

Cambridge University Press

978-1-107-40964-4 - Materials Research Society Symposium Proceedings: Volume 272:

Chemical Processes in Inorganic Materials: Metal and Semiconductor Clusters and Colloids

Editors: Peter D. Persans, John S. Bradley, R. R. Chianelli and Gunter Schmid

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PART I

Non-Metals: Synthesis

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SOL-GEL SYNTHESIS OF METAL OXIDE CLUSTERS AND COLLOIDS

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ABSTRACT

The hydrolysis and condensation of metal alkoxides $M(OR)_2$ allows the formation of oxo-polymers or oxide colloids under mild conditions in solution. The molecular design of these precursors provides a chemical control over the formation of condensed phases. This can be conveniently performed via the chemical modification of alkoxides by nucleophilic species such as carboxylates or β -diketones. Condensation can be tailored with two chemical parameters ; the hydrolysis ratio which leads to more condensed species and the amount of complexation which prevents condensation. Molecular clusters or colloidal particles can be obtained instead of precipitates. Moreover, non hydrolyzable complexing organic ligands lead to the formation of hybrid materials in which organic and inorganic moieties are chemically bonded. These hybrid clusters and colloids are important starting points for producing solids and films with novel physical properties.

INTRODUCTION

The sol-gel synthesis of glasses and ceramics received a great amount of scientific and technological interest during the last decade [1]. It is based on the inorganic polymerization of molecular precursors and provides a new way for producing oxide materials under mild conditions in solution [2]. Hydrolysis and condensation reactions lead to the formation of oxo-polymers which are then transformed into an oxide network. Sol-gel chemistry offers the possibility to design molecular precursors and control polymerization reactions so that tailor made materials can be obtained. The chemical modification of metal alkoxides by nucleophilic ligands leads to the formation of new molecular precursors which exhibit different chemical reactivity and functionality [3]. Monodispersed powders or long chain polymers can then be synthesized. Homogeneous multi-component glasses and ceramics can be obtained at low temperature by mixing precursors solutions at a molecular level. The rheological properties of sols and gels allow the production of fibers or films by such techniques as spinning or dip-coating. Organically modified ceramics known as "Ormocers" in which organic and inorganic components are mixed at a nanoscale have been also produced via the sol-gel route [4].

The sol-gel process usually leads to glasses and ceramics in which an oxide network is formed. This paper describes how hydrolysis and condensations reactions can be controlled in order to form smaller species such as clusters and colloids. Discussion is focussed on transition

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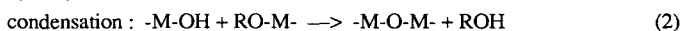
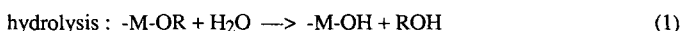
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metal oxides which are known to exhibit electronic properties. These properties arise either from delocalized electrons in the conduction band or from electron hopping between transition metal ions in different valence states. Electronic materials such as semiconducting V_2O_5 coatings, electrochromic WO_3 layers or ferrimagnetic Fe_3O_4 colloids have been synthesized via the sol-gel route [3].

HYDROLYSIS AND CONDENSATION OF METAL ALKOXIDES

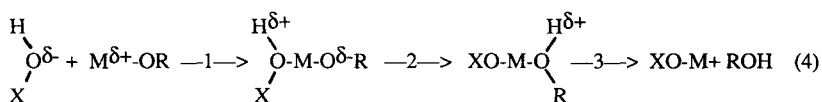
Sol-gel chemistry is based on the hydrolysis and condensation of metal alkoxides.



Condensed species are progressively formed giving rise to oligomers, oxo-polymers, colloids, gels or precipitates. At the end of the process hydrous oxides or hydroxides are obtained. These reactions correspond to the nucleophilic substitution of alkoxy ligands by hydroxylated species XOH as follows :



where X stands for H (hydrolysis) or M (condensation). They can be described according to a S_N2 mechanism [3] :



The first step (1) corresponds to the nucleophilic addition of a negatively charged $HO^{\delta-}$ group onto the positively charged metal atom $M^{\delta+}$ which increases its coordination number in the transition state. A proton transfer then occurs within the transition state (2) toward an OR group. This positively charged protonated alkoxide ligand ROH is then removed while the negatively charged OX group remains bonded to the metal atom.

According to this mechanism, the chemical reactivity of metal alkoxides toward hydrolysis and condensation mainly depends on the positive charge of the metal atom δ_M and its ability to increase its coordination number "n". As a general rule the electronegativity of metal atoms decreases, their size increases and the chemical reactivity of the corresponding alkoxides increases when going down the periodic table. Silicon alkoxides $Si(OR)_4$ react very slowly. Gelation occurs within several days after water has been added while most transition metal alkoxides are very sensitive to moisture. They have to be handled in a dry atmosphere otherwise precipitation occurs as soon as water is present.

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The sol-gel synthesis of silica is usually performed in the presence of catalysts. However acid or base catalysis does not only increase gelation rates, it also leads to completely different silica materials [1].

. Inorganic acids reversibly protonate negatively charged alkoxide ligands and increase the reaction kinetics by producing better leaving groups. The partial charge of OR groups increases as the electron-providing power of alkoxy, hydroxo and oxo ligands increases. The ease of protonation of OR groups therefore decreases as the connectivity of the adjacent Si atom increases. Acid-catalyzed condensation is directed preferentially toward the ends of oligomeric species resulting in entangled chain polymers [5].

. Base catalysis provides better nucleophilic OH⁻ groups for hydrolysis while deprotonated silanol groups Si-O⁻ enhance condensation rates. The positive partial charge δ_{Si} increases with its connectivity and nucleophilic addition of Si-O⁻ is directed preferentially toward the middles of oligomers leading to highly crosslinked polymeric clusters. Monodispersed silica spheres can be produced via the hydrolysis of silicon alkoxides in the presence of ammonia [6].

MOLECULAR STRUCTURE OF METAL ALKOXIDES

The oxidation state M^{z+} of most metal ions is usually smaller than their coordination state in the oxide $MO_{z/2}$. As a consequence coordination expansion is a general tendency of the sol-gel chemistry of transition metal alkoxides $M(OR)_z$. Positively charged metal atoms tend to increase their coordination number by using vacant d orbitals to accept electrons from nucleophilic ligands [7]. This currently occurs via solvation or oligomerization. Therefore transition metal alkoxides exhibit either monomeric or oligomeric structures. Several species are often simultaneously in equilibrium and the molecular complexity of metal alkoxides $M(OR)_z$ depends on physical parameters (concentration, temperature) as well as chemical factors (solvent, oxidation state M^{z+} , steric hindrance of OR).

Oligomerization

The molecular complexity of metal alkoxides increases with the size of the metal atom. Titanium ($r_{COV}=1.32\text{\AA}$) for instance gives monomeric $Ti(OPr^i)_4$ species while dimeric $[Zr(OPr^i)_4]_2$ oligomers are observed for zirconium ($r_{COV}=1.45\text{\AA}$). However the steric hindrance of alkoxide ligands also appears to be a major parameter. Bulky secondary or tertiary alkoxide groups tend to prevent oligomerization while primary alkoxides are usually oligomeric (Fig.1). Oligomeric species $[Ti(OEt)_4]_n$ ($n=2,3$) have been evidenced in the pure liquid alkoxide whereas titanium iso-propoxide is monomeric $Ti(OPr^i)_4$ [8]. Monomeric titanium alkoxides with bulky OR groups, in which Ti has a lower coordination number, are more reactive toward hydrolysis. Spherical monodispersed TiO_2 powders can be produced via the controlled hydrolysis of diluted solutions of $Ti(OEt)_4$ in EtOH while $Ti(OPr^i)_4$ leads to polydispersed precipitates [9][10].

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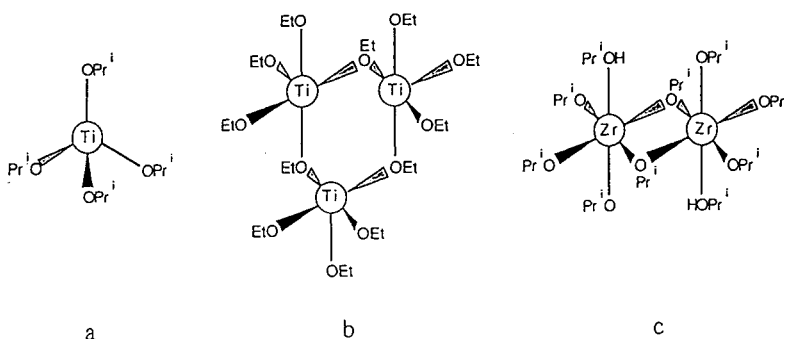
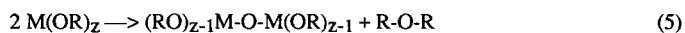


Figure 1. Molecular structure of metal alkoxides. (a) $\text{Ti}(\text{OPr}^i)_4$, (b) $[\text{Ti}(\text{OEt})_4]_3$,
 (c) $[\text{Zr}(\text{OPr}^i)_4.\text{Pr}^i\text{OH}]_2$

Condensation sometimes occurs via ether formation, specially when metal alkoxides are heated. It leads to the formation of oxo-alkoxides as follows :



Oxo-alkoxides are often formed during the purification of metal alkoxides via distillation. Condensation is favored by the smaller size of oxo ligands O^{2-} and their ability to exhibit higher coordination numbers. This leads to a coordination expansion of the metal atom and oxo-alkoxides are more stable than the corresponding alkoxides [11]. They are of course less reactive toward hydrolysis and condensation. Large and electropositive metals are known to give oxoalkoxides such as $\text{Pb}_4\text{O}(\text{OEt})_6$ [12] or $\text{Y}_5\text{O}(\text{OPr}^i)_{13}$ [13]. It has been observed that liquid $\text{NbO}(\text{OEt})_3$ crystallizes slowly in a dry atmosphere giving $\text{Nb}_8\text{O}_{10}(\text{OEt})_{20}$ crystals. Mass spectroscopy shows that ether molecules $(\text{Et})_2\text{O}$ are released so that condensation arises from ether elimination rather than hydrolysis [14]. Ether elimination should also be responsible for the formation of $\text{Ti}_{16}\text{O}_{16}(\text{OEt})_{32}$ crystals upon heating an equimolar solution of $\text{Ti}(\text{OEt})_4$ in EtOH . These crystals appear to be stable and do not hydrolyze any further when left in air for one month [15].

Solvation and alcoholysis

Metal alkoxides are not soluble into water. Therefore a common solvent has to be used. This is usually an alcohol ROH but the choice of this solvent is also very important. Coordination expansion via solvate formation occurs when alkoxides are dissolved in their parent alcohol. The stability of such solvates increases with the size and the electropositive character of the metal, *i.e.* when going down the periodic table. At room temperature monomeric $\text{Ti}(\text{OPr}^i)_4$ is not solvated

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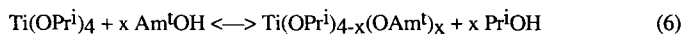
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while solvated dimeric species $[\text{Zr}(\text{OPr}^i)_4\text{Pr}^i\text{OH}]_2$ and $[\text{Ce}(\text{OPr}^i)_4\text{Pr}^i\text{OH}]_2$ have been observed in solution (Fig. 1c) and even isolated as single crystals [16][17].

Coordination expansion can occur either via alkoxide bridging or solvation. The molecular complexity of metal alkoxides can then be controlled by an appropriate choice of the solvent [18]. $[\text{Zr}(\text{OPr}^n)_4]_n$ oligomers are formed ($n \leq 4$) in non polar solvents such as cyclohexane allowing slow hydrolysis rates and the formation of clear gels. Less condensed solvates are formed in n-propanol. Hydrolysis becomes much faster and leads to precipitation [19].

Alcohol interchange reactions also occur when metal alkoxides are dissolved in non parent alcohols. These reactions are rather slow with silicon alkoxides while they can be very fast with transition metal alkoxides. They lead to the formation of mixed alkoxides. Five different species for instance are readily formed when $\text{Ti}(\text{OPr}^i)_4$ is dissolved in Am^iOH :



with x ranging from 0 to 4. Again it is possible to control hydrolysis and condensation by varying the value of x . Precipitation occurs readily with $x=0$, stable colloids are obtained for $x=4$ while polymeric gels are formed around $x=2$ [20].

Decameric species $[\text{Y}(\text{OC}_2\text{H}_4\text{OMe})_3]_{10}$, made of a cyclic arrangement of 10 yttrium atoms, have been obtained in nearly quantitative yield via the alcoholysis of $\text{Y}_5\text{O}(\text{OPr}^i)_{15}$ in 2-methoxyethanol at room temperature [21]. The reaction of cerium iso-propoxide with 2(2-dimethylaminoethyl-methylamino)ethanol gives dimeric $[\text{Ce}_2(\text{OPr}^i)_6(\text{OC}_2\text{H}_4\text{NMeC}_2\text{H}_4\text{NMe}_2)_2]$ and trimeric $[\text{Ce}_3\text{O}_4(\text{OPr}^i)_2(\text{OC}_2\text{H}_4\text{NMeC}_2\text{H}_4\text{NMe}_2)_2]$ species [22].

Formation of hetero-alkoxides.

Coordination expansion sometimes occurs via the formation of double alkoxides. Such a reaction appears to be quite easy to perform via the simple mixing of different alkoxides [11] $\text{Pb}_4\text{O}(\text{OEt})_6$ for instance undergoes complete dissolution in ethanol when $\text{Nb}(\text{OEt})_5$ is added, leading to $[\text{Pb}_6\text{O}_4(\text{OEt})_4][\text{Nb}(\text{OEt})_5]_4$. This heterometallic alkoxide has the right $\text{Pb}/\text{Nb}=6/4$ ratio for the sol-gel synthesis of PMN ceramics [12]. Double alkoxides or oxo-alkoxides are often obtained when two alkoxides are heated under reflux before hydrolysis. Such a procedure is currently performed in order to obtain a better mixing but it could also lead to heterometallic alkoxides. The formation of these heterometallic alkoxides is favored by a large difference in the electronegativity of metal atoms such as $\text{LiNb}(\text{OEt})_6$ which is used for the sol-gel synthesis of LiNbO_3 ceramics [23]. Condensation occurs via the nucleophilic addition of alkoxide groups, both metal atoms are then linked together by alkoxide bridges. It can also result from ether elimination or esterification leading to μ -oxo bridges.

Heterometallic alkoxides are often more soluble than their parent alkoxides, a property that can be advantageously used for the sol-gel chemistry of insoluble alkoxides. They also provide

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precursors for multicomponent materials. The molecular precursor has the right M'/M stoichiometry and some M-O-M' bonds are already formed. Alkoxide bridges are usually hydrolyzed during the sol-gel synthesis whereas oxo bridges are strong enough not to be broken.

Chemical modification of metal alkoxides.

Transition metal alkoxides are very prone to nucleophilic reagents. They react readily with hydroxylated ligands XOH giving $[M(OR)_z-n(OX)_n]$ species [7]. Such reactions lead to important modifications of the molecular structure of the alkoxide. A new precursor is formed the chemical reactivity and functionality of which can be completely different [3]. Chemical modification can be performed via alcoholysis reactions as shown previously for cerium and yttrium alkoxides [21][22]. Nucleophilic chemical additives are also currently employed in order to stabilize highly reactive transition metal alkoxides and control the condensation reactions.

It has been observed for instance that adding acetic acid to titanium alkoxides prevents the precipitation of TiO_2 and increases the gelation time [24]. Acetate groups OAc^- (CH_3COO^-) behave as bidentate bridging ligands toward titanium. The coordination number of titanium increases from four to six and oligomeric species $[Ti(OPr^i)_3(OAc)]_n$ ($n=2$ or 3) are formed for a molar ratio $AcOH/Ti=1$. Acetate ligands are less easily hydrolyzed than alkoxy groups therefore slowing down condensation reactions. The functionality of the new precursor decreases leading to the anisotropic growth of oxo-polymers rather than the precipitation of oxide particles.

Similar reactions are observed with acetyl acetone ($acacH=CH_3-CO-CH_2-CO-CH_3$). Its enolic form contains hydroxyl groups which react with metal alkoxides as chelating ligands [25]. Oligomers are not readily formed and for a stoichiometric $acac/Ti = 1$ ratio, nucleophilic substitution leads to $[Ti(OPr^i)_3(acac)]$ monomers in which Ti is only fivefold coordinated. This strongly chelating ligand cannot be removed upon hydrolysis (unless $pH < 2$) even in the presence of a large excess of water. Condensation is then prevented and only small oligomers are formed [26].

MOLECULAR DESIGN OF CLUSTERS AND COLLOIDS

Metal alkoxides react with water molecules (hydrolysis) and nucleophilic species (complexation). The first reaction gives reactive M-OH bonds. It is followed by condensation and leads to the formation of larger species. Complexing ligands XOH lead to non reactive M-OX bonds which prevent condensation and favor the formation of smaller species. A large variety of oligomeric species can then be obtained upon hydrolysis and condensation. Molecular clusters or colloidal particles can be synthesized depending on the relative amount of hydrolysis ($h=H_2O/M$) and complexation ($x=X/M$). More condensed species are obtained as x decreases and h increases as shown by the following examples.

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Titanium oxide clusters and colloids.

Pure titanium alkoxides $Ti(OR)_4$ are highly reactive toward hydrolysis and lead to the uncontrolled precipitation of TiO_2 when water is added. However, for very low hydrolysis ratio ($h < 1$), condensation is mainly governed by the formation of μ -oxo and alkoxide bridges. Solute molecular oxo-alkoxides such as $Ti_7O_4(OEt)_{20}$ ($h=0.6$), $Ti_{10}O_8(OEt)_{24}$ ($h=0.8$) and even $Ti_{16}O_{16}(OEt)_{32}$ ($h=1$) have been obtained from $Ti(OEt)_4$ and isolated as single crystals from the solution [27][28][15].

Titanium iso-propoxide reacts with acetic acid in a one to one ratio ($x=1$) giving oligomeric $[Ti(OPr^i)_3(OAc)]_n$ species. Esterification occurs when more than one mole of $AcOH$ is added. Acetic acid in excess reacts with alcohol molecules released during complexation providing the *in-situ* generation of water and giving rise to more condensed species. Only solute oligomeric species are obtained in the presence of small amounts of water. Single crystals of hexameric $Ti_6O_4(OPr^i)_{12}(OAc)_4$ have been obtained upon aging an equimolar mixture of $AcOH$ and $Ti(OPr^i)_4$ in a closed vessel (Fig.2). Water, provided via esterification reactions arising from acetic acid in excess ($x=4/6=0.66$), leads to the slow hydrolysis of alkoxide groups which are replaced by oxo bridges [29]. All organic groups can be removed and clear transparent titanium dioxide gels are obtained in the presence of an excess of water.

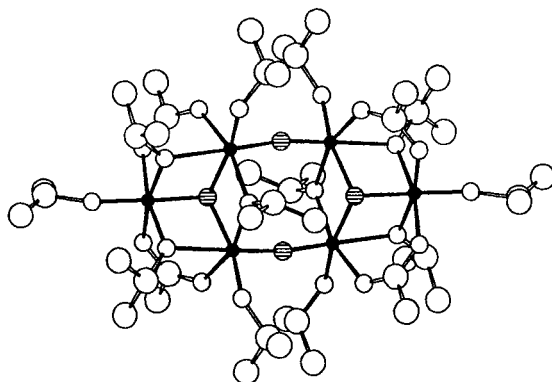


Figure 2. Molecular structure of hexameric $Ti_6O_4(OPr^i)_{12}(OAc)_4$. (O=Ti, \ominus =oxo bridges)

The reaction of titanium alkoxides with acetylacetonone also leads to oligomeric compounds. $[TiO(acac)]_2$ is formed upon hydrolysis of $Ti(acac)_2(OR)_2$. Single crystals have been isolated and X-ray diffraction experiments show dimers with sixfold coordinated Ti atoms linked through oxygen bridges [30]. Strongly complexing acac ligands cannot be hydrolyzed easily and condensation does not go any further. Larger molecular species can be obtained for smaller amounts of acetylacetonone. Single crystals of $Ti_{18}O_{22}(OBu)_{26}(acac)_2$ have been obtained recently

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(Fig.3). They are made of eighteen $[\text{TiO}_6]$ octahedra sharing edges or corners and correspond to $x=0.1$, $h=1.2$. Complexing acac ligands remain outside of the $\text{Ti}_{18}\text{O}_{22}$ core of the molecule [31].

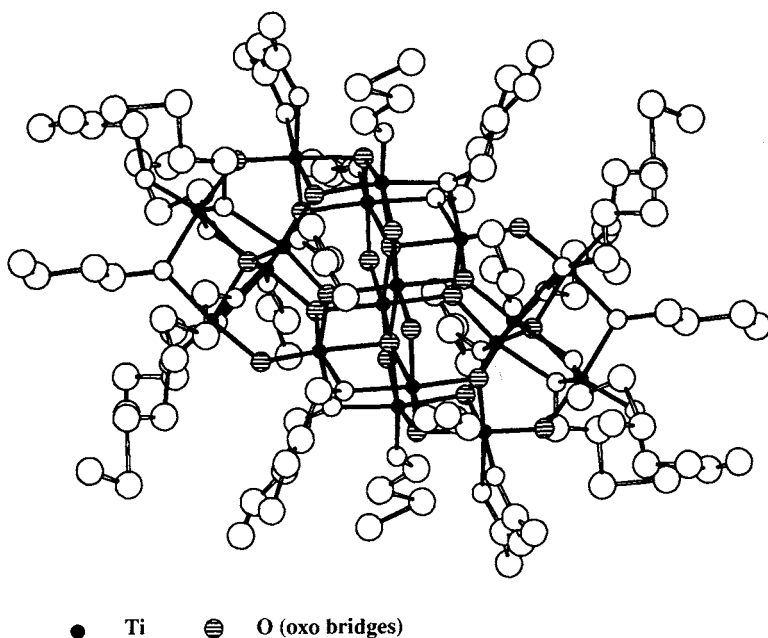


Figure 3. Molecular structure of $\text{Ti}_{18}\text{O}_{22}(\text{OBu})_{26}(\text{acac})_2$.

Clear sols are obtained when $\text{Ti}(\text{OBu}^n)_4$ is hydrolyzed in the presence of acetylacetonate. The mean hydrodynamic diameter of the colloidal particles, measured by quasi-elastic light scattering, increases from 2nm to 40nm as the hydrolysis ratio increases from $h=1$ to $h=4$ (for $x=0.3$). It decreases from 40nm to 3nm when the amount of acetylacetonate increases from $x=0.3$ to $x=1$ (for $h=4$) [31].

Zirconium oxide clusters and colloids.

Similar experiments have been performed with zirconium alkoxides. Solvated dimeric species are formed when zirconium propoxide is dissolved in its parent alcohol. Tetrameric species $\text{Zr}_4\text{O}(\text{OPr}^n)_{10}(\text{acac})_4$ are obtained with acetylacetonate ($x=\text{Acac}/\text{Zr}=1$) in the presence of a very small amount of water ($h=0.2$) [32]. Larger molecular clusters can be formed by decreasing x and increasing h as shown by the decameric species $[\text{Zr}_{10}\text{O}_6(\text{OH})_4(\text{OPr}^n)_{18}\text{L}_6]$ obtained for $x=0.6$, $h=1$ and $\text{L}=\text{allylacetoacetate}$ (Fig.4) [33].