Mixed metal oxide aerogels from tailor-made precursors

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ABSTRACT

Highly porous mixed oxides and metal-doped materials are relevant for many applications including filters, sorption media or photocatalysts, in medical, or electrochemical and optical applications, etc. Mixed oxides are of special interest for several reasons: the chemical properties of an otherwise "inert" support can be improved by the second component, i.e. comprising characteristics, such as higher acidity, larger surface areas, thermal stability, etc. However, the properties of the final material strongly depend on the chemical homogeneity or degree of demixing of the various components. The development of general, cost-effective routes allowing for the synthesis of such mixed metal oxides with deliberately designed structural features on all length scales (from the atomic level to the macroscopic morphology) is still a demanding task. In this paper, we will provide an overview over different solution-based chemical approaches, e.g. sol–gel processes, to highly porous (monolithic) mixed metal oxide aerogels.

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1. Introduction

Aerogels are solid materials that are characterized by extremely low densities combined with high porosities, and large inner surface areas [1]. One intriguing feature of aerogels is that all constituting elements are in the nanoscale regime, providing a unique combination of properties that make the materials attractive for a variety of applications, such as catalysis, adsorbents, drug delivery, thermoresistors, piezoelectrics, or sensors. Although the first aerogel was already prepared in 1931 by Kistler [2], the development and application-oriented research of aerogels only started in the late 1960s, concomitant with the rapid development of the sol–gel process. Since then, many different chemical compositions, including purely inorganic gels, e.g., metal oxides and sulfides (tellurides and selenides), carbides, metal-doped or mixed metal oxides, as well as inorganic–organic hybrid gels, organic polymeric gels, including resorcinol/formaldehyde, polyurethane, polyamide, conducting polymers (e.g. polythiophenes) and many more, graphene and carbon aerogels, have been prepared. There are some excellent review articles summarizing the recent progress in aerogel science [1,3–7].

In this review, we will focus on aerogels that are composed of two or more different metal/semimetal oxide centers. These binary of multinary oxides (e.g. ZrO_2/SiO_2, TiO_2/SiO_2, TiO_2/ZrO_2, Al_2O_3/SiO_2, $CoTiO_2/TiO_2$, etc.) are of significant

technological importance, however, the properties strongly depend on parameters such as (1) the M^aO_x/M^bO_y ratio, (2) the dispersion of one component in the other and with that the chemical homogeneity of the network, (3) the accessibility of the different metal/semimetal centers as well as (4) the textural properties of the material, all of which are governed not only by the synthetic approach, but also the drying procedures [8–14].

The rapid development of sol–gel processes during the past decades has led major steps forward in the deliberate synthesis of porous, mixed metal oxide networks. Sol–gel procedures complement the broad range of other conventional methods used for the preparation of mixed metal oxide nanostructures, such as ceramic synthesis, flame hydrolysis, ion exchange on supported oxides, precipitation or impregnation methods, typically followed by high temperature treatment [15–24]. Most of these procedures, are however not suited for the production of highly porous aerogel monoliths. The advantages of sol–gel processing are that (i) the hydrolysis and condensation reactions already proceed at room temperature and (ii) by the use of liquid precursor molecules molecular mixing of the different metal/semimetal centers is in principle possible, (iii) particle sizes can be easily controlled by the manifold processing variables, as well as (iv) the application of templates allows for a deliberate tailoring of the porous network architecture.

Developing and designing materials from a molecular/atomic level requires the ability to deliberately control the positioning of the building blocks within a material. This is also an essential requirement in the synthesis of porous materials, such as aerogels, in which the arrangement of different building blocks (particles) forming the solid framework determines the pores' size, shape
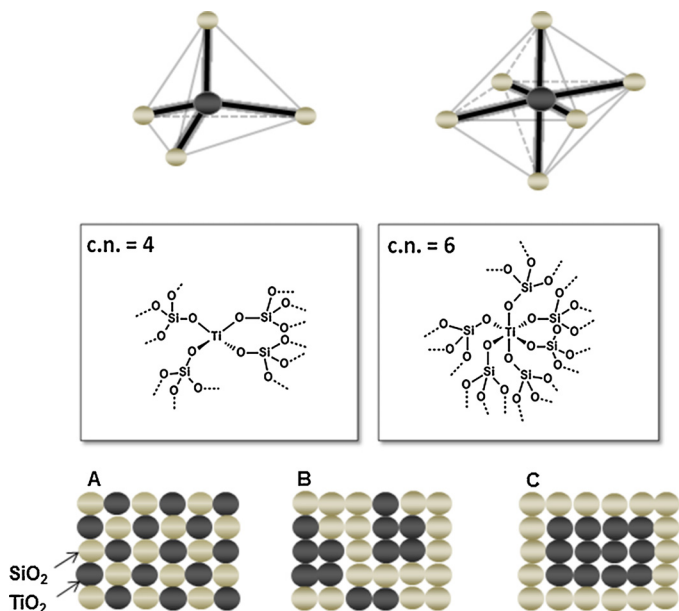
and arrangement. In the following a strong focus will be given to SiO_2/TiO_2 mixed oxide aerogels as a model system, however, the underlying concepts are very general and can easily be transferred to other mixed oxide and even chalcogenide systems.
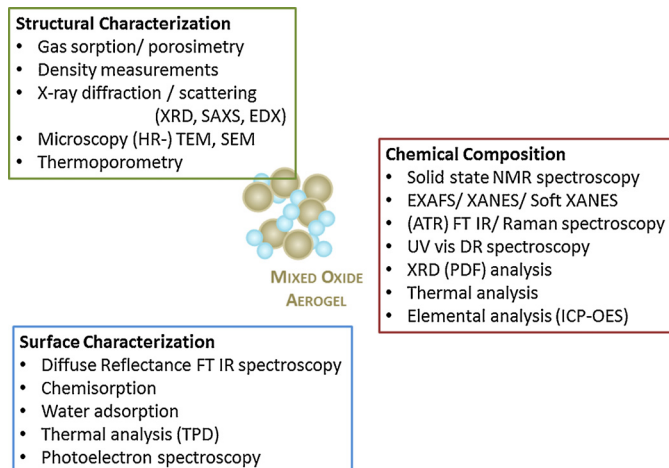
2. Chemical homogeneity

What exactly is meant with chemical homogeneity: Looking at the atomic level, the degree of homogeneity is commonly associated with the relative amount of Si—O—Ti linkages in the mixed oxide. Depending on the reaction conditions, different scenarios have to be distinguished (see Fig. 1, top and middle). Titanium can be dispersed in the silica framework on an atomic level (isomorphic substitution), resulting in tetrahedrally coordinated metal centers as it is found for the zeolitic system titanosilicalite 1 (TS-1) [25]. This is not the regular case, since one has to consider that for transition metals the coordination number (c.n.) can be higher than the valency, resulting in a coordination expansion, i.e. for titanium the valency is typically four but up to six ligands are octahedrally coordinated to the metal center as present in the crystalline titanium dioxide phases, anatase or rutile (Fig. 1, top right) [13].

If larger segregated titania domains are present, those can either be homogeneously distributed in the silica matrix (Fig. 1A, bottom) or demixed domain structures can be formed to different extent (Fig. 1B and C, bottom). The size of these domains strongly depends on the reaction and drying conditions and can vary from a few nanometers up to micrometer-sized domains. For these phase separated systems one also has to consider that the particles can either be crystalline or amorphous, depending on the synthetic approach. Unfortunately, in many cases, no or only very limited information on the chemical homogeneity, neither on the atomic nor on the particulate level is given.

Starting from solution as in sol–gel processes, the key to design the desired dispersion and mixing of the different metal centers lies in an understanding of the chemical reactivity and the structural

Fig. 2. Schematic overview of some typical methodologies available for the characterization of mixed metal oxide aerogels.

chemistry of the precursors. Typical precursors for sol–gel processes are metal alkoxides, e.g. $Ti(OR)_4$ for titania, or $Si(OR)_4$ for silica. A major challenge in sol–gel processes in the presence of water is the different reaction rate for the hydrolysis reaction. This reaction typically proceeds via a nucleophilic substitution mechanism and therefore depends on the partial charge, δ^+, on the metal atom (Si or Ti). The titanium atom, e.g. Ti^{4+} in $Ti(O^iPr)_4$, is a strong Lewis acid with a significant positive partial charge imparting a much higher reactivity towards hydrolysis than the Si atoms in tetraalkoxysilanes (Si^{4+}) [26]. This can easily be observed by the vigorous reaction of titanium alkoxides with water resulting in ill-defined titanium-oxo/hydroxo compounds.

In 2001, Gash et al. developed a new sol–gel route based on metal ion salts in the presence of epoxides as gelation agents to synthesize different transition metal and main group metal oxide aerogels [27]. The versatility of this procedure has been shown with the synthesis of a large variety of metal/Si mixed oxide aerogels [28]. The choice of epoxide proved to give a good control over composition regarding the M/Si ratio, even allowing for the synthesis of gels with the metal oxide – not silica – as the major component. Due to the compositional generality of the method, the obtained nanocomposites are built-up from a variety of metal oxides with several oxidation states. For these gels not only the structure, but also the dispersion of the different elements in the gels has been investigated by using electron energy-loss spectroscopy (EELS) in tandem with TEM. The authors have shown that the different elements are uniformly dispersed throughout the materials and no large silica domains appear to be present.

Recent progress in the synthesis of mixed oxides applying this epoxide-based approach, e.g. for ZrO_2/SiO_2 mixtures, starting from low-cost commercially available precursors, such as water glass or metal salts, has been shown by Ratke et al. However, no information on the chemical homogeneity of the mixed oxides is given [29].

As seen above, porous mixed metal oxide materials are easily accessible from a synthesis point of view. However, a detailed characterization, especially with a focus on the molecular/atomic level chemical homogeneity of the material remains notoriously difficult. To get a complete picture of the structure, morphology, composition and chemical homogeneity typically a combination of different analytical techniques has to be applied (see Fig. 2).

Regarding structural features, such as microstructure, morphology, specific surface areas, pore sizes and pore size distributions, etc., standard methods including X-ray scattering or diffraction, electron microscopy, gas sorption or porosimetry have been used. However, one has to keep in mind that due to the amorphous or

Fig. 1. Isolated metal species in tetrahedral (top, left) or octahedral (top, right) coordination; atomic dispersion for mixed metal oxides in tetrahedral (c.n. = 4) or octahedral (c.n. = 6) geometry for titanium centers by Si—O—Ti bridges (middle) and segregated titania domains either homogeneously dispersed in the silica matrix (A) or phase separated to different extents (B and C); (note that in the bottom images A–C, the colored spheres represent silica or titania particles not atoms). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)