

DESIGN OF PRECURSORS FOR SOL-GEL ROUTE TOMETAL/MIXED METAL OXIDES

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ABSTRACT

The requirement for metal/heterometal oxides as useful materials in the electronics industry has stimulated research and spurred activity in the area of sol-gel technique in this field in recent years. This led to renewed interest in the preparation of these materials. This article discusses the increasingly sophisticated design strategies for precursor complexes through a series of case studies on sol-gel technique for metal/mixed oxide.

INTRODUCTION

The synthesis and characterization of nanoparticles have attracted considerable attention in recent years. It is well known that nano-sized particles, because of their small size and high surface area display many unique properties such as electrical¹, optical², and magnetic^{3, 4}, somewhat different if compared to those of the bulk system. Nanoparticles, thanks to their special physical and chemical properties, now exhibit interesting applications also, in biology, catalysis, sensors, mechanics and electronics fields.⁵⁻⁷ If nano-scaled particles are dispersed in a host matrix, a new nanocomposite material will be formed that possesses some unique properties both of the nanoparticles and the matrix. The sol-gel synthesis of inorganic nanocomposites based on highly dispersed and nanosized active phases that exhibit catalytic, electro-optic, ferroelectric, and non-linear optical properties. Particular attention was addressed to the thin films preparation, fundamental for the realization of electronic devices. Compared with the conventional ceramic routes, such as coprecipitation, grafting, impregnation, the sol-gel exhibits many advantages, among them the low process temperature, the high control of purity, composition, microstructure and textural properties of the final material.⁸⁻¹⁰ Particularly, for mixed-oxides this synthesis procedure allows to obtain materials characterized by a high dispersion of the active phase in the matrix on both molecular and nanometer scale.¹¹⁻¹⁶ Moreover, the versatility of the sol-gel route makes possible to obtain the final material as powders, bulk and coating films. For films fabrication, in comparison with the conventional deposition techniques, such as chemical vapor deposition, sputtering and pulsed laser deposition, the sol-gel offers a better control of the chemical composition, excellent homogeneity, low process temperature, uniformity over large area allowing to produce high-quality films up to micron thickness.^{8, 17}

A report of the most recent literature data about these materials is later on reported. This effort aims to provide a clear picture of the state of the art to clarify the actual interest and the novelty of the work done in recent years. Special emphasis is attributed to the influence of the process parameters on the control of the dispersion degree of the active phase.

SOL-GEL CHEMISTRY

The role of the precursors commonly, the most preferred starting reagents are alkoxides with general formula:

$M_x(OR)_y$ where M = element with valence y; R = alkoxide group

These alkoxides must exhibit useful properties to control the chemical synthesis of oxides: 1. easy to purify, a lot of alkoxides can be distilled in order to obtain highly pure products; 2. wide variety, it is possible to choose R among a large number of alkylic groups in order to obtain the required reactivity; 3. possible control, of the alkoxides hydrolysis and the polycondensation of hydrolysed species; 4. mixed alkoxides, as a further control means of the stoichiometry and homogeneity of the final products. Gelation: hydrolysis and polycondensation. The transition from sol to gel involves two key steps, such as hydrolysis and polycondensation reactions. The hydrolysis takes place also by small amounts of water. Because water and alkoxides are immiscible, a mutual solvent such as alcohol, is normally used as a homogenizing agent. In the hydrolysis reaction, the alkoxide groups (OR) are replaced stepwise by hydroxyl groups (OH): The hydrolysis rate depends on many factors. Indeed, the reaction can favourably be promoted by an increase in the charge density on the metal, the number of metal ions bridged by a hydroxo- or oxo-ligand, and the size of the alkyl groups.^{18,19}

CASE STUDIES OF SOL-GEL PRECURSORS FOR METAL/MIXED METAL OXIDES

High surface area nanocrystalline metal oxides of magnesium, calcium, aluminium, and transition metals have proven to be exceptional adsorbents and catalysts.²⁰⁻²⁵ Core/shell bimetallic mixtures, such as MgO coated with V_2O_3 , possess their own unique sorption and catalytic properties.²⁶ Furthermore, mixed oxides of the type MAI_2O_4 (M=Ca, Mg, Mn, Co, Fe, Ni, Zn) have found uses in many important processes, such as Fischer-Tropsch catalysts or as precursors to new ceramics.^{27,28} Generally, these oxides, especially those of the MAI_2O_4 type, have been prepared by three methods. (i) Co-precipitation of metal hydroxides followed by heat treatment at high temperatures, as for $CaAl_2O_4$, for example:
 $Ca(OH)_2 + 2Al(OH)_3 \xrightarrow{\text{co-precipitation}} CaAl_2O_4 + 4H_2O$

Unfortunately, this method is affected by the tendency of the two hydroxides to precipitate at different rates, leading to at least partial segregation to CaO and Al_2O_3 individual solid oxides as final products (phase segregation). (ii) Physical mixing of hydroxides, oxides, alkoxides, or nitrates followed by high temperature treatment.

This method is also complicated by the tendency toward phase segregation. (iii) Hydrolysis of bimetallic bridged alkoxides, such as $M[Al(OR)_4]_2$, shown below.²⁹⁻³⁰

In theory, if hydrolysis of all OR groups ($OR \rightarrow OH$) were to occur at the same rate, then a homogeneous hydroxide (and after dehydration, a homogeneous oxide) could be obtained. However, the doubly bridged Al-O(R)-Al groups, due to the presence of two Al cations, would probably be hydrolyzed faster than the terminal RO-Al groups, thus the bridge would be cleaved and segregation of phases would occur. Due to the problems inherent in all these synthetic methods (if the goal is to prepare a homogeneous phase), a new method needs to be developed where the M-O-Al bridges in the pure molecular precursor are not cleaved upon hydrolysis. Therefore, we have prepared bimetallic m-oxo molecular precursors of the form $(RO)_2Al-O-M-O-Al(OR)_2$. The M-O-Al bridging oxo group is much less sensitive to hydrolysis compared to the M-O(R)-Al group and, therefore, a homogeneous phase can be maintained throughout hydrolysis and subsequent dehydration. In practice, this approach has worked well in our laboratory. In addition, a modified aerogel synthesis approach has been included in the technology so that high surface area nanocrystalline MAI_2O_4 materials can be obtained. It entailed controlled stoichiometric hydrolysis of the bimetallic m-oxo alkoxide in an alcohol-toluene solvent mixture, such that a high quality gel was formed rather rapidly. The gel was placed in an autoclave which was heated to near supercritical conditions (300 °C) and the solvent quickly vented and removed. In this way, high surface area hydroxides were formed and were dehydrated under vacuum conditions, leading to high surface area nanocrystalline MAI_2O_4 oxide as a homogeneous phase.

This is an important feature when the goal is to prepare homogeneous phase bimetallic oxides. Zircon, $ZrSiO_4$, is the only crystalline phase in the binary SiO_2-ZrO_2 system that is stable under 1676 °C. This oxide exhibits low thermal expansion, low thermal conductivity, and high resistance to thermal shock. To take advantage of such properties, which are very interesting for high temperature applications, the zircon should be highly pure. Indeed, impurities such as Al_2O_3 , Fe_2O_3 , TiO_2 and SiO_2 , found in natural zircon sand, can lead to a lowering of its decomposition temperature and alteration of its mechanical properties. Although difficult, the preparation of high-purity $ZrSiO_4$ has already been the subject of a great number of research papers. Various different synthetic routes have been investigated. The formation of zircon powders at temperatures as low as 150 °C is possible under hydrothermal conditions.³¹⁻³³ Sol-gel processing has also been used by combining numerous precursors in aqueous or organic media, including sols, salts and alkoxides.³⁴⁻⁴⁸ In this case, literature data indicate that pure zircon is produced at high temperatures varying between 1100-1500 °C according to the procedure followed. However, Mosset et al.³² have shown that partially crystallized zircon can be formed at 100 °C. The work discusses zircon synthesis by a new aqueous semi-alkoxide route, combining tetraethoxysilane (TEOS) with zirconyl nitrate $ZrO(NO_3)_2 \cdot xH_2O$: an aqueous solution of zirconyl nitrate in which TEOS has been hydrolysed into silicic acid constitutes a homogeneous zircon precursor. A procedure for the preparation of spherical $ZrSiO_4$ particles from the starting precursor solution is also mentioned in literature which is used for obtaining pure zircon powders with controlled morphology.

Titanium dioxide nanostructures have been widely investigated as materials for solar cells,⁴⁹ photocatalysis,⁵⁰⁻⁵¹ optoelectronic devices,⁵² photoelectrochromic windows,⁵³ and sensors.⁵⁴ For these applications, the forms of titania—their crystal size, shape, and structure are critically important to their performance. The simplest and most commonly reported synthetic procedure for preparing TiO₂ nanostructures is the sol-gel method in which titanium alkoxide or titanium chloride precursors are hydrolyzed in an aqueous solution. Nanoparticles,⁵⁵ nanowires,⁵⁶⁻⁵⁷ nanotubes,⁵⁸⁻⁵⁹ and ordered 2- and 3-dimensional porous films⁶⁰ are just some of the architectures available to researchers via sol-gel chemistry. Despite the research advances in this area, it is still challenging to predict a priori the crystal size and structure from a particular synthetic protocol. Furthermore, the reproducible synthesis of small-batch TiO₂ nanocrystals remains a challenge. The synthetic knowledge to vary systematically the morphological and electronic properties of nanostructured systems in a reproducible way is important for advancing both fundamental and applied research. This is especially true for TiO₂ nanoparticles used in the fabrication of mesoporous films for dye-sensitized solar cells (DSSCs; Grätzel cells),⁶¹⁻⁶² one of the promising unconventional future technologies of interest to the solar cell community. For instance, varying the particle shape can affect the particle packing density, which, in turn, can alter light harvesting⁶³ and electron transport in TiO₂ films.⁶⁴ Variation in the particle density (porosity) changes the average coordination number of particles in films, the consequence of which alters the electron transport pathway and, therefore, the electron dynamics.⁶³

Volatile organometallic oxide precursors offer several advantages for the synthesis of nano-scaled metal oxides in different environments because they can be used in chemical-vapour-synthesis (CVS), in solution (non-hydrolytic and hydrolytic sol-gel-synthesis) or in solid state synthesis (synthesis of nanoscaled solids).⁶⁵ We are currently using organozinc-alkoxide⁶⁶ and -siloxide clusters⁶⁷ as molecular models and volatile multiple precursors for nanoscaled ZnO, Zn and ortho-zinc silicate (Zn₂SiO₄) particles.⁶⁸ ZnO is one of the most important substrates in heterogeneous catalysis⁶⁹ but its (micro)-structure-reactivity relationship is not yet well understood even after more than 30 years of intensive research. We have shown that organozinc siloxide clusters⁶⁷ can be used as remarkable versatile precursors for the synthesis of highly active nanocrystalline ZnO and heterometal ZnO supports for the conversion of CO₂ and H₂ into methanol and H₂O.⁶⁹ Remarkably, alkali metal ion-modified ZnO supports show uncommonly strong one- and two-electron donor properties and are unusual super basic heterogeneous catalysts.⁷⁰ Since the catalytic activity of ZnO supports can be drastically enhanced in the presence of several promotor components (*e.g.*, Cu particles, alkali metal ions, *etc.*) it is furthermore highly desirable to gain access to appropriate single-source precursors for such multi-component ZnO substrates which are far less developed or hitherto unknown. Therefore we are also currently focusing on the synthesis of structurally defined heterometal zinc-alkoxide and-siloxide clusters as molecular single-source precursors for alkali metal-modified ZnO systems.

We learned that the structural chemistry of seemingly simple mixed alkali metal and zinc alkoxides is only scarcely developed, although they have a long tradition as reactive species in both organic and inorganic synthesis. For example, it is well known that dialkylzinc compounds can be highly activated as alkyl transfer reagents towards unsaturated organic substrates in the presence of alkali metal alkoxides,⁷¹ and diorganozinc compounds react with CO to give acyloins but only in the presence of alkali metal alkoxides as promoters.⁷²

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