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Book of abstracts
Ceria MCE 2015

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Invited talks:

Dr. M. Elm

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Electrical transport in mesoporous oxides with high surface area

Oxygen ion conductors, such as ceria and yttria-stabilized zirconia, are of great interest for various applications such as ionic membranes, solid oxide fuel cells or gas sensors. However, for most technical applications a sufficient ionic conductivity requires elevated temperatures making it necessary to find ways of increasing it. One possible strategy for improving the transport properties is nanostructuring. By changing morphology or thickness of oxide thin films enhancements in ionic conductivity were reported, which were attributed to a reduction of the grain boundary resistance, the influence of strain and misfit dislocations, or surface effects. But also reports of no enhancement or even a decreasing conductivity due to nanostructuring can be found resulting in a wide range of reported conductivity values for ceria and zirconia-based oxides. Especially in nanometer thick thin films were the conductivity is measured parallel to the substrate the surface region may have a considerable effect on the transport properties as it can show different physical properties compared to bulk. The role of strain, grain boundaries and the surface region on the transport properties will be discussed, focusing on the influence of surface effects on the transport properties in mesoporous $Ce_xZr_{1-x}O_2$ and 8 mol-% yttria-stabilized zirconia thin films. Due to their regular structure of pores with diameters ranging typically between 5 and 20 nm mesoporous materials can be considered as a closed packaged, interconnected 3D network of nano-crystallites with a high surface to volume ratio. This architecture makes these materials an ideal model system to study the influence of surface effects and the surrounding gas atmosphere on the transport properties. The mesoporous thin films were prepared by a solution-phase coassembly of chloride and nitrate salt precursors with an amphiphilic diblock copolymer using an evaporation-induced self-assembly process (EISA). Structural characterization of the mesoporous thin films was performed using high-resolution transmission electron microscopy (HR-TEM), wide-angle X-ray diffraction (WAXD), secondary-ion mass spectroscopy (SIMS), X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy confirming the high structural quality of the mesoporous films with a regular pore structure of cubic symmetry and crystalline walls consisting of single nano-sized grains. Using impedance spectroscopy the electrical transport properties were investigated as a function of temperature and oxygen partial pressure. For reducing atmosphere the $Ce_xZr_{1-x}O_2$ thin films with high Ce content show a $p(O_2)$-dependence of the total conductivity proportional to $p(O_2)^{1/6}$ as expected for mixed electronic-ionic conductors, while with increasing Zr content the total conductivity varies proportional to $p(O_2)^{1/3}$. This behavior cannot be described with the standard defect model for bulk CeO_2-ZrO_2 solid solutions and seems to results from the high surface to volume ratio. In the case of the mesoporous YSZ thin films, the total conductivity is constant in the investigated $p(O_2)$ range (comparable to bulk YSZ) revealing dominating ionic conductivity. However, the temperature-dependence of the conductivity strongly varies under dry and ambient atmospheric conditions. The results obtained indicate a strong influence of the surface region on the transport properties in mesoporous oxides, which will be discussed using a qualitative defect model including surface effects.

Dr. V. Ganduglia-Pirovano

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

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 model ceria-based catalysts using CeO_2(111) [1], VO_x/CeO_2(111) [2,3], and Ni/CeO_2(111) [4,5] will be discussed, as examples of catalysts for partial alkyne hydrogenation, oxidative dehydrogenation, and hydrogen production, 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 [6].

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Sustainable low temperature wet chemistry route to crystalline inorganic nanostructures and their spectroscopic and structural characterization

The paradigms of green chemistry are currently entailing all the fields of chemistry [1-4] and particularly inorganic chemistry represents an exciting playground for the design and optimisation of green chemistry -inspired and sustainable routes [5-6]. Environmentally friendly methodologies for the controlled synthesis of inorganic nanostructures are a noticeably stimulating research field since this encompasses not only the control of the final composition but also, and more importantly, a fine tuning of the obtained materials in terms of crystallinity (crystalline phase, crystallite size), shape, and morphology.

Controlling size, shape and morphology, at the same time adopting mild conditions of processing parameters (mainly in terms of temperature and pressure) as well as safe, cost-effective, earth-abundant and common chemicals and solvents are relevant conditions to be met for sustainable and cost-efficient production of functional inorganic materials.

In this framework, wet-chemical routes are preferred to solid state ones for preparing inorganic crystalline materials since the liquid phase is more versatile with respect to the variation of structural, compositional and morphological features of the resulting compound materials. Furthermore, the molecular homogeneity of the starting solution or the microscopic homogeneity of the suspensions typically used in colloidal based methods are generally retained in the final materials.

In this contribution, selected synthetic routes for the low or room temperature of inorganic nanomaterials will be presented and described, with particular focus on hydrothermal synthesis [5,7], miniemulsion [5,8] and colloidal-based methods [5,6].

The last part of this talk will be instead devoted to outline the tight interplay among spectroscopic and diffraction-based methods for a sound and thorough characterization of inorganic nanostructures. Structural determination over different length scales combined with a detailed investigation of chemical environment and oxidation states of the involved species are important information to be collected in order to orient also the functional properties of the final nanomaterials.

As a working example, the combined use of XPS, XAS and Raman spectroscopies and of XRD to unravel the chemico-physical and structural features of a complex system such as the ceria zirconia so-called “κ-phase will be shortly discussed.

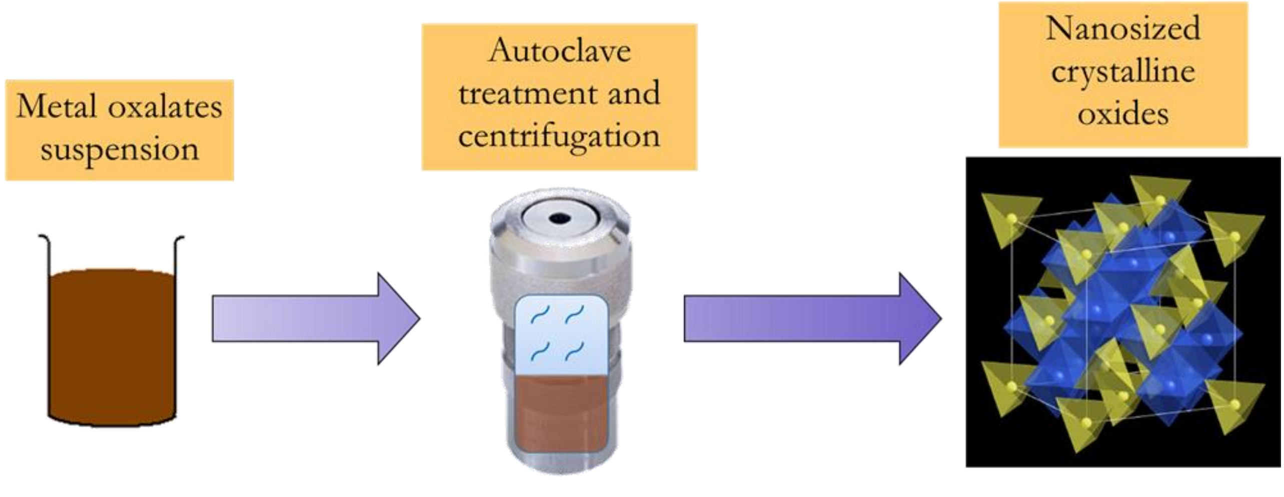

Fig. 1 Combination of coprecipitation of oxalates and hydrothermal treatment

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CeO_2 as an oxygen storage material in three way catalysts

From an economic point of view, the three-way catalyst for the purification of automotive exhaust is the most important application of ceria in catalysis. Modern three-way catalysts contain ceria in form of a precious metal activated Ce/Zr mixed oxide and the main role of this mixed oxide is to act as an oxygen buffer. Under rich conditions, ceria can be partially reduced to Ce^{III} while at oxidizing conditions it can be oxidized back to Ce^{IV}. In the vehicle application, this oxygen buffering function is required, since the three-way catalyst only works well in a narrow range of exhaust stoichiometry, the so-called lambda window. Despite the application of complex control schemes and two lambda sensors, dynamic driving situations unavoidably lead to momentary deviations from the ideal exhaust stoichiometry so that a high conversion of the pollutants can only be maintained due to the application of oxygen buffer materials.

A special focus of this presentation will be on identifying those material properties that control the oxygen storage performance under real world conditions. It will be shown that the dynamic behavior of the oxygen storage is more complicated than previously thought. Much of the complexity arises due to the fact that even under nominally reducing conditions, ceria is permanently oxidized by H_2O and CO_2 so that the filling state of the oxygen storage is determined by the equilibrium of the reactions:

$$CO + Ce_2O_4 \leftrightarrow CO_2 + Ce_2O_3 \qquad (1)$$
$$H_2 + Ce_2O_4 \leftrightarrow H_2O + Ce_2O_3 \qquad (2)$$

In consequence, a number of experimental observations can only be understood if the equilibrium properties of reactions 1 and 2 are correctly taken into account. These include:

- The oxygen storage capacity is lowered by the presence of H_2O and CO_2.
- The oxygen storage capacity depends on the amplitude of the lambda-oscillations.
- Following a rich-lean step the catalyst emits CO/H_2 when there is no CO/H_2 in the inlet.
- Delayed CO/H_2 emissions in the so-called fuel cut-off scenario.
- The capability of the oxygen storage to dump lambda-oscillations, even if the average lambda is slightly rich.

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Defect Chemistry at the Interfaces in Ceria: What should be considered?

In-depth knowledge about the concentration of mobile defects and their local variation in a solid electrolyte is a pre-requisite for understanding and even predicting physical properties of such materials. Ceria is one of the most extensively studied oxides for redox catalyst and electrochemical applications because of its outstanding chemical capacity for oxygen and ionic conductivity when doped. Owing to such effort, defect chemistry of ceria in the bulk has been reasonably well understood, the studies on the concentration and mobility and the interactions of the defects at/near the interface has begun relatively recently along with the huge interest in nano-scale science. It is well accepted by now that the surface or internal interfaces in oxides are not electrically neutral due to thermodynamic reasons such that the electroneutrality no longer holds near interface. This fact results in local variation in the concentration of the mobile defects adjacent to the surface/interfaces, leading to local changes in physical properties associated with it. For instance, the concentration of oxygen vacancy at the surface may be higher than the corresponding bulk value. The current across the grain boundaries in ceria is substantially hampered compared to that in the bulk.

In this contribution, local variation in the concentration of oxygen vacancies in acceptor doped ceria will be discussed in a quantitative way. A new model that accurately describes the current-voltage behavior across the grain boundary in ceria resulted from the change in the local variation in the concentration will be introduced.

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Crystal growth of ceria-based materials

Skull-melting is an outstanding method for the growth of very pure single crystals with, in theory, no limitation concerning the melting temperature [1,2]. It can be described as quasicrucible- free high frequency (HF) process where the material is included in a water-cooled copper crucible. Power transfer occurs via an HF-field. By addition of a small amount of ignition metal to the oxide material, it can be coupled to the HF-field and heated up to its melting point. Between the molten material and the cool crucible a thin ceramic layer (the skull) remains, protecting the melt from impurities. After the whole interior becomes molten, the crucible is slowly moved out of the HF-field and crystals grow in a Bridgman-like process from the bottom of the skull.

In the lecture the Skull-melting technique is explained in detail and ceria-based single crystals grown in Berlin are presented.

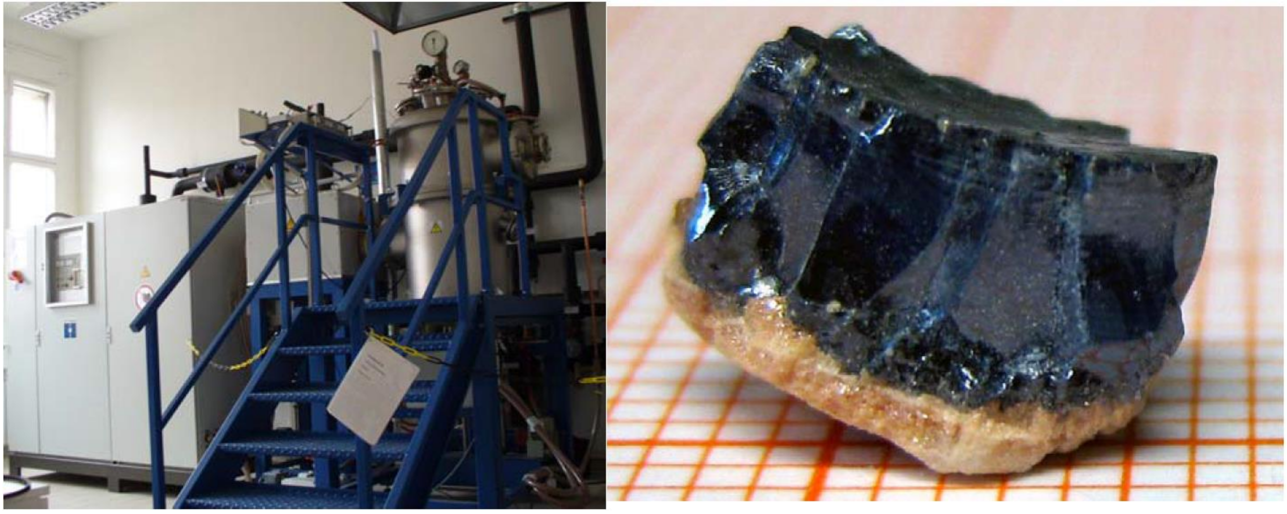

Fig. 1: Skull-melter at TU Berlin (left) together with $CeO_{2-\delta}$ single crystals (right).

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Ceria-based catalysts in low-temperature fuel cells: from surface science to in-situ spectroelectrochemistry

Ceria-based catalytic materials are among the most fascinating ones in environmental and energy technology, with applications ranging from exhaust catalysis via hydrogen production to fuel cell technology. Their surface nanostructure is the key to control and tune their surface reactivity. When used as supports for noble metal nanoparticles, it is the oxide nanostructure which controls the energetics of spillover and reverse spillover processes. Very importantly, the support nanostructure also affects the dispersion of the supported noble metal itself. In the ultimate limit, nanostructured ceria supports even allow the preparation thermally stable atomically-dispersed noble metal catalysts.

Following a surface-science approach, we develop a hierarchy of model systems for ceria-based catalytic materials. We start from the preparation of ordered ceria thin films on single crystal metal supports, and review the characterization of the film structure, the defect structure, methods to modify the stoichiometry and methods for metal deposition and metal doping. Using these models, detailed insights into their geometric and electronic structure, stability, adsorption properties, and reactivity are obtained from ultrahigh vacuum to realistic reaction conditions. The surface structure of these systems is studied, for example, studied by scanning tunneling microscopy (STM), electronic properties are investigated by photoelectron spectroscopy (PES) including synchrotron-radiation-based methods (SR-PES), vibrational properties are probed by infrared reflection absorption spectroscopy (IRAS) and the adsorption and reaction kinetics is studied using molecular beam (MB) techniques and temperature programmed desorption (TPD).

Three aspects are discussed in specific which are related to the catalytic and electro-catalytic properties of ceria-based catalysts: The first topic is related to spillover processes, which are important mechanistic steps in numerous catalytic reactions. The term describes the transfer of activated reactants via phase boundaries between different regions of a nanostructured catalyst, e.g. nanoparticles and support. For reducible oxides, spillover is often linked to the surface redox chemistry. It is discussed how hydrogen, oxygen, hydrocarbons, and sulfur spillover can be investigated, for example by resonant photoelectron spectroscopy (RPES) and how these mechanistic steps relate to complex reaction mechanisms, e.g. in hydrogen production. The second aspect is related to the stabilization of catalytically active noble metals. Noble metals such as Pt can be stabilized on ceria surfaces in atomically dispersed form and model systems for such atomically dispersed catalysts can be prepared using a surface science approach. These atomically defined model systems help to explore the geometric, electronic, and chemical properties of such systems. Finally, applications of ceria-based catalytic coatings in proton exchange membrane fuel cells (PEM-FCs) are discussed. Here, porous coatings of Pt-doped ceria show high noble metal efficiency and excellent stability. Comparative experiments on model systems and thin film catalysts help to explore the related reaction mechanisms. The reactivity of Pt-CeO_2 thin films towards H_2, CO, and CH_3OH is studied in both ultrahigh vacuum (UHV) and in-situ under electrochemically controlled conditions. UHV studies suggest that hydrogen activation requires traces of metallic Pt to be present at the surface, whereas CH_3OH activation is facile, even in the absence of any metallic Pt. Subtractively normalized interfacial Fourier Transform infrared spectroscopy (SNIFTIRS) indicates that under electrochemically controlled conditions the ceria support helps to stabilize very small metallic Pt aggregates which show a reduced tendency for poisoning.

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Ceria based materials for automotive catalysis, focus in Diesel Exhaust Catalysis

I. Abstract :

Ceria main application in automotive catalysis is the three-way catalysts for gasoline engines. In the early years, ceria was co-impregnated with precious metals onto alumina in a very simple manner. Ceria is now combined in solid solution with Zirconia to achieve high OSC performance even after severe ageing conditions. The development of such Ceria-Zirconia mixed oxide materials began in the late 80s and ultimately achieved widespread incorporation into TWC's by the mid 90s under the name of advanced TWC formulations. Since then, driven by the successive legislation severisation and the recurrent need to reduce the PGM, there are continuous needs to develop the performances of such materials.

The reduction of NOx from Diesel Engines is a major issue in automotive catalysis. Over the last several years, many solutions to remove NOx under lean operating conditions have been considered. Attention is now focused on two main technologies: (i) NOx-Storage Catalyst (NSC) (ii) Selective Catalytic Reduction using ammonia as reductant (urea SCR) and

The evolution of the legislation and particularly the testing cycle procedure (WLPT cycle, RDE) will require the evolution of the NOx control strategies with a particular focus on low temperatures NOx elimination. Therefore, there is a regain of interest for materials that can deal with low temperature NOx storage and be compatible with traditional Diesel Catalyst functionalities such as the oxidations of CO and Hydrocarbons. Ceria is an oxidising material that is known to be efficient for storing NOx at low temperature. This is the reason why it is already implemented in some of the most advanced emission control technologies.

Selective Catalytic Reduction (SCR) of NOx using NH3 as a reducer shows extremely high potential to comply with the most stringent regulations on NOx emissions. This technology initially developed for the NOx abatement of stationary sources has been successfully applied in the last decade on trucks in Europe and US. NH3-SCR process shows growing interest for passenger cars applications as well. In this context, the nature of the washcoat material is of first order of interest:

- The vanadium oxide based catalysts exhibit high NOx conversion in a wide range of temperatures (from 250°C to 500°C) but a very limited thermal stability
- The metal - exchanged zeolite based catalysts, as i.e. Fe-zeolites and Cu-zeolites, have been also extensively investigated. Zeolite based catalysts show high NOx conversion and good thermal stability.

New Mixed Metal Oxides have been also proposed as alternative catalysts for the NH3-SCR process. These systems may obey the need for higher activity at low temperature and better thermal durability, particularly when the SCR function is combined with a Diesel Particulate Filter.

With increasingly severe Particulate Matter (PM)/ Particle Number (PN) regulations across the world the use of Diesel Particulate Filters (DPFs) have become widespread. DPFs using a Fuel Borne Catalyst (FBC) to assist filter regeneration provide a uniquely advantaged DPF technology: The FBC, added to the fuel, is mixed within the soot during the combustion in the engine and the additivated soot is collected in the DPF. This intimate contact between the catalyst and the soot leads to a drastic reduction of the soot combustion temperature (starting at 300°C) and very fast soot combustion kinetic (down to few minutes) allowing fast and complete DPF regeneration even in the very challenging city driving conditions.

The paper will focus on recent development made on ceria based materials with the objective to meet legislation targets in LNT, SCR and DPF.

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Expanding the horizons of ceria in oxidation and hydrogenation catalysis

This talk will present novel applications of ceria in catalyzed reactions of technological importance. Firstly, the development of ceria-based catalysts in the recovery of chlorine via the gas-phase HCl oxidation will be described and further bridged with the more recent application of this oxide in bromine recovery within the context of alkene functionalization and in ethylene oxychlorination as an alternative to copper-based catalysts in PVC manufacture. Finally, the scope of ceria in the selective hydrogenation of alkynes will be demonstrated. The opposite requirements in the design of ceria for optimal oxidation and hydrogenation performance will be discussed.

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Concepts for the solution-based synthesis of CeO2 materials with defined nanoscaled porosity

In the past years, CeO_2 and CeO_2-based solution solutions (Zr, Gd, …) has received increasing attention as potential catalyst, e.g. in the Deacon process. While catalytic processes can generally be improved by a high surface area, enhancing the activity, the Deacon process exemplifies the need for catalysts also possessing sufficient stability. Furthermore, the role of the oxygen storage capacity (OSC) is still a matter of current research, in particular the influence of the surface layers which requires the materials to possess a high surface area. Thus, basic research on CeO_2-based catalysts benefits from porous materials possessing a defined nanoscaled porosity, i.e. in terms of pore shape and a narrow pore-size distribution.

The talk is going to present concepts for the generation of such materials, especially mesoporous materials (Pore size between 2 nm and 50 nm) with defined pore shapes such as cylinders or sphere, allowing for fine control of the pore volume and hence the surface area. Such mesoporous CeO_2 can be achieved by self-assembly strategies in combination with suitable sol-gel chemistry. The general idea of using surfactants as templates is based on the fact that amphiphilic organic molecules self-assemble in certain solvents to give regular superstructures that feature structural motifs on the nanometer scale (lyotropic liquid-crystalline phases). Typically, the constituting entities are spherical or cylindrical micelles or lamellar sheets with a characteristic cross-section of 5–100 nm. In the templating procedure, such regularly ordered mesostructures of amphiphiles in water are converted into their 1:1 replica (their "negative") by solidifying the hydrophilic or solvatophilic domains between the micelles.[1] This is done by replacing the majority of the solvent by either preformed CeO_2 nanoparticles [2] or by a metal oxide precursor and condensing this precursor around the micelles.[3,4] The final mesoporous CeO_2 is achieved by removal of the surfactant template, either by burning or dissolving the surfactant. Although this process appears to be simple, several problems had to be overcome to achieve a homogeneous and well-defined mesoporosity throughout the material. For instance, such high-surface area materials can only be generated if the involved interfacial energies are adjusted. Also, the condensation rates of precursor mixtures (e.g. in the case of mesoporous Ce-Zr-oxide solid solutions) need to be considered.

Since the proof of a homogeneous mesoporosity is of high relevance, the presentation also provides an overview about suitable quantitative characterization tools.

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Key issues in the development of ceria-based catalysts

Rare-earth oxides have been widely investigated as structural and electronic promoters to improve the activity, selectivity and thermal stability of catalysts. The most significant of the oxides of rare-earth elements in industrial catalysis is certainly CeO2. Enormous effort has been dedicated in the past 40 years in studying the role of ceria in three-way-catalysts; the origin of this success dates back to the late ‘70s when CeO2 was first employed as an oxygen storage component of TWCs formulation. The ability of ceria to rapidly modify its average oxidation state in a suitable temperature range by maintaining structural integrity is the key of application; after several years, its ability to do so is still unsurpassed. There are also several other applications or processes for which ceria-based materials are currently being actively investigated. More specifically, cerium oxide is used as a key component in catalyst materials for soot oxidation, reforming, partial oxidation and water gas shift reaction. Other energy-related uses are in the fuel cell technology where CeO2 and other rare earth materials are fundamental components to reduce the operating temperature of solid oxide fuel cells. All these applications may benefit primarily from the unique redox properties of cerium dioxide and from the possibility of fine tuning the interaction between ceria and other elements (metal or oxides) in order to improve catalytic performances. Additional effects like stabilization of metal dispersion, change of crystal shape/morphology and structural/textural stability, can affect catalytic properties as well.

As a contribution to these areas, we have been investigating in the last few years a number of issues concerning the preparation and characterization of nanostructured and nanoshaped cerias as active materials for applications in soot and CO oxidation reaction and the use of noble metal ceria combinations in catalytic combustion of methane. Some of these issues will be reviewed here, with a special focus on the understanding of the relationships between activity and morphology in the former case, and the preparation of active noble metal/ceria formulation in the latter. In addition, a brief historical overview on the development of first and second generation of ceria-based catalysts will be presented.

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Understanding and managing mixed ionic-electronic conduction in ceria and the role of suitable doping strategies

Ceria and many related ceria containing solid oxides have gained a wide interest with respect to their particular combination of interesting properties as functional materials. In this contribution, the bulk defect properties and their control represent the central topic. A large number of isovalent and aliovalent dopants can be used to modify concentrations of ionic and electronic defects and their mobility in a wide range. Widely differing properties can be generated by suitable dopant strategies ranging from a material usable as a solid electrolyte with very good oxygen ion conduction for fuel cells and chemical sensors up to a typical semiconducting material or a material for optical applications e.g. as UV absorber or as component in LED materials.

In this presentation, a particular focus is on applications which profit from mixed ionic-electronic conduction such as reversible short term oxygen storage in heterogeneous catalysts or oxygen permeation membranes for gas separation. The coexistence of mobile electronic and ionic defects in ceria resulting from the choice of suitable dopants is the basis for many selective redox catalysts in production of chemicals. Therefore, a detailed understanding of dopant effects is desirable for being able to predict optimized functional properties.

A basic starting point is the formulation of chemical defect equilibria interacting with each other and coupled to bulk diffusion and exchange with neighbouring phases. A very good possibility to illustrate dopant effects is the combined use of Brouwer diagrams, chemical potentials, electronic band scheme and Fermi level. Such concepts facilitate to discuss and define what is needed to achieve particular properties of a mixed conducting functional material, e.g. how to enhance oxygen storage properties, electrochemistry and activity towards oxygen related redox processes and oxygen permeation.

Examples are given based on a recent experimental studies of dopant influences in ceria based oxides covering a) the differences between doped single crystalline and polycrystalline materials, b) a wide temperature range between room temperature and 800 °C, and c) a detailed measurement of electron and ion transport properties such as partial conductivities, chemical diffusion coefficients, and transference numbers.

Acknowledgements

A considerable part of this contribution cites results of a joint research project with the participation of three groups, i.e. at the University Giessen (Prof. Jürgen Janek), the Technical University Berlin (Prof. Martin Lerch) and the University Münster. At present, the project is funded by the DFG within the project grants JA 648/21-1, WI 952/9-1 and LE 781/14-1.

Contributed talks:

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Ceria nanostructures on titania: from model studies to core shell nanoparticles with biomimetic activity

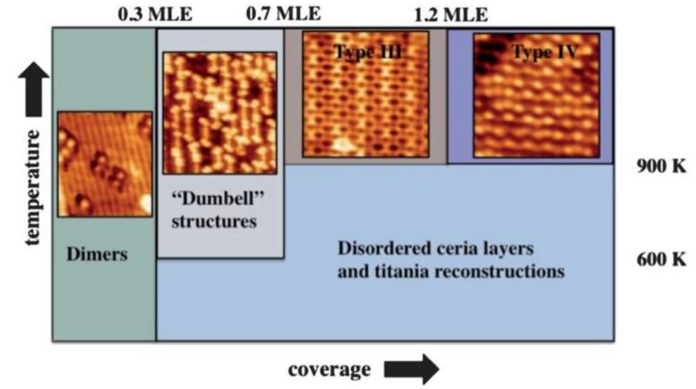

Figure 2: Phase diagram of Ceria ultrathin films deposited on the $TiO_2(110)$ surface

The bedrock on which all the exceptional properties of ceria are founded is its ability to form, with little energy cost, oxygen vacancies. Therefore, all materials science studies focused on ceria try to answer to one simple question: how to promote even more this natural tendency? Several approaches have been attempted such as doping, introduction of strain, reduction of size, etc. A radically new route however, is the formation of an interface with another oxide with the aim of exploiting the electronic transfer at the interface as a tool for tailoring the electron occupancy in the defects states of ceria (Ce 4*f* orbitals). In order to prove this concept, we studied the deposition of ceria on the (110) surface of rutile-TiO_2 single crystal. We obtained several different nanophases (fig. 1) than have no bulk counterpart, exhibiting quite unusual structural and chemical properties.[i] On all this phases for example, methanol can undergo oxidative dehydrogenation to formaldehyde at unprecedented low temperature (330 K). [1] The key for explaining this behaviour has been traced back to the systematic presence of reduced ceria species (Ce^{3+}), which is made possible by the energy stabilisation of the Ce 4*f* states below the Ti 3*d* band operated by the hybridisation with O 2*p* band of titania. Therefore the electrons otherwise trapped into titania defects (Ti^{3+}) are readily injected into ceria defect band. This process has been monitored *in situ* by resonant photoemission spectroscopy across the Ce 4*d*-4*f* threshold during the adsorption of reducing and oxidizing gases. The possibility to shuttle electrons with minimal energy cost between the Ce 4*f* and Ti 3*d* defects bands modifies profoundly the normal redox chemistry of ceria, making this composite system an excellent catalyst. Therefore, we developed a new method based on a surface limited sol-gel reaction, to produce core@shell titania@ceria nanoparticles with monolayer precise thickness (fig. 2) that reproduce on a large scale the special interface studied in model systems in ultra high vacuum conditions.[ii] These composite powders were tested as peroxidase like mimics demonstrating an excellent catalytic activity even better than the natural horseradish peroxidase enzyme. [2]

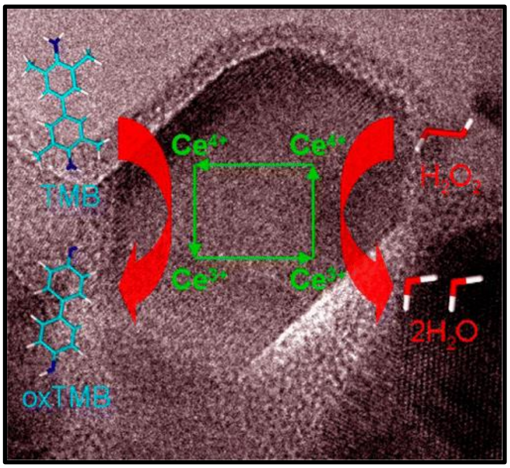

Figure 1 Schematic visualisation of the catalytic cycle explaining the peroxidase like activity of titania@ceria nanoparticles

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Ceria-stabilized molten tin in SOFC anodes

Due to its relatively low cost and good oxygen storage properties ceria has been studied in a wide variety of catalytic and electro-catalytic applications[1]. One successful approach towards the improvement of its catalytic properties is to add a metal co-catalyst in the anode. Tin, despite evidence showin a strong interaction with ceria[2,3], has not been fully investigated as a co-catalyst in electro-catalytic applications where ceria sees widespread use, that is solid oxide fuel cells (SOFCs). We describe, for the first time, the effect of tin on the catalytic properties of ceria towards the oxidation of hydrogen in intermediate temperature solid oxide fuel cells (IT-SOFC) at 873K. Ceria and tin oxides were infiltrated in a porous Ce0.8Sm0.2O2 (SDC) scaffold and tested in button cell configuration. The cell was electrolyte supported and the electrolyte used was a commercial SDC powder.

It was found that when tin oxide is present alone it is reduced to metal which, being in liquid form due to the relatively high temperature (873K), segregates to the surface of the anode. This in turn negatively affects performance by causing a significant increase in polarization resistance. When cerium and tin are both present in SDC anodic scaffolds, on the other hand, a 10-fold increase in power output when compared to ceria alone, with a concomitant decrease in cell polarization resistance. The performance was found to be stable over a period of 20 hours at 873K with the open circuit voltage (OCV) remaining at 0.92V, 400mV higher than the OCV developed by a cell infiltrated with ceria alone. Tests were also performed up to 700°C without registering significant degradation for the ceria/tin anodes.

SEM/EDX analysis shows that tin localizes preferentially on the ceria particles. This is in stark contrast with the behavior of tin when alone in the anodic scaffold, in which case EDX spectra reveal that the metal is more uniformly spread inside the anode, and rapidly segragates to the surface. Structural analysis (XRD, XPS, HR-TEM) performed on tin impregnated ceria powders revealed that tin is present in operational conditions as a molten metal, and that its stabilization on ceria nanoparticles is due to the formation of a nanometric layer of tin oxide which acts as a ”glue” between the metal and ceria. This, in stark contrast with previous literature data, without evidence of the formation of ceria-tin solid solutions. At the same time the interfacial oxide layer can be used to explain the increase in SOFC performance, since with tin acting as an oxygen relay between ceria and hydrogen the oxygen exchange kinetics of ceria are significantly improved[4].

The increased electrocatalytic performance towards hydrogen oxidation together with the stabilization of a molten metal in the form of nanoparticles at a temperature almost 400K above its melting point make this ceria-tin system an interesting new model for the development of novel catalysts.

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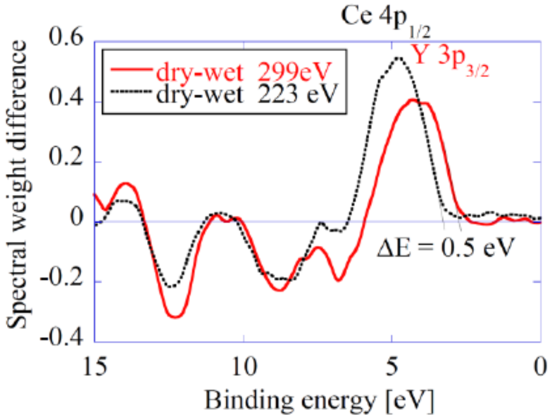
Observation of oxygen vacancy filling under water vapor in ceramic proton conductors in-situ with ambient pressure XPS

Super-protonic conductivity is a highly-wished-for functionality of solid electrolytes for intermediate temperature ceramic fuel cells and steam electrolyzers. Y-substituted barium cerate - conventional ceramics with ABO3-type perovskite structure, is a well-studied candidate for this purpose. We have investigated the functional oxygen vacancy filling of engineered oxygen deficient BCY by water molecules with electro-analytical methods and ambient pressure XPS [1], which enabled to sketch a detailed picture of the correlation of molecular and electronic structure changes, and the concomitant onset of proton conductivity at elevated temperatures. With this information we were able to design experiments, where the proton phonon coupling could be quantitatively investigated with high pressure-high temperature electrochemical impedance spectroscopy combined with quasi-elastic neutron scattering [2,3]. Supported with pressure dependent XRD and Raman scattering data [4,5] we were able to correlate the proton jumping parameters with the temperature and found that the proton jump times follow a Holstein polaron relation [6,7].



VB XPS difference spectra containing the spectral signature of oxygen defects in BaCeY-oxide, recorded in resonant condition for Y and Ce. The maxima of the pronounced difference peak at a binding energy of around 5 eV are shifted by about 0.5 eV, revealing that the gap state of oxygen vacancies next to Y is by 0.5 eV closer to the Fermi level than a gap state from an oxygen vacancy next to Ce.

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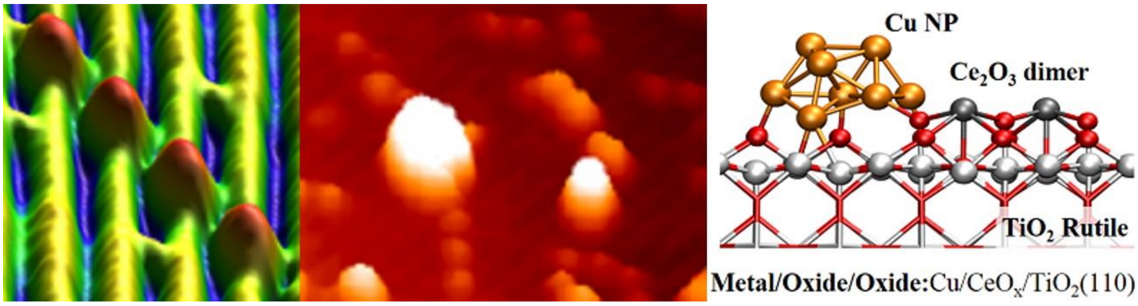
Understanding Ceria-based nanostructured catalysts: Water Gas Shift and Methanol Synthesis reactions example

We briefly review the main conclusions, from both theoretical and experimental points of view, harvested until now in our previous works regarding the Methanol Synthesis from CO$_2$ and WGS reactions,[1, 2, 3, 4, 5] together with key ideas for designing nanostructured catalysts based on ceria. Most of the ideas and general statements included in the present work may be also very useful for designing catalysts for other reactions that require the presence and combination of metals and oxides. Particularly relevant is the description of the nature, properties and future implications of the nano-mixed-oxide phase "naturally" generated at the interface of some systems which modifies and activates the whole catalytic process. Co-supporting metal and reducible-oxide nanoparticles on another oxide-support in systems with a strong oxide–oxide interaction opens the door to a new family of highly active catalysts suitable for reactions such as water gas shift, CO oxidation or methanol synthesis, among others.



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Nanostructured Cu-Ce-O Catalysts for CO Preferential Oxidation (PROX) in H2-rich Gases and Water Gas Shift (WGS) Reaction

Highly ordered mesoporous and shape controlled nano Cu-Ce-O catalysts with different Cu contents (1 – 70 wt. %) and high specific surface areas (70 – 160 $m^2 \cdot g^{-1}$) have been synthesized by using nanocasting method with ordered mesoporous silica KIT-6 and functional SBA-15 as hard templates or by using co-precipitation method.[1,2] The catalytic activity in preferential oxidation of CO in H_2-rich gases (PROX) was tested at a space velocity of 60,000 $mL \cdot h^{-1} \cdot gcat^{-1}$. The activity of the mesoporous catalysts increases with the concentration of Cu and becomes stable for Cu concentrations higher than 20 mol%. A CO conversion around 100 % can be attained with $Cu_{0.20}Ce_{0.80}O_2$ as catalyst at 160 °C. The exit CO concentration can be as low as 70 ppm under these conditions. The CO_2 selectivity can reach 100 % at low temperature (60 – 80 °C). The influence of the pretreatment atmosphere on activity was also studied. Oxidationreduction- oxidation cycling can improve the catalytic activity of the catalysts. In addition, a series of Cu-Ce-O nanoparticles with different shapes and Cu concentrations have been synthesized by a simple low temperature co-precipitation method. These catalysts show much superior catalytic activity than the high temperature prepared nanocast samples in PROX, suggesting the preparation method has great influence on the activity of Cu- Ce-O catalysts. Moreover, these fresh prepared shaped Cu-Ce-O catalysts also show very high catalytic activity for WGS reaction at a high space velocity of 42,000 $mL \cdot h^{-1} \cdot gcat^{-1}$ and low temperature (below 300 °C), which is much superior than that of the CeO_2 supported gold catalysts.[3] Moreover, this catalyst is very stable at least up to 15 h in the same reaction conditions with a CO conversion only drops from 98.7 to 97.5 %.

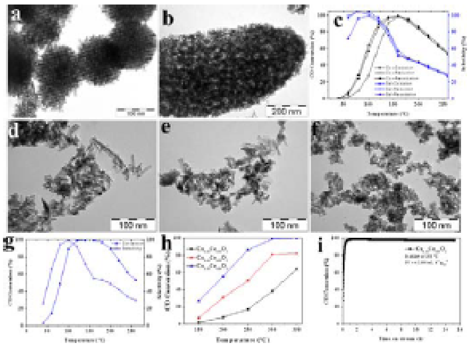

Figure 1. (a) TEM image of $Cu_{0.20}Ce_{0.80}O_2$ nanocast from mesoporous silica KIT-6; (b) TEM image of $Cu_{0.20}Ce_{0.80}O_2$ nanocast from functional mesoporous silica SBA-15; (c) PROX activity and CO_2 selectivity of mesoporous $Cu_{0.20}Ce_{0.80}O_2$ nanocast from KIT-6: influence of pretreatment conditions; (d-f) TEM images of $Cu_{0.01}Ce_{0.99}O_2$, $Cu_{0.05}Ce_{0.95}O_2$ and Cu0.20Ce0.80O2 synthesized by co-precipitation method; (g) PROX activity and CO selectivity of $Cu_{0.20}Ce_{0.80}O_2$ nanoparticles synthesized by co-precipitation method; (h) WGS activities of Cu-Ce-Onanoparticles with different Cu contents synthesized by coprecipitation method; and (i) performance of the $Cu_{0.20}Ce_{0.80}O_2$ catalyst synthesized by co-precipitation method at constant temperature of 300 °C. Operation conditions: for PROX, WHSV = 60,000 $mL \cdot h^{-1} \cdot gcat^{-1}$; for WGS, WHSV = 42,000 $mL \cdot h^{-1} \cdot gcat^{-1}$.

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A first-principles approach to the attempt frequency for oxygen diffusion in pure and doped ceria

The rate of oxygen ion jumps in a solid oxide depends not only on the activation energy but also on the pre-exponential factor of diffusion. In order to allow a fully ab initio prediction of the oxygen ion conductivity in pure and samarium doped ceria we calculated the attempt frequency for an oxygen ion jump from first principles using DFT+U, NEB, phonon calculations and the transition state theory. The equivalence of the Eyring and the Vineyard method is shown without restriction to the Gamma point. Convergence checks of the phonon mesh show that the common reduction to the Gamma point is not sufficient to calculate the attempt frequency. The pre-exponential factor is unaffected by doping with a single Sm ion at the migration edge while a Sm-Sm edge exhibits a significantly larger attempt frequency. The attempt frequencies for the constant volume and constant pressure case in harmonic and quasi-harmonic approximation are in agreement with literature approximations and experiments.

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New approach for the in-situ monitoring of oxygen storage in ultra-thin ceria films

We assess a novel optical approach aiming at the in-situ monitoring of oxygen storage processes in ultra-thin layers of ceria. It is based on the photoluminescence response of ceria-coated group III-nitride nanowires to variations in the ambient reducing or oxidizing atmosphere.

Group III-nitride nanowires were grown by plasma-assisted molecular beam epitaxy using a self-assembled growth process. [1] The photoluminescence intensity of the as-grown nanowires shows a high sensitivity to adsorbed oxygen which makes them suitable as transducer elements whit optical readout in gas sensing applications. [2, 3, 4] Within the presented work the nanowires were coated with an ultrathin layer of ceria used as an optical probe for the characterization oxygen-related processes in the ceria-layer.

Ceria coating was performed by atomic layer deposition and a homogeneous ceria coverage with uniform film thickness was achieved (cf. Fig. 1). [5]

The transient photoluminescence intensity of the nanowire probes was measured during exposition to reducing and oxidizing gas atmospheres for samples with different thicknesses of the ceria layer. In oxidizing gas atmosphere both ceria coated and as-grown nanowires show a decrease in photoluminescence intensity. However, we find significant influence of the ceria film thickness on the time constant of the response. The underlying mechanism will be discussed based on a microscopic model taking photogeneration and transfer of charge carriers into account.

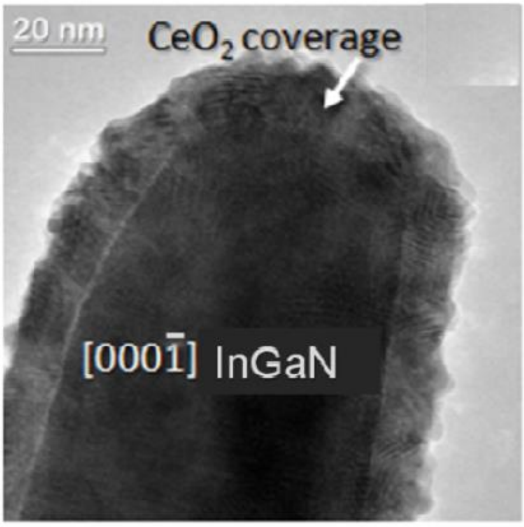

Figure 1: TEM-image of ceria coated InGaN/GaN-nanowire.

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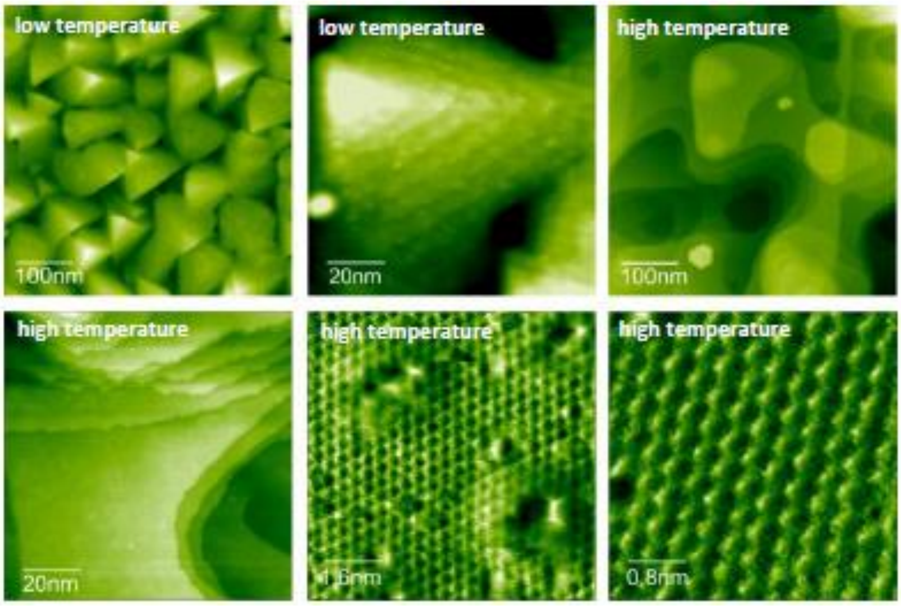
A well-structured metastable ceria surface grown as a film on Si(111)

Changes in the surface morphology of a 180 nm thick film of ceria grown on Si (111) with a Pr_2O_3 buffer layer[1] are studied with non-contact atomic force microscopy (NC-AFM) and Kelvin probe force microscopy (KPFM). A preparation with annealing cycles in the ultra-high vacuum leads to a morphology with significant differences when comparing the temperature regime from room temperature to 900 K (low temperature regime; LT) compared to 900 K to 1100 K (high temperature regime; HT).

For the LT-regime pyramidal, terraced triangular structures are observed which are formed due to a “wedding cake” like growth mechanism of the ceria film. This surface morphology undergoes a transition for the HT-regime where flat terraces and step structures develop on the film surface. Within the HT regime the width of the terraces increases with increasing annealing temperature until a decomposition of the film occurs at temperatures higher than 1100 K.[2] The structural transformation is confirmed by a high resolution low energy electron diffraction experiments combined with spot profile analysis (SPA-LEED).

Although the surface morphology of the HT regime is similar to structures observed on CeO_2(111) surfaces of bulk crystals,[3] we find much more atomic scale irregularities on the film surface. These irregularities are interpreted as an effect of surface defects caused by the reduction of the ceria film.[4]



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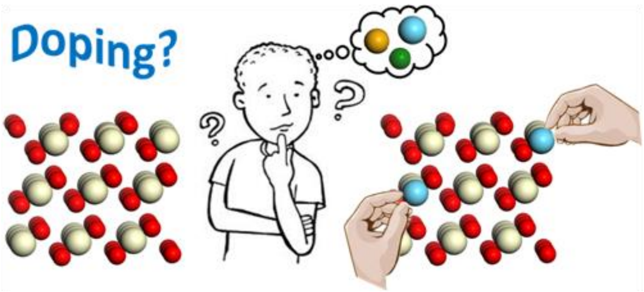
Promoted Ceria: A Structural, Catalytic and Computational Study



The role of trivalent (La, Sm, Gd, and Y) and tetravalent (Hf, Zr, and Ti) dopants in the catalytic, structural, and electronic properties of ceria was investigated.[1] Promoted ceria catalysts were synthesized by coprecipitation with ammonia and tested in HCl and CO oxidation. Ceria catalysts exhibit a medium high reactivity and excellent stability in HCl oxidation. The intrinsic reactivity of ceria in HCl oxidation can be improved by a factor of 2 when doping with Hf and Zr in appropriate quantities, whereas trivalent dopants are detrimental. Although both oxidation reactions rely on the existence of oxygen vacancies, the order of reactivity in HCl and CO oxidation is not completely parallel. The effects of promoters on the electronic conductivity and the vacancy formation energy were studied by contactless conductivity experiments using the microwave cavity perturbation technique and by density functional theory calculations. Furthermore, transport properties were also assessed on the basis of theoretical calculations. The order of oxygen vacancy formation energy follows well the order of conductivity (polaron mobility) (trivalent > tetravalent > undoped) observed under inert and oxidizing conditions. This implies that none of these properties correlates with the reactivity. On the other hand, reducing conditions strongly enhanced the conductivity of Hf- and Zr-doped ceria. In HCl oxidation, only the balanced reduction of both Cl and O vacancy formation energies allows for an enhanced reactivity. Promoters give rise to lattice contraction–expansion modifying vacancy formation energies, adsorption properties, and surface coverages.

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Relations between dynamic redox behavior and catalytic performance of $VO_x/Ce_xZr_{1-x}O_2$ catalysts during low-temperature NH_3-SCR of NO studied by *in situ* spectroscopy

The selective catalytic reduction (SCR) of NO_x by NH_3 belongs to the most important processes for cleaning of exhaust gases. While the operation of industrial V_2O_5-WO_3/TiO_2 catalysts for power plants is limited to a narrow range of 400-500°C, there is still a need to develop stable and active catalysts for NO_x abatement at low temperature (needed, e. g., for diesel and lean-burn engines). Promising candidates could be V_2O_5 highly dispersed on modified CeO_2, due to their high oxygen mobility and interesting redox properties [1-3]. However, knowledge about structure-reactivity relationships in NH_3-SCR of NO_x over ceria-supported vanadia catalysts is still very limited so far.

In this work, we have explored the potential of catalysts containing 5% V_2O_5 dispersed on mixed CeO_2/ZrO_2 supports for the SCR of NO by NH_3 at low temperature. *In situ*- UV-Vis diffuse reflectance spectra were recorded at 200 °C using the same gas composition of catalytic tests with a flow rate of 25 mL/min after 1h pretreatment at 275 °C in air. Kinetic studies of reduction and reoxidation were performed by *in situ*-UV-vis-DRS monitoring the absorbance at 700 nm in the range of d-d-transitions of reduced V-species [4]. *Operando* EPR spectra were recorded in X-band under similar conditions as in the catalytic tests. Simultaneous *in situ*-UV-vis/H_2-reduction measurements have been performed as reference in 5% H_2/Ar at 400°C to quantify the mean V valence state under SCR conditions. Based on *in situ*-EPR and *in situ*-UV-Vis and coupled *in situ*-UV-Vis/H_2-TPR studies we discuss relations between catalytic performance, structure and redox properties of V sites in these catalysts.

Highest catalytic performance was measured with catalyst 5 % V_2O_5/ $Ce_{0.7}Zr_{0.3}O_2$ which, compared to literature values [2] reached full conversion of NO at a significantly lower temperature (200 °C compared to 240 °C) and at nearly 6-fold GHSV of 70000 h^{-1} (compared to 12000 h^{-1}). These are the best results ever achieved with this catalytic system.

In situ-EPR and -UV-vis measurements revealed the presence of preferentially polymerized octahedral vanadium species on the highly active 5 % $V_2O_5/Ce_{0.7}Zr_{0.3}O_2$ catalyst while polymerized tetrahedral surface VO_4 species dominate on 5% V_2O_5/ZrO_2. Fitting of the time-dependent redox behavior of the V sites (derived from *in situ*-UV-vis-DRS) by a first-order rate law revealed the presence of two types of oxidized and reduced VO_x species (probably on the surface and in the bulk) in all these catalysts. Maximum rate constants for both reduction and reoxidation were obtained for the highly active 5 % $V_2O_5/Ce_{0.7}Zr_{0.3}O_2$ (compared to the less active catalysts supported on pure CeO_2 and ZrO_2). Comparison of the absorbance of reduced V species in the *in situ*-UV-Vis-DR spectra under SCR conditions with that in the H_2-reduction calibration curves indicates that the amount of V species participating in reversible redox cycles is highest for the most active catalyst 5 % $V_2O_5/Ce_{0.7}Zr_{0.3}O_2$.

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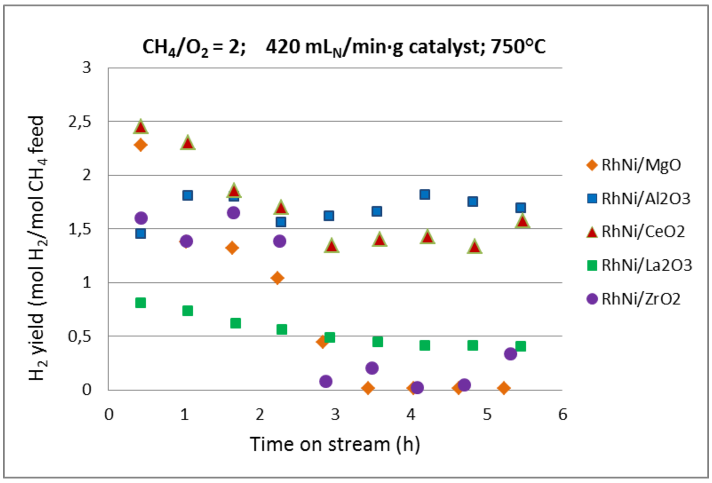
Catalytic performance of oxide-supported Rh-Ni catalysts for partial oxidation of methane: the ceria-support effect

There is a great economic incentive in developing an efficient catalyst for the conversion of natural gas in hydrogen or synthesis gas, suitable for methanol and Fischer-Tropsch synthesis processes by Partial Oxidation of Methane (POM), since this is a much less energy-intensive reaction than that used nowadays, based on highly endothermic methane steam reforming.

Supported Ni catalysts were found to be active for this process, but suffer from fast deactivation caused by coke formation as well as sintering of Ni particles. In comparison, noble metal catalysts exhibit higher activities and stabilities; however, they are much more expensive and less readily available. Previous studies show that the combination of a small amount of group VIII metal with transition metals may be a way to decrease the catalyst cost and improve the catalyst performance. Thus, it has been suggested that the presence of noble metals contributes to maintaining a higher content of the transition metal in the metallic state, which appears to lead to an increase in the rate of methane decomposition and to promote the formation and stabilization of smaller transition metal particles [1].The higher degree of active phase in the metallic state also appears to help to decrease the hot spot formation [2]. On the other hand, the support has also a role in the catalyst efficiency changing the adsorption and reactivity of reactant molecules.



In this work, supported catalysts based on nickel as active phase with a small amount of rhodium as promoter have been prepared (by solid state reaction) and tested for POM. The interaction of above phases with different supports (Al_2O_3, CeO_2, La_2O_3, MgO, ZrO_2) has been studied and correlated with the catalytic behavior. Some of these supports could act to the reactivity process and could decrease the coke formation due to their basicity, by creating oxygen vacancies, by contributing to the storage of oxygen and by enhancing oxygen mobility, or via the formation of carbonates in the surface.

In order to establish structure-activity relationships, different characterization techniques (Adsorption-desorption of N_2 at 77 K XRD, XPS, TPR, Raman spectroscopy) have been used. Obtained results point out that the support plays a crucial role in the catalytic activity, selectivity and stability. Among all the studied catalysts, those based on ceria and alumina are the most active and selective, presenting low carbon deposition. Ceria seems to be a promising support if it is combined with another such as alumina, which confers the former a higher resistance to sintering.

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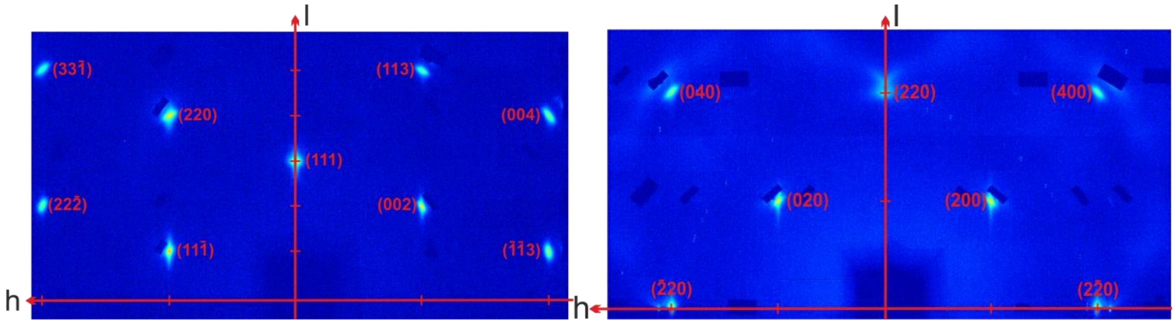
Structure and stability of 10% Gd-doped CeO2 thin films grown on Yttria-Stabilized Zirconia

Cerium oxide is used as an anode as well as an electrolyte material in solid oxide fuel cells, due to its ability to form oxygen vacancies and therefore store and release oxygen. Doping ceria with Gadolinium (Gd) induces oxygen vacancies, making them available under non-reducing conditions. The interfacial and crystalline stability of Ceria films under reducing conditions plays an important role for both the mechanical stability and the oxygen ion conductivity. In addition to that, ceria films could also replace single crystals with difficult to obtain sufficient quality. However, there are also challenges to obtain sufficient quality on films.

To study both the interfacial and crystalline stability of ceria, 25 nm thick 10% Gd-doped ceria films were grown by pulsed laser on Yttria-Stabilized Zirconia substrates with (110) and (111) orientation, inducing a nominally 5% vacancy concentration. Both samples were pre-characterised with x-ray reflectivity, gracing incident x-ray diffraction, X-ray photoelectron spectroscopy and atomic force microscopy. The x-ray measurements were done at the ID03 beamline at the ESRF as well as with a lab source. After annealing at 1300°C in ultra-high vacuum, reflectivity measurements and reciprocal space mapping were done at the Petra III P07 high-energy beamline. Both the (110) and (111)-oriented films were atomically smooth and epitaxial to the YSZ substrates, with good crystalline quality and no defects like twinning. Upon reduction due to the annealing in vacuum, both samples show an increase in lattice parameter while maintaining their crystalline quality. The reflectivity measurements show interdiffusion at the interface to the substrate without any change in film thickness or density. The measurements on the (110) oriented sample indicate faceting at the surface. The XPS analysis of the surface reveals an increase in the concentration of Ce^{3+} and Yttrium upon annealing, indicating diffusion of yttrium to the surface as well as slight reduction of the surface.



Maps of reciprocal space of the (h,l)-plane from the (111) (left) and (110) (right) oriented sample after annealing.

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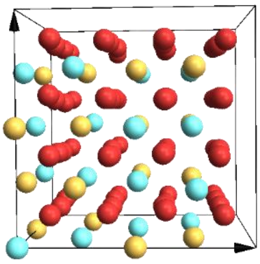
Ab initio investigations of $Zr_{1-x}Ce_xO_2$

CeO_2 based composites have a high oxygen storage-release capacity (OSC). A common CeO_2 based composite that exhibits a very high OSC is $Zr_{1-x}Ce_xO_2$. The highest OSC can be achieved with a Ce to Zr ration of 1, which correspond to an x of 0.5. [1]

$Zr_5Ce_5O_2$ can occur in two different phases. A tetragonal phase, where the Ce and Zr ions are distributed randomly across the crystal and a so called kappa-phase, where the Ce and Zr ions are well ordered. The OSC of the kappa-phase is nearly twice as high as the OSC of the unordered phase. Hence the difference in the formation of oxygen vacancies between these two phases are from special interest. We present results of DFT calculations, where we investigate the electronic and structural properties of these two phases. In particular we focus our investigations on the Raman-spectra.

Furthermore we investigate the electronic and structural properties of $Zr_{1-x}Ce_xO_2$ as a function of the Ce concentration x.



$Zr_5Ce_5O_2$ in kappa-phase

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Structural and Textural Investigations of CeO_2-based Glass-Ceramics synthesized by Crystallization and Leaching of Glasses in the CeO_2-Na_2O-Al_2O_3-B_2O_3 System

CeO_2 is widely used as catalyst and co-catalyst (or support) due to its oxygen storage capacity and oxygen ion conductivity. Applications are investigated for solid oxide fuel cells, as well as catalyst for the, e.g., HCl oxidation [1], CO oxidation [2], soot combustion [3], and dry reforming [4]. Besides chemical properties of the catalyst, also textural properties like porosity and pore size play an important role for applications in heterogeneous catalysis. Various methods exist for the preparation of CeO_2 materials. Nanorods can be produced by electrospinning [1], nanoparticles by hydrothermal synthesis [5], and membranes with controlled porosity by e.g., inverse replication of porous glasses [6].

In this study we investigate a route to CeO_2-based glass ceramics, which comprises the crystallization and leaching of a mixed-oxide silica-free glass. Literature which is dedicated to that topic is rather scarce. Promising results have been published by Res et al. [7] describing a phase separation in the prepared glasses which leads to the occurence of cubic CeO_2. Though, the results are incomplete and have moved out of focus since then. The lack of available literature on glasses containing large amounts of cerium oxide suggests that a study of these glasses would be useful.

Therefore, we prepared different glasses within the CeO_2-B_2O_3-Na_2O-Al_2O_3-system. These glasses were heat treated at different temperatures and time periods and finally subjected to a treatment with water or mineral acids for selective leaching of the soluble phases, thus generating a pore system. The initial materials as well as the leached samples have been characterized by XRF and XRD for the determination of the composition and occurrence of crystalline phases. Furthermore, DTA and dilatometric measurements have been conducted to obtain information on the glass transition and the crystallization temperatures, i.e., Tg and Tcryst. respectively. Finally, the leached samples have been characterized by nitrogen sorption, mercury intrusion porosimetry, and scanning electron microscopy.

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Migration of cation defects in cerium dioxide

CeO_2 serves as a model fluorite-type oxide since it adopts cubic symmetry under ambient conditions without the need for stabilizing substituents in contrast to other notable fluorite-type oxides, such as ZrO_2 and HfO_2. In this study we investigated the migration of cerium ions in CeO_2 by means of static lattice simulations. Activation energies for migration were obtained from classical simulations based on various sets of empirical pair potentials (EPP) and from quantum mechanical simulations employing density functional theory (DFT) calculations. Vacancy, interstitial and interstitialcy mechanisms were considered. In addition, the influence of adjacent oxygen vacancies on cation migration mechanisms was examined, since the defect chemistry of nominally undoped and acceptor-doped systems is dominated by oxygen vacancies. Results show strong indications for a cerium vacancy diffusion mechanism and are in accordance with literature data on other fluorite oxides.

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Electrochemical In-situ IR Spectroscopy on Pt Electrodes: Single Crystals, Metallic Thin-Films, Pt Nanoparticles, and Pt-Doped CeO_2

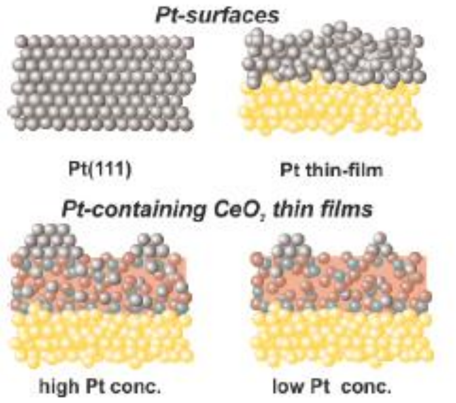
Pt-doped CeO_2 has been identified as a potential novel anode material in proton exchange membrane fuel cells (PEMFC). Providing very high noble metal efficiency, the material may help to decrease the demand for Pt, while simultaneously increasing the tolerance against CO posining. [1]

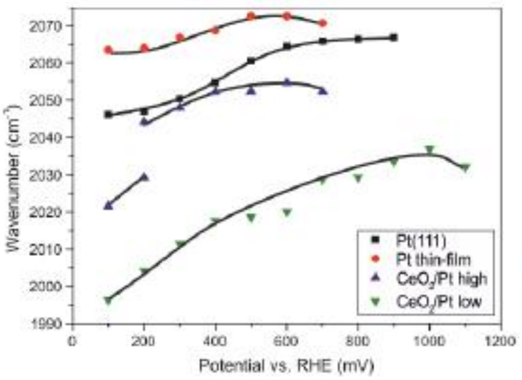
To explore the chemical state of Pt species in the ceria matrix under reaction conditions we apply in-situ electrochemical IR spectroscopy. Towards this am we have set up a new IR spectro-electrochemistry system that includes a state-of-the-art vacuum FTIR spectrometer and an optimized external reflection cell. We demonstrate that the system is functional and provides an excellent signal/noise ratio.

Using this setu, we have investigated methanol oxidation in acidic solution on different Pt catalysts by Substractively Normalizet Interfacial Fourier Transform Infrared Spectra (SNIFTIRS). Using the CO that is formed during the reaction as a probe for the Pt surface sites, we compare Pt(111) electrodes, Pt thin-film electrodes, and Pt- containgin CeO_2 thin-film electrodes with different Pt-concentration. All thin-film samples were prepared by magneton sputtering and characterized by SEM, EDS and cyclic voltammetry. Before measurement we cleaned the surface by potential cycling.

On all samples, the IR spectra in the CO stretching frequency region are dominated by the on-top CO band between 2000 and 2100 cm-1. A slight blue shift is observed for the Pt thin-film sample in comparison to Pt(111). Possible explanations involve the co-adsorption of electron withdrawing species and/or an increased CO density. Most importantly, the rougher surface of the thin-film induces higher reactivity and leads to earlier CO formation, which is also reflected by the more pronounced s-shape of the CO band (Stark shift).

For the Pt-doped CeO2 electrode with the higher Pt concentration two different CO on-top peaks are identified, which can be assigned to edges and terraces. The signals are shifted to lower wavenumbers (red shift) and the oxidation of CO occurs at lower potentials. The Pt-doped CeO_2 electrode with the lower concentration of Pt shows an even stronger red shift and a broadening of the signal. For both Pt concentrations we conclude, that a fraction of Pt^{2+} is reduced to Pt^0 and stabilized in form of nanoparticles. Their size decreases with decreasing Pt concentration.





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Ceria-based Materials and Components for Solar-thermochemical Fuels Production

The ease of transportation and high power density create the basis for hydrocarbon fuels' privileged position in our energy mix. Therefore processes that use renewable energy sources to produce liquid hydrocarbon fuels from H_2O and CO_2 are of crucial importance. Concentrated solar radiation can be employed as the only energy source for the renewable production of hydrogen from water either indirectly, e.g. by supplying the electricity for electrolysis, or directly by supplying the necessary heat for thermochemically producing hydrogen and syngas. Among the various thermochemical cycles tested so far for solar-driven hydrogen production via water splitting, those based on redox-pair oxide systems, are directly adaptable to carbon dioxide splitting and/or combined CO_2/H_2O splitting for the production of CO or syngas, respectively. The Helmholtz Virtual Institute *SolarSynGas* brings together expertise from solar energy research and materials science to develop metal oxide based redox materials and to integrate them into suitable process technologies for such processes. Due to preliminary theoretical studies as well as reported in the literature, ceria-based materials are viable candidate materials for such cycles. In screening campaigns, the performance of ceria was enhanced via doping with zirconium and trivalent lanthanides. The most promising compositions were subjected to equilibrium reduction experiments with the aid of thermogravimetry analysis under varying conditions such as the temperature and the partial pressure of oxygen. Applying a basic reaction model, the thermodynamic properties of the material were determined. Further than that, kinetical parameters such as the chemical surface exchange coefficient and chemical diffusivity of oxygen were determined. Thereby, the basic understanding of interrelations between atomic structure and transport, microstructure, reactivity and life time of the materials is gained, which is crucial for the development of optimized reactor and process concepts based on ceria.

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Structural Studies of $Zr_xCe_{1-x}O_2$ Nanofibers and Bulk Material by Raman Spectroscopy

Ceria based materials are used in various catalytic applications and in solid oxide fuel cell (SOFC) application etc., because of its unique oxygen storage capacities (OSC) and reversible reduction/oxidation of Ce^{4+} to/from Ce^{3+}. Mixing ZrO_2 with CeO_2 is reported to improve the OSC and the thermal properties of ceria. Alloying the two oxides results in more efficient catalytic properties which makes $Zr_xCe_{1-x}O_2$ a good candidate as a catalyst, e.g. for the heterogeneous catalysis process of HCl by oxygen. Mixed oxides in form of 1D nanofibers allow one to assess the morphological stability of the catalysts more easily.

The composition of the mixed ZrO_2 and CeO_2 alloy strongly affects its crystal structure. Pure CeO_2 has a cubic fluorite structure. With the increasing of ZrO_2 in CeO_2, the crystal structure changes normally to various tetragonal phases and finally to a monoclinic phase. With Raman spectroscopy, the crystal structures are studied. By comparing $Zr_xCe_{1-x}O_2$ fibers of various compositions before and after the HCl oxidation, and by comparing fibers which underwent different reaction conditions, we obtained useful information about the impact of the crystal structure and composition of $Zr_xCe_{1-x}O_2$ on its catalytic activity.

A unique metastable kappa phase, κ-$Zr_{0.5}Ce_{0.5}O_2$, which possesses an ordered arrangement of cations is reported to have a further improved OSC and to possess an excellent oxygen releasing ability at low temperatures. κ-$Zr_{0.5}Ce_{0.5}O_2$ can be formed by oxidizing the pyrochlore-type $Ce_2Zr_2O_{7+x}$ at 873K. The complicated synthetic process of the κ-phase $Zr_{0.5}Ce_{0.5}O_2$, its precursors and its derivative phases are also studied by Raman spectroscopy.

The Raman study allows us to optimize $Zr_xCe_{1-x}O_2$ alloy system as a catalyst for recovering HCl waste to pure Cl_2.

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Ordered Mesoporous Thin Films of CeO_2 - ZrO_2 as a promising Model Catalyst in the HCl Oxidation

Selectivity and long-term stability are significant parameters in the evaluation of new catalysts. While high-surface-area materials have the distinction of possessing a high catalytic activity, the morphological investigations of the surface are accompanied by difficulties in terms of using electron spectroscopy. Herein, we present the preparation of ordered mesoporous thin films of pure CeO_2 and ZrO_2 as well as the mixed oxide (mp-CZO).The films were dip-coated from a solution of the respective metal chlorides and the polymer polyisobutylene (PIB). The mesoporosity was introduced by the evaporation induced self-assembly process (EISA). These thin films are promising model catalysts in the HCl oxidation. Therefore, we are able to analyze the structural changes of the mp-CZO surface under the harsh conditions of this model reaction. From these changes the morphological stability of the mesoporous mixed oxides can be deduced.

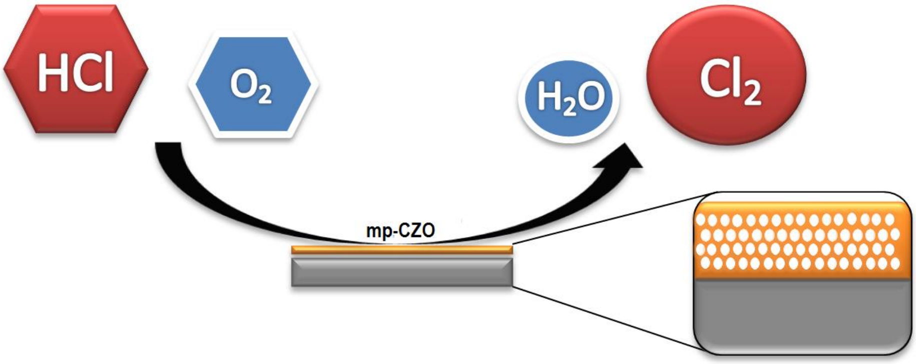

Figure 3: Scheme of the HCl oxidation and their reactants with a mesoporous ceria-zirconia thin film catalyst on a substrate like silicon or sapphire.

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Local structure investigation in ceria-zirconia “κ –phase” by XAFS: unraveling the reason for outstanding oxygen storage capacity

Ceria zirconia solid solutions ($Ce_xZr_{1-x}O_2$, CZ) are well known for buffering oxygen due to fast and easy switch between the oxidation states Ce^{3+}/Ce^{4+} [1,2], showing remarkable oxygen storage capacity (OSC) and, thanks to the presence of the zirconium, increased thermal stability with respect to pure ceria. Hence, CZ is used as catalyst carrier in three way catalysts (TWC) also for their high surface carrier density and as oxygen release material in oxygen deficient atmospheres. In addition to the known properties of ceria, the mixed oxide system has proven to improve the catalytic activity in HCl oxidation (Deacon process)[3] with respect to pure CeO_2.
Particularly interesting among the ceria zirconia solutions is the so-called “κ-phase”.[4] This phase is known to increase the OSC since its high degree of homogeneity, without local enrichments of Ce or Zr, allows oxygen atoms to rapidly move into and out of the lattice. In addition, the ordered arrangement of the Ce and Zr atoms along the <110> direction limits reduction-induced lattice stress.
The exact role of the ZrO_2 in the increase of the OSC, on the other hand, is still debated[5]. The OSC is strongly dependent on the atomic structure of the ceria-zirconia solutions, and it is therefore necessary to have a thorough description of the structural features of these systems. In this regard, Xray absorption fine structure (XAFS) is the method of choice to investigate the local structure around both the Ce and Zr cations and determine the cation-cation network and the oxygen environment around these.
In this framework, we investigated the structural evolution of a series of ceria zirconia solutions characterized by different synthetic approaches and/or thermal history, with the aim of finding the optimal conditions for an easy preparation of the desired “κ-phase”. This evolution was followed by means of both XRD and XAFS measurements, evidencing how the correct thermal treatment is necessary to obtain a homogenous solid solution.

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One-pot synthesis of noble/transition metal-doped CeO_2 nanocrystal assembled spheres

Introduction

The introduction of noble metals or aliovalent transition metals into the CeO_2 matrix can often improve the functionalities of CeO_2-based materials. Here we present a generalized and simple one-pot method to obtain noble metal/transition metal incorporated CeO_2 nanocrystal assembled spheres. This can shed some in-sights in developing novel strategies to fabricate active CeO_2-based nanocatalysts.

Experiment:

Typical synthetic procedure for Pd-CeO_2 spheres: The stocking solution was prepared by dissolving $CeCl_3$ in ethylene glycol. An appropriate amount of Na_2PdCl_4, PVP and co-solvent/surfactant was added respectively. The solution was heated in an oil bath and the product was obtained by centrifugation.

Results:

From the TEM images we can see that the product was monodispersed spheres stacked by ultrasmall nano-crystals. The Pd elements is randomly scattered on the spheres, which is evidenced by HAADF-STEM images. The XRD showed typical peaks of CeO_2.

This method can also well applied to other noble metal or transition metal doped with CeO_2 nanocrystals in one-pot process and the calcined samples showed good catalytic activity in CO oxidation reaction.

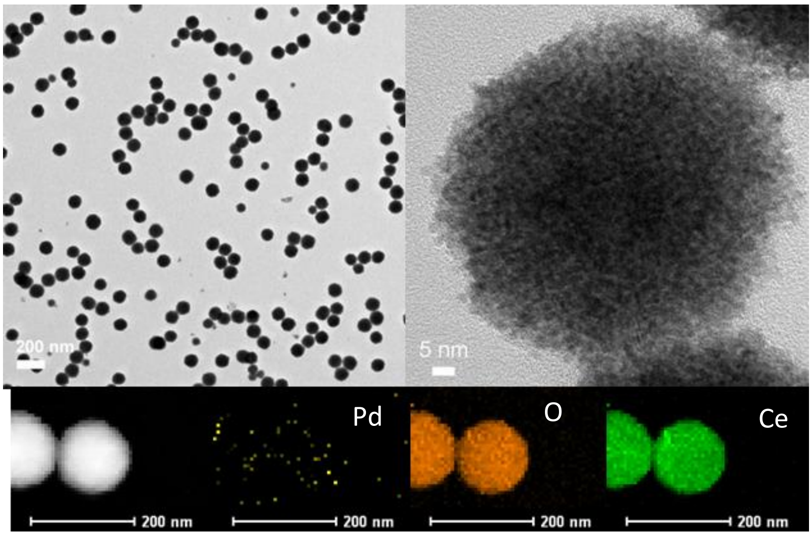

Figure 1. TEM and HAADF-STEM images of Pd-CeO_2 spheres

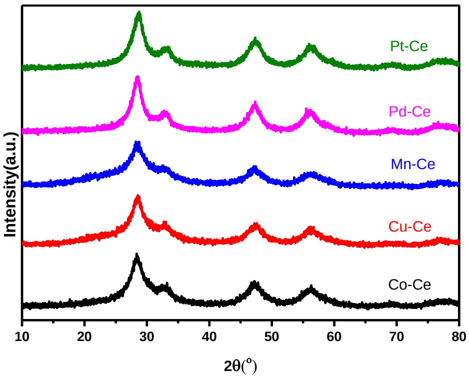

Figure 2. XRD profile of different samples

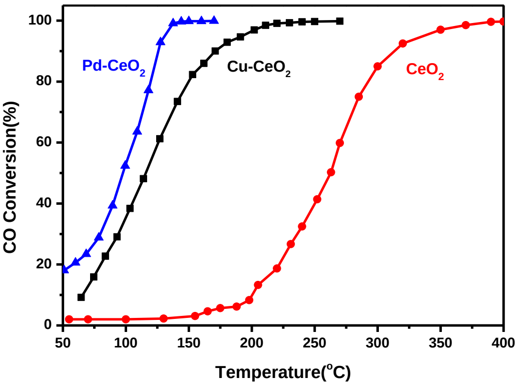

Figure 3. CO oxidation activity of Pd-, Cu-CeO_2 and pure CeO_2

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Conductivity and Relaxation Processes in $Pr^{3+/4+}$ doped Ceria

Acceptor-doped ceria is a well known oxygen ion conductor.[1] However, the growing interest in mixed conducting doped ceria, lead the focus on doping with multivalent $Pr^{3+/4+}$. This dopant is outstanding as it increases the ionic as well as the electronic conductivity. In case of larger amounts of Pr doping (≥2%), polaron hopping between Pr^{3+} and Pr^{4+} leads to a maximum of electronic conductivity in the intermediate oxygen partial pressure range. This phenomenon was investigated in a Hebb-Wagner setup with an encapsulated ion blocking microelectrode. Polycrystalline samples were prepared by sol-gel method and sintered at 1600 °C for 8 h after uniaxial-pressing at 400 MPa. A single crystal with the composition $Ce_{0.85}Pr_{0.14}Zr_{0.01}O_{2-\delta}$ was produced by skull-melting in the facility of TU Berlin. Measurements were performed in voltage range -0.9 to 0.3 V resulting in oxygen partial pressures between $10^{-22.5}$ and $10^{7.5}$ bar. Polycrystalline $Ce_{0.98}Pr_{0.02}O_{2-\delta}$ shows three types of electronic conductivity: $Ce^{3+/4+}$ polaron-hopping, $Pr^{3+/4+}$ polaron-hopping and hole bandmotion, which are dependent on the oxygen partial pressure.

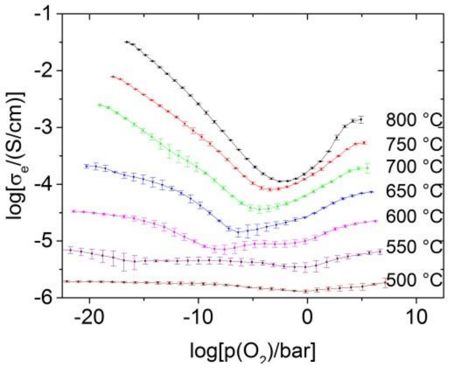

Figure 1. The electronic conductivity dependence on partial pressure of oxygen in polycrystalline $Ce_{0.98}Pr_{0.02}O_{2-\delta}$ at various temperatures.

Kelvin probe force microscopy (KPFM) is a scanning probe microscopy based technique for the measurement of the surface potential. Similar to the ion-blocking micro electrodes, changes in the surface potential can be used to monitor polarization-relaxation processes near the sample surface at low temperatures. KPFM measurements at room temperature on 20 mol% Pr-doped pellets were performed to further investigate the relaxation process after polarization (application of ± 5 V for up to 300 s) with the KPFM measurement tip. Circular shaped domains of changed surface potential were found after polarization, which faded with time.

Acknowledgements

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Three different synthetic methods for $Ce_{0.7}Zr_{0.3}O_2$ catalysts applied in CO and soot oxidation

Introduction Ceria and ceria materials doped with different transition and rare earth metals are intensively studied in literature with respect to their structural and catalytic properties, especially in the field of emission reduction [1]. One reason is that ceria can undergo a redox-switch between Ce^{4+} and Ce^{3+} and, thereby, store and release oxygen to compensate rich and lean exhaust gas compositions. Incorporation of zirconia enhances the catalytic performance by both stabilizing the ceria catalyst against sintering at elevated temperatures and by vacancy formation which leads to an enhanced ion mobility, allowing several layers of ceria to be involved in this oxygen storage process. However, under oxidizing conditions, no clear correlation can be drawn between common characterization results and the catalytic performance under oxidizing conditions. In this contribution we studied three different preparation methods with respect to their surface and textural properties as well as their catalytic performance in oxidation reactions such as the CO and soot oxidation [2].

Experimental Ceria-zirconia catalysts were synthesized by three different methods: Solid Grinding (*SG*), Sol-gel synthesis (*SOL*) and co-precipitation (*CP*). Each batch preparation was split and the as-prepared precursor calcined at 450 and 650 °C yielding six samples in total. Catalysts were characterized by N_2 physisorption (BET/BJH), XRD, Raman spectroscopy, TPR, XPS and CO-OSC puls titration. CO and soot oxidation experiments were performed to study the oxygen activation under oxidizing conditions.

Results and Discussion

We found that the preparation method strongly influences the properties of the catalyst with respect to surface atomic ratios, ion mobility and reducibility, thermal stability and, therefore, the resulting catalytic activity to activate oxygen on the surface. BET/BJH results demonstrated a high thermal stability for the SG and CP, and lower thermal stability for the SOL samples. Powder XRD measured with an internal standard identified Ce-Zr binary oxides by their shift of 2 angles and confirmed a size-relation between particle sizes and lattice parameters. Raman spectra confirm the mainly cubic (*c*) phase with some small contributions of two different tetragonal phases (*t´* and *t´´*) indicating an oxygen displacement [3]. TPR results showed different reducibilities according to structural properties of the catalysts. Supported by the XPS analysis we correlate small specific surface areas and high Zr/Ce atomic ratios found for SOL samples with the weak reducibility observed in TPR and insignificant activity in CO-OSC experiments. Further, the results confirm that the solid-state grinding method is a promising route to produce stable catalysts with good catalytic properties under both oxidizing and reducing atmosphere. Co-precipitation leads to small and stable particles with the highest CO-OSC values among all methods but weak activity for oxygen activation in soot oxidation.

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Characterization of electrochemically deposited thin CeO_2 films

Electrodeposition is widely used for industrial applications to deposit thin films, coatings, and adhesion layers. Herein, CeO_2 thin films were deposited on highly oriented pyrolytic graphite (HOPG) and polycrystalline platinum substrates by cathodic electrodeposition. The influence of deposition parameters on the yield and on film morphologies is studied and discussed. The morphology and composition of the electrodeposited films were characterized by in-situ and ex-situ atomic force microscopy (AFM), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), and X-ray photoelectron spectroscopy (XPS). The AFM results indicate that the thickness of the CeO_2 films strongly depends on the Ce3+ concentration and the deposition time. After exposing the films to ambient air, cracking structures are formed, which were analyzed in detail by AFM. The XPS data indicates formation of stoichiometric CeO_2. Good corrosion resistivity of the CeO_2 films was confirmed for electrochemically deposited ceria on HOPG.

A possible application of above mentioned films involves their use in electro-catalytic layers for methanol oxidation in fuel cells. Therefore the electro-catalytic activity of electrochemically deposited CeO_2 thin films was investigated using cyclic voltammetry (CV). Indeed, Pt doped CeO_2 layers show promising catalytic properties with respect to oxidation rates required potentials.

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New insight into ceria and its defect structure: A combined spectroscopic approach

Ceria is used in many applications like hydrogen production and purification, in exhaust catalysis and as an electrolyte in solid oxide fuel cells. For the comprehension of the underlying reactions it is crucial to understand the properties and reactivity of ceria itself. Many of these applications are based on the ease of oxygen removal from the ceria crystal and the formation of defects.[1-3] In this contribution we report on the properties of synthesized and commercial ceria powder samples. To obtain new insight into the types of ceria defects a combined spectroscopic approach has been applied.

The ceria samples were studied by Raman, Diffuse Reflectance Infrared Fourier Transform (DRIFT) and UV-Vis spectroscopy. Further investigations were done by X-Ray Diffraction (XRD) and by use of the phonon confinement model (PCM). Bulk defects were characterized in the Raman spectra by the ratio of the defect signal intensity (around 540 cm^{-1} and 595 cm^{-1}) to 2LO signal intensity (1170 cm^{-1}).[4] By a combination of XRD and Raman data with simulations using PCM the spectral behaviour (asymmetry, full width at half maximum (FWHM) and position) of the F_{2g} signal (465 cm^{-1}) could be described.[5] Additional information on the ceria bulk structure as well as bulk defects was obtained by UV-Vis spectroscopy. The amount of Ce(3+) in ceria could be correlated with the absorption edge.[6] Insight into surface defects was obtained based on the influence of defects on the spectral position of hydroxyl groups detected in the Raman and DRIFT spectra.[7]

By using a combined spectroscopic approach important characteristics of the synthesized and commercial ceria samples could be determined. In particular, new insight into the ceria defect structure was obtained.

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Performance of CeO_2 prepared by modified precipitation route on dry reforming of methane

Catalytic dry reforming of methane (CH_4+CO_2) to synthesis gas (CO and H_2) has received considerable attention in recent years due to the H_2/CO product ratio close to unity. This is suitable for the liquid hydrocarbon production via Fischer-Tropsch synthesis and, in conjunction with the water-gas-shift reaction lead to the production of H_2 for fuel cell applications. Cerium oxide was suggested as a promising candidate for anode component in Solid Oxide Fuel Cells (SOFCs), due to its catalytic activity in reforming and enhanced resistance against coke formation. The preparation method affects properties such as the surface area, defects concentration and thermal stability. The present work aims at studying the effect of adding H_2O_2 during the synthesis, alone or with cetyltrimethylammonium bromide (CTAB), a template agent, on morphologic, structural and catalytic properties of ceria. The samples were characterized by powder X-ray diffraction (PXRD), scanning electron microscopy (SEM), isotherms of adsorption-desorption of nitrogen at -196 ^oC, thermogravimetric and differential thermal analysis (TG-DTA), Raman spectroscopy, and temperature programmed reduction experiments in CH_4 (TPR-CH_4) or H_2 (TPR-H_2). Catalytic properties in methane dry reforming were investigated in view of the potential use of ceria as SOFC anodes operating on CH_4+CO_2 mixtures such as in biogas.

Samples were all active in the conversion of CH_4/CO_2 mixtures, CO and H_2 being produced. H_2/CO ratios much lower than unity were obtained. This was explained by the contribution of the reverse water gas shift reaction which becomes predominant above 850 °C in the experimental conditions used. Table 1 shows methane conversion rates at 900 °C in stoichiometric and oxidizing conditions.

Table 1. Comparison between the surface areas of the CeO_2 powders calcined at 900 °C and the specific methane conversion rates obtained at 900 °C in CH_4/CO_2 reaction mixtures

Sample	CH_4 consumption rate (mmol/h.g)		Surface area (m^2/g)
	Stoichiometric	Oxidizing	
CeO_2	5.6	4.0	5.6
CeO_2_CTAB	5.2	3.4	7.6
CeO_2_H_2O_2	6.8	4.6	13.7
CeO_2_CTAB_H_2O_2	6.7	4.5	20.1

The improved methane conversion in the presence of CeO_2_H_2O_2 compared with CeO_2_pp and CeO_2_CTAB_pp can be only partly correlated with higher surface areas, but most probably due to improved bulk redox properties when alternating between oxidizing and reducing treatments and resistance to deposition of graphitic carbon. As the presence of Ce^{3+} (O vacancies) at the surface was evidenced by Raman measurements, the distribution of Ce^{3+}/Ce^{4+} throughout the ceria surface could be a possible factor influencing the catalytic behavior.

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Resonant Inelastic X-ray Scattering on ceria thin films during reduction/oxidation processes

Cerium oxide is a promising material for applications in different fields because of its unique properties. It is able to store, transport and release oxygen depending on the ambient conditions, and therefore it is the subject of studies in view of its application in catalysis, fuel cells, memories and energy conversion. However a complete understanding of the mechanisms responsible of these properties is still missing. The ease with which cerium ions reversibly switch their oxidation state from 3+ to 4+ is currently a matter of debate and it is of great interest in order to optimize materials based on cerium oxide. At the origin of this behavior there is clearly its particular electronic structure that is linked to the crystal structure. Therefore, a deep study of the rearrangement of the electronic configuration during oxidation and reduction processes is necessary [1].

In the last few years we have studied cerium oxide in the form of ultrathin film [2,3]. It was shown that cerium oxide, with the CeO_2 stoichiometry (the so called ceria), can be grown epitaxially on the (111) surface of Pt single crystals. Heating treatments in ultrahigh vacuum or in oxygen-rich atmosphere respectively induce controlled reduction or oxidation [4].

Resonant Inelastic X-ray Scattering (RIXS) technique allows to understand how the electronic structure of ceria-based materials evolves when oxygen vacancies are formed. RIXS is an innovative high-resolution technique particularly suited for the investigation of lanthanide systems [5]. The use of spectrometers both on the incident and on the emitted radiation gives the opportunity to excite a particular electronic transition of the studied material and to measure the response at a specific decay channel. The increased resolution of the emission spectrometer analyser compared to common fluorescence detectors used in normal XAS results in highly resolved spectral features, which give more accurate information that are not accessible when measuring in total fluorescence yield.

High-Energy Resolution Fluorescence Detected (HERFD) XANES measurements on ceria films of different thickness and morphology were performed at the ID26 beam line of ESRF (Grenoble). Tuning the incident energy at the Ce L3 edge and the emitted photon spectrometer at the energy of the Lα1 fluorescence line (i.e. $3d^{5/2}$-$2p^{3/2}$ transition) we checked the evolution of Ce electronic structure during reduction/oxidation processes. The pre-edge region (i.e. 2p-4f transitions) gives specific information on the 4f electronic configuration, while the post-edge region shows the evolution of the 5d band which is directly related to the modification of the Ce oxidation state. We also measured two-dimensional RIXS maps (scanning both incident and emitted photon energies) to obtain additional information about the electronic correlations in the excited state at different degree of reduction.

We used this high-resolution technique on ceria film characterized by different thickness and morphology to better understand the charge compensation mechanisms during reduction and oxidation cycles, with the aim of improving the knowledge of ceria-based material.

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Interfaces in Ceria: Cation Reduction and Mobile Charge Carriers Concentration Redistribution

The ability of reducing cerium cations and the possibility of obtaining acceptors solid solutions over a broad compositional range make ceria a key material for applications such as catalysis and oxide fuel cell electrolytes. For both oxygen exchange and electrical transport properties, the full understanding of the charge carrier chemistry is crucial. Interestingly, while the bulk defect chemistry of ceria has been extensively investigated and the bulk charge carrier concentrations can be accurately predicted (as far as temperature, oxygen partial pressure and dopant concentration are known), the concentration of mobile charge carriers at interfaces (e.g. grain boundaries in ceramics or interfaces in thin films) can deviate drastically from the boundary-free bulk situation. In the case of grain boundaries, this can be often rationalized in terms of space charge effects arising from a positive excess charge in the grain boundary core.

In the present contribution, a selection of fascinating since rather unexpected effects are illustrated, which emphasize the relevance of interface/boundary effects on the overall electrical transport properties of this material particularly at the nano-scale: (i) a significant electronic conductivity in nanocrystalline fully dense, heavily acceptor-doped thin films ($Ce_{0.9}Gd_{0.1}O_{1.95}$) under oxidizing conditions and at temperatures as low as 280 °C; (ii) blocking grain boundaries in donor-doped CeO_2 films; (iii) the enhanced electron concentration at the interface between epitaxial ceria films and zirconia substrate; (iv) low temperature ($T < 250$ °C) proton conduction in mesoporous samples under wet conditions. All these examples indicate that in addition to dopant, oxygen partial pressure and temperature also interfaces have a profound impact for the determination of the effective mobile charge carrier chemistry and thus could be exploited as novel adjusting screw to set the transport properties of this material.

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Defect association in doped non-stoichiometric ceria from first principles

Rare-earth oxide doped ceria is a promising candidate for the application as electrolyte in solid oxide fuel cells (SOFC). The efficiency of SOFCs strongly depends on the oxygen ion conductivity of the electrolyte. Furthermore, its reduction and degradation affect the performance of the cells. Computational methods provide valuable tools for the investigation of properties like defect formation, defect distribution and conductivity on a microscopic length scale. By utilizing these methods microscopic mechanisms can be analyzed and macroscopic properties predicted.

We combine density functional theory calculations and Monte Carlo simulations to investigate the defect distribution in doped ceria under oxidizing and reducing conditions. Major defects in doped stoichiometric ceria are oxygen vacancies and dopant ions. Reduction leads to localization of excess electrons at cerium ions, so called small polarons.

We calculate the energy of association for defect pairs in bulk ceria including interaction between dopant ions, oxygen vacancies and polarons by means of DFT+*U*. The association energy between trivalent cations and oxygen vacancies shows a clear dependence on the cation radius (Fig. 1). As a consequence, polarons prefer the next nearest neighbor (NNN) position to oxygen vacancies rather than the nearest neighbor (NN) position as suggested experimental observations.[1]

The equilibrium distribution of defects in doped stoichiometric and non-stoichiometric ceria is simulated applying the Metropolis Monte Carlo algorithm with the calculated association energies. The resulting coordination numbers are in remarkable agreement with experimental data.[2] Above all we find a decrease of the lattice energy due to defect interaction in doped non-stoichiometric ceria which enhances the reducibility with increasing dopant fraction.

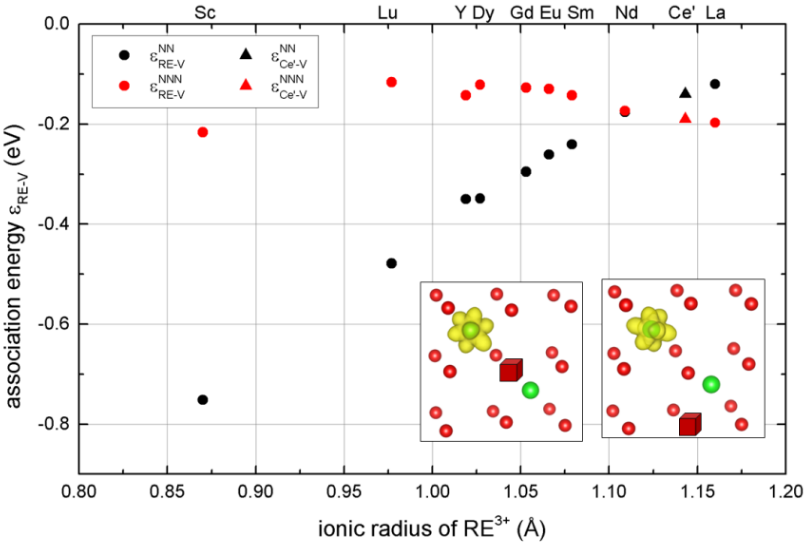

Figure 1: Energy of association between a trivalent cation and an oxygen vacancy in ceria in NN (black) and NNN (red) position for dopant ions (circles) and polarons (triangles). The insets show the magnetization density of a polaron in NN (left) and NNN (right) position to the vacancy (red box).

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Surface X-ray diffraction as a tool for the oxide surfaces characterization

Surface X-ray diffraction (SXRD) allows the exact structural determination of surfaces, interfaces and thin films. In comparison with other diffraction surface sensitive methods, like electron or helium atom diffraction, the main advantage of SXRD is capability to penetrate deeply into matter allowing the investigation of different types of materials, including insulators, in conditions ranging from UHV to high pressure or in liquid environment. SXRD is frequently used in the characterization of oxide surfaces, allowing to obtain information about crystallographic structure and morphology of thin oxide films, *in situ* monitoring of their growth, or buried interfaces allowing the comprehension of the peculiar electronic properties shown oxide interfaces. The ID03 beamline, which is part of ESRF, offers ideal conditions for the fast characterization of the oxide surfaces in different environments, thanks to the high brilliance synchrotron X-ray beam, use of highly sensitive 2D detectors, and the recently developed software for the fast analysis of collected data. Its access is open to the European community and aim of this contribution is to provide some examples focused to the structural determination of oxides surfaces and interfaces.

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Method for clean transfer of UHV-prepared samples to the electrolyte solution

We have used previously described method for clean transfer of samples from UHV to electrolyte solution to relate STM images in UHV with electrochemical AFM measurements on the same sample. CeO_x/Pt(111) sample was prepared in UHV and characterized with STM. Then the chamber with the sample was filled with inert gas (Ar), the sample surface was covered with a drop of ultrapure water (Type I) and the sample was taken out of the chamber and inserted into the electrochemical AFM cell. No changes in surface morphology were observed in the following AFM measurements.

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The influence of aging and humidity on transport properties of ceria thin films at low temperatures

Cerium oxide has been frequently studied as a model system for the class of mix ionic electronic conductor (MIEC) with fluorite structure. High surface area nanocrystalline CeO_{2-x} is an exceptional catalyst for redox reactions. It is one of the most studied compounds for oxygen-ion incorporation. Further, there has been growing interest in CeO_2 as an interface material for silicon on insulator (SOI) applications.

The microstructure of the CeO_{2-x} thin films strongly affects their electrical properties, as space charge zones within the grain boundaries influence the ionic and electronic conductivity. For electronic conduction, parallel space charge zones bypass the bulk conductivity due to accumulation of electrons. Due to the same space charge zones oxygen vacancies are strongly depleted in the grain boundaries, resulting in an conduction pathway via the bulk resulting in large boundary resistances due to serial depletion zones.[1] Especially at high temperatures, the microstructure might undergo changes during long-term electrochemical impedance spectroscopy (EIS) measurements, due to crystallite growth or aging effects.

Additionally the influence of water on the conductivity of nanostructured ceria at low temperatures due to proton conductivity was reported. The origin of the enhanced proton conductivity is still controversial.[2]

We present results on PLD deposited ceria thin films, which were investigated according to the change of their microstructure via XRD, SEM and EBSD under thermal treatment.

Further, we present studies on the electrical response via EIS measurements at moderate temperatures and various humidities, showing no significant enhancement of the conductivity except for temperatures below 50°C for nanocrystalline thin films.

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Characterization of microfabricated free-standing GDC membranes

Doping ceria with gadolinium leads to the formation of oxygen vacancies which significantly improves the ionic transport properties of ceria. As the oxygen ion conductivity of gadolinium-doped ceria (GDC) is even higher than that of the widely used yttria-stabilized zirconia, GDC is one of the most important solid electrolytes for technological applications, especially for solid oxide fuel cells (SOFC). Considering GDC as solid electrolyte in SOFCs, the operation temperature typically lies in the temperature range between 500 °C - 800 °C to ensure high ionic conductivity. Decreasing these high temperatures is desirable in order to improve device stability, life time and to extend the application of SOFCs to portable devices. One way of reducing the operating temperature of SOFCs is miniaturization, i.e. the reduction of the electrolyte thickness.

Here, we report on the fabrication of free-standing GDC membranes on micro-structured Si substrates. For the fabrication a GDC thin film was deposited by sputtering and then etched free by different steps of photolithography and wet-chemical etching. Depending on the window size the fabricated membranes with a lateral edge length between 10 µm to 40 µm show different buckling patterns, which are caused by tensile and compressive strain in the membrane. Optical light microscopy and Raman analysis were performed in order to characterize the strain of the free-standing membranes. For the characterization of the transport properties, electrical contacts were prepared in an additional micro-fabrication step. Using electrochemical impedance spectroscopy the total conductivity will be investigated.

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Novel catalysed gasoline particulate filter formulations based on Mixed ionic-electronic conducting catalysts

Future changes in Europe regulation (Euro 6c in 2017) concerning particle matter (PM) abatement will probably lead to the implementation of filter devices in direct injection gasoline (GDI) engines. Catalyzed-Gasoline Particulate Filter (cGPF) can be combined with conventional three way converter (TWC) to meet pollutants standards. Recently, electro-promoted nano-dispersed catalysts for vehicles exhaust after-treatment is getting growing attention since they can combine electrochemical promotion of catalysis and high metallic active site availability. Nano-cell catalysts are composed of nano-electrodes (two different natures of metallic nanoparticles) supported on a mixed ionic-electronic conductor (MIEC). This study reports the preparation and catalytic performances of MIEC based-cGPFs for GDI exhaust treatment. Catalysts were composed of Pd and Rh nanoparticles dispersed on gadolinia-doped ceria (CGO), a mixed oxygen-electronic conductor. These materials have been washcoated in SiC mini-GPFs equipped or not with a filtration membrane (Table 1). Catalytic activity measurements have been performed independently in lean and rich feed conditions for different catalyst loadings and locations inside mini-cGPFs. Finally, the impact of PM on catalytic performances has been explored.

Table 1. Characteristic of the tested GPFs **cGPF**	**Catalyst loading in porous walls / g/L**	**SiC Filtration Membrane**	**Catalyst loading onto the membrane/ g/L**
Config 0	86	No	-
Config 1	-	Yes	12
Config 2	80	Yes	12
Config 3	80	Yes	12 (only CGO)
Config 4	80	Yes	-

Figure 1 displays catalytic results (NO reduction and CO oxidation) together with the filtering efficiency in lean operating conditions (O_2/CO/CO_2/NO/C_3H_6/C_3H_8/H_2O : 1 vol.%/ 6000 ppmv/ 14 vol.%/ 740 ppmv/ 1125 ppmv/ 375 ppmv/1%). Differences between samples are only significant at high conversions since the commercial mini-TWC placed upstream cGPFs is very active. The maximum CO conversion was reached in a short temperature interval (250-280 ºC). All the samples showed high performances for NOx conversion, especially those equipped with a catalytic layer on the filtration membrane such as Config 2. This can be attributed to a higher availability of catalytic sites. The filtration membrane has a strong impact on the filtering efficiency (Fig. 1C). Furthermore, in a lesser extent, the presence of catalyst in the porosity of the membrane also improves the soot filtration. On the other hand, the higher the catalyst loading, the higher the pressure drop.

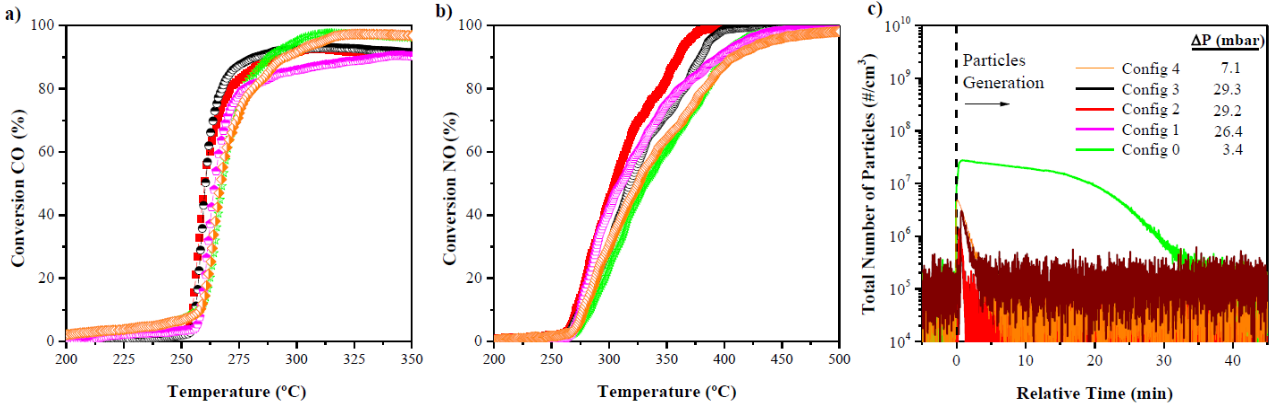

Fig. 1. Catalytic results of the different c-GPFs: a) CO conversion, b) NO conversion and c) Particles number

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Manipulating grain boundary impedance by using doping strategies

In the past decades, doped/co-doped CeO_2 has been investigated for its use as SOFC electrolytes, anode additive, in catalysis etc. However, there are lots of possibilities to manipulate the properties of CeO_2 by various doping strategies as well as by composites with other materials. Especially, composites open the possibility of including the properties of two or more materials in one single material. A recent study will be described here with two examples: i) CeO_2-Na_2CO_3 as an improved electrolyte and ii) CeO_2-ZrO_2-Na_2CO_3 composites as a possible mixed conducting electrode material. The examples demonstrate the potential of a careful design by doping strategies.

(i). The composite CeO_2-Na_2CO_3 is developed with the aim to produce an efficient and low cost solid oxide fuel cell (SOFC) electrolyte material for application at low temperatures. It includes calcia doped ceria with Ca^{2+} substituting part of the Ce^{4+} ions as base material and Na_2CO_3 as an additive phase. Na_2CO_3 mainly accumulates at the grain interfaces during sintering and thereby forms an amorphous percolation network surrounding the ceria particles. This percolation layer remarkably enhances the grain boundary conductivity and hence, increases the net total conductivity by a factor of 25 at 300 °C. The amount of calcia dopant was optimized at the composition $Ce_{0.95}Ca_{0.05}O_{2-\delta}$. After subsequent optimization of the amount of Na_2CO_3 (at 20 wt%), the net total conductivity was increased by a factor of 10 to 25 with respect to the Na_2CO_3 free $Ce_{0.95}Ca_{0.05}O_{2-\delta}$. Which clearly was identified by a remarkable decrease in grain boundary resistance down to very low frequencies (10 mHz). Hence, it resulted from an enhanced oxygen ion transport through the grain interfaces favoring its usage as an electrolyte material in SOFCs. Although the detailed mechanism of the oxide ion transport is under debate, the very probable participation of the carbonate phase suggests that carbonate ions act as net O^{2-} carriers (vehicle mechanism). This does not exclude a possible additional role of water and participation of proton mobility at medium and low temperatures. The ionic mobility of univalent Na+ ions may be advantageous, as the other carbonates such as $SrCO_3$, $BaCO_3$ do not show the same enhancement effect as Na_2CO_3.

(ii). The second composite (the three phase system CeO_2-ZrO_2-Na_2CO_3) was developed with the aim to produce a mixed ionic-electronic conductor (MIEC) useful for their application as cathode or anode additive in SOFCs. As a first step, a two phase system consisting of Ta5+ doped ceria (3 mole%) as electronic conductor and YSZ as oxygen ion conductor was prepared. Its overall conductivity was lower than that of each of the two separate constituents. This can be attributed to a highly resistive interface between the ceria and zirconia particles. In order to decrease this interface resistivity, in a first attempt the electronic resistance was reduced by CoO as an additional additive (1 mol%). A further reduction of the grain boundary resistivity was achieved (again as in i) by adding Na_2CO_3 followed by annealing. We attribute this to an additional improvement of the ionic part of the grain boundary conductivity. The results overall showed a nearly 10 times higher conductivity with Co^{2+} and a nearly 10 000 times higher conductivity after Na_2CO_3 addition in the final Ce(Ta)O_2-YSZ composite. Hence, the use of both CoO and Na_2CO_3 as additives lead to a greatly optimized mixed conducting ceramic composite with a remarkably increased net conductivity for ions and electrons in the intermediate temperature range.

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Surface properties of CeO_2(111) within kinetic montecarlo simulations

Recently Kullgren and coworkers claim a incompatibility between density functional theory (DFT) and experimental results of Esch about the density and structure of the vacancies for the surface (111) of CeO_2 under UHV condition and they assume that the claimed oxygen vacancies are in fact fluorine impurities. In order to examine the possibility of a significant fluorine contamination we perform a twice investigation of the ceria surface within kinetic Montecarlo simulations. Firstly, assuming the formation of vacancies and neglecting fluorine impurities we confirm that this possibility is incompatible with the relevant DFT results, even if microscopic dynamics is considered. Secondly, we investigate the competition between fluorine and oxygen vacancies finding a direct correlation between fluorine and vacancies concentration. This may suggest, that, in this simplified scenario, the absence of vacancies and the presence of fluorine only should be unlikely.

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Combining two redox active rare earth elements – electrical properties and defect chemistry of praseodymium-doped ceria single crystals

The combination of good electrical conductivity with high oxygen storage capacity (OSC) at intermediate temperatures qualifies the redox active material ceria and its doped analogues for utilization in different electrochemical applications, such as catalysis, solid electrolyte fuel cells (SOFC) and oxygen membranes. By choosing the type and range of doping, electrical properties can be adjusted in various ways. Therefore a precise knowledge of the transport behavior of doped oxides at intermediate temperatures and different oxygen partial pressures is necessary to design compatible defect models. Many doped systems of ceria have already been investigated in their polycrystalline state. Especially co-doping with praseodymium is attractive as it enhances the redox activity, oxygen storage capacity and oxygen surface kinetics of the material. Within this work single crystals of praseodymium-doped ceria have been investigated to get a better understanding of the influence of co-doping on transport processes in bulk material, i.e. without the influence of grain boundaries. Beside the characterization of structural changes caused by doping using XRD and Raman spectroscopy, investigations of electrochemical transport properties of the Pr-doped ceria single crystals have been realized. Measurements of the total electrical conductivity, the ionic transference number and the non-stoichiometry of $Ce_{0.85}Pr_{0.14}Zr_{0.01}O_2$ were performed in an oxygen partial pressure range of $-25 < \lg(pO_2) < 0$ for temperatures between 500 °C and 800 °C. With praseodymium being redox active itself, higher values of oxygen deficiency and electrical conductivity than in pure ceria have been observed at high oxygen partial pressures, while no significant structural changes occur due to the similar ionic radii of both cations.

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Synthesis and physicochemical characterization of $Ce_{1-x}Gd_xO_{2-\delta}$: A case study on the impact of the oxygen storage capacity in the HCl oxidation reaction

In order to be able to understand the results of catalytic tests the catalyst material needs to be properly characterized. This is of utmost importance for mixed oxides as a segregation of the phase has to be excluded. The present study reports the sophisticated synthesis of high surface area $Ce_{1-x}Gd_xO_{2-\delta}$ (CGO) fibers used as catalysts for the oxidation of HCl. Special emphasis is put on the role of oxygen storage capacity (OSC) of Gd-CeO_2 on the catalytic performance. An in-depth physicochemical characterization of high surface area Gd-CeO_2 was achieved by employing a multitude of dedicated spectroscopic techniques.

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$Ce_{1-x}Zr_xO_2$ catalysts for the liquid-phase DMC-synthesis: The influence of the preparation method

Introduction

$Ce_{1-x}Zr_xO_2$ mixed oxide solid solutions are highly interesting materials for catalytic applications due to their chemical and structural properties. However, these properties are strongly influenced by the chosen preparation method.

For instance, Tomishige and Ikeda reported that materials based on ZrO_2 and CeO_2 seem to be suitable catalysts for the liquid-phase synthesis of dimethyl carbonate (DMC) from methanol and CO2 [1]. Current DMC synthesis routes require toxic and corrosive chemicals. Therefore, alternative methods such as direct synthesis from CO_2 and MeOH in the liquid-phase ($CO_2 + 2\ MeOH \rightleftharpoons DMC + H_2O$) have to be developed.

$Ce_{1-x}Zr_xO_2$ mixed oxide solid solutions are promising systems with acid and base properties that can be tuned by the choice of composition and preparation method. The present contribution deals with the preparation and extensive characterization of different Ce-Zr mixed oxide applied as catalysts in the liquid-phase DMC synthesis.

Experimental

The cerium/zirconium mixed oxides were synthesized using three different precipitation agents: i) sodium hydroxide, ii) sodium carbonate and iii) urea. $Ce(NO_3)_3{*}6H_2O$ and $ZrO(NO_3)_2{*}H_2O$ were used as the cerium and the zirconium source, respectively. Different $Ce_{1-x}Zr_xO_2$ mixed oxides with varying Zr contents (0, 10, 30, 50, 70, 90, 100 mol%) were synthesized.

Coprecipitation was performed in an automated reactor system with pH 10 and temperature control (RT). After precipitation, the precipitate was aged for additional 2 h in its mother liquor.

For homogeneous precipitation, a solution containing urea and the appropriate amounts of the metal nitrates was heated up to 95 °C (2 °C/min) leading to an increase of the pH value (7-8) due to the thermal decomposition of urea. The precipitates were dried at 105 °C for 24 h followed by calcination in air at 490 °C for 3 h. All samples were thoroughly characterized with respect to their bulk and surface properties by X-ray diffraction (XRD), Raman spectroscopy, N_2 physisorption (BET method), thermal analysis (TG), and temperature-programmed desorption (NH3- and CO2-TPD).

Results and Discussion

X-ray powder diffraction revealed that Ce-Zr mixed oxides were successfully obtained by coprecipitation with NaOH (Fig.1.). The XRD patterns reveal the presence of phase-pure $Ce_{1-x}Zr_xO_2$. Shifting of the reflexes toward higher 2θ values with increasing Zr amount is caused by the gradual replacement of Ce^{4+} cations by smaller Zr^{4+} cations according to Vegard's law. In contrast, separate CeO_2 and ZrO_2 phases were observed for samples prepared by coprecipitation with Na_2CO_3 as well as by homogeneous precipitation with urea.

The results show that coprecipitation with NaOH provides a suitable method to prepare $Ce_{1-x}Zr_xO_2$ mixed oxides with tunable surface properties which can be further optimized for their application as catalysts in the liquid-phase DMC synthesis

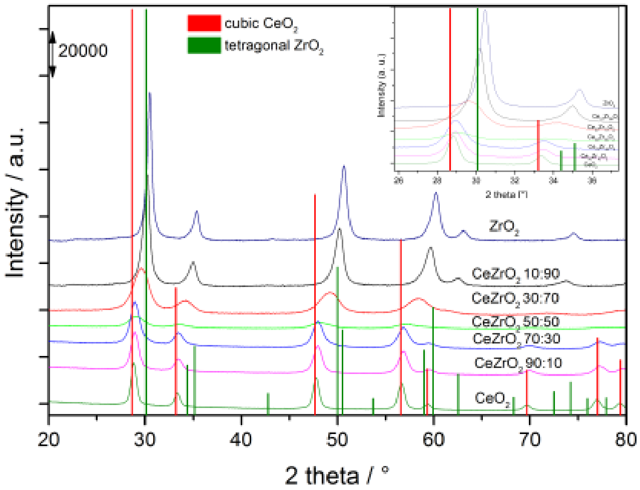

Fig.1. Powder XRD patterns of the pure and mixed oxides precipitated with NaOH

Acknowledgements

This work is supported by the Cluster of Excellence RESOLV (EXC 1069) funded by the Deutsche Forschungsgemeinschaft

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Ceria on Cu(110): formation of nanostripe strain defects

The growth morphology and atomic geometry of ceria nanostructures on Cu(110) have been investigated by STM, LEED, XPS, and DFT calculations. Ceria grows epitaxially in a two-dimensional (2-D) hexagonal layer, which is associated with a CeO_2(111)-type trilayer structure forming a (3x11) coincidence lattice. An important experimental parameter is the oxygen pressure during growth: it influences the stoichiometry of the ceria overlayer as well as the Cu surface oxide phase, which coexists with the ceria for coverages below the full monolayer. For oxygen pressures in excess of 10^{-7} mbar, stoichiometric CeO_2 and coexisting CuO-c(6x2) surface oxide are formed, whereas for lower oxygen pressures, in the 10^{-8} mbar range, slightly substoichiometric ceria ($CeO_{\sim 1.9}$) and a CuO-(2x1) surface oxide are observed. The DFT + U calculations have been performed on a somewhat simplified (3x2) overlayer lattice. They reveal that the most stable situation is a single CeO_2(111)-type trilayer on a strongly reconstructed Cu-O interfacial layer. The measured STM height of the ceria overlayer with respect to the substrate depends on the bias voltage, but converges to ~ 4.25 Å for bias values beyond the ceria conduction band edge. This is compatible with the geometry parameters derived from the DFT model. The ceria overlayer grows essentially 2-D, but displays a peculiar nanostripe pattern, with varying periodicities ranging from 4-8 nm and a corrugation amplitude of 0.2-0.3 nm. This nanostripe pattern is interpreted as due to a topographic modulation of the overlayer, caused by the frustration of the overlayer-substrate bonding as a result of the epitaxial mismatch at the ceria-Cu interface, as it has been postulated recently for a 2-D NaCl layer on Cu(110) [1]. Detailed STM investigations with ultrahigh resolution reveal that the ceria lattice is distorted in the transition region between dark (low) and bright (high) stripes, which gives rise to periodic regions of anisotropic lattice strain - so called "lattice strain defects". It is speculated that these lattice strain defects may support a particular surface chemistry.

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Microelectrode-EIS for the investigation of electrode kinetics of solid electrolytes

The oxygen reduction and exchange kinetics at the electrode solid electrolyte interface are important parts of energy conversion devices like SOFCs and sensor systems like Lambda probes. To address the question of geometry dependent interface resistances and energy barriers quasi-reference-free impedance spectroscopy measurements with model type microelectrodes are promising.

These microelectrode measurements were successfully performed on YSZ as solid electrolyte[1]. In this system, the concentration of the Yttrium dopant exhibits a direct impact on the oxygen exchange kinetics[2]. Based on these results it is planned to apply the microelectrode impedance measurements to CeO2-based solid electrolytes to quantify the impact of the chemical nature and concentration of dopants on the oxygen exchange kinetics.

To establish the microelectrode technique we prepared in a first step the wellknown Pt/YSZ system using pulsed laser deopsition. The Platinum was ablated onto single crystalline YSZ discs at substrate temperatures of 500 °C to produce dense and highly crystalline thin films. The films were microstructured using photo lithography and ion beam etching. The resulting electrodes are of cylindrical shape with a diameter of 100 µm.

Impedance spectroscopy measurements were performed through the crystal using a full area pasted counter electrode at the backside of the crystal. The microelectrode geometry ensures, that the charge transfer resistance is the dominant contribution to the cell impedance. Furthermore, due to the high potential drop at the microelectrode interface only the area of the microelectrode contributes to the cell impedance. Hence, non-ideally shaped electrolytes can be measured quasi-reference-free.

The resulting impedance spectra exhibited three contributions: A high frequency semi circle, whose resistance corresponded to the ionic conductivity of YSZ, a mid-frequency semi circle which was attributed to the oxygen exchange reaction and an non-ideal low-frequency arc, whose physical equivalent could not be assigned unambiguously and which will be subject of further investigation.

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Grain orientation in CeO_2 thin films after high temperature treatment

Cerium oxides are widely investigated materials in the class of mixed or ionic conductors. Doped CeO_2 thin films have applications in redox reaction catalysis, as solid electrolytes for SOFCs, and as oxygen sensors due to the ability of ceria to change its oxidation state and thus allow oxygen transport. The catalytic capability of CeO_2 thin films varies with the surface structure, whose orientation strongly depends on the crystal orientation of the substrate as well as the processing parameters like growth rate, temperature, and oxygen partial pressure. Thus, it is important to understand the morphological changes of cerium oxide surfaces due to external conditions.

In the work presented here, thin films of nominally pure CeO_2 were deposited on single crystalline (0001)-sapphire substrates via pulsed laser deposition. In order to investigate the influence of high temperature treatment on the crystal orientation electron backscatter diffraction and X-ray diffraction were performed on the CeO_2 thin films after annealing at 1000 °C and 1500 °C. The grain size and surface morphology of the samples strongly differ depending on the heating procedure. Contrary to expectations almost no pure (001)- or (111)-orientation of grains at the surface could be observed. Nevertheless, one of both orientations is favored on each sample, i.e. the orientation of most grains has a deviation of 20 degree or less from perfect (001)- or (111)-orientation, respectively. In accordance to literature XRD measurements show a (111)-orientation or a mixture of (111)/(001)-orientation of the grains, but do not always correspond to the domination grain orientation obtained by EBSD.

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Synergic effect of $CePrO_x$ and Cu/$CePrO_x$ physical mixture for soot oxidation

Introduction

Soot particles are formed as undesired by-product in combustion processes, being one of the main pollutants emitted by diesel engines together with NO_x, CO and unburned hydrocarbons. A vast amount of catalysts have been reported to accelerate soot combustion [1]; among them ceria-based catalysts have been proposed as promising substitutes of platinum catalysts, as a result of the extremely good soot oxidation temperatures displayed [2-4]. In particular the doping of ceria with praseodymia enhances the physicochemical properties and catalyst reducibility [5,6]. During recent years, improvement of ceria-based materials properties has been carried out by doping ceria and loading more economic metals to the support, but the synergic effect of a physical mixture of two kind of catalysts, one with a metal loaded and the other without, in order to obtain two different active sites has not been reported. Therefore the objective of this work is to study the existence of a synergic effect on a physical mixture of 5%Cu/$Ce_{0.5}Pr_{0.5}O_x$ and $Ce_{0.5}Pr_{0.5}O_x$ used for soot oxidation.

Materials and Methods

Six catalysts were used in this study, consisting of different mixtures of 5% Cu/$Ce_{0.5}Pr_{0.5}O_x$ and $Ce_{0.5}Pr_{0.5}O_x$. Catalysts are referred to as xCuCePr, where x is the wt. fraction of 5%Cu/$Ce_{0.5}Pr_{0.5}O_x$ in the physical mixture. Cerium and praseodymium nitrate precursors were mixed in an agate mortar to obtain Ce0.5Pr0.5Ox after calcination at 500 ºC for 3 h (heating rate 10 ºC). Copper loading was carried out by incipient wetness impregnation to obtain 5 wt.% Cu using the proper amount of $Cu(NO_3)_2 \cdot 2.5H_2O$ (Sigma-Aldrich 98%).The catalysts were characterized by XRD, Raman Spectroscopy, N_2 adsorption, H_2-TPR and XPS. The catalytic activity for the combustion of soot was determined from peak-top temperature (Tm) during temperature programmed oxidation (TPO) of catalyst–soot mixtures using 500 ml/min gas flow (10% O_2 or 500 ppm NO and 10% O_2 with N_2 as balance). Each catalyst was accurately mixed with soot (Printex-U soot by Degussa AG) in diverse manner in order to achieve loose or tight contact. A catalyst/soot weight ratio of 20:1 to 4:1 was adopted. In addition, as a measure of activity we used the temperature at which 50% of weight loss is observed (T50, corresponding to removal of 50% of soot) by running TGA experiments using an air flow (60 ml/min) tangent to the sample.

Results and Discussion

Figure 1 shows the soot conversion results obtained for the optimum catalyst mixture (0.6CuCePr) and for those with the highest (CuCePr) and lowest (CePr) copper amount. The onset temperature for soot combustion is lower with 0.6CuCePr confirming a synergic effect between CePr and CuCePr sites. Together with the characterization (not included for brevity) these results shows that activity in CuCePr is closely related to NO oxidation to NO_2, while Cu-free CePr sites play an important role in the direct oxidation of soot with active oxygen species coming from gas phase oxygen. However, it is shown that copper hinders the active oxygen soot combustion mechanism and therefore, the two sites, must be located on different particles. In addition the study confirms the existence of two different mechanisms: i) soot combustion by active oxygen and ii) NO_2-assisted soot combustion.

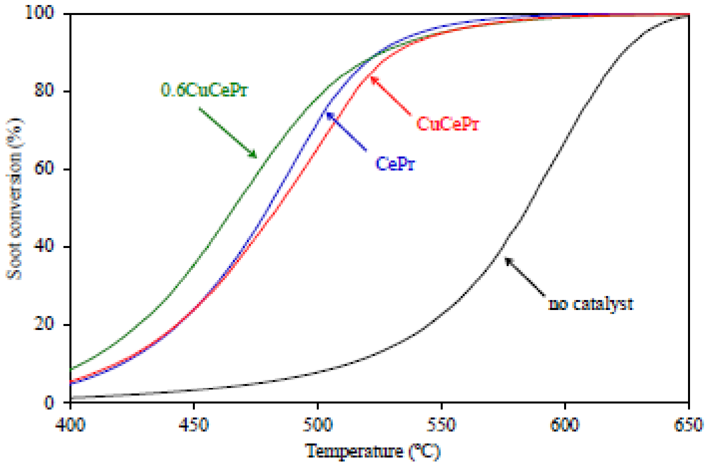

Figure 1. Soot conversion profiles carried out in 500 ppm NO/ 10%O_2/N_2 balance and using catalyst/soot ratio 4:1 in loose contact.

Significance:
The results show that activity of CuCePr sites is mainly related with the low temperature NO oxidation to NO_2, while Cu-free CePr sites play an important role in the direct oxidation of soot with active oxygen. The existence of two different mechanisms relying on soot combustion by active oxygen and NO_2-assisted soot combustion is also confirmed.

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Effect of cerium dioxide on transient pulse experiments for three-way-catalysts

Introduction

The oxygen storage material (OSM) of three-way-catalysts (TWCs) consists largely of cerium dioxide and plays a major role in the purification of exhaust gas. Consequently, a better understanding of the underlying mechanisms is beneficial for the development of improved catalysts.

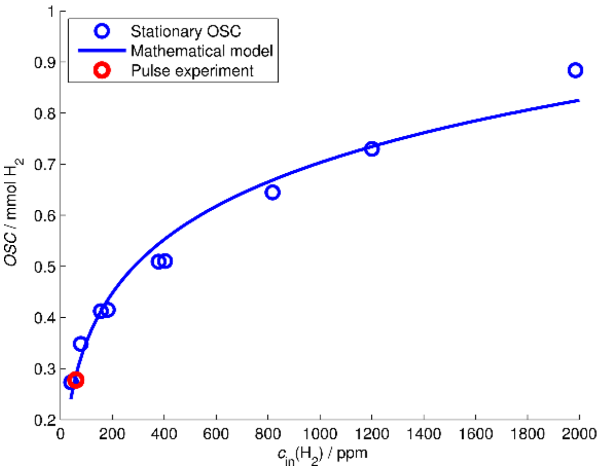
The reduction of cerium dioxide by H_2/CO and the reoxidation by H_2O/CO_2 is widely recognized and both reaction pathways have to be considered for TWC application due to the high H_2O/CO_2 concentrations of about 10 % in the exhaust gas. Accordingly, the performance of TWCs is highly affected by the thermodynamics of the OSM [1]. Recently, we have demonstrated the applicability of these thermodynamics determined experimentally in computational simulations of TWCs [2].

In this contribution, the ability of the model to predict real-world behavior of TWCs, i.e. highly transient operations, is investigated. As representation of such transient operations, pulse experiments are used.

Results and Discussion

The thermodynamics of the OSM has been determined by titration methods [2], [3]. For the implementation into the computational model, a second order polynomial has been fit to the experimental data (figure 1a). The kinetic parameters were not optimized and are taken from [1].

The pulse experiments were carried out as follows. First, exhaust gas with a composition of 60 ppm H_2 and 10 % H_2O in N_2 was fed into the catalyst until steady-state is reached. The composition was chosen to represent a typical operating point for TWCs, i.e. a lambda signal of 650 mV behind the catalytic converter. Then, a short pulse of 1200 ppm O_2 is added to the exhaust gas. This procedure was repeated for several pulse durations. The outlet for four different pulse durations are shown in figure 1b. For short pulses, the applied O_2 is completely stored by the OSM. With increasing pulse duration, progressively more O_2 is detected behind the catalyst, until steady-state is reached.



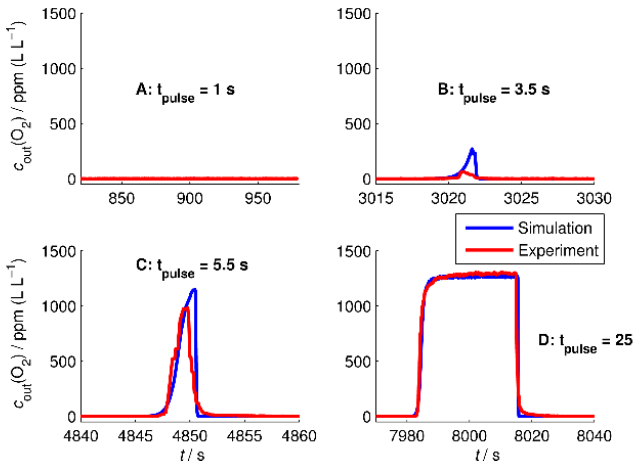


Figure 1a) depicts the experimental values of the oxygen storage capacity (OSC) determined by titration methods (blue circles) for different exhaust gas compositions (10 % H_2O, N_2 balance, T = 400 °C) and the applied mathematical model (blue line). The experimental value for the pulse experiments is shown in red.

Figure 1b) shows the experimental (red) and simulated (blue) O2 concentrations behind the catalyst for different pulse durations (60 ppm H_2, 10 % H_2O, N_2 balance, T = 400 °C).

As can be seen in figure 1a, the OSC for the pulse experiments is well predicted by the mathematical model and in thermodynamically controlled regimes, there is a perfect agreement between simulation and experiment, as can be seen by the longest pulse in figure 1b (Pulse D). For short pulses, the breakthrough of O_2 is affected not only by thermodynamics, but by kinetics and transport phenomena as well. This becomes obvious for pulses B and C in figure 1b, which are generally described by the computational model, underlining the dominant effect of the thermodynamics. However, the slight deviations suggest further effects superposing the thermodynamics.

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Probing the influence of defects in gold loaded ceria during CO oxidation by a combined in situ spectroscopic approach

Ceria is known for its oxygen storage capacity in automotive exhaust treatment. Due to the easy valence shift of Ce^{4+} to Ce^{3+} and vice versa ceria builds oxygen vacancy forming defects upon reduction of the stoichiometric CeO_2. Here we use defect rich nanocomposite ceria (ca) synthesized by decomposition of cerium(III) nitrate and commercial ceria (co) as support for gold particles. Ceria supported Au (0,1 – 1 wt %) catalysts are prepared by deposition precipitation and studied for CO oxidation. During reaction complementary Raman- and diffuse reflectance IR (DRIFT) - as well as UV/Vis- and X-ray photoelectron (XP) spectroscopy are applied (*in situ* approach). In the multi *in situ*-setup Raman-, UV/Vis- and quasi *in situ* XP spectroscopy are combined measuring simultaneously at the same spot of the catalyst.[1] Another setup provides DRIFTS at absolutely comparable conditions (flow rate, conversion, temperature) while using a slightly different cell geometry. For both setups conversion is monitored by gas phase IR spectroscopy (*operando*). XP spectra of Au/CeO_2 (ca) and (co) indicate the presence of about 6% oxidized gold species (Au_+) besides metallic gold (Au_0). Gold oxidation is accompanied by ceria reduction upon gold loading as indicated by a broad UV/Vis band centered at around 575 nm. Raman spectra show a broadening and softening of the F_{2g} peak around 465 cm_{-1} upon exposure to reaction conditions (5% CO, 25% O_2 in Argon). Moreover, an increase in the defect band at 590 cm_{-1} is observed. Both aspects indicate defect formation in ceria. An increase in the number of ceria surface defects is deduced from the peroxide band at 830 cm_{-1}. Complementary DRIFT spectra provide insight into adsorbed species, e.g. under reactions conditions Au/CeO_2 (co) shows a rapid buildup of carbonate species. In conclusion, a combined spectroscopic approach is presented providing new insight into the mode of operation of ceria supported catalysts in oxidation reactions. Depending on gas environment a distinct spectral signature of adsorbed CO, hydroxyl, carbonate and formate species as well as ceria phonons is observed.

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Ab-initio analysis of the defect structure of ceria

Due to its vast number of applications in catalysis, solid oxide fuel cells and membranes, ceria – especially in its acceptor-doped form – has been extensively studied. With the demonstration of the resistive switching properties of the undoped material, however, pure ceria is increasingly attracting interest. We have determined the formation energies of all ionic defects, considering all possible charge states, with Density Functional Theory (DFT) calculations employing the GGA+U method.[1] We have further determined the formation energies of polarons, electrons and of clusters of polarons and oxygen vacancies. From the individual defect energies we have extracted Schottky, Frenkel and anti-Frenkel energies. In order to be able to compare our results further with experimental data we have finally determined energies of reduction and hydration, as well as point-defect concentrations and conductivities. The quantities predicted by our calculations show very good agreement with experiment.

In order to shed light on the migration process of fast oxygen conduction in ceria we have further studied the migration by a vacancy mechanism of diverse anion moieties in ceria. Analysis of our results indicates a new paradigm for understanding fast oxygen-ion migration in solids.

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S. Sharath

(001) and (111) single-oriented highly epitaxial CeO_2 thin films on r-cut sapphire substrates

Stabilisation of epitaxial (001) and (111) single oriented ceria films on increasingly relevant sapphire substrates is important for use as buffer layers for epitaxial growth of complex oxides. High quality epitaxial thin films of CeO_2 were thus grown using molecular beam epitaxy (MBE) on r-cut sapphire substrates (Al_2O_3 (1-102). The films were grown by evaporating CeO_2 at different rates at substrate temperatures from 500°C to 750°C. The thin films were chararacterized using X-ray diffraction (XRD) and reflection high energy electron diffraction (RHEED). The oxidation state of the substrate as well as the rate of evaporation was found to affect the growth orientation of CeO_2. While oxygen pre-annealed substrates favor (001) growth, oxygen vacancies lead to a mixed (001) and (111) orientation. A combination of pre-annealing of the substrate and post-annealing of the film was used to achieve single oriented CeO_2 in both (001) and (111) directions on Al_2O_3 (1-102). Furthermore, post-annealing resulted in a dramatic increase of crystallinity with a rocking curve width of the (002) reflection as small as 0.004°. The higher quality of the films were also evident from the highly defined Laue oscillations after annealing the films. The interface and surface roughness of the films were also reduced as observed from fitting the X-ray reflectivity oscillations and atomic force microscopy (AFM). The in plane epitaxial relationships were determined using ϕ-scan measurements as CeO_2 [100] || Al_2O_3 [1-10-1] for CeO_2 (001) films and multidomain growth with CeO_2 [10-1] || Al_2O_3 [02-21] ± 2.64° for CeO_2 (111) oriented films respectively. A consistent growth model involving oxygen vacancies at the substrate to thin film interface is suggested to explain the growth model as shown in the figure 1. Polarity enhanced epitaxial growth of CeO_2 (001) is promoted on fully oxidised surface of r-cut Al_2O_3 and surface with larger amount of oxygen vacancies tends to stabilize CeO_2 (111) growth direction. [1] D.S. Bick et al., *Accepted,* J. Electronic Materials. (2015).

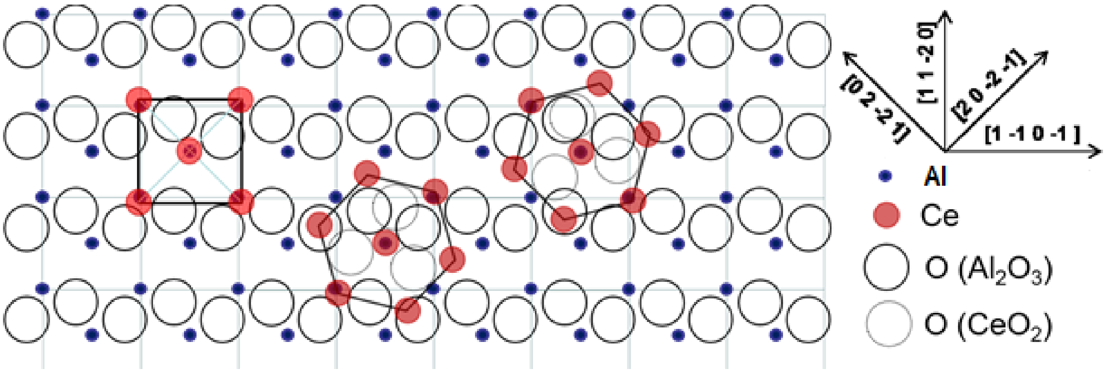

Fig 01. Suggested epitaxial growth model; CeO_2 (002) (left square) and (111) (two hexagonal rotated domains on right)

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Defect Chemistry, Redox Kinetics and Chemical Diffusion of Ce-containing Yttria Stablized Zirconia

Oxides of the fluorite structure are of importance for energy conversion and storage devices. For example, ceria-based oxides are promising solid electrolytes for SOFC operating at intermediate temperatures and catalysts for a catalytic converter to produce fuels from CO_2. The performance of these devices is largely influenced by the defect chemistry, reactivity and related kinetic processes occurring in the materials at operating conditions. To understand the mechanism of reactivity and atomic transport processes in oxides, optical in-situ spectroscopy has been developed to study the defect chemistry and reaction kinetics at elevated temperatures under various atmospheres. In this contribution, we will present an optical in-situ study of defects equilibrium and redox kinetics of Ce-containing yttria stabilized zirconia single crystals. The optical absorption of defects in equilibrium can be described in terms of a defect model involving oxygen vacancies and electrons. Chemical diffusion coefficients obtained from modelling redox processes upon rapid changes in oxygen activity will be discussed by considering defect interactions and their effects on ionic diffusion.

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Shape-controlled CeO_2 nanostructures as model heterogeneous oxidation catalysts

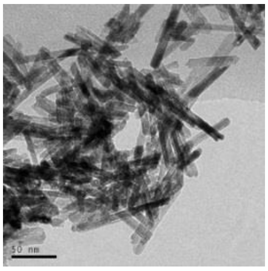
CeO_2 is an important technological material that finds numerous applications, such as in the clean-up of tail gases of gasoline engines, solid oxide fuel cells and O_2 sensors. It can be synthesized using a wide array of techniques, for instance hydrothermal treatment, microwave-assisted processes or Flame-Spray Pyrolysis (FSP).

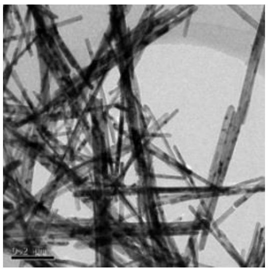
Cerium dioxide is also a well-known support for a wide variety of noble metals, as it proves capable not only to favor the formation and stability of metal nanoparticles, but also to take an active role by undergoing reduction and supplying oxygen atoms.

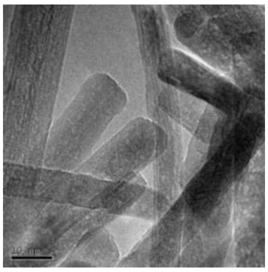
It has been evidenced that the extent of metal-ceria synergy is strongly dependent on the termination of the ceria support [1]. With hydrothermal methods it is possible to prepare nanostructured CeO_2 in the shape of nanorods, nanocubes or nanooctahedra [2].

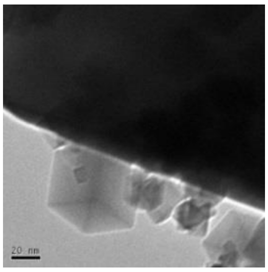
In our approach we aim at developing well-defined systems made of ceria-supported Pd atoms, clusters and nanoparticles for CO and CH_4 oxidation. By varying the morphology of the CeO_2 we can relate the nature and activity of the active Pd phase to the reducibility of the ceria support surface.

A simple and reproducible hydrothermal method was followed, and the influence of parameters such as cerium precursor, base and treatment temperature was assessed. The samples were characterized with Transmission Electron Microscopy, as shown below:









A H_2-TPR study showed that CeO_2 nanorods can be reduced more extensively and at lower temperatures than nanocubes.

The CeO_2 nanostructures were successfully impregnated with $Pd(NO_3)_2$, resulting in homogeneously dispersed Pd nanoparticles whose size ranged below 2 nm.

In situ X-ray Near Edge Absorption Structure (XANES) was applied on selected Pd-impregnated samples during CO oxidation reaction. Different CeO_2 nanostructures proved to have a substantial influence on the chemical state of Pd during the reaction.

Our intent is to further develop these promising systems as well-defined model catalysts for complete methane oxidation at low temperatures.

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Ordered phases of reduced ceria thin films on Cu(111) observed by STM

Different stoichiometry of cerium oxide (CeO_x) invokes different ordering of oxygen vacancies. We study the structure of thin films of reduced ceria with stoichiometry, 1,5<x<2. With the help of Scanning Tunneling Microscopy we observe three types of surface reconstructions of reduced ceria: a $(\sqrt{7} \times \sqrt{7})R19.1$ degrees reconstruction representing a bulk termination of the t-Ce_7O_{12}, a (3×3) reconstruction representing a bulk termination of the $CeO_{1.67}$, and a (4×4) reconstruction representing a bulk termination of the Ce_2O_3. The perspective applications include advanced model catalyst studies controlling both the concentration and the coordination of oxygen vacancies [1-3].

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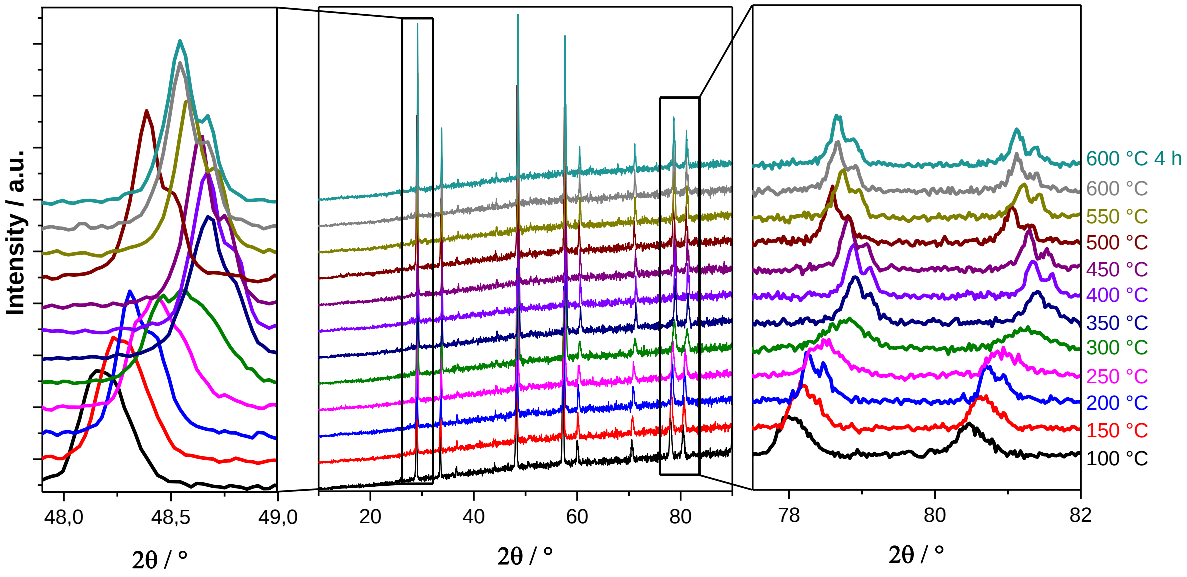
$Ce_2Zr_2O_8$ κ-phase – Mechanistic Insights in the Synthesis Process

The $Ce_2Zr_2O_8$ κ-phase is a crystal structure, which exhibits a remarkably low temperature of reduction[1] and an extreme high capacity of possible oxygen storage (oxygen storage capacity, OSC).[2] These features derive from the ordered arrangement of cerium and zirconium atoms along the ‹110› direction. This arrangement reduces lattice stress due to oxygen vacancy formation.
We show mechanistic insights processes of the synthesis process of the κ-phase, especially the transformation from the precursor, the pyrochlore structure. In this transformation, the pyrochlore phase of the ceria-zirconia mixed oxide is heated up to 600 °C under air. Oxygen vacancies are filled up with oxygen, while the cation arrangement is unaffected.



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In situ EPR study on redox properties of CuO-CeO$_2$

Understanding of the redox properties of metal oxides is a major task in catalysis research. *In situ* study provides with direct observation of change of valences and formation of active sites during redox or reaction conditions, and thus helps unveil the ongoing redox pathways. Here *in situ* electron paramagnetic resonance, combined with online gas analysis, mass spectrometry, x-ray photoelectron spectroscopy, x-ray diffraction and temporal analysis of products reactor, has been utilized to study the thermodynamic and kinetic redox behaviors of CuO-CeO$_2$. A synergetic mechanism that involves the redox pair of Ce^{4+}/Ce^{3+} is observed via studying the sample under subsequent CO/N$_2$/O$_2$ flow at *in situ* conditions (Figure 1). In addition, a direct mechanism that bypasses Ce^{4+}/Ce^{3+} has also been identified using isotopic $^{17}O_2$ labelling. Both two mechanisms suggest that strong interactions between Cu and Ce lead to better catalytic performance. With such guideline, CuO-CeO$_2$ is optimized and shows 11 K of operation window ranging from 377 K to 388 K, with 99% conversion and selectivity, in preferential oxidation of CO in excess of H$_2$ feed gas.

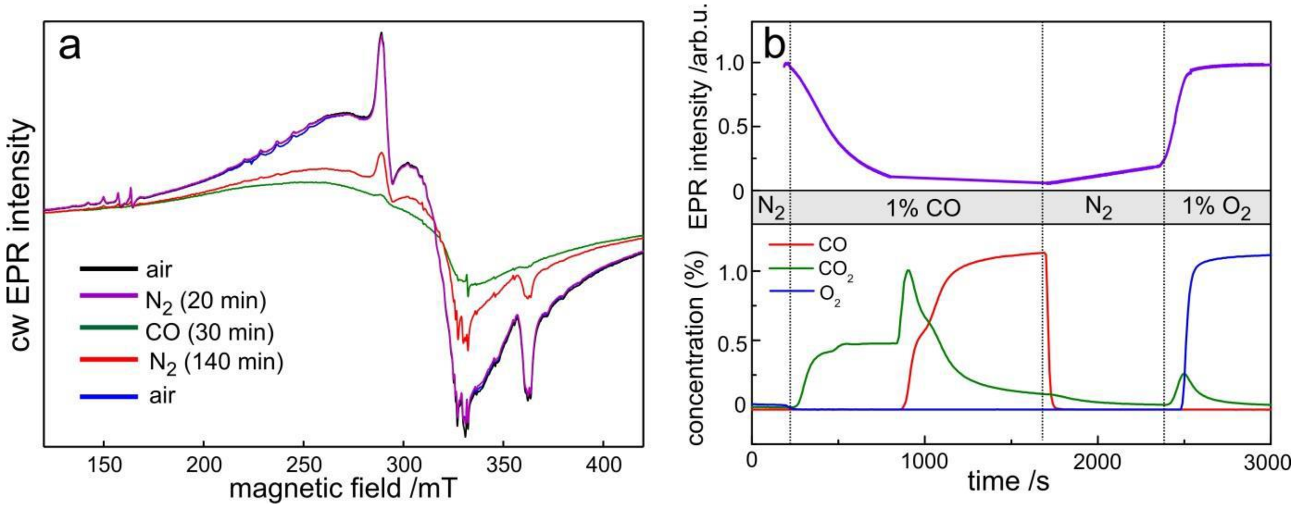

Figure 1. (a) X-band cw EPR spectra of 20wt% CuO-CeO$_2$ recorded at 453 K during the treatment with air/N$_2$/CO/N$_2$/air cycle. The times of the particular gas treatment are indicated. (b) Upper trace: Time dependence of Cu^{2+} dimer EPR intensity at 289 mT during N$_2$/CO/N$_2$/air cycle at 453 K. Lower traces: Corresponding CO, CO$_2$ and O$_2$ concentration simultaneously recorded by gas analytic system.

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In-situ Photoelectron Spectroscopy of Differently Oriented CeO_2 Thin Films Deposited by Magnetron Sputtering

CeO_2 is widely used as oxygen ion conductor and in catalysts. For these applications the surface properties of the material are of great importance. In oxide semiconductors the ionization potential and work function can be strongly influenced by the crystal orientation and termination of the surface. Differences of more than 1 eV in the ionization potential of SnO_2 have been reported depending on surface orientation and termination [1]. A similar dependence for CeO_2 has not been investigated to date and is therefore of great interest.
We conducted *in-situ* X-ray and UV photoemission spectroscopy of (111), (110) and (100) oriented CeO_2 thin films. The films were deposited by magnetron sputtering from a ceramic target on Al_2O_3(0001)/Pt(111), MgO(110)/Pt(110), MgO(100)/Pt(100) and $SrTiO_3$:Nb(100) substrates. We present ionization potential, work function and Fermi level position of ceria in dependence of crystal orientation, deposition condition and post-deposition treatment in reducing and/or oxidizing atmosphere. We have found ionization potentials and work functions ranging from 7.1 to 7.7 eV and 4.2 to 5.0 eV, respectively, with a maximum variation of Fermi level at the surface of 0.7 eV . In addition, the films were characterized *ex-situ* by X-ray diffraction to determine their crystal orientation.

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UHV-IR spectroscopy study of carbon monoxide adsorption on CeO_2(111) single crystal surface

Ceria, one of the most easily reducible metal oxides, exhibits extraordinary activities in diverse catalytic processes.[1] In all cases, the oxidation reduction cycle (Ce^{4+}/Ce^{3+} cations – and the associated oxygen vacancies) is the most determining factor. The importance of this material has triggered numerous experimental and theoretical studies, in particular aiming at elucidating the properties of oxygen vacancies.

Here we used a novel apparatus[2] combining a state-of-the-art FT-IR spectrometer with a dedicated UHV-chamber to monitor the adsorption of the most frequently used probe molecule carbon monoxide (CO) on stoichiometric and defective bulk CeO_2(111) single crystal surfaces. The obtained data can construct a database for reliable assignments of the bands in the complicated infrared spectra for CO on ceria powders. More importantly, it also allows identifying defect sites formed on CeO_2 surfaces. Since no previous measurements are available, the assignment of the CO ν_1 stretch frequency as determined by IR-spectroscopy for the stoichiometric and defective surfaces are aided by ab-initio electronic structure calculations using density functional theory (DFT).[3]

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On the fabrication of microelectrodes to measure the conductivity of single grains and grain boundaries in ceria thin films

The resistance of a polycrystalline ceramic thin film strongly depends on its microstructure as not only the bulk resistance of the grains themselves but also the resistance of the grain boundaries contributes to the overall resistance. Using electrochemical impedance spectroscopy the two contributions can often be separated as they show different capacities resulting in two semicircles in the impedance spectrum. However, depending on the thickness and the microstructure of the thin films the two semicircles may overlap making a separation of both contributions difficult. Here, we present a method for the fabrication of microelectrodes to measure the resistance of a single grain and its grain boundary directly.

Ceria thin films were prepared by pulsed laser deposition on sapphire and MgO substrates using a KrF-Excimer laser. The as-prepared thin films show a columnar structure with grain sizes of about 100 nm. To obtain crystallites in the µm-range, grain growth was induced by annealing of the samples at a temperature of 1500°C. This temperature treatment resulted in thin films consisting of multiple crystallites with diameters of 50 µm or more and a large surface roughness. Subsequently, the thin films were characterized by X-ray diffraction, SEM and Raman spectroscopy to confirm that a clean phase of cubic ceria was prepared. Due to the high film roughness a bilayer coating of PMMA A4 and MMA (8.5 EL) MAA was necessary for a successful fabrication of the microelectrodes using electron beam lithography. Stable electrode structures on the thin films could only be achieved by the evaporation of gold with a thickness of 400 nm or more.
