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Critical review

Pure and mixed-oxide thin film model systems grown on sodium chloride templates for structural and catalytic studies

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ABSTRACT

Preparation and application possibilities for thin film model systems of isolated pure oxides and mixed oxide systems are reviewed. Vacuum deposition of oxides on NaCl(001) growth templates or post-oxidation of initially prepared metal particles almost exclusively led to well-structured and -defined systems, which are perfect starting systems for in-depth structural, compositional and property characterization. The advantages of the chosen preparation pathways are exemplarily discussed for a number of case studies, showing the full range of application possibilities, including easy and reproducible preparation of oxide nanoarchitectures, studies of detailed monitoring of phase transformations in oxide systems and more complex applications such as the influence of the oxide's properties on intermetallic formation in supported metal/oxide systems or the preparation of mixed oxide model systems with defined morphology and structure. Particular emphasis is placed on how structural characterization (high-resolution transmission electron microscopy, atomic force microscopy), spectroscopic methods (X-ray photoelectron spectroscopy) and kinetic measurements can be successfully combined to result in unambiguous structure–activity/selectivity and property relationships, leading to an in-depth understanding of the participating oxide structures on an atomic and molecular level.

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Contents

1. Introduction	0
2. Experimental overview	0
3. Case studies	0
3.1. Case study 1 – Preparation of well-defined oxide films: CeO ₂ and Y ₂ O ₃	0
3.2. Case study 2 – Preparation of oxide nano-architectures: In ₂ O ₃ , Ga ₂ O ₃ , V ₂ O ₅ and NiO	0
3.3. Case study 3 – Structural transformations between different oxide polymorphs: WO ₃ and ZrO ₂	0
3.4. Case study 4 – Structural transformations between different oxide structures: V ₂ O ₃ , SnO ₂ and CuO	0
3.5. Case study 5 – Use of oxide model systems for catalytic studies: In ₂ O ₃ and Ga ₂ O ₃	0
3.6. Case study 6 – Studies on the strong metal–support interaction: Reductive formation of intermetallic phases: Pt/SiO ₂ , Pd/Ga ₂ O ₃ and Rh/VO _x	0
3.7. Case study 7 – Preparation and characterization of mixed oxide systems: Ga ₂ O ₃ –WO ₃ and Y ₂ O ₃ -stabilized ZrO ₂	0
4. Conclusions	0
Acknowledgments	0
References	0

1. Introduction

Metal oxides are one of the most promising materials at the intersection of the primary research areas in chemistry, physics, and materials science. Potential application areas range from protective coatings over

solar cells and sensors to microelectronics and the use as catalysts in a variety of chemical reactions [1,2]. Yet, despite these advantages, the use of oxides does not come without strings attached. The latter are usually connected with the complex chemistry of these materials, which subsequently hampers drawing decisive conclusions, e.g. regarding reaction mechanisms or structure–property relationships [1]. As a representative example, nicely showing the drawbacks of using oxides, is the large research field of catalysis [1]. In this case, oxides are typically

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either used as supports for other catalytically active, mostly metallic, materials or as catalysts themselves. However, whereas the catalysis of noble metals is already well understood, several factors have to be additionally considered if oxides are used, including: surface vs. bulk structural terminations, the presence of various oxidation states, possible phase transformations between different polymorphic modifications, hydroxylation or other chemical modifications of the oxide surface or the presence of defects in general [1]. All these factors govern the geometric and electronic structure of the oxidic materials, with possible and likely influences on their use. To extend these considerations, mixed oxides gain increased interest especially in sensor technology or (photo-) catalysis [3,4]. As the corresponding pure oxide systems, they might be present as supported systems, combined with a dopant or as bulk mixed-oxide phases [1]. One of the well-known examples of the former are supported vanadium oxide catalysts, which have been scrutinized for catalytic applications over the last three decades [4]. Mixed bulk Mo–V–Te–Nb oxides employed as selective oxidation catalysts are an example of the latter [5,6].

Interestingly, simple physical mixtures of two oxides, e.g. Ga₂O₃–WO₃ or Ga₂O₃–MoO₃, have recently been identified as promising methanol conversion catalysts, thereby synergistically exceeding the catalytic properties of both pure oxides [3,7]. Nevertheless, these examples already highlight a major difficulty in mixed-oxide characterization, that is, the identification of the active working sites is even more complicated than for pure oxides and additionally comprise mixed oxidation states, phase distribution, different surface terminations, co-existing surface and bulk structures, altered local bonding geometries or the simultaneous presence of amorphous and crystalline structures [4]. From this discussion, the need to precisely know and control the structure and morphology of the respective oxide phases, and the subsequent use of dedicated well-defined and -structured model systems, is obvious. The preparation and characterization of such model systems represent a never-ending discussion, especially in the catalysis community, and are usually connected to the terms “pressure” and “materials” gaps [8,9].

Although advances to overcome the material's gap have been achieved upon preparation of “inverse” model catalysts (growth of oxide on metal substrates) [10,11] or the preparation of planar nano-particulate metal catalysts (e.g. well-defined metal particles supported on thin oxide substrates) [12–15], these studies suffer from the still existing pressure gap, since usually these model catalyst studies are conducted under ultra-high vacuum (UHV) conditions, i.e. in pressure regimes far from the usual technical conditions. The latter gap is increasingly circumvented by the use of high-pressure reaction cells attached to UHV chambers [16–18] or the development of in-situ high-pressure spectroscopic methods [19–23], also applicable to more technically relevant catalytic systems. The usual drawback of these industrial catalysts, nevertheless, is the presence of less-defined and -ordered particles alongside a large particle size distribution, significantly hampering detailed structural analysis. One way to overcome these problems is the use of thin film model systems, already successfully exploited to prepare and study the growth of small noble metal catalyst particles of e.g. Pt, Rh, Pd, Ir or Re on different templates such as NaCl, KCl, KBr or MgO facets [23–30].

NaCl(001) single crystals have evolved as particularly promising materials, due to their very easy handling and use. This approach offers several advantages: The use of a well-defined and structured growth template results in very well-defined and ordered particle morphologies and structures which are ideally suited for structural analysis by electron microscopy and related techniques [30]. Studies on structural, chemical and compositional changes during catalyst activation or annealing treatments in various gas atmospheres are especially favorable due to the large contact area, especially if interfaces between oxides or oxide-metal are expected to play a dominant role. By combining these investigations with catalytic studies in a dedicated micro-reactor set-up under relevant catalytic conditions or with the determination of material

properties, the establishment of structure–activity/selectivity/property correlations is greatly facilitated [31].

This method is even more powerful if these studies are also related to more industrially relevant powder systems, which can be characterized regarding structure, morphology or catalytic properties in the same experimental set-up under comparable conditions. Since so far the focus was mainly on metal particle morphology characterization after different annealing treatments and the preparation of supported metal/oxide systems [30], the present review tries to extend this thin film model concept to an in-depth discussion about the preparation of oxide films by exploiting the same properties of the growth template that led to the preparation of noble metal particles.

This knowledge-based approach offers a tremendous variety of possibilities in preparation and characterization of oxide phases, including pure oxides, the specific analysis of metal–support interaction in oxide-supported bimetallic particles by reductive treatments and successful pathways to prepare model systems of mixed-oxide systems, to name just a few. In close correlation to this preparative approach, this review will show how related structural (atomic force microscopy, (scanning) electron microscopy), spectroscopic (X-ray photoelectron spectroscopy) and catalytic/property information can be gained from these thin film model systems. Such combined studies appear to be underrepresented for technologically relevant model systems so far. Wherever applicable, cross-correlations to structurally less-defined systems are attempted.

The following contribution exemplarily reviews the possibilities of oxide model thin film preparation and analysis. Seven case study groups are presented, which cover the full range of applications of the oxide model systems in materials science and catalysis. This will encompass (1) preparation routines to well-ordered oxide films, which subsequently are compared regarding their stability under reducing conditions, (2) preparation routines to oxide nanoarchitectures, (3) studies of phase transformations between different oxide polymorphs, (4) studies of structural transformations between different oxide structures, (5) use of pure oxide model systems for catalytic studies, (6) studies of the strong metal–support interaction and the reactive formation of oxide-supported intermetallic phases and (7) preparation routines to mixed oxide phases. Details regarding the individual systems are given in the respective sections as a short introduction to the research field.

2. Experimental overview

In order to prepare thin film systems applicable to both structural and spectroscopic characterization by, for example, electron microscopy techniques, X-ray photoelectron spectroscopy, atomic force microscopy as well as kinetic analysis by gas chromatography/mass spectrometry, a well-established setup is used [1]. Fig. 1 shows a representative flow chart for the preparation of oxide thin films, which is, with small amendments, also applicable to the preparation of oxide-supported bimetallic particles and mixed-oxide films.

Pure oxide films and nano-particles were vacuum-grown on water-soluble NaCl(001) single crystals (0.25 cm²) or freshly prepared NaCl films (up to 100 cm²) by evaporation of the respective oxide in a background pressure of O₂ or H₂. Experimental conditions include thermal evaporation in 10^{−4} mbar O₂ for Ga₂O₃ [32], In₂O₃ [33], SiO₂, ZnO [34], WO₃ [35], V₂O₃ [36], Y₂O₃ [37] and GeO₂ [38] at varying template temperatures between 300 and 623 K. SnO films were prepared in 10^{−3} mbar O₂ due to formation of metallic Sn within the oxide matrix at lower oxygen pressures [38,39]. Al₂O₃ was prepared by reactive evaporation of Al metal in 10^{−4} mbar O₂ [31]. The preparation of SnO₂ [39], V₂O₅ [36] and VO [36] thin films required post-oxidation (at 673 K for SnO₂ and V₂O₅) or post-reduction (at 673 K, VO) treatments. ZrO₂ films had to be prepared by thermal evaporation of ZrO₂ powder in a background pressure of 10^{−5} mbar H₂ to suppress the formation of volatile tungsten oxide species (from the W filament) [37]. Thin films of yttria-stabilized ZrO₂ (YSZ) were prepared by sputtering from a pressed YSZ powder target. For this purpose, a home-built sputter source was used [40]. In

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