

Chemistry and Molecular Sciences and Technologies

COST Action CM1104

Reducible oxide chemistry, structure and functions

Working Groups 1-Fundamentals and 3-Reactivity Meeting

April 18-19, 2013

Organizers

- **Günther Rupprechter – local organizer**
Vienna University of Technology, Vienna
- **M. Verónica Ganduglia-Pirovano – WG1 coordinator**
Institute of Catalysis and Petrochemistry-CSIC, Madrid
- **Jörg Libuda – WG3 coordinator**
University of Erlangen-Nuremberg

Program

Day 1 – April 18, 2013

Opening:

- 9:00 to 9:10 – **Welcome by the Organizers**

Session I: **Metal/oxide systems I** – Chair: **Günther Rupprechter**

- 9:10 to 9:30 – **Henrik Grönbeck**
A first-principles view of the Cabrera-Mott model for metal oxidation
- 9:30 to 9:50 – **Shamil Shaikhutdinov**
CO oxidation over metal-supported ultrathin oxide films
- 9:50 to 10:10 – **Claude R. Henry**
Reactivity of regular arrays of Pd and PdAu clusters supported on nanostructured alumina ultrathin films

10:10 to 10:40: Coffee Break

- 10:40 to 11:00 – **Konstantin Neyman**
On the concept of ionic platinum species in catalytic materials based on Pt-CeO₂ nanocomposites
- 11:00 to 11:20 – **Rubén Pérez**
A combined nc-AFM and DFT study of Pt atoms adsorbed on TiO₂(110)
- 11:20 to 11:40 – **Niklas Nilius**
Adsorption of gold adatoms on ceria thin films
- 11:40 to 12:00 – **Lasse B. Vilhelmsen**
Catalysis at oxidized gold clusters on TiO₂(110)

12:00 to 13:30: Lunch Break

Session II: **Metal/oxide systems II** – Chair: **M. Veónica Ganduglia-Pirovano**

- 13:30 to 13:50 – **Paolo Fornasiero**
Nanoscale engineering of the metal-ceria interface
- 13:50 to 14:10 – **Albert Bruix**
Strong metal-support interactions on Pt/CeO₂
- 14:10 to 14:30 – **Peter Broqvist**
Ceria at the nano scale: impact of environment
- 14:30 to 14:50 – **Mónica Calatayud**
Measuring reducibility of metal oxides from DFT calculations
- 14:50 to 15:10 – **Michael Nolan**
Surface modified TiO₂ photocatalysts: Insights from first principles simulations

15:10 to 17:00: Coffee Break and Poster Session

Session III: Reactivity – Chair: Jörg Libuda

- 17:00 to 17:20 – **Stefano Fabris**
Unifying Concepts in water oxidation catalysed by RuO₂-based materials: Surface mechanisms replicated at molecular sites
- 17:20 to 17:40 – **Javier Carrasco**
DFT study of ethyne hydrogenation on CeO₂(111)
- 17:40 to 18:00 – **Yaroslava Lykhach**
C-C bond cleavage in carboxylic acid and alcohols on Pt/ceria model catalysts
- 18:00 to 18:20 – **Arturo Martínez-Arias**
CuO_x dispersed on different ceria surfaces: influence on activity and selectivity for the CO-PrOX process
- 18:20 to 18:40 – **Adrián Bonivardi**
Hydrogen-assisted surface reduction mechanism of cerium-gallium mixed oxide with enhanced redox properties

20:00: Conference Dinner

Day 2 – April 19, 2013

Session IV: Oxide formation, defects and characterization – Chair: Michael Reichling

- 9:00 to 9:30 – **Edvin Lundgren**
Novel in situ techniques for studies of model catalysts
- 9:30 to 9:50 – **Vladimir Matolín**
Growth of Ce_2O_3 thin film model catalysts
- 9:50 to 10:10 – **M. Alexander Schneider**
Properties of a bilayer $\text{CoO}(111)$ film on $\text{Ir}(100)$

10:10 to 10:40: Coffee Break

- 10:40 to 11:00 – **Sergey M. Kozlov**
Steps on $\text{CeO}_2(111)$: Step energies, STM appearance, O vacancy formation
- 11:00 to 11:20 – **Jeppe V. Lauritsen**
Atom-resolved NC-AFM studies of polar surfaces of insulating metal oxides: $\text{ZnO}(0001)$ -O and $\text{MgAl}_2\text{O}_4(100)$
- 11:20 to 11:40 – **Milica Todorović**
STM contrast mechanisms on a metal-oxide surface: Towards chemically selective imaging by controlling tip apex chemistry
- 11:40 to 12:00 – **Željko Šljivančanin**
Modelling graphene oxidation: From small epoxy clusters to a fully oxidized surface

12:00 to 13:40: Lunch Break

Session V: Doped titania and ceria, and other oxide systems – Chair: Kersti Hermansson

- 13:40 to 14:00 – **Gianfranco Pacchioni**
The unusual properties of oxide ultrathin films: how to make MgO from a non-reducible to a “reducible oxide”
- 14:00 to 14:20 – **Tiziano Montini**
Metal/ TiO_2 -B,N nanocomposites as photocatalysts for production of valuable chemicals under solar irradiation
- 14:20 to 14:40 – **José C. Conesa**
DFT+U modelling of a Mo-containing oxide catalyst
- 14:40 to 15:00 – **Soghomon Boghosian**
Ceria doped with lanthana and zirconia. Probing structural defects of the ceria cubic matrix by high temperature Raman spectroscopy
- 15:00 to 15:20 – **Carmen Tiseanu**
Nanoscale heterogeneity in CeO_2 - ZrO_2 revealed by luminescence spectroscopy
- 15:20 to 15:40 – **Verónica Vildosola**
Two-dimensional electron gas generation at the surface of the charge ordered BaBiO_3 semiconductor: a new physical mechanism

15:40 to 16:00: Discussion and Closing

Talks

A first-principles view of the Cabrera-Mott Model for Metal Oxidation

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Oxidation of metals is an every-day phenomenon of significant practical importance within, for example, catalysis and corrosion. The work of Cabrera and Mott (CM) in the mid-twenty century still remains the main theoretical basis for thin oxide growth on metals [1]. According to CM, electrons from the Fermi level of the metal substrate traverse the developing oxide film to acceptor levels of oxygen molecules to form different anions (O_2^{2-} , O_2^- , O^{2-} , O^-) on the oxide surface. The negative anions and their positive counterpart at the metal-oxide interface generate an electric potential, called the Mott potential, which effectively lowers the energy barriers for migration of ions through the oxide. As the oxide thickness increases, the effect of the Mott potential on the oxidation rate diminishes and the process is terminated at some limiting thickness. Recently, Zhou et al. [2] demonstrated that limiting thickness of the aluminium oxide on Al(111) can be tuned by oxygen pressure. In particular, it was observed that the thickness of the alumina film increases with increasing oxygen pressure up to 1 Torr after which the oxide film it remains constant at thickness of 12.4 Å.

In this study [3], we have explored some key features of Al_2O_3 thin film growth on metallic on Al(111) by first-principles calculations. Our results support many of the assumptions of the CM model. For example, the estimated limiting thickness of Al_2O_3 on Al(111) is found to be 16 Å, which agrees well with the experimental data. Furthermore, the charge transfer to adsorbed oxygen molecules generates a Mott potential with a value in close agreement with experimental observations. Interestingly, however, our results suggest an alternative interpretation as to the underlying reason for the limiting thickness.

[1] N. Cabrera, N.F. Mott, Reports on Progress in Physics **12**, 163 (1948).

[2] N. Cai et al. Phys. Rev. Lett. **107**, 035502 (2011).

[3] J. Baran, H. Grönbeck, A. Hellman, (submitted).

CO oxidation over metal-supported ultrathin oxide films

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Well-ordered thin oxide films grown on single crystal substrates have drawn some attention in recent years as suitable oxide supports for modeling highly dispersed metal catalysts at the atomic scale. A continuously growing body of experimental and theoretical results points to that *ultrathin* oxide films, those below one nanometer in thickness, may exhibit interesting catalytic properties in their own right, which may not be observed on thicker films or respective single crystal surfaces. [1,2]

In this work, we have studied catalytic properties of ultrathin oxide films by the low temperature CO oxidation reaction at near-atmospheric pressures. The systems include Fe, Mn, Zn, and Ru-oxide films [3,4]. In particular, we focused on possible effects of the film thickness and metal support on the reaction rate. Structural characterization was performed by a number of surface-science techniques such as a low energy electron diffraction (LEED), Auger electron spectroscopy (AES), a temperature programmed desorption (TPD), and scanning tunneling microscopy (STM). The activity was measured by gas chromatography.

The results reveal a strong correlation between the reaction rate and the desorption temperature of the most weakly bound oxygen species present on these films under net oxidizing conditions. The results suggest oxygen binding energy as a suitable descriptor for this reaction.

- [1] L. Giordano, G. Pacchioni, *Acc. Chem. Res.*, **44**,1244 (2011).
- [2] S. Shaikhutdinov, H.-J. Freund, *Ann. Rev. Phys. Chem.*, **63**, 619 (2012).
- [3] Y. Martynova, B. Yang, et al., *Catal. Lett.*, **142**, 657 (2012).
- [4] Y. Martynova, B.-H. Liu, et al., *submitted*.

Reactivity of regular arrays of Pd and PdAu clusters supported on nanostructured alumina ultrathin films

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The reactivity of metal clusters depends on their size, shape, on the support [1] and also on the distance between them through the reverse spillover effect [2]. Moreover it is known that for tiny clusters reactivity can vary as a function of the exact number of atoms they contain [1]. In order to understand the variation of the reactivity as a function of cluster size it is necessary to be able to prepare uniform (in size, shape and spatial distribution) collections of clusters in a broad size range. This goal has been reached by growing, in a controllable way, the metal clusters on a nanostructured alumina film grown on Ni₃Al (111) surface presenting an hexagonal arrangement of point defects separated by 4.1 nm [3] which play the role a template to grow regular arrays of pure metal clusters [4] or bimetallic clusters with adjustable size and composition [5]. The spatial distribution is very uniform on the whole substrate, as checked by GISAXS [6] and this organization is stable up to 600 K [7]. The reactivity towards CO of Pd clusters has been studied by molecular beam relaxation spectroscopy (MBRS) on a very broad range of size: from 5 atoms to 6 nm. From the measurement of the life time of CO molecules adsorbed on the clusters, at various temperatures, the adsorption energy of CO is measured as a function of cluster size. For the first time, it has been possible to observe quantitatively the evolution of the reactivity of metal clusters between the molecular regime, where the electronic structure depends on the exact number of atoms in the cluster, and the bulk regime, where the electronic structure varies monotonously as a function of size. In the case of bimetallic PdAu clusters of a mean size of 2 nm the adsorption energy of CO decreases continuously when the Au content increases until the equal concentration is reached where CO does no longer adsorbs. These results are explained by an ensemble effect and a core-shell structure of the of the bimetallic clusters

[1] "NANOCATALYSIS" Eds. U. Heiz, U. Landman; Springer, Berlin (2007).

[2] M.A. Röttgen, S. Abbet, K. Judai, J.M. Antonietti, A.S. Wörz, M. Arenz, C.R. Henry, U. Heiz, J. Am. Chem. Soc. **129**, 9635(2007).

[3] G. Hamm, C. Barth, C. Becker, K. Wandelt, C.R. Henry, Phys. Rev. Lett. **97** 126106(2006).

[4] S. Degen, C. Becker, C. Wandelt, Farad. Discuss. **125**, 343(2003).

[5] G. Hamm, C. Becker, C.R. Henry, Nanotechnology **17**, 1943(2006).

[6] G. Sitja, M. Marsault, F. Leroy, S. Le Moal, C.R. Henry, Int. J. Nanotechnol. **9**, 567(2011).

[7] M. Marsault, *PhD thesis* Marseille (2010).

On the concept of ionic platinum species in catalytic materials based on Pt-CeO₂ nanocomposites

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Catalysts containing oxide-supported Pt are of utmost importance for automobile catalytic converters, which ‘consume’ 40% of the worldwide manufactured Pt-group metals. Pt-CeO₂ catalysts are also widely used for the water-gas-shift (WGS) reaction, a key step in fuel processing to generate hydrogen. Too high costs for the noble metal is the major problem for Pt-based catalysts. But formulations containing only traces of Pt would be economical [1]. This requirement seems to be fulfilled for novel Pt-CeO₂ material highly active and CO-tolerant anode fuel cell (FC) catalyst [2]. Its characterization revealed that most of the small loaded Pt amount is present as cations, indicating that cationic Pt atomically dispersed on nanostructured ceria may be essential for the anode FC catalysis. Preparation of a highly active Pt-CeO₂ catalyst with very low Pt loading requires that most of Pt forms atomic cations is located in positions accessible for the reactants [3]. The formation of surface Ptⁿ⁺ species in Pt-CeO₂ nanostructures and their possible importance for several catalytic reactions has been reported [4]. However, atomic-level information on the active sites of such complex catalytic structures remains lacking [5].

We present an overview of computational density functional modelling studies of atomic Pt species interacting with various forms of CeO₂ ranging from the most stable regular surface CeO₂(111) [6] to recently developed nanoparticulate models [7]. The focus is on the electronic state of Pt as well as on the geometric structure and stability of the surface complexes.

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- [1] Q. Fu, H. Saltsburg, M. Flytzani-Stephanopoulos, *Science* **301**, 935 (2003).
 - [2] V. Matolín, I. Matolínová, M. Vaclavu et al., *Langmuir* **26**, 12824 (2010).
 - [3] M. Hatanaga, N. Takahashi, T. Tanabe et al., *Appl. Catal. B* **99**, 336 (2010).
 - [4] M. S. Hedge, G. Madras, K. C. Patil, *Acc. Chem. Res.* **42**, 704 (2009).
 - [5] M. Flytzani-Stephanopoulos, B. C. Gates, *Annu. Rev. Chem. Biomol. Eng.* **3**, 545 (2012).
 - [6] A. Bruix, A. Migani, G. N. Vayssilov, K. M. Neyman, J. Libuda, F. Illas, *Phys. Chem. Chem. Phys.* **13**, 11384 (2011).
 - [7] A. Migani, K. M. Neyman, S. T. Bromley, *Chem. Commun.* **48**, 4199 (2012).

A combined nc-AFM and DFT study of Pt atoms adsorbed on TiO₂(110)

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A first step to understand the role of Pt/TiO₂ systems as heterogeneous catalysts is to probe their structural and electronic properties at the atomic scale. Here, we work along this line by studying single Pt atoms adsorbed on hydroxylated TiO₂(110)-1x1 with a combination of non-contact atomic force microscopy (nc-AFM) and first-principles calculations. The calculations are based on tip models which have been recently proposed to explain the observed tip-sample forces for the most frequent contrast modes of hydroxylated TiO₂(110) [1]. The experiments are performed with the microscope in a Kelvin-Probe Force Microscopy (KPFM) setup and both force and local contact potential difference (LCPD) curves have been obtained. From the nc-AFM images associated with the most frequent contrast modes we deduce that the region where the Pt atom is adsorbed and subjected to diffusion at room temperature is around the fivefold coordinated titanium rows and confined between two bridging oxygen rows (see Fig 1a). By comparing the force spectroscopy data and the simulated forces (see Fig 1b and c), we find the microscopic mechanisms causing the image contrast, and, in particular, we explain the puzzling fact that for each contrast mode the Pt atom always appears as the brightest surface feature. Furthermore, we analyze the charge state of the Pt atom by means of KPFM images and Bader charge calculations, and we discuss the relation between the LCPD curves and the collapse of the vacuum barrier between tip and surface that provokes a sudden change in the calculated workfunction of the tip-sample system.

[1] A. Yurtsever et al., Phys. Rev. B **85**, 125416 (2012).

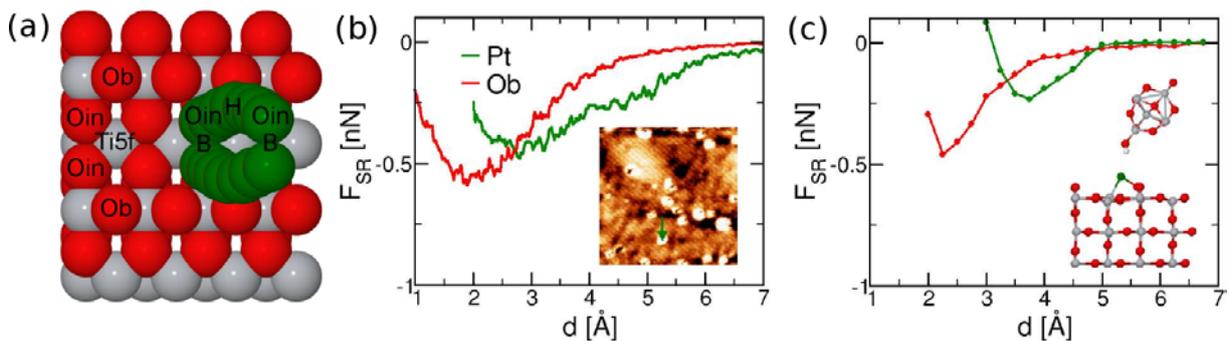


Fig 1. (a) Ball-and-stick representation of the TiO₂(110) surface with the Pt adsorption sites which are reachable at room temperature. Color code: O atoms are red, Ti atoms are grey, and Pt atoms are green. The nomenclature for each site is indicated in black. (b) Experimental short-range tip-sample forces over Pt (green line) and bridging O (red line) sites indicated in the inset image. (c) Calculated tip-sample forces over the same sites as in (b) using the tip model of the inset.

Adsorption of gold adatoms on ceria thin films

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Low-temperature scanning tunnelling microscopy and spectroscopy are employed to study the adsorption of individual Au atoms on well-defined CeO₂(111) films grown on Ru(0001). For slightly reduced films, two types of Au species are found on the surface. While the first one shows up as isolated protrusion, the second type develops a distinct Sombrero-shape and always appears in pairs of 8-10 Å distance. The relative abundance of the two species sensitively depends on the reduction state of ceria lattice, i.e. the density of oxygen vacancies. According to DFT calculations, we assign the two species to Au atoms in two different charge states. While the simple protrusion corresponds to positively-charged Au bound to O-sites on the ideal, defect-free surface, the paired species are negatively charged and decorate subsurface O-defects. The pair formation reflects the nature of O vacancies to generate always two Ce³⁺ ions that are able to transfer electrons to two Au atoms above. The observation of Au pairs therefore provides evidence for charge-transfer between reduced Ce³⁺ and electronegative Au ad-species, but also represents an intrinsic ruler to measure the mean distance between the two Ce³⁺ generated by each O defect.

Catalysis at Oxidized Gold Clusters on TiO₂(110)

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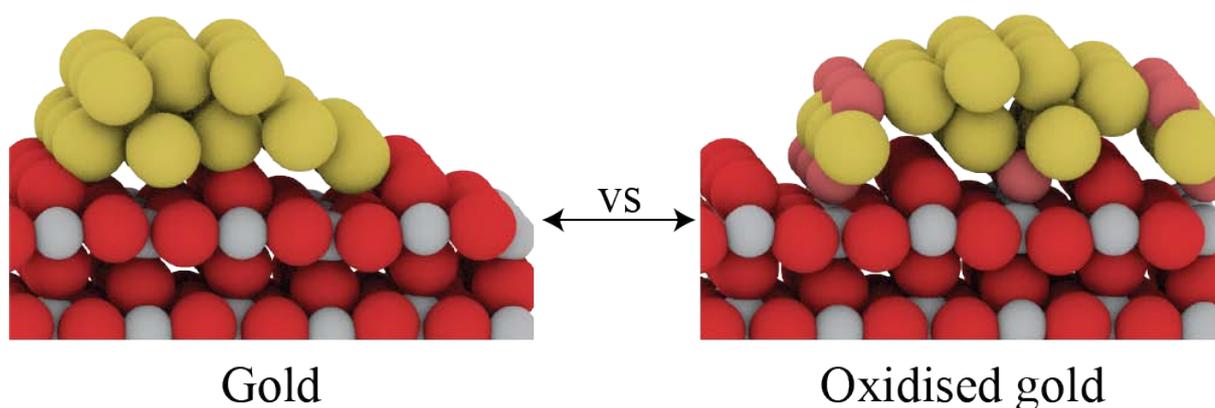
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One of the major challenges in gold catalysis is the high structural fluxionality of supported gold clusters during chemical reactions. To investigate the structural and catalytic changes induced by an increasing amount of oxygen we look at the structure of gold rods on the TiO₂(110) surface with varying amounts of oxygen present. The investigations are done with a specialized genetic algorithm (GA) together with density functional theory calculations. The GA has previously been used successfully in the prediction of gold clusters on MgO(100) [1] and in MOFs [2] and for the prediction of step reconstructions on the TiO₂(110) surface [3]. The GA enables a systematic and unbiased investigation of rods with different stoichiometries.

We predict that the interface between the TiO₂(110) surface and the gold rods will oxidize under ambient conditions, whereas the edge of the gold rods will only fully oxidize in a CO-free environment. Under reactive conditions the gold rod catalyses the splitting of molecular oxygen at the TiO₂/gold interface with a barrier of less than 0.5eV thus enabling a CO-oxidation reaction on these supported structures at mild conditions.

One important aspect in these investigations is the reduction state of the TiO₂ crystal. Unsurprisingly the stability of the oxidised gold rods increase with increased reduction of the crystal. It is however shown that the most significant change happens when going from a stoichiometric crystal to a slightly reduced crystal, whereas the energetics is less affected by a higher reduction.

These investigations expand on the recent investigations by Yates et al. [4] where the authors consider the low temperature and pressure CO oxidation reaction at an idealised gold rod on stoichiometric TiO₂. Using the genetic algorithm in the structure prediction together with investigations of the reduction of the crystal enables a more detailed description of the gold rod oxidation and charge transfer in the system.



[1] Vilhelmsen, L.B.; Hammer, B. *Phys. Rev. Lett.* 2012, 108, 126101

[2] Vilhelmsen, L.B.; Walton, K.S.; Sholl, D.S. *J. Am. Chem. Soc.*, 2012, 134 (30), pp 12807–12816

[3] Martinez, U.; Vilhelmsen, L.B.; et al.; *Phys. Rev. B*, 2011, 84 (20), 205434

[4] Green, I.X.; Tang, W.; et al.; *JACS*, 2012, 134, 12717-12723

Nanoscale engineering of the metal-ceria interface

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Ceria (CeO₂) is an key example of an “active support”, meaning that it plays a fundamental role in the reaction mechanism of many industrially important catalytic processes, especially those involving redox steps, such as methane oxidation, CO oxidation, Water-Gas Shift (WGS), steam reforming, and organic transformations.[1-3] This support improves the catalytic activity of deposited metals by orders of magnitude especially for oxidation reactions. The increased activity of metal-ceria catalysts is typically attributed to the capability of ceria to store and release lattice oxygen which participates in the catalytic cycle. The observed enhancement must result from active sites at the metal-ceria interface, since the rate is higher than what is expected based simply on the rates over ceria and the metal individually. Furthermore, the activity changes with particle size as associated with the metal-support interface.[4] Understanding size-activity relationships for ceria-based catalysts is fundamental towards improving catalyst performance. A precise structural and morphological control of metal supported on CeO₂, coupled with the possibility to modulate the metal-support interactions, allowed us to better understand the and CO oxidation reactivity of ceria based catalysts.

References

- [1] A. Trovarelli, *Cat Rev. Sci. Eng* **38**, 439 (1996).
- [2] T. Bunluesin, et al. *Appl. Catal. B: Environ.* **15**, 107 (1998).
- [3] M. Cargnello, et al. *Science* **337**, 713 (2012).
- [4] M. Cargnello, et al. *Catal. Lett.* **142**, 1043 (2012).

Strong Metal-Support Interactions on Pt/CeO₂

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We have examined the electronic properties of Pt nanoparticles deposited on CeO₂(111) and CeO_x/TiO₂(110) model catalysts using photoemission and density-functional (DF) calculations. The results of valence photoemission and DF calculations point to a new type of Strong Metal-Support Interaction (SMSI) which produces large electronic perturbations for small Pt particles in contact with ceria. This significantly enhances the ability of the admetal to dissociate the O-H bonds in water, which directly affects the production of H₂. When going from Pt(111) to Pt₈/CeO₂(111), the dissociation of water becomes a very exothermic process. The ceria-supported Pt₈ appears as a fluxional system that can change geometry and charge distribution to better accommodate adsorbates. Compared to other WGS catalysts {Cu(111), Pt(111), Cu/CeO₂(111) and Au/CeO₂(111)}, the Pt/CeO₂(111) surface has the unique property that the admetal is able to dissociate water in an efficient way.[1]

[1] A. Bruix, J. A. Rodríguez, P. J. Ramírez, S. D. Senanayake, J. Evans, J. B. Park, D. J. Stacchiola, P. Liu, J. Hrbek, F. Illas, *J. Am. Chem. Soc.*, 134, 8968–8974 (2012)

Ceria at the nano scale: impact of environment

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The chemical composition, shape and structure of small metal-oxide nanoparticles can be strongly affected by its surrounding environment. In a recent study [1], we demonstrated how reduced ceria nanoparticles could be stabilized in an oxidative environment through the adsorption of many O₂ molecules. Rather than being re-oxidized to form a CeO₂ nanoparticle, such reduced particles become supercharged with O₂⁻ species leading to a dramatically enhanced oxygen storage capacity.

In the current work, we study the chemical composition, shape and structure of ceria nanoparticles in reducing, oxidative and humid environments. We search for the global minimum structures using a force-field based evolutionary algorithm. From the initial screening, candidate structures are further geometry-optimized using density functional calculations and the effect of the environment is introduced through standard thermodynamic relations. Based on our calculations, we predict that small stoichiometric ceria nanoparticles will have a very limited stability range in both oxidative and humid environments. Instead, as illustrated in **Fig. 1**, the reduced ceria nanoclusters are stabilized through the adsorption of oxygen molecules in the form of superoxo species and water in the form of hydroxo species.

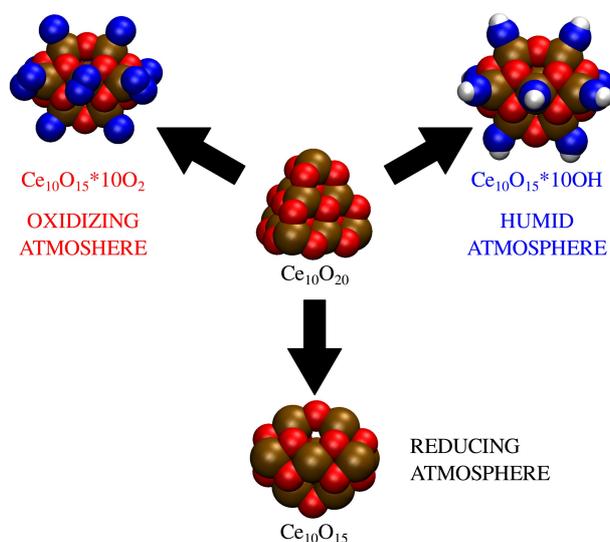


Fig. 1 Our calculations predict that stoichiometric clusters have limited stability and readily transform into reduced clusters in oxidizing, humid and reducing atmospheres. This is exemplified in the figure for the $Ce_{10}O_{20}$ (stoichiometric) and $Ce_{10}O_{15}$ (reduced) clusters.

[1] J. Kullgren et al., J. Phys. Chem. Lett. **4**, 604–608 (2013)

Measuring reducibility of metal oxides from DFT calculations

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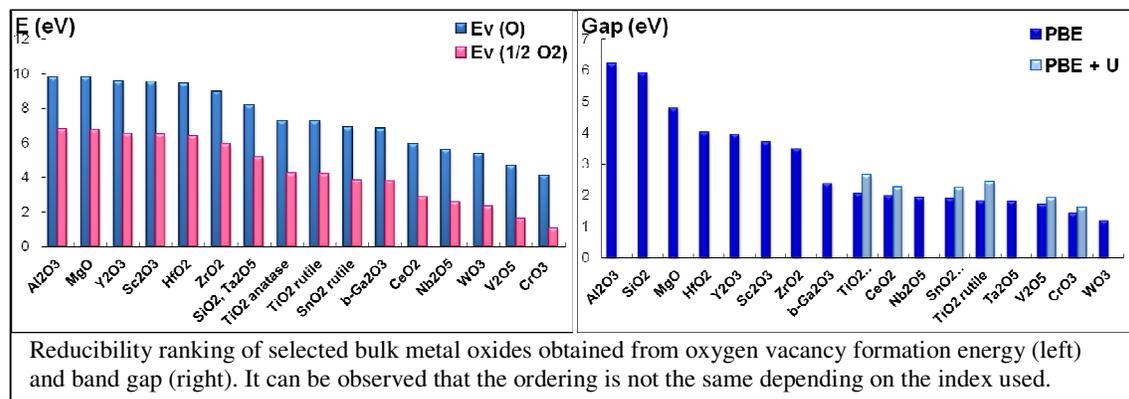
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Reducibility is one of the main properties determining the oxide chemical behaviour. If the meaning of “reducible metal oxide” is clear for both chemists and physicists, the term is far from being unambiguous.

From the theoretical point of view, some reactivity descriptors have been used to understand the nature and the extent of reducibility in a variety of materials. Among the most widely used, the oxygen vacancy formation energy E_v allows measuring the cost of removing an oxygen out of the lattice. The electronic description of the reduced system is also a critical index to understand reducibility: the band gap is correlated with the ability of a system to be reduced. Also, the localization of the electrons left by the removal of a lattice oxygen can be used as index: they may be transferred to the cation if it is reducible, or may stay at the lattice point if it is not.

In the present work we perform periodic density functional theory based calculations on a series of bulk metal oxides to establish a ranking of reducibility based on two criteria: the E_v value and the electronic structure. We will show that the two criteria do not lead to the same ordering, and we will discuss case examples of reducible, irreducible and intermediate behaviour.

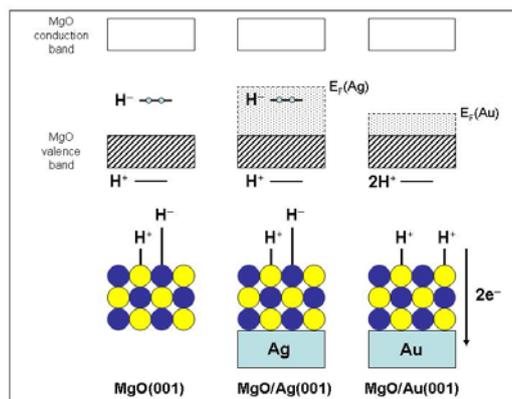


The unusual properties of oxide ultrathin films: how to make MgO from a non-reducible to a “reducible oxide”

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We will report on the unusual properties of oxides at the nanoscale, and in particular on the completely different behavior of MgO towards H_2 dissociation. It is well known that the H_2 molecule dissociates heterolytically on stepped MgO surfaces with formation of protons bound to O^{2-} anions (OH groups), and hydride ions bound to Mg cations (MgH groups). This is typical of non-reducible oxides. Homolytic splitting on MgO, with formation of a pair of OH groups per adsorbed H_2 molecule, is only possible in special conditions, like for polar MgO(111) surfaces or under irradiation due to the generation of O^{\cdot} radicals. On the contrary, homolytic splitting, with formation of adsorbed protons and transfer of the H_2 electrons to the empty d states of transition metal ions is the typical dissociation mechanism on reducible oxides like TiO_2 or CeO_2 . We demonstrate, based on first principles DFT calculations, that homolytic splitting of H_2 is the thermodynamically most favored dissociation mode if MgO(001) films of few atomic layers are deposited on a metal support. The choice of the support is crucial. In fact, while on MgO/Ag(001) ultrathin films H_2 dissociation resembles the behavior of the bare MgO surface, on MgO/Au(001) homolytic dissociation is preferred. The reason lies in the different position of the Fermi level in the two metal/oxide interfaces. The lower Fermi level (higher work function) of MgO/Au(001) favors the transfer of the H_2 electrons to the metal support via electron tunneling through the ultrathin insulating (adsorption of protons). This is another manifestation of the unusual behavior of oxides at the nanoscale. It is of general relevance for the splitting and reactivity of covalently bound molecules.



[1] Hsin-Yi Tiffany Chen, Livia Giordano, Gianfranco Pacchioni, submitted

Unifying Concepts in Water Oxidation Catalysed by RuO₂-based materials: Surface Mechanisms Replicated at Molecular Sites

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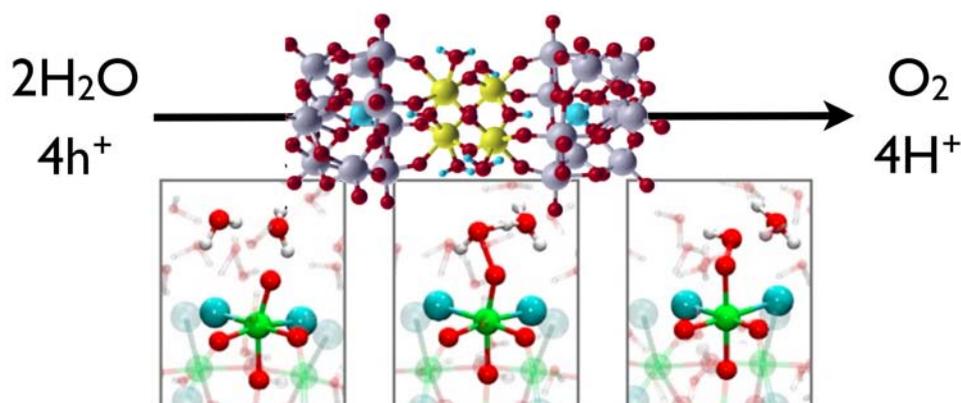
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Solar-to-fuel energy conversion relies on the invention of efficient catalysts enabling water oxidation through low energy pathways. Our aerobic life is based on this strategy, mastered by the natural Photosystem II enzyme, using a tetra-nuclear Mn-oxo complex as oxygen evolving center. Within artificial devices, water can be oxidized efficiently on tailored metal-oxide surfaces such as RuO₂. The quest for catalyst optimization in-vitro is plagued by the elusive description of the active sites on bulk oxides. Although molecular mimics of the natural catalyst have been proposed, they generally suffer from oxidative degradation under multi-turnover regime. Here we investigate a nano-sized tetraruthenium-polyoxometalate (Ru₄-POM), standing as one of the most efficient artificial catalysts reported so far and featuring a totally inorganic molecular structure with enhanced stability [1-3].

Experimental and computational evidence indicates that this is a unique molecular species mimicking oxygenic RuO₂ surfaces. Density functional theory calculations show that the catalytic efficiency of Ru₄-POM stems from the optimal distribution of the free energy cost to form reaction intermediates, in analogy with metal-oxide catalysts, thus providing a unifying picture for the homogeneous and heterogeneous water oxidation catalysis[4,5]. These correlations among the mechanism of reaction, thermodynamic efficiency, and local structure of the active sites provide guidelines for the rational design of superior molecular catalysts and composite materials designed with a bottom up approach and atomic control.



[1] A. Sartorel et al. *J. Am. Chem. Soc.* **130**, 5006 (2008).

[2] Y. Geletti et al. *Angew. Chem. Int. Ed.* **47**, 3896 (2008).

[3] F.M. Toma et al., *Nature Chemistry* **2**, 826 (2010).

[4] S. Piccinin and S. Fabris, *Phys. Chem. Chem. Phys.* **13**, 7666 (2011)

[5] S. Piccinin, A. Sartorel, G. Aquilanti, A. Goldoni, M. Bonchio and S. Fabris, to appear in *PNAS* (2013)

DFT study of ethyne hydrogenation on CeO₂(111)

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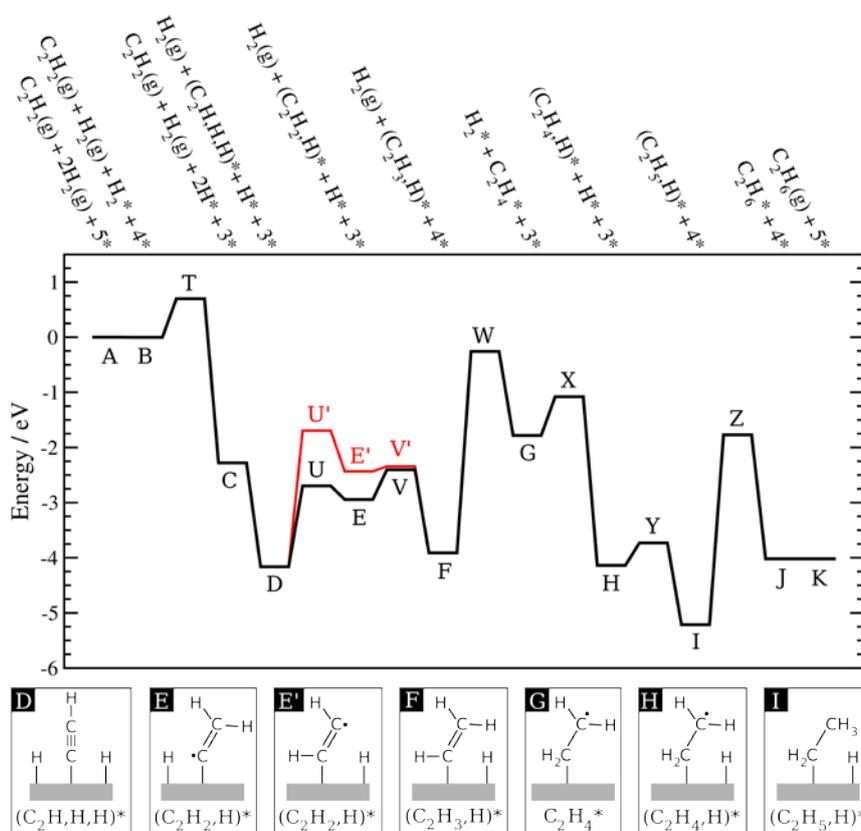
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Ceria is a key component in many heterogeneous catalysts. In typical applications ceria magnifies the performance of the active phase, but the stand-alone catalytic function of ceria is rare and usually related to oxidations. Interestingly, in a recent experimental study by some of us, we reported an unprecedented performance of pure ceria for the partial hydrogenation of alkynes to olefins with outstanding selectivity [1]. Experimental evidence shows that (111) facets are especially prone to hydrogenation and, therefore, here we combine in-depth characterization, catalytic tests, and density-functional theory (DFT) mechanistic studies to provide a molecular-level understanding of the hydrogenation of ethyne on the CeO₂(111) surface. From this study we find that (i) hydrogen activation is the most probable rate-limiting step (B→C in the figure) and (ii) a high-energy barrier of *ca.* 4 eV (F→G in the figure) hinders the over-hydrogenation process, in line with the experimentally observed virtual absence of ethane at the reactor outlet. Our results open exciting perspectives for investigating the ability of pure ceria as a catalyst for the selective hydrogenation of alkynes and other functional groups.



[1] G. Vilé et al., *Angew. Chem. Int. Ed.* **53**, 8620 (2012).

C-C bond cleavage in carboxylic acid and alcohols on Pt/ceria model catalysts

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Catalytic conversion of biomass-derived oxygenates, i.e. mixtures of carboxylic acids, alcohols, and aldehydes, is a prospective means for hydrogen production from renewable resources [1]. The fundamental challenge of this technology resides in the development of a catalyst with high selectivity towards C–C bond cleavage.

In the current study, we explored the C–C bond cleavage in acetic acid [2], ethanol [3], and ethylene glycol [3] on ceria based catalysts. The decomposition pathways of these molecules were investigated by means of synchrotron photoelectron spectroscopy (SRPES) and temperature programmed desorption (TPD) on single crystal Pt(111), well-ordered stoichiometric CeO₂(111)/Cu(111), partially reduced CeO_{2-x}/Cu(111), and Pt/CeO₂/Cu(111) model catalysts.

We found that C–C bond cleavage does not occur on Pt(111) and stoichiometric CeO₂(111)/Cu(111). There, the principal desorption products included aldehydes, ketones, and water. Ethylene was identified as the main precursor to C₂ carbonaceous deposits on Pt(111). On CeO_{2-x}/Cu(111) and Pt/CeO₂/Cu(111), partial cleavage of C-C bond leads to deposition of hydrocarbon species, CH_x. CH_x formed from acetic acid are the most stable on CeO_{2-x}/Cu(111). At high temperature, a minor fraction of CH_x desorbs as acetylene while the major part forms stable C–Ce³⁺ bonds. High yields of hydrogen were achieved only in the presence of Pt due to complete dehydrogenation of the molecules. Moreover, the remaining carbonaceous species were completely removed upon interaction with oxygen released by ceria to Pt.

Additionally, the tendency to the C-C bond cleavage is discussed with respect to the structure of the functional group in the studied molecules and their orientation on the catalytically active surfaces.

[1] B.M. Güell, G. van Rossum, W.P.M. van Swaij, S.R.A. Kersten, L. Lefferts, K. Seshan, *Appl. Catal., B*, **101**, 587 (2011).

[2] A. Neitzel, Y. Lykhach, V. Jóhanek, N. Tsud, T. Skála, K.C. Prince, V. Matolín, J. Libuda, *J. Catal.*, (2013), submitted.

[3] A. Neitzel, Y. Lykhach, V. Jóhanek, T. Skála, K. Ševčíková, N. Tsud, K.C. Prince, V. Matolín, J. Libuda, (2013), in preparation.

CuO_x dispersed on different ceria surfaces: influence on activity and selectivity for the CO-PrOx process

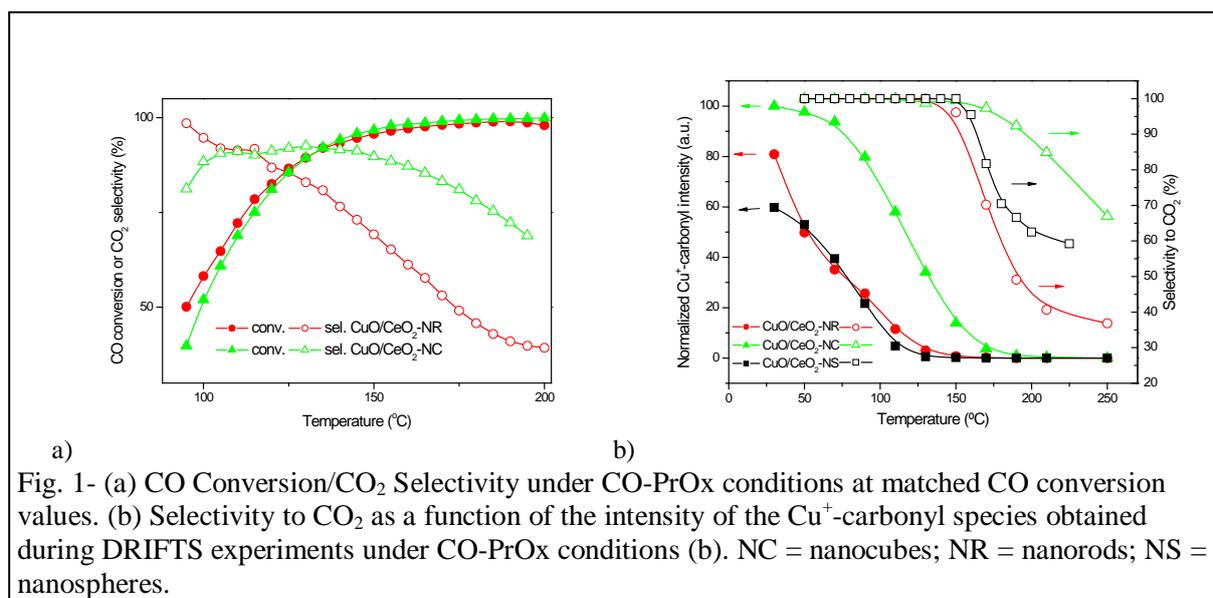
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Catalytic preferential oxidation of CO in the presence of H₂ (CO-PrOx process) is employed for purifying H₂ produced from hydrocarbons and fed to low temperature fuel cells in order to avoid CO poisoning of the Pt-based anode employed in such type of fuel cells. Our recent work [1] shows that the selectivity (related to the portion of oxygen used to oxidise CO vs. that employed to oxidise H₂, which are basically the two competing reactions in the process) of ceria-supported CuO_x in the process is appreciably improved (Fig. 1a) if one uses as support a specially prepared CeO₂ having cubic nanoparticle shape (i.e. exposing mostly the (001) surface, less stable) rather than rounded or rod-like CeO₂ nanoparticles which, like those obtained in typical syntheses of high surface area ceria, expose mainly other surfaces. Detailed characterization using XRD and TEM along with XPS and EPR evidences that the Cu oxide phase disperses very efficiently on the nanocube-shaped CeO₂, suggesting stronger CuO-ceria interaction on the (001) surface of the latter. This could be the reason for the higher stability of surface Cu⁺ carbonyls during reaction, which apparently could retard the reduction of copper to the non-selective metallic state, as evidenced by DRIFTS data obtained under reaction conditions (Fig. 1b); XPS experiments under gas atmosphere using synchrotron radiation are expected to be completed shortly in order to get further support for this hypothesis. In turn, differences in the catalytic activity of the dispersed CuO_x entities as a function of the exposed face present in the underlying CeO₂ support are also revealed by such DRIFTS experiments. The experimental results are also complemented by DFT+U calculations on slab models of CuO_x nanoparticles supported on different CeO₂ surfaces.



[1] D. Gamarra et al., Appl. Catal. B: Environmental, **130-131**, 224, (2013).

Hydrogen-assisted surface reduction mechanism of cerium-gallium mixed oxide with enhanced redox properties

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The relevance of the cerium based catalytic supports is primarily based on the remarkable oxygen storage capacity of these materials, which is linked to the creation, stabilization and diffusion of oxygen vacancies, especially in the oxide surface, due to the reversible redox property of the $\text{Ce}^{4+}/\text{Ce}^{3+}$ pair. Temperature-programmed reduction in H_2 and in CO results showed that the redox behavior is noticeably enhanced in the gallium-doped ceria powder materials as compared to pure cerium oxide. These last results were in agreement with ultimate oxygen storage capacity, in situ time-resolved X-ray diffraction (TR-XRD) and x-ray absorption near edge (XANES) measurements. The XANES Ga K-edge spectrum of ceria-gallia samples show that a change in the oxidation state of Ga^{3+} is undetectable even after exposing the sample to H_2 at temperatures up to 623 K. The redox properties of the cerium-gallium oxide were evaluated in-situ using time-resolved infrared spectroscopy in transmittance and diffuse reflectance mode. Two characteristic infrared bands were analyzed (Figure 1): a peak at 2127 cm^{-1} , which is assigned to the forbidden electronic transition ${}^2F_{5/2} \rightarrow {}^2F_{7/2}$ of Ce^{3+} cations, and a band at approximately 2000 cm^{-1} attributed to the stretching mode of the Ga-H surface bond. Based on these combined spectroscopic studies, a novel mechanism is proposed for the reduction of Ce^{4+} to Ce^{3+} where Ga-H species are suggested to be directly involved in this surface process (Figure 2). The results of temperature-programmed oxidation by O_2 (O_2 -TPO), obtained by in situ IR and TR-XRD, indicate that the Ce^{3+} of reduced samples is oxidized immediately to Ce^{4+} in both CeO_2 and in the gallium-cerium mixed oxide when exposed to O_2 at 300 K. However, the H_2O -TPO experiments showed that the reoxidation of Ce^{3+} to Ce^{4+} is partial in both materials; however, the reoxidized fraction of Ce^{3+} is 50% higher on pure ceria than on cerium-gallium mixed oxide. The proposed reduction mechanism on the gallium-ceria samples, and the lower oxidation power observed for water, as compared to oxygen, may help in the future to gain better understanding of catalytic redox processes involving mixed-oxides of ceria.

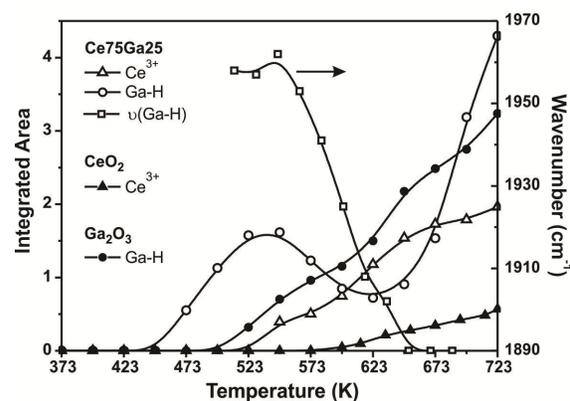


Figure 1. Thermal evolution of the concentration of the Ce^{3+} and Ga-H species under H_2 on CeO_2 , $\text{Ce}_{75}\text{Ga}_{25}$ (mixed oxide) and Ga_2O_3 .

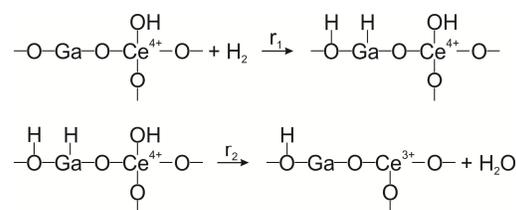


Figure 2. Surface reduction mechanism of Ce^{4+} to Ce^{3+} on the cerium-gallium mixed oxides.

Novel in situ techniques for studies of model catalysts

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We have in recent years explored the possibilities to perform experiments at conditions closer to those of a technical catalyst, in particular at increased pressures. In this contribution, results from catalytic CO oxidation over a Pd single crystal surfaces using High Pressure X-ray Photo emission Spectroscopy (HPXPS), Planar Laser Induced Fluorescence (PLIF), and High Energy Surface X-Ray Diffraction (HESXRD) will be presented.

Armed with structural knowledge from ultra-high vacuum experiments, the presence of adsorbed molecules and gas-phase induced structures can be identified, and related to changes in the reactivity and/or to reaction induced gas-flow limitations. The strength and weaknesses of the experimental techniques will be discussed.

Growth of Ce_2O_3 thin film model catalysts

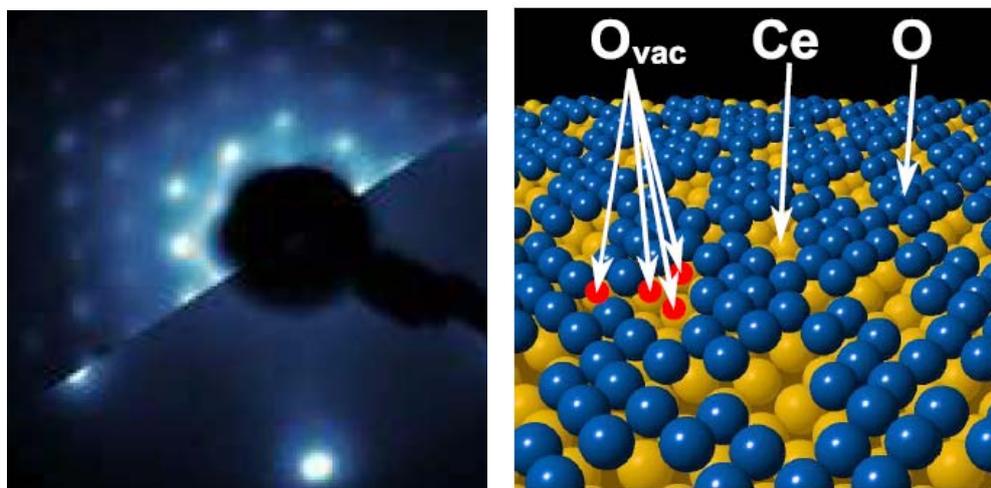
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Thin films of reduced ceria supported on metals are often applied as substrates in model studies of the chemical reactivity of ceria based catalysts. Of special interest are the properties of oxygen vacancies in ceria. However, thin films of ceria prepared by established methods become gradually disordered as the concentration of vacancies increases. We propose an alternative method for preparing ordered reduced ceria films based on the physical vapor deposition and interfacial reaction of Ce with CeO_2 films. The method yields bulk-truncated layers of cubic c- Ce_2O_3 . These layers contain 25% of perfectly ordered vacancies in the surface and subsurface allowing well-defined measurements of the properties of ceria in the limit of extreme reduction. These layers also represent a normally unstable polymorph of Ce_2O_3 , which is most likely stabilized by the tetragonal distortion of the ceria layers on Cu. The c- $\text{Ce}_2\text{O}_3(111)$ surface exhibits a characteristic 4×4 reconstruction with respect to $\text{CeO}_2(111)$ allowing its easy identification in surface science experiments.



4×4 reconstruction of the $\text{Ce}_2\text{O}_3(111)$ surface: LEED (left), model (right)

Properties of a bilayer CoO(111) film on Ir(100)

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Thin films are often a way to allow applying surface science tools -notably STM- to otherwise insulating oxide systems. Cobalt oxide films can be grown in a great variety of configurations on Ir(100). Growth of ultra-thin layers of varying oxygen content [1] but also of thick, stoichiometric, bulk-like phases can be achieved resulting in (111) surfaces perfectly ordered on a 10 nm or larger scale [2].

We concentrate here on ultra-thin CoO films to study the interaction of the oxide film with the underlying metal substrate by STM and DFT. The complete stoichiometric bilayer of CoO(111) on Ir(100) is a strongly corrugated, incommensurate, one-dimensional Moiré overlayer. DFT calculations show that the corrugation is the result of strong repulsion and attraction points in the potential landscape of the Co and O atoms on the Ir surface. Hence this overlayer is an example of an incommensurate, relaxed film with strong local binding to the underlying substrate [3]. With different preparation temperatures the Moiré periodicity and hence the binding lengths can be slightly tuned. Remarkably, however, this is not due to the increased formation of defects, the density of oxygen vacancies in these films is of the order of 5 per (10nm)². Due to the low density of defects adsorption and self-assembly of larger organic molecules can be studied on the CoO films similar to the growth on metal surfaces as demonstrated by the growth of sub-monolayer Cobalt-Phthalocyanine films.

- [1] M. Gubo, C. Ebensperger, W. Meyer, L. Hammer, K. Heinz, Phys. Rev. B **83**, 075435 (2011)
- [2] K. Biedermann, M. Gubo, L. Hammer, K. Heinz, J. Phys.: Cond. Matter **21**, 185003 (2009)
- [3] C. Tröppner, et al., Phys. Rev. B **86**, 235407 (2012)

Steps on CeO₂(111): Step energies, STM appearance, O vacancy formation

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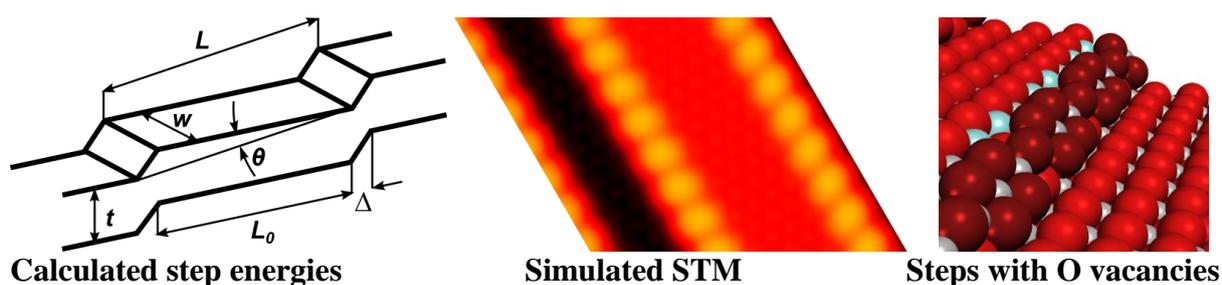
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Ceria attracts a lot of attention due to its usage in catalysis and energy technologies. Probably the most important features of ceria, high oxygen storage capacity and facile oxygen release, may be greatly amplified by nanostructuring. Steps on nanoislands, formed upon annealing, are elements of such a nanostructure, which were shown to have unique properties, for example, the ability to dissociate water [1].

In this work, by means of Density Functional Theory methods combined with Scanning Tunnelling Microscopy (STM) we determined geometric and electronic structure of three types of steps as well as their energies. Electronic structures of type I and type III steps feature split-off states, which manifest themselves in experimentally measured differential conductance curves. These states emerge due to the effect of missing O anions on the steps and make steps appear bright in STM [2]. To investigate the stabilities of the steps, we have devised two new methods to derive step energies from electronic structure calculations, which are more accurate and computationally efficient than the existing one. Results of all three methods agree with each other and also with the experimental results [3]. The reason why the steps on CeO₂(111) surface are expected to have promising properties is because low coordinated O atoms on ceria steps are thought to be bound less strongly than O atoms on the most stable {111} terraces. In this work, we also attempt to computationally investigate O vacancy formation energies on the experimentally observed step structures taking into account various possible arrangements of Ce³⁺ ions near the vacancy. O vacancy formation was found to be less endothermic on the steps and in some cases to cause step reconstruction.



- [1] Y. Lykhach, V. Johánek, H. A. Aleksandrov, S. M. Kozlov, M. Happel, T. Skála, P. St. Petkov, N. Tsud, G. N. Vayssilov, K. C. Prince, K. M. Neyman, V. Matolín, J. Libuda, J. Phys. Chem. C **116**, 12103 (2012).
- [2] N. Nilius, S. M. Kozlov, J.-F. Jerratsch, M. Baron, X. Shao, F. Vines, S. Shaikhutdinov, K. M. Neyman, H.-J. Freund, ACS Nano **6**, 1126 (2012).
- [3] S. M. Kozlov, F. Viñes, N. Nilius, S. Shaikhutdinov, K. M. Neyman, J. Phys. Chem. Lett. **3**, 1956 (2012).

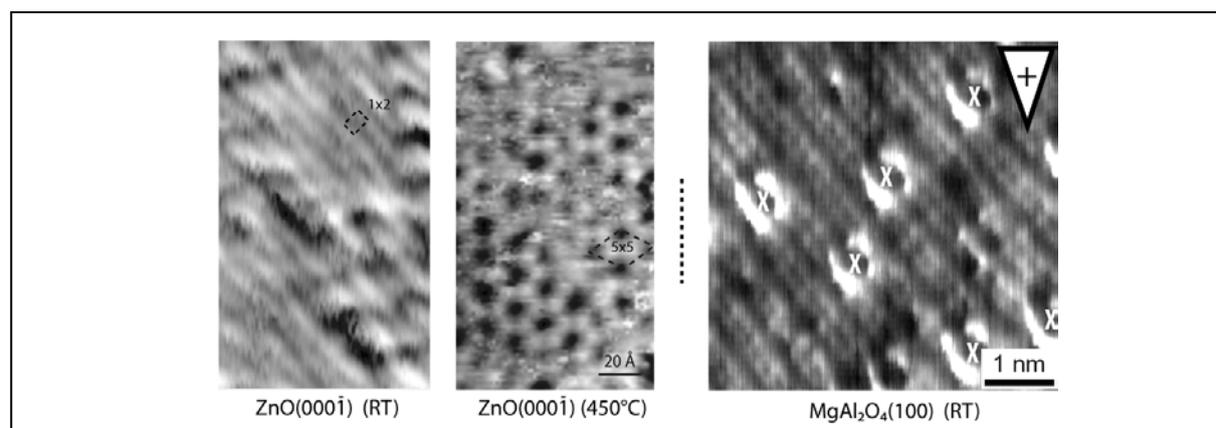
Atom-resolved NC-AFM studies of polar surfaces of insulating metal oxides: ZnO(0001)-O and MgAl₂O₄(100)

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Polar metal oxide surfaces formed by crystal truncation are unstable due to a diverging surface dipole, and the surface must therefore be compensated by adopting a modified or reconstructed surface [1]. For insulating metal oxides, the field remains very poorly explored experimentally, but with atom-resolved NC-AFM it is possible to provide new atomic-scale understanding. Here we demonstrate how NC-AFM has been successfully applied in the determination of the atomic-scale structure of two pronounced polar surfaces, namely the O-terminated ZnO(000-1) and MgAl₂O₄(100). NC-AFM imaging of O-terminated ZnO(000-1) reveals that the surface at room temperature adopts a (1×2) striped surface attributed to a regular structure of OH groups on the ZnO(000-1) lattice. Calculations show that this structure reflects 0.5ML of adsorbed H which fully compensates the polarity. At elevated temperatures, above 300°C, H begins to desorb, and to uphold a non-polar configuration the ZnO undergoes a reconstruction reflected by a (5×5) structure and, at higher temperatures, a (2×2) surface reconstruction composed of patches with alternating wurtzite and an unusual zinc-blende ZnO stacking. The findings are supported by NEXAFS spectroscopy and DFT calculations, and interestingly show that the stabilization mechanism for ZnO(000-1) is in distinct contrast to the morphology-driven stabilization previously observed to be predominant on the opposite Zn(0001) surface [2]. In the case of polar MgAl₂O₄(100), complementary tip-dependent NC-AFM images could be obtained with both negatively (O-terminated) or positively (Mg-terminated) charged tips, which revealed the structure of the surface cation and oxygen lattices, respectively. The surface is in this case shown to be O and Al terminated. NC-AFM images, however, also reveal a distinct atomic defect type shown to be so-called Mg-Al antisites formed by an interchange of surface Al and Mg in the subsurface. Surprisingly, the antisite formation is calculated to be very favorable, and the antisites therefore contribute to an overall stabilization of the otherwise polar MgAl₂O₄(100) surface [3].



- [1] J. Goniakowski, F. Finocchi, and C. Noguera, *Rep. Prog. Phys.* **71**, 016501 (2008).
- [2] J. V. Lauritsen, S. Porsgaard, M. K. Rasmussen, et al., *ACS Nano* **5**, 5987 (2011).
- [3] M. K. Rasmussen, A. S. Foster, B. Hinemann, et al., *Physical Review Letters* **107** (2011).

STM Contrast Mechanisms on a Metal-Oxide Surface: Towards Chemically Selective Imaging by Controlling Tip Apex Chemistry

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In the present study on a model high-symmetry Cu(100)-O surface, we combine STM experiments with density-functional theory (DFT) and Non-Equilibrium Green's Function (NEGF) calculations [1] to investigate the role of tip apex chemistry in contrast formation mechanisms and understand how it may be exploited to achieve functional imaging. At the outset, we systematically applied calculations to explore the STM imaging characteristics of Cu-O tips with different chemical terminations as a function of STM tip height and bias voltage. We were able to identify the imaging modes of tips terminating in a metal, non-metal and an intermediate adatom-contamination geometry and interpret them in terms of the contrasting tunnelling properties of Cu and O chemical species for a range of typical experimental parameters. Simulated imaging of a high-symmetry surface with asymmetric tip structures produced insight into asymmetric image features, STM image offsets and the imaging of surface domains on Cu(100)-O.

Based on these results, we conducted an extensive comparison of the computed STM image database with the bank of experimental image. We found remarkable agreement, which validated the chosen tip models. Our simulations show that dynamic contamination of metallic tips on the Cu(100)-O surface is highly likely, leading to STM image offsets and varied asymmetry effects observed in experiments. O-terminated tips were particularly stable and frequently identified in experimental images: our simulations of their conducting properties show their imaging mode could be experimentally manipulated to selectively image metallic or non-metal surface species. By providing a comprehensive understanding into STM contrast formation mechanisms, we suggest how controlled changes in tip apex chemistry could be employed to enhance the functionality of SPM probes, thus allowing in-depth, species-specific analysis of complex compounds.

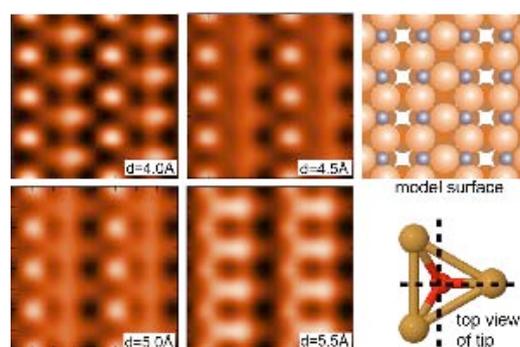


Figure 1: STM contrast variation with CuO tip approach from 5.5 Å to 4.0 Å ($V=+0.4V$)

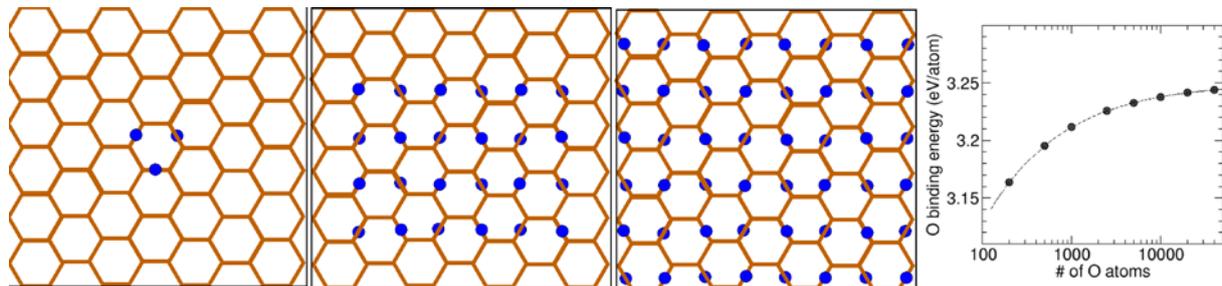
[1] J. M. Blanco, F. Flores and R. Pérez, Prog. Surf. Sci. **81**, 403 (2006).

Modelling graphene oxidation: from small epoxy clusters to a fully oxidized surface

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We used ab initio calculations based on density functional theory (DFT) to investigate the binding of atomic oxygen on graphene, considering adsorption structures with sizes varying from sub-nanometric clusters to infinite overlayers. From an extensive set of studied configurations of oxygen dimers, trimers and tetramers we demonstrated a strong tendency of adsorbates to form close-packed structures. In the high O coverage regime, corresponding to a C/O ratio of 2:1, we identified two very favourable structures with a distribution of O adatoms which enables both the hybridization of all C- $2p_z$ states from the graphene pi electron network with the O- $2p$ states, as well as the minimization of the electrostatic repulsion between negatively charged O atoms attached to the same side of the graphene sheet. Using DFT results obtained for small clusters we constructed a simple model able to describe the energetics of the O islands with sizes beyond those that can be directly treated by first principles methods.



[1] Ž. Šljivančanin et al., Carbon **54**, 482 (2013).

Surface modified TiO₂ photocatalysts: Insights from first principles simulations

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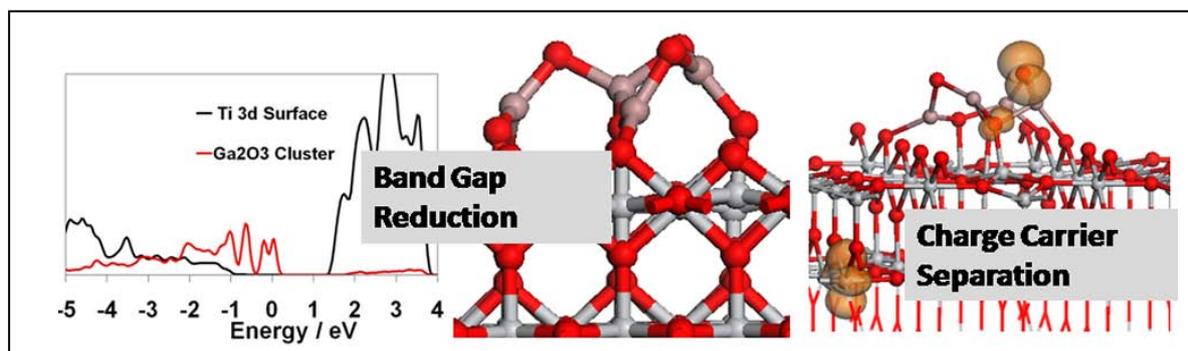
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Photocatalysts based on TiO₂ have been intensely studied, with an emphasis on two key challenges: (1) to shift the TiO₂ band gap to the visible region and (2) enhance charge separation after photoexcitation. This could be achieved by metal or anion doping. However, doping suffers from limitations, such as dopant solubility, stability and reproducibility. We are investigating other mechanisms for engineering band gap narrowing in a controlled fashion, namely surface modification of TiO₂ with metal oxide nanoclusters. This contribution describes our results from density functional theory (DFT) simulations and experiments of TiO₂ rutile and anatase surfaces modified with nanoclusters of metal oxides, including FeO_x, TiO₂, SnO₂/SnO, and Ga₂O₃.

The results from experiment and DFT models of FeO_x (with Fe²⁺ or ³⁺ oxidation states) show that this modifications of TiO₂ can lead to visible light activity, by introducing nanocluster states above the TiO₂ valence band edge, thus shifting the top of the VB to higher energy and reducing the band gap [1,2]. Furthermore, simulations of the photoexcited state show enhanced electron-hole separation upon excitation. Tin oxide modification of anatase shows how the tin oxidation state can tune the light absorption and charge separation properties [3-5]: anatase modified with SnO₂ shows only UV light activity [3,4], since there are no tin oxide derived states in the TiO₂ band gap, but SnO modified anatase is predicted to have a reduced band gap [5], arising from the Sn²⁺-O lone pair. For TiO₂ [6] and Ga₂O₃ [7] modified rutile (110), we find a band gap reduction and charge separation, so that these modifications of rutile would be good candidates for visible light active photocatalysts. A set of design principles for modifying TiO₂ to induce visible light photocatalytic activity are discussed.



- [1] H. Tada, et al. *Angew. Chem. Int. Ed.* **50**, 3501 (2011)
- [2] M. Nolan, *Phys Chem. Chem. Phys.* **13**, 18194 (2011).
- [3] Q. Jin et al., *J. Phys. Chem. C*, **116**, 12621 (2012)
- [4] M. Fujishima et al., *Phys. Chem. Chem. Phys.*, **14**, 705 (2012)
- [5] A. Iwaszuk and M. Nolan, *J. Mat. Chem. A*, submitted (2013)
- [6] A. Iwaszuk, et al., *J. Mat. Chem. A*, **1**, 2515 (2013)
- [7] M. Nolan, *ACS Applied Materials and Interfaces*, **4**, 6765 (2012)

Metal/TiO₂-B,N nanocomposites as photocatalysts for production of valuable chemicals under solar irradiation

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The use of solar light as energy source is a fundamental aspect for the development of sustainable processes for the production of energy and products. Therefore, the development of innovative and efficient photocatalysts able to convert solar energy into chemical energy or to promote chemical reactions is a must. TiO₂-based materials are widely investigated as photocatalysts for many important processes, such as water depollution and H₂ production [1,2]. Doping of TiO₂ is a common way to reduce the band gap and increase the activity under visible light illumination. In this work, TiO₂ is doped with B and N both in the bulk of the materials, adding H₃BO₃ and urea during the sol-gel synthesis. Similar materials have already demonstrated an increased activity for dyes decolourization with respect to un-doped TiO₂ [3]. Metal/TiO₂-B,N (Metal = Pd, Pt, Ag, Ru, Cu) were prepared by photodeposition of metal nanoparticles from metal precursors (nitrates or chlorides) in ethanolic aqueous solutions by UV-vis irradiation for 2h. The catalysts prepared were characterized in terms of N₂ physisorption, powder XRD, HAADF-STEM and photocatalytic activity for the sustainable production of valuable chemicals (H₂ or value-added organic compounds). All the samples presents high surface area (90 – 130 m²/g) and are composed by a mixture of TiO₂ polymorphs (~70% anatase, ~10% rutile and ~20% brookite). Metals were deposited as highly dispersed metal nanoparticles, in agreement with our previous report on un-doped TiO₂ [4]. The photocatalytic activity of the Metal/TiO₂-B,N nanocomposites has been evaluated with respect to the H₂ production by means of photoreforming of aqueous solutions containing renewable sacrificial agents, such as ethanol and glycerol, under irradiation with a Solar Simulator. Finally, Metal/TiO₂-B,N nanocomposites were employed as photocatalysts for the synthesis of substituted benzimidazoles from substituted 2-nitroaniline, discussing the effect of the nature of the metal on the selectivity.

References

1. U.G. Akpan, et al., *J. Hazard. Mater.* **170**, 520 (2009).
2. X. Chen et al., *Chem. Rev.* **110**, 6503 (2010).
3. V. Gombac, et al., *Chem. Phys.* **339**, 111(2007).
4. T. Montini et al., *ChemCatChem* **3**, 574 (2011).

DFT+U modelling of a Mo-containing oxide catalyst

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Complex mixed oxide catalysts are frequently used today for selective hydrocarbon oxidation processes. A system receiving attention lately is that constituted by the Mo-V-Nb-Te oxide system, in which the so-called M1 phase has shown interesting performances for the selective ammoxidation of propane and dehydrogenation of ethane [1]. The layered structure of this phase [2] is formed by a system of 5-, 6- and 7-member rings of MO_6 octahedra ($M=\text{Mo},\text{V}$) containing $(-\text{Te}-\text{O}-)_n$ and $(-\text{Nb}-\text{O}-)_n$ chains in tunnels formed by the 6- and 5- member rings respectively. The unit cell (neglecting the disorder at the M sites) has an overall stoichiometry similar to $(\text{MO}_3)_{36}(\text{TeO})_4(\text{NbO})_4$, i.e. 160 atoms in total. Furthermore all M sites have an occupancy by V of at most ~ 0.5 , suggesting that all V atoms alternate with Mo along the $\text{M}=\text{O}\dots\text{M}$ chains perpendicular to the layers, which would need double cells with 320 atoms for a correct modelling. Careful topological analysis has allowed to identify in this lab a half-size model (Fig. 1) which is equivalent enough to the M1 phase structure in all relevant aspects and makes more tractable its DFT modelling. The latter has been thus undertaken.

A typical $\text{Mo}_{30}\text{V}_6\text{Te}_4\text{Nb}_4\text{O}_{116}$ stoichiometry (160 atoms) is adopted for modelling the two-layer cell. Assuming the redox states V^{4+} , Te^{4+} and Nb^{5+} (experimentally verified), 8 excess electrons must be distributed over 30 Mo atoms, giving the average redox state $\text{Mo}^{+5.733}$. The system is indeed akin to a Mo bronze. The question arises, whether these electrons are localized. It is known that spurious self-interaction in DFT may lead to unphysical delocalization. This problem has been much studied for systems containing 3d or 4f partially filled shells, but much less for partially filled 4d shells. On the other hand recent work [3] claims that the experimental value of the energetics of the reduction of MoO_3 to MoO_2 is reproduced with a DFT+U treatment, not with just DFT. Thus a first principles determination of U for Mo has been undertaken here, following Cococcioni's method [4] (as implemented in program Quantum-Espresso) and using a simple ideal NaMo_2O_6 structure model derived from the high temperature tetragonal WO_3 lattice.

The results indicate a value of $U \approx 4$ eV (ca. half that given in [2]). Its suitability is tested on other Mo bronzes of experimentally known structure and average Mo redox state between 5.0 and 6.0 which are known to display semiconducting or metallic behaviour and charge density wave effects at low temperature. With this Mo U value a modelling of the $(\text{Mo},\text{V},\text{Nb},\text{Te})\text{Ox}$ catalyst using the said 160-atom two-layer cell has been then started using program VASP. It shows that most, but not necessarily all, of the excess electrons are localized on specific Mo ions, but only if the DFT+U approach is used. A study on the preferred location of V in the several M sites (a relevant issue [5]) is under way; its progress will be reported.

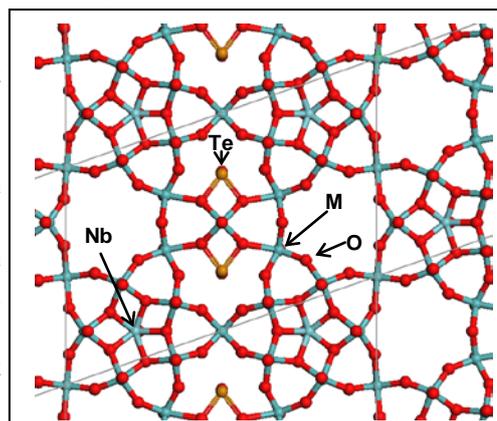


Fig. 1- Structure of half-size model (with unit cell shown) of $(\text{Mo},\text{V},\text{Nb},\text{Te})\text{Ox}$ catalyst

- [1] a) K. Asakura et al., *J. Catal.* **194**, 309, (2000); b) P. Botella et al., *Catal. Today* **142**, 272 (2009).
- [2] X. Li et al., *Top Catal* **54**, 614, (2011).
- [3] S. Lutfalla et al., *J. Chem. Theory Comput.* **7**, 2218, (2011).
- [4] M. Cococcioni, S. de Gironcoli, *Phys. Rev. B* **71**, 035105, (2005).
- [5] F. N. Naraschewski et al., *Top Catal* **54**, 639, (2011).

Ceria doped with lanthana and zirconia. Probing structural defects of the ceria cubic matrix by high temperature Raman spectroscopy

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Ceria with a fluorite-type cubic structure, space group $Fm\bar{3}m$ (O_h^5), has an exceptionally simple vibrational structure with *one* Raman active mode (F_{2g}) which is typically observed around 460 cm^{-1} and is due to symmetric breathing mode of O atoms surrounding each Ce^{4+} . Because this vibrational mode is only dependent of the oxygen movement, its band characteristics (width and position) are *extremely dependent* on the *disorder* induced in the oxygen ion sublattice of the oxide and is therefore sensitive to both Ce–O bond arrangements and lattice defects. Punctual defects may exist even in the cubic matrix of *pure* ceria, caused by the non-stoichiometric condition due to the presence of Ce^{3+} . The resulting effective negative charge is compensated by O vacancies in the pure ceria sublattice. This is manifested in the Raman spectra by weak bands (e.g. a longitudinal optical mode at $\sim 620\text{ cm}^{-1}$, otherwise Raman inactive) that are leaking due to the pertinent partial relaxation of the symmetry rules.

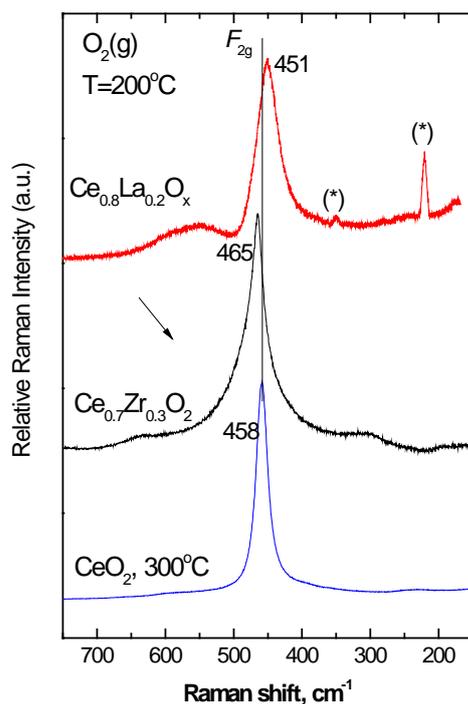


Figure 1. *In situ* Raman spectra of ceria-based materials obtained under flowing $\text{O}_2(\text{g})$ at temperatures as indicated by each spectrum.

leaking of weak bands due to local lowering of symmetry, etc. Temperature and composition effects on the Raman spectra are discussed and interpreted.

Doping the CeO_2 matrix by other oxides such as La_2O_3 or ZrO_2 leads to $\text{Ce}_{1-x}\text{La}_x\text{O}_y$ and $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ materials. Although no distinct lanthana or zirconia crystalline phases are formed, the inclusion of La^{3+} or Zr^{4+} in the ceria cubic matrix largely affects the lattice parameters. The ionic radius of La^{3+} (1.15 \AA) is larger than that of Ce^{4+} (1.01 \AA), and the incorporation of La^{3+} into the fluorite-type CeO_2 lattice results in an increase in the value of the lattice parameter (lattice expansion). Thus, the occurring structural perturbation is expected to be manifested in the Raman spectra (see Fig. 1) by a red shift of the F_{2g} mode upon doping with La_2O_3 due to the *longer* Ce–O bonds. To the contrary, as Zr^{4+} (0.80 \AA) is smaller than Ce^{4+} (1.01 \AA), most probably a lattice contraction occurs upon substitution of Ce^{4+} by Zr^{4+} . A corresponding moderate shortening of Ce–O bond distances is expected, thereby leading to a blue shift in the F_{2g} band. Moreover, a larger distribution of Ce–O sites is resulting and is accounted for by the broadening of the F_{2g} band. Generally, the structural defects activate shifts of the main band, band broadening,

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Nanoscale heterogeneity in CeO₂ - ZrO₂ revealed by luminescence spectroscopy

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In this talk, we present some of our recent results on the nanoscale heterogeneity in CeO₂-ZrO₂ solid solutions (Ce/Zr=1). The main approach was based on the spectrally and temporarily resolved luminescence of europium (Eu³⁺) used as a structural probe [1]. It has been established by now that the emission properties of Eu³⁺ depend strongly on the local symmetry of sites it substitutes in the lattice of CeO₂ or ZrO₂. Since both tetragonal and cubic symmetries characterize the oxygen environments in Eu³⁺-CeO₂-ZrO₂ (calcined at 750 and 1000 °C) the luminescence of Eu³⁺ doped into CeO₂ and tetragonal ZrO₂ was also measured.

The oxides were also characterized by X-ray diffraction (XRD), Raman spectroscopy, transmission electron microscopy (TEM) and evaluated for their phase content and homogeneity. Upon calcination at 750 °C, we found that Eu³⁺-CeO₂-ZrO₂ appears as single, homogeneous phase following XRD and Raman characterization. However, luminescence data evidence several tetragonal oxygen environments around Eu³⁺ differing by local symmetry, Fig. 1. The distinctive character of these tetragonal environments was inferred from the relative intensities, widths and peak positions of the emission transitions. Increasing the calcination temperature at 1000 °C, an additional luminescence, typical of Eu³⁺ in CeO₂ was found, which relates the observed asymmetry of XRD patterns to the onset of ceria phase separation. Finally, we believe that our approach can complement the existing methods used to investigate the nanoscale homogeneity and local structure of CeO₂ - ZrO₂.

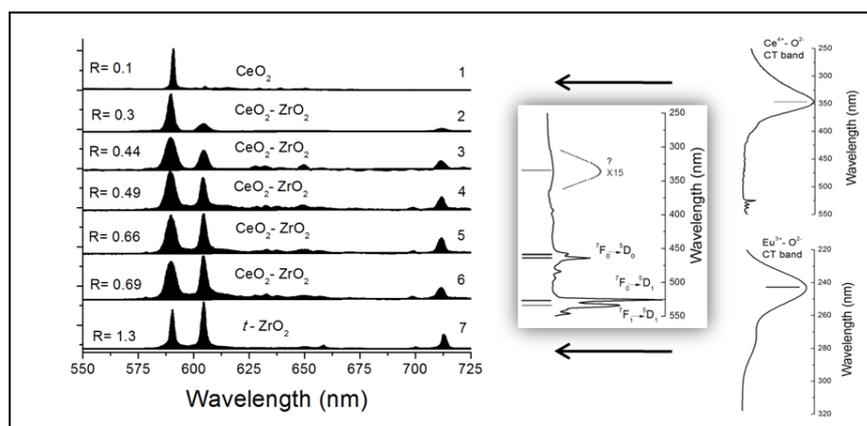


Fig. 1. Luminescence (left) and excitation (right) spectra of Eu³⁺ in CeO₂ - ZrO₂, CeO₂ and ZrO₂ (all samples were calcined at 750 °C). The shapes of the emission spectra of Eu³⁺ in the mixed oxide (spectra 2 - 6) fall between those in CeO₂ (spectrum 1) and tetragonal ZrO₂ (spectrum 7). The intensity ratio (R) corresponding to the 605 and 591 nm centered emissions is directly correlated to the local (a)symmetry of Eu³⁺- oxygen polyhedron.

[1]. C. Tiseanu, B. Cojocaru, V. Parvulescu, M. Sanchez Dominguez, P. A. Primus and M. Boutonnet, Phys. Chem. Chem. Phys. **14**, 12970, (2012).

Two-dimensional electron gas generation at the surface of the charge ordered BaBiO₃ semiconductor: a new physical mechanism

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In this work, we find by means of first-principles calculations a new physical mechanism to generate a two-dimensional electron gas, namely, the breaking of charge ordering at the surface of a charge ordered semiconductor due to the incomplete oxygen environment of the surface ions. The emergence of the 2D gas is independent of the presence of oxygen vacancies or polar discontinuities; this is a self-doping effect. This mechanism might apply to many charge ordered systems, in particular, we study the case of BaBiO₃(001). In bulk, this material is a prototype of a “forbidden valence” compound in

which the formal “metallic” Bi⁴⁺ is skipped exhibiting a charge disproportionated Bi³⁺-Bi⁵⁺ ordered structure. At room temperature, this charge disproportionation together with the breathing distortions gives rise to a Peierls semiconductor with monoclinic crystal structure. At higher temperatures ($T > 750\text{K}$) or upon doping, it turns cubic and metallic. Interestingly, doped BaBiO₃ was one of the first non-cuprates high-T_c superconductors discovered. Our calculations show that the outer layer of the Bi-terminated simulated surface turns more cubic-like and metallic while the inner layers remain in the insulating monoclinic state that the system present in the bulk form. On the other hand, the metallization does not occur for the Ba termination, a fact that makes this system appealing for nanostructuring.

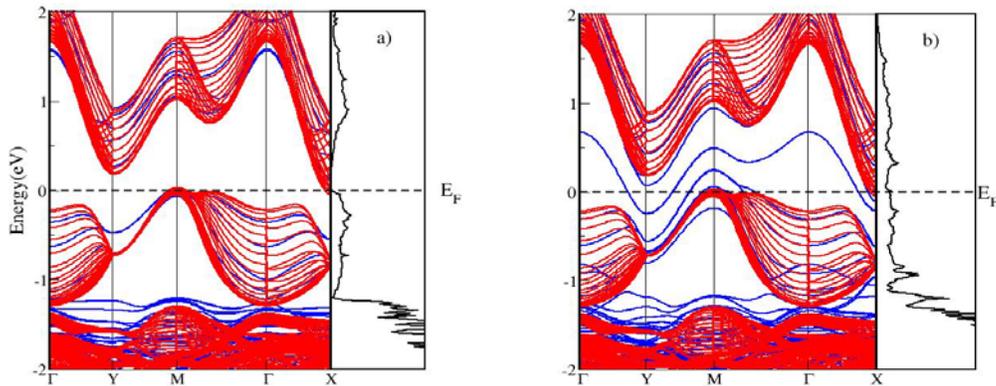


Figure 1

In Fig. 1a), we show the obtained bandstructure for a 11 layer Ba-terminated slab and in Fig1b) the corresponding to a 13-layer Bi terminated slab. The red bands are the bulk projected (001) states. Finally, in view of the bulk properties of this material under doping, this particular finding sets another possible route for future exploration: the potential scenario of 2D superconductivity at the BaBiO₃ surface.

Posters

Adsorption and decomposition of ethylene glycol and ethanol on ceria-based model catalysts

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We have investigated the adsorption and decomposition of ethylene glycol and ethanol on single crystal Pt(111) and on thin films of stoichiometric CeO₂(111), partially reduced CeO_{2-x}, and Pt/CeO₂ on Cu(111) by means of synchrotron radiation photoelectron spectroscopy (SRPES). The reaction of both alcohols with the ceria-based catalysts is discussed in terms of the redox properties of ceria. The oxidation state of cerium cations is monitored with highest surface sensitivity by means of the resonant photoemission spectroscopy (RPES).^[1]

During adsorption at 150 K, deprotonation of ethylene glycol and ethanol leads to formation of ethylenedioxy and ethoxy species on all surfaces, respectively. Additionally, formation of methoxy is observed as a result of partial C-C bond cleavage in ethanol adsorbed on CeO_{2-x} at 150 K. Part of the molecules adsorb also intact. Molecularly adsorbed ethylene glycol and ethanol desorb from all surfaces upon annealing between 180 and 225 K. On CeO₂(111) and CeO_{2-x}, ethylenedioxy are stable up to 500 and 475 K, respectively. Decomposition of ethylenedioxy above 500 K results in C_xH_y moieties and surface carbon on both surfaces. In addition, formate is found on CeO₂(111). The decomposition of ethylene glycol leads to reduction of stoichiometric ceria and partial re-oxidation of reduced ceria. In contrast, decomposition of ethoxy does not significantly alter the oxidation state of ceria on CeO₂(111). Only slight re-oxidation is observed on CeO_{2-x}. On CeO₂(111) and CeO_{2-x}, ethoxy are stable up to 550 and 475 K, respectively. Except for methoxy on CeO_{2-x}, no other surface species have been detected during decomposition.

Decomposition of ethanol and ethylene glycol adsorbed on Pt(111) at 150 K follows a complex decomposition pattern leading to formation of CO, ethylene, ethylidene, ethylidyne and CH species. Stable carbonaceous deposits are formed that remained on the surface above 500 K.

During decomposition of ethanol and ethylene glycol on Pt/CeO₂, species are found on Pt particles that are similar to those formed on Pt(111). Additionally, C-C and C-H bond breakage is enhanced in presence of Pt particles. Hydrogen spillover and reverse spillover accompanied by reduction and re-oxidation of ceria support has been observed during annealing of the adsorbates between 150 and 300 K. Further annealing to 500 K leads to aggregation of carbonaceous deposits on Pt and at Ce³⁺ cations along the perimeter of Pt particles. Above 500 K, the onset of oxygen reverse spillover initiates a self-cleaning process on Pt/CeO₂.

[1] V. Matolín, I. Matolínová, L. Sedláček, K. C. Prince, T. Skála, *Nanotechnology* **2009**, 20(21), 215706.

Cobalt Oxide Model Catalysis across the Materials and Pressure Gap

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Cobalt oxide has recently turned out to be a novel, highly active heterogeneous catalyst for key processes in future energy and environmental technology. This includes e.g. low-temperature CO oxidation, the related PROX reaction (preferential oxidation of CO in excess H₂), the total oxidation of VOCs (volatile organic compounds), and the reforming of hydrocarbon oxygenates for hydrogen production. Most importantly, cobalt-oxide-based catalysts hold a unique potential for replacing or reducing the demand for critical materials (noble metals and rare earth oxides). Despite these outstanding prospects, the origin of the surprising cobalt oxide surface chemistry has remained a mystery up to date. Neither the extreme dependence of activity on surface structure nor the mechanisms by which metal (e.g. Pd) and oxide (e.g. CeO₂) modifiers enhance stability and activity are truly understood.

In this contribution we present a joint project that aims at acquiring an understanding of the catalytic activity of cobalt oxide materials at the molecular level. Towards this aim the three project partners bring together the complementary expertise for a state-of-the-art model catalysis and surface science approach: (A) the atomic-level structural characterization of reactive sites on complex model catalysts, (B) mechanistic and microkinetic studies of catalytic reactions under UHV conditions, and (C) transfer of this knowledge to realistic reaction conditions by in-situ spectroscopy up to realistic ambient pressure conditions. We will take advantage of the expertise of one project partner in preparation of ordered cobalt oxide films (presented in detail in other contributions), providing access to a unique library of bulk and surfaces structures. We will probe adsorption and reaction on these surface structures, characterize relevant defects at the atomic scale with respect to their geometric and electronic properties, and subsequently modify these structures by metal (Pd) and oxide (CeO₂) cocatalysts. In this project, we will mainly focus on low-temperature CO-oxidation and PROX, but perform first explorative work towards oxidation and reforming reactions. Simultaneously, we will cross the materials gap and the pressure gap for cobalt oxide catalysts for the first time and, finally, link the obtained knowledge to industrial-grade powder catalysts by in-situ spectroscopy from UHV to realistic reaction conditions. The interdisciplinary approach of this project will allow us to identify structure-functionality relationships of catalytic processes at an unprecedented level of detail and will guide rational strategies towards future development of complex multifunctional cobalt oxide catalysts.

Preparation and characterization of ZrO₂ thin films grown on Pt₃Zr

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Introduction

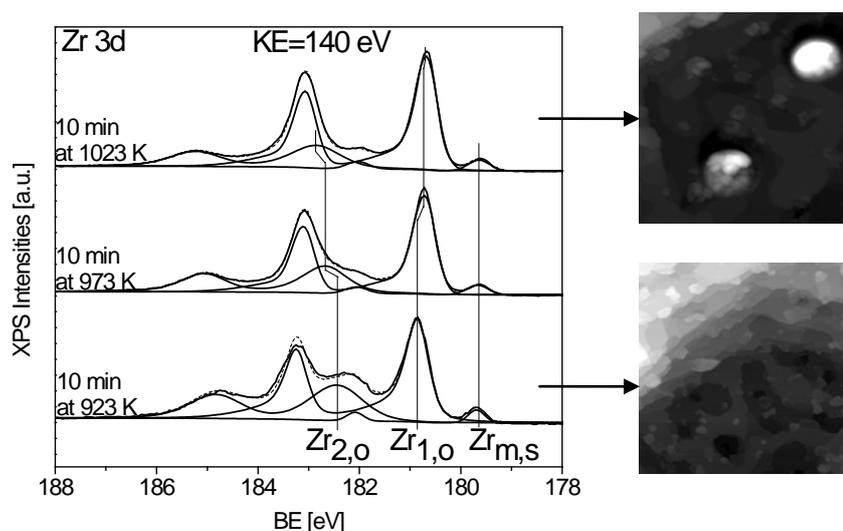
ZrO₂ is widely used in the field of heterogeneous catalysis, and is known as an excellent support and catalysts material itself [1]. However, microscopic mechanisms of the functions of ZrO₂ and of the oxide-metal interactions need to be better understood. In order to conduct fundamental studies on ZrO₂ via a surface science approach, thin film model catalysts have been prepared and characterized.

Experimental

In this study, a previously described route was followed to obtain well-ordered and ultra-thin zirconia film [2]: A cleaned Pt₃Zr (0001) alloy substrate was oxidized at 673 K, followed by post-annealing at 1023 K. The chemical composition of the film is investigated by high resolution X-ray Photoelectron Spectroscopy (XPS). The structure of the film is characterized by Scanning Tunneling Microscopy (STM).

Results

Besides a signal for metallic zirconium from the substrate (Zr_{m,s}), XPS showed two distinctive oxidic species (Zr_{1,o} and Zr_{2,o}) upon oxidation at 673 K and post-annealing at 1023 K. With increasing photon energy, the ratio between Zr_{2,o} and Zr_{1,o} increased, indicating that Zr_{2,o} are located in a deeper layer than Zr_{1,o}. After post-annealing of the oxide at 923 K, STM detected many small clusters with a height of about 1nm, in addition to the film terraces. Increasing the annealing temperature to 1023 K led to the disappearance of a considerable amount of the small clusters, accompanied by the significant decrease of the intensities of Zr_{2,o} shown by XPS. Therefore, Zr_{1,o} and Zr_{2,o} could be assigned to Zr oxide species within the trilayer thin film and Zr oxide species in the clusters, respectively.



- [1] K. Tanabe, T. Yamaguchi, Catal. Today., **20**, 185, (1994).
- [2] M. Antlanger, et al., Phys. Rev. B., **86**, 03451, (2012).

Ni/CeO₂(111): a model catalyst for water-gas shift reaction

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Ceria is an extensively used heterogeneous catalyst carrier due to its unique oxygen storage capabilities associated with the easy conversion between Ce³⁺ and Ce⁴⁺ ions [1]. In addition, strong metal-ceria interactions result in an enhanced performance by avoiding sintering of the active phase [2]. One important example that boosted the use of ceria as a catalyst support is the water-gas shift (WGS) reaction for the production of syngas (H₂ + CO₂), where supported coinage metals (Au, Cu, or Pt) are typically employed as the active phase. Experimental insight revealed that nickel-based catalysts can also be stable, inexpensive and highly active, showing an excellent potential for the WGS reaction at small Ni coverages, whilst catalysing the production of methane from CO and H₂ at medium and large coverages [3].

Here we study the electronic structure, geometries, and adsorption of C, CO, and H₂O on small Ni_n (n=1 and 4) particles supported on CeO₂(111) using density-functional theory (DFT) with the DFT+U approach and compared to Ni(111) and CeO₂(111). We show that the CO bond strength follows the trend: Ni(111) < Ni₄/CeO₂(111) < Ni₁/CeO₂(111) [4]. The stronger CO bond found for the smallest particles provides an explanation for the experimentally reported Ni coverage dependence of the CO methanation reaction on Ni/CeO₂(111). Ni-ceria interactions are crucial for the interpretation of these results. In addition, we explore the adsorption and dissociation of water on these systems, since a good WGS catalyst should be able to oxidize and remove CO efficiently, but still be active enough to dissociate water. We observe that the molecular adsorption of water on the bare CeO₂(111) surface (−0.55 eV) [5] is similar to the adsorption under the presence of supported single Ni atoms (−0.62 eV). Nevertheless, dissociative water adsorption is more favourable on the Ni₁/CeO₂(111) (−1.00 eV) than on the bare CeO₂(111) surface (−0.60 eV) [5]. We have established computational models for Ni/ceria systems for the WGS reaction that are consistent with experimental knowledge for powder catalysts and experimental model catalysts and thus help to bridge the gap between them.

[1] A. Trovarelli, *Catal. Rev.-Sci. Eng.* **38**, 439 (1996).

[2] J. A. Farmer and C. T. Campbell, *Science* **329**, 933 (2010).

[3] L. Barrio, A. Kubacka, G. Zhou, M. Estrella, A. Martínez-Arias, J. C. Hanson, M. Fernández-García, and J. A. Rodríguez, *J. Phys. Chem. C* **114**, 12689 (2010).

[4] J. Carrasco, L. Barrio, P. Liu, J. A. Rodríguez, and M. V. Ganduglia-Pirovano, submitted.

[5] D. Fernández-Torre, K. Kośmider, J. Carrasco, M. Verónica Ganduglia-Pirovano, and R. Pérez, *J. Phys. Chem. C* **116**, 13584 (2012).

Adsorption induced arrangement of atoms in bimetallic PdZn/Pd(111) surface alloys

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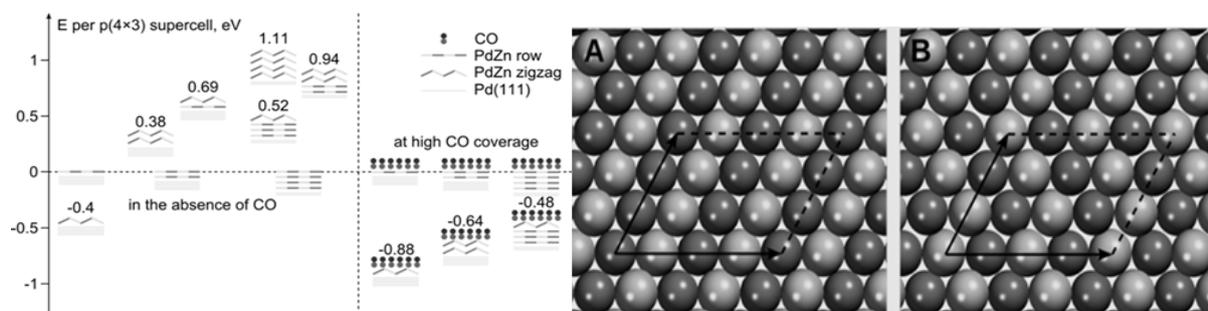
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PdZn alloys have recently raised great interest as catalysts for hydrogen production via methanol steam reforming (MSR) since they show good conversion and high selectivity towards CO₂ and hydrogen. We have utilized well-defined model 1:1 PdZn/Pd(111) surface alloys to study the process of alloy formation and thermal stability in different gas atmospheres applying XPS, TPD, and PM-IRAS (Polarization-Modulation IR Reflection Absorption Spectroscopy). Combining DFT calculations with experimental data gives strong indications for structural rearrangement of Pd and Zn atoms in PdZn surface alloys on Pd(111) at elevated CO coverage.

Pd/Zn model catalysts were prepared by physical vapor deposition of Zn onto a clean Pd(111) single crystal substrate in ultrahigh vacuum. The surface alloys on Pd(111) were modeled by 6 layers thick p(4×3) supercell [1]. PdZn surface alloys could be characterized experimentally by a characteristic IR band of adsorbed CO and a corresponding CO-TPD desorption peak. By following the spectral evolution during annealing (in UHV or 10⁻⁶ mbar CO) upon Zn deposition, a window for alloy formation at annealing temperatures between ~473 K and 623 K was deduced from XPS, TPD and PM-IRAS.

By comparing the relative stabilities of different PdZn surface structures with and without CO adsorbed, it was calculated, that at high CO coverage (i.e. high CO pressure) a PdZn reconstructed “zigzag” structure of PdZn is more stable compared to the conventional “row” 2x1 structure [1].



Contrary to conventional “row” structure, reconstructed “zigzag” structure is calculated to adsorb CO on-top of Pd atoms at coverage up to 0.5 ML in agreement with observation in PM-IRAS and TPD experiments, respectively.

A first hint for the experimental relevance of proposed “zigzag” structure is the 0.5 ML CO saturation coverage determined by TPD, which was calculated to be only possible for the reconstructed surface. On the non-reconstructed surface arranged in rows, CO is stable only at coverage $\theta \leq 0.33$, with sharp decrease of stability at higher coverage. Currently STM investigations are underway to get full microscopic understanding of the system.

[1] C. Weilach, S. M. Kozlov, H. H. Holzzapfel, K. Föttinger, K. M. Neyman, G. Rupprechter (2012) 2012, J. Phys. Chem. C 116 (35)

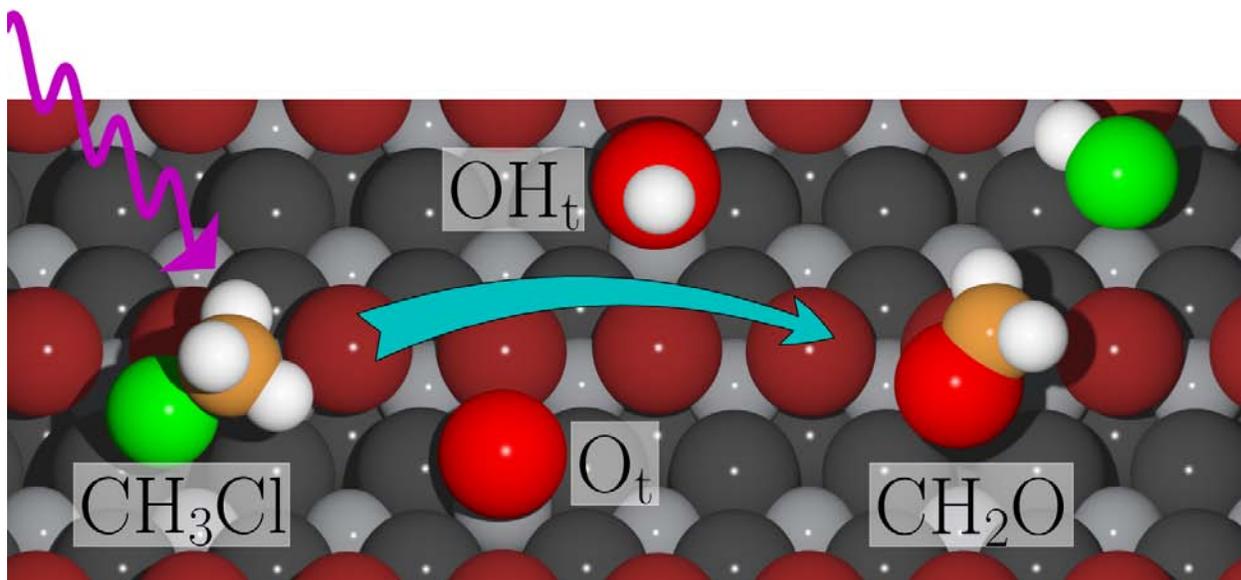
Photo oxidation mechanisms on rutile TiO₂ (110)

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Photo chemistry on rutile TiO₂ has received much attention lately, but theoretical insight is difficult to obtain, due to the combination of excited states and extended systems. In this work the presence of a photo-generated hole in the TiO₂ valence band is assumed, while the corresponding photo-electron is omitted from the models. This prohibits the electron-hole recombination and changes the photo oxidation reaction into a fictitious electronic ground state problem, tractable by density functional theory. This approach is used to study the photo oxidation of two simple molecules on the rutile TiO₂ (110) surface, namely methyl chloride (CH₃Cl) and ethanol (EtOH).

Experimentally it is found that the rutile TiO₂ (110) surface can only photo oxidize CH₃Cl in the presence of both bridging oxygen vacancies (O_{br} vac.) and oxygen molecules [1]. The experimental conditions may lead to formation of terminal oxygen atoms (O_t) and terminal hydroxyls (OH_t). We show that O_t and OH_t indeed facilitate the photo oxidation of CH₃Cl into CH₂O, while bridging oxygen atoms (O_{br}) that are native to the (110) surface do not (See figure).

In the study of EtOH, we find that only deprotonated EtO⁻ can undergo photo oxidation on the rutile TiO₂ (110) surface. This is analog to the proposed mechanism for methanol photo oxidation [2]. The presence of O_t and OH_t do therefore increase the rate of photo oxidation by deprotonating EtOH, but unlike methanol they are not required, since a minority of EtOH deprotonate thermally on the reduced (110) surface [3].



- [1] G. Lu et al., J. Phys. Chem. **99**, 7626 (1995)
- [2] M. Shen and M. A. Henderson, J. Phys. Chem. C **116**, 18788 (2012)
- [3] J. Ø. Hansen et al., Phys. Rev. Lett. **107**, 136102 (2011)

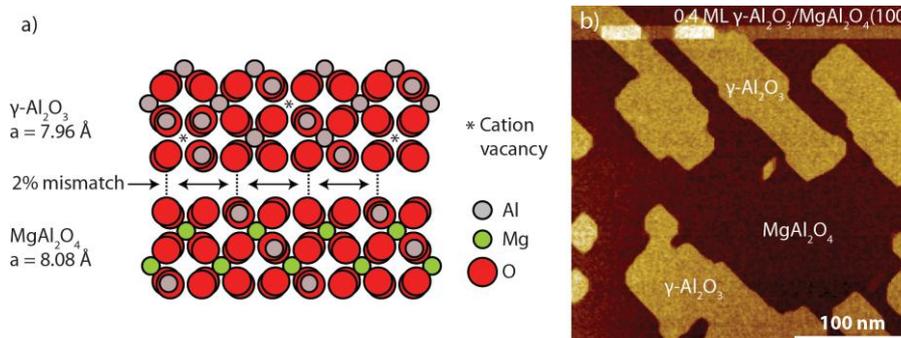
Non-contact atomic force microscopy characterization of a crystalline transition Al_2O_3 surface

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Heterogeneous catalysis plays a crucial role in the society today, both as the means for environmental protection and as the backbone technology for most of the chemical industries. The development of new catalysts is given a very high priority since they facilitate a much better utilization of our scarce energy reserves and it can drive the concept of waste-free 'green' chemistry and the development of a sustainable energy sector. Metal oxides like Al_2O_3 play major roles in heterogeneous catalysis as supports for catalytically active nanoclusters because of their excellent mechanical and thermal stability. Of all the transitional aluminas, $\gamma\text{-Al}_2\text{O}_3$ is the most important in catalysis, but so far surface science studies have been unable to address the surface structure of this insulating material in detail. A better understanding of the surface structure of support materials seems to be a prerequisite for the synthesis of more sintering stable catalysts and the realization of nanocatalysts implementing catalyst particles with a tailored size and morphology.

Benefitting from a nearly perfect structural match between the (100) surface of MgAl_2O_4 and $\gamma\text{-Al}_2\text{O}_3$ (see Fig. 1a), we show that we can use $\text{MgAl}_2\text{O}_4(100)$ as a template to grow thermodynamically stable and crystalline alumina films with $\gamma\text{-Al}_2\text{O}_3$ -like properties. Previous atom-resolved nc-AFM studies have shown that the $\text{MgAl}_2\text{O}_4(100)$ surfaces terminates by an Al-O rich termination, which turns out to be ideal for the continuously grown alumina films [1]. Preliminary nc-AFM studies reveals a perfect crystalline film-like growth (see Fig. 1b), where up to 4ML thick films of Al_2O_3 were prepared using e-beam evaporation of pure Al onto a $\text{MgAl}_2\text{O}_4(100)$ substrate followed by annealing at 1473 K in an oxygen atmosphere (1×10^{-7} mbar). Subsequent analysis of atom-resolved NC-AFM images reveals a structure with a quadratic grid and a high concentration of atomic defects on Mg positions, which is suggesting a surface structure reflecting Al-terminated $\gamma\text{-Al}_2\text{O}_3$.

The stable $\gamma\text{-Al}_2\text{O}_3(100)$ films make it possible to open up a whole new range of fundamental studies of the metal/support interaction for catalytic systems based on surfaces with real $\gamma\text{-Al}_2\text{O}_3$ properties. The synthesis of stable well-defined alumina films with transition alumina characteristics will allow us to address important catalytic properties such as acid-based properties, cluster adhesion strength and sintering scenarios for model systems of supported nanoclusters that incorporate the real oxide support structure.



[1] M. Rasmussen et al., Phys. Rev. Lett. **107**, 036102 (2011).

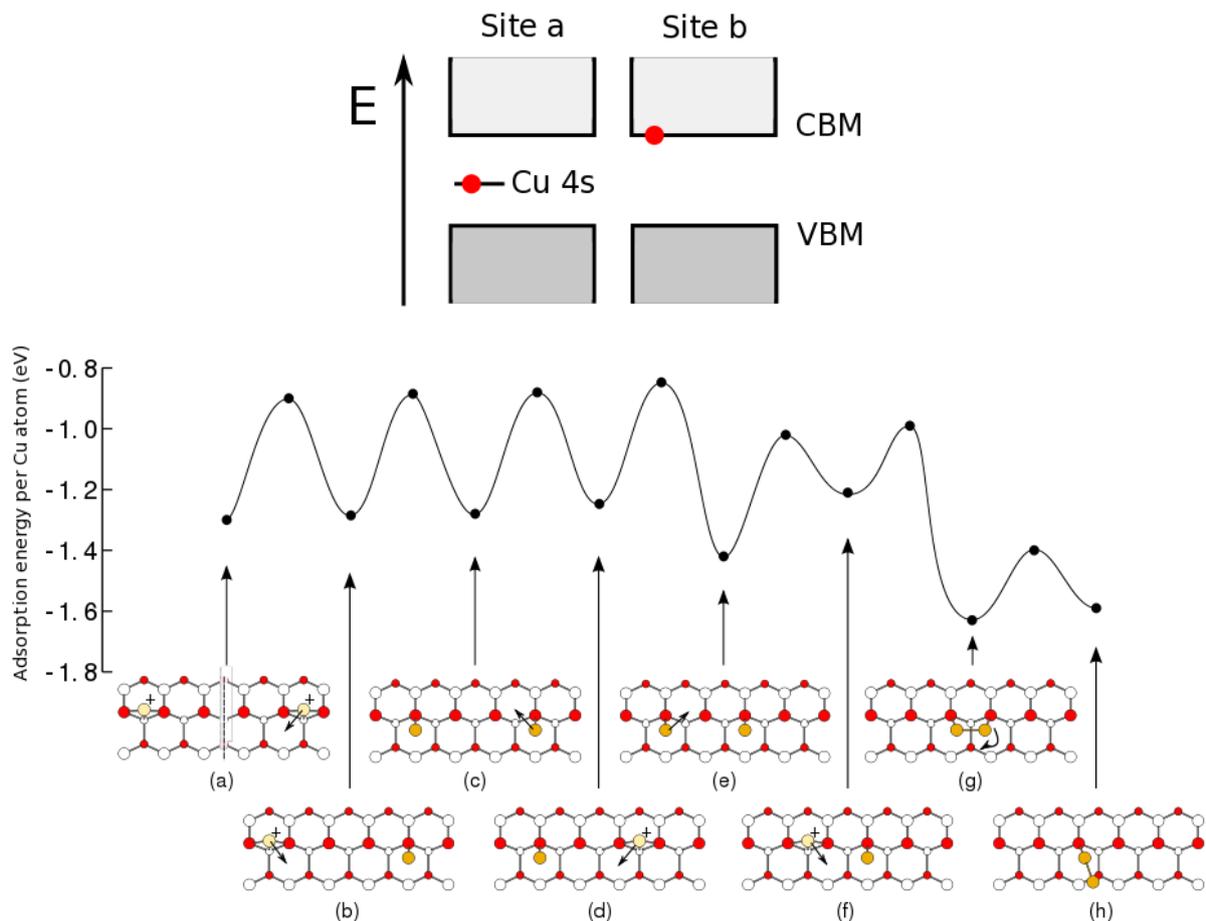
Cu dimer formation on a ZnO surface: the effect of alternating charge states

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Cu/ZnO catalysts are industrially used to catalyze methanol synthesis and the water-gas shift reaction. In this work [1], the formation of Cu dimers on the ZnO(1010) surface has been studied using hybrid density functional theory. Depending on the adsorption site, Cu atoms are found to adsorb with either oxidation state 0 or +1. In the latter case, the Cu atom has donated an electron to the ZnO conduction band. The two modes of adsorption display similar stability at low coverages, while at higher coverages the neutral species is more stable. Single Cu atoms diffuse across the ZnO(1010) surface with small barriers of migration (0.3–0.4 eV) along ZnO[1210], repeatedly switching their oxidation states, while the barrier along ZnO[0001] is significantly higher (>1.5 eV). The formation of a Cu dimer from two adsorbed Cu atoms is energetically favorable with two competing structures of similar stability, both being charge neutral. The minimum energy paths for Cu atom diffusion and dimer formation are characterized by at least one of the two Cu atoms being in oxidation state 0.



[1] M. Hellström, D. Spångberg, K. Hermansson, P. Broqvist, *Phys. Rev. B* **86**, 235302 (2012).

Formic acid adsorption on the reduced TiO_2 (110) surface

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In this work, we have studied the adsorption of a formic acid molecule (HCOOH) on the reduced rutile TiO_2 (110) surface with the presence of scarce oxygen vacancies. Molecular dynamics (MD) simulations with the self-consistent charge density functional tight-binding (SCC-DFTB) method were performed in order to find the stable adsorption configurations. Their stabilities were then confirmed using standard density functional theory (DFT) within the Hubbard-U approximation.

In our MD simulations, HCOOH instantaneously dissociates when brought into contact with the surface, forming an adsorbed formate ion (HCOO^-) and a proton. The different stable adsorption configurations are illustrated in Fig. 1. We note that besides the bi-dentate bridge configuration previously found in experiments on the stoichiometric TiO_2 (110) surfaces, we observe several configurations that heal oxygen vacancies. Our validation tests show that the relative stabilization energies of the different adsorption configurations using SCC-DFTB are in quantitative agreement with the DFT+U results, but there is a shift in absolute adsorption energies. The stable adsorption configurations have also been characterized through vibrational analysis, to be used as an aid in the assignment of peaks from Infrared spectroscopic experiments of the same system.

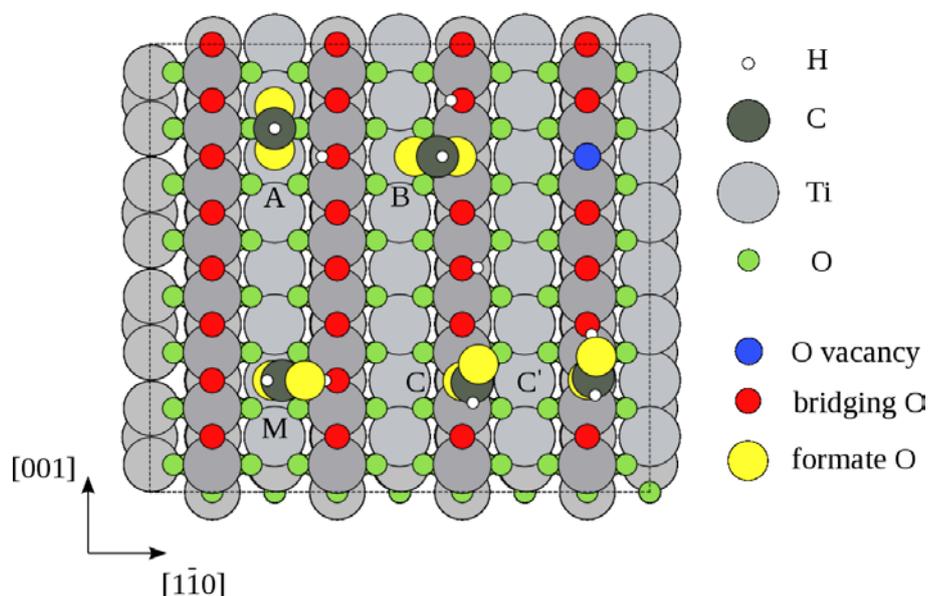


Fig. 1 Stable adsorption configurations of formic acid over the reduced TiO_2 (110) surface.

Driving structural and electronic properties of thick CoO films via the interface chemistry

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We have investigated the growth and electronic structure of CoO films of several bilayers thickness on an unreconstructed Ir(100) substrate by LEED, STM and UPS. When starting with a clean iridium surface and reactively depositing cobalt in an 10^{-6} mbar oxygen atmosphere a hexagonal, [111]-oriented CoO film is formed despite the square symmetry of the underlying substrate. The situation changes completely when the oxygen film is grown reactively on one or several interfacial layers of pure cobalt. Now the growth of the CoO film occurs exclusively in the [100] direction. Since the unreacted Co layers at the interface are pseudomorphic with respect to the Ir(100) substrate, the switch of the CoO growth orientation is not driven by stress reduction but entirely by the local chemical interaction at the interface. The different film orientations at the interface are also not kinetically driven but indeed energetically stable (up to film decomposition temperatures above 1000°C), which is corroborated by DFT calculations for monolayer thick films grown on the two different substrates [1]. The surface of the CoO(111) film, however, is only metastable and forms (100) facets at around 600°C.

The surfaces of the so grown (100) and (111) oriented films differ also dramatically in their electronic properties as shown by means of photoelectron and scanning tunneling spectroscopy. While the non-polar CoO(100) films are insulating, the CoO(111) films exhibit a metallic surface layer, which is caused by a stacking fault in the outermost subsurface Co layer [2]. This structural switch from rocksalt- to wurtzite-type stacking thus compensates the dipole moment of the otherwise polar (111) film.

[1] M.Gubo et al., Phys. Rev. Lett. **108**, 066101 (2012).

[2] W. Meyer, K. Biedermann, M. Gubo, L. Hammer and K. Heinz, Phys. Rev. Lett. **101**, 016103 (2008)

Reduction of PdO(101) with H₂: A combined DFT and XPS study

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Transition metals for catalytic oxidation reactions often form oxides under realistic reaction conditions. One example is palladium, where the PdO(101) facet recently has been suggested to be the most active facet for methane oxidation [1]. The elementary reaction steps for methane oxidation over PdO(101) are, however, still under debate and the catalytic cycle may include reduction of the surface. In this study, we have explored the reduction of PdO(101) by H₂ combining Density Functional Theory (DFT) calculations and high-resolution core-level photo-emission spectroscopy.

The calculated potential energy landscape for H₂ adsorption and dissociation over PdO(101) is shown in Figure 1. H₂ adsorbs weakly (2) and the stable configuration of atomic hydrogen on the surface corresponds to H adsorbed on a pair of three-fold coordinated Pd and O close to each other (3). Reduction of the surface and formation of adsorbed H₂O (6) turns out to be energetically favoured (6). Water formation is at low temperatures, however, kinetically hindered due to substantial energy barriers.

The Pd (3d) and O (1s) core level shifts during exposure of PdO(101) to H₂ were measured at 100 K. Comparing the measured and the calculated core level shifts reveals that only atomic hydrogen is present on the surface. This is consistent with the prediction of high barriers for water formation.

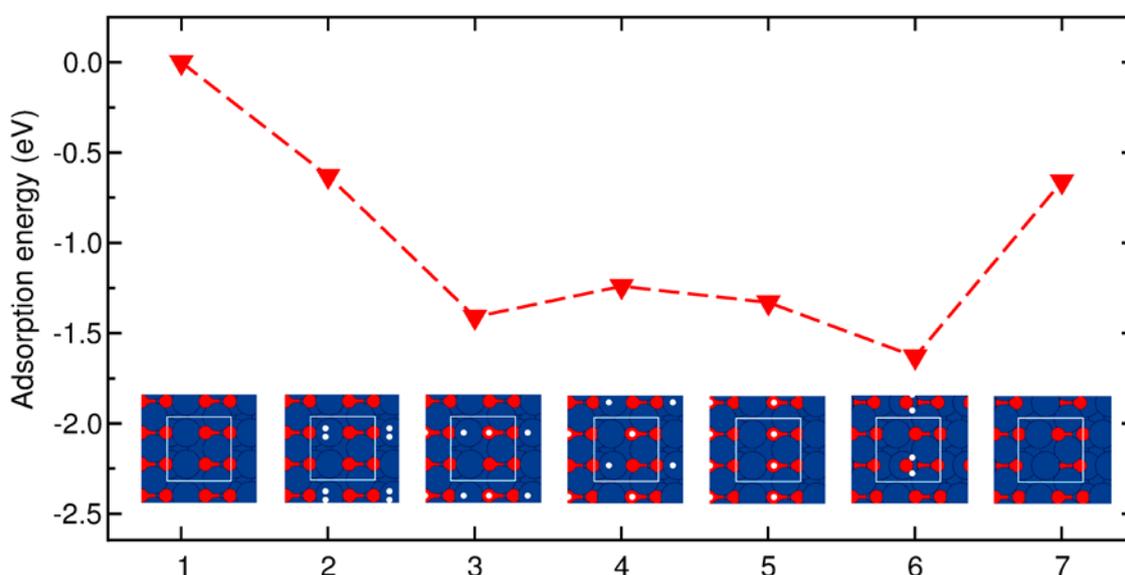


Figure 1. Potential energy landscape for H₂ adsorption and dissociation on Pd(101). The energies are given with respect to the bare surface and H₂ in the gas phase. Structures (1) and (7) correspond to the bare surface and the surface with an oxygen vacancy, respectively. Atomic color codes: Red(bright) – oxygen, Blue(dark) – palladium, White – hydrogen. The surface cell is indicated.

[1] A. Hellman et al., *J. Phys. Chem. Lett.*, **3**, 678, (2012).

THE ROLE OF WATER IN THE LOW-TEMPERATURE CO OXIDATION CATALYZED BY THE Au/TiO₂ INTERFACE: A DFT ANALYSIS

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Au nanoparticles supported by reducible oxides such as TiO₂ are among the most effective catalysts for low-temperature CO oxidation [1]. The origins of such exceptional catalytic activity are still under debate. Bond and Thompson [2] proposed a new mechanism for the CO oxidation which takes place at the interface between the Au nano particles and the TiO₂ support involving OH and carbonate like groups.

We employ DFT calculations to investigate the role of water in the CO oxidation reaction catalyzed by Au/TiO₂ interfaces, focusing in particular on the characterization of reaction intermediates based on carbonate ad-species.

First we determined the structure of our catalyst model by optimizing a 2-layer gold strip on TiO₂ (110) rutile surface both in the presence and absence of oxygen vacancies and the electronic structure of the gold strip is calculated. Then the most favourable adsorption sites of the reactants, intermediates and the products are located and the diffusion of these species on the catalytic system is demonstrated. Finally we report the reaction pathways and the transition state along the minimum energy path using a climbing-image nudged-elastic band method.

[1] M. Hatura, *et al.*, *J. Catal.* **115**, 301, (1989).

[2] G.C. Bond, and D.T. Thompson, *Gold Bulletin.* **33**, 41 (2004).

Equilibrium shape of supported silver clusters

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Metallic nanoparticles embedded in an oxide substrate or supported on its surface are encountered in a large number of applications. Best known examples are catalysis, environmental chemistry, plasmonics, magnetic information storage and medical applications. Broad spectrum of applications results from properties that are strongly determined by their size, shape and crystallographic orientation of exposed facets.

We studied the morphology of silver nanoparticles supported on MgO smoke crystallites by combining Transmission Electron Microscopy (TEM) and atomistic simulations of clusters of realistic size [1]. An advantage was taken of the occurrence of complex – but well-defined – MgO surfaces to analyze Ag clusters of various orientations. Silver clusters were seen to adopt systematically the shape of a truncated octahedron irrespectively of the supports' morphology. The (100)Ag/(100)MgO epitaxy was evidenced and (100), (111) and (110) facets were identified. The agreement between observed shapes and simulated profiles demonstrated that the formers were close to equilibrium which allowed the use of Wulff-Kaisheew construction to determine the anisotropy ratios $\gamma_{100}/\gamma_{111}$ (1.03 ± 0.03) and $\gamma_{110}/\gamma_{111}$ (1.08 ± 0.03) and Ag(100)/MgO(100) adhesion energy (0.58 ± 0.10 J.m⁻²) for clusters large enough to escape stress effects.

The existence of the open (110) facet in the case of silver raise the question of its occurrence in the equilibrium shape of clusters of other fcc metals. Moreover, the existing experimental and theoretical evidence is somewhat contradictory in case of Au clusters. Preliminary results will be presented in this regard.

[1] S. Stankic et al., *Nanoscale*, 2013, DOI: 10.1039/C3NR33896G

Interaction of hydrogen with ZnO nanopowders – evidence of bulk and surface processes

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There have been many investigations to reveal the nature of the hydrogen gas and ZnO nanopowder interaction. Conclusive experimental studies are, however, far fewer in numbers. We use metal combustion technique for the production of ZnO nanopowders. Transmission Electron Microscopy (TEM) revealed tetrapod-like shapes to be the predominant ones while an influence of synthesis parameters on ZnO morphology was also observed (see Figure). The interaction with hydrogen was studied by various spectroscopic techniques. The diffusion of H₂ into the bulk of ZnO was demonstrated to be in line with IR results obtained by Wöll and co-workers [1]. We observed strong depletion of non-polar Raman modes when ZnO powder was exposed to hydrogen. These results – that were also accomplished by X-ray diffraction measurements – show that hydrogen induces significant changes in the crystal structure of ZnO. Finally, the intensity of photoluminescence emission band centered in visible region at ~2.9 eV was found to be fully recovered after pumping hydrogen – suggesting that this optical process in ZnO may be attributed to its surface.

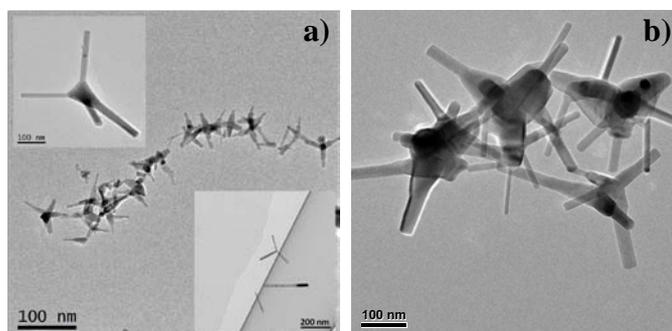


Figure: TEM images of ZnO powders produced by combusting Zn in a) air, b) Ar/O₂ = 95/5

[1] H. Noei, H. Qiu, Y. Wang, M. Muhler and C. Wöll, *ChemPhysChem*, **11**, 3604, (2011).

Energetics of CO₂ adsorption and formation of carbonates on CeO₂ nanoparticle determined by computational modeling

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Using DFT modeling within DFT+U approach we investigated the energetics of the adsorption of CO₂ and formation of surface carbonates on ceria nanoparticle using the model reported earlier [1]. In a previous study we used computational modeling and FTIR spectroscopy to assign various experimentally observed vibrational modes to individual types of surface carbonates formed after interaction of CO₂ with ceria [2]. The type of coordination (via two or three oxygen centers) of the carbonates on the surface was found as the most important factor for vibrational frequencies. Now, we differentiated modeled carbonates on the base of their stability with respect to CO₂ and ceria nanoparticle. In order to verify the adsorption energies of CO₂ calculated by DFT+U method (using gradient corrected PW91 functional and U = 4 eV), we determined adsorption energies of the same structures using a hybrid exchange-correlation functional, PBE0. The adsorption energies calculated with PBE0 were found by only 0.01 to 0.08 eV higher than those calculated with the GGA functional. From the modeled structures we distinguished several groups of carbonates: at less coordinates cerium ions (at edges) with BE(CO₂) around 1.2, 0.7, and 0.5 eV, depending on the coordination; at facets with BE(CO₂) around 0.4 to 0.2 eV; as part of polycarbonates with BE(CO₂) around 0.2 eV. These values are in reasonable agreement with recent experimental measurement [3] showing two plateaus at 1.1 and 0.5 eV.

In order to clarify the influence of the surface coverage on the adsorption energy of CO₂ on ceria we modeled several systems with increasing number of carbonate species on the ceria nanoparticle, up to 9 carbonates. The total adsorption energy is found essentially additive when the ratio of the number of carbonate species and cerium ions at which they are adsorbed is less than 1/2, while above this value the total energy becomes lower than the sum of the individual adsorption energies of the different species.

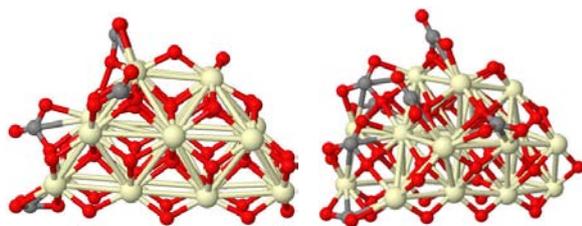


Fig. 1. Examples of models with five and seven carbonate species on ceria nanoparticles.

Acknowledgements

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References

- [1] A. Migani, G.N. Vayssilov, S.T. Bromley, F. Illas, K.M. Neyman, *Chem. Commun.* 2010, 46, 5936.
- [2] G.N. Vayssilov, M. Mihaylov, P.St. Petkov, K.I. Hadjiivanov, K.M. Neyman, *J. Phys. Chem. C* 2011, 115, 23435.
- [3] R. Farra, S. Wrabetz, M.E. Schuster, E. Stotz, N.G. Hamilton, A.P. Amrute, J. Pérez-Ramírez, N. López, D. Teschner, *Phys. Chem. Chem. Phys.*, 2013,15, 3454.

Distinguishing different Pt sites in Pt/CeO₂ via CO Adsorption: A DFT Study

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Here we report results of computational modelling of CO adsorption on a platinum cluster (Pt₈) and Pt containing CeO₂ nanoparticles (Fig. 1) [1] in order to check preferable adsorption site for CO and changes of the C-O vibrational frequency on different positions, as one of the most common characterization approaches for heterogeneous catalytic systems [2,3].

For CO adsorption on platinum cluster our results suggest that the variation of the CO frequency is influenced stronger by the coordination of the Pt atom at which it is bound in the cluster, than on the state of the support (stoichiometric or reduced), or by presence of a single O atom transferred to the Pt₈ cluster, as suggested earlier [4]. Although the oxygen spillover has minor influence on the CO frequency, it decreases the binding energy of CO to the Pt atoms neighbouring O significantly, by 35 kJ/mol with respect to the value for the corresponding position in the pristine structure, 263 kJ/mol.

In addition, our calculations suggest that the adsorption of a single CO molecule cannot induce electron transfer from the reduced CeO₂ back to Pt₈ and cannot reduce the number of Ce³⁺ ions in this way. Such reverse electron transfer is not observed also in the system with large number of oxygen vacancies (up to 4 on the nanoparticle, in which about 50% of cerium ions are Ce³⁺).

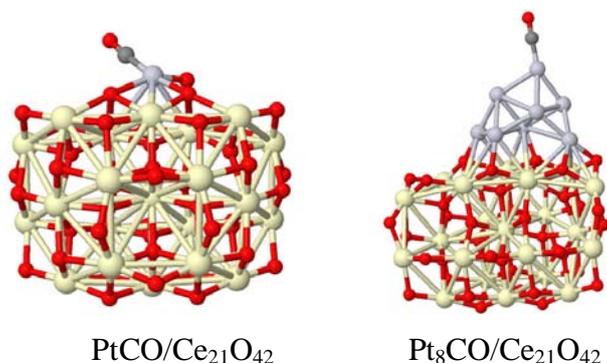


Fig. 1. Selected structures where a CO is adsorbed on bare Pt/Ce₂₁O₄₂ and Pt₈/Ce₂₁O₄₂.

Acknowledgements

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References

- [1] A. Migani, et al. *J. Mater. Chem.* **20**, 10535, (2010).
- [2] K. I. Hadjiivanov, G. N. Vayssilov *Adv. Catal.* **47**, 307, (2002).
- [3] M. Happel et al. *J. Catal.* **289**, 118, (2012).
- [4] G. N. Vayssilov, et al. *Nat. Mater.* **10**, 310, (2011).

Nickel-Based Zirconia and Ceria-Zirconia Catalysts for CH₄ Reforming

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Ni/ZrO₂ is used as a catalyst for methane reforming, which are key processes for hydrogen production in industry and in solid oxide fuel cells. Nickel shows a good activity but is rapidly deactivated by coke formation, which is a major problem. One approach to inhibit coke formation is controlling the size of the nickel particles on the surface, since the ensembles necessary for carbon formation are larger than those needed for methane reforming [1,2]. Furthermore, the addition of copper and formation of a CuNi alloy are expected to reduce coke formation [3].

In this contribution we have characterized zirconia and ceria-zirconia based nickel and bimetallic copper/nickel catalysts and explored the formation of the CuNi alloy. The catalytic properties of the catalysts were tested for CH₄ decomposition and CO₂ reforming of CH₄.

The mixed oxide support was prepared by surfactant assisted coprecipitation of zirconyl and cerium nitrates with cetyltrimethylammoniumbromide as cationic surfactant. The catalysts were prepared by impregnation of ZrO₂ and CeO₂/ZrO₂ with nickel and copper nitrate and calcined at 450 °C. The catalysts contain 5 % w/w metal.

Characterization techniques used include *in situ* X-Ray Photoelectron Spectroscopy, IR spectroscopy of CO as a probe molecule as well as applied *in situ* during methane decomposition, oxidation and CO₂ reforming. X-Ray Absorption Near Edge Structure (XANES), transmission electron microscopy (TEM), H₂ chemisorption and temperature programmed reaction (TPReaction), oxidation (TPO) and reduction (TPRed). These methods provided information on Cu and Ni oxidation states, reduction temperature, catalytic performance, morphology and metal distribution on the surface.

The ceria/zirconia support prepared by coprecipitation effects a higher nickel dispersion on the much higher surface area compared to the zirconia supported catalyst. Therefore, it causes higher catalytic activity in terms of CO₂ reforming of methane and a lower coke formation rate which was determined by temperature programmed oxidation after the reaction.

Formation of a copper-nickel alloy during reduction was confirmed by various techniques. X-Ray Absorption Spectroscopy and Temperature Programmed Reduction showed a decrease in the reduction temperature of nickel by copper addition.

In order to get information about the Cu:Ni ratio on the surface, chemisorption of hydrogen as adsorbing agent was performed. Hydrogen was chosen because it adsorbs irreversibly on nickel but not on copper. The results of these experiments showed, that the surface was enriched in copper, in agreement with FTIR spectroscopy of CO adsorption [4].

TPReaction with MS detection showed that the methane decomposition rate to hydrogen in absence of oxygen was about the same on the CuNi as on the Ni catalyst but started at higher temperature. By repeating the TPReaction measurements H₂ production was already observed at lower temperature and was comparable with the monometallic Ni catalyst. During comparable catalytic activity the addition of copper causes a lower amount of carbonaceous species on the catalyst which could be burnt off at a lower oxidation temperature.

[1] Y. Hu, E. Ruckenstein, *Adv. Catal.*, **48**, 297, (2004).

[2] M.C. Bradford, M.A. Vannice, *Catal. Rev.-Sci. Eng.*, **41**, 1 (1999).

[3] S. McIntosh, R. J. Gorte, *Chem. Rev.*, **104**, 4845-4865 (2004).

[4] A. Kitla, O. Safonova, K. Föttinger, *submitted*.

Surface properties of thick ceria films grown on Si(111)

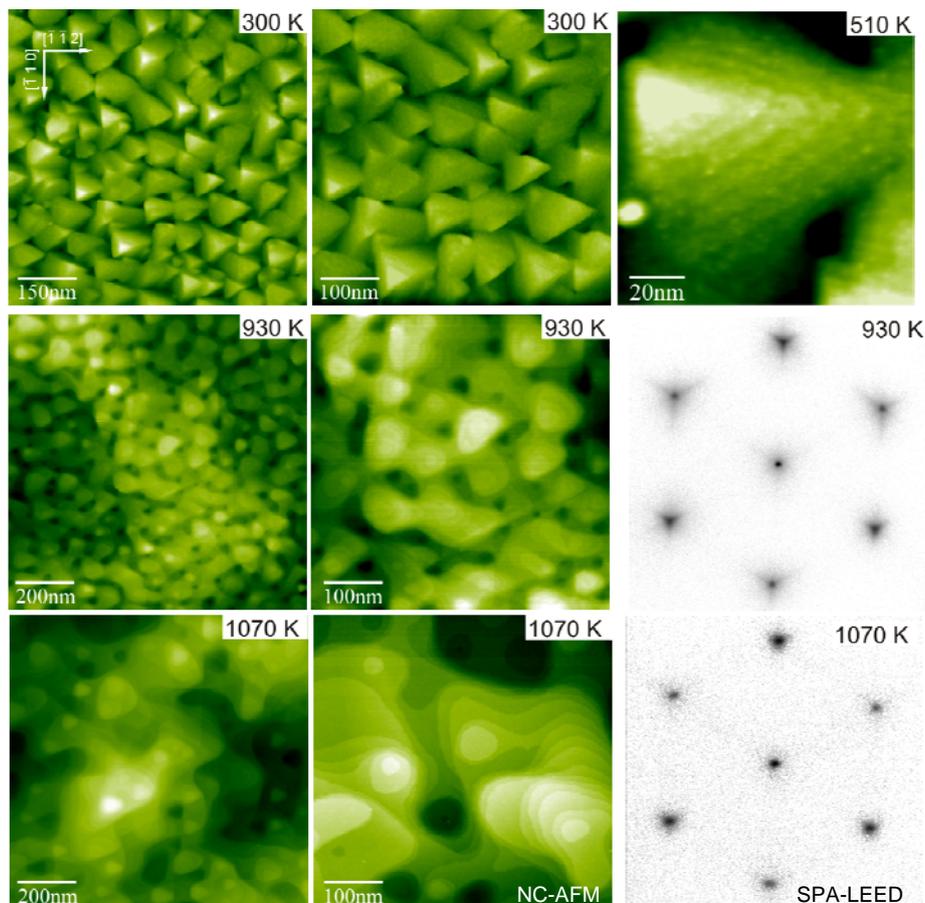
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A 180 nm thick film of ceria grown on Si(111) with a Pr₂O₃ buffer layer [1] is studied with non-contact atomic force microscopy (NC-AFM) and Kelvin probe force microscopy (KPFM). The film is prepared by annealing to different temperatures in the ultra-high vacuum. Up to a temperature of 845 K, pyramidal, terraced triangular structures are observed. In a temperature range from 515 K to 780 K, 6 to 12 nm high spikes appear between the triangle structures. After annealing, the film to 930 K and higher temperatures flat terraces and step structures develop on the film surface that are similar to structures observed on CeO₂(111) surfaces of bulk crystals. The structural transformation is confirmed by a high resolution low energy electron diffraction experiments combined with spot profile analysis (SPA-LEED). Annealing temperatures over 1100 K cause a decomposition of the film. Sputtering the ceria film and annealing at 1090 K generates the best result with large terraces and well defined step structures [2]. Terraces are not atomically flat and KPFM measurements reveal a negative local potential at step edges and potential variations on terraces what is in strong contrast to results found on surfaces of bulk ceria crystals [2].



[1] M. H. Zoellner *et al.*, Phys. Rev. B **85**, 035302 (2012).

[2] H. H. Pieper *et al.*, Phys. Chem. Chem. Phys. **14**, 15361 (2012).

Reactivity vs. Morphology – Steps on TiO₂(110)

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The promising applications of TiO₂-based materials have spurred tremendous research both in fundamental as well as in more applied research fields. However, in surface science studies particularly flat rutile TiO₂(110)-(1×1) has been investigated intensely, whereas step edges and kink sites have often been ignored so far.

In applications such as photocatalysis, photodegradation of organic pollutants and the photo-generation of hydrophilic films the interaction of O₂ with TiO₂ plays an important role. In recent years the oxygen chemistry occurring on flat TiO₂(110) surfaces has been understood in great detail and the role of bulk and surface defects has been unraveled [1-3]. However, the role of step edges in this important interaction is today still unexplored.

Generally, the presence of step edges and kink sites is considered to be beneficial for surface catalyzed reactions. On the surface of rutile TiO₂(110) single crystals two distinct types of stable step edges exist, namely <001> and <1-11> steps [4].

We have studied TiO₂(110) surfaces characterized by different densities of <001> and <1-11> steps by a combination of scanning tunneling microscopy (STM), ultraviolet photoelectron spectroscopy (UPS) and temperature programmed desorption (TPD). The samples were prepared with identical bulk reduction in order to facilitate comparability of the obtained results.

By STM we imaged the surfaces with atomic resolution and unraveled differences in morphology that result from the different step concentrations [5]. UPS allows for studying the distribution of the valence electrons and the defect state of TiO₂. We characterize the chemical environment of surface atoms and discuss differences in the surface reduction state. We used TPD to sample the interaction of oxygen with the surfaces. Therefore, we dosed O₂ at low temperature and detected the desorbing O₂ molecules while heating the sample. We characterized changes in surface morphology and reduction state after the O₂ TPD. This enables us to draw conclusions on the re-oxidation behavior and, hence, the efficiency for oxygen reduction.

We discuss how the differences in surface reactivity can be correlated to the surface morphology, i.e. to the step edges representing the different surfaces.

- [1] E. Lira et al., Surf. Sci. **604**, 1945 (2010).
- [2] Z.-T. Wang et al., J. Phys. Chem. Lett. **1**, 3524 (2010).
- [3] S. Tan et al., J. Am. Chem. Soc. **133**, 2002 (2011).
- [4] U. Diebold et al., Surf. Sci. **411**, 137 (1998).
- [5] R. Bechstein et al., Phys. Rev. Lett. **108**, 236103 (2012).

Adsorption of Pd and Au over Fe₃O₄(001) surface

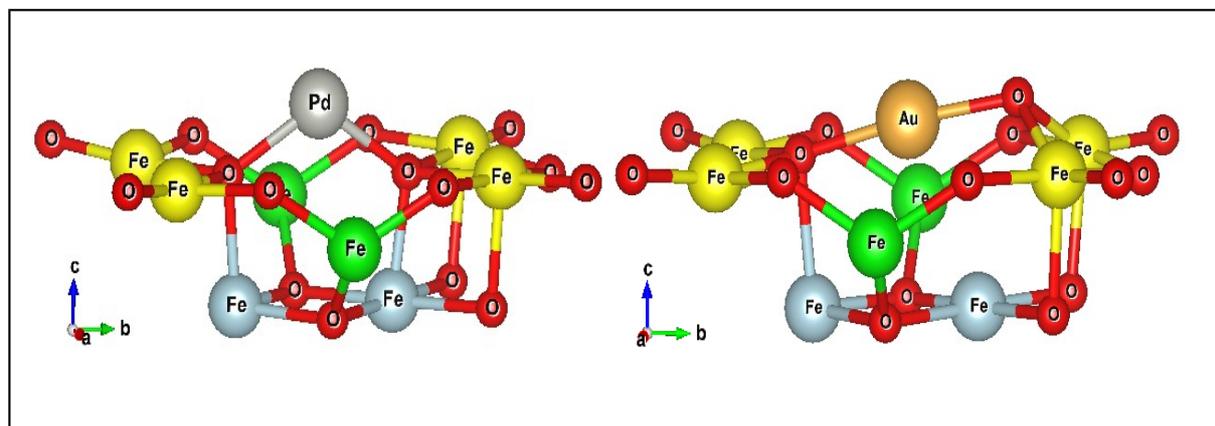
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In order to understand the catalytic activity of magnetite supported palladium and gold catalysts, the adsorption configurations and energies of single Pd and Au atoms on the Fe₃O₄(001) surfaces were studied using density functional theory based GGA+U calculations. Various adsorption sites for Pd and Au atoms on 9-layer and 17-layer slabs were considered, from which two strongly favored geometries emerged. Gold atoms prefer to be linearly coordinated to two surface oxygen atoms (as in the case of Cu₂O). This is facilitated in a tilted geometry, in which one surface oxygen atom relaxes into the surface and one relaxes outward; gold is accommodated in the surface plane. Palladium is also twofold coordinated to surface oxygens in a bent molecular geometry, therefore protrudes from the surface; the oxygen atoms remain in the surface plane. Both adsorbates are positively charged, resulting in reduced magnetic moments and altered orbital occupancies on iron atoms. In addition, the effect of CO addition was investigated, and found to differ significantly for two precious metals. CO binds weakly to Au, but strongly to Pd, having a strong effect on the Pd-surface geometry and the electronic structure. The activation barriers that clarify possible diffusion pathways were calculated for both adsorbates.



Defect Structures And Energies In Ceria Nanoparticles

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In spite of a number of studies, both experimental [1,2] and computational [3], how the properties of ceria nanoparticles (NP) differ from the bulk behavior is still not completely clear. We have used atomistic computational methods to probe the defect structure of ceria NP in the 1 to 2 nm diameter size range. Both classical atomistic simulations and QM calculations were carried out. Structural optimizations and defect calculations were conducted with the GULP package [4] using a set of empirical potentials from Gotte et al. [5]. The cp2k code [6] was used for the QM calculations. NP of stoichiometries, Ce₁₅O₃₀ (1 nm diameter), Ce₈₀O₁₆₀ and Ce₁₄₀O₂₈₀ (~ 2nm diameter). The small number of atoms in these NP allowed the calculation of defect formation energies on every site: vacancies on each oxygen position and Ce³⁺ substitutional energies on each cation site were obtained. Neutral [V_o·2Ce'_{ce}] triplet energies were also calculated, and heats of reduction were thus obtained.

For the 1 nm NP, the lattice expansion of ~ 6% seen experimentally was reproduced in the simulations (Fig. 1). The presence of Ce³⁺, suggested by some, is thus not necessary for the expansion. Furthermore, reduction (incorporation of neutral triplets) leads to substantial distortion of the shape of the 1 nm NP, thus limiting the degree of reduction.

For the 2 nm NP, the most favourable position for the oxygen vacancy was found to lie below the surface, as a result of concomitant structural rearrangement. This suggests a natural mechanism for the continuing reduction of the NP, since oxygen atoms removed from the surface are replenished by this rearrangement. The QM calculations showed that the electrons released by removal of the oxygen were localized on the neighbouring cerium ions predicted by the classical simulations to provide the lowest energy neutral triplet.

Further calculations showed that whilst the incorporation of lanthanum into the NP was energetically favoured, Fe additions were predicted not to be favoured. Both predictions have been born out experimentally.

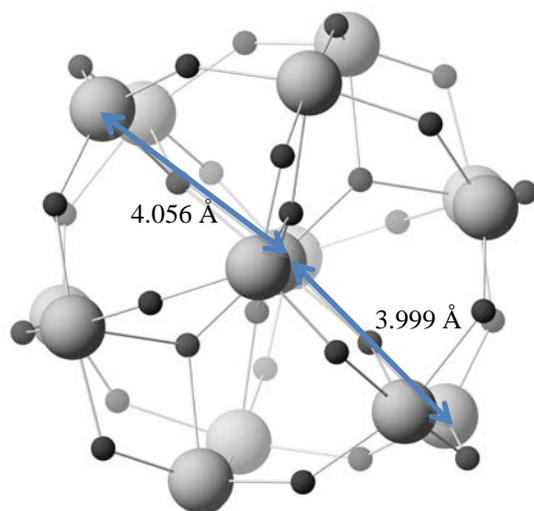


Fig. 1. 1 nm NP. Indicated Ce – Ce distances compare to a bond length of 3.825 Å in simulated bulk ceria.

References

- [1]. R. K. Hailstone, A. G. DiFrancesco, J. G. Leong, T. D. Allston and K. J. Reed, *J. Phys. Chem. C* **113** (2009) 15155
- [2]. J. Guzman, S. Carretin and A. Corma, *J. Amer. Chem. Soc.* **127** (2005) 3286
- [3]. A. Migani, G. N. Vayssilov, S. T. Bromley, F. Illas, and K. M. Neyman, *J. Mater. Chem.* **20**, (2010) 10535
- [4] J.D. Gale, A.L. Rohl, *Molecular Simulation* **29** (2003) 291.
- [5] A. Gotte, D. Spangberg, K. Hermansson and M. Baudin, *Solid State Ionics*, **178**, (2007), 1421.
- [6] www.cp2k.org

Sol-gel synthesis of CeO₂ by using cerium tert-butoxide as precursor

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CeO₂ materials have been extensively studied and employed in applications, and various methods were adopted to synthesize CeO₂, including sol-gel method [1]. The sol-gel method has many advantages for material synthesis and design, which can easily control the materials' composition and structure [2]. In the literature, inorganic cerium salts were mainly used as starting material in sol-gel processes to prepare CeO₂, as they are commercially available. Nevertheless, cerium alkoxides are more beneficial to the materials' properties because the oxo network is formed stepwise during the sol-gel process.

In this work cerium tert-butoxide (Ce(O*t*Bu)₄) was synthesized from ammonium cerium nitrate ((NH₄)₂[Ce(NO₃)₆], CAN) [3], and it was further used to synthesize CeO₂ by sol-gel processing. Acetaldoxime and the surfactant F127 were added as chelating ligand and pore-forming agent respectively, to adjust the structure of the synthesized CeO₂. In order to figure out the advantage of Ce(O*t*Bu)₄, CAN was also used to synthesize CeO₂ by the same procedure for comparison. The synthesized materials were characterized by TGA, IR, XRD, BET and others. The results indicated that CeO₂ made from Ce(O*t*Bu)₄ had higher thermal stability and higher surface area than that prepared from CAN. The surface area can reach 165 m²/g for the best preparation conditions.

- [1] E. Smolentseva, et al., Appl. Cataly. B, **115**,117 (2012).
- [2] U. Schubert, Acc. Chem. Res., **40**, 730 (2007).
- [3] W.J. Evans, et al., Inorg. Chem., **28**, 4027 (1989).

Effect of organic group addition on catalytic properties and therapeutic drug and vitamin administration of niobosilicates

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A direct synthesis route was used to prepare promising functionalized materials, ordered mesoporous nioboorganosilicas (Nb-PMOs), which exhibited high surface area (up to 1400 sq. m/g) and uniform mesopores of width ca. 3-15 nm. For materials synthesized using bridged organosilica precursors (having organic groups inside the silica walls) obtained results showed both nanopores with hexagonal ordering and crystalline structure of walls, which is typical for microporous material (MAPO-39 zeolite). It has been suggested that the obtained structure is a mesoporous material with zeolitic walls. In the case of materials synthesized using organosilica precursors in terminal positions, all materials showed well defined hexagonal array of pores and decrease in degree of order with increasing amount of organic moieties. The presence of niobium at two different localizations (inside the silica skeleton and outside it) was evidenced.

Since Nb-PMOs were expected to find application as a water-tolerant solid catalyst for reactions that require weak acidic sites and low temperatures, they were tested for various oxidation reactions. It was shown that the novel Nb-containing organosilica materials are suitable for epoxidation of olefins. All the catalysts with the functionalized framework exhibited higher epoxide selectivity (~99%) than the pure niobosilica catalyst, although they had similar structural/textural properties, but barely improved (or sometimes decrease) the olefin conversion. An increase in the chain length of organic precursor was a contributing factor for higher hydrophobicity and thus a better selectivity. It is noteworthy that low amounts of water do not interfere with the reaction in the Nb-PMOs systems. Moreover, the results demonstrated that even a small fraction of organic groups (10%) in the framework can lead to materials with greatly improved catalytic activity.

Very promising results showed the experiments on adsorption of active compounds such as drugs (ibuprofen) or vitamin derivatives (vitamin A acid – isotretinoin) inside the pores. Results of this process showed dependence of: type of organic group present inside the silica material, its amount and localization (within the framework or onto the inner surface of pores - inward the pore center). For the majority of samples the amount of adsorbed active substance increased with increasing length of carbon chain, degree of unsaturation and increasing number of organic groups. The organic compounds introduced into the matrix with the use of a terminal precursor were found to block the active substance in the matrix for the steric reasons. Functionalised silicas of SBA-15 structure show better adsorption properties than the corresponding MCM-41 type materials. This observation is explained by the fact that MCM-41 type material has only mesopores, while SBA-15 has also micropores, in which substances of smaller particles such as ibuprofen prefer to localise. The adsorption abilities of silicas modified with niobium and organic functional groups are in general almost twice greater than those of pure mesoporous silicas, organosilica or niobium-silica structures.

Preparation of mesoporous silica thin films supported on Fe₂O₃

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It is well known that ordered mesoporous materials (OMM), since their discovery in 1992, have had a great impact in the whole world of material science. Among others, a very important feature of OMM is their ability to form thin films. Due to specific parameters, like surface roughness, symmetry, strictly defined pores with specific orientation and geometry, mesoporous thin films (MTF) have a high technological potential as membranes, sensors, surfaces for heterogeneous catalysis [1] and even as insulating layers of low dielectric constant for microelectronics. MTF can be also modified with heteroatoms, for example Ti, in order to enhance their potential applications, especially in catalysis [2]. The aim of our work was to prepare mesoporous silica thin films with hexagonally oriented pores' structure and to deposit it on the surface of Fe₂O₃.

Deposited mesoporous silica thin films were prepared using the growth from solution technique. Synthesis was done in the open poly-ethylene vessel, in acidic or basic conditions. Tetraethylortosilicate (TEOS) and 1,1,1,3,5,5,5-heptamethyltrisiloxane (HMTS) were used as a silica source. Hexadecyltrimethylammonium chloride (cTOCl) was applied as a template. After 1 hour of stirring, the vessel containing a mixture of silica film precursor and Fe₂O₃ was moved to the dryer in order to remove the solution. Different temperatures were employed and their influence on textural parameters was evaluated. The last step in the synthesis procedure was a template extraction which was done with different mixtures of ethanol and HCl.

Several analytic methods were applied for the physicochemical characterization of the obtained materials, namely FT-IR, XRD and TEM/SEM analysis, as well as low temperature N₂ sorption measurements.

According to our research, an elevated temperature during substrates stirring has a negative influence on the film formation and ordering of its structure. However, the solvent evaporation before the gelation step should be done in higher temperatures, that enable the preparation of well define mesoporous structures. Influence of the pH value in the reaction mixture was also examined during our studies. It was revealed that the acidic character of the reaction mixture is more preferable than the basic one, especially when it comes to the level of ordering in the structure of created films. FT-IR and XRD analysis confirmed that highly ordered mesoporus silica films were successfully deposited on the surface of other inorganic oxide (Fe₂O₃). Also changes in the textural parameters, that were observed for Fe₂O₃ samples, confirmed that their surface was covered with silica films. The catalytic activity is under investigation.

National Science Centre is kindly acknowledged for financial support (grant number: N N204 538839).

[1] J.Y. Ying, C.P. Mehnert, M.S. Wong, *Angew. Chem. Int. Ed.* (1999), 38, 56-77

[2] Y. Shioya, K. Ikeue, M. Ogawa, M. Anpo, *Appl. Catal. A*, (20030, 254, 251-259

