

Chapter 2

Aqueous and Nonaqueous Sol-Gel Chemistry

2.1 Introduction

The most widely used synthetic technique for bulk metal oxides has been the ceramic method, which is based on the direct reaction of powder mixtures. These reactions are completely controlled by the diffusion of the atomic or ionic species through the reactants and products. To bring the reaction partners sufficiently close together and to provide high mobility, these solid state processes require high temperature and small particle sizes. Although the harsh reaction conditions only lead to thermodynamically stable phases, preventing the formation of metastable solids, these approaches gave access to a large number of new solid compounds, enabling the development of structure-properties relationships. However, in comparison to organic chemistry, where highly sophisticated synthetic pathways are employed to make and break chemical bonds in a controlled way, the ceramic method is a rather crude approach. It is therefore no surprise that for the size- and shape-controlled synthesis of nanoparticles especially liquid-phase routes represent the most promising alternatives. In contrast to solid-state processes, but analogous to organic chemistry, “chimie douce” approaches offer the possibility to control the reaction pathways on a molecular level during the transformation of the precursor species to the final product, enabling the synthesis of nanoparticles with well-defined and uniform crystal morphologies and with superior purity and homogeneity [12]. Among the various soft-chemistry routes, sol-gel procedures were particularly successful in the preparation of bulk metal oxides (e.g., ceramics, glasses, films and fibers) [33, 20], and therefore they have also been applied for nanoparticle synthesis. But in spite of great efforts, the number of oxidic nanoparticles obtained by sol-gel chemistry is still rather small compared to the variety of compounds obtained via powder routes. It turned out that in many cases a synthesis protocol developed for a bulk metal oxide could not directly be adapted to its corresponding counterpart on the nanoscale. The reasons for this observation are manifold. Aqueous sol-gel

chemistry is quite complex, on the one hand due to the high reactivity of the metal oxide precursors towards water and the double role of water as ligand and solvent, and, on the other hand, due to the large number of reaction parameters that have to be strictly controlled (hydrolysis and condensation rate of the metal oxide precursors, pH, temperature, method of mixing, rate of oxidation, the nature and concentration of anions, ...) in order to provide good reproducibility of the synthesis protocol [33]. Another fundamental problem of aqueous sol-gel chemistry is that the as-synthesized precipitates are generally amorphous. The required post-synthetic annealing step to induce the crystallization process prevents any subtle control over crystal size and shape. For the preparation of bulk metal oxides these limitations play only a minor role, however, in the case of nanoparticle synthesis they constitute a major issue.

Nonaqueous (or non-hydrolytic) sol-gel processes in organic solvents, generally under exclusion of water, are able to overcome some of the major limitations of aqueous systems, and thus represent a powerful and versatile alternative [30, 40, 38, 37, 41]. The advantages are a direct consequence of the manifold role of the organic components in the reaction system (e.g., solvent, organic ligand of the precursor molecule, surfactants, or *in situ* formed organic condensation products). On the one hand they act as oxygen-supplier for the oxide formation and strongly determine the particle size and shape as well as the surface properties due to their coordination properties, and on the other hand the moderate reactivity of the oxygen carbon bond generally results in slower reaction rates. Altogether these parameters lead to the situation, where nonaqueous synthesis routes generally yield metal oxide nanoparticles with uniform, yet complex crystal morphologies, crystallite sizes in the range of just a few nanometers, and good dispersibility in organic solvents. Another important point is the fact that the chemistry of the oxygen-carbon bond is well-known from organic chemistry. This aspect is of utmost significance considering the fundamental role of organic reaction pathways in nonaqueous sol-gel chemistry approaches (cf. Chapter 5). Parallel to the formation of the inorganic nanoparticles, also the initial organic species undergo transformation reactions often following elementary mechanisms of organic chemistry [39]. Based on the identification and quantification of these organic by-products, it is possible to correlate the processes leading to these organic species by retro-synthetical analysis to the growth mechanisms of the oxide nanoparticles. The connection of organic chemistry with the synthesis of inorganic nanomaterials thus represents first, but fundamental steps towards a future rational synthesis design for inorganic nanoparticles.

We have to point out that many examples discussed in this book do not strictly follow the definition of sol-gel chemistry, i.e., the transformation of the molecular precursor does not exclusively proceed along the formation of a sol and then a gel. However, we denote any process as “sol-gel”, as long as the transformation of the molecular precursor into the final oxidic compound involves chemical condensation reactions in liquid-phase under mild condi-

tions. This definition allows us to draw comparisons between aqueous and nonaqueous sol-gel processes, highlighting the analogy between the mechanistic pathways found in both methods. We will also discuss some examples in this book that are not based on sol-gel chemistry, but on simple thermal decomposition of molecular precursors in liquid media. Furthermore, in the current literature the synthesis of metal oxides in organic solvents is typically denoted as “nonhydrolytic”. However, in some cases these procedures involve the use of hydrated metal oxide precursors and/or water is produced *in situ*, so that a hydrolytic reaction pathway cannot be excluded. Therefore, we prefer to name these routes as “nonaqueous sol-gel chemistry”.

2.2 Aqueous Sol-Gel Chemistry

The aqueous sol-gel process can shortly be defined as the conversion of a precursor solution into an inorganic solid via inorganic polymerization reactions induced by water. In general, the precursor or starting compound is either an inorganic (no carbon) metal salt (chloride, nitrate, sulfate, ...) or a metal organic compound such as an alkoxide. Metal alkoxides are the most widely used precursors, because they react readily with water and are known for many metals [47, 6]. Some alkoxides, which are widely used in industry, are commercially available at low cost (Si, Ti, Al, Zr), whereas other ones are hardly available, or only at very high costs (Mn, Fe, Co, Ni, Cu, Y, Nb, Ta, ...). In comparison to the preparation of silicates from silicon alkoxides, sol-gel processing of transition metal oxides has much less been studied, mainly due to the high reactivity of transition metal alkoxides.

In general, the sol-gel process consists of the following steps (Figure 2.1) [34]: i) Preparation of a homogeneous solution either by dissolution of metal organic precursors in an organic solvent that is miscible with water, or by dissolution of inorganic salts in water; ii) conversion of the homogeneous solution into a sol by treatment with a suitable reagent (generally water with or without any acid/base); iii) aging; iv) shaping; and v) thermal treatment/sintering. The first step in a sol-gel reaction is the formation of an inorganic polymer by hydrolysis and condensation reactions, i.e., the transformation of the molecular precursor into a highly crosslinked solid. Hydrolysis leads to a sol, a dispersion of colloidal particles in a liquid, and further condensation results in a gel, an interconnected, rigid and porous inorganic network enclosing a continuous liquid phase. This transformation is called the sol-gel transition. There are two possibilities to dry the gels. Upon removal of the pore liquid under hypercritical conditions, the network does not collapse and aerogels are produced. When the gel is dried under ambient conditions, shrinkage of the pores occurs, yielding a xerogel. One of the highly attractive features of the sol-gel process is the possibility to shape the material into any

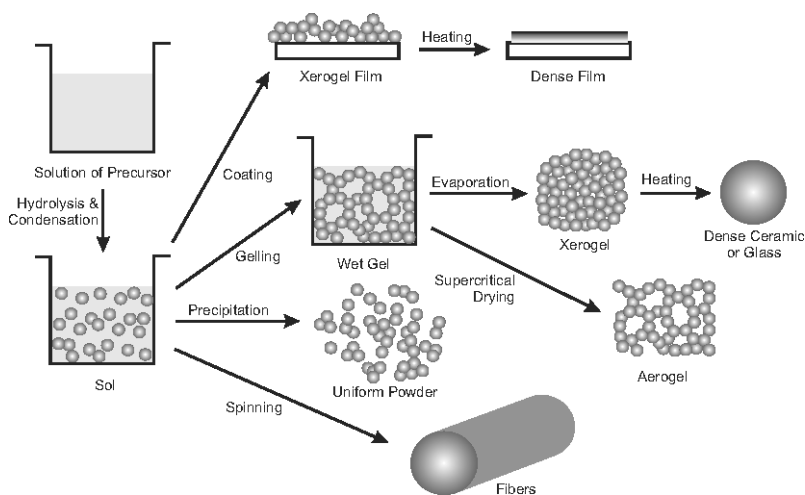


Fig. 2.1. Various steps in the sol-gel process to control the final morphology of the product

desired form such as monoliths, films, fibers, and monosized powders, and subsequently to convert it into a ceramic material by heat treatment.

As mentioned before, the sol-gel processes can be classified into two different routes depending on the nature of the precursors: a) the precursor is an aqueous solution of an inorganic salt or b) a metal organic compound [33]. The inorganic route involves the formation of condensed species from aqueous solutions of inorganic salts by adjusting the pH, by increasing the temperature or by changing the oxidation state. But this method has several disadvantages. The aqueous chemistry of transition metal ions can be rather complicated because of the formation of a large number of oligomeric species, depending on the oxidation state, the pH or the concentration. The role of the counter anions, which are able to coordinate the metal ion giving rise to a new molecular precursor with different chemical reactivity towards hydrolysis and condensation, is almost impossible to predict. These ions can influence the morphology, the structure and even the chemical composition of the resulting solid phase. Also the removal of these anions from the final metal oxide product is often a problem. Many of these issues can be avoided by using metal alkoxides as precursors. They are often soluble in organic solvents, providing high homogeneity, and they can easily be converted to the corresponding oxide.

The sol-gel conversion of metal alkoxides involves two main reaction types: hydrolysis and condensation (Scheme 2.1). During hydrolysis, the alkoxide groups ($-OR$) are replaced via the nucleophilic attack of the oxygen atom of a water molecule under release of alcohol and the formation of a metal hydroxide. Condensation reactions between two hydroxylated metal species

leads to M-O-M bonds under release of water (oxolation), whereas the reaction between a hydroxide and an alkoxide leads to M-O-M bonds under release of an alcohol (alkoxolation).



Scheme 2.1. Main reactions in the sol-gel process using metal alkoxides. Hydrolysis (Eq. 2.1) and condensation, involving oxolation (Eq. 2.2) and alkoxolation (Eq. 2.3)

Chemical aspects play an important role in studying and controlling the sol-gel process. The chemical reactivity of metal alkoxides towards hydrolysis and condensation depends mainly on the electronegativity of the metal atom, its ability to increase the coordination number, the steric hindrance of the alkoxy group, and on the molecular structure of the metal alkoxides (monomeric or oligomeric). The amount of added water in the hydrolysis step and how the water is added, determines, whether the alkoxides are completely hydrolyzed or not and which oligomeric intermediate species are formed. Additional parameters are the polarity, the dipole moment, and the acidity of the solvent.

The major problem of sol-gel methods based on the hydrolysis and condensation of molecular precursors is the control over the reaction rates. For most transition metal oxide precursors, these reactions are too fast, resulting in loss of morphological and also structural control over the final oxide material. Furthermore, the different reactivities of metal alkoxides make it difficult to control the composition and the homogeneity of complex multi-metal oxides by the sol-gel process. One possibility to decrease and to adjust the reactivity of the precursors is the use of organic additives like carboxylic acids, β -diketones or functional alcohols, which act as chelating ligands and modify the reactivity of the precursors [33, 21]. An alternative strategy involves the slow release of water by chemical or physical processes, allowing control over the local water concentration and thus, over the hydrolysis of the metal oxide precursors [9]. In spite of all these efforts, the strong sensitivity of aqueous sol-gel processes towards any slight changes in the synthesis conditions and the simultaneous occurrence of hydrolysis and condensation reactions makes it still impossible to fully control the sol-gel processing of metal oxides in aqueous medium.

More information and mechanistic details about the aqueous sol-gel processing of metal oxides can be found in several excellent books and reviews [33, 20, 7, 29].

2.3 Nonaqueous Sol-Gel Chemistry

In nonaqueous sol-gel chemistry the transformation of the precursor takes place in an organic solvent under exclusion of water. In comparison to aqueous sol-gel chemistry, the list of potential precursors is longer and includes, in addition to inorganic metal salts and metal alkoxides, also metal acetates and metal acetylacetonates. Organometallic compounds are also frequently used, but then the process is rather based on thermal decomposition than sol-gel (remember: organometallic compounds are defined as having a direct metal-carbon bond, whereas metal organic compounds have a metal-hetero atom (usually oxygen) bond between the metal center and the organic ligand).

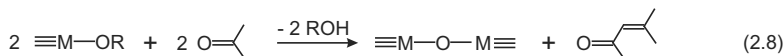
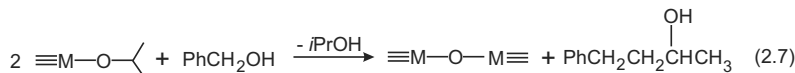
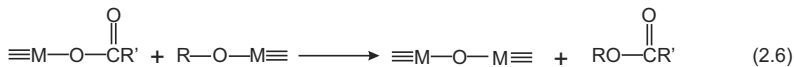
Nonaqueous sol-gel processes have a long history, although they never became as popular as their aqueous analogs. Early studies on nonaqueous sol-gel processes date back to the middle of the 19th century, when the reaction between various metal chlorides and alcohols were investigated. Ebelmen, for example, found that silicon tetrachloride forms silica gels in ethanol [14]. More than 80 years later, Dearing and Reid presented their work on “Alkyl Orthosilicates”, proposing an aqueous and nonaqueous route to silica gels, assuming that they might show “different absorptive power” [13]. Many other groups continued to work on this topic [42, 17, 16], including peculiar but interesting examples like the conversion of chlorosilanes to oligosiloxanes and of silicon and titanium tetrachloride to the respective oxide by refluxing in dimethylformamide [43], the reaction of silicon tetrachloride with benzaldehyde [49] and organic ethers [45], or the synthesis of silica-sodalite from nonaqueous systems [4]. Nevertheless, these publications were more or less isolated efforts without receiving much attention. However, in the middle of the 1980s, and more intense around the beginning of the 1990s, research on nonhydrolytic preparation routes to metal oxides became popular to a larger scientific community [9, 48, 19]. Two main research directions could be distinguished: One focusing on the preparation of metal oxide gels, the other on metal oxide powders. Several groups worked on the preparation of powders using metal alkoxides and alcohols [15, 23, 25] or inert organic solvents [25, 26, 24]. Especially the glycothermal method involving the reaction of metal alkoxides or acetylacetonates with 1,4-butanediol is a versatile approach to various metal oxides [31] and has recently been reviewed [22]. On the other side, in 1992 Corriu et al. published their work on monolithic silica, alumina, and titania gels, as well as on gels containing two metals [8, 11, 10]. In the same year, the synthesis of zinc oxide gels was presented, using zinc alkoxides as precursors and acetone as condensation agent [18]. Upon aging, the gels formed a precipitate, which contained 4 nm zincite nanocrystals. An analogous approach was later on used for TiO_2 , BaO , and BaTiO_3 [3]. Following these examples, a large variety of metal oxide gels were synthesized and reported, including silica, alumina, titania, mixed Al/Si and transition metal oxides from the corresponding metal chlorides and metal alkoxides or ethers as oxygen donors [1, 2], metal ferrites from the metal nitrates and ethylene glycol

[44], and zirconia and zircon from metal carboxylates and metal alkoxides [28]. Although some of these “earlier” examples also led to the formation of nanoscale materials, it was probably the work on the synthesis of titanium oxide nanoparticles, published in 1999 by three independent groups [46, 32, 27] that gave the starting signal for the intensified search of new synthesis routes to metal oxide nanoparticles under nonaqueous and/or nonhydrolytic reaction conditions. Nowadays, the family of metal oxide nanoparticles that are prepared by nonaqueous processes has grown immensely and ranges from simple binary metal oxides to more complex ternary, multi-metal and doped systems.

In aqueous systems, metal alkoxides are the most widely used precursors, and their chemical transformation into the oxidic network involves hydrolysis and condensation reactions. In aqueous sol-gel processes the oxygen for the formation of the oxidic compound is supplied by the water molecules. In nonaqueous systems, where intrinsically no water is present, the question arises, where the oxygen for the metal oxide comes from. Analogous to the nonhydrolytic preparation of bulk metal oxide gels [25], the oxygen for nanoparticle formation is provided by the solvent (ethers, alcohols, ketones or aldehydes) or by the organic constituent of the precursor (alkoxides or acetylacetonates). It is interesting to note that in spite of the large number of methodologies reported for the nonaqueous synthesis of metal oxide nanoparticles, and independent whether surfactants are used or not, most of the known condensation steps, i.e., the formation of the metal-oxygen-metal bond as basic structural unit, can be summarized in only five distinct pathways (Scheme 2.2) [37, 39]:

- Alkyl halide elimination (Eq. 2.4)
- Ether elimination (Eq. 2.5)
- Condensation of carboxylate groups (ester and amide eliminations) (Eq. 2.6)
- C-C coupling of benzylic alcohols and alkoxide molecules (Eq. 2.7)
- Aldol/ketimine condensation (Eq. 2.8).

Alkyl halide elimination, the condensation between metal halides and metal alkoxides (either initially added, or formed upon the reaction of metal halides with alcohols) under release of an alkyl halide, is shown in Eq. 2.4. Ether elimination (Eq. 2.5) is the result of the reaction between two metal alkoxides. The ester elimination process involves the reaction between metal carboxylates and metal alkoxides or between metal carboxylates and alcohols (Eq. 2.6). Analogous to ester eliminations are amide eliminations, e.g. reactions between metal carboxylates and amines. Alkyl halide, ether and ester eliminations are the most commonly reported routes. However, due to the excellent catalytic activity of the metal centres in the precursor species peculiar and more complex organic reactions such as C-C bond formation between alkoxy groups were also observed (Eq. 2.7). Whereas in some cases the presence of a basic species was a prerequisite for C-C bond formation, transition metals with high Lewis acidity, such as Nb, Y, and Ce, were able to directly catal-



Scheme 2.2. Main condensation steps in nonaqueous sol-gel processes resulting in the formation of a metal-oxygen-metal bond. Alkyl halide elimination (Eq. 2.4), ether elimination (Eq. 2.5), ester elimination (Eq. 2.6), C-C bond formation between benzylic alcohols and alkoxides (Eq. 2.7), aldol condensation reactions (Eq. 2.8)

use this Guerbet-like reaction. If ketones are used as solvents, the release of oxygen usually involves aldol condensation, where two carbonyl compounds react with each other under formal elimination of water (Eq. 2.8). The water molecules act as oxygen supplying agent for the metal oxide formation. However, all these condensation mechanisms are discussed in more details in Chapter 5.

2.4 Surfactant-Directed vs. Solvent-Controlled Nonaqueous Sol-Gel Approaches

Nonaqueous processes can roughly be divided into surfactant- and solvent-controlled approaches. Surfactant-controlled synthesis routes involve the transformation of the precursor species into the oxidic compound in the presence of stabilizing ligands in a typical temperature range of 250 to 350 °C. The most popular and successful approach within this strategy is the hot injection method, where the reagents are injected into a hot surfactant solution, which was particularly successfully applied in the synthesis of semiconductor nanocrystals [35].

An elegant alternative to surfactants is the use of common organic solvents, which act as reactant as well as control agent for particle growth, enabling the synthesis of high-purity nanomaterials in surfactant-free medium [41]. In comparison to the synthesis of metal oxides in the presence of surfactants the solvent-controlled approaches are simpler, because the initial reaction mixture just consists of two components, the metal oxide precursor(s) and a common organic solvent. The small number of reactants simplifies the char-

acterization of the final reaction solution and, related to that, the elucidation of the chemical reaction mechanisms. The synthesis temperature is typically in the range of 50 to 200 °C, which is notably lower than in the hot-injection method.

A comparison of the literature on both approaches clearly shows that surfactant routes permit outstanding control over the growth of metal oxide nanoparticles, leading to almost perfectly monodisperse samples [40]. The ability of surfactants to cap the surface of the nanoparticles, sometimes combined with selectivity towards specific crystal faces, provides advantages such as shape control, low agglomeration tendency, good dispersibility in organic solvents, and the potential to tailor the surface properties. However, drawbacks resulting from surface-adsorbed surfactants are the unpredictable influence on the toxicity of the nanoparticles [36, 5], and the diminished accessibility of the particle surface, which is a serious issue regarding applications in gas sensing or catalysis. Although solvent-controlled approaches generally result in some agglomeration, the dispersibility properties of the nanoparticles can be improved by a post-synthetic functionalization step. In some cases a tiny amount of surfactants suffices to lead to completely transparent nanoparticle dispersions. However, surfactant-assisted and surfactant-free synthesis approaches both have advantages and limitations. Table 2.1 summarizes the pros and cons of the two strategies, clearly underlining that they are rather complementary [41]. Of course, one always has to be careful with such general trends, because selected reaction systems can behave in a completely opposite way.

Table 2.1. Pros and cons of surfactant-directed and solvent-controlled nonaqueous liquid-phase routes to metal oxide nanoparticles

	Surfactant-directed approaches	Solvent-controlled approaches
Pros	<ul style="list-style-type: none"> • Excellent control over crystal size • Narrow size distribution • Good control over crystal shape • Low agglomeration tendency • Good redispersibility 	<ul style="list-style-type: none"> • Low amount of organic impurities • Non-toxic solvents • Simple, robust and widely applicable synthesis protocols • Good accessibility of the nanoparticle surface
Cons	<ul style="list-style-type: none"> • Large amount of organic impurities • Toxicity of surfactants • Restricted accessibility of the nanoparticle surface • Complex reaction mixtures 	<ul style="list-style-type: none"> • Less control over crystallite size and shape • Broader size distributions • Formation of agglomerates • Restricted redispersibility

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