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From Pure Oxides to Mixed Oxides: Model Systems for Structural and Catalytic Studies

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As pure oxides and mixed oxide systems play an ever-increasing role in a variety of research fields ranging from catalysis over electrochemical applications to microelectronics, the present contribution aims at introducing a straightforward concept for the easy and reproducible preparation of well-defined and well-structured thin film model systems both for pure and mixed oxide systems. Exploiting the special structural and surface properties of vacuum-cleaved NaCl (001) growth templates, the concept is exemplified for the formation of nano-spheres (Ga_2O_3), nano-pyramids (In_2O_3), plates and needles (V_2O_5) and dendritic structures (Ga_2O_3-WO_3). Careful tuning of the preparation conditions (substrate temperature, deposition rate, oxygen partial pressure or post-annealing temperature) allows the formation of special particle morphologies at much lower substrate temperatures (less than 400°C) than previously and usually applied.

Keywords: Model systems, Electron microscopy, Thin film, Epitaxy, Heterogeneous catalysis, Oxide, Mixed oxide.

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1. INTRODUCTION

Metal oxides, both pure and as mixed oxide systems, are of exceptional importance in a variety of research areas, basically encompassing the fields of chemistry, physics and materials science. In turn, they are utilized in catalysis, as sensors, as corrosion protective coatings, in electrochemical applications or in microelectronics, to name just a few. Regarding heterogeneous catalysis, for example, oxides are widely used either as a catalyst itself or as support for other oxides, metal particles or functional groups. This at the same time shows the usual challenge faced, when dealing with oxide systems: while for example the catalysis on metal particles is well-understood, oxides are significantly more complex because of their structural and chemical flexibility. This might involve different oxidation states, polymorphism, surface termination, hydroxylation, doping or the general role of surface and bulk defects [1]. Similar considerations also hold for other research areas. The complexity is evidently multiplied, if mixed oxide systems are discussed. The latter recently got more attention due to their promising behavior in various research areas, such as sensor technology or (photo-) catalysis [2]. Obviously, the need for specially prepared model systems exhibiting well-defined particle shapes and structures that can be studied by the full artillery of state-of-the-art structural and spectroscopic characterization methods (e.g. electron microscopy techniques) is even more imperative. One particular promising pathway to prepare such model systems is the use of the well-defined cleavage facet of NaCl(001) to structurally and energetically facilitate the growth of nanoparticles. It has already proven its capabilities in mediating the growth of well-shaped metal nanoparticles (Pt, Rh, Pd, Ir or Re) [3]. The present contribution extends these studies to oxidic systems and highlights the possibilities in not only modeling particular particle shapes, morphologies and structures, but also in establishing structure-property and structure-activity relationships.

2. EXPERIMENTAL

In order to prepare oxide systems that are well-suited for characterization by high-resolution electron microscopy (HRTEM), selected area electron diffraction (SAED), atomic force microscopy (AFM) or X-ray photoelectron spectroscopy (XPS), as well as for kinetic studies by gas chromatography (GC), pure oxide and mixed oxide nanoparticles (and films) were vacuum-grown on a crystalline soluble substrate (i.e. NaCl(001), 0.25 cm²) via oxide or metal evaporation in a low background pressure (~10^{-2} Pa) of oxygen at substrate temperatures between 300 and 623 K. For some oxides, post-annealing treatments (oxidative or reductive) had to be performed. Following this routine, a variety of oxide films have been prepared, including Ga_2O_3, bcc-In_2O_3, cubic VO, monoclinic V_2O_5, ZnO, SiO_2, TiO_2, fcc-CeO_2, WO_3, cubic SnO_2, SnO, tetragonal PdO, GeO_2, bcc-Y_2O_3, tetragonal ZrO_2, cubic Cu_2O, cubic CuO, cubic NiO, as well as Ga_2O_3-WO_3. Film thicknesses of ~25 nm are usually obtained to achieve self-supporting samples. Mixed oxide systems were prepared in a similar fashion, by either co-deposition or consecutive deposition of the respective oxides. In addition, the same films were prepared in parallel on freshly grown polycrystalline NaCl(001) films (up to 100 cm²) to obtain films suitable for micro-kinetic measurements. A strengthening layer of 500-1000 nm SiO_2 was added to all the latter films to improve the mechanical stability. All prepared films were in turn floated into distilled water, dried and either mounted on gold grids for electron microscopy or mounted on quartz wool inside the micro-reactor [1].

3. RESULTS AND DISCUSSION

3.1 Ga₂O₃

Gallium oxides and Ga-containing materials are catalytically active in a variety of reactions, including hydrocarbon isomerization, dehydrogenation or methanol steam reforming/methanol synthesis. Various methods have been proposed as access routes to Ga-containing systems, including sputtering, laser deposi-

tion, chemical vapor deposition or oxidation of GaAs or GaN surfaces [1]. For our proposed routine, Ga_2O_3 powder was thermally evaporated onto different NaCl surfaces between 300 and 580 K at varying deposition rates (~ 0.3-10Å s^{-1}) and O_2 background pressures. Uniformly sized Ga_2O_3 spheres with diameters between 20-25 nm were obtained at substrate temperatures T > 530 K. The formation of Ga_2O_3 spheres was explained by a growth mechanism based on highly mobile quasi-liquid sub-stoichiometric oxides of gallium, including an equilibrium between desorption of these gallium oxides and fast re-oxidation to Ga_2O_3 (Figure 1a). The sizes of these spheres was found to be highly depend on the oxygen partial pressure, leading to larger spheres at lower O_2-pressures (Figure 1b). The size control occurs via (surface) re-oxidation of gallia spheres, which suppresses coalescence by Ostwald ripening. The XPS spectra reveal a stoichiometry close to Ga_2O_3, at least in the surface-near regions (Figure 1c). AFM topography confirms the formation of the sphere-like aggregates (Figure 1d), whose exact shape and size is even more evident in the phase image. Catalytic testing in methanol steam reforming reveals Ga_2O_3 being a highly active catalyst, but without pronounced selectivity towards CO_2 (Figure 1e) [4].

3.2 In_2O_3

In_2O_3-containing catalysts, particular in combinations with other oxides, such as Al_2O_3, TiO_2 or zeolithes, have shown high activity and selectivity in $deNO_x$ reactions and for ethanol and methanol steam reforming. For the latter two cases, CO formation was almost completely suppressed down to the ppm-level. As for Ga_2O_3, several methods for the preparation of In_2O_3 nanoparticles and thin films exist: evaporation, sputtering, laser deposition, spray pyrolysis, thermal oxidation of pre-deposited In and electrochemical deposition [1]. Especially the preparation of nanostructures (nanocrystals and wires) has received increased attention due to the potential use as catalyst systems [5]. However, one of the main drawbacks is related to the very high substrate temperatures, usually being in the range of 1000-1200 K [5]. As for the In_2O_3 system, after deposition at 580 K in 10^{-2} Pa O_2, the TEM images show particles with square, triangular and quasi-rhombohedral outlines (Figure 1a), giving rise to an almost single-crystalline SAED pattern of bcc-In_2O_3 (Figure 1b). This is also confirmed by the HRTEM images (Figure 1c). Cubic NaCl acts as a "structural mediator" for the growth of crystalline In_2O_3, as the crystallographic matching between the lattice planes of both structures is almost perfect. Regarding catalytic behavior in methanol steam reforming, In_2O_3 particles turn out to be promising CO_2-selective catalysts (Figure 2d) [6].

3.3 V_2O_3 and V_2O_5-based compounds

VO_x- and V_2O_5-based systems are widely used in a variety of industrially important chemical processes such
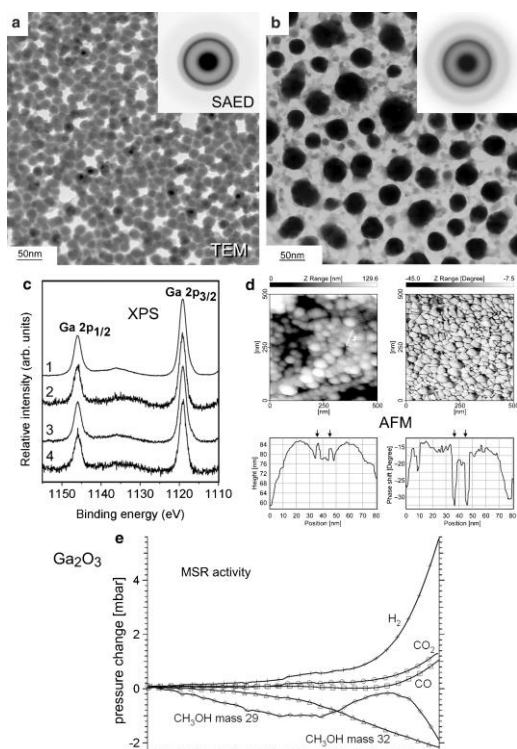

Fig. 1 – Characterization of the thin film Ga_2O_3 catalyst. (a) TEM image of spheres, obtained at substrate temperatures of 580 K in 10^{-2} Pa O_2. (b) Same film, but without additional oxygen partial pressure. the insets show the respective SAED patterns. (c) Ga 2p XPS spectra obtained in the as-grown state and after different annealing treatments. (d) AFM topography (left) and phase signal (right) of the film shown in (a). (e) Temperature-programmed methanol steam reforming reaction on the Ga_2O_3 thin film (adapted from [1]).
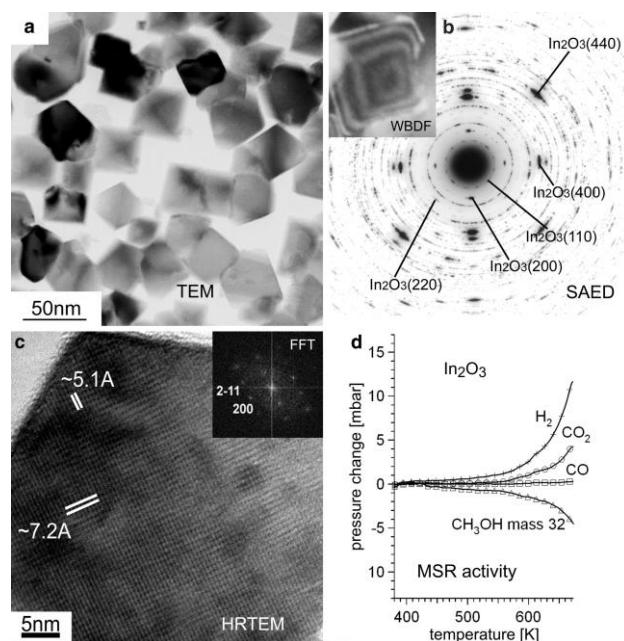

Fig. 2 – Characterization of the epitaxial thin film In_2O_3 catalyst. (a) TEM image of pyramidal-shaped particles, obtained at substrate temperatures of 580 K in 10^{-2} Pa O_2. (b) SAED pattern with dark-field image of a single particle shown as inset. (c) HRTEM image of a [001]-oriented particle with FFT as inset. (d) Temperature-programmed methanol steam reforming reaction on the In_2O_3 particles (adapted from [1]).

as the oxidation of SO_2 to SO_3 during the production of sulphuric acid, the oxidation of benzene to maleic anhydride or the selective reduction of NO_x with NH_3. For this purpose, vanadium oxides are almost exclusively supported on other oxide systems, including SiO_2, Al_2O_3, TiO_2 or ZrO_2. Although previously assumed to only act as a structural stabilizer, the structural and energetic situation at the interface is considerably more complex, also due to the redox behavior of VO_x [1]. Vanadium oxides were grown by reactive deposition of V metal in 10^{-2} Pa O_2 at 600 K. This typically yields well-ordered V_2O_3 thin films, which can be converted to V_2O_5 by post-oxidation at 673 K. Upon oxidation at 723 K and above, elongated V_2O_5 needles form (Figure 3b), with typical diameters between 20 and 30 nm and average lengths between 20 and 300 nm. V_2O_5 crystals with near-square outlines and oblong particles are also frequently observed (Figure 3a). SAED patterns and HRTEM images reveal the exclusive presence of V_2O_5 (Figure 3c and d). Subsequently, these nanocrystals can serve as a convenient tool for reduction treatments as access to other nano-particulate vanadium oxides and as nanostructured support for Pd or PdO particles [7].
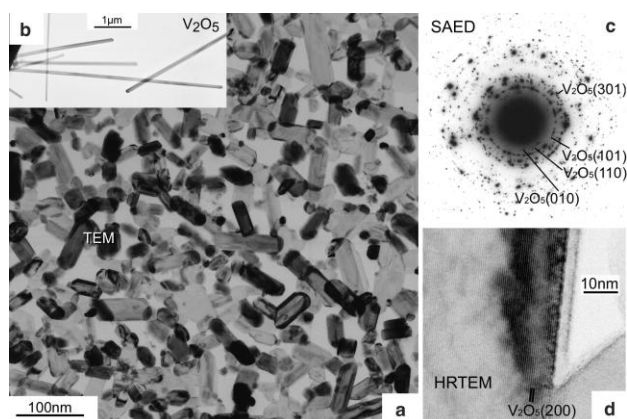

Fig. 3 – Characterization of the epitaxial thin film V_2O_5 catalyst. (a) TEM image of elongated V_2O_5 particles, obtained at substrate temperatures of 580 K in 10^{-2} Pa O_2 followed by post-annealing at 773 K. (b) Three separated V_2O_5 needles. (c) SAED pattern. (d) HRTEM image with atomically-resolved (200) fringes running parallel to the particle edges of single V_2O_5 needles (adapted from [1]).

3.4 Mixed Ga_2O_3-WO_3 systems

Considered as the most ambitious goal of the presented studies, the thin film model system preparation routine is successfully taken to a new complexity level in establishing a new pathway to model mixed-oxide systems. Exemplarily discussed for binary Ga_2O_3/WO_3, it is shown that this preparation routine also offers exciting new possibilities to access a full range of oxide combinations relevant in a variety of research areas including catalysis, sensor technology and materials chemistry. Similarly to the pure oxide systems, careful tuning of the experimental conditions yields a nano-architectured mixed oxide system. Ga_2O_3/WO_3 itself is an interesting system due to its catalytic action in methanol synthesis, where the oxide-oxide interface is assumed to govern the catalytic activity and selectivity [8]. The film morphology and structure are observed to strongly differ from those of the pure oxides and upon co-deposition of both oxides

also leads to a branched network of Ga-enriched dendrites within a W-enriched binary oxide matrix (Figure 4 a-b). The Ga-enriched dendrites are easily seen in high-angle annular dark-field (HAADF) images, due to the pronounced differences of Ga_2O_3 and WO_3 in the average atom number Z (Figure 4c, with the associated line profile of the energy-dispersive X-ray (EDX) spectra shown in 4d). Mediated by the GaO_x/NaCl(001) contact area, the formation rather appears to be a surface-related phenomenon than being an intrinsic property of the mixed-oxide bulk [9].
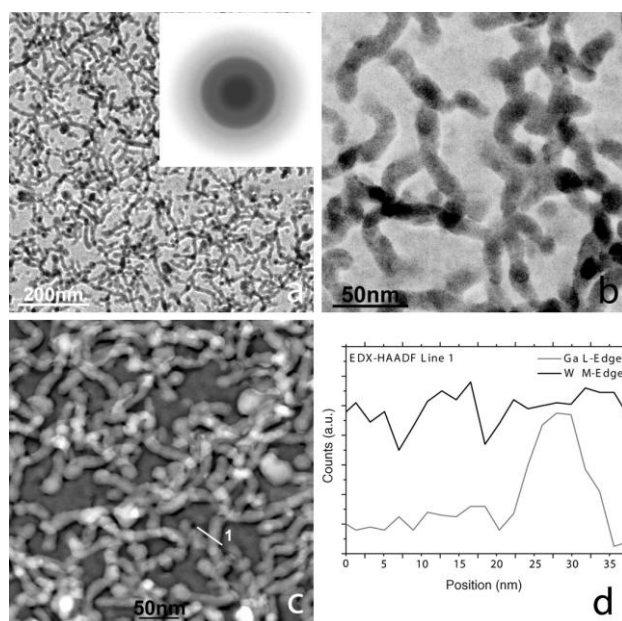

Fig. 4 – Characterization of the mixed Ga_2O_3-WO_3 thin film deposited at 600 K in 10^{-2} Pa O_2. (a-b) TEM images of the Ga-enriched dendrites, with the amorphous SAED pattern shown as inset (c) HAADF image of the Ga dendrites with EDX line profile. (d) Ga L-edge and W M-edge intensity along the line shown in (c) (adapted from [9]).

4. CONCLUSION

Model systems for transition and noble metal oxide systems, either as thin films or nanoparticles, were prepared by vacuum deposition of oxides or oxidation of metals. These systems are well suited for atomic scale characterization by surface-specific methods, bulk determination methods and catalytic tests. The exploitation of the special surface and structural properties of NaCl, either influencing the growth of the oxide species by structural similarities or by energetic properties (i.e. wetting phenomena) allows overcoming the general structural, morphological and compositional flexibility of oxides. These usually lead to significant challenges in their characterization, being intimately connected to their peculiar, but sometimes exceptional structural, catalytic and materials properties. As shown in Figure 5, the chosen preparation pathway is rather easy and has the tremendous advantage of in-parallel preparation of samples for structural and spectroscopic characterization as well as for determination of its materials properties (sensor, catalytic or other physicochemical), which makes the establishment of structure-activity and structure-property relationships straightforward.
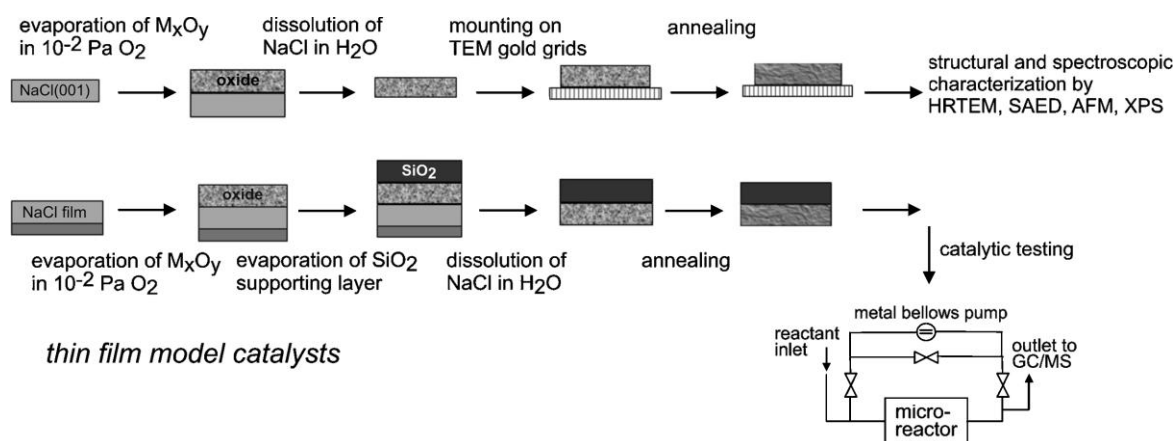
Fig. 5 – Scheme of the preparation concept of epitaxially grown oxide model catalysts for structural, spectroscopic and catalytic characterization, including a scheme of the recirculated micro-reactor setup in the right lower corner.

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