

Dr Witold Piskorz

Uniwersytet Jagielloński w Krakowie

Wydział Chemii

Zakład Chemii Nieorganicznej

Zespół Katalizy i Fizykochemii Ciała Stałego

Autoreferat

„Kwantowo-chemiczne modelowanie zależności między strukturą i morfologią nanoziaren tlenków a ich własnościami elektronowymi i aktywnością katalityczną”

w związku z wnioskiem o przeprowadzenie przewodu habilitacyjnego

Kraków, 09.2013 r.



UNIVERSITAS IAGELLONICA
CRACOVIENSIS

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Tom 1

Informacje o autorze, dane osobowe i życiorys naukowy

1.1 *Curriculum vitae*, dane kontaktowe

Dane osobowe:

Imię i nazwisko: Witold Piskorz

Data i miejsce urodzenia: 02.09.1973 r., Kraków

Stan cywilny: żonaty, dwoje dzieci

Posiadane dyplomy, stopnie naukowe

1. Stopień naukowy doktora nauk chemicznych – 2001 r., Wydział Chemii Uniwersytetu Jagiellońskiego, Zakład Chemii Teoretycznej. Tytuł pracy: „Molekularny mechanizm aktywacji wiązania C-H w węglowodorach oddziałujących z tlenkami metali przejściowych”, promotor: doc. dr hab. E. Broclawik.
2. Dyplom magistra chemii – 1997 r., Wydział Chemii Uniwersytetu Jagiellońskiego. Tytuł pracy: „Zastosowanie termicznej desorpcji potasu do charakterystyki katalizatorów syntezy amoniaku”. Promotor: prof. dr hab. A. Barański, ocena: celująca.

Informacje o dotychczasowym zatrudnieniu w jednostkach naukowych

1997 – 2001	Studia Doktoranckie na Wydziale Chemii Uniwersytetu Jagiellońskiego w Zakładzie Chemii Teoretycznej
2001 – 2004	Wydział Chemii UJ, Zakład Chemii Nieorganicznej, stanowisko asystenta
2004 – obecnie	Wydział Chemii UJ, Zakład Chemii Nieorganicznej, mianowanie na stanowisko adiunkta
2008 – 2009	roczny staż post-doktorski w Uniwersytecie Humboldtów, Berlin, Niemcy

Informacje kontaktowe

Zespół Katalizy i Fizykochemii Ciała Stałego

Wydział Chemii

Uniwersytet Jagielloński w Krakowie

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1.2 Potwierdzona kopia dyplomu doktora nauk chemicznych

ODPIS

(GODŁO PAŃSTWOWE)

RZECZPOSPOLITA POLSKA
UNIwersytet Jagielloński w Krakowie

WYDZIAŁ CHEMII

DYPLOM

PAN WITOLD PISKORZURODZONY DNIA 2 WRZEŚNIA 1973 ROKU W KRAKOWIE

NA PODSTAWIE PRZEDSTAWIONEJ ROZPRAWY DOKTORSKIEJ POD TYTUŁEM

" MOLEKULARNY MECHANIZM AKTYWACJI WIĄZANIA C-H W WĘGLOWODORACH ODDZIAŁUJĄCYCH
Z TLENKAMI METALI PRZEJŚCIOWYCH "

ORAZ PO ZŁOŻENIU PRZEPISANYCH EGZAMINÓW UZYSKAŁ STOPIEŃ NAUKOWY

DOKTORA

NAUK CHEMICZNYCHNADANY UCHWAŁĄ RADY WYDZIAŁU CHEMIIZ DNIA 24 MAJA 2001 R.PROMOTOREM W PRZEWODZIE DOKTORSKIM BYŁ DOC. DR HAB. EWA BROCLAWIK

RECENZENTAMI W PRZEWODZIE DOKTORSKIM BYLI

PROF. DR HAB. BARBARA GRZYBOWSKA - ŚWIERKOSZ - INSTYTUT KATALIZY PAN, KRAKÓWPROF. DR HAB. LUDWIK KOMOROWSKI - POLITECHNIKA WROCŁAWSKAKRAKÓW, 28 LISTOPADA 2001 R.

REKTOR

/-/PROF. DR HAB. FRANCISZEK ZIEJKA

DZIEKAN

/-/PROF. DR HAB. ROMAN DZIEMBAJ

Nr

4363

PROMOTOR

/-/DOC. DR HAB. EWA BROCLAWIK

Stwierdzam zgodność odpisu z oryginałem
Kraków, dnia 28.11.2001
podpis [signature]

1.3 Tematyka badań

W pracy badawczej stosuję metody chemii obliczeniowej do całościowego, wieloskalowego opisu interesujących katalitycznych układów heterogenicznych – od struktury w skali atomowej do właściwości makroskopowych. Mój dorobek naukowy można zakwalifikować do następujących kategorii:

1. kwantowo-chemiczne modelowanie struktury elektronowej, struktury powierzchni i morfologii nanoziaren,
2. modyfikacja ich właściwości, w tym także funkcjonalizacja i modelowanie własności powierzchni, symulacja obrazów mikroskopowych STM,
3. poszukiwanie związków między własnościami w skali atomowej a własnościami makroskopowymi, w szczególności własnościami katalitycznymi, oraz
4. modelowanie mikrokinezy i termodynamiczne *ab initio*.

Zagadnienia te można określić mianem „**katalizy komputerowej**”. Badania wykonuję za pomocą oprogramowania komercyjnego i należącego do kategorii *Open Source*, adaptowanego do niestandardowych zastosowań, a także programów własnych. W swej pracy stosuję metody obliczeniowe i poziom teorii optymalnie dobrane do problemu pod względem dokładności i złożoności obliczeniowej oraz pozwalające na najlepsze odtworzenie więzów eksperymentalnych.

Mam także doświadczenie w budowie i rozwoju oprogramowania do klasycznej dynamiki molekularnej oraz w badaniach prowadzonych z wykorzystaniem tej metodologii. Zaprojektowałem także, skonstruowałem i oprogramowałem elektronikę sterującą próżniowym stanowiskiem pomiarowym. Jestem także administratorem komputerów dużej mocy obliczeniowej.

1.4 Pełna lista artykułów naukowych

1.4.1 Analiza scjentometryczna

- Liczba publikacji: **26** (w tym jedna po pozytywnych recenzjach)
 - w siedmiu jestem autorem korespondującym
- Liczba publikacji w czasopismach z Listy Filadelfijskiej (uwzględnionych w *Science Citation Reports*): **24**
- Sumaryczny IF = **103,07**
- Cytowania:
 - Całkowita liczba cytowań: **212** (bez samocytowań: **196**)
 - Liczba cytowań za ostatnie 4 lata (w latach 2009-2012): **13 + 12 + 35 + 35 = 95**
 - Średnia liczba cytowań na 1 artykuł: **9,22**

Wskaźniki te przytoczone zostały za portalem *Web of Science* i nie różnią się one istotnie od wartości podanych przez inne bazy danych (*Scopus*, *Google Scholar*)

- Indeks Hirscha **h = 9**
- Udział w ponad **60** konferencjach
 - **44** wygłoszone wykłady i komunikaty (pełna lista w Aneksie 1, str. 18)
 - **44** postery (pełna lista w Aneksie 1, str. 21)

1.4.2 Wykaz publikacji

Gwiazdką oznaczono autora/-ów korespondującego/-ych. Podany jest mój wkład osobisty oraz oszacowaną wartość udziału w procentach.

Przed uzyskaniem stopnia doktora

1. E. Broclawik*, A. Endou, R. Yamauchi, T. Kanougi, W. Piskorz, M. Kubo, A. Miyamoto, „Methane activation in heterogeneous active sites”, Abstracts of papers of the American Chemical Society, 215: 064-COMP Part 1 Apr 2 1998, ISSN: 0065-7727.

Wkład osobisty: część obliczeń DFT wybranych ścieżek aktywacji metanu (15 %).

2. E. Broclawik*, W. Piskorz, K. Adamska „On the ground electronic state of MoO^+ : Upgrade density functional theory calculations”, *J. Chem. Phys.*, **24** (1999) 11685. **IF = 3,149**.

Wkład osobisty: Przygotowanie i wykonanie części kwantowo-chemicznych obliczeń struktury elektronowej, z wykorzystaniem kilku funkcjonałów DFT, oraz obliczenia anharmonicznej struktury oscylacyjnej kationu MoO^+ (30 %).

3. E. Broclawik*, J. Datka, B. Gil, W. Piskorz, P. Kozyra „The interaction of CO, N_2 and NO with Cu cations in ZSM-5: quantum chemical description and IR study”, *Topics in Catalysis*, **11/12** (2000), 335. **IF = 2,212**.

Wkład osobisty: Część obliczeń kwantowo-chemicznych, udział w redakcji manuskryptu (20 %).

4. E. Broclawik, J. Datka, B. Gil, W. Piskorz, P. Kozyra „Combined theoretical and experimental study on exchanged cations in ZSM-5: activity in DENOX processes”, *Polish Journal of Environmental Studies*, **9**, supl. I, (2000), 11. **IF = 0,888**.

Wkład osobisty: Część obliczeń kwantowo-chemicznych, udział w redakcji manuskryptu (15 %).

Po uzyskaniu stopnia doktora

5. A. Tomsic, P. U. Andersson, N. Marković, W. Piskorz, M. Svanberg, J. B. C. Pettersson* „Molecular-dynamics simulations of cluster-surface collisions: Emission of large fragments”, *J. Chem. Phys.*, **115** (2001), 10509. **IF = 3,149**.

Wkład osobisty: Opracowanie części programu do obliczeń dynamiki molekularnej — implementacja potencjału oddziaływania H_2O -grafit oraz C-C; drobne korekty manuskryptu (15 %).

6. E. Brocławik*, J. Haber, W. Piskorz „Molecular mechanism of C–H bond cleavage at transition metal oxide clusters”, *Chem. Phys. Lett.*, **333** (2001), 332. **IF = 2,169.**

Wkład osobisty: Praca oparta na wynikach mojego doktoratu. Znaczna część obliczeń kwantowo-chemicznych, udział w tworzeniu manuskryptu (50 %).

7. P. Pietrzyk, W. Piskorz, Z. Sojka*, E. Brocławik „Molecular structure, spin density distribution and hyperfine coupling constants of the $\eta^1\{\text{CuNO}\}^{11}$ adduct formed in ZSM-5 zeolite: DFT calculations and comparison with EPR data”, *J. Phys. Chem. B*, **107** (2003), 6105. **IF = 4,189.**

Wkład osobisty: Część obliczeń kwantowo-chemicznych struktury geometrycznej wykorzystanych klastrów wyciętych z sieci zeolitu ZSM-5 (30 %).

8. A. Kotarba*, G. Adamski, W. Piskorz, Z. Sojka, C. Sayag, G. Djéga-Mariadassou „Modification of electronic properties of Mo_2C catalyst by potassium doping: Impact on the reactivity in hydrodenitrogenation reaction of indole”, *J. Phys. Chem. B*, **108** (2004), 2885. **IF = 4,189.**

Wkład osobisty: Całość obliczeń kwantowo-chemicznych, udział w opracowaniu manuskryptu (40 %).

9. W. Piskorz, E. Brocławik, „Molecular mechanism of the methane dissociation on the vanadium oxides clusters. DFT calculations” w: E. G. Derouane, V. Parmon, F. Lemos, F. Ramoa (eds.) “Sustainable Strategies for the Upgrading of Natural Gas: Fundamentals, Challenges, and Opportunities”, NATO Advanced Study Institute Series, **191** (2005), 317; ISBN: 1-4020-3308-7.

Wkład osobisty: Praca oparta o wyniki mojego doktoratu. Większość obliczeń kwantowo-chemicznych, znaczący udział w opracowaniu manuskryptu (50 %).

10. W. Piskorz*, G. Adamski, A. Kotarba, Z. Sojka, C. Sayag, G. Djéga-Mariadassou, „Hydrodenitrogenation of indole over Mo_2C catalyst: Insights into mechanistic events through DFT modeling”, *Catal. Today* (APAC 2005), **119** (2007) 39. **IF = 3,004.**

Wkład osobisty: Całość obliczeń kwantowo-chemicznych, opracowanie obliczeniowej części artykułu, udział w dyskusji nad manuskrytem (40 %).

11. P. Pietrzyk, F. Zasada, W. Piskorz, A. Kotarba, Z. Sojka*, „Computational spectroscopy and DFT investigations into nitrogen and oxygen bond breaking and bond making processes in model deNO_x and deN₂O reactions”, *Catal. Today* (APAC 2005), **119** (2007) 219. **IF = 3,004.**

Wkład osobisty: Istotna część obliczeń kwantowo-chemicznych dotyczących procesu rozkładu N₂O (20 %).

12. P. Stelmachowski, F. Zasada, W. Piskorz, A. Kotarba, Z. Sojka* „Experimental and DFT studies of N₂O decomposition over bare and Co doped magnesium oxide – insights into the role of active sites topology in dry and wet conditions”, *Catal. Today*, **137** (2008), 423. **IF = 3,526.**

Wkład osobisty: Istotna część obliczeń kwantowo-chemicznych, udział w opracowaniu manuskryptu (30 %).

13. W. Piskorz, F. Zasada, P. Stelmachowski, A. Kotarba, Z. Sojka*, „Decomposition of N₂O over the surface of cobalt spinel: A DFT account of reactivity experiments”, *Catal. Today*, **137** (2008), 418. **IF = 3,526.**

Wkład osobisty: Opracowanie klastrowych modeli obliczeniowych, w tym także z wykorzystaniem **autorskiego oprogramowania** [1]. Znaczna część obliczeń kwantowo-chemicznych, dyskusja wyników, udział w tworzeniu manuskryptu.

Jestem **pierwszym autorem** (50 %).

14. M. Inger, M. Saromka, M. Wilk*, P. Stelmachowski, F. Zasada, G. Maniak, W. Piskorz, A. Adamski, A. Kotarba, Z. Sojka, P. Granger, „Low temperature catalyst for nitrous oxide decomposition from nitric acid plant tail gases (Katalizator do niskotemperaturowego rozkładu tlenku azotu(I) ze strumienia gazów resztkowych z instalacji kwasu azotowego)”, *Przem. Chem.* **88** (2009). **IF = 0,254**.

Wkład osobisty: Opracowanie modeli obliczeniowych, istotna część obliczeń kwantowo-chemicznych, udział w dyskusji wyników i opracowaniu manuskryptu (30 %).

15. F. Zasada*, W. Piskorz, S. Cristol, J.-F. Paul, A. Kotarba, Z. Sojka*, „Periodic Density Functional Theory and Atomistic Thermodynamic Studies of Cobalt Spinel Nanocrystals in Wet Environment: Molecular Interpretation of Water Adsorption Equilibria”, *J. Phys. Chem. C* **114** (2010), 22245. **IF = 4,224**.

H1

Artykuł wybrany do wniosku o przeprowadzenie przewodu habilitacyjnego (**H1**), pełny tekst na str. 49, opis wkładu osobistego na str. 27 (40 %).

16. G. Maniak, P. Stelmachowski, F. Zasada, W. Piskorz, A. Kotarba*, Z. Sojka, „Guidelines for optimization of catalytic activity of 3d transition metal oxides catalysts in N₂O decomposition by potassium promotion”, *Catal. Today* **176** (2011), 369. **IF = 3,526**.

Wkład osobisty: Opracowanie modeli obliczeniowych, udział w wykonaniu obliczeń kwantowo-chemicznych oraz dyskusji wyników (25 %).

17. F. Zasada, W. Piskorz*, S. Godlewski*, J. S. Prauzner-Bechcicki, A. Tekiel, J. Budzioch, P. Cyganik, M. Szymonski, Z. Sojka, „Chemical Functionalization of the TiO₂(110)-(1×1) Surface by Deposition of Terephthalic Acid Molecules – a DFT and STM Study”, *J. Phys. Chem. C* **115** (2011), 4134. **IF = 4,224**.

H5

Artykuł wybrany do wniosku o przeprowadzenie przewodu habilitacyjnego (**H5**), pełny tekst na str. 99, opis wkładu osobistego na str. 28 (40 %).

18. F. Zasada, W. Piskorz, P. Stelmachowski, A. Kotarba, J.-F. Paul, T. Płociński, K. J. Kurzydłowski, Z. Sojka* „Periodic DFT and HR-STEM Studies of Surface Structure and Morphology of Cobalt Spinel Nanocrystals. Retrieving 3D Shapes from 2D Images”, *J. Phys. Chem. C* **115** (2011) 6423. **IF = 4,224**.

H2

Artykuł wybrany do wniosku o przeprowadzenie przewodu habilitacyjnego (**H2**), pełny tekst na str. 59, opis wkładu osobistego na str. 27 (30 %).

19. W. Piskorz*, F. Zasada, P. Stelmachowski, O. Diwald, A. Kotarba, Z. Sojka* „Computational and Experimental Investigations into N₂O Decomposition over MgO Nanocrystals – From Thorough Molecular Mechanism to Ab Initio Microkinetics”, *J. Phys. Chem. C* **115** (2011), 22451. **IF = 4,224**.

H8

Artykuł wybrany do wniosku o przeprowadzenie przewodu habilitacyjnego (**H8**), pełny tekst na str. 128, opis wkładu osobistego na str. 28 (60 %).

20. W. Piskorz*, J. Gryboś, F. Zasada, S. Cristol, J.-F. Paul, A. Adamski, Z. Sojka* „Periodic DFT and Atomistic Thermodynamic Modeling of Surface Hydration Equilibria and Morphology Prediction of Monoclinic ZrO₂ Nanocrystals”, *J. Phys. Chem. C*, **115** (2011), 24274. **IF = 4,224**.

H3

Artykuł wybrany do wniosku o przeprowadzenie przewodu habilitacyjnego (**H3**), pełny tekst na str. 70, opis wkładu osobistego na str. 27 (50 %).

21. W. Piskorz*, J. Gryboś, F. Zasada, P. Zapala, S. Cristol, J.-F. Paul, Z. Sojka* „Periodic DFT Study of the Tetragonal ZrO₂ Nanocrystals – Equilibrium Morphology Modeling and Atomistic Surface Hydration Thermodynamics”, *J. Phys. Chem. C*, **116** (2012), 19307. **IF = 4,224**.

H4

Artykuł wybrany do wniosku o przeprowadzenie przewodu habilitacyjnego (**H4**), pełny tekst na str. 84, opis wkładu osobistego na str. 27 (50 %).

22. S. Godlewski*, A. Tekiel, W. Piskorz*, F. Zasada, J. S. Prauzner-Bechcicki, Z. Sojka, M. Szymonski „Supramolecular Ordering of PTCDA Molecules – the Key Role of Dispersion Forces in an Unusual Transition from Physisorbed into Chemisorbed State”, *ACS Nano*, **6** (2012), 8536. **IF = 11,421**.

H6

Artykuł wybrany do wniosku o przeprowadzenie przewodu habilitacyjnego (**H6**), pełny tekst na str. 111, opis wkładu osobistego na str. 28 (45 %).

23. P. Stelmachowski*, G. Maniak, F. Zasada, W. Piskorz, A. Kotarba, Z. Sojka „Substituted Cobalt Spinels as Catalysts for Low Temperature deN₂O – Evidence for Octahedral Co³⁺ Active Sites”, *Appl. Catal. B*, DOI: 10.1016/j.apcatb.2013.05.027. **IF = 6,052**.

Wkład osobisty: Część obliczeń kwantowo-chemicznych, udział w dyskusji wyników (20 %).

24. M. Kolmer, A. A. Ahmad Zebari, J. S. Prauzner-Bechcicki*, W. Piskorz, F. Zasada, S. Godlewski, B. Such, Z. Sojka, M. Szymonski, „On-Surface Polymerization on Titanium Dioxide: Polyanthrylene on TiO₂(011)-(2×1) surface”, *Angew. Chem. Int. Ed.*, **52**, (2013), 1. DOI: 10.1002/ange.201303657. **IF = 13,455**.

H7

Artykuł wybrany do wniosku o przeprowadzenie przewodu habilitacyjnego (**H7**), pełny tekst na str. 122, opis wkładu osobistego na str. 28 (45 %).

25. W. Piskorz*, F. Zasada, P. Stelmachowski, A. Kotarba, Z. Sojka* „Molecular Mechanism and Microkinetics of deN₂O Reaction over Alkaline Earth Oxides – The Role of Static and Dynamic Recombination of Peroxy Intermediates”, *J. Phys. Chem. C.*, DOI: 10.1021/jp405459g. **IF = 4,224**.

H9

Artykuł wybrany do wniosku o przeprowadzenie przewodu habilitacyjnego (**H9**), pełny tekst na str. 139, opis wkładu osobistego na str. 29 (65 %).

26. M. Kolmer, A. A. Zebari, M. Goryl, F. Buatier de Mongeot, F. Zasada, W. Piskorz, P. Pietrzyk, Z. Sojka, F. Krok, M. Szymonski „Temperature dependent orientation of self-organised nanopatterns on the ion-irradiated TiO₂(110)“, *Phys. Rev. B*, po pozytywnych recenzjach.

Wkład osobisty: znaczna część obliczeń kwantowo-chemicznych, zaproponowanie mechanizmu zmiany orientacji zmarszczek, całość wykonanych symulacji obrazów STM, udział w dyskusji wyników (30 %).

Pełna lista **wystąpień konferencyjnych** oraz **posterów** zamieszczona jest w Aneksie 1 (str. 18).

1.5 Pozostałe osiągnięcia naukowo-badawcze

W skład mojego dorobku naukowego, oprócz omówionych wyżej artykułów, wystąpień konferencyjnych i posterów, wchodzi:

- 8 nagród indywidualnych i zespołowych, opis na str. 11;
- 3 patenty i zgłoszenia patentowe, w tym 1 międzynarodowy (europejski), opis na str. 13;
- 8 projektów badawczych KBN/MNiSW/NCN (w tym kierownictwo jednego projektu), opis na str. 11;
- 4 granty instytucji międzynarodowych, opis na str. 12;

1.6 Działalność recenzencka

- 9 recenzji artykułów – *New Journal of Chemistry* (RSC): 2010 r.; *Journal of Physical Chemistry* (ACS): 2011 r., 2013 r. (×3); *Physical Chemistry Chemical Physics* (RSC): 2011 r.; *ACS Nano* (ACS): 2011 r., *Structural Chemistry* (Springer): 2011 r.; *Heteroatom Chemistry* (Wiley), 2013 r.;
- 1 recenzja projektu badawczego dla Narodowego Centrum Nauki, 2012 r.;

1.7 Nagrody i wyróżnienia

1. Zespołowa Nagroda Ministra Edukacji Narodowej (Warszawa 2000 r).
2. Stypendium im. St. Estreichera (Kraków 2000 r).
3. Zespołowa nagroda Rektora Uniwersytetu Jagiellońskiego za szczególne osiągnięcia w pracy naukowej (Kraków 2004 r).
4. Nagroda Zespołowa I stopnia Rektora Uniwersytetu Jagiellońskiego za szczególne osiągnięcia w pracy organizacyjnej: opracowanie systemu elektronicznej kolejki (EOKD, *vide* 1.13 na stronie 16), Kraków 2007 r.
5. Złoty medal na Międzynarodowej Wystawie Wynalazków IVIS 2008 w Warszawie.
6. Brązowy medal na 57. Światowej Wystawie Innowacji, Badań Naukowych i Nowoczesnej Techniki „Brussels Innova 2008”; 13-15.11.2008 r, Bruksela.
7. Dyplom Ministra Nauki i Szkolnictwa Wyższego za wyróżniający się projekt badawczy w 2008 r.
8. Złoty medal na wystawie „*Salon International des Inventions 2009*” w Genewie.
9. Zespołowa nagroda Rektora UJ, 2012 r.
10. Złoty medal na XVI Moskiewskim Salonie Wynalazków i Innowacyjnych Technologii „*Archimedes 2013*” za „Kompozytowy katalizator do niskotemperaturowego rozkładu podtlenku azotu”.

1.8 Udział w projektach badawczych

1.8.1 Uczestnictwo w projektach badawczych finansowanych przez KBN/Ministerstwo Nauki i Szkolnictwa Wyższego/Narodowe Centrum Nauki

Kierowanie

1. Grant „Symulacje metodami DFT procesu oddziaływania metali alkalicznych z powierzchnią tlenków metali”, nr 4 T09A 139 23, zakończenie przyjęte 06.2004 r.

Wykonawstwo

2. Grant promotorski „Molekularny mechanizm aktywacji wiązania C–H w węglowodorach oddziałujących z tlenkami metali przejściowych”, nr 3 T09A 065 19, zakończenie przyjęte 31.01.2002 r.
3. Grant „Reakcje DeNO_x na zeolitach: badania spektroskopowe IR, EPR, TPD–MS, modelowanie metodami chemii kwantowej oraz badania katalityczne”, nr 3 T09A 073 14, zakończony w 2000 r. (publikacja nr 3)
4. Grant „Aktywatory i aktywacja wiązania C–H w metanie oraz jego selektywne utlenianie do związków tlenowych”, nr PBZ/KBN/018/T09/99/1b, zakończony: 12.2003 r.
5. Grant „Węglik molibdenu dotowany alkaliem jako katalizator reakcji z udziałem wodoru”, nr 3 T09A 172 19, zakończony: 05.2003 r. (publikacje nr 10 i 8)
6. Grant „Inżynieria procesów ograniczania emisji oraz utylizacji gazów szkodliwych i ciepłarnianych”, nr PBZ-MEiN 3/2/2006 r. (publikacje nr 12 i 14)
7. Grant „Badania ścieżek aktywacji i przemian spinowo-elektronowych towarzyszących oddziaływaniu cząsteczek NO_x, CO_x, O₂ oraz małych węglowodorów z powierzchniowymi kompleksami metali przejściowych w kontekście reakcji deNO_x”, nr 3 T09A 147 26, zakończony: 2007 r. (publikacja nr 11)
8. Grant „Funkcjonalizowane tlenki lite i nanomateriały tlenkowe – badania spektroskopowe i modelowanie molekularne związków pomiędzy strukturą a reaktywnością” nr 299/N-COST/2008/0. (publikacje nr 15, 16, 19, 20, 17 i 18)
9. Grant Iuventus Plus „Morfologia tlenkowych nanomateriałów katalitycznych – badania metodami DFT i symulacja zdjęć HR-TEM”, nr IP2011 063371.
10. Grant „Chemia katalitycznego dopalania sadzy na nanostrukturalnych układach tlenkowych promowanych alkaliem”, nr 2011/01/B/ST4/00574.
11. Grant „Katalityczne usuwanie gazów ciepłarnianych na modelowych nanostrukturalnych układach spinelowych”, nr 2011/03/B/ST5/01564 (publikacja: nr 25).

1.8.2 Uczestnictwo w zagranicznych projektach badawczych

1. Projekt polsko-francuski nr 6523 „Application of novel and cheap catalytic materials: (oxy)carbides and (oxy)nitrides of transition metals as the substitutes of noble metals in the commercial hydrotreatments catalysts” (1996–2001);
2. Program międzynarodowy „Jumelage «Matériaux pour l’environnement»” (publikacje nr 10 i 10);
3. Projekt europejski „Eureka – Abatement of N₂O and NO_x from industry plants and fossil fuel combustion devices over novel catalysts – STATIONOCAT E!3230” (publikacja nr 13);
4. COST Action D41 „Oxides Surface Chemistry” (publikacje nr 15, 19, 20, 17 i 18);
5. COST Action CM1104 „Reducible oxide chemistry, structure and functions” (publikacja: nr 21);
6. GDRI CNRS-PAN: Groupement De Recherche International „Catalysis for polluting emissions aftertreatment and production of renewable energies” (publikacja nr 12);

1.9 Patenty i zgłoszenia patentowe

1. P-385251 (2008) „Katalizator do niskotemperaturowego rozkładu podtlenku azotu”, Instytut Nawozów Sztucznych, Puławy i Uniwersytet Jagielloński, Kraków.
2. P-388518 (2009) „Katalizator do wysokotemperaturowego rozkładu podtlenku azotu”, Instytut Nawozów Sztucznych, Puławy i Uniwersytet Jagielloński, Kraków.
3. Patent europejski PCT/PL2009/000050 (2009) „Catalyst for low-temperature decomposition of dinitrogen oxide and a process for the preparation thereof”, Instytut Nawozów Sztucznych, Puławy i Uniwersytet Jagielloński, Kraków.

1.10 Przynależność do stowarzyszeń naukowych

1. Polskie Towarzystwo Chemiczne (od 2001),
2. Polski Klub Katalizy (od 2001).

1.11 Współpraca krajowa i międzynarodowa

1. Goeteborg University, Szwecja, prof. Jan B. C. Pettersson
 - (a) 1998 r., stypendium trzymiesięczne. Udział w opracowaniu programu do symulacji metodą dynamiki molekularnej zderzeń klasterów wody z powierzchnią grafitu (publikacja 5);
2. Emory University, Atlanta, GA, USA, prof. Keiji Morokuma
 - (a) 2000 r., stypendium sześciomiesięczne. Wstępne obliczenia DFT do rozprawy doktorskiej oraz studia literaturowe (publikacja 6);
3. CNRS (Centre national de la recherche scientifique) i Université Pierre et Marie Curie Paris 6, Francja, prof. Gerald Djéga-Mariadassou. Współpraca polega na badaniu azotków i węglików metali przejściowych w ramach projektu International Group of Research (GDRI) „Catalyse pour l’environnement” (publikacje: 8 i 10);
4. Humboldt Universität zu Berlin, RFN, prof. Joachim Sauer.
 - (a) 02.2008-02.2009 r., roczny staż. Rozwój oprogramowania kwantowo-chemicznego: implementacja półempirycznej parametryzacji energii dyspersyjnej w programie Turbomole 5.10 oraz implementacja metody całkowania termodynamicznego (QMPot); obliczenia DFT odwodornienia propanu na klasterach $\text{Si}_x\text{O}_y\text{VO}$; publikacja w końcowej fazie przygotowania (W. Piskorz *et al.*, „C-H bond activation in propane by silica supported vanadia catalyst: free energy calculation for stationary and transition states by molecular dynamics compared to harmonic approximation”).
5. Friedrich-Schiller-Universität Jena, RFN, prof. Marek Sierka. Współpraca datuje się od czasu mojego pobytu na stypendium post-doktorskiego w Uniwersytecie Humboldtów w 2008/09 roku i polega na rozwoju oprogramowania kwantowo-chemicznego (Turbomole, QMPot);

6. Unite de Catalyse et de Chimie du Solide - UMR CNRS 8181 Uniwersytet w Lille, Francja. Zespół prof. Sylvaina Cristola i prof. Jean-François Paula. Współpraca w dziedzinie modelowania morfologii nanoziaren i obrazów HR-TEM.
7. Department of Materials Science and Physics University of Salzburg, prof. Oliver Diwald. Współpraca w ramach COST Action D41 „Oxides Surface Chemistry” w dziedzinie syntezy nanoziaren MgO.
8. Centrum Badań Układów Nanoskopowych i Zaawansowanych Materiałów NANOSAM, Instytut Fizyki, Uniwersytet Jagielloński w Krakowie, zespół pod kierownictwem prof. M. Szymońskiego. Współpraca polega na badaniach funkcjonalizacji powierzchni tlenkowych – strona odpowiedzialna na część doświadczalną: mikroskopię STM (publikacje 17, 22, 24).
9. Instytut Nawozów Sztucznych, Puławy. Współpraca w dziedzinie opracowanie katalizatora do rozkładu N_2O (publikacje: 14, 16; patenty: wykaz w rozdz. 1.9).

1.12 Dorobek dydaktyczny i popularyzatorski

1.12.1 Opracowanie wykładów, seminariów i kierowanie kursami

Opracowanie autorskiego sylabusu oraz kierowanie i prowadzenie zajęć (koordynator) kursów dla kierunku Chemia:

1. „Urządzenia pomiarowe i technika eksperymentalna” dla studentów III roku (od 2009 r. do teraz) – wykład i seminarium,
2. „Urządzenia pomiarowe i technika eksperymentalna” dla studentów III roku, studia niestacjonarne (2009/10 r.) – wykład i seminarium,
3. „Modelowanie Molekularne Materiałów” dla studentów I roku studiów II stopnia (od 2010 r. do teraz) – wykład i seminarium,

Opracowanie autorskiego sylabusu oraz kierowanie i prowadzenie zajęć (koordynator) kursów dla kierunku Zaawansowane Materiały i Nanotechnologia:

1. „Modelowanie Metodami Chemii Kwantowej” dla studentów III roku (od 2010 r. do teraz) – wykład i seminarium,

1.12.2 Inne prowadzone zajęcia dydaktyczne

1. Pracownia specjalizacyjna profilu „Chemia nowych materiałów i kataliza” (IV rok kierunku Chemia) w roku 2002/3.
2. Ćwiczenia do przedmiotu „Programowanie w języku Fortran 77” (III rok kierunku Chemia) w latach 1998/9, 1999/2000 i 2003/4.
3. Ćwiczenia laboratoryjne „Podstawy chemii” (I rok kierunku Chemia) w latach 2001-12.
4. Ćwiczenia laboratoryjne „Chemia nieorganiczna” (I rok kierunku Inżynieria Materiałowa) w roku 2004/5.

5. Ćwiczenia laboratoryjne „Chemia nieorganiczna II” (II rok kierunku Chemia) w latach 2008-13.
6. Ćwiczenia „Pakiet Microsoft Office: PowerPoint” (I rok kierunku Chemia) w rok 2002/3.
7. Ćwiczenia rachunkowe z matematyki: rachunek różniczkowy i całkowy, podstawy algebry liniowej (I rok kierunku Chemia) w latach 2002/3-2004/5 i 2006/7.
8. Ćwiczenia laboratoryjne „Spektroskopia molekularna UV-Vis” (III rok kierunku Chemia) w roku 2002/3.

1.12.3 Udział w projektach edukacyjnych

1. Projekt POKL.04.01.02-00-097/09 „Zwiększenie liczby wysoko wykwalifikowanych absolwentów kierunków ścisłych Uniwersytetu Jagiellońskiego”, **przygotowanie materiałów dydaktycznych** z przedmiotu “Urządzenia Pomiarowe i Technika Eksperymentalna”,
2. Projekt POKL.04.01.02-00-097/09 „Zwiększenie liczby wysoko wykwalifikowanych absolwentów kierunków ścisłych Uniwersytetu Jagiellońskiego”, **przygotowanie materiałów dydaktycznych** z działu “Kwantowy opis atomów II”.

1.12.4 Pozostałe zagadnienia dorobku dydaktycznego

- Wkład w tworzeniu kwantowo-chemicznego kodu wykorzystywanego do celów dydaktycznych [2] (główny autor i koordynator: dr Grzegorz Mazur, Zakład Chemii Teoretycznej, Wydział Chemii UJ).

1.12.5 Opieka nad doktoratami

- Promotorstwo pomocnicze pracy doktorskiej mgr Joanny Gryboś. Tematyka badawcza mgr Gryboś obejmuje badania za pomocą wysokorozdzielczej mikroskopii elektronowej struktury nanoziaren tlenkowych oraz modelowanie w formalizmie DFT tych struktur.

1.12.6 Prowadzenie seminariów magisterskich

- Seminaria magisterskie dla kierunku Zaawansowane Materiały i Nanotechnologia: „Nanomateriały i Biomateriały” oraz „Fotonika i Nanotechnologia”.

1.12.7 Opieka nad licencjatami

1. „Ocena wpływu warunków przygotowania próbki polikrystalicznego spinelu kobaltowego na wartość jej pracy wyjścia”, Katarzyna Ćmil, 06.2013 r.
2. „Badanie pracy wyjścia *in-situ* polikrystalicznego spinelu kobaltowego w obecności O₂ i NO”, Joanna Duch, 06.2013 r.

1.12.8 Publikacje w czasopismach popularno-naukowych

- Artykuł w „*Uranii*” nr 11 (598) 1991, str. 306,
- Artykuł w miesięczniku „*Wszechświat*”, tom 93, nr 4, 1992, str. 105,
- Recenzja dla czasopisma studenckiego „*Studenckie Zeszyty Naukowe UJ*”(2013 r.).

1.12.9 Działalność na polu popularyzacji nauki

- Warsztaty Olimpijskie dla uczniów liceum, 2002/3 r., przedmiot Chemia.
 - Działalność w Polskim Towarzystwie Miłośników Astronomii oraz w Sekcji Obserwacji Pozycji i Zakryć PTMA (astronomia obserwacyjna – obserwacje pozycyjne i zjawisk zakryciowych, astrofotografia)
 - Pierwsza transkontynentalna obserwacja zakrycia planetoidalnego: 144 *Vibilia* / SAO 78468, 31.12.1993 r., (np. <http://mpocc.astro.cz/world/12.txt>, <http://mpocc.astro.cz/world/mpocc1.txt>, lub: David W. Dunham, *Sky & Telescope*, Feb. 1995, str. 72, gdzie obserwację określono jako „jedną z nielicznych transkontynentalnych”).
 - Pokazy dla publiczności przejścia Merkurego (2001 r.) i Wenus (2004 r.) przed tarczą Słońca.
 - Ekspedycje popularno-naukowe na zaćmienie Słońca:
 - * Meksyk 07.1991 r.
 - * Węgry 07.1999 r.
 - * Republika Południowej Afryki 11-12.2002 r.
- Do dorobku popularyzatorskiego tych ekspedycji zaliczam wykonanie fotografii fazy całkowitej i częściowej zaćmienia Słońca (opublikowane, a także dystrybuowane przez Młodzieżowe Obserwatorium Astronomiczne w Niepołomicach k. Krakowa, www.moa.pl).

1.13 Dorobek organizacyjny

- Udział w organizacji XLV Zjazdu Polskiego Towarzystwa Chemicznego Kraków 2002 — serwis informatyczny umożliwiający rejestrację uczestników *on-line* oraz generujący potrzebne organizatorowi zestawienia i potwierdzenia.
- Udział w organizacji konferencji Current Trends in Theoretical Chemistry VI, 1-5.09.2013, Kraków; Uczestnictwo w obsłudze informatycznej konferencji.
- Konstrukcja i konfiguracja klastra obliczeniowego (> 300 rdzeni procesorów AMD opteron). Usługi: PXE booting, DNS, DHCP, NIS+, NFS, ups-shutdown, MPICH+ssh(RSA keys), ganglia, SAMBA, bezdyskowe węzły obliczeniowe. Administracja tym klastrerem oraz jego rozbudowa i utrzymanie.
- Opracowanie systemu „elektronicznej kolejki” (EOKD) dla celów zarządzania przyjmowaniem studentów w dziekanacie Wydziału Chemii, <http://www.student.chemia.uj.edu.pl/eokd/>, Kraków 2007 r.; do chwili obecnej: dalsza konserwacja kodu i jego usprawnienia.
- Udział w tworzeniu oprogramowania internetu/intranetu Wydziału Chemii UJ; Komputeryzacja pracowni EPR; Konfiguracja i utrzymywanie serwera grupy roboczej Zespołu Katalizy i Fizykochemii Ciała Stałego.

1.14 Zainteresowania naukowe

- Fizykochemia ciała stałego, kwantowo-chemiczne modelowanie materiałów, chemia powierzchni, kataliza heterogeniczna, metody spektroskopowe,
- Chemia obliczeniowa, metody numeryczne chemii, obliczenia DFT z wykorzystaniem programów VASP, DMOL, ADF, CASTEP, TURBOMOLE, i CRYSTAL.
- Rozwój oprogramowania kwantowo-chemicznego
 - QMPot: moduły do obliczeń dynamiki molekularnej (MD) i poszukiwania stanów przejściowych algorytmem LST/CG/QST
 - półempiryczna dyspersja w TURBOMOLE 5.10
 - udział w budowie programu do obliczeń kwantowo-chemicznych, ukierunkowanego na zastosowania dydaktyczne [2]. Praca nad zagadnieniami:
 - * wyznaczanie grupy punktowej symetrii i wyrównanie geometrii do znalezionej, z zadaną dokładnością, grupy symetrii,
 - * wielofunkcyjny *logger*.
- Konstrukcja aparatury naukowej, projektowanie i konstrukcja układów elektronicznych (technika analogowa i cyfrowa, w tym mikroprocesorowa),
- Biegła znajomość języków programowania: C/C++, Fortran 90, AWK, symboliczny 80x86, sh/bash, PHP, SQL, Python oraz systemu składu tekstu $\text{\TeX}$ / $\text{\LaTeX}$.
- Biegła znajomość zagadnień administracji i konfiguracji systemów uniksowych,
- Biegła znajomość technologii internetowych i baz danych, w tym programowania asynchronicznych aplikacji internetowych (AJAX).
- Dobra znajomość technologii stosowanych w obliczeniach równoległych, w tym technologii związanych z sieciami *infiniband*.

1.15 Zainteresowania pozanaukowe

- Astronomia obserwacyjna, astrofotografia, fotografia przyrodnicza, pływanie, narciarstwo.



1.16 Aneks tomu 1 (udział w konferencjach)

1.16.1 Lista referatów i komunikatów

Przed uzyskaniem stopnia doktora

1. A. Barański, A. Kotarba, W. Piskorz, „Termiczna desorpcja potasu z modelowych katalizatorów syntezy amoniaku”, Kongres Technologii Chemicznej, Wrocław, 1997 r.
2. E. Broclawik, W. Piskorz, „Properties of a metal site moderated by oxygen ligands: DFT study of methane dissociation on $[\text{VO}_n, n = 0 - 4]$ vanadium-oxygen systems”, Cetraro, Włochy, 1998 r.
3. E. Broclawik, T. Borowski, W. Piskorz, „Oddziaływanie centrów aktywnych w układach katalitycznych i biologicznych z ligandami: modelowanie kwantowo-chemiczne”, Polanica-Zdrój, 14-18.09.1998 r.

Po uzyskaniu stopnia doktora

4. W. Piskorz, Z. Sojka, „Influence of potassium promotion on electronic structure of Mo_2C and its interaction with H_2 “, Fifty Years of Theoretical Chemistry in Poland, Kraków, 13-15.05.2002 r.
5. W. Piskorz, Z. Sojka „DFT modeling of active ensembles in Mo_2C catalyst”, „Matériaux Carbonés et Catalytiques pour l'Environnement”, Zakopane, 25.09.2003 r.
6. W. Piskorz, A. Kotarba, G. Adamski, Z. Sojka, C. Sayag „Hydrodenitrogenation of indole over Mo_2C catalyst: insight into mechanistic events through DFT modeling”, International Symposium on Air Pollution Abatement Catalysis (APAC), Kraków, 21-24.09.2005 r.
7. W. Piskorz, A. Kotarba, G. Adamski, Z. Sojka, C. Sayag – komunikat, „Hydrodenitrogenation of indole over Mo_2C catalyst: insight into mechanistic events through DFT modeling”, International Symposium on Air Pollution Abatement Catalysis (APAC), Kraków, 21-24.09.2005 r.
8. A. Kotarba, A. Adamski, F. Zasada, P. Stelmachowski, W. Piskorz, Z. Sojka „Decomposition of N_2O over Perovskites and Spinel”, Annual meeting of the EUREKA Project E!3230, Kraków, 2005 r.
9. F. Zasada, P. Stelmachowski, A. Adamski, W. Piskorz, A. Kotarba, Ch. Dujardin, J.-F. Dacquin, P. Granger, Z. Sojka „Low-temperature N_2O Decomposition on Perovskite and Spinel Systems” Annual meeting of the EUREKA Project E!3230, Paryż, Francja, 16-17.02.2006 r.
10. F. Zasada, W. Piskorz, Z. Sojka „Modelowanie DFT oddziaływania N_2O z powierzchnią MgO — wpływ defektów morfologicznych”, XXXVIII Ogólnopolskie Kolokwium Katalityczne, Kraków, 15-18.03.2006 r.
11. F. Zasada, P. Stelmachowski, A. Adamski, W. Piskorz, A. Kotarba, „Abatement of N_2O over perovskite and spinel catalyst”, Annual meeting of the EUREKA Project E!3230, Zakopane, 18-19.09.2006 r.
12. F. Zasada, W. Piskorz, P. Pietrzyk, A. Kotarba, Z. Sojka: „Decomposition of N_2O at Mild Temperatures – CSMM Investigations”, Catalysis for Environment: Depollution, Renewable Energy and Clean Fuels, International Annual Meeting 2006, Zakopane, 20-23.09.2006 r.

13. F. Zasada, P. Stelmachowski, W. Piskorz, A. Adamski, A. Kotarba, Z. Sojka „Decomposition of N_2O via Anionic Redox Mechanism on Oxide Surfaces”, 35. Inorganic Reaction Mechanisms Meeting, Kraków, 2006 r.
14. F. Zasada, W. Piskorz, A. Adamski, P. Stelmachowski, A. Kotarba, Z. Sojka „Mechanisms of N_2O Decomposition over Perovskite and Spinel Systems”, Annual Meeting of the EUREKA Project E!-3230, Paryż, Francja, 15-16.02.2007 r.
15. F. Zasada, W. Piskorz, Z. Sojka „Zastosowanie obliczeń klasterowych i periodycznych w formalizmie DFT, jako narzędzie badań struktury elektronowej perowskitu $LaCoO_3$ w kontekście reaktywności katalitycznej”, XXXIX Ogólnopolskie Kolokwium Katalityczne, Kraków, 14-16.03.2007 r.
16. W. Piskorz, F. Zasada, P. Stelmachowski, A. Kotarba, Z. Sojka „Decomposition of N_2O over Co_3O_4 (100) surface – influence of H_2O and O_2 : DFT studies supported by TPSR experiment”, AWP 2007 – International Symposium on Air and Water Pollution Abatement, Zakopane, 21-23.06.2007 r.
17. P. Stelmachowski, W. Piskorz, F. Zasada, A. Kotarba, Z. Sojka „Catalytic decomposition of N_2O over bare and hydroxylated MgO ”, AWP 2007 – International Symposium on Air and Water Pollution Abatement, Zakopane, 21-23.06.2007 r.
18. F. Zasada, P. Stelmachowski, W. Piskorz, A. Kotarba, Z. Sojka „Electronic properties and reactivity of Sr- and Ce-doped $LaCoO_3$ in N_2O decomposition” AWP 2007 – International Symposium on Air and Water Pollution Abatement, Zakopane, 21-23.06.2007 r.
19. F. Zasada, W. Piskorz, A. Adamski, P. Stelmachowski, A. Kotarba, Z. Sojka „Mechanisms of N_2O Decomposition over Perovskite and Spinel Systems – continuation”, Annual Meeting of the EUREKA Project E!-3230, Zakopane, 17-18.09.2007 r.
20. Z. Sojka, F. Zasada, P. Stelmachowski, W. Piskorz, A. Kotarba, „Reactivity of bare and Co/Ni-doped magnesium oxide in N_2O decomposition in dry and wet conditions: experimental and DFT investigations”, Annual Meeting of the COST Action D41, Berlin, Niemcy, 21-23.10.2007 r.
21. W. Piskorz, J. Sauer, „DFT modeling of propane ODH on V_2O_5/SiO_2 ”, Annual Meeting of the COST Action D41, Kraków, 30.04-02.05.2009 r.
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23. P. Stelmachowski, G. Maniak, F. Zasada, W. Piskorz, A. Kotarba, Z. Sojka, M. Inger, M. Wilk, komunikat, „Optimization of Oxide Catalyst for Low Temperature N_2O Abatement – Synergy of Bulk and Surface Double Doping”, EuropaCatIX, Catalysis for a Sustainable World, Salamanca, Hiszpania, 30.08-04.09.2009 r.
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Tom 2

Opis badań naukowych ujętych w ramach wniosku habilitacyjnego

2.1 Wprowadzenie

Z punktu widzenia filozofii nauki rzeczywistość nie może zostać poznana w całej swej złożoności w sposób pełny. Tworzone w umyśle badacza modele są koniecznym uproszczeniem rzeczywistości, natomiast jego wiedza o nich jest pełna. Modelowanie rzeczywistości sprowadza się do uzyskiwania z postulowanego modelu – za pomocą wybranej teorii – obserwabli, czyli wielkości matematycznych o bardzo różnej złożoności – są to np. wielkości skalarne, tensorowe, czy też tzw. wolumetryczne, czyli określone na siatce punktów. Eksperyment naukowy również prowadzi do wyznaczania wielkości liczbowych, które formalnie również można potraktować jako obserwabli. Proces weryfikacji modelu sprowadza się zatem do konfrontacji obserwabli uzyskanych wskutek modelowania z tymi uzyskanymi doświadczalnie. Aby model uznać za poprawnie odzwierciedlający układ rzeczywisty konieczny jest zatem proces sukcesywnej weryfikacji założeń tego modelu względem kolejnych zastosowanych metod doświadczalnych.

Wskutek znacznego postępu metod obliczeniowych chemii teoretycznej oraz gwałtownego wzrostu wydajności obliczeniowej sprzętu komputerowego w ostatnich dekadach modelowanie kwantowo-chemiczne może być obecnie w wielu wypadkach uważane za nieodzowną metodę komplementarną do metod doświadczalnych.

Przyjąłem więc, jako rutynowy sposób postępowania, połączenie w sposób „samouzgodniony” własnego modelowania kwantowo-chemicznego z doświadczalnymi wynikami otrzymanymi przez współpracowników w obrębie zespołu oraz spoza tej grupy – z innych krajowych i zagranicznych ośrodków naukowych.

W niniejszym rozdziale (podrozdział 2.3.1) opisane są wybrane aspekty metodologiczne, przede wszystkim niestandardowe, w odniesieniu do własnych artykułów. Podane są tam również odnośniki do literatury. Dalej omówione zostaną kolejno zagadnienia prowadzące od badań morfologii nanoziaren (rozdział 2.3.2), modelowanie adsorpcji za pomocą termodynamiki *ab initio*, poprzez funkcjonalizację i badanie powierzchni (rozdział 2.3.3) aż do symulacji *ab initio* kinetyki reakcji w układach heterogenicznych (rozdział 2.3.4).

Modelowanie właściwości chemicznych ciała stałego obejmuje szeroki zakres struktur zawartych między dwoma skrajnymi przypadkami, którymi są **proszki** o niekontrolowanej morfologii ziaren, a z drugiej strony

dokładnie zdefiniowane **monokryształy i cienkie filmy**. W obszarze pomiędzy nimi znajdują się, bardzo interesujące z punktu widzenia możliwości uzyskania żądanych właściwości, **nanostrukturalne** układy o dobrze zdefiniowanej morfologii.

Osią przewodnią mojego dorobku jest **badanie właściwości ciała stałego**, takich jak **morfologia, stabilność termodynamiczna** czy **struktura elektronowa**, w kontekście **aktywności katalitycznej oraz fotochemicznej**, a także **właściwości** eksponowanych płaszczyzn. Dorobek ten koncentruje się także wokół zagadnień poszukiwania **związków** między własnościami **w skali atomowej**, a właściwościami **makroskopowymi**, szczególnie **aktywnością katalityczną**.

Złożoność układów rzeczywistych stawia **znaczące wymagania** w odniesieniu do **warsztatu** badawczego. Efektywne wykorzystanie oprogramowania kwantowo-chemicznego do badania **niestandardowych** układów i **nietrywialnych** modeli, wymaganych do opisu **realnych** układów, wymagało opracowania przeze mnie szeregu narzędzi – programów służących do budowy struktur, do konwersji danych między różnymi formatami, oraz do ekstrakcji interesujących informacji z powstałych plików wynikowych, a przede wszystkich modyfikacji i rozbudowy istniejącego oprogramowania kwantowo-chemicznego.

Zapotrzebowanie na stały i niezawodny dostęp do znacznych zasobów obliczeniowych, a także potrzeba wpływu na sposób ich funkcjonowania, skłoniły mnie do konstrukcji **własnego klastra** obliczeniowego (*vide* punkt 2.6.6 na stronie 189).

W modelowaniu procesów heterogenicznych zaznacza się, oprócz wymienionych wyżej zagadnień, także **dyskretna natura** procesów elementarnych. Powoduje to konieczność zastosowania takich modeli, jak dwuwymiarowy gaz, czy kinetyka Monte-Carlo. Z kolei, na ogół wysoka temperatura heterogenicznych procesów katalitycznych wymusza **uwzględnienie takich parametrów termodynamicznych**, jak realistyczna temperatura i ciśnienie. Sama zaś natura **słabych oddziaływań** z powierzchnią w stadium pre-adsorpcji powoduje konieczność uwzględnienia oddziaływań dyspersyjnych. Obsadzenie **wyższych oscylacyjnych stanów wzbudzonych** (płaska w okolicach minimum powierzchni energii potencjalnej, wysoka temperatura) wymaga uwzględnienia ich **anharmoniczności**, a także **sprzężeń oscylacyjno-rotacyjnych**.

Nie można zapomnieć, że podczas adsorpcji rozpoczyna się oddziaływanie struktury elektronowej adsorbentu i adsorbentu. Poprawne modelowanie heterogenicznych procesów katalitycznych wymaga zbadania **kanałów komunikacji elektronowej** między adsorbentem a powierzchnią katalizatora, a także między powierzchnią a wnętrzem ciała stałego.

2.2 Lista artykułów stanowiących podstawę do wniosku habilitacyjnego wraz z uwzględnieniem wkładu osobistego habilitanta

Do postępowania habilitacyjnego zgłoszone zostały osiągnięcia naukowe przedstawione w cyklu **9 artykułów** opublikowanych w latach 2010-2013. Prace te zostały ujęte tytułem: „**Kwantowo-chemiczne modelowanie zależności między strukturą i morfologią nanoziaren tlenków a ich własnościami elektronowymi i aktywnością katalityczną**” i charakteryzują się wskaźnikami sejentometrycznymi o następujących wartościach:

- Sumaryczny współczynnik oddziaływania (ang. *impact factor*, IF) za rok 2012 równy **59,49**,
- Punktacja MNiSW równa **335**,
- Średnia wartość współczynnika oddziaływania, wyznaczona na jedną publikację z tego cyklu, wynosi **6,61**,

- Liczba cytowań: **212** (z wyłączeniem cytowań własnych: **196**).

[H1] F. Zasada*, **W. Piskorz**, S. Cristol, J.-F. Paul, A. Kotarba, Z. Sojka*, „Periodic Density Functional Theory and Atomistic Thermodynamic Studies of Cobalt Spinel Nanocrystals in Wet Environment: Molecular Interpretation of Water Adsorption Equilibria”, *J. Phys. Chem. C* **114** (2010), 22245.

(IF = 4,805; MNiSW = 35, liczba cytowań = 10).

Wkład osobisty: 40%. Zaprojektowanie modeli obliczeniowych; wykonanie części obliczeń kwantowo-chemicznych, przygotowanie oprogramowania do wizualizacji i pomiarów konstrukcji Wulffa, udział w dyskusji wyników oraz opracowaniu manuskryptu, wykonanie części rysunków.

[H2] F. Zasada, **W. Piskorz**, P. Stelmachowski, A. Kotarba, J.-F. Paul, T. Płociński, K. J. Kurzydłowski, Z. Sojka* „Periodic DFT and HR-STEM Studies of Surface Structure and Morphology of Cobalt Spinel Nanocrystals. Retrieving 3D Shapes from 2D Images”, *J. Phys. Chem. C* **115** (2011), 6423.

(IF = 4,805; MNiSW = 35, liczba cytowań = 9).

Wkład osobisty: 30%. Część obliczeń kwantowo-chemicznych, ustalenie optymalnego parametru Hubbarda i pozostałych parametrów obliczeniowych. Udział w dyskusji wyników i redakcji manuskryptu.

[H3] **W. Piskorz***, J. Gryboś, F. Zasada, S. Cristol, J.-F. Paul, A. Adamski, Z. Sojka* „Periodic DFT and Atomistic Thermodynamic Modeling of Surface Hydration Equilibria and Morphology Prediction of Monoclinic ZrO₂ Nanocrystals”, *J. Phys. Chem. C*, **115** (2011), 24274.

(IF = 4,805; MNiSW = 35, liczba cytowań = 3).

Wkład osobisty: 50%. Część obliczeń kwantowo-chemicznych; przygotowanie oprogramowania do analizy morfologii (konstrukcja Wulffa). Modelowanie zależności energii swobodnej (a stąd także równowagowej **morfologii**) od rozmiaru ziarna za pomocą **autorskiego programu** [3] (*vide* rozdział 2.3.2 na stronie 31). Analiza wyników w ujęciu izotermy Fowlera-Guggenheima (umożliwiającej łatwą analizę energii adsorpcji, w tym oddziaływań lateralnych, poszczególnych cząsteczek adsorbentu).

Jestem **pierwszym autorem** tego artykułu i jednym z **autorów korespondujących**.

[H4] **W. Piskorz***, J. Gryboś, F. Zasada, P. Zapała, S. Cristol, J.-F. Paul, Z. Sojka* „Periodic DFT Study of the Tetragonal ZrO₂ Nanocrystals – Equilibrium Morphology Modeling and Atomistic Surface Hydration Thermodynamics”, *J. Phys. Chem. C*, **116** (2012), 19307.

(IF = 4,805; MNiSW = 35, liczba cytowań = 0).

Wkład osobisty: 50%. Istotna część obliczeń kwantowo-chemicznych. Modelowanie zależności energii swobodnej oraz **równowagowej morfologii** od rozmiaru ziarna za pomocą **autorskiego programu** [3] (*vide* rozdział 2.3.2 na stronie 31). Analiza wyników w ujęciu izotermy Fowlera-Guggenheima.

*Tu i poniżej gwiazdką wyróżniono nazwisko autora korespondującego / autorów korespondujących

Jestem **pierwszym autorem** i jednym z **autorów korespondujących**.

[H5] F. Zasada, **W. Piskorz**^{*}, S. Godlewski^{*}, J. S. Prauzner-Bechcicki, A. Tekiel, J. Budzioch, P. Cyganik, M. Szymonski, Z. Sojka, „Chemical Functionalization of the TiO₂(110)-(1×1) Surface by Deposition of Terephthalic Acid Molecules - a DFT and STM Study”, *J. Phys. Chem. C* **115** (2011), 4134.

(IF = 4,805; MNiSW = 35, liczba cytowań = 10).

Wkład osobisty: 40%. Wykonanie **istotnej części obliczeń DFT** struktury geometrycznej cząsteczek TPA zaadsorbowanych na TiO₂(110) oraz wykonanie **wszystkich symulacji** obrazów mikroskopii tunelowej (STM) w formalizmie Tersoffa-Hamanna, a także uczestnictwo w redakcji artykułu.

Jestem jednym z **autorów korespondujących**.

[H6] S. Godlewski^{*}, A. Tekiel, **W. Piskorz**^{*}, F. Zasada, J. S. Prauzner-Bechcicki, Z. Sojka, M. Szymonski „Supramolecular Ordering of PTCDA Molecules – the Key Role of Dispersion Forces in an Unusual Transition from Physisorbed into Chemisorbed State”, *ACS Nano*, **6** (2012), 8536.

(IF = 11,421; MNiSW = 45, liczba cytowań = 2).

Wkład osobisty: 45%. **Zaplanowanie szeregu modeli** (zapewniających zgodność z eksperymentem LEED) i wykonanie części obliczeń DFT struktury geometrycznej cząsteczek PTCDA zaadsorbowanych na powierzchni TiO₂(110), włączając w to obliczenia **dynamiki molekularnej *ab initio***, oraz wykonanie **wszystkich symulacji** obrazów mikroskopii tunelowej (STM) w formalizmie Tersoffa-Hamanna oraz Bardeena, wykonanie **obliczeń gęstości stanów elektronowych**, a także uczestnictwo w redakcji artykułu.

Jestem jednym z **autorów korespondujących**.

[H7] M. Kolmer, A. A. Ahmad Zebari, J. S. Prauzner-Bechcicki^{*}, **W. Piskorz**, F. Zasada, S. Godlewski, B. Such, Z. Sojka, M. Szymonski, „On-Surface Polymerization on Titanium Dioxide: Polyanthrylene on TiO₂(011)-(2×1) surface”, *Angew. Chem. Int. Ed.*, **52**, (2013), 1. DOI: 10.1002/ange.201303657.

(IF = 13,455; MNiSW = 45).

Wkład osobisty: 45%. Planowanie modelowania kwantowo-chemicznego; wykonanie obliczeń DFT struktury geometrycznej cząsteczek 10,10'-dibromo-9,9'-biantrylu (DBBA) zaadsorbowanych na powierzchni TiO₂(110) oraz wykonanie **wszystkich symulacji** obrazów mikroskopii tunelowej (STM) w formalizmie Tersoffa-Hamanna. Istotny wkład w **interpretację** obrazów STM oraz w **opracowanie mechanizmu** reakcji polimeryzacji DBBA na powierzchni TiO₂(110). Uczestnictwo w redakcji artykułu.

[H8] **W. Piskorz**^{*}, F. Zasada, P. Stelmachowski, O. Diwald, A. Kotarba, Z. Sojka^{*} „Computational and Experimental Investigations into N₂O Decomposition over MgO Nanocrystals – From Thorough Molecular Mechanism to *ab initio* Microkinetics”, *J. Phys. Chem. C* **115** (2011), 22451.

(IF = 4,805; MNiSW = 35, liczba cytowań = 2).

Wkład osobisty: 60%. Większość obliczeń kwantowo-chemicznych. **Całość obliczeń mikrokinetycznych**, zarówno w domenie czasowej, jak i wielkości asymptotycznych (równowagowych) — całkowicie z wykorzystaniem **autorskiego oprogramowania** [4, 5]. Weryfikacja energii swobodnej stanu przejściowego za pomocą **autorskiego programu** [6] realizującego **metodologię TI** (*vide* rozdział „Wyjście poza przybliżenie harmoniczne — całkowanie termodynamiczne” na str. 189). Istotny udział w **dyskusji wyników** oraz redakcji manuskryptu, wykonanie wszystkich figur dotyczących symulacji mikrokinetycznych.

Jestem **pierwszym autorem** i jednym z **autorów korespondujących**.

[H9] **W. Piskorz***, F. Zasada, P. Stelmachowski, A. Kotarba, Z. Sojka* „Molecular Mechanism and Microkinetics of deN₂O Reaction over Alkaline Earth Oxides – The Role of Static and Dynamic Recombination of Peroxy Intermediates”, DOI: 10.1021/jp405459g, *J. Phys. Chem. C*.

(IF = 4,805; MNiSW = 35).

Wkład osobisty: 65%. Znaczna część obliczeń kwantowo-chemicznych. **Całość obliczeń mikrokinetycznych**, zarówno w domenie czasowej, jak i wielkości asymptotycznych (równowagowych) – całkowicie z wykorzystaniem **autorskiego oprogramowania** [4, 5], a także **modelowanie Monte Carlo** dyskretnych procesów powierzchniowych – całkowicie z wykorzystaniem **autorskiego oprogramowania** [7]. Istotny udział w **dyskusji wyników** oraz redakcji manuskryptu, wykonanie wszystkich figur dotyczących symulacji mikrokinetycznych.

Jestem **pierwszym autorem** i **autorem korespondującym**.

Za istotny element mojej pracy naukowej zaliczam także bezpośrednią współpracę z młodszymi kolegami, w tym także wprowadzanie ich w specjalistyczne zagadnienia modelowania molekularnego, oraz przygotowanie im warsztatu naukowego. W szczególności chciałbym podkreślić swój udział w rozwoju naukowym dra Filipa Zasady oraz mgr Joanny Gryboś, z którymi współpracuję od czasu ich studiów magisterskich. Młodszych współpracowników wprowadzałem w zagadnienia modelowania kwantowo-chemicznego ciała stałego. Rutynowo korzystają oni z programów mojego autorstwa do wspomagania konstrukcji modeli i przetwarzania wyników programów kwantowo-chemicznych.

Wartym podkreślenia jest też fakt, że **skonstruowany** i **zarządzany** przeze mnie **klaster komputerowy** jest istotnym narzędziem dla **innych zespołów** czy **grup badawczych** (prof. prof. Ewa Brocławik, Jerzy Datka, Janusz Szklarzewicz).

2.3 Krótkie omówienie publikacji włączonych do wniosku habilitacyjnego

2.3.1 Aspekty metodologiczne

W swoich badaniach stosowałem metody chemii kwantowej, poziomu teorii oraz sposoby modelowania wybrane optymalnie do danego zagadnienia.

Wykorzystywałem przede wszystkim modelowanie w symetrii periodycznych warunków brzegowych, w tym typu płytowego (*slab*). Stosowałem także modele klasterowe, klasterzy wbudowane w sieć ładunków punktowych, wbudowane w struktury pseudopotencjałów pozbawionych bazy funkcyjnej, czy wbudowane w periodyczne (3D) sieci ładunków punktowych (PEECM [8]).

W niniejszym rozdziale skrótowo omówię wybrane **niestandardowe** zagadnienia metodologiczne, zastosowane przeze mnie w badaniach. Przez “niestandardowe” rozumiem niewystępujące w programach kwantowo-chemicznych w wersjach, z których korzystałem w trakcie danego etapu badań, a które zaimplementowałem na użytek tych badań, albo takie, które wymagają indywidualnej parametryzacji do danego zagadnienia.

2.3.1.1 Rozwinięcia metodologii obliczeniowej opartej na DFT

DFT+D Teoria funkcjonałów gęstości, DFT, pomimo jej licznych zalet, wynikających przede wszystkim z uwzględnienia w znacznym stopniu elektronowej korelacji kulombowskiej, jest teorią jednowyznacznikową i, jako taka, nie może poprawnie oddać wielkości wielowyznacznikowych z natury, do jakich należą oddziaływania dyspersyjne (typu londonowskiego). Metody opierające się na wielowyznacznikowym rozwinięciu wieloelektronowej funkcji falowej, takie jak metoda zupełnej przestrzeni aktywnej (CASSCF) czy metody sprzężonych klasterów (CC), które te oddziaływania mogą opisać, charakteryzują się złożonością obliczeniową o kilka rzędów wielkości większą, niż DFT. Pomocny tu staje się formalizm półempirycznej parametryzacji oddziaływań dyspersyjnych S. Grimme’a [9]. Szczegóły zostały przedstawione w aneksie, w rozdziale 2.6.2.1.

Zaimplementowałem obliczanie energii, gradientów i hesjanu oddziaływań dyspersyjnych w programie do molekularnych obliczeń kwantowo-chemicznych Turbomole 5.10 [10] oraz w programie do obliczeń z periodycznymi warunkami brzegowymi VASP [11–14]. W przypadku tego ostatniego proces optymalizacji geometrii był przeprowadzany w zewnętrznej pętli **programu autorskiego**, realizującego algorytm BFGS [15], gdzie program VASP był wykorzystywany do obliczania jedynie całkowitej energii i jej gradientów, zaś krok optymalizacji, zgodnie z wymienionym wyżej algorytmem, był obliczany w programie autorskim. W ten sposób unikałem modyfikacji kodu źródłowego programu VASP, a dzięki przechowywaniu plików pomocniczych na tzw. ramdisku narzut czasowy był akceptowalny. Tak rozbudowane programy wykorzystałem m.in. w publikacji [H5], [H6] i [H9].

DFT+U Układy charakteryzujące się istotnym udziałem efektów korelacji kulombowskiej (zwane kolokwialnie „silnie skorelowanymi”), np. tlenki metali przejściowych, często wymagają wprowadzenia korekty tych oddziaływań, których opis w standardowych parametryzacji funkcjonału korelacyjno-wymennego w DFT jest niewystarczający. Opierając się na przybliżeniu homogenicznego lub niemal homogenicznego gazu elektronowego parametryzacje te prowadzą często do niedoszacowania szerokości przerwy energetycznej, a nawet prowadzą do przewidywania metalicznego stanu podstawowego tych tlenków.

Poprawkę taką można wprowadzić w formalizmie Hubbarda [16, 17], szeroko stosowanym pod nazwą DFT+*U* do opisu silnie skorelowanych układów (dalszy komentarz w rozdziale 2.6.2.2). Wartość parametru *U* z reguły dobiera się tak, aby uzyskać dobrą zgodność obliczonego widma gęstości stanów z wyznaczonym doświadczalnie. W wielu wypadkach wystarczy skalibrować parametr *U* na doświadczalną wartość przerwy energetycznej lub na wartość przerwy obliczoną z użyciem funkcjonału hybrydowego (np. B3LYP).

Metodologia DFT+*U* była przeze mnie wykorzystywana podczas modelowania, w trybie periodycznych warunków brzegowych, struktury elektronowej spinelu kobaltowego [H5] oraz rutylu [H2].

2.3.2 Modelowanie morfologii z wykorzystaniem termodynamiki *ab initio* nanoziaren tlenkowych w funkcji ich hydratacji oraz konfrontacja modelowania z obrazami HR-TEM

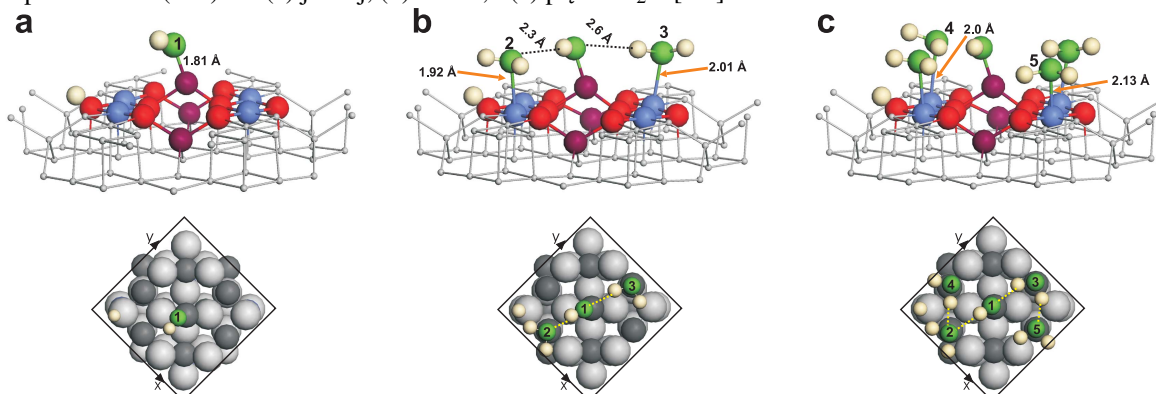
Zasadniczym elementem umożliwiającym modelowanie morfologii nanoziaren jest poznanie ich struktury elektronowej oraz równowagowej geometrii komórki elementarnej. Stosując standardowe narzędzia optymalizacji parametrów komórki, zaimplementowane w programach kwantowo-chemicznych, takich jak VASP, można napotkać na powstanie artefaktu zwanego naprężeniem Pulaya. W rozdziale 2.6.1, str. 186, zarysowane są przyczyny powstawania tego artefaktu oraz zastosowane przeze mnie sposoby uniknięcia go.

Uzyskawszy optymalną strukturę komórki elementarnej można obliczyć powierzchnię energii swobodnej ścian, charakteryzujących się kierunkiem krystalograficznym (hkl), przed adsorpcją, a następnie, korzystając z konstrukcji Wulffa [18], morfologię ziarna. Otrzymaną równowagową morfologię nanoziaren można skorygować uwzględniając poprawki wynikające z adsorpcji cząsteczek/jonów koreagentów lub pochodzących ze środowiska syntezy, a także obecnych w środowisku pracy katalizatora (*vide* 2.3.2). Termodynamika atomistyczna (inaczej termodynamika *ab initio*) opiera się na założeniu równowagi między fazą gazową, stanowiącą rezerwuuar cząsteczek adsorbentu, a powierzchnią krystalitów. Wówczas entalpię swobodną ściany (o polu powierzchni równym A) można wyrazić następującym wzorem: $G_{hkl}^a(T, p, \Theta) = \frac{1}{A} [G^{\text{slab}}(T, p, \{n_i^{\text{ads}}\}) - \sum_i n_i^{\text{ads}} \mu(T, p)]$, gdzie $\mu(T, p)$ jest potencjałem chemicznym adsorbentu, w przypadku artykułów **H1-H4** – wody. Minimum funkcji $\Delta_a G_{hkl}(T, p, n\text{H}_2\text{O})$ nie było wyznaczane bezpośrednio, natomiast wykonano obliczenia DFT dla różnych ilości zaadsorbowanych cząsteczek wody i przez porównanie wartości kolejnych $\Delta_a G_{hkl}(T, p, n\text{H}_2\text{O})$ w funkcji T i p wybrano wartość najniższą, definiującą pokrycie najstabilniejszej w tych warunkach formy.

2.3.2.1 Morfologia nanoziaren Co_3O_4 i modelowanie procesów hydratacji powierzchni

Spinele, z uwagi na wyjątkowe własności strukturalne i elektronowe, oraz wynikające z nich właściwości magnetyczne, należą do najbardziej interesujących naukowo oraz technologicznie tlenków i mają szerokie zastosowanie jako materiały ceramiczne i elektrodowe, sensory oraz katalizatory. Spinel kobaltowy, Co_3O_4 jest szczególnie często stosowany jako katalizator; w ostatnich latach stał się szczególnie interesujący jako katalizator do niskotemperaturowego rozkładu N_2O (patenty, rozdział 1.9, str. 13 oraz publikacje: 14 i 16). Funkcjonalizacja w postaci powierzchniowej promocji potasem i cynkiem skutkuje znaczną aktywnością katalityczną w temperaturze poniżej 350°C w obecności takich inhibitorów, jak H_2O , O_2 czy NO_x , powszechnie występujących w przemysłowych gazach odlotowych. Oczywistym jest zatem, że pełne zrozumienie mechanizmu procesów katalitycznych oraz konkurencyjnych procesów inhibicji nie jest możliwe bez zbadania procesu sorpcji wody na poszczególnych ścianach krystalitów spinelu kobaltowego.

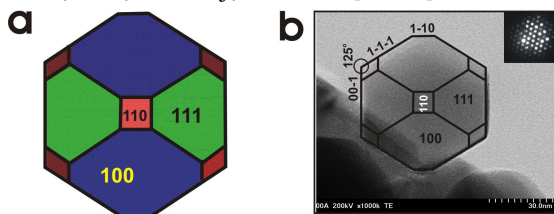
Rysunek 2.1: Widok z boku (lewa strona) i z góry (prawa strona) geometrii zaadsorbowanych cząsteczek wody na powierzchni (100) dla (a) jednej, (b) trzech, i (c) pięciu H₂O [H1].



W publikacjach [H1 i H2] przeprowadziłem badania sorpcji wody na nanokrystalitach za pomocą termodynamiki *ab initio*. Warto zaznaczyć, że wartości energii swobodnej, uzyskane z obliczeń DFT, nie były skalowane.

Określenie równowagowej morfologii nanoziaren jest przyczynkiem do badania wpływu substancji adsorbujących się na powierzchniach ziaren (w tym uwodnienia) o różnych wskaźnikach Millera na własności tych ścian, w tym także na ich udział w wypadkowej morfologii ziarna [H2].

Rysunek 2.2: Morfologia bezwodnego nanoziarna Co₃O₄ wizualizowana za pomocą konstrukcji Wulffa (a); Typowy obraz TEM (b) wraz z obrazem dyfrakcyjnym równoległej wiązki dla wybranego obszaru SAED (wstawka), który wskazuje na taką samą orientację obrazów; [za H1]



2.3.2.2 Morfologia *t* – ZrO₂ i *m* – ZrO₂

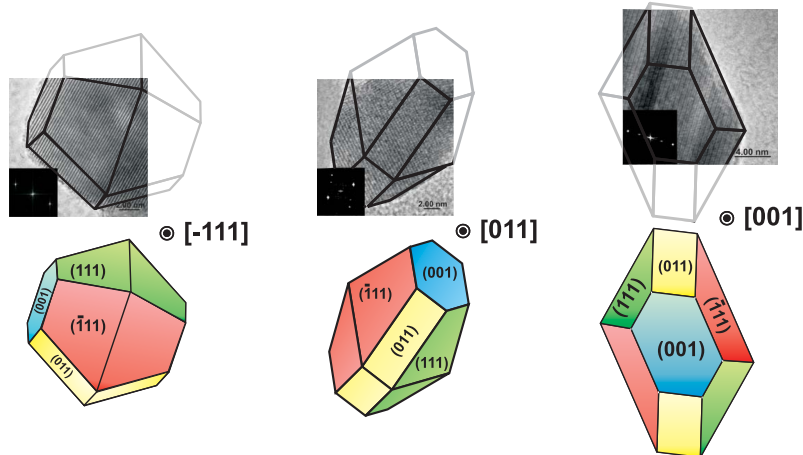
Zasadniczym wątkiem publikacji [H3 i H4] jest modelowanie morfologii tetragonalnej [H3] i jednoskośnej [H4] formy polimorficznej ZrO₂ — materiału charakteryzującego się wysoką stabilnością temperaturową [19], znaczną twardością [20], niską przewodnością cieplną oraz znacznym przewodnictwem jonowym tlenu [21]. Jest też wyjątkowo szeroko stosowanym katalizatorem [22–26] oraz podłożem katalitycznym [27–29].

ZrO₂ występuje w trzech najczęściej spotykanych formach polimorficznych: jednoskośnej *m* – ZrO₂ (oznaczenie grupy symetrii *P2₁c*), tetragonalnej *t* – ZrO₂ (*P4₂/nmc*) i regularnej *r* – ZrO₂ (*Fm $\bar{3}$ m*). W postaci większych ziaren jednoskośny ZrO₂ jest stabilny do temperatury 1175 °C, powyżej której przechodzi w formę *t* – ZrO₂, jednakże dla nanoziaren relacja względnej trwałości jest odwrócona.

Dwutlenek cyrkonu często znajduje się w środowisku zawierającym wodę, zarówno pochodzącą z syntezy, jak i z substratów lub produktów katalizowanej reakcji. Wiadomo też, że hydratacja powierzchni zachodzi zarówno w postaci niezdyssocjowanych cząsteczek H₂O, jak i w postaci zdysocjowanej [30–33], i powoduje znaczącą modyfikację natury centrów aktywnych [34] oraz ma także zasadniczy wpływ na stabilność form polimorficznych [35–37].

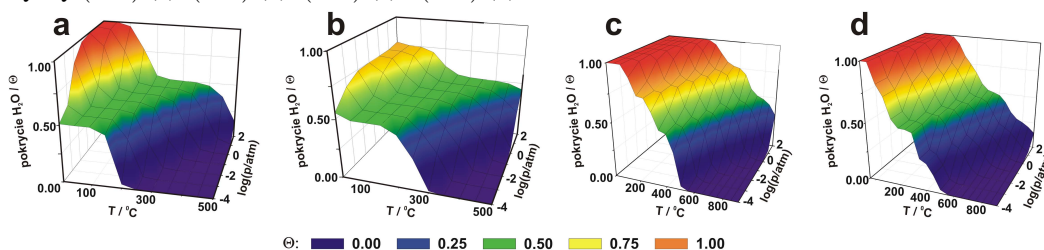
Przewidziane morfologie nanoziaren zostały skonfrontowane z obrazami wysokorozdzielczej mikroskopii elektronowej (HR-TEM) uzyskując znakomitą zgodność.

Rysunek 2.3: Obrazy mikroskopii TEM *m* – ZrO₂ oraz konstrukcje Wulffa zorientowane wzdłuż kierunków $[\bar{1}11]$, $[011]$ i $[001]$ w celu nałożenia ich na obrazy 2D.



Warto tu zauważyć, iż, w przypadku wysokiej heterogeniczności ścian w procesie adsorpcji, należy dla każdej z nich zastosować równanie wielocentrowej izotermy Langmuira: $\Theta_{hkl} = \sum_{i=1}^n x_i \frac{\beta_i^n}{1 + \sum_{i=1}^n \beta_i^n}$, gdzie β_i^n jest skumulowaną stałą trwałości adsorpcji. W tym ujęciu całkowite pokrycie $\Theta = \sum_{hkl} f_{hkl} \Theta_{hkl}$, gdzie f_{hkl} jest udziałem (ułamkiem) powierzchni ścian (hkl) w powierzchni całkowitej. Równanie wielocentrowej izotermy Langmuira może być przekształcone do postaci równania Fowlera-Guggenheima: $\ln\left(\frac{\Theta}{1-\Theta}\right) - \ln p = \alpha\Theta + \ln K$, które zakłada istnienie monowarstwy oddziałujących lateralnie molekuł, których uśrednione oddziaływanie jest określone przez parametr α . Taka właśnie analiza została przeprowadzona w artykułach [H3 i H4]. Otrzymana zależność pokrycia od temperatury i ciśnienia cząstkowego pary wodnej przedstawiona jest na Rys. 33.

Rysunek 2.4: Zależność równowagowego pokrycia *m* – ZrO₂ wodą od temperatury i ciśnienia p_{H_2O} dla płaszczyzny $(\bar{1}11)$ (a), (111) (b), (011) (c) i (001) (d).



Na rysunku tym wyraźnie zaznacza się bimodalna (a, b), trimodalna (c) i tetramodalna charakterystyka desorpcji.

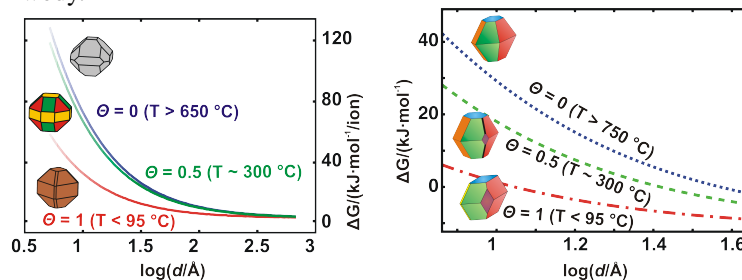
Wpływ wielkości ziaren różnych polimorfów na ich względną stabilność

Względna stabilność krystalitu jest wynikiem kompromisu pomiędzy **energią wnętrza** krystalitu (ang. *bulk energy*) a **energią powierzchniową**, związaną z obecnością ścian, krawędzi i wierzchołków [38], i skutkującą kompresją krystalitu. Energia związana z naprężeniem wnętrza, o postaci tensora typu (0,2), wyznaczanym poprzez różniczkowanie energii względem deformacji kryształu, może być przybliżona energią wynikającą

z **wewnętrznego ciśnienia hydrostatycznego**, gdyż energia związana z wytworzeniem krawędzi i naroży może być **zaniedbana** przy rozmiarach ziaren 5-100 nm. W modelowaniu przyjąłem powyższe założenia oraz stosowalność równania Younga-Laplace'a: $\Delta V/V = e = P_{\text{eff}} \cdot \beta$, gdzie β jest współczynnikiem ściśliwości objętościowej, a P_{eff} jest ciśnieniem. Z powodu wymaganej znacznej dokładności wyznaczenia modułu sprężystości, wielkość tę wyznaczyłem z dopasowania równania stanu Bircha-Murnaghana ze względną niepewnością $< 10^{-4}$.

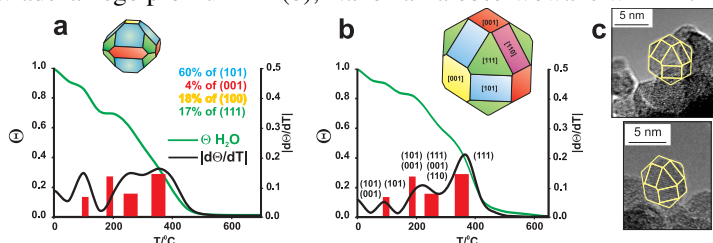
Obliczenia względnej stabilności wykonałem za pomocą **autorskiego programu** i dotyczyły one dwóch polimorficznych odmian ZrO_2 : jednoskośnej [H3] i tetragonalnej [H4].

Rysunek 2.5: Diagram względnej stabilności $t\text{-ZrO}_2$ (lewa, [H3]) i $m\text{-ZrO}_2$ (prawa, [H4]) dla trzech wartości pokryć cząsteczkami wody.



Uzyskano bardzo dobrą zgodność termicznego profilu pokrycia z doświadczalnym profilem TPD, *vide* Rys. 2.6, gdzie czerwone słupki oznaczają maksima sygnału TPD.

Rysunek 2.6: Zależność pokrycia w funkcji temperatury wyznaczona dla kształtu bezwodnego nanokryształu $t\text{-ZrO}_2$ (a); Odwrotna konstrukcja Wulffa, wraz z termiczną zależnością Θ i $\frac{d\Theta}{dT}$, przeprowadzona dla optymalnego dopasowania do doświadczalnego profilu TPD (b); Nanoziarna obserwowane w TEM.



Artykuły [H3] i [H4] są, według mojej najlepszej wiedzy, **pierwszym** tak **systematycznym studium** wyjaśniającym, **na poziomie molekularnym**, szczegóły **termodynamiki** procesu sorpcji wody na nanokryształach ZrO_2 w dobrze **zdefiniowanym środowisku**, wykonanym w oparciu o **modelowanie *ab initio***, popartym **doświadczalnie**.

2.3.3 Funkcjonalizacja powierzchni tlenkowych za pomocą cząsteczek organicznych

Samoorganizacja warstw cząsteczek organicznych na podłożach jest ważnym zagadnieniem w tzw. nanoprodukcji: w konstrukcji sensorów, w fotowoltaice, optoelektronice, fotokatalizie czy medycynie [39–44]. Zasadniczym wyzwaniem jest zrozumienie natury oddziaływań międzycząsteczkowych oraz pomiędzy zaadsorbowanymi cząsteczkami a powierzchnią, oraz uzyskanie wpływu na wzajemne relacje między tymi oddziaływaniami. Rutyl, polimorficzna odmiana TiO_2 jest szeroko badanym półprzewodnikiem i fotokatalizatorem, jest też

perspektywnym podłożem dla samoorganizujących struktur organicznych (grupy karboksylowe z alkilowymi lub aryłowymi resztami) z uwagi na wszechstronne właściwości chemiczne i łatwo modyfikowalną strukturę elektronową. Powierzchnia $\text{TiO}_2(110)$ jest bardzo stabilna i przez to często eksponowana w ziarnach i szeroko omawiana w literaturze.

2.3.3.1 Modelowanie obrazów mikroskopii tunelowej

Skaningowa mikroskopia tunelowa, STM, jest szeroko stosowanym rodzajem mikroskopii ze skanującą sondą o rozdzielczości atomowej, wykorzystującym tunelowanie prądu od elektronowych stanów zajętych próbki do sondy lub w przeciwną stronę, do wolnych stanów elektronowych próbki. Tak więc, nie rejestruje ona rzeczywistej topografii próbki, a jedynie dokonuje skaningowo pomiaru stanów elektronowych próbki w pobliżu poziomu Fermiego. Z tego względu bezpośrednia interpretacja może być trudna, a wręcz niemożliwa, stąd powszechnie stosuje się modelowanie obrazów tej mikroskopii.

Najczęściej stosowanym formalizmem modelowania obrazów mikroskopii tunelowej (STM) jest teoria Tersoffa-Hamanna [45] (T-H). Zakłada ona proporcjonalność natężenia prądu tunelowania od lokalnej gęstości stanów elektronowych (DOS) w otoczeniu poziomu Fermiego próbki w punkcie przyłożenia igły, scałkowanej po energii w ustalonym jej przedziale, wyznaczonym przez napięcie podkładu (ang. *bias voltage*). Przybliżenie to jest proste pojęciowo i bardzo szybkie obliczeniowo, jednakże daje ograniczoną rozdzielczość w płaszczyźnie próbki (przybliżenie sferycznej symetrycznej funkcji falowej, a więc orbitalu typu *s*), a także zaniedbuje geometrię i strukturę elektronową igły.

Bardziej zaawansowaną teorię rozpraszania Bardeena [46] (BST) wykorzystuje się wtedy, gdy stosowalność teorii T-H staje się dyskusyjna. Teoria BST wynika z zależnego od czasu rachunku zaburzeń Oppenheimera i jest stosowana zarówno do modelowania procesu tunelowania w mikroskopii STM, jak również do modelowania polowej emisji elektronów przy projektowaniu źródeł emisji polowej, np. w mikroskopii elektronowej. W teorii Bardeena natężenie prądu tunelowego jest proporcjonalne do splotu lokalnej DOS podłoża i DOS igły. Można w tym miejscu łatwo zauważyć, że teoria ta sprowadza się do teorii T-H jeśli w miejsce całej rozmaitości stanów elektronowych igły przyjąć pojedynczą funkcję falową o symetrii kulistej.

W teorii Bardeena układ jest podzielony na 2 podukłady, dla których znane są hamiltoniany oraz rozwiązania ich zagadnienia własnego. Ponieważ oba zagadnienia są rozwiązywane osobno, można potraktować tunelowanie igła $\leftrightarrow$ podłoże jako proces wertykalny, nieadiabaticzny. Pełny hamiltonian układu jest sumą tych hamiltonianów z dodanym tzw. hamiltonianem przeniesienia. Dzięki temu założeniu możliwe jest rozszerzenie podejścia BST, np. o rozpraszanie w obrębie bariery potencjału.

Teoria BST charakteryzuje się nieporównywalnie większą, w porównaniu do teorii T-H, złożonością obliczeniową, stąd też do tej pory stosowana była do układów niewielkich.

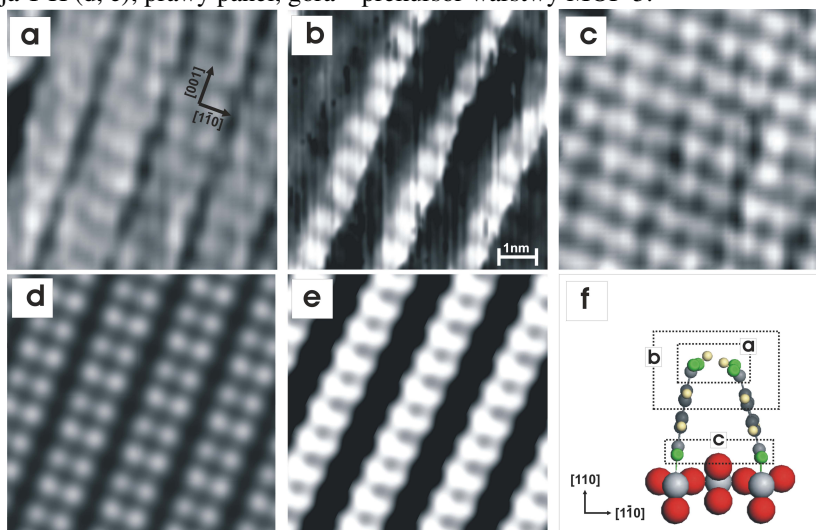
W pracach [H5, H6 i H7] wykorzystałem teorię Tersoffa-Hamanna, zaś w artykule [H6] zastosowałem dodatkowo teorię Bardeena w implementacji programu bSKAN [47, 48] do modelowania obrazu układu o **niespo-tykanym wcześniej w literaturze rozmiarze**.

2.3.3.2 Samoorganizacja TPA na powierzchni $\text{TiO}_2(110)$

Kwas tereftalowy (TPA) – kwas benzeno-1,4-dikarboksylowy – jest strukturą prototypową, bifunkcjonalną, posiadającą 2 grupy karboksylowe, z których jedna może wiązać się z powierzchnią, a druga umożliwia rozbudowę struktury, a także może stanowić warstwę buforową, zapobiegającą silnym sprzężeniom elektronowym między

adsorbatem a podłożem, które mogłoby spowodować zniszczenie właściwości optoelektronicznych [49, 50]. Właściwości monowarstwy TPA są interesujące jeszcze z uwagi na to, iż rozbudowa struktury może prowadzić do epitaksjalnego wzrostu warstwy struktur metaloorganicznych typu MOF [51]. Przegląd szeregu konformacji [H5] doprowadził do konkluzji, że przy niewielkim pokryciu preferowana energetycznie jest horyzontalna orientacja cząsteczek TPA względem powierzchni $\text{TiO}_2(110)$, natomiast przy pokryciu bliskim 1 molekuły TPA orientują się w kierunku normalnym do powierzchni i tworzą **struktury dimeryczne**. **Obrazy STM** (wykonane w Centrum Badań Układów Nanoskopowych i Zaawansowanych Materiałów NANOSAM Instytutu Fizyki UJ) **wykazują faktycznie takie zjawisko** (Rys. 2.7 a, b) i **zgodność z modelowanymi obrazami** (Rys. 2.7 d, e) **jest bardzo dobra**. Natomiast przy innych parametrach eksperymentu **struktura dimeryczna** w obrazie STM **zanika** (Rys. 2.7 c), co również uzasadniłem modelowaniem wykazując, że w tym wypadku obserwowane jest tunelowanie **do stanów atomów bliskich powierzchni** (Rys. 2.7 f).

Rysunek 2.7: Dimeryczna i monomeryczna struktura obrazów STM wraz z ich interpretacją – obraz STM (a, b, c) oraz symulacja T-H (d, e); prawy panel, góra – prekursor warstwy MOF-5.



Z pewnością warta podkreślenia jest nietrywialna interpretacja obrazów STM, a także zbadanie wpływu zaadsorbowanych cząsteczek organicznych na **właściwości elektronowe podłoża** (gęstość stanów elektronowych), a przez to na jego postulowane **właściwości fotokatalityczne** [H5].

2.3.3.3 Samoorganizacja PTCDA na powierzchni $\text{TiO}_2(110)$

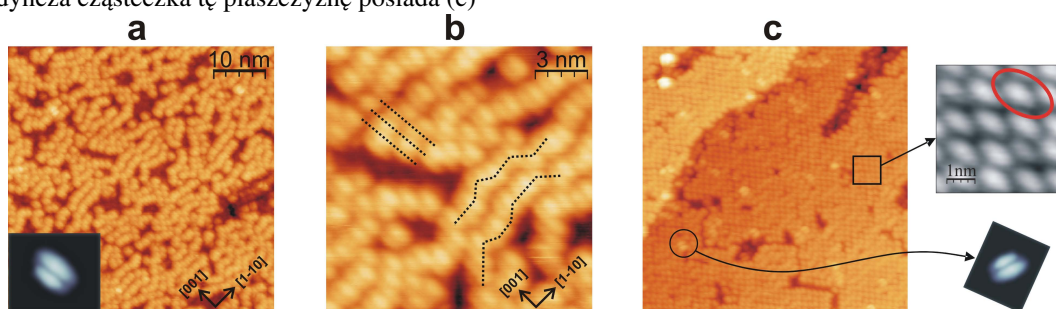
Dalsze badania nad samoorganizacją cząsteczek organicznych na TiO_2 przeprowadzono w odniesieniu do bezwodnika kwasu perylenotetrakarboksylowego, PTCDA, prototypowej cząsteczki π -sprężonej, należącej do grupy szeroko stosowanej w optoelektronice i fotowoltaice [52, 53].

Otrzymane w Centrum NANOSAM obrazy STM cząsteczek PTCDA zaadsorbowanych na powierzchni $\text{TiO}_2(110)$ przy $T = 77\text{ K}$ wykazują **różną jakościowo** postać w zależności od wielkości pokrycia. Dla $\Theta \in (0; 0,5)$ obserwuje się wyraźną **płaszczyznę węzłową** w obrębie obrazu pojedynczej cząsteczki PTCDA (Rys. 2.8 a i 2.9 a, b) oraz tworzenie **łańcuchowych struktur**, w których kątowa orientacja sąsiednich molekuł ma naturę dyskretną – charakteryzuje się kilkoma **preferowanymi wartościami kątami** (Rys. 2.8 b). Dla dużych pokryć, $\Theta \simeq 1$, obserwuje się z kolei **zanik płaszczyzny węzłowej** oraz tworzenie upakowanych **domen** budujących monowarstwę (Rys. 2.8 c; warto zauważyć, że na tym samym obrazie pojedyncza molekula leżąca

na monowarstwie zachowuje płaszczyznę węzłową). Eksperyment LEED wskazuje na współmierność $c(6 \times 2)$ monowarstwy PTCDA (kierunki $[001]$ i $[1\bar{1}0]$) względem podłoża.

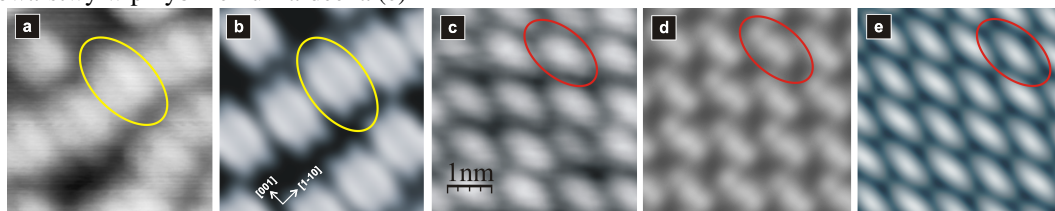
Dyskretne wartości kąta między sąsiednimi PTCDA przy niskim Θ uzasadniłem złożeniem **periodycznego potencjału** PTCDA-TiO₂ oraz oddziaływania **momentów kwadrupolowych** cząsteczek PTCDA, gdzie wypadkowy potencjał ma wyraźne minima dla kątów ok. 30° oraz 45°. Wykazałem, że płaszczyzna węzłowa, odwzorowująca płaszczyznę węzłową orbitalu LUMO, zanika przy dużych pokryciach wskutek **częściowej dearomatyzacji** wywołanej wyraźnym **odkształceniem** cząsteczki. Odkształcenie to wynika z wzajemnego oddziaływania (stłoczenia) cząsteczek adsorbentu oraz ich oddziaływaniem z powierzchnią, które to oddziaływania są zdominowane przez wkład **dyspersyjny** [H6].

Rysunek 2.8: Obrazy STM dla $\Theta \in (0; 0,5)$, widoczna płaszczyzna węzłowa (a); kątowe relacje między cząsteczkami PTCDA (b); zanik płaszczyzny węzłowej PTCDA w monowarstwie ($\Theta \simeq 1$), dla porównania pojedyncza cząsteczka tę płaszczyznę posiada (c)



Dla geometrii otrzymanej w wyniku modelowania monowarstwy PTCDA wykonałem symulację obrazu STM, który wykazuje pewien udział struktury typu jodełkowego (Rys. 2.9 d) i symetrię (6×2) , co jest odstępstwem od wyników LEED. Struktura jodełkowa jest często spotykana w przypadku adsorpcji PTCDA na jednorodnej („płaskiej”) powierzchni metalicznej, natomiast na powierzchni TiO₂(110) cząsteczki PTCDA ulegają odkształceniu wskutek oddziaływania ze skorugowaną powierzchnią. **Optymalną strukturę** znalazłem modelując adsorpcję w formalizmie **dynamiki molekularnej ab initio** (stochastyczny algorytm symulowanego wyżarzania). Wziąwszy pod uwagę znane słabe strony przybliżenia Tersoffa-Hamanna, zastosowałem modelowanie w formalizmie **Bardeena** [46] (*vide* rozdział „Modelowanie obrazów mikroskopii tunelowej” na str. 35) i tak otrzymany obraz wykazuje **znakomitą zgodność** z eksperymentem STM (Rys. 2.9 c, e) [H6].

Rysunek 2.9: Obrazy doświadczalne STM przy niskim pokryciu (a) i dla monowarstwy (c); symulacja obrazów STM w przybliżeniu Tersoffa-Hamanna dla niskiego pokrycia (b) i dla monowarstwy (d); symulacja dla monowarstwy w przybliżeniu Bardeena (e)



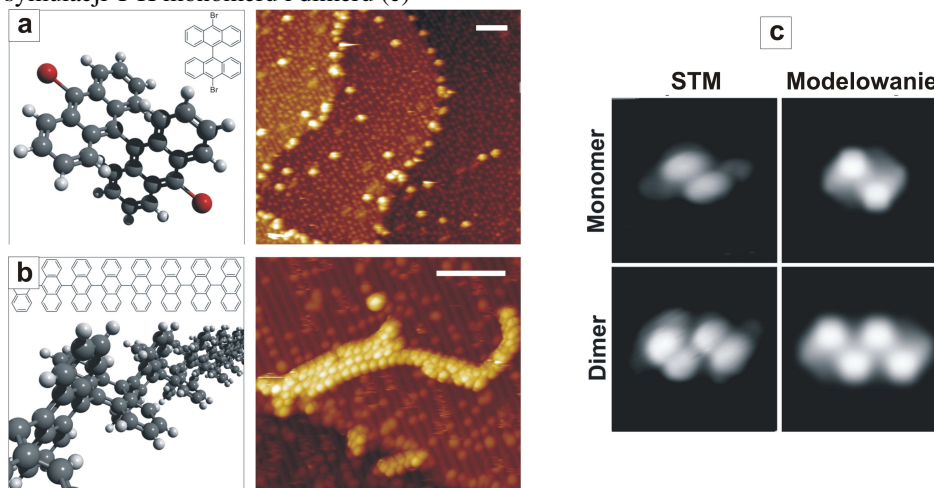
Badania te, według mej najlepszej wiedzy, stanowią **pierwszy w świecie** przypadek modelowania adsorpcji i samoorganizacji molekuł aromatycznych w postaci monowarstwy na wybranej powierzchni tlenkowej. Jest to również **pierwszy** przypadek modelowania obrazów STM **tak dużego układu** w formalizmie **Bardeena**.

Unikalne w skali światowej jest połączenie stochastycznego algorytmu poszukiwania geometrii odpowiadającej minimalnej energii (a przez to znalezienie konformacji, której **nie znajdują deterministyczne algorytmy minimalizacji**, np. BFGS) oraz wykorzystanie najbardziej zaawansowanej metodologii modelowania obrazów STM w układzie o niemal 300 atomach w komórce elementarnej.

2.3.3.4 Polikondensacja DBBA na powierzchni (011)TiO₂

Jednym z zasadniczych zadań nanotechnologii jest możliwość sterowania powstawaniem struktur oraz maszyn i urządzeń w skali nanometrowej. Jak dotąd, znane są przypadki subtelnego sterowania strukturami zaadsorbowanymi na metalach za pomocą igły STM. Jednakże taka metodologia jest niemożliwa do zastosowania przy tworzeniu większych struktur jedno- czy dwuwymiarowych z uwagi na nieakceptowalną pracochłonność. W takich sytuacjach obiecująca wydaje się samoorganizacja wyzwalana termicznie. Samoorganizacja monomerów ulegających kowalencyjnemu łączeniu została stwierdzona na powierzchniach metalicznych. Natomiast wykorzystanie powierzchni tlenkowych daje **niezwykle szerokie możliwości sterowaniem** zarówno strukturą i morfologią powierzchni, jak i jej własnościami chemicznymi, w tym kwasowością. Praca [H7] jest, według mojej wiedzy, **pierwszą na świecie**, w której **samoorganizująca polikondensacja** została stwierdzona **na powierzchniach tlenkowych** (Rys. 2.10). Zostało wykazane, że tlenki, w odróżnieniu od metali, dają znacznie większe możliwości **manipulacji morfologią** powierzchni, a przez to większą elastyczność w **planowaniu** otrzymanych w wyniku polikondensacji struktur. W pracy [H7] wykonałem **symulacje obrazowania STM** i **zinterpretowałem** wyniki doświadczalne poprzez zaproponowanie **oryginalnego mechanizmu polimeryzacji** katalizowanego przez **powierzchniowe centra protonowe**. Mechanizm ten jest **całkowicie różny**, niż znany w literaturze wolnorodnikowy mechanizm na powierzchniach metalicznych.

Rysunek 2.10: Obrazy STM monomerów DBBA (a) oraz łańcuchów oligomerycznych (b); Zestawienie obrazów STM oraz symulacji T-H monomeru i dimeru (c)



2.3.4 Mikrokinetyczne modelowanie *ab initio* katalitycznych reakcji na powierzchniach tlenków

Zrozumienie, w wyniku modelowania, wpływu szeregu czynników na morfologię ziaren i funkcjonalizację ich powierzchni pozwala na kontrolowanie tych zjawisk. Można dzięki temu racjonalnie, systematycznie i owocnie poszukiwać **optymalnej procedury** otrzymania **aktywnego katalizatora**, np. do rozkładu podtlenku azotu [H8].

Poznanie na **poziomie atomowym** wszystkich prawdopodobnych ścieżek reakcji elementarnych sprowadza się do wyznaczenia ich energii lub entalpii swobodnych. Swoje badania rozpocząłem od układów **modelowych** – tlenków metali alkalicznych, a uzyskane wyniki były pomocne przy modelowaniu katalizatora o własnościach akceptowalnych w warunkach **przemysłowych**: spinelu kobaltowego promowanego potasem i cynkiem (publikacje: nr 13, 14, 16, 23), za który zostały przyznane **patenty** (wymienione w sekcji 1.9 na stronie 13), których jestem współwłaścicielem. Opracowany katalizator do niskotemperaturowego rozkładu N_2O jest obecnie testowany w **półprzemysłowej skali** w Instytucie Nawozów Sztucznych w Puławach.

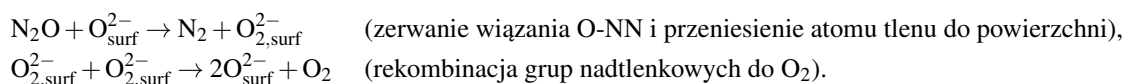
Obliczenie parametrów kinetycznych etapów elementarnych prowadzi do zaproponowania układu **równań kinetycznych**. Znakomitą weryfikacją postulowanej sieci reakcji elementarnych jest konfrontacja wynikających z rozwiązania tych równań **wielkości makroskopowych**, takich jak **parametry stanu**, z wielkościami **wyznaczonymi eksperymentalnie**. Taki też był cel publikacji [H8]. Mostem łączącym wielkości właściwych dla skali atomowej (energii swobodne) z parametrami stanu jest **modelowanie mikrokinetyczne**, które stanowi rozwiązanie w **dziedzinie czasowej** równań różniczkowych lub też ich **analiza asymptotyczna**, pozwalająca określić stany ustalone.

Procesy katalityczne z udziałem **aktywnych form tlenowych** (ROS), takich jak O^- , O^{2-} , O_2^{2-} , w układach heterogenicznych należą do jednej z **najważniejszych** grup procesów technologii chemicznej. Do tej klasy należą zarówno procesy katalitycznego utleniania, np. $deCH_4$, jak i rozkładu (np. deN_2O). Występujące we wszystkich tych procesach powierzchniowe formy ROS **zmieniają** formalny **stopień utlenienia** wskutek wymiany gęstości elektronowej z fazą stałą. Natura tych procesów wymaga zrozumienia zarówno procesów dyfuzji form ROS na powierzchnię, jak również transportu ładunku (w formie elektronów lub dziur) w obrębie ciała stałego.

I tak, zasadniczo, katalityczny rozkład N_2O może przebiegać wzdłuż kationowego mechanizmu redoks **CRM** [54–56] (przeniesienie elektronu, zachodzi np. na spinelu kobaltowym) lub anionowego mechanizmu redoks **ARM** (przeniesienie atomu tlenu, zaproponowany dla MgO [H8] i majenitu [57]).

2.3.4.1 Prosty układ modelowy: tlenki metali ziem alkalicznych

Mechanizm ARM może być, w dużym uproszczeniu, opisany w postaci dwóch etapów:



Mechanizm ten obserwuje się w przypadku tlenków o dużej pasmowej **przerwie energetycznej**, gdy nie ma dostępnych kationów o własnościach elektrodonorowych. W artykule **H8** jako modelowy tlenek o takich własnościach wybrany został przedstawiciel tlenków metali ziem alkalicznych (AEO) – MgO . Dogłębne zrozumienie tej, z pozoru banalnej, struktury i bogactwa elementarnych procesów zachodzących na ich powierzchni, jest dobrym wstępem do dalszych badań nad tlenkami zawierającymi centra zarówno ARM, jak i CRM, np. spineli.

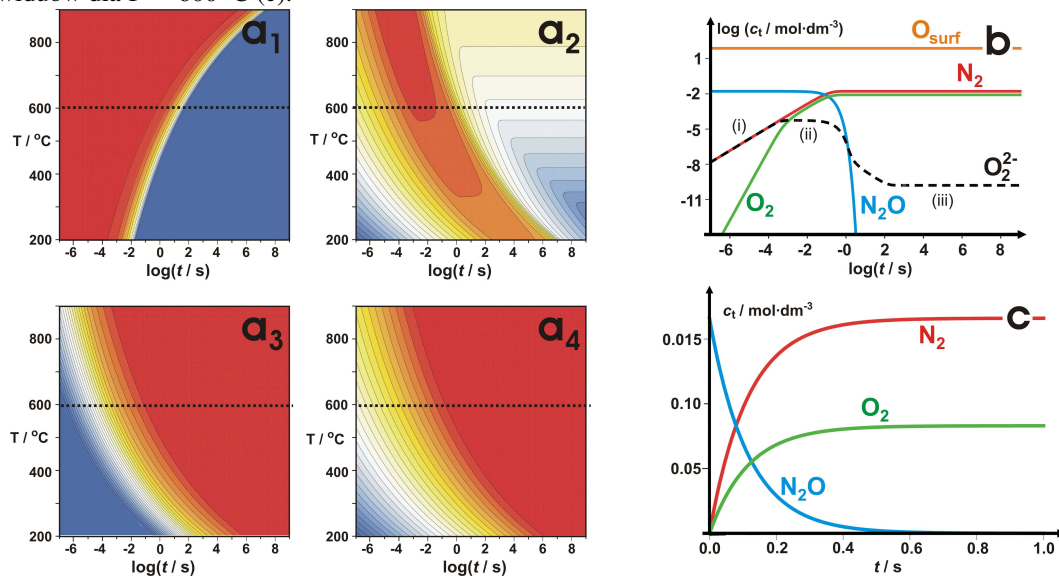
Zaproponowany układ równań kinetycznych:

$$\begin{aligned} r_1 &= k_1 \frac{p_{N_2O}}{p_0} (1 - \Theta) && \text{transfer tlenu; dysocjacja } N_2O \text{ (OAT),} \\ r_2 &= k_2 \Theta^2 && \text{rekombinacja Langmuira-Hinshelwooda (LH), } (1/k_2 = 1/k_{diff} + 1/k_{rec}) \\ r_3 &= k_3 \frac{p_{O_2}}{p_0} (1 - \Theta) && \text{readsorpcja } O_2, \\ r_4 &= k_4 \frac{p_{N_2O}}{p_0} \Theta && \text{rekombinacja Eleya-Rideala,} \end{aligned}$$

rozwiązałem za pomocą **autorskiego programu** algorytmem BDF [58] na podstawie stałych szybkości obliczonych w formalizmie teorii stanu stacjonarnego (TST) z energii swobodnych aktywacji. Funkcje rozdziału zostały obliczone z wykorzystaniem wyidealizowanych modeli: oscylatora harmonicznego, rotatora sztywnego i gazu

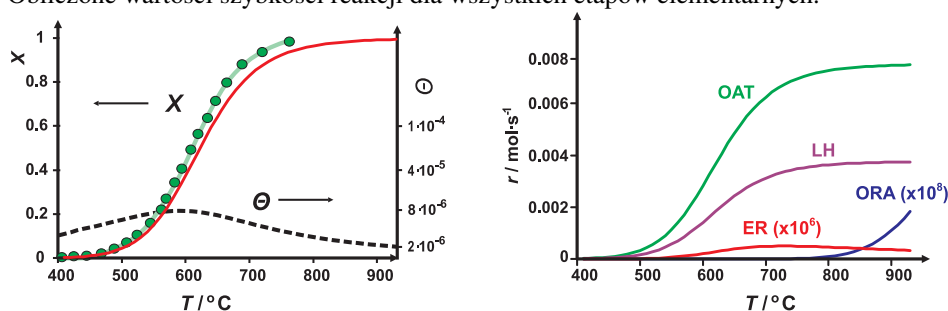
doskonałego. W celu weryfikacji dwóch pierwszych modeli obliczyłem **energię swobodną aktywacji** etapu przeniesienia atomu O dodatkowo za pomocą schematu **całkowania termodynamicznego** (TI, *vide* rozdział 2.6.5, str. 189) uzyskując wartość bardzo zbliżoną do wartości wynikającej z przybliżenia harmonicznego (odpowiednio 54,4 kcal/mol i 51,9 kcal/mol dla $T = 600^\circ\text{C}$). Żadne **skalowanie** wartości energii swobodnej (DFT) **nie było** stosowane. Wyniki modelowania reaktora TAP przedstawione są na Rys. 2.11.

Rysunek 2.11: Modelowanie zależności od temperatury i czasu stężenia N_2O (a_1), grup nadtlenkowych (a_2), O_2 (a_3) i N_2 (a_4); Wykres log – log stężeń indywiduów w funkcji czasu dla $T = 600^\circ\text{C}$ (b); Wykres liniowy stężeń indywiduów dla $T = 600^\circ\text{C}$ (c).



Wyniki modelowania asymptotycznego wraz z danymi doświadczalnymi uzyskanymi z eksperymentu TPSR przedstawione są na Rys. 2.12.

Rysunek 2.12: Zestawienie obliczonych i doświadczalnych konwersji w stanie stacjonarnym w funkcji temperatury (a); Obliczone wartości szybkości reakcji dla wszystkich etapów elementarnych.



Poprawność przewidzianego teoretycznie modelu mikrokinetycznego była także **zweryfikowana** za pomocą symulacji kinetycznego efektu izotopowego dla ^{18}O i ^{15}N (*vide* rozdział 2.6.3). Uzyskane w publikacji [H8] wyniki pozostają w **bardzo dobrej zgodności** z danymi doświadczalnymi [59].

W toku badań **wykazalem**, że nawet przy nanometrycznym rozdrobnieniu MgO , **naroża i krawędzie** krystalitów **nie są istotne** w przebiegu reakcji deN_2O , gdyż pomimo niższej energii aktywacji procesu OAT na tych centrach, niż dla eksponowanych ścian, centra te ulegają **deaktywacji** wskutek wysokiej **stabilności kinety-**

cznej powierzchniowych grup O_2^{2-} (bardzo wysokiej bariery energetycznej dla dyfuzji tych grup), wyższej, niż to ma miejsce dla eksponowanych ścian.

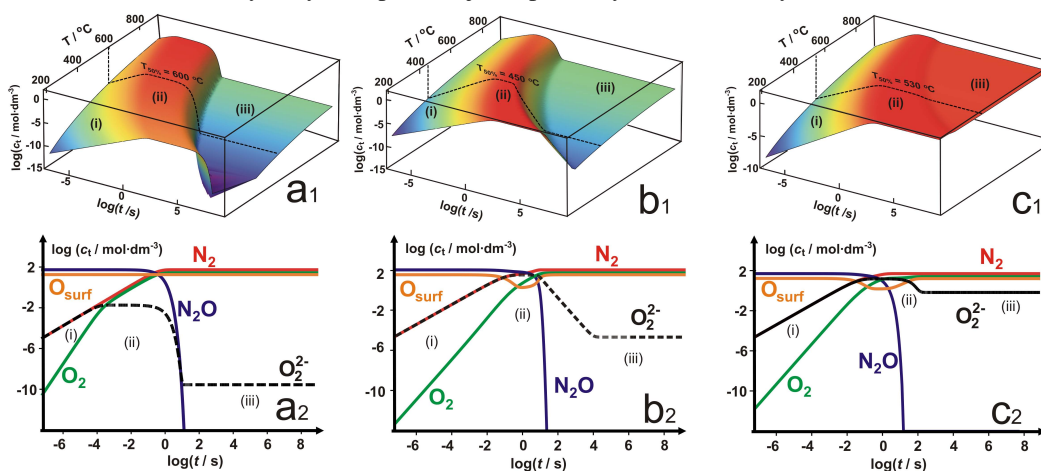
2.3.4.2 Mechanizm dyfuzyjny i bezdyfuzyjny etapu LH

Zagadnienie **dyfuzji i rekombinacji** grup nadtlennokowych (mechanizm LH) na MgO, CaO i SrO okazało się na tyle interesujące, że tematyce tej poświęcony został artykuł **H9**. Najważniejszym zagadnieniem tam rozstrzygniętym było wykazanie, w jakich warunkach zachodzi **rekombinacja bezdyfuzyjna**, a w jakich musi dojść do **dyfuzji powierzchniowej** grup nadtlennokowych.

W tym celu przeprowadziłem analogiczne modelowanie, jak w artykule **H8**, jednakże jednoetapowy proces rekombinacji LH zastąpiłem superpozycją dwóch procesów: dyfuzji powierzchniowej i rekombinacji. Z uwagi na znaczną wartość bariery energetycznej procesu dyfuzji zastosowałem model **dyskretnego gazu 2D**. W modelu tym zakłada się, że grupy nadtlennokowe mogą zajmować położenia tworzące siatkę kwadratową z węzłami zlokalizowanymi w pozycjach powierzchniowych anionów tlenkowych. Grupy te mogą wykonywać przeskoki i, jeśli dwie z nich zajmą sąsiednie węzły siatki, może dojść do ich rekombinacji. W takiej sytuacji rutynowo stosowany model **średniego pola** nie może być adekwatny.

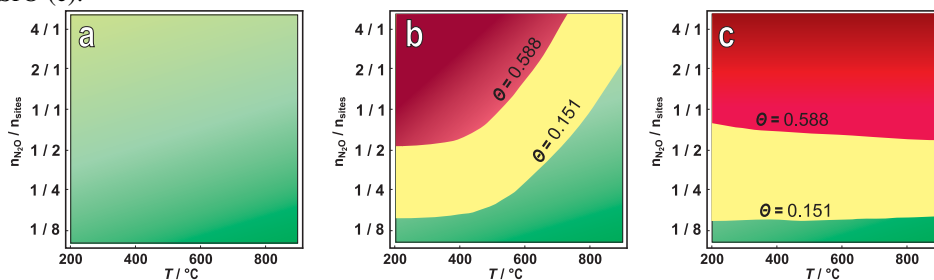
Zastosowane modelowanie mikrokinetyki dyskretniej (*vide* Aneks rozdziału 2, podrozdział 2.6.4.1, str. 188) pozwoliło na dołączenie efektów wychodzących **poza przybliżenie pole średniego** na skutek uwzględnienia **korelacji** w obsadzaniu centrów aktywnych i stosowną modyfikację wyrażenia na szybkość r_{LH} . Uzyskaną postać szybkości r_{LH} włączyłem do układu równań różniczkowych [**H9**], a wyniki symulacji przedstawione są na Rys. 2.13.

Rysunek 2.13: Wykresy 2D ewolucji w czasie pokrycia grupami nadtlennokowymi w temperaturze T dla: MgO (a_1), CaO (b_1) i SrO (c_1); Wykresy log – log stężeń poszczególnych indywiduów w czasie dla $T_{50\%}$ dla: MgO (a_2), CaO (b_2) i SrO (c_2) – wykresy te odpowiadają kropkowanym liniom na wykresach a_1 – c_1 .



Na rysunku 2.14 przedstawiono, w funkcji temperatury oraz stosunku ilości N_2O do ilości centrów powierzchniowych, obszary, w których zachodzi praktycznie wyłącznie **rekombinacja dyfuzyjna** (obszary zielone) oraz te, w których **rekombinacja nie jest poprzedzona przeskokami** (obszar czerwony). W obszarze żółtym zachodzi mechanizm mieszany.

Rysunek 2.14: Zależność pokrycia w stanie stacjonarnym od temperatury i stosunku $n_{\text{N}_2\text{O}}/n_{\text{sites}}$ dla: MgO (a), CaO (b) i SrO (c).



2.3.5 Najważniejsze wyniki i wnioski. Elementy nowości w pracach autora

Studia opisane w ramach niniejszego wniosku habilitacyjnego są oparte o **kwantowo-chemiczne modelowanie obserwabli** – wyników różnych metod badawczych, między innymi **mikroskopii tunelowej (STM)**, wysoko-rozdzielczej **mikroskopii elektronowej (HR-TEM)**, **oscylacyjnej spektroskopii** w podczerwieni (IR), czy **termoprogramowanej reaktywności**. Rezultaty modelowania konfrontowałem z wynikami doświadczeń wykonanych przez pracowników zespołu, którego jestem członkiem, oraz osób spoza Zespołu, z którymi współpracuję.

Modelowana przeze mnie morfologia bezwodnych i uwodnionych nanoziaren (**H1-H4**) charakteryzuje się **bardzo dużą zgodnością** z doświadczeniem (HR-TEM). Artykuł **H1** jest **pierwszym systematycznym studium *ab initio*** termodynamiki hydratacji nanoziaren spinelu kobaltowego o ogólnym fasetowaniu – w postaci rombikubooktaedru. Artykuł **H2** rozwinął tę tematykę weryfikując pozytywnie morfologię nanoziaren za pomocą obrazów mikroskopii HR-TEM. W artykułach **H3** i **H4** wprowadziłem do modelowania morfologii także zagadnienie **naprężenia** wewnątrz krystalitu oraz **analizę adsorpcji** w ujęciu wielocentrowej izotermi Langmuira oraz izotermi Fowlera-Guggenheima i są one, według mojej wiedzy, **pierwszym tak całościowym** opisem hydratacji i hydroksylacji nanoziaren *m*-ZrO₂ (**H3**) i *t*-ZrO₂ (**H4**) w metodologii obliczeniowej DFT, popartej mikroskopią HR-TEM oraz eksperymentem TPD wody.

Prace **H5**, **H6** i **H7** dotyczą modelowania samoorganizacji cząsteczek organicznych na powierzchniach rutylu, **wyjaśnianiu mechanizmów** rządzących tym procesem, oraz symulacji obrazów STM struktur powierzchniowych.

W pracy **H5** wykazałem, że monowarstwa TPA może **fotosensybilizować** rutyl oraz stanowić szkielet kotwiczący do powierzchni TiO₂ strukturę **MOF-5**.

W ramach publikacji **H6** wykonałem modelowanie obrazów STM w formalizmie **Bardeena** dla **największych układów** – umożliwiło to interpretację nieoczywistej konformacji cząsteczek PTCDA zaadsorbowanych na powierzchni rutylu, wynikającej z ich **samoorganizacji**, pojawiającej się przy osiągnięciu pokrycia ~1. **Wykazałem**, że utworzenie tej fazy uwarunkowane jest deformacją (a przez to częściową dearomatyzacją) cząsteczek, w którym to procesie dominującą rolę odgrywają **oddziaływania dyspersyjne**, są one swoistym „wyzwalaczem”, prowadzącym do silnej chemisorpcji.

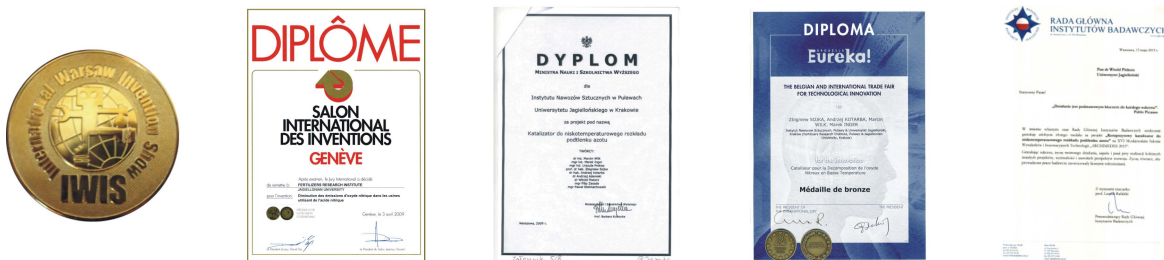
Praca **H7**, w której miałem istotny wkład w część obliczeniową, udowodniła, **po raz pierwszy**, możliwość **polikondensacji poliantryli na podłożach tlenkowych**. Opracowałem **oryginalny mechanizm polikondensacji**, katalizowanej przez powierzchniowe centra protonowe.

Artykuły **H8** i **H9** dotyczą mikrokinetycznego modelowania rozkładu N₂O na powierzchniach tlenków metali ziem alkalicznych. Przeprowadziłem w nich modelowanie adsorpcji i procesów powierzchniowych w aspekcie

statycznym (mechanizm) i dynamicznym (kinetyka). I tak, w publikacji **H8** przeprowadziłem **szczegółową analizę** etapów elementarnych tego procesu uzyskując **bardzo dobrą zgodność** z doświadczeniem (KIE, kinetyka reaktora przepływowego). Wyjaśniłem także latentną fazę eksperymentu impulsowego za pomocą analizy dynamiki pokrycia powierzchni grupami nadtlenkowymi (produktem pośrednim rekombinacji L-H).

W dalszych badaniach mikrokinetycznych (**H9**) zbadałem ilościowo dwa możliwe **scenariusze rekombinacji** w mechanizmie Langmuira-Hinshelwooda: **dynamiczną (dyfuzyjną) i statyczną (bezdyfuzyjną)**. W rozważaniach mikrokinetycznych wprowadziłem etapy o **naturze dyskretnej** oraz połączyłem modelowanie Monte Carlo z kinetycznymi równaniami różniczkowymi. Wykazałem, że pomimo **pozornego podobieństwa**, szczegóły mechanizmu rekombinacji L-H na tlenkach poszczególnych metali ziem alkalicznych są zgoła inne: dla MgO **dyfuzja** jest etapem niezbędnym w **całym badanym przedziale** stężeń N_2O i temperatur, natomiast dla SrO w przeważającym zakresie parametrów rekombinacja jest natury **bezdyfuzyjnej**.

Wątek modelowania procesu deN_2O katalizowanego domieszkowanym spinelem Co_3O_4 przyczynił się do nawiązania **współpracy z przemysłem** (Instytut Nawozów Sztucznych w Puławach), co z kolei zaowocowało **trzema patentami** (*vide* rozdział 1.9 na stronie 13). Patenty te zostały przedstawione i docenione na targach i wystawach (rozdział 1.7 na stronie 11).



Uczestniczyłem w **tworzeniu i rozwoju programów** do obliczeń kwantowo-chemicznych. **Zaimplementowałem** półempiryczne oddziaływania dyspersyjne w programie **TURBOMOLE 5.10**, **napisałem 2 moduły** do programu **QMPot** [60]: pierwszy, realizujący dynamikę Borna-Oppenheimera *ab initio*, w szczególności wykorzystywaną do obliczania zmiany **energii swobodnej algorytmem TI** oraz do **symulacji dipolowych widm oscylacyjnych** metodą **funkcji autokorelacji**, i drugi, służący do **poszukiwania stanów przejściowych** na powierzchni energii potencjalnej za pomocą algorytmu LST/CG/QST. Brałem także udział w opracowaniu programu do obliczeń kwantowo-chemicznych [2], tworzonemu z naciskiem na **przejrzystość kodu, łatwość implementacji i testowania nowych metod**, stosowany także **do celów dydaktycznych**. W toku tych prac **opracowałem i wykonałem** moduły do **wyznaczania grupy punktowej symetrii cząsteczek** oraz moduł elastycznego, wielofunkcyjnego *loggera*. Wykonane przeze mnie **oprogramowanie pośredniczące** umożliwia przygotowanie plików wejściowych (ang. *input files*) dla programu VASP za pomocą graficznego środowiska do modelowania Accelrys Materials Studio. Zastosowane rozwiązanie jest dużym ułatwieniem dla początkujących użytkowników programu VASP.

Konstrukcja **klastera obliczeniowego** Zespołu Katalizy i Fizykochemii Ciała Stałego, z wykorzystaniem **autorskiej** dystrybucji systemu Linux, będącej rozwinięciem otwartej dystrybucji CentOS, a także późniejsze zarządzanie nim oraz rozbudowa, są **moim wyłącznym osiągnięciem**. Zdecydowana większość obliczeń kwantowo-chemicznych wchodzących w skład mojego dorobku naukowego została wykonana z wykorzystaniem tego klastera: był on **jedynym komputerem** dużej mocy obliczeniowej wykorzystanym w publikacjach **H3-H6 i H8-H9**, zaś w pozostałych był wykorzystywany w istotnej części obliczeń (szczegółowe informacje zawarte są w rozdziale 2.6.6). Klaster ten jest też szeroko wykorzystywany przez osoby **spoza Zespołu**.

Opracowane przeze mnie i zainstalowania na klastrze drobne programy ułatwiły obliczenia i zdecydowanie zmniejszyły ryzyko błędów.

Wyżej opisane osiągnięcia mogą wskazywać na nabytą przeze mnie pewną **autonomię** na poziomie **zarządzania sprzętem obliczeniowym, twórczego** wykorzystywania, **adaptowania** i **rozwijania** oprogramowania kwantowo-chemicznego, oraz **stosowania** metod **chemii kwantowej** do **kompleksowego** i **skutecznego** rozwiązywania **ważkich problemów katalizy heterogenicznej**.

2.3.5.1 Zebranie technik badawczych i metod obliczeniowych stosowanych przeze mnie w pracy naukowej

Kwantowo-chemiczne obliczenia w reżimie **molekularnym** oraz z **periodycznymi warunkami brzegowymi**; modelowanie właściwości ciała stałego, takich jak: **morfologia krystalitów** (konstrukcja Wulffa) *ab initio* oraz modyfikacja ich powierzchni (izotermy adsorpcji, **funkcjonalizacja** za pomocą molekuł organicznych), wyznaczanie współczynnika ściśliwości objętościowej, **modelowanie obrazów mikroskopii STM** (formalizm **Tersoffa-Hamanna** oraz **Bardeena**) i TEM, modelowanie *ab initio* **reakcji powierzchniowych**; klasyczna dynamika molekularna; obliczenia **zmiany energii swobodnej** metodą całkowania termodynamicznego (**oprogramowanie autorskie**), symulacje **mikrokinetyczne** heterogenicznych reakcji katalitycznych (**oprogramowanie autorskie**); opracowanie **autorskiej dystrybucji** systemu operacyjnego (klastr obliczeniowy);

Do zagadnień wykraczających poza materiał włączony do wniosku habilitacyjnego należą **pomiary strumienia potasu** (atomy, jony, stany Rydberga) powstałe podczas desorpcji z powierzchni materiałów katalitycznych.

Spis literatury omówienia publikacji włączonych do wniosku habilitacyjnego

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- [4] W. Piskorz; „mikrokinetyka_t, program do rozwiązywania kinetycznych równań różniczkowych w domenie czasowej”.
- [5] W. Piskorz; „mikrokinetyka_asympt, program do rozwiązywania kinetycznych równań różniczkowych w stanie stacjonarnym, model reaktora okresowego”.
- [6] W. Piskorz; „ti.py, program do obliczania energii swobodnej metodą całkowania termodynamicznego”.
- [7] W. Piskorz; „MC_surf.c, program do symulacji Monte Carlo dyskretnej dyfuzji powierzchniowej”.
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2.4 Pełne teksty publikacji wchodzących w skład prezentowanego osiągnięcia naukowego

2.4.1 Tekst artykułu H1

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Periodic Density Functional Theory and Atomistic Thermodynamic Studies of Cobalt Spinel Nanocrystals in Wet Environment: Molecular Interpretation of Water Adsorption Equilibria

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In this paper we present a theoretical study of water sorption on cobalt spinel nanocrystals by means of plane-wave periodic density functional theory (DFT) calculations jointly with statistical thermodynamics. The three most stable (100), (110), and (111) planes exposed by Co_3O_4 were considered, and their stabilization upon water adsorption is discussed in detail. The calculated changes in free enthalpy of the investigated system under different hydration conditions along with the Wulff construction were used to predict the rhombicuboctahedral equilibrium morphology of cobalt spinel nanocrystals in different conditions, which corresponds very well to the experimental transmission electron microscopic (TEM) images. Two-dimensional surface coverage versus temperature and pressure diagrams were constructed for each of the examined (100), (110), and (111) planes to illustrate water adsorption processes in a concise way.

Introduction

Owing to their unique structure and related electronic and magnetic properties, spinels belong to one of the scientifically and technologically most attractive oxides, and they have a remarkable record of widespread applications as spintronic materials, ceramics, electrode materials, gas sensors, and catalysts.^{1–4} In particular the cobalt spinel (Co_3O_4), frequently used as a catalyst,^{5–7} has recently received a great deal of theoretical and practical attention because of its high activity in the low-temperature decomposition of nitrous oxide.^{8–10} Functionalized by surface doping with potassium and bulk doping with zinc or nickel, the resultant multicomponent catalysts exhibit excellent catalytic performance at the threshold temperature of 350 °C, even in the presence of inhibiting coreactants such as water, dioxygen, and NO_x , ubiquitously present in tail gases of nitric acid plants.¹¹

The well-described reaction of N_2O decomposition via cationic redox mechanism (CRM) depends on the ability of the catalyst to facilitate efficient NN–O bond breaking and subsequent Langmuir–Hinshelwood recombination of the resultant oxygen intermediates into molecular oxygen, mediated by surface diffusion.^{12,13} It is then not surprising that various surface planes of Co_3O_4 exhibit different activities due to distinct differences in their structure and concentration of the exposed active sites.¹⁴ However, under industrial conditions they are easily blocked by inhibitors; among them, water has been found to be the most harmful for catalyst activity.¹¹ Indeed, the deN_2O temperature-programmed surface reaction (TPSR) experiments have indicated that the coadsorbed water shifts the temperature of half-conversion of N_2O by 200 °C toward higher values.^{7,15} Nonetheless, it has been recently shown that cobalt spinel catalysts promoted by double-doping with potassium and zinc

are active enough to meet the target level of N_2O decomposition in a low-temperature regime, despite considerable inhibition by preferential adsorption of water.⁸ Furthermore, possible changes in the morphology of the catalyst upon prolonged exposure to wet conditions at elevated temperature should also be elucidated for practical applications. Detailed quantitative evaluation of the surface coverage by water admolecules at working conditions (T and $p_{\text{H}_2\text{O}}$) is thus crucial for understanding both the number and the nature of the available active centers during the deN_2O reaction and for molecular-level description of the inhibition effect of water.

Co_3O_4 is a readily accessible and thermodynamically stable form of cobalt oxide under ambient temperatures and partial pressures of oxygen. It has the structure of a normal spinel ($Fm\bar{3}m$) where half-filled octahedral sites contain $\text{Co}^{3+}(\text{d}^6)$ cations (denoted hereafter as Co^{O}), whereas tetrahedral sites exhibiting $1/8$ occupancy are filled by $\text{Co}^{2+}(\text{d}^7)$ cations (denoted as Co^{T}). Oxygen ions surrounded by one Co^{T} and three Co^{O} cations exhibit 4-fold coordination. Careful inspection of the experimental data reveals that (100), (110), and (111) planes are exposed in a number of Co_3O_4 specimens prepared by various methods.^{9,16,17} Under working conditions, the presence of adsorbed H_2O leads to surface hydroxylation, modifying thereby the surface energies of the exposed facets, which may influence the shape of the spinel nanocrystals.

In the present work we investigated the surface structure and morphology of hydroxylated Co_3O_4 rhombicuboctahedral nanocrystals by means of density functional theory (DFT) periodic calculations in conjunction with *ab initio* thermodynamics. Molecular description of water sorption, surface geometry relaxation, and stability of the (100), (110), and (111) planes at wet conditions are discussed in detail. The results are summarized in terms of theoretical water adsorption isobars. Despite extensive applications of cobalt spinel, there are only few theoretical papers devoted explicitly to DFT calculations of

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Co_3O_4 ;^{13,14} however, among them none has dealt with the surface hydroxylation and water sorption issues.

Calculation Scheme and Models

For all calculations, the DFT level of theory was chosen with use of the Vienna ab initio simulation package (VASP)¹⁸ based on Mermin's finite temperature DFT.¹⁹ The projector-augmented plane-wave (PAW)^{20,21} method for describing electron-ion interactions, together with PW91 GGA exchange functional, as parametrized by Perdew and Wang,²² were employed. All calculations were performed by use of a standard Monkhorst-Pack²³ grid with $2 \times 2 \times 2$ sampling mesh for bulk calculations and $2 \times 2 \times 1$ for slab calculations. The number of ionic layers for the proposed slab models (100), (110), and (111) were equal to 10, 7, and 12, respectively. The layer was defined by the subset of the ions lying in the same plane perpendicular to the given Miller index in the idealized structure. Although the number of layers differs, the thickness of the crystal part for all models was very similar [8.05, 8.05, and 9.35 Å for the (100), (110), and (111) planes, respectively]. The cutoff energy of 400 eV and the Methfessel-Paxton²⁴ smearing with σ parameter set to 0.1 eV were used. For solving the self-consistent field (SCF) convergence of Kohn-Sham equations, we set the energy change convergence criterion to 1×10^{-5} eV between two successive iterations. In the bulk calculations the positions of all ions were relaxed, and for the slab model the ions from the four topmost layers were relaxed, to render the net forces acting upon the ions smaller than 1×10^{-2} eV·Å⁻¹.

Starting surface geometries were obtained by cleaving the solid spinel in the normal (100), (110), and (111) directions (Figures S1–S3 and Table S1 in Supporting Information). For all planes, (1×1) unit cells were used because they expose adequate room to model high and low water coverages. The same structure of the top and bottom slab terminations, together with a vacuum separation of 10 Å between two periodically repeated slabs, allowed avoiding any unphysical interactions between slabs. To test that, the vacuum thickness was varied in the range of 8 Å up to 30 Å and a very good convergence of water adsorption energy was achieved at 10 Å, so the latter value was used for further modeling.

In the adopted computational model, both the stoichiometry of the bulk Co_3O_4 and the proper $\text{Co}^{\text{T}}:\text{Co}^{\text{O}}$ ratio of 1:2 were preserved. A more detailed description of the adopted models and the calculation schemes and their thorough validation against the experimental data was discussed in our previous paper.²⁵ In the latter case several bulk properties of Co_3O_4 , such as lattice parameters, Γ – Γ , X–X, and Γ –X band gaps, electronic and magnetic structure, were computed.²⁵ They all remain in good agreement with the experimental structure of cobalt spinel²⁶ and its magnetic and electronic properties reported elsewhere.^{27,14,28} We can thus reasonably assume that the employed formalism along with the used parametrization is capable of describing the Co_3O_4 system with adequate accuracy.

In order to compare the stability of the exposed hydroxylated facets, the interaction with water vapor should be calculated as a function of temperature and H_2O partial pressure. Beginning with adsorption energies derived from static calculations, the entropic contributions were evaluated by means of atomistic thermodynamics, where surface with the adspecies is set in equilibrium with a gas phase described beyond the usual ideal gas approximation (vide infra). The Wulffman program²⁹ in tandem with Geomview interactive 3D visualization software³⁰ was used to predict theoretical equilibrium habit of the nanocrystals (minimum surface

energy convex polyhedra), in the presence of water, following the rule

$$\gamma_{hkl}(\mathbf{n})/r_{hkl} = \text{const}; \forall hkl \quad (1)$$

where γ_{hkl} is the surface energy of the hydroxylated exposed (hkl) plane and r_{hkl} is the distance from the center of the nanocrystal to the (hkl) face.

Thermodynamic Approach

In order to describe water adsorption on various surface planes of faceted cobalt spinel nanocrystals under real process conditions, we used the well-established atomistic thermodynamic modeling.^{31–33} In this approach the gas phase plays the role of reservoir in equilibrium with the solid surface and the adsorbed molecules. We can then define the free enthalpy of a surface (A) as a function of the thermodynamic parameters (T, p) and the number of adsorbed molecules n_i^{ads} using a general expression:

$$G_{hkl}^a(T, p, \theta) = \frac{1}{A} \left[G^{\text{slab}}(T, p, \{n_i^{\text{ads}}\}) - \sum_i n_i^{\text{ads}} \mu(T, p) \right] \quad (2)$$

where $\mu(T, p)$ is the chemical potential of water.

The minimum of a given function $\Delta_a G_{hkl}(p, T, n\text{H}_2\text{O})$ is not searched directly, but instead several adsorption models that differ in number of water admolecules are compared to find the most stable one in given conditions. Hence, for each of the proposed adsorption models the free enthalpy $\Delta_a G_{hkl}(p, T, n\text{H}_2\text{O})$ is plotted as a function of T and p parameters, and the lowest one defines the most stable system in given equilibrium circumstances. The pristine, totally dehydroxylated surface with Gibbs free energy of $G^s(\text{Co}_3\text{O}_4(hkl)) = E^{\text{el}} + E_{\text{ZPE}} - RT \ln Q'_{\text{vib}}$ is taken as a reference.³⁴ Using the above tenets and notation, we may thus write down the adsorption process in the following way:



The related adsorption Gibbs energy, $\Delta_a G_{hkl}(p, T)$, can be expressed as

$$\Delta_a G_{hkl}(p, T, n\text{H}_2\text{O}) = G^s(\text{Co}_3\text{O}_4(hkl)/\{\text{H}_2\text{O}\}) - [G^s(\text{Co}_3\text{O}_4(hkl)) + G^e(\text{H}_2\text{O})] \quad (4)$$

where $G^e(\text{H}_2\text{O}) = n\mu(\text{H}_2\text{O})$. Assuming that the vibrational terms of the surface do not vary upon water adsorption in a significant degree (i.e., $\Delta G^s \approx \Delta E^{\text{el}}$), we can factorize the free energy of adsorption in two parts: an electronic contribution, $\Delta_a E^{\text{el}}$, calculated as difference of the corresponding static DFT energies at 0 K, and the change in the chemical potential of water molecules upon adsorption:

$$\Delta_a G_{hkl}(p, T, n\text{H}_2\text{O}) = \Delta_a E^{\text{el}} - n\Delta\mu(\text{H}_2\text{O}) \quad (5)$$

where $\Delta_a E^{\text{el}} = E^{\text{el}}(\text{Co}_3\text{O}_4(hkl)/\{\text{H}_2\text{O}\}) - E^{\text{el}}(\text{Co}_3\text{O}_4(hkl)) - nE^{\text{el}}(\text{H}_2\text{O})$. In turn, changes in the chemical potential of gas phase and adsorbed water are described in a classic way:

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$$\Delta\mu(p, T) = \Delta\mu^\circ(T) + RT \ln(p/p^\circ) \quad (6)$$

and can be computed by use of standard statistical thermodynamics:³⁵

$$\Delta\mu^\circ(T) = \Delta[E_{\text{ZPE}} + E^{\text{osc}}(0 \rightarrow T) + E^{\text{rot}} + E^{\text{trans}}] + RT - T(S^{\text{osc}} + S^{\text{rot}} + S^{\text{trans}}) \quad (7)$$

Those thermal contributions cover changes in the translational, rotational, and vibrational degrees of freedom upon adsorption of n molecules. In the adsorbed state the parent gas-phase translations and rotations are converted into low-frequency soft oscillations (so-called frustrated rotations and translations), whereas the hard stretching OH modes were only slightly modified (by 20 cm⁻¹ toward lower values) when water adsorbs associatively and by about ~200 cm⁻¹ for dissociative mode of adsorption. The frustrated modes due to strong binding of H₂O to the surface exhibit rather elevated, as for those type of molecular motion, frequencies of 200–300 cm⁻¹. However, the contribution to entropy and energy changes from the frustrated modes are quite small, and the major part of the thermal contribution to the chemical potential of the adsorbed water species comes from hard vibrations and is approximated by ZPE of the gas-phase H₂O molecule:

$$\Delta\mu^\circ(T, p) = \mu^\circ(T) - E_{\text{ZPE}}^{\text{g}}(\text{H}_2\text{O}) + RT \ln(p/p^\circ) \quad (8)$$

The pressure term in expression 8 was corrected by using virial expansion up to the first power of the molar volume:

$$pV_{\text{m}} = RT(1 + B/V_{\text{m}}) \quad (9)$$

The values of the coefficient B , fitted with fourth-order polynomials for various temperatures, were taken from the work of Kell et al.³⁶

The expression of the surface energy $\gamma_{\text{hkl}}(\text{H}_2\text{O})$ as a function of n adsorbed water molecules and temperature is given by

$$\gamma_{\text{hkl}}(\text{H}_2\text{O}) = \gamma_{\text{hkl}}^\circ + \Theta_{\text{hkl}} \Delta_a G_{\text{hkl}}(p, T, n\text{H}_2\text{O})/2n \quad (10)$$

with $\Theta_{\text{hkl}} = 2n/A_{\text{hkl}}$, where Θ_{hkl} stands for the surface coverage by H₂O admolecules, A_{hkl} is the area of the hkl plane, and $\gamma_{\text{hkl}}^\circ$ is the surface energy in the fully dehydrated state ($\Theta_{\text{hkl}} = 0$), calculated as

$$\gamma_{\text{hkl}}^\circ = [E_{\text{slab}}(hkl) - mE_{\text{bulk}}]/2A_{\text{hkl}} \quad (11)$$

where E_{slab} denotes the slab energy and mE_{bulk} is the energy of the m Co₃O₄ units in the bulk model.

Combination of eqs 5 and 6 gave the $\Delta_a G_{\text{hkl}}(p, T, n\text{H}_2\text{O})$ free energy as a function of $\ln(p/p^\circ)$. The calculated Gibbs free energies were used to construct Wulff shapes^{37,38} representing morphology of the cobalt spinel nanocrystalites under specified conditions (T , $p_{\text{H}_2\text{O}}$).

Free enthalpies of water adsorption for the particular surface planes hkl can be translated into changes in the surface coverage with temperature and partial pressure by use of a multisite Langmuir equation.^{39,40} In this approach the total surface

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coverage Θ_{total} is expressed as a sum of water species adsorbed on different sites in the following way:

$$\Theta_{\text{total}} = \sum_{i=1} x_i \frac{\beta_i^n}{1 + \sum_{i=1} \beta_i^n} \quad (12)$$

The expression describes adsorption on the i th site, taking into account that H₂O binds to it only if the sites with lower index number are already occupied; $x_i = N_i/N$ is the ratio of N_i sites per total number of possible N adsorption sites, whereas $\beta^n = K_1, K_2, \dots, K_n$ is the cumulative adsorption equilibrium constant, with the component K_i values describing the adsorption equilibrium constant between subsequent surface phases that differ in the number of H₂O admolecules:

$$K_i = \exp\left(-\frac{\Delta G_i - \Delta G_{i+1}}{RT}\right) \quad (13)$$

By using eq 12 we can plot Θ as a function of temperature or pressure.

Results and Discussion

Bulk Properties and Structure of Dry Surfaces. The optimized lattice constant of Co₃O₄ spinel, $a_{\text{PW91}} = 8.051$ Å, and the u parameter (describing the position of oxygen anions in the unit cell) of 0.263 Å compare well with the experimental values of 8.082 and 0.263 Å, respectively.²⁵ The calculated octahedral cobalt–oxygen and tetrahedral cobalt–oxygen bond lengths were equal to $d_{\text{Co}^{\text{O}}-\text{O}} = 1.917$ Å and $d_{\text{Co}^{\text{T}}-\text{O}} = 1.924$ Å. Both values are in a good agreement with the experimental Co^O–O and Co^T–O bond distances of 1.920 and 1.935 Å.²⁵ The stability of the bare low indexes surfaces of cobalt spinel was studied in the previous work.²⁵ Energies calculated for these surfaces are 1.39, 1.65, and 1.48 J/m² for (100), (110), and (111) planes, respectively. The microstructure of the chosen planes upon reconstruction was described in detail in our previous work, nevertheless, their basic characteristics are recalled here for the sake of clarity.

Upon cleaving of the (100) plane, each of the exposed Co^O ions loses one, and each Co^T loses two, oxygen neighbors. The concentration of the exposed tetrahedral ions (0.015 Å⁻²) is 4 times lower than the octahedral ones (0.060 Å⁻²). The Co^O_{5c} cations (the subscript “nc” describes hereafter the coordination number) located in the truncated edge-sharing octahedra (constituted by five lattice O²⁻ anions) form regularly spaced strips sequentially interconnected by the Co^T cations (Figure S4 in Supporting Information). The tetrahedral cobalt ions, in turn, are placed below the strips (Co^T_{4c} ions) and above them (Co^T_{2c} ions). There are two types of exposed oxygen ions: 4-fold O_{4c} species, preserving bulk coordination, and truncated 3-fold O_{3c} ones (with one missing bond to Co^T). The resultant slab model exhibits the surface composition {1Co^T_{2c}, 4Co^O_{5c}, 2Co^T_{4c}, 6O_{3c}, 2O_{4c}}.

Among two principal types of terminations for the (110) surface, occasionally labeled as A and B,¹⁴ for further calculations only the more stable (110)-A plane,²⁵ containing less dangling bonds, was taken into account. The (110)-A plane is terminated by 4-fold Co^O_{4c} ions with two missing oxygen bonds (Figure S5 in Supporting Information). The tetrahedral cobalt ions are surrounded by three oxygens, giving rise to 3-fold Co^T_{3c} surface species. The exposed oxygen anions (O_{3c}) exhibit the

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TABLE 1: Characterization of the Exposed (100), (110), and (111) Surface Planes

plane	$\gamma/J \cdot m^{-2}$	slab area $A_{\text{hk}}/\text{\AA}^2$	surface composition		
			Co ^O	Co ^T	O
(100)	1.39	64.8	4 Co ^O _{3c}	1 Co ^T _{2c} 2 Co ^T _{4c}	6 O _{3c} 2 O _{4c}
(110)	1.65	96.7	4 Co ^O _{4c}	3 Co ^T _{3c}	4 O _{3c} 4 O _{2c}
(111)	1.48	112.3	2 Co ^O _{3c}	4 Co ^T _{3c}	10 O _{3c} 6 O _{4c}

same trigonal coordination. The concentration of both cobalt species, equal to 0.044 and 0.033 $\text{\AA}^{-2}$ for Co^O_{4c} and Co^T_{3c}, respectively are comparable in this case. The resultant stoichiometry of the A-(110) slab model can be described as {3Co^T_{3c}, 4Co^O_{4c}, 4O_{3c}, 4O_{2c}}.

Cleavage of Co₃O₄ across the (111) plane can produce six conceivable nonequivalent terminations. The most stable one (with the lowest number of dangling bonds) is characterized by strong undersaturation of four Co^O ions, which are reduced to 3-fold coordination (Co^O_{3c}), whereas in the case of four Co^T only one O²⁻ ligand is lost (Co^T_{3c}); see Figure S6 in Supporting Information. The surface contains 10 O_{3c} and six O_{4c} oxygen species per unit cell. The concentrations of cobalt species were found to be 0.018 $\text{\AA}^{-2}$ for Co^O_{3c} and 0.036 $\text{\AA}^{-2}$ for Co^T_{3c}. The composition of the devised slab model is described by the ensemble {4Co^T_{3c}, 2Co^O_{3c}, 10O_{3c}, 6O_{4c}}. The surface compositions of all investigated planes are summarized in Table 1.

The calculated surface energies of the dry planes were next used to reveal the habit of the Co₃O₄ crystallites by using Wulff construction (Figure 1a).^{37,41} The predicted rhombicuboctahedral shape remains in an excellent agreement with the corresponding TEM picture (Figure 1b) of typically observed cobalt spinel crystallites obtained by pH-controlled precipitation.²⁵ The resultant nanocrystals expose predominantly six (100) and eight (111) low energy facets, truncated by twelve minor (110) planes of higher energy. More detail account of the morphology of nanocrystalline Co₃O₄ can be found in our other paper.²⁵

Water Adsorption. For water adsorption modeling, H₂O molecules were added to coordinatively unsaturated cobalt ions in a successive fashion to obtain full surface coverage corresponding to a monolayer. A large number of starting geometries of water admolecules was explored to find the most stable adsorption mode. To begin with, for each exposed Co site both dissociative and associative adsorption geometries were tested, whereas for highly unsaturated cobalt ions (with more than one Co–O bond missing) the multiple adsorption was assumed. For all investigated planes, the most stable sites for water adsorption are those having the most unsaturated Co ions.

(100) Plane. The optimized structure of a water molecule adsorbed on (100) plane (corresponding to H₂O coverage of $\Theta_{(100)} = 1.54 \text{ nm}^{-2}$) is shown in Figure 2a. Water adsorbs

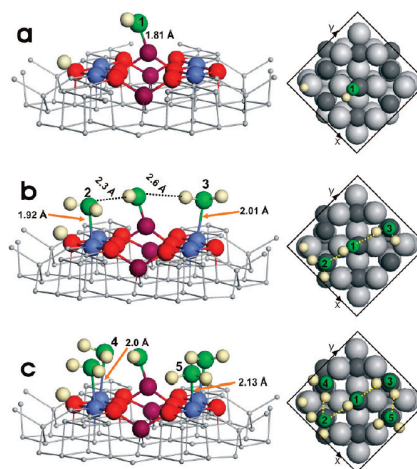


Figure 2. Lateral and top views of water adsorption geometries on (100) surface for (a) one, (b) three, and (c) five H₂O admolecules. Only the two topmost layers of the slab model are shown. Color coding: Co^O, blue; Co^T, purple; spinel O, red; water O, green; H, yellow.

dissociatively on the Co^T_{2c} sites, leading to formation of terminal hydroxyl groups (with a Co^T_{2c}–OH distance of 1.81 Å) and bridging hydroxyl groups by involving an O_{3c} surface ion. The calculated energy for this adsorption mode was found to be 1.18 eV.

As shown in Figure 2b, the second water molecule chemisorbs on Co^O_{3c} sites without dissociation. The adsorption energy of 1.04 eV includes a contribution from the hydrogen bond formed by the superficial hydroxyl group (1) and the oxygen moiety of water admolecule (2) with a Co–O(H₂) distance of ~2.3 Å. The third water molecule was deposited on the surface in a similar way (Figure 2b), but the adsorption energy is now lowered to 0.89 eV. The Co–O(H₂) bond lengths were 1.92 and 2.01 Å for the second and third water molecule, respectively. The corresponding surface density was 4.62 H₂O nm⁻² (Figure 2b). Figure 2c shows an optimized structure for five adsorbed molecules ($\Theta_{(100)} = 7.71 \text{ nm}^{-2}$). Adsorption of the last two water molecules occurs in an associative manner. The molecules reorient themselves to form a network of weak hydrogen bonds stabilizing the resultant structure. The calculated adsorption energies fall to 0.70 and 0.71 eV for the fourth and fifth admolecule, respectively. Analysis of the adsorption geometry and energetics of the last molecules indicates that the main part of their interaction is due to H-bond formation and that the interaction with the surface is rather weak. Once the fifth H₂O molecule had been accommodated, all cobalt sites were covered by water. The sixth water molecule, when deposited on the still-unsaturated cobalt sites (Co^T_{2c}–OH), is only weakly attracted, so due to quite low adsorption energy ($\Delta E_{\text{ads}} = 0.2 \text{ eV}$), this adsorption mode was not considered in further thermodynamic calculations.

(110) Plane. Adsorption of water on the (110) plane is more complex, since two types of cobalt sites (four unsaturated Co^O_{4c} ions and three Co^T_{3c} ions) are present. The most stable adsorption form of water results from dissociative coordination on the Co^O_{4c} sites ($\Delta E_{\text{ads}} = 1.45 \text{ eV}$) and corresponds to surface coverage of $\Theta_{(110)} = 1.09 \text{ nm}^{-2}$. The ensuing terminal hydroxyl group (with a Co^O_{4c}–OH distance of 1.79 Å) together with the bridging hydroxyl group, produced by interaction between the proton of the adsorbed water molecule and the surface O_{3c} ion,

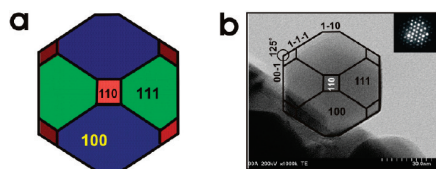


Figure 1. (a) Morphology of a dry Co₃O₄ nanocrystallite visualized by Wulff construction. (b) Typical TEM picture together with the parallel beam selected area electron diffraction (SAED) pattern (inset), revealing the same orientation of both images.²⁵

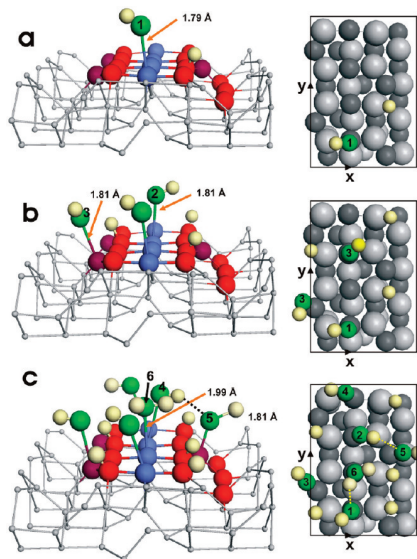
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Figure 3. Lateral and top views of water adsorption geometries on (110) surface for (a) one, (b) three, and (c) six H₂O admolecules. Only three topmost layers of the slab model are shown. Color coding: Co^O, blue; Co^T, purple; spinel O, red; water O, green; H, yellow.

are shown in Figure 3a. The second water molecule dissociates upon adsorption on Co^O_{4c} ion, and when the DFT accuracy is considered, the results are quite similar, since the energy gain is $\Delta E_{\text{ads}} = 1.40$ eV, whereas the Co^O_{4c}–OH bond length increased to 1.81 Å. The released proton forms a bridging hydroxyl group with the surface O_{3c} ion. The third water molecule binds to Co^T_{3c} sites ($\Delta E_{\text{ads}} = 1.01$ eV and $d_{\text{Co-OH}} = 1.81$ Å) in a dissociative way, forming another bridging hydroxyl group. The structure of all three adsorbed water molecules is shown in Figure 3b. The next two molecules also adsorb dissociatively: the first one on the Co^O_{4c} sites and the second on the Co^T_{3c} sites, forming a terminating (both Co–OH bonds of 1.80 Å) and a bridging hydroxyl group, similarly to the previously adsorbed molecules (Figure 3c). On the contrary, the last water molecule is adsorbed on the remaining Co^O_{4c} center in an associative fashion ($d_{\text{Co-OH}_2} = 1.84$ Å in both cases). The adsorption energies of water molecules 4, 5, and 6 (Figure 3) were 0.80, 0.63, and 0.70 eV, respectively. Surprisingly the adsorption energy of the last H₂O (no. 6) is higher than that of the preceding one (no. 5). This can be explained by reconstruction energy cost for the fifth molecule and by the fact that the last molecule forms two hydrogen bonds with the adjacent hydroxyl groups. Upon adsorption of sixth water molecule, the coverage of the (110) surface is completed.

(111) Plane. For the (111) plane the most stable form of adsorbed water is a dissociative attachment to the most exposed Co^O_{3c} sites, stabilized by interaction with the adjacent Co^T_{3c} ions. Since in our model we deal with two such sites (separated by 9.86 Å), adsorption of two first H₂O molecules can be treated independently (Figure 4a). The resultant coverage corresponds to 1.78 H₂O nm⁻². Both bridging hydroxyls, with adsorption energy of $\Delta E_{\text{ads}} = 1.55$ eV, have similar geometry with Co^O_{3c}–OH and Co^T_{3c}–OH distances of 1.80 and 2.1 Å, respectively. The surface reconstruction is rather large in the case of the first two molecules since the Co^T ion is forced to move toward the OH group by about 0.15 Å. This surface

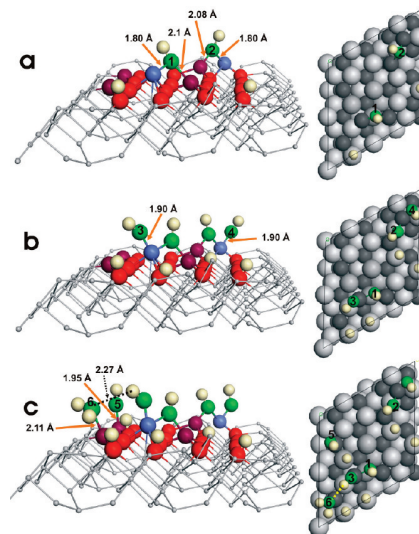


Figure 4. Lateral and top views of the water adsorption geometries on (111) plane for (a) two, (b) four, and (c) six H₂O molecules (full monolayer). Only the three topmost layers of the slab model are shown. Color coding: Co^O, blue; Co^T, purple; spinel O, red; water O, green; H, yellow.

corrugation can explain why the third and fourth molecules (no. 3 and 4 in Figure 4b) adsorbed in a nonbridging mode. They are also dissociatively adsorbed on the same Co^O_{3c} sites, giving rise to doubly hydroxylated surface Co^O_{3c} ions; however there are no adjacent unoccupied surface Co^T ions to stabilize those OH groups. The adsorption energy is considerably reduced to 0.9 eV in this case. The water coverage was further enhanced by dissociative adsorption of molecule no. 5 ($\Delta E_{\text{ads}} = 0.71$ eV) and associative adsorption of molecule no. 6 ($\Delta E_{\text{ads}} = 0.68$ eV) on the Co^T sites. Adsorption of the latter one has induced appreciable reconstruction of the previously adsorbed molecule no. 3 (Figure 4b), which resulted in formation of a new hydrogen bond ($d_{\text{O-H}} = 2.27$ Å). The calculation revealed that adsorption of the seventh H₂O molecule was too weak ($\Delta E_{\text{ads}} = 0.3$ eV) to be included in the thermodynamic model. Thus, full water coverage of the (111) plane corresponds to six admolecules per slab area, corresponding to $\Theta_{(111)} = 5.34$ H₂O nm⁻².

The calculated adsorption energies and surface coverage, together with the prime geometric parameters of the adsorbed water species, are summarized in Table 2. From a quick inspection of the results it is clear that the hydroxylation process for the (100) plane occurs in a different way than for (110) and (111) surfaces. Highly undercoordinated cobalt Co_{3c} and Co_{4c} sites located on the (110) and (111) planes bind water much more strongly than the more saturated Co_{5c} centers located on the (100) planes. Furthermore, we can assume that water dissociation is induced by a strong adsorption on the unsaturated Co ions, since we observe H₂O splitting only for the first adsorbing molecule [case of the (100) plane]. It can be concluded that the abundant surface oxygen (O_{3c}) sites are not basic enough to deprotonate a water molecule, which is clearly seen for the (100) plane.

Because the density of cationic adsorption sites is higher on the (100) plane, distances between the adjacent surface hydroxyl groups are smaller, favoring formation of hydrogen bonds. The relaxation of the (100) and (111) surfaces upon hydroxylation

TABLE 2: Basic Characteristics of Water Adsorption on the Surface of Co₃O₄ Nanocrystals^a

no.	(100) plane				(110) plane				(111) plane			
	$\Delta E_{\text{ads}}/\text{eV}$	ads center	ads type	$d_{\text{Co-O(H}_2\text{)}}/\text{\AA}$	$\Delta E_{\text{ads}}/\text{eV}$	ads center	ads type	$d_{\text{Co-O(H}_2\text{)}}/\text{\AA}$	$\Delta E_{\text{ads}}/\text{eV}$	ads center	ads type	$d_{\text{Co-O(H}_2\text{)}}/\text{\AA}$
1	1.18	Co ^T _{2c}	d	1.81	1.49	Co ^O _{4c}	d	1.79	1.56	Co ^O _{3c}	d	1.80
2	1.04	Co ^O _{3c}	a	1.92	1.40	Co ^T _{3c}	d	1.81	1.53	Co ^O _{3c}	d	1.80
3	0.89	Co ^O _{5c}	a	2.01	1.01	Co ^O _{4c}	d	1.81	0.92	Co ^O _{3c}	d	1.90
4	0.70	Co ^O _{5c}	a	2.00	0.80	Co ^O _{4c}	d	1.80	0.90	Co ^O _{3c}	d	1.90
5	0.71	Co ^O _{5c}	a	2.13	0.63	Co ^T _{3c}	d	1.81	0.71	Co ^T _{3c}	d	1.95
6					0.70	Co ^O _{4c}	a	1.99	0.68	Co ^T _{3c}	a	2.11

^a ΔE_{ads} , adsorption energy; d, dissociative mode; a, associative mode; $d_{\text{Co-O(H}_2\text{)}}$, bond length in angstroms.

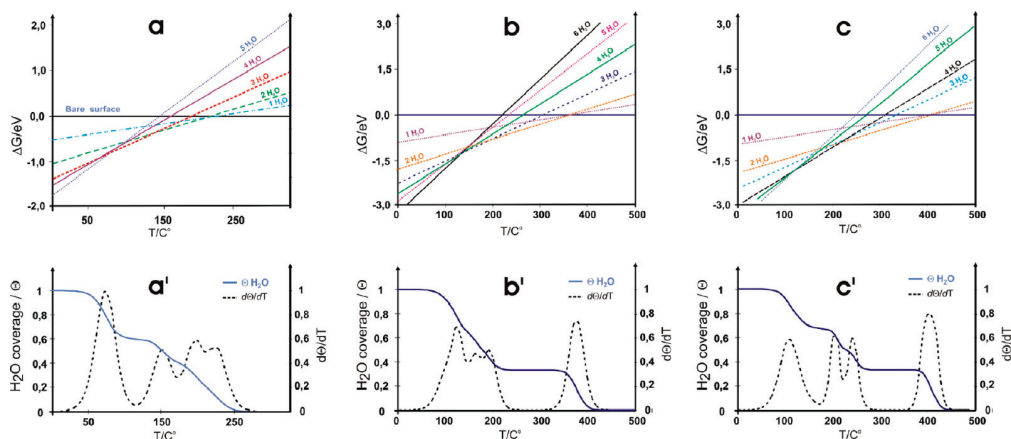


Figure 5. Gibbs free energy of water adsorption as a function of temperature at $p/p^\circ = 0.01$ bar for different numbers of adsorbed H₂O molecules, together with the corresponding surface coverage Θ and a differential curve $d\Theta/dT$, for (a) (100), (b) (110), and (c) (111) planes.

is negligible, and only for the (111) plane do we observe significant movements of surface ions upon adsorption of water. What is important is the observation that the adsorption energies of the last molecules on all the surfaces are quite similar (they all resemble the strong H-bond energy). Thus, desorption of the first molecule in temperature-programmed desorption (TPD) H₂O experiments should start at almost the same temperature for all the surfaces.

Once the molecular structure and energetics of water sorption were successfully determined by static DFT calculations, atomistic thermodynamics could be employed to construct adsorption diagrams as a function of temperature and partial pressure of water.

Surface Hydration Diagrams. The free enthalpy of water adsorption on the (100) surface plane as a function of temperature for partial pressure of water equal to 0.01 atm is plotted in Figure 5a, together with the corresponding water coverage $\Theta_{(100)}$ and a differential curve $d\Theta/dT$. The most stable adsorption form of water at a given temperature corresponds to the lowest value of the Gibbs energy in the surface energy diagram, defining variation of water coverage as a function of temperature. At low-temperature regime (below 50 °C), a monolayer of water (corresponding to five molecules) is formed by the hydroxylated Co^T_{2c} species and water adsorbed molecularly on the Co^O_{5c} sites (Figure 5a). Around 70 °C, two molecules of weakly adsorbed water leave the surface, liberating the Co^O_{5c} centers of lower affinity to water, which is easily seen as a pronounced peak in the corresponding $d\Theta/dT$ curve (dotted line in Figure 5a'). The resulting surface coverage is then reduced to $\Theta = 0.6$. The second desorption peak occurs at $T \sim 150$ °C when the next H₂O molecule leaves the surface. Finally, the

two water molecules desorb sequentially in the temperature range 200–250 °C, and above 250 °C the (100) plane becomes completely dehydrated ($\Theta = 0$).

The thermal behavior of the hydrated (110) surface (Figure 5b) is clearly different from that of the (100) surface. The monolayer of water consisting of six H₂O molecules (attached dissociatively and molecularly to the Co^O_{4c} and Co^T_{3c} sites) is stable now up to ~ 110 °C. The first portion of adsorbed water leave the surface in the temperature range of 120–210 °C, in a sequence of $2 \rightarrow 1 \rightarrow 1$ molecules, and the surface coverage falls down to $\Theta = 0.4$ (Figure 5b'). This region with two dissociatively adsorbed H₂O molecules is stable in a wider temperature window from 210 to 350 °C. Finally, around 400 °C two remaining molecules of water depart simultaneously, leaving the (110) plane in a fully dehydroxylated state (Figure 5b).

For the (111) termination, the situation is quite similar to that observed in the case of the (110) plane. The monolayer of water consists again of six H₂O molecules attached dissociatively to the Co^O_{3c} sites and molecularly to the Co^T_{3c} sites, but it is now slightly less stable (up to 80 °C). The first peak with the maximum at 100 °C (Figure 5c') is related to two water molecules desorbing from the Co^T_{3c} sites. The next two molecules associated with the Co^O_{3c} sites are released sequentially in the temperature range 210–240 °C. The resultant surface coverage of $\Theta = 0.4$ corresponds to two H₂O species dissociatively adsorbed on Co^O_{3c} sites and is stable over a wider range of temperatures (250–400 °C). The two residual water molecules dissociatively adsorbed on the Co^O_{3c} centers (stabilized additionally by interaction with the adjacent Co^T_{3c}) desorb

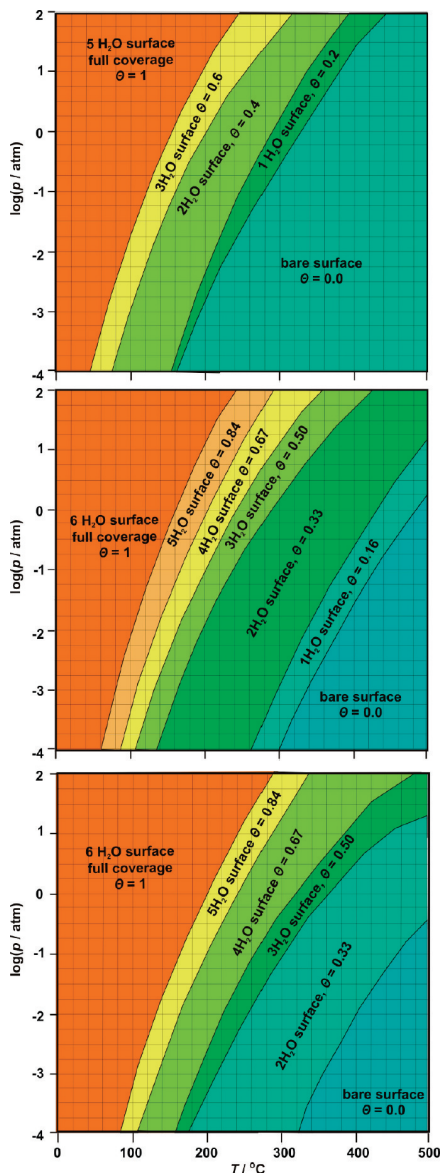


Figure 6. Two-dimensional diagrams of water coverage as a function of temperature and partial pressure of water for (a, top panel) (100), (b, middle panel) (110), and (c, bottom panel) (111) planes of cobalt spinel.

together at about 400 °C. Consequently, above 450 °C the anhydrous (111) plane is completely exposed (Figure 5c,c').

The highly exothermic adsorption of the incipient amounts of water ($\Delta E_{\text{ads}} \sim 1.5$ eV) observed on both (111) and (110) surfaces has also been found in other oxides like TiO₂,⁴² ZrO₂,⁴³ and γ -Al₂O₃.⁴⁴ It can be explained by strong Lewis acidity of the unsaturated cationic centers situated on the surface. The lower adsorption energy on the (100) plane, in turn, can be associated with its higher stability owing to the presence of the abundant Co^{O_{5c}} sites.

In Figure 6, two-dimensional $\Theta(p,T)$ diagrams of water sorption on the exposed (100), (110), and (111) planes of Co₃O₄ are shown. They help to define easily the surface coverage as a function of pressure and temperature, which is essential in explaining the harmful effect of water present in the feed on the catalytic performance of cobalt spinel.¹¹

Changes in Spinel Morphology upon Hydroxylation. Obviously, adsorption of water gives rise to anisotropic changes in the surface energy of the exposed facets of the Co₃O₄ nanocrystals. The calculated γ_{hkl} values for various temperatures are collected in Table 3. They can be used to reveal the changes in equilibrium morphology of the spinel nanocrystals as a function of experimental conditions by means of Wulff construction (Figure 7). The corresponding variation of the relative abundance of the (100), (110), and (111) planes is shown in Table 3.

Inspection of Table 3 shows that although the surface energy as a function of temperature changes in a monotonous fashion for all investigated facets, their relative abundances exhibit more involved behavior. However, the resultant modifications of the spinel shape are rather small. The most affected is the relative contribution of the (110) plane, which is neatly illustrated in Figure 7. Nonetheless, the Co₃O₄ spinel as a whole preserves essentially its rhombicuboctahedral habit, regardless of the conditions, corroborating nicely the TEM observations (Figure 1).

Once the shape of the spinel grains and the relative abundance of the exposed planes are known, we may calculate the total surface coverage as a function of temperature, since this property can directly be compared with experiment. Figure 8 shows the $\Theta_{\text{total}}(T)$ and $d\Theta_{\text{total}}/dT(T)$ profiles for water partial pressure $p = 0.01$ atm, with the relative contributions of the particular planes taken from the computed shape of spinel grains in dry (panel a) and wet (panel b) conditions.

Since those contributions do not differ much, the corresponding plots exhibit quite similar character. We can now define readily three main temperature regions of changes in water surface coverage (equivalent to water desorption peaks in equilibrium conditions). The first one occurs between 70 and 120 °C and is related to the release of molecularly adsorbed water. The second region of 180–260 °C corresponds to deletion of the dissociatively adsorbed water from the (100) plane, whereas the high-temperature region (350–420 °C) can be attributed to the last portion of water desorbing from the highly unsaturated Co^{O_{3c}} ions located on the (111) plane. In our thermodynamic model, only a monolayer adsorption of water was taken into account. Obviously, with the increasing p/p°

TABLE 3: Surface Energies of Partially Hydroxylated Planes of Co₃O₄ at Various Temperatures, Together with Their Relative Abundances^a

surface energy	room temperature	100 °C	200 °C	300 °C	>400 °C
$\gamma_{100}/\text{J} \cdot \text{m}^{-2}$ (abundance %)	1.02 (39%)	1.19 (37%)	1.36 (36%)	1.39 (39%)	1.39 (48%)
$\gamma_{110}/\text{J} \cdot \text{m}^{-2}$ (abundance %)	1.16 (13%)	1.39 (4%)	1.51 (9%)	1.58 (11%)	1.65 (11%)
$\gamma_{111}/\text{J} \cdot \text{m}^{-2}$ (abundance %)	1.04 (47%)	1.17 (59%)	1.31 (54%)	1.39 (50%)	1.48 (41%)

^a For $p = 0.01$ atm.

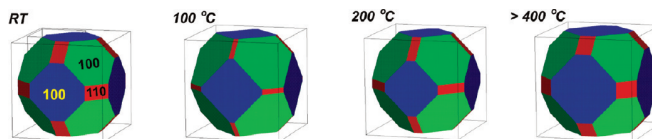


Figure 7. Wulff shapes for Co_3O_4 nanocrystals as a function of temperature for $p_{\text{H}_2\text{O}}$ set to 0.01 atm.

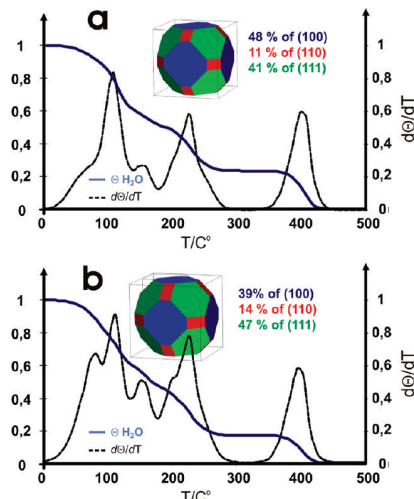


Figure 8. Total surface coverage as a function of temperature for cobalt spinel rhombicuboctahedral grains with percentage plane contributions from molecular modeling. (a) Shape calculated for bare surfaces; (b) shape calculated for hydroxylated surfaces.

values a multilayer (physical) adsorption is expected to occur by formation of hydrogen bonds with the water adspecies, desorbing usually below 100 °C. Therefore, in this region our diagrams may not be congruent with the experiment.

To our knowledge, an experimental study of water adsorption/desorption at equilibrium conditions on faceted Co_3O_4 has not been reported as yet. In a rather old paper, Takita et al.⁴³ have reported the presence of four water TPD peaks occurring at 60–80, 100–180, 200–400, and above 430 °C. Apart from the first one, obviously associated with desorption of physisorbed water, the number and the positions of the remaining maxima are in good agreement with our theoretical predictions.

Conclusions

By a combination of DFT calculations and atomistic thermodynamics, water sorption on the three most stable (100), (110), and (111) planes exposed by faceted Co_3O_4 nanograins was modeled. The calculated surface energies together with the Wulff construction demonstrate that it is possible to predict accurately the equilibrium rhombicuboctahedral shape of cobalt spinel nanocrystals under different hydration conditions in excellent agreement with the experimental TEM images. Two-dimensional (surface coverage versus temperature and pressure) diagrams constructed for each of the examined (100), (110), and (111) planes, allowed us to epitomize water adsorption processes in a concise way. By use of the shape-dependent thermodynamic model, variations of the total surface coverage with temperature were rationalized in terms of molecular structure and the stability of the corresponding water adspecies. This paper, as far as we know, is the first attempt to explain

water adsorption thermodynamics on faceted cobalt spinel nanocrystals under defined conditions in a systematic way by means of ab initio calculations.

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Supporting Information Available: Six figures, showing supercell side and top views of (100), (110), and (111) Co_3O_4 termination and perspective views of (100), (110), and (111) surfaces, and one table, listing parameters for supercells of different Co_3O_4 terminations. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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2.4.2 Tekst artykułu H2

[H2] F. Zasada, W. Piskorz, P. Stelmachowski, A. Kotarba, J.-F. Paul, T. Płociński, K. J. Kurzydłowski, Z. Sojka* „Periodic DFT and HR-STEM Studies of Surface Structure and Morphology of Cobalt Spinel Nanocrystals. Retrieving 3D Shapes from 2D Images”, *Journal of Physical Chemistry C* **115** (2011), 6423.

Periodic DFT and HR-STEM Studies of Surface Structure and Morphology of Cobalt Spinel Nanocrystals. Retrieving 3D Shapes from 2D Images

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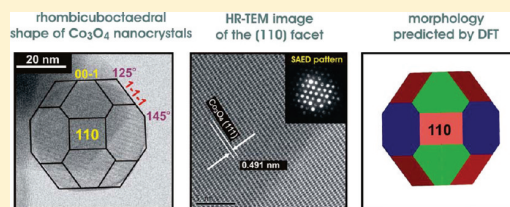
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S Supporting Information

ABSTRACT: In this study, we investigated the morphology of Co_3O_4 nanocrystals using periodic PW91 and PW91+U density functional calculations and Wulff construction. Theoretical investigations were combined with high resolution scanning transmission electron microscopy, which revealed that the examined spinel samples, obtained by pH-controlled precipitation, exhibit well-developed faceted crystallites. The results of slab calculations enabled to characterize the surface structure and reconstruction of the low index (100), (110), and (111) planes that were observed in HR-STEM pictures. The surface energies of the relaxed facets increased in the following order 1.39 J m^{-2} (100) < 1.48 J m^{-2} (111) < 1.65 J m^{-2} (110). These ab initio calculated values were used to predict a rhombicuboctaedra equilibrium habit of the cobalt spinel crystallites, by means of the Wulff plot. The obtained results were in remarkable agreement with the experimental shapes retrieved by matching 3D Wulff polyhedra to 2D STEM images observed along three different [100], [110], and [111] directions. Thus, the joined theoretical and experimental approach applied successfully herein, allowed not only for univocal shape determination and surface structure reconstruction of the faceted Co_3O_4 nanocrystals, but also provided the in-depth understanding of the observed features at the atomic level.



INTRODUCTION

Many important properties of nanostructured oxides depend on their size, dimensionality and shape.^{1–4} Obvious examples include optical, electronic and magnetic properties, interfacial phenomena and chemical reactivity.^{5–7} Owing to the clear-cut structure and substantial surface area, oxide nanocrystals provide excellent model systems for joined experimental and theoretical investigations into surface related properties at nanometric scale, in more realistic pressure and temperature conditions, than in the case of conventional high vacuum single crystal studies.^{8–10} Faceted polyhedral crystals expose well-defined crystallographic planes, depending on the synthesis method, allowing for sensible investigations into structure–reactivity relationships at practical conditions.^{11–13} This assists in designing of new catalytic materials of enhanced activity and selectivity by preferential development of more active planes or by enhancement of the density of active sites.¹¹

From the thermodynamic point of view, the equilibrium shape of a nanocrystal is determined by the free energies of various facets $\gamma_{hkl}(n)$, and can be revealed by classic Wulff construction that minimizes the total surface free energy at a fixed volume.¹⁴ The Wulff theorem provides a simple relation between the $\gamma_{hkl}(n)$

energy of the (hkl) plane and its distance r_{hkl} in the normal direction n from the center of the crystallite. Later on, the thermodynamic stability of faceted and rounded shapes was revisited by Herring.¹⁵ In the case when the morphology of a nanocrystal is known from microscopic observations, $\gamma(n)$ can be assessed by iterative way until the resulting shape matches the observed one, by using Wulff construction in the inverse fashion.¹⁶ In addition to the thermodynamic driving forces, kinetics also plays an important role in determination of the morphology in the real growth conditions. In such a case, the approach advanced by Chernov can be applied to predict the steady-state shapes of nanocrystals.¹⁷

In recent years sophisticated tools, such as synchrotron X-ray diffraction, scanning probe microscopy, Cs-corrected high resolution transmission electron microscopy,¹⁸ or electron tomography^{19,20} have been applied for nanocrystals characterization and to retrieve correct and comprehensive structural and morphological information. Yet, several challenges still remain, especially with regard to 3-D

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Table 1. Supercell Parameters of Different Co₃O₄ Planes

supercell			supercell size	number of Co ₃ O ₄ units/stoichiometry
(100)	regular	$\alpha = \beta = \gamma = 90^\circ$	$a = b = 8.051 \text{ \AA}$ $c = 20.061 \text{ \AA}$	10/Co ₃₀ O ₄₀
(110)	regular	$\alpha = \beta = \gamma = 90^\circ$	$a = 8.051 \text{ \AA}$, $b = 11.388 \text{ \AA}$ $c = 18.544 \text{ \AA}$	14/Co ₄₂ O ₅₆
(111)	hexagonal	$\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$	$a = b = 11.388 \text{ \AA}$ $c = 20.460 \text{ \AA}$	16/Co ₄₈ O ₆₄

reconstruction of the nanocrystals shape. To reach a satisfactory tomographic reconstruction, for instance, some essential aspects of the acquisition procedure such as application of special high tilt holders preventing shadowing of the viewable grid area, use of small tilt increments, precise alignment of the component images should be carefully addressed.^{19,20}

Owing to recent progress in computational chemistry, fairly accurate first principles calculations of nanoparticles surface structure and theoretical predictions of the resultant nanomorphology are made possible.^{5,10,21} By invoking a simple approach of the Wulff construction along with the *ab initio* thermodynamics one can account also for more realistic environment conditions.²¹ For number of nanomaterials, such approach has proved its excellent predictive and explanatory capabilities. It has been used, for instance, to examine the equilibrium geometry of titanium dioxide^{22,23} and alumina polymorphs,²⁴ maghemite,^{25,26} magnesium oxide in dry and wet conditions,²⁷ as well as lead oxide in arbitrary oxygen pressure.²⁸ Convergence of theory with high resolution electron microscopy becomes especially productive for detailed understanding the habit of nanocrystals, their surface structure and for shape modeling as well. Examples are provided by thorough investigations of MgO by Jupille et al.²⁷ or by Stroppa et al. work on antimony-doped tin dioxide.²⁹

The cobalt spinel belongs to one of the most attractive oxides with remarkable record of widespread applications.^{11,30,31,32} In particular Co₃O₄ frequently used as a catalyst,^{33–35} has recently received a great deal of theoretical and practical attention because of its outstanding activity in low temperature decomposition of N₂O.^{36–38} Noting the particular structure with disparate concentration of the active sites it is not surprising that distinct surface planes of Co₃O₄ exhibit different activities. Shape-dependent oxygen storage capacity of ceria nanocrystals³⁹ and carbon monoxide oxidation over nanostructured cobalt spinel,¹¹ may serve here as paramount examples.

In the present work we investigated the surface properties and the shape of Co₃O₄ spinel by *ab initio* periodic calculations based on DFT theory. The surface geometry relaxation and stability of the exposed low index (100), (110), and (111) planes were examined in detail. We use combination of the information obtained from images taken by high resolution Cs-corrected STEM and the calculated DFT surface energies for three-dimensional Wulff reconstruction of the shape of spinel nanocrystals. Despite widespread use of the cobalt spinel there are only few theoretical papers devoted to explicit DFT calculations of Co₃O₄,^{34,40} but no one has been dealing with surface structure and morphology elucidation as yet.

EXPERIMENTAL SECTION

Calculation Details. For all calculations DFT level of theory was chosen with use of the Vienna *ab initio* simulations package

(VASP)⁴¹ based on Mermin's finite temperature DFT.⁴² Projector augmented plane wave (PAW)^{43,44} method for describing electron-ion interactions together with generalized gradient GGA-PW91 exchange-functional as parametrized by Perdew et al.⁴⁵ were employed. In addition to DFT scheme, in accounting for electron correlation effects the DFT+U method developed by Anisimov was used. While the values of *U* from 2 to 5 eV, all produced qualitatively similar results in terms of the converged electronic structure, eventually the value of the Hubbard parameter equal to *U* = 3.5 eV was used, in accordance with earlier papers.⁴⁶ The DFT+U calculations were performed only to describe bulk properties, since they had little influence on the calculated surface properties (*vide infra*).

A number of tests were initially performed to verify the accuracy of the method (cutoff energy from 350 to 500 eV and *k*-point set from $1 \times 1 \times 1$ to $5 \times 5 \times 5$). As a result all slab calculations were performed using standard Monkhorst-Pack⁴⁷ grid ($2 \times 2 \times 1$ sampling mesh) with cutoff energy of 400 eV and a Methfessel–Paxton⁴⁸ smearing with σ parameter set to 0.1 eV. For solving the Kohn–Sham SCF convergence, a constraint was set to be an energy change of 10^{-5} eV between two successive iterations. The geometry optimization of Co₃O₄ indicated that for bulk calculations a good agreement between predicted and experimental structure⁴⁹ was obtained. Surface geometries were constructed by cleaving the solid in the normal (100), (110), and (111) directions, thus obtaining large supercells containing ca. 10 atomic layers. Vacuum space of 10 Å was located above modeled surfaces in the *z* direction to separate oxides layers from the interactions (Table 1).

The stoichiometry of the bulk Co₃O₄ was preserved in the constructed slab model, together with the tetrahedral to octahedral cobalt ratio of 1:2. Furthermore, the same structure of the top and the bottom slab terminations was ascertained. Relaxation of the atomic positions in the four top layers was assumed to render forces acting upon the ions below $1 \times 10^{-2} \text{ eV} \cdot \text{\AA}^{-1}$.

The Wulffman program^{16,50} in tandem with Geomview interactive 3D visualization software⁵¹ were used to predict theoretical equilibrium habit of the nanocrystals (minimum surface energy convex polyhedra), following the rule

$$\gamma_{hkl}(n)/r_{hkl} = \text{constant}, \quad \forall hkl \quad (1)$$

where γ_{hkl} is the surface energy of the exposed (*hkl*) plane and r_{hkl} is the distance from the center of the nanocrystal to the surface of the *hkl* plane.

Materials and Characterization. The Co₃O₄ spinel samples were prepared by pH-controlled precipitation method as described elsewhere in more detail.^{36,37} The samples were calcined at 400 °C in air for 2 h prior characterization measurements. The phase verification of the synthesized material was performed by

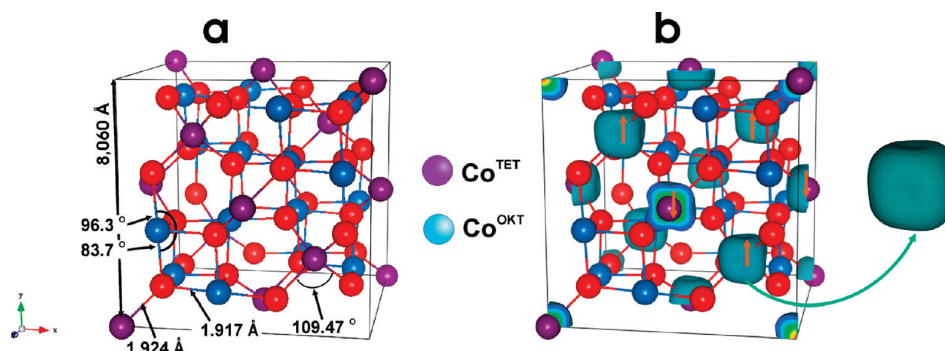


Figure 1. (a) Illustration of the cubic Co₃O₄ spinel structure. The Co²⁺ ions, colored blue, occupy tetrahedral sites and the Co³⁺ ions, colored purple, occupy octahedral sites within a fcc oxygen sublattice, colored red. (b) Spin density repartition revealing two networks of paramagnetic tetrahedral Co²⁺ ($S = 3/2$) ions, and a diamagnetic octahedral Co³⁺ ($S = 0$) ions.

means of an X'pert Pro (PANalytical) powder diffractometer with Cu K α radiation in the Bragg–Brentano geometry. The data were recorded in the 2θ range of 15–128 deg. with the resolution of 0.01 deg. and the acquisition time of 6 s per step. Diffraction pattern was simulated by Rietveld method using the DBWS program,⁵² according to the Young procedure.⁵³ The unit cell parameters were refined as cubic structure ($Fd\bar{3}m$, space group 227), and the starting parameters were taken from the ICSD file data 63164.

High resolution scanning transmission electron microscopy and parallel beam electron diffractions were carried out with a Hitachi dedicated STEM microscope operating at an accelerating voltage of 200 keV, and equipped with a field emission electron gun (FEG) together with Cs corrector of the spherical aberration. For the STEM experiments the powder specimens were deposited on a copper grid with the holey carbon thin film from alcohol solution and were cleaned with plasma generated from the mixture of hydrogen and oxygen gases for 20 s. Particle shapes were observed in the secondary electron image mode and the orientation was checked and reoriented by using the Kikuchi line diffraction pattern, obtained with the high convergence angle diffraction mode. Spot diffraction patterns were taken by parallel beam diffraction mode with beam diameter around 2 nm stopped on the particle. The fast Fourier transform was performed on high resolution images of atomic structure, taken in STEM brightfield imaging mode.

RESULTS AND DISCUSSION

Co₃O₄ has a normal spinel structure ($Fd\bar{3}m$, space group 227), and the unit cell containing eight formula units (56 ions) exhibits a lattice constant $a = 8.084$ Å.⁵⁴ Cobalt cations occupy 8a and 16d Wyckoff positions at $(1/8, 1/8, 1/8)$ and $(1/2, 1/2, 1/2)$, whereas oxygen atoms occupy the 32e oxygen positions at (u, u, u) , where u is the so-called oxygen parameter (Figure 1a). Only the lattice parameter a and the oxygen parameter u are required to completely determine the atomic positions of this structure. Distribution of the cations among the spinel interstitials can be characterized by the degree of inversion x . For Co₃O₄ with $x = 0$ half-field octahedral sites contain Co³⁺(d⁶) cations (denoted hereafter as Co^O), whereas tetrahedral sites exhibiting one-eighth occupancy are filled by Co²⁺(d⁷) cations (denoted Co^T).⁵⁵ Oxygen ions being

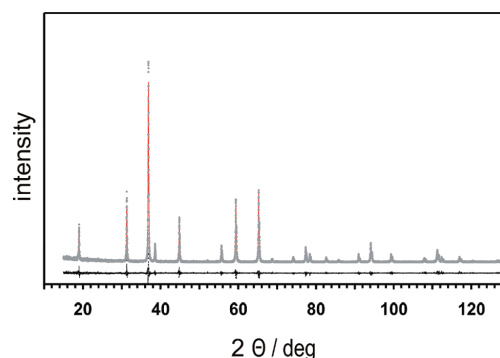


Figure 2. XRD pattern (gray points) together with Rietveld refinement (red line) of the nanostructured cobalt spinel.

surrounded by 1 Co^T and 3 Co^O cations exhibit a 4-fold coordination (O_{4c}). This ideal site occupancy may be perturbed, however, by partial inversion ($x > 0$). Weak magnetic interactions among the tetrahedral cobalt ions have been discussed recently,⁵⁶ and results in a low Néel temperature of 40 K.^{57,58}

Bulk Structure and Properties. Validation of the Computational Scheme. Bulk properties of Co₃O₄ were computed and compared with experimental data to verify the adequacy of the employed DFT approach. Experimental structural parameters were derived from the recorded XRD pattern of the Co₃O₄ sample by means of the Rietveld refinement simulation (Figure 2), and the results are summarized in Table 2.

The optimized lattice constant ($a_{\text{PW91}} = 8.051$ Å and $a_{\text{PW91+U}} = 8.060$ Å) are within $\sim 0.4\%$ difference with the experimental value of 8.082 Å. Previous plane-wave DFT calculations using other gradient functionals led to similar level of the accuracy.⁴⁰ The calculated octahedral cobalt–oxygen and tetrahedral cobalt–oxygen bond lengths were equal to $d_{\text{Co}^{\text{O}}-\text{O}} = 1.917$ Å and $d_{\text{Co}^{\text{T}}-\text{O}} = 1.924$ Å, respectively. Both values compare well with the experimental Co^O–O and Co^T–O bond distances (Table 2). The $d_{\text{Co}^{\text{O}}-\text{O}}$ and $d_{\text{Co}^{\text{T}}-\text{O}}$ bond lengths were derived from the value of $u = 0.263$, extracted from Rietveld refinement of the diffraction pattern (Figure 2), using the following

Table 2. Calculated and Experimental Bulk Properties of Co₃O₄

property	calculated value (DFT+U)	experimental value
unit cell parameter/Å	8.060	8.082 ^a
unit cell volume/Å ³	523.64	528.29 ^a
<i>u</i> parameter	0.263	0.263 ^a
Co ^T –O distance/Å	1.924	1.935 ^b
Co ^O –O distance/Å	1.917	1.920 ^b
octahedral angle (O–Co–O)/deg	96.3	90 ^b
	83.7	
tetrahedral angle (O–Co–O)/deg	109.47	-
electronic gap/eV	1.53	1.6

^a Derived from Rietveld refinement simulations. ^b Calculated from experimental *u* value.equations.⁵⁹

$$\begin{aligned} d_{\text{Co}^{\text{O}}-\text{O}}^{\text{O}} &= a\sqrt{3u^2 + 2u - 3/8} \\ d_{\text{Co}^{\text{T}}-\text{O}}^{\text{T}} &= a\sqrt{3(u - 1/4)} \end{aligned} \quad (2)$$

Variation of the *u* parameter reflects the adjustment of the oxygen positions to accommodate differences in the actual radius of the Co^T and Co^O cations. When *u* increases with respect to the reference value of 0.250, characteristic of ideal spinel geometry, the tetrahedral bond length increases, whereas the octahedral bond length decreases. The bond length $d_{\text{Co}^{\text{T}}-\text{O}} > d_{\text{Co}^{\text{O}}-\text{O}}$ is consistent with the crystal radius of the divalent high spin Co^T ($r_{\text{Co}^{\text{T}}} = 0.72$ Å) greater than the crystal radius of the trivalent low spin Co^O ($r_{\text{Co}^{\text{O}}} = 0.685$ Å for low spin and $r_{\text{Co}^{\text{O}}} = 0.75$ Å for high spin configuration), implying different spin states of both cations, which is nicely confirmed by the more accurate calculations (vide infra).

The calculated spin magnetic moment of the divalent Co^T ions was found to be 2.27 μ_{B} and 2.61 μ_{B} for PW91 and PW91+U, respectively, and remains in good agreement with preceding calculations.⁴⁶ Each of the Co^T ions of high spin $e^4t_2^3$ configuration is surrounded by four nearest neighbor Co^T ions of opposite spin, giving rise to an antiferromagnetic network (Figure 1b), in line with empirical observations.^{57,58} The trivalent Co^O ions, as already mentioned, exhibit a closed shell t_{2g}^6 configuration and consequently a nil magnetic moment, clearly revealed by spin density repartition within the unit cell (Figure 1b) and by the spin polarized band structure calculations (Figure 2). As a result the experimental magnetic state of cobalt spinel was well reproduced. The antiferromagnetic state was found to be situated about 0.1 eV below the energy level of a ferromagnetic alignment, again in line with magnetic studies.^{57,58} The calculated value of the electronic gap of 1.53 eV compares well with the experimental value of 1.6 eV. The projected electronic density of states (DOS) for Co^O, Co^T, and oxygen ions are discussed in more detail in Supporting Information S1.

We can thus reasonably assume that the employed formalism along with the used parametrization is capable to describe the Co₃O₄ system with the adequate accuracy.

Surface Energies and Reconstruction. For surface energy modeling we considered three low index (100), (110), and (111) planes with the largest interplanar spacing, as they are predicted to be the most stable, following Bravais–Friedel–Donnay–Harker theory.⁶⁰ Indeed, a careful scrutiny of the experimental data reveals that only those planes are exposed in a number of Co₃O₄ specimens prepared by various methods.^{9,61,62}

Table 3. Surface Energies Calculated with and without Inclusion of Hubbard *U* Parameter for Co₃O₄ Spinel

method	surface energy [J/m ²]		
	(100)	(110)	(111)
DFT	1.38	1.65	1.48
DFT+U	1.38	1.65	1.47

Theoretical surface energies γ corresponding to the energy difference of the surface and bulk ions per unit area were calculated as follows:

$$\gamma = (E_{\text{slab}} - nE_{\text{bulk}})/2A \quad (3)$$

where E_{slab} denotes the slab energy and nE_{bulk} energy of the *n* Co₃O₄ units in the bulk model, whereas *A* is the surface exposed by the slab model for a given *hkl* plane. The entropic contribution can be added by using the computed full phonon density of states⁶³ or alternatively, in a simplified treatment, by inclusion of the most relevant vibration modes.⁶⁴ However, with quite good approximation we may neglect this term, which is a common approach in this type of calculations,^{25,10,21,65} as it shall not affect the conclusions drawn in a significant way.^{23,28,25} Indeed, crystal habits are principally determined by relative energies of the exposed planes, and entropy terms normally do not alter this ordering.²⁵ Groundwork DFT and DFT+U calculations for (100), (110), and (111) planes revealed that the surface energy is also quite insensitive to inclusion of the Hubbard parameter (Table 3). Therefore, all the calculations of the surface properties and shape prediction were performed within the DFT (GGA-PW91) approach alone.

For (100) plane modeling, we used a slab composed of 10 layers (8.35 Å). Among possible terminations, the most stable structure of this plane consists of four coordinatively unsaturated 5-fold Co^O_{5c} (with one missing oxygen ligand), two recessed, fully coordinated 4-fold Co^T_{4c} and two protruding 2-fold Co^T_{2c} ions (with two missing O ligands). The surface concentration of the Co^T ions (0.015 Å⁻²) is four times lower than the Co^O_{5c} ones (0.060 Å⁻²). The Co^O_{5c} cations located in truncated edge-sharing octahedra, constituted by five lattice O²⁻ anions, form regularly spaced strips joined sequentially by the Co^T cations (Figure 3a). The tetrahedral cobalt ions, in turn, are placed below the strips (Co^T_{4c} ions) and above them (Co^T_{2c} ions). The distance between the nearest Co^O cations is equal to 2.89 Å, whereas the tetrahedral cobalt species are separated by 8.051 Å. There are two types of exposed oxygen ions: the 4-fold O_{4c} species, preserving

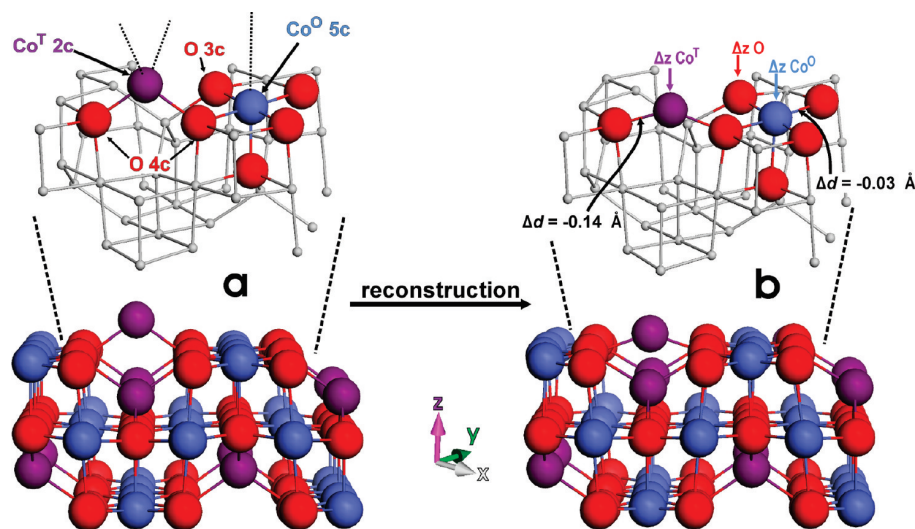


Figure 3. Top-lateral view of the optimized unrelaxed (a) and relaxed (b) structure of the (100) plane of Co_3O_4 , with major displacements of the exposed ions marked by arrows.

bulk coordination, and truncated 3-fold O_{3c} ones (with one missing bond to Co^{T}). In order to ensure equivalence of both surfaces in the slab model and preserve the surface stoichiometry, one Co^{T} cation per unit cell was displaced from upper to lower plane of the slab, giving rise to the following surface composition $\{1\text{Co}^{\text{T}}_{2c}, 4\text{Co}^{\text{O}}_{5c}, 2\text{Co}^{\text{T}}_{4c}, 6\text{O}_{3c}, 2\text{O}_{4c}\}$ of the computational model for the (100) plane.

There are two principal types of terminations for the (110) surface, occasionally labeled as A and B in the literature.⁴⁰ They were modeled by slabs containing 7 (8.54 Å) and 9 layers (11.5 Å), respectively. The (110)-A plane is terminated with octahedral ions, the coordination of which is lowered to 4-fold ($\text{Co}^{\text{O}}_{4c}$) one, which is caused by two missing oxygen bonds. The tetrahedral cobalt ions are surrounded by three oxygens, giving rise to 3-fold $\text{Co}^{\text{T}}_{3c}$ surface centers (Figure 4a). The same trigonal coordination exhibit exposed oxygen anions (O_{3c}). The (110)-B termination is a bit more deprived, exhibiting only 4-fold $\text{Co}^{\text{O}}_{4c}$ cations and two types of 3-fold anions, with a $\text{Co}^{\text{O}}(\text{O}_{3c})$ or a $\text{Co}^{\text{T}}(\text{O}_{3c})$ neighbor missing. In contrast to the (100) plane, the concentration of both cobalt species, equal to $0.044 \text{ \AA}^{-2}$ and $0.033 \text{ \AA}^{-2}$ for Co^{O} and Co^{T} , respectively are comparable here. The $\text{Co}^{\text{O}}\text{--Co}^{\text{O}}$ distance for the (110) plane was found to be 2.95 Å, whereas the $\text{Co}^{\text{T}}\text{--Co}^{\text{T}}$ spacing equals to 3.48 Å (for A termination).

In order to ensure the proper stoichiometry and parity of the lower and upper planes the (110)-A termination was modified by removing one Co^{T} cation from both sides. The resultant computational model of the (110)-A plane exhibits the following composition $\{3\text{Co}^{\text{T}}_{3c}, 4\text{Co}^{\text{O}}_{4c}, 4\text{O}_{3c}, 4\text{O}_{2c}\}$. In the case of the (110)-B termination more severe modifications involving deletion of two cobalt and four oxygen atoms were needed. The resultant model of this termination consist of $\{4\text{Co}^{\text{T}}_{3c}, 2\text{Co}^{\text{O}}_{3c}, 4\text{O}_{3c}, 4\text{O}'_{3c}\}$ surface ions. For further calculations only the more stable (110)-A plane, containing less dangling ions ($\gamma_{(110)\text{-A}} = 1.65 \text{ J/m}^2$ and $\gamma_{(110)\text{-B}} = 1.92 \text{ J/m}^2$, *vide infra*), was taken into account.

The (111) plane was modeled using a slab comprising 13 layers (9.88 Å). Cleavage of Co_3O_4 across this plane can produce six conceivable nonequivalent terminations. The most stable (111) surface with the smallest number of dangling bonds (Figure 5a) is characterized by strong under-saturation of four Co^{O} ions, which is reduced to 3-fold coordination ($\text{Co}^{\text{O}}_{3c}$), whereas in the case of four Co^{T} only one O^{2-} ligand is lost ($\text{Co}^{\text{T}}_{3c}$). The exposed oxygen ions, in turn, take account of ten O_{3c} and six O_{4c} species per unit cell. The concentration of both cobalt species is equal to $0.018 \text{ \AA}^{-2}$ and $0.036 \text{ \AA}^{-2}$ for Co^{O} and Co^{T} , respectively. The shortest $\text{Co}\text{--Co}$ distance of 3.41 Å is larger than that observed for (100) and (110) planes, and is defined by the adjacent Co^{O} and Co^{T} ions (Figure 5a). In order to preserve the stoichiometry and equivalence of both surfaces of the slab, one Co^{T} ion was displaced from the upper into the lower plane, giving rise to the following composition $\{4\text{Co}^{\text{T}}_{3c}, 2\text{Co}^{\text{O}}_{3c}, 10\text{O}_{3c}, 6\text{O}_{4c}\}$ of the computational model for the (111) plane.

Surface reconstruction for all investigated planes is significant only for the highly unsaturated surface ions, and can be described as prevailing relaxation in z-direction (toward the bulk). For the (100) termination the unsaturated $\text{Co}^{\text{T}}_{2c}$ ions move about $-0.45 \text{ \AA}$ inward and the $\text{Co}^{\text{O}}\text{--O}_{3c}\text{--Co}^{\text{T}}$ central oxygen by $-0.06 \text{ \AA}$. The Co^{O} ions remained almost unperturbed (Table 4, Figure 3b). Those changes are accompanied by considerable reduction of the $\text{Co}^{\text{O}}\text{--O}$ and $\text{Co}^{\text{T}}\text{--O}$ bond lengths by $-0.14 \text{ \AA}$ and $-0.07 \text{ \AA}$, respectively. A substantial increase of the $\text{O}\text{--Co}^{\text{T}}_{2c}\text{--O}$ angles by 33.4 deg and almost intact $\text{O}\text{--Co}^{\text{O}}_{5c}\text{--O}$ angles (with a mere drop of -4.2 deg) were observed. For the (110) plane both the tetrahedral and the octahedral cobalt ions were considerably shifted inward by -0.25 and $-0.13 \text{ \AA}$, respectively (Table 4, Figure 4b). Relaxation of the $\text{Co}^{\text{O}}\text{--O}_{3c}\text{--Co}^{\text{T}}$ oxygen anion, up to $-0.07 \text{ \AA}$ was close to that observed for the (100) plane. The shrinking of the $\text{Co}^{\text{O}}\text{--O}$ bond ($\Delta d_{\text{Co}^{\text{O}}\text{--O}} = -0.08 \text{ \AA}$ and $-0.10 \text{ \AA}$) and the $\text{Co}^{\text{T}}\text{--O}$ bond lengths ($\Delta d_{\text{Co}^{\text{T}}\text{--O}} = -0.13 \text{ \AA}$ and $-0.12 \text{ \AA}$) was more pronounced in this case. The associated changes in

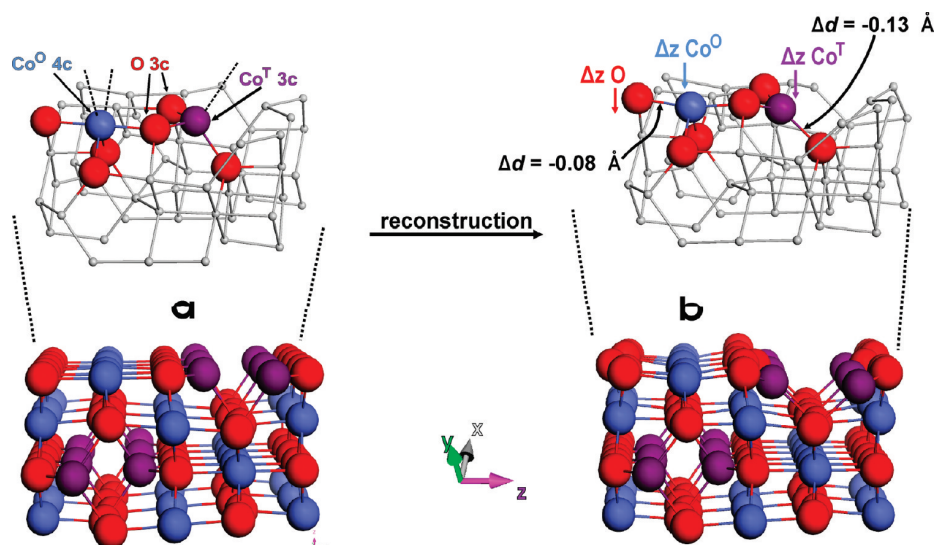


Figure 4. Top-lateral view of the optimized unrelaxed (a) and relaxed (b) structure of the (110) plane of Co_3O_4 , with major displacements of the exposed ions marked by arrows.

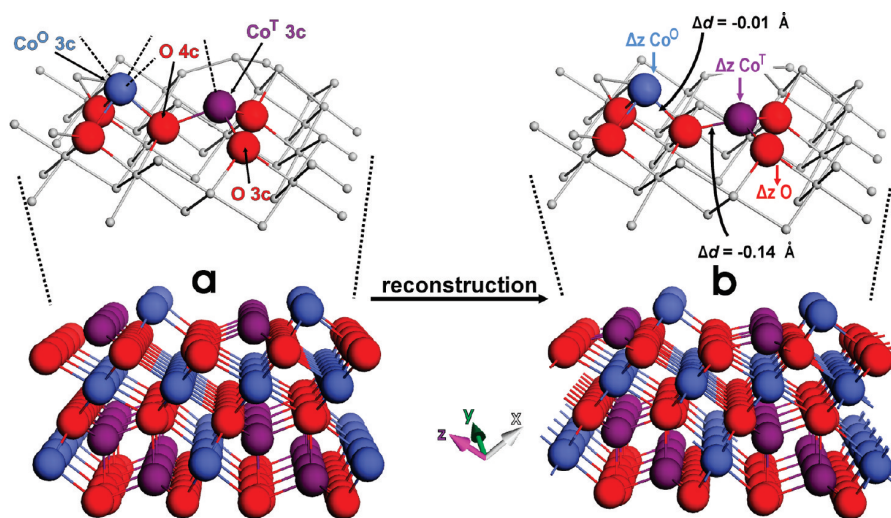


Figure 5. Top-lateral view of the optimized unrelaxed (a) and relaxed (b) structure of the (111) plane of Co_3O_4 , with major displacements of the exposed ions marked by arrows.

the $\text{O}-\text{Co}^{\text{T}}_{3\text{c}}-\text{O}$ angle by 11.1 deg, and the $\text{O}-\text{Co}^{\text{O}}_{4\text{c}}-\text{O}$ angle by 4.2 deg, were both positive, in contrast to what was observed for the (100) plane.

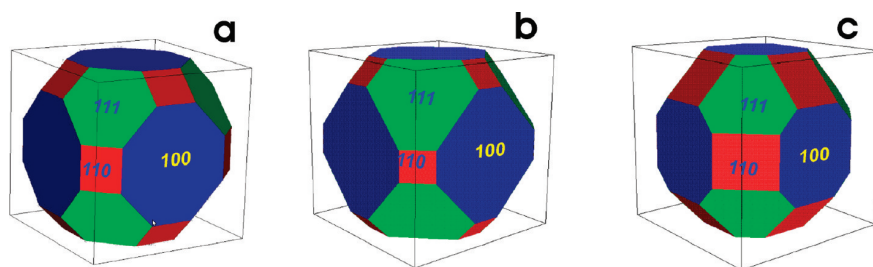
The highly unsaturated $\text{Co}^{\text{O}}_{3\text{c}}$ ions in the (111) plane relax their position by moving along the z -axis by -0.06 Å, and similar displacement (-0.07 Å) was observed for surface $\text{O}_{3\text{c}}$ anions. Again, the most exposed tetrahedral Co^{T} ions shifted by -0.22 Å, exhibit the highest relaxation. The resultant contraction of the $\text{Co}^{\text{O}}-\text{O}$

bond length was quite small ($\Delta d_{\text{Co}^{\text{O}}-\text{O}} = -0.01$ Å) in contrast to more distinct decrease of the $\text{Co}^{\text{T}}-\text{O}$ bond lengths ($\Delta d_{\text{Co}^{\text{T}}-\text{O}} = -0.05$ Å and -0.14 Å). Furthermore, the reconstruction of the (111) surface involved rather small outward distortion of the $\text{O}-\text{Co}^{\text{T}}_{3\text{c}}-\text{O}$ and the $\text{O}-\text{Co}^{\text{O}}_{3\text{c}}-\text{O}$ angles (Table 4, Figure 5b).

The relaxation described above is responsible for considerable lowering of the surface energy by 0.19, 0.21, and 0.28 J/m² for the (100), (110) and (111) planes, respectively, in comparison to the

Table 4. Surface Energy and Relaxation for the Most Stable (100), (110), and (111) Planes of Co_3O_4

plane	$\gamma/\text{J}\cdot\text{m}^{-2}$		$\Delta z/\text{\AA}$			$\Delta d/\text{\AA}$		$\Delta\alpha/\text{deg}$	
	rigid	relaxed	Co^{T}	Co^{O}	O	$\text{Co}^{\text{O}}-\text{O}$	$\text{Co}^{\text{T}}-\text{O}$	$\text{O}-\text{Co}^{\text{T}}-\text{O}$	$\text{O}-\text{Co}^{\text{O}}-\text{O}$
(100)	1.57	1.38	−0.45	−0.01	−0.06	−0.03	−0.14 −0.07	33.4	−4.2
(110)	1.86	1.65	−0.25	−0.13	−0.07	−0.08 −0.10	−0.13 −0.12	11.1	3.1
(111)	1.75	1.48	−0.22	−0.06	−0.07	−0.01	−0.05 −0.14	7.2	4.4

Figure 6. Theoretical shapes for nanocrystalline Co_3O_4 (a) calculated without surface reconstruction, (b) including surface reconstruction and (c) experimental shape retrieved by means of the Wulff method.

parent geometries. The calculated γ values for the rigid and relaxed surfaces together with the most important displacements of the surface ions along with the changes in the nearest cobalt–oxygen distances and angles observed upon the relaxation are collected in Table 4.

Although calculations of the surface energies for the (110) and (111) planes of cobalt spinel have been already undertaken by other authors,⁴⁰ a consistent and complete set of γ values is required to provide an appropriate input for reliable theoretical shape modeling, and this is performed for the first time in this paper. We have also found that the (110)-A termination is more stable than the (110)-B one, in contrast to previous data obtained with PBE functional.⁴⁰

For validation of the results, we have used the computed surface energies from Table 4 to visualize the equilibrium morphologies of the relaxed and unrelaxed spinel crystals, using the Wulff construction (Figure 6, parts a and b). The resultant theoretical rhombicuboctahedral crystals expose predominantly six (100) and eight (111) low energy facets, truncated by 12 minor (110) planes of higher energy. The computed shape can be next compared with the morphology of the synthesized Co_3O_4 nanocrystals, retrieved by matching the corresponding STEM images to the predicted three-dimensional rhombicuboctahedral shape, by means of the Wulffman software (Figure 6c). As implied by Figure 6, relaxation of the surface geometry leads to preferential development of the (111) planes at the expense of the (110) ones.

Selected projections of the reconstructed polyhedral shapes of the Co_3O_4 crystallites, the high resolution Cs-corrected STEM images at two magnifications of the synthesized nanoparticles together with the corresponding Fast Fourier Transform (FFT) patterns are gathered in Figure 7. The high resolution images and parallel beam electron diffractions (see inserts in Figure 7a1–c1) revealed that the observed spinel nanoparticles were single crystals.

Furthermore, the nanoparticles are faceted on the (100), (111), and (110) planes, in excellent agreement with the theoretical calculations (Figure 7a–c). The indicated spacing of 0.292 and 0.491 nm corresponds well to the interlayer distances of the (110) and (111) crystallographic planes of Co_3O_4 , respectively (Figure 7a2–c2). The symmetry of the diffraction spots in the FFT patterns (Figure 7a3–c3) reveals the orientation of the observed faceted particles along the [100], [110] and [111] axes, allowing for univocal alignment of the predicted 3D Wulff shapes with respect to the experimental 2D images.

The angles measured between the exposed facets, 125 deg, 135 deg, and 145 deg (Figure 7, parts a1, b1, and c1), are consistent with those expected between the (100)/(111), (100)/(110) and (110)/(111) planes of the spinel $Fd\bar{3}m$ structure. This confirms that, indeed, the observed polyhedrons assume the computed rhombicuboctahedral habit.

The presented nanocrystallites observed by STEM (Figure 7) were selected from larger population, the fragment of which is shown in Supporting Information (Figure S2). As can be seen therein, in the synthesized material we observed exclusively the spinel nanocrystals with the exposed (111), (110), and (100) facets. Depending on their abundance the crystallites assumed the predominant rhombicuboctahedral shape with the prevailing (100) and (111) planes or less frequent truncated octahedral shapes with the main (111) plane. The actual morphology is a matter of thermodynamic and kinetic factors as discussed below. However, for comparison with the Wulff derived theoretical habits only those exhibiting equilibrium shapes can meaningfully be taken into account.

Closer inspection of Figure 6 and Figure 7 revealed some appreciable differences between the morphologies of the pristine Wulff construction and the experimental habit (manifested mainly by a slightly enlarged abundance of the (110) plane). The stability of nanoparticles is gauged by the Gibbs energy

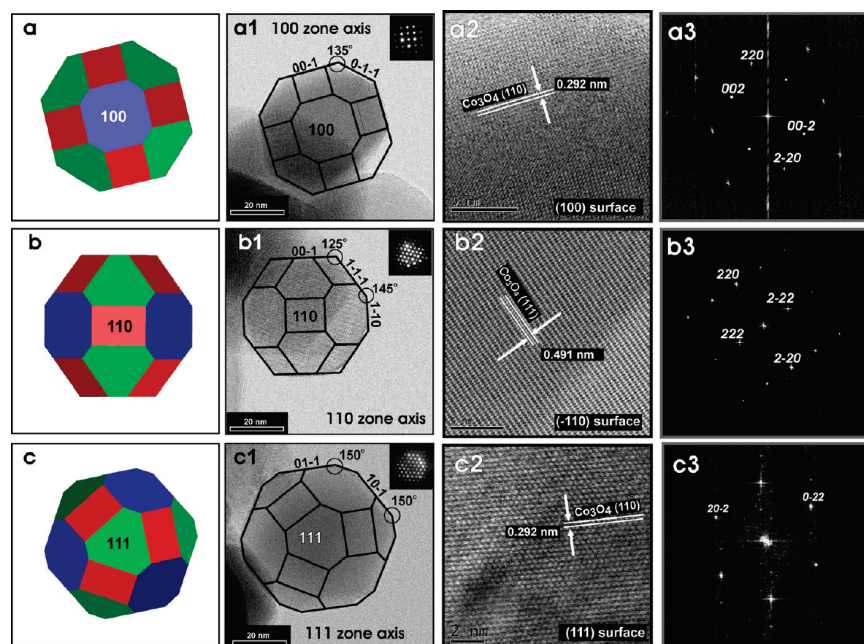


Figure 7. Thermodynamical Wulff shape (a–c) together with reconstructed STEM shapes (a1–c1) of cobalt nanocrystals viewed along the [100], [110], and [111] directions. HRTEM images of the exposed Co₃O₄ planes (a2–c2), together with the corresponding fast Fourier transform (a3–c3) indexed within the *Fm*3*m* space group.

$G(T) = G_{\text{bulk}}(T) + G_{\text{surf}}(T) \approx \Delta_f G^\circ + (M/\rho)q\sum f_i \gamma_i$, where M is the molar mass, ρ is the density, q is the surface-to-volume ratio, and f_i are weight factors for surface energies γ_i .²¹ Substitution of the computed numerical values showed that the total surface energy normalized to the volume of the nanocrystal of an average size, $V_{\text{ncryst}} = 55809 \text{ nm}^3$, changes from 1.095 to 1.111 fJ for the DFT-predicted and the experimental shapes, respectively. Such small enhancement of the surface energy by 1.5% can certainly be accommodated by the limited accuracy of the adopted model. In the most straightforward way, this phenomenon can be accounted for by residual hydroxylation of the surface (not taken into account), which obviously modifies the energy of the exposed planes.⁶⁶ However, our calculation of surface energy of the hydroxylated planes revealed that in such a case the abundance of the exposed (110) planes is disfavored by adsorbed water (Supporting Information, Figure S3). Furthermore, comparison of the calculated habit of the Co₃O₄ nanocrystals in dry ($\Theta_{\text{OH}/\text{H}_2\text{O}} = 0$) and wet conditions ($\Theta_{\text{OH}/\text{H}_2\text{O}} = 0.8$) indicates that hydroxylation has only a slight effect on the overall spinel morphology⁶⁶ and cannot be associated with the observed minor contribution of the truncated octahedral shapes.

It is well-known, that appearance of the crystallites may also be influenced by anisotropy in the rate of crystal growth, under particular experimental conditions (Wulff–Chernov plot).^{17,22,27} In the case of nanocrystals that have still not reached the equilibrium, but are in the stage of a steady-state growth, the lowest perpendicular extension rate $v_{\text{hkl}}(n)$ modifies the shape, asymptotically evolving into the thermodynamic habit. By proper adjusting the relative speed of growth for different terminations ($v_{100} : v_{110} : v_{111} =$

1:0.88:0.95) both shapes can be match satisfactorily. The total surface energy of the resultant average-size nanocrystal (with the same volume of 55809 nm³) was assessed to be equal to 1.045 fJ, using the experimental γ -values. It is only slightly smaller than that obtained in the DFT calculations, suggesting that in fact there is no substantial difference between thermodynamic stability of the predicted and observed shapes. Therefore, a plausible origin of the observed fine differences in the morphology can be associated with the kinetic effects quite reasonably. Indeed, the observed minor truncated octahedral nanocrystals can be associated with only slightly slower speed of growth of the (111) plane ($v_{100} : v_{110} : v_{111} = 1:1:0.88$). Current more comprehensive work carried out in our laboratory includes size effects or the extent of surface complexation, in accounting for the experimental morphologies of the Co₃O₄ nanostructures obtained in various conditions.

Once the polyhedral form of the crystallites is determined, from the areas of the exposed planes, we can calculate their fractional abundance, total surface area, and the areal concentration of cobalt ions. Such data are useful for calculation of turnover frequencies or for establishing quantitative relationships between preparation conditions and profusion of specific crystallographic facets that are catalytically most active, allowing for development of improved catalytic materials based on cobalt spinel structure.^{37,36} Such studies belong to one of the leading direction in shape dependent nanocatalysis on oxides including cobalt spinel, where controlled faceting allows for optimization of its catalytic properties. In fact, the (100) plane has been found to be the most active in N₂O decomposition reaction,³⁶ the (110) has

been recognized much more active than (100) for CH₄ activation and CO oxidation,^{11,67} whereas the (111) plane populated by highly unsaturated ions, being easily contaminated by inhibitors, such as water,⁶⁸ seems to be catalytically less important.

CONCLUSIONS

The bulk structure, shape, and surface energies of the low index (100), (110), and (111) planes exposed by Co₃O₄ nanocrystals were investigated by means of periodic PW91 and PW91+U density functional (DFT) calculations, combined with high resolution STEM studies. The calculated surface energies γ for the relaxed planes were found to increase in the following order 1.38 J m^{-2} (100) < 1.48 J m^{-2} (111) < 1.65 J m^{-2} (110). The consistent set of computed γ values was used to predict the equilibrium shape of Co₃O₄ crystallites using Wulff construction. The rhombicuboctahedral habit predicted by DFT modeling compares well with the experimental shape of the synthesized spinel nanocrystals, retrieved by matching the corresponding 2D TEM images to 3D Wulff shapes for three principal [100], [110], and [111] directions.

ASSOCIATED CONTENT

S Supporting Information. Detailed information on the cobalt spinel electronic structure, STEM picture of Co₃O₄ nanocrystallites and Wulff shapes of dry and partially hydroxylated Co₃O₄. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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2.4.3 Tekst artykułu H3

[H3] W. Piskorz*, J. Gryboś, F. Zasada, S. Cristol, J.-F. Paul, A. Adamski, Z. Sojka* „Periodic DFT and Atomistic Thermodynamic Modeling of Surface Hydration Equilibria and Morphology Prediction of Monoclinic ZrO₂ Nanocrystals”, *Journal of Physical Chemistry C*, **115** (2011), 24274.

Periodic DFT and Atomistic Thermodynamic Modeling of the Surface Hydration Equilibria and Morphology of Monoclinic ZrO₂ Nanocrystals

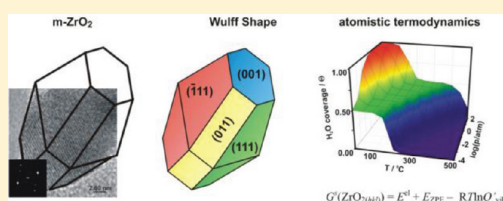
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S Supporting Information

ABSTRACT: A comprehensive DFT study of water sorption ($0.25 < \theta < 1$) on monoclinic ZrO₂ ($P2_1/c$) nanocrystals was performed by means of plane wave periodic DFT/PW91 calculations jointly with statistical thermodynamics. All planes, (001), (110), (011), (-101), (111), and (-111), exposed by m -ZrO₂ crystallites of the equilibrium morphology were taken into account, and their atomic structure, reconstruction, and stabilization upon water adsorption were elucidated and discussed in detail. Using the calculated surface energy values, the truncated hexagonal bipyramidal shapes of the monoclinic zirconia nanocrystallites in dry and wet states were predicted by means of the Wulff construction. The results compare very well with the experimental TEM images. The computed changes in the free enthalpy of adsorption under different hydration conditions were used to construct two-dimensional surface coverage versus temperature and pressure diagrams, $\theta_{hkl} = f(T, p_{H_2O})$, for each of the exposed planes. It was shown that full coverage of water on the more stable (-111) and (111) planes was achieved in a bimodal way ($1 \rightarrow 2$ and $2 \rightarrow 2$, respectively), whereas for less stable (011) and (001) terminations it occurs via a trimodal $1 \rightarrow 1 \rightarrow 2$ and a tetramodal $1 \rightarrow 1 \rightarrow 1 \rightarrow 1$ process. In addition, to illustrate water adsorption processes in a more concise way, multisite Langmuir and Fowler–Guggenheim isotherms were calculated and interpreted in terms of molecular interactions within the adsorbate layer and with the surface.



1. INTRODUCTION

Owing to its versatile properties such as high temperature stability,¹ high refractive index, low thermal conductivity, hardness,² and pronounced oxygen ion conduction,³ zirconia belongs to one of the scientifically and technologically most attractive oxides with a remarkable record of widespread applications. It is also extensively used in catalysis as a robust support^{4–7} and catalyst component in a number of industrially important processes.^{8–12} In this latter context, one of the most important features of the polycrystalline ZrO₂ is the nature of the exposed facets, reconstruction of their structure, and the ability to sustain high surface area under the reaction conditions. Shape-dependent catalysis and microkinetics on nano oxides, where controlled faceting allows for optimization of their catalytic performance, provide a good example of fundamental role of such investigations.

As a real catalyst or support, zirconia is often applied in wet conditions, where water can be the product of the catalyzed reaction (e.g., oxidation of hydrocarbons) or a component of the feed ($deNO_x$, deN_2O).^{13,14} Furthermore, water is inevitably present during the preparation of zirconia-supported catalysts by impregnation or ion-exchange methods, and also during hydrothermal synthesis of highly dispersed zirconia. It has been reported that water molecules may adsorb on the ZrO₂ surface,

forming single or multiple layers, involving both dissociative and molecular modes of adsorption.^{15–18} Water admolecules not only modify the nature of the active sites¹⁹ but also may severely influence stability of the ZrO₂ polymorphs as well.^{20–22}

Zirconia can exist in a monoclinic ($P2_1/c$), tetragonal ($P4_1/nmc$), and a cubic ($Fm\bar{3}m$) form. The coarse grain monoclinic phase is stable below 1175 °C, transforming next into the tetragonal one. But in the case of fine grain powders, this order can easily be reversed.²³ Careful inspection of the experimental data reveals that low-index (001), (110), (011), (-101), (111), and (-111) planes are exposed in a number of m -ZrO₂ specimens prepared by various methods.^{24–27} From the thermodynamic point of view, the shape of such nanocrystals is determined by the free energies of the exposed facets, γ_{hkl} , and can be revealed by Wulff construction.²⁸ In the case when the morphology of a zirconia nanocrystal is known from microscopic TEM observations, γ_{hkl} values can be assessed in an iterative process until the trial shape matches the observed one, by using the Wulff construction in an inverse fashion.²⁹ Presence of water leads to

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profound surface hydroxylation and hydration, modifying thereby the surface energies of the exposed facets, which may influence the form of the zirconia nanocrystals. Detailed quantitative evaluation of the surface coverage by water at working conditions (T and $p_{\text{H}_2\text{O}}$) is thus crucial for understanding the number and the nature of the available active centers. Another important parameter that may influence the morphology is the size of crystallites grains, as revealed by Barnard et al.³⁰

Despite the clear significance of the interfacial chemistry for understanding zirconia properties, among the number of theoretical papers devoted to ZrO_2 molecular modeling^{31–33} only a few have dealt with surface hydroxylation, however, mostly in a rather scarce fashion.^{34,35} There is also lack of a systematic study of the surface faceting and structure in relation to equilibrium morphology of the monoclinic zirconia in dry and wet conditions.

In the present work, we investigated the surface energetics and shape of the bare and hydroxylated $m\text{-ZrO}_2$ nanocrystals by means of periodic DFT calculations and atomistic thermodynamic modeling. Molecular description of water sorption processes, surface geometry relaxation, stability of all the exposed planes and water adsorption equilibria were discussed in detail. The results were summarized in terms of theoretical multisite Langmuir and Fowler–Guggenheim adsorption isotherms, and compared with experimental TEM and thermogravimetric results.

2. METHODS AND MATERIALS

2.1. Calculation Scheme and Structural Models. For all calculations the Vienna ab Initio Simulation Package (VASP)³⁶ based on Mermin's finite temperature DFT was applied.³⁷ The following electron configurations $[\text{Kr}]4d^25s^2$ and $[\text{He}]2s^22p^4$ were used for the zirconium and oxygen atoms, respectively. The core electrons were kept frozen and replaced by PAW pseudopotentials.³⁸ The PW91 GGA exchange functional, as parametrized by Perdew et al.,³⁹ was employed together with the Methfessel–Paxton⁴⁰ smearing with the γ parameter set to 0.1 eV. To evaluate the accuracy of the adopted method, a number of tests were initially performed by changing the cutoff energy from 350 to 700 eV and the k -point sampling mesh from $2 \times 2 \times 2$ to $4 \times 4 \times 4$ (using standard Monkhorst–Pack⁴¹ grid). As a result, the valence electrons were described using the plane wave basis set with the cutoff of 400 eV. The integration in the Brillouin zone was preformed as follows: $3 \times 3 \times 3$ for the bulk unit cell, $2 \times 2 \times 1$ for the (-101) plane, $3 \times 3 \times 1$ for the (111) and (-111) planes, $3 \times 2 \times 1$ for the (101) plane and finally $2 \times 3 \times 1$ for the remaining surface terminations. For solving the SCF convergence of the Kohn–Sham equations, we set the energy changes of 1×10^{-5} eV between two successive iterations. During the calculations, the positions of all bulk ions, and for the slab model the positions of all ions located within the four topmost layers, were relaxed to render the net forces acting upon them smaller than 1×10^{-2} eV·Å⁻¹.

According to the $P2_1/c$ space group symmetry, the nonequivalent, low index facets of the monoclinic zirconia include (001) , (010) , (100) , (110) , (101) , (011) , (-101) , (111) , and (-111) planes. Their starting geometries were obtained by cleaving the solid ZrO_2 along the corresponding normal directions. For all the investigated planes, a (1×1) unit cell was used since it exposes sufficient space to model high and low water coverages. In order to avoid surface–surface interactions, a vacuum

separation of 12 Å was set between two periodically repeated slabs composed of 4–6 atomic layers.³¹ The influence of the slab thickness on the electronic energy was investigated too, and the results revealed that only the three outermost ZrO_2 layers are important for the relaxation. In the developed model, the bulk stoichiometry of the ZrO_2 was preserved, and the same composition and structure of the top and the bottom slab terminations were ascertained (see Table S1 in the Supporting Information). Due to the structural and chemical complexity of the monoclinic zirconia, it is not straightforward to select the appropriate structure of the exposed Miller planes.³¹ Among possible terminations, only the stoichiometric structures of lowest surface energy were taken into account (Table S2 in the Supporting Information).

For adsorption modeling, the energies of water ad molecules obtained from the static DFT calculations were complemented by entropic contributions derived by means of the atomistic thermodynamics. The gas phase–surface equilibrium was described within the usual perfect gas approximation. The Wulffman program⁴² in tandem with Geomview interactive 3D visualization software⁴³ was used to predict the theoretical equilibrium shape of the $m\text{-ZrO}_2$ nanocrystals in the absence and presence of water. Theoretical surface energies corresponding to the energy difference between the surface and bulk ions per unit area were calculated as $\gamma = (E_{\text{slab}} - nE_{\text{bulk}})/2A$, where E_{slab} denotes the slab energy and nE_{bulk} energy of the n ZrO_2 units in the bulk model, whereas A is the surface exposed by the slab for a given hkl plane. Since the crystal habits are principally determined by relative energies of the exposed planes, the entropy terms may be neglected, since they normally do not alter this results in a significant way.^{44–46}

2.2. Atomistic Thermodynamics and Theoretical Isotherms. The adopted calculation scheme of the thermodynamic modeling^{47–49} was described in our previous work in more detail.⁵⁰ For each of the proposed adsorption scenarios, the free enthalpy $\Delta_a G_{hkl}(p, T, n\text{H}_2\text{O})$ was calculated as a function of T and p parameters, and the lowest value defines the most stable system in given equilibrium circumstances. The pristine, totally dehydroxylated, surface with the Gibbs free energy equal to $G_{hkl}(\text{ZrO}_2) = E^{\text{el}} + E_{\text{ZPE}} - RT \ln Q'_{\text{vib}}$, was taken as a reference state.⁵¹ Supposing that the vibrational terms do not vary upon water adsorption in a significant degree (i.e., $\Delta G \cong \Delta E^{\text{el}}$), we can factorize the free enthalpy of adsorption in two parts: an electronic contribution, $\Delta_a E^{\text{el}}$, calculated as a difference of the corresponding static DFT energies, and the change in the chemical potential of water molecules upon adsorption: $\Delta_a G_{hkl}(p, T, n\text{H}_2\text{O}) = \Delta_a E^{\text{el}} - n\Delta\mu(\text{H}_2\text{O})$. Noting that the contribution to entropy and energy changes due to the soft modes originating from the frustrated translations and rotations of water ad molecules are small, and that the major part of the thermal contribution comes from hard normal H_2O vibrations (approximated by ZPE), the chemical potential of the adsorbed water species can be expressed as $\Delta\mu(p, T) = \Delta\mu^0(T) + RT \ln(p/p^0)$, where $\Delta\mu^0(T) = \Delta(E_{\text{ZPE}} + E^{\text{osc}}(0 \rightarrow T) + E^{\text{rot}} + E^{\text{trans}} + RT - T(S^{\text{osc}} + S^{\text{rot}} + S^{\text{trans}}))$. The surface energy, $\gamma_{hkl}(\text{H}_2\text{O})$, as a function of the n adsorbed water molecules and temperature can be described by the following formula

$$\gamma_{hkl}(\text{H}_2\text{O}) = \gamma_{hkl}^0 + \theta_{hkl} \Delta_a G_{hkl}(p, T, n\text{H}_2\text{O})/2n \quad (1)$$

with $\theta_{hkl} = 2n/A_{hkl}$, where θ_{hkl} stands for the surface coverage by water, A_{hkl} is the area of the exposed hkl plane, and γ_{hkl}^0 is the

Table 1. Surface Energies of the Most Stable Monoclinic Zirconia Planes

	exposed plane	(-111)	(111)	(-101)	(101)	(011)	(110)	(001)	(010)	(100)
$\gamma/(\text{J}\cdot\text{m}^{-2})$	rigid surface	1.34	1.39	1.71	2.37	1.89	2.26	1.97	2.53	1.88
	relaxed surface	0.87	1.06	1.23	1.52	1.34	1.42	1.35	1.75	1.47
relative relaxation energy/%		35	24	28	36	29	37	31	31	22

surface energy in the fully dehydrated state ($\theta_{hkl} = 0$). The calculated $\Delta_a G_{hkl}(p, T, n\text{H}_2\text{O})$ values were next used to predict the Wulff morphology of the zirconia nanocrystallites under specified thermodynamic conditions ($T, p_{\text{H}_2\text{O}}$).

The temperature and pressure dependence of the anisotropic adsorption of water on the particular hkl planes are expressed in terms of the surface coverage, θ_{hkl} , using a multisite Langmuir isotherm.^{52,50}

$$\theta_{hkl} = \sum_{i=1} x_i \frac{\beta_i^n}{1 + \sum_{i=1} \beta_i^n} \quad (2)$$

where $x_i = N_i/N$ is the ratio of the N_i sites per total number N of the available adsorption centers, whereas β_i^n is the calculated cumulative adsorption equilibrium constant. Total surface coverage Θ , which actually is measured experimentally, can be then expressed as $\Theta = \sum_{hkl} \theta_{hkl}$.

The multisite Langmuir isotherm can be transformed into the empirical Fowler–Guggenheim (F-G) equation^{53,54}

$$\ln\left(\frac{\Theta}{1-\Theta}\right) - \ln p = \alpha\Theta + \ln K \quad (3)$$

which assumes the existence of a monolayer of the laterally interacting molecules, accounted for within the mean field approximation by the α parameter.

2.3. Size Effect. The relative stability of a given nanocrystal results from the compromise between the bulk energy including the stress contribution (the stress tensor of the (0,2) type can be derived by differentiation of the energy with respect to the deformation of the crystal), and the interfacial energy, associated with the presence of surface, edges, and corners as was shown by Barnard et al.⁵⁵ The surface energy outperforms the other interfacial energies, whereas the stress energy can be approximated by the internal hydrostatic pressure.^{30,55} Furthermore, for nanocrystals with sizes in the range of 3–100 nm, the edge and corner contributions are negligible and can safely be ignored together with slight effects related to the simultaneous minimization of the total surface to volume ratio and total surface energy.^{55,56} Indeed, it has been shown recently that for monoclinic ZrO_2 nanocrystals with diameters greater than ~ 7.5 nm the optimized nanomorphology converges to that of the Wulff shape.⁵⁶

In this article, the volume compressive dilation caused by the surface energy and validity of the Laplace–Young equation were assumed for energy calculations. A set of energy versus volume calculations was performed, and the results were fitted to the Birch–Murnaghan equation of state (the root mean square was $<10^{-4}$). The compressibility of the bulk was calculated as a second derivative of the energy with respect to the cell volume at the equilibrium point.

2.4. Sample Preparation and Microscopic Investigations. The synthesis of the $m\text{-ZrO}_2$ nanocrystals is described in the Supporting Information in more detail. Transmission electron microscopy (TEM) measurements were carried out using a Philips

CM20 instrument operating at 200 kV. Prior to TEM analysis the samples were ultrasonically dispersed in ethanol, on a holey carbon film supported on a copper grid (400 mesh). The grid was dried for 45 min and subjected to plasma cleaning (Solarus Gatan Model 950) to eliminate surface contamination.

3. RESULTS AND DISCUSSION

3.1. Bulk Structure. The monoclinic phase of ZrO_2 (baddeleyite) possess a $P2_1/c$ structure, and the X-ray analysis reveals that the elementary cell consists of four ZrO_2 stoichiometric units. Each Zr^{4+} ion is surrounded by seven O^{2-} anions, with the Zr–O distances ranging from 2.02 to 2.07 Å, whereas four oxygen ions exhibit 4-fold coordination, and four trigonal one.⁵⁷ The correctness of the computational approach was proved by comparison of the calculated lattice parameters, unit cell volume, coordinates of the atoms, and the enthalpy of formation of $m\text{-ZrO}_2$ with the corresponding experimental values (see Supporting Information, Table S3).^{58,59} Very good agreement shows that the employed formalism with the adopted parametrization is capable of describing the investigated monoclinic zirconia with an adequate accuracy.

3.2. Equilibrium Shape. In order to correctly predict and visualize the equilibrium morphology of the monoclinic zirconia nanocrystals, a complete set of consistent γ_{hkl} values is required. For DFT modeling, we selected a set of low index planes with the largest interplanar spacing as they are predicted to be the most stable, following the Bravais–Friedel–Donnay–Harker theory.⁶⁰ In Table 1 surface energies of the exposed rigid and relaxed planes, together with the percentage of the relaxation energy, are summarized. The latter parameter was defined in the following way: $(\gamma_{\text{rigid surface}} - \gamma_{\text{relaxed surface}})/\gamma_{\text{rigid surface}} \times 100\%$. As shown in Table 1, the surface energies of the relaxed facets increase in the following order: $(-111) < (111) < (-101) < (011) < (001) < (110) < (100) < (101) < (010)$. Similar tendency has been observed previously by Christiansen and Carter within the less adequate LDA approximation.³²

The calculated γ_{hkl} values were next used to predict equilibrium morphologies of the rigid and relaxed monoclinic ZrO_2 crystals, which generally are quite similar (Figure 1). As can be inferred from this figure, only four (-111) , (111) , (011) , and (001) facets are eventually exposed. Their relative abundances are summarized in Table S4 in the Supporting Information. Upon relaxation, the contribution of the (-111) plane increases, reducing simultaneously the area of the (111) plane. Interestingly, the (-101) termination disappears, even though the less stable planes such as (011) and (001) are still exposed (Table 1).

Comparison of the experimental TEM images of the zirconia nanocrystals (a–c) with the appropriately oriented Wulff shapes (a_1 – c_1) along the $[-111]$, $[011]$, and $[001]$ directions is shown in Figure 2. As it can be readily seen, the theoretically predicted shape of $m\text{-ZrO}_2$ fits quite well to the corresponding TEM pictures (Figure 2a–c). The synthesized zirconia nanoparticles are terminated with the (-111) , (111) , (011) , and (001) planes,

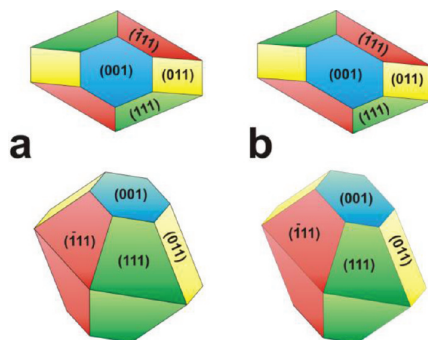


Figure 1. Top and lateral view of the theoretical equilibrium shapes for nanocrystalline *m*-ZrO₂, calculated without (a) and with (b) surface reconstruction effect.

in agreement with the theoretical predictions. The symmetry of the diffraction spots in the inserted FFT patterns (Figure 2a–c) reveals the $[-111]$, $[011]$, and $[001]$ orientation of the observed crystallites, allowing for univocal alignment of the predicted 3D Wulff shapes with respect to the experimental 2D images (Figure 2a₁–c₁). Some discrepancies between the morphologies predicted by the Wulff construction and the experimental habit of the obtained *m*-ZrO₂ nanocrystals might be caused by the anisotropy in the rate of the crystal growth, the influence of synthesis environment and the residual hydroxylation of the surface, which can affect the energy of the exposed planes.⁶¹

3.3. Atomic Structure of the Exposed Planes. Detailed atomic structures of the exposed surfaces of the *m*-ZrO₂ nanocrystal are shown in Figure 3 (the blue and the red balls symbolize zirconium and oxygen ions, respectively). There are two kinds of the bulk oxygen ions of different coordination: a trigonal, O_{3c}, and a tetrahedral, O_{4c}, one. The bulk zirconium cations, in turn, all exhibit a 7-fold coordination. The coordination number of the surface ions is lowered as revealed in Figure 3a–d, where the dangling bonds are indicated with dashed lines. The direction and the magnitude of displacements of the surface ions upon the relaxation, as well as the numbering of the surface ions, are shown in Figure 3a₁–d₁.

The (-111) plane consists of four zirconium cations (Figure 3a). Three of them (no. 1, 2, and 3 in Figure 3a₁) exhibit a reduced 6-fold coordination due to one missing oxygen ligand, whereas the Zr4 cation preserves its bulk 7-fold surrounding. Among seven surface oxygen ions, four exhibit a trigonal coordination (O_{3c}) and two a tetrahedral one (O_{4c}), and the most exposed oxygen anion is attached to two Zr cations only (O7_(2c)) in Figure 3a₁. Displacements of the oxygen ions upon surface relaxation are generally directed toward the undercoordinated Zr cations (Figure 3a₁). The following surface composition of the slab was used for modeling of the (-111) plane $\{1\text{Zr}_{7c} (2.2 \text{ nm}^{-2}), 3\text{Zr}_{6c} (6.7 \text{ nm}^{-2}), 1\text{O}_{2c} (2.2 \text{ nm}^{-2}), 4\text{O}_{3c} (8.9 \text{ nm}^{-2}), 2\text{O}_{4c} (4.5 \text{ nm}^{-2})\}$. The numbers in the parentheses indicate the surface concentration of the indicated ions.

On the (111) plane, all exposed zirconium ions exhibit a 6-fold arrangement. The bulk coordination of the oxygen atoms O1 and O5 is preserved, whereas all others exhibit one missing bond, giving rise to 2O_{3c} and 2O_{2c} undercoordinated species (Figure 3, b and b₁). Hence, in comparison to the (-111) plane, formation

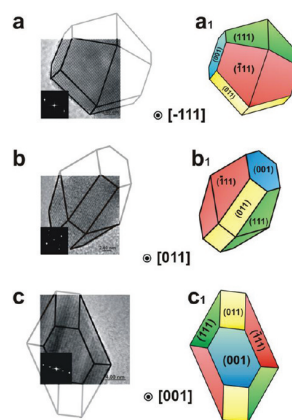


Figure 2. TEM pictures of the monoclinic zirconia nanocrystals (a–c) together with the calculated Wulff shapes (a₁–c₁), oriented along $[-111]$, $[011]$, and $[001]$ directions to align with the observed 2D images.

of the (111) facet requires the cleavage of a larger number of bonds, and therefore it exhibits higher surface energy ($\gamma_{(111)} = 1.06 \text{ J/m}^2$ versus 0.87 J/m^2 $\gamma_{(-111)}$). Reconstruction of the (111) plane induces significant movement of all the coordinatively unsaturated ions (Figure 3b₁). The resultant model of the (111) plane consists of $\{4\text{Zr}_{6c} (7.3 \text{ nm}^{-2}), 2\text{O}_{2c} (3.7 \text{ nm}^{-2}), 3\text{O}_{3c} (5.5 \text{ nm}^{-2}), 1\text{O}_{4c} (1.8 \text{ nm}^{-2})\}$ surface ions.

The doubled unit cell of the (011) plane contains four zirconium and four oxygen ions that preserve their bulk coordination. For two Zr cations the coordination is reduced to six (Zr2 and Zr4) and to five (Zr1 and Zr3), whereas in the case of oxygen trigonal (O1, O2, O4, O5, O6, O7) and digonal (O3, O8) species with one and two dangling bonds, respectively, can be distinguished (Figure 4c). The atomic surface composition can be described in the following way: $\{2\text{Zr}_{5c} (2.6 \text{ nm}^{-2}), 2\text{Zr}_{6c} (2.6 \text{ nm}^{-2}), 2\text{O}_{2c} (2.6 \text{ nm}^{-2}), 6\text{O}_{3c} (10.4 \text{ nm}^{-2})\}$. The reduction of the coordination number for the exposed ions is higher than in the case of the previous planes, accounting for the enhanced surface energy (1.34 J/m^2) of the (011) facet. Displacements of the surface ions upon relaxation (Figure 4c₁) show that the positions of the trigonal O_{3c} anions (no. 1, 5, 6, and 10) are mostly affected.

The (001) termination, in turn, has the same number of dangling bonds as the previous one, and therefore, a comparable surface energy of 1.35 J/m^2 (Table 1). The bulk coordination of the Zr cations is reduced to 6 (Zr2, Zr4) and 5 (Zr1, Zr3), and that of the anions to 3 (O1 and O5) and 2 (O2, O3, O6, and O7). However, one tetrahedral and two trigonal oxygen anions maintain their bulk coordination (Figure 3d). The resultant composition of the slab model can be expressed as $\{2\text{Zr}_{5c} (9.3 \text{ nm}^{-2}), 2\text{Zr}_{6c} (9.3 \text{ nm}^{-2}), 4\text{O}_{2c} (18.6 \text{ nm}^{-2}), 2\text{O}_{3c} (9.3 \text{ nm}^{-2}), 2\text{O}_{4c} (9.3 \text{ nm}^{-2})\}$. As expected, the diagonal oxygen anions exhibit the largest displacement upon the surface relaxation (Figure 3d₁).

In the each investigated case, the surface relaxation affects also the distance between the first and the second layer. According to Noguera, for metal oxides the topmost oxygen ions are generally displaced outward, whereas topmost cations are displaced inward upon the surface relaxation.⁶² However, such rearrangement was

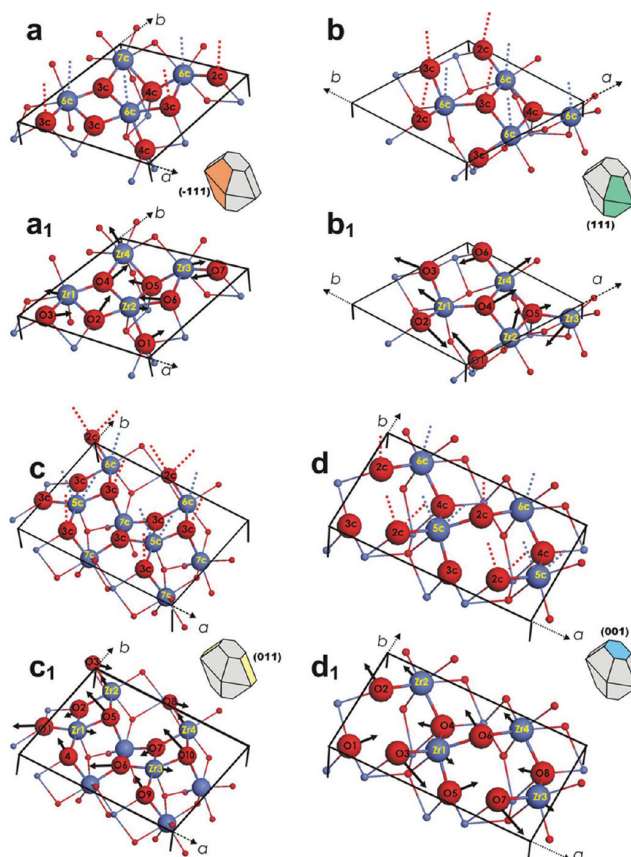


Figure 3. Top-lateral view of the surface structure of the exposed planes of the *m*-ZrO₂ nanocrystal (a–d). The dotted lines indicate missing bonds for the surface ions. Principal directions of the movement of the surface ions upon relaxation are indicated by black arrows (a₁–d₁).

not observed by us, in agreement with previous reports of Christensen and Carter.³²

3.4. Water Sorption—Molecular Picture and Thermodynamics. For water adsorption modeling, H₂O molecules were attached successively to the coordinatively unsaturated surface zirconium ions until the full monolayer coverage was achieved. A large number of starting geometries of the adspecies were explored to determine their most stable adsorption modes. To begin with, for each exposed zirconium site both dissociative and associative adsorption modes were tested, whereas for highly unsaturated zircon ions (with two Zr–O bond missing) a multiple water adsorption was assumed. The most stable adsorption forms of water at given temperature and pressure were determined on the base of the calculated Gibbs free energies. Since each unit cell contains four exposed zirconium atoms (Figure 3), the following water coverages $\Theta = 0.25, 0.5, 0.75, 1.0$ are amenable for the modeling.

Hydration of the (–111) Plane. The optimized structure of first water molecule (W1) adsorbed on the (–111) plane is shown in Figure 4a. Water adsorbs dissociatively on the Zr2_(6c) site ($\Delta_a E = -1.10$ eV), and the Zr2_(6c)–OH distance is equal to

2.14 Å (Figure 4a). The detached proton is accommodated by the neighboring O7_(2c) atom, and the corresponding surface coverage is equal to 2.2 H₂O/nm². The second water molecule (W2) adsorbs in an associative fashion on the Zr1_(6c) site, enhancing the coverage to 4.5 H₂O/nm² (Figure 4a). The Zr2_(6c)–O distance of 2.37 Å is longer than that observed for the hydroxyl ligand, and consequently the adsorption energy is increased to –1.13 eV (Table 2). The H₂O adspecies is stabilized by a hydrogen bond established with the nearby hydroxyl group. At higher coverage (6.7 H₂O/nm²), coexistence of both adsorption modes was observed, and an associative adsorption of the third water molecule (W3) on the Zr3_(6c) site (Figure 4 a₁) was accompanied by the energy gain decreased to $\Delta_a E = -0.93$ eV. The adsorbed H₂O molecule exhibited the Zr3_(6c)–O(H₂) bond length of 2.36 Å, and it was additionally stabilized via H-bonds (to reveal the emerging network of hydrogen bonds, water molecules from the adjacent unit cells, labeled with apostrophe, were added in Figure 4). The last H₂O molecule physisorbs on the remaining Zr4_(7c) bare sites exhibiting the Zr4_(7c)–O(H₂) bond length of 2.35 and $\Delta_a E$ of –0.85 eV. As revealed by Figure 4a₁, it is stabilized by two hydrogen bonds with W1 and

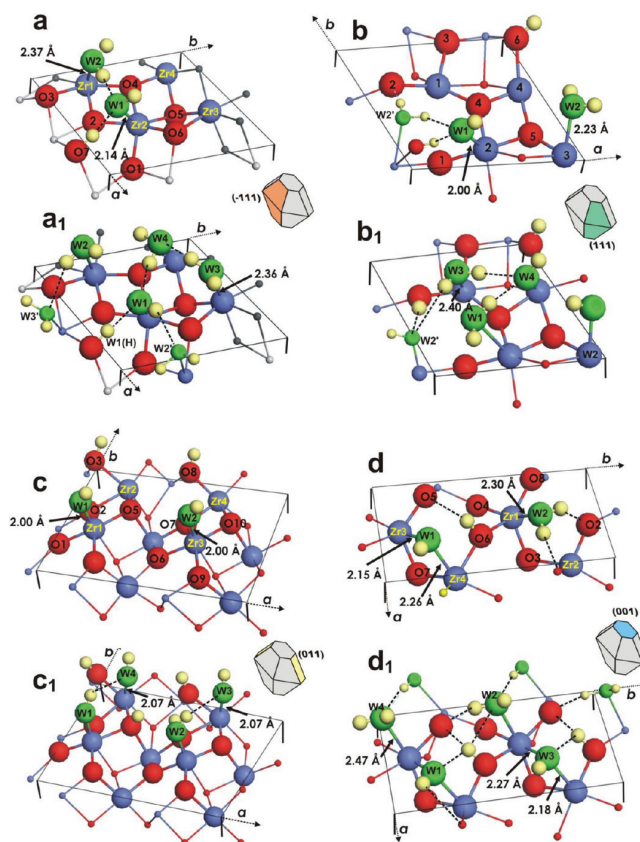


Figure 4. Top—lateral view of surface hydration of *m*-ZrO: (a–d) half-hydroxylated planes with two water molecules, (a₁–d₁) fully hydroxylated planes with four water molecules.

Table 2. Basic Characteristics of Water Adsorption on the (−111) Plane of the Monoclinic Zirconia^a

$n_{\text{H}_2\text{O}}$ ($\theta \cdot \text{nm}^{-2}$)	$\Delta_a E/\text{eV}$	adsorption center	adsorption type	$d_{\text{Zr}-\text{O}(\text{H}_2)}/\text{\AA}$
1 (2.2)	−1.10 ^b	Zr2 _(6c)	dissociative	2.14
2 (4.5)	−1.13	Zr1 _(6c)	associative	2.37
3 (6.7)	−0.93	Zr3 _(6c)	associative	2.36
4 (8.9)	−0.85	Zr4 _(7c)	associative	2.38

^a $n_{\text{H}_2\text{O}}$, number of water molecules per unit cell; θ , surface coverage; $\Delta_a E$, adsorption energy per H₂O molecule; and $d_{\text{Zr}-\text{O}(\text{H}_2)}/\text{\AA}$, bond length. ^b The calculated adsorption energies agree well with the values published earlier,¹⁸ equal to −1.20, −1.05, −0.93, −0.85, respectively.

W3 ad molecules of water (Figure 4a₁). These results remain in good agreement with previous literature data.^{18,63}

The values summarized in Table 2 indicate that the effect of stabilization decreases when surface coverage increases. A sudden increase observed on passing from $\theta_{(-111)} = 0.25$ to $\theta_{(-111)} = 0.5$ can be accounted for by the appearance of the H-bonds.

Hydration of the (111) Plane. The optimized structure of the first water molecule (W1) adsorbed on the (111) facet (giving rise to coverage of $1.8 \text{ H}_2\text{O nm}^{-2}$) is shown in Figure 4b. Water adsorbs dissociatively on the Zr2_(6c) site, forming a terminal hydroxyl group (with the Zr2_(6c)–OH distance of 2.00 Å) and a bridging hydroxyl group, by involving an adjacent surface O_{2c} ion. The calculated energy gain for this mode of adsorption is equal to −1.24 eV. The second water molecule (W2) chemisorbs on the Zr3_(6c) sites associatively and is additionally stabilized by strong hydrogen bonds (Figure 4b). The resultant adsorption energy −1.41 eV is therefore higher than that found for the first H₂O ad molecule, despite the Zr3_(6c)–O(H₂) distance of 2.23 Å being now longer. The surface coverage at this step equals to $3.7 \text{ H}_2\text{O nm}^{-2}$. The third water molecule was accommodated on the Zr1_(6c) cation in a similar associative way with the adsorption energy increased to −1.13 eV, enhancing $\theta_{(111)}$ value to $5.3 \text{ H}_2\text{O nm}^{-2}$. As indicated in Figure 4b₁, the Zr–O(H₂) bond length is elongated to 2.40 Å. Associative adsorption of the last water molecule (W4) takes place on the Zr4_(6c) centers. Even though the Zr4_(6c)–O(H₂) distance is becoming shorter (2.35 Å), the adsorption energy, $\Delta_a E = -0.92 \text{ eV}$, decreased.

Table 3. Basic Characteristics of Water Adsorption on the (111) Plane of the Monoclinic Zirconia^a

$n_{\text{H}_2\text{O}}$ ($\theta \cdot \text{nm}^2$)	$\Delta_a E/\text{eV}$	adsorption center	adsorption type	$d_{\text{Zr}-\text{O}(\text{H}_2)}/\text{\AA}$
1 (1.8)	-1.24	Zr2 _(6c)	dissociative	2.00
2 (3.7)	-1.41	Zr3 _(6c)	associative	2.23
3 (5.3)	-1.13	Zr1 _(6c)	associative	2.40
4 (7.1)	-0.92	Zr4 _(7c)	associative	2.35

^a $n_{\text{H}_2\text{O}}$, number of water molecules per unit cell; θ , surface coverage; $\Delta_a E$, adsorption energy per molecule; $d_{\text{Zr}-\text{O}(\text{H}_2)}/\text{\AA}$, bond length.

Table 4. Basic Characteristics of Water Adsorption on the (011) Plane of the Monoclinic Zirconia^a

$n_{\text{H}_2\text{O}}$ ($\theta \cdot \text{nm}^2$)	$\Delta_a E/\text{eV}$	adsorption center	adsorption type	$d_{\text{Zr}-\text{O}(\text{H}_2)}/\text{\AA}$
1 (1.3)	-1.91	Zr1 _(5c)	dissociative	2.00
2 (2.6)	-1.98	Zr3 _(5c)	dissociative	2.00
3 (3.9)	-1.67	Zr2 _(6c)	mixed	2.07
4 (5.2)	-1.73	Zr4 _(6c)	associative	2.07

^a $n_{\text{H}_2\text{O}}$, number of water molecules per unit cell; θ , surface coverage; $\Delta_a E$, adsorption energy per molecule; $d_{\text{Zr}-\text{O}(\text{H}_2)}/\text{\AA}$, bond length.

This is caused by the fact that water admolecules reorient themselves to form a system of hydrogen bonds. However, being weaker they do not compensate the lateral repulsion between the adspecies, and hence the full surface coverage is not thermodynamically stable above 0 °C (vide infra). The principal parameters describing the adsorption process on the (111) plane are summarized Table 3.

Hydration of the (011) Plane. Water adsorption on the (011) facet is determined by its specific structure with half of the exposed zirconium sites being coordinatively fully saturated. Therefore, to preserve the total number of the adsorption sites the relevant elementary cell was doubled. The first (W1) and the second (W2) water molecules adsorb dissociatively on the Zr1_(5c) and Zr3_(5c) sites, leading to the concurrent formation of terminal and bridging (by entailing an adjacent O_{2c} surface ion) hydroxyl group with $\Delta_a E = -1.91$ and -1.98 eV, respectively, and the same Zr_{5c}-OH bond length of 2.00 Å (Figure 4c). Due to the relatively large distance between those sites (5.11 Å), both adsorption events can be treated independently. The resultant coverage corresponds to 2.6 H₂O/nm². Adsorption of the third H₂O molecule (W3) enhances the water coverage to 3.9 H₂O/nm². It occurs in a dissociative way on the Zr2_(6c) sites with the released proton attached to the adjacent O8_(3c) ion (Figure 3c₁). The calculated adsorption energy was equal to -1.67 eV, and the Zr2_(6c)-OH distance was found to be 2.07 Å.

For the last water molecule (W4) the adsorption occurs in a dissociative way on the Zr4_(6c) sites with the energy slightly enhanced to -1.73 eV, in comparison to the previous step. The Zr2_(6c)-OH distance of 2.07 Å and $\theta = 5.2$ H₂O/nm² were determined Figure 4c₁). The crucial parameters characterizing the adsorption process on the (011) plane are summarized in Table 4.

Hydration of the (001) Plane. In the case of the (001) plane, the most stable form of adsorbed water (W1) is a dissociative bidentate mode (Figure 4d), with attachment of the resultant hydroxyl group to the Zr3_(5c) and Zr4_(6c) centers ($\Delta_a E = -1.95$ eV).

Table 5. Basic Characteristics of Water Adsorption on the (001) Plane of the Monoclinic Zirconia^a

$n_{\text{H}_2\text{O}}$ ($\theta \cdot \text{nm}^2$)	$\Delta_a E/\text{eV}$	adsorption center	adsorption type	$d_{\text{Zr}-\text{O}(\text{H}_2)}/\text{\AA}$
1 (1.9)	-1.95	Zr _{5c} (Zr3)/Zr _{6c} (Zr4)	dissociative	2.15/2.26
2 (3.7)	-1.57	Zr _{5c} (Zr1)	associative	2.30
3 (5.6)	-1.38	Zr _{5c} (Zr1)/Zr _{6c} (Zr2)	dissociative	2.18/2.27
4 (7.5)	-1.23	Zr _{5c} (Zr3)	associative	2.47

^a $n_{\text{H}_2\text{O}}$, number of water molecules per unit cell; θ , surface coverage; $\Delta_a E$, adsorption energy per molecule; $d_{\text{Zr}-\text{O}(\text{H}_2)}/\text{\AA}$, bond length.

The liberated proton is accommodated by the nearby O6_(2c) anion. The ensuing surface coverage corresponds to 1.9 nm⁻². The Zr3_(5c)-OH bond is markedly shorter (2.15 Å) in comparison to that of the Zr4_(6c)-OH one (2.26 Å), whereas in the (Zr1_(5c))-(O6_(2c))-(Zr4_(6c)) moiety the bond lengths are almost equal (2.22 and 2.20 Å, respectively); see Figure 4d.

The next H₂O molecule (W2) adsorbs on the Zr1_(5c) cation in an associative fashion, with the adsorption energy of $\Delta_a E = -1.57$ eV, increasing the surface coverage to 3.7 nm⁻² (Figure 4d). The Zr1_(5c)-OH₂ bond length is equal to 2.30 Å, and this adspecies is stabilized by strong hydrogen bonds. The presence of the W2 water leads also to an appreciable increase of the bond lengths within the bridging hydroxyl groups, produced in the previous step.

Owing to the similar local environment of the Zr1, Zr2, and the Zr3, Zr4 sites, subsequent water molecules (W3 and W4) adsorb in a similar way (Figure 4d₁). The third H₂O species, upon dissociation on the surface, forms two OH groups (a bridging Zr1_(5c)-OH-Zr2_(6c) and a terminal O2_(2c)-H one), with the adsorption energy of $\Delta_a E = -1.38$ eV. The surface coverage at this stage is equal to 5.6 H₂O nm⁻². The last water molecule is attached associatively ($\Delta_a E = -1.23$ eV), again to the Zr1_(5c) site completing its coordination sphere. As a result, all exposed zirconium ions became fully saturated by complete hydration of the surface, corresponding to $\theta = 7.5$ H₂O nm⁻².

The main difference between the half and full monolayer coverage is development of a more extensive hydrogen bond system. At higher coverage, the H-bonds are reorganized and become longer, giving rise (along with the enhanced lateral repulsion between the positively charged protons) to lowering of the adsorption energy. The basic characteristics of water adsorption on the (001) plane is provided in Table 5.

Comparison with experiment reveals that the calculated mean adsorption energies of -1.1 eV/H₂O molecule in the coverage range of 4 molecules per nm² remain in good agreement with the empirical value of ca. -1.0 eV/H₂O molecule observed by Ushakov and Navrotsky.⁶⁴ for the same coverage. Moreover, the average density of the hydroxyl sites equal to 2.54 μmol/m² for fully covered *m*-ZrO₂ surface (calculated by taking into account the particular areas of the exposed planes) corresponds well with the experimental value of 2.29 μmol/m² reported by B. Pawelec,⁶⁵ supporting nicely the proposed theoretical model of water sorption experimentally.

3.5. Thermodynamic Diagrams of Surface Hydration Equilibria. The free enthalpy (Gibbs energy) of water adsorption on the exposed planes of the *m*-ZrO₂ nanocrystal as a function of temperature (for partial pressure of water equal to 0.01 atm) are plotted in Figure 5, together with the associated water coverage, θ_{hkl} , and differential, $d\theta_{\text{hkl}}/dT$, curves. In these diagrams, the

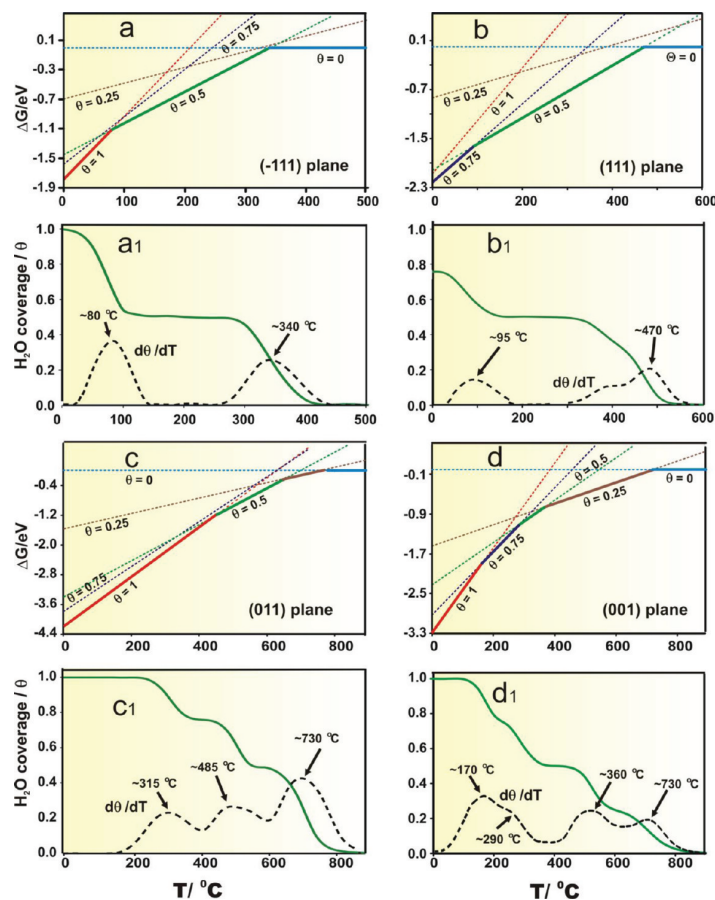


Figure 5. Gibbs free energy of water adsorption as a function of temperature at $p/p^\circ = 0.01$ bar for different number of adsorbed H_2O molecules (a–d) together with the corresponding surface coverage θ and a differential curve $d\theta/dT$ (a₁–d₁) for all terminations of the $m\text{-ZrO}_2$ nanocrystal.

most stable adsorption form of water at given temperature corresponds to the lowest Gibbs energy. However, for proper description of the θ_{hkl} variation as a function of temperature (Figure 5a₁, b₁, c₁, and d₁), the close-lying $\Delta_a G_{hkl}(T)$ lines, especially in the vicinity of the crossing points, have also been taken into account. The resultant coexistence of various water adspecies leads to smooth variation of the surface coverage with temperature, instead of the abrupt changes implied by simplified lowest Gibbs energy criterion only.

As shown in Figure 5a at the low-temperature regime (below 80 °C), a monolayer of water (corresponding to four ad molecules) is formed on the (–111) plane (Figure 5a₁). Around 80 °C two H_2O molecules leave the surface, liberating the $\text{Zr}4_{(7c)}$ and $\text{Zr}3_{(6c)}$ sites of the lowest affinity to water (Table 2), which can easily be seen as a pronounced peak in Figure 5a₁ (dotted line $d\theta/dT$). Such desorption leads to the drop of the coverage to $\theta_{(-111)} = 0.5$ (intermediate stages with $\theta_{(-111)} = 0.25$ and 0.75 were found to be unstable, in contrast to earlier calculations of Korhonen et al.¹⁸). The adsorbate half-monolayer contains both dissociatively and molecularly adsorbed water species associated with the

$\text{Zr}2_{(7c)}$ and $\text{Zr}1_{(7c)}$ sites. Dehydration of the (–111) facet is completed at above ~340 °C (Figure 5a₁), remaining in nice agreement with the previously reported value of ~350 °C.¹⁸

Thermal stability of the hydrated (111) facet (Figure 5b) is somewhat different from that of the (–111) one, as water molecules leave this plane in a sequence $1 \rightarrow 2$ instead of $2 \rightarrow 1$. The highest coverage of $\theta_{(111)} = 0.75$ (corresponding to 3 H_2O molecules) is stable up to ~95 °C. The first desorbing water molecule was associatively attached to the $\text{Zr}4_{(6c)}$ sites without formation of the stabilizing auxiliary hydrogen bonds. The region of $\theta_{(111)} = 0.5$ related with two associatively and dissociatively adsorbed water molecules is stable in a wider temperature window (95–470 °C), which can be accounted for by strong stabilization effect of the resultant hydrogen bond network. Around 470 °C, the two remaining molecules of water depart consecutively, as can be inferred from the corresponding differential $d\theta/dT$ curve, leaving the analyzed (111) plane in a fully dehydroxylated state (Figure 5b₁). In fact, the high-temperature desorption peak exhibits two clear maxima located at ~350 and 470 °C that can be associated with stepwise

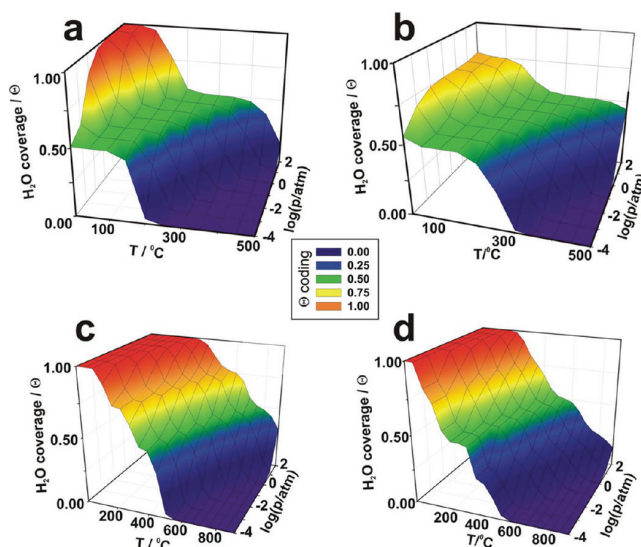


Figure 6. Two-dimensional diagrams of the equilibrium water coverage as a function of temperature and partial pressure for (a) (-111) , (b) (111) , (c) (011) , and (d) (001) planes of the monoclinic zirconia, revealing a bimodal (a,b), trimodal (c), and tetramodal (d) desorption characteristics.

reduction of the surface coverage from $\theta_{(111)} = 0.5$ to $\theta_{(111)} = 0$ via transient $\theta_{(111)} = 0.25$ state.

In the case of the (011) plane, the monolayer of water is much more stable as the two earliest desorption peaks, associated with the $\text{Zr}2_{(6c)}$ and $\text{Zr}3_{(6c)}$ centers, are observed at ~ 300 and ~ 470 °C (Figure 5c,c₁). It is quite surprising that the surface coverage is reduced in this range of temperatures, since the free enthalpy for $\theta_{(111)} = 1$ remains the lowest until 485 °C. However, a more careful inspection of the water sorption diagrams shows that there is a nearby crossing of two $\Delta_a G(T)$ lines for $\theta_{(011)} = 0.75$ and $\theta_{(011)} = 0.5$ at ~ 315 °C with the energy only slightly higher than that corresponding to the full coverage. Apparently, it is responsible for desorption of the first portion of water (Figure 5c₁). The next H_2O molecule desorbs at the temperature of ~ 485 °C, defined by the crossing of the $\theta_{(011)} = 1.0$ and $\theta_{(011)} = 0.5$ lines, whereas the last H_2O leaves the surface at ~ 730 °C, as it can be inferred from the intersection of the $\theta_{(011)} = 0.5$ and the bare surface plots.

For the (001) plane, the H_2O monolayer persists until ~ 170 °C (Figure 5d). Above this temperature, the first molecule of the associatively adsorbed water leaves the surface liberating the $\text{Zr}3_{(5c)}$ center. The next reduction of the surface coverage from $\theta_{(001)} = 0.75$ and $\theta_{(001)} = 0.5$ occurs at ~ 290 °C. It corresponds to desorption of water dissociatively adsorbed on the $\text{Zr}1_{(5c)}/\text{Zr}2_{(6c)}$ site. The second associatively attached H_2O molecule departs at ~ 360 °C, exposing the bare $\text{Zr}1_{(5c)}$ center. The last desorption peak of the dissociatively accommodated water on the dual $\text{Zr}3_{(5c)}/\text{Zr}4_{(6c)}$ site is observed at ~ 730 °C, and then the (001) termination assumes a fully dehydroxylated state.

The results of our calculations revealed that the less stable (001) and (011) planes exhibit much higher affinity toward water adsorption than the more stable (-111) and (111) ones. Whereas in the previous case water sorption exhibits a bimodal

desorption characteristics ($1 \rightarrow 2$ and $2 \rightarrow 2$, respectively, see Figures 5a₁,b₁ and 6a,b), in the case of the (011) facets a trimodal $1 \rightarrow 1 \rightarrow 2$, and for (001) a tetramodal $1 \rightarrow 1 \rightarrow 1 \rightarrow 1$, desorption takes place (Figures 5c₁,d₁ and 6c,d). The calculated sorption parameters collected in Tables 2–5 remain in full agreement with the experimental values published by Ushakov and Navrotsky. The adsorption enthalpies derived from their calorimetric measurements for half-monolayer water coverage of the $m\text{-ZrO}_2$ varied from -1.14 to -1.76 eV.⁶⁴

In Figure 6, more involved two-dimensional $\theta_{hkl}(p,T)$ diagrams of water sorption on the exposed (-111) , (111) , (011) , and (001) planes of $m\text{-ZrO}_2$ are shown. They help to analyze the surface coverage as a function of both water partial pressure (adsorption isotherms) and temperature (adsorption isobars) in an integral way. Such plots may be used, i.e., for explaining poisoning effect of water present in the feed on the catalytic performance of the zirconia-based catalysts or the changes in the morphology of the $m\text{-ZrO}_2$ nanocrystals in different conditions, discussed below.

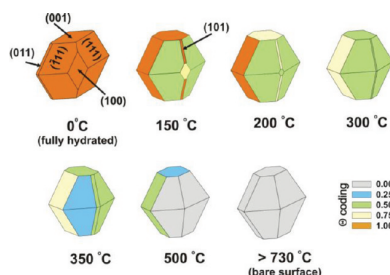
3.6. Changes of Morphology upon Hydration. As it was explained above, adsorption of water gives rise to pronounced anisotropic variation of the surface energy of the exposed facets of the monoclinic ZrO_2 . The calculated γ_{hkl} values at various temperatures for all terminations, along with the corresponding changes in their relative abundance, are collected in Table 6.

The calculated $\gamma_{hkl}(T)$ values can next be used to predict changes in the equilibrium morphology of the monoclinic zirconia nanocrystals, as a function of the experimental conditions (calcination temperature, humidity) using Wulff construction (Figure 7).

Analysis of the data presented in Table 6 and Figure 7 shows that, in spite of the monotonous increase of the surface energy with the increasing temperature (caused by the decreasing water coverage), the relative abundances of the exposed planes exhibit a

Table 6. Surface Energies of the Exposed Partially Hydrated Planes of the Monoclinic Zirconium Dioxide at Various Temperatures, Together with Their Relative Abundances, Calculated for $p/p_0 = 0.01$

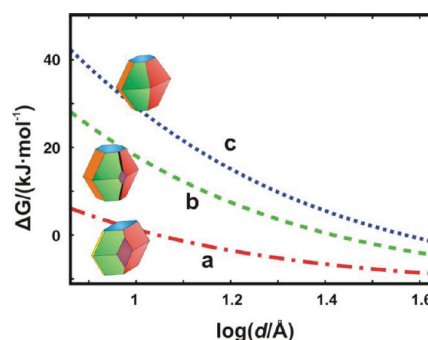
	0 °C	150 °C	200 °C	300 °C	350 °C	500 °C
$\gamma_{(-111)}/\text{J}\cdot\text{m}^{-2}$ (% abundance)	0.25 (45%)	0.57 (24%)	0.64 (21%)	0.79 (20%)	0.87 (18%)	0.87 (27%)
$\gamma_{(111)}/\text{J}\cdot\text{m}^{-2}$ (% abundance)	0.36 (24%)	0.61 (21%)	0.67 (21%)	0.81 (22%)	0.88 (15%)	1.06 (13%)
$\gamma_{(011)}/\text{J}\cdot\text{m}^{-2}$ (% abundance)	0.53 (6%)	0.59 (38%)	0.61 (45%)	0.65 (45.5%)	0.68 (54%)	0.75 (56%)
$\gamma_{(001)}/\text{J}\cdot\text{m}^{-2}$ (% abundance)	0.39 (16%)	0.74 (11%)	0.84 (10%)	1.02 (12%)	1.11 (7%)	1.20 (4%)
$\gamma_{101}/\text{J}\cdot\text{m}^{-2}$ (% abundance)	0.37 (0%)	0.63 (3%)	0.71 (2.8%)	0.88 (0.5%)	0.93 (6%)	1.06 (0%)
$\gamma_{(100)}/\text{J}\cdot\text{m}^{-2}$ (% abundance)	0.26 (10%)	0.60 (3%)	0.72 (0.2%)	0.97 (0%)	1.09 (0%)	1.35 (0%)

**Figure 7.** Wulff shapes of the monoclinic zirconia nanocrystals as a function of temperature for $p_{\text{H}_2\text{O}} = 0.01$ atm.

more complicated variation. Moreover, water adsorption gives rise to the appearance of new (100) and (101) facets, not observed in the dry ZrO_2 . The first one (100) is observed at low-temperature region (< 300 °C), whereas the ephemeral (101) plane appears from 150 to 350 °C. Nonetheless, the general truncated squeezed hexagonal bipyramid shape of the monoclinic zirconia nanocrystals is preserved in large range of the experimental conditions (Figure 7).

To evaluate the grain size dependence of the $m\text{-ZrO}_2$ shape, the Gibbs energy was plotted as a function of the average dimension, d , for three differently hydroxylated nanocrystals (Figure 8). Due to their rather intricate morphology, the size of an equivalent cube of the same volume was taken as a convenient dimension measure of the $m\text{-ZrO}_2$ crystallites. As revealed in Figure 8, in the case of very small grains ($d < 20$ Å) the differences in ΔG are quite pronounced, strongly favoring the hydroxylated state of the surface. However, with increasing size these discrepancies monotonously converge, and for crystallites with the typical size about 50–200 nm, hydration of the surface has rather small influence on the stability of the monoclinic zirconia nanocrystals. As a result, small crystallites formed in a nonhydrous environment (e.g., by calcination at elevated temperatures) are disfavored and exhibit a marked tendency for conversion into the morphology appropriate for the hydrated state when placed in a humid environment. In contrast, such tendency for large crystallites is attenuated as the corresponding thermodynamic driving force is apparently ceasing (Figure 8).

Once the polyhedral shape of the $m\text{-ZrO}_2$ nanocrystals is determined, from the particular areas of the exposed planes we can easily calculate their fractional abundance, the theoretical total surface area, and the areal concentration of the exposed zircon ions. Such data is useful for calculation of turnover frequencies in catalysis or for establishing quantitative relationships between the preparation conditions and profusion of the specific

**Figure 8.** Size dependence of the Gibbs free energy of the $m\text{-ZrO}_2$ nanocrystals for (a) fully hydroxylated ($T < 95$ °C), (b) half-hydroxylated ($\Theta = 0.5$, $T \sim 300$ °C), and (c) bare surface ($T > 750$ °C).

crystallographic facets that are most active, allowing for development of improved catalytic materials based on zirconia. Furthermore, from the relative abundance of all the exposed facets, one can calculate the total surface coverage by water as a function of temperature, $\Theta(T)$, since only this quantity can be directly measured in practice. In Figure 9, the $\Theta(T)$ and $d\Theta/dT$ profiles for water total adsorption at $p_{\text{H}_2\text{O}}/p_0 = 0.01$ are shown for $m\text{-ZrO}_2$ crystallites with dry and hydrated state morphologies. The results are compared with the gravimetric thermal desorption data (gray bars) published by Nawrocki et al.⁶⁶ and shown in Figure 9a,b. A quick inspection of this figure shows that, even if the contribution of the particular facets changes significantly for both model nanocrystals chosen for the comparison, the overall five-modal water desorption behavior is qualitatively well preserved.

The first peaks in the $d\Theta/dT$ curves shown in Figure 9a,b occur below 100 °C and are assigned to desorption of molecular water attached to the Zr_{6c} sites located on the (-111) and (111) planes. The second region of $\sim 200\text{--}400$ °C corresponds to depletion of the dissociatively adsorbed water from the (-111) plane as well as to the associatively adsorbed H_2O from the Zr_{6c} centers situated on the (011) and (001) terminations. Further decrease of the surface coverage in the temperature range of $400\text{--}600$ °C is associated with desorption of the water molecules adsorbed dissociatively on the Zr_{6c} sites located on the (111) and (011) planes. The highest temperature region around 750 °C can be attributed to elimination of the last portion of water from the highly unsaturated Zr_{6c} sites on the (011) and (001) planes. The investigated model of water adsorption considered only a monolayer coverage, however, a multilayer physisorption

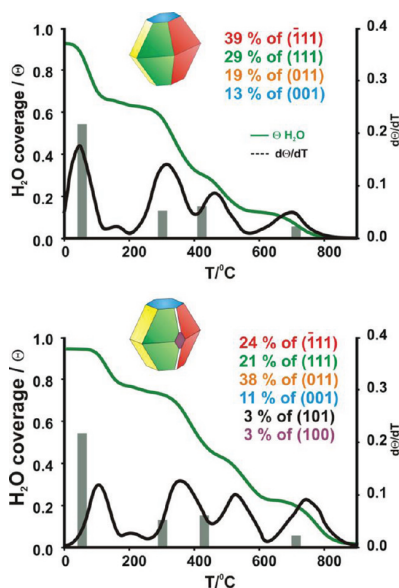


Figure 9. Total surface coverage as a function of temperature for the monoclinic zirconium dioxide. Calculated for the shape of the nanocrystals with bare surface (top) and partially hydroxylated ($\Theta = 75\%$) surface (bottom).

is expected to occur at low temperatures and higher p/p_0 values. Such weakly attached water molecules are usually desorbing below $100\text{--}120^\circ\text{C}$, so this region of the calculated diagram may not be fully consistent with the experimental data.

Experimental investigations of water adsorption/desorption processes on monoclinic zirconia are rather scarce.^{66,67} Thermogravimetric measurements of Nawrocki et al. have reported the presence of four maxima of the departing water located at 80, 300, 430, and 700°C . Except for a weak peak at around 200°C , associated with water release from the less abundant (001) planes, the number and the positions of the remaining bands correspond very well to the predicted values, calculated for the $m\text{-ZrO}_2$ nanocrystals with the equilibrium morphology of the dry state. For the nanocrystals with the shape of the hydrated state, such agreement is apparently less satisfactory, indicating that water adsorption does not lead to any appreciable changes in the habit of the $m\text{-ZrO}_2$ crystallites during the investigations.

As an alternative to adsorption isobars shown in Figure 9, variation of the coverage can be analyzed in terms of the Langmuir multisite or Fowler–Guggenheim isotherms (Figure 10). In the latter case, the repulsion between the adspecies is semiempirically taken into account within the mean field model.

Two distinct linear regions of different slope can be distinguished in the calculated F-G plot, with a distinct turning point at $\Theta = 0.27$. The effective energy of the mutual repulsive interactions between the adsorbed water molecules (gauged by the parameter α in eq 6) was equal to -0.29 eV for $\Theta \leq 0.27$, decreasing down to -0.13 eV for $\Theta \geq 0.27$. The negative value of the α parameter, following the F-G model, reveals repulsive character of the lateral energy, which is associated with dipolar interactions between the positively charge hydrogen atoms of the

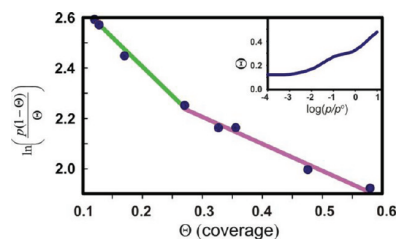


Figure 10. Fowler–Guggenheim isotherm at 400°C , and the corresponding multisite Langmuir isotherm at the same temperature (inset).

surface hydroxyl groups as discussed elsewhere.⁶⁸ It should be noted that the repulsion energy term is equal to $\alpha \times \Theta$, and therefore, for instance, in the case of $\Theta = 0.25$ and 0.75 they are equal to $-0.29 \times 0.25 = -0.07\text{ eV}$ and $-0.13 \times 0.75 = -0.10\text{ eV}$, respectively, in accordance with the values derived directly from DFT calculations. The corresponding DFT values of -0.05 eV for $\Theta = 0.25$, and -0.12 eV for $\Theta = 0.75$ were calculated for the hydration state of the $m\text{-ZrO}_2$ nanocrystal in the specified thermodynamic conditions as a difference between the adsorption energies of water admolecules accommodated sequentially on the zirconia surface. Careful inspection of the obtained results reveals that the abrupt change in the slope of the F-G plot can be assigned to passage from strong adsorption of water on the doubly unsaturated $\text{Zr}_{(\text{sc})}$ sites located on the (011) and (001) planes ($\Delta_a E \approx -1.9\text{ eV}$, Tables 4 and 5) to weaker adsorption on the singly unsaturated zirconium sites situated on the all (001), (011), (-111) , and (111) planes ($\Delta_a E \approx -1.2$ to -0.8 eV , Tables 2–5).

4. CONCLUSIONS

Combining the DFT calculations and atomistic thermodynamic modeling, water sorption on the (-111) , (111), (011), and (001) planes exposed by faceted monoclinic ZrO_2 nanocrystals was modeled. The calculated surface energies together with the Wulff construction demonstrate that it is possible to predict accurately the equilibrium shape of $m\text{-ZrO}_2$ crystallites under different hydration conditions and temperatures. The results remain in excellent agreement with the experimental TEM images. It was shown that water adsorption on the more stable (-111) and (111) planes exhibits a bimodal characteristics ($1 \rightarrow 2$ and $2 \rightarrow 2$, respectively), whereas for less stable (011) and (001) terminations a trimodal $1 \rightarrow 1 \rightarrow 2$ and a tetramodal $1 \rightarrow 1 \rightarrow 1 \rightarrow 1$ process were observed. Two-dimensional (surface coverage versus temperature and pressure) diagrams constructed for each of the examined planes allowed to describe water adsorption processes in a concise way. Using the shape- and size-dependent thermodynamic models, variations of the total surface coverage and the morphology of nanocrystals with temperature were rationalized in terms of the molecular structure and the stability of water adspecies. Macroscopic picture of water adsorption process was provided by the calculated multisite Langmuir and Fowler–Guggenheim isotherms. As far as we know, this is the first systematic attempt to explain at the molecular level water adsorption thermodynamics on faceted $m\text{-ZrO}_2$ nanocrystals under defined conditions in a comprehensive way by means of ab initio calculations confronted with experiment directly.

■ ASSOCIATED CONTENT

S Supporting Information. Supercell parameters of monoclinic ZrO_2 planes; stoichiometric terminations of (001), (010), and (101) slab models; parameters of calculated bulk unit cell for monoclinic zirconia; contribution of the exposed facets in the equilibrium shape of $m\text{-ZrO}_2$ crystal; and description of the synthesis of the $m\text{-ZrO}_2$ nanocrystals. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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2.4.4 Tekst artykułu H4

[H4] W. Piskorz*, J. Gryboś, F. Zasada, P. Zapała, S. Cristol, J.-F. Paul, Z. Sojka* „Periodic DFT Study of the Tetragonal ZrO₂ Nanocrystals – Equilibrium Morphology Modeling and Atomistic Surface Hydration Thermodynamics”, *Journal of Physical Chemistry C*, **116** (2012), 19307.

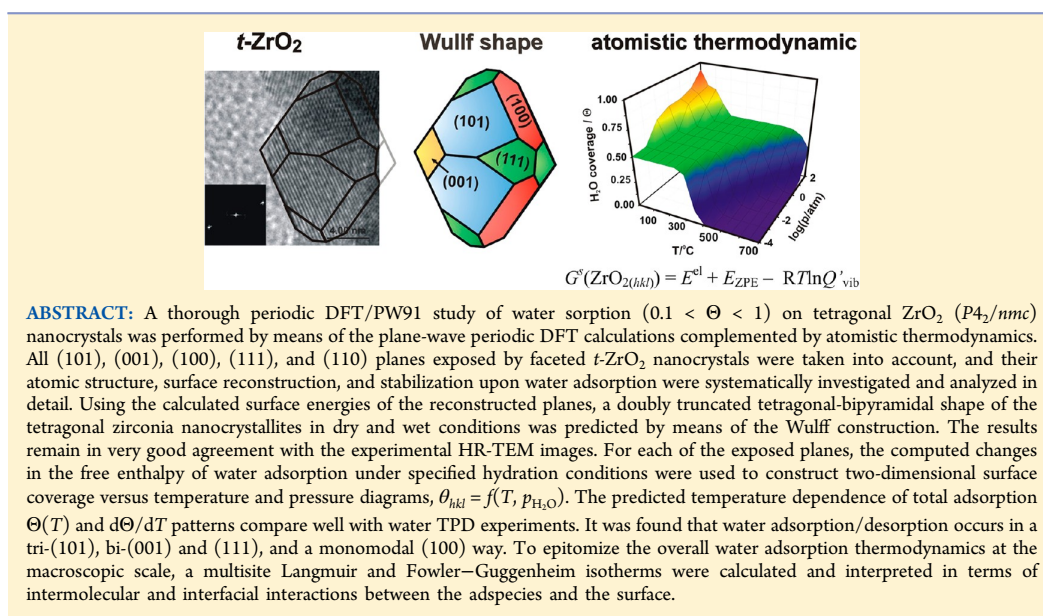
Periodic DFT Study of the Tetragonal ZrO₂ Nanocrystals: Equilibrium Morphology Modeling and Atomistic Surface Hydration Thermodynamics

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Supporting Information



1. INTRODUCTION

Zirconium dioxide (ZrO₂), owing to its unique properties, such as high hardness¹ and thermal stability,² high refractive index, and low thermal conductivity,³ is one of the most widely researched ceramic materials of high scientific and technological importance for fuel cell technology⁴ or in semiconductor and bioceramic applications.^{5–7} Moreover, having unique acid–base characteristics and redox properties, zirconia is used in catalysis as a robust support^{8–11} and catalyst component^{12–15} in a number of vital industrial processes.^{16–19}

Under normal pressures, the coarse grain zirconium dioxide can exist in monoclinic, *m*-ZrO₂, ($P2_1/c$); tetragonal, *t*-ZrO₂, ($P4_2/nmc$); and cubic, *c*-ZrO₂, ($Fm\bar{3}m$) forms depending on the temperature. The monoclinic phase is stable up to 1175 °C, transforming martensitically into the tetragonal one and, over 2370 °C, into the cubic polymorph. Yet, despite their apparent

thermodynamic instability, the tetragonal and the cubic phases are also observed at lower temperatures, when zirconia is doped with alien oxides, such as Y₂O₃,²⁰ CaO, or MgO,²¹ or upon decreasing the size of the crystallites below critical dimensions discussed elsewhere.^{22–24} Indeed, it has been shown that *t*-ZrO₂ is stable at ambient conditions when the size of the nanocrystals (NCs) is lower than ~20 nm.²⁵ The metastable tetragonal phase preserves the structural characteristic for high temperature, *t*-ZrO₂.²⁶ The nature and the concentration of dopants determine not only which polymorphic phase is actually present but also allow preventing the NC sintering and the tetragonal-to-monoclinic phase transition. Because of the

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remarkable technological importance of the tetragonal zirconia and versatile catalytic properties,^{27–29} this transition was deeply analyzed in the literature.^{30–32} It has been found that a number of different factors affect this transition, yet some discrepancies between the literature data are still persistent.^{33–35}

One of the key issues in the heterogeneous catalysis on zirconia materials is the proper recognition of the nature of the exposed facets and their surface reconstruction under the reaction conditions.³⁶ Indeed, successful control of the faceting allows for efficient optimization of their catalytic performance³⁷ and clear-cut morphology engineering. Careful inspection of abundant experimental data reveals that low-index (101), (001), (100), (111), and (110) planes are exposed in a number of *t*-ZrO₂ specimens prepared by various methods.^{38–40} Their relative abundance is influenced by the preparation conditions and the presence of dopands and auxiliary species, such as surfactants or structure-directing agents.^{41–43}

As a catalyst, zirconia nanocrystals are often exploited in wet conditions, since water can be the byproduct of the catalyzed reaction or the undesired harmful component of a real feed.^{44–47} Water is also unavoidably present during hydrothermal synthesis of highly dispersed ZrO₂ or in the course of the preparation of zirconia-supported catalysts, when classic impregnation or ion-exchange methods are used.⁴⁸ It is well known that water admolecules not only modify the nature of the active sites⁴⁹ but also may severely influence the stability of the ZrO₂ polymorphs as well.^{50–52} This effect is connected with surface hydroxylation and hydration processes that modify surface energies of the exposed facets. It has been reported that water molecules may adsorb on the ZrO₂ surface, forming single or multiple layers, involving both dissociative and molecular modes of adsorption.^{53–56}

Despite the clear role of nanomorphology and interfacial phenomena for appropriate understanding of the zirconia properties, among a number of papers on molecular modeling of bulk and surface zirconia,^{60–62} only a few have been devoted to investigations of surface hydration processes, mostly in a rather scant fashion.^{63,64} There is also lack of a systematic study of the *t*-ZrO₂ surface structure reconstruction and faceting in relation to the equilibrium morphology of the tetragonal zirconia in dry and wet conditions. Detailed quantitative evaluation of the surface coverage by water at working conditions (*T* and *p*_{H₂O}) of the zirconia-based catalysts is thus crucial for understanding the nature and quantification of the available active centers. Such knowledge is important for the molecular-level modeling of the catalytic reactions over the *t*-ZrO₂ nanocrystals.

The present paper, which continues our previous study on the monoclinic zirconia nanocrystals,⁶⁵ describes the results of DFT and atomistic thermodynamic modeling of the morphology and water adsorption equilibria for the bare and hydroxylated *t*-ZrO₂ nanocrystals. The molecular description of surface geometry relaxation, stability of all of the exposed planes, and the mechanism of water sorption processes were analyzed in detail. The calculated adsorption results, recapitulated in the form of the multisite Langmuir and Fowler–Guggenheim isotherms, were compared with experimental HR-TEM and water TPD results.

2. METHODS AND MATERIALS

2.1. Calculation Scheme and Structural Models. All computations were performed using the Vienna Ab initio

Simulation Package (VASP)⁶⁶ based on Mermin's finite temperature DFT.⁶⁷ The adopted calculation scheme was justified in our previous paper on *m*-ZrO₂.⁶⁵ The following electron configurations [Kr]4d²5s² and [He]2s²2p⁴ were used for the zirconium and oxygen atoms, respectively. The core electrons were kept frozen and replaced by PAW pseudopotentials.⁶⁸ The PW91 GGA exchange functional, as parametrized by Perdew et al.,⁶⁹ was employed together with the Methfessel–Paxton⁷⁰ smearing with the γ parameter set to 0.1 eV. To evaluate the accuracy of the adopted method, a number of tests were initially performed, by changing the cutoff energy from 350 to 700 eV, and the *k*-point sampling mesh from $2 \times 2 \times 2$ to $4 \times 4 \times 4$ (using a standard Monkhorst–Pack⁷¹ grid). As a result, the valence electrons were described using the plane-wave basis set with the cutoff at 400 eV. The integration in the Brillouin zone was carried out with the following mesh density: $2 \times 2 \times 2$ for the bulk unit cell and $2 \times 2 \times 1$ for each analyzed surface termination. We set the convergence criteria of $1 \cdot 10^{-5}$ eV between two successive SCF iterations. During the calculations, the positions of all bulk ions and, for the slab model, the positions of all ions located within the four topmost layers were relaxed, to keep the net forces acting on the atoms smaller than $1 \cdot 10^{-2}$ eV·Å⁻¹.

According to the *P4₂/nmc* space group symmetry, the nonequivalent, low index facets of the tetragonal zirconia include the (101), (001), (100), (111), and (110) planes. Their starting geometries were obtained by cleaving the solid *t*-ZrO₂ along the appropriate normal directions. For all the investigated planes, a (1×1) unit cell was used since it is sufficiently large to model high and low water coverages. To avoid any unphysical surface–surface interactions, a vacuum separation of 12 Å was set between two periodically repeated slabs composed of four to seven atomic layers. The influence of the slab thickness on the electronic energy was carefully verified, revealing that only three outermost ZrO₂ layers are significant in properly accounting for the surface relaxation. The developed slab model of *t*-ZrO₂ preserved both the bulk stoichiometry and the same structure of the top and the bottom surfaces (see Table S1 in the Supporting Information). Among several possible terminations, only the stoichiometric structures of the lowest surface energy were taken into account (Table S2 in the Supporting Information).

For water adsorption modeling, the energies of the admolecules determined in the static DFT calculations were complemented by entropic contributions derived by using the atomistic thermodynamics machinery. The gas phase–solid surface equilibrium was accounted for within the usual perfect gas approximation. The Wulffman program⁷² along with the Geomview interactive 3D visualization software⁷³ was used to reveal the theoretical equilibrium shape of the *t*-ZrO₂ nanocrystals in dry and wet conditions. Theoretical surface energies were calculated as $\gamma = (E_{\text{slab}} - nE_{\text{bulk}})/2A$, where E_{slab} denotes the slab energy, nE_{bulk} is the energy of the *nt*-ZrO₂ units in the bulk model, and A is the surface area exposed by the slab for a given *hkl* plane. Taking into account that the crystal shapes are essentially determined by the relative energies of the exposed planes, the entropy terms may safely be neglected, as they usually do not influence the results in a considerable way.^{74–76}

2.2. Thermodynamic Modeling and Adsorption Isotherms. Details of the calculation scheme used in the thermodynamic modeling^{77–79} were described and evaluated in our previous work.⁸⁰ For each of the proposed adsorption

modes, the corresponding free enthalpies $\Delta G_{hkl}(p, T, n\text{H}_2\text{O})$ were calculated as a function of temperature, T , and pressure, p . The lowest value of $\Delta G_{hkl}(p, T, n\text{H}_2\text{O})$ defines the most stable system in the given equilibrium conditions. For quantitative analysis of the results, a pristine (completely dehydroxylated) surface with the Gibbs energy equal to $G_{hkl}(\text{ZrO}_2) = E^{\text{el}} + E_{\text{ZPE}}^{\text{el}} - RT \ln Q'_{\text{vib}}$ was taken as a suitable reference state.⁸⁶ Assuming that the vibrational terms do not vary upon water sorption in a meaningful way (i.e., $\Delta G \cong \Delta E^{\text{el}}$), we can factorize the free enthalpy of adsorption in two parts: an electronic contribution, ΔE^{el} , calculated as a difference of the corresponding static DFT energies, and a change in the chemical potential of water upon adsorption: $\Delta G_{hkl}(p, T, n\text{H}_2\text{O}) = \Delta E^{\text{el}} - n\Delta\mu(p, T, \text{H}_2\text{O})$. Taking into account that the contribution to entropy and energy changes due to the soft modes associated with the frustrated translations and rotations of the H_2O admolecules is small, the major part of the thermal component comes from hard normal H_2O vibrations approximated by the leading ZPE term. In that case, the chemical potential of the adsorbed water species can be expressed as $\Delta\mu(p, T, \text{H}_2\text{O}) = \Delta\mu^0(T, \text{H}_2\text{O}) + RT \ln(p/p^0)$, where $\Delta\mu^0(T, \text{H}_2\text{O}) = \Delta(E_{\text{ZPE}}(\text{H}_2\text{O}) + E^{\text{osc}}(0 \rightarrow T) + E^{\text{rot}} + E^{\text{trans}} + RT - T(S^{\text{osc}} + S^{\text{rot}} + S^{\text{trans}}))$. The surface energy variation as a function of the n adsorbed water molecules and temperature, $\gamma_{hkl}(T, n\text{H}_2\text{O})$, can then be described in the following way

$$\gamma_{hkl}(T, n\text{H}_2\text{O}) = \gamma_{hkl}^0 + \theta_{hkl}\Delta G_{hkl}(p, T, n\text{H}_2\text{O})/2n \quad (1)$$

with $\theta_{hkl} = 2n/A_{hkl}$, where θ_{hkl} stands for the surface coverage by water, A_{hkl} is the area of the exposed hkl plane, and γ_{hkl}^0 is the surface energy in the fully dehydrated state ($\theta_{hkl} = 0$). The calculated $\Delta G_{hkl}(p, T, n\text{H}_2\text{O})$ values were subsequently used to predict the Wulff shape of the tetragonal zirconia nanocrystals under given thermodynamic conditions ($T, p_{\text{H}_2\text{O}}$).

The temperature and pressure dependence of the anisotropic adsorption of water on the exposed hkl planes was expressed in terms of the surface coverage, θ_{hkl} , using the multisite Langmuir isotherm^{82,80}

$$\theta_{hkl} = \sum_{i=1} x_i \frac{\beta_i^n}{1 + \sum_{i=1} \beta_i^n} \quad (2)$$

where $x_i = N_i/N$ is the ratio of the N_i sites per total number N of the available adsorption centers, whereas β^n represents the calculated cumulative adsorption equilibrium constant. The resultant total surface coverage $\Theta(T, p)$, the quantity actually accessible by experiment, is defined as $\Theta(T, p) = \sum_{hkl} \theta_{hkl}$. The multisite Langmuir isotherm can, in turn, be transformed into the empirical Fowler–Guggenheim (F-G) equation^{83,84}

$$\ln\left(\frac{\Theta}{1-\Theta}\right) - \ln\left(\frac{p}{\text{bar}}\right) = \alpha\Theta + \ln K \quad (3)$$

where a monolayer of the laterally interacting water molecules is described within the mean field approximation by the parameter α , with K being the corresponding adsorption equilibrium constant.

2.3. Size Effect. Relative thermodynamic stability of $t\text{-ZrO}_2$ nanocrystals results from the competition between the bulk energy (including the stress contribution) and the interfacial energy related to the surface structure and its specific topology (edges, corners, kinks, steps), as discussed elsewhere.⁸⁵ For nanocrystals with the size in the range of 7–200 nm, the surface

energy usually dominates the other interfacial components; therefore, the edge and corner contributions for the investigated $t\text{-ZrO}_2$ NCs with dimensions around 50 nm (vide infra) can safely be ignored (together with minor effects related to simultaneous minimization of the total surface-to-volume ratio together with the total surface energy).⁸⁶ For the stress energy calculations, the volume compressive dilation caused by the surface energy and the validity of the Laplace–Young equation were assumed. A set of energy versus volume calculations were performed, and the results were fitted to the Birch–Murnaghan equation of state (with the root-mean-square $< 10^{-4}$). The compressibility of the bulk was calculated as a second derivative of the energy with respect to the cell volume at the equilibrium point, whereas the stress tensor of the (0, 2) type can be derived by differentiation of the energy with respect to the deformation of the investigated $t\text{-ZrO}_2$ nanocrystal.

2.4. Synthesis of the Samples and TEM Measurements. The synthesis of the $t\text{-ZrO}_2$ nanocrystals is described in the Supporting Information in more detail. Transmission electron microscopy (TEM) measurements were carried out using a Tecnai Osiris instrument (FEI) operating at 200 kV. Prior to TEM analysis, the samples were ultrasonically dispersed in methanol on a holey carbon film supported on a copper grid (400 mesh). The grid was dried for 45 min, and then plasma-cleaning (Solaris Gatan model 950) treatment was applied to remove surface contamination.

3. RESULTS AND DISCUSSION

3.1. Bulk Structure. The tetragonal zirconia exhibits a slightly distorted fluorite ($P4_2/nmc$) structure with two ZrO_2 molecules in the elementary cell with the lattice parameters of $a = b = 3.64$ Å and $c = 5.27$ Å. Each zirconium atom is surrounded by eight oxygen atoms: four at a distance of 2.06 Å (forming a flattened tetrahedron), and four at a distance of 2.45 Å (giving an elongated tetrahedron, which is rotated by 90° relative to the former one). Each oxygen atom has two oxygen neighbors at 2.63 Å and four at 2.65 Å and is bound to two zirconium atoms at 2.06 Å, while two more Zr atoms are 2.45 Å away.⁸⁷ The accuracy of the applied computational approach was proved by comparison of the calculated lattice parameters, the unit cell volume, and the d_z parameter describing displacements of the oxygen atoms due to the fluorite structure distortion⁸⁸ with the corresponding experimental values (see the Supporting Information, Table S3).^{87,89} A very good agreement between both results shows that the employed formalism and parametrization, validated already in our previous modeling of $m\text{-ZrO}_2$,⁶⁵ are also capable of describing the tetragonal zirconia nanocrystals in an adequate quantitative way.

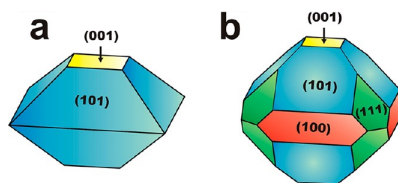
3.2. Equilibrium Morphology. For DFT calculations, we selected the most stable low index planes with the largest interplanar spacing according to the Bravais–Friedel–Donnay–Harker theory. Indeed, the (100), (101), and (001) terminations have been predominantly observed in the experimental TEM studies of ZrO_2 .^{90,91} In Table 1, the surface energies of the rigid and relaxed facets, together with the percentage of the relaxation energy (defined in our previous paper²⁷), are collated. The surface energies of the relaxed planes increase in the following order: (101) < (001) < (100) < (111) < (110). A similar tendency has been observed earlier by Christiansen and Carter.⁶¹ Haase et al.⁶² have reported the γ value of the relaxed tetragonal (101) plane to be equal to 1.04

Table 1. Surface Energies of the Most Stable Terminations of the Tetragonal Zirconia Nanocrystals

	exposed plane				
	(101)	(001)	(100)	(111)	(110)
γ /(J/m ²) rigid surface	1.33	1.21	2.10	3.14	3.18
γ /(J/m ²) relaxed surface	1.06	1.17	1.23	1.25	1.77
relative relaxation energy (%)	20	3	41	60	44

J/m². The values obtained by Iskandrova et al.⁶⁴ for the (101) and (001) facets are equal to 1.09 and 1.13 J/m², respectively, and, along with those values calculated by Anez et al.⁶⁵ (1.07 J/m² for (101) and 1.63 J/m² for the (110) plane), remain in good agreement with the values presented in Table 1.

The calculated γ_{hkl} values were subsequently used to predict the equilibrium shape of the rigid and relaxed tetragonal ZrO₂ nanocrystals (Figure 1). The morphology of the rigid crystal is

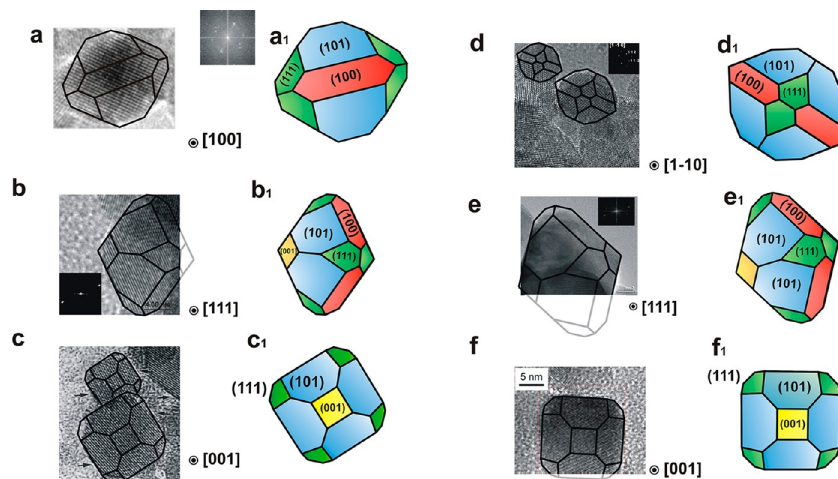
**Figure 1.** Top-lateral views of the theoretical equilibrium shapes of the nanocrystalline *t*-ZrO₂, calculated without (a) and with (b) inclusion of the surface reconstruction effects.

dictated by two (101) and (001) facets only, whereas, upon relaxation, four different facets, (101), (001), (100), and (111), are exposed. Thus, the surface relaxation leads to dramatic changes in the equilibrium morphology of the *t*-ZrO₂ nanocrystal. The new (100) and (111) facets are produced at the expense of the abundance of the (101) and (001) planes

that is substantially reduced, as shown in Table S4 (Supporting Information). The polar, and, therefore, the least stable, (110) facet is not present, neither in the rigid nor in the relaxed form (Table 1).

In Figure 2a, comparison of the experimental TEM images of the tetragonal zirconia nanocrystals (a–f) with the suitably oriented (i.e., along the [100], [111], and [001] directions) Wulff shapes is presented (a₁–f₁). As it can be easily noticed, the predicted shape of *t*-ZrO₂ fits quite well to the corresponding TEM images (Figure 2a–f). All analyzed zirconia nanoparticles are terminated with the (101), (001), (100), and (111) planes, in agreement with the theoretical calculations. The diffraction spots in the inserted FFT patterns (Figure 2a–f) confirm the particular [100], [111], and [001] orientation of the observed crystallites definitely, allowing for univocal alignment of the predicted 3D Wulff shapes with respect to the corresponding experimental 2D images Figure 2a₁–c₁. The TEM pictures (Figure 2c–f) of *t*-ZrO₂ nanocrystals were adopted from the paper of Chraska et al.,⁹² Angeles-Chavez et al.,⁹³ Suzuki-Muresan et al.,⁹⁴ and Barnard et al.,⁹⁵ respectively. Some discrepancies between the morphologies predicted by the Wulff construction and the experimental habit of the obtained *t*-ZrO₂ nanocrystals (see, for example, panels a and a₁, Figure 2) might be caused by kinetic effects, influence of the synthesis environment, or residual hydroxylation of the surface, which can modify the energy of the facets.⁹⁶

3.3. Structure of the Exposed Planes. Atomic structures of the exposed (101), (001), (100), and (111) crystallographic planes of the *t*-ZrO₂ nanocrystal are shown in Figure 3a–d, where the blue and the red balls symbolize zirconium and oxygen ions, respectively. Only one kind of the bulk oxygen of tetrahedral coordination, O_{4c} (the subscript defines the coordination number), can be distinguished, contrary to the monoclinic phase, whereas all bulk zirconium cations exhibit an 8-fold coordination (Zr_{8c}). The numbering of the surface ions (Zr_n and O_m) is shown in Figure 3a–d, and their actual coordination states are shown in Figure 3a₁–d₁. Additionally,

**Figure 2.** TEM pictures of the tetragonal zirconia nanocrystals (a–c) together with the calculated Wulff shapes (a₁–c₁), oriented along the [100], [111], [110], and [001] directions to align with the observed 2D images. Images c₁, d₁, e₁, and f₁ were adopted from Chraska et al.,⁹² Angeles-Chavez et al.,⁹³ Suzuki-Muresan et al.,⁹⁴ and Barnard et al.,⁹⁵ respectively.

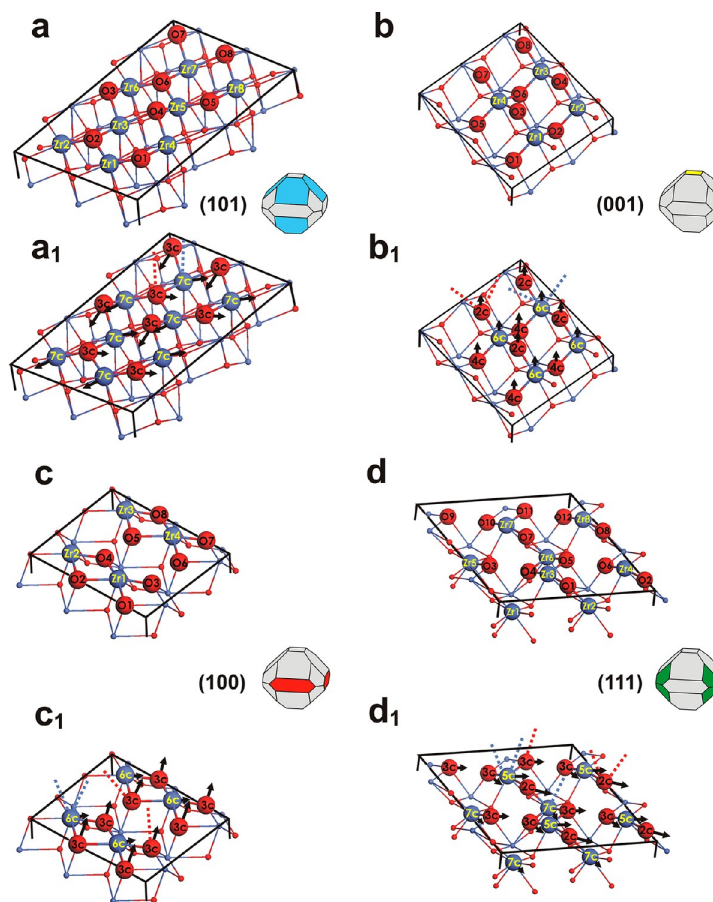


Figure 3. Top-lateral views of the surface structure of the exposed planes of the *t*-ZrO₂ nanocrystal (a–d). The dotted lines indicate missing bonds of the surface ions. Principal directions of the movement of the surface ions upon relaxation are indicated by black arrows (a₁–d₁).

the dangling bonds are marked with dashed lines, whereas the direction and the magnitude of displacements of the surface ions upon relaxation are indicated with thick black arrows.

A unit cell representing the (101) plane consists of eight surface zirconium cations (Figure 3a). Each of them exhibits a reduced 7-fold coordination (Zr_{7c}) due to one missing oxygen ligand. Among 16 surface oxygen ions, 8 have a trigonal coordination (O_{3c}) and 8 a tetragonal one (O_{4c}). Since the 4-fold coordinated oxygen ions are located beneath the plane of the zirconium cations, being hardly accessible for water adsorption, they are not emphasized in Figure 3a, a₁. Because of the mere reduction of the coordination numbers, displacements of the surface ions upon the relaxation are rather small and are restricted to the topmost layer only (Figure 3a₁). The following surface composition of the slab was used for modeling of the (101) plane: {8 Zr_{7c} (6.1 nm⁻²), 8 O_{3c} (6.1 nm⁻²), 8 O_{4c} (6.1 nm⁻²)}. The numbers in the parentheses indicate surface concentrations of the corresponding ions.

All of the exposed zirconium ions located on the (001) plane exhibit a 6-fold arrangement. The bulk coordination of the four

oxygen atoms (O1, O2, O5, and O6) is preserved, whereas the two remaining ones have two missing bonds (O_{2c}); see Figure 3b, b₁. Hence, in comparison to the (101) plane, formation of the (001) facet requires the cleavage of a larger number of the bonds and, consequently, exhibits higher surface energy ($\gamma_{(001)} = 1.17 \text{ J/m}^2$ vs $\gamma_{(101)} = 1.06 \text{ J/m}^2$). Even though the coordination numbers of the surface ions are significantly lowered in comparison with those of the bulk, the surface relaxation does not cause significant shifts of their positions (Figure 3b₁). Being coordinatively unsaturated, these ions are more strongly bonded, and apparently quite rigid. The resultant model of the (001) plane consists of the following set, {4-Zr_{6c} (7.5 nm⁻²), 4-O_{2c} (7.5 nm⁻²), 4-O_{4c} (7.5 nm⁻²)}, of the surface ions.

The unit cell of the (100) plane contains four zirconium and eight oxygen ions. Each Zr cation has the coordination number reduced to six, whereas, in the case of the surface oxygen ions, only trigonal species with one dangling bond are present (Figure 3c₁). The atomic surface composition can be described by the following set of ions: {4-Zr_{6c} (5.2 nm⁻²), 8-O_{3c} (10.4

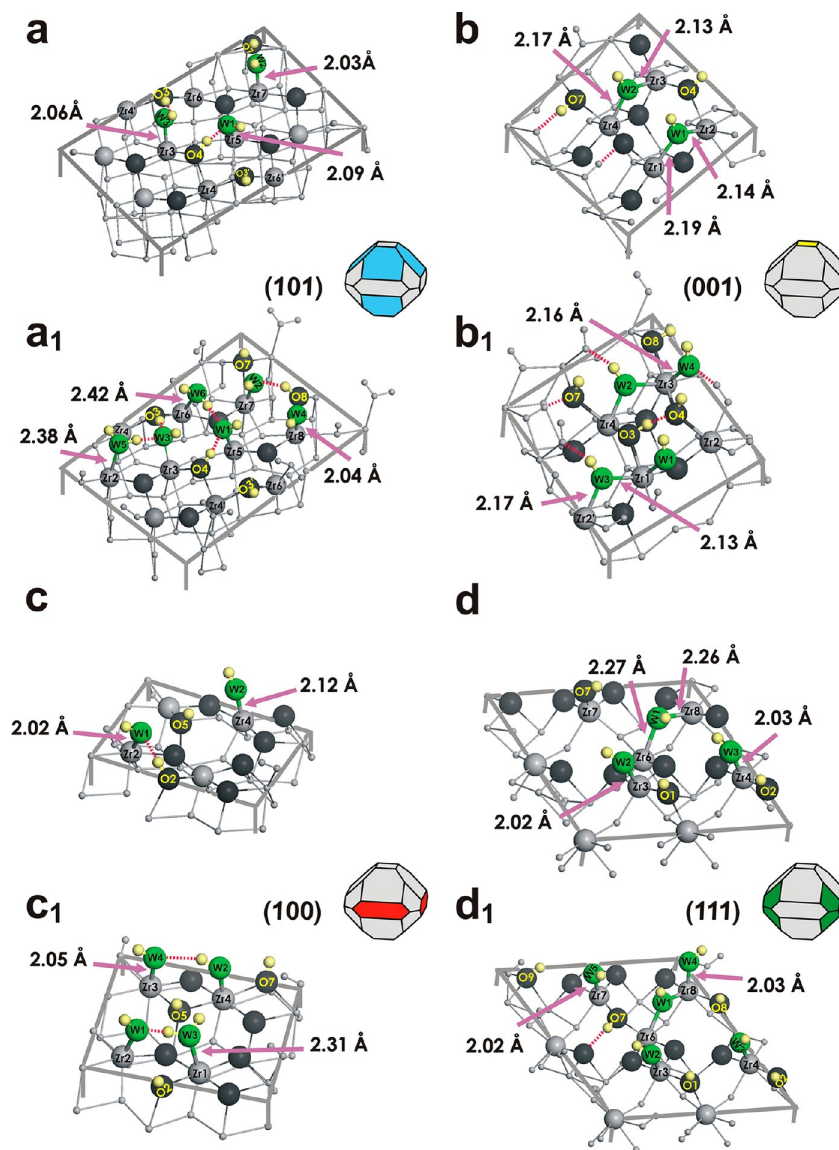


Figure 4. Top-lateral views of the surface hydration of *t*-ZrO₂: (a–d) the half-hydroxylated planes with three or two water molecules and (a₁–d₁) the fully hydroxylated planes with six, five, or four water molecules. The surface ions repeated by virtue of the translational symmetry are marked with primes.

nm⁻²). The reduction of the coordination number for the exposed species is higher than that observed for the previous planes, accounting for considerable enhancement of the surface energy of the (100) facet (1.23 J/m²). Accordingly, displacements of the surface ions upon relaxation are also significant (Figure 3c₁). As a result, the surface structure becomes more uniform.

As the least stable among all of the exposed facets, the (111) termination, with $\gamma = 1.25$ J/m², is corrugated and compact. The coordination of the Zr cations is reduced to 5c (Zr3, Zr4, Zr7, Zr8) and 7c (Zr1, Zr2, Zr5, Zr6), and that of the anions to 2c (O1, O2, O7 and O8), and 3c for the rest of the oxygen ions (Figure 3d,d₁). The resultant composition of the corresponding slab model can be expressed as {4 Zr_{5c} (3.3 nm⁻²), 4 Zr_{7c} (3.3 nm⁻²), 4 O_{2c} (3.3 nm⁻²), 8 O_{3c} (6.6 nm⁻²)}. As expected, the

dicoordinated oxygen anions and the pentacoordinated zirconium cations exhibit the largest displacement upon the surface relaxation (Figure 3d₁).

3.4. Water Sorption: A Molecular Picture and Thermodynamics. For molecular modeling of the water adsorption process, H₂O molecules were attached successively to the coordinatively unsaturated surface zirconium ions until a complete monolayer coverage was achieved. To determine the most stable adsorption modes, a large number of various starting geometries of the adspecies were thoroughly explored. For each of the exposed zirconium sites, both dissociative and associative adsorption ways were tested, whereas for highly unsaturated zircon ions (with two Zr–O bond missing) a multiple water adsorption mode was taken into account. The most stable adsorption forms of the adsorbed water at a given temperature and pressure were determined on the basis of the calculated Gibbs free energies. Since the unit cells contains four or eight exposed zirconium atoms (Figure 3), the following water coverages, $\theta_{\text{H}_2\text{O}} = 0.125, 0.25, 0.375, 0.5, 0.625, 0.75, 0.875, 1.0$, were amenable for our modeling.

Hydration of the (101) Plane. The optimized structure of the first water molecule (W1) adsorbed on the (101) plane is shown in Figure 4a. Water adsorbs dissociatively on the Zr5_(7c) sites ($\Delta E = -1.33$ eV), and the resultant Zr5_(7c)–OH distance is equal to 2.09 Å. The detached proton is accommodated by the neighboring O4_(3c) atom, and the corresponding surface coverage is equal to 1.1 H₂O/nm². Proton attachment leads to modification of the O4_(3c) coordination from the tricoordinated to the dicoordinated bridging state, by loosing the bond with Zr5_(7c). This structure is additionally stabilized by a strong hydrogen bond, marked with the dotted red line in Figure 4a. The second water molecule (W2) adsorbs in a dissociative fashion on the Zr7_(7c) site ($\Delta E = -1.41$ eV) with the Zr7_(7c)–O distance of 2.03 Å, enhancing the surface coverage to 2.1 H₂O/nm². The remaining proton is attached to the adjacent O7_(3c) atom (Figure 4a) and stabilized by a hydrogen bond with the nearby hydroxyl group. Owing to the similar local environment of the Zr3, Zr5 and the Zr4, Zr7 sites, subsequent water molecules W3 and W4 adsorb in an analogous way (Figure 4a₁). The third H₂O species (W3), upon dissociation, forms two surface OH groups (a terminal Zr3_(7c)–OH, and a bridging Zr4_(7c)–O3'_(3c)–H–Zr6'_(7c) one), with the adsorption energy of $\Delta E = -1.34$ eV. The surface coverage at this step is equal to 3.2 H₂O nm⁻². The fourth water molecule (W4) is again attached dissociatively to the Zr8_(7c) ($\Delta E = -1.20$ eV) with the remaining proton being accommodated by the neighboring O8_(3c) atom and stabilized by the hydrogen bond. The resultant surface coverage corresponds to $\theta = 4.3$ H₂O nm⁻².

At higher coverage (5.4 H₂O/nm²), a coexistence of two adsorption modes takes place, since the fifth water molecule (W5) is attached to the Zr2_(7c) site in an associative fashion (Figure 4a₁) with $\Delta E = -1.14$ eV. The adsorbed H₂O molecule exhibits the Zr2_(7c)–OH₂ bond length elongated to 2.38 Å, and it is additionally stabilized via H bonds with W3 adspecies. The last H₂O molecule (W6) adsorbs associatively on the Zr6_(7c) bare site, exhibiting the Zr6_(7c)–OH₂ bond length of 2.42 Å and ΔE of -1.05 eV. As revealed in Figure 4a₁, it is stabilized by hydrogen bonds with W1 admolecules. Higher surface coverages are not available due to the high coordination number (7c) of all surface ions for the (101) termination. These results remain in good agreement with previous literature data⁶³ and are summarized Table 2.

Table 2. Basic Characteristics of Water Adsorption on the (101) Plane of the Tetragonal Zirconia^a

$n_{\text{H}_2\text{O}}$ (θ/nm^2)	$\Delta E/\text{eV}$	adsorption center	adsorption type	$d_{\text{Zr}-\text{O}(\text{H}_2)}/\text{\AA}$
1 (1.1)	-1.33	Zr5 _(7c)	dissociative/H bond	2.09
2 (2.1)	-1.41	Zr7 _(7c)	dissociative/H bond	2.03
3 (3.2)	-1.34	Zr3 _(7c)	dissociative/H bond	2.06
4 (4.3)	-1.20	Zr8 _(7c)	dissociative	2.04
5 (5.4)	-1.14	Zr2 _(7c)	associative/H bond	2.38
6 (6.4)	-1.05	Zr6 _(7c)	associative/H bond	2.42

^a $n_{\text{H}_2\text{O}}$, number of water molecules per unit cell; θ , surface concentration; ΔE , adsorption energy per H₂O molecule; $d_{\text{Zr}-\text{O}(\text{H}_2)}$ (Å), bond length.

Hydration of the (001) Plane. In the case of the (001) plane, the most stable form of the first adsorbed water (W1) is a dissociative bidentate mode with $\Delta E = -1.58$ eV (Figure 4b), and attachment of the resultant bridging hydroxyl group to the Zr1_(6c) and Zr2_(6c) sites. The liberated proton is accommodated by the nearby O4_(2c) anion. The ensuing surface coverage corresponds to 1.9 nm⁻², and the Zr1_(6c)–OH bond length (2.19 Å) is comparable to that of the Zr2_(6c)–OH one (2.14 Å).

The next H₂O molecule (W2) adsorbs in a similar dissociative fashion ($\Delta E = -1.60$ eV) on the Zr4_(6c) and Zr3_(6c) cations (bridged by the resultant OH group), with the remaining proton attached to the O7_(2c) anion (Figure 4b), increasing the surface coverage to 3.8 nm⁻². The Zr4_(6c)–OH and the Zr3_(6c)–OH bonds are equal to 2.17 and 2.13 Å, respectively, and those adspecies are additionally stabilized by strong hydrogen bonds. The adsorbed W2 species only slightly influences the bond lengths of the bridging hydroxyl groups associated with the previous W1 water adsorption.

The optimized structure of the third water molecule (W3) is quite similar to those described before (Figure 4b₁). The adsorption occurs in a dissociative way, giving rise to a bridging hydroxyl group, Zr2'_(6c)–OH–Zr1_(6c), with the Zr2'_(6c)–OH and Zr1_(6c)–OH distances of 2.17 and 2.13 Å, respectively. The liberated proton is accommodated by the nearby O3_(2c) anion, and the whole structure is stabilized by hydrogen bonds. The calculated energy gain for this mode of adsorption is equal to -1.18 eV, and the surface coverage was enhanced to 5.7 H₂O nm⁻².

The dissociative adsorption mode was also observed for the last W4 water molecule (Figure 4b₁). It takes place on the Zr3_(6c) centers, with the detached proton being accommodated by O8_(2c), enhancing the coverage to 7.5 H₂O/nm². Despite that the Zr3_(6c)–OH distance (2.16 Å) is comparable to those previously described, the adsorption energy, $\Delta E = -1.05$ eV, is increased, since the whole structure is stabilized by strong H bonds. Although the exposed zirconium cations were not fully coordinatively saturated at this stage, a multiple water adsorption was not observed. The principal parameters describing the adsorption process on the (001) plane are summarized in Table 3.

Hydration of the (100) Plane. In the case of the (100) plane, the first (W1) and the second (W2) water molecules adsorb dissociatively on the Zr2_(6c) and Zr4_(6c) sites (Figure 4c), leading to the concurrent formation of terminal and bridging hydroxyl groups (by entailing the adjacent O_{3c} ions) with $\Delta E = -1.15$ and -1.51 eV, respectively. The Zr2_(6c)–OH bond length is equal to 2.02 and 2.12 Å, for the first and the second water molecules, respectively. Additionally, the first admolecule

Table 3. Basic Characteristics of Water Adsorption on the (001) Plane of the Tetragonal Zirconia^a

$n_{\text{H}_2\text{O}}$ (θ/nm^2)	$\Delta E/\text{eV}$	adsorption center	adsorption type	$d_{\text{Zr}-\text{O}(\text{H}_2)}/\text{\AA}$
1 (1.9)	-1.58	Zr1 _(6c) /Zr2 _(6c)	dissociative/H bond	2.19/2.14 ^b
2 (3.8)	-1.60	Zr4 _(6c) /Zr3 _(6c)	dissociative/H bond	2.17/2.13
3 (5.7)	-1.18	Zr2 _(6c) /Zr1 _(6c)	dissociative/H bond	2.17/2.13
4 (7.5)	-1.07	Zr3 _(6c)	associative/H bond	2.16

^a $n_{\text{H}_2\text{O}}$, number of water molecules per unit cell; θ , surface concentration; ΔE , adsorption energy per molecule; $d_{\text{Zr}-\text{O}(\text{H}_2)}$ ($\text{\AA}$), bond length. ^bThe mode of water adsorption changes when the surface coverage increases. When $\theta = 1$, the OH group originating from the W1 water is attached only to the Zr1 cation with the Zr_{6c}1–OH distance equal 2.17 $\text{\AA}$, in contrast to the $\theta < 0.75$ coverage.

of water is stabilized by a strong hydrogen bond. Because of the relatively large distance between those sites (6.69 $\text{\AA}$), both adsorption events can be treated independently, and the resultant coverage corresponds to 2.6 $\text{H}_2\text{O}/\text{nm}^2$. Adsorption of the third H_2O molecule (W3) increases the water coverage to 3.9 $\text{H}_2\text{O}/\text{nm}^2$. It occurs in an associative way on the Zr1_(6c) sites (Figure 4c₁). The calculated adsorption energy is equal to -1.41 eV, and the Zr1_(6c)–OH₂ distance is elongated to 2.31 $\text{\AA}$. As revealed by Figure 4c₁, the W3 species is stabilized by a hydrogen bond with the W1 admolecule.

For the last molecule of water (W4), the adsorption occurs in a dissociative way on the Zr3_(6c) sites with the energy increased to -1.33 eV, in comparison to the previous step. The Zr3_(6c)–OH distance of 2.05 $\text{\AA}$ and the maximal surface concentration of $\theta = 5.2 \text{ H}_2\text{O}/\text{nm}^2$ are acquired (Figure 4c₁). This structure is stabilized by a rather weak hydrogen bond with the W2 admolecule of water. The parameters characterizing the water adsorption process on the (100) plane are summarized in Table 4.

Table 4. Basic Characteristics of Water Adsorption on the (100) Plane of the Tetragonal Zirconia^a

$n_{\text{H}_2\text{O}}$ (θ/nm^2)	$\Delta E/\text{eV}$	adsorption center	adsorption type	$d_{\text{Zr}-\text{O}(\text{H}_2)}/\text{\AA}$
1 (1.3)	-1.15	Zr2 _(6c)	dissociative/H bond	2.02
2 (2.6)	-1.51	Zr4 _(6c)	dissociative	2.12
3 (3.9)	-1.41	Zr1 _(6c)	associative/H bond	2.31
4 (5.2)	-1.33	Zr3 _(6c)	dissociative/H bond	2.05

^a $n_{\text{H}_2\text{O}}$, number of water molecules per unit cell; θ , surface concentration; ΔE , adsorption energy per molecule; $d_{\text{Zr}-\text{O}(\text{H}_2)}$ ($\text{\AA}$), bond length.

Hydration of the (111) Plane. The basic characteristics of water adsorption on the (111) plane are collated in Table 5. The first H_2O molecule (W1) adsorbs on the Zr6_(7c) and Zr8_(5c) cations in a dissociative bidentate mode, with the released proton attached to the adjacent O7_(2c), which breaks its bond with Zr6_(7c), creating a terminal OH group simultaneously (Figure 4d). The adsorption energy is equal to -1.65 eV. The surface coverage at this step is equal to 0.8 nm^{-2} , whereas the Zr6_(7c)–OH and the Zr7_(5c)–OH bond lengths are equal to 2.27 and 2.26 $\text{\AA}$, respectively. Owing to the similar local environment of the Zr3, Zr4, Zr7, and Zr8 sites, subsequent water molecules (W2, W3, and W4) adsorb in a similar dissociative way (Figure 4d₁). The resultant hydroxyl

Table 5. Basic Characteristics of Water Adsorption on the (111) Plane of the Tetragonal Zirconia^a

$n_{\text{H}_2\text{O}}$ (θ/nm^2)	$\Delta E/\text{eV}$	adsorption center	adsorption type	$d_{\text{Zr}-\text{O}(\text{H}_2)}/\text{\AA}$
1 (0.8)	-1.65	Zr6 _(7c) /Zr8 _(5c)	dissociative/H bond	2.27/2.26
2 (1.6)	-1.63	Zr3 _(5c)	dissociative	2.02
3 (2.5)	-1.57	Zr4 _(5c)	dissociative	2.03
4 (3.3)	-1.59	Zr8 _(5c)	dissociative	2.03
5 (4.1)	-1.50	Zr7 _(5c)	dissociative	2.02

^a $n_{\text{H}_2\text{O}}$, number of water molecules per unit cell; θ , surface concentration; ΔE , adsorption energy per molecule; $d_{\text{Zr}-\text{O}(\text{H}_2)}$ ($\text{\AA}$), bond length.

groups are accommodated by the Zr3_(5c), Zr4_(5c), and Zr8_(5c) cations, respectively, and the released protons are attached to the adjacent O_(2c) anions. As revealed by Table 5, subsequent adsorption energies for W2, W3, and W4 as well as the corresponding Zr_(5c)–OH distances are almost equal. Upon accommodation of four water molecules, the coverage corresponds to $\theta = 3.3 \text{ H}_2\text{O}/\text{nm}^2$.

The most stable form of the fifth adsorbed water (W5) is a dissociative mode (Figure 4d₁), with attachment of the resultant hydroxyl group to the Zr7_(5c) center ($\Delta E = -1.50 \text{ eV}$). The liberated proton is accommodated by the nearby O9_(3c) anion. The resultant surface coverage corresponds to 4.1 nm^{-2} . Higher surface coverage was not observed, despite the fact that most of the surface Zr ions are rather significantly unsaturated (5c); see Figure 4d₁.

3.5. Thermodynamic Diagrams of Surface Hydration.

The free enthalpy (Gibbs energy) of water adsorption on the exposed planes of the *t*-ZrO₂ nanocrystals as a function of temperature for a partial pressure of water equal to 0.01 atm is plotted in Figure 5, together with the associated water coverage, $\theta_{\text{H}_2\text{O}}(T, p_{\text{H}_2\text{O}} = 0.01)$, and auxiliary differential curves ($d\theta_{\text{H}_2\text{O}}/dT$). Generally, the most stable adsorption form of water at a given temperature corresponds to the lowest Gibbs energy plotted in the diagrams. However, for correct description of the $\theta_{\text{H}_2\text{O}}(T, p_{\text{H}_2\text{O}} = 0.01)$ variation with temperature (Figure 5a₁–d₁), the close-lying $\Delta G_{\text{H}_2\text{O}}(T, p_{\text{H}_2\text{O}} = 0.01)$ lines, especially in the vicinity of the crossing points, were also taken into account. The resultant coexistence of various water adspecies leads to a smooth variation of the surface concentration with temperature, instead of the abrupt changes implied by a hard lowest Gibbs energy criterion only.

As shown in Figure 5a, at the low-temperature regime (below 30 °C), a monolayer of water (corresponding to six admolecules) is present on the (101) plane. The first desorbing water molecule is that associatively attached to the Zr6_(7c) site and stabilized by the ancillary hydrogen bonds. Around 130 °C, two H_2O molecules leave the surface, liberating the Zr2_(7c) and Zr8_(7c) sites of the relatively low affinity to water (Table 2). This can easily be seen as a pronounced peak in Figure 5a₁ (dotted $d\theta/dT$ line). Such a desorption leads to a pronounced drop of the coverage down to $\theta_{(101)} = 0.5$, since an intermediate stage with $\theta_{(101)} = 0.66$ was found to be unstable. A subsequent decrease of the surface coverage from $\theta_{(101)} = 0.5$ to $\theta_{(101)} = 0.33$ occurs at ~280 °C (Figure 5a) and corresponds to desorption of water dissociatively adsorbed on the Zr3_(7c) site. This transformation, being unresolved in the $d\theta/dT$ plot (Figure 5a₁, dotted line), is covered by a broad peak at ~350 °C corresponding to complete dehydration of the (101) facet.

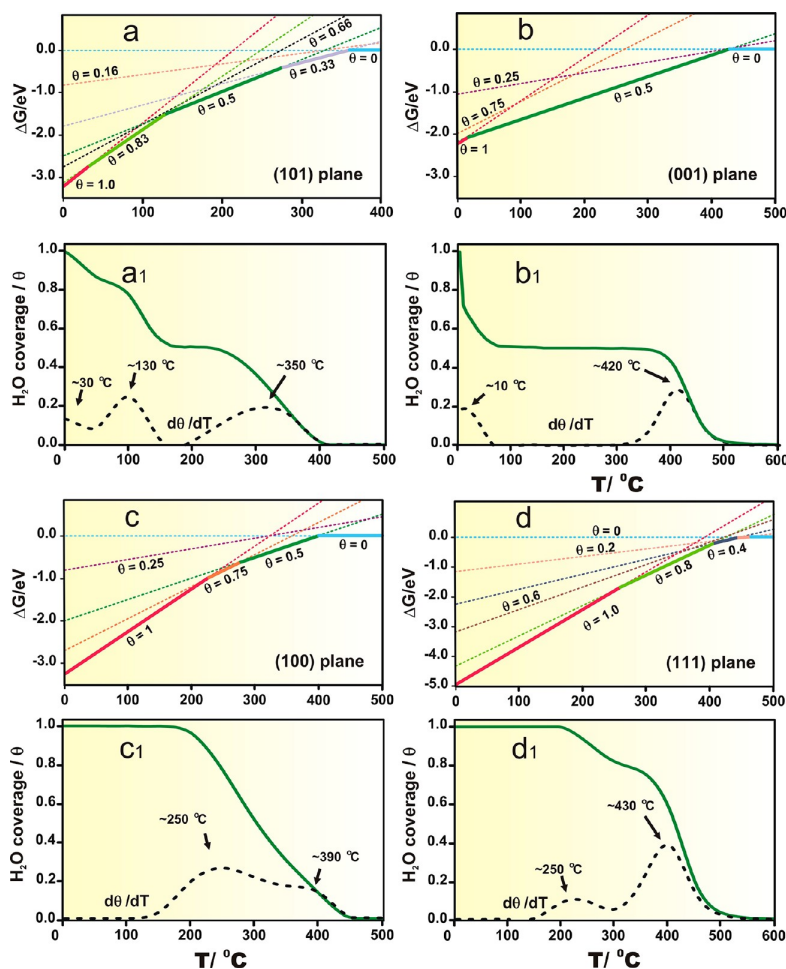


Figure 5. Gibbs free energy of water adsorption as a function of temperature at $p/p^\circ = 0.01$ bar for different numbers of adsorbed H_2O molecules (a–d) together with the corresponding surface coverage θ and a differential curve $d\theta/dT$ (a₁–d₁) for all terminations of the $t\text{-ZrO}_2$ nanocrystal.

Overall, the sequence of trimodal water desorption can be express as $1 \rightarrow 2 \rightarrow (1 + 2)$, where the numbers in the parentheses indicate the steps revealed by intersection of the corresponding ΔG lines.

Thermal stability of the hydrated (001) plane (Figure 5b) is somewhat different from that of the (101) one, as water molecules leave this plane in the sequence $2 \rightarrow 2$. The highest coverage of $\theta_{(001)} = 1.0$ (corresponding to four H_2O molecules) is stable only up to $\sim 10^\circ\text{C}$. Above 10°C , the two molecules of water depart simultaneously, as it can be inferred from the corresponding θ and $d\theta/dT$ curves (Figure 5b₁). It may be surprising that the surface coverage is reduced in such a low-temperature range, yet a more careful inspection of the water adsorption diagrams shows that those easily desorbing molecules correspond to W4 molecules weakly attached to $\text{Zr3}_{(6c)}$ and W3 attached to the $\text{Zr1}_{(6c)}$ (with the already attached W1) and $\text{Zr2}_{(6c)}$ sites. The half-monolayer of water is

apparently much more stable, and two water molecules associated with the $\text{Zr1}_{(6c)}/\text{Zr2}_{(6c)}$ and $\text{Zr4}_{(6c)}/\text{Zr3}_{(6c)}$ centers leave the (001) plane in a concerted way at $\sim 420^\circ\text{C}$, completing the dehydroxylation process (Figure 5b₁).

In the case of the (100) plane, the monolayer of water is stable until ca. 230°C , when the first H_2O connected with the $\text{Zr3}_{(6c)}$ center desorbs (Figure 5c). The desorption of the next water molecule, associatively attached to $\text{Zr1}_{(6c)}$, occurs at the temperature of $\sim 280^\circ\text{C}$ and is defined by the crossing of the $\theta_{(100)} = 0.75$ and $\theta_{(100)} = 0.5$ lines. However, the corresponding differential $d\theta/dT$ curve shows only one broad peak with the maximum at the temperature of $\sim 250^\circ\text{C}$ (Figure 5c₁). Indeed, a more careful inspection of the water sorption diagrams shows that there is a nearby crossing of two $\Delta G(T)$ lines for $\theta_{(100)} = 1.0$ and $\theta_{(100)} = 0.5$ at $\sim 260^\circ\text{C}$, with the energy only slightly higher than that corresponding to the $\theta_{(100)} = 0.75$. Thus, the mentioned broad peak results from these effects. The last two

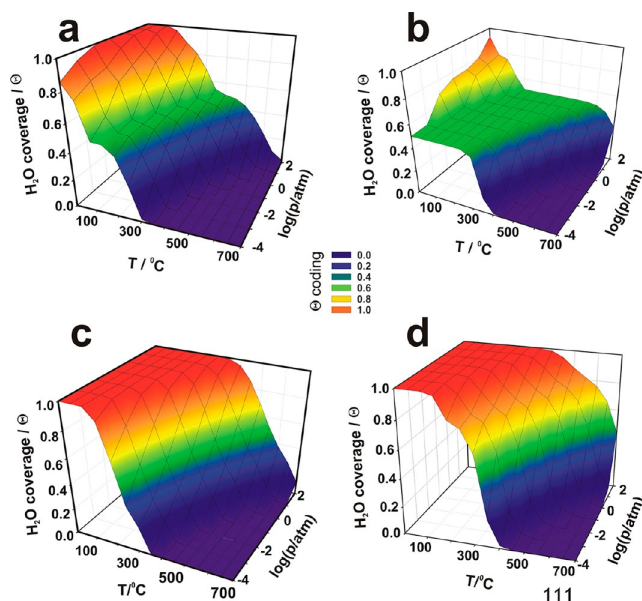


Figure 6. Two-dimensional diagrams of the equilibrium water coverage as a function of temperature and partial pressure for (101) (a), (001) (b), (100) (c), and (111) (d) planes of the tetragonal zirconia.

Table 6. Surface Energies of the Exposed Partially Hydrated Planes of the Tetragonal Zirconium Dioxide at Various Temperatures, Together with Their Relative Abundances, Calculated for $p/p^0 = 0.01$

	0 °C	150 °C	300 °C	450 °C	550 °C	650 °C
$\gamma_{(101)}/\text{J}\cdot\text{m}^{-2}$ (% abundance)	0.52 (6%)	0.82 (12%)	1.01 (35%)	1.06 (66%)	1.06 (61%)	1.06 (60%)
$\gamma_{(001)}/\text{J}\cdot\text{m}^{-2}$ (% abundance)	0.51 (8%)	0.74 (12%)	0.96 (11%)	1.17 (4%)	1.17 (4%)	1.17 (4%)
$\gamma_{(100)}/\text{J}\cdot\text{m}^{-2}$ (% abundance)	0.56 (8%)	0.85 (13%)	1.12 (13%)	1.23 (11%)	1.23 (17%)	1.23 (18%)
$\gamma_{(111)}/\text{J}\cdot\text{m}^{-2}$ (% abundance)	0.45 (49%)	0.74 (48%)	1.02 (26%)	1.24 (7%)	1.25 (15%)	1.25 (17%)
$\gamma_{(110)}/\text{J}\cdot\text{m}^{-2}$ (% abundance)	0.42 (28%)	0.77 (15%)	1.06 (15%)	1.29 (12%)	1.44 (3%)	1.56 (0%)

H₂O leave the surface at ~ 390 °C, as it can be deduced from the intersection of the $\theta_{(100)} = 0.5$ and the bare surface lines. As a result, water leaves the (100) plane in a monomodal way (1 + 1 + 2).

For the (111) plane, the H₂O monolayer (corresponding to five ad molecules) persists until ~ 250 °C (Figure 5d). Above this temperature, first molecule of the dissociatively adsorbed water leaves the surface, liberating the Zr7_(sc) center. The next reduction of the surface coverage from $\theta_{(111)} = 0.8$ to $\theta_{(111)} = 0.4$ occurs at ~ 410 °C. It corresponds to desorption of two water molecules dissociatively adsorbed on the Zr4_(sc) and Zr8_(6c) sites. The fourth dissociatively attached H₂O molecule departs at ~ 430 °C, exposing the bare Zr3_(sc) center. The last reduction of the surface coverage occurs at ~ 450 °C. Above this temperature, the (111) termination assumes a fully dehydroxylated state. The corresponding differential $d\theta/dT$ curve shows only one pronounced peak with the maximum at the temperature of ~ 430 °C (Figure 5d₁). This is caused by the fact that the stepwise reduction of the surface coverage from $\theta_{(111)} = 0.8$ to $\theta_{(111)} = 0.0$ via transient $\theta_{(111)} = 0.4$ and $\theta_{(111)} = 0.2$ states occurs in a narrow range of the temperature (~ 40 °C). Furthermore, between 400 and 450 °C, there are several close crossings of the $\Delta G(T)$ lines with the energy only slightly higher than that corresponding to the $\theta_{(111)} = 0.4$ or $\theta_{(111)} = 0.2$

ones. Therefore, the mentioned peak at 430 °C in the differential curve reflects aptly such modifications in the surface coverage. The resultant sequence of water departure from the (100) plane is the following: 1 $\rightarrow$ (2 + 1 + 1).

The results of our calculations revealed that the affinity toward water adsorption exhibited by the (101) and (001) planes with a low-temperature desorption peak below 30 °C is different from that of the (100) and (111) planes with the first desorption peak above 100 °C. In the case of the (001) and (111) facets, water exhibits a bimodal desorption characteristics (1 + 1) $\rightarrow$ 2 and 1 $\rightarrow$ (2 + 1 + 1), respectively (see Figure 5b₁, d₁), in the case of the (101) facet, a trimodal 1 $\rightarrow$ 2 $\rightarrow$ (1 + 2) (Figure 5a₁), and for (100), a monomodal (1 + 1 + 2) desorption takes place (Figure 5c₁). The calculated sorption parameters collected in Tables 2–5 remain in full agreement with the experimental values published by Ushakov and Navrotsky.⁹⁷ The adsorption enthalpies derived from their calorimetric measurements for half-monolayer water coverage of the *t*-ZrO₂ vary from -1.61 to -0.95 eV.

In Figure 6, more comprehensive two-dimensional $\theta_{\text{H}_2\text{O}}(p, T)$ diagrams of water sorption on all of the exposed (101), (001), (100), and (111) planes of the *t*-ZrO₂ nanocrystals are shown. They help to analyze the surface coverage as a function of both water partial pressure (adsorption isotherms) and temperature

(adsorption isobars) in an integral way. For instance, such plots may be used for clarification of the poisoning effect of water present in the feed on the activity of zirconia-based catalysts or for discussion of morphological changes of the t -ZrO₂ nanocrystals in different conditions, as discussed below.

3.6. Morphological Changes Induced by Hydration. As it was explained above, adsorption of water gives rise to pronounced anisotropic variation of the surface energy of the exposed facets of the tetragonal ZrO₂. The calculated $\gamma_{hkl}(T)$ values at various temperatures for all terminations, along with the corresponding changes in their relative abundance, are collected in Table 6.

Using Wulff construction, the calculated $\gamma_{hkl}(T)$ values can next be used to predict variations of the equilibrium morphology of the tetragonal zirconia nanocrystals as a function of the experimental conditions (calcination temperature and humidity) (Figure 7).

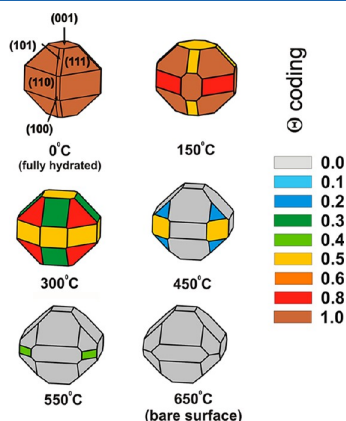


Figure 7. Wulff shapes of the tetragonal zirconia nanocrystals as a function of temperature for $p_{\text{H}_2\text{O}} = 0.01$ atm.

Analysis of the data presented in Table 6 and Figure 7 shows that, despite the monotonous increase of the surface energy with the increasing temperature (caused by the decreasing water coverage), the relative abundances of the exposed planes exhibit a more complicated variation. Moreover, water adsorption gives rise to the appearance of a new (110) facet, not observed in the dry ZrO₂. From the experimental point of view, the presence of this polar, and hence intrinsically unstable termination, has been confirmed by microscopic studies.⁹⁸ Nonetheless, the general doubly truncated tetragonal-bipyramidal shape of the tetragonal zirconia nanocrystals is preserved in the large range of the experimental conditions (Figure 7).

To evaluate the grain size dependence of the t -ZrO₂ habit, the Gibbs energy was plotted as a function of the average dimension, d , for bare and partially and fully hydrated nanocrystals (Figure 8). Because of their rather intricate morphology, the size of an equivalent cube of the same volume was taken as a convenient dimensional measure of the real t -ZrO₂ nanocrystallites. As revealed in Figure 8, in the case of very small grains ($d < 20$ Å), the differences in ΔG are quite pronounced, strongly favoring the fully hydrated state of the surface. With increasing size, these discrepancies monotonously

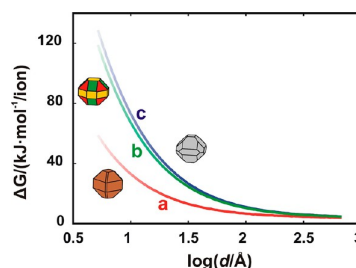


Figure 8. Size dependence of the Gibbs free energy of the m -ZrO₂ nanocrystals for (a) fully hydroxylated ($T < 95$ °C), (b) half-hydroxylated ($\Theta = 0.5$, $T \sim 300$ °C), and (c) bare surface ($T > 650$ °C).

converge to the same value, and for crystallites with the size of about 50–200 nm, the hydration of the surface has a rather small influence on the stability of the tetragonal zirconia nanocrystals. However, due to the negligence of the off-diagonal terms of the compressibility tensor as well as the contributions of the edges and corners to the ΔG values, our model loses its applicability for very small sizes of the nanocrystals, which is indicated in Figure 8 by the gradually fading lines.

Once the correct polyhedral shape of the t -ZrO₂ nanocrystals is determined, we can easily calculate the fractional abundance of the facets, theoretical total surface area, and the aerial concentration of the exposed ions. Such data are indispensable for calculation of the turnover frequencies in catalysis and also for establishing quantitative relationships between the preparation conditions and profusion of the specific crystallographic facets that are most active. It thus allows for development of improved catalytic materials based on zirconia. Furthermore, from the relative abundance of all of the exposed facets, one can calculate the total surface coverage by the adsorbed water as a function of temperature, $\Theta(T)$, since this quantity can be directly measured in practice. In Figure 9, the $\Theta(T)$ and $d\Theta/dT$ profiles for total adsorption of water at $p_{\text{H}_2\text{O}}/p^0 = 0.01$ are shown for t -ZrO₂ crystallites with the calculated equilibrium shape and the experimental morphology retrieved by an inverse Wulff reconstruction of the synthesized nanocrystals observed in TEM (Figure 9b, bottom panel). The latter were used in water TPD experiments. The first peaks in the $d\Theta/dT$ curves shown in Figure 9a occur below 50 °C and, hence, are mainly assigned to desorption of molecular water attached to the Zr_{6c} sites located on the (101) plane, and water dissociatively attached to the Zr_{6c} sites located on the (001) plane. The second region of ~100–170 °C corresponds to depletion of the associatively and dissociatively adsorbed water from the (101) plane. Further decrease of the surface coverage at the temperature range of 190–320 °C is associated with desorption of the water molecules adsorbed dissociatively or associatively on the Zr_{5c}, Zr_{6c}, and Zr_{7c} sites located on the analyzed planes. The highest-temperature region around 420 °C can be attributed to elimination of the last portion of water from the highly unsaturated Zr_{5c} sites located on the (111) plane, and the bridging water molecules from the Zr_{6c} centers on the (001) plane. The investigated model of water adsorption takes into account only the monolayer coverage; however, a multilayer physisorption is expected to occur at low temperatures and higher p/p^0 values. Such weakly attached water

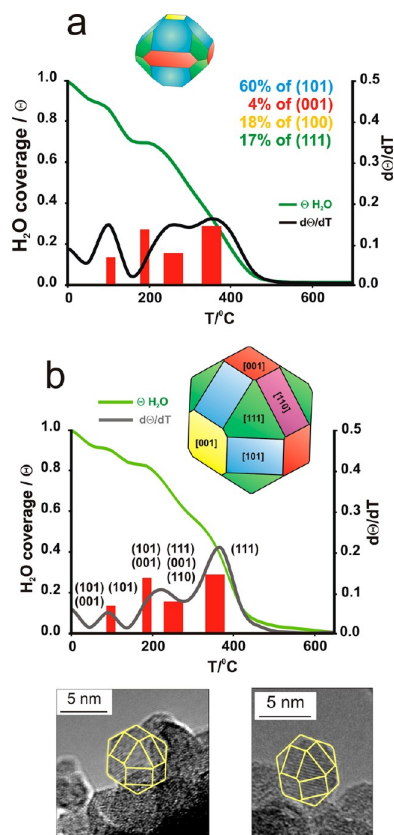


Figure 9. (a) Total coverage as a function of temperature for the tetragonal zirconium dioxide, calculated for the shape of the bare nanocrystals. (b) Reverse Wulff reconstruction of the tetragonal zirconia nanocrystal shape observed in TEM (bottom panel) together with the calculated $\Theta(T)$ and $d\Theta/dT$ curves that correspond at best to the experimental TPD results. The red bars indicate the positions of the desorption maxima in the TPD profiles.

molecules are usually desorbing below 100–120 °C, so this region of the calculated thermodynamic diagram may not be fully consistent with the experimental data.

Given that the experimental investigations of water adsorption/desorption processes on tetragonal zirconia are rather scarce,^{99,100} we performed temperature-programmed water desorption measurements to link our theoretical results with the experimental data. The procedure of an experiment is described in the Supporting Information in more detail. The TPD profile revealed that water desorption peaks are observed at temperatures around 120, 190, 240, and 330 °C (see the Gaussian decomposition of the TPD curve in Figure S1, Supporting Information). The TPD peaks are indicated by red bars with the size proportional to the amount of the desorbed water. A comparison with the calculated $d\Theta/dT$ profiles for the *t*-ZrO₂ nanocrystals of the equilibrium morphology in the dry state (Figure 9a) reveals that, although the gross features of the experimental line are reproduced quite reasonably, there are some apparent discrepancies (in terms of the intensity) at 190

and 240 °C. Nonetheless, a much better agreement with the experiment can be achieved by using, instead of the calculated equilibrium shape, an experimental morphology retrieved by an inversed Wulff construction from TEM images recorded for the same sample on which the TPD was measured (Figure 9b). For the sake of clarity, each TPD peak is associated with the facets from which water is desorbing.

In an alternative approach to water adsorption isobars (Figure 9), changes in the total surface coverage, Θ , can be analyzed in terms of the multisite Langmuir (m-sL) or Fowler–Guggenheim (F-G) isotherms (Figure 10). In the case of the F-G isotherm, the repulsion between the adspecies is semiempirically described using the mean field model.

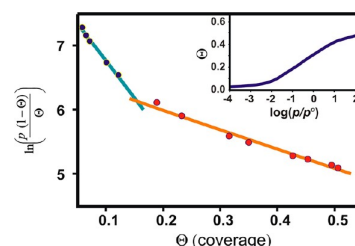


Figure 10. Fowler–Guggenheim isotherm at 400 °C and the corresponding multisite Langmuir isotherm at the same temperature (inset).

A quick inspection of the calculated F-G plot shows that two distinct linear regions of different slopes, with a discrete turning point at $\Theta = 0.15$, can be distinguished. The effective energy of the mutual repulsive interactions between the adsorbed water molecules (gauged by the parameter α in eq 3) was equal to -0.67 eV for $\Theta \leq 0.15$, decreasing down to -0.18 eV for $\Theta \geq 0.15$. The negative value of the α parameter, following the F-G model, reveals the repulsive character of the lateral energy, which is associated with dipolar interactions between the positively charged hydrogen atoms of the surface hydroxyl groups, as discussed elsewhere.^{65,101} The repulsion energy term is equal to $\alpha \cdot \Theta$; thus, for $\Theta = 0.1$ and 0.5 , the corresponding values are equal to $-0.67 \cdot 0.1 = -0.07$ eV and $-0.18 \cdot 0.5 = -0.09$ eV, respectively, in accordance with the values derived directly from the DFT calculations (-0.06 eV for $\Theta = 0.1$, and -0.11 eV for $\Theta = 0.5$). A more involved analysis of the obtained results reveals that the abrupt change in the slope of the F-G plot can be assigned to passage from the region of stronger adsorption of water molecules in the bridge conformations on the (001) planes (with ΔE of -1.60 eV $\div$ -1.58 eV; see Table 3) and adsorption on the doubly unsaturated Zr_(sc) sites located on the (111) planes ($\Delta E \approx -1.65$ eV– -1.59 eV, Table 5), to the region of weaker adsorption of water on the singly unsaturated zirconia sites situated on the (101), (001), (011), and (111) planes ($\Delta E \approx -1.2$ eV $\div$ -0.8 eV, Tables 2 and 5).

4. CONCLUSIONS

Water adsorption on the (101), (001), (100), and (111) planes exposed by faceted tetragonal ZrO₂ nanocrystals was successfully modeled by combining the periodic density functional calculations with atomistic thermodynamics. The calculated DFT/PW91 surface energies of the reconstructed

terminations demonstrate that it is possible to predict correctly the equilibrium shape of t -ZrO₂ crystallites under different hydration conditions and temperatures using the Wulff construction. The results remain in good agreement with the experimental TEM images. It was shown that water desorption on the (001) and (111) planes occurs in a bimodal fashion, $(1 + 1) \rightarrow 2$ and $1 \rightarrow (2 + 1 + 1)$, respectively, whereas, for (101), a trimodal $1 \rightarrow 2 \rightarrow (1 + 2)$ and, for (100) terminations, a monomodal $(1 + 1 + 2)$ pathway were observed. Thermodynamic two-dimensional diagrams (surface coverage versus temperature and pressure) calculated for all facets allowed us to describe water adsorption processes in a comprehensive quantitative way. The predicted changes in the total surface coverage and the morphology of nanocrystals with temperature were further rationalized in terms of the molecular structure and energetic stability of water adspecies. A concise macroscopic description of water adsorption equilibria was afforded by the calculated multisite Langmuir and Fowler–Guggenheim isotherms. To our best knowledge, this is the first systematic molecular level account of the water adsorption thermodynamics on the faceted t -ZrO₂ nanocrystals under specified conditions by means of ab initio calculations compared directly to experiment.

■ ASSOCIATED CONTENT

■ Supporting Information

Supercell parameters of tetragonal ZrO₂ planes, different terminations of t -zirconia slab models, t -ZrO₂ nanocrystal synthesis procedure, comparison of the calculated lattice parameters with literature data, contribution of the exposed facets in the equilibrium shape of the t -ZrO₂ crystal, TPD experimental procedure, and Gaussian decomposition of the TPD plot. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

Dedicated to Professor Adam Bielański on the occasion of his 100th birthday.

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2.4.5 Tekst artykułu H5

[H5] F. Zasada, W. Piskorz*, S. Godlewski*, J. S. Prauzner-Bechcicki, A. Tekiel, J. Budzioch, P. Cyganik, M. Szymonski, Z. Sojka, „Chemical Functionalization of the $\text{TiO}_2(110)-(1\times 1)$ Surface by Deposition of Terephthalic Acid Molecules - a DFT and STM Study”, *Journal of Physical Chemistry C* **115** (2011), 4134.

Chemical Functionalization of the $\text{TiO}_2(110)-(1 \times 1)$ Surface by Deposition of Terephthalic Acid Molecules. A Density Functional Theory and Scanning Tunneling Microscopy Study

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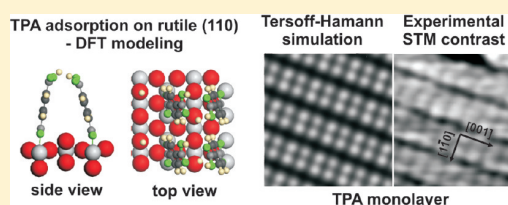
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 Supporting Information

ABSTRACT: Periodic DFT calculations were used to explore structural properties of terephthalic acid (TPA) deposited on the rutile $\text{TiO}_2(110)-(1 \times 1)$ surface at low and high coverage. Theoretical results were compared with scanning tunneling microscopy imaging data. At low loading the TPA molecules adsorb dissociatively as discrete entities adopting a flat-lying *plane-on* geometry. The resultant terephthalic anion is attached to the surface by two covalent bonds between the carboxylic oxygens and the 5-fold coordinated Ti atoms with an additional stabilization due to the hydrogen bond formation with the adjacent surface hydroxyls. When the saturation coverage is achieved, a well-ordered monolayer of the vertically oriented molecules is formed. In both cases the TPA ad molecules bind to the surface via carboxylic groups as terephthalic anions. Formation of dimers results from the formation of hydrogen bonds between the adjacent TPA molecules. To elucidate the reactivity of the functionalized surface, we deposited zinc formate ions on top of the compact TPA monolayer. Calculations showed that the anchoring properties of the TiO_2/TPA system are not perturbed by the dimer formation, auguring well for its prospective application as a promising chemically functionalized surface for on-top growth of metal organic frameworks.



INTRODUCTION

Controlled chemical functionalization of surfaces leading to modification of their chemical and physical properties plays an important role in modern nanostructuring^{1–4} and has been the goal of numerous experimental and theoretical studies.^{5–15} In recent years fabrication of functionalized systems with desired properties has been extended into nanocrystals, nanoparticles, and nanowires.^{16–18} The rapidly growing interest in surface functionalization arises from the large range of its possible applications in medicine, biology, organic electronics, and optoelectronics. In particular, the self-assembly of monolayers allows production of stable, flexible, and high-quality nanostructures, where organic monolayers are directly used as linkers between the monocrystal template and the on-top built structures.^{11,15} In the last case, one can deposit molecules having several functional groups such that one of them anchors at the surface. The remaining functional groups can then be used for further modification of the resultant composite structure by reaction with the intentionally designed ancillary molecules, conferring the desired structural and electronic properties to the whole system.

The most extensively studied class of self-assembled monolayers (SAMs) exhibiting promising structure stability is derived from alkanethiols deposited on metal surfaces such as gold, silver, or copper.^{2,15} Recently, also the oxide surfaces have been used as templates for growing self-assembled monolayers of carboxylic acids with alkane chains and aromatic rings.^{19–26} Although a range of metal oxides including ZnO , AgO , Al_2O_3 , or ZrO_2 have been investigated,¹⁹ undoubtedly the most explored substrate is TiO_2 .²⁵ Its popularity stems from the wide range of practical applications such as catalysis, surface coatings, fabrication of sensors, and optoelectronic industry and medical usage.^{20,27–32} Among a wide variety of the examined molecules, the 1,4-benzenedicarboxylic acid (terephthalic acid) can be regarded as a prototypical structure containing two functional groups, one of them providing stable attachment to the substrate, whereas the second one is apt for generation of chemically functionalized nanostructures. As recently shown, the TPA molecules form

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well-ordered monolayer structures of upright-oriented molecules when deposited on the titanium dioxide.^{7,8} This model system combines the well-known advantages of chemically functionalized self-assembled monolayers with the semiconducting and monocrystalline properties of titanium dioxide substrate. The layers formed by the TPA molecules have an epitaxial character, which opens several potential applications for the TPA/TiO₂ system. For instance, the TPA monolayer could be used as a buffer layer for further deposition of functionalized molecules without strong surface–adsorbate electronic coupling which could destroy the originally designed optoelectronic properties.⁵ Indeed, as recently demonstrated by Palmgren et al.,⁵ incorporation of single bipirydyne layer could isolate FePc molecules from the electronic influence of titania, providing a barrier layer that efficiently prevents modification of the electronic properties of the deposited molecules. The TPA monolayer could also be used as a starting point in an epitaxial growth of metal organic frameworks (MOFs).³⁴ MOFs are the most porous materials available today and attract enormous attention due to their prospective applications in hydrogen storage,³⁵ catalysis,³⁶ drug release,³⁷ and modern sensor technologies.^{38,39}

The MOF structures consist of inorganic–organic hybrid pores that are made of inorganic units connected by organic ligands. So far they were prepared in the form of powders by conventional chemical methods and only recently an epitaxial layer-by-layer growth of the MOF materials was demonstrated.^{40–42} This new approach to MOF synthesis in the form of thin films opens up new possibilities for better controlling their structure (e.g., by avoiding two interpenetrating networks),⁴⁰ and for nanosensor applications.³⁹ Terephthalic acid is one of the commonly used ligands in the MOF synthesis. For example it links the [Zn₄O]⁶⁺ clusters in model MOF-5 structure.⁴³ The TPA/TiO₂ monolayer has, therefore, a practical potential of mimicking a single 2D sheet of this framework, allowing for an epitaxial growth of a 3D structure of the MOF-5, in a layer-by-layer fashion.

Although the TPA/TiO₂ system has been explored experimentally by several techniques (like atomic force microscopy (AFM), scanning tunneling microscopy (STM), and near edge X-ray absorption fine structure (NEXAFS) spectroscopy),^{7,8,33} the results still do not provide a definite explanation of the adsorption scheme, the film structure, and the chemical functionality of the modified surface. For instance it has been still a matter of debate whether molecules forming the congested layer bind to the substrate in a molecular or dissociated form. Generally, it has been assumed that the carboxylic acid group dissociates upon adsorption, although some theoretical calculations provide similar binding energies for both the dissociative and the molecular adsorption forms.^{44–46} Furthermore, it has been discussed that released protons stabilize the carboxylic acid layer.^{47,48} Another issue to be addressed refers to the postulated adsorbate–adsorbate interactions leading to dimer formation in the congested layer of the upright oriented TPA molecules.^{7,8} The nature of these interactions has not been explained so far. Guo and Williams reported formation of dimers for benzoic acid and, at the same time, lack of dimer formation for the adsorbed acetic acid molecules,⁴⁹ attributing formation of dimers to interactions between the benzene rings. However, in a more likely case where the dimer formation is driven by the interactions among the top carboxyl groups, the surface functionalization with the TPA monolayer could be hampered, as indicated by Martin et al.⁵⁰ Thus, in the context of controlled surface

functionalization, it is of great importance to examine the intermolecular interactions within the TPA monolayer in detail, as they could substantially influence the layer structure and its functionality.

In light of above-mentioned questions, we address our work to density functional theory (DFT) modeling of the TPA adsorption process at low (discrete adsorption modes, single molecules) and high coverage (congested adsorption modes, molecular monolayer) and formation of well-ordered structures. The simulated STM images of the TPA adspecies were compared with available STM data.^{7,8} Potential application of the TPA/TiO₂ system for MOF synthesis was verified by interaction of the packed TPA monolayer with deposited [(HCOO)Zn]⁺ cations.

■ EXPERIMENTAL SECTION

Computational Details. For all calculations we chose the DFT theory implemented in the Vienna ab initio simulations package (VASP)⁵¹ based on Mermin's finite temperature DFT.⁵² We employ the projector augmented plane wave (PAW)^{53,54} method for describing electron–ion interactions together with PW91 GGA exchange–correlation functional as parametrized by Perdew et al.⁵⁵ knowing that the GGA functionals have been proven to produce reliable results in describing electronic structure of such systems like titania.^{56–58}

A number of tests were initially performed to verify the accuracy of the method (variation of the cutoff energy and *k*-point set) when applied to bulk properties of TiO₂. Presented results were obtained for the standard Monkhorst–Pack⁵⁹ grid (3 × 3 × 2 sampling mesh for bulk calculations and 2 × 2 × 1 for slab calculations) with the cutoff energy of 400 eV and the Methfessel–Paxton⁶⁰ smearing with σ parameter set to 0.1 eV. For solving the Kohn–Sham equations the SCF convergence criterion was set to be an energy change of 10^{−5} eV between two successive iterations. Geometry optimization was performed until the changes in the forces acting upon the ions were smaller than 0.001 eV/Å per atom.

Surface geometries were constructed by cleaving the solid in the [110] direction. The Ti₄₈O₉₆ supercell model (for details see Table S3 in the Supporting Information) used for calculations consisted of nine atomic layers (thickness of 9.01 Å) and a vacuum layer of 18 Å, located above the modeled surface in the [110] direction, to separate the slabs to avoid mutual interactions. Both the stoichiometry of the bulk TiO₂ and the identical structure of the top and the bottom slab terminations were preserved. The four outermost atomic layers were allowed to relax, while the remaining deeper layers were kept fixed at the optimized atomic bulk positions. The size of the surface model was adequate to accommodate up to 4 TPA molecules in the supercell. We started with calculations of an isolated TPA molecule adsorbed on TiO₂, and then we added other molecules to reach a monolayer coverage. The adsorption energy (ΔE_{ads}) per one molecule was defined as

$$\Delta E_{\text{ads}} = (E_{\text{total}} - (E_{\text{surf}} + nE_{\text{TPA}}))/n$$

where E_{total} is the energy of the optimized model describing TPA adsorption, E_{surf} denotes energy of the bare surface, and nE_{TPA} stands for the energy of *n* isolated TPA molecules. Since in total energy calculations we employed a symmetric slab exposing a surface of 154.2 Å² and TPA molecules were adsorbed on one side only, the specific $\Delta E_{\text{ads}}^{\text{s}}$ energy normalized to the surface

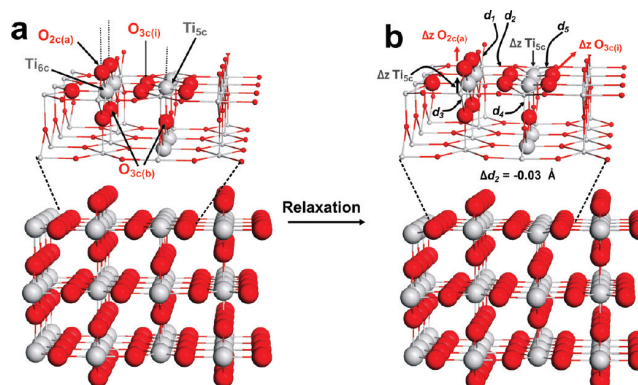


Figure 1. Top-lateral view of the optimized unrelaxed and relaxed (a) structure of the (110) plane of the TiO₂ with major displacements of the exposed ions marked by arrows together with top view (b) of relaxed surface with Ti–Ti distances indicated.

area was calculated following the formula:

$$\Delta E_{\text{ads}}^{\text{S}} = \Delta E_{\text{ads}} / 154.2 \text{ \AA}$$

The latter value is helpful for comparing energy gains upon adsorption of molecules with different surface areas per molecule.

With the optimized geometries of the surface species the resultant STM image simulations were performed within the Tersoff–Hamann theory.⁶¹ The images were simulated in the constant current mode applied in the STM experiments. The *k*-point sampling was done with Monkhorst–Pack mesh; the $2 \times 2 \times 1$ density was used initially and the convergence of the results was verified up to $4 \times 4 \times 4$ mesh, for both TiO₂ and TiO₂/TPA. The compromise was reached at $4 \times 4 \times 2$ mesh density. For acceleration of convergence the Methfessel–Paxton smearing with the width of $\sigma = 0.01$ eV was utilized. In addition to the PW91 functional the PBE⁶² functional was also tested, and in both cases the obtained results were in perfect agreement.

Sample Preparation and STM Imaging. The experiments were carried out in an ultrahigh vacuum (UHV) system containing preparation, surface analysis, and radial distribution chambers. The STM measurements were performed with the Omicron variable temperature scanning probe microscope (VT-STM/AFM). The base pressure was in the low 10^{-10} mbar range. The preparation chamber was supplied with a noble gas ion gun, effusion cells, an infrared pyrometer, and a quartz microbalance thickness monitor. The surface quality was monitored with a low-energy electron diffraction (LEED) setup. The TiO₂(110) wafers (MaTecK GmbH) were mounted on sample holders with a silicon wafer acting as a resistive heater. The samples were first annealed for 6 h at 800 K, and subsequently the cycles of 1 keV Ar⁺ sputtering for 15 min and annealing at 960 K for 15 min were repeated until a clean surface was reached. The annealing temperature was controlled by the infrared pyrometer. The TPA molecules were evaporated at about 370 K from a Knudsen cell on the TiO₂(110) surface kept at room temperature. Prior to the evaporation procedure, terephthalic acid powder (Fluka, $\geq 99\%$ purity) was outgassed for several hours in vacuum. The STM imaging was carried out in a constant current mode at positive bias voltages (empty state imaging) with etched tungsten tips used as probes. For image processing and

STM data analysis, WSxM and Mathematica 7.0 software were employed.⁶³

RESULTS AND DISCUSSION

The investigated single crystal titanium dioxide exhibits a rutile structure ($D_{4h}^{14}-P4_2/mnm$, $a = b = 9.16$, and $c = 5.90$ Å), where each titanium ion is linked to six oxygen neighbors, forming a slightly perturbed octahedron that is linked by corners and edges. In such a structure two different Ti–O bond lengths of 1.976 Å (two oxygen atoms) and 1.954 Å (four oxygen atoms) can be distinguished. As shown in Table S1 (Supporting Information), differences between the calculated and the experimental parameters are less than 1%.

Surface Structure Optimization. The unreconstructed (110) surface of rutile exhibits the titanium atoms in two different coordination environments.²⁰ Along the [001] direction, the rows of fully coordinated Ti ions (Ti_{6c}) (the *nc* subscript hereafter denotes the coordination number of *n*) occupying octahedral interstitials (of approximately the same geometry as in the bulk) alternate with the rows of pentacoordinated Ti_{5c} ions, occupying truncated octahedral sites and exposing one dangling bond in the [110] direction (Figure 1a). Analogously, we can distinguish three kinds of the surface oxygen anions: those lying beneath the exposed plane, and having a trigonal coordination, O_{3c(b)} with the geometry similar to the bulk species (“b” in subscript denotes “bulk”), oxygen O_{3c(i)} anions (“i” in subscript for “interlayer”) connecting the rows of the Ti_{6c} and Ti_{5c} cations, and exposed O_{2c(a)} anions (“a” for “above”) that are located above the uppermost titanium layer. The latter are coordinated to only two Ti neighbors and exhibit one dangling bond perpendicular to the (110) plane (Figure 1a). The calculated surface energy of the unreconstructed (110) plane was equal to $1.35 \text{ J} \cdot \text{m}^{-2}$.

Prior to TPA adsorption modeling, the TiO₂ slab was relaxed. Only slight changes in the atomic positions were observed (Figure 1b), in good agreement with previous experimental and theoretical findings.²⁰ The relaxation process can be described as slight displacements of the topmost atoms in the *z* direction perpendicular to the (110) plane. The Ti_{6c}, O_{3c(i)}, and O_{2c(a)} ions are moved outward by 0.23, 0.20, and 0.04 Å,

respectively, whereas Ti_{5c} cations are moved in the opposite direction by 0.1 Å. Such displacements influence the interatomic bond lengths in the topmost layers, and the results are given in Table S2 (Supporting Information). As shown in Figure S1 (Supporting Information), the l_1 distance between the Ti_{5c} cations in the [001] row is equal to 2.96 Å, whereas for the Ti_{5c} cations located in the [110] rows the l_2 distance of 6.50 Å was found. Upon relaxation the surface energy was substantially lowered to $0.67 \text{ J} \cdot \text{m}^{-2}$, in line with earlier calculations of Ramamoorthy and Vanderbilt.⁶⁴ Such low surface energy can be accounted for by electrostatic considerations²⁰ and a relatively low number (0.1 per Å²) of the dangling bonds ($0.05/\text{Å}^2$ for Ti_{5c} and $0.05/\text{Å}^2$ for $\text{O}_{2\text{c(a)}}$).

Low Coverage Limit. Discrete Adsorption Modes. In the following section we will focus our attention on discrete adsorption modes of TPA molecules in the low coverage limit, where single molecules adsorb on the surface. For geometry optimization of the gas-phase molecule, a crystallographic structure of the terephthalic acid was used as a starting point.^{65,66} Following previous suggestions,⁴⁷ adsorption of carboxylic acids is not significantly affected by surface defects, such as oxygen vacancies or superficial hydroxyls; therefore all calculations were performed within a pristine TiO_2 surface model.

The calculated geometry of the reference gas phase TPA molecule (along with the corresponding bond lengths and angles) is presented in Figure S2 and Table S4 in the Supporting Information. The results obtained are in perfect agreement with earlier experimental and theoretical data.^{65–67} The TPA molecule was next placed on the $\text{TiO}_2(110)$ slab in different starting conformations (see Figure S3 in the Supporting Information). From the four proposed geometries, three led to significant adsorption energies, and the geometry denoted as *side-on* (Figure S3c, Supporting Information), exhibiting ΔE_{ads} lower than 0.02 eV/molecule was excluded from further analysis.

The highest adsorption energy per molecule ($\Delta E_{\text{ads}} = 3.33 \text{ eV/molecule}$) is associated with the *plane-on* adsorption geometry (Figure 2), where the binding occurs through the oxygen atoms of both carboxylic groups and the surface Ti_{5c} ions, involving a 90° rotation of the molecule around the bond between the aromatic ring and the carboxylic group. The adsorption centers (Ti_{5c}) for both carboxylic groups were separated by an intact Ti_{5c} ion, and the attached carboxylic oxygen atoms complete their coordination sphere. The resultant $\text{Ti}_{\text{5c}}\text{--O}_{\text{TPA}}$ bond length was equal to 1.93 Å. Even for the starting geometry with an undissociated TPA molecule, the structure optimization causes the hydrogen atoms from both carboxyl groups to migrate to the nearest bridging oxygen atoms ($\text{O}_{2\text{c(a)}}$) forming surface hydroxyls with a O--H bond length of 0.99 Å. This accounts for an additional stabilization of the adsorbed TPA molecule by formation of hydrogen bonds between the deprotonated carboxylic groups and the surface hydroxyls, characterized by a $\text{O}_{\text{TPA}}\text{--HO}_{\text{surf}}$ distance of 2.21 Å (Figure 2a). The main axis of the TPA molecule is not parallel to the [001] direction, as can be inferred from Figure 2b, where the lines are parallel to Ti_{5c} rows and the molecule main axis forms an angle of approximately 19° . Such positioning allows the carboxylic groups of the TPA admolecules to better interact with the surface Ti ions. Analysis of the changes in the structure of the TPA molecule upon adsorption (Table S4, Supporting Information) showed no significant modification of the aromatic ring. The only relevant changes include the previously described rotation of the carboxylic groups and reduction of the C1--O1 bond length by 0.05

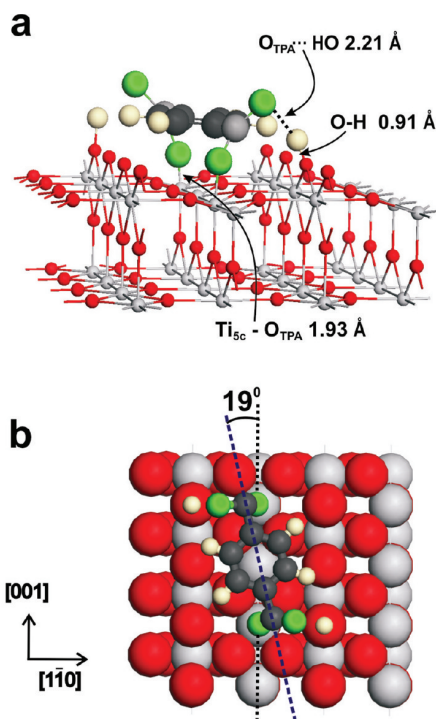


Figure 2. Plane-on adsorption mode of the TPA molecule on the (110) surface of rutile TiO_2 : (a) side view of the topmost trilayers (smaller spheres) of titanium dioxide and adsorbed molecule (larger spheres); (b) top view of the TPA admolecule. Surface atoms are colored in the following way: oxygen, red; titanium, light gray. TPA atoms are colored as: oxygen, green; hydrogen, yellow; carbon, gray.

Å, resulting from 2-fold deprotonation of the TPA molecule. Relaxation of the surface upon adsorption was found to be rather small. The titanium ions of the topmost layer are moved slightly toward the molecule along the [110] direction by about 0.01 Å, while all other atoms remain essentially in their initial positions.

For *top-on* (vertical) adsorption of the TPA molecules, two starting geometries of different orientation of the carboxylic group were proposed (see Figure S3 in the Supporting Information). In the so-called bridge configuration the adsorption is accompanied by deprotonation of the carboxyl group, and the TPA admolecule is oriented along the [001] direction (Figure 3), giving rise to the adsorption energy of ΔE_{ads} of 2.42 eV/molecule. In this configuration the two carboxylic oxygen atoms are attached to two adjacent surface Ti_{5c} ions with the $\text{Ti}_{\text{5c}}\text{--O}_{\text{TPA}}$ bond length equal to 2.0 Å. Such bridging geometry of the carboxylic group was reported for titanium dioxide with adsorbed monocarboxylic acids such as formic,^{68,69} acetic,²⁰ trimethylacetic,⁷⁰ benzoic, and isonicotinic^{71–73} acids and also for $\text{Cu}(110)$ surface upon TPA deposition.^{67,74} As seen in Figure 3 the released proton is attached to the distal bridging $\text{O}_{2\text{c}}$ atom, without any significant interaction with the TPA admolecule. Detailed analysis of the geometry changes upon the adsorption (Table S4, Supporting Information) indicates

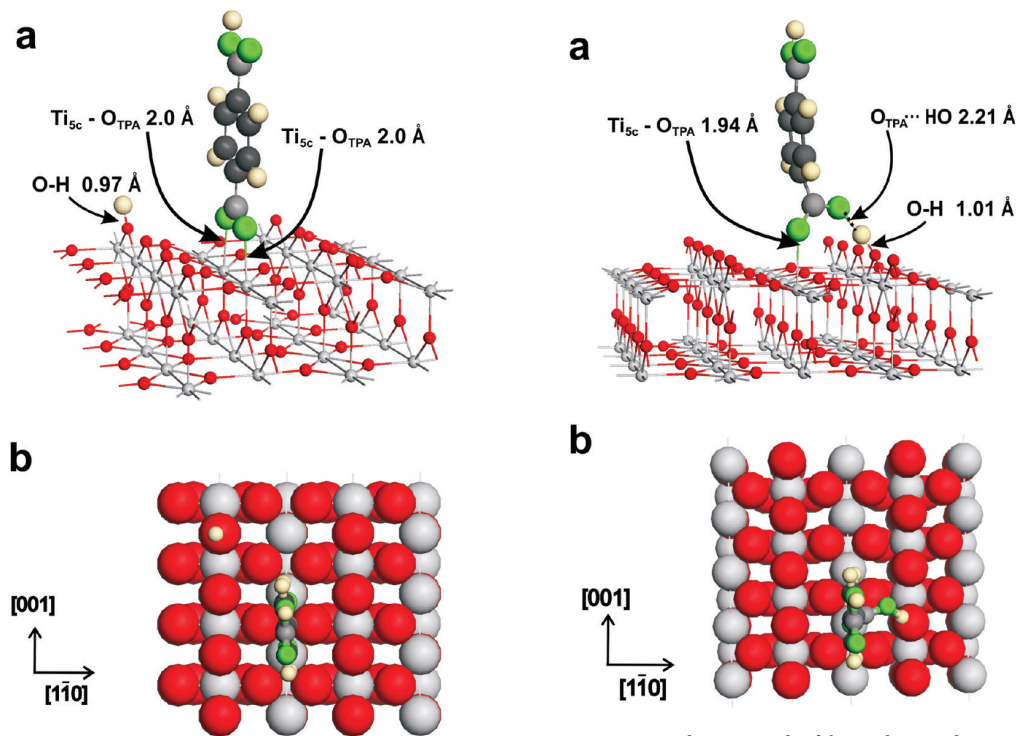


Figure 3. Top-on adsorption mode of the predissociated TPA molecule on the TiO₂(110) surface: (a) side view of the topmost trilayers (smaller spheres) of the titanium dioxide and the adsorbed molecule (larger spheres); (b) top view of the adsorbed TPA molecule (color coding of atoms is the same as that in Figure 2).

that the aromatic ring remains essentially intact, whereas the C–O bonds of the deprotonated bound carboxylic group became as expected, equivalent. The surface Ti_{5c} ions involved in the adsorption move slightly toward the bulk of the titania substrate along the [110] direction, while all other surface and bulk atoms remain in their initial positions.

The second top-on adsorption mode occurs without predissociation (see Supporting Information). The optimized geometry (Figure 4a) is featured by a Ti_{5c}–O_{TPA} bond of $d_{\text{Ti}–\text{O}} = 1.94$ Å, which is accompanied by an auxiliary hydrogen bond produced by the released carboxylic proton with the nearest surface bridging O_{2c(a)} oxygen ($d_{\text{O} \cdots \text{HO}} = 2.21$ Å) along with $\sim 90^\circ$ rotation of the aromatic ring. The resultant adsorption energy was found to be $\Delta E_{\text{ads}} = 1.35$ eV/molecule. Again, the relaxation of the oxide surface was negligible.

The discrete adsorption modes of the TPA molecules on the rutile TiO₂(110) surface were experimentally characterized by noncontact atomic force microscopy (NC-AFM) and NEXAFS techniques.³³ It has been shown that for low coverages (below ~ 0.3 monolayers) the TPA molecules, adsorbed as single, well-isolated entities, adopt a nearly flat-lying geometry and do not form any organized structure. Earlier force field theoretical

Figure 4. Top-on adsorption mode of the nondissociated TPA molecule on TiO₂(110) surface: (a) side view of the topmost trilayers (smaller spheres) of titanium dioxide and the adsorbed TPA molecule (larger spheres); (b) top view of the admolecule (color coding of atoms is the same as that in Figure 2).

calculations indicated that discrete molecules lie flat on the surface and are bound via both carboxylic groups to the same titanium row by monodentate bonds.⁴⁴ Additionally, hydrogen bonds were also formed between the TPA OH groups and the surface bridging O_{2c(a)} oxygens. The deprotonated adsorption mode was shown to adopt similar geometry but without formation of hydrogen bonds. Surprisingly, the adsorption energy was equal to 2.35 eV/molecule for both adspecies.

Due to the lack of the hydrogen bonds stabilizing the dissociatively adsorbed TPA, Sushko et al.⁴⁴ reported the molecules to be extremely mobile on the surface with the diffusion barrier of only 0.22 eV (the protonated form exhibits the barrier of 0.39 eV). Rahe et al.³³ based on NC-AFM measurements found the TPA molecules to be immobile at room temperature, associating this fact with pinning of the admolecules to the surface defects. A small discrepancy in the orientation of the aromatic ring plane (NEXAFS has revealed a tilting by $\sim 18^\circ$) was attributed to the adsorption on morphological irregularities or to thermal excitations into low-energy vibrational states.³³

Our DFT calculations for the low coverage limit indicate that the TPA molecules adsorb dissociatively in a flat plane-on geometry, forming two covalent bonds between surface titanium atoms and oxygen atoms from the molecule dissociated carboxyl groups. The DFT results are in good agreement with the NC-AFM and NEXAFS experiments, and contrary to the results of

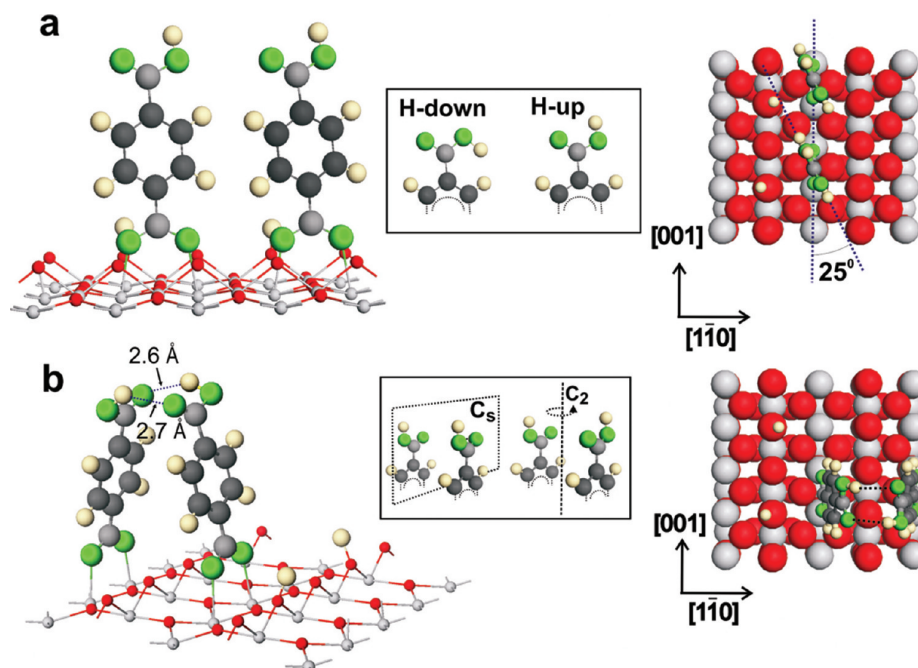


Figure 5. Side and top views of optimized structures for dimer adsorption of TPA on the TiO_2 (110) surface with lateral side-to-side (a) and frontal plane-to-plane arrangements (b). Inserts represent starting geometries of the carboxylic groups (coloring of atoms is the same as that in Figure 2).

Sushko et al.,⁴⁴ we show that the terephthalic anion upon deprotonation forms hydrogen bonds with the nearby surface hydroxyls stabilizing the adsorbed state.

High Coverage Limit. Congested Adsorption Modes.

When only the adsorption energy per molecule alone is considered, one may presume that the flat-lying geometry is preferred and the upright adsorbed TPA molecules should not be observed. However, from quick inspection of Figures 2 and 3 it can readily be noticed that the flat-lying molecules occupy three Ti_{5c} adsorption centers, whereas the vertically adsorbed molecule only two such sites. As a result the calculated adsorption energy gain per surface area is equal to 0.057 and $0.068 \text{ eV} \cdot \text{\AA}^{-2}$ for horizontally and vertically adsorbed molecules, respectively. These numbers indicate clearly that in the low-coverage limit, when single molecules adsorb on the surface, the plane-on adsorption geometry is favored, whereas in the high coverage limit, when the monolayer structure is formed, the TPA admolecules are preferably stabilized in the top-on (vertical) fashion. Due to the large difference in the adsorption energy between the associative (molecular) and the dissociative forms (1.35 and 2.42 eV per molecule, respectively), it is plausible that in the monolayer all molecules are adsorbed in the dissociative upright conformation. However, to interpret the experimental results showing formation of a monolayer with the vertically oriented molecules,^{7,8,33} mutual interactions between the adspecies have to be taken into account.

For modeling a dense monolayer of the TPA molecules, we approximate the intermolecular interactions by sorting them out into two categories: (1) the interaction between the TPA molecules adsorbed in a side-to-side (lateral) arrangement on

the Ti_{5c} sites of the same [001] row, and (2) the interaction between the TPA molecules occupying the Ti_{5c} sites in a plane-to-plane (frontal) fashion (Figure 5).

In the case of the side-to-side geometry, we considered two conformations of the unbound top carboxylic group, with the hydrogen atoms in an up and a down geometry (insert of Figure 5a), since Atodiresei et al. reported that these arrangements differ in energy for TPA adsorbed on the $\text{Cu}(110)$ plane.⁶⁷ In contrast to that paper, our results indicated that the hydrogen-up conformation is slightly more favorable ($\sim 0.04 \text{ eV/molecule}$) than the hydrogen-down one. Such a difference may be associated with a larger distance between the adsorbed TPA molecules, which is primary defined by the (110) interplanar spacings of the TiO_2 ($2.9 \text{ \AA}$) and Cu ($2.5 \text{ \AA}$) substrates. Upon optimization, the TPA admolecules rotate around the $\text{C1}-\text{C2}$ bond by 25° to avoid steric interaction between the phenyl rings. The rotation leads to energy gain of 0.13 eV/molecule . The total adsorption energy per molecule equal to 2.35 eV is slightly lower than that for the isolated admolecules. The optimal geometry of the adsorbed TPA molecule in the most stable hydrogen-up conformation is shown in Figure 5a.

For the plane-to-plane mode we can consider two different arrangements of the top carboxylic groups, exhibiting a C_s and a C_2 local symmetry (see insert in Figure 5b). Optimization of the starting C_s conformation leads to an essentially vertical adsorption of both TPA admolecules with no apparent interaction between them. The C_2 geometry leads to formation of double hydrogen bonds between the hydroxyl and carbonyl oxygens of both carboxylic groups. In such a case, the significant energy gain of 0.17 eV per molecule leads to a total adsorption energy of 2.61

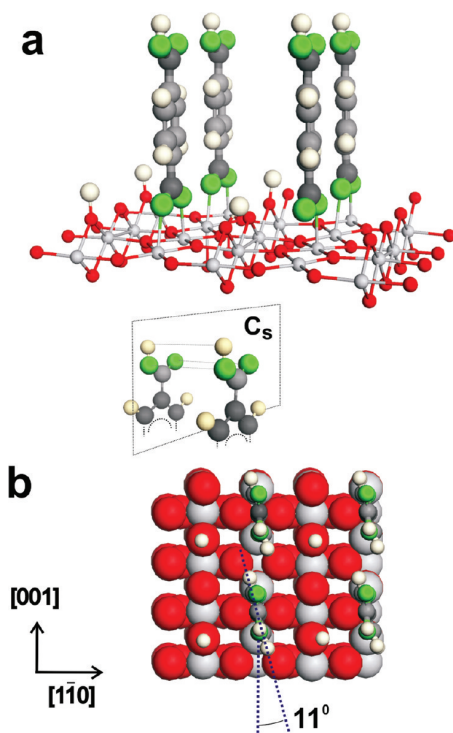


Figure 6. Optimized nondimer structure of a dense TPA monolayer on the $\text{TiO}_2(110)$ surface. Side view with the insert showing geometry of the apical carboxylic groups (a) and top view (b).

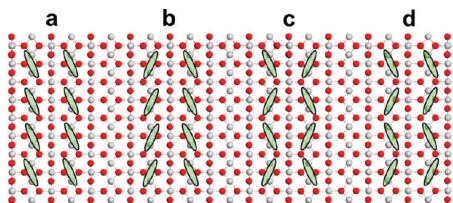


Figure 7. Four typical patterns of a TPA monolayer connected with the rotation of the admolecules (for the sake of simplicity the scheme neglects interactions between the apical carboxylic groups).

eV/molecule. Analysis of the dimeric adsorption modes indicates that occupation of two adjacent adsorption sites by TPA molecules leads to a significant energy rise due to repulsive interactions between the phenyl rings, while hydrogen bonds produced by the interacting TPA admolecules sitting on the neighboring sites of the parallel Ti_{5c} rows stabilize the dimer structure.

As a next step in approximating the structure of the dense TPA monolayer formed on the $\text{TiO}_2(110)$ surface, we have considered a more realistic model with four adsorbed TPA molecules. As in the previous case, we have considered two adsorption modes with the top carboxylic groups in either C_s or C_2

symmetry. For the C_s configuration, shown in Figure 6, we have obtained the adsorption energy $\Delta E_{\text{ads}} = 2.23$ eV/molecule.

The C_2 -based model is more complex since together with the hydrogen bond formation detailed analysis of the relaxed TPA monolayer revealed (i) phenyl ring rotation to reduce repulsive side-to-side interactions between the neighboring TPA molecules and (ii) mutual plane-to-plane inward tilting of the TPA molecules adsorbed on the adjacent Ti_{5c} rows. As a consequence of these two effects four different TPA patterns (variants of the C_2 model) are possible, as shown schematically in Figure 7. A more detailed picture of the four spatial arrangements of the TPA molecules in a congested monolayer is presented in Figure 8. For each of these geometries, an additional stabilization by formation of the hydrogen bonds is possible. However, two hydrogen bonds formed between the neighboring TPA admolecules are not symmetric (show different bond lengths), which is a direct consequence of the simultaneous rotation and inward inclination of the TPA molecules. The ΔE_{ads} energies calculated for the four structures shown in panels a–d of Figure 8 correspond to 2.42, 2.42, 2.38, and 2.39 eV per molecule, respectively. Each of these four geometries implied by the C_2 model allowing for dimer formation exhibits the ΔE_{ads} energy lower than the C_s structure ($\Delta E_{\text{ads}} = 2.23$ eV/molecule) where the dimerization is not feasible. The C_s and the four C_2 structures are separated by an energy barrier of 0.27 eV/molecule associated with rotation of the top carboxylic group, leading to easy transition between the C_s and C_2 configurations. The height of this barrier was assessed using the NEB approach.⁷⁵ It is low enough to allow smooth relaxation of the C_s structure to one of the four possible C_2 arrangements, strongly suggesting that the stable layer involves formation of dimers, and this process is kinetically accessible even at ambient conditions. The differences in ΔE_{ads} energies for all dimer geometries implied by the C_2 model are negligible. Thus, for a real congested TPA monolayer we may expect a mixed phase structure involving the four discussed dimeric species, and all amid phenyl ring rotation angles.

To perform a more direct comparison of our results with the STM data, we have simulated STM images of the TPA structures obtained from the DFT calculations (see Figure 9). Whereas the calculations of the C_2 structures provide a clear distinction between the four geometries, such delineation is not possible in STM measurements at room temperature, due to thermal drift that smears out their detailed appearance.^{7,8} The simulated STM images are featured by clear submolecular resolution, which is unattainable in the experiment. Therefore, for the sake of comparison between the simulated and the experimental STM images, a smearing procedure was used by convolution with the Gaussian function. The standard deviation was equal to the diameter (in pixels) of the circle occupied by a TPA molecule in the simulated image, whereas the integration area had the radius of 2 standard deviations. In Figure 10 simulated STM images of the TPA monolayer convoluted with a Gaussian function are compared with the STM pictures obtained at room temperature. The experimental contrast could be categorized into three main groups exhibiting: (i) a dimer configuration (Figure 10a), (ii) bright rows of the adjacent TPA molecules (Figure 10b), or (iii) a (2×1) pattern (Figure 10c). The dimer configuration clearly seen in Figure 10a can be associated with the calculated dimer structures, stabilized by hydrogen bonds (Figures 8 and 10d). Due to the limited STM resolution (which may arise from thermal excitations and the size of the tip apex) it is impossible to decide whether any of the four predicted dimer geometries

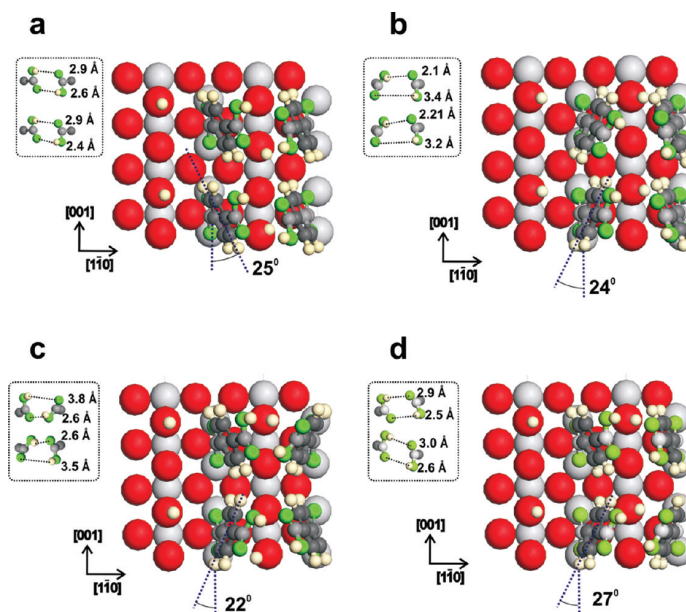


Figure 8. Optimized dimer structures of a TPA dense monolayer adsorbed on the $\text{TiO}_2(110)$ surface. Top view with inserts showing the geometry of the apical carboxylic groups.

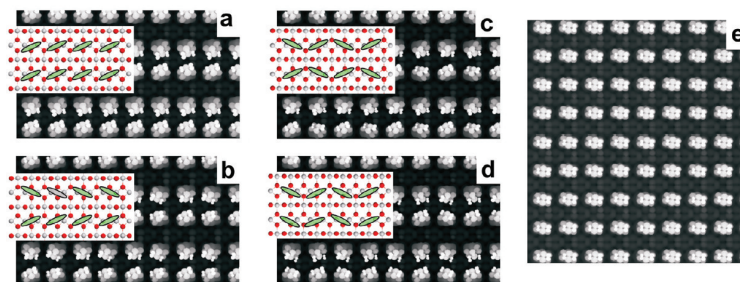


Figure 9. Simulated empty-state STM images (tunneling current 2.0 pA, bias voltage +2.0 V) of a congested TPA monolayer with (a–d) and without (e) inclusion of the stabilization by hydrogen bonds.

(Figures 7 and 8) is actually preferred. As discussed above, we expect that they all may be present in a mixed phase. Similarly, the STM image shown in Figure 10b, previously attributed to the dimer configuration with an enhanced contrast on the top carboxylic groups (arising from a spontaneous tip modification; see ref 8), corresponds very well to the image presented in Figure 10e. The latter shows the same dimer structure as in Figure 10d but was calculated for a larger bias voltage (3 V instead of 2 V). The observed changes of the STM appearance shown in panels d and e of Figure 10 could then result from adding new states that take part in the tunneling process by broadening of the energy window when the bias voltage increases. Alternatively, it may also be connected with the tip rise/restructuring upon spontaneous modification of the apex occurring in the experiment which corresponds to increased bias voltage in the calculated STM pictures.

The question of whether the STM contrast shown in Figure 10c and assigned to the (2×1) motif could imply the existence of a nondimer structure (see Figure 6) can be analyzed by invoking the following arguments. As shown previously the STM experiments exclude coexistence of the dimer and nondimer phases (for details see ref 8). Furthermore, the STM contrast switching is not recorded continuously but in certain random time intervals that are long enough to allow collection of the whole $50 \text{ nm} \times 50 \text{ nm}$ scan frame for a given pattern. These findings exclude also the possibility of spontaneous recurring switching between the (2×1) and the dimer structures. The DFT adsorption energy of the dimer structure is decreased by approximately 0.27 eV/molecule with respect to the 2×1 pattern, and the low energy barrier between the nondimer and dimer structures suggests the predominance of the TPA dimers. Therefore we can judiciously conclude that the congested TPA

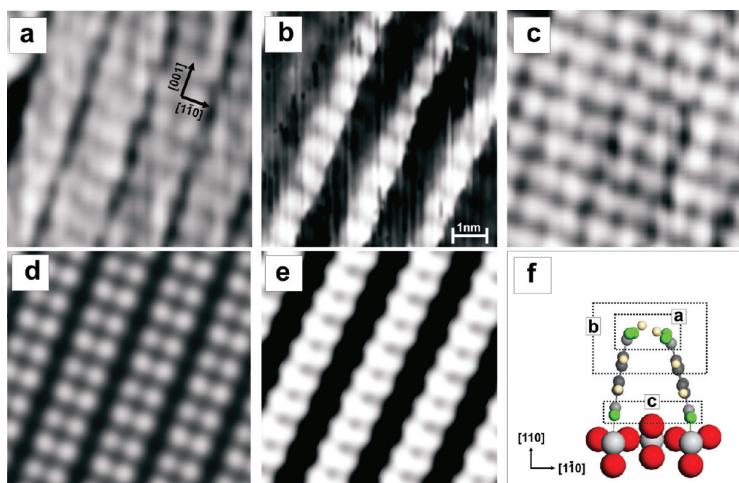


Figure 10. Simulated and experimental empty-state STM images of a congested TPA monolayer; (a), (b), and (c) show experimental images exhibiting a dimer motif, enhanced contrast on top of dimer rows, and a (2×1) pattern, respectively. All images acquired at +2.0 V bias voltage. (d) and (e) Simulated images exhibiting a dimer motif (at bias voltage of +2.0 V) and contrast enhancement achieved on top of the dimer rows (bias voltage +3.0 V), respectively. (f) Schematic representation of the STM contrast origin. All images were acquired and simulated with the tunneling current of 2.0 pA.

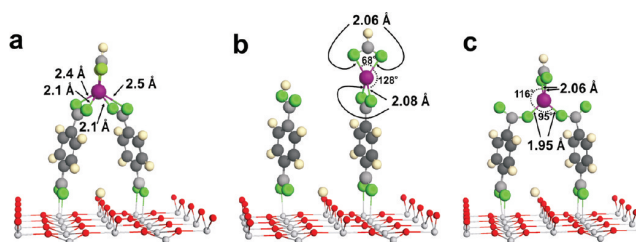


Figure 11. Optimized structures of the zinc ions attached to the TPA monolayer deposited on the (110) surface of TiO_2 (for the sake of simplicity only two TPA molecules per unit cell are shown). Zinc ion is terminated by formate ion.

layer assumes a stable dimer configuration (Figures 7 and 8) and that the experimental STM data shown in Figure 10, due to specific tip modification, reveal essentially different parts of the electronic structure of the dimer TPA/ TiO_2 layer, as proposed elsewhere.⁸ Consequently, the observed (2×1) STM contrast in Figure 10c could be attributed to the imaging of the bottom part of the TPA admolecules. Unfortunately, direct theoretical modeling of this contrast is behind the abilities of the Tersoff–Hamann approach applied in our work.

Surface-Mediated Building of Metal Organic Frameworks (MOFs). Formation of a stable TPA monolayer on the TiO_2 surface results in its functionalization by terminal carboxylic groups. It is, however, still a matter of debate³⁰ whether the intermolecular stabilization of the TPA monolayer effected by hydrogen bonds between the carboxylic groups of the adjacent admolecules may be the detriment of such functionalization. To address this issue we have investigated formation of the MOF-5 structures using the TPA monolayer as a template. The key interaction in the MOF-5 structure occurs between the zinc ions and the dissociated carboxylic group of the TPA molecules.⁴³ To evaluate these processes we studied adsorption

of $[(\text{HCOO})\text{Zn}]^+$ species on the TPA functionalized titanium dioxide, mimicking in that way the embedding of the zinc ions within the MOF-5 framework. Our goal was to check whether the top carboxylic groups of the congested TPA monolayer, despite being in the dimer state, can effectively bind the metal ions, allowing for effective MOF structure growth on the TPA/ TiO_2 surface.

In the DFT modeling we explored three possible attachment modes of the $[(\text{HCOO})\text{Zn}]^+$ cation: (i) directly to both carboxylic groups bonded by hydrogen bonds (the geometry is shown in Figure 11a); (ii) to a lone carboxylic group not involved in hydrogen bonds (Figure 11b); (iii) to two oxygen atoms of the adjacent carboxylic groups, giving rise to bridgelike conformation (Figure 11c). In general, for all three conformations a rather strong interaction between the zinc ions and the TPA admolecules was observed. Conformation (ii) shown in Figure 11b exhibits the highest adsorption energy equal to 2.78 eV. In this case two oxygen ions of the top carboxylic group and the two oxygen atoms of the adsorbed formic acid form a distorted tetrahedral surrounding of the central zinc ion, characterized by the bond lengths of ~ 2.1 Å and the bond angles equal to 68° and 128° . Conformation (i)

shown in Figure 11a is characterized by the adsorption energy of 2.16 eV and is significantly less stable than conformation (ii). This may result from the larger coordination number of the zinc ion, which leads to larger metal–ligand bond lengths (Figure 11a). Geometry (iii) shown in Figure 11c is characterized by the lowest adsorption energy of 1.50 eV. This results most probably from the position of the TPA carboxylic groups (perpendicular to the phenyl ring plane), which are forced to twist in order to coordinate the zinc ion effectively. The obtained values of the adsorption energy clearly indicate that upon interaction with the $[(\text{HCOO})\text{Zn}]^+$ cation, the TPA molecules adsorbed on the rutile $\text{TiO}_2(110)$ surface are forced to release the hydrogen bonds, and each TPA ad molecule is able to host one $(\text{HCOO})\text{Zn}^+$ cation.

CONCLUSIONS

Periodic DFT modeling and room temperature STM measurements were used to explore structural properties of the terephthalic acid deposited on the rutile $\text{TiO}_2(110)-(1 \times 1)$ surface. At low coverage the molecules adsorb dissociatively as single entities adopting a flat-lying plane-on geometry ($\Delta E_{\text{ads}} = 3.33$ eV/molecule). At the saturation coverage a complete well-ordered monolayer of the upright-oriented TPA molecules, bound to the surface in a bidentate top-on fashion, is formed ($\Delta E_{\text{ads}} \sim 2.4$ eV/molecule). Within the monolayer the intermolecular interactions lead to rotation and inclination of the molecule resulting in linkage effects and formation of stable dimer rows running along the surface $[001]$ direction. A notable agreement between simulated and experimental STM data provides clear support of the proposed dimer model. We show that the interaction between the phenyl rings is relatively weak and the nature of dimer structure arises from the hydrogen bond formation between the apical carboxyl groups of adjacent molecules. Finally, to directly address effective chemical functionality of the dimerized TPA/ TiO_2 surface, we perform calculations of the stable adsorption geometries of the zinc formate ion on top of the dimerized TPA monolayer. Calculations indicate that the covalent bonding of zinc in a tetrahedral configuration is accompanied by the hydrogen bond breaking between the TPA molecules. Thus, we conclude that the anchoring properties of the TPA/ TiO_2 system are not suppressed by the TPA dimer formation, allowing for straightforward on-top growth of the MOF structures.

ASSOCIATED CONTENT

S Supporting Information. Detailed information on the surface unit cell parameters, relaxed molecule geometry, interatomic bond length changes upon relaxation, and starting geometries for the TPA adsorption calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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2.4.6 Tekst artykułu H6

[H6] S. Godlewski*, A. Tekiel, W. Piskorz*, F. Zasada, J. S. Prauzner-Bechcicki, Z. Sojka, M. Szymonski „Supramolecular Ordering of PTCDA Molecules – the Key Role of Dispersion Forces in an Unusual Transition from Physisorbed into Chemisorbed State”, *ACS Nano*, **6** (2012), 8536.

Supramolecular Ordering of PTCDA Molecules: The Key Role of Dispersion Forces in an Unusual Transition from Physisorbed into Chemisorbed State

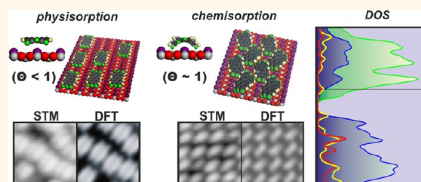
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Supramolecular self-assembly of organic molecules on surfaces plays an important role in nanofabrication. It can control formation and properties of nanostructures, leading to a wide range of applications in photovoltaics, (opto)electronics, gas sensing, (photo)catalysis, and in medicine.^{1–7} Among many types of substrates used for surface-supported supramolecular assembly, metal oxides appear very attractive due to their tunable electronic structure and versatile chemical properties. TiO₂, the most frequently studied material among transition metal oxides, plays a dominant role in model studies and practical applications, especially in conjunction with organic dye sensitization for photovoltaic devices.^{8–11} One of the key challenges for molecular nanofabrication is an effective control of the intermolecular interactions and the binding between the deposited species and the substrate surface. In our work, we have chosen PTCDA molecules,^{12–19} which are extensively studied prototypes of large π -conjugated molecules and are widely used in optoelectronic and photovoltaic devices, to demonstrate the central role of collective intermolecular dispersion forces in controlling the supramolecular ordering of ad molecules on the TiO₂ surface.

Although the density functional theory (DFT) methods have been widely used in analysis of surface-supported molecular systems,^{20–28} still little is known about the nature of the binding of large aromatic planar molecules on metal oxide surfaces. Most studies, so far, have been based on standard DFT calculations,^{29–31} without an explicit account for sizable van der Waals interactions that can actually play a significant role due to the

ABSTRACT



Adsorption and self-assembly of large π -conjugated 3,4,9,10-perylene tetracarboxylic dianhydride (PTCDA) molecules on rutile TiO₂(110) surface have been investigated using a combination of high-resolution scanning tunneling microscopy (STM), low-energy electron diffraction, and density functional theory calculations with inclusion of Grimme treatment of the dispersion forces (DFT-D). Evolution of the STM images as a function of PTCDA coverage is caused by transition of the adsorption mode from physisorbed single adspecies and meandering stripes into spontaneously ordered chemisorbed molecular assemblies. This change in the adsorption fashion is accompanied by significant bending of the intrinsically flat, yet elastic, PTCDA molecule, which allows for strong electronic coupling of the dye adspecies with the TiO₂ substrate. Extensive DFT-D modeling has revealed that adsorption is controlled by interfacial and intermolecular dispersion forces playing a dominant role in the adsorption of single PTCDA species, their self-organization into the meandering stripes, and at the monolayer coverage acting collectively to surmount the chemisorption energy barrier associated with the molecule bending. Analysis of the resulting density of states has revealed that alignment of the energy levels and strong electronic coupling at the PTCDA/TiO₂ interface are beneficial for dye sensitization purposes.

KEYWORDS: supramolecular ordering · titanium dioxide · TiO₂ · PTCDA · dye sensitization · photovoltaics · STM · DFT-D · van der Waals · semi-empirical dispersion · adsorption · DOS · surface functionalization

presence of large and highly polarizable polyaromatic rings.^{32,33} The size limitation makes the semi-empirical Grimme extension of the standard DFT method (denoted as DFT-D) an attractive and computationally cost-effective way of incorporating dispersion interactions.^{32,34–41} In recent years, this approach has demonstrated its ability to provide reliable modeling of molecular

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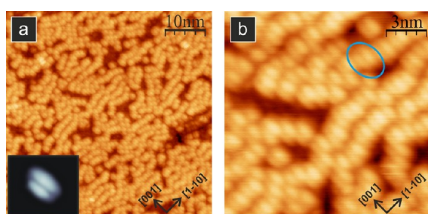


Figure 1. (a) Empty state STM images of meandering molecular stripes together with an isolated molecule (inset). (b) Magnification of the left image reveals the characteristic two-lobe appearance and the orientation of PTCDA with the longer axis parallel to the [001] direction (blue ellipse indicates a single molecule). Both STM images were acquired with the bias voltage of +2.0 V and the tunneling current of 2 pA.

geometries and better description of the molecule–metal substrate binding.^{33,42,43} Until now, in the case of metal oxide substrates, the DFT-D methods have been used for modeling small inorganic systems^{44,45} and alkyl chains only.⁴⁶ In particular, almost no attempt has been made yet to analyze adsorption of large aromatic systems.

In the present work, we examined the role of the interfacial and intermolecular dispersion forces in nanofabrication of large π -conjugated systems on metal oxide surfaces by thorough experimental and theoretical investigations of PTCDA molecules deposited on the $\text{TiO}_2(110)$ surface. The PTCDA/ TiO_2 system was characterized by high-resolution low-temperature scanning tunneling microscopy (STM) and low-energy electron diffraction (LEED), complemented by DFT-D modeling, including the Tersoff–Hamann⁴⁷ and more advanced Bardeen⁴⁸ simulations of the STM images.

RESULTS AND DISCUSSION

Low Coverage Limit: Physisorbed PTCDA Molecules. PTCDA molecules were thermally deposited on the $\text{TiO}_2(110)$ substrate at room temperature under ultrahigh vacuum conditions. At low coverage, the molecules adsorb flat as single entities with their longer molecular axis oriented along the [001] direction of the titania substrate, that is, along the surface bridging oxygen rows. The characteristic two-lobe appearance in the STM images (two dominant lobes of the LUMO orbital spread parallel to the longer molecular axis; see inset in Figure 1a) was rationalized through the DFT-D calculations as a physisorption state that essentially only slightly deforms the intrinsically flat geometry of PTCDA. By increasing the coverage to a submonolayer range, the enhanced intermolecular interactions led to formation of meandering molecular stripes running essentially across surface oxygen rows, as shown by STM images in Figure 1 (both panels). The detailed analysis of the STM image (recorded with larger scale in Figure 1b) revealed that the characteristic two-lobe

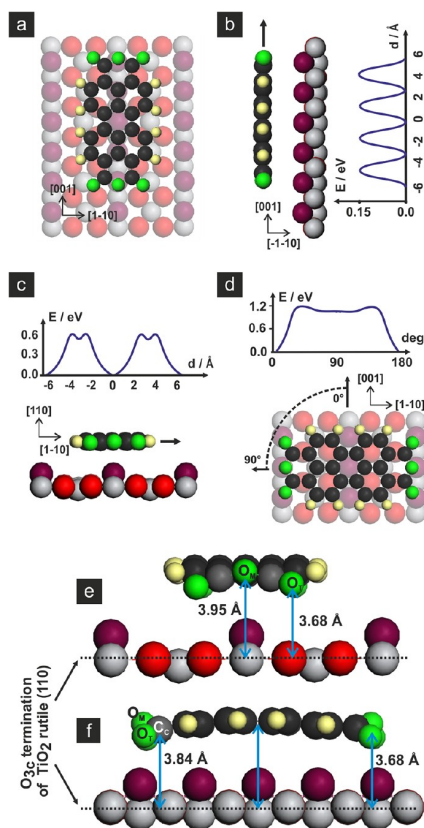


Figure 2. Different views of the most stable adsorption geometry of an isolated PTCDA molecule on the $\text{TiO}_2(110)$ surface. Stable adsorption geometry (a), dependence of the adsorption energy (with respect to the most stable geometry) on the lateral displacement along (b) and across (c) the reconstruction rows. Dependence of the interaction energy on the rotation of the molecule around the axis normal to the surface (d), and deformation of the adsorbed molecule in the most stable geometry (e,f).

appearance of the PTCDA molecules persists, indicating that in this state the ad molecules are still bound to the surface by a similar mechanism as in the case of the isolated molecules.

Preliminary GGA-DFT calculations for the flat-lying PTCDA molecule on the $\text{TiO}_2(110)$ surface revealed the presence of weak (about 0.15 eV per molecule) attractive molecule–substrate interactions only, which do not favor any specific orientation of the molecules, in apparent contradiction to the STM observations. Thus, to correctly describe the adsorption, we used the DFT-D scheme to investigate the potential energy surface (PES) of the PTCDA/ TiO_2 system in more detail. The starting point was the fully optimized PTCDA molecule located directly above the protruding oxygen rows, as

shown in Figure 2a. The TiO_2 surface was then scanned by dragging the PTCDA molecule along the [001] (Figure 2b) and [1–10] (Figure 2c) directions and by rotating it around the [110] axis (Figure 2d). As presented in the corresponding energetic profiles, the movement along the [001] direction was accompanied by a periodic variation of the potential energy with the amplitude of 0.15 eV (Figure 2b). The movement across the protruding oxygen rows exhibited two energetic minima: a shallow one of 0.1 eV and a deeper one of 0.6 eV (Figure 2c), whereas the rotation around the [110] axis was accompanied by the highest energetic barrier of 1.2 eV (Figure 2d). Thus in the DFT-D scheme, the most stable position of the PTCDA molecule corresponds to the orientation with its main axis parallel to the [001] direction, in a perfect agreement with the STM experiments (see Figure 1). Inspection of Figure 2 reveals that the surface–molecule interactions give rise to only a slight deformation of the polyaromatic backbone with the terminal oxygen atoms (O_T) of the anhydride groups (placed 3.68 Å above the reference plane defined by the surface trigonal oxygen ions) pointing toward the titanium atoms, and the middle part of the carbon ring displaced away from this plane by 4.02 Å. Analysis of the geometry of the anhydride groups indicated that attraction of the O_T atoms toward the surface titanium ions is balanced by repulsion between the middle O_M atoms and bridging oxygens of the TiO_2 substrate (Figure 2f). The elucidated structure of the PTCDA species exhibited the binding energy of 1.76 eV with a dominant contribution of the interfacial dispersion interactions (1.45 eV), which is tantamount with a virtually van der Waals character of the PTCDA– TiO_2 interactions. The appreciable distortion of the inherently planar PTCDA molecule upon adsorption, revealed for the first time on oxide surfaces, is analogous to the morphologies that previously have been observed for PTCDA on the metallic Ag(111) substrate.⁴⁹

The obtained results indicate an excellent agreement between the calculated and experimentally observed geometries of the PTCDA/ TiO_2 (110) system, confirming the adequacy of the applied DFT-D scheme. Thorough analysis of the results (see Supporting Information Table S1) showed that screening effects are negligible, revealing a dominant role of the dispersion interactions in the adsorption of large polyaromatic molecules on titanium dioxide.

The corresponding Tersoff–Hamann simulations performed for the adsorbed PTCDA in the most stable position (Figure 2a) remain in good agreement with the above conclusions. The simulated image appears as a two-lobe feature characteristic of an essentially intact molecule in the physisorbed state (Figure 3b,c, simulated with different values of Gaussian blurring to include tip broadening effects), which is very similar to that observed in the experimental images recorded for

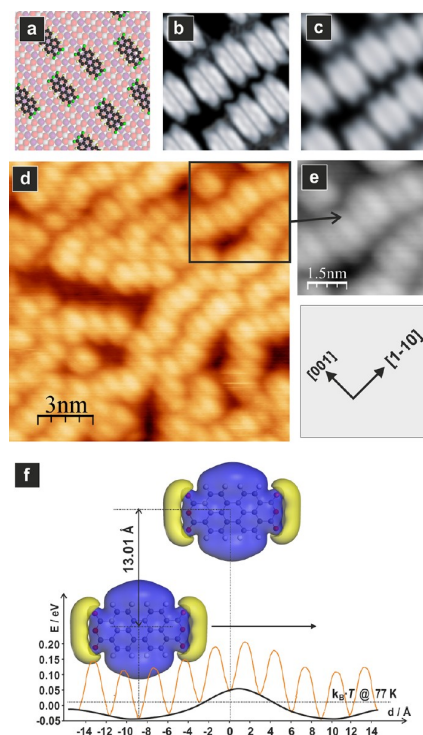


Figure 3. Adsorption of PTCDA molecules on TiO_2 at submonolayer coverage. (a) Schematic model of meandering molecular lines. (b,c) Tersoff–Hamann simulated STM images with varied Gaussian blurring to include tip broadening of the images. (d,e) Empty state STM images of meandering molecular stripes. (f) Overall potential (undulated orange line) produced by interaction potential between two PTCDA molecules while passing by each other (thick black line), superimposed on the PTCDA-surface interaction potential; yellow/violet contour visualizes the negative/positive electrostatic potential isosurfaces. All STM images were acquired with the bias voltage of +2.0 V and the tunneling current of 2 pA.

the submonolayer coverages (Figure 3d,e). As a result, it shows that the PTCDA admolecules in both the isolated and the submonolayer case are essentially physisorbed on the TiO_2 surface. Thus, formation of the meandering molecular stripes can be attributed to the collective action of the intermolecular dispersive forces, which are further enhanced by mutual interactions between the sizable permanent quadrupole moments of the adjacent PTCDA molecules. The development of the stripes was rationalized by a series of DFT-D calculations for a fixed PTCDA molecule being passed (without geometry relaxation) by another one at the distance equal to that observed on the TiO_2 surface in STM scans (the neighboring molecules are located on every second protruding oxygen row, i.e., 13.01 Å apart). Although such a simplified approach does not include the substrate explicitly, it allows for a

quick and rough estimation of the intermolecular interaction potential at low computational costs. The results are shown in Figure 3f, where the solid black line indicates the estimated intermolecular potential that is superimposed on the periodic interaction potential between the PTCDA molecule and the TiO_2 surface (Figure 3f; as a benchmark, the average thermal energy, kT , at 77 K is also indicated). The resultant overall potential (marked with the orange line in Figure 3f) exhibits a regular pattern of the preferred energetic positions of the PTCDA molecules relative to the adjacent one. Consequently, alignment of neighboring molecules along specific directions, such as $[2-20]$, $[2-2\pm1]$, and $[2-2\pm2]$, is preferred. This model based on intermolecular dispersion forces rationalizes the self-assembly of the meandering PTCDA stripes on the TiO_2 surface at medium submonolayer coverages (Figures 1 and 3) in a straightforward way. It is worth noting that exclusion of the dispersion forces (apart from the seizing interfacial stabilization) smears out the intermolecular interaction potential by reducing it from 0.11 to 0.01 eV, which would substantially attenuate the driving force of self-organization into the observed pattern.

Since the interactions between the adjacent PTCDA molecules are rather weak, the meandering stripes are metastable and, upon thermal annealing, can readily be transformed into more robust supramolecular assemblies.

Development of Monolayer Coverage: Chemisorption Forced by Dispersion Interactions. The impact of the dispersion forces was even more pronounced once a full PTCDA monolayer was deposited. Indeed, upon increasing the number of the neighboring molecules, an entirely new ordered PTCDA phase was formed. The LEED measurements (see Supporting Information, Figure S1) showed that the new molecular layer exhibits a six-fold commensurability along the protruding oxygen rows ($[001]$ direction), and a two-fold periodicity across the rows ($[1-10]$ direction). Close examination by low-temperature STM indicated that the PTCDA molecules form the structure of a brick-wall-like appearance with a $c(6 \times 2)$ symmetry in the STM images (Figure 4, both panels). On the basis of those observations, we can deduce that this new structure is so densely packed that the accommodation of the flat-lying molecules as nearest neighbors is no longer possible, taking into account sole geometrical constraints of the flat intact molecule only. Noting the large size of the PTCDA molecule and its possible deformation upon adsorption, we have analyzed its flexibility along vertical (long), horizontal (short), and diagonal axes (see Supporting Information, Figure S7). Calculations revealed that the most likely direction of the PTCDA deformation is along the diagonal axis with the elastic modulus of $3.1 \text{ eV/\AA}^2$. Deformations along the vertical and horizontal axes are substantially smaller due to considerably higher

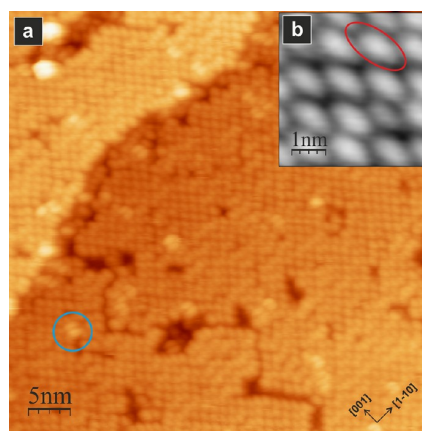


Figure 4. STM image of a densely packed molecular structure (approximately 1 ML). (a) Closed layer (blue circle indicates a single molecule adsorbed on top of the first monolayer). (b) Magnification of the monolayer structure (red ellipse indicates a single molecule). The STM image was acquired with the bias voltage of +2.0 V and the tunneling current of 2 pA.

rigidity of the molecule in these directions (5.4 and $21.7 \text{ eV/\AA}^2$, respectively). Such diagonal deformation might rationalize the observed enhanced packing and is beneficial for formation of the strong bonds with the surface that will be discussed in the following paragraph.

Furthermore, there is a striking difference between the typical two-lobe STM contrast of the physisorbed PTCDA molecules observed at the submonolayer coverage and the PTCDA appearance within the dense monolayer, where each molecule was recorded as a single-lobe feature only (a red ellipse in Figure 4b indicates a PTCDA molecule discriminated in the monolayer). It is worth noting that in the same picture there are some individual molecules adsorbed on top of the first monolayer, and they consequently exhibit the two-lobe appearance typical for the physisorbed state (see blue circle in Figure 4a). These observations indicate clearly that there is a significant difference in the electronic structure of the PTCDA molecules adsorbed within the first monolayer, which are recorded as the single-lobe features, and the physisorbed PTCDA molecules (single molecules, meandering stripes, and single molecules adsorbed on top of the first layer) exhibiting the two-lobe STM appearance. To elucidate the structure of the PTCDA molecules in the first monolayer in more detail, a corroborative DFT-D modeling was next performed.

Figure 5a,b shows the most stable monolayer model that adequately reproduces both the surface packing density and the symmetry of the molecular species deduced from the LEED and STM measurements (for analysis of other examined models, see Supporting

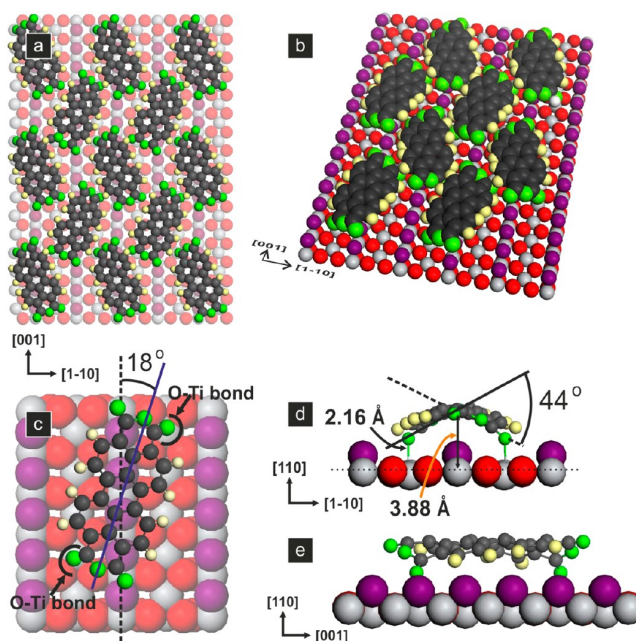


Figure 5. Optimized geometry of the (6×2) closed monolayer. Molecules are bent due to dispersion interactions resulting in a quasi-herringbone structure: (a) top view, (b) perspective view, (c–e) single molecule position extracted from the monolayer.

Information, Figure S2 and Table S2). In the optimized geometry exhibiting symmetry compatible with the one observed experimentally, the PTCDA molecules are arched over the protruding surface oxygen rows, with one of their diagonals located on top of the oxygen row (Figure 5c). As a result, two strong covalent bonds between the terminal (O_T) oxygen atoms of PTCDA and the surface titanium atoms can be formed, giving rise to robust coupling between PTCDA and TiO_2 moieties that is beneficial for efficient photosensitization. The two oxygen atoms involved in the bonds creation come from two opposite anhydride terminal groups and are located along one of the molecule diagonals (Figure 5c). In this geometry, the twisting angle between the anhydride groups is 44° and the O_T-Ti_{surf} distance is equal to 2.16 Å. The average distance between the middle aromatic ring of the PTCDA molecule and the surface O_{3c} atoms is 3.88 Å (Figure 5d). The characteristic feature of this configuration is that diagonal hydrogen atoms point toward the surface, in contrast to another slightly less stable configuration (by 0.11 eV) with hydrogen atoms pointing outward from the surface. However, such small difference in geometry has dramatic consequences on the appearance of the STM images (see below).

The described geometrical parameters show dramatic deformation of the PTCDA molecules upon adsorption. Reaching this conformation requires either

tight packing leading to increased intermolecular dispersive interactions (approximately 2.22 eV per molecule) or thermal annealing of the meandering stripes to 100 °C. Both of these factors assist in the formation of quite strong chemical bonds (1.08 eV) between the arched PTCDA molecules and the TiO_2 surface. Although the deformation of the intrinsically flat PTCDA molecule implies an energy rise of 0.52 eV, the overall adsorption energy of 2.79 eV per molecule is still sizable. As a result, the enhanced dispersion interactions developed within the dense monolayer are crucial for bending of the PTCDA ad molecules and make the chemisorption state accessible by removing the corresponding energy barrier.

Tersoff–Hamann STM image simulations performed for the optimized densely packed structure revealed a significantly different appearance of the chemisorbed PTCDA molecules in comparison to the physisorbed species. Thus, the observed dramatic contrast change can be assigned to the large distortion of the PTCDA molecule backbone giving rise to breaking of the two-fold symmetry of the chemisorbed state STM contrast. Consequently, instead of the two-lobe feature, which is typical for the physisorbed PTCDA molecules (Figure 6a,b), a uniform single-lobe appearance was recorded for the molecules tightly packed within the monolayer (Figure 6c–e).

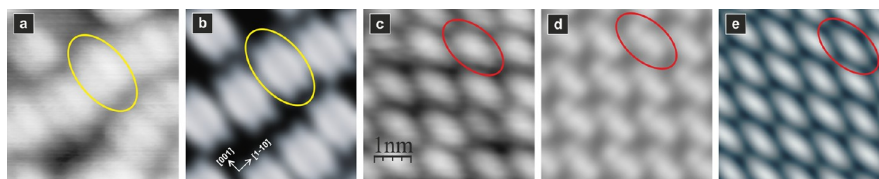


Figure 6. Comparison of the STM contrasts for the physisorbed and chemisorbed PTCDA molecules. Experimental (a) and calculated Tersoff–Hamann (b) images of the physisorbed meandering molecular stripes (yellow ellipses indicate single molecules). Experimental (c) and calculated Tersoff–Hamann (d) and Bardeen (e) images of the chemisorbed (6×2) superstructure (red ellipses indicate single molecules). Images (a–d) were simulated with the bias voltage of +2.0 V and the tunneling current of 2 pA; image (e) was simulated in the constant height mode at bias voltage of +2.0 V.

The supramolecular structure obtained at the monolayer coverage can be described as a well-known PTCDA herringbone phase,¹⁴ which is additionally distorted due to significant non-uniform rotation of the molecules and unidirectional arching of all molecules over the surface oxygen rows, leading to the (6×2) symmetry of the superstructure unit cell. Despite the two distinct orientations of the molecules within the monolayer of the herringbone structure, such collective bulging of the central part of each molecule leads to an unexpected almost brick-wall (6×2) appearance in the STM images seen in Figure 6c–e.

The herringbone structure is typically formed by PTCDA molecules deposited on well-defined substrates with a “flat” surface–molecule interaction potential that is significantly weaker than the intermolecular ordering forces and therefore does not provide any specific adsorption sites. On such substrates, the supramolecular structures can be ordered readily by intermolecular forces, as for example, on the Au(111) surface.⁴⁹ In the present study on the PTCDA/TiO₂(110) system, the supramolecular ordering is strongly affected by the pronounced anisotropy of the surface structure with the crucial role played by the protruding oxygen rows. The latter create a ripple-like surface potential that in conjunction with the intermolecular dispersion forces have a significant effect on the ordering and configuration of the PTCDA molecules. Consequently, the structure of the full monolayer is very similar to the herringbone pattern, comprising considerably distorted PTCDA molecules that adopt their own geometry to the (110) surface landscape by arching over the terminal oxygen rows. Such configuration with hydrogen atoms directed toward the surface is stabilized by collective action of intermolecular dispersion forces and establishment of chemical bonds with surface titanium atoms. Interestingly, for the alternative configuration with the hydrogen atoms directed out of the surface a Tersoff–Hamann based simulation gives rise to significantly different STM pattern (see Figure S6 in Supporting Information) with molecule images

rotated with respect to the direction pointed by substrate surface oxygen rows. Noting a rather crude approximation of the Tersoff–Hamann approach, we supplemented the simulations for the most stable configuration by the much more advanced Bardeen approach in order to minimize the uncertainties associated with STM image simulations. Indeed, this more accurate method gives rise to even better agreement with the experimental pictures (Figure 6e).

In order to factorize the stabilization energy (2.79 eV) of a PTCDA admolecule within the monolayer into the admolecule–surface and the intermolecular contributions, we performed calculations for the isolated PTCDA admolecule in a frozen geometry adopted from the monolayer coverage. The calculated PTCDA–surface interaction energy was equal to 1.75 eV, allowing for extraction of the intermolecular stabilization energy for the molecule within the densely packed layer, which reaches 1.04 eV. Hence, overcoming the energetic barrier (0.52 eV) of the pronounced distortion of the chemisorbed PTCDA species can be explained by the enhancement of the intermolecular dispersion forces caused by an increased number of the adjacent molecules once the dense monolayer is being formed. It is thus clear that the intermolecular contribution plays a key role in the bending of the molecule backbone and the formation of chemical bonds, which due to steric constraints imposed by the protruding oxygen rows cannot be achieved for a single PTCDA molecule. Yet, the structural relaxation of the single PTCDA molecule with the bent geometry taken from the monolayer structure is only moderate and, accidentally, its total binding energy ($E_{\text{ads}} = 1.80$ eV) is very similar to that obtained for the physisorbed PTCDA (1.76 eV). However, the lack of the chemisorbed states in STM images at the low coverage limit can be clarified not only by the already discussed bending energy barrier but also by unfavorable adsorption thermodynamics. Indeed, the free enthalpy of the adsorption, ΔG_{ads} , showed that at the temperature above 50 K only the physisorbed state of the

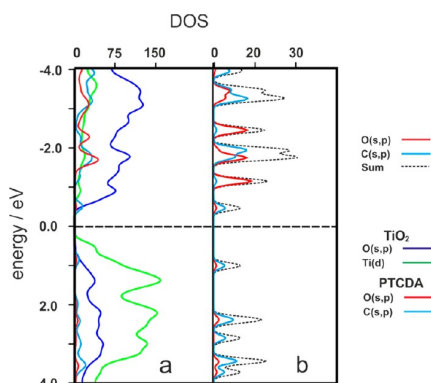


Figure 7. Density of states (DOS) diagrams for the PTCDA monolayer on rutile (110) surface (a) and an isolated physisorbed PTCDA molecule (b).

PTCDA ad molecules is clearly preferred once the entropic term is taken into account (see Supporting Information Figure S3).

To illustrate the importance of dispersion forces in monolayer self-assembly, we repeated modeling within the pure DFT method without inclusion of the dispersion interactions. The results showed that PTCDA molecules remain essentially flat upon adsorption and their stacking due to the space limitation gives rise to a roof-tiles structure (see Supporting Information, Figure S5) in which the protruding ad molecules are not evenly distributed on the surface. This result clearly contradicts the STM and LEED experiments. In such a geometry, PTCDA stabilization energy falls to mere 0.24 eV in dramatic contrast to PTCDA stabilization of 2.79 eV in a monolayer with dispersion interactions incorporated.

Influence of the Adsorption Mode on the Electronic Structure of the PTCDA/TiO₂ Assembly. The observed transformation from the flat physisorbed into the bent chemisorbed state can be used to control the electronic and optoelectronic properties of the organic dye sensitizers, which strongly depend on the molecular structure of the adspecies. It also demonstrates feasibility of controlled structural transitions in the supramolecular surface assemblies and the resultant alteration in the functional behavior of the oxide photonic devices with variation of the surface coverage.

To study the influence of the PTCDA adsorption mode on photosensitization properties of the PTCDA/TiO₂ system, we discussed the energy level alignment at the PTCDA/TiO₂(110) interface by calculating density of states (DOS) diagrams. In Figure 7, the DOS for the PTCDA/TiO₂(110) monolayer (left panel) and single physisorbed PTCDA molecule (right panel) are shown. The pattern for the single molecule consists

of narrow bands, which originate from strongly localized electrons on the s and p orbitals of the carbon (mainly in the sp² hybridization) and oxygen PTCDA atoms. The highest occupied states (originating from HOMO) lie 1.5 eV below the lowest unoccupied states (originating from LUMO). The overall DOS structure is very close to that of a molecule in the gas phase, indicating only weak electronic coupling between rutile and PTCDA, which is unfavorable for photonic applications.

The left panel in Figure 7 shows the DOS of the PTCDA monolayer chemisorbed on the (110) rutile surface. Due to the bending of PTCDA molecules, the DOS bands are clearly broadened. Furthermore, when compared to the DOS of the physisorbed molecule, the HOMO band remains practically unshifted while the LUMO band is lowered by 0.02 eV. The C(s,p) states emerge above the top of the valence band, indicating the electronic promotion of TiO₂. The bottom of the conduction band of TiO₂ remains almost intact, whereas the LUMO band is located directly above the bottom of the conduction band in accordance with recent experimental studies.⁵⁰ Such relative energy alignment and strong electronic coupling between the chemisorbed PTCDA adspecies and the TiO₂ substrate due to covalent C–O–Ti bonds are favorable for electron injection from the photoexcited PTCDA dye into the sensitized titanium oxide and for interfacial charge delocalization as discussed by Cao *et al.*⁵⁰

CONCLUSIONS

We have demonstrated experimentally and rationalized by modeling the ability of large, planar organic molecules, exemplified by PTCDA, to arch over the protruding oxygen rows on the TiO₂(110) surface by collective action of the intermolecular dispersive forces, which allows for strong electronic coupling between the dye adspecies and the TiO₂ substrate. This effect is of particular importance on highly anisotropic surfaces, where the dispersive forces can dominate the intrinsically complex molecule–substrate interaction landscape. High-resolution STM and LEED results complemented by DFT-D calculations have demonstrated remarkable transition in the mode of PTCDA adsorption as a function of coverage, which is directly controlled by the strength of the interfacial and the intermolecular dispersion interactions. At submonolayer coverage, the interfacial dispersion forces play a dominant role in the adsorption of single flat-lying PTCDA molecules in a nearly intact state, whereas the intermolecular dispersion interactions are decisive in the self-organization of PTCDA at higher submonolayer coverages into meandering molecular stripes. When a monolayer is formed, molecule–substrate and intermolecular dispersion forces lead collectively to the formation of a commensurate

dense structure, built of bent chemisorbed species. The resultant alignment of the energy levels and strong electronic coupling at the PTCDA/TiO₂

interface, due to formation of covalent C–O–Ti bonds, are advantageous for potential dye sensitization applications.

METHODS

Experimental Details. The experiments were carried out in an ultrahigh vacuum (UHV) system containing preparation, surface analysis, and radial distribution chambers. The STM measurements were performed with an Omicron variable-temperature scanning probe microscope (VT STM/AFM). The base pressure was in the low 10^{−10} mbar range. The preparation chamber was supplied with a noble gas ion gun, effusion cells, an infrared pyrometer, and a quartz microbalance thickness monitor. The surface quality was monitored with a low-energy electron diffraction (LEED) setup. The TiO₂(110) wafers (MaTeck GmbH) were mounted on sample holders with a silicon wafer underneath acting as a resistive heater. The samples were first annealed for 6 h at 800 K, and subsequently, the cycles of 1 keV Ar⁺ sputtering for 15 min and annealing at 960 K for 15 min were repeated until a clean, well-defined surface was obtained, as checked by LEED and STM measurements. The annealing temperature was controlled by the infrared pyrometer. The experimental procedure was adjusted to keep the sample as clean as possible, as the contamination could affect seriously the growth of molecular structures on metal oxides. The PTCDA molecules were evaporated at about 580 K from a Knudsen cell on the TiO₂(110) surface kept at room or elevated temperature. For molecule deposition, the sample was heated by a resistive heater and the temperature was monitored by type K thermocouple. Prior to the evaporation procedure, PTCDA powder (Fluka) was outgassed for several hours in vacuum at the temperature slightly below the sublimation point. The STM imaging was carried out at reduced temperature of around 90 K (flow cryostat, liquid nitrogen) in a constant current mode at positive bias voltages (empty state imaging) with etched tungsten tips used as probes. For image processing and STM data analysis, WSxM software⁵¹ was used.

Calculation Scheme. For all calculations, we chose the first principles DFT theory implemented in the Vienna Ab initio Simulations Package (VASP)⁵² based on Mermin's finite temperature DFT.⁵³ We employed the projector augmented plane wave (PAW) method^{54,55} for describing electron–ion interactions together with PW91 GGA exchange–correlation functional as parametrized by Perdew *et al.* based on the fact that the GGA functionals can produce reliable results in describing electronic structure of oxide systems like titania.^{56–58}

Presented results were obtained for the standard Monkhorst-Pack grid⁵⁹ (3 × 3 × 2 sampling mesh for bulk calculations and 2 × 2 × 1 for slab calculations) with the cutoff energy of 380 eV and the Methfessel–Paxton smearing⁶⁰ with σ parameter set to 0.1 eV. For solving the Kohn–Sham equations, the self-consistent field (SCF) convergence criterion was set to be an energy change not larger than 10^{−5} eV between two successive iterations.

Surface geometries were constructed by cleaving the crystal along the (110) plane. The supercell models with stoichiometry of Ti₇₂O₁₄₄ were built to describe both adsorption of an isolated PTCDA molecule and monolayer structure (for periodic model details, see Figure S4 and Tables S3 and S4 in the Supporting Information). The size of the surface model was adequate to accommodate two PTCDA molecules in the supercell. Geometry optimization was performed until the changes in the forces acting on the ions were smaller than 0.001 eV/Å per atom. The molecular dynamics (MD) calculations of monolayer were carried with the following settings: Nose–Hoover chain (2) thermostat, time step 10 fs, and the Nose coupling parameter of 2.0. The integration was performed for the total of 1000 steps.

With the optimized geometries of the PTCDA molecules, the resultant STM image simulations were performed as topographs of constant local density of states within the Tersoff–Hamann theory.⁴⁷ The images were simulated in the constant current ($I = 2$ pA) mode applied in the STM

experiments and the local density of states as constructed from electronic states in an energy window between 0 and 2 eV above the Fermi level (*i.e.*, empty states). Taking into account the complexity of the monolayer, we have verified the Tersoff–Hamann simulations with much more advanced Bardeen approach⁴⁸ as implemented in the bSKAN code.^{61,62} The tunneling current was evaluated in a constant height mode as a convolution of the substrate and tip densities of states. In the simulations, bias voltage (from 0.75 to 2.0 V), tip–surface distance (from 1 to 3 Å), and the tip geometries (square pyramid, square pyramid with single W atom, and square pyramid terminated with 2 × 2 ensemble of W atoms) were tested.

In the computation procedure, the dispersion semi-empirical terms parametrized by Grimme and applied successfully for modeling interactions between hydrocarbons and metal oxides^{34,35} were added to the quantum-mechanical energies and gradients (DFT-D method).

Conflict of Interest: The authors declare no competing financial interest.

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Supporting Information Available: Additional experimental and calculations details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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2.4.7 Tekst artykułu H7

[H7] M. Kolmer, A. A. Ahmad Zebari, J. S. Prauzner-Bechcicki*, W. Piskorz, F. Zasada, S. Godlewski, B. Such, Z. Sojka, M. Szymonski, „On-Surface Polymerization on Titanium Dioxide: Polyanthrylene on TiO₂(011)-(2×1) surface”, *Angew. Chem. Int. Ed.*, **52**, (2013), 1. DOI: 10.1002/ange.201303657.

Surface Chemistry

Polymerization of Polyanthrylene on a Titanium Dioxide (011)-(2 × 1) Surface**

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One of the most challenging promises of nanotechnology is an ultimate level of control in fabrication of nanoscale structures, machines, and devices. Fine positioning of single atoms demonstrated by Eigler and Schweizer,^[1] or precise control over Ullmann reaction on Cu surface reported by Hla and co-workers,^[2] are excellent examples of achievable mastery in the field of scanning tip-induced processes. However, if larger one-dimensional and two-dimensional nanostructures are targeted, the tip-induced methods are not the most favorable: they would require tremendous amount of time for accomplishment. Thus, taking an advantage of self-assembly and thermal triggering is a very encouraging strategy among others in delivering the highest possible precision and efficiency in fabrication of large nanostructures.^[3] It has been envisaged that functionalizing individual molecular precursors (building blocks) with precisely chosen linking sites should allow for future bottom-up construction of miscellaneous molecular devices.^[3d,4] Accordingly, many research groups have recently reported successful direct on-surface formation of covalently bonded molecular structures with use of various thermally triggered chemical reactions on metallic surfaces.^[3b–d,4,5] These reports refer to formation of a wide range of structures, spanning from simple dimers to longer oligomers, or even two-dimensional molecular networks. Yet, to the best of our knowledge, the on-surface fabrication of covalently bonded molecular structures accomplished on semiconducting surfaces has not been reported.

An approach that offers direct formation of complex molecular structures in a predefined form on a desired substrate surface, by itself, is a very attractive idea from a technological point of view. A possibility to merge, in a bottom-up fashion, a substrate possessing chosen bulk and

surface properties (for example, appropriate band gap, catalytic reactivity, and so on) with specifically designed large molecular architectures (for example, networks with pores of uniform size and preferred shape) is a key advantage of the discussed method. Understanding the on-surface processes leading to the formation of such molecular objects will advance many technological branches, such as nano-electronics, gas- and bio-sensing, solar cells, and many others.

Herein, we present the on-surface polymerization on a semiconducting metal oxide surface, namely TiO₂. Molecular precursors 10,10'-dibromo-9,9'-bianthryl (DBBA, see Figure 1 A, commercially available from St-Jean Photochemicals Inc.), are deposited on a (011) face of the rutile titania (Figure 1 C) using a standard Knudsen cell. The polymerization is thermally activated, either through post- or during-deposition annealing. Formation of extended polyanthrylenes

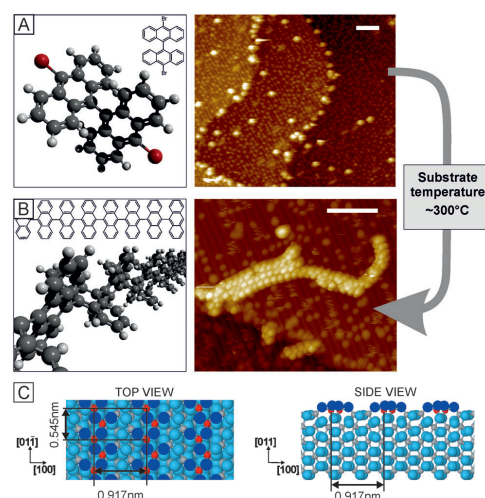


Figure 1. On-surface polymerization of DBBA molecules on a TiO₂ surface. Models and STM images (white scale bars: 5 nm) of A) DBBA monomers and B) polyanthrylenes. STM images: small bright dots on the zigzag rows are ascribed to surface hydroxyl groups.^[9] C) Model of the TiO₂(011)-(2 × 1) surface, top and side views. Oxygen atoms are marked blue (dark blue is reserved for the two-fold coordinated oxygen atoms forming the characteristic double zigzag rows, running along the [01 $\bar{1}$] crystallographic direction of the surface).^[10] Titanium atoms are marked gray; five-fold coordinated titanium atoms are shown in red.

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(see Figure 1B) from DBBA molecules directly on the Au(111) surface has been reported quite recently.^[5b,6]

Oligomer formation requires substantial mobility of the adsorbed precursors. It has been shown for several molecular species studied on the (011) face of rutile that the admolecules are mobile enough to form different 1D or 2D weakly bonded structures,^[7] including formation of non-covalently bonded PTCDA molecular wires.^[8] The interaction of the polyaromatic core of PTCDA with the underlying substrate forces a planar adsorption geometry and does not impede the mobility of the admolecules. Thus, we anticipate rather high mobility of the DBBA molecules on the (011) face of rutile.

As expected, DBBA molecules deposited at low coverage on the substrate kept at room temperature are so mobile that stable scanning tunneling microscopy (STM) imaging conditions at room temperature (RT) are hardly achievable. Imaging at liquid nitrogen temperature (LNT) allows to resolve single molecules distributed on terraces and attached to step-edges (Figure 1A). There is no trace of polymeric species on the surface, suggesting that the deposited precursors still possess their halogen substituents. The polymerization reaction is triggered thermally. We annealed the sample with the molecules at 300 °C. As a result, we observed randomly distributed, short oligomers. Further annealing at the same temperature does not result in formation of more ordered or more extended structures.

Better conditions for efficient polymerization into longer chains were achieved when molecules are deposited on the substrate kept at 270 °C. During deposition we kept a low molecular flux; that is, the temperature of the evaporator was set to 135 °C to assure a submonolayer coverage and disallow a dissociation reaction in the evaporator. Monomers, dimers, and longer oligomers are obtained (Figure 2). Analysis of the STM images reveals an excellent agreement in appearance of the polymer chains between our data and the results reported for the Au(111) substrate.^[5b] Namely, along the chains there are observed protrusions appearing alternately on both sides with a periodicity of 0.86 nm, which is in line with previous observations for the DBBA polymers on the Au(111) surface, and with the periodicity of the bianthryl core.^[5b] 0.86 nm and

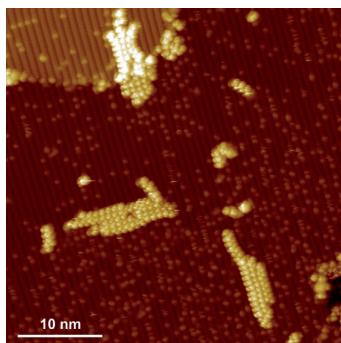


Figure 2. DBBA molecules deposited on the TiO₂(011) surface kept at 270 °C; STM imaging at LNT (10 pA, +2 V). 50 nm × 50 nm.

0.85 nm, respectively (Figure 2). The width of the polyanthrylenes expected from their structural model is about 1 nm, and as it can be inferred by comparison with the substrate periodicity (the distance between the surface reconstruction rows is about 0.92 nm; see the model in Figure 1), it is the value observed in the presented data.

Interestingly, when molecular precursors are deposited at low coverage, longer polyanthrylenes are often observed in bunches rather than as single, long entities (Figure 2, and Figure 3A). As the main building block of the oligomer is the bianthryl core, it is expected that oligomers in a bunch

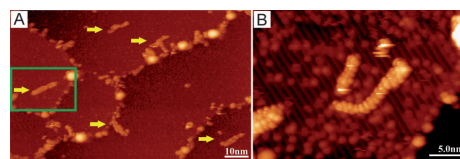


Figure 3. STM images of DBBA oligomers assembled on TiO₂(011) (imaging at LNT, 10 pA, +2 V) (A) 100 nm × 60 nm (scale bar 10 nm), longer oligomers and bunches of oligomers (marked with yellow, horizontal arrows); (B) 25 nm × 17.5 nm (scale bar 5.0 nm), enlargement of the region marked with the green rectangle in (A), showing a disentangled bunch of polymers as a result of a tip-induced manipulation obtained by 100 pA constant current scanning conditions.

interact through the van der Waals or π -interactions. In line with such conjecture, we observed the bunches with molecular chains mostly laying parallel to each other. The interaction between oligomers is of non-covalent character, and therefore it is much weaker than the coupling that connects bianthryl monomers. Applying a tip-induced manipulation allows the oligomers to be disentangled from a bunch, as demonstrated by two subsequent STM scans (Figure 3). As predicted for oligomers, the polyanthrylene chains survive such harsh scanning conditions, in contrast to the bunches of chains. Our result is similar to that reported by Grill et al.^[3d] In their work, porphyrin dimers were obtained by deposition of porphyrin molecules with a single Br substituent on the Au(111) surface and subsequent annealing. The heating triggered the C–Br bond cleavage, diffusion of the organic fragments, and their recombination into dimers. Eventually, the resulting porphyrin dimers were found to form clusters. Intact dimers can be easily separated from these clusters by the lateral manipulation with the STM tip. In this way, it is demonstrated that two porphyrin molecules in the dimer are bonded by a strong covalent bond in comparison to rather weak non-covalent bonds binding the clusters.^[3d]

As reported by Cai et al.,^[5b] further annealing of the polyanthrylene chains on the Au(111) surface to 400 °C leads to a cyclodehydrogenation reaction and formation of a fully aromatic system, that is, graphene nanoribbons. To test if such a reaction is feasible on the surface of titanium dioxide we decided to anneal the sample covered with oligomers. To promote formation of longer oligomers, we increased the coverage (three times longer deposition) and substrate

temperature during the deposition to 350°C. The resulting unordered network of long molecular chains is so stable that it was possible to achieve good imaging conditions in RT STM (not shown). After further annealing of the sample at 400°C and 450°C (for 30 minutes at each temperature), the molecular network remained practically intact. It is concluded that up to 450°C the cyclodehydrogenation reaction is not initialized on the $\text{TiO}_2(011)-(2 \times 1)$ surface. Additionally, it is evident that the obtained polyanthrylenes are quite robust to thermal treatment. The question whether the cyclodehydrogenation reaction leading to planarization and thus to formation of graphene nanoribbons could be thermally triggered at higher temperatures on the $\text{TiO}_2(011)$ surface remains unanswered, and is subjected for further, on-going research.

Our experimental findings are corroborated with density functional theory (DFT) modeling of the DBBA monomer and dimer adsorbed on the $\text{TiO}_2(011)-(2 \times 1)$ surface. We used the Vienna ab initio simulations package (VASP).^[11] For reliable description of the electronic structure of rutile titanium dioxide we employed projector augmented plane wave (PAW)^[12] method for description of the electron-ion interactions, and PW91 GGA exchange-correlation functional, as parameterized by Perdew and Wang.^[13] Additionally, to account for dispersion forces that play important role in the adsorption of polycyclic molecules on the surface of rutile,^[14] we used the semi-empirical Grimme extension^[15] of the DFT method (DFT-D). The GGA/DFT-D calculations revealed a weak adsorption energy (0.11 eV per molecule) of DBBA that is dominated by the dispersion term (0.08 eV per molecule). It results from the molecule–substrate attractive interactions (−1.09 eV) counterbalanced by the ad molecule deformation (+0.98 eV). Owing to the presence of the bianthryl core in the DBBA molecule (see Figure 1), the adsorption geometry is governed by tendency to keep each anthryl as parallel to the substrate as possible. In contrast, the short C–C bond, connecting the anthryl moieties in the bianthryl core, does not let the molecule to arrive at flat geometry. Consequently, although the adsorbed molecule preserves its 90° dihedral angle between the anthryl planes, one of them is significantly deformed owing to the interaction with the protruding surface ions, thereby partly losing its aromatic character. As a result, the C–Br bond in the adsorbed DBBA is elongated ($\Delta d_{\text{C-Br}} = 0.09 \text{ \AA}$) and weakened ($\Delta B O(\text{Mayer}) = -0.16$). In the optimized geometry, the hydrogen atoms closest to the surface are 1.8 Å above the topmost ions of the substrate; additionally, the bromine atoms are 4.95 Å above the topmost ions. These results strongly suggest that no chemical interaction is expected between the molecule and the substrate. Translations along and across the zigzag rows, and rotation with respect to the surface normal, change the adsorption energy only by 2–5%. Such observations are in line with the fact that the direction-independent dispersion forces dominate the surface–molecule interactions and suggest that the monomers should be able to diffuse on the surface. Applying the same calculation for a dimer adsorbed on the (011) face gives coherent result: the dimer adsorption energy is nearly twice the monomer, namely 0.21 eV per molecule. Finally, simulations of STM images

were performed as topographs of the constant local density of states within the Tersoff–Hamann theory^[16] with additional Gaussian blurring to include tip broadening effects. As can be seen in Figure 4, there is an excellent agreement between the calculated and the measured images.

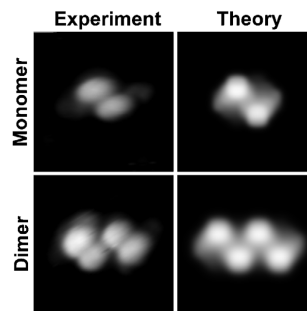


Figure 4. Comparison between experimental and theoretical STM images of DBBA monomer and dimer. Left column: in the experimental images the contrast is set to expose the molecules. The right panel: simulated images with Gaussian blurring mimicking the tip broadening of experimental images. (Both experiment and theory: 3 nm × 3 nm, 2 pA, +2 V).

For metallic surfaces and molecular precursors containing halogen atoms at linking sites, the on-surface polymerization reaction has been described as a two-step process:^[3d] 1) selective thermal C–X (X = I, Br) bond cleavage, resulting in radical/ion formation, followed by 2) radical/ion recombination, resulting in formation of oligomers. At increased substrate temperatures, there are several processes that could take place simultaneously and compete with each other, that is, cleavage of the C–X bond, diffusion of molecular precursors and radicals/ions, recombination of the radicals/ions, and desorption of smaller molecular species. Proper balance between these processes results in formation of long oligomers.^[5f]

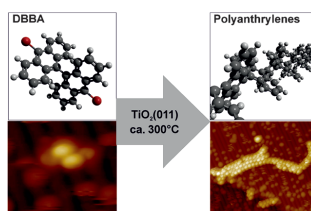
Replacing the metal surface with titanium dioxide changes the reaction environment drastically, and thus it is rather unlikely that the on-surface polymerization will necessarily follow the same pathway. In the case of titanium dioxide surfaces, the most important issue is their distinct chemical nature and the related properties. Among several possible routes of C–C bond formation explored by DFT screening, a concerted process of early C–C bond formation accompanied by late C–Br bond cleavage and a multistep proton assisted coupling exhibited the lowest activation barriers (below 1.95 eV). The latter, being energetically most preferred and specific for oxides, is featured by proton transfer from surface hydroxyl groups to DBBA ad molecules (1.39 eV), the rather easy migration of this species on the aromatic framework (0.65–1.13 eV), and preferred attachment to the Br-bearing carbon atom. The resultant rehybridization and substantial weakening of the C–Br bond facilitates the carbon–carbon bond formation and release of Br_2 byproduct, which only requires 0.82 eV. Certainly, an exact

Communications

Surface Chemistry

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Polymerization of Polyanthrylene on
a Titanium Dioxide (011)-(2×1) Surface



On-surface polymerization is feasible on semiconducting surfaces. Thermally triggered covalent coupling of 10,10'-dibromo-9,9'-bianthryl molecules on the $\text{TiO}_2(011)-(2 \times 1)$ surface is demonstrated. The result paves the way for application of the thermally driven on-surface polymerization on semiconducting surfaces and indicates that methods based on such a reaction are more universal than previously thought.

2.4.8 Tekst artykułu H8

[H8] W. Piskorz^{*}, F. Zasada, P. Stelmachowski, O. Diwald, A. Kotarba, Z. Sojka^{*} „Computational and Experimental Investigations into N₂O Decomposition over MgO Nanocrystals – From Thorough Molecular Mechanism to ab initio Microkinetics”, *Journal of Physical Chemistry C* **115** (2011), 22451.

Computational and Experimental Investigations into N₂O Decomposition over MgO Nanocrystals from Thorough Molecular Mechanism to ab initio Microkinetics

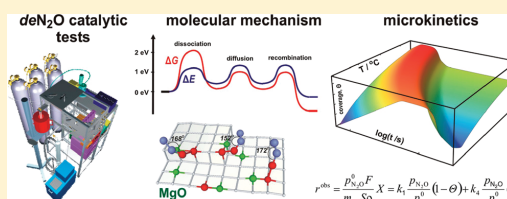
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S Supporting Information

ABSTRACT: In this article a comprehensive molecular modeling of the reaction mechanism complemented by ab initio microkinetic modeling of the catalytic decomposition of N₂O on MgO nanocrystals is discussed. The density functional level of theory was used to study the molecular mechanism of conceivable elementary steps of the *de*N₂O reaction over the most stable (100) surface, including the effect of surface morphology. It is shown that terrace sites are responsible for steady state reactivity, whereas the more basic and reactive sites located on edges and corners are involved only in the initial stages of the reaction because of poisoning. Detailed analysis of the reaction progress in terms of the energy profiles and the evolution of partial charges and bond orders for each step allowed for an in-depth insight at the atomic scale into the nature of the catalytic N₂O decomposition over anionic redox active sites constituted by surface O²⁻ ions. The harmonic transition state theory along with the calculated free enthalpies of activation were used to model the reaction progress in pulse (transient) and steady state regimes as well as to predict the kinetic isotopic effects (KIE) for ¹⁵N and ¹⁸O labeled reactants. The proposed kinetic scheme was able to reproduce the results of temperature-programmed surface reaction and KIE experiments with high accuracy without fitting of any parameters.

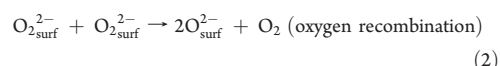
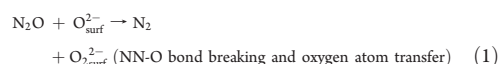


INTRODUCTION

Catalytic decomposition of nitrous oxide has long been recorded due to both fundamental and practical interests.^{1,2} As one of the three most important greenhouse gases,^{3–5} and being destructive for the stratospheric ozone layer,^{6,7} anthropogenic emissions of N₂O have to be reduced substantially, preferably by catalytic processes operating at low temperatures. In this context, reactivity of the vast range of catalysts such as supported metals,^{8–10} simple^{11,12} and complex oxides,^{5,13,14} as well as metallozeolites^{15–17} have been extensively explored. Furthermore, owing to its simplicity, N₂O dissociation has widely been used in model studies probing redox properties of catalytic surfaces in mild oxidation catalysis and as an electron scavenger used in radiolysis. Cleavage of the N–O bond by the electroprotonic 2e⁻/2H⁺ process is also a key step of the enzymatic N₂O reductase.¹⁸

The principal mechanisms along which nitrous oxide can be activated and decomposed on oxide surfaces involve dissociative electron transfer sustained by cationic sites^{19–21} (cationic redox mechanism) and oxygen atom transfer effected by anionic sites^{11,22,23} (anionic redox mechanism). For wide band gap oxide catalysts (characterized by the absence of cationic electron donor centers), the oxygen atom transfer route, defined by the

following principal steps



is preferred. Obviously, some other possible variants of the oxygen recombination events are possible, and they are discussed below in more detail. The activity of an anionic redox catalyst is thus directly related to the ability of surface oxygen ions to abstract the oxygen atom from the N₂O reactant to form O₂²⁻ intermediates (eq 1), and their straightforward recombination into O₂ molecule (eq 2).

Because of its simplicity, chemical stability, and well-known surface chemistry, MgO is an excellent model system for detailed examination of the anionic redox mechanism of N₂O

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decomposition.^{21,22,24} Magnesia is a highly ionic wide band gap ($E_g = 9$ eV) compound²⁵ with the face-centered cubic structure (space group $Fm\bar{3}m$) and the unit cell parameter $a = 4.21$ Å.²³ The thermodynamically most stable (100) termination of MgO is only slightly relaxed (surface corrugation remains within 2% of the interionic distance), giving rise to predominant characteristic cubic shape of the crystallites.^{26–28}

Catalytic properties of MgO are associated with the Lewis basicity of surface oxygen anions for acid–base type reactions.^{29,30} In N_2O decomposition the pristine MgO is found to be a moderately active catalyst (temperature of 50 % conversion ≈ 600 °C),⁴ where the anionic redox mechanism operates exclusively.^{12,31,32} Although morphological irregularities of the catalyst surface such as corners and edges change many important parameters, like ionic charges, electrostatic potential anisotropy, and basicity of the exposed anions, their kinetic significance is observed only for the samples of high surface area.²¹ Whereas the surface anionic vacancies can take part in N_2O dissociation step, but due to the high barrier for the subsequent oxygen recombination and very low abundance, they can be disregarded as the possible active sites. The latter conjecture is also valid for the Lewis acid sites constituted by surface magnesium cations. Interaction of N_2O with empty Mg 3d orbitals shall depopulate the $2\tau_u$ highest-occupied molecular orbital, which is of antibonding character between the O–N₂. As a result, such interaction leads to strengthening of the O–N₂ bond that hinders the dissociation step.

Despite the fact that the decomposition of nitrous oxide over MgO has been extensively studied both experimentally and theoretically,^{12,20,33} systematic investigations into the elementary surface events and their surface dynamics, including topographic effects and free enthalpy calculations, is still missing. In this paper a comprehensive molecular mechanism of the N_2O decomposition over a model MgO catalyst, which takes into account conceivable elementary steps and the impact of surface topology, was developed and connected with microkinetic modeling for transient and steady state regimes. The results of density functional theory (DFT) calculations were confronted with the experimental catalytic data for MgO catalyst of various particle size for wide range of reaction parameters.

■ COMPUTATIONAL AND EXPERIMENTAL DETAILS

Calculations. All calculations were performed with the DMol³ program package³⁴ (Materials Studio of Accelrys Inc.),³⁵ using a rPBE GGA-type functional developed by Perdew, Burke, and Ernzerhof (PBE)³⁶ with corrections added by Hammer et al.³⁷ This functional has been successfully used for description of magnesium oxide surface properties consistent with experimental data.^{38–40} The molecular orbitals were expanded into a double-numerical basis with polarization functions (DNP), which are equivalent to the Pople's Gaussian basis set of 6-31G**. For all ions the DSPP (DFT semicore pseudopotential),⁴¹ a Fermi smearing of 0.01 hartree, and a cutoff energy of 4.5 Å were used. The self-consistent field convergence criterion was set to 10^{-6} Hartree, whereas for optimal geometry the gradient convergence was set to 1×10^{-5} Hartree/Å. Geometry optimization was carried out following the BFGS scheme.^{42,43}

The Brillouin zone integrations were performed using a $3 \times 3 \times 3$ Monkhorst–Pack grids⁴⁴ for the bulk and $2 \times 2 \times 1$ for the slab model of the (100) surface. The influence of the k-points sampling up to $6 \times 6 \times 6$ for the bulk and $4 \times 4 \times 3$ for the slab models was tested, and it was found that the calculated energies

are not changed at the larger k-points density. The MgO (100) surface was simulated by means of a symmetric periodic $Mg_{32}O_{32}$ slab (Figure S1 in Supporting Information). The slab was repeated periodically with a 15 Å vacuum between the slabs to avoid unphysical interactions. The four topmost layers of surface ions were fully optimized. After introduction of N_2O molecule the stable stationary and transition state geometries were determined. Transition states were located using a LST/QST guess⁴⁵ followed by BFGS⁴⁶ refinement. For stationary points on the potential energy surface full vibrational analysis was carried out to calculate the corresponding Gibbs energies (free enthalpies) of activation.

Calculation of the Reaction Rate Constant. Reaction rate constants were calculated within the harmonic transition state theory (HTST) using the classic equation⁴⁷

$$k = \frac{k_B T}{h} \exp\left(\frac{-\Delta G_a}{RT}\right) \quad (3)$$

where k_B is the Boltzmann constant, ΔG_a stands for activation Gibbs energy, and h , T , and R denotes Planck constant, temperature, and gas constant, respectively. To calculate Gibbs energy of activation for the considered elementary steps we used partition functions of the investigated system as proposed by Hirano.⁴⁸ By use of the ideal gas approximation we defined the enthalpy as the sum of static DFT electronic energy (E^{el}), zero point energy (ZPE), and thermal contributions associated with vibrational, rotational, and translational degrees of freedom: $H(T) = E^{el} + ZPE + E^{osc}(0 \rightarrow T) + E^{rot}(T) + E^{trans}(T) + RT$, assuming that $pV = RT$. The entropy, likewise, contains three contributions: $S(T) = S^{osc}(T) + S^{rot}(T) + S^{trans}(T)$. For the surface species the translations and rotations converted into frustrated oscillation modes and were included in the vibration analysis. Within such model the Gibbs energy may be factorized into temperature independent static E^{el} and ZPE contributions, and temperature-dependent $G(0 \rightarrow T)$ part: $G = E^{el} + ZPE + G(0 \rightarrow T)$. The difference between the free enthalpies of the transition state and the reactant state defines the free enthalpy of activation $\Delta G_a = G_{TS} - G_R$, which was used to calculate the rate constants.

To verify the applicability of the classic approximation (harmonic oscillator, rigid rotor), thermodynamic integration⁴⁹ (TI) was also employed. A molecular dynamics code based on Newtonian equation of motion was used.⁵⁰ The velocity Verlet integrator with the RATTLE⁵¹ constraint algorithm and the Nosé–Hoover⁵² chain thermostat was used. The constraint reaction force along the reaction pathway was integrated yielding the free energy changes. The obtained value for the activation free enthalpy of the oxygen atom transfer step ($\Delta G_a = 51.9$ kcal/mol at 600 K) remains in a very good agreement with the results obtained within the classic approximation ($\Delta G_a = 54.4$ kcal/mol at 600 K). Thus, the validity of the HTST treatment was assured, and because of the time cost of the TI calculations, this approximation was used for further calculations. The free enthalpies obtained from the vibrational analysis were used as input into the set of differential kinetic equations, solved with Mathematica⁵³ software implementing the BDF⁵⁴ algorithm.

Samples Preparation, Characterization, and Catalytic Measurements. Nanostructured magnesium oxide samples were synthesized and characterized by several methods (X-ray diffraction, XRD; scanning electron microscopy, SEM; Brunauer–Emmett–Teller, BET); see Table S1 in the Supporting Information

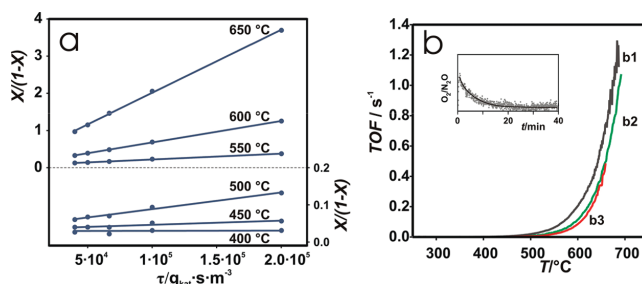


Figure 1. (a) Plot of $X/(1-X)$ as a function of the contact time. (b) Plot of steady state turnover frequency for MgO samples of different grain size: b_1 , 10 nm; b_2 , 23 nm; b_3 , 170 nm. In the insert transient changes in the deN_2O reactivity at 550 °C in the initial period are shown.

for more details. The characteristic aspect of the MgO morphology obtained by various methods is the predominance of cubic shapes of the nano- and sub-micro-crystals of different aggregation extend.⁵⁵ This allows for study the influence of the MgO particle size on the reactivity for a wide range of dimensions of the nanocrystals, preserving essentially their shape. The deN_2O activity of the catalysts was measured in a fixed bed microreactor (inside diameter = 15 mm), using 100 mg of catalyst (200–300 μm sieve fraction, and 1 mm of the catalyst bed height). The gas mixture of 5% N_2O in He and the variable flow rate of 30, 60, 90, 120, and 150 $\text{mL} \cdot \text{min}^{-1}$ were used. The gas-phase analysis was performed by means of a compact quadrupole mass spectrometer (RGA200, SRS). The Péclet number ($Pe \approx 0.005$) and Damköhler number ($Da \approx 0.1$) indicate that a perfect mixing regime was achieved for all the measurements. The temperature-programmed surface reaction (TPSR) and stepwise steady-state experiments were carried out to measure the activity of the MgO catalysts.

In the case of the flow microreactor with (quasi) ideal mixing the reaction rate, r , for an active site (turnover frequency) can be related to the conversion, X , in the following way: $rm_{\text{cat}}S_{\text{BET}}c_{\text{surf}} = F_{N_2O}X$, where F_{N_2O} is the inlet N_2O flow, m_{cat} is the catalyst mass, S_{BET} stands for the specific surface area, and $c_{\text{surf}} = 1.13 \times 10^{19} \text{ m}^{-2}$ is the surface concentration of the active sites.⁵⁶ By substitution of $r = k^{\text{obs}}X_{N_2O}$ we obtain the relation between the apparent rate constant and the conversion: $k^{\text{obs}}\tau = (X)/(1-X)$, where τ is the contact time. Thus, from the linear plot of $X/(1-X)$ as a function of the contact time τ , the rate constants, k^{obs} , were obtained for various temperatures (Figure 1a). The value of the prefactor, $4.1 \times 10^{-18} \text{ m}^3 \text{ s}^{-1}$, and the activation energy of N_2O decomposition over MgO, $E_a = 35.0 \text{ kcal mol}^{-1}$, were obtained from the corresponding Arrhenius plot (Figure S3 of Supporting Information) exhibiting a good agreement with the literature data ($E_a = 35\text{--}36.1 \text{ kcal mol}^{-1}$).^{12,57}

The dependence of the N_2O conversion on the MgO particle size is shown in Figure 1b. The turnover frequency (TOF) plotted as a function of temperature for the MgO samples with the crystallite size varying from 10 to 170 nm indicate that there is a little influence (within the experimental error) of the nanocrystals morphology on the steady-state kinetics. Yet, the results of transient measurements (Figure 1b insert) show that the initial activity is slightly higher than the steady state asymptote, declining progressively with time on stream. This effect was more pronounced for smaller MgO crystallites. Such behavior can be explained by progressive saturation of the most active minor active sites located on edges and corners (morphology-dependent kinetics) and involvement at the steady state of

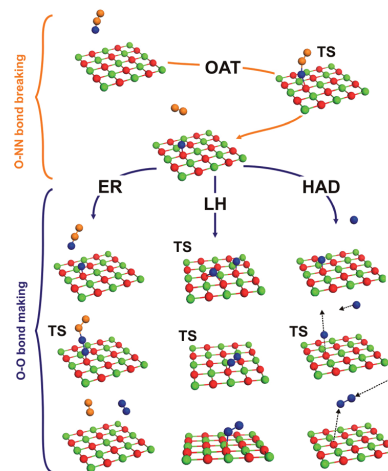


Figure 2. The conceivable mechanistic pathways of N_2O decomposition including the common OAT step of the O–N bond breaking, and three parallel routes: Langmuir–Hinshelwood (LH), Eley–Rideal (ER), and hot atom desorption (HAD) of the O–O bond-making step.

the less active but predominant sites located on terraces, the abundance of which is practically morphology independent. Theoretical rational for this observation is discussed below in detail.

RESULTS AND DISCUSSION

Mechanistic Pathways of N_2O Decomposition. To build a suitable mechanistic background for molecular modeling we analyzed all possible elementary steps of N_2O decomposition over MgO, presented in Figure 2. For each elementary step the geometries of the reactants, transition states, and products are presented. The elementary steps were grouped into three main reaction pathways; however, the first step was assumed to be the same in each case. It involves the N_2 –O bond cleavage (at the surface O^{2-} active sites), followed by the oxygen atom transfer (OAT), forming a surface peroxy group O_2^{2-} – the key intermediate of the deN_2O process (eq 1). This reaction step exhibiting bent transition state is presented in Figure 2 (OAT). The resultant surface peroxy group can recombine into a final

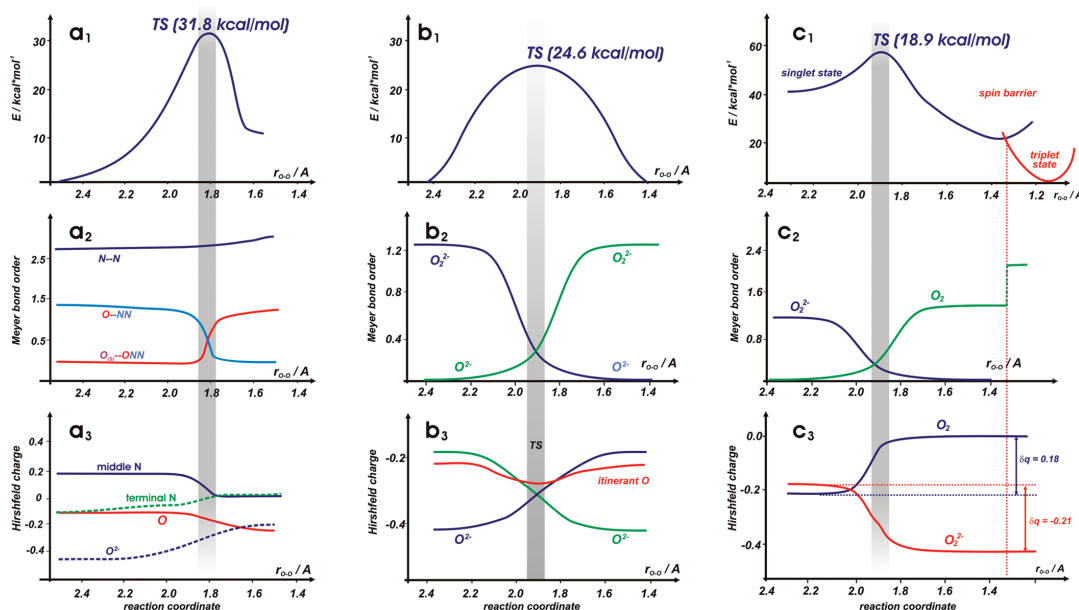
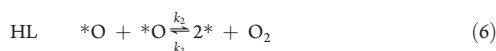
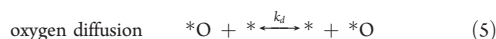
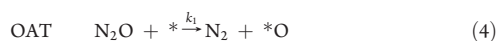


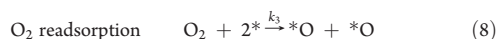
Figure 3. Energetic profile (a_1 – c_1) and evolution of bond orders (a_2 – c_2) and atomic charges (a_3 – c_3) for O–NN dissociation, O–atom surface diffusion, and O–O recombination steps in the LH route of N_2O decomposition.

dioxygen following three different pathways: Eley–Rideal (ER),²³ Langmuir–Hinshelwood (HL),^{23,58} and hot atom desorption (HAD), where the hyperthermal oxygen atoms of the peroxy groups escape into the gas phase and recombine into O_2 . Laser-induced desorption of the hyperthermal O atoms was observed previously by one of us.⁵⁹

DFT calculations of activation energies (see below) revealed that among three possible pathways of O–O bond formation the HAD route with the barrier of 55.1 kcal/mol (much higher than 31.8 kcal/mol for LH and 40.8 kcal/mol for ER routes) can be excluded from the kinetic considerations. As a result the following elementary steps were taken into account for detailed mechanistic and kinetic analysis



The symbol $\rightleftharpoons$ indicates that the surface diffusion of oxygen atom is a symmetrical process, as discussed below. The asterisk (*) denotes the active sites ($\text{O}_{\text{surf}}^{2-}$ anions) at the catalyst surface. We also assume that the reaction of oxygen recombination is reversible with dissociative readsorption of dioxygen.



As implied by the scheme shown in Figure 2, the surface peroxy species play a central role in all mechanistic variants of the N_2O decomposition.

Molecular Insight into Elementary Steps of N_2O Decomposition. As already mentioned, the reactivity of MgO is related to the ability of surface oxygen anions to abstract the oxygen atom from N_2O molecule to form O_2^{2-} species. Both steps, the O atom transfer and recombination of the peroxide ions, were modeled by DFT on the (100) plane of MgO. The mechanistic molecular level picture of the elementary steps implicated in the N_2O decomposition was analyzed in terms of energy profiles, Mayer bond orders, and Hirshfeld charges as a function of the reaction coordinate $r_{\text{O-O}}$ (the distance between NN–O and $\text{O}_{\text{surf}}^{2-}$ or between surface oxygen species). Evolution of these parameters during the reaction progress is shown in Figure 3.

The key peroxide intermediate is produced via bent transition state NN–O– $\text{O}_{\text{surf}}^{2-}$ located at 31.8 kcal/mol (Figure 2 OAT, Figure 3a₁) with the NN–O bond stretched from 1.18 to 1.48 Å and at the $\text{O}_{\text{surf}}^{2-}$ –ONN distance of 1.89 Å and the N–N–O angle of 156°. The corresponding transition-state imaginary stretching frequency was found to be -520 cm^{-1} . Further approach of the oxygen atom to the surface results in the NN–O bond cleavage and formation of the incipient O_2^{2-} species with the O–O intermolecular bond length decreased to 1.45 Å. A deeper understanding of the oxygen atom transfer process can be inferred from the analysis of evolution of the bond orders along the reaction coordinate (Figure 3a₂). Inspection of this figure reveals that the N–NO bond order increases during the reaction, and the nascent NNO– $\text{O}_{\text{surf}}^{2-}$ bond is produced at the expense of the vanishing NN–O bond, as expected. A particular feature of this bond rearrangement is that it occurs in a narrow range of the

Table 1. Energetic Barriers, Stretching Frequency, and Thermal Contributions to the Activation Free Enthalpy at 600 °C, Calculated for the Elementary Steps of N₂O Decomposition over MgO

deN ₂ O elementary step	$\Delta E_a/\text{kcal mol}^{-1}$	$\Delta(\text{ZPE})/\text{kcal mol}^{-1}$	TS stretching frequency/cm ⁻¹	$G(0 \rightarrow \text{T})$ 600 °C/kcal mol ⁻¹
oxygen transfer	31.8	-2.17	-520	25.34
O ₂ ²⁻ diffusion	24.6	-1.08	-258	-1.27
O ₂ ²⁻ recombination	18.9	-1.37	-341	1.47
O ₂ readsorption	62.6	-0.01	-341	33.14
ER recombination	40.8	-2.44	-800	24.48

NNO–O_{surf} distances, revealing a hard nature of the involved chemical interactions. More insightful changes were observed in the Hirshfeld partial charge redistribution plots (Figure 3a₃). For the oxygen atom in the N₂O reactant, a moderate change of the charge from -0.1 (in the intact molecule) to -0.26 (in the surface peroxide intermediate) was observed. The partial charge on the terminal nitrogen is close to -0.09, and evolves during the reaction course to zero. Yet, the greatest alternation occurs on the middle nitrogen (from 0.19 to 0.0) and on the surface oxygen (from -0.42 to -0.19), showing that the main flow of the electron density during the N₂O activation takes place between these two atoms. It may be then concluded that the oxygen atom transfer step consists in two stages of the charge flow. The initial stage is associated with the bent transition state and provokes charge flow from the surface O²⁻ anion to the middle nitrogen, to yield a nascent peroxy group. In the next stage, further charge redistribution within the O₂²⁻ unit is caused by relaxation of the emerged peroxy group into its final tilted configuration (with the O_{ext}–O_{surf}–Mg angle of 58.6°). In the latter case, interaction of the terminal oxygen atom O_{ext} with the adjacent Mg²⁺ cation leads to appreciable electric polarization of the surface O₂²⁻ species ($q_{\text{O}_{\text{surf}}} = -0.19$, $q_{\text{O}_{\text{ext}}} = -0.26$). Overall, the anionic redox sites are clearly constituted by the surface oxygen ions (O_{surf}), which upon accommodation of oxygen atoms abstracted from N₂O change their formal oxidation state from starting -2 in O²⁻_{surf} to -1 in the O₂²⁻ intermediate. The most important molecular signatures of the peroxy groups are summarized in Table S2 of Supporting Information. It should be noted that the stabilization energy of two adjacent surface peroxy groups (the parameter important for discussion of surface diffusion) is nearly the same as for two distal O₂²⁻. This fact shows that the lateral interaction between two peroxy species is rather weak; therefore their surface diffusion should be not much influenced by the coverage.

Surface diffusion of the peroxy species is shown in parts b₁–b₃ of Figure 3. The transition-state energy was found to be located at 24.6 kcal/mol, and the distance between the diffusing O atom and the surface O²⁻ anion was equal to $r_{\text{O-O}} = 1.91$ Å. The Mayer bond order and the Hirshfeld population analysis (parts b₂ and b₃ of Figure 3) indicate that at the beginning of the O atom movement ($r_{\text{O-O}} = 2.2$ Å), while the O–O bond is appreciably elongated, there is only slight concomitant redistribution of the electron density. Close to the transition state concerted formation of the new O–O²⁻ bond and cleavage of the old one is clearly visible, not only through the analysis of bond orders but also through comparison of the atomic charges. Analysis of Figure 3b₃ indicates that reaching the TS configuration is accompanied by uneven charge redistribution within the vanishing and the nascent peroxy groups. As a result, the itinerant

oxygen atom acquires a noteworthy negative charge in the transition state. The energetic barrier for diffusion can be rationalized by the large distance between adjacent surface anions (3.13 Å) in comparison to the O–O separation in the peroxy group, which indicates that the configuration of the transition state for oxygen diffusion can be reached only when the overwhelming part of the old O–O²⁻ bond is already lost (bond order decreases by 80% at TS), whereas the new one is still in its incipient state (20%).

The recombination pathway of two peroxy surface species leading to the eventual O₂ molecule is shown in parts c₁–c₃ of Figure 2. The reaction energetics is plotted as a function of $r_{\text{O-O}}$ for the singlet state of the nascent dioxygen with the superimposed diabatic potential energy curve for the triplet ground state (³Σ_g⁻) of dioxygen in the gas phase. Along the reaction coordinate two characteristic turning points can be distinguished. At larger distances ($r_{\text{O-O}} = 2.0$ Å) the charge comproportionation ($2\text{O}_2^{2-} \rightarrow \text{O}_2 + 2\text{O}^{2-}$) begins until the TS configuration is reached at $r_{\text{O-O}} = 1.88$ Å, giving rise to the activation barrier of 18.9 kcal/mol. At shorter distances ($r_{\text{O-O}} = 1.33$ Å, close to the interatomic separation of O₂ in the singlet ¹Δ_g state), the curve of singlet dioxygen crosses with that characteristic for molecular oxygen in the triplet state (³Σ_g⁻). As a result a spin barrier emerges from the diabatic crossing of the singlet and triplet potential energy (¹Δ_g → ³Σ_g⁻). Since the energetic and the spin barriers are separated along the reaction coordinate, the spin recombination can occur still at the surface or even in the gas phase.

In the ER mechanism the distance between the oxygen atom of N₂O and the terminal oxygen in the surface peroxy group was used as a reaction coordinate. The approach of the N₂O molecule toward the peroxy group leads to highly energetic, concerted cleavage of the N₂–O bond and formation of the O–O²⁻ one. The distortion of the peroxy group is significant, as revealed by its elongation of about 0.5 Å, and concomitant with distortion of the activated N₂O molecule as revealed by the N–N–O angle of 162.4°. The resultant lowering of the lowest-unoccupied molecular orbital (LUMO) level facilitates the charge transfer from the peroxy group to the N₂O molecule, and elongation of the N–O bond (1.14 to 1.49 Å). The high energetic barrier of 40.8 kcal/mol suggests that for the MgO surface the preferred mechanism of oxygen recombination involves LH rather than the ER pathway.^{21,60} The ER mechanism, in turn, may be preferred in the case of high activation barrier for diffusion (immobile intermediates) and high surface coverage by intermediates, which is expected for more basic alkaline earth oxides such as CaO or SrO.^{32,61} The principal thermodynamic parameters defining each elementary step are summarized in Table 1.

Inspection of the data collected in Table 1 shows that the oxygen transfer and ER recombination steps exhibit the highest

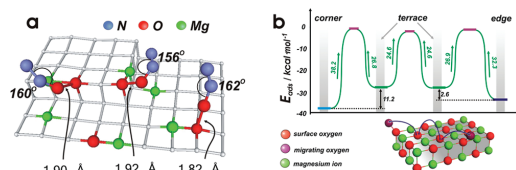


Figure 4. Transition-state geometries of the oxygen transfer step for various topological location of the active centers (a), and the energy barriers of O_2^{2-} diffusion on the MgO surface along various pathways (marked by arrows) (b).

negative entropy contribution associated with the loss of translational and rotational degrees of freedom. Therefore, the free enthalpy of activation, ΔG_a , of these two steps significantly increases with the reaction temperature (leading to thermal self-hindrance of these steps) in contrast to LH recombination step, for which the entropic term is much smaller and positive (Figure S3 of Supporting Information).⁶² The transition states associated with the surface diffusion step resemble the structure of the peroxy intermediate, so the thermal contributions to its activation free enthalpy $\Delta G_a(0 \rightarrow T)$ exhibit weak temperature dependence as well.

Some of the elementary steps described above were studied previously,^{63,64} and similar results were obtained for the activation energy and the geometry of the OAT transition state ($E_a = 31.6$ kcal/mol,⁶² 37.1 kcal/mol,²³ and 32.4 kcal/mol¹²) as well as for the surface oxygen diffusion.⁶⁵ Experimental results also suggest that the oxygen transfer process is energetically the most demanding molecular event (the rate-determining step) of the N_2O decomposition over MgO (32.3 kcal/mol,⁶⁶ 36.0 kcal/mol⁶⁷). The calculated height of the energetic barrier for the recombination of oxygen (18.9 kcal/mol) was confirmed experimentally (16 kcal/mol) in our earlier work.²¹ Both experimental and computational results indicate that the high activation energy of N_2O dissociation implies that this process is feasible at higher temperatures ($>400^\circ\text{C}$), whereas the recombination of peroxy group can take place at much lower temperature range (120°C).²¹ These facts lead to bare surface ($\Theta \approx 0$) regime of the N_2O decomposition kinetics.

ROLE OF MORPHOLOGY

An idealized model of a fragment of the MgO surface exhibiting principal topological features, i.e., terraces (with 5-fold coordination of the exposed ions), edges (4-fold), and corners (3-fold) is shown in Figure 4. Because of lowering of the Madelung potential caused by reduction of the coordination number of the surface O^{2-} sites located at edges and corners they exhibit enhanced Lewis basicity.^{68,69}

As already discussed, in the case of the oxygen transfer step the transition state energy barrier is associated with the charge density flow from the surface O^{2-} sites into the antibonding LUMO orbital of the reacting N_2O molecules.²² Indeed, as shown in Figure 4a the bending of the activated N_2O molecule ($\angle \text{N}-\text{N}-\text{O} = 162^\circ$) on the less basic terrace sites is smaller than that observed for the more basic edge ($\angle \text{N}-\text{N}-\text{O} = 160^\circ$) and corner ($\angle \text{N}-\text{N}-\text{O} = 156^\circ$) centers, whereas the $\text{N}_2\text{O}-\text{O}_{\text{surf}}$ distance follows the opposite trend (1.82, 1.90, and 1.92 Å for terraces, edges, and corners, respectively). Since the extension of the bending associated with the N_2O activation

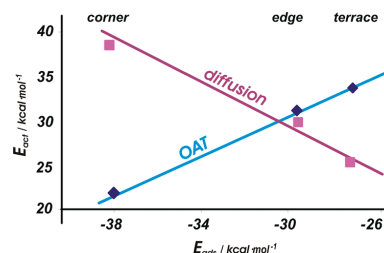


Figure 5. Sabatier plot for the oxygen atom transfer and surface diffusion steps of N_2O decomposition for corner, edge, and terrace sites of the MgO catalyst.

depends on the population of the antibonding LUMO orbital,²² the observed angular distortions of N_2O in the transition state for various topological locations of the electron donor O^{2-} sites are consistent with their different basicity (gauged by the local Madelung energy). In the case of the hard terrace O^{2-} centers, to reach the transition state configuration the N_2O molecule has to approach the surface quite intimately. This leads to strong Pauli repulsion of the fully occupied oxygen levels within the $\text{N}_2\text{O} \cdots \text{O}_{\text{surf}}$ moiety, giving rise to high activation barrier (31.8 kcal/mol). This barrier is lowered to 29.1 kcal/mol for the O^{2-} centers located at edges decreasing down to 22.4 kcal/mol in the case of the softest corner sites, where the oxygen–oxygen distance is the smallest, minimizing the Pauli repulsion. Yet, the enhanced basicity of these coordinatively unsaturated sites assures strong activation of the N_2O molecule (as can be inferred from the bending angle) due to an efficient electron density transfer from the O^{2-} sites into the LUMO level of N_2O . It might appear then, that improvement of the deN_2O activity can easily be achieved by increasing the abundance of the most basic corner/edge anionic active sites by appropriate morphology engineering.

However, to close the catalytic cycle following the most preferable LH mechanism, the peroxy species produced in the OAT step have to diffuse on the MgO surface to recombine into the final O_2 product (eq 6). Such recombination is possible exclusively on the terraces, since movement of the peroxy groups along the edges is prohibited by very high energy barrier (>60 kcal/mol) in comparison to that observed on terraces (24.6 kcal/mol). Although the barrier for diffusion from edges and corners toward terraces is lower (32.3 and 38.2 kcal/mol, see Figure 4b), the peroxy groups located at these sites exhibit higher stability than on terraces, and the only driving force for O_2^{2-} spreading would be associated with the increase of the configurational entropy. The latter can play a significant role at high temperatures only. The energetic competition between the OAT and diffusion steps of N_2O decomposition for various topological sites can be better illustrated in the form of a Sabatier plot (Figure 5). As a result the most active basic sites located at edges and corners are involved mostly at the beginning stages of the N_2O decomposition, and their saturation during the reaction progress is responsible for the observed gradual decrease of the initially higher MgO activity, which is morphology sensitive (Figure 1b, insert). However, the steady state TOF does not depend on the catalyst morphology, as it is associated with the involvement of terrace active sites mainly.

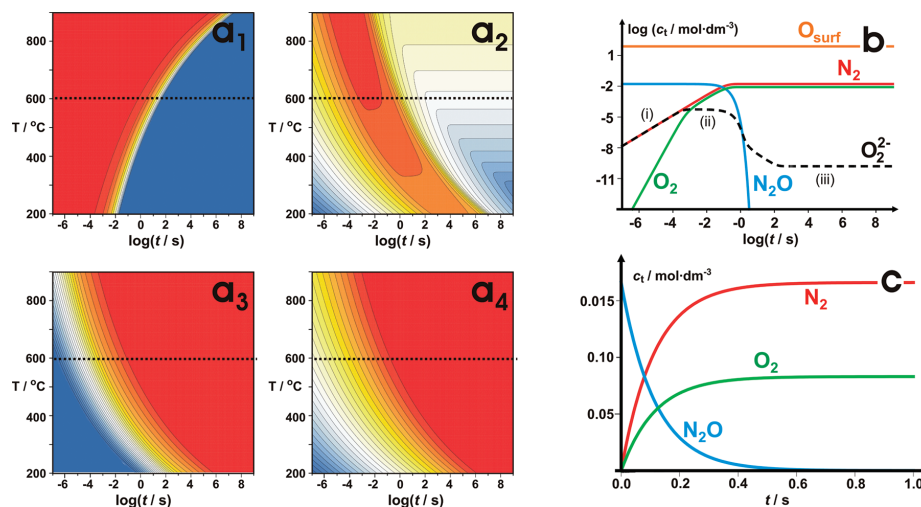


Figure 6. Time-resolved simulations of N_2O (a_1), peroxy (a_2), O_2 (a_3), N_2 (a_4). log–log plot of species concentration as a function of time (for 600 °C) (b). Linear plot of species concentration as a function of time (for 600 °C) (c).

Microkinetic Modeling. Molecular level mechanistic considerations of N_2O decomposition allows to propose the following kinetic equations for the relevant elementary steps

$$\text{OAT} \quad (\text{N}_2\text{O dissociation}) r_1 = k_1 \frac{p_{\text{N}_2\text{O}}}{p^0} (1 - \Theta) \quad (9)$$

$$\text{LH recombination} \quad r_2 = k_2 \Theta^2 \quad (10)$$

$$\text{O}_2 \text{ readsorption} \quad r_3 = k_3 \frac{p_{\text{O}_2}}{p^0} (1 - \Theta) \quad (11)$$

$$\text{ER recombination} \quad r_4 = k_4 \frac{p_{\text{N}_2\text{O}}}{p^0} \Theta \quad (12)$$

where Θ is the surface coverage by the peroxy intermediates and k_3 encompasses the sequential surface diffusion (k_{diff}) and recombination (k_{rec}) steps, merged in the following way: $(1)/(k_3) = (1)/(k_{\text{diff}}) + (1)/(k_{\text{rec}})$.⁷⁰

For the ab initio microkinetic modeling all the necessary kinetic data are calculated by DFT, and no fitting was used for comparison with experiment.

Pulse Reactor Transient Kinetics. The results of the microkinetic simulations for pulse reactor are shown in Figure 6. The set of the operational parameters chosen for modeling was based on the literature data for TAP reactor.^{71,72} The parameters and units used in the simulation are collected in Table S3 in Supporting Information.

A two-dimensional plot shows the evolution of all reacting species: N_2O (a_1), O_2^{2-} (a_2), O_2 (a_3), N_2 (a_4) as a function of the elapsing time, t , and the reaction temperature, T . The cross sections for 600 °C (corresponding to ~50% conversion) in the logarithmic and linear scales are shown in parts b and c of Figure 6, respectively. In the case of N_2O decomposition the 2D diagram shows its expected monotonous decay with the reaction progress, and the resultant emergence of the N_2 and O_2 products

in the whole range of the temperature and time. The most interesting is the surface dynamics of the O_2^{2-} intermediate (a_2), where three mechanistically distinct regions can be defined: (i) a transient stage of incipient increase of the coverage, (ii) steady state plateau of maximum surface coverage, and (iii) transient switch into another region of Θ , the level of which depends on the temperature but is independent of time. These three regions can be better seen in Figure 6b on the dotted line. In the first stage of the reaction (from μs to ms time range) changes in the N_2 and O_2^{2-} concentration are concerted in accordance with the OAT reaction step, whereas the concentration of N_2 exceeds that of O_2 until ~0.1 ms. Since at the initial period of the reaction the surface coverage by the peroxy groups is very small, formation of O_2 following the LH step is delayed in comparison to the OAT step. Once the elapsing time reaches the value of about 0.1 ms, corresponding to the maximum quasi stable concentration of the O_2^{2-} intermediates (in the range from ~0.1 ms to ~1 s), the production of N_2 and O_2 is mutually balanced. It is noteworthy that the maximal O_2^{2-} concentration is more than 3 orders of magnitude smaller than the concentration of active sites, so the fraction of the occupied sites remains small, and the recombination of the peroxy groups is possible due to the fast surface diffusion of the O_2^{2-} species (leading to the bare surface, $\Theta \approx 0$, kinetic regime).

In region ii, a rapid conversion of N_2O takes place, which is well seen in Figure 6c, where the linear time scale is used. Once the N_2O molecules delivered within the reactant pulse are becoming nearly depleted, the maximum concentration of the peroxy groups cannot be maintained due to decaying supply of the oxygen atoms, and Θ gradually drops to a new level that corresponds to equilibrium between the gas phase dioxygen and surface O_2^{2-} . It can be noted that due to a short time interval (below ms) and low concentration of intermediates and the reaction products, the first region (i) is not accessible even for TAP experiments and remains a latent stage. Interestingly

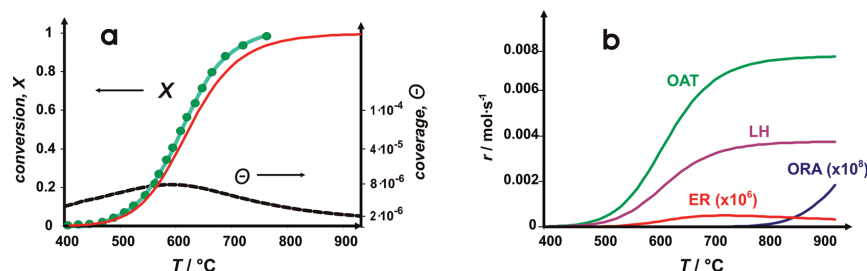


Figure 7. Comparison of the calculated and experimental steady state conversions for various temperatures for the 0.1 g of MgO catalyst with surface area of $72.4 \text{ m}^2 \text{ g}^{-1}$ and flow rate of $30 \text{ cm}^3 \text{ min}^{-1}$ (5% $\text{N}_2\text{O}/\text{He}$) (a) and specific rates for all elementary reactions steps (b).

in this stage the reaction progress is controlled not by the activation energy of the involved OAT and LH steps but by the surface coverage of the intermediates. The region amenable for experimental investigations is shown in Figure 6c, where the theoretically predicted profiles of the reactants are presented.

■ FLOW REACTOR STEADY STATE KINETICS

In the steady state, the surface coverage, Θ , of the adsorbed peroxy species is constant, therefore the production (OAT, r_1 , and O_2 readsorption, $2r_3$) and consumption (HL, $2r_2$, and ER, r_4)

rates of the peroxy species are equal

$$r_1 + 2r_3 = 2r_2 + r_4 \quad (13)$$

The observed overall rate of N_2O decomposition, r^{obs} , is given by the sum of the rates of the elementary reactions r_1 and r_4

$$r^{\text{obs}} = r_1 + r_4 \quad (14)$$

As a result the asymptotic (steady state) concentration of the peroxy intermediates (Θ) at given temperature can be described by the following formula⁷³

$$\Theta = \frac{(X-1)k_1p_{\text{N}_2\text{O}}^0 - Xk_3p_{\text{N}_2\text{O}}^0 - k_4p_{\text{N}_2\text{O}}^0 + k_4Xp_{\text{N}_2\text{O}}^0 - 2k_3p_{\text{O}_2}^0}{\sqrt{8k_2(k_3(Xp_{\text{N}_2\text{O}}^0 + 2p_{\text{O}_2}^0) - (X-1)k_1p_{\text{N}_2\text{O}}^0) + ((X-1)k_1 - Xk_3 + (X-1)k_4)p_{\text{N}_2\text{O}}^0 - 2k_3p_{\text{O}_2}^0)^2/4k_2}} \quad (15)$$

Upon neglecting the contributions due to the minor O_2 readsorption and ER steps, this equation assumes a much simpler form

$$\Theta = \frac{(X-1)k_1p_{\text{N}_2\text{O}}^0 - \sqrt{((X-1)k_1p_{\text{N}_2\text{O}}^0)^2 - (X-1)k_1p_{\text{N}_2\text{O}}^0}}{4k_2} \quad (16)$$

For the sake of conciseness, $p_{\text{N}_2\text{O}}^0$ is used instead of $p_{\text{N}_2\text{O}}^0/p^0$ and $p_{\text{O}_2}^0$ instead of $p_{\text{O}_2}^0/p^0$. The actual concentration of nitrous oxide, $p_{\text{N}_2\text{O}}$, is expressed as $p_{\text{N}_2\text{O}} = p_{\text{N}_2\text{O}}^0(1-X)$, where $p_{\text{N}_2\text{O}}^0$ is the initial N_2O concentration in the feed. The concentration of oxygen, p_{O_2} , is expressed as a sum of O_2 present in the feed, $p_{\text{O}_2}^0$, and oxygen produced from the decomposed N_2O , $0.5(p_{\text{N}_2\text{O}}^0X)$. The overall rate of the deN_2O reaction, r^{obs} , can be next associated with the observed N_2O conversion in the microreactor with a quasi-ideal mixing, and with the rates of the nitrous oxide consuming elementary steps (OAT and ER)

$$r^{\text{obs}} = \frac{p_{\text{N}_2\text{O}}^0 F}{m_{\text{cat}} S \rho} X = r_1 + r_4 \quad (17)$$

where m_{cat} is the mass of the catalyst, S is specific surface area, ρ is the concentration of active sites, and F is the gas flow. Equation 17 allows for modeling of the temperature dependence of the N_2O conversion on the reaction rate constants of all elementary steps linked by Θ (which implicitly depends on k_1 , k_2 , k_3 , and k_4). For $S = 72.4 \text{ m}^2 \text{ g}^{-1}$, $m_{\text{cat}} = 0.1 \text{ g}$, $F = 30 \text{ cm}^3 \text{ min}^{-1}$ used in typical

experimental catalytic tests (Figure 7a, dotted line), substituting the DFT calculated values of the activation enthalpies, the theoretical kinetic curve can be obtained without any fitting (Figure 7a solid curve). A remarkable agreement between the experiment and theory confirms the adequacy of the microkinetic model, as well as the applied DFT machinery. Once the correct model is established, an in-depth insight into the variation of the kinetic parameters such as surface coverage (Θ curve in Figure 7a) or the kinetic relevance of minor ER and oxygen readsorption (ORA) pathways (Figure 7b), which are not directly accessible from the experiment is possible. As expected, the maximum surface coverage Θ corresponds to maximum reaction rate. It should be noted, however, that the stationary Θ values are quite small ($<10^{-3}$) indicating that the catalyst surface remains essentially bare during the whole reaction, as it was already mentioned. As a result of the fast surface diffusion of the peroxy intermediates, the contribution of the ER step to overall turnover is negligible (6 orders of magnitude lower than the LH step) in the whole range of the temperatures. Similarly, the readsorption of oxygen, with even lower share in the total N_2O conversion, can also be abandoned. These two processes gain, however, in importance considerably for more basic alkali earth oxides.

To further confirm the predicted theoretical microkinetic model we have calculated the kinetic isotopic effect (KIE) for ^{18}O and ^{15}N . The KIE were calculated following Bigeleisen formalism, based on the absolute rate theory.⁷⁴ The rate constant ratios k_1/k_0 , k_2/k_0 , and k_3/k_0 (where k_0 , k_1 , k_2 , and k_3 are the rate constants for $^{14}\text{N}^{14}\text{N}^{16}\text{O}$, $^{15}\text{N}^{14}\text{N}^{16}\text{O}$, $^{14}\text{N}^{15}\text{N}^{16}\text{O}$, and $^{14}\text{N}^{14}\text{N}^{18}\text{O}$

Table 2. Calculated KIE (^{15}N and ^{18}O) Parameters at Various Temperatures along with the Experimental KIE (^{15}N) Values for N_2O Decomposition over MgO

T/K	KIE (^{18}O) _{calcd} (this work)	KIE (^{15}N) _{calcd} (this work)	KIE (^{15}N) _{exptl} (ref 77)
675	5.80	2.19	2.23
725	5.50	2.12	2.12
775	5.30	1.94	1.98
825	5.10	1.85	1.83

isotopomers, respectively) were calculated using the following formula^{75,76}

$$\frac{k_0}{k_i} = \frac{\nu_{L_0}}{\nu_{L_i}} \prod_{j=1}^{3n-6} \frac{u_{ij} \sinh(u_{0j}/2)}{u_{0j} \sinh(u_{ij}/2)} \prod_{j=1}^{3n-7} \frac{u_{0j} \sinh(u_{ij}/2)}{u_{ij} \sinh(u_{0j}/2)} \quad (19)$$

where the pound sign denotes the transition state. The first product refers to the frequencies of the reactants and the second one to the transition states. ν_L is the frequency of the normal mode associated with the reaction coordinate, and $u = hc\omega/k_B T$ (h = Planck constant, c = speed of the light, ω = angular frequency, k_B = Boltzmann constant, and T = temperature). The frequencies for all investigated N_2O isotopomers in the stationary and the transition states were calculated by DFT. For ^{15}N the predicted KIE values are in an excellent agreement with experimental results of Žemva et al.⁷⁷ in the whole investigated T range (Table 2), unfortunately for ^{18}O such experimental data are not available.

CONCLUSIONS

The microkinetic model of the catalytic decomposition of N_2O on MgO nanocrystals of various sizes was developed based on comprehensive mechanistic studies by joined DFT calculations and reactivity experiments. The elementary steps of the reaction over most stable (100) surface were analyzed in terms of the energy profiles and evolution of the bond orders and partial charges during the NN–O bond braking and N–N and O–O bond making processes. It was shown that the steady state decomposition of N_2O involves anionic redox centers located on terraces, whereas the more active edge and corner sites are gradually poisoned by the intermediate products, and therefore they are less important for sustainable activity. The energetic profiles of all elementary steps were determined and the reaction intermediates and transition state geometries were ascertained. The kinetically relevant steps of the reaction include a dissociative activation of N_2O via oxygen atom transfer (slow step) and a LH recombination of peroxy intermediates (fast step), giving rise to bare surface regime of $de\text{N}_2\text{O}$ kinetics. The ER desorption of hyperthermal oxygen atom and the oxygen readsorption steps were found to be kinetically irrelevant. The calculated free enthalpies together with the harmonic transition state theory were used for ab initio modeling of the kinetic parameters. The proposed scheme reproduces the results of temperature programmed and steady state catalytic $de\text{N}_2\text{O}$ experiments, including kinetic isotopic effects, with high accuracy. The latent stage of the $de\text{N}_2\text{O}$ pulse kinetic was clarified in terms of the dynamics of the surface coverage of the peroxy intermediates. On the basis of the obtained results a complete mechanistic description at atomic scale of all involved elementary steps and prediction of turnover rates were provided.

ASSOCIATED CONTENT

S Supporting Information. Model of the symmetric periodic $\text{Mg}_{32}\text{O}_{32}$ slab, table of synthesis methods for various micro- and nanostructured magnesium oxide along with the basic characteristics, an Arrhenius plot for N_2O decomposition over MgO , basic molecular signatures of surface peroxy group, ΔG_a , ΔH_a , and rate constants, and parameters and units used for simulations of pulse reactor kinetics. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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2.4.9 Tekst artykułu H9

[H9] W. Piskorz*, F. Zasada, P. Stelmachowski, A. Kotarba, Z. Sojka* „Molecular Mechanism and Microkinetics of deN₂O Reaction over Alkaline Earth Oxides – The Role of Static and Dynamic Recombination of Peroxy Intermediates” DOI: 10.1021/jp405459g, *J. Phys. Chem. C*.

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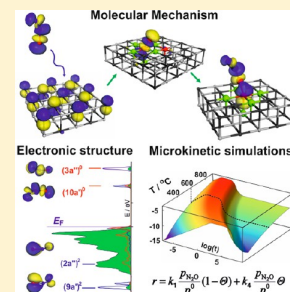
DFT Modeling of Reaction Mechanism and Ab Initio Microkinetics of Catalytic N₂O Decomposition over Alkaline Earth Oxides: From Molecular Orbital Picture Account to Simulation of Transient and Stationary Rate Profiles

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Supporting Information

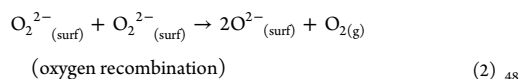
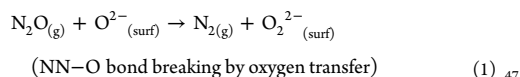
ABSTRACT: A comprehensive molecular modeling of the reaction mechanism, complemented by ab initio microkinetic studies of the catalytic decomposition of N₂O on a series of the alkaline earth oxides (MgO, CaO, and SrO), was performed. The DFT level of theory was used to study the intimate mechanism of conceivable elementary steps of the *de*N₂O reaction over the terrace sites of the most stable (100) planes. The principal mechanistic events were thoroughly analyzed in terms of the frontier molecular orbital picture, and a multiple role of the anionic redox active centers constituted by surface O²⁻_(surf) ions was revealed. The harmonic transition state theory along with the calculated free enthalpies of activation were used to model the reaction progress with the elementary step resolution in pulse (transient) and steady state regimes. For modeling the surface diffusion and recombination of the reaction key intermediates (peroxy groups), a Monte Carlo approach was applied to rationalize dioxygen formation along the static and dynamic routes. The developed kinetic scheme was able to reproduce the results of temperature-programmed surface reaction (TPSR) and isothermal steady state experiments with high accuracy without fitting any parameters. On the basis of obtained results, a complete molecular mechanistic description of the *de*N₂O reaction was proposed, resolving definitely the dependence of the particular elementary steps on the strength of anionic redox centers and their Lewis basicity.



INTRODUCTION

Nitrous oxide is well-known for its destructive influence on the stratospheric ozone layer¹ and is also recognized as a strong greenhouse gas.^{2,3} Due to its harmful impact on the environment, direct decomposition of N₂O into N₂ and O₂ is of great scientific and practical importance.^{4,5} Although catalytic decomposition of nitrous oxide has been widely studied over many classes of compounds, including supported metals,^{6–8} simple^{9–11} and complex oxides,^{3,12–14} as well as zeolites,^{15,16} a thorough understanding of the intimate mechanism and the resultant microkinetics of the *de*N₂O reaction is still not fully accomplished. The progress can be made, inter alia, by establishing quantitative structure–activity relationships and a detailed molecular description of the reaction steps, including determination of their energetics and unavoidably also the entropic part.

The principal mechanisms along which the nitrous oxide can be decomposed involve electron transfer^{17,13,18} (cationic redox mechanism operating, e.g., on cobalt spinel) and oxygen atom transfer¹⁹ (anionic redox mechanism originally proposed for magnesium oxide²⁰ and mayenite²¹ catalysts). The latter involves the following principal steps, described elsewhere in more detail²⁰



According to these equations the performance of the catalyst is determined by the ability of surface oxygen ions (anionic redox active sites) to abstract the oxygen atom from N₂O to form O₂²⁻ intermediates (eq 1) and to release surface oxygen into the final O₂ molecule (eq 2). The first step is initiated by the simultaneous NN–O bond breaking and formation of peroxide ion on the catalyst surface and is essentially controlled by the Lewis basicity of the O²⁻_(surf) active sites. Owing to their structural simplicity, well-defined cubic morphology, countable active sites (surface O²⁻), and easily controlled basicity by mere variation of the cationic radius, alkali earth oxides (AEOs) are excellent model systems for detailed examination of the anionic redox mechanism of N₂O decomposition and the interplay between the reaction and surface diffusion steps.^{18,19}

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Alkaline earth oxides are typical ionic compounds with the same rock-salt structure (space group $Fm\bar{3}m$) characterized by highest density packing (fcc), where both cations and anions occupy the octahedral interstitials. MgO, CaO, and SrO are wide band gap insulators²² with the same structure of the thermodynamically most stable (100) surface. Surface corrugation is lower than 2% of the interionic distance, and the outermost atomic plane relaxes inward by 1% of the interlayer spacing in each case.²³ The quite large difference in the stabilization energy of the (100) and other low-index terminations is reflected in the typical cubic shape of the AEO crystallites.^{24,25} The (100) terraces are characterized further more by lowering of the coordination of the surface ions from six to five.²⁶ Owing to their highly ionic nature, to a large extent the reactivity of the alkaline earth oxides is dictated by anisotropy of the surface Madelung energy (E_{Mad}), which varies for different coordination of $\text{O}^{2-}_{(\text{surf})}$ sites, depending on their topological locations and on the interionic distances $d = r_{\text{A}^{2+}} + r_{\text{O}^{2-}}$. Thus, the pronounced difference in basicity of the $\text{O}^{2-}_{(\text{surf})}$ active sites originates from different lattice parameter (MgO: $a = 4.21 \text{ \AA}$; CaO: $a = 4.81 \text{ \AA}$; and SrO: $a = 5.16 \text{ \AA}$)¹¹ and is reflected in their activity toward CO_2 adsorption²⁷ and N_2O decomposition.²⁸

Although there is a great deal of theoretical and experimental data about the MgO surface,^{29–33} less information is available for CaO and SrO.^{34–36} An overall agreement has been reached that the oxygen abstraction takes place at an $\text{O}^{2-}_{(\text{surf})}$ site, leaving a peroxide intermediate at the surface.^{37,38} Since all the considered oxides have the same surface structure, one would expect decomposition of N_2O to be correlated with the lattice constant and therefore the basicity sequence. Actually, previous studies on N_2O decomposition have shown that CaO is more active than magnesia;³⁹ however, SrO and BaO (despite their higher basicity) do not follow the trend, being distinctly less reactive.^{40,43}

Indeed, Snis and Miettinen on the basis of experiment and DFT calculations predicted that CaO is a more active deN_2O catalyst than MgO.¹⁰ The reactivity of AEO series toward deN_2O reaction has also been addressed by Karlsen et al.,^{11,41} using embedded cluster calculations. The authors focused on the regeneration of the catalyst surface (eq 2), which proceeds along different mechanisms for the different oxides. In the case of MgO and CaO, recombination of the surface peroxide species into dioxygen has been proposed, whereas for SrO and BaO direct reaction of N_2O with a surface peroxide ion has been found to prevail. However, since in this study merely the activation barriers of the elementary steps have been computed, the results can be confronted with the experiments only in the limited way. To directly confront catalytic results on different alkaline earth oxide activities with theoretical predictions in a more adequate fashion, we developed a thorough microkinetic model of the deN_2O reaction over the series of AEOs. Such an approach, taking into account the entropic contributions explicitly, allows for calculation of rate constants of all elementary steps and their temperature responses. The transient and stationary kinetic analysis was complemented by a detailed molecular level description of the reaction mechanism.

■ EXPERIMENTAL AND COMPUTATIONAL DETAILS

As already mentioned the advantage of using the AEO as model catalysts is that owing to their predominantly cubic morphology they possess well-defined easily countable anionic redox O^{2-}

sites, provided that careful in situ surface depassivation (dehydration, dehydroxylation, and decarboxylation) is performed prior to each kinetic measurement.¹⁸ Additionally, their activity can be controlled easily by mere changes in the cationic radius on passing from magnesium to strontium, allowing us to probe fine nuances of the deN_2O reaction mechanism.

Materials Preparation, Characterization, And Catalytic Studies. Three alkaline earth oxides were used in the experiments: MgO, CaO, and SrO. Magnesium oxide was obtained from Ubichem ($72.4 \text{ m}^2\text{g}^{-1}$), whereas calcium and strontium oxides were obtained by calcination of the respective oxalates, prepared by the precipitation method. The metal oxalates were obtained by adding dropwise 1 M solution of oxalic acid to a 1 M solution of calcium or strontium nitrate (Aldrich, p.p.a.). The oxalates were dried at 100°C for 10 h and calcined for 2 h at 900°C in the case of CaO and 2 h at 1000°C in the case of SrO. Specific surface areas (Quantasorb Junior, Quantachrome) of the obtained oxides were equal to 7.4 and $2.9 \text{ m}^2\text{g}^{-1}$ for CaO and SrO, respectively.

Powder X-ray diffraction (XRD) patterns (Figure S1, Supporting Information) were recorded with a Philips X'Pert PW 3020 diffractometer using $\text{Cu K}\alpha$ radiation. Both synthesized samples were found to be well-crystalline. In the case of air exposed calcium oxide (CaO: ICSD-28905) low amounts of $\text{Ca}(\text{OH})_2$ were detected by XRD (ICSD-202229), whereas for SrO the substantial contribution of SrCO_3 (ICSD-15195), due to reaction with atmospheric CO_2 caused by exposure to air, was observed. To ensure phase purity and cleanliness of the catalyst surface, all oxides were heated in situ prior to the reaction in the flowing He up to temperatures MgO , 1000°C ; CaO , 700°C ; and SrO , 1100°C , where virtually no more CO_2 or H_2O (checked by QMS) traces were desorbing from the surface (Figure S2, in Supporting Information).

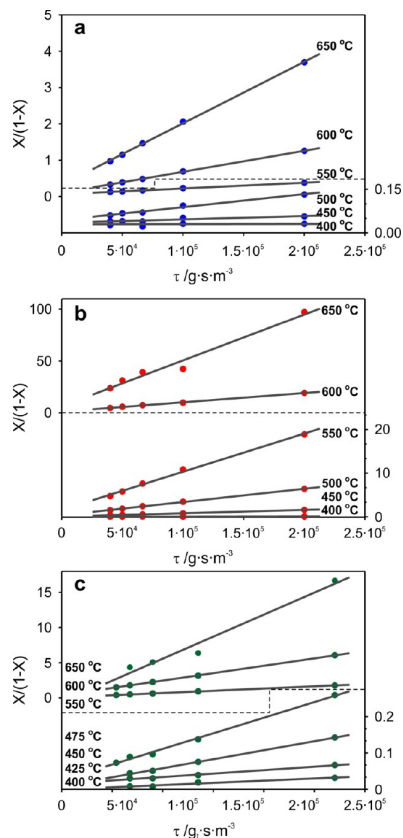
The deN_2O activity of the catalysts was measured in a fixed bed microreactor (i.d. 15 mm), using 100 mg of catalyst (200–300 μm sieve fraction, $\sim 1 \text{ mm}$ catalyst bed height). The gas mixture of 5% N_2O in He and the variable flow rate of 30, 60, 90, 120, and 150 $\text{mL}\cdot\text{min}^{-1}$ were used. The gas-phase analysis was performed by means of a compact quadrupole mass spectrometer (RGA200, SRS). To ensure that the reactor is operating in the kinetic regime, the criterial numbers for extra- and intragranular diffusion limitations were checked according to the eurokin procedure.⁴² The Péclet number ($Pe \sim 0.005$) and Damköhler number ($Dk \sim 0.1$) indicated that practically a perfect mixing regime was achieved for all the measurements. The temperature-programmed reaction and the isothermal stepwise steady state experiments were carried out to measure the activity of the alkaline earth oxide catalysts.

In the case of the flow microreactor with (quasi) ideal mixing the first-order reaction rate, r^{obs} , for an active site (turnover frequency) can be related to the conversion, X , in the following way: $r^{\text{obs}} m_{\text{cat}} S_{\text{BET}} c_{\text{surf}} = F_{\text{N}_2\text{O}} X$, where $F_{\text{N}_2\text{O}}$ is the inlet N_2O flow; m_{cat} is the catalyst mass; S_{BET} stands for the specific surface area; and c_{surf} is the surface concentration of the active sites (Table 1).

As a result the following relation between the apparent rate constant and the conversion can be obtained: $k^{\text{obs}} \tau = (X/(1-X))$, where τ is the contact time defined as: $((m_{\text{cat}} S_{\text{BET}} c_{\text{surf}})/F^0)$. Thus, from the linear plot of $X/(1-X)$ as a function of the contact time τ , the rate constants, k^{obs} , were obtained for various temperatures (Figure 1). The apparent activation

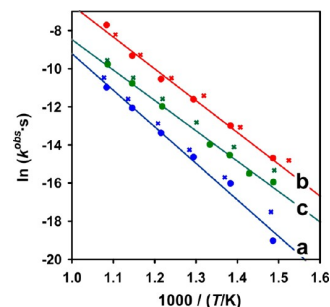
Table 1. Experimental Activation Energies, E_a , and Pre-Exponential Factors

sample	$S_{\text{BET}}/\text{m}^2\cdot\text{g}^{-1}$	$c_{\text{surf}}/\text{m}^{-2}$	apparent activation energy $E_a/\text{kcal}\cdot\text{mol}^{-1}$	
			experiment	DFT
MgO	72.4	1.13×10^{19}	35.0 ± 0.8	33.4 ± 0.2
CaO	7.4	8.64×10^{18}	30.9 ± 1.4	29.1 ± 0.4
SrO	2.9	7.51×10^{18}	33.0 ± 0.5	31.1 ± 0.1

**Figure 1.** Plot of $X/(1-X)$ versus contact time for the series of steady state reaction temperatures for N_2O decomposition over (a) MgO, (b) CaO, and (c) SrO.

188 energies (E_a) of N_2O decomposition were calculated from the
 189 corresponding Arrhenius plots (Figure 2), exhibiting a good
 190 agreement with the literature data ($E_a = 35 \pm 36.1 \text{ kcal}\cdot\text{mol}^{-1}$)⁴³ and the theoretical calculations (vide infra). The
 191 obtained values together with the theoretical apparent
 192 activation energies are presented in Table 1.

194 **Calculations Scheme.** All the calculations were performed
 195 with the DMol³ program⁴⁴ from Materials Studio package of
 196 Accelrys Inc.⁴⁵ In the DFT computations, electron exchange-
 197 correlation effects were described by the generalized gradient
 198 approximation (GGA) developed by Perdew, Burke, and
 199 Ernzerhof (PBE)⁴⁶ with corrections added by Hammer et
 200 al.⁴⁷ The molecular orbitals were expanded into a double-

**Figure 2.** Arrhenius plots of the nitrous oxide decomposition rate constants over (a) MgO, (b) CaO, and (c) SrO. Circles indicate the experimental points whereas crosses the corresponding calculated values.

numerical basis set with polarization functions (DNP),
 comparable to Pople's Gaussian basis set of 6-31G**.
 For all ions of the DSPP (DFT Semicore Pseudopotential),⁴⁸ a Fermi
 smearing of 0.01 Ha and a basis set cutoff distance of 4.5 Å
 were employed. The SCF convergence criterion was set to be
 an energy change of 1×10^{-6} Ha. The convergence criterion of
 optimal geometry was set to 1×10^{-5} Ha difference between
 two successive iterations.

The Brillouin zone integrations were performed using 3×3
 $\times 3$ Monkhorst–Pack grids⁴⁹ for the bulk and $2 \times 2 \times 1$ for the
 slab models of the (100) surface. The alkaline earth oxide (100)
 facets were simulated by using a symmetric periodic slab model
 with the 15 Å vacuum region between the slabs to avoid mutual
 interactions. The four topmost layers of surface ions were fully
 optimized. Upon introduction of the N_2O molecule for each
 postulated elementary step the stable substrate and product
 geometries were determined with the use of the BFGS
 scheme.^{50,51} The transition states were located starting with
 the LST/QST guess⁵² followed by BFGS⁵³ refinement. For
 each stationary point on the potential energy surface full
 vibrational analysis was employed to calculate the free energies.

Calculation of Reaction Rate Constants. Reaction rate
 constants were calculated within the Harmonic Transition State
 Theory (HTST) using a classic equation⁵⁴

$$k = \frac{k_B T}{h} \exp\left(\frac{-\Delta G_a}{RT}\right) \quad (3)$$

where k_B is the Boltzmann constant; ΔG_a stands for activation
 Gibbs free energy; and h , T , and R denote the Planck constant,
 temperature, and gas constant, respectively. The ΔG_a values of
 considered elementary steps were calculated as described in
 detail in our previous paper.²⁰ Within the ideal gas
 approximation ΔG_a was expressed as the sum of static DFT
 electronic energy (E^{el}), zero point energy (ZPE), and thermal
 contributions associated with the vibrational, rotational, and
 translational degrees of freedom supplemented by the three
 entropic contributions: $S(T) = S^{\text{osc}}(T) + S^{\text{rot}}(T) + S^{\text{trans}}(T)$.
 The difference between the Gibbs free energies of the transition
 states and the reactant states ($G_{\text{TS}} - G_{\text{R}}$) defines ΔG_a . The
 kinetic differential equations were solved with Mathematica⁵⁵
 software using the BDF⁵⁶ algorithm.

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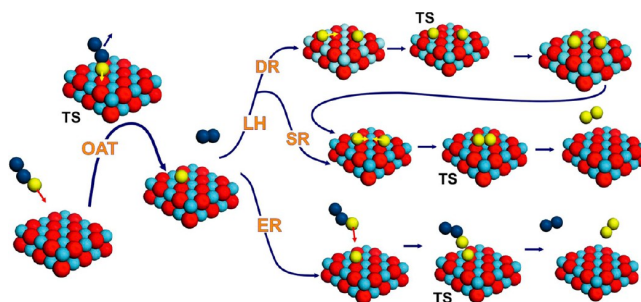


Figure 3. Conceivable mechanistic pathways of N_2O decomposition including the common oxygen atom transfer (OAT) step of the O–N₂ bond breaking and two parallel routes: Langmuir–Hinshelwood (LH), divided into dynamic (DR) and static recombination (SR) of the peroxy group and Eley–Rideal (ER). Color coding of atoms: magnesium, light blue; MgO, oxygen, red; N_2O /surface/ O_2 oxygen, yellow; nitrogen, navy blue.

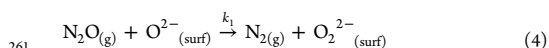
RESULTS AND DISCUSSION

Mechanistic Pathways of Catalytic N_2O Decomposition

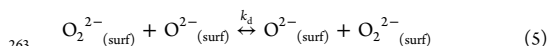
For thorough molecular modeling of the reaction kinetics we analyzed the conceivable elementary steps of N_2O decomposition over AEO shown in Figure 3. The proposed elementary steps were grouped into two main reaction pathways, with the first step assumed to be the same in each case. It involves the N_2O bond cleavage on the surface O^{2-} active site and the concerted oxygen atom transfer (OAT), leading to formation a surface peroxy group O_2^{2-} —the key intermediate of the deN_2O process (eq 1). The resultant surface peroxy group can recombine into final dioxygen following two different routes: Langmuir–Hinshelwood (LH)^{11,39} with static (SR) or dynamic (DR) recombination and Eley–Rideal (ER).¹¹ As implied by this scheme the surface peroxy species play a central role in all mechanistic variants of the N_2O decomposition.

As a result the following elementary steps were taken into account for detailed mechanistic and kinetic analysis (SD denotes surface diffusion)

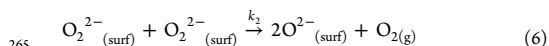
OAT



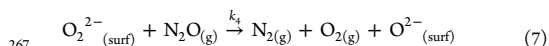
SD



LH

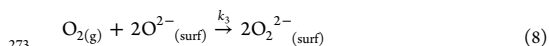


ER



The symbol $\leftrightarrow$ denotes that the surface diffusion of oxygen atoms is a symmetrical process, as discussed below in more detail. In the microkinetic modeling we also took into account the possibility of dissociative readsorption of dioxygen.

O_2 readsorption (ORA)



The influence of topological effects such as corners, steps, and edges on the deN_2O reactivity is, however, not taken into

account herein. Since it has been discussed in our previous paper¹⁸ we only recall the main ideas for the sake of clarity. Due to lowering of the Madelung potential caused by reduction of the coordination number of the active surface O^{2-} sites located at edges and corners, they exhibit enhanced Lewis basicity in comparison to terrace sites. In the case of the electronically hard terrace O^{2-} centers, to reach the transition state configuration, the N_2O molecule has to approach the surface quite intimately. This leads to strong Pauli repulsion of the fully occupied oxygen levels within the $\text{N}_2\text{O} \cdots \text{O}_{\text{surf}}$ moiety, giving rise to high activation barriers (see Table 3). These barriers are lowered for the softer O^{2-} centers located at the edges and corner where the interoxygen approach is smaller, minimizing the Pauli repulsion. Yet, their enhanced basicity gives rise to stronger activation of the N_2O molecule due to an efficient electron density transfer from the low coordinated O^{2-} centers into the LUMO level of N_2O . To close the catalytic cycle, the peroxy species produced in the OAT step have to diffuse on the AEO surface to recombine into O_2 . Such recombination is possible exclusively at the terraces since the movement of the peroxy groups along the edges is prohibited by a very high energy barrier (>60 kcal/mol for MgO) in comparison to that observed on terraces. However, the peroxy groups located at these topographic sites exhibit higher stability than on terraces, and the only driving force for O_2^{2-} to spread on the surface is associated with the configuration entropy increase. The latter can play a significant role at high temperatures only. As a result the most active basic sites located at the edges and corners of the AEO catalysts may be involved mostly at the initial stages of the N_2O decomposition, and their saturation during the reaction progress is responsible for the observed morphology-sensitive gradual decay of the initially higher activity.

Molecular Picture of the Surface Reaction Events. The molecular level picture of the elementary steps of N_2O decomposition over AEO was analyzed in terms of the corresponding energetics, evolution of the bond lengths, Bader^{57,58} charges, and frontier molecular orbital interactions as a function of the reaction coordinate. The mechanistic considerations, supported by calculation of the free enthalpy barriers, provide a suitable, functional background for microkinetic simulations. The emphasis was focused on the detailed description of the surface diffusion of oxygen intermediates, which is essentially governed by the lattice constant of the investigated oxides. The surface oxygen ions $\text{O}^{2-}_{(\text{surf})}$, constituting the anionic redox active sites, upon accommodation of an oxygen atom abstracted from N_2O , change their

Table 2. Peroxy Intermediate Characteristics for Different AEO Surfaces

	MgO	CaO	SrO
$\text{O}^{2-}_{(\text{surf})}-\text{O}^{2-}_{(\text{surf})}$ distance/Å	2.98	3.40	3.62
peroxy group bond length/Å	1.54	1.51	1.52
peroxy group stabilization energy ^a /kcal·mol ⁻¹	27.0	53.1	65.4
peroxy group polarization/ $\Delta\delta_{\text{Hirshfeld}}$	0.050	0.065	0.066
O–O stretching frequency/cm ⁻¹	828	854	867

^aPeroxy group stabilization energy is defined as the sum of the energies of the isolated, triplet state O atom and the fully relaxed clean slab minus the energy of the fully relaxed slab containing adsorbed O.

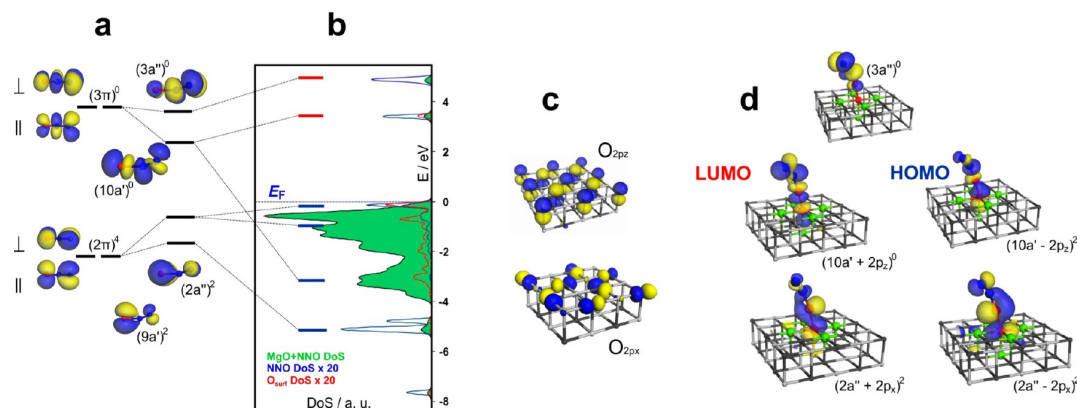


Figure 4. Molecular orbital diagram of the NN–O bond cleavage step over MgO. FMO of linear and bent geometry of the gas-phase N₂O molecule (a), the TS energy levels of N₂O orbitals and DOS diagram of the MgO–NNO system (b), p_z and p_x orbitals of surface oxygen anions (c), and FMO picture of the transition state (d).

formal oxidation state from -2 ($\text{O}^{2-}_{(\text{surf})}$) to -1 ($\text{O}^{2-}_{(\text{surf})}$ intermediate).

NN–O Bond Breaking: Oxygen Atom Transfer Step (OAT). The N₂–O bond cleavage (on the $\text{O}^{2-}_{(\text{surf})}$ sites), followed by the oxygen atom transfer (OAT), exhibits a bent transition state (Figure S3 in Supporting Information) with the N–N–O angle decreasing from 156° through 138° to 134° for MgO, CaO, and SrO, respectively. The geometry of N₂O in the TS configuration is characterized by slight shortening of the N–NO bond (0.07, 0.04, 0.04 Å) and a more pronounced lengthening of the N₂–O bond (0.37, 0.54, 0.45 Å). The N₂O– $\text{O}^{2-}_{(\text{surf})}$ distance changes as 1.89 (MgO), 2.14 (CaO), and 2.09 Å (SrO). The corresponding TS energies, equal to 31.8, 24.6, and 20.1 kcal/mol for MgO, CaO, and SrO, respectively, dramatically decreased with the $\text{O}^{2-}_{(\text{surf})}$ basicity. This is reflected in charge redistribution within the N₂O moiety in the TS configuration. Whereas for the intact N₂O molecule in its ground state the negative charges of $q_{\text{O}} = -0.11$ and $q_{\text{Nt}} = -0.08$ are counterbalanced by the positive charge on the middle nitrogen $q_{\text{Nm}} = +0.18$, in the TS geometry the partial charges of both nitrogen atoms, $q_{\text{Nt}} = 0.02$ and $q_{\text{Nm}} = 0.06$, merge nearly to zero (approaching obviously the nitrogen charges in the N₂ molecule). The negative charge $q = -0.50$ accumulated on the antibonding LUMO of the oxygen moiety leads to weakening of the N₂–O bond, favoring the formation of an incipient peroxy molecule (vide infra). The overall charge transfer from $\text{O}^{2-}_{(\text{surf})}$ to N₂O equals to -0.42 for MgO, -0.51 (CaO), and -0.58 (SrO), following the order of their Lewis (optical) basicity (namely, 0.68, 0.97, and 1.14 from MgO, CaO, and

SrO, respectively).⁵⁹ Stabilization energies of the resultant peroxy groups on different oxides are collected in Table 2.

A deeper understanding of the molecular nature of the TS can be inferred from the analysis of the N₂O frontier orbitals (FMO) in relation to DOS structure of AEO. Interaction of the degenerate 2π , 3π in-plane ($\parallel$) and out-of-plane ($\perp$) pairs of N₂O with the corresponding $2p_z$ and $2p_x$ orbitals of the $\text{O}^{2-}_{(\text{surf})}$ active sites on the MgO can be taken as an illustration (Figure 4a–d).

The dramatic modification of the N₂O FMO upon bending to 156° is shown in Figure 4a, whereas the interaction energetics with the catalysts are epitomized in Figure 4b. As can be inferred from Figure 4d the empty $3a''$ ($\perp$) orbital plays a spectator role for the transition state, whereas the $10a'$ ($\parallel$) orbital interacts strongly with the surface $\text{O}2p_z$ orbitals in the σ -type bonding (blue levels in panel b) and antibonding (red levels) fashion. Among the HOMO levels of N₂O the $2a''$ ($\perp$) orbital is involved in a weaker π -type overlap with the surface $\text{O}2p_x$ (Figure 4d). The splitting between the bonding and antibonding levels in this case is much smaller than for the corresponding σ overlap (Figure 4b). This is in contrast to the TS of N₂O on the SrO surface, where the π interaction splitting dominates the σ one (Figure S4, Supporting Information). Such behavior is caused by the higher bending of N₂O in the TS configuration 134° , which gives rise to augmentation of the oxygen lobe of the $2a''$ orbital, beneficial for enhancement of the π overlap.

Peroxy Surface Diffusion. As implied by Figure 3 the peroxy group can either diffuse on the surface eventually recombining upon encounter along the Langmuir–Hinshel-

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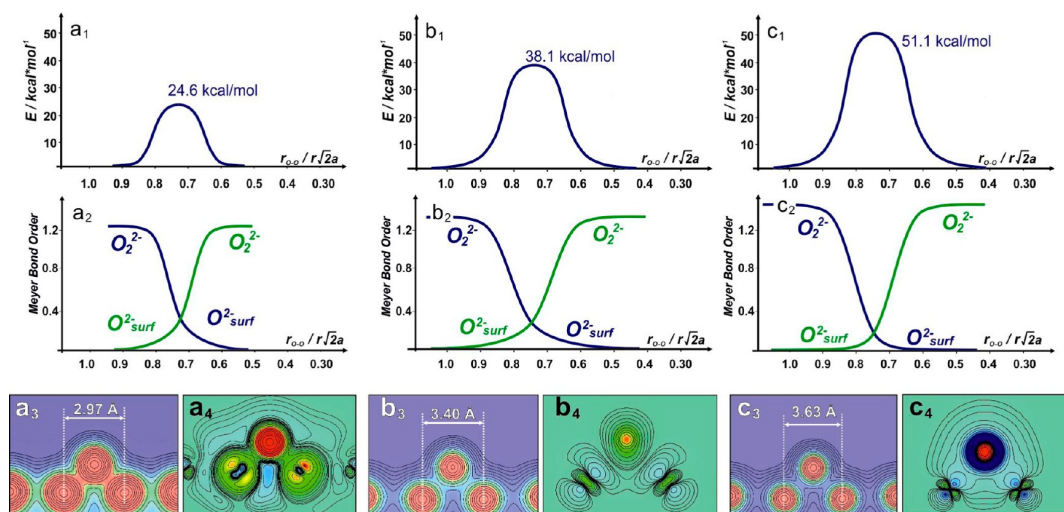


Figure 5. Energetic profile (a₁–c₁), evolution of the bond orders (a₂–c₂), charge density distribution (a₃–c₃), and differential electron density maps of the transition state of oxygen diffusion over MgO (a), CaO (b), and SrO (c).

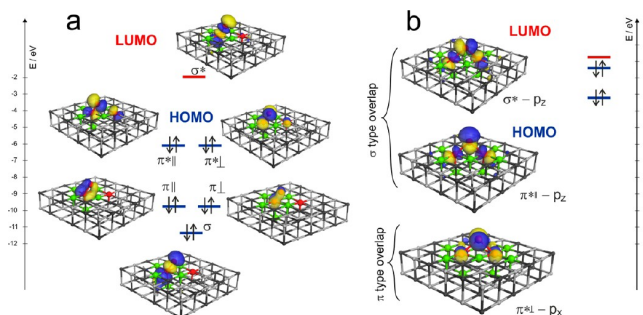


Figure 6. Frontier molecular orbital diagram for surface peroxy group (a) and for oxygen diffusion TS geometry (b) on MgO.

wood route (LH) or in the Eley–Rideal route (ER) be attacked by another gas-phase N_2O molecule to yield N_2 and O_2 molecules and restore the $O_2^{2-}(\text{surf})$ active site. Evolution of the energy, bond orders, and the electron density distribution in the transition state for surface diffusion of the peroxy species is shown in Figure 5, whereas the most important parameters characterizing the stable peroxy ion are collected in Table 2. The transition state energies for the surface diffusion on MgO, CaO, and SrO were found to be 24.6, 38.1, and 51.1 kcal/mol, respectively (Figure 5 a₁–c₁, note that the values on the abscissa axis are expressed in units of lattice constant divided by $\sqrt{2}$). The increase of the energetic barrier can be rationalized simply by the gradually increasing distance between adjacent surface ions $O_2^{2-}(\text{surf})$ – $O_2^{2-}(\text{surf})$ in comparison to the O–O separation in the peroxy group (see Table 2). The distances between the diffusing O atom and the surface $O_2^{2-}(\text{surf})$ anion (r_{O-O}) in the transition state are equal to 2.14, 2.51, and 2.69 Å for the MgO, CaO, and SrO, respectively, indicating that the TS configuration for oxygen diffusion can be reached only when the overwhelming part of the initial O– $O_2^{2-}(\text{surf})$ bond is already lost (the Mayer bond order decreases by 80%, 90%, and

95% at TS for MgO, CaO, and SrO), whereas the final one is still in its incipient state (Figure 5 a₂–c₂).

The charge density distribution (Figure 5 a₃–c₃) and the differential electron density maps of the transition state for MgO, CaO, and SrO (Figure 5 a₄–c₄) reveal nicely differences in the electronic nature of the TS caused by the increasing cationic radius. Whereas in the case of MgO the transition state resembles the ozone-like structure with clear accumulation of the electron density between the itinerant oxygen and the $O_2^{2-}(\text{surf})$ ions (Figure 5 a₃–a₄), for CaO, and more clearly for SrO, in the transition state configuration the itinerant oxygen is only loosely associated with the $O_2^{2-}(\text{surf})$ ions, assuming an adatom-like state (Figure 5 b₃, b₄ and c₃, c₄).

The key molecular orbitals and the corresponding energy levels for surface peroxy intermediate, and their involvement in the formation of the transition state, are shown in Figure 6a for the MgO(100) surface. In agreement with previous calculations³² the $O_2^{2-}(\text{surf})$ group is tilted (21.5° from the normal direction of the (100) plane) toward the adjacent $O_2^{2-}(\text{surf})$ anion, and the relatively long peroxy bond of 1.54 Å results from the following electronic configuration: $\sigma^2(\pi_L, \pi||)^4(\pi^*L, \pi^*L, \pi^*L, \pi^*L)^4$.

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423 $\pi^*||\rangle^4$ with the full occupation of both π antibonding orbitals.
 424 In the case of the most basic SrO surface the tilting of the
 425 corresponding peroxy group is suppressed due to the distal
 426 position of the adjacent Sr^{2+} cations (Figure S5 in Supporting
 427 Information).

428 The O–O stretching frequencies of 828, 854, and 867 cm^{-1}
 429 for MgO, CaO, and SrO reveal the corresponding increase of
 430 the peroxy bond strength. Indeed, the straight configuration of
 431 the peroxy intermediate on the SrO surface is more beneficial
 432 for the orbital overlapping in comparison to the tilted one
 433 observed on MgO. The most striking feature of the surface
 434 peroxy intermediates is, however, a dramatic difference in the
 435 stabilization energies increasing from 27.1 for MgO to 65.4
 436 kcal/mol for SrO, caused by the increased bond order within
 437 the peroxy group and decreased Pauli repulsion with the
 438 adjacent $\text{O}^{2-}_{(\text{surf})}$ anions. This fact plays a decisive role for the
 439 deN_2O kinetics (vide infra).

440 In the FMO picture, shown in Figure 6b, the transition state
 441 for diffusion is produced by the antibonding σ -type overlap of
 442 the $\sigma^*(\text{O}_2^{2-})-\text{p}_z(\text{O}^{2-}_{(\text{surf})})$ and $\pi^*||(\text{O}_2^{2-})-\text{p}_z(\text{O}^{2-}_{(\text{surf})})$ in-
 443 plane orbitals, giving rise to LUMO and HOMO, and π -type
 444 overlap $\pi^*\perp(\text{O}_2^{2-})-\text{p}_x(\text{O}^{2-}_{(\text{surf})})$ of the out-of-plane orbitals
 445 (HOMO-1).

446 To quantify the surface peroxy transport, assuming
 447 homogeneous distribution of the O_2^{2-} species we calculated
 448 the diffusion coefficients (D) for a series of AEOs using the
 449 Einstein–Smoluchowski⁶⁰ random walk model

$$D = \frac{k_B T}{h} \frac{n l^2}{2d} \exp\left(\frac{-\Delta G_a}{k_B T}\right) \quad (9)$$

450 where n defines the number of nearest-neighbor sites; d is the
 451 dimensionality of the motion; l denotes the distance between
 452 adjacent sites; and ΔG_a is the Gibbs free energy of activation for
 453 the elementary jump. For MgO at $T_{50\%} = 600\text{ °C}$ the diffusion
 454 coefficient equals to $1.4 \times 10^{-12}\text{ m}^2\cdot\text{s}^{-1}$, and the related
 455 hopping frequency is $1.58 \times 10^7\text{ s}^{-1}$, which indicates high
 456 mobility of the peroxy groups. The corresponding parameters
 457 dramatically decrease to $7.60 \times 10^{-18}\text{ m}^2\cdot\text{s}^{-1}$ and $6.58 \times 10^1\text{ s}^{-1}$,
 458 for CaO and to $3.06 \times 10^{-20}\text{ m}^2\cdot\text{s}^{-1}$ and $2.33 \times 10^{-1}\text{ s}^{-1}$ for
 459 SrO.

460 The calculated diffusion coefficients normalized to the AEO
 461 lattice constants (hopping frequencies) are presented in Figure
 462 7 as a function of temperature. The solid lines superimposed on
 463 the 3D-plot correspond to the activation free enthalpies of the

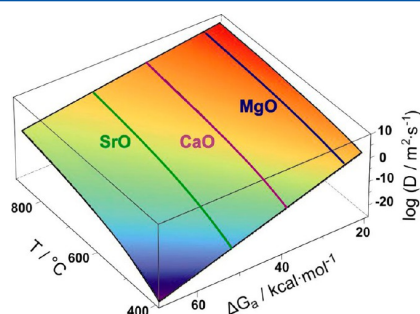


Figure 7. Surface diffusion coefficients D of peroxy species as a function of Gibbs free energy of activation (ΔG_a) and temperature (T) presented in the logarithmic scale.

peroxy group diffusion on the MgO, CaO, and SrO surfaces, 465
 showing that on MgO the O_2^{2-} intermediates are mobile, 466
 whereas on SrO they are quite immobilized in most of the 467
 temperature range of the deN_2O reaction. 468

O–O Bond-Making Step: Recombination of Surface Oxygen Intermediates. 469

As implied by Figure 3 the LH route 470
 may occur through the static (SR) or dynamic (DR) 471
 recombination of the intermediate oxygen species, which 472
 regenerate the $\text{O}^{2-}_{(\text{surf})}$ active sites enclosing the catalytic 473
 cycle. Whereas for $\Theta \ll 1$ surface diffusion is a necessary step 474
 for recombination of the peroxy group, in the case of $\Theta \rightarrow 1$ 475
 the adjacent peroxy groups may recombine without any 476
 preceding displacement. Therefore, we distinguished the static 477
 (without diffusion) and dynamic (with diffusion) recombina- 478
 tion regimes, which to large extent are controlled by the lattice 479
 constant of AEO. The LH route is favored by the low activation 480
 energy for the diffusion of the surface oxygen,^{18,61} whereas the 481
 alternative ER route, discussed below, is preferable at high 482
 activation barrier for diffusion (immobile intermediates), high 483
 coverage by O_2^{2-} , and high partial pressure of N_2O .^{11,41} 484

For modeling of the LH recombination, the distance between 485
 the oxygen atom in the N_2O molecule and the terminal oxygen 486
 in the surface peroxy group was used as a reaction coordinate. 487
 The encounter of two O_2^{2-} groups gives rise to formation of an 488
 incipient O–O bond, with the transition states located at 18.9, 489
 39.3, and 56.1 kcal/mol for MgO, CaO, and SrO, respectively. 490
 In the asymmetric TS geometry with the $\text{O}^{2-}_{(\text{surf})}-\text{O}-\text{O}$ and 491
 $\text{O}-\text{O}-\text{O}^{2-}_{(\text{surf})}$ angles ranging from 85° to 102° and 135° to 492
 129° for the series of the investigated AEO (Figure S6 in the 493
 Supporting Information), the shorter $\text{O}^{2-}_{(\text{surf})}-\text{O}$ bond changes 494
 from 1.55 Å (MgO) to 1.47 Å (SrO) and the longer one from 495
 2.02 Å (MgO) to 2.37 Å (SrO). The O–O bond length of the 496
 nascent dioxygen molecule equals to 1.88 Å (MgO) and 1.85 Å 497
 (CaO and SrO), being evidently less affected by the nature of 498
 the AEO surface. The frontier molecular orbitals associated 499
 with the transition state are shown in Figure 8, taking MgO as 500 88

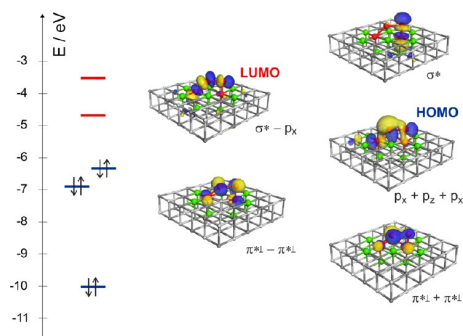


Figure 8. Frontier molecular orbital diagram of the transition state for recombination of peroxy intermediates along the Langmuir–Hinshelwood pathway on the MgO surface.

an example. The overlap of the out-of-plane $\pi^*\perp(\text{O}_2^{2-})$ orbitals 501
 of the two adjacent peroxy groups gives rise to HOMO-1 502
 (antibonding combination) and HOMO-2 (bonding combina- 503
 tion). In turn, the overlap of the in-plane orbitals leads to 504
 HOMO and LUMO, whereas LUMO+1 is essentially confined 505
 to σ^* MO of one of the two peroxy groups. 506

Table 3. Energetic Barriers Calculated for deN_2O Elementary Steps over Alkaline Earth Oxides

all energies/kcal/mol	MgO ($T = 600\text{ }^{\circ}\text{C}$)		CaO ($T = 450\text{ }^{\circ}\text{C}$)		SrO ($T = 530\text{ }^{\circ}\text{C}$)	
	ΔE_a	$\Delta G_{(0 \rightarrow T)}$	ΔE_a	$\Delta G_{(0 \rightarrow T)}$	ΔE_a	$\Delta G_{(0 \rightarrow T)}$
oxygen atom transfer (OAT)	31.8	25.3	24.6	24.11	20.1	33.12
O_2^{2-} diffusion (SD)	24.6	-1.27	38.1	-0.66	51.1	-0.77
Langmuir–Hinshelwood (LH) O_2^{2-} recombination	18.9	-1.47	39.3	-1.70	56.1	-1.88
O_2 readsorption	75.6	33.15	61.3	24.54	42.8	28.21
Eley–Rideal (ER) recombination	34.8	24.48	31.2	21.59	26.9	26.43

507 In the ER route the approach of the N_2O molecule toward
 508 the peroxy group leads to highly energetic, concerted cleavage
 509 of the N_2 –O bond and concomitant formation of the O–
 510 O_2^{2-} (surf) bond. In the case of the MgO surface significant
 511 distortion of the peroxy group in the TS state consists of an
 512 elongation of the N_2 –O (from 1.14 to about 1.49 Å) and O–
 513 O_2^{2-} (surf) (from 1.54 to 2.04 Å) bonds and formation of the
 514 N_2O –peroxy bond with the length of 1.43 Å (corresponding to
 515 the O–O distance in the nascent dioxygen). For CaO and SrO
 516 the analogous bond distances change from 1.14 to 1.57 and
 517 1.69 Å (N_2 –O), from 1.51 to 2.09 Å, and from 1.52 to 1.92 Å
 518 (O– O_2^{2-} (surf)), whereas the N_2O –peroxy bond lengths are
 519 equal to 1.69 and 1.71 Å, respectively. The bending of the N–
 520 N–O is about 155° in each case. As discussed for the OAT step
 521 such deformation facilitates the charge transfer from the peroxy
 522 group to the N_2O molecule. The resultant energetic barrier
 523 decreases in the following order: 34.8 kcal/mol (MgO), 31.2
 524 kcal/mol (CaO), and 26.9 kcal/mol (SrO).
 525 **Energetic Barriers.** The calculated activation energies of all
 526 the key steps of the deN_2O reaction on the AEO (100) surfaces
 527 are summarized in Table 3. Those values are complemented by the
 528 entropic contribution, and the values calculated for the
 529 temperature of 50% conversion are shown as an example.
 530 Inspection of the data collected in Table 3 reveals that the free
 531 enthalpy of activation, ΔG_a , of the oxygen transfer and the ER
 532 recombination steps significantly increases with the reaction
 533 temperature, leading to thermal self-hindrance of these steps.
 534 This effect is related with the high negative entropy
 535 contribution due to the loss of translational and rotational
 536 degrees of freedom upon N_2O adsorption. In contrast, the
 537 transition states associated with the surface diffusion and the
 538 LH recombination steps resemble the structure of the
 539 substrates, and therefore the corresponding entropic terms
 540 are much smaller and positive. As a result, both thermal
 541 contributions to activation free enthalpies $\Delta G_{(0 \rightarrow T)}$ exhibit
 542 rather weak temperature dependence.
 543 Molecular modeling of the energetics of some of the
 544 elementary steps of N_2O decomposition over AEO surfaces
 545 has been carried out by other researchers. Most of the papers,
 546 however, were confined to magnesium oxide, and the activation
 547 energies of the OAT step ranging from 31.6 to 37.4 kcal/
 548 mol^{10,18,11,62} and for oxygen diffusion from 24.6 to 27.7 kcal/
 549 mol^{18,62} have been reported. For the LH recombination step
 550 calculations of Karlsen et al. give $\Delta E_a = 19.6$ kcal/mol, in nice
 551 agreement with our results, showing that the value of $E_a = 25.8$
 552 kcal/mol obtained by Scagnelli et al. is apparently exagger-
 553 ated.^{11,62} In the case of nitrous oxide decomposition over CaO,
 554 the oxygen atom transfer step has been addressed in a few
 555 papers,^{10,11,63} and the activation energies varying from 19.4 to
 556 27.7 kcal/mol have been calculated. The upper values that are
 557 consistent with our results seem to be more reliable. In turn,
 558 the reported energetic barrier of 39.0 kcal/mol for the LH
 559 step¹¹ remains in excellent agreement with our data. For

strontium oxide among the previously obtained activation
 energies of the AOT (19.7 kcal/mol) and ER (25.9 kcal/mol)
 steps¹¹ both remain again in an excellent agreement with our
 result.

Microkinetic Modeling. In the previous article on N_2O
 decomposition²⁰ we have modeled the LH route as a sequence
 of the elementary steps of the surface peroxy diffusion and
 recombination. For very fast diffusion (MgO) and low
 coverages a conventional mean field kinetic approach ($r_{LH} =$
 $k\Theta^2$) is fully adequate. However, in the case of slow diffusion
 and high coverages ($0.6 < \Theta \rightarrow 1$), when most of the peroxy
 groups occupy adjacent sites and a discrete nature of the AEO
 surface becomes apparent, the overall reaction rate is
 progressively controlled by the static recombination.

To address the kinetics of these processes in an explicit way,
 uncorrelated jumps of the peroxy intermediates on the surface
 covered stochastically by O_2^{2-} were modeled by Monte Carlo
 simulations to determine functional dependence of the average
 number of diffusion hops, $\langle n \rangle$, leading to the peroxy groups
 encounter on Θ . During the MC simulations, the coverage-
 dependent probability of the surface site to be occupied was
 corrected by the correlation coefficient accounting for the
 mutual interaction between the O_2^{2-} species, derived from the
 DFT calculations (see Supporting Information). The number
 of the required jumps, n , was derived from the random walk
 model on the square lattice using the Einstein–Smoluchowski
 equation, $\langle r^2 \rangle = nl^2$, where r is the Cartesian distance between
 the nearest peroxy species and l is the lattice constant, hence n
 $= (\langle r^2 \rangle / l^2)$. Next, following Allen et al.,⁶⁴ the catalyst surface
 was divided into the equal virtual squares in such a way that on
 average two O_2^{2-} species are present in each square. In such a
 case, $\Theta = 2/M$, and the surface of a square equals $M \cdot l^2$, where
 M stands for the total number of active sites in the square. The
 time at which in each virtual square a molecule of dioxygen is
 produced via the LH route (resulting from diffusion and
 reaction events) can be expressed as

$$\tau_{LH} = \langle n \rangle \tau_d + \frac{\tau_2}{P_1(\Theta, z) \cdot P_2(\tau_2, \tau_d)} \quad (10)$$

In eq 10 the first term accounts for the time of an elementary
 diffusion jump, τ_d , multiplied by the mean number of hops, $\langle n \rangle$,
 needed for a peroxy pair formation. In the second term $P_1(\Theta, z)$
 is the geometrical probability of recombination, $P_1(\Theta, z) = ((z$
 $- 1)\Theta + 1/z)$ (for the square lattice $z = 4$), whereas $P_2(\tau_2, \tau_d) =$
 $1 - \exp(-\tau_d/\tau_2)$ describes the probability of transfer from the
 diffusion to the recombination state used in kinetic MC
 simulations,⁶⁵ and τ_2 is the mean time of the recombination
 event. Taking into account that in each virtual square one O_2
 molecule is produced, by definition the LH reaction rate can be
 expressed as $r_{LH} = 1 \cdot (O_2 \text{ molecule}) / (\tau_{LH} \cdot M \cdot l^2)$. Noting that $1/$
 $M = \Theta/2$ we get the following final equation for the LH
 recombination rate r_{LH}

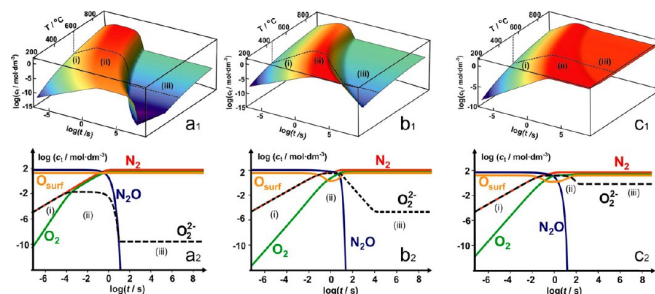


Figure 9. Two-dimensional plots showing evolution of surface coverage (by O₂²⁻ ions) as a function of the elapsing time, t , and the reaction temperature, T , for MgO (a₁), CaO (b₁), and SrO (c₁), together with the log–log plot of species concentration as a function of time at $T_{50\%}$ for MgO (a₂), CaO (b₂), and SrO (c₂). The plots a₂–c₂ correspond to the cross sections indicated by dotted lines in the a₁–c₁ plots.

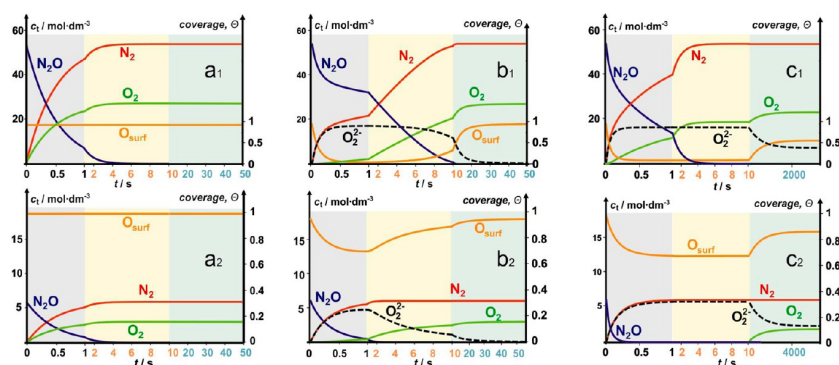


Figure 10. Time-resolved simulations. Evolution of reaction species for N₂O-rich conditions (a₁–c₁) and N₂O-lean conditions (a₂–c₂) at $T_{50\%}$. Please note three different time scales distinguished by gray, yellow, and pale green shadings.

$$r_{\text{LH}} = \frac{\Theta}{2 \left(\langle n \rangle \tau_d + \frac{\tau_2}{P_1(\Theta, z) \cdot P_2(\tau_2, \tau_d)} \right)} \quad (11)$$

This approach allows us to treat the diffusion and recombination steps in an equivalent way, yet being controlled by the average number of jumps and geometrical probability factor, which are functions of the coverage. Expressing τ_2 and τ_d as $1/k_2$ and $1/k_d$, respectively, and taking into account that $\langle n \rangle \sim 1/\Theta$ and $(2/M = \Theta)$, for the fast recombination limit ($k_d \ll k_2$) eq 11 converges to the diffusion-controlled form $r_{\text{LH}} \rightarrow (k_d/M) \Theta^2$. In the case of fast diffusion ($k_d \gg k_2$), it converges in turn to $r_{\text{LH}} \rightarrow (1/M) P_1(\Theta)^{-1} P_2(\tau_2, \tau_d)^{-1} \tau_2$ and hence $r_{\text{LH}} = k_2 \Theta^2$. On the basis of the above discussion we propose the following kinetic equations for the relevant elementary steps

AOT (N₂O dissociation)

$$r_1 = k_1 \frac{p_{\text{N}_2\text{O}}}{p^0} (1 - \Theta) \quad (12)$$

LH recombination

$$r_2 = \frac{\Theta}{2 \left(\frac{\langle n \rangle}{k_d} + \frac{1}{P_1(\Theta, z) P_2(k_2, k_d) k_2} \right)} \quad (13)$$

O₂ readsorption

$$r_3 = k_3 \frac{p_{\text{O}_2}}{p^0} (1 - \Theta) \quad (14)$$

ER recombination

$$r_4 = k_4 \frac{p_{\text{N}_2\text{O}}}{p^0} \Theta \quad (15)$$

Pulse Reactor: Transient Kinetics. For the ab initio microkinetic modeling all the necessary kinetic data were calculated by DFT, and no fitting was used for comparison with experiment. The set of the operational parameters chosen for modeling was based on the literature data for the TAP reactor.^{66,67} The parameters and units used in the simulations are collected in Table S1 (Supporting Information). The results of the microkinetic simulations for the pulse reactor are shown in Figure 9.

Since we are focused on the surface dynamics of the O₂²⁻ intermediates we present two-dimensional plots (Figure 9 a₁–c₁), showing the evolution of the surface coverage (by peroxy ions) as a function of the elapsing time, t , and the reaction temperature, T , for each oxide. The cross sections (corresponding to arbitrary, yet representative, 50% conversion temperature, 600 °C, 450 °C, and 530 °C, for MgO, CaO, and SrO, respectively) presented in the logarithmic scale (Figure 9 a₂–c₂) illustrate the evolution of all deN₂O species.

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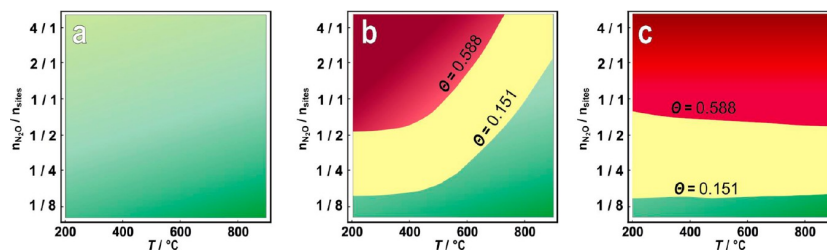


Figure 11. Two-dimensional plot presenting temporal steady state Θ value as a function of temperature and $n_{\text{N}_2\text{O}}/n_{\text{sites}}$ ratio for MgO (a), CaO (b), and SrO (c).

For all studied oxides the surface coverage presented as a function of time and temperature has similar shape, where three regions can be distinguished (Figure 9 a₂–c₂). In the first region (noted as (i)) the transient stage of an incipient increase of the coverage is observed, while changes in the O_2^{2-} and N_2 concentrations are concerted in accordance with the kinetics of the OAT step. Since at the initial stage of the reaction the surface coverage is very small, the formation of O_2 following the LH step is delayed in comparison to OAT. In the second region, (ii), a plateau of maximum surface O_2^{2-} coverage can be attributed to a temporal steady state situation, in which the peroxy groups production (via OAT) and decay (via LH and ER) have the same rate. The third region, (iii), appearing after depletion of the last portion of N_2O , is defined by the ability of the given oxide to recombine the peroxy ions into O_2 and its readsorption rate. The temperature dependence of the coverage (Figure 9 a₁–c₁) is generally similar in each case. For higher temperatures the maximum coverage in the region (ii) is reached in shorter time, and the equilibrium coverage in the region (iii) is higher (readsorption rate increases faster with the temperature than recombination).

The results collated in Figure 9 are redrawn for temperature $T_{50\%}$ in Figure 10 a₁–c₁ using a linear scale for N_2O -rich conditions ($n_{\text{N}_2\text{O}}/n_{\text{sites}} = 3/1$) and in Figure 10 a₂–c₂ for N_2O -lean conditions ($n_{\text{N}_2\text{O}}/n_{\text{sites}} = 1/3$). Such representation emphasizes kinetic data for the experimentally accessible time and concentration ranges, providing better insight into the evolution of the concentration profiles of the reactants and intermediates. From Figure 10 we can infer that the deN_2O reaction course over MgO is distinctly different in comparison to CaO and SrO. For MgO the surface coverage by O_2^{2-} is virtually infinitesimal throughout the reaction (see the straight orange lines of constant $\text{O}_2^{2-}(\text{surf})$ concentration in Figure 10 a₁, a₂). Oxygen is produced simultaneously with nitrogen with the stoichiometric ratio, and the full conversion is reached fast (after about 4 s) for both investigated $n_{\text{N}_2\text{O}}/n_{\text{sites}}$ values. Such behavior is characteristic of a bare surface kinetics.²⁰

In the case of calcium and strontium oxides different catalyst performance can be observed. In the rich N_2O regime in the first second of reaction time, N_2O is decomposed rapidly into N_2 and the peroxy intermediate until nearly full surface coverage is reached (after ~0.4 and ~0.1 s for CaO and SrO, respectively). Then the decomposition rate is reduced (due to decreased number of the free active sites), and the reaction moves into the region of nearly equal rates of the peroxy production and recombination, giving rise to the temporal steady concentration of the surface O_2^{2-} species. This behavior is clearly seen in the middle region in Figure 10 b₁ and c₁ (black dotted line). In this region we observe slow production of

oxygen shifted toward longer time in comparison to MgO, consistent with experimental transient deN_2O studies, where simultaneous production of O_2 and N_2 over MgO ⁶⁸ and a delay in the oxygen evolution for CaO were observed. The temporal steady state period decays when the pulsed nitrous oxide is decomposed completely (after 10 and 4 s for CaO and SrO, respectively). The last stage of the transient reaction consists of recombination of the peroxy ions, competing with the O_2 readsorption. The temporal steady state is reached after ca. 50 s in the case of calcium oxide and is extended dramatically until 2000 s for strontium oxide (Figure 10 b₁, c₁).

The kinetic situation is somehow different in the lean N_2O conditions. Initial fast decomposition of N_2O is no longer hindered by blocking of all the active sites since there are not enough pulsed N_2O molecules to fully cover the surface with the peroxy groups. Nitrous oxide is entirely decomposed after about 2, 1, and 0.3 s for MgO, CaO, and SrO, respectively. A full possible surface coverage (~0.3) is reached very fast (~1 s for CaO and 0.7–0.8 s for SrO). In the next few seconds (2–10 s) the different behavior of CaO and SrO becomes more apparent. For the calcium oxide catalyst a steady decrease of the surface coverage by O_2^{2-} (via the LH route) takes place, and after about 10 s the surface is cleared by 80%. However, the final $\text{O}_2^{2-}(\text{surf}) + \text{O}_2^{2-}(\text{surf}) \rightleftharpoons 2\text{O}_2^{2-}(\text{surf}) + \text{O}_2(\text{g})$ equilibrium is not reached in the assumed time scale (Figure 10 b₂). Inspection of Figure 10 b₂ reveals that this process occurs after 3000 s. On SrO the slow recombination leads in the first ten seconds to stable coverage (Figure 10 c₂), in contrast to CaO. However, slow recombination (coverage reduction and O_2 production) can be observed at a much longer time scale (green shadowed region in Figure 10 c₂). After 4000 s the O_2^{2-} recombination and O_2 readsorption processes have the equal rates. It is worth noting that in lean conditions the amount of produced dioxygen is about ten times smaller than in rich conditions, leading to the smaller final coverage $\Theta = 0.16$, than in the reach conditions characterized by $\Theta = 0.4$.

Static versus Dynamic Recombination. The discussion presented in the previous section does not answer explicitly which kind of recombination mechanism (static or dynamic) actually takes place for a given AEO oxide. We resolved this problem by means of MC simulations, calculating an average local site occupation (the number of adjacent sites occupied by O_2^{2-}) for a selected peroxy group as a function of coverage (the data averaging was performed for 10^6 simulations). The elementary occupation probabilities were generated in the same way as for calculating the 1-norm distance (see Supporting Information). For the average local site occupation higher than 3.9, the occupation vs log Θ curve flattens (see the turning point in Figure S7b, Supporting Information). This

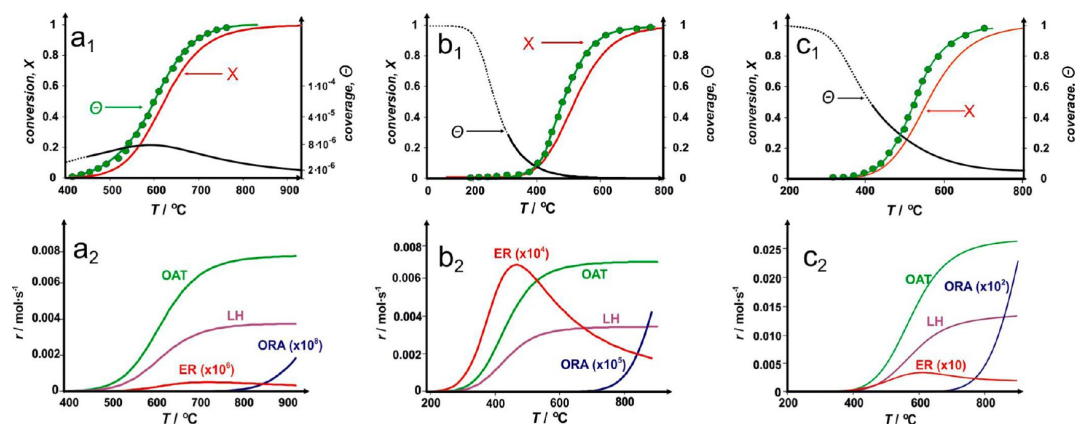


Figure 12. Comparison of the calculated and experimental steady state conversions for various temperatures for the 0.1 g of MgO catalyst with surface area of $72.4 \text{ m}^2 \text{ g}^{-1}$ and the flow rate of $30 \text{ cm}^3 \text{ min}^{-1}$ (5% $\text{N}_2\text{O}/\text{He}$) (a) and specific rates for all elementary reactions steps (b).

implies that for the surface coverages corresponding to the local site occupation range from 3.9 to 4 the diffusion step is needless since the peroxide ions practically occupy all the neighboring sites in the square lattice of AEO (static recombination region). On the other hand, when the average occupation is lower than 1, on average $\langle m \rangle$ jumps of the intermediate O_2^{2-} are needed for O_2 production (dynamic recombination region). Thus, between the average occupations of 3.9 and 1 a mixed recombination region occurs, and the values of the corresponding threshold coverages were found to be $\Theta_{3.9} = 0.588$ and $\Theta_1 = 0.151$, respectively. In Figure 11 we plotted the temporal steady state Θ values (see region (ii) in Figure 9 a₁–c₁) as a function of the reaction temperature and the $n_{\text{N}_2\text{O}}/n_{\text{Sites}}$ ratio for MgO (a), CaO (b), and SrO (c). The threshold $\Theta_{3.9}(T, n_{\text{N}_2\text{O}}/n_{\text{Sites}}) = 0.588$ and $\Theta_1(T, n_{\text{N}_2\text{O}}/n_{\text{Sites}}) = 0.151$ values define three regions shown in Figure 11 in green, yellow and red. In the first region ($\Theta \geq 0.588$, red area) all the adjacent sites are practically occupied, so the static recombination scheme is valid. For the $\Theta \leq 0.151$ (green area) the distance between two peroxy intermediates is too large, and for their encountering surface diffusion is necessary. In the region $0.17 < \Theta < 0.588$ (yellow area) two mechanisms operate simultaneously.

Flow Reactor: Steady State Kinetics. In the flow reactor kinetics when the steady state is reached, the surface coverage, Θ , of the adsorbed peroxy species is constant; therefore, the production (AOT, r_1 , and O_2 readsorption, $2 \cdot r_3$) and consumption (LH, $2 \cdot r_2$, and ER, r_4) rates of the peroxy species are equal

$$r_1 + 2r_3 = 2r_2 + r_4 \quad (16)$$

The observed overall rate of the N_2O decomposition, r^{obs} , is given by the sum of the rates of the elementary reactions r_1 and r_4

$$r^{\text{obs}} = r_1 + r_4 \quad (17)$$

The r^{obs} rate can be next associated with the observed N_2O conversion in the microreactor with a quasi-ideal mixing and with the rates of the elementary steps (AOT and ER) consuming nitrous oxide.²⁰

$$r^{\text{obs}} = \frac{p_{\text{N}_2\text{O}}^0 F}{m_{\text{cat}} S \rho} X = r_1 + r_4 \quad (18)$$

where m_{cat} is the mass of the catalyst; S is specific surface area; ρ is the concentration of active sites; and F is the gas flow. Using the calculated dependence of $k^{\text{obs}}_{\text{(theo)}}$ on temperature the theoretical Arrhenius plot (Figure 2) allows for derivation of the theoretical apparent activation energies summarized in Table 1, which remain in nice agreement with the corresponding experimental values.

Equation 18 allows for modeling of the temperature dependence of the N_2O conversion on the reaction rate constants of all elementary steps linked by $\Theta(k_1, k_2, k_3, k_4)$. From the DFT calculated values of the activation enthalpies the theoretical kinetic curve can be obtained without any fitting. In Figure 12 a₁–c₁ typical TPSR data for all oxides are presented (green line fitted to experimental points) together with theoretically predicted conversions (red line). A remarkable agreement between the experiment and theory confirms the adequacy of the microkinetic model, as well as the applied DFT machinery. Once the correct model is established, an in-depth insight into the variation of the individual kinetic parameters, surface coverages (Figure 12 a–c₁, Θ curve), and the mechanistic role of minor ER and ORA pathways (Figure 12 b₁–c₁), which are hardly accessible from the experiment, is made possible.

In the case of MgO, the contribution of the ER step to overall turnover is negligible (6 orders of magnitude lower than the LH step) in the whole range of temperatures, and the catalyst surface remains essentially bare during the whole reaction. Similarly, the readsorption of oxygen, with even lower share in the total N_2O conversion, can also be abandoned.

For more basic CaO and SrO oxides, kinetic relevance of the elementary steps is somewhat different. At low temperatures (<400 °C) the expected surface coverages are high, yet due to the hindrance of the first step (OAT) the achievement of this limit is severely delayed and in the conventional TPSR experiment can not be observed (this is why it is indicated by the broken line in Figure 12 a₁–c₁). Increasing of the temperature leads, together with conversion increase, to

enhancing of the O_2^{2-} recombination and the ensuing reduction of the surface coverage. Analysis of the rates of the elementary steps reveals that similarly to MgO the OAT and LH steps are the most relevant in the deN_2O kinetics on CaO and SrO, but the rate-determining step is shifted to LH. The ER step that depends on both the surface peroxy and N_2O concentrations at higher temperatures (where it would play some kinetic role) is quenched since at such conditions the CaO and to a less extent SrO surfaces are becoming O_2^{2-} depleted due to their enhanced recombination (Figure 12).

CONCLUSIONS

The microkinetic model of the catalytic decomposition of N_2O on alkali earth oxide nanocrystals was developed, based on comprehensive mechanistic and microkinetic studies by joined DFT calculations and catalytic measurements. All elementary steps, reaction intermediates, and transition state geometries were ascertained and discussed thoroughly in terms of the frontier molecular orbital picture. It is shown that surface oxygen ions $\text{O}^{2-}_{(\text{surf})}$ play the role of the anionic redox active centers, constituting a $\text{O}^{2-}_{(\text{surf})} \leftrightarrow \text{O}_{2(\text{surf})}^{2-}$ redox couple, the strength of which is gauged by the lattice constant of the alkaline earth oxide. The dynamics of the elementary steps over the most stable (100) surfaces was analyzed in terms of the free energy profiles. The calculated free enthalpies together with the harmonic transition state theory were used for ab initio modeling of the kinetic parameters of the individual reaction steps. The kinetically relevant steps of the reaction for all oxides include a dissociative activation of N_2O via oxygen atom transfer and a Langmuir–Hinshelwood recombination of peroxy intermediates, whereas the Eley–Rideal and oxygen readsorption pathways play a negligible role. The static (without surface diffusion) and dynamic (with surface diffusion) recombination steps were identified, and their relative relevance in overall mechanism was determined as a function of temperature and the $n_{\text{N}_2\text{O}}/n_{\text{active sites}}$ ratio. On the basis of obtained results a complete molecular level mechanistic description of the deN_2O reaction and the resultant quantitative microkinetic scheme were developed. The proposed model reproduces the results of temperature programmed and steady state catalytic deN_2O experiments with high accuracy.

ASSOCIATED CONTENT

Supporting Information

Monte Carlo modeling details, Figures S1–S7, and Table S1. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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2. Oświadczenie mgra Amira A. Ahmada Zebariego o jego roli w powstaniu pracy **H7**;
3. Oświadczenie dra Janusza Budziocha o jego roli w powstaniu pracy **H5**;
4. Oświadczenie prof. Sylvaina Cristola o jego roli w powstaniu prac **H1, H3 i H4**;
5. Oświadczenie prof. dra hab. Piotra Cyganika o jego roli w powstaniu pracy **H5**;
6. Oświadczenie prof. Olivera Diwalda o jego roli w powstaniu pracy **H8**;
7. Oświadczenie dra Szymona Godlewskiego o jego roli w powstaniu prac **H5, H6 i H7**;
8. Oświadczenie mgr Joanny Gryboś o jej roli w powstaniu prac **H3 i H4**;
9. Oświadczenie mgra Marka Kolmera o jego roli w powstaniu pracy **H7**;
10. Oświadczenie dra hab. Andrzeja Kotarby, prof. UJ, o jego roli w powstaniu prac **H1, H2 i H8**;
11. Oświadczenie prof. zw. dra hab. inż. Krzysztofa J. Kurzydłowskiego oraz dra inż. Tomasza Płocińskiego o ich roli w powstaniu pracy **H2**;
12. Oświadczenie prof. Jean-François Paula o jego roli w powstaniu prac **H1, H2, H3 i H4**;
13. Oświadczenie dra Jakuba S. Prauznera-Bechcickiego o jego roli w powstaniu prac **H5, H6 i H7**;
14. Oświadczenie prof. dra hab. Zbigniewa Sojki o jego roli w powstaniu prac **H1, H2, H3, H4, H5, H6, H7, H8 i H9**;
15. Oświadczenie dra Pawła Stelmachowskiego o jego roli w powstaniu prac **H2, i H8**;
16. Oświadczenie dra Bartosza Sucha o jego roli w powstaniu pracy **H7**;
17. Oświadczenie prof. dra hab. Marka Szymońskiego o jego roli w powstaniu prac **H5, H6 i H7**;
18. Oświadczenie dra Antoniego Tekiela o jego roli w powstaniu prac **H5 i H6**;
19. Oświadczenie dra Filipa Zasady o jego roli w powstaniu prac **H1, H2, H3, H4, H5, H6, H7, H8 i H9**;
20. Oświadczenie dra Piotra Zapały o jego roli w powstaniu pracy **H4**;

2.5.1 Oświadczenie dra hab. Andrzeja Adamskiego o jego roli w powstaniu pracy H3

Dr hab. Andrzej Adamski
Uniwersytet Jagielloński
Wydział Chemii
ul. Ingardena 3, 30-060 Kraków
tel. 12 663-22-24, fax 12 634-05-15
e-mail: adamski@chemia.uj.edu.pl

w Krakowie, 17 lipca, 2013 r.

OŚWIADCZENIE

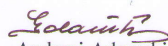
W związku z postępowaniem habilitacyjnym Dr. Witolda Piskorza, oświadczam niniejszym, jako współautor pracy:

W. Piskorz, J. Gryboś, F. Zasada, S. Cristol, J.-F. Paul, A. Adamski, Z. Sojka

Periodic DFT and Atomistic Thermodynamic Modeling of Surface Hydration Equilibria and Morphology Prediction of Monoclinic ZrO₂ Nanocrystals

J. Phys. Chem. C, 115 (2011) 24274,

iż moje zaangażowanie w jej powstanie ograniczało się do preparatyki opisanych próbek jednoskośnego ZrO₂ oraz elementów badań strukturalnych. Swoją udział szacuję na nie więcej, niż 5 %.


Andrzej Adamski

2.5.2 Oświadczenie mgra Amira A. Ahmeda Zebariego o jego roli w powstaniu pracy H7

Name: Amir A.Ahmad Zebari

Krakow, 11 July 2013

Faculty of Physics, Astronomy and Applied Computer Science
Jagiellonian University
Reymonta 4, 30-059 Krakow, Poland

In the manuscript

M. Kolmer, A. A. Ahmad Zebari, J. S. Prauzner-Bechcicki, W. Piskorz, F. Zasada, S. Godlewski, B. Such,

Z. Sojka, M. Szymonski, "On-Surface Polymerization on Titanium Dioxide: Polyanthrylene on $\text{TiO}_2(011)-(2\times 1)$ surface".

Angewandte Chemie, DOI: 10.1002/anie.201303657 and 10.1002/ange.201303657.

I was preparing samples and performing scanning tunneling microscopy measurements and took part in preparation of the manuscript.

Amir Zebari

2.5.3 Oświadczenie dra Janusza Budziocha o jego roli w powstaniu pracy H5

Janusz Budzioch

Kraków dn. 10.07.2013

Afiliacja obecna:

Janusz Budzioch MEASLINE

ul. Rozrywka 20/9

31-417 Kraków

Afiliacja w trakcie powstawania pracy:

Instytut Fizyki Uniwersytetu Jagiellońskiego

ul. Reymonta 4

30-059 Kraków

OŚWIADCZENIE

Oświadczam, że w pracy *F. Zasada, W. Piskorz, S. Godlewski, J. S. Prauzner-Bechcicki, A. Tekiel, J. Budzioch, P. Cyganik, M. Szymonski, Z. Sojka, "Chemical Functionalization of the TiO₂(110)-(1×1) Surface by Deposition of Terephthalic Acid Molecules - a DFT and STM Study", J. Phys. Chem. C 115 (2011), 4134* mój udział polegał na przygotowaniu aparatury pomiarowej do przeprowadzenia eksperymentu oraz wykonaniu pomiarów wstępnych.

Janusz Budzioch

2.5.4 Oświadczenie prof. Sylvaina Cristola o jego roli w powstaniu prac H1, H3 i H4

**UNITE DE CATALYSE ET DE CHIMIE DU SOLIDE - UMR CNRS 8181**

Université Lille Nord de France
Centre National de la Recherche Scientifique
Université des Sciences et Technologies de Lille
Université d'Artois
Ecole Nationale Supérieure de Chimie de Lille
Ecole Centrale de Lille

Sylvain CRISTOL

UCCS · USTL · Bâtiment C3 · 59655 Villeneuve d'Ascq Cedex

Tél : +33(0)3.20.43.454.03 · Email : sylvain.cristol@univ-lille1.fr

To :
Whom it may concern

Villeneuve d'Ascq, le 11 juillet 2013

I was contacted by Dr Witold Piskorz to provide a statement about my contribution to the following papers:

- 1) F. Zasada, W. Piskorz, S. Cristol, J.-F. Paul, A. Kotarba, Z. Sojka,
Periodic Density Functional Theory and Atomistic Thermodynamic Studies of Cobalt Spinel Nanocrystals in Wet
Environment: Molecular Interpretation of Water Adsorption Equilibria
J. Phys. Chem. C 114 (2010), 22245.
- 2) W. Piskorz, J. Gryboś, F. Zasada, S. Cristol, J.-F. Paul, A. Adamski, Z. Sojka
Periodic DFT and Atomistic Thermodynamic Modeling of Surface Hydration Equilibria and Morphology Prediction of
Monoclinic ZrO₂ Nanocrystals
J. Phys. Chem. C, 115 (2011), 24274.
- 3) W. Piskorz, J. Gryboś, F. Zasada, P. Zapala, S. Cristol, J.-F. Paul, Z. Sojka
Periodic DFT Study of the Tetragonal ZrO₂ Nanocrystals Equilibrium Morphology Modeling and Atomistic Surface
Hydration Thermodynamics
J. Phys. Chem. C, 116 (2012), 19307.

I would like to declare that my contribution to those articles was connected with the training in the UCCS laboratory of University Lille 1 of two students: F. Zasada and J. Grybos. During their stay, I explained them how to take in ton account the contribution of pressure and temperature effects within DFT calculations, supervised their work and check the obtained results. The contribution of Dr Piskorz was definitely dominating in the above mentioned articles; hence he was the first and corresponding author in two of them.

Should any further information be required, please do not hesitate to contact me.

Yours sincerely,

Sylvain Cristol,

2.5.5 Oświadczenie prof. dra hab. Piotra Cyganika o jego roli w powstaniu pracy H5

UNIwersytet Jagielloński
Instytut Fizyki im. Mariana Smoluchowskiego
Zakład Fizyki Nanostruktur i Nanotechnologii

dr hab. Piotr Cyganik

ul. Reymonta 4
30-059 Kraków

Tel: (+48) 12 663 55 40
Fax: (+48) 12 633 70 86
E-mail: piotr.cyganik@uj.edu.pl

Oświadczenie

Oświadczam, że w pracy: F. Zasada, W. Piskorz, S. Godlewski, J. S. Prauzner-Bechcicki, A. Tekiel, J. Budzioch, P. Cyganik, M. Szymonski, Z. Sojka, "Chemical Functionalization of the $\text{TiO}_2(110)-(1 \times 1)$ Surface by Deposition of Terephthalic Acid Molecules - a DFT and STM Study", J. Phys. Chem. C 115 (2011), 4134, mój udział polegał na współkierowaniu badaniami doświadczalnymi (STM) oraz na współredakcji tekstu manuskryptu.

Piotr Cyganik,

Kraków 15.07.2013

2.5.6 Oświadczenie prof. Olivera Diwalda o jego roli w powstaniu pracy H8



Department of
Materials Science and Physics
University of Salzburg

Univ. Prof. Dr. Oliver Diwald
Hellbrunnerstrasse 34/ III
A-5020 Salzburg – Austria
Europe

Phone: +43 / (0) 662 / 8044 5444
Fax.: +43 / (0) 662 / 8044 622
www.uni-salzburg.at
oliver.diwald@sbg.ac.at

To whom it may concern

Salzburg, 17.07.2013

Dear Ladies and Gentlemen,

I was contacted by Dr. Witold Piskorz to provide a statement about my contribution to the following paper:

W. Piskorz, F. Zasada, P. Stelmachowski, O. Diwald, A. Kotarba, Z. Sojka
"Computational and Experimental Investigations into N₂O Decomposition over MgO Nanocrystals - From Thorough Molecular Mechanism to ab initio Microkinetics",
J. Phys. Chem. C 115 (2011), 22451.

I would like to declare that my contribution to those articles was connected with providing materials and basic materials characterization data.

In my opinion the contribution of Dr Piskorz was definitely dominating in the above mentioned article, hence he was the first and corresponding author.

Should any further information be required, please do not hesitate to contact me.

With kind regards

Oliver Diwald

2.5.7 Oświadczenie dra Szymona Godlewskiego o jego roli w powstaniu prac H5, H6 i H7

Kraków, 15.07.2013

dr Szymon Godlewski

Centrum Badań Układów Nanoskopowych i Zaawansowanych Materiałów NANOSAM Instytut Fizyki,
Wydział Fizyki, Astronomii i Informatyki Stosowanej, Reymonta 4, 30-059 Kraków

OŚWIADCZENIE

Oświadczam, że w pracy „Supramolecular Ordering of PTCDA Molecules: The Key Role of Dispersion Forces in an Unusual Transition from Physisorbed into Chemisorbed State”, S. Godlewski, A. Tekiel, W. Piskorz, F. Zasada, J.S. Prauzner-Bechcicki, Z. Sojka, M. Szymonski, ACS Nano 6 (2012) 8536–8545 mój udział polegał na opracowaniu koncepcji prowadzonych badań, przeprowadzeniu eksperymentu, analizie i interpretowaniu uzyskanych wyników doświadczalnych, uczestniczeniu w interpretacji porównawczej wyników eksperymentu i obliczeń oraz przygotowaniu tekstu manuskryptu.

Podpis

Kraków, 15.07.2013

dr Szymon Godlewski

Centrum Badań Układów Nanoskopowych i Zaawansowanych Materiałów NANOSAM Instytut Fizyki,
Wydział Fizyki, Astronomii i Informatyki Stosowanej, Reymonta 4, 30-059 Kraków

OŚWIADCZENIE

Oświadczam, że w pracy M. Kolmer, A.A. Ahmad Zebari, J.S. Prauzner-Bechcicki, W. Piskorz, F. Zasada, S. Godlewski, B. Such, Z. Sojka, M. Szymonski „On-Surface Polymerization on Titanium Dioxide: Polyanthrylene on $\text{TiO}_2(011)-(2\times 1)$ surface”, *Angewandte Chemie International Edition*, DOI:10.1002/ange.201303657 mój udział polegał na przygotowywaniu powierzchni ditlenku tytanu i uczestniczeniu w interpretacji uzyskanych wyników.

Podpis

Kraków, 15.07.2013

dr Szymon Godlewski

Centrum Badań Układów Nanoskopowych i Zaawansowanych Materiałów NANOSAM Instytut Fizyki,
Wydział Fizyki, Astronomii i Informatyki Stosowanej, Reymonta 4, 30-059 Kraków

OŚWIADCZENIE

Oświadczam, że w pracy "Chemical Functionalization of the $\text{TiO}_2(110)-(1 \times 1)$ Surface by Deposition of Terephthalic Acid Molecules – a DFT and STM Study", F. Zasada, W. Piskorz, S. Godlewski, J.S. Prauzner-Bechcicki, A. Tekiel, J. Budzioch, P. Cyganik, M. Szymoński, Z. Sojka, J. Phys. Chem. C 115 (2011) 4134-4144 mój udział polegał na przeprowadzeniu części prac doświadczalnych, częściowym interpretowaniu uzyskanych wyników doświadczalnych, uczestniczeniu w interpretacji porównawczej wyników eksperymentu i obliczeni oraz przygotowaniu tekstu manuskryptu.

Podpis

2.5.8 Oświadczenie mgr Joanny Gryboś o jej roli w powstaniu prac H3 i H4

Gryboś Joanna
Kraków, 1.06.2013
Wydział Chemii,
Uniwersytet Jagielloński,
ul. Ingardena 3,
30-060 Kraków, Polska

OŚWIADCZENIE

Oświadczam, że w pracy:

Witold Piskorz, Joanna Gryboś, Filip Zasada, Piotr Zapala, Sylvain Cristol, Jean Francois Paul, Zbigniew Sojka, 2012, *"Periodic DFT Study of the Tetragonal ZrO₂ Nanocrystals: Equilibrium Morphology Modeling and Atomistic Surface Hydration Thermodynamics"*, J. Phys. Chem. C, 116 (36), 19307-19320

mój udział polegał na:

wykonaniu obliczeń metodą DFT/PW91 w formalizmie periodycznym pozwalających określić równowagową morfologię nanokryształów tetragonalnej odmiany ditlenku cyrkonu oraz proces relaksacji i rekonstrukcji analizowanych powierzchni. Następnie porównałam wyniki obliczeń teoretycznych z wykonanymi przeze mnie i zaczerpniętymi z literatury zdjęciami mikroskopowymi (HR TEM). Ponadto, w oparciu o termodynamikę statystyczną, przeprowadziłam analizę adsorpcji wody na zoptymalizowanych powierzchniach nanokryształów w funkcji temperatury i ciśnienia (diagramy termodynamiczne oraz wykresy przedstawiające zmianę pokrycia powierzchni wodą w ujęciu wielocentrowej izotermy Langmuira). Zanalizowałam również zmiany morfologii związane z procesem adsorpcji. Przygotowałam także wstępną wersję manuskryptu (wraz z rysunkami) obejmującą wymieniony przeze mnie zakres materiału.


Podpis

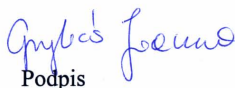
OŚWIADCZENIE

Oświadczam, że w pracy:

Witold Piskorz, Joanna Gryboś, Filip Zasada, Sylvain Cristol, Jean Francois Paul, Andrzej Adamski, Zbigniew Sojka, 2011, "*Periodic DFT and Atomistic Thermodynamic Modeling of the Surface hydration Equilibria and morphology of Monoclinic ZrO₂ Nanocrystals*" J. Phys. Chem. C 115, 24274-24286

mój udział polegał na:

wykonaniu obliczeń metodą DFT/PW91 w formalizmie periodycznym, pozwalających określić równowagową morfologię nanokryształów jednoskośnej odmiany ditlenku cyrkonu oraz proces relaksacji i rekonstrukcji analizowanych powierzchni. Następnie porównałam wyniki obliczeń teoretycznych ze zdjęciami mikroskopowymi (HR TEM). Ponadto, w oparciu o termodynamikę statystyczną, przeprowadziłam analizę adsorpcji wody na zoptymalizowanych powierzchniach nanokryształów w funkcji temperatury i ciśnienia (diagramy termodynamiczne oraz wykresy przedstawiające zmianę pokrycia powierzchni wodą w ujęciu wielocentrowej izotermy Langmuira). Zanalizowałam również zmiany morfologii związanej z procesem adsorpcji.


Podpis

2.5.9 Oświadczenie mgra Marka Kolmera o jego roli w powstaniu pracy H7

OŚWIADCZENIE WSPÓŁAUTORA

mgr Marek Kolmer

Kraków, 12/07/2013

Centrum Badań Układów Nanoskopowych i Zaawansowanych Materiałów,
NANOSAM, Instytut Fizyki, Uniwersytet Jagielloński,
Reymonta 4, 30-059 Kraków

OŚWIADCZENIE

Oświadczam, że w pracy: M. Kolmer, A. A. Ahmad Zebari, J. S. Prauzner-Bechcicki, W. Piskorz, F. Zasada, S. Godlewski, B. Such, Z. Sojka, M. Szymonski, "On-Surface Polymerization on Titanium Dioxide: Polyanthrylene on TiO₂(011)-(2×1) surface", Angew. Chem. Int. Ed. mój udział polegał na wykonaniu oraz opracowaniu danych z części eksperymentalnej dotyczącej obrazowania niskotemperaturowym mikroskopem STM molekuł DBBA na powierzchni TiO₂(011)-(2×1) przed i po zainicjowaniu reakcji ich polimeryzacji. Brałem także udział w interpretacji uzyskanych wyników oraz w tworzeniu tekstu artykułu.

Podpis


2.5.10 Oświadczenie dra hab. Andrzeja Kotarby, prof. UJ, o jego roli w powstaniu prac H1, H2, H8 i H9

Kraków, dn. 10.07.2013 r.

dr hab. Andrzej Kotarba, prof. UJ
Zakład Chemii Nieorganicznej
Wydział Chemii
Uniwersytet Jagielloński
ul. Ingardena 3, 30-060 Kraków

OŚWIADCZENIE

Oświadczam, że w pracach:

- 1) F. Zasada*, W. Piskorz, S. Cristol, J.-F. Paul, A. Kotarba, Z. Sojka*, "Periodic Density Functional Theory and Atomistic Thermodynamic Studies of Cobalt Spinel Nanocrystals in Wet Environment: Molecular Interpretation of Water Adsorption Equilibria", *J. Phys. Chem. C* **114** (2010), 22245
- 2) F. Zasada, W. Piskorz, P. Stelmachowski, A. Kotarba, J.-F. Paul, T. Płociński, K. J. Kurzydłowski, Z. Sojka* "Periodic DFT and HR-STEM Studies of Surface Structure and Morphology of Cobalt Spinel Nanocrystals. Retrieving 3D Shapes from 2D Images", *J. Phys. Chem. C* **115** (2011), 6423
- 3) W. Piskorz*, F. Zasada, P. Stelmachowski, O. Diwald, A. Kotarba, Z. Sojka* "Computational and Experimental Investigations into N₂O Decomposition over MgO Nanocrystals – From Thorough Molecular Mechanism to ab initio Microkinetics", *J. Phys. Chem. C* **115** (2011), 22451
- 4) W. Piskorz*, F. Zasada, P. Stelmachowski, A. Kotarba, Z. Sojka* "Molecular Mechanism and Microkinetics of deN₂O Reaction over Alkaline Earth Oxides – The Role of Static and Dynamic Recombination of Peroxy Intermediates", przyjęte do druku. DOI: 10.1021/jp405459g, *J. Phys. Chem. C*

mój udział polegał na zaprojektowaniu eksperymentów pomiarów aktywności badanych układów tlenkowych, pomiarów pracy wyjścia, oraz interpretacji i dyskusji wyników.



2.5.11 Oświadczenie prof. zw. dra hab. inż. Krzysztofa J. Kurzydłowskiego oraz dra inż. Tomasza Płocińskiego o ich roli w powstaniu pracy H2

Prof. zw. Dr hab. inż. Krzysztof Jan Kurzydłowski
dr inż. Tomasz Płociński
Wydział Inżynierii Materiałowej
Politechniki Warszawskiej
ul. Wołoska 141
02-507 Warszawa

Oświadczenie

W związku z włączeniem publikacji: F. Zasada, W. Piskorz, P. Stelmachowski, A. Kotarba, J.-F. Paul, T. Płociński, K. J. Kurzydłowski, Z. Sojka "Periodic dft and hr-stem studies of surface structure and morphology of cobalt spinel nanocrystals. Retrieving 3d shapes from 2d images", j. Phys. Chem. C 115 (2011), 6423 do rozprawy habilitacyjnej dr Witolda Piskorza oświadczamy, że nasz wkład do w/w publikacji ograniczył się do części pomiarów mikroskopowych. Modelowanie kwantowo-chemiczne morfologii nanokrystalitów Co₃O₄ to w dominującej części wkład Pana dr Piskorza.



/podpisy/



2.5.12 Oświadczenie prof. Jean-François Paula o jego roli w powstaniu prac H1, H2, H3 i H4



UNITE DE CATALYSE ET DE CHIMIE DU SOLIDE - UMR CNRS 8181
Université Lille Nord de France
Centre National de la Recherche Scientifique
Université des Sciences et Technologies de Lille
Université d'Artois
Ecole Nationale Supérieure de Chimie de Lille
Ecole Centrale de Lille

Jean-François Paul

UCCS · USTL · Bâtiment C3 · 59655 Villeneuve d'Ascq Cedex
Tél : +33(0)3.20.33.77.34 · Email : Jean-francois.paul@univ-lille1.fr

Villeneuve d'Ascq, le 26 août 2013

To whom it may concern

During the last years, ours group work in collaboration with the Jagiellonian University and more precisely with the Faculty of Chemistry. This strong collaboration leads to the publication of the following paper in high quality international journal

- 1) F. Zasada, W. Piskorz, S. Cristol, J.-F. Paul, A. Kotarba, Z. Sojka,
"Periodic Density Functional Theory and Atomistic Thermodynamic Studies of Cobalt Spinel Nanocrystals in Wet Environment: Molecular Interpretation of Water Adsorption Equilibria", J. Phys. Chem. C 114 (2010), 22245.
- 2) F. Zasada, W. Piskorz, P. Stelmachowski, A. Kotarba, J.-F. Paul, T. Płociński, K. J. Kurzydłowski, Z. Sojka
"Periodic DFT and HR-STEM Studies of Surface Structure and Morphology of Cobalt Spinel Nanocrystals. Retrieving 3D Shapes from 2D Images", J. Phys. Chem. C 115 (2011), 6423.
- 3) W. Piskorz, J. Gryboś, F. Zasada, S. Cristol, J.-F. Paul, A. Adamski, Z. Sojka
"Periodic DFT and Atomistic Thermodynamic Modeling of Surface Hydration Equilibria and Morphology Prediction of Monoclinic ZrO₂ Nanocrystals", J. Phys. Chem. C, 115 (2011), 24274.
- 4) W. Piskorz, J. Gryboś, F. Zasada, P. Zapala, S. Cristol, J.-F. Paul, Z. Sojka
"Periodic DFT Study of the Tetragonal ZrO₂ Nanocrystals - Equilibrium Morphology Modeling and Atomistic Surface Hydration Thermodynamics", J. Phys. Chem. C, 116 (2012), 19307.

The major part of the work has been performed in the Jagiellonian University, including the submission of the calculation and the main part of the redaction. The work performed in Lille is mainly focus on the introduction of the thermodynamic corrections to include temperature and pressure effects in the ab-initio calculations. Thanks to the collaboration, these methods are now currently used by researcher at the Jagiellonian University.

Jean-Francois Paul
Professor.

Secrétariat Général : Unité de Catalyse et de Chimie du Solide · USTL · Bât. C3 · 59655 Villeneuve d'Ascq Cedex
Tél : +33(0)3.20.43.49.49 · Fax : +33(0)3.20.43.65.61 · Web : <http://uccs.univ-lille1.fr>

2.5.13 Oświadczenie dra Jakuba S. Prauznera-Behcickiego o jego roli w powstaniu prac H5, H6 i H7

Kraków, dn. 10.07.2013 r.

Jakub Prauzner-Behcicki
Centrum NANOSAM,
Wydział Fizyki, Astronomii i Informatyki Stosowanej,
Uniwersytet Jagielloński
ul. Reymonta 4, 30-059 Kraków

OŚWIADCZENIE

Oświadczam, że w pracy

Filip Zasada, Witold Piskorz, Szymon Godlewski, Jakub S. Prauzner-Behcicki, Antoni Tekiel, Janusz Budzioch, Piotr Cyganik, Marek Szymonski, and Zbigniew Sojka,
“*Chemical Functionalization of the $\text{TiO}_2(110)-(1 \times 1)$ Surface by Deposition of Terephthalic Acid Molecules. A Density Functional Theory and Scanning Tunneling Microscopy Study*”
J. Phys. Chem. C 2011, 115, 4134–4144

mój udział polegał na przygotowaniu próbek, przeprowadzaniu pomiarów techniką mikroskopii bliskich oddziaływań, analizie otrzymanych wyników eksperymentalnych, zaproponowaniu możliwego modelu adsorpcji molekuł w warstwie, dyskusji i analizie wyników obliczeń, przygotowaniu tekstu manuskryptu.



Kraków, dn. 10.07.2013 r.

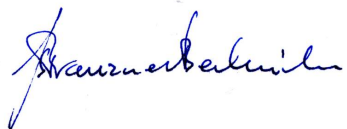
Jakub Prauzner-Bechcicki
Centrum NANOSAM,
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Uniwersytet Jagielloński
ul. Reymonta 4, 30-059 Kraków

OŚWIADCZENIE

Oświadczam, że w pracy

Szymon Godlewski, Antoni Tekiel, Witold Piskorz, Filip Zasada, Jakub S. Prauzner-Bechcicki, Zbigniew Sojka, Marek Szymonski
"Supramolecular Ordering of PTCDA Molecules: The Key Role of Dispersion Forces in an Unusual Transition from Physisorbed into Chemisorbed State"
ACS Nano **2012**, *6*, 8536

mój udział polegał na analizie i dyskusji otrzymanych wyników eksperymentalnych, pracach nad przygotowaniem tekstu manuskryptu.



Kraków, dn. 10.07.2013 r.

Jakub Prauzner-Bechcicki
Centrum NANOSAM,
Wydział Fizyki, Astronomii i Informatyki Stosowanej
Uniwersytet Jagielloński
ul. Reymonta 4, 30-059 Kraków

OŚWIADCZENIE

Oświadczam, że w pracy

Marek Kolmer, Amir A. Ahmad Zebari, Jakub S. Prauzner-Bechcicki, Witold Piskorz, Filip Zasada, Szymon Godlewski, Bartosz Such, Zbigniew Sojka, Marek Szymonski,
"On-Surface Polymerization on Titanium Dioxide: Polyanthrylene on TiO₂(011)-(2×1) surface"
Angewandte Chemie, DOI: 10.1002/anie.201303657 and 10.1002/ange.201303657

mój udział polegał na pracach eksperymentalnych, dyskusji i analizie danych eksperymentalnych, dyskusji i analizie wyników obliczeń, przygotowaniu tekstu manuskryptu.



2.5.14 Oświadczenie prof. dra hab. Zbigniewa Sojki o jego roli w powstaniu prac H1, H2, H3, H4, H5, H6, H7, H8 i H9

Kraków, dn. 20.08.2013 r.

Prof. dr hab. Zbigniew Sojka
Zakład Chemii Nieorganicznej
Wydział Chemii
Uniwersytet Jagielloński
ul. Ingardena 3, 30-060 Kraków

OŚWIADCZENIE

Oświadczam, że w pracy:

1) F. Zasada*, W. Piskorz, S. Cristol, J.-F. Paul, A. Kotarba, Z. Sojka*, "Periodic Density Functional Theory and Atomistic Thermodynamic Studies of Cobalt Spinel Nanocrystals in Wet Environment: Molecular Interpretation of Water Adsorption Equilibria", *J. Phys. Chem. C* **114** (2010), 22245

mój udział polegał na planowaniu eksperymentów, dyskusji wyników, współredakcji publikacji

w pracy:

2) F. Zasada, W. Piskorz, P. Stelmachowski, A. Kotarba, J.-F. Paul, T. Płociński, K. J. Kurzydłowski, Z. Sojka* "Periodic DFT and HR-STEM Studies of Surface Structure and Morphology of Cobalt Spinel Nanocrystals. Retrieving 3D Shapes from 2D Images", *J. Phys. Chem. C* **115** (2011), 6423

mój udział polegał na planowaniu eksperymentów, dyskusji wyników, współredakcji publikacji

w pracy:

3) W. Piskorz*, J. Gryboś, F. Zasada, S. Cristol, J.-F. Paul, A. Adamski, Z. Sojka* "Periodic DFT and Atomistic Thermodynamic Modeling of Surface Hydration Equilibria and Morphology Prediction of Monoclinic ZrO₂ Nanocrystals", *J. Phys. Chem. C*, **115** (2011), 24274

mój udział polegał na planowaniu eksperymentów, dyskusji wyników, współredakcji publikacji

w pracy:

4) W. Piskorz*, J. Gryboś, F. Zasada, P. Zapała, S. Cristol, J.-F. Paul, Z. Sojka* "Periodic DFT Study of the Tetragonal ZrO₂ Nanocrystals – Equilibrium Morphology Modeling and Atomistic Surface Hydration Thermodynamics", *J. Phys. Chem. C*, **116** (2012), 19307

mój udział polegał na planowaniu eksperymentów, dyskusji wyników, współredakcji publikacji

w pracy:

5) F. Zasada, W. Piskorz*, S. Godlewski*, J. S. Prauzner-Bechcicki, A. Tekiel, J. Budzioch, P. Cyganik, M. Szymonski, Z. Sojka, "Chemical Functionalization of the TiO₂(110)-(1×1) Surface by Deposition of Terephthalic Acid Molecules - a DFT and STM Study", *J. Phys. Chem. C* **115** (2011), 4134

mój udział polegał na dyskusji wyników, współredakcji publikacji

w pracy:

- 6) S. Godlewski*, A. Tekiel, W. Piskorz*, F. Zasada, J. S. Prauzner-Bechcicki, Z. Sojka, M. Szymonski "Supramolecular Ordering of PTCDA Molecules – the Key Role of Dispersion Forces in an Unusual Transition from Physisorbed into Chemisorbed State", *ACS Nano*, **6** (2012), 8536

mój udział polegał na dyskusji wyników, współredakcji publikacji

w pracy:

- 7) M. Kolmer, A. A. Ahmad Zebari, J. S. Prauzner-Bechcicki*, W. Piskorz, F. Zasada, S. Godlewski, B. Such, Z. Sojka, M. Szymonski, "On-Surface Polymerization on Titanium Dioxide: Polyanthrylene on $\text{TiO}_2(011)-(2 \times 1)$ surface", *Angew. Chem. Int. Ed.*, przyjęte do druku. DOI: 10.1002/ange.201303657

mój udział polegał na dyskusji wyników, współredakcji publikacji

w pracy:

- 8) W. Piskorz*, F. Zasada, P. Stelmachowski, O. Diwald, A. Kotarba, Z. Sojka* "Computational and Experimental Investigations into N_2O Decomposition over MgO Nanocrystals – From Thorough Molecular Mechanism to ab initio Microkinetics", *J. Phys. Chem. C* **115** (2011), 22451

mój udział polegał na planowaniu eksperymentów, dyskusji wyników, współredakcji publikacji

w pracy:

- 9) W. Piskorz*, F. Zasada, P. Stelmachowski, A. Kotarba, Z. Sojka "Molecular Mechanism and Microkinetics of deN_2O Reaction over Alkaline Earth Oxides - The Role of Static and Dynamic Recombination of Peroxy Intermediates", DOI: 10.1021/jp405459g, *J. Phys. Chem. C*.

mój udział polegał na planowaniu eksperymentów, dyskusji wyników, współredakcji publikacji



2.5.15 Oświadczenie dra Pawła Stelmachowskiego o jego roli w powstaniu prac H2, H8 i H9

Paweł Stelmachowski

Kraków, 20.08.2013

Uniwersytet Jagielloński, Wydział Chemii

OŚWIADCZENIE

Oświadczam, że w pracy

1. F. Zasada, W. Piskorz, P. Stelmachowski, A. Kotarba, J.-F. Paul, T. Płociński, K. J. Kurzydłowski, Z. Sojka „Periodic DFT and HR-STEM Studies of Surface Structure and Morphology of Cobalt Spinel Nanocrystals. Retrieving 3D Shapes from 2D Images”, J. Phys. Chem. C 115 (2011), 6423
mój udział polegał na:

syntezie badanego materiału, analizie i opracowaniu danych z badań strukturalnych materiału.

2. W. Piskorz, F. Zasada, P. Stelmachowski, O. Diwald, A. Kotarba, Z. Sojka „Computational and Experimental Investigations into N₂O Decomposition over MgO Nanocrystals – From Thorough Molecular Mechanism to ab initio Microkinetics”, J. Phys. Chem. C 115 (2011), 22451
mój udział polegał na:

syntezie badanego materiału, pomiarów powierzchni właściwej materiału, opracowaniu danych z badań strukturalnych materiału, wykonaniu testów katalitycznych i analizie wyników eksperymentalnych.

3. W. Piskorz, F. Zasada, P. Stelmachowski, A. Kotarba, Z. Sojka „Molecular Mechanism and Microkinetics of N₂O Reaction over Alkaline Earth Oxides – The Role of Static and Dynamic Recombination of Peroxy Intermediates”, DOI: 10.1021/jp405459g, J. Phys. Chem. C, mój udział polegał na:

syntezie badanego materiału, pomiarów powierzchni właściwej materiału, opracowaniu danych z badań strukturalnych materiału, wykonaniu testów katalitycznych i analizie wyników eksperymentalnych.

Podpis



2.5.16 Oświadczenie dra Bartosza Sucha o jego roli w powstaniu pracy H7

Kraków, 24.07.2013

Bartosz Such
Instytut Fizyki
Uniwersytet Jagielloński

OŚWIADCZENIE

Oświadczam, że współpracowałem z Panem dr Witoldem Piskorzem, czego efektem jest praca:

M. Kolmer, A.A. Ahmad Zebari, J.S. Prauzner-Bechcicki, W. Piskorz, F. Zasada, S. Godlewski, B. Such, Z. Sojka, M. Szymonski „*On-Surface Polymerization on Titanium Dioxide: Polyanthrylene on TiO₂(011)-(2×1) surface*”, *Angewandte Chemie International Edition*, DOI:10.1002/ange.201303657.

W trakcie przygotowywania pracy brałem udział w dyskusji otrzymanych rezultatów i komentowałem powstający manuskrypt.



Dr Bartosz Such

2.5.17 Oświadczenie prof. dra hab. Marka Szymońskiego o jego roli w powstaniu prac H5, H6 i H7

Kraków, 16.07.2013

Prof. Dr hab. Marek Szymoński

Centrum Badań Układów Nanoskopowych i Zaawansowanych
Materiałów NANOSAM,
Instytut Fizyki,
Wydział Fizyki, Astronomii i Informatyki Stosowanej,
Uniwersytet Jagielloński
Reymonta 4, 30-059 Kraków

OŚWIADCZENIE

Oświadczam, że w pracy "Chemical Functionalization of the $\text{TiO}_2(110)-(1 \times 1)$ Surface by Deposition of Terephthalic Acid Molecules – a DFT and STM Study", F. Zasada, W. Piskorz, S. Godlewski, J.S. Prauzner-Bechcicki, A. Tekiel, J. Budzioch, P. Cyganik, M. Szymoński, Z. Sojka, J. Phys. Chem. C 115 (2011) 4134-4144 mój udział polegał na kierowaniu grupą naukowców wykonujących eksperymenty, planowaniu doświadczeń, dyskusji wyników i współudziale w redagowaniu publikacji.

Podpis

Kraków, 16.07.2013

Prof. Dr hab. Marek Szymoński

Centrum Badań Układów Nanoskopowych i Zaawansowanych
Materiałów NANOSAM,
Instytut Fizyki,
Wydział Fizyki, Astronomii i Informatyki Stosowanej,
Uniwersytet Jagielloński
Reymonta 4, 30-059 Kraków

OŚWIADCZENIE

Oświadczam, że w pracy „Supramolecular Ordering of PTCDA Molecules: The Key Role of Dispersion Forces in an Unusual Transition from Physisorbed into Chemisorbed State”, S. Godlewski, A. Tekiel, W. Piskorz, F. Zasada, J.S. Prauzner-Bechcicki, Z. Sojka, M. Szymonski, ACS Nano 6 (2012) 8536–8545 mój udział polegał na kierowaniu grupą naukowców wykonujących eksperymenty, planowaniu doświadczeń, dyskusji wyników i współudziale w redagowaniu publikacji.

Podpis



Kraków, 16.07.2013

Prof. Dr hab. Marek Szymoński

Centrum Badań Układów Nanoskopowych i Zaawansowanych
Materiałów NANOSAM,
Instytut Fizyki,
Wydział Fizyki, Astronomii i Informatyki Stosowanej,
Uniwersytet Jagielloński
Reymonta 4, 30-059 Kraków

OŚWIADCZENIE

Oświadczam, że w pracy M. Kolmer, A.A. Ahmad Zebari, J.S. Prauzner-Bechcicki, W. Piskorz, F. Zasada, S. Godlewski, B. Such, Z. Sojka, M. Szymoński „On-Surface Polymerization on Titanium Dioxide: Polyanthrylene on $\text{TiO}_2(011)-(2\times 1)$ surface”, Angewandte Chemie International Edition, DOI:10.1002/ange.201303657 mój udział polegał na kierowaniu grupą naukowców wykonujących eksperymenty, planowaniu doświadczeń, dyskusji wyników i współudziale w redagowaniu publikacji.

Podpis

2.5.18 Oświadczenie dra Antoniego Tekiela o jego roli w powstaniu prac H5 i H6

Antoni Tekiel
Physics Department, McGill University
3600 University St
Montreal, QC H3A 2T8
Kanada

Toronto, 10. lipiec 2013 r.

OŚWIADCZENIE

Oświadczam, że w następujących pracach:

1. F. Zasada, W. Piskorz, S. Godlewski, J. S. Prauzner-Bechcicki, A. Tekiel, J. Budzioch, P. Cyganik, M. Szymonski, Z. Sojka (2011) "Chemical Functionalization of the $\text{TiO}_2(110)-(1 \times 1)$ Surface by Deposition of Terephthalic Acid Molecules - a DFT and STM Study", J. Phys. Chem. C 115, 4134

mój udział (razem z Dr. Szymonem Godlewskim) polegał na przygotowaniu eksperymentu oraz wykonaniu doświadczeń techniką skaningowej mikroskopii tunelowej. Ponadto brałem aktywny udział w dyskusji wyników ze współautorami oraz przygotowaniu manuskryptu, w tym pracy nad rycinami prezentującymi wyniki teoretyczne i eksperymentalne.

2. S. Godlewski, A. Tekiel, W. Piskorz, F. Zasada, J. S. Prauzner-Bechcicki, Z. Sojka, M. Szymonski (2012) "Supramolecular Ordering of PTCDA Molecules; the Key Role of Dispersion Forces in an Unusual Transition from Physisorbed into Chemisorbed State", ACS Nano 6, 8536

mój udział polegał na dyskusji koncepcji badawczej, wyników naukowych oraz przygotowaniu manuskryptu, w tym pracy nad rycinami prezentującymi wyniki teoretyczne i eksperymentalne.

Antoni Tekiel

2.5.19 Oświadczenie dra Filipa Zasady o jego roli w powstaniu prac H1, H2, H3, H4, H5, H6, H7, H8 i H9

Dr Filip Zasada
Wydział Chemii
ul. Ingardena 3, 30-060 Kraków

Kraków, 01.08.2013

W związku z włączeniem publikacji:

1. F. Zasada, W. Piskorz, S. Cristol, J.-F. Paul, A. Kotarba, Z. Sojka, „Periodic Density Functional Theory and Atomistic Thermodynamic Studies of Cobalt Spinel Nanocrystals in Wet Environment: Molecular Interpretation of Water Adsorption Equilibria”, *J. Phys. Chem. C* 114 (2010), 22245.
2. F. Zasada, W. Piskorz, P. Stelmachowski, A. Kotarba, J.-F. Paul, T. Płociński, K. J. Kurzydłowski, Z. Sojka „Periodic DFT and HR-STEM Studies of Surface Structure and Morphology of Cobalt Spinel Nanocrystals. Retrieving 3D Shapes from 2D Images”, *J. Phys. Chem. C* 115 (2011), 6423.
3. W. Piskorz, J. Gryboś, F. Zasada, S. Cristol, J.-F. Paul, A. Adamski, Z. Sojka „Periodic DFT and Atomistic Thermodynamic Modeling of Surface Hydration Equilibria and Morphology Prediction of Monoclinic ZrO₂ Nanocrystals”, *J. Phys. Chem. C*, 115 (2011), 24274.
4. W. Piskorz, J. Gryboś, F. Zasada, P. Zapała, S. Cristol, J.-F. Paul, Z. Sojka „Periodic DFT Study of the Tetragonal ZrO₂ Nanocrystals – Equilibrium Morphology Modeling and Atomistic Surface Hydration Thermodynamics”, *J. Phys. Chem. C*, 116 (2012), 19307.
5. F. Zasada, W. Piskorz, S. Godlewski, J. S. Prauzner-Bechcicki, A. Tekiel, J. Budzioch, P. Cyganik, M. Szymonski, Z. Sojka, „Chemical Functionalization of the TiO₂ (110)-(1×1) Surface by Deposition of Terephthalic Acid Molecules - a DFT and STM Study”, *J. Phys. Chem. C* 115 (2011), 4134.
6. S. Godlewski, A. Tekiel, W. Piskorz, F. Zasada, J. S. Prauzner-Bechcicki, Z. Sojka, M. Szymonski „Supramolecular Ordering of PTCDA Molecules – the Key Role of Dispersion Forces in an Unusual Transition from Physisorbed into Chemisorbed State”, *ACS Nano*, 6 (2012), 8536.
7. M. Kolmer, A. A. Ahmad Zebari, J. S. Prauzner-Bechcicki, W. Piskorz, F. Zasada, S. Godlewski, B. Such, Z. Sojka, M. Szymonski, „On-Surface Polymerization on Titanium Dioxide: Polyanthrylene on TiO₂(011)-(2×1) surface”, *Angew. Chem. Int. Ed.*, 52, (2013), 1. DOI: 10.1002/ange.201303657.
8. W. Piskorz, F. Zasada, P. Stelmachowski, O. Diwald, A. Kotarba, Z. Sojka „Computational and Experimental Investigations into N₂O Decomposition over MgO Nanocrystals – From Thorough Molecular Mechanism to ab initio Microkinetics”, *J. Phys. Chem. C* 115 (2011), 22451.

9. W. Piskorz, F. Zasada, P. Stelmachowski, A. Kotarba, Z. Sojka „Molecular Mechanism and Microkinetics of deN₂O Reaction over Alkaline Earth Oxides – The Role of Static and Dynamic Recombination of Peroxy Intermediates”, DOI: 10.1021/jp405459g, J. Phys. Chem. C.

do rozprawy habilitacyjnej pana dr Witolda Piskorza oświadczam że prace te są częścią naszych wspólnych badań dotyczących w ogólnym ujęciu modelowania molekularnego struktury, własności i reaktywności powierzchni tlenków metali. Mój udział w powyżej wymienionych pracach związany był z:

współudziałem w opracowaniu i optymalizacją modeli kwantowochemicznych wykorzystywanych w symulacjach (prace 1-9),
współudziałem w badaniu ścieżek reakcji w formalizmie DFT (prace 7, 8),
prowadzeniem i analizą wyników transmisyjnej mikroskopii elektronowej i opracowaniem wyników termodynamiki atomistycznej (prace 1, 2, 3, 4)
pomocą w przygotowaniu rysunków i redagowaniu tekstu publikacji (prace 1-9)

Kraków 01.08.2013

Dr Filip Zasada

2.5.20 Oświadczenie dra Piotra Zapalę o jego roli w powstaniu pracy H4

mgr Piotr Zapalę
Synthos SA
Chemików 1
30-600 Oświęcim

Bath, 15.07.2013

Wydział Chemii Uniwersytetu Jagiellońskiego
Ingardena 3
30-060 Kraków

E-mail: pzapala@gmail.com

OŚWIADCZENIE

Oświadczam, że w pracy *Periodic DFT Study of the Tetragonal ZrO₂ Nanocrystals: Equilibrium Morphology Modeling and Atomistic Surface Hydration Thermodynamics* opublikowanej w The Journal of Physical Chemistry C w 2012 r (vol. 116 str. 19307 – 19320) mój udział polegał na syntezie tetragonalnej odmiany ZrO₂ oraz wykonaniu eksperymentu termoprogramowanej desorpcji wody z powierzchni ZrO₂.

2.6 Aneks tomu 2

W aneksie przedstawiłem skrótowy opis niestandardowych metodologii oraz architekturę autorskiego klastra obliczeniowego.

2.6.1 Naprężenia Pulaya

Standardowe narzędzia optymalizacji geometrii, zaimplementowane np. w programie VASP, stosują optymalizację położeń jonów w komórce elementarnej oraz parametrów komórki. Optymalizacja ta prowadzona jest dla **ustalonej** wartości **energii odcięcia** fal płaskich. Zmiana rozmiarów komórki prowadzi do tzw. naprężenia Pulaya (ang. *Pulay stress*). Wynika to z niezupełności *skończonej* bazy fal płaskich względem zmiany objętości komórki. Możliwe jest **wyeliminowanie** w znacznym stopniu naprężenia Pulaya poprzez bardzo znaczną rozbudowę bazy funkcyjnej, najlepiej w połączeniu z kontrolą zbieżności energii względem rozmiaru (energii odcięcia) bazy. Innym podejściem, znacznie mniej wymagającym obliczeniowo, jest wykonanie **serii** obliczeń z **ustaloną energią** odcięcia (relatywnie *niewielką*) i następnie dopasowanie **równania stanu** Bircha-Murnaghana (B-M), $B = V \frac{\partial^2 E}{\partial V^2}$, do zależności energii względem objętości komórki (*vide infra*). Dane literaturowe, uzyskane dla szeregu programów kwantowo-chemicznych, wskazują, że metodologia taka daje **bardzo dobre** wyniki (małe błędy wynikające z niezupełności bazy funkcyjnej), szczególnie, gdy zastosuje się względnie duże zmiany objętości komórki (5-10 %).

Naprężenie Pulaya, wynikające z niezupełności bazy funkcyjnej, jest **podobnej natury**, jak błąd superpozycji bazy (ang. *basis set superposition error*, BSSE), aczkolwiek sam termin BSSE stosuje się w odniesieniu do baz **centrowanych na atomach**.

Wyznaczanie parametrów komórki za pomocą równania stanu W celu wyznaczenia **współczynnika ściśliwości objętościowej** (ang. *bulk modulus*) wykonywałem serię obliczeń energii w funkcji objętości komórki elementarnej i wyniki aproksymowałem (ze średnim względnym błędem kwadratowym $< 10^{-4}$) za pomocą równania stanu B-M. Obliczenie parametrów aproksymującej funkcji kwadratowej pozwoliło na wyznaczenie **współczynnika ściśliwości**, a wartość objętości w minimum energii, V_0 , w tym równaniu stanu określiła przy okazji optymalny rozmiar komórki elementarnej ze znacznie lepszą dokładnością, niż standardowe algorytmy optymalizacji stałej sieciowej wykorzystywane w programie VASP. Z tego względu ta technika wyznaczania stałej sieciowej jest wykorzystywana przeze mnie powszechnie.

2.6.2 Rozwinięcia teorii DFT

2.6.2.1 DFT+D

Zgodnie z półempiryczną teorią Grimmea [9], energia oddziaływań dyspersyjnych, E_{disp} , jest funkcją **homo-graficzną** $\sim \frac{1}{R_{ij}^6}$ tłumioną, dla małych odległości, przez **funkcję wykładniczą** f_D , i ma postać:

$$E_{\text{disp}} = -S_6 \sum_{i=1}^{n_{\text{at}}} \sum_{j>i}^{n_{\text{at}}} \underbrace{\frac{C_6^{ij}}{R_{ij}^6} f_D(R_{ij}, R_{ij}^{\text{vdW}})}_{\text{funkcja tłumiąca}}.$$

Funkcja tłumiąca ma postać $f_D = \left(1 + \exp \left(-d \left(\frac{R_{ij}}{R_i^{\text{vdW}} + R_j^{\text{vdW}}} - 1 \right) \right) \right)^{-1}$, zaś współczynnik $C_6^{ij} = 2 \frac{C_6^i C_6^j}{C_6^i + C_6^j}$ jest parametrem zależnym od dwóch atomów. Wielkość stałej C_6^i , charakterystycznej dla danego pierwiastka, wynika z parametryzacji. Zmienna R_i^{vdW} jest promieniem van der Waalsa atomu i , natomiast R_{ij}^{vdW} jest sumą promieni van der Waalsa atomów i oraz j . Stałe d i S_6 są parametrami teorii, zależnymi od przyjętego **funkcjonału DFT**.

W układach o periodycznych warunkach brzegowych wyrażenie na energię ma postać ($\mathbf{L}$ indeksuje komórki):

$$E_{\text{disp}} = -\frac{S_6}{2} \sum_{i=1}^{n_{\text{at}}} \sum_{j>i}^{n_{\text{at}}} \sum_{\mathbf{L}} \frac{C_6^{ij}}{|\mathbf{r}^{i,0} - \mathbf{r}^{j,\mathbf{L}}|^6} \underbrace{f_D(|\mathbf{r}^{i,0} - \mathbf{r}^{j,\mathbf{L}}|)}_{\text{funkcja tłumiąca}}.$$

Kluczową zaletą parametryzacji Grimme'a jest **znikoma złożoność obliczeniowa**, którą można naiwnie i pesymistycznie oszacować na $O(n^2)$, gdzie n jest **liczbą atomów** w układzie (jest to ograniczenie od góry, nie uwzględniające tzw. *pre-screeningu*, czyli np. pomijania *a priori* par, w których wzajemna odległość atomów jest większa od ustalonego kryterium).

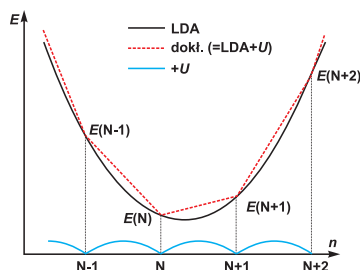
2.6.2.2 DFT+U

W modelu Hubbarda dokonuje się wyboru niewielkiego **podzbioru orbitali** i korelację elektronową, związaną z nimi, traktuje się w sposób **odrębny**. Uzyskane wyniki zależą, oczywiście, od sposobu wyboru tych orbitali oraz od wyboru parametrów użytych do ich opisu. Istnieją metody [17] nieodwołujące się do doświadczalnych wartości przerw energetycznych, oparte na teorii odpowiedzi (ang. *linear response approach*), pozwalające na obliczenie wartości parametrów metody DFT+U.

Np. dla orbitali d : $U = E(d^{n+1}) + E(d^{n-1}) - 2E(d^n)$, co oznacza zmianę energii kulombowskiej towarzyszącą przeniesieniu 2 elektronów na to samo centrum atomowe.

Hamiltonian w modelu Hubbarda jest uzupełniony o człon U , równy $E_{\text{DFT}+U}[n(\mathbf{r})] = E_{\text{DFT}}[n(\mathbf{r})] + E_{\text{Hubb.}}[\{n_m^{I\sigma}\}] - E_{\text{DC}}[\{n_m^{I\sigma}\}]$, gdzie $n(\mathbf{r})$ jest gęstością elektronową, $n_m^{I\sigma}$ oznacza obsadzenia orbitalu atomu I , który podlega oddziaływaniu Hubbarda. Wyraz $E_{\text{DC}}[\{n_m^{I\sigma}\}]$ („DC” od ang. „double counting”) pochodzi od konieczności uniknięcia **podwójnego zliczania** oddziaływania obliczonego z wyrazu Hubbarda i, w sposób przybliżony, z energii DFT.

Uwzględnienie członu Hubbarda powoduje, iż **zależność energii od liczby obsadzeń** w DFT przestaje być (w niewielkim otoczeniu minimum) funkcją kwadratową, a uzyskuje jakościowo kształt **dokładnej** zależności funkcyjnej E od n :



2.6.3 Modelowanie kinetycznego efektu izotopowego

Modelowanie kinetycznego efektu izotopowego (ang. *kinetic isotopic effect*, KIE) wykonałem w oparciu o formalizm Bigeleisena [61]. Otrzymane stosunki stałych szybkości k_1/k_0 , k_2/k_0 i k_3/k_0 (gdzie k_0 , k_1 , k_2 i k_3 oznaczają stałe szybkości odpowiednio dla izotopomerów: $^{14}\text{N}^{14}\text{N}^{16}\text{O}$, $^{15}\text{N}^{14}\text{N}^{16}\text{O}$, $^{14}\text{N}^{15}\text{N}^{16}\text{O}$ oraz $^{14}\text{N}^{14}\text{N}^{18}\text{O}$) zostały obliczone z równania [62, 63]

$$\frac{k_0}{k_i} = \frac{v_{L0}^\#}{v_{Li}^\#} \underbrace{\prod_{j=1}^{3n-6} \frac{u_{ij} \sinh(u_{0j}/2)}{u_{0j} \sinh(u_{ij}/2)}}_{\text{substrat}} \underbrace{\prod_{j=1}^{3n^\#-7} \frac{u_{0j}^\# \sinh(u_{ij}^\#/2)}{u_{ij}^\# \sinh(u_{0j}^\#/2)}}_{\text{stan przejściowy}}$$

W powyższym wzorze v_L jest liczbą falową drgania związanego ze współrzędną reakcji. Wielkość $u = hc\omega/(k_B T)$, gdzie ω jest częstością, h – stałą Plancka, c – prędkością światła, k_B – stałą Boltzmanna zaś T – temperaturą.

2.6.4 Mikrokinetyka

Mikrokinetyka *ab initio* jest to badanie **kinetyki całego procesu** w oparciu o kwantowo-chemiczną analizę jego **etapów elementarnych**. Jest to zatem swoisty **łącznik** między wielkościami kwantowo-mechanicznego **mikroświata**, takimi jak energia swobodna aktywacji czy częstotliwość zderzeń aktywnych, a takimi wielkościami **makroskopowymi**, jak szybkość reakcji czy stężenie. Nieodłącznym zagadnieniem jest tu **poprawne pojęciowo**, a przez to jak **najdokładniejsze** wyznaczenie funkcji termodynamicznych: w przybliżeniu Born-Oppenheimera jest to energia elektronowa, oraz funkcja rozdziału, albo też energia swobodna wyznaczona ze statystyki przebiegu dynamiki molekularnej *ab initio* (*vide* następny podrozdział).

Posiadając pełny zestaw **energii swobodnych** dla **wszystkich** rozważanych etapów elementarnych można, w oparciu o stechiometrię, zaproponować układ **kinetycznych równań różniczkowych**. Rozwiązawszy go, uzyskuje się **czasową zależność** wielkości **makroskopowych** (typowo: stężenia/ciśnienia cząstkowego), które można **zweryfikować doświadczalnie**. Można także obliczyć stężenia asymptotyczne, które z kolei mogą być porównane z wielkościami uzyskanymi z eksperymentu równowagowego.

2.6.4.1 Mikrokinetyka dyskretna

Do opisu **dyskretnej** dyfuzji i **następczej rekombinacji** zastosowałem model **błądzenia przypadkowego** Smoluchowskiego-Einsteina [64], natomiast zależność średniej odległości (w metryce ∞) od pokrycia modelowałem metodą **Monte Carlo** (program autorski [7]), uwzględniając **korelację** obsadzeń węzłów wynikającą ze wzajemnego oddziaływania grup nadtlenkowych, znajdujących się w pozycjach sąsiednich (poprawka energetyczna jest **różna** dla **różnej liczby sąsiednich grup**).

Uzyskane w wyniku tych rozważań równanie na **szybkość procesu LH** ma postać: $r_{LH} = \frac{\Theta}{2 \left(\langle n \rangle \tau_d + \frac{\tau_2}{P_1(\Theta, z) \cdot P_2(\tau_2, \tau_d)} \right)}$, gdzie $\langle n \rangle$ jest średnią wartością liczby skoków dyfuzji, potrzebną do utworzenia pary sąsiadujących grup nadtlenkowych (otrzymaną z modelowania Monte Carlo), zależną od pokrycia, τ_d jest czasem pojedynczego skoku dyfuzji, a τ_2 jest czasem charakterystycznym rekombinacji. $P_1(\Theta, z)$ jest geometrycznym prawdopodobieństwem rekombinacji $P_1(\Theta, z) = \frac{(z-1)\Theta+1}{z}$ (z jest liczbą sąsiednich węzłów, dla siatki kwadratowej $z = 4$), zaś $P_2(\tau_2, \tau_d) = 1 - \exp(-\tau_d/\tau_2)$ określa prawdopodobieństwo przejścia ze stanu dyfuzyjnego do

rekombinacji. Szczególnie istotna jest **prawidłowa asymptotyka** zaproponowanego równania na r_{LH} dla **obu skrajnych przypadków** – szybkiej **rekombinacji** ($k_2 \gg k_d$) oraz dla szybkiej **dyfuzji** ($k_2 \gg k_d$): $r_{LH} \rightarrow k_d \Theta^2$.

2.6.5 Obliczanie funkcji termodynamicznych

Wyjście poza przybliżenie harmoniczne — całkowanie termodynamiczne Adekwatne obliczenia *ab initio* **wysokości barier** energetycznych oraz **czynnیکów przedeksponencjalnych** są kluczowe dla wiarygodnych symulacji reakcji chemicznych. Obliczenie czynników przedeksponencjalnych (równoważne obliczeniu energii swobodnej) stanowi często poważną **trudność**. Standardowym podejściem jest przybliżenie **oscylatora harmonicznego, rotatora sztywnego oraz gazu doskonałego** do wyznaczenia funkcji rozdziału odpowiednio: oscylacyjnej, rotacyjnej i translacyjnej [65]. W procesach heterogenicznych, z reguły, zanim dojdzie do procesu katalitycznego substraty muszą ulec adsorpcji. Oddziaływanie substratów, produktów czy stanów pośrednich często ma naturę oddziaływań van der Waalsa z dominującym członem dyspersyjnym i charakteryzujących się płaskim, anharmonicznym potencjałem o wielu minimach i niskich dzielących je barierach [66, 67]. Typowym przykładem są węglowodory w zeolitach [68–71]. Przybliżenie oscylatora harmonicznego i rotatora sztywnego (ang. *harmonic oscillator, rigid rotor*, HO-RR) zawodzi szczególnie w przypadku obsadzenia wyższych stanów oscylacyjnych i rotacyjnych, czyli w **podwyższonych temperaturach**, typowych dla wielu procesów **katalizy heterogenicznej**. Ogólnie, problem anharmoniczności może zostać rozwiązany przez **próbkowanie** powierzchni energii potencjalnej (PES). Następnie, uzyskane wartości energii mogą zostać aproksymowane **funkcją analityczną**, dla której rozwiązuje się **oscylacyjne i rotacyjne zagadnienie własne**. Można także zastosować metodę **Monte-Carlo** [72–75] lub **dynamikę molekularną *ab initio*** (AIMD) [76]. Dynamika molekularna jest jednakże na ogół realizowana jako dynamika **klasyczna**, newtonowska, i jako taka **zaniedbuje** ona kwantowo-mechaniczny ruch jąder, a zatem także energię oscylacyjnego **stanu podstawowego** (ang. *zero point energy*, ZPE). W dynamice molekularnej zmiana energii swobodnej między stanami 1 i 2 może być obliczona wprost, jako funkcja **prawdopodobieństwa** realizacji tych **stanów** w zespole kanonicznym: $\Delta G_{1 \rightarrow 2} = -RT \ln \frac{p(2)}{p(1)}$, gdzie R oznacza stałą gazową, T temperaturę, zaś $p(x)$ oznacza prawdopodobieństwo stanu x . Ze podejścia tego można skorzystać, jeśli prawdopodobieństwo stanu 2 jest **wystarczająco wysokie** (problem rzadkich zdarzeń, ang. *rare event problem*). W przeciwnym wypadku można zastosować tzw. **próbkowanie parasolowe** (ang. *umbrella sampling*) [77] lub właśnie **całkowanie termodynamiczne** (ang. *thermodynamic integration*) [78–80].

2.6.6 Architektura autorskiego klastra obliczeniowego

W niniejszym rozdziale opisuję wybrane, niestandardowe rozwiązania, które zastosowałem przy konstrukcji klastra obliczeniowego.

- Opracowałem własny systemu automatycznej konfiguracji nowych węzłów obliczeniowych – konfiguracja jest uzależniona od architektury i zasobów komputera, a także od tego, czy na lokalnym dysku twardym ma zostać zainstalowany system operacyjny, czy też ma on służyć wyłącznie jako pamięć masowa do przechowywania plików tymczasowych (ang. *scratch disk*) o znacznym rozmiarze, natomiast system operacyjny jest ładowany z zasobu sieciowego.
- Wybór ładowanych bibliotek dzielonych uzależniony jest od architektury procesorów węzłów obliczeniowych: AMD opteron/(mikroarchitektura *bulldozer*), opteron/(mikroarchitektura K10), intel/Xeon. Występujące między nimi niewielkie z pozoru różnice muszą być uwzględnione w celu zapewnienia maksymalnej wydajności, a czasem wręcz stabilności kodu.

- Do komunikacji poszczególnych komputerów, wchodzących w skład klastra, służą dwie sieci:
 - jedna, służąca do uwierzytelnienia zadań użytkowników (za pomocą wymiany kluczy kryptografii niesymetrycznej, RSA): typowy *gigabit ethernet*.
 - druga, charakteryzująca się bardzo dużą przepustowością oraz wyjątkowo krótkim opóźnieniem (czasem dostępu) — Infiniband (*ib*) dla celów komunikacji międzyprocesowej, w tym zdalnego, bezpośredniego dostępu do pamięci (ang. *remote direct memory access*, RDMA). Zastosowano sieć w postaci zrównoleglonej, czterokanałowej ($4\times$), o poczwórnej przepustowości (QDR, przesył w 4 punktach okresu zegara taktującego), co daje całkowitą przepustowość równą 32 Gbit/s. Obecnie infiniband jest najczęściej wykorzystywaną infrastrukturą komunikacyjną w konstrukcji superkomputerów. Topologię sieci *ib* określa się w literaturze anglojęzycznej mianem *switched fabric*. Ponieważ w literaturze polskiej brak jest ugruntowanego tłumaczenia, proponuję określenie *topologia przełączanego medium*, gdyż działanie jej polega na zastosowaniu przełączanej/adaptowanej topologii, zależnej od chwilowego przepływu pakietów w taki sposób, że dla każdej trasy pakietów tworzony jest wirtualny kanał komunikacji, nie kolidujący z innymi możliwymi w tym samym czasie transmisjami. Przełączanie kanałów odbywa się sprzętowo, za pomocą dedykowanych układów scalonych. Technologia *switched fabric* jest rozwinięciem koncepcji *crossbar switch* wywodzącej się z telekomunikacji i polegającej na bezpośrednim łączeniu wybranego wejścia z wybranym wyjściem (w analogowej centrali telekomunikacyjnej), i stąd pochodzi jej nazwa. Warto tu zaznaczyć, że technologia *ib* jest rozwojowa — obecnie trwają prace nad osiągnięciem przepustowości 300 Gbit/s, charakteryzuje się też znaczną niezawodnością i dzięki temu jest stosowana w bankowości czy w obsłudze centrów danych.
- Pamięć masowa: programowa macierz dyskowa typu RAID (ang. *redundant array of independent disks*), poziom 1 (ang. *mirroring*). Zastosowana została replikacja całego dysku, a nie tylko wybranych partycji. Spowodowało to konieczność dostosowania jądra systemu operacyjnego do możliwości uruchamiania systemu z urządzenia objętego replikacją. Zaletą macierzy RAID 1, oprócz znacznie zwiększonej niezawodności, jest też dwukrotny wzrost przepustowości dysku przy odczycie (tryb sekwencyjny). Dużą zaletą macierzy programowej (ang. *software RAID*), opartej o rozwiązania otwarte (ang. *open software*), jest jej wyjątkowa elastyczność (zarówno dotyczy to szerokiego spektrum obsługiwanego sprzętu, jak i konfigurowalności, które w rozwiązaniach sprzętowych są spotykane jedynie w bardzo kosztownych sterownikach), dostępność narzędzi naprawczych oraz możliwość analizy i zrozumienia szczegółów działania. Narzut w postaci przeliczania adresów bloków dyskowych przez procesor jest niezauważalna.
- Usługa zdalnego pulpitu w technologii NX z wykorzystaniem otwartego oprogramowania firmy *nomachine*. Zaletą tej technologii jest znakomita kompresja przesyłanych danych, a dzięki temu wyjątkowo niewielkie wymagania co do przepustowości sieci. Umożliwiająca to interaktywną pracę w środowisku graficznym nawet z wykorzystaniem połączenia modemowego. Każdy użytkownik uzyskuje dostęp do pulpitu, który może zostać w dowolnym momencie wielokrotnie odłączany (ang. *suspended*) i ponownie podłączany (ang. *resumed*), nawet z fizycznie innego terminala. Stan wszystkich uruchomionych programów zostanie zachowany na czas odłączenia sesji, natomiast funkcjonowanie programów nie jest zawieszane („zamrożone”). Według deklaracji producenta, możliwe jest uzyskanie stopnia kompresji od 10:1 to 1000:1 w typowych zastosowaniach. Co więcej, technologia NX wykorzystuje do przesyłu danych i uwierzytelnienia użytkowników powszechnie uznany protokół *secure shell* (SSH).