FOXSI
Functional Oxide Surfaces and Interfaces
International FOXSI Conference, May 23-25, 2016

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Functional Oxide Surfaces and Interfaces (FOXSI)

International FOXSI Conference, May 23-25, 2016

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Structure and reactions on catalysts surfaces in ambient gas pressure and under liquids

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Over the past century the science of surfaces has undergone an enormous progress. The atomic and electronic structure, reactivity, and dynamics of many material surfaces have been uncovered. Several Nobel prizes have marked the great accomplishments of our predecessors, from I. Langmuir in 1932 to G. Ertl in 2007. This progress has been fostered and propelled by the continuous development of powerful techniques that have provided atomic and molecular level details of surfaces, adsorption and desorption phenomena, vibration and electronic spectra, electron diffraction and real space imaging by the Scanning Tunneling Microscope. The nature of many techniques has constrained Surface Science to ultra-high vacuum environments, and often under cryogenic temperature to achieve a measurable coverage of weakly bound adsorbates. And yet practical surfaces are surrounded by gases and liquids at ambient conditions of pressure and temperature. Under these conditions the surfaces are covered with dense layers of adsorbed molecules in equilibrium with the gas phase, while the relevant ambient temperature unlocks many kinetic processes that are frozen at low temperatures. Here I will review the physics and chemistry of surfaces with dense layers of adsorbates and show new phenomena that derive from this, including the effect of reactant gases such as O2, C2H4, and CO on the structure of Pt and Cu surfaces. Prospects for similar studies of the solid-liquid interface, a new frontier in the field, and their impact in environmental science, electrochemistry and energy storage will be discussed in view of recent advances in x-ray based spectroscopic techniques.

Ultrathin Oxide Films on Metal Substrates: Case studies

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Ultrathin oxide films become interesting materials in modern technological applications. In addition, such films are considered as suitable models to elucidate the atomic structures and mechanisms of chemical reactions at oxide surfaces and oxide/metal interfaces. In this talk, I will discuss some general aspects of using such systems in catalysis and highlight important role of the oxide/metal interfaces. Several case studies will be discussed in details. The first one addresses atomic structure of ZnO and FeO films, used in CO oxidation at nearly atmospheric pressures. In the second case, interaction of water with metal supported silica films will be addressed in order to create hydroxo species as anchoring sites for active “monomeric” species.

From Ultrathin to Thin Zirconia Films

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Zirconia (ZrO_2) is a catalyst support and, in doped form, an oxygen ion conductor employed as solid-state electrolyte for gas sensors and solid-oxide fuel cells. For these applications, it is essential to understand the surface science of ZrO_2. Since zirconia (pure and doped) is an electronic insulator up to high temperatures, most analysis methods involving charged particles such as scanning tunnelling microscopy (STM) are possible only on (ultra-)thin ZrO_2 films on a metal support. We have developed methods to grow ultrathin ZrO_2 films by oxidation of suitable alloys; the resulting films are O–Zr–O trilayers with a structure closely related to cubic ZrO_2(111) [1,2]. Metal deposition experiments on these films and DFT calculations show that the interaction increases with decreasing electronegativity of the metal (stronger bonding to oxygen), with the exception of Pt and Au, which bind mainly to the Zr cations [3].

Somewhat thicker (few-layer) ZrO_2 films were grown by an ultrahigh-vacuum (UHV) compatible sputter deposition source (inspired by [4]) and also show ZrO_2(111)-like surfaces with different superstructures, which can be linked to the bulk phases of the oxide. Upon annealing in oxygen, the oxide dewets the metal (Pt or Rh) support, and oxide islands remain on the surface. Annealing in UHV leads to an ultrathin (trilayer) oxide covering the metal surface between thicker (bulk-like) ZrO_2 islands. This phenomenon is usually known as strong metal-support interaction (SMSI) and related to a sub-stoichiometric ultrathin oxide. As ZrO_2 is an essentially non-reducible oxide, the SMSI effect has to be explained by a different process. We propose a novel SMSI mechanism, based on alloying of Zr with the substrate, which changes the adhesion of the ultrathin oxide film on the support.

Supported by the Austrian Science Fund (Project F45, FOXSI)

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Oxygen defects and the reactivity of ceria

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The formation of oxygen defects and their identification by STM is discussed based on DFT calculations.[1,2]

Supported transition metal oxide catalysts are used for the selective oxidations involving C-H bond activations. Examples are the oxidative dehydrogenation of propane to propene and of methanol to formaldehyde. According to the Mars-van Krevelen mechanism the feed molecules exchange redox-equivalents with the catalysts and the oxygen defect formation energy of the latter has been proposed as reactivity descriptor.

Here, the focus is on support effects for vanadium oxide catalysts, in particular in the difference between reducible (VO_x/CeO_2)[3,4,5,6] and non-reducible[7] (VO_x/SiO_2) supports for methanol[8] oxidation. For VO_x/CeO_2, two pathways are found[6] that explain the observed TPD peaks: (i) methanol can chemisorb on the CeO_2 surface filling a so-called pseudovacancy and the H atom is transferred to an V–O–Ce interphase bond or (ii) CH_3OH may chemisorb at the V–O–Ce interphase bond and forms a V–OCH_3 species from which H is transferred to the ceria surface, providing evidence for true cooperativity.

CeO_2 turns out to be a very special support - it easily accommodates electrons in f-states. In the VO_x/CeO_2 system this leads to stabilization of V^{+5} also under reducing conditions. The VO_x/CeO_2 system is more reactive than each component alone.

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LEED intensity analyses of oxide films - structural surprises and reliability

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The surfaces of transition metal oxides are quite often not just bulk-like terminated but chemically and geometrically reconstructed. There can be vacancies within either the oxygen or cation lattice as well as site switches towards interstitial position. These processes are not restricted to the very surface but can also occur - even exclusively - within subsurface layers as e.g. in the cases of Fe_3O_4(100) [1] and CoO(111) [2] and by that remain largely hidden to imaging methods like STM. For ultra-thin oxide films grown on reactive substrates the situation further complicates by the competition of binding forces within the film and towards the substrate [3]. This may even lead to Moire-type films with a laterally modulated structure as found for a CoO(111)-type bilayer on Ir(100) [4]. In the sub-monolayer regime there is a further competition between 2D-oxide island growth and 1D-nanostructure formation. On the plain Ir(100) surface for example, linear metal-oxide hybrid structures with TMO_2 stoichiometry (TM = Mn, Fe, Co, Ni) develop self-organised in threefold lateral distance (for $\Theta_{TM} = 0.33$), inducing a missing row substrate reconstruction below. With increasing TM coverage these quasi-1D structures are successively substituted by 2D islands of TMO(111) bi- or trilayers.

As demonstrated above, the structural solutions of nature for oxide surfaces and films are often complex and rather surprising, which makes the initial guess of the correct structure - the inevitable starting point of every structure determination - a demanding task. This is the more crucial the larger the surface unit cell becomes, since in such a case the contribution of one extra (or missing) atom alters the total wave field only moderately. This means that neglecting such an element in the model structure will also not lead to dramatic changes in the intensity spectra and so still seemingly plausible fits may result. As an example, LEED-IV analyses for the c(2×2)-reconstructed surface of Fe_3O_4(100) using models which neglect either the Fe vacancies or the interstitial ions of the correct model [1] still produce “best-fit” Pendry R-factors in the range 0.2 - 0.3, which are commonly called “acceptable fits”! As a consequence it has to be pointed out that trustworthy LEED fits in particular for complex structures have to be of significantly better quality ($R_P < 0.15$). Approaches to improve the quality of a LEED intensity analysis as well as consistency checks to detect incomplete structural models are presented and discussed.

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Ir-based electrocatalysts for the oxygen evolution reaction

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Water electrolysis, combined with renewable electric power generation technologies, such as solar electric, solar-thermal, hydro, or wind power plants, is expected to emerge as a low-emission method for storing excess electricity and for producing hydrogen fuel as part of a solar refinery. The challenge in electrocatalytic water splitting is the high overpotential required for the anodic oxygen evolution reaction (OER). Relatively low overpotential is attainable in acid electrolyzers using IrOx-based electrocatalysts, however they are expensive and of limited sustainability. Furthermore, the complexity of iridium oxide's electronic structure makes it particularly difficult to experimentally determine the chemical state of the active surface species. In the first part of this contribution, an accurate understanding of the electronic structure of iridium oxide surfaces will be provided based on combined synchrotron-based X-ray photoemission and absorption spectroscopies with ab initio calculations.[1]

In the second part I address the challenges related to noble metal content and durability of water splitting catalysts presenting a low-Ir content OER catalyst on a corrosion-stable oxide support with excellent electrochemical performance and durability.[2]

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Hydroxylation and dissolution of model thin film oxides: MgO, CaO and SiO_2

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Water-oxide interaction is of great importance in a number of technologically relevant fields, among them heterogeneous catalysis. Several studies report on the promoting effect of water in catalytic reactions, the participation of surface hydroxyls in reaction, and the influence of hydroxylation on the binding of metals to oxide surfaces. Achieving a fundamental atomic scale understanding of water-oxide interaction at environmentally and catalytically relevant conditions (e.g. ambient pressure) represents, therefore, a challenge for surface science studies related to heterogeneous catalysis. In this contribution, I will present results of our recent studies related to the interaction of water with thin, single crystalline oxide films (MgO(001)/Ag(001), CaO(001)/Mo(001), SiO_2/Ru(0001)) carried out in a wide range of water chemical potential, from UHV to mbar water pressures (hydroxylation) and liquid water (dissolution).

We combine results for infrared reflection absorption and X-ray photoemission spectroscopy with scanning tunneling microscopy and calculations using density functional theory to characterize the different hydroxylation states of MgO(001) and CaO(001). As proposed by calculations, we find different stable hydroxyl/water adsorption structures (2-dimensional and 1-dimensional) on the two oxide surfaces, which form as a consequence of the relative importance of intermolecular coupling (hydrogen bonding) within the adsorbed layer and the strength of the molecule-substrate interaction as a function of basicity and lattice constants of the oxide surfaces.[1-3] In contrast to MgO and CaO, silica is quite inert toward water interaction. Its hydroxylation requires additional electron bombardment of adsorbed ice layers.[4] By combining results of thermal desorption spectroscopy of hydroxylated silica and dissolution studies carried out over a wide range of solution pH and temperature, a hydroxylation mechanism based on the activation of siloxane bonds by water radiolysis products (e.g. hydroxyl) is proposed.[5]

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Interaction of water with ultrathin ZrO_2 films

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It is well accepted that surface science based planar model catalysts are well-suited for fundamental studies of surfaces processes, despite the inherent differences between model and technological catalysts [1-3]. Methodological advances also allow to examine active functioning model catalysts, at (near) atmospheric pressure and at elevated temperature. Frequently applied methods encompass polarization-modulation infrared reflection absorption spectroscopy (PM-IRAS), sum frequency generation (SFG) laser spectroscopy and near atmospheric pressure X-ray photoelectron spectroscopy (NAP-XPS). In the current contribution this approach is utilized to examine Ni-ZrO_2 „cermet“ anodes that are employed in Solid Oxide Fuel Cells (SOFCs) for CH_4 reforming to H_2 and/or H_2 oxidation.

In order to model SOFC anodes well-ordered ultrathin films of ZrO_2 were grown in UHV by oxidation and annealing of $Pt_3Zr(0001)$ single crystals [4]. Ni was deposited by physical vapor deposition. Low Energy Electron Diffraction (LEED), Scanning Tunneling Microscopy (STM), high resolution X-ray Photoelectron Spectroscopy (XPS) and Density Functional Theory (DFT) indicated the formation of a well-structured ZrO_2 trilayer film, corresponding to the (111) facet of cubic ZrO_2. Whereas the interaction of the ZrO_2 film with CO or CO_2 was very weak (desorption temperatures of 155 and 117 K, respectively), its interaction with water was very strong (desorption temperature of 485 K). NAP-XPS (O1s and Zr3d) and PM-IRAS were thus applied to examine water adsorption/dissociation and hydroxylation of the O-Zr-O film. Backed by DFT, three channels of water adsorption (molecular vs. dissociative, reversible vs. non-reversible) could be identified. Creation of defects by ion bombardment strongly enhanced water dissociation.

Once hydroxylated the ZrO_2 film exhibited exceptional activity for reaction with CO_2 (whereas the non-hydroxylated film did not). IRAS, using formic acid (HCOOH) and formaldehyde (HCHO) as reference, was used to identify the functional groups of the species formed. Ni nanoparticles grown on the ZrO_2 trilayer were examinded by PM-IRAS and XPS.

Support by the Austrian Science Fund (FWF SFB-F45 FOXSI) is gratefully acknowledged.

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Theory of oxide surfaces and metal/oxide interfaces – Adsorption on ZrO2 films and bulk surfaces

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Doped and un-doped Zirconia (ZrO_2) is an important material with many interesting properties, which makes it also very useful for various technological applications, e.g. for solid-oxide fuel-cells or gas sensors and three-way catalysts, to name only a few. Hence, a detailed understanding of its adsorption and interface properties on an atomic level is very important. Here we present results of DFT calculations for the adsorption of metal ad-atoms and water on bulk surfaces and on thin Zirconia films grown by oxidation of a Pt_3Zr substrate [1]. The calculations were performed using the Vienna Ab-Initio Simulation Package (VASP) employing van-der-Waals density-functionals [2]. Concerning the metal ad-atoms the bonding and adsorption mechanism was studied for both noble Au and Ag and reactive Ni and Pd [3]. Our calculations for single ad-atoms show that the metal-oxide interaction strength increases in the sequence Ag<Au<Pd<Ni on monoclinic ZrO_2, and Ag≈Au<Pd<Ni on the supported ultra-thin ZrO_2 film. On monoclinic bulk surfaces Au and Ag bind weakly (0.8-1.2eV), while reactive Ni and Pd show significantly higher adsorption energies (> 2.0 eV). On the supported ultra-thin ZrO_2 film a general increase of the adsorption energies by more than 0.5eV is found, resulting a chemisorbed state for Ag, whereas Au remains more weakly bound. The metal ad-atoms bind mainly to the oxygen anions of the oxide and remain charge-neutral or become positive charged. Au is an exception as it can bind strongly to the Zr cations of a thin film, and change its charge state between −1 and +1, depending on the adsorption site. Hence the possibility of charge transfer to the substrate differentiates between the supported ultra-thin zirconia films and the surface of bulk m-ZrO_2.

Concerning the adsorption of water, the interesting question to answer is whether H_2O dissociates on the ZrO_2 surface. Our calculations reveal that the dissociation on bulk ZrO_2 surfaces is preferred, but barriers around 100meV exist. On a thin film the situation is slightly ambiguous, as sites exist (close to protruding O atoms) where dissociation happens spontaneously (no barrier). For other sites barriers around 60meV are predicted. Despite these small barriers the binding energy of the dissociated state is only slightly higher than that of the molecular state. As compared to the bulk surface the thin film is generally less reactive with respect to water dissociation, but a few sites exist where H_2O dissociates spontaneously. Calculations of the O_{1s} core levels show that molecularly adsorbed and dissociated water can be distinguished unambiguously, in contrast to STM simulations which look rather similar for both cases.

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Mass Transport and Mass Storage in Functional Oxides

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The first part of the contribution refers to oxygen incorporation in oxides and discusses thermodynamics and kinetics. Particular emphasis is laid on the effects of grain boundaries and the corresponding confinement in nanocrystalline mesoscopic oxides.

The second part studies the H_2O incorporation thermodynamics and kinetics in oxides. Owing to the presence of oxygen ion conductivity, electron conductivity and proton conductivity exciting non-monotonic kinetic phenomena emerge. The solution of this “three-carrier-problem” is presented.

The third part considers recent results on “job-sharing composites”, where storage in space charge zones at the interface between oxides and metals enable storage of Li or H_2, whereby both could not be stored in the individual phases alone. Thermodynamics and kinetics of this novel materials concept are presented.

Elastic Strain and Dislocations in Oxide Thin Films: Hand-in-hand or counter in oxide ion conduction?

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Enhancement of ionic conductivity in thin films or multilayers of oxide materials, i.e. doped zirconia and ceria, has sparked great interest in the search for fast ion conducting structures for fuel cells as well as for red-ox based resistive memories. The enhancement in ionic conductivity in such structures could be attributed to elastic strain arising from the lattice mismatch at the interface. However, this assumes that the interface between two materials is perfectly coherent, while in most cases a high density of dislocations are observed, and these dislocations relax the interfacial elastic strain. The strain field and the electrostatic field that arises from the dislocations can also impact the defect stability, distribution and mobility in these materials; and yet, the role of dislocation on the ionic conductivity is not consistently reported in the literature nor is it clearly understood. The aim of our work is to quantitatively assess the dislocation's influence on the ionic conductivity in fluorite and perovskite oxides, exemplified by doped CeO_2 and $SrTiO_3$, respectively. Edge dislocations in in these materials are studied by atomistic simulations combining the Monte Carlo, Molecular Dynamics and Nudge Elastic Band calculations. Asymmetric distribution profiles of dopant cations and oxygen vacancies are found as a result of the strain field of the dislocation, giving rise to counterintuitive results for diffusion kinetics along and across the dislocations. The studied dislocations in such highly doped or reducible oxides trap oxygen vacancies, and create vacancy-depleted space charge zones, and thus, reduce the oxide ion mobility along the dislocation, as opposed to the fast pathways that dislocations present for atomic diffusion in metals. As a result, the potential role of elastic strain and dislocations will be contrasted in oxide ion diffusion in these reducible or doped oxides.

Nucleation and Growth of Anatase TiO_2 (001) on the $SrTiO_3$ (001) Surface

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Nanostructured TiO_2 is a widely used material for catalysis applications. The anatase phase is more catalytically active under ultraviolet irradiation for photocatalytic applications than the rutile polymorph. However, anatase TiO_2 is generally only found in small crystal sizes, but is not thermodynamically stable for large crystals. To be able to study the surface of anatase an epitaxial growth method can be applied to grow anatase (001) onto the $SrTiO_3$ (001) surface. The lattice of anatase is only 3.1% smaller than that of $SrTiO_3$. This method allows the production of high quality and large anatase (001) films which are stable at temperatures up to 600 °C.

Scanning tunneling microscopy reveals that following certain surface processing steps a class of TiO_x nanostructures are formed on the $SrTiO_3$ (001) surface. $SrTiO_3$ single crystals doped with 0.5wt% Nb (n-type) were used in these experiments. The sample surfaces were prepared by Ar^+ ion sputtering and ultra-high vacuum (UHV) annealing in the temperature range 850 – 900 °C. Annealing samples at different temperatures and for different lengths of time results in a different degree of TiO_x segregation to the $SrTiO_3$ (001) surface. The excessive TiO_x on the sample surfaces form different types of epitaxial TiO_x-rich nanostructures. These nanostructures can be classified as parallel packed nanolines (dilines, metadilines, trilines and tetralines) or small dot features. Upon extensive UHV annealing leading to significant TiO_x surface enrichment, the TiO_2 (001) anatase phase starts to nucleate on the nanostructured $SrTiO_3$ (001) surfaces. This occurs after several annealing cycles at temperatures around 880-900 °C. The growth of anatase TiO_2 (001) can be further enhanced through the evaporation of Ti onto the nanostructured $SrTiO_3$ (001) surface followed by an annealing step at 750 – 900 °C. Anatase TiO_2 (001) epitaxially grown on $SrTiO_3$ (001) surfaces can have large surface areas of (1×4) reconstructions. These surfaces are ideally suited for the study of metal nanoparticle (e.g. Pd) growth.

Coupled Optical and Electrochemical Investigation of Oxygen Exchange and Diffusion at Oxide Thin Film Surfaces

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Oxides are playing an increasing critical role as functional components in the fields of energy conversion/storage, microelectronics, displays, sensors/actuators and catalysis. In turn, their electrical (ionic & electronic), optical, magnetic and catalytic properties depend sensitively on their oxygen nonstoichiometry, often frozen in during processing, and rarely well defined. This is particularly true for thin films, where conventional methods, appropriate to bulk materials, do not apply. In this presentation, we review in-situ optical, electrochemical and dilatometric methods, developed or refined in our laboratory, to monitor, analyze and control defect equilbria, nonstoichiometry, charge and mass transport/exchange and optical properties of oxide thin films and nano-sized particles. Examples will include materials of interest as electrodes in fuel cells, sensors, and oxidation catalysts.

Voltage and light affecting defects in oxides

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Voltage and light are two important drivers of defect chemical processes or solid state electrochemical reactions in metal oxides. This is illustrated by several examples. A voltage affects the width of reaction zones of solid state electrochemical electrodes, leads to unusual electrode migration in PZT or modifies local conductivities in $SrTiO_3$ thin films. Similarities are emphasized between oxides used in different fields, e.g. in piezo actuators and solid oxide fuel cells. The effect of light on defect chemical processes is essential when aiming at solid state photo-electrochemical cells. An oxide based high temperature solar cell, operating at >400°C, is introduced which can be used to chemically store energy [1]. Moreover, oxygen stoichiometry changes in $SrTiO_3$ under UV illumination lead to a voltage in an electrochemical cell and thus the charging of a kind of battery by light could be realized.

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High-temperature superconductivity in La_2CuO_4-based heterostructures induced by interface effects

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In advanced materials, interface effects have been proven to be a powerful tool for improving or even inducing novel functionalities. These encompass magnetism, electronic and ionic transport, as well as superconductivity at the nanoscale.

Here, we present the results of our investigations on lanthanum cuprate (La_2CuO_4)-based heterostructures grown by atomic-layer-by-layer Oxide MBE, in which an insulator-to-superconductor electronic phase transformation was induced by the ad-hoc introduction of interfaces.

In the first example, superlattices of two-dimensionally doped La_2CuO_4, in which single LaO lattices planes were replaced by negatively charged SrO planes with a predefined periodicity, have been studied.[1] By employing a series of complementary techniques such as DC low-temperature transport measurements, high-resolution electron spectroscopy and microscopy, Zinc tomography, we observed the following exciting findings. (i) By appropriately tuning the distance between neighbouring SrO planes, superconducting critical temperatures up to ≈ 35 K could be obtained; (ii) the Sr concentration profile is highly asymmetric, as a result of the MBE deposition process, being abrupt at the interface side facing the substrate but rather diffused in the growth direction; (iii) at the side of the SrO planes where the Sr concentration profile is abrupt, high-temperature superconductivity results from space-charge effects, namely the local accumulation of holes required to compensate the negatively charged SrO layers.

In the second example, the properties of the superconducting interface obtained at the contact between lanthanum cuprate and lanthanum strontium nickelate ($La_{2-x}Sr_xNiO4$) are presented. In particular, the relation between the electrical properties (superconductivity up to ≈ 40 K), the local interface structure and composition (e.g. possible cationic intermixing) is critically discussed. The two studies represent successful examples of the implementation of two dimensional doping for inducing high-temperature superconductivity in oxide heterostructures and shed light onto the complex interplay between different phenomena occurring at interfaces.

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Homoepitaxial Growth and Surface Reactivity of SrTiO$_3$(110)

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We report the first results from our new experimental setup that combines pulsed-laser deposition (PLD), controlled by high-pressure Reflection Electron Energy Diffraction (RHEED), with state-of-the-art surface science techniques (STM, LEED, XPS, LEIS, etc.) A tight control of all film preparation parameters and appropriate interfacing with UHV based-techniques allows investigating growth morphologies with exquisite detail.

We have investigated the homoeptitaxial growth of Nb-doped SrTiO$_3$(110). This surface forms a variety of reconstructions; one can reversibly and reproducibly switch back-and-forth between the various surface structures. This is achieved by evaporating a set amount of Sr or Ti, and annealing in O$_2$, i.e., by adjusting the chemical potential of the constituents. The most stable reconstruction has a (4×1) symmetry; which, it was argued, forms in order to compensate the intrinsic polarity of this surface orientation [1]. This structure and its homologous (n×1) series consist of corner-sharing units of tetrahedrally-coordinated Ti atoms that form rings with various sizes [2]. By varying the O chemical potential one can adjust defect clusters at domain boundaries [3]. At the Ti-rich side of the phase diagram, the surface is terminated with an (m×l) layer, which consists of octahedrally-coordinated Ti [4]. Systematic investigations on how these two different types of terminations affect reactivity towards $^{18}O_2$ are currently underway.

For the growth experiments we used the SrTiO$_3$(110)-(4x1) surface as a starting point. The reconstruction layer floats to the top during homoepitaxial growth [5]. We show how the growth depends on the substrate temperature, O$_2$ partial pressure, laser fluence, pulse frequency, and initial surface structure. When the deposited material is slightly off-stochiometric, formation of reconstructions with different symmetries strongly affects the growth.

Supported by the Austrian Science Fund (Project F45, FOXSI) and the ERC Advanced Grant ‘OxideSurfaces’.

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$SrRuO_3$ thin films as active layers for resistive switching

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Investigating the process of surface redox processes on the nanoscale is a key for understanding the mechanistic details of resistive switching. In this work we use scanning tunneling microscopy (STM) in combination with photoelectron emission microscopy (PEEM) for studying the influence of tip-induced electric fields on the morphological and electronic properties of ultrathin strontium ruthenate ($SrRuO_3$) films. Due to its high electronic conductance $SrRuO_3$ is a widely used electrode material in ReRAM devices, but we can show in this work, that it also shows resistive switching properties. This finding may have a significant influence on the interpretation of switching properties of ReRAM devices using SRO as the electrode material.
In comparison to most other scanning probe methods the STM technique benefits from its potentially atomic resolution and also eliminates the artefacts that can arise between the electrode-oxide contact. Here the STM tip acts as a non-contact top electrode in our “simulated ReRAM cell”. The obtained results allow us to develop a well-grounded mechanistic model for resistive switching of $SrRuO_3$ thin films based on oxygen vacancy creation and migration.

Adsorption on Ruthenate Perovskite Surfaces – a DFT study

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Perovskite oxides are promising materials for various applications in the field of energy production and conversion, such as solid oxide fuel cells. Nevertheless, an atomistic insight into the surface chemistry of these materials is only starting to emerge. For example, we could recently show that a strontium ruthenate surface shows a surprisingly high chemical activity for the adsorption of CO [1]. In this presentation, I will discuss the adsorption of common molecules, such as H_2O and O_2, on the (001) surface of the Ruddlesden-Popper perovskites $Sr_3Ru_2O_7$ (SRO) and $Ca_3Ru_2O_7$ (CRO).

Although both surfaces are structurally closely related, the addition tilting of the Ru octahedra at the CRO (001) surface leads to the formation of wide and narrow rows at the surface. This additional patterning results in a pronounced difference between the surfaces for both adsorbates. While the calculations predict a similar dissociative adsorption of H_2O in the low coverage limit, the attractive interaction of the dissociated water molecules leads to the formation of dimers and finally cage-like network structures at the SRO surfaces [2]. Water dimers can still form at the CRO surface, yet the formation of lateral interconnections of the water network is supressed by the lower symmetry of the substrate.

In contrast to H_2O, we predict a molecular adsorption of O_2 on both surfaces. Still also in this case pronounced differences become evident at higher coverages. While the SRO surfaces can be uniformly covered up the saturation coverage, the striped pattern at the CRO surface is directly reflected in the adsorption energies of the O_2 molecule, as the adsorption in the wide channels is preferred by ~0.3 eV. Consequently the saturation coverage is already reached at an O_2 coverage of 0.5 ML, where the dense packing leads to the formation of a zig-zag arrangement of the O_2 molecules.

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Charge Transfer across Quantum Dot-Oxide Interfaces for High-Efficiency Photovoltaics

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Metal oxides constitute robust and relatively cheap semiconductor materials that are finding increasing applications in opto-electronics, but their band gaps are typically prohibitively wide for the generation of free charges through the absorption of visible light. Several approaches have been developed to circumvent this drawback. Specifically, the sensitization of mesoporous oxides by semiconductor quantum dot (QD) nanocrystals represents a promising route for the development of low-cost photovoltaics in QD sensitized solar cells.

In addition to their tuneable band gap, QDs have the ability to generate multiple charge carriers from single photons by a process called carrier multiplication (CM), which potentially provides a means towards high-efficiency photovoltaics. Although CM has been widely interrogated in colloidal QDs in solution, the collection of those multiple charge carriers at oxide electrodes has not been clearly elucidated. The contribution of CM towards the overall device performance is ultimately determined by a competition between transfer to the electrode material and charge recombination within the QDs.

We report interfacial electron transfer dynamics from quantum dots grown directly onto mesoporous oxide films. Such systems are well-suited for achieving efficient multiple charge transfer by CM, as electron transfer from QD-to-oxide is substantially faster than charge recombination. However, despite CM occurring efficiently in colloidal systems, only one electron is transferred to the oxide. This seemingly counterintuitive result can be understood by noting that efficient hot electron transfer at the QD-oxide interface can compete with CM within the QDs. Hot electron transfer is observed to occur on sub-100 fs timescales, nulling the CM efficiency. Implications of these results for solar energy conversion are discussed.

In situ mesoscopic and microscopic visualisation of catalytic reactions on metal-oxide systems

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The focus of the research in the SFB project part 04 is currently directed to the catalytic oxidation of CO and of H_2 on stepped Rh surfaces. Such surfaces are of particular interest, since the catalytic particles exhibiting high-index facets are nowadays increasingly considered as promising objects for synthesis of fine chemicals, oil refining processes, automobile catalytic converters and energy conversion technology [1].

In the present study, an innovative approach is applied which allows to avoid repeated experiments with differently oriented high-index single crystal surfaces: a polycrystalline Rh foil can be prepared in such a way, that several µm-sized grains exhibit different high-index orientations within the field of view of a photoemission electron microscope (PEEM). Using the *kinetics by imaging* procedure, based, instead of mass spectrometry, on analysis of the PEEM video-sequences taken during the visualisation of the ongoing reaction, the local kinetics for each individual surface domain can be evaluated. This occurs in one experiment, i.e. under identical conditions for all regions in the PEEM field of view [2]. The same approach was applied on the nanoscale, using the field emission microscope (FEM) to image *in situ* the CO and H_2 oxidation on a Rh nanotip. In the present study, a row of Rh surfaces, vicinal to the [100]-, [110]- and [111]-directions was evaluated and kinetic phase diagrams in the pressure range of 10^{-6} mbar were constructed for CO and H_2 oxidation. Analysis of the obtained phase diagrams provided new insights into the bistable behaviour of both reactions and into the role of step density in the catalytic activity of Rh, e.g. an increased step density increases the tolerance of the (100)- and (111)-type vicinals to the CO poisoning in contrary to the (110)-type vicinals, where an opposite behaviour was observed.

In the case of the H_2 oxidation on the same high-index Rh surfaces, apart from the construction of kinetic phase diagrams, the oscillating behaviour of this reaction was found. In high vacuum conditions, such self-sustaining oscillations were previously observed only by FIM, i.e. in the presence of high electric field which is participating in the oscillation mechanism [3]. Present observations, in turn, have been performed on plane Rh surfaces (by PEEM) or on a nanotip (by FEM, where the field effect on the reaction is negligible [4]). Structure dependent frequencies and a nanoclock behaviour were observed. A model which includes the Rh surface oxide formation as a presumable feedback mechanism leading to the appearance of oscillations in a bistable $H_{ad}/O_{ad}/Rh$ system is proposed.

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The non-innocent role of cerium oxide in heterogeneous catalysis:

A theoretical perspective

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Ceria (CeO_2) is the most significant of the oxides of rare-earth elements in industrial catalysis with its reducibility being essential to its functionality in catalytic applications. The complexity of real (powder) catalysts hinders the fundamental understanding of how they work. Specifically, the role of ceria in the catalytic activity of ceria-based systems is still not fully understood. To unreveal it, well-defined ceria-based model catalysts are prepared experimentally or created theoretically and studied. In this talk, recent results on CeO_2(111) and Ni/CeO_2(111) model ceria-based catalysts will be discussed, as examples of catalysts for partial alkyne hydrogenation,[1] and hydrogen production,[2,3] respectively. The emphasis is here put on theoretical studies and special attention is given to the effects of ceria as catalyst support and to the ability of state-of-the-art quantum-mechanical methods to provide reliable energies and an accurate description of the electronic structure of reducible ceria-based systems.[4]

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Promotional Zr-Metal Interactions in Fuel Reforming Processes

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An in situ activating bimetallic $Cu/Cu_{51}Zr_{14}$ pre-catalyst for hydrogen generation from methanol and water, prepared by intermetallic co-melting, yields very high CO_2-selectivity (>99.9 %) and thus H_2 yields. With respect to the geometric surface area of our model catalyst, at least one order of magnitude higher activity was observed in comparison to supported Cu-ZrO_2 and Cu-ZnO-Al_2O_3 reference catalysts. Evolution of structural activation monitored by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and electron microscopy indicates transformation of the initially bimetallic $Cu/Cu_{51}Zr_{14}$ pre-catalyst into an active, selective and self-stabilizing state with coexistence of dispersed Cu and partially hydroxylated tetragonal ZrO_2. The outstanding performance of this active state is assigned to the presence of a high interface site concentration following in situ decomposition of the intermetallic compound. The active interfacial sites result from a teamwork of Cu, responsible for methanol activation, and tetragonal ZrO_2, activating water via surface hydroxylation.

Beyond intermetallic melt preparation, inverse Pd-ZrO_xH_y and Cu-ZrO_xH_y model catalysts were prepared by chemical vapor deposition (CVD) using zirconium-t-butoxide (ZTB) as an organometallic precursor. Depending on post-treatments, either ZrO_xH_y or ZrO_2 overlayers or Zr as sub-nanometer metal clusters could be obtained. Following decomposition of ZTB on Pd(111), a partially hydroxylated Zr^{4+}-containing layer was formed, which can be reduced to metallic Zr by thermal annealing in ultrahigh vacuum, leading to redox active Zr^0 sub-nanometer clusters. Alternatively, a fully oxidised ZrO_2 layer can be prepared by annealing in $5x10^{-7}$ mbar O_2. Complementary DFT calculations showed that a single layer of ZrO_2 on Pd(111) can be more easily reduced than a double- and triple layer. Also, the initial and resultant layer compositions greatly depend on the oxidation potential of the gas environment: The better the background pressure, the faster and more complete the reduction of Zr on Pd takes place. As a practical consequence of Zr redox activity, the initially bimetallic Pd-Zr precatalysts showed pronounced activity for dry reforming of methane, which is attributed to the synergistic bifunctional cooperation of Pd and ZrO_xC_y surface species.

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Pt/ZrO_2 interfaces: from ultrathin films to ion transport conditions

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The Pt / YSZ (yttria stabilized zirconia) interface represents a prototypical model system for the investigation of metal / oxide interfaces under oxygen ion transport conditions relevant for high temperature solid oxide fuel cell and sensor applications. The primary in-situ investigation method of these interfaces is impedance spectroscopy which delivers information on possible transport mechanisms for which a direct correlation with structural parameters is desirable.

Here we present in-situ high energy surface x-ray diffraction data (70 keV photon energy) from the Pt / YSZ(111) interface, which we obtained at a sample temperature of 750 K in controlled oxygen atmosphere of 0.5 bar under different sample polarization conditions. Using hard x-rays allows us to access the Pt/YSZ interface buried below a 150 nm thick Pt electrode at the atomic scale. We deduce subtle changes of the interfacial structure from crystal truncation rod data when switching from cathodic to anodic polarization of the Pt electrode. At the buried interface, a similar atomic scale morphology is observed as for the clean YSZ(111) surface under UHV conditions [1]. The evaluation of the powder diffraction pattern of the Pt electrode does not give evidence for the formation of a substantial amount of Pt oxide under anodic polarization and Pt bubble formation.

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Interfacial dynamics in nanocarbon-inorganic hybrid photocatalysts

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What are nanocarbon-inorganic hybrids? Hybridising nanocarbon materials, i.e. CNTs and graphene, with active inorganic nanomaterials constitutes a powerful strategy towards designing new-generation functional materials for many applications where efficient charge separation and extraction is required, including photovoltaics, photocatalysis, batteries, supercapacitors and biosensors [1,2]. In contrast to nanocomposites, which merely combine the intrinsic properties of both compounds, nanocarbon hybrids additionally provide access to both a large surface area required for gas/liquid-solid interactions and an extended interface, through which charge and energy transfer processes create synergistic effects that result in unique properties and superior performances.

How can they be improved? I will demonstrate that the performance of these hybrids can be further enhanced through purposefully engineering interfaces and morphology, e.g. fewer grain boundaries alleviate electron transport within the catalyst and the formation of an Ohmic junction facilitates charge transfer and separation at the interface with the nanocarbon [3].

How do they function? I will present a model system that allows for measuring and tuning of interfacial charge and energy transfer processes and for revealing the nature of catalytically active sites in nanocarbon hybrids.

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Čerenkov Spectrometry and Electron Energy Loss Spectrometry for Quantitative Bandgap Determination in Oxides

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Čerenkov radiation is emitted as soon as the speed of the swift probe electron exceeds the one of light inside the probed medium [1]. Consequently, the electron beam has to emit energy by slowing down. This effect can be either measured by means of an optical detector – such as the cathodoluminescence (CL) detector – and by means of electron energy loss spectrometry (EELS). The radiation emission is damped unless it is completely suppressed with increasing absorption coefficient. Thus the band gap can be determined from spectral analysis of the emitted radiation. On the other hand the presence of interband transitions being excited by means of sample irradiation with an electron beam leads also to a strong increase in intensity of the inelastically scattered electrons. This is observed by means of EELS.

In the present work we discuss the emission of Čerenkov radiation and their usability for the determination of band gaps in oxides. We compare the accuracy of this new method with electron energy loss spectrometry (EELS). Due to the fact that both, the Čerenkov losses and the interband transitions contribute to the inelastic part of the spectrum, the beam energy is reduced such that the Čerenkov effect is avoided [2].

We find that the accuracy of the band gap measurement is much higher in Čerenkov spectrometry, because the energy resolution is independent from the energy spread of the electron source, whereas in EELS the energy resolution of the source limits the accuracy. In optical spectrometry the absorption behavior of the used light guide limits the determination of band gaps being larger than 4.13 eV (corresponds to 300 nm wave length).

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Surface Chemistry of Oxygen and Water on Anatase TiO_2(101)

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TiO_2 is a prototypical material used in photocatalytic reactions, e.g. in water remediation, photocatalytic water splitting or in the oxidation of organic molecules [1, 2]. Two polymorphs of TiO_2 are used industrially - rutile and anatase, where the anatase is typically preferred in applications. Surface chemistry of water and oxygen is the base of many important processes such as photocatalytic water splitting or oxygen reduction reaction, which are essentially inverse mechanisms mediated by holes and electrons, respectively. Here we study adsorption and reactions of oxygen and water on a reduced anatase TiO_2(101) using Scanning Tunneling Microscopy (STM), Atomic Force Microscopy (AFM), Temperature Programmed Desorption (TPD), Photoemission Spectroscopy (PES) and Density Functional Theory (DFT).

While water exhibits molecular adsorption [3] on the Anatase (101) surface and desorbs below room temperature, reaction with oxygen results in the dissociation and formation of terminal OH groups. The terminal OH groups are the final product of the reaction and are stable at room temperature. We identify OOH as an important metastable intermediate of the reaction. Based on DFT calculations, we discuss the energy balance of the single reaction steps in dependence on the number of excess electrons available in the slab. The reactions mentioned above are energetically favorable as long as the substrate provides enough excess electrons. We compare the results on anatase (101) surface to equivalent reactions reported on the rutile (110), and point out key differences between these two TiO_2 polymorphs.

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Surface Structures of Ultrathin Ti_2O_3 Films on Au(111)

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Titanium oxides are materials used in photocatalysis [1] and gas sensing [2]. Most of the studies are based on the two common TiO_2 polymorphous – rutile and anatase. However, new titanium oxide structures can be created in ultrathin film forms that are very different from the bulk crystal terminations. There is increasing interest in this field because these novel structures may be associated with enhanced properties.

We have carried out growth of TiO_x ultrathin films on (22 × √3)-reconstructed Au(111) substrates through Ti deposition and post-deposition oxidation and annealing. In the growth of the thin films three different structures were observed: a (2 × 2)-reconstructed Ti_2O_3 structure resembling a honeycomb pattern, a TiO pinwheel shape and triangular shaped TiO_x islands [3,4]. The (2 x 2) honeycomb structure has two crystallographically unique domain boundaries (DBs) along the <1-10> directions, and also two unique DBs along the <11-2> directions. Along the <11-2> directions the preferred boundary structure is to have alternating rings of 4 and 8 Ti atoms. Along the <1-10> directions there are two commonly observed DBs with either double 5-fold and single 8-fold rings or with alternating 5-fold and 7-fold rings. Scanning tunnelling microscopy (STM) images of these three DBs are shown in figure 1. Density functional theory (DFT) calculations were used to model the DB structures and to calculate their formation energies. Two DBs that are crystallographically unique, but are not observed by STM over long repeat periods, were also modelled.

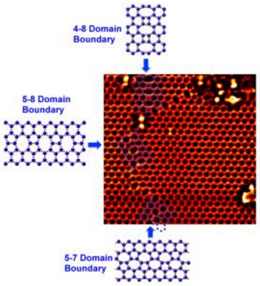

Figure 1: STM image of Ti_2O_3 honeycomb thin films with 4-8, 5-8 & 5-7 DBs (image size: 14 × 14 nm^2, $V_s = 0.9$ V, $I_t = 0.22$ nA). Ti atoms are draw as big blue balls; O atoms are small red balls.

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Special Research Program SFB F45

Functional Oxide Surfaces and Interfaces (FOXSI)

International FOXSI Conference, May 23-25, 2016

TUtheSky Lounge, TU Vienna

POSTERS

Adsorption and Thermally Activated Metalation of Carboxy-functionalized Porphyrins on MgO Nanoparticles

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Metal oxide surfaces functionalized with organic molecules are of great interest for various applications, for example in catalysis, in sensor technology or in solar cells. For devices such as dye-sensitized solar cells functionalization with porphyrins is a common procedure. However, the influence of the surface structure of the oxide on the binding to the linker groups and the reactivity of the organic molecules are poorly understood, especially for particulate systems.

In a previous research effort we explored the reactivity of the non-functionalized free-base tetraphenyl-porphyrin (2HTPP) on well-defined MgO nanocubes of very small (~ 10 nm) and larger (100 – 1000 nm) sizes. In the former case metalation occurred spontaneously at room temperature in a toluene-2HTPP solution.[1] We associated this effect to the release of Mg ions from defect sites such as particle edges.

In this project, we investigated the binding of unfunctionalized and carboxy-functionalized free-base porphyrins to nanometer-sized MgO particles of various structures. 5-(4- carboxyphenyl)-10,15,20-triphenyl-21,23H-porphyrin (MCTPP), 5,10,15,20-tetrakis-(4- carboxyphenyl)-21,23H-porphyrin (TCPP) as well as 2HTPP were adsorbed from solution on MgO nanocubes (~ 10 nm) as well as larger, non-shape-defined MgO nanoparticles (< 50 nm). The adsorption behaviour was analysed using diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS). In specific, we explored the behaviour upon heating via temperature-programmed DRIFTS.

In contrast to non-functionalized 2HTPP, we found that MCTPP and TCPP bind to the oxide surfaces via the carboxylic acid groups as carboxylate species. Interestingly, no indications for metalation were found for either sample at room temperature. Upon heating, however, we observed partial metalation for TCPP for both kinds of particles. MCTPP even showed almost complete metalation after heating for either particle size. In view of the fact that complete metalation occurs for 2HTPP on the nanocubes, this finding demonstrates the influence of the surface structure and the adsorption geometry on the metalation reaction.

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Oxygen exchange kinetics of $La_{0.9}Ca_{0.1}FeO_{3-\delta}$

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Mixed ionic-electronic conducting perovskites from the series $(La,Sr)(Co,Fe)O_{3-\delta}$ have a wide range of applications, for example as cathodes for solid oxide fuel cells (SOFCs), gas sensors or catalysts. Unfortunately, the long-term stability of these materials is insufficient. Thermodynamic considerations guide to the conclusion that the replacement of Sr with Ca and of Co with Fe will result in more stable compounds. Furthermore, only a few studies on the mass and charge transport properties of $(La,Ca)FeO_{3-\delta}$ are found in the literature. By now, no data on the oxygen exchange kinetics of these materials are available. In the present work, the composition $La_{0.9}Ca_{0.1}FeO_{3-\delta}$ (LCF91) was synthesized via a glycine-nitrate process. XRD measurements and Rietveld analysis showed LCF91 as the main phase and a minor amount of brownmillerite $Ca_2Fe_2O_5$ as secondary phase. The electronic conductivity and the oxygen exchange kinetics of LCF91 were determined as functions of oxygen partial pressure ($1\text{x}10^{-3} \leq pO_2/\text{bar} \leq 0.1$) and temperature ($600 \leq T/°\text{C} \leq 800$). In-situ dc-conductivity relaxation experiments revealed the chemical surface exchange coefficient k_{chem} and the chemical diffusion coefficient of oxygen D_{chem}. High values of $k_{chem}=9\text{x}10^{-4}$ cm s^{-1} and $D_{chem}=7\text{x}10^{-6}$ cm^2 s^{-1} were obtained at 800°C and $pO_2=0.01$ bar. The activation energies for k_{chem} and D_{chem} were in the range of $33 \leq E_a/\text{kJ mol}^{-1} \leq 43$ and $61 \leq E_a/\text{kJ mol}^{-1} \leq 67$, respectively. To obtain the thermodynamic factor of oxygen and to estimate the self-diffusion coefficients of oxygen, data on the oxygen nonstoichiometry of LCF91 from the literature were utilised [1]. In addition, the ionic conductivity of LCF91 was calculated via the Nernst-Einstein relation.

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Mechanism of the oxygen reduction reaction at SOFC cathodes: combined experimental and ab-initio investigations

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Slow kinetics of the oxygen reduction reaction at the cathode is a main limiting factors for the performance of solid oxide fuel cells (SOFC). Mixed conducting (La,Sr,Ba)(Mn,Fe,Co)$O_{3-\delta}$ perovskite cathode materials for use on oxide ion conducting electrolytes exhibit a sufficient oxide ion conductivity enabling an extension of the reactive zone beyond the electrolyte/electrode/gas three-phase boundary for thin-film electrodes. The mechanism of the oxygen exchange reaction is discussed on the basis of experimental findings (dependence of effective surface rate constant on pO_2 and concentration and mobility of oxygen vacancies in the cathode material [1]) and results from ab-initio calculations (concentration and mobility of surface defects, energies of intermediates and transition states [2]). Oxygen vacancies are found to play an important role for the surface kinetics.

In order to extend the reactive zone, cathode materials used on proton conducting electrolytes such as Ba(Zr,Y)$O_{3-\delta}$ should exhibit also some proton conductivity. The defect chemistry will be discussed for the example of $Ba_{0.5}Sr_{0.5}Fe_{0.8}Zn_{0.2}O_{3-\delta}$ (BSFZ) based on thermogravimetry experiments [3]. In order to obtain an atomistic picture of protons in a mixed conducting cathode materials, ab-initio calculations of $La_{1-x}Sr_xFeO_{3-\delta}$ (LSF) with different concentrations of oxygen vacancies and protons were carried out [4]. The protons are bound to an O^{2-} ion forming a hydroxide ion on a oxide site, similar as in Ba(Zr,Y)$O_{3-\delta}$ electrolyte materials. However, the enthalpy of water incorporation into oxygen vacancies is significantly lower (in good agreement with the experimentally found low proton concentrations). The reasons for this difference will be discussed.

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Determining optical properties of $LaSrMnO_3$-$LaAlO_3$ interfaces by VEELS investigations

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In this study we have investigated the optical and electronic properties of thin layered $LaSrMnO_3$-$LaAlO_3$ interfaces. These Sr-doped $LaMnO_3$ (LSM) perovskite-type oxides are a promising cathode material in solid oxide fuel cells (SOFC) for high temperature applications. [1]
Since conventional optical methods for determining the dielectric properties are limited by the wave length of the light, a high spatial resolution can be obtained by the usage of electrons. Therefore a combined investigation by transmission electron microscopy (TEM) and electron energy loss spectrometry (EELS) offers a possible solution.

The layer structure of the specimen consists of a single crystalline $LaAlO_3$ (100) substrate and an epitaxial LSM (100) layer of 100 nm. The synthesis of these thin films were done by pulsed laser deposition. For TEM investigation the specimen was prepared by the focused ion beam (FIB) lift-out specimen preparation technique (Quanta 200 3D DualBeam FIB) as a cross section sample. Subsequently the FIB prepared TEM-lamellae was thinned by using a Technoorg-Linda GentleMill in order to achieve a sample thickness smaller than 80 nm. The TEM analysis were performed by a FEI TECNAI F20 TEM equipped with a Gatan GIF Tridiem energy filter and a FEI TECNAI G20 TEM using a Gatan GIF 2001 energy filter. The microstructure of the interface was observed at 200 keV. For the valence EELS measurements of the optical and electronic properties the operation voltage was set to 60 kV. This was done in order to eliminate retardation effects and inelastic delocalization, which alter the VEELS signal at higher energies. [2]

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Structure-activity relationships in methanol steam reforming on Cu/t-ZrO_2-catalysts

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The system Cu/ZrO_2 is investigated with respect to the influence of the preparation procedure of the catalyst on the physicochemical and catalytic properties. As a model reaction, methanol steam reforming (MSR) was chosen. The catalytic activity and selectivity is determined using a batch micro-reactor connected to a mass spectrometer for analysis of the gas phase composition. The interest in the system Cu/ZrO_2 is mainly fuelled by the previously reported high selectivity of Cu particles impregnated on tetragonal ZrO_2. Amongst others, Purnama et al. [1], who used a templating technique for the preparation of their catalyst, were able to create such a catalyst that exhibited improved long term stability, higher activity per copper mass and less CO production in comparison with a commercial Cu/ZnO/Al_2O_3 catalyst with approximately 50 wt% Cu. Despite the recent advances in catalyst preparation, the role of tetragonal ZrO_2 and especially the Cu-ZrO_2 interface remains largely unknown. The prime motivation thus was the elucidation of the influence of the preparation technique on the selectivity in MSR. Especially the interaction of the metallic Cu and the ZrO_2 and their interface in catalysis is considered to be a potential key parameter influencing the catalytic performance and the selectivity by control of the reaction path.

To eventually fill this knowledge gap, alternative preparation pathways have been followed using isopropoxide precursors. Recently, highly structurally stable tetragonal ZrO_2 phases could be prepared this way [2]. The Cu/t-ZrO_2 catalysts were thus prepared either by impregnation of tetragonal ZrO_2 with copper-isopropoxide or by co-precipitation of zirconium-isopropoxide and copper-isopropoxide. Calcination at 400 °C followed preparation in both cases, thus creating the CuO/t-ZrO_2 catalysts.

X-ray diffraction measurements of the catalysts after calcination showed that the impregnated catalyst contains both monoclinic and tetragonal ZrO_2, whereas the contribution of the former is rather small in comparison to the latter. The two strongest reflections of CuO can be observed in both of the catalysts. In contrast to the impregnated catalyst, no monoclinic ZrO_2 is present in the co-precipitated catalyst. They were both tested under MSR conditions and improved CO_2-selectivity could already be observed on the co-precipitated catalyst.

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Water chemistry on Y_2O_3, YSZ and ZrO_2

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The present study focuses on the adsorption and conduction behavior of H_2O and D_2O on the oxides YSZ (8 mol% Y_2O_3), ZrO_2 and Y_2O_3. For YSZ, a sequential dissociative water – "ice-like" layer - polymeric chained water – "liquid-like" water adsorption model for isothermal and isobaric conditions over a pressure range of 10^{-5} mbar up to 24 mbar and a temperature range from room temperature up to 1173 K could be established and experimentally verified, using a combination of *operando* Fourier-Transform infrared spectroscopy, *operando* electrochemical impedance spectroscopy and moisture sorption measurements. In contrast to YSZ, a high surface concentration of OH groups from water chemisorption is absent at any temperature/pressure and thus the ice-like and following molecular water layers on pure monoclinic ZrO_2 exhibit no measurable protonic conduction. The characteristic changes of the related infrared bands could directly be linked to the associated conductivity and moisture sorption data. As the chemisorbed and physisorbed water layers are relevant to (electro)catalytically active (mixed) oxide surfaces, the presented data provide the specific reactivity of the chosen oxides towards water over a pressure/temperature parameter range extending up to SOFC-relevant conditions. Thus, they are supposed to provide an extended basis for further investigation of close-to-real gas adsorption or catalyzed heterogeneous reactions.

Catalytic CO oxidation on stepped Rh surfaces

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Studies of catalytic reactions on stepped surfaces are performed usually either on single crystal surfaces with high Miller indexes or on curved crystals with the step density varying across the sample surface. To reveal the effect of steps, the first approach requires separated experiments with differently structured surfaces, this implies known difficulties with keeping the parameters, such as pressure and temperature, identical in different experiments. Using the second approach, it is hardly possible to resolve the reaction kinetics on differently stepped regions of the curved surface, due to the basically averaging principle of mass-spectrometry.

In the present contribution, we use the *kinetics by imaging* approach, which relies on the analysis of the video-files taken during the visualisation of the ongoing reaction by a work function based surface microscope (e.g. PEEM) instead of mass spectrometry [1]. We apply herewith the above approach to the stepped Rh surfaces present on the differently oriented µm-sized grains of a polycrystalline Rh foil.

To compare the Rh surfaces with big differences in the step density, a curved crystal surface with an extremely high curvature, namely an apex of a Rh nanotip was used for a comparative study. Such an nm-sized apex may serve also as a model for a single catalytic particle with a highly stepped surface. In contrary to such a particle, the surface of a nanotip can be prepared in a controlled way by field evaporation and characterised by FIM with atomic resolution. Switching to the FEM imaging mode (just reversing the tip-polarity) the reaction can be imaged *in situ* on a nanoscale [2]. Applying the same approach as for the µm-sized samples, i.e. analysing the *in situ* obtained FEM video-files, the local reaction kinetics can be evaluated for individual, differently oriented nanofacets of the tip apex [3].

The ongoing CO oxidation reaction on Rh was visualized in the 10^{-6} mbar pressure range on differently oriented high-index domains of a polycrystalline Rh foil and on the apex of a Rh nanotip. From the analysis of the *in situ* recorded PEEM and FEM video data, kinetic transitions between the steady states of high and low catalytic activity were determined and kinetic phase diagrams for the CO oxidation were constructed for all studied Rh surfaces. The observed structure- and size-effects are discussed.

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The Influence of the Substrate on Zirconia Thin Films

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Investigating zirconia (ZrO_2) is challenging due to its high band gap (> 5eV). As an insulator it is not accessible to measurement methods relying on electronic conduction, such as scanning tunneling microscopy (STM), at room temperature. To circumvent this issue, thin ZrO_2 films can be studied [1]. We have grown zirconia on single crystals of varying material using a sputter deposition source similar to [2].
The influence of the substrate material is investigated in two different measurement regimes: Continuous, ordered films on the one hand and islands plus monolayers on the other hand.

We present STM data that show the effect of varying substrates on ordered films of well-defined thickness. STM measurements are possible up to a film thickness of ≈7 monolayers. Changing the substrate of a 5 monolayer-thick film from Rh(111) to $Pt_3Zr(0001)$ changes both the size as well as the number of orientational domains.

When studying islands and growth of monolayers via the SMSI (strong metal-support interaction) effect [3,4], the diffusivity of metallic Zr into the substrate is the crucial factor. We have measured the diffusion of Zr into Pt(111) and Rh(111) using X-ray photoelectron spectroscopy (XPS) and present the effects of this property on the growth of ultra-thin layers, investigated with STM and XPS.

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Operando Spectroscopy Studies of Co_3O_4 and $LaCoO_3$ Catalysts during Preferential CO Oxidation

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Catalytic preferential CO oxidation (PROX, $CO+H_2+0.5O_2 \rightarrow CO_2+H_2$) is a key reaction for removing traces of CO from the H_2-rich stream for hydrogen-fueled proton exchange membrane fuel cells. Due to the price and the limited availability of noble metals, increasing attention has been paid to noble-metal-free alternatives. Transition metal oxides, especially cobalt-based materials, are perspective catalysts for PROX. However, the current understanding of PROX over these catalysts is mainly based on pre- and post-catalyst characterization, and open questions include the nature of active sites and reaction pathways.

Therefore, we have performed an operando spectroscopy study on the catalyst structure and oxidation state during the PROX reaction while simultaneously monitoring catalytic activity by mass spectrometry. To investigate the bulk structure, we utilized in situ X-ray absorption spectroscopy (XAS) at the Co K edge performed at the I811 beamline at Max-lab II in Lund, whereas surface composition was monitored by in situ near atmospheric pressure X-ray photoelectron spectroscopy (NAP-XPS) at the ISISS beamline at BESSY II of the Helmholtz-Zentrum Berlin. The reactivity of cobalt in different chemical compounds and oxidation states (Co_3O_4, CoO and $LaCoO_3$) was compared. Apart from the reaction mixture (CO, O_2, H_2), reduction in pure CO or H_2 atmospheres were examined as well.

The operando XAS and NAP-XPS results indicated that under conditions of high selectivity for PROX both the bulk and surface of Co_3O_4 appeared fully oxidized (up to 250°C). In the C1s region NAP-XPS detected adsorbed carbonates, molecular CO and elementary carbon on the surface. When surface reduction started at higher temperature, the selectivity changed to methanation. The rather easy surface reduction in pure CO (starting already at ~100 °C) and the fast reoxidation suggest that adsorbed CO reacts with lattice oxygen, which is replenished by gas phase O_2, and the reoxidation by O_2 during PROX is fast enough to prevent overall reduction. We have explored further the potential of cobalt-based materials for PROX by focusing on the $LaCoO_3$ perovskite. The analysis of operando Co K-edge XANES for $LaCoO_3$ revealed that from RT to 400 °C the perovskite phase remained stable, and no methane production was observed below 400 °C. Thus, preserving cobalt in a high oxidation state (+3) in $LaCoO_3$ during PROX explains the wider temperature window for the selective CO oxidation in excess of hydrogen as compared to Co_3O_4.

Acknowledgements:
This work was supported by the Austrian Science Fund (FWF) under projects F4502-N16 (SFB FOXSI) and W1243 (Doctoral School “Building Solids for Function”). We acknowledge Dr. Detre Teschner for the support and the Helmholtz-Zentrum Berlin for provision of synchrotron radiation beamtime at the ISISS beamline of BESSY II, and the beamtime granted at the I811 beamline at the MAX-lab synchrotron radiation source in Lund and support by Dr. Stefan Carlson. We are grateful to Dr. Michael Stöger-Pollach and Dr. Johannes Bernardi for assistance with TEM and Dr. Klaudia Hradil for help with XRD measurements.

Adsorption of Water and Oxygen on $Ca_3Ru_2O_7$(001)

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Complex ternary perovskite oxides are increasingly used in solid oxide fuel cells and catalysis [1]. Therefore it is highly desirable to obtain a better understanding of their surface chemical properties. We use low-temperature STM, XPS and DFT to investigate the adsorption of water and oxygen on Ca3Ru2O7.

Dosing small amounts of water on the clean surface at 105 K leads to bright dots sitting on the bright lines of the substrate along the [010] direction. We propose that water dissociates and that the bright dots correspond to OH groups sitting on Ca bridge sites. The OH groups are immobile at 78 K, in contrast to the interesting dynamic behavior observed on the Sr3Ru2O7(001) surface [2]. The O*1s* XPS spectrum shows the growth of a shoulder at 531.0 eV binding energy, 1.8 eV above the bulk oxygen peak. We attribute the shoulder to dissociated water, in agreement with our DFT calculations. At higher doses various superstructures are formed, with long-range order that depends on the coverage, dosing temperature and annealing time. Molecular water is observed only after all sites available for dissociation have been occupied. The O*1s* XPS spectrum shows the molecular water at 533.1 eV binding energy, 3.9 eV above the bulk oxygen peak.

Oxygen adsorbs weakly and is moved around by the STM tip. At higher coverages the oxygen becomes partially immobile and can be imaged by STM. Upon adsorption of oxygen the O*1s* XPS spectrum shows a peak at 532.7 eV binding energy, 3.7 eV above the bulk oxygen peak. We attribute the peak to molecularly adsorbed O2, in agreement with our DFT calculations.

This work was supported by the Austrian Science Fund (FWF project F45) and the ERC Advanced Grant “OxideSurfaces”.

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Water-Induced Decoupling of Tracer and Electrochemical Oxygen Exchange Kinetics on Mixed Conducting Electrodes

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Isotope exchange depth profiling and electrochemical impedance spectroscopy are usually regarded as complementary tools for measuring the oxygen exchange activity of mixed conducting oxides, for example used in solid oxide fuel cell (SOFC) electrodes. Only very few studies directly correlate electrical (k^q) and tracer (k^*) exchange coefficient at the solid-gas interface measured under identical conditions[1,2] and the 1:1 correlation between k^q and k^* is more an assumption than being an experimentally verified fact. In this study we report that the measured rates of electrical and tracer exchange of oxygen may strongly differ. The oxygen isotope exchange experiments (k^*) with in-situ impedance spectroscopy measurements (k^q) on $La_{0.6}Sr_{0.4}FeO_{3-\delta}$ and $SrTi_{0.3}Fe_{0.7}O_{3-\delta}$ thin film electrodes revealed that $k^* > 100\ k^q$ in humid oxidizing ($^{16}O_2$+$H_2{}^{18}O$) and humid reducing (H_2+$H_2{}^{18}O$) atmospheres. These results are explained by fast water adsorption on surface oxygen vacancies and subsequent dissociation into two surface hydroxyl groups. This rules out water dissociation as the rate limiting step in solid oxide water electrolysis.

Moreover, electrochemically driven oxygen exchange and isotope exchange was performed in $O_2/H_2{}^{18}O$ and $^{18}O_2$ atmospheres on $Nd_2NiO_{4+\delta}$ microelectrodes deposited on single crystalline YSZ substrates. Electrochemical impedance measurements revealed a strong dependence of k^q on the applied bias voltage. However, no effect of bias variation was found for the tracer surface exchange coefficient $(k)^*$. This again can be explained by a different mechanism of oxygen exchange when driven by tracer or by electrochemistry. Altogether, the measurements indicate that straightforward interpretation of the experimentally determined k^* values in terms of electrochemical surface exchange resistances may be misleading.

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DFT calculations on Zirconia films of increasing thickness

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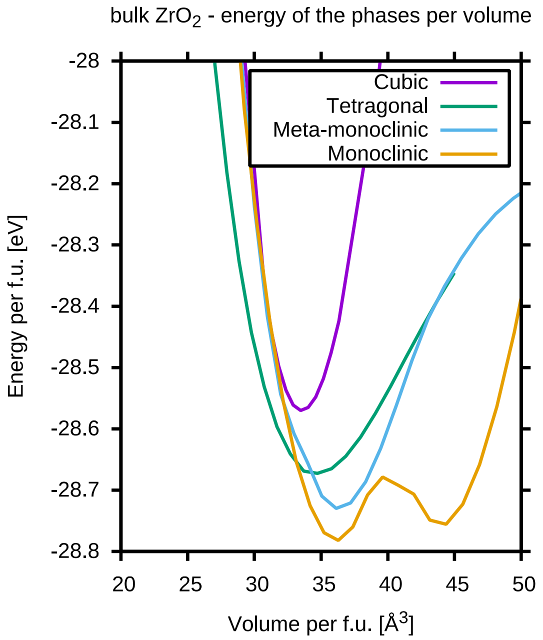
Ultrathin films of ZrO2 on metallic substrates are different from bulk surfaces not only by different surface geometries but also electronically, allowing a charge transfer between adsorbates and the substrate, leading to e.g. different charge states of adsorbed ad-atoms [1]. Here we present a systematic study of the stability and structure of (111)-type ZrO_2 films with varying thickness using the Vienna Ab-Initio Simulation Package (VASP) employing semi-local functionals of GGA type and van-der-Waals density-functionals [2]. Since ZrO_2 is known to undergo quite a few pressure and temperature dependent phase-transitions, we start out with a careful investigation of bulk phase stabilities confirming our findings independently with the USPEX code, which is based on genetic search algorithms [3] to find the best structures for a given stoichiometry. We recover the well-known stability sequence monoclinic<tetragonal <cubic, but also detect a stable high volume phase and a meta-monoclinic phase only slightly less stable than the monoclinic ground-state.



These findings hold as well for unsupported (111)-type films for thicknesses larger than five (111)-type ZrO_2 tri-layers. For ultrathin layers (1-2 tri-layers) a cubic or tetragonal film is preferred, while the monoclinic is most stable from three layers upwards. For the monoclinic films we also investigated the stability of different (111)-cuts, in order to shed some light on the structure of thicker ZrO_2 films grown experimentally on Rh(111).

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Ethanol electro-oxidation on valve metal (oxy)carbide supported Pt (alloy) catalysts

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Direct Ethanol Fuel Cells (DEFC) have been the subject of numerous studies in recent years, however, the complete oxidation of ethanol to CO_2 at the anode side is still one of the main challenges. The enhanced electro oxidation of ethanol requires the use of expensive platinum based electrodes. Moreover, the catalysts are mainly supported on carbon, which can be corroded under certain conditions resulting in detachment and agglomeration of catalyst nanoparticles [1].

Titanium oxycarbide (TiO_xC_y) and group 6 metal carbides (MC_x, M = Mo,W) are used as innovative supports for platinum and platinum alloy nanoparticles in this study. The chemical composition of the catalyst surfaces has been characterized using X-ray Photoelectron Spectroscopy (XPS). Cyclic Voltammetry (CV) and current transients at temperatures up to 70 °C have been recorded in 0.5 M H_2SO_4 with 1 M EtOH. For a quantitative estimation of the EOR products, Differential Electrochemical Mass Spectrometry (DEMS) measurements are in progress.

Acknowledgements: This work was supported by the European Union Seventh Framework Programme via the EU project DECORE (project 309741).

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Water adsorption on magnetite (001)

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Magnetite (Fe_3O_4) exhibits interesting properties which makes it attractive for applications e.g. in catalysis, where it is used to catalyze the water-gas shift reaction. The (001) surface of magnetite shows a ($\sqrt{2}\times\sqrt{2}$)R45° non-stoichiometric surface reconstruction upon preparation in UHV [1], which gets lifted upon adsorption of water vapor at room temperature and water vapor pressures higher than 10^{-4} mbar. Previous studies on this system by XPS [2], LEED I-V and DFT [3] predict a mixed-adsorption mode of water on this surface, but were all based on an older, bulk truncated model for the surface reconstruction. Therefore, the structure of this unreconstructed surface as well as the mechanisms that are involved in the lifting of the reconstruction remain unclear.

We present our recent results on the surface structure and morphology of the unreconstructed surface composition as well as the lifting process upon dosing water vapor at pressures up to 10 mbar. These are based on surface x-ray diffraction (SXRD) experiments performed at the ID03 beamline at the ESRF and the MPI beamline at ANKA, which allowed for in-situ measurement of the surface structure and morphology over the whole pressure range starting at UHV conditions. They are complemented by infrared reflection absorption spectroscopy (IRRAS) measurements in our own UHV lab.

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Dimerization of benzoic acid on TiO_2 surfaces - an ab-initio study

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Hierarchical structures including inorganic and organic constituents allow for excellent mechanical properties found in natural biological composites such as nacre. In order to design new materials mimicking the natural role models, at first, it is essential to understand the involved processes on each hierarchical level. Starting from the smallest relevant length scale this includes the interactions at the interface between inorganic and organic components at the atomistic level. Particularly, carboxylic acids and metal oxides have proven to be excellent choices for the organic and inorganic constituents, respectively [1].

At the hybrid organic--metal-oxide interface intermolecular forces may contribute to an improved mechanical stability. For instance, linker molecules possessing an aromatic side chain interact with each other via van-der-Waals interaction.

In this regard, the adsorption of benzoic acids on TiO_2 (110) rutile serves as a prototype system. A very regular 2 x 2 overlayer due to dimerization via the phenyl groups has recently been reported [2].

Here, we present a density functional theory analysis of the dimerization of benzoic acids on a rutile TiO_2 surface. To properly describe the attractive interaction of adsorbing molecules among each other, we applied an exchange correlation functional with van-der-Waals correction. For all surface orientations, the preferred dimer formation mode (hydrogen - to - π - orbital or tilted and twisted π - to - π) as well as the amount of energy gain resulting from dimerization will be discussed.

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Supported by DFG, SFB 986, project A4.

C–H Bond Activation at Ceria-supported Vanadia Clusters

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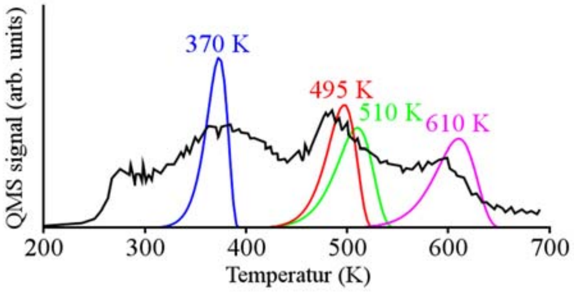
Monomeric and oligomeric vanadia species supported on CeO_2(111) represent very active catalysts for the selective oxidation of methanol to formaldehyde.[1] By virtue of temperature- programmed desorption spectroscopy (TPD) as well as scanning tunneling microscopy, vanadia monomers were found to be more active than their aggregations of higher nuclearity.[2] On the basis of a Mars-van Krevelen mechanism, different reaction pathways exploiting the cooperative effect between catalyst and support have been calculated for ceria-supported vanadium monoxide.[3]

Assuming first-order kinetics with a rate-determining hydrogen transfer, desorption rates were calculated for these reaction pathways using density functional theory. The resulting desorption peaks can be compared directly with the experimental TPD spectrum.



Theory and experiment are in good agreement and it is possible to assign each desorption peak to a certain reaction pathway. This was not possible after comparing calculated intrinsic barriers with the desorption barriers obtained via Redhead analysis, since the latter assumes a constant pre-exponential factor of 10^{-13} s^{-1}, which leads to deviations of up to 20% for desorption barriers.

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New atomically designed catalytic active phases: $Co_x(SR)_m$ and Co doped $Au_n(SR)_m$ clusters

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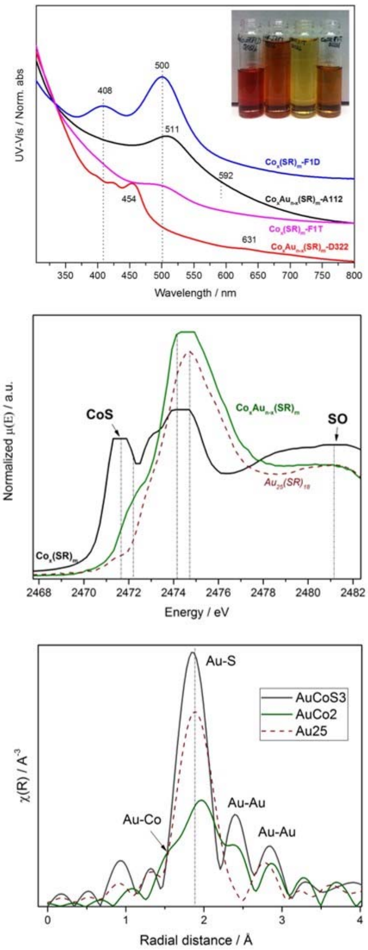

Figure 1: UV-Vis, XANES (S Kedge) and EXAFS (Au L3 edge) results

The understanding and controlling of nanoparticles' catalytic behavior at the molecular level is the key point for the design and optimization of the high active and selective catalysts. Metal cluster research has been widely focused on thiolated-protected gold clusters with the general formula $[Au_x(SR)_y]^z$; z: charge. It has been shown that doping these systems with a heteroatom metal provides an exciting opportunity to fine-tune the properties [1, 2]. But why only gold? Besides, recent studies show the possibility to synthesize thiolate-protected clusters with defined atom composition with metals such as Pd, Ni, Cu or Ag, thus expanding metal clusters beyond Au. It represents another completely broad field to explore the focus on catalytic applications, where the active sites for a defined reaction can be atomically designed. Based on Brust method, we developed the synthesis for Co doped $Au_{25}(SC_2H_4Ph)_{18}$ and $Co_x(SC_2H_4Ph)_m$ clusters. Isolation of different sizes and compositions has been performed based on previous experience and characterized by several techniques such as UV-Vis, MALDI, FIR, Raman, XPS and XAFS. Preliminary results indicate the formation of two kinds of monometallic thiolated cobalt clusters dealing with different UV-Vis spectra and different solubility in toluene. This could be related to the presence of oxygen detected in one of the samples. XAFS, FIR, XPS and UV-Vis indicate also the formation of Co doped $Au_{25}(SR)_{18}$ keeping the core structure and staple configuration. Besides, additional sizes and combinations have been obtained in the synthesis and isolated. However, the exact composition is still under study. These materials represent new atomically designed catalytic active phases with broad numbers of applications. One of the main critical points for catalytic application of thiolated metal clusters is the removal of the ligands, due to the poisoning effect of sulfur. Besides, cobalt sulphide has been recently discovered to improve catalytic performance in hydrogen evolution in photoelectrocatalysis and other photoelectrochemical processes [3].

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Crystalline mesoporous tantalum oxide photocatalysts: tuning pore sizes and injection barriers

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Mesoporous materials engineering has emerged as a promising strategy for designing high-performance (photo)catalysts in various energy related applications. Among the benefits of a mesoporous matrix are an increased active surface area and shorter diffusion paths for charge carriers.

Such mesoporous structures have been produced mainly by block copolymer self-assembly, ligand- or surfactant-assisted templating or by using anodized alumina as hard templates. Resulting films, however, typically exhibit cubic micellar, hexagonally-ordered cylindrical or undefined pores thus restricting 3D access to the interior. Furthermore, the mesoporous are generally rather small (< 5 nm) and induce kinetic limitations for reactant diffusion in liquid environments. As a consequence, the surface area in such materials is not fully available for the photocatalytic conversion and restricts the apparent benefits of the mesoporous matrix.

This work goes beyond mere synthesis of novel ordered mesoporous photocatalysts. We deliberately tune the pore sizes to 20-40 nm to eliminate kinetic limitations and allow access to the entire pore area. In addition, we create well-ordered mesoporous matrix with three-dimensional architecture to further facilitate reactant diffusion in liquid environments.

By using tailor-made block-copolymers we obtained well-ordered, highly crystalline Ta_2O_5 films with alternating gyroid structure and large pore dimensions. Our photocatalytic results demonstrate close to linear correlation between the activity and the surface area, confirming that the mesoporous Ta_2O_5 photocatalysts offer unrestricted access to large inner surface area. The catalysts evolve hydrogen with high apparent quantum yields up to 3.7 % – one of the highest reported for binary metal oxides optimized only via morphology and structure engineering.

We further compare gyroid Ta_2O_5 with Ta_2O_5 nanotubes exhibiting similar crystal structure, porosity and surface area, yet different overall morphology and pore structure and demonstrate that the nature of the template (soft polymer vs robust carbon nanotubes) has a strong effect on crystallization and surface termination of Ta_2O_5 (e.g. by changing injection barriers), and, consequently, the photocatalytic performance of the resulting mesostructures.

Strong-metal support interaction (SMSI) effects under ambient conditions in liquid-phase photocatalysis

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Heterogeneous photocatalysis is a field with a wide array of applications including solar H_2 production from water. Pt-loaded TiO_2, in particular P25 (20% rutile and 80% anatase), is a benchmark material with remarkable activities in this context. Mechanisms for H_2 evolution as well as the exact role of the co-catalyst and the often used sacrificial agents (e.g. alcohols) have been under on-going investigation and debate. [*1-3*] A setup with an online gas analyzer, which allows for simultaneous recording of up to four gases, combined with the *in situ* photodeposition of Pt enables us to continuously monitor the initial stages of photocatalytic H_2 evolution.

We observed a sudden deactivation of Pt-loaded TiO_2 (P25) during these initial stages of photocatalytic H_2 evolution from aqueous methanol solutions. Further experiments and characterization led us to the hypothesis, that strong metal-support interactions (SMSI) – known from classical heterogeneous catalysis – may be the reason for this unusual behavior. [*4*] Several key parameters that can be related to the amount of defects present in our system can influence the behavior of Pt/TiO_2, including UV intensity, Pt loading and pretreatment of the oxide. We thus suspect that the amount of surface defects compared to the amount of Pt particles plays a critical role in triggering deactivation. Indeed, HRTEM images indicated an encapsulation of the Pt, while diffuse reflectance spectroscopy (DRS-UV-vis) and Raman spectroscopy evidenced defect formation, particularly in the anatase phase of P25. However, *in situ* characterization techniques (e.g *in situ* DRIFT) might provide further insight into the process of deactivation.

SMSI effects are usually only considered after high temperature treatments ($T > 450$ K) in reducing atmospheres, but we argue that the local conditions during H_2 evolution are reductive enough to cause encapsulation even at ambient temperature.This effect should be considered in future investigations and would require data acquisition during the first minutes of an experiment.

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Methane Dry Reforming studied on Inverse Pt/ZrO_2 Model Catalyst

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Abstract

Being a carbon source, the utilization of carbon dioxide (CO_2) became attractive from both an environmental and economical perspective. However, CO_2 is a very stable molecule, thus to induce a reaction the activation of CO_2 by catalysts is required [1]. One way of activating CO_2 is dry reforming of methane (DRM), when CH_4 is reformed by CO_2 on Ni or Pt particles supported by zirconia (ZrO_2), $CH_4 + CO_2 \rightarrow 2\ CO + 2\ H_2$. During DRM, CO_2 is reduced to carbon monoxide (CO) via reaction precursors or intermediates, which can further oxidize the carbon formed via CH_4 dissociation. Such activation can occur on the ZrO_2 or on the interfacial sites [2]. As a support, technical ZrO_2 powder material can activate CO_2 by forming carbonate with basic anionic sites, or by forming formate with hydroxyl groups [2]. However, due to the possible different reaction pathways, microscopic mechanisms of the functions of ZrO_2 need to be further understood via a surface science approach. We therefore conducted a systematic study of the interaction between CO_2/CH_4 and ZrO_2 particles supported on Pt single crystals and with the Pt support itself.

Prior to actual dry reforming experiments the model catalyst surface was exposed only to either CH_4 or CO_2. By dosing CH_4 in the Zr 3d region a shift of 0.8 eV towards the lower binding energy side was observed, which can be induced by the change of oxidation state of Zr or the change of the ZrO_2 particle size. In the C 1s region the formed carbon species, that was present in CH_4 gas atmosphere, was completely removed by switching from CH_4 to CO_2 gas atmosphere. This is only possible when CO_2 reacts with the carbon on the surface to CO ($CO_2 + C \rightarrow 2\ CO$).
During methane dry reforming a shift of the Zr3d signal to 182.0 eV could be observed at temperatures above 400°C. At elevated reaction temperatures the surface stays free of carbon contaminations. Only below 150°C carbon and carbonate species could be observed. The Pt 4f signal stays at 71.0 eV during DRM.

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