We show how large-scale computer simulations based on density functional theory can be used to obtain insights into the performance of spinel anode materials for water splitting or alcohol oxidation as important catalytic processes in the chemical industry. The results highlight the role of surface orientation and termination and point towards octahedral cobalt as a possible active site in these systems.

# Supercomputing for energy conversion and catalysis applications

Modelling and understanding the catalytic activity of transition metal oxide surfaces using high-performance computer simulations

By Rossitza Pentcheva & Hamidreza Hajiyani

The development and improvement of catalysts for the relevant processes in the chemical industry, such as (photo-) electrocatalytic water splitting or alcohol oxidation, requires mechanistic understanding at the atomic/molecular level. Quantum-mechanical simulations based on density functional theory (DFT) have advanced to become a powerful tool to predict the properties of materials and their efficiency for various energy conversion applications. Here we outline two examples that show how such simulations can be applied to model, understand and improve the catalytic activity of anode materials for water splitting or alcohol oxidation. In particular, we focus on the performance of transition metal oxides with a so-called spinel structure, containing cobalt, iron and oxygen, $CoFe_2O_4$ and Co_3O_4, which are in the focus of investigation in the Collaborative Research Centre (CRC) TRR 247. By splitting the reactions into elementary steps, the simulations allow us to evaluate their energetics and determine the catalytic performance, which can be compared to experimental measurements. Moreover, analysis of the electronic, magnetic and structural properties offers insight into the underlying mechanisms in order to explain the energetic trends. Specifically, we address the oxygen evolution reaction (OER) at two orientations of the $CoFe_2O_4$ surface, namely (001) and (111), and different surface terminations. The results indicate that the (001) surface has an improved performance compared to the (111) and identify an octahedral cobalt ion at the (001) surface as a potential active site with the lowest overpotential of 0.26 V. Its activity correlates with the specific local environment and bonding of intermediates. In the second application, we consider different paths for the isopropanol oxidation to acetone on the $Co_3O_4(001)$ surface, which involve the release of H_2 vs water as by-products, the latter necessitating either the presence of additional oxygen species or oxygen from the lattice. The calculated relative energies of the intermediate steps for the different pathways support a Langmuir-Hinshelwood mechanism with additional adsorbed oxygen, consistent with experiments within the CRC/TRR 247.

Rossitza Pentcheva. Foto: Vladimir Unkovic
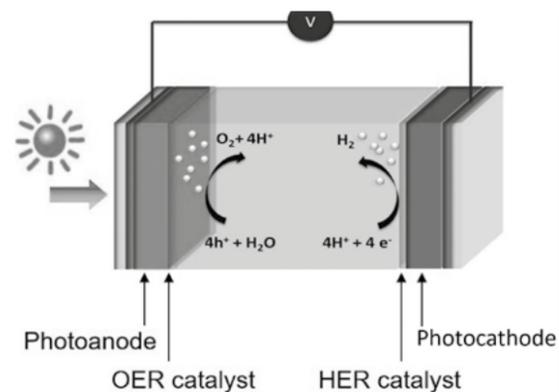
(1) Schematic representation of a photo-electrochemical cell for water splitting composed of a photoanode and a photocathode where the oxygen/hydrogen evolution reaction (OER/HER) take place respectively.
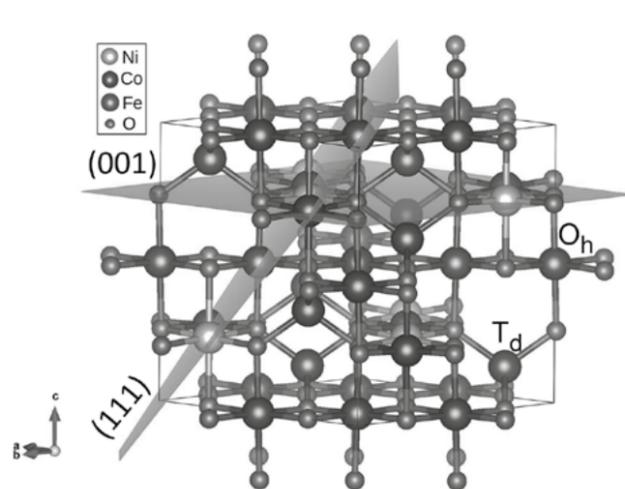Source: own illustration

Introduction

A major concern in our society is finding ways to reduce emissions caused by fossil fuels. In accordance with the Paris Agreement from 2015, global warming should be limited to well below 2° C, preferably 1.5° C, compared to pre-industrial levels. To achieve this goal, further progress should be made in using sustainable energy sources, such as wind power and sunlight[1]. Beside harvesting sunlight and converting it into electricity, the main challenge is large-scale energy storage, which is essential in order to bridge the time and place gap between supply and demand. One of the most promising approaches is to convert sunlight into chemical energy, i.e. use hydrogen gas as a fuel produced by photo-electrochemical (PEC) water splitting ($H_2O \rightarrow H_2 + 1/2 O_2$). However, the hydrogen production efficiency at the cathode in photo-electrochemical cells (PECs) is limited by the sluggish kinetics of the oxygen evolution reaction (OER) taking place at the photoanode (see Fig. 1). Another technologically relevant process is the selective oxidation of alcohols, such as isopropanol, to the corresponding aldehydes and ketones, which is a key technology in the chemical industry, providing important intermediates for pharmaceuticals and fine chemicals. To improve performance, cost-effective and stable compounds with a low overpotential for water oxidation are required. Traditionally, catalysts applied in total oxidation reactions often contain noble metals, such as gold, platinum, and iridium as in IrO_2, but their high cost and low availability limits applications. On the other hand, transition metal oxides (TMO) are cheap and abundant, thermally and chemically stable and environmentally benign and at the same time have a promising catalytic activity, which makes them interesting for energy conversion applications. While a lot of research has so far focused on the catalytic activity of metal surfaces, the understanding of the processes at TMO surfaces lags behind due to their complex structure and electronic behaviour. To fill this gap, the research in CRC/TRR 247 focuses on the heterogeneous oxidation catalysis at cobalt and iron-containing oxides with a spinel or perovskite structure as an attractive class of materials for such applications and for a systematic study of the structure-property relation.

In the spinel structure, the oxygen ions form a slightly distorted face-centred cubic lattice and the cations fill one eighth of the tetrahedral (Td) and half of the octahedral (Oh) sites, where they are surrounded by four or six oxygen ions respectively (see Fig. 2). Catalytic processes take place at surfaces, e.g. of a nanoparticle, which generally exhibit facets with different surface orientations depending on reaction conditions. Two of the most common low-index surface orientations, (111) and (001), are shown as planes cutting through the bulk crystal in Figure (2). For the (001) direction, the plane goes through a layer containing octahedrally coordinated cations and oxygen, typically called the B-layer. On the other hand, one could also cut the crystal in a parallel plane slightly above, containing tetrahedrally coordinated cations, the so-called A-layer. Thus one has to consider not only a variety of surface orientations, but also different surface terminations, e.g. the aforementioned A and B-layers. The availability of different cation coordinations (fourfold, sixfold), multiple oxidation states, suitable gap sizes and high surface reactivity makes spinels interesting for catalytic applications. Co_3O_4 and $CoFe_2O_4$ are two prominent representatives from the spinel family that are investigated within CRC/TRR 247.
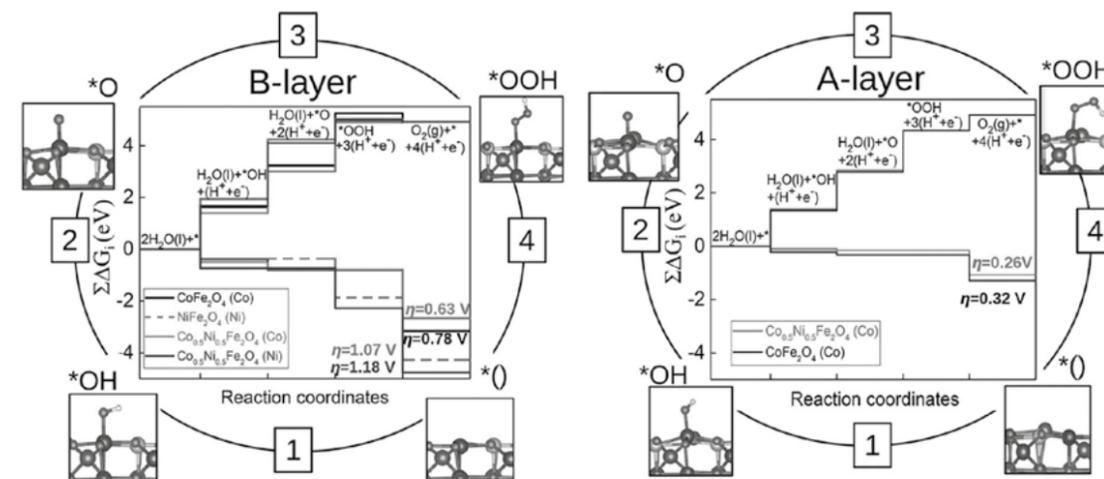
So how can theoretical simulations contribute towards understanding the catalytic processes at such materials? The behaviour of the system at the atomic/molecular scale follows the rules of quantum mechanics. However, a quantum mechanical description of systems with many atoms and electrons is extremely challenging. A breakthrough was achieved with the development of density functional theory in the 1960s by Walter Kohn and collaborators, for which he and John A. Pople were awarded the Nobel Prize in Chemistry in 1998. Since the numerical cost of such simulations increases cubically with the number of electrons in the system, such simulations for the systems of interest here are very demanding and require the use of supercomputers, such as MagnitUDE at UDE. Moreover, the description of transition metal oxides and their surfaces is challenging as the electrons in these systems are strongly correlated and require methods beyond standard DFT, such as the DFT+U method[2] that is suitable for the system sizes of interest here. More computationally involved methods are also applied to obtain accurate electronic and spectroscopic properties of the materials. In the following, we discuss two examples for the application of density functional theory with a Hubbard U term to understand and possibly improve the performance of spinels as anode materials for water splitting and for isopropanol oxidation.

Improving the OER performance by cation mixing in $Co_xNi_{1-x}Fe_2O_4$ [3,4]

A typical photo-electrochemical cell, as shown schematically in Figure (1), is composed of two electrodes: hydrogen is formed from water at the cathode with the hydrogen evolution reaction (HER), whereas the oxygen evolution reaction (OER) takes place at the anode (see Fig. 2). While HER is a two electron-transfer reaction process, OER is a four electron-proton coupled reaction ($2H_2O \rightarrow O_2 + 4H^+ + 4e^-$), which requires a higher voltage beyond the 1.23 V needed to split water to drive the reaction, the so-called overpotential. Due to this overpotential, OER is typically the bottleneck and the main focus of research is to find anode materials with the lowest possible overpotential. In experiments on spinel nanoparticles synthesized within CRC/TRR 247, our collaboration partners found that $CoFe_2O_4$ has a lower overpotential than $NiFe_2O_4$; however, the overpotential is lowest (0.34 V) for a 50:50 mix of Co and Ni, i.e. $Co_{0.5}Ni_{0.5}Fe_2O_4$[3]. In order to shed light on the origin of improved OER performance, we explored the effect of cation mixing, surface orientation and termination in the $Co_xNi_{1-x}Fe_2O_4$ spinel with (111) and (001) surface orientation[3,4]. Due to the broken bonds at the surface and unsaturated charges, the ions at the surface undergo substantial relaxations

(2) Spinel structure with oxygen and cations shown by small and large spheres, also indicated are the tetrahedral (T_d) and octahedral cation sites (O_h) and the crystal planes showing (001) and (111) orientation.
Source: own illustration

(3) Side view of the relaxed structure of the intermediates during OER at the B and A-layer of the $Co_{1-x}Ni_xFe_2O_4$ (001) surface (x=0, 0.5, 1) together with the cumulative free energies and overpotentials.
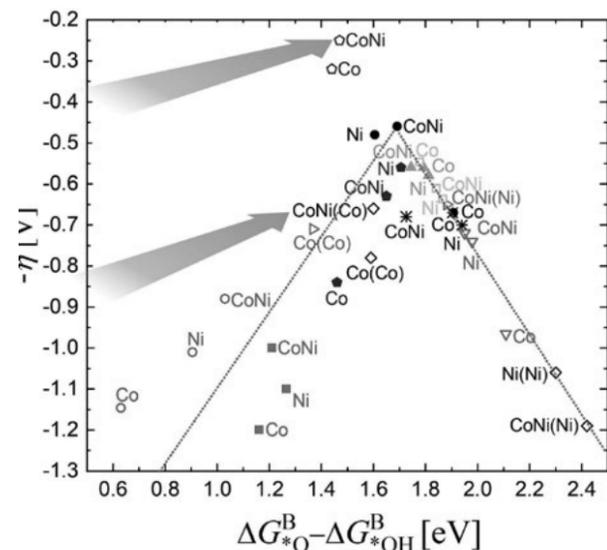Source: H. Hajiyani, R. Pentcheva, Surface termination and composition control of activity of the $Co_xNi_{1-x}Fe_2O_4$(001) surface for water oxidation: insights from DFT+U calculations, ACS Catal., 8, 11773–11782 (2018), reprinted with permission from and copyright of the American Chemical Society

from their ideal bulk positions, thus an important and computationally time-consuming step is the optimization of the surface structure. Next, one needs to determine the relative energetic stability of different surface orientations and terminations under different oxygen pressures and reaction conditions. This investigation showed that the prevailing terminations are the (001) surface orientation with A and B-layer termination in oxygen-poor and oxygen-rich conditions but with significant relaxations of the surface ions, which influences the OER activity of these surfaces.

In order to assess the OER activity of the studied surfaces and calculate the overpotential, we follow the approach of Rossmeisl et al., in which the OER process is split into four intermediate steps[5]. The first comprises the adsorption and dissociation of a water molecule into an *OH group bound to the surface (typically on top of a cation) and the release of a proton and an electron: $* + H_2O \rightarrow *OH + H^+ + e^-$, where * denotes the oxide surface. The next step is the deprotonation of the *OH group and the release of another proton and electron: $*OH \rightarrow *O + H^+ + e^-$. In the third step, another water molecule is dissociated on top of *O and forms *OOH: $*O + H_2O \rightarrow *OOH + H^+ + e^-$. Finally, *OOH is deprotonated and leaves the surface as an O_2 molecule $*OOH \rightarrow * + O_2 + H^+ + e^-$ and the surface is in its initial state, ready for the next OER cycle.

At standard conditions (pH = 0, p = 1 bar, and T = 298 K), the reaction free energy of the individual steps is calculated as the energy difference between the intermediates presented above, including zero-point energy (ZPE) and entropic (TΔS) contributions: $\Delta G_i = \Delta E + \Delta ZPE - T\Delta S - e\phi$.

Figure (3) shows the side views of the relaxed structures and the corresponding cumulative free energies of intermediates and overpotentials during OER for the B-layer (left) and the A-layer (right) terminations

(4) Overpotential versus the binding energy difference of *OH and *OOH groups for different reaction sites and terminations of the Co$_x$Ni$_{1-x}$Fe$_2$O$_4$ (001) and (111) surfaces.
Source: H. Hajiyani, R. Pentcheva, Surface termination and composition control of activity of the Co$_x$Ni$_{1-x}$Fe$_2$O$_4$ (001) surface for water oxidation: insights from DFT+U calculations, ACS Catal., 8, 11773–11782 (2018), reprinted with permission from and copyright of the American Chemical Society

of the Co$_{1-x}$Ni$_x$Fe$_2$O$_4$ (001) surface with x=0, 0.5 and 1. As one can see, the cumulative free energy is a step-like function with uphill steps. In order to run the reaction, an additional potential ϕ_{OER}, equal to the highest step, needs to be applied to make those steps downhill. Subtracting 1.23 V from ϕ_{OER}, one obtains the overpotential η. Our results show that overall the overpotential is lowest for a cobalt octahedral reaction site (Co) at the mixed Co$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$ (001) surface, followed by a Co at the CoFe$_2$O$_4$ (001) surface, while the overpotential at a Ni reaction site at the mixed Co$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$ (001) or NiFe$_2$O$_4$ (001) surface is beyond 1 V. Moreover, Co at the A-layer shows much lower overpotentials (0.26-0.32 V) than at the B-layer. The same trend with regard to Ni-mixing is observed for the (111) surface, yet the overpotential is higher overall (0.55 V for a Fe site)[3]. To gain further insight into the origin of this behaviour, we plotted -η as a function of the energy difference to bind two of the intermediates, *O and *OH, which results in the so-called

volcano plot as shown in Figure (4) for the studied (001) and (111) surface orientation, terminations and reaction sites. The cases with the lowest overpotential are located at the top of the volcano, while those for the Co-site at the A-layer of the mixed Co$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$ (001) and mixed CoFe$_2$O$_4$ (001) lie even above the volcano, which is associated with the particular bonding geometry of the *OOH intermediate that is not only bonded to the surface cation by O but H also forms a bond to a surface oxygen, lowering the energy of this typically potential-determining step. Further analysis of the electronic properties (not shown here) gives insight into the variation of the oxidation states during OER for the different systems[4].

The DFT results indicate that the overpotential strongly depends on surface orientation, termination and reaction site and the trend with Ni-mixing is consistent with experimental findings[3]. In particular, when terminated with an additional tetrahedral layer (A-layer), Co$_{0.5}$Ni$_{0.5}$Fe$_2$O$_4$ (001) and mixed CoFe$_2$O$_4$ (001) exhibit one of the lowest theoretically reported over-

potentials of 0.26-0.32 V, in good agreement with the measured value of 0.34 V. Moreover, the results point towards octahedral surface cobalt ions as a candidate for the active site. Ongoing studies focus on further spinel surfaces such as Co$_3$O$_4$ (001)[6] as well as perovskite surfaces to obtain a comprehensive picture of the activity at cobalt and iron containing oxides depending on structure and local environment. Further aspects of ongoing work are the effect of solvation and liquid water as well as the role of defects. Another challenge to be tackled is the incorporation of kinetic effects, i.e. information on the barriers that need to be overcome between the intermediate steps.

Isopropanol oxidation at the Co$_3$O$_4$ (001) surface: mechanistic insights into the aerobic oxidation of alcohols[7]

The second example comprises the 2-propanol oxidation to acetone at the Co$_3$O$_4$ (001) surface. This reaction can proceed over several paths: besides the product acetone, hydrogen can be released from the surface in what is known as dehydrogenation: $(CH_3)_2CHOH \rightarrow (CH_3)_2CO + H_2$

Another possibility is oxidative dehydrogenation, where water is released:

$$2(CH_3)_2CHOH + O_2 \rightarrow 2(CH_3)_2CO + 2H_2O$$

In this case, either additional adsorbed oxygen species (Langmuir-Hinshelwood mechanism) or oxygen from the oxide lattice (Mars-van Krevelen mechanism) are needed to form the water molecule, and in the latter case an oxygen vacancy is then left at the surface. Using DFT+U calculations we have considered four different pathways for the (001) surface of Co$_3$O$_4$, which is abundant under common synthesis conditions. Figure (5) shows the Co$_3$O$_4$ (001) surface with a B-layer termination of octahedral cobalt and oxygen prior to and following the adsorption of an isopropanol molecule and oxygen. The spin density and magnetic moments at the cation sites are also shown, giving an indication of changes in the electronic properties of the surface compared to bulk. In bulk Co$_3$O$_4$ (Co^{2+}Co$^{3+}_2$O$^{2-}_4$), Co^{2+} occupies the tetrahedral sites (Td) with a magnetic moment of 2.6 μ_B (three unpaired spins from a total of seven electrons), whereas Co^{3+} resides at the octahedral sites and has six electrons, three with spin up and three with spin down, which results in a zero magnetic moment (termed low spin, LS). Our results indicate that at the B-layer of the (001) surface, the fivefold-coordinated Co acquires a

finite magnetic moment of 1.9 μ_B due to the broken bonds at the surface pointing towards Co^{3+} in the intermediate spin (IS) state. The DFT calculations show that both 2-propanol and additional oxygen prefer to adsorb on top of the octahedral Co surface sites. Interestingly, Co underneath both adsorbates, 2-propanol or additional O, has an oxidation state of +3 (low spin, LS) as in bulk Co$_3$O$_4$. This is consistent with spectroscopic measurements within CRC/TRR 247[7].

In Figure (6) we provide a first assessment of the different mechanisms by comparing the relative stability of intermediates following four pathways of 2-propanol to acetone oxidation on the Co$_3$O$_4$ (100) surface: the dehydrogenation pathways A and B involve the desorption of acetone and H$_2$, while the oxidative dehydrogenation pathways C and D result in the formation of acetone and H$_2$O. They differ, however, concerning the origin of oxygen in the desorbing H$_2$O molecule: in the Mars–van Krevelen pathway C, it stems from a surface/lattice oxygen, leaving a surface with an oxygen vacancy, and in the Langmuir–Hinshelwood pathway D it stems from a coadsorbed oxygen, leaving a defect-free surface. We note that the coadsorption of 2-propoxide next to so-called reactive oxygen species (ROS) is favoured in comparison to the adsorption on the bare surface. Our results illustrate that the latter pathway D results in the highest energy gain with respect to the initial configuration and in comparison to the dehydrogenation pathways A and B. As can be seen from Figure (6), reaction mechanisms C and D are both downhill with a higher energy gain for D of −1.81 eV versus −1.1 eV for C. Ongoing studies assess the dependence on other surface orientations, chemical compositions and defects at the surface.
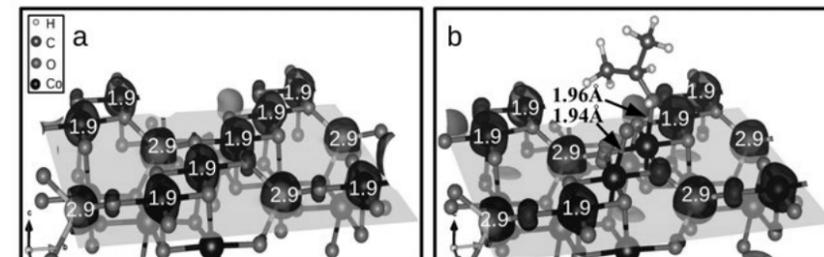

(5) Structure and spin density of (a) the bare Co$_3$O$_4$ (001) surface and (b) the surface with adsorbed 2-propanol and ROS at a neighbouring site. The bond lengths of adsorbates to the surface in Å are also shown in black and the magnetic moments at the Co sites in μB in white. Note that the surface octahedral Co acquires a finite magnetic moment and is in an intermediate spin state, while after adsorption of either oxygen or isopropanol on top of Co its magnetic moment is quenched as in the bulk material.
Source: adapted and modified from S. Anke, G. Bendt, I. Sinev, H. Hajiyani, H. Antoni, I. Zegkinoglou, H. Jeon, R. Pentcheva, B. Roldan Cuenya, S. Schulz, M. Muhler, Selective 2-Propanol Oxidation over Unsupported Co$_3$O$_4$ Spinel Nanoparticles: Mechanistic Insights into Aerobic Oxidation of Alcohols, ACS Catal., 9, 5974–5985 (2019), with permission from and copyright of American Chemical Society
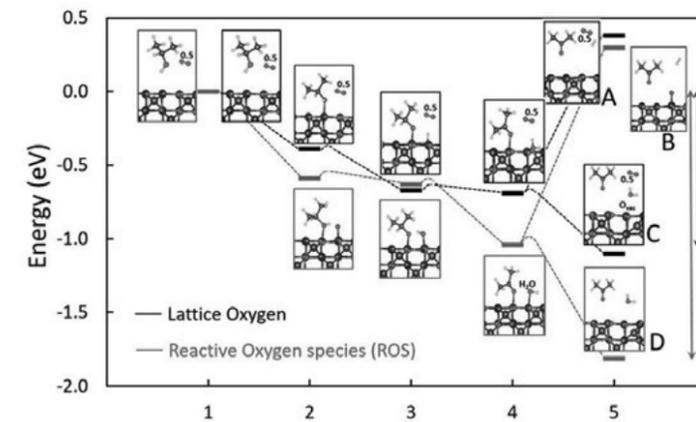
(6) Energetics of intermediates during 2-propanol to acetone oxidation with respect to the initial configuration (2-propanol in the gas phase). Four mechanisms were studied: in A and B acetone desorbs from the surface together with H_2, and in C and D the products are acetone and water. In C an oxygen vacancy is created at the surface (Mars–van Krevelen mechanism), and in D the oxygen of desorbed water stems from co-adsorbed oxygen on the surface (Langmuir–Hinshelwood mechanism). In the intermediate stages, hydrogen from the deprotonation of 2-propanol adsorbs at a surface oxygen or an OH group (A, C) or at ROS (D). In order to compare the relative stability of intermediates for the four pathways, $0.5E_{O_2}$ is added to the total energy for paths A and C.
Source: Adapted from S. Anke, G. Bendt, I. Sinev, H. Hajiyani, H. Antoni, I. Zegkinoglou, H. Jeon, R. Pentcheva, B. Roldan Cuenya, S. Schulz, M. Muhler, Selective 2-Propanol Oxidation over Unsupported Co_3O_4 Spinel Nano-particles: Mechanistic Insights into Aerobic Oxidation of Alcohols, ACS Catal., 9, 5974–5985 (2019) , with permission of the American Chemical Society

Zusammenfassung

Wir haben zwei Beispiele vorgestellt, die zeigen, wie großskalige Computersimulationen basierend auf der Dichtefunktionaltheorie genutzt werden können, um einen Einblick in die Eigenschaften von Spinell-Anoden-Materialien für die Wasserspaltung oder Alkohol-Oxidation als wichtige katalytische Prozesse in der chemischen Industrie zu bekommen. Die Ergebnisse unterstreichen die Rolle der Oberflächenorientierung und -terminierung und weisen auf oktaedrisches Kobalt als potentielles aktives Zentrum in diesen Systemen hin. Weitere Studien zielen darauf ab, ein systematisches Verständnis der Rolle von strukturellen Mustern für die katalytische Aktivität von gemischten Kobalt-Eisen-Oxiden und die aktiven Zentren zu identifizieren und Reaktivitätstrends zu extrahieren, um das Design von Katalysatoren zu ermöglichen. Künftige wichtige Herausforderungen, die angegangen werden müssen, sind die Modellierung der Grenzfläche zum flüssigen Wasser sowie von kinetischen Effekten. Eine enge Zusammenarbeit mit experimentellen und anderen theoretischen Gruppen innerhalb des CRC/TRR 247 und Zugang zu Supercomputing-Ressourcen wie MagnitUDE sind wichtige Voraussetzungen hierzu.

Annotations/Publications

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Rossitza Pentcheva studied Physics at Sofia University and at the University of Cologne, concluding her studies with a diploma thesis at the Forschungszentrum Jülich. In 2000, she received her PhD at the Free University of Berlin and the Fritz Haber Institute of the Max Planck Society in Berlin. She continued as a DFG project leader and held positions as a lecturer and senior lecturer at the Ludwig Maximilian University of Munich (LMU) and as a visiting scientist at the University of California, Davis. She completed her habilitation in the field of Materials Science at LMU in 2008. In 2014, she was appointed Professor of Theoretical Physics at the University of Duisburg-Essen (UDE), where she is a board member of the Center for Computational Science and Simulation (CCSS) and a member of the Center for Nanointegration (CENIDE). Moreover, she is a founding member, project leader and board member of the Collaborative Research Centre (CRC) TRR 80 'From Electronic Correlations to Functionality', as well as a founding member and project leader within the CRC 1242 'Non-Equilibrium Dynamics of Condensed Matter in the Time Domain' and CRC/TRR 247 'Heterogeneous Oxidation Catalysis in the Liquid Phase'. Her research focuses on the theoretical modelling of novel electronic and topologically non-trivial phases as well as on non-equilibrium dynamics at oxide interfaces with an application potential in electronics, spintronics or energy conversion (thermoelectrics, water splitting).

Hamidreza Hajiyani. Foto: Vladimir Unkovic