

Electron microscopy investigations of Metal-Support Interaction effects in M/Y₂O₃ and M/ZrO₂ 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 $\text{Cu}/\text{Cu}_2\text{O}$ 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 (~ 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 $\text{Cu}/\text{Cu}_2\text{O}$ 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

ZrO₂- and Y₂O₃-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: α -Y₂O₃ with cubic structure; a high-temperature β -Y₂O₃ phase stable at 2653 K with hexagonal structure and a high-pressure γ -Y₂O₃ 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 ZrO₂ structure, which is the thermodynamically stable phase under ambient conditions, a tetragonal and a cubic ZrO₂ phase [1,10]. Far too exhaustive to be reviewed in detail at this point, the cubic phase is formed upon cooling the ZrO₂ melt to 2953 K, followed by the transformation into tetragonal ZrO₂ 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, 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 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 ZrO_2 amorphous \rightarrow

ZrO₂ tetragonal → ZrO₂ 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/Y₂O₃ and M/ZrO₂ (M=Cu, Ni), referenced to the corresponding M/SiO₂ 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

Y₂O₃ (from a tantalum crucible) and ZrO₂ (from a tungsten crucible) have been both prepared in a dedicated high vacuum chamber (base pressure 10⁻⁶ mbar) by thermal evaporation of Y metal in 10⁻⁴ mbar O₂ or ZrO₂ in 10⁻⁵ mbar H₂, respectively, onto vacuum-cleaved NaCl(001) single crystal facets. The latter is introduced in the case of ZrO₂ 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 Y_2O_3 , ZrO_2 , or, in the case of the reference sample, in a 25 nm thick layer of amorphous 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\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 Y_2O_3 and ZrO_2

Starting from the already well-characterized initial states, comprising highly-ordered bcc Y_2O_3 (at template temperatures of 573 K), amorphous ZrO_2 (at 300 K) and ordered tetragonal 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 Y_2O_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. Y_2O_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 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 ZrO_2 film deposited at 300 K, panels B, D and F those of the 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 ZrO₂ phase at 573 K (panel B). Details have been discussed in previous work [30]. Panels C and D highlight the structures of the ZrO₂ samples after reduction at 673 K. Whereas the initially tetragonal ZrO₂ 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 ZrO₂ is detected), the initially amorphous ZrO₂ 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 ZrO₂ 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 ZrO₂ 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 ZrO₂ → monoclinic ZrO₂. 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 ZrO₂ 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 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 ZrO_2 material [1]. Whereas 1223 K are reported for bulk 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 ZrO_2 phase, but forms the tetragonal phase first, which subsequently transforms into the monoclinic phase. The energetic situation at the ZrO_2/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 Ga_2O_3 nanospheres was

found to be triggered by wetting phenomena between sub-stoichiometric GaO_x and $\text{NaCl}(001)$ [32], whereas the formation of well-shaped In_2O_3 nanopillars was due to epitaxial relations between the In_2O_3 and 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 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 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 ZrO_2 structure [31]. Hence, we can exclude substantial variations of the electronic structure/chemical environment of the 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 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 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 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 ~ 833 K (panel B), the tetragonal ZrO_2 phase starts to develop. However, the subsequent transition to monoclinic 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 (~ 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 M/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 Ni/NiO particles embedded in the respective oxides. For comparison, the same metal particles have also been supported on 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-Y₂O₃ (panel A) and the Cu-ZrO₂ (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. Y₂O₃ is represented by the grey structure in-between the metal particles. The SAED pattern (inset) reveals that although Y₂O₃ was deposited at room temperature, polycrystalline bcc-Y₂O₃, alongside a mixture of Cu and Cu₂O for the particle structure/composition is present. Due to the crystallinity of Y₂O₃, detection of the Cu/Cu₂O is therefore not straightforward. Particle analysis, as shown in Figure 6 B, yields an average diameter of the Cu/Cu₂O particles of ~ 11 nm and a particle density of 2.1 · 10¹¹ particles cm⁻², both of which are comparable to the reference Cu/Cu₂O-SiO₂ system (discussed in detail in [34]). Cu/Cu₂O particles embedded in ZrO₂ are very hard to detect, also due the inherently higher contrast of the amorphous ZrO₂ structure. SAED patterns (inset) indeed reveal that ZrO₂ is amorphous and that the copper particles are in fact mostly Cu₂O. The presence of Cu₂O is nicely corroborated in HRTEM images, where Figure 7 shows an agglomerate of two Cu₂O 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 Cu₂O is additionally confirmed. Figure 8 in turn shows the corresponding TEM-images of the Ni-Y₂O₃ and Ni-ZrO₂ 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-Y₂O₃ (panel A) and amorphous ZrO₂ (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 Y₂O₃, HAADF imaging (panel C) has been carried out. The HAADF intensity roughly follows the trend $I \sim \rho \cdot t \cdot Z^{1.5}$ (ρ ...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 g cm^{-3}) and Y_2O_3 (5.0 g cm^{-3}) and the average atom number Z of Ni (28) and Y_2O_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/Cu₂O and Ni/NiO particles on SiO₂, we refer to previous work [34].

3.3. Metal-Support interaction in the M/Y₂O₃ and M/ZrO₂ (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 Ni₃Si₂ intermetallic phase. An assignment of the experimentally determined lattice spacings to those of the base-centered orthorhombic Ni₃Si₂ 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 Ni₃Si₂ 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/Cu₂O 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 Y_2O_3 - and 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 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 Ni/SiO_2 counterpart. For copper, Figure 11 A and B show the state of $\text{Cu-Y}_2\text{O}_3$ and 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 Y_2O_3 , again, no further signs of metal-support interaction are detectable, even at the highest annealing temperatures. For Cu on amorphous ZrO_2 the phase transformation into tetragonal and subsequently monoclinic 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 ZrO_2 is present, i.e. the presence of Cu obviously stabilizes this particular ZrO_2 phase. For pure ZrO_2 , treatments under similar experimental conditions already led to the beginning transformation into the monoclinic ZrO_2 phase (see section 3.1.). This stabilization is even more astonishing, since the initial starting point was amorphous 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 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 SiO_2 (-747 kJ mol^{-1}) $<$ ZrO_2 (-926 kJ mol^{-1}) $<$ Y_2O_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 ZrO_2 and Y_2O_3 . This is, however, only a relative estimation, since also SiO_2 is usually considered a hardly reducible oxide, if compared to classical reducible “SMSI” oxides like TiO_2 or 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/ 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/ SiO_2 interface by reaction of diffusing atomic hydrogen with the 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. Y_2O_3 represents an extraordinarily stable system up to very high temperatures, even under reductive conditions, whereas the 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 ZrO_2 , whose properties could be studied separately. Moreover, by adding Cu and Ni to the

Y₂O₃- and ZrO₂-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.

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Tables

Table 1: Correlation of the experimentally determined lattice spacings $d(hkl)_{\text{exp}}$ [Å] on Y_2O_3 and ZrO_2 after different reductive thermal treatments to those of bcc- Y_2O_3 , tetragonal ZrO_2 or monoclinic ZrO_2 , alongside assignment to distinct theoretical lattice planes, characterized by $d(hkl)_{\text{theor}}$.

Y_2O_3 H 1073K			ZrO_2 H 673			ZrO_2 H 1073		
$d(hkl)_{\text{exp}}$	Lattice plane	$d(hkl)_{\text{theor}}$	$d(hkl)_{\text{exp}}$	Lattice plane	$d(hkl)_{\text{theor}}$	$d(hkl)_{\text{exp}}$	Lattice plane	$d(hkl)_{\text{theor}}$
4.36	Y_2O_3 (211)	4.33	2.97	t- ZrO_2 (101)	2.96	3.69	m- ZrO_2 (011)	3.69
3.03	Y_2O_3 (222)	3.06	2.59	t- ZrO_2 (002)	2.59	3.18	m- ZrO_2 (-111)	3.16
2.64	Y_2O_3 (400)	2.65	2.12	t- ZrO_2 (102)	2.12	2.97	t- ZrO_2 (101)	2.96
2.48	Y_2O_3 (411)	2.50	1.83	t- ZrO_2 (112)	1.82	2.84	m- ZrO_2 (111)	2.84
2.39	Y_2O_3 (420)	2.37	1.58	t- ZrO_2 (103)	1.55	2.62	t- ZrO_2 (002)	2.59
2.24	Y_2O_3 (332)	2.26	1.51	t- ZrO_2 (211)	1.53	2.55	t- ZrO_2 (110)	2.54
2.07	Y_2O_3 (134)	2.08	1.38	t- ZrO_2 (212)	1.37	2.34	m- ZrO_2 (021)	2.33
1.87	Y_2O_3 (440)	1.87	1.28	t- ZrO_2 (004)	1.28	2.21	m- ZrO_2 (-211)	2.21
1.71	Y_2O_3 (611)	1.72				2.19	m- ZrO_2 (102)	2.19
1.61	Y_2O_3 (622)	1.60				2.02	m- ZrO_2 (112)	2.02
1.55	Y_2O_3 (136)	1.56				1.84	m- ZrO_2 (022)	1.84
1.43	Y_2O_3 (642)	1.42				1.83	t- ZrO_2 (112)	1.83
1.31	Y_2O_3 (800)	1.32				1.78	m- ZrO_2 (-221)	1.78
1.25	Y_2O_3 (831)	1.23				1.69	m- 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-ZrO₂ and Cu-Y₂O₃ after different reductive thermal treatments to those of fcc Cu, cubic Cu₂O, bcc-Y₂O₃, tetragonal or monoclinic ZrO₂, alongside assignment to distinct theoretical lattice planes, characterized by $d(hkl)_{theor}$.

Cu/Y ₂ O ₃ as grown			Cu/Y ₂ O ₃ H1073 K			Cu/ZrO ₂ 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 ₂ O ₃ (222)	3.05	4.35	Y ₂ O ₃ (211)	4.32	3.08	Cu ₂ O (110)	3.01
2.64	Y ₂ O ₃ (400)	2.65	3.09	Y ₂ O ₃ (222)	3.06	2.49	Cu ₂ O (111)	2.46
2.10	Cu (111)	2.09	2.66	Y ₂ O ₃ (400)	2.65	2.16	Cu ₂ O (200)	2.13
1.91	Y ₂ O ₃ (125)	1.93	2.38	Y ₂ O ₃ (420)	2.37	1.55	Cu ₂ O (220)	1.51
1.81	Cu (200)	1.81	2.13	Cu (111)	2.09			
1.63	Y ₂ O ₃ (622)	1.60	1.94	Y ₂ O ₃ (125)	1.93			
1.29	Cu (220)	1.28	1.83	Cu (200)	1.81			
			1.62	Y ₂ O ₃ (622)	1.60			
Cu/ZrO ₂ H1073 K								
Assignment								
$d(hkl)_{exp}$	Lattice plane	$d(hkl)_{theor}$						
2.97	t-ZrO ₂ (101)	2.96						
2.65	t-ZrO ₂ (002)	2.59						
2.30	m-ZrO ₂ (021)	2.33						
2.10	t-ZrO ₂ (102)	2.12						
2.06	Cu (111)	2.09						
1.81	t-ZrO ₂ (112) Cu (200)	1.82 1.81						
1.54	t-ZrO ₂ (103)	1.55						
1.42	t-ZrO ₂ (212)	1.37						
1.27	t-ZrO ₂ (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-ZrO₂, Ni-Y₂O₃ and Ni-SiO₂ after different reductive thermal treatments to those of fcc Ni, cubic NiO, bcc-Y₂O₃, tetragonal or monoclinic ZrO₂ and base-centered orthorhombic Ni₃Si₂ alongside assignment to distinct theoretical lattice planes, characterized by $d(\text{hkl})_{\text{theor}}$.

Ni/Y ₂ O ₃ as grown			Ni/Y ₂ O ₃ H673 K			Ni/ZrO ₂ 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 ₂ O ₃ (222)	3.06	3.07	Y ₂ O ₃ (222)	3.06	2.08	NiO (200)	2.09
2.69	Y ₂ O ₃ (400)	2.65	2.65	Y ₂ O ₃ (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 ₂ O ₃ (125)	1.93	1.92	Y ₂ O ₃ (125)	1.93			
1.77	Ni (200)	1.76	1.88	Y ₂ O ₃ (440)	1.87			
1.64	Y ₂ O ₃ (622)	1.60	1.59	Y ₂ O ₃ (622)	1.60			
1.49	NiO (220)	1.48	1.33	Y ₂ O ₃ (156)	1.35			
1.36	Y ₂ O ₃ (156)	1.35	1.22	Ni (220)	1.25			
1.26	Ni (220)	1.25						
Ni/ZrO ₂ H673 K			Ni/SiO ₂ 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 ₂ (101)	2.96	3.31	Ni ₃ Si ₂ (311)	3.34			
2.59	t-ZrO ₂ (002)	2.59	3.23	Ni ₃ Si ₂ (112)	3.18			
2.54	t-ZrO ₂ (110)	2.54	3.10	Ni ₃ Si ₂ (131)	3.09			
2.12	t-ZrO ₂ (102)	2.12	2.94	Ni ₃ Si ₂ (022)	2.91			
2.04	NiO (200)	2.09	2.73	Ni ₃ Si ₂ (330)	2.70			
1.99	Ni (111)	2.03	2.66	Ni ₃ Si ₂ (420)	2.66			
1.81	t-ZrO ₂ (112)	1.83	2.61	Ni ₃ Si ₂ (222)	2.63			
1.58	t-ZrO ₂ (103)	1.55	2.12	Ni ₃ Si ₂ (150)	2.12			
1.54	t-ZrO ₂ (211)	1.53	1.99	Ni ₃ Si ₂ (313)	1.98			
1.49	t-ZrO ₂ (202)	1.48	1.94	Ni ₃ Si ₂ (531)	1.94			
1.37	t-ZrO ₂ (212)	1.37	1.87	Ni ₃ Si ₂ (350)	1.91			
1.28	t-ZrO ₂ (004)	1.28	1.79	Ni ₃ Si ₂ (621)	1.83			
1.19	t-ZrO ₂ (213)	1.18	1.76	Ni ₃ Si ₂ (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 Y_2O_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- Y_2O_3 in both cases.

Figure 2: Overview bright-field TEM image of a free-standing 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 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 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 ZrO_2 , respectively.

Figure 5: Selected Area Electron Diffraction patterns of a 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/Cu₂O particles embedded in bcc-Y₂O₃ (panel A) and amorphous ZrO₂ (panel C), respectively. Panel B shows the particle analysis of the Cu/Y₂O₃ film. The SAED patterns are shown as insets.

Figure 7: High-resolution TEM image of two agglomerated Cu₂O 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-Y₂O₃ (panel A) and amorphous ZrO₂ (panel B). Panel C shows the HAADF image of the Ni/Y₂O₃ sample for better imaging of the Ni/NiO particles.

Figure 9: Structure of the reference Ni/SiO₂ 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 Ni₃Si₂ particle with (512) and (311) lattice fringes.

Figure 10: Overview bright-field TEM images of Ni/NiO particles embedded in bcc-Y₂O₃ (panel A) and amorphous ZrO₂ (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/Cu₂O particles embedded in bcc-Y₂O₃ (panel A) and amorphous ZrO₂ (panel B) and subsequently reduced in hydrogen for 1 hour at 873 K and 973 K, respectively. The SAED patterns are shown as insets

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