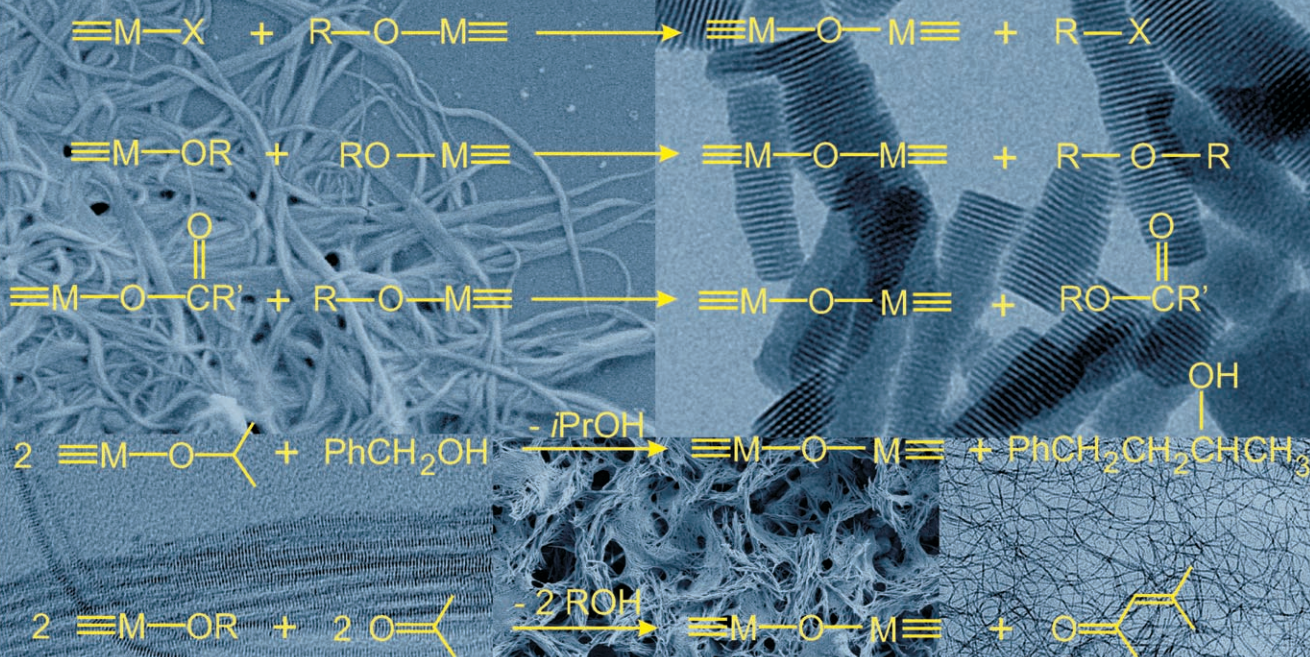


Organic Reaction Pathways in the Nonaqueous Synthesis of Metal Oxide Nanoparticles

Metal Oxide Precursor
+
Organic Solvent



Organic Reaction Pathways in the Nonaqueous Synthesis of Metal Oxide Nanoparticles

Markus Niederberger* and Georg Garnweitner^[a]

Abstract: Nonaqueous-solution routes to metal oxide nanoparticles are a valuable alternative to the known aqueous sol–gel processes, offering advantages such as high crystallinity at low temperatures, robust synthesis parameters and ability to control the crystal growth without the use of surfactants. In the first part of the review we give a detailed overview of the various solution routes to metal oxides in organic solvents, with a strong focus on surfactant-free processes. In most of these synthesis approaches, the organic solvent plays the role of the reactant that provides the oxygen for the metal oxide, controls the crystal growth, influences particle shape, and, in some cases, also determines the assembly behavior. We have a closer look at the following reaction systems in this order: 1) metal halides in alcohols, 2) metal alkoxides, acetates, and acetylacetonates in alcohols, 3) metal alkoxides in ketones, and 4) metal acetylacetonates in benzylamine. All

these systems offer some peculiarities with respect to each other, providing many possibilities to control and tailor the particle size and shape, as well as the surface and assembly properties. In the second part we present general mechanistic principles for aqueous and nonaqueous sol–gel processes, followed by the discussion of reaction pathways relevant for nanoparticle formation in organic solvents. Depending on the system several mechanisms have been postulated: 1) alkyl halide elimination, 2) elimination of organic ethers, 3) ester elimination, 4) C–C bond formation between benzylic alcohols and alkoxides, 5) ketimine and aldol-like condensation reactions, 6) oxidation of metal nanoparticles, and 7) thermal decomposition methods.

Keywords: metal oxides • nanostructures • nonhydrolytic synthesis • reaction mechanisms • sol–gel processes

Introduction

The synthesis of particles with control over size, shape, and size distribution has been a major part of colloid chemistry for decades. For quite a while, most efforts invested in the preparation of uniform, finely dispersed particles were essentially considered as due to the curiosity of colloid scientists, and, with the exception of polymer colloids (latexes), without any practical significance.^[1] However, this attitude has changed dramatically and nowadays there is no doubt about the fundamental role of uniform powders in many areas of science and technology. Hand-in-hand with the development of highly advanced analytical tools, enabling the characterization of small structures with atomic resolution, the size of the targeted objects and devices decreased rapid-

ly below the 100 nm limit. This new direction of research is broadly defined as “nanoscience” and involves “the ability to do things—measure, see, predict, and make—on the scale of atoms and molecules to exploit the novel properties found at that scale”.^[2] Although this “definition” goes far beyond the simple preparation of nanomaterials, the synthesis of nanoparticles still remains one of the main tasks of chemists working in this area. As a matter of fact, many discoveries related to nanoparticle synthesis can be regarded as milestones in the history of nanoscience; for example, the discovery of carbon nanotubes,^[3] the synthesis of well-defined quantum dots,^[4] and the shape control of CdSe nanocrystals.^[5] On the other hand, these synthesis strategies are often isolated efforts, that is, they do not offer any underlying physical or chemical principles that would allow either the generalization of the processes involved for any kind of nanomaterial or the development of a mechanistic understanding of nanoparticle formation.

The fascination of nanoparticles is founded on the one hand in their use as nanobuilding blocks for nanocomposites,^[6,7] and on the other hand in the size-dependence of

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electronic properties in semiconducting crystallites.^[8–12] Intensive work on semiconductor-doped glasses^[13] and on the photocatalytic properties of colloidal CdS^[14,15] finally resulted in the description of the quantum-size effect more than 20 years ago. Brus et al. found that CdS crystallites in the size range of a few nanometers did not have the electronic spectra of the bulk material, even though they exhibited the same unit cell and bond length as the bulk material.^[16,17] These findings opened up a new and exciting possibility to tailor the chemical and physical properties of a material. New applications and properties are a result of controlling particle size and shape on a nanometer scale rather than of altering the composition.^[12] The high interest in quantum-sized materials, as well as in nanoparticles in general, is reflected in the huge library of nanoparticles reported in literature, covering a broad spectrum of compositions, structures, and shapes, and this is similarly true for the synthesis methods applied for these nanomaterials. Nevertheless, some methods have been proven to be particularly successful. Vapor-phase synthesis, for example, is presumably the most extensively explored approach to the formation of one-dimensional nanostructures.^[18,19] Solution-based techniques are more versatile with regard to particle morphology, due to the broadness of these approaches, which involve coprecipitation, sol–gel chemistry, microemulsion, hydrothermal/solvothermal processing and template syntheses.^[20]

Among all the functional materials to be synthesized on the nanoscale, metal oxides are particularly attractive candidates, from a scientific as well as from a technological point of view. The unique characteristics of metal oxides make them the most diverse class of materials, with properties covering almost all aspects of materials science and solid-state physics. The great variety of structures and properties made them the primary target in solid-state chemistry and provides the basis for designing new materials. The crystal chemistry of metal oxides, representing not only the crystal structure, but also the nature of bonding, ranges from simple rock salt to highly complex incommensurately modulated structures, and the bonding can vary anywhere between highly ionic to covalent or metallic.^[21,22] Associated with such changes in structure and bonding, oxidic materials exhibit fascinating electronic and magnetic properties, including metallic or insulating and ferro-, ferri-, or antiferromagnetic behavior. Some oxides possess switchable orientation states as in ferroelectrics, others are superconducting or show colossal magnetoresistance. All these properties make metal oxides a vital constituent in technological applications like gas sensing,^[23,24] electroceramics,^[25–28] catalysis^[29] or energy conversion^[30] and storage,^[31–33] to name but a few.

The conventional and also traditional synthesis of oxidic materials involves the direct reaction of a mixture of powders. To bring the reaction partners sufficiently close together and to provide high mobility, these solid-state reactions require high temperature and small particle sizes. However, these harsh conditions preclude subtle control of the reactions and impede the formation of thermally labile and metastable solids.^[34] Nevertheless, these approaches generat-

ed an overwhelming plethora of solid compounds and fulfilled, in addition to the synthesis and characterization, the main goal of correlating structure–property relationships of bulk materials. It is evident that for nanoparticle synthesis, in which size and shape are crucial factors in determining the properties, other preparation methodologies have to be developed. The most promising alternatives are soft-chemistry routes,^[35,36] in which good control from the molecular precursor to the final product is achieved, offering high purity and homogeneity, and low processing temperatures. It is not surprising that the concepts of sol–gel chemistry, which had a long and successful tradition in the synthesis of bulk metal oxides,^[37,38] have been adapted for nanoparticle synthesis.^[20] In spite of all the recent efforts, the number of oxidic nanoparticles obtained by sol–gel chemistry is still minuscule compared to the variety of compounds obtained from powder routes. This is not only a question of the time-frame, but also due to the fact that the conventionally applied aqueous sol–gel chemistry suffers from some major drawbacks. In the most cases the as-synthesized precipitates are amorphous and subsequent heat treatment is necessary to induce crystallization. However, this additional step results in alteration, mainly particle growth, or even destruction of the well-defined particle morphology. Further disadvantages of aqueous systems are reaction parameters that are difficult to control, such as fast hydrolysis rate of the metal alkoxides, pH, method of mixing, rate of oxidation, and, especially, the nature and concentration of anions.^[37,39] The high complexity of aqueous solutions leads to a situation in which slight changes in experimental conditions have a strong influence on particle morphology.^[40,41] Nonaqueous sol–gel processes in organic solvents are able to overcome many of these specific problems typical for aqueous systems. Although these ideas are not new and the basic reaction principles were established almost a century ago, only recently have they been implemented in nanoparticle synthesis in a more systematic fashion.

In this review we will discuss advances in the development of soft-chemistry routes to inorganic nanoparticles, with a strong focus on metal oxides and nonaqueous reaction processes. In contrast to other reviews on nanoparticle synthesis, we will direct our attention not so much on the characteristics of the nanoparticles, but particularly on the primary mechanisms leading to their formation. Nanoparticle formation is often accompanied by processes involving basic organic chemistry principles and, therefore, information about reaction pathways can be found by identification of the organic byproducts, which are either present in the final reaction mixture or escape during the synthesis as gaseous compounds. By retro-synthetic approaches one can correlate the processes leading to these organic species to the growth mechanisms of the oxide particles. We are convinced that understanding these processes is an important step towards the rational synthesis design of inorganic nanoparticles, not only for metal oxides, but also for metal nitrides and sulfides, which however are not in the scope of this review. In spite of the immense progress in nanoparticle

research, the development of synthesis concepts based on a rational design has remained a primary objective, and yet we are far from achieving this goal. It is still impossible to prepare a certain compound on the nanoscale with a desired composition, structure, size, and shape, or even properties, intentionally and in a predicted way. This problem has been a serious issue in solid-state chemistry for a long time and “has led to the widely accepted, and often somewhat resigned, attitude that experimental solid-state chemistry is not amenable to detailed design and thus is intrinsically of an explorative nature”.^[34] In contrast to powder synthesis, but similar to most of the reactions in organic chemistry, nanoparticle preparation is predominantly performed in liquid solutions. Accordingly, the adaptation of organic chemistry principles to nanoparticle synthesis would lead to the ideal case in which a toolbox of well-known chemical reactions is available to prepare the targeted nanoparticles by following a sequence of predictable synthesis steps, so that it is possible to use the basic concepts developed in molecular chemistry for the rational design of inorganic nanoparticles.

Processes involving the transformation of molecular precursors into metal oxides are generally termed as sol–gel procedures in this review, although they do not strictly proceed through the formation of a sol and a gel, but are often based on simple precipitation. In the literature, the synthesis of metal oxides in organic solvents is often 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”.

Nonaqueous Sol–gel Chemistry for Metal Oxide Synthesis

History of nonaqueous sol–gel chemistry: As often in science, it is difficult to date exactly the starting point of the investigations on the nonaqueous synthesis of oxidic compounds. Early work on the reaction of alcohols with silicon tetrachloride can be traced back to the year 1928, when Dearing and Reid presented their work on “Alkyl Orthosilicates”.^[42] Amazingly, already these authors proposed an aqueous and nonaqueous route to silica gels, assuming that they might show “different absorptive power”. Although many other groups continued to work on this topic,^[43–45] 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,^[46] the reaction of silicon tetrachloride with benzaldehyde^[47] and organic ethers,^[48] or the synthesis of silica–sodalite from nonaqueous systems,^[49] it was only at the beginning of the nineties that these concepts became popular to a larger scientific community.^[50,51] Emanating from the preparation of monolithic silica gels from the reaction of silicon tetrachloride with oxygen donors such as alkoxides, aldehydes, and ethers,^[52] the Corriu and Vioux

groups were particularly active in the field of nonhydrolytic sol–gel chemistry. They and others reported the synthesis of several metal oxide gels, including silica, alumina, titania, binary phases thereof, tin oxide, and various titanates.^[53–61] At about the same time, Inoue et al. and others worked on the preparation of oxidic powders using the reaction between metal alkoxides and alcohols^[62–64] or inert organic solvents.^[64–66] In particular, the glycothermal method involving the reaction of metal alkoxides or acetylacetonates in 1,4-butanediol is a versatile approach to various metal oxides^[67,68] and has recently been reviewed.^[69] All these results represent an important basis for the use of nonaqueous sol–gel processes for the synthesis of metal oxide nanoparticles.

Surfactant- versus solvent-controlled synthesis of metal oxide nanoparticles: The extension of the nonhydrolytic reaction processes to the synthesis of zincite,^[70] zirconia,^[64] and titania nanocrystals^[65,71–73] were further steps in opening up new pathways to a large variety of metal oxide nanoparticles. Nowadays, nonaqueous synthesis approaches have become a valuable alternative to aqueous systems and the family of metal oxide nanoparticles synthesized by nonhydrolytic reaction routes is growing rapidly,^[74–77] including TiO₂,^[78–85] FeO_x,^[86–99] MnO,^[86,90,100–104] Mn₃O₄,^[84,100,105] CeO₂,^[106] CuO_x,^[105,107] Cr₂O₃,^[90] Co₃O₄,^[90,108] CoO,^[105,109] NiO,^[90,102,110] ReO₃,^[111] ZrO₂,^[112,113] HfO₂/Hf_xZr_{1–x}O₂,^[113,114] V₂O₅,^[84] ZnO,^[115–121] Y₂O₃:Eu,^[122] In₂O₃,^[123,124] SnO₂,^[121] WO_x,^[84,125,126] Sm₂O₃,^[127] and ferrites.^[96,128–132] Some of these procedures offer peculiar features such as extraordinary size control, like in the case of magnetic iron oxide nanoparticles,^[97] or easy scale-up to tens-of-grams quantities.^[133]

A wide variety of metal oxide precursors is used in these procedures, ranging from organometallic complexes to metal halides, alkoxides, and acetylacetonates. Some of the precursor salts are hydrated, so that a hydrolytic formation of the metal oxide network cannot be excluded. For most of these processes, a common feature is the presence of surfactants and coordinating solvents as stabilizing agents, and in general, the reactions occur at high temperatures between 200 and 300 °C. The use of coordination chemistry provides several advantages. The surface capping agents can be exchanged against other ones, offering control over the surface properties. Furthermore, agglomeration of the nanocrystals can be prevented, so that they are highly dispersible in (organic) solvents. On the other hand, the surface functionalization with surfactants bears the problem that it influences the toxicity of the nanoparticles.^[134] The cytotoxicity of quantum dots, for example, strongly depends on the molecules attached to the surface.^[135,136]

An elegant alternative to surfactants is the use of nontoxic solvents that act as a reactant as well as control agent for particle growth, thereby allowing the synthesis of high-purity nanomaterials.^[77] In the past two decades, several pathways have been developed enabling the surfactant-free synthesis of nanocrystalline materials. In principle, one can distinguish between methods in which the solvent itself, or a

reaction product, acts as capping agent, binding to the particle surface and hence limiting particle growth and agglomeration, and methods which employ hydrophobic solvents, which are in principle analogous to emulsion-like systems. The latter, however, lack the ability of stabilization of the formed particles against aggregation, and hence we will focus on solvent-stabilized routes.

The probably most widely explored approach to synthesize metal oxide nanoparticles in nonaqueous medium in the absence of any surfactants is based on the use of metal halides and alcohols. Especially the reaction between TiCl_4 and various alcohols is well documented.^[137–139] One of the particularly versatile solvents in this context is benzyl alcohol, because it enables the synthesis of titania nanoparticles with good control not only over particle size,^[140,141] but also over surface properties^[142] and assembly behavior.^[143,144] The low reaction temperature of the TiCl_4 /benzyl alcohol system offers the possibility to functionalize the surface of the nanoparticles in an in situ process; that is, the addition of enediol ligands such as dopamine and 4-*tert*-butylcatechol to the reaction mixture provides a simple route to surface-functionalized nanoparticles that are dispersible either in water or in organic solvents.^[142] If the same reaction is performed in the presence of 2-amino-2-(hydroxymethyl)-1,3-propanediol ($\text{HOCH}_2)_3\text{CNH}_2$ (Trizma), the as-synthesized titania nanocrystals assemble into pearl-necklace structures upon redispersion in water (Figure 1a). Interestingly, these nanowirelike arrangements are composed of a continuous string of precisely ordered nanoparticles. HRTEM investigations give evidence that the nanoparticles assemble along the [001] direction through oriented attachment,^[143] exhibiting monocystal-like lattice fringes (Figure 1b). In spite of the formation of a supercrystal, an AFM image still reveals the particulate features and nicely presents the possibility of branching events in the wirelike structures (Figure 1c). Experimental data suggest that the anisotropic assembly is a consequence of the water-promoted desorption of the organic ligands selectively from the {001} faces of the crystalline nanosized building blocks together with the dissociative adsorption of water on these crystal faces. Both processes induce the preferred attachment of the titania nanoparticles along the [001] direction.^[144]

In addition to TiCl_4 other metal chlorides such as FeCl_3 ,^[145] VOCl_3 ,^[141] CoCl_2 ,^[146] and WCl_6 ^[141,147] readily react with alcohols to the corresponding metal oxides. SnCl_4 and benzyl alcohol are an exceptional case, as this system on the one hand yields nanocrystalline SnO_2 particles with a small particle size distribution in the range of 2–6 nm (Figure 2a). On the other hand it allows the formation of a transparent and stable sol in tetrahydrofuran without any additional stabilizer and without any indication of agglomeration.^[148] Addition of a polybutadiene-*block*-poly(ethylene oxide) block copolymer as template to the THF solution and subsequent evaporation of the solvent induces the cooperative assembly of the nanoparticles and the PB-PEO block copolymer micelles, resulting in the formation of a highly ordered porous mesostructure (Figure 2b).^[148] It is interesting to note that in

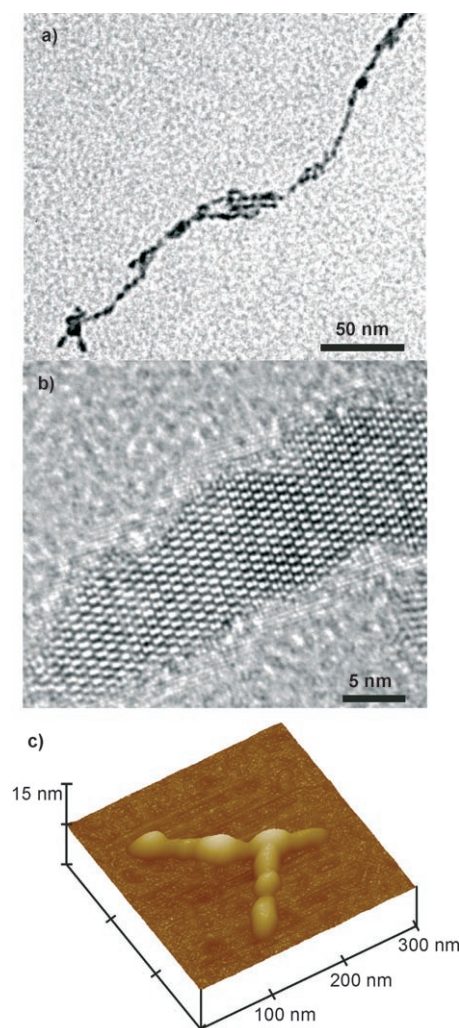


Figure 1. a) TEM image of titania nanoparticle assemblies in water, b) HRTEM image of a part of a titania nanostructure, and c) AFM image of titania nanoparticle assemblies.

contrast to previously reported procedures, in which aqueous ceria nanoparticle sols^[149] were used for the assembly into mesoporous materials,^[150] here throughout the whole process no addition of water is required. The reaction of benzyl alcohol with WCl_6 results in the formation of tungstate nanoplatelets with sides ranging from 30 to 100 nm (Figure 2c).^[141] Addition of the bioligand deferoxamine mesylate, a siderophore, changes the particle morphology completely from a pseudo-2D shape to 1D nanowires (Figure 2d). These nanowires are single-crystalline and exhibit a uniform diameter of 1.3 nm (Figure 2d, inset).^[151]

These examples show that the metal halide/alcohol system with its low reaction temperature is particularly useful and versatile in cases in which either surface functionalization of the nanoparticles with organic ligands is desired, or in which biomimetic reaction principles based on the use of organic templates have to be applied to tailor particle morphology. On the other hand, metal halide precursors are a problem when high purity of the product is required, as halide impurities often remain in the final oxidic material, and this con-

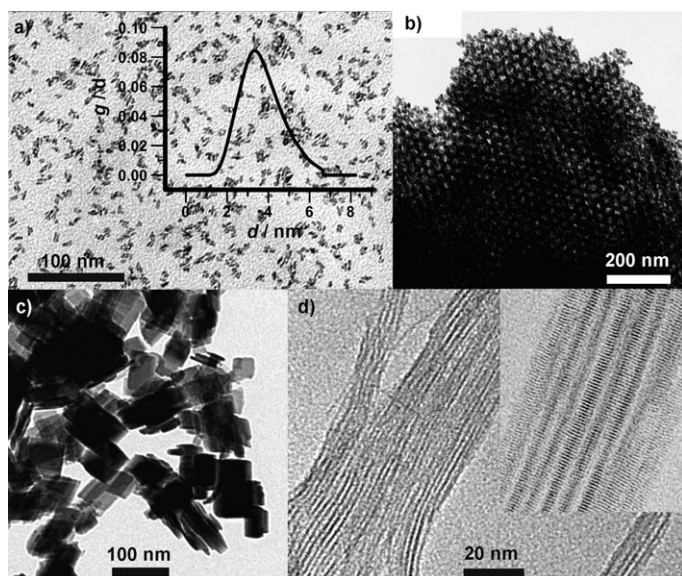


Figure 2. a) TEM overview image of tin oxide nanoparticles (inset: particle size distribution measured by analytical ultracentrifugation), b) TEM image of mesoporous tin oxide after calcination at 550 °C, c) TEM image of tungsten oxide platelets, and d) TEM image of tungsten oxide nanowire bundles (inset: HRTEM image).

tamination is detrimental for applications in catalysis or gas sensing.

An alternative halide-free route to crystalline metal oxides involves the reaction of metal alkoxides, acetates, or acetylacetonates with alcohols or glycols. The majority of the publications deal with the reaction of metal alkoxides in various alcohols, but also a few other examples have been reported. CuO nanoparticles in the size range of about 5–10 nm were obtained by means of alcohol thermal treatment of copper acetate in ethanol.^[152] Solvothermal treatment of iron acetylacetonate in benzyl alcohol resulted in the formation of nanocrystalline magnetite particles with a spherical morphology and diameters of 12–25 nm.^[153] The reaction of zirconium *n*-propoxide in various glycols yielded nanocrystalline zirconia powders at 300 °C. The crystallite sizes could be varied in the range of 3 to 5 nm by adjusting the zirconium *n*-propoxide/solvent ratio,^[154] but the size was also influenced by the nature of the solvent. Whereas 1,2-ethanediol (ethylene glycol) led to the smallest particles due to the strong coordination of the solvent to the particles, 1,4-butanediol (and not 1,6-hexanediol) yielded the largest particles, which was a consequence of the facile intramolecular ether formation.^[64] This example nicely highlights the importance of the formation mechanism, when one wants to predict the properties of nanoparticles in a specific reaction system—just considering the binding strength of the glycols is evidently not sufficient.

A wide variety of binary and ternary metal oxide nanoparticles has been obtained by reacting metal alkoxides with alcohols, most of the work, however, being dedicated to the synthesis of nanocrystalline titania. Titanium *n*-butoxide in 1,4-butanediol formed anatase nanocrystals of about 10–

15 nm in diameter after solvothermal reaction.^[155,156] When heating titanium *n*-butoxide in toluene, only amorphous products were obtained.^[156] Ethylene glycol reacts with titanium *n*-butoxide to titanium glycolate, which can easily be transformed into crystalline anatase nanowires by calcination. Based on the same process, SnO₂, In₂O₃, and PbO nanowires with diameters of 50 nm and lengths up to 30 μm were prepared.^[157]

Among the various alcohols, benzyl alcohol plays an outstanding role in the nonaqueous preparation of metal oxide nanocrystals, because it allows the synthesis of a large selection of nanocrystalline metal oxides such as V₂O₅, Nb₂O₅,^[158] Ta₂O₅, HfO₂,^[159] SnO₂, In₂O₃,^[160,161] indium tin oxide,^[162] CeO₂, ZrO₂,^[161] NaNbO₃, NaTaO₃,^[77] BaTiO₃, LiNbO₃, BaZrO₃,^[163] SrTiO₃, and (Ba,Sr)TiO₃.^[164] TEM images of nanocrystalline ceria, zirconia, indium tin oxide and barium titanate are presented in Figure 3. In all these cases, the par-

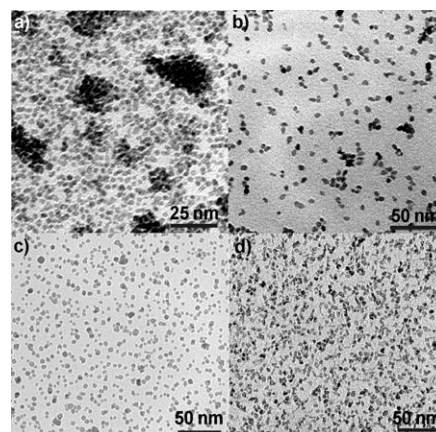


Figure 3. TEM overview images of various metal oxide nanoparticles obtained from halide-free precursors in benzyl alcohol. a) CeO₂, b) ZrO₂, c) SnO₂-doped In₂O₃, and d) BaTiO₃.

ticles exhibit a spherical morphology with uniform shapes, small size distributions, and good dispersibility. Ceria, obtained from cerium isopropoxide and benzyl alcohol at 200 °C, has an average particle size of 3–4 nm (Figure 3a). The reaction of zirconium isopropoxide with benzyl alcohol at 230 °C resulted in zirconia nanocrystals with diameters of 4–6 nm (Figure 3b). In the case of indium tin oxide, the two precursors tin *tert*-butoxide and indium acetylacetonate were reacted in benzyl alcohol at 200 °C, yielding indium tin oxide nanoparticles in the size range of 5–10 nm (Figure 3c).^[162] The SnO₂ content was varied in the range of 2–30 wt % with a maximum electrical conductivity at a dopant concentration of 15 wt %. The synthesis of BaTiO₃ involves the dissolution of metallic barium in benzyl alcohol, addition of titanium isopropoxide and subsequent solvothermal treatment at 200 °C for 48 h.^[163,164] This procedure leads to barium titanate nanoparticles with diameters of 5–8 nm (Figure 3d). Interestingly, in spite of the small particle size the structure of these nanoparticles is not completely cubic. Although it is cubicalike on average, it shows locally slight dis-

tortions of a tetragonal type.^[165] The structural information might help to understand the dielectric properties of these nanomaterials. A first step toward application of the BaTiO₃ nanoparticles was taken by the fabrication of thin film coatings by means of electrophoretic deposition technique.^[166]

It is interesting to note that in certain cases the reaction between metal alkoxides and benzyl alcohol results in the formation of more complex structures than just spherical particles. When using yttrium isopropoxide as precursor, the reaction with benzyl alcohol at 250 °C yields a lamellar nanohybrid consisting of crystalline, 0.6 nm thick yttrium oxide layers with intercalated benzoate molecules.^[167] Evidently, the yttrium oxide species is able to catalyze the oxidation of benzyl alcohol to benzoic acid, thus limiting the growth in thickness of the yttrium oxide lamellae (Figure 4a). Bundles of tungsten oxide nanowires are obtained after the reaction of tungsten isopropoxide in benzyl alcohol without the use of any additional structure-directing templates (Figure 4b).^[168] The bundles can be split up into individual nanowires by the addition of formamide to a dispersion of the nanobundles in ethanol. The small diameter of about 1 nm makes these wires structurally highly flexible (Figure 4c). The high surface-to-volume ratio combined with the high purity of the material makes these nanowire bun-

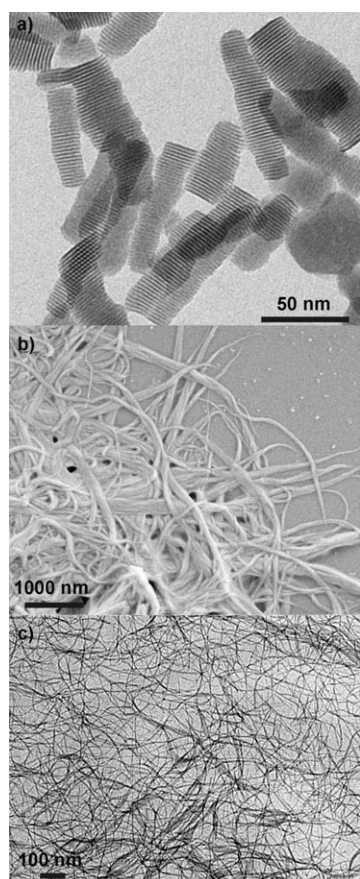


Figure 4. a) TEM image of the lamellar yttrium oxide/benzoate nanohybrid, b) SEM image of tungsten oxide bundles, and c) TEM image of individual tungsten oxide nanowires.

dles ideal candidates for gas-sensing devices. Preliminary results confirm this assumption, as these nanowires show an extraordinarily good sensitivity to NO₂ concentrations in the ppb range.^[168]

Metal oxides containing cations that are sensitive towards reduction to the respective metals by alcohols (in particular copper and lead-containing compounds) are not accessible by the “benzyl alcohol route”. In these cases, the use of non-reductive solvents like ketones or aldehydes instead of benzyl alcohol is required. The applicability of this approach has already been reported for the synthesis of ZnO, TiO₂, In₂O₃, and BaTiO₃. The addition of acetone to solutions of zinc dialkoxides in benzene resulted in the formation of transparent gels, which transformed into 4 nm zincite nanocrystals.^[70] During this process, acetone is transformed into mesityl oxide via aldolate ligands (β -diketonates) as transition products (see later discussion on aldol condensation), which can also act as chelating ligands, stabilizing the formed nanocrystals. The use of different ketones and aldehydes as oxygen-supplying agents in the nonaqueous, solvothermal synthesis of anatase nanocrystals made it possible to tailor the particle size to some extent, as sterically unfavorable alicyclic and aromatic ketones and aldehydes resulted in smaller particles than aliphatic compounds.^[169] Crystalline BaTiO₃ was obtained by transformation of the bimetallic alkoxide complex [(BaTiO)₄(iPrO)₁₆] \cdot 3*i*PrOH in acetone under stirring at room temperature for 21 days.^[170] BaTiO₃ was also synthesized in acetophenone starting from metallic barium and titanium isopropoxide.^[171] In comparison to BaTiO₃ prepared by the benzyl alcohol route, these nanoparticles are larger, namely in the size range of 10–15 nm. A similar synthesis method was employed for piezoelectrics such as PbTiO₃, Pb(Zr,Ti)O₃, and PbZrO₃.^[172] These technologically important materials are traditionally synthesized by solid-state reactions at temperatures between 600 and 1100 °C and nonaqueous sol-gel chemistry offers now a simple soft-chemistry route to amorphous powder precursors that can be transformed into the nanocrystalline oxides at temperatures between 400 °C and 600 °C.^[172] Interestingly, the synthesis of BaSnO₃ nanoparticles is only possible in ketones, but not in alcohols; this phenomenon is not yet understood.^[77]

In addition to the reaction of metal halides, alkoxides, acetates, or acetylacetonates with oxygen-containing solvents, another synthesis procedure involving the reaction of metal acetylacetonates with benzylamine was reported. This route is quite generally applicable and resulted in the formation of various metal oxide nanoparticles such as iron, zinc, indium and gallium oxide.^[173]

In the surfactant-free synthesis of metal oxide nanoparticles, the organic solvents play a crucial role in determining the particle size, shape, and size distribution. Nanoparticles with the same composition, but synthesized from different precursors and solvents, can exhibit a range of particle morphologies. Consequently, by choosing the appropriate reaction system, it is possible to gain control over all these crystal parameters. Figure 5 illustrates these possibilities show-

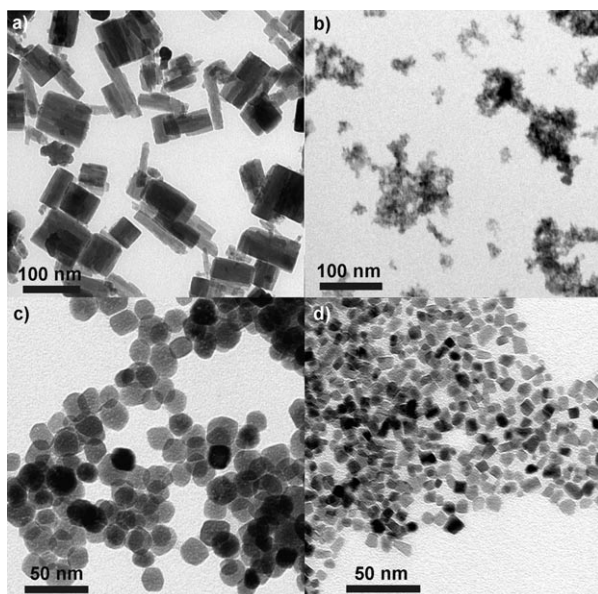


Figure 5. TEM images of a) Nb_2O_5 obtained from niobium ethoxide and benzyl alcohol, b) Nb_2O_5 obtained from niobium chloride and benzyl alcohol, c) In_2O_3 prepared from indium isopropoxide and acetophenone, and d) In_2O_3 obtained from indium acetylacetonate and benzylamine.

ing indium and niobium oxide nanoparticles as representative examples for the synthesis of metal oxides in different reaction systems. The reaction of niobium ethoxide in benzyl alcohol yielded after solvothermal treatment at 220°C orthorhombic Nb_2O_5 with a platelet-like morphology with sides ranging from 50 to 80 nm (Figure 5a).^[158] If NbCl_5 is used as precursor, the reaction in benzyl alcohol leads to small, slightly agglomerated crystallites of just a few nanometers. In the case of indium oxide, the indium isopropoxide/acetophenone system resulted in the formation of nearly spherical particles with diameters ranging from 15 to 30 nm. If a similar reaction is performed starting from indium acetylacetonate in benzylamine, the nanoparticles are much smaller with pronounced crystal facets.^[161]

General Mechanistic Principles of Sol-gel Processes

Introduction into aqueous sol-gel chemistry: The sol-gel process can shortly be defined as the conversion of a precursor solution into an inorganic solid by chemical reactions. In general, the precursor or starting compound is either an inorganic metal salt (acetate, chloride, nitrate, sulfate,...) or an organic species like a metal alkoxide. Indeed, metal alkoxides constitute the most widely used class of precursors in aqueous sol-gel processes^[174–177] and their chemistry is well established.^[178–180] In a first step, the metal alkoxide is transformed into a sol (dispersion of colloidal particles in a liquid), which reacts further to a gel, an interconnected, rigid, and porous inorganic network enclosing a continuous

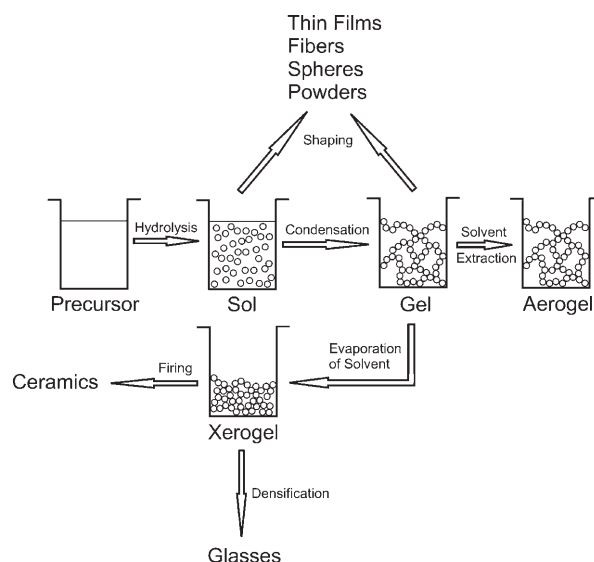


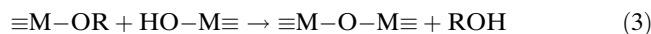
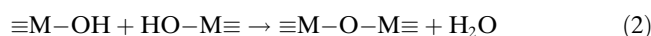
Figure 6. Various steps in the sol-gel process to control the final morphology of the product (according to reference [182]).

liquid phase (Figure 6). This conversion involves two main reaction types: hydrolysis and condensation [Eqs. (1)–(3)].

Hydrolysis



Condensation



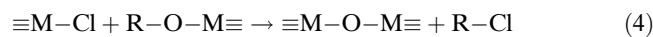
During hydrolysis, the alkoxide groups (-OR) are replaced through the nucleophilic attack of the oxygen atom of a water molecule under release of alcohol and the formation of a metal hydroxide [Eq. (1)]. Condensation reactions between two hydroxylated metal species leads to M-O-M bonds under release of water (oxolation) [Eq. (2)], whereas the reaction between a hydroxide and an alkoxide leads to M-O-M bonds under release of an alcohol (alkoxolation) [Eq. (3)]. Although these processes have been investigated for decades, the simultaneous occurrence of hydrolysis and condensation reactions leads to a wide variety of different species,^[181] which cannot be identified, and, therefore, aqueous sol-gel chemistry is not yet fully controllable. More detailed information about aqueous sol-gel processes can be found elsewhere.^[36–38, 182–186]

The advantage of the aqueous sol-gel approach lies in the fact that the sol or the gel can be shaped to the finally desired form such as monoliths, films, fibers, and monosized powders, and subsequently converted into the ceramic material by heat treatment. The versatility of the whole process is summarized in Figure 6, presenting a schematic of the various routes one can follow within the sol-gel synthesis of an inorganic material.^[182]

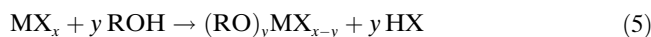
Introduction into nonaqueous sol-gel chemistry: The major problem of sol-gel methods based on the hydrolysis and condensation of molecular precursors is the control over the reaction rates. For most transition metal oxide precursors, these reactions are too fast, resulting in loss of morphological and 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 multicomponent 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.^[36,37,181,187-189] 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.^[184] Even the slow dissolution of water from the gas-phase in an inert solvent has been employed as a similar strategy.^[190-192]

However, it is also possible to completely avoid the presence of water in the reaction medium, which is usually referred to as nonhydrolytic or nonaqueous sol-gel chemistry. The oxygen is provided by donors such as ethers, alcohols, or alkoxides rather than water, which leads to a completely different chemistry based on the reactivity of the oxygen-carbon bond.^[184] Formation of the M-O-M bridge occurs through the condensation reaction between the ligands coordinated to two different metal centers followed by the elimination of an organic fragment. Nonhydrolytic sol-gel routes to oxides and organic-inorganic hybrids have been reviewed by Vioux,^[50] Inoue,^[69] Hay et al.,^[51,61] and also partly by Cushing et al.^[20] Therefore we will focus here just on some examples and general principles particularly important for nanoparticle synthesis.

Alkyl halide elimination: Due to the broad availability and low cost of metal halides, the first systematic investigations of the nonaqueous synthesis of metal oxide gels were carried out on alkyl halide elimination reactions. They involve the condensation between metal alkoxides and metal halides under release of an alkyl halide [Eq. (4)].

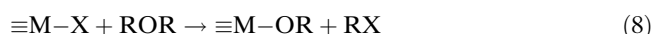


The metal alkoxide species can also be produced in situ by the alcoholysis or the etherolysis of metal halides [Eq. (5)]. In the first case, metal halides react to the respective metal alkoxides. It depends mainly on the metal center, how many halides are exchanged.^[179] As a second step, the alkoxide groups formed in situ react with unsolvolyzed M-Cl species according to [Eq. (4)]. Secondary and especially benzylic alcohols, however, prefer to directly eliminate alkyl halides [Eq. (6)] instead of hydrogen halides [Eq. (5)], which may be adequately termed as a *hydroxylation* process,^[52] and with subsequent condensation according to Equation (7).

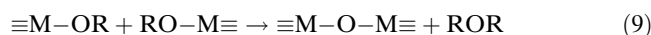


Even though the overall reaction is the same, it is not purely academic to distinguish between these two mechanisms. The intermediate hydroxyl groups are significantly more reactive than alkoxide species, leading to higher rates of gelation in secondary and benzylic alcohols. This is in agreement with experimental results.^[52]

For the reaction between metal halides and ethers, only one mechanism has been observed [Eq. (8)], with a second step as in Equation (4).^[55]



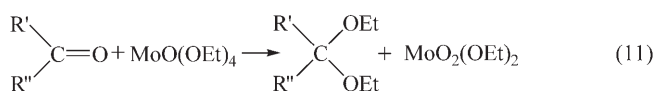
Ether elimination: In the case of the ether elimination process, the M-O-M bond is formed by the reaction between two metal alkoxides [Eq. (9)].



The interest in the mechanistic aspects of metal alkoxide transformation into oxoalkoxides as intermediates for oxides led to the discovery of the ether elimination process half a century ago by Bradley et al., who reported the tendency of niobium alkoxides to split off carbonium ions.^[193,194] Ether elimination reactions are characteristic of the derivatives of multivalent early transition elements such as Mo^{VI}, W^{VI}, and Nb^V, for which the inorganic molybdates or tungstates are directly produced in the presence of pronouncedly basic (alkaline, alkaline earth) alkoxides [Eq. (10)].^[195,196]

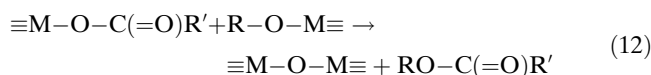


The formation of the oxo species is analogously possible in reactions of metal alkoxides with aldehydes and ketones.^[196,197] The molybdenum alkoxides MoO(OCH₃)₄ and MoO(OCH₂CH₃)₄ transform carbonyl compounds like acetaldehyde and acetone into acetals and ketals, respectively [Eq. (11)]. Finally, this reaction results in the quantitative formation of the colloidal oxidic compound.^[197]

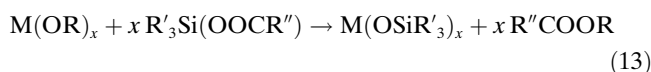


The condensation of metal alkoxides on action of carbonyl compounds can, however, also proceed by other pathways, as discussed below (under the section Other Mechanisms) and reported in the literature.^[198]

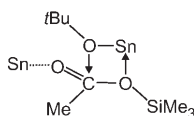
Ester elimination: The ester elimination process involves the reaction between metal carboxylates and metal alkoxides [Eq. (12)].



This approach has been used for the preparation of alkylsilyloxy derivatives of titanium, zirconium, niobium, and tantalum.^[199,200] The reaction between the metal alkoxides $\text{M}(\text{OR})_x$ and the silyl esters $\text{R}'_3\text{Si}(\text{OOCR}'')$ results in the formation of the trialkylsilyloxides $\text{M}(\text{OSiR}'_3)_x$ under elimination of the corresponding ester [Eq. (13)].

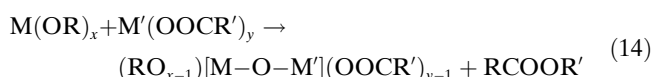


In the case of tin(IV) *tert*-butoxide and trimethylsilyl acetate, experiments in nonpolar solvents showed that the alkoxide group is transferred to the carbonyl ligand of the silyl acetate, similar to acid-catalyzed transesterification.^[201] The electropositive and coordinatively unsaturated Sn center acts as a Lewis acid center by coordinating to the carbonyl oxygen atom of the acetate, decreasing the electron density and thus, allowing the nucleophilic attack of the alkoxide (Scheme 1).



Scheme 1. Possible transition state of the ester elimination reaction between $\text{Sn}(\text{O}t\text{Bu})_4$ and $\text{Me}_3\text{Si}(\text{OAc})$ under formation of an Sn-O-Si bond (according to reference [201]).

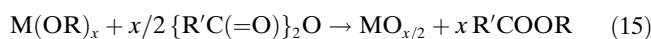
Compared to ether elimination, the ester elimination process seems to be more versatile, and several examples of nonhydrolytic preparations of (multicomponent) oxide gels have been reported. Anhydrous ZrO_2 and ZrSiO_4 gels were synthesized by using a direct condensation reaction of metal alkoxides $\text{M}(\text{OR})_x$ ($\text{M} = \text{Zr}$; $\text{R} = \text{C}_3\text{H}_7$) with metal carboxylates $\text{M}'(\text{O}_2\text{CR}')_y$ ($\text{M}' = \text{Si}$, Zr ; $\text{R}' = \text{CH}_3$) releasing a carboxylic acid ester as coproduct [Eq. (14)].^[202]



Similarly, $\text{Sn}(\text{OAc})_4$ and $\text{Sn}(\text{O}t\text{Bu})$ yield the tin-oxo cluster $[\text{Sn}_6(\text{O}_6)(\text{O}t\text{Bu})_6(\text{OAc})_6]$ and *t*BuOAc upon reflux in toluene.^[59] Interestingly, these clusters form highly oriented cassiterite-phase SnO_2 films upon processing the respective solution by aerosol-assisted chemical vapor deposition on a silicon substrate.^[59] The authors proposed several criteria required for successful ester elimination between a metal carboxylate and metal alkoxide: 1) a nonchelating carboxylate

ligand, 2) a non-coordinating solvent, 3) an electropositive metal alkoxide, and 4) vacant coordination sites on the metal alkoxide center.

The ester elimination route can also be carried out in a modified fashion. Already Pande and Mehrotra investigated the reactions of titanium isopropoxide with acetic anhydride.^[203] This approach offers the advantage of a completely hydroxyl-free and thus nonhydrolytic process [Eq. (15)]. It has later been employed to prepare silica gels^[204] and TiO_2 nanopowders.^[205]



Esterification reactions also play an important role in the synthesis of various polyoxometalate and metal-oxo clusters.^[6,177] To achieve perfectly defined structures, the water required for cluster formation is generated in situ through esterification or aldolization reactions in the presence of chelating or bridging organic ligands as stabilizing agents. The preparation involved the use of the corresponding metal isopropoxides in carboxylic acids, giving access to various titanium-oxo-isopropoxo clusters,^[206] a niobium-oxo-acetate complex,^[207] and several titanium-, zirconium-, and vanadium-oxo clusters,^[208] to name but a few. Two possible formation mechanisms based on direct esterification (intra-coordination-sphere mechanism, i.e., water is only virtually formed) or esterification between the slowly exchanged organic acid and the alcohol molecules (water is produced in situ) were proposed.^[206] It is interesting to note in this context that the formation of two titanium-oxo clusters has also been obtained through the reaction of titanium isopropoxide with diverse ketones.^[209] This process is discussed in more detail later in the section on aldol condensation. A detailed review on titanium-oxo clusters was recently published by Sanchez et al.^[210]

Organic Reaction Mechanisms in the Nonaqueous Synthesis of Metal Oxide Nanoparticles

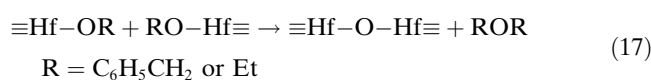
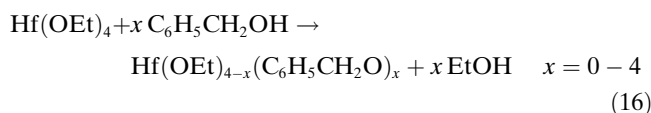
Alkyl halide elimination: Following intensive studies on the formation of oxide gels by the direct reaction between metal halides and alcohols or alkoxides (cf. section on alkyl halide elimination), Trentler et al. published in 1999 the first synthesis of crystalline anatase nanoparticles based on an alkyl halide elimination process.^[72] Relatively high temperatures of 300 °C and the presence of trioctylphosphine oxide (TOPO) as surfactant were required to yield phase-pure materials. This strategy has later been successfully applied to the synthesis of titania and zirconia nanocrystals by reacting the respective metal chloride and metal isopropoxide in hot TOPO.^[81,112,114] In the case of zirconia, the organic side products were analyzed. Aside from *i*PrCl, substantial amounts of propene were found, formed by dehydrochlorination of *i*PrCl, which was due to the rather high reaction temperature of 340 °C.^[112] Nevertheless, mechanistic studies of the alkyl halide elimination process for nanoparticle synthesis

are rather scarce, even though it is known that many metal halides, for example, bismuth chlorides, result in a variety of products upon reaction with alcohols.^[211] Trentler et al. proposed that the high-temperature reaction between TiX_4 and $\text{Ti}(\text{OR})_4$ essentially follows an S_N^1 mechanism, with reaction rates strongly decreasing with increased branching of the substituent R, but unaffected by the nature of X. Our own recent results indicated that even in such a simple reaction system involving metal halides in an alcohol the primary path of reaction is far from being straightforward.^[212] Although alkyl halide elimination is reported as the main pathway for the nonaqueous synthesis of TiO_2 in benzyl alcohol due to stabilization of the transient carbocation by the mesomeric effect of the phenyl ring,^[50] the presence of surface modifiers, such as dopamine, in the system^[142] significantly alters the ratio of reaction products. Whereas in the pure TiCl_4 /benzyl alcohol system the final reaction solution contained a benzyl chloride/benzyl ether molar ratio of 3:1, the dopamine system in fact contained a 1:3 ratio. In all these reaction systems, both benzyl ether and benzyl chloride were present as reaction products, but in varying amounts depending on the system.^[212] Also in the absence of organic ligands after solvothermal treatment in alcohols the formation of ethers was observed to a large extent.^[138] Furthermore, one has to keep in mind that the nanocrystals formed in the reaction mixture may even be able to catalyze side reactions, such as ether elimination, making it impossible to distinguish between direct products of nanoparticle formation and products of side processes. For example, the reaction between SnCl_4 and benzyl alcohol resulted in SnO_2 nanoparticles,^[148] but during the synthesis the benzyl alcohol solvent, being in 20-fold surplus, is almost completely transformed into dibenzyl ether. In addition, because metal halides are known to catalyze etherification reactions,^[213] it is not possible to determine whether the metal halide itself or the growing nanocrystals constitute the catalyst for this side reaction.

Ether elimination: Although termed as “thermal decomposition” or “thermal dehydration” in the early days, ether elimination routes in fact have been proven much earlier than the alkyl halide elimination mechanism to constitute viable pathways to amorphous and nanocrystalline oxides. Already in 1986, Fanelli and Burlew reacted aluminum alkoxides in 2-butanol and obtained amorphous Al_2O_3 in the form of agglomerated particles only 20 nm in size.^[62] They proposed “thermal dehydration” of the solvent to result in situ formation of water. Soon after, the so-called glycothermal method was developed by Inoue and co-workers, who subjected metal hydroxides and alkoxides to solvothermal treatment in glycols under autogenous pressure at temperatures of 325–450 °C.^[64, 65, 214, 215] The formation mechanism of zirconia upon treatment of $\text{Zr}(\text{OnPr})_4$ in 1,4-butanediol was proposed as a two-step process. First, 1,4-butanediol binds to the metal center, forming a glycoxide, which in a second step undergoes intramolecular condensation to tetrahydrofuran, which was as a matter of fact identified in the final re-

action mixture by gas chromatography.^[64] This mechanism shows that the dehydration process is catalyzed by the metal itself, and thus the reaction does not simply involve thermal dehydration.

We have recently reported the synthesis of HfO_2 and Ta_2O_5 nanoparticles by mixing the respective ethoxide with benzyl alcohol followed by solvothermal treatment, and we investigated also the reaction mechanisms by studying the organic composition of the final reaction mixture.^[159] The results point to a two step process involving ligand exchange reactions and ether elimination [Eqs. (16) and (17)].



In a first step, a significant amount of the ethoxy ligand is exchanged against benzyl alcohol to form ethanol and a benzyl alkoxide species [Eq. (16)]. It is known that such ligand-exchange processes take place already at room temperature.^[216, 217] Next the alkoxy species undergo condensation to form M–O–M bonds and organic ether [Eq. (17)]. The amount of dibenzyl ether found in the final reaction mixture was substantially higher than the amount of diethyl ether or benzyl ethyl ether (benzyl ether/diethyl ether plus mixed ether molar ratio of about 1.0:0.3), which means that most ethoxy groups are exchanged. These findings can be explained on the one hand by the surplus of benzyl alcohol in the system, but on the other the better stabilization of transition states due to mesomeric effects of the benzyl group plays an important role too.

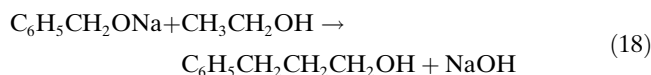
In addition, the reaction of titanium alkoxides in benzyl alcohol proceeds by this mechanism. Crystalline anatase resulted upon solvothermal treatment of $\text{Ti}(\text{OiPr})_4$ in benzyl alcohol at 200 °C for two days.^[212] The final reaction solution contained benzyl ether and isopropyl ethers in a molar ratio of 1.0:0.46. The fact that the amount of isopropyl ether and mixed benzyl isopropyl ether is significantly higher as compared to the ethyl ethers found in the HfO_2 synthesis reflects the better stability of secondary carbocations compared to primary ones.

Ester elimination: Over the last years, ester elimination processes have become a frequently applied route for the synthesis of metal oxide nanoparticles. Early experiments were generally aimed to supply water in situ by the reaction between acids and alcohols. In a second step, the generated water reacted with the metal oxide precursor, usually a metal alkoxide.^[73] Metal halides such as TiCl_4 were also used as precursors and added to alcohol/acid mixtures followed by solvothermal treatment and leading to highly crystalline anatase at rather mild conditions. It is interesting to

note that in this case ester formation between the alcohol and acid provided the water to hydrolyze the titania precursor, but nanoparticle formation occurred through alkyl halide elimination.^[137] However, it seems more straightforward to use the precursors directly as the reactant for esterification. One has the choice of either treating a metal carboxylate with an alcohol solvent or starting from a metal alkoxide, which is then reacted with an acid. Both pathways have become quite broadly employed. The latter one was particularly successful for the synthesis of transition-metal oxides like TiO₂ nanoparticles and nanorods,^[85,218,219] because the respective alkoxides are available commercially, and certain acids, in particular higher acids like oleic acid, additionally act as capping and structure-directing agents. Other metals, such as copper and zinc, are more stable in the form of acetates or carboxylates and are thus synthesized by reacting the carboxylates with alcohols or diols.^[118,152] Quite analogous to ester eliminations are amide eliminations. By reacting metal oleates with amines one can induce the controlled growth of oxides such as titania nanorods.^[83]

Other mechanisms

C–C bond formation: The systematic study of C–C bond formation between alcohols started more than 100 years ago by Marcel Guerbet. He investigated the reaction of sodium alkoxides with the parent and with other alcohols.^[220] In particular, the condensation products of sodium benzyl alcoholate with various alcohols attracted his attention.^[221,222] He found that sodium benzyl alcoholate reacted with ethanol at a temperature of 220 °C to 2-benzylethanol [Eq. (18)].^[222]

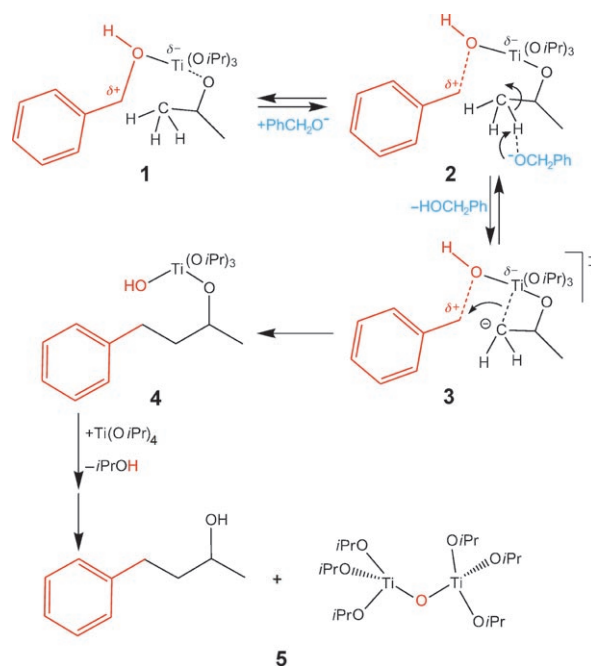


Decades later, Pratt and Kubler presented a modified Guerbet reaction involving the condensation reaction of benzyl alcohol with primary alcohols.^[223] Generally, the Guerbet reaction can be defined as the reaction between two alcohols at high temperatures, generally under catalytic conditions, resulting in a β -branched primary alcohol with twice the molecular weight of the reactant alcohol minus a mole of water [Eq. (19)].^[224,225]



The Guerbet reaction proceeds through a number of sequential steps including dehydrogenation of the alcohol to the corresponding carbonyl compounds; aldol condensation between the carbonyl compounds, followed by elimination of water; and hydrogenation of the unsaturated aldehydes to a saturated alcohol.^[224,225] As a side reaction, two molecules of aldehyde may undergo Cannizzaro-like disproportionation into alcohol and carboxylic acid.^[224] A review on Guerbet chemistry is provided by O'Lenick, Jr.^[225]

Remarkably, many investigations regarding the Guerbet reaction were focused on active primary alcohols, such as benzyl alcohol and *p*-methoxybenzyl alcohol. Accordingly, it is not surprising that benzyl alcohol also provides unique reaction mechanisms for the transformation of metal oxide precursors to oxides due to the chemical properties of the phenyl group. Whereas under “neutral” conditions metal chlorides and alkoxides undergo the aforementioned alkyl halide and ether elimination mechanisms, in the presence of alkaline species metal alkoxides react with benzyl alcohol by means of a C–C coupling mechanism, analogous to Guerbet chemistry. This reaction was recently described when studying the nonaqueous formation of BaTiO₃ and SrTiO₃ by solvothermal reaction of the respective alkaline earth metal and titanium isopropoxide in benzyl alcohol.^[163,164] In comparison to the standard reaction of metal alkoxides in alcohols, which usually proceeds through ether elimination (see above), the only difference from the experimental point of view is the dissolution of metallic barium in the alcohol prior to addition of the alkoxide Ti(O*i*Pr)₄. Nevertheless, the reaction mechanism changes completely and only negligible quantities of ethers were found in the final reaction mixture. The major components detected were 4-phenyl-2-butanol and 1,5-diphenyl-3-pentanol, which was proposed to form through deprotonation of the β -position of the isopropoxide ligand, followed by nucleophilic attack of the benzylic carbon atom (Scheme 2).^[164] The mechanism can be divided into several steps, starting with the coordination of benzyl alcohol (shown in red for better illustration) to the Ti atom of the metal oxide precursor. This bonding activates the benzylic carbon atom toward nucleophilic attack (1). The deprotonation of a β -carbon atom of the isopropoxy



Scheme 2. Proposed reaction mechanism for the simultaneous formation of BaTiO₃ nanoparticles and 4-phenyl-2-butanol.

group by benzyl alcoholate (**2**), which was formed upon dissolution of barium in benzyl alcohol, formally leads to a carbanion. The negative charge is stabilized by interaction with the Ti center (**3**), similar to an agostic bond,^[226] this fact also explains why deprotonation occurs in the β - and not in the α -position. The subsequent nucleophilic attack results in the formation of 4-phenyl-2-butoxide (**4**) and a metal-bound hydroxyl group. This M–OH group promotes further condensation under release of the alcohol (**5**), finally leading to the oxidic nanoparticles. The complete absence of acetone and unsaturated species as well as only small amounts of benzaldehyde and other carbonyl compounds in the final BaTiO₃ reaction mixture strongly supports this mechanism; however, it does not exclude completely a Guerbet-like process involving oxidation, aldol condensation, and reduction.

It is worth noting that the high crystallinity of the nanoparticles is presumably a direct consequence of the complexity of the organic reactions, because the slow and controlled provision of the hydroxyl species as condensation agents decreases the reaction rates and facilitates the formation of this ternary oxide in nanocrystalline form.

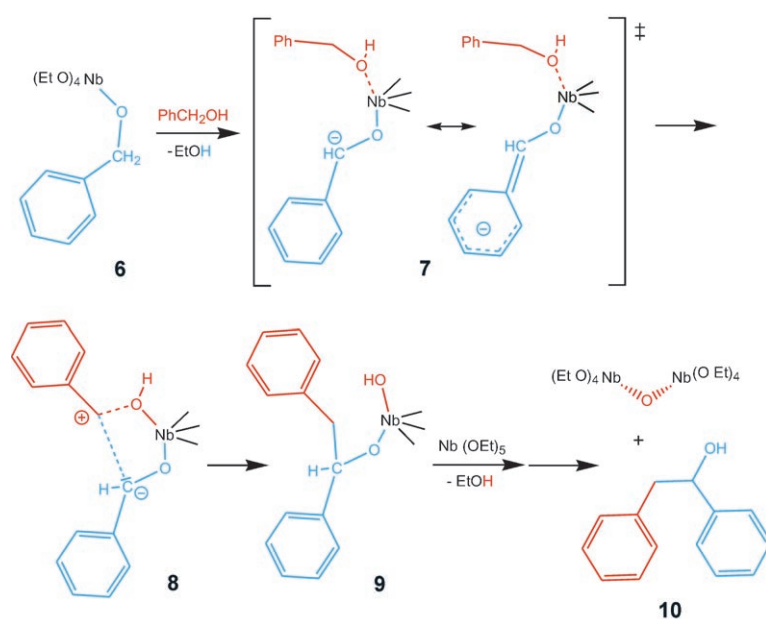
This C–C coupling mechanism was not observed when Ti(O*i*Pr)₄ alone was treated in benzyl alcohol under otherwise equal experimental conditions. In this case, benzyl ether or isopropyl ethers were formed, as initially expected, yielding crystalline anatase nanoparticles. In the presence of an alkaline species, such as Na(OEt) or K(O*t*Bu), the C–C coupling mechanism occurred to a comparable extent as for the BaTiO₃ system, but leading to amorphous gels.^[212] These results point to the conclusion that evidently “alkaline” conditions are a prerequisite for the occurrence of the C–C coupling mechanism in the Ti system. The coupling reaction is rather insensitive regarding the alkoxide precursor, as also Ti(OEt)₄, Ti(O*n*Pr)₄ and Ti(O*n*Bu)₄ could be used as precursors, resulting in the respective coupling products 3-phenylpropanol, 3-phenyl-2-methylpropanol and 2-benzylbutanol in good to almost stoichiometric yields.^[212]

Derivatives of benzyl alcohol, such as 1-phenylethanol, may also be used as solvents for the synthesis of titania and titanate nanoparticles under analogous conditions. For the system Ba/Ti(O*i*Pr)₄/1-phenylethanol, crystalline BaTiO₃ nanoparticles were obtained, as well as 2-phenyl-4-pentanol as the product of C–C coupling between an isopropoxy ligand and the solvent. 2-Phenylethanol, with the alcohol function bound to the vicinal instead of the benzylic carbon, does not

undergo nucleophilic attack and only amorphous gels were obtained. Accordingly it seems that the C–C coupling mechanism is strictly limited to the benzylic carbon atom and hence to benzylic alcohols as solvents.

On the other hand, the occurrence of this coupling reaction is by no means restricted to Ti centers as catalysts. A similar pathway was reported for yttrium isopropoxide, but leading to a lamellar nanocomposite instead of nanoparticles (Figure 4a).^[167] In addition to the C–C coupling, there is a high tendency for disproportionation of benzyl alcohol to toluene and benzaldehyde/benzoic acid, catalyzed by the yttrium centers. It is a peculiarity of this system that the coupling reaction even takes place in the absence of any alkaline species, which was attributed to the high Lewis acidity of the yttrium complex.^[167]

Also Nb can catalyze the C–C coupling reaction, as was observed for the reaction of Nb(OEt)₅ in benzyl alcohol at 220 °C.^[212] In this case, however, aside from the main reaction product 3-phenylpropanol, an abundance of side products was formed, including quite substantial amounts of 1,2-diphenylethanol and 1-ethoxy-1,2-diphenylethane. These compounds were not found in the BaTiO₃ and yttrium oxide systems. They must be formed through a C–C coupling reaction between two benzyl moieties. In this context, one has to keep in mind that the solvothermal treatment is performed at 220 °C, relatively close to the temperature of 250 °C, at which benzyl alcohol starts to undergo thermolysis reactions forming dibenzyl and various disproportionation products in an inert solvent such as cyclohexane without any catalyzing metals present.^[227] The proposed side reaction on the way to Nb₂O₅ leading to 1,2-diphenylethanol is presented in Scheme 3. Benzyl alcohol is coordinated to Nb centers in large amounts due to ligand exchange reactions.^[216] The



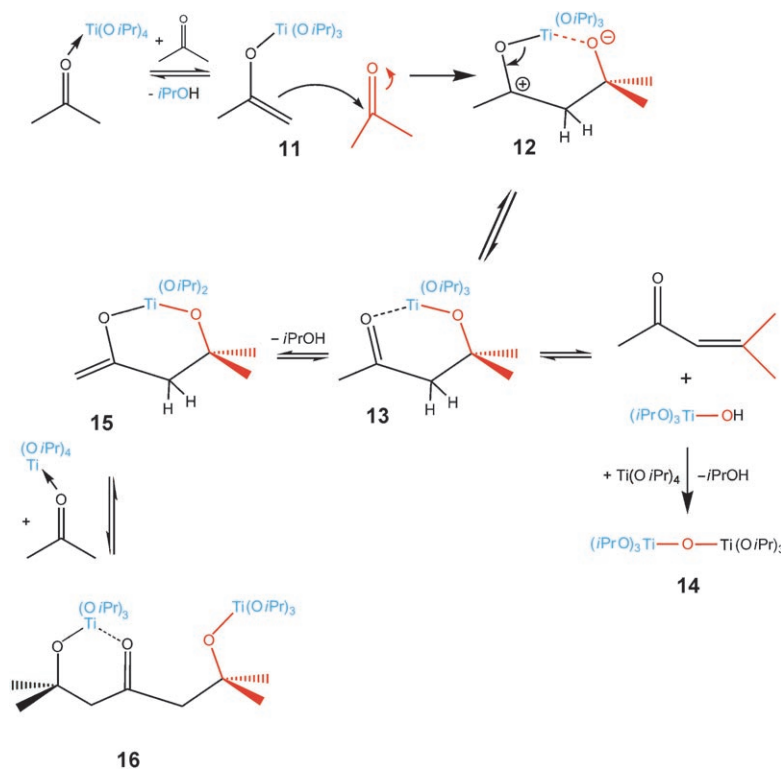
Scheme 3. Proposed side reaction involving a C–C bond formation of two benzylic species to form 1,2-diphenylethanol occurring to a large extent upon solvothermal reaction of Nb(OEt)₅ in benzyl alcohol.

resulting benzyl alcoholate (**6**) can be deprotonated at the α -position and the negative charge is stabilized by the electrophilic niobium center as well as by charge delocalization in the aromatic system (**7**). Subsequently, another benzyl alcohol species coordinates with the Nb center, and an attack of the negatively charged ligand onto the electrophilic second benzyl group (**8**) via a five-membered ring as transition state results in C–C bond formation (**9**). The simultaneously formed hydroxyl group leads to formation of Nb–O–Nb bridges under release of ethanol and 1,2-diphenylethanol (**10**).

Aldol condensation: The largest majority of sol–gel synthesis approaches to metal oxides (aside from water) employ alcohols, amines, or acids as solvents, even though other organic compounds, such as ketones, amides, or esters, also constitute attractive reaction media, as they are cheap, non-reductive and nontoxic. In the case of ketones, the main disadvantage may be their generally low boiling points, a problem that can easily be circumvented by using autoclaves for solvothermal treatment if elevated temperatures are necessary.

Ketones or aldehydes can also be used as the oxygen source in nonaqueous processes, just like ethers and alcohols. However, the release of oxygen from carbonyl compounds generally involves more complicated elimination processes. Ketones and related compounds undergo aldol condensation under elimination of water and formation of α,β -unsaturated carbonyl compounds. Such aldol elimination processes are known to be catalyzed by metal complexes,^[228] which are present in the system anyway as the metal oxide precursors. The eliminated water is consumed for the formation of the oxide, thus driving the equilibrium to complete turnover. These condensation processes take place already at moderate temperatures, as demonstrated by Goel et al.,^[70] who reacted $\text{Zn}[\text{OC}(\text{CH}_2\text{CH}_3)_3]_2$ with acetone in benzene or toluene as inert solvents. Acetone is deprotonated and coordinates to Zn to form an enolate complex. In a second step, the enolate ligand nucleophilically attacks another acetone species by means of an aldol condensation to yield Zn–OH and mesityl oxide as condensation products. These reactions occurred even at room temperature, leading to transparent gels that transformed to precipitates consisting of hydrated zincite nanocrystals upon aging.^[70] In a simi-

lar approach, titanium–oxo clusters were prepared by the reaction of titanium isopropoxide with ketones, such as acetone, acetylaceton, and diacetone alcohol, at room temperature.^[209] Organic condensation products detected in the acetone system were mesityl oxide and the tridentate ligand 2,6-dimethylhept-3-en-2,4,6-triol ($\text{O}_3\text{C}_9\text{H}_{18}$). The proposed reaction mechanism is depicted in Scheme 4 and is quite similar to the mechanism reported by Goel et al.^[70] First,



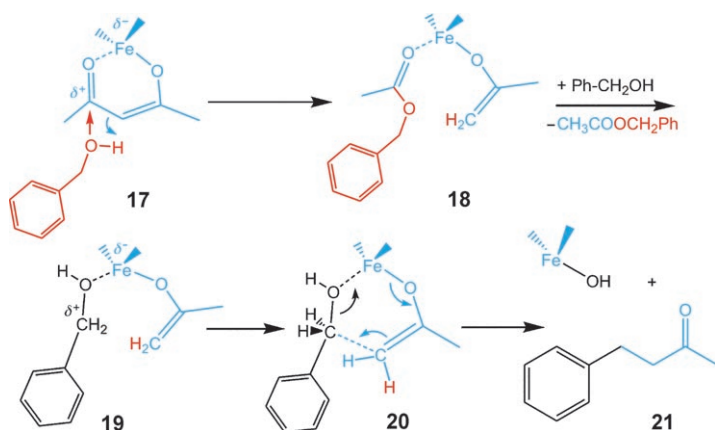
Scheme 4. Proposed formation mechanism of TiO_2 in acetone through aldol condensation.

acetone is coordinated to the titanium center, and deprotonation leads to the enolate complex under concurrent release of isopropanol (**11**). The enolate ligand nucleophilically attacks a second acetone molecule to form a C–C bond (**12**), and the aldolate ligand is coordinated to the Ti center (**13**). This titanium diacetone alcoholate complex can either react to give a Ti–OH species under release of mesityl oxide and further proceed to the formation of a Ti–O–Ti bond (**14**), or undergo further condensation reaction with a third acetone molecule.^[209] In the latter process, complex **15** is transformed into the tridentate ligand **16**, which is an excellent stabilizing agent. If the reaction is performed at room temperature, well-defined titanium–oxo clusters are obtained,^[209] whereas the solvothermal treatment of $\text{Ti}(\text{O}i\text{Pr})_4$ in ketones and aldehydes extended the size of the products beyond clusters and led to the formation of nanocrystalline anatase in the size range of 7 to 20 nm, depending on the solvent.^[169] In this case, even higher condensation products of acetone such as phorone and mesitylene were observed.^[169]

Also the preparation of BaTiO₃ nanocrystals 6–15 nm in size was achieved at room temperature by the long-time stirring of solutions of a pre-synthesized mixed barium/titanium oxoalkoxide in acetone.^[170]

In some cases, a side mechanism closely related to the Meerwein–Ponndorf–Verley reaction was observed, as first described to occur upon heating of aluminum alkoxides in acetone.^[229–231] This pathway has also been observed as side reaction in the formation of BaTiO₃ in cyclohexanone,^[170] in which the ligand is oxidized to the respective ketone through a hydride transfer from the alkoxide ligand to a coordinated solvent molecule, whilst the solvent is reduced to an alkoxy group. In this particular case starting from Ti(OiPr)₄ in cyclohexanone, acetone and cyclohexanol are formed. Due to the presence of the two ketone species acetone and cyclohexanone, the subsequent aldol condensation produces a variety of addition products, but essentially follows the reaction pathway as depicted in Scheme 4. BaTiO₃ can also be synthesized in acetone and acetophenone.^[171] Metallic barium was dissolved in the ketones at room temperature, resulting in the formation of barium enolates, followed by addition of Ti(OiPr)₄ and solvothermal treatment at 180–200 °C. The reaction pathway is not altered but enhanced by the presence of barium enolates, because the enolates constituted the reactive species inducing the aldol condensation process.

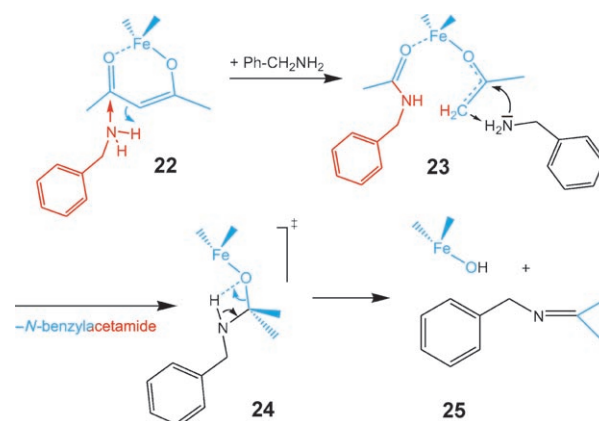
Aldol condensation reactions were also found as a part of the formation mechanism on the way to metal oxides starting from metal acetylacetonates in organic solvents. It was recently reported that the solvothermal reaction of metal acetylacetonates with benzyl alcohol or benzylamine was a particularly successful and versatile pathway to nanocrystalline Fe₃O₄, In₂O₃, Ga₂O₃, and ZnO at relatively mild conditions (175–200 °C).^[153,173] The analysis of the organic species in the final synthesis liquid revealed that in fact the reaction commences with a solvolysis of the acetylacetonate species, followed by aldol or ketimine condensation reactions. The mechanism for the reaction of Fe(acac)₃ in benzyl alcohol yielding magnetite nanocrystals is depicted in Scheme 5.



Scheme 5. Main reaction occurring upon solvothermal treatment of Fe(acac)₃ in benzyl alcohol involving solvolysis of the acetylacetonate, followed by condensation reactions.

Benzyl alcohol nucleophilically attacks one carbonyl group of the acetylacetonate ligand (17). Alcoholysis leads to benzyl acetate and an enolate ligand (18). In a next step, benzyl alcohol coordinates to the Fe center, releasing benzyl acetate in a ligand exchange reaction. Then, the enolate attacks the coordinated benzyl alkoxide (19, 20), and 4-phenyl-2-butanone is released (21). The Fe-bound hydroxyl group binds to another Fe center, representing the starting point of nanoparticle formation. A number of side products were also identified in the final reaction mixture. 4-Phenyl-3-buten-2-one, which was found in small amounts, is an oxidation product of 4-phenyl-2-butanone. Starting from Fe^{III}, one third of the iron must be reduced to Fe^{II} to obtain phase-pure magnetite. Therefore, 4-phenyl-3-buten-2-one is proposed to form from 4-phenyl-2-butanone by dehydrogenative oxidation, concurrently reducing two iron centers, which means that in principle the benzyl alcohol solvent leads to partial reduction of iron and provides for the correct stoichiometry of the oxide product.

The analogous reaction of Fe(acac)₃ in benzylamine proceeds quite similarly (Scheme 6), with the second step of the



Scheme 6. Main pathway of the reaction of Fe(acac)₃ in benzylamine leading to an oxygen transfer to the iron to enable nanoparticle formation.

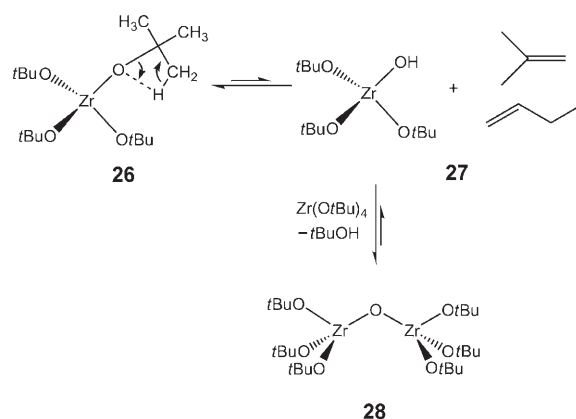
reaction, however, being a ketimine condensation, in which the enolate ligand functions as an electrophile (in contrast to the reaction in benzyl alcohol, in which the enolate ligand was the nucleophile). Due to the higher Lewis basicity of benzylamine, the solvolysis is enhanced (22), resulting in *N*-benzylacetamide and an enolate species (23), which undergoes the aforementioned ketimine condensation (23, 24) to form an imine under release of a hydroxyl group (25).

Surprisingly, it is even possible to utilize amides as solvents for the nonaqueous synthesis of metal oxides. The solvothermal reaction of Ti(OiPr)₄ with benzamide yielded highly crystalline anatase nanoparticles. In this case, due to the nature of the amide, the oxygen cannot be supplied by the solvent but stems from the alkoxide precursor. Indeed our preliminary results indicate the formation of *N*-isopropylbenzamide as the main organic condensation product,

which would go hand-in-hand with the release of the oxygen of the alkoxy group to enable the building of oxidic nanoparticles.^[212]

Thermal decomposition: The pathways and mechanisms discussed so far all rely on reactions between the precursor species and the solvent, or between two precursor species, and take place at moderate temperatures below 350 °C. There is, however, also a large number of nonaqueous synthesis procedures based on the high-temperature treatment of metal oxide precursors, in which, in principle, the presence of a solvent is not a prerequisite for the oxide formation, but merely serves to create a homogeneous distribution of the metal oxide precursor. These strategies may be grouped under “thermal decomposition routes”, even though in many cases the actual mechanism of oxide formation is not clear from a chemical point of view, as organic condensation reactions may just as well be responsible for the formation of initial clusters or even the oxide itself. Already the earliest of these “thermal decomposition routes”, the Pechini method,^[232] is such a confusing case. It is based on the preparation of solutions containing metal ions of Ti, Zr or Nb in ethylene glycol, stabilized as citrate complexes, which form oligomers through polyesterification reactions with the solvent. For the preparation of mixed metal oxides, such as perovskites, alkaline earth metal salts are dissolved in these precursor solutions. Subsequent heat treatment of the homogeneous solution in an open container removed excess solvent. The residual “resin-like” intermediate is subsequently fired at high temperature (500–730 °C), leading to thermal decomposition of the organic components and formation of the oxide. Although water is added to some of the mixtures, in others the water is generated in situ during the polycondensation, in principle leading to a nonaqueous sol–gel-based approach allowing the synthesis of metal oxides (but requiring high temperatures to obtain crystalline materials). The Pechini method has since been the focus of intensive research, and the interested reader is referred to more specific reviews.^[20,233]

The temperature required for the formation of crystalline nanoparticles can be substantially reduced by using other, easier to decompose precursor species. Only one year after Pechini developed his combustion method, Mazdiyasi and co-workers presented an approach involving the simple decomposition of metal alkoxides in the vapor phase at temperatures above 350 °C.^[234,235] They suggested an elimination reaction to occur upon thermolysis of $\text{Zr}(\text{O}t\text{Bu})_4$ according to Scheme 7. When the alkoxide vapor comes into contact with hot inert gas (325–500 °C), elimination of an alkoxide ligand (**26**) produces a metal-coordinated hydroxyl group and the respective olefin (or its isomers; **27**). The hydroxyl group reacts with another metal center to form oxygen bridges (**28**) as the starting point of oxide formation. The last reaction steps were reported to occur rapidly, and today common understanding is that elimination of the alcohol goes hand-in-hand with the formation of metal–oxygen–metal bridges.



Scheme 7. Reaction mechanism for the thermolysis of $\text{Zr}(\text{O}t\text{Bu})_4$ proposed by Mazdiyasi et al.^[234]

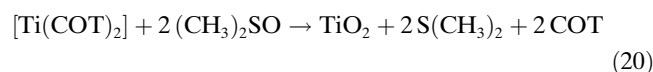
It seems to be more convenient to perform thermal decomposition of precursor species like metal alkoxides, acetylacetonates, or carboxylates in inert solvents with high boiling points. This technique was successfully employed in the 1990s by Inoue et al.^[64,215] In the last years a large number of reports based on this approach were published, including the synthesis of iron oxide/ferrite^[91,128,129,131,133] and titanium oxide nanoparticles,^[71,78,236] sometimes using complex mixtures of organic solvents and surfactants.^[90,100,123,237]

Although the reaction temperatures required for these systems are still considerably higher than for the sol–gel-type reaction pathways, the versatility of the approach is astonishing and even morphological control can be achieved to some extent through the nature and ratio of solvent or surfactant used.^[119] Many of these reports present important and fascinating new protocols to metal oxide nanoparticles. However, the study of these processes regarding detailed formation mechanisms, whether simple thermal decomposition or other pathways take place, would open new opportunities for the improvement of this synthesis strategy. Taking into account that often oleic acid is used as solvent together with long-chain aliphatic amines as surfactant, and that other groups have identified ester elimination processes as responsible for the formation of oxide nanoparticles under such conditions,^[218] it seems that “thermal decomposition” is misused for convenience in a broad and generalized sense as encompassing all reactions taking place at high temperatures. Especially with respect to a particular oxidation state of a metal in the final oxidic material it is crucial to investigate and to understand the role of the organic species in the synthesis mixture.

Nevertheless, it is now widely recognized that efforts to perform mechanistic studies for newly developed approaches to oxide nanoparticles are worthwhile, leading to surprising results. For example, when Li et al. presented a novel nonaqueous method to Fe_3O_4 nanocrystals in 2-pyrrolidone, the transformation of the precursor $\text{Fe}(\text{acac})_3$ to Fe_3O_4 was simply termed as a “thermal decomposition”, not giving any indication about why one third of the iron ions

are reduced to Fe^{II} required for the formation of Fe₃O₄.^[91] Upon reporting a slightly altered protocol in their following publication, however, they also included mechanistic studies based on photoelectric spectroscopy analysis of the gaseous reaction products. These investigations revealed that in fact 2-pyrrolidone is unstable under the employed reflux conditions, releasing carbon monoxide, which leads to a partial reduction of Fe^{III} to Fe^{II}.^[98] This example highlights again the role of the organics in the reaction system. Evidently, the solvent is crucial not only with respect to the stabilization of nanoparticles, leading to control over the size and shape, but also towards the intrinsic composition of the material.

Other mechanisms: Apart from these more generally applicable reaction routes, other more specialized methods that are nonetheless interesting can be found in the literature. Tang et al. recently reported the reaction of bis(cyclooctatetraene)titanium, [Ti(COT)₂], with dimethyl sulfoxide (DMSO) in *o*-dichlorobenzene at room temperature [Eq. (20)].



In this case, the oxygen is formally supplied from the DMSO, which is reduced by [Ti(COT)₂] to the disulfide.^[82] This route is especially interesting, as in contrast to the other low-temperature methods discussed before, at no stage is there a formation of hydroxyl groups or water. Hence the presence of surface-adsorbed hydroxyl groups can be excluded. On the other hand, the requirement of a prior synthesis of the very reactive titanium complex bis(cyclooctatetraene)titanium may prove detrimental with respect to a more general application of this synthesis approach.

If the metals are easily achievable on the nanoscale, the conversion of metal nanoparticles into the respective metal oxides by means of an oxidation process constitutes another alternative route, as reported for FeO_x, NiO, ZnO, or CuO.^[87,107,110,117,130] Mild organic oxidants, such as trimethylamine oxide, may be used, but in some cases even exposure to air or stirring in organic solvents for a longer period of time is sufficient to complete oxidation.^[107,110,238] This approach takes advantage of the good size and shape control as provided by some preparation methods for nearly monodisperse metal nanoparticles. If carefully performed, no alteration of particle size and morphology occurs during transformation into the oxide. This two-step process, synthesis of metal nanoparticles and oxidation to the oxide, can be combined into one by directly adding the oxidizing agent prior to the formation of the metal nanoparticles, or by performing the synthesis under aerobic conditions.^[87,94,95,125,126] Similarly, core-shell nanoparticles consisting of a metal core and a shell of the respective metal oxide are accessible.^[239]

If stable organometallic compounds of a particular metal exist, a viable pathway is the dissolution of the compound in an anhydrous organic solvent followed by oxidation by air

or moisture. Whereas the formation of ZnO from dicyclohexylzinc at room temperature was reported to rely on the presence of moisture^[240] and thus cannot be termed nonaqueous, in hot TOPO diethylzinc could be reacted to crystalline ZnO in the complete absence of water.^[115]

Summary and Outlook

In comparison to aqueous sol-gel chemistry, the synthesis of metal oxide nanoparticles in organic solvents under exclusion of water provides some peculiar features, which allow for better control over particle size, shape, crystallinity, and surface properties. The main advantage of nonaqueous chemistry lies in the accessibility of highly crystalline products at moderate temperatures. This behavior is strongly related to the fact that switching from aqueous sol-gel chemistry and its high reactivity of water to nonhydrolytic processes, which are based on the more controllable reactivity of the oxygen-carbon bond, drastically decreases the reaction rates and leads to controlled crystallization. At the same time, the chemistry of the oxygen-carbon bond is well-known from organic chemistry and therefore, these routes open the possibility to adapt reaction principles from organic chemistry to the synthesis of inorganic nanomaterials. The role of the organic species in the reaction system is much broader than just to act as oxygen supplying agent. In many cases, the nanoparticle growth is highly restricted, which means that either the organic solvent or the in situ formed organic species are able to function as stabilizing agents. Furthermore, the organics can directly influence the composition of the final oxidic material. The diverse redox properties of organic compounds make it possible to tailor the oxidation state of the metal ions, which is particularly attractive for metal oxides with mixed oxidation numbers.

In contrast to aqueous systems, in which the smallest changes in the experimental conditions result in alteration of the products, nonaqueous procedures are very robust within one system. As a consequence, most of these processes are highly reproducible, easy to scale-up to gram quantities (or more), and applicable to a broad family of metal oxides. On the other hand, the morphology of the final product strongly depends on the precursor and solvent used, that is, metal oxides with the same composition and crystal structure, but obtained from different precursors and/or solvents, are often characterized by different particle sizes and shapes. This observation highlights the crucial role of the organic side of the process, and also provides a precious tool to tailor particle morphology.

In spite of the intense research efforts in the area of nonaqueous synthesis of metal oxide nanoparticles, and related to that, of the large number of published methodologies, it is in principle possible to summarize these processes in only seven distinct mechanisms: 1) alkyl halide elimination; 2) ether elimination; 3) condensation of carboxylate groups (ester and amide elimination); 4) C-C coupling of benzylic alcohols and alkoxide precursors; 5) aldol/ketimine conden-

sation, which may be preceded by solvolysis of the precursor as in the case of acetylacetonates; 6) oxidation of metal nanoparticles; and 7) thermal decomposition methods. Although this list is in some cases rather arbitrary, it is a first step towards the rationalization of these approaches and should help to develop some general synthesis concepts.

Although the investigation and also the classification of these reaction mechanisms represent important progress in nanoparticle synthesis, the ultimate goal of a rational synthesis design is still far away. By choosing the appropriate reaction system, one is on the way to gain control over particle composition and, to some extent, over the particle size. But the big question of finding a relationship between a particular synthesis system and the final particle morphology remains a challenging task. How is it possible that in such a simple reaction system like metal alkoxides and benzyl alcohol completely different particle morphologies are found? Since the particle morphology cannot always be put into relation with the crystal structure, the answer has to be found in the function of the organics. Evidently the organic solvent and/or the organic products formed in situ interact with the inorganic species in a synergetic manner, so that crystallization occurs in a highly controlled way. Although the importance of the organic–inorganic interface is well recognized, it also reflects the dilemma on the long way to a rational synthesis design. Yin and Alivisatos recently summarized the problem as follows: “We are still far from a quantitative description of how organic molecules bind and pack on nanocrystal surfaces. To move beyond the qualitative phenomenology and general framework for kinetic shape control..., detailed knowledge of selective surface-adhesion energies on nanocrystals, including the dependence of adhesion energy on coverage and co-adhesion, is essential.”^[241] Another major issue lies in the comprehension of the crystallization process. The universal applicability of the classical crystallization mechanism was already questioned a few years ago.^[242] An increasing number of examples, mainly originating from biomineralization, but more and more also from nanoparticle synthesis, point to the fact that alternative crystallization pathways play an important role, too. These so-called nonclassical crystallization mechanisms are based on particle-mediated processes like oriented attachment and mesocrystal formation and they are highly complex and not yet well understood.^[243,244] Crystallization may seem to be well-established; however there is evidence that the need to focus attention on the investigation of crystallization mechanisms is still required.

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