

## Electron microscopy investigations of Metal-Support Interaction effects in $M/Y_2O_3$ and $M/ZrO_2$ thin films (M=Cu, Ni)

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## Abstract

Model systems of the clean and pure oxides  $Y_2O_3$  and  $ZrO_2$ , as well as  $Cu/Cu_2O$  and  $Ni/NiO$  particles embedded in the respective oxides have been used to study the reduction behavior of the oxides and the eventually associated metal-support interaction effects in oxide-supported systems. Particular emphasis has also been given to the influence of the phase transformation in  $ZrO_2$ -containing systems on metal-support interaction. Whereas  $Y_2O_3$  has been found to be an outstandingly structurally and thermally stable oxide even upon reduction in hydrogen up to 1073 K,  $ZrO_2$  was found to undergo a series of phase transformations from amorphous  $ZrO_2$  to polycrystalline tetragonal  $ZrO_2$  ( $\sim 673$  K) and subsequently to monoclinic  $ZrO_2$  (above 873 K). Both phase transformations were found to be basically dependent on gas partial pressure and annealing rate. However, substantial reduction of the oxides did not take place during the phase transformations. In turn, both Cu- and Ni-containing systems were not observed to be substantially affected by any (strong) metal-support interaction effects such as encapsulation by sub-stoichiometric oxides or reductive formation of intermetallic phases, at least up to temperatures of 1073 K. Equally, for the  $ZrO_2$ -containing systems, also the phase transformations occurring at elevated temperatures did not cause structural or thermochemical alterations of the Cu or Ni-particles. Differences in the metal-support interaction between Cu- and Ni-particles have only been obtained in the structural “reference” systems, that is, if supported on  $SiO_2$ . Whereas  $Cu/Cu_2O$  particles on  $SiO_2$  are basically unaffected by the reductive treatment at elevated temperatures, a  $Ni_3Si_2$  intermetallic phase is formed if  $SiO_2$ -supported  $Ni/NiO$  particles are treated in hydrogen at 673 K and above.

## 1. Introduction

ZrO<sub>2</sub>- and Y<sub>2</sub>O<sub>3</sub>-based systems have evolved as promising materials in a wide range of technological applications, ranging from ceramics over toughening agents and optical coatings to catalysis. The strength of these materials is intimately connected to their high chemical and thermomechanical stability, therefore e.g. also withstanding the demanding operating conditions of solid-oxide fuel cells or reactive melts of Ti or U [1-10]. Structural stability under the desired experimental conditions is therefore also imperative. This includes knowledge about possible phase transformations, presence of distinct grain structures or the general presence of oxygen vacancies. Whereas little is known about the structural transformations within the Y-O systems (three phases are known to exist:  $\alpha$ -Y<sub>2</sub>O<sub>3</sub> with cubic structure; a high-temperature  $\beta$ -Y<sub>2</sub>O<sub>3</sub> phase stable at 2653 K with hexagonal structure and a high-pressure  $\gamma$ -Y<sub>2</sub>O<sub>3</sub> phase with monoclinic structure) [11], a wealth of literature already exists on almost all aspects of the phase transformation in the Zr-O systems [1,12-20]. This includes the monoclinic ZrO<sub>2</sub> structure, which is the thermodynamically stable phase under ambient conditions, a tetragonal and a cubic ZrO<sub>2</sub> phase [1,10]. Far too exhaustive to be reviewed in detail at this point, the cubic phase is formed upon cooling the ZrO<sub>2</sub> melt to 2953 K, followed by the transformation into tetragonal ZrO<sub>2</sub> at 2643 K and subsequently by transformation into the monoclinic structure at 1223 K [1]. The monoclinic-to-tetragonal transformation occurs in the other direction (i.e. upon heating) at 1423 K [1]. The tetragonal-to-monoclinic phase transformation is by far the most studied one [1,12-20] and it is widely accepted, that this phase transformation is of martensitic-type [1], that is, a diffusionless and athermic process arising from cooperative shear movements of the initial microstructure [1,18,19,21]. Particle size and matrix effects in particular have been reported to play a dominant role [1,22]. Less focus has nevertheless been put on the structural transformation between the other phases. Unfortunately, especially the martensitic transformation occurs at

close to technologically relevant temperatures and typically results in crack formation within the microstructure following volume expansion by  $\sim 4\%$ , eventually leading to e.g. de-adhesion of the ceramic coatings [1]. Regarding the previously mentioned applications within catalytic entities,  $\text{ZrO}_2$  is mostly combined with copper and nickel to result in oxide-supported systems of particular technological importance in carbon dioxide reforming of methane [10], steam reforming of methanol [9] or as anode materials in solid-oxide fuel cells [8]. With the exception of steam reforming of methanol, these reactions are typically examined at very high temperatures (at and above 973 K), i.e. at temperatures where phase transformations, at least in the  $\text{ZrO}_2$  case, could possibly start to play a role and affect the behavior of the whole catalytic entity. Extending the influence of the stability of the supporting oxides, we might include also so-called strong metal-support interaction effects, typically observed for, but not limited to, reducible oxides under strongly reducing conditions in hydrogen at elevated temperatures ( $\sim T \geq 773$  K) [22]. Possible structural manifestations include encapsulation of active metal particles by sub-stoichiometric oxides or reductive formation of intermetallic particles [23,24].

A particular promising pathway to tackle a number of problems prevailing in research, also encompassing the oxides discussed above, is the use of well-defined model systems, epitaxially grown on vacuum-cleaved  $\text{NaCl}(001)$  facets. This enabled us to prepare both metal and oxide systems with well-defined grain size, particle morphology and structure. They are in turn especially well-suited not only to eventually prepare different polymorphic forms of oxides or to study phase transformations between the different structures on well-defined systems, but, extending the complexity, also to study the interaction between metal and oxide and to eventually establish structure/morphology - activity/selectivity/property relationships [25-30]. In the present case, we aim at providing answers to specific important questions in  $\text{ZrO}_2/\text{Y}_2\text{O}_3$ -related research, that is, (i) investigate the phase transition  $\text{ZrO}_2$  amorphous  $\rightarrow$

ZrO<sub>2</sub> tetragonal → ZrO<sub>2</sub> monoclinic by the use of a well-defined model system, (ii) to investigate if the phase transition temperatures are distinctly different by the use of a crystallographic well-defined system, (iii) to study the influence of external parameters, such as high pressure vs. low pressure and simple annealing vs. reduction in hydrogen and (iv) to extend these studies to metal-support interaction effects in more complex systems of M/Y<sub>2</sub>O<sub>3</sub> and M/ZrO<sub>2</sub> (M=Cu, Ni), referenced to the corresponding M/SiO<sub>2</sub> systems. As the perfect tool to provide answers to these questions, analytical high-resolution electron microscopy is chosen, with special emphasis on selected area electron diffraction (SAED), high-angle annular dark field imaging (HAADF), high-resolution imaging (HRTEM) and electron-energy loss spectroscopy (EELS).

## 2. Experimental

### *Sample preparation and annealing treatments*

Y<sub>2</sub>O<sub>3</sub> (from a tantalum crucible) and ZrO<sub>2</sub> (from a tungsten crucible) have been both prepared in a dedicated high vacuum chamber (base pressure 10<sup>-6</sup> mbar) by thermal evaporation of Y metal in 10<sup>-4</sup> mbar O<sub>2</sub> or ZrO<sub>2</sub> in 10<sup>-5</sup> mbar H<sub>2</sub>, respectively, onto vacuum-cleaved NaCl(001) single crystal facets. The latter is introduced in the case of ZrO<sub>2</sub> to reduce the formation of volatile tungsten oxides during the preparation process [31]. Template temperatures were chosen as 300 K and 573 K, respectively. Film thicknesses of ~25 nm are usually obtained. Details of preparation have been given elsewhere [31]. Metal/metal oxide particles have been deposited via electron beam evaporation of copper (99.9999% purity Alfa Aesar) or nickel (99.98% purity, Alfa Aesar) onto similar NaCl (001) single crystal facets at a substrate temperature of 573 K. Particle sizes of 10-20 nm for copper and 10-30 nm for nickel were obtained, corresponding to nominal metal layer thicknesses of about 5 nm. Subsequently, the

Cu or Ni particles are embedded in  $\text{Y}_2\text{O}_3$ ,  $\text{ZrO}_2$ , or, in the case of the reference sample, in a 25 nm thick layer of amorphous  $\text{SiO}_2$ , prepared by reactive deposition of SiO in an oxygen partial pressure of  $10^{-4}$  mbar. Generally, the NaCl template is subsequently dissolved in water and the resulting thin film is transferred to a gold grid for electron microscopy. Routine inspection of the impurity level is carried out by energy-dispersive X-ray spectroscopy and basically revealed only peaks due to the film constituents with all other impurities well below the detection level. The purity of the substrate was also ensured by freshly cleaving the NaCl(001) crystals immediately before deposition of either oxide or metal.

Thermal treatments in helium and hydrogen are carried out under flowing conditions of either 1 ml/s pure helium or hydrogen up to temperatures of about 1073 K. After mounting the samples (i.e. the films on the gold grids) into the furnace, the temperature is ramped in 5 K/min to the desired temperature, typically followed by an isothermal period of 60 minutes. Finally, the samples are cooled down to room temperature in the respective gas atmosphere. Thermal treatments in vacuum were performed in-situ in a dedicated heating holder of a JEOL 4000FX microscope up to 1150 K.

#### *Electron Microscopy characterization*

Structural characterization of the samples was carried out by a 100 kV Zeiss EM 10C microscope, by a 200 kV FEI TECNAI F20 STWIN Analytical (Scanning-) Transmission Electron Microscopes (S)TEM equipped with a GATAN Tridiem energy filter and by a JEOL 4000FX microscope operated at 400kV. Using the latter microscope, a heating holder, capable of reaching 1270 K in vacuo, was used. As a result of the limited resolution of this microscope at high temperatures (point-to-point  $2.8\text{\AA}$ ) due to increased thermal drift, only selected area electron diffraction patterns were recorded. Prior to imaging, the samples were

without exception plasma-cleaned to remove surface carbon impurities. The SAED patterns were subsequently externally calibrated with respect to the Pd spots in a separately prepared sample, investigated under identical conditions. Electron-energy loss (EEL) spectra are background-corrected and corrected for plural scattering.

### 3. Results and Discussion

#### 3.1. Reduction of the pure oxides $\text{Y}_2\text{O}_3$ and $\text{ZrO}_2$

Starting from the already well-characterized initial states, comprising highly-ordered bcc  $\text{Y}_2\text{O}_3$  (at template temperatures of 573 K), amorphous  $\text{ZrO}_2$  (at 300 K) and ordered tetragonal  $\text{ZrO}_2$  (at 573 K) [31], their thermal stability and reducibility was tested. This is a crucial requirement, as for potential applications as model systems in e.g. solid-oxide fuel cell research, structural and thermo-chemical stability, especially at very high temperatures, is a prerequisite. Figure 1 therefore shows a comparison of an  $\text{Y}_2\text{O}_3$  thin film prepared at 573 K in the initial state (left panel) and after reduction in hydrogen at 1073 K (right panel). In short, despite the harsh reductive conditions, both the characteristic microstructure, consisting of well-shaped elongated grains, as well as the high crystallographic ordering basically remain unaffected by the treatment.  $\text{Y}_2\text{O}_3$  films prepared at 300 K are initially amorphous, but crystallize in the same bcc structure (however, only polycrystalline Debye-Scherrer-type patterns are obtained), if treated under comparable conditions. For an assignment of the SAED patterns to distinct structures we refer to Table 1. In case of the  $\text{ZrO}_2$  samples, the situation is much more complex and eventually enabled us to follow the phase transformation within the Zr-O system in detail. Figure 2 summarizes these experiments. Panels A, C and E show the structural evolution of the  $\text{ZrO}_2$  film deposited at 300 K, panels B, D and F those of the  $\text{ZrO}_2$  film deposited at 573 K. As it can be clearly seen, the initial states (panels A and B) are already strikingly different and comprise amorphous structures at 300 K (panel A), but a

somewhat ordered tetragonal ZrO<sub>2</sub> phase at 573 K (panel B). Details have been discussed in previous work [30]. Panels C and D highlight the structures of the ZrO<sub>2</sub> samples after reduction at 673 K. Whereas the initially tetragonal ZrO<sub>2</sub> film remains unaffected by the treatment and only minor changes in the grain structure has been observed (also reflected in the respective SAED patterns, where still only tetragonal ZrO<sub>2</sub> is detected), the initially amorphous ZrO<sub>2</sub> film has undergone a rather pronounced structural reconstruction with associated re-crystallization. Some areas of the film rather seem to be unaffected, but generally, the films consist of an arrangement of plate-like, rather large grains (average diameter about several hundreds of nm, marked in Figure 2 C). A careful analysis of the corresponding SAED pattern reveals the presence of the same tetragonal ZrO<sub>2</sub> phase being present right after deposition at elevated temperatures. However, the microstructure seems to be crucially dependent on the initial state of the sample, since in panel D, such plate-like structures have never been observed. It appears that the high ordering of the initial film deposited at 573 K prevents the formation of the larger grains, at least at comparable temperatures. Note that at this stage, preparative access to two types of tetragonal ZrO<sub>2</sub> phases is provided, a more ordered and a more structurally chaotic one. Raising the reduction temperature to temperatures above 873 K, yet another phase transformation is observed, namely tetragonal ZrO<sub>2</sub> → monoclinic ZrO<sub>2</sub>. Panels E and F show the microstructures of the two films after reduction at 1073 K (deposition at 300 K) and 873 K (deposition at 573 K), respectively. In both cases, a porous structure, consisting of large-area, strained and defective grains (marked by an arrow in Figure 2F, separated by cracks (marked by arrows in Figure 2E)), is observed. This is very typical of a martensitic-type phase transformation [1], which has been already previously discussed for the transition between the two ZrO<sub>2</sub> structures [1,13,20]. Characteristic of this special phase transformation is its diffusionless, athermic process developing from transformation strains, leading to volume increase of the structure and finally, reconstruction of the particles and grains. Several parameters, influencing the

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specific type of phase transformation, have been reported to play a role, including particle size and matrix effects [1,22]. Specifically, embedding of the grains in a matrix has been shown to oppose the transformation [1]. Electron microscopy has been shown in the past to be a particular useful tool for investigating all aspects of this phase transformation [1,12,13,16,17,20]. One aspect, being relevant also for the present case, is the possibility to induce the tetragonal  $\rightarrow$  monoclinic phase transformation by irradiation with the electron beam of an electron microscope [1]. This has, however, in the present case never been observed by the use of any of the microscopes. Regarding the question what exactly stabilizes the tetragonal structure in our systems, epitaxial relations of the tetragonal  $\text{ZrO}_2$  structure with the underlying fcc NaCl lattice have been held responsible for the stabilization [31], alongside a small particle size being definitely below the experimentally estimated critical size for stabilization of the tetragonal phase (10-40 nm) [12,31].

It should be noted, that the tetragonal  $\rightarrow$  monoclinic phase transition in the present samples occurs at much lower temperatures than reported for bulk  $\text{ZrO}_2$  material [1]. Whereas 1223 K are reported for bulk  $\text{ZrO}_2$  [1], by the use of the special thin film system, this phase transformation temperature is lowered to about 873 K. Moreover, to our knowledge, no transition temperatures for the amorphous  $\rightarrow$  tetragonal transition are reported so far. While it is not particularly surprising, that the tetragonal phase, once it is (especially epitaxially) stabilized, remains up to very high annealing temperatures, the amorphous structure does interestingly not transform directly into the thermodynamically most stable monoclinic  $\text{ZrO}_2$  phase, but forms the tetragonal phase first, which subsequently transforms into the monoclinic phase. The energetic situation at the  $\text{ZrO}_2/\text{NaCl}$  interface is expected to play a crucial role in the stabilization of this particular tetragonal phase, either due to altered wetting behavior or due to possibly formed small nucleation seeds of the tetragonal phase. Both extreme situations have already been observed for various oxides: the formation of  $\text{Ga}_2\text{O}_3$  nanospheres was

found to be triggered by wetting phenomena between sub-stoichiometric  $\text{GaO}_x$  and  $\text{NaCl}(001)$  [32], whereas the formation of well-shaped  $\text{In}_2\text{O}_3$  nanopillars was due to epitaxial relations between the  $\text{In}_2\text{O}_3$  and  $\text{NaCl}$  lattices [27]. Following this argumentation, the well-ordered structure shown in Figure 2 D is still dominated by the initial epitaxial relations, whereas the structure shown in Figure 2 C might represent the true “thermodynamical” equilibrated structure, since the latter coincides with the micro-structures reported for tetragonal  $\text{ZrO}_2$  previously (see e.g. Figure 17 in reference [1]). Figure 3 subsequently highlights a more detailed look on the structure of the tetragonal phase, as shown in Figure 2 C. Panel A depicts a large-scale image of that structure, where the irregular plates of tetragonal  $\text{ZrO}_2$  can be seen in detail (marked by an arrow in Figure 3A), exhibiting strong Bragg contrast and a pronounced internal structure revealing the defective and strained structure. In contrast, panel B shows a corresponding STEM image taken under HAADF contrast conditions (camera length 30 mm), revealing that the contrast variations in the bright-field image are in fact due to Bragg contrast and not due to variations in chemical composition. This assumption is basically corroborated by the EEL spectrum shown in panel C, whose Zr-M and O-K edges are identical to the ones of the initial  $\text{ZrO}_2$  structure [31]. Hence, we can exclude substantial variations of the electronic structure/chemical environment of the  $\text{ZrO}_2$  structure upon reduction. Finally, panel D shows a high-resolution electron micrograph of a representative interface of two plate-like grains, with sets of differently oriented  $\text{ZrO}_2$  grains with (101) lattice fringes ( $d_{\text{exp}}=3.01 \text{ \AA}$ ,  $d_{\text{theor}(101)}=2.98 \text{ \AA}$  [33]). This further reveals that in fact only tetragonal  $\text{ZrO}_2$  is present. To finalize the experiments on the sequence of phase transformations, additional experiments at varying pressures and gas atmospheres have been performed. Figure 4 in short reveals, that also annealing in 1 bar pure He leads to the same phase transitions at similar temperatures. Panel A shows the structure after annealing at 673 K, panel B at 1073 K. The SAED patterns reveal the presence of the tetragonal and monoclinic phases with at the same time very similar microstructures as those presented in

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Figure 2. Hence, as already anticipated from the EELS experiments shown in Figure 3 C, formation of oxygen vacancies or changes in the chemical environment are less an issue. Figure 5, in contrast, shows that kinetics play a dominant role in the phase transformations of both amorphous  $\rightarrow$  tetragonal and tetragonal  $\rightarrow$  monoclinic  $\text{ZrO}_2$ . In panels A-C, the evolution of the SAED patterns upon heating in vacuum inside the electron microscope is shown. Panel A reveals that even after annealing the sample at 753 K, only amorphous structures are obtained. Starting at  $\sim$  833 K (panel B), the tetragonal  $\text{ZrO}_2$  phase starts to develop. However, the subsequent transition to monoclinic  $\text{ZrO}_2$  has never been observed, even at the highest annealing temperatures (panel C shows the SAED pattern taken at 1173 K). As the annealing in this case is very fast ( $\sim$ 1 K/s, no prolonged heating at a certain temperature is experimentally possible), it appears that the system is far from its equilibrium structure and formation of the phases is largely suppressed due to kinetic reasons.

### 3.2. Preparation and characterization of the $\text{M}/\text{Y}_2\text{O}_3$ and $\text{M}/\text{ZrO}_2$ ( $\text{M}=\text{Cu}, \text{Ni}$ ) samples

To further shed light on the consequences of the (de-)stability of the respective oxide phases on the structure, morphology and properties of more complex metal/oxide systems, the above-discussed results are extended to investigations of small  $\text{Cu}/\text{Cu}_2\text{O}$  and  $\text{Ni}/\text{NiO}$  particles embedded in the respective oxides. For comparison, the same metal particles have also been supported on  $\text{SiO}_2$  and treated under similar conditions. Section 3.2. deals with the details of preparation of the systems, section 3.3. with the implications upon reduction. To increase the TEM contrast and subsequently, the detection of copper and nickel, both oxides have been deposited at 300 K. The assignment of the SAED patterns to the different structures is summarizingly depicted in Table 2 (Cu-systems) and Table 3 (Ni-systems).

Figure 6 highlights bright-field overview TEM images of the structure of the Cu-Y<sub>2</sub>O<sub>3</sub> (panel A) and the Cu-ZrO<sub>2</sub> (panel C) samples. In Figure 6 A, the Cu particles can be detected as rounded grey and black aggregates, the contrast differences mainly arising from Bragg contrast variations. Y<sub>2</sub>O<sub>3</sub> is represented by the grey structure in-between the metal particles. The SAED pattern (inset) reveals that although Y<sub>2</sub>O<sub>3</sub> was deposited at room temperature, polycrystalline bcc-Y<sub>2</sub>O<sub>3</sub>, alongside a mixture of Cu and Cu<sub>2</sub>O for the particle structure/composition is present. Due to the crystallinity of Y<sub>2</sub>O<sub>3</sub>, detection of the Cu/Cu<sub>2</sub>O is therefore not straightforward. Particle analysis, as shown in Figure 6 B, yields an average diameter of the Cu/Cu<sub>2</sub>O particles of ~ 11 nm and a particle density of 2.1 · 10<sup>11</sup> particles cm<sup>-2</sup>, both of which are comparable to the reference Cu/Cu<sub>2</sub>O-SiO<sub>2</sub> system (discussed in detail in [34]). Cu/Cu<sub>2</sub>O particles embedded in ZrO<sub>2</sub> are very hard to detect, also due the inherently higher contrast of the amorphous ZrO<sub>2</sub> structure. SAED patterns (inset) indeed reveal that ZrO<sub>2</sub> is amorphous and that the copper particles are in fact mostly Cu<sub>2</sub>O. The presence of Cu<sub>2</sub>O is nicely corroborated in HRTEM images, where Figure 7 shows an agglomerate of two Cu<sub>2</sub>O particles exhibiting (200) and (111) lattice fringes [35], further giving rise to a translational Moiré-pattern with an experimentally determined fringe distance of 17.4 nm. Theoretical calculations on the basis of two overlapping parallel (200) and (111) lattice distances without rotation yield a value of 17.6 nm. Thus, the presence of Cu<sub>2</sub>O is additionally confirmed. Figure 8 in turn shows the corresponding TEM-images of the Ni-Y<sub>2</sub>O<sub>3</sub> and Ni-ZrO<sub>2</sub> catalysts. Generally, as shown in Figure 8 A and B, the nickel particles are equally hard to detect as their copper counterparts and the SAED patterns are (supporting oxide-wise) similar. Crystalline bcc-Y<sub>2</sub>O<sub>3</sub> (panel A) and amorphous ZrO<sub>2</sub> (panel B) are present, as well as a compositional mixture of Ni and NiO in case of the metal particles. Average particle diameters of about 10 nm are obtained. For an exemplified better visualization of the Ni particles on Y<sub>2</sub>O<sub>3</sub>, HAADF imaging (panel C) has been carried out. The HAADF intensity roughly follows the trend  $I \sim \rho \cdot t \cdot Z^{1.5}$  ( $\rho$ ...density,  $t$ ...thickness,  $Z$ ...atom number) under the

chosen imaging conditions (camera length 30 mm). Hence, constant thickness and density provided, regions with a higher atom number  $Z$  appear brighter in HAADF images and vice versa. For a qualitative estimation of the HAADF contrast, the intensity of the image has been calculated on the basis of the density of Ni ( $8.9 \text{ g cm}^{-3}$ ) and  $\text{Y}_2\text{O}_3$  ( $5.0 \text{ g cm}^{-3}$ ) and the average atom number  $Z$  of Ni (28) and  $\text{Y}_2\text{O}_3$  (20.4) to be  $I(\text{Ni}) = 8.9 \cdot 28^{1.5} = 1318$  and  $I(\text{Y}_2\text{O}_3) = 5.0 \cdot 20.4^{1.5} = 610$ . Therefore, the bright spots in Figure 8 C represent the location of the Ni particles (for simplification, the particles have been treated as solid Ni particles). For a discussion of the Cu/Cu<sub>2</sub>O and Ni/NiO particles on SiO<sub>2</sub>, we refer to previous work [34].

### 3.3. Metal-Support interaction in the M/Y<sub>2</sub>O<sub>3</sub> and M/ZrO<sub>2</sub> (M=Cu, Ni) samples

For instructive comparison of the metal-support interaction, the results on the reference catalysts are presented first. Figure 9 highlights the size and structure of the nickel particles after a reduction in hydrogen at 673 K. Very large particles with sometimes straight edges and distinct particle morphologies (pentagonal or hexagonal outlines) are encountered. The SAED pattern still reveals the presence of metallic Ni, but also rather faint reflections of a second phase. This second phase is identified as a Ni-rich Ni<sub>3</sub>Si<sub>2</sub> intermetallic phase. An assignment of the experimentally determined lattice spacings to those of the base-centered orthorhombic Ni<sub>3</sub>Si<sub>2</sub> structure ( $a=12.22\text{\AA}$ ,  $b=10.80\text{\AA}$ ,  $c=6.92\text{\AA}$ , space group Cmc21, pattern number 00-017-0881 [36]) is shown in Table 3. Figure 9 B shows a high-resolution electron micrograph of a single Ni<sub>3</sub>Si<sub>2</sub> particle with faint (512) and more pronounced (311) lattice spacings, both marked by circles in the Fast Fourier Transform pattern shown as inset ( $d_{\text{exp}}=3.31 \text{ \AA}$ ,  $d_{\text{theor}}(311)=3.34 \text{ \AA}$ ;  $d_{\text{exp}}=1.92 \text{ \AA}$ ,  $d_{\text{theor}}(512)=1.94 \text{ \AA}$ ) [36]. It is worth to note, that this is the same intermetallic Ni-Si compound, that is formed upon reductive decomposition of bulk NiO particles in hydrogen at temperatures of  $\sim 673 \text{ K}$  [34]. The corresponding Cu/Cu<sub>2</sub>O particles

do not show changes in particle morphology or composition, especially no silicide formation is observed if treated under comparable conditions (not shown).

The extension of these experiments to the  $\text{Y}_2\text{O}_3$ - and  $\text{ZrO}_2$ -based samples is shown in the subsequent Figures 10 (nickel) and 11 (copper). Reduction of either  $\text{Ni-Y}_2\text{O}_3$  (Figure 10 A) or  $\text{Ni-ZrO}_2$  (Figure 10 B) at comparable temperatures did not yield (strong) metal-support interaction effects, such as encapsulation of metal particles or formation of intermetallic compounds. However, sintering is observed, with increased particle diameters between 20-30 nm. Both systems structure-, morphology-, and composition-wise represent very stable systems, as compared to the  $\text{Ni/SiO}_2$  counterpart. For copper, Figure 11 A and B show the state of  $\text{Cu-Y}_2\text{O}_3$  and  $\text{Cu-ZrO}_2$  after reduction in hydrogen at 873 K (panel A) and 973 K (panel B), respectively. Despite strong sintering of Cu particles on  $\text{Y}_2\text{O}_3$ , again, no further signs of metal-support interaction are detectable, even at the highest annealing temperatures. For Cu on amorphous  $\text{ZrO}_2$  the phase transformation into tetragonal and subsequently monoclinic  $\text{ZrO}_2$  (as evidenced by the SAED pattern), does not affect the shape or structure of the Cu particles substantially, again except thermal sintering. Undisputable formation of Cu-Y or Cu-Zr intermetallic phases has not been observed. We note, however, that even after reduction at the highest temperatures, only tetragonal  $\text{ZrO}_2$  is present, i.e. the presence of Cu obviously stabilizes this particular  $\text{ZrO}_2$  phase. For pure  $\text{ZrO}_2$ , treatments under similar experimental conditions already led to the beginning transformation into the monoclinic  $\text{ZrO}_2$  phase (see section 3.1.). This stabilization is even more astonishing, since the initial starting point was amorphous  $\text{ZrO}_2$ , with no obvious crystallographic (or epitaxial) relationships to either NaCl or  $\text{Cu/Cu}_2\text{O}$ . We might expect a matrix effect by  $\text{Cu/Cu}_2\text{O}$ , which opposes the transformation to the monoclinic  $\text{ZrO}_2$  phase. To summarizingly discuss the possibility of strong metal-support interaction in the outlined systems, we firstly note the prerequisite of reductive formation of an intermetallic phase starting from any metal/oxide system, that is, the

reduction of the oxide support. If and how prone any given oxide is to eventually be reduced to the metallic state, may be roughly estimated by its free enthalpy of formation. Therefore, the free enthalpy of formation (at 900 K), and, hence, its stability, increases in the line  $\text{SiO}_2$  ( $-747 \text{ kJ mol}^{-1}$ )  $<$   $\text{ZrO}_2$  ( $-926 \text{ kJ mol}^{-1}$ )  $<$   $\text{Y}_2\text{O}_3$  ( $-1670 \text{ kJ mol}^{-1}$ ) [37]. Reduction of the respective oxide and therefore, the tendency for intermetallic formation, is hence less pronounced in the case of  $\text{ZrO}_2$  and  $\text{Y}_2\text{O}_3$ . This is, however, only a relative estimation, since also  $\text{SiO}_2$  is usually considered a hardly reducible oxide, if compared to classical reducible “SMSI” oxides like  $\text{TiO}_2$  or  $\text{CeO}_2$  [23]. Classical structural manifestations of strong metal-support interaction like the reversible encapsulation of metal particles by a reduced sub-stoichiometric oxide are not anticipated, less so intermetallic formation as an extreme case. However, reductive Ni-silicide formation has been observed in a number of catalytic supported Ni/ $\text{SiO}_2$  systems upon treatment in hydrogen [38,39]. As the reaction is performed under flowing conditions, the driving force of the reaction  $3\text{Ni} + 2\text{SiO}_2 + 4\text{H}_2 \leftrightarrow \text{Ni}_3\text{Si}_2 + 4\text{H}_2\text{O}$  is the permanent removal of water and thus, the water partial pressure is kept on a low level and the reaction forced to the products. Water formation will most likely occur at the Ni/ $\text{SiO}_2$  interface by reaction of diffusing atomic hydrogen with the  $\text{SiO}_2$  substrate.

#### 4. Conclusions

In conclusion, we have shown that the presented model systems are excellent starting materials to eventually shed light on some important topics in materials science.  $\text{Y}_2\text{O}_3$  represents an extraordinarily stable system up to very high temperatures, even under reductive conditions, whereas the  $\text{ZrO}_2$  model system is an excellent basis for studying the important phase transformations between its amorphous, tetragonal and monoclinic structure. In turn, the chosen preparation pathway provides a convenient access to different polymorphic forms of  $\text{ZrO}_2$ , whose properties could be studied separately. Moreover, by adding Cu and Ni to the

Y<sub>2</sub>O<sub>3</sub>- and ZrO<sub>2</sub>-containing samples, catalytic model systems for more complex reactions like methanol steam reforming or methane reforming in solid-oxide fuel cells, are easily established. The combination of catalytic testing/determination of materials properties and the use of well-defined model systems being at the same time not too far from technologically realistic systems makes the establishment of structure-activity/selectivity/property relationships straightforward.

## **5. Acknowledgements**

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## Tables

**Table 1:** Correlation of the experimentally determined lattice spacings  $d(\text{hkl})_{\text{exp}}$  [Å] on  $\text{Y}_2\text{O}_3$  and  $\text{ZrO}_2$  after different reductive thermal treatments to those of bcc- $\text{Y}_2\text{O}_3$ , tetragonal  $\text{ZrO}_2$  or monoclinic  $\text{ZrO}_2$ , alongside assignment to distinct theoretical lattice planes, characterized by  $d(\text{hkl})_{\text{theor}}$ .

<b><math>\text{Y}_2\text{O}_3</math> H 1073K</b>			<b><math>\text{ZrO}_2</math> H 673</b>			<b><math>\text{ZrO}_2</math> H 1073</b>		
<b>d (hkl)<sub>exp</sub></b>	<b>Lattice plane</b>	<b>d (hkl)<sub>theor</sub></b>	<b>d (hkl)<sub>exp</sub></b>	<b>Lattice plane</b>	<b>d (hkl)<sub>theor</sub></b>	<b>d (hkl)<sub>exp</sub></b>	<b>Lattice plane</b>	<b>d (hkl)<sub>theor</sub></b>
4.36	$\text{Y}_2\text{O}_3$ (211)	4.33	2.97	t- $\text{ZrO}_2$ (101)	2.96	3.69	m- $\text{ZrO}_2$ (011)	3.69
3.03	$\text{Y}_2\text{O}_3$ (222)	3.06	2.59	t- $\text{ZrO}_2$ (002)	2.59	3.18	m- $\text{ZrO}_2$ (-111)	3.16
2.64	$\text{Y}_2\text{O}_3$ (400)	2.65	2.12	t- $\text{ZrO}_2$ (102)	2.12	2.97	t- $\text{ZrO}_2$ (101)	2.96
2.48	$\text{Y}_2\text{O}_3$ (411)	2.50	1.83	t- $\text{ZrO}_2$ (112)	1.82	2.84	m- $\text{ZrO}_2$ (111)	2.84
2.39	$\text{Y}_2\text{O}_3$ (420)	2.37	1.58	t- $\text{ZrO}_2$ (103)	1.55	2.62	t- $\text{ZrO}_2$ (002)	2.59
2.24	$\text{Y}_2\text{O}_3$ (332)	2.26	1.51	t- $\text{ZrO}_2$ (211)	1.53	2.55	t- $\text{ZrO}_2$ (110)	2.54
2.07	$\text{Y}_2\text{O}_3$ (134)	2.08	1.38	t- $\text{ZrO}_2$ (212)	1.37	2.34	m- $\text{ZrO}_2$ (021)	2.33
1.87	$\text{Y}_2\text{O}_3$ (440)	1.87	1.28	t- $\text{ZrO}_2$ (004)	1.28	2.21	m- $\text{ZrO}_2$ (-211)	2.21
1.71	$\text{Y}_2\text{O}_3$ (611)	1.72				2.19	m- $\text{ZrO}_2$ (102)	2.19
1.61	$\text{Y}_2\text{O}_3$ (622)	1.60				2.02	m- $\text{ZrO}_2$ (112)	2.02
1.55	$\text{Y}_2\text{O}_3$ (136)	1.56				1.84	m- $\text{ZrO}_2$ (022)	1.84
1.43	$\text{Y}_2\text{O}_3$ (642)	1.42				1.83	t- $\text{ZrO}_2$ (112)	1.83
1.31	$\text{Y}_2\text{O}_3$ (800)	1.32				1.78	m- $\text{ZrO}_2$ (-221)	1.78
1.25	$\text{Y}_2\text{O}_3$ (831)	1.23				1.69	m- $\text{ZrO}_2$ (202)	1.70

**Kommentar [PS4]:** Response to Reviewer 2 and 3; addressing of the hkl-indices thoroughly revised (all changes in red). Applies to the whole Table

**Table 2:** Correlation of the experimentally determined lattice spacings  $d(hkl)_{exp}$  [Å] on Cu-ZrO<sub>2</sub> and Cu-Y<sub>2</sub>O<sub>3</sub> after different reductive thermal treatments to those of fcc Cu, cubic Cu<sub>2</sub>O, bcc-Y<sub>2</sub>O<sub>3</sub>, tetragonal or monoclinic ZrO<sub>2</sub>, alongside assignment to distinct theoretical lattice planes, characterized by  $d(hkl)_{theor}$ .

Cu/Y <sub>2</sub> O <sub>3</sub> as grown			Cu/Y <sub>2</sub> O <sub>3</sub> H1073 K			Cu/ZrO <sub>2</sub> as grown		
Assignment			Assignment			Assignment		
$d(hkl)_{exp}$	Lattice plane	$d(hkl)_{theor}$	$d(hkl)_{exp}$	Lattice plane	$d(hkl)_{theor}$	$d(hkl)_{exp}$	Lattice plane	$d(hkl)_{theor}$
3.02	Y <sub>2</sub> O <sub>3</sub> (222)	3.05	4.35	Y <sub>2</sub> O <sub>3</sub> (211)	4.32	3.08	Cu <sub>2</sub> O (110)	3.01
2.64	Y <sub>2</sub> O <sub>3</sub> (400)	2.65	3.09	Y <sub>2</sub> O <sub>3</sub> (222)	3.06	2.49	Cu <sub>2</sub> O (111)	2.46
2.10	Cu (111)	2.09	2.66	Y <sub>2</sub> O <sub>3</sub> (400)	2.65	2.16	Cu <sub>2</sub> O (200)	2.13
1.91	Y <sub>2</sub> O <sub>3</sub> (125)	1.93	2.38	Y <sub>2</sub> O <sub>3</sub> (420)	2.37	1.55	Cu <sub>2</sub> O (220)	1.51
1.81	Cu (200)	1.81	2.13	Cu (111)	2.09			
1.63	Y <sub>2</sub> O <sub>3</sub> (622)	1.60	1.94	Y <sub>2</sub> O <sub>3</sub> (125)	1.93			
1.29	Cu (220)	1.28	1.83	Cu (200)	1.81			
			1.62	Y <sub>2</sub> O <sub>3</sub> (622)	1.60			
Cu/ZrO <sub>2</sub> H1073 K								
Assignment								
$d(hkl)_{exp}$	Lattice plane	$d(hkl)_{theor}$						
2.97	t-ZrO <sub>2</sub> (101)	2.96						
2.65	t-ZrO <sub>2</sub> (002)	2.59						
2.30	m-ZrO <sub>2</sub> (021)	2.33						
2.10	t-ZrO <sub>2</sub> (102)	2.12						
2.06	Cu (111)	2.09						
1.81	t-ZrO <sub>2</sub> (112) Cu (200)	1.82 1.81						
1.54	t-ZrO <sub>2</sub> (103)	1.55						
1.42	t-ZrO <sub>2</sub> (212)	1.37						
1.27	t-ZrO <sub>2</sub> (004)	1.28						

**Kommentar [PS5]:** Response to Reviewer 2 and 3; addressing of the hkl-indices thoroughly revised (all changes in red). Applies to the whole Table

Table 3: Correlation of the experimentally determined lattice spacings  $d(\text{hkl})_{\text{exp}}$  [Å] on Ni-ZrO<sub>2</sub>, Ni-Y<sub>2</sub>O<sub>3</sub> and Ni-SiO<sub>2</sub> after different reductive thermal treatments to those of fcc Ni, cubic NiO, bcc-Y<sub>2</sub>O<sub>3</sub>, tetragonal or monoclinic ZrO<sub>2</sub> and base-centered orthorhombic Ni<sub>3</sub>Si<sub>2</sub> alongside assignment to distinct theoretical lattice planes, characterized by  $d(\text{hkl})_{\text{theor}}$ .

Ni/Y <sub>2</sub> O <sub>3</sub> as grown			Ni/Y <sub>2</sub> O <sub>3</sub> H673 K			Ni/ZrO <sub>2</sub> as grown		
Assignment			Assignment			Assignment		
$d(\text{hkl})_{\text{exp}}$	Lattice plane	$d(\text{hkl})_{\text{theor}}$	$d(\text{hkl})_{\text{exp}}$	Lattice plane	$d(\text{hkl})_{\text{theor}}$ or	$d(\text{hkl})_{\text{exp}}$	Lattice plane	$d(\text{hkl})_{\text{theor}}$
3.08	Y <sub>2</sub> O <sub>3</sub> (222)	3.06	3.07	Y <sub>2</sub> O <sub>3</sub> (222)	3.06	2.08	NiO (200)	2.09
2.69	Y <sub>2</sub> O <sub>3</sub> (400)	2.65	2.65	Y <sub>2</sub> O <sub>3</sub> (400)	2.65	1.79	Ni (200)	1.77
2.41	NiO (111)	2.41	2.09	NiO (200)	2.09	1.51	NiO (220)	1.48
2.05	Ni (111)	2.03	2.00	Ni (111)	2.03	1.27	Ni (220)	1.25
1.91	Y <sub>2</sub> O <sub>3</sub> (125)	1.93	1.92	Y <sub>2</sub> O <sub>3</sub> (125)	1.93			
1.77	Ni (200)	1.76	1.88	Y <sub>2</sub> O <sub>3</sub> (440)	1.87			
1.64	Y <sub>2</sub> O <sub>3</sub> (622)	1.60	1.59	Y <sub>2</sub> O <sub>3</sub> (622)	1.60			
1.49	NiO (220)	1.48	1.33	Y <sub>2</sub> O <sub>3</sub> (156)	1.35			
1.36	Y <sub>2</sub> O <sub>3</sub> (156)	1.35	1.22	Ni (220)	1.25			
1.26	Ni (220)	1.25						
Ni/ZrO <sub>2</sub> H673 K			Ni/SiO <sub>2</sub> H673 K					
Assignment			Assignment					
$d(\text{hkl})_{\text{exp}}$	Lattice plane	$d(\text{hkl})_{\text{theor}}$	$d(\text{hkl})_{\text{exp}}$	Lattice plane	$d(\text{hkl})_{\text{theor}}$ or			
2.96	t-ZrO <sub>2</sub> (101)	2.96	3.31	Ni <sub>3</sub> Si <sub>2</sub> (311)	3.34			
2.59	t-ZrO <sub>2</sub> (002)	2.59	3.23	Ni <sub>3</sub> Si <sub>2</sub> (112)	3.18			
2.54	t-ZrO <sub>2</sub> (110)	2.54	3.10	Ni <sub>3</sub> Si <sub>2</sub> (131)	3.09			
2.12	t-ZrO <sub>2</sub> (102)	2.12	2.94	Ni <sub>3</sub> Si <sub>2</sub> (022)	2.91			
2.04	NiO (200)	2.09	2.73	Ni <sub>3</sub> Si <sub>2</sub> (330)	2.70			
1.99	Ni (111)	2.03	2.66	Ni <sub>3</sub> Si <sub>2</sub> (420)	2.66			
1.81	t-ZrO <sub>2</sub> (112)	1.83	2.61	Ni <sub>3</sub> Si <sub>2</sub> (222)	2.63			
1.58	t-ZrO <sub>2</sub> (103)	1.55	2.12	Ni <sub>3</sub> Si <sub>2</sub> (150)	2.12			
1.54	t-ZrO <sub>2</sub> (211)	1.53	1.99	Ni <sub>3</sub> Si <sub>2</sub> (313)	1.98			
1.49	t-ZrO <sub>2</sub> (202)	1.48	1.94	Ni <sub>3</sub> Si <sub>2</sub> (531)	1.94			
1.37	t-ZrO <sub>2</sub> (212)	1.37	1.87	Ni <sub>3</sub> Si <sub>2</sub> (350)	1.91			
1.28	t-ZrO <sub>2</sub> (004)	1.28	1.79	Ni <sub>3</sub> Si <sub>2</sub> (621)	1.83			
1.19	t-ZrO <sub>2</sub> (213)	1.18	1.76	Ni <sub>3</sub> Si <sub>2</sub> (043)	1.76			

**Kommentar [PS6]:** Response to Reviewer 2 and 3; addressing of the hkl-indices thoroughly revised (all changes in red). Applies to the whole Table

## Figure Captions

Figure 1: Overview bright-field TEM image of a free-standing  $\text{Y}_2\text{O}_3$  thin film in the as-grown state (A) and after reduction at 1073 K in hydrogen for 1 hour (B). The insets highlight the corresponding SAED patterns, indicating the presence of bcc- $\text{Y}_2\text{O}_3$  in both cases.

Figure 2: Overview bright-field TEM image of a free-standing  $\text{ZrO}_2$  thin film deposited at 300 K (panels A, C and E) and deposited at 573 K (panels B, D and F). Panels A and B highlight the respective initial, as-grown samples, C and D the structure of the film after reduction at 673 K in hydrogen for 1 hour and panels E and F the structure of the films after reduction at 1073 K and 873 K in hydrogen for 1 hour, respectively. The insets show the corresponding SAED patterns.

Figure 3: Structure of the  $\text{ZrO}_2$  thin film after reduction at 673 K. (A) Overview bright-field TEM image, (B) HAADF image, (C) Zr-M and O-K EEL edges and (D) high-resolution TEM image of the interface of neighbouring bright and dark grains as shown in panel A.

Figure 4: Overview bright-field TEM image of a free-standing  $\text{ZrO}_2$  thin film deposited at 300 K and subsequently annealed in 1 bar He for 1 hour at 673 K (panel A) and at 1073 K (panel B). The insets highlight the corresponding SAED patterns, indicating the presence of tetragonal and monoclinic  $\text{ZrO}_2$ , respectively.

Figure 5: Selected Area Electron Diffraction patterns of a  $\text{ZrO}_2$  thin film deposited at 300 K and subsequently annealed in-situ in vacuum in the electron microscope. SAED patterns taken at 753 K (A), 833 K (B) and 1173 K (C), respectively.

Figure 6: Overview bright-field TEM images of Cu/Cu<sub>2</sub>O particles embedded in bcc-Y<sub>2</sub>O<sub>3</sub> (panel A) and amorphous ZrO<sub>2</sub> (panel C), respectively. Panel B shows the particle analysis of the Cu/Y<sub>2</sub>O<sub>3</sub> film. The SAED patterns are shown as insets.

Figure 7: High-resolution TEM image of two agglomerated Cu<sub>2</sub>O particles highlighting (111) and (200) lattice fringes, as well as a Moiré-pattern caused by the overlap of both structures.

Figure 8: Overview bright-field TEM images of Ni/NiO particles embedded in bcc-Y<sub>2</sub>O<sub>3</sub> (panel A) and amorphous ZrO<sub>2</sub> (panel B). Panel C shows the HAADF image of the Ni/Y<sub>2</sub>O<sub>3</sub> sample for better imaging of the Ni/NiO particles.

Figure 9: Structure of the reference Ni/SiO<sub>2</sub> thin film after reduction at 673 K in hydrogen for 1 hour. Panel (A) highlights the bright-field overview TEM image alongside its SAED pattern (inset), panel B a rounded Ni<sub>3</sub>Si<sub>2</sub> particle with (512) and (311) lattice fringes.

Figure 10: Overview bright-field TEM images of Ni/NiO particles embedded in bcc-Y<sub>2</sub>O<sub>3</sub> (panel A) and amorphous ZrO<sub>2</sub> (panel B) and subsequently reduced at 673 K in hydrogen for 1 hour. The SAED patterns are shown as insets.

Figure 11: Overview bright-field TEM images of Cu/Cu<sub>2</sub>O particles embedded in bcc-Y<sub>2</sub>O<sub>3</sub> (panel A) and amorphous ZrO<sub>2</sub> (panel B) and subsequently reduced in hydrogen for 1 hour at 873 K and 973 K, respectively. The SAED patterns are shown as insets

## References

- [1] M. Rühle, *Adv. Mater.* 9 (1997) 195 and references therein
- [2] F. Jollet, C. Noguera, N. Thomat, M. Gautier, J.P. Duraud, *Phys. Rev. B* 42 (1990) 7587-7595
- [3] Y. Shen, S. Shao, H. Yu, Z. Fan, H. He, J. Shao, *Appl. Surf. Sci* 254 (2007) 552-556
- [4] F. Pailloux, D. Imhoff, M. Jublot, F. Paumier, R.J. Gaboriaud, M. Jaouen, *Micron* 37 (2006) 420-425
- [5] V.P. Oleshko, J.M. Howe, S. Shukla, S. Seal *J. Nanosci. Nanotech.* 4 (2004) 867-875
- [6] T. Gougousi, Z. Chen, *Thin Solid Films* 516 (2008) 6197-6204
- [7] J. D. Cawley, W. F. Lee, *Structure and Properties of Ceramics, Materials Science and Technology*, Vol. 11 (Ed. M. V. Swain), VCH, Weinheim 1994, p.47
- [8] S. McIntosh, R.J. Gorte, *Chem. Rev.* 104 (2004) 4845-4865
- [9] H. Purnama, F. Girgsdies, T. Ressler, J. H. Schattka, R. A. Caruso, R. Schomäcker, R. Schlögl, *Catal. Lett.* 94 (2004) 61
- [10] B. Xu, J. Wie, Y. Yu, J. Li, Q. Zhu, *Top. Catal.* 22 (2003) 77
- [11] Landolt-Börnstein, *Phase equilibria, crystallographic and thermodynamic data of Binary Alloys, Group IV/5/H* (Ed. B. Predel), Springer, Berlin, 1997
- [12] I. Kasatkin, F. Girgsdies, T. Ressler, R. a. Caruso, J. H. Schattka, J. Urban, K. Weiss, *J. Mater. Sci.* 39 (2004) 2151
- [13] P. M. Kelley, C. J. Ball, *J. Am. Ceram. Soc.* 69 (1986) 259

- [14] N. K. Shima, *J. Mech. Phys. Solids* 45 (1997) 261
- [15] B. Budiansky, L. Truskinovsky, *J. Mech. Phys. Solids* 41 (1993) 1445
- [16] G. K. Bansal, A. H. Heuer, *Acta Metallurgica* 20 (1972) 1281
- [17] G. K. Bansal, A. H. Heuer, *Acta Metallurgica* 22 (1974) 409
- [18] J. M. MacKenzie, J. S. Bowles, *Acta Metallurgica* 2 (1954) 138
- [19] J. M. MacKenzie, J. S. Bowles, *Acta Metallurgica* 2 (1954) 129
- [20] J. E. Bailey, *Proc. R. Soc. Lond. A* 279 (1964) 395
- [21] C. M. Wayman, *Materials Characterization* 39 (1997) 235
- [22] A. G. Evans, N. Burlingame, M. Drory, W. M. Kriven, *Acta Metallographica* 29 (1981) 447
- [23] S. J. Tauster, *Accounts of Chemical Research* 1 (1986) 389
- [24] J. Liu, *ChemCatchem* 3 (2011) 934
- [25] G. Rupprechter, K. Hayek, H. Hofmeister, *Nanostructured Materials* 9 (1997) 311-314
- [26] S. Penner, H. Lorenz, B. Klötzer, D. Wang, M. Stöger-Pollach, C. Rameshan, W. Jochum, *Appl. Catal. A* 358 (2009) 193-202
- [27] H. Lorenz, M. Stöger-Pollach, S. Schwarz, J. Bernardi, K. Pfaller, B. Klötzer, S. Penner, *J. Phys. Chem. C* 112 (2008) 918-925
- [28] S. Penner, B. Klötzer, B. Jenewein, X. Liu, E. Bertel, F. Klauser, *Thin Solid Films* 516 (2008) 4742-4749
- [29] S. Penner, B. Jenewein, B. Klötzer, *PhysChemChemPhys* 9 (2007) 2428-2433

- [30] H. Lorenz, S. Penner, B. Klötzer, C. Rameshan, W. Jochum, *Appl. Catal. A* 358 (2009) 203-210
- [31] R. Thalinger, M. Stöger-Pollach, B. Klötzer, S. Penner, *Mat. Chem. Phys.* 138 (2013) 384
- [32] S. Penner, B. Klötzer, B. Jenewein, X. Liu, E. Bertel, F. Klauser, *Thin Solid Films* 516 (2008) 4742-4749
- [33] B. Bondars, G. Heidemane, J. Grabis, K. Laschke, H. Boysen, J. Schneider, F. Frey, *J. Mater. Sci.* 30 (1995) 1621
- [34] R. Thalinger, M. Heggen, D. Stroppa, M. Stöger-Pollach, B. Klötzer, S. Penner, *Mater. Chem. Phys.* (2013), submitted
- [35] A. Kirfel, K. D. Eichhorn, *Acta Crystallogr. A* 46 (1990) 271
- [36] Y. D. Yin, R. M. Rioux, C. K. Erdonnez, S. Hughes, G. A. Somorjai, A. P. Alivisatos, *Science* 304 (2004) 711
- [37] I. Bahrin, *Thermochemical Data of Pure Substances, Part II La-Zr*, VCH, Weinheim, 1993
- [38] H. Praliand, G. A. Martin, *J. Catal.* 72 (1981) 394
- [39] R. Lamber, N. Jaeger, G. Schultz-Ekloff, *Surf. Sci.* 227 (1990) 268