

## THE CHEMISTRY OF THE SOL-GEL PROCESS

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The sol-gel process is based on inorganic polymerization chemistry. Starting from molecular precursors an oxide is obtained via hydroxylation-condensation reactions. A chemical control of the morphology and structure becomes therefore possible. This paper presents an analysis of the role of anions on the chemical reactions involved in the sol-gel process. Some anions exhibit complexing properties toward the metal atom, leading to a chemical modification of the molecular precursor. The whole hydroxylation-condensation process is therefore modified leading to tailor-made materials. Examples are described for both inorganic and metal organic precursors.

### 1. Introduction

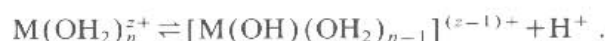
The sol-gel process offers new approaches to the synthesis of oxide materials. Starting from molecular precursors, an oxide network is obtained via inorganic polymerization reactions [1]. These reactions mainly occur in solutions and the term "sol-gel processing" is often broadly used to describe the synthesis of inorganic oxides by wet chemical methods. It offers many advantages compared to the conventional "powder" route, such as lower temperature processing or better homogeneity for multi-component materials. The rheological properties of sols and gels allow the fabrication of fibres [2] or films by such techniques as spinning or dip-coating [3].

The sol-gel chemistry is based on inorganic polymerization reactions. Two routes are usually described in the literature depending on whether the precursor is an aqueous solution of an inorganic salt or an alkoxide in an organic solvent [4]. In both cases, the reaction can be described as follows:

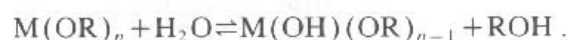
(i) Hydroxylation of the precursor leading to the formation of M-OH bonds: the hydroxylation of inorganic precursor is performed via *pH* modification of the aqueous solution [3] leading to the protonation of anionic oxo-ions:



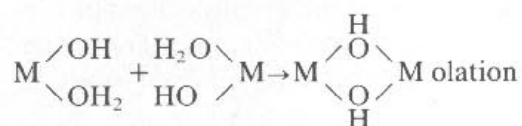
or the deprotonation of cationic aquo-ions:



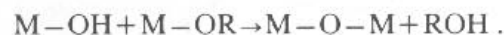
The hydroxylation of alkoxides is simply performed via hydrolysis by adding water [6]



(ii) Condensation: a polycondensation process follows the hydroxylation reaction leading to the departure of a water molecule:



M-OH + M-OH → M-O-M + H<sub>2</sub>O oxolation,  
 or an alcohol molecule:



In both cases hydroxy or oxygen bridges are formed leading to condensed species. At the end of the process all oxygen atoms are bridging oxygens and a hydrated oxide network is obtained.

Such a description of the sol-gel chemistry is however too simplified. A survey of the literature shows that foreign species are always present either as counter ions [7], solvents [8] or chemical additives [9]. It has been observed that they actually play an important role. The structure, the morphology and even the chemical composition of the oxide material

strongly depends on the presence of such foreign species, even in small amounts.

This paper reports an experimental analysis and a discussion of the chemical role of anionic species on the hydroxylation-condensation reactions of metal cations. Both inorganic and metal-organic routes will be described.

## 2. The metal-organic route

Acid is often used in the sol-gel chemistry of silica in order to increase the rate of hydrolysis [11]. The gelation time of TEOS ( $\text{Si}(\text{OC}_2\text{H}_5)_4$ ) decreases from 1000 h down to 92 h in the presence of HCl [12]. Such an effect can be easily explained in terms of the nucleophilic substitution of OR groups by OH ones. Acid catalysts lead to the protonation of alkoxy groups that become better leaving groups.

However, it has been reported that the gelation time of TEOS depends on the acid used. Acetic acid for instance leads to a shorter gelation time (72 h) than HCl despite a higher *pH* [12]. This may be due to nucleophilic activation of silicon by acetic acid [4,13]. The reverse effect is actually observed in the case of titanium alkoxides. The gelation time increases significantly in the presence of acetic acid [14].

A detailed analysis of the chemical reactions involved all along the sol-gel route was therefore undertaken in order to provide information about the chemical role of the acetate group [15].

X-ray absorption experiments performed on pure  $\text{Ti}(\text{OPr}^i)_4$  clearly show that such an alkoxide exhibits a tetrahedral monomeric structure in the liquid state (fig. 1a). A single Ti-O distance of 1.76 Å is observed (fig. 1b) and all alkoxy groups appear to be equivalent by  $^1\text{H}$  and  $^{13}\text{C}$  NMR [15].

An exothermic reaction occurs when pure acetic acid is added to the alkoxide leading to a clear solution. XANES experiments then show that the coordination number of Ti increases up to 6 (fig. 1c) while different Ti-O distances (1.80 Å and 2.06 Å) are observed in the Fourier transform of the EXAFS spectrum (fig. 1d). Moreover, some Ti...Ti correlations are observed corresponding to a Ti...Ti distance of 3.11 Å suggesting an oligomeric structure made of edge sharing octahedral species. Chemical

shifts of  $^1\text{H}$  and  $^{13}\text{C}$  NMR peaks show that acetate groups are bonded to titanium while infra-red spectra indicate that OAc groups behave as bidentate bridging ligands. A stoichiometric reaction takes place for a 1/1 ratio that can be written as follows:



A modified precursor is then obtained which could correspond to dimeric species  $\text{Ti}_2(\text{OAc})_2(\text{OPr}^i)_6$  made of two octahedral  $\text{Ti}(\text{OAc})(\text{OPr}^i)_3$  units linked together by both  $(\text{OPr}^i)$  and  $(\text{OAc})$  bridges.

The hydrolysis of such precursors was followed by X-ray absorption, infra-red spectroscopy and NMR [15]. These experiments have shown that alkoxy ligands are hydrolyzed first while OAc groups remain bonded to the titanium even when an excess of water is added.

The previous experiments show that acetates do not behave as counter ions in the acid hydrolysis of titanium alkoxides. They act as nucleophilic agents and react with the alkoxide giving rise to a new molecular precursor, therefore modifying the whole hydrolysis-condensation process.

The reactivity of  $\text{Ti}(\text{OPr}^i)_4$  towards acetic acid can be described in terms of the nucleophilic substitution of  $(\text{OPr}^i)$  by  $(\text{OAc})$  groups. Acetates are stronger ligands. They are also able to behave as bidentate species and give rise to acetate bridges. Moreover, because of the steric hindrance of  $(\text{OPr}^i)$  groups, Ti is only four coordinate in the pure alkoxide  $\text{Ti}(\text{OPr}^i)_4$ . Consequently the metal atom is able to increase its coordination number upon complexation with acetates leading to six coordinate titanium species.

This increase in coordination leads to a decrease of the overall reactivity of the modified molecular precursors. A new charge repartition is set up which promotes a decoupling between hydrolysis and condensation.

Less electronegative ligands  $(\text{OPr}^i)$  are first and rather quickly removed upon hydrolysis while more electronegative ones  $(\text{OAc})$  should be mainly removed during condensation reactions. As a consequence, the growth of the particles becomes more anisotropic promoting the formation of polymeric gels [10].

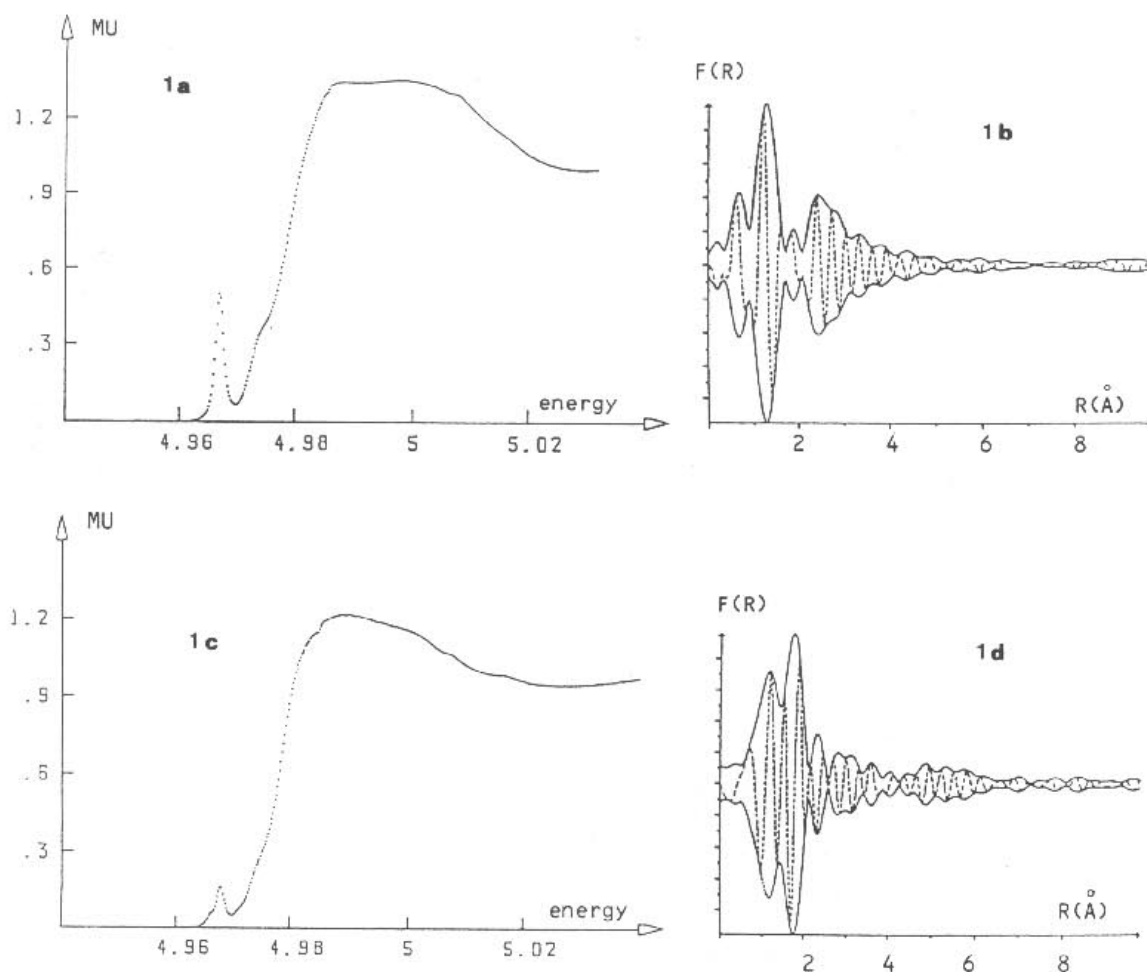


Fig. 1. X-ray absorption spectra at the Ti K-edge: (a) XANES spectrum of the  $\text{Ti}(\text{OPr}^i)_4$  precursor, (b)  $k^3$  Fourier transform of the EXAFS spectrum of  $\text{Ti}(\text{OPr}^i)_4$ , (c) XANES spectrum of  $\text{Ti}(\text{OPr}^i)_3$  OAc modified precursor, (d)  $k^3$  Fourier transform of the EXAFS spectrum of  $\text{Ti}(\text{OPr}^i)_3$  OAc.

### 3. The inorganic route

It is well known that anions play an important role in homogeneous precipitation of metal oxides from aqueous solutions [7]. They affect both the particle morphology and colloid stability. Some of them even remain strongly coordinated to the metal cation and thus end up in the precipitate giving basic salts while others can be removed by leaching.

As in the metal-organic route, some anions  $X^-$  can enter the coordination sphere of metal cations in aqueous solution.

This can be clearly evidenced by  $^{27}\text{Al}$  NMR. A single peak is observed when an aluminium nitrate or chloride is dissolved into water. The chemical shift is typical of solvated  $[\text{Al}(\text{OH}_2)_6]^{3+}$  species (fig. 2a).  $\text{Cl}^-$  and  $\text{NO}_3^-$  clearly behave as counter ions. They

do not enter the coordination sphere of the cation. A drastic change occurs as soon as some phosphoric acid is added to the solution (fig. 2b). Several peaks appear that correspond to the formation of  $\text{Al}-(\text{H}_2\text{PO}_4)-(\text{H}_2\text{O})$  species. These phosphate groups remain strongly bonded to the metal cations until the end of the process thus leading to aluminum phosphates rather than aluminum hydroxides.

The question therefore arises to be able to predict whether such  $\text{M}-\text{X}$  associated species are formed in aqueous solutions.

Water actually plays a double role in aqueous chemistry:

It behaves as a solvent with a high dielectric constant ( $\epsilon=80$ ) that favors the dissociation of ionic species:

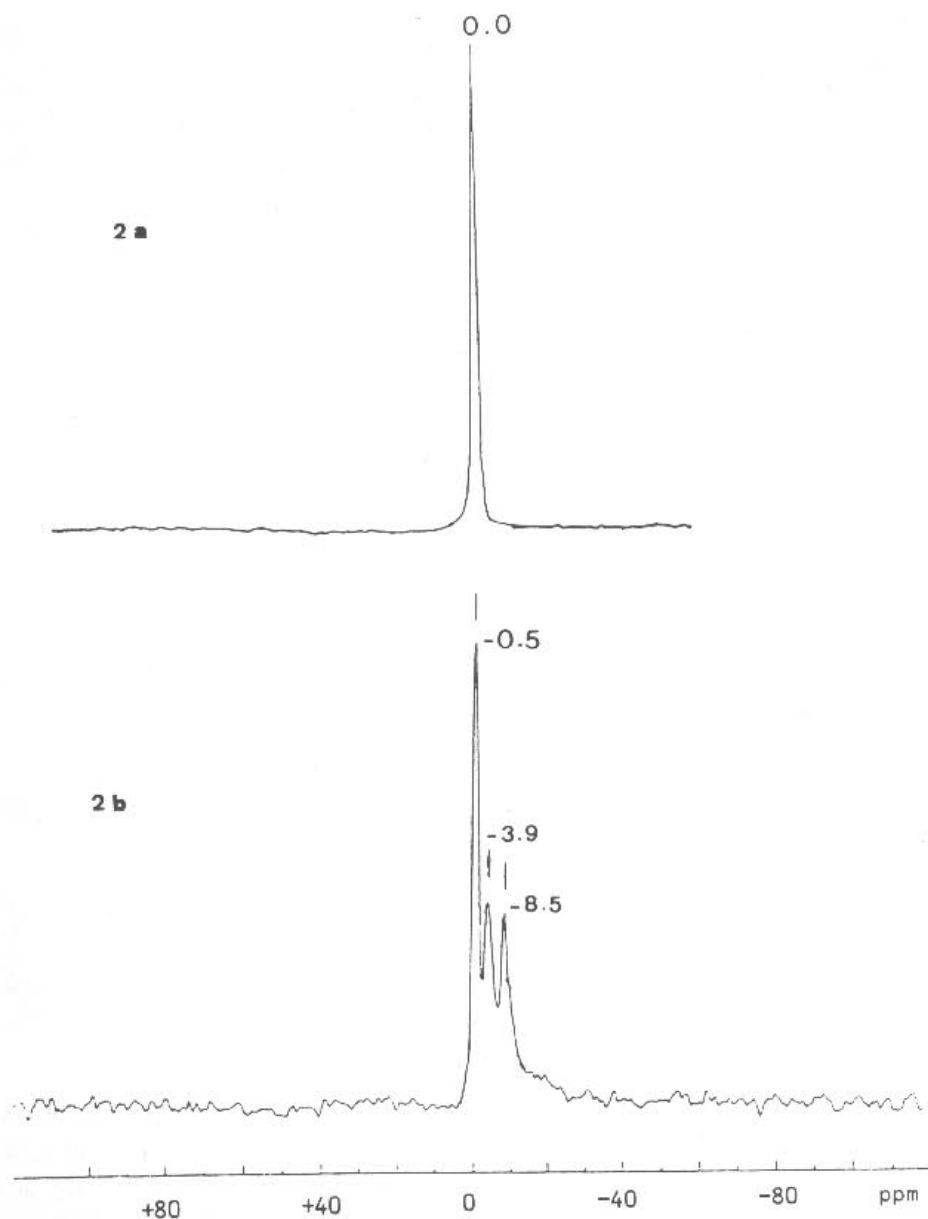
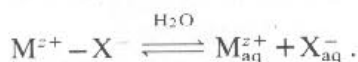


Fig. 2.  $^{27}\text{Al}$  NMR: (a) NMR spectrum of  $(\text{Al}(\text{H}_2\text{O})_6)^{3+}$  species, (b) NMR spectrum after addition of phosphates anions.



It also behaves as a  $\sigma$ -donor molecule and reacts as a nucleophilic ligand giving solvated species  $\text{M}(\text{OH}_2)_n^{z+}$ .

The stability of an M-X bond mainly depends on the electronegativity of the anion [4].

Highly electronegative anions ( $\chi_{\text{X}^-} > \chi_{\text{H}_2\text{O}}$ ) are able to substitute water molecules within the solvation sphere of the cation  $\text{M}^{z+}$ . However, the M-X

bond may be strongly polar and the high dielectric constant of the solvent leads to ion pair formation.

Anions with a low electronegativity ( $\chi_{\text{X}^-} < \chi_{\text{H}_2\text{O}}$ ) however are not able to substitute water molecules.

An M-X bond can be formed within a rather narrow electronegativity range only. The anion  $\text{X}^-$  then behaves as a complexing agent toward the aqueous cation  $\text{M}^{z+}(\text{H}_2\text{O})_n$  leading to the formation of a modified precursor. This electronegativity range depends on the metal cation  $\text{M}^{z+}$  and varies with the *pH* of the solution. As a general rule, it shifts toward

lower electronegativities when the *pH* increases, i.e. with the hydrolysis ratio "h" of the precursor increases:



For a given precursor, the electronegativity range can be calculated using the Partial Charge Model [16]. Results of such calculations are reported in table 1 for aqueous solutions of zirconium salts.

As a consequence, highly electronegative anions such as  $\text{ClO}_4^-$  ( $\bar{\chi}=2.86$ ) behave as counter ions because of ionic dissociation. They are not able to substitute water molecules in the solvation sphere of  $\text{Zr}^{4+}$  and are not involved in the formation of condensed species. When dissolved into water,  $\text{ZrO}(\text{ClO}_4)_2$  gives rise to cyclic tetramers  $[\text{Zr}(\text{OH}_2)(\text{OH}_2)_4]_4^{4+}$  in which zirconium is surrounded by four water molecules and four bridging OH groups [17]. Hydroxylation of the precursor occurs when the *pH* increases, leading to the precipitation of hydrous zirconia  $\text{ZrO}_2 \cdot n\text{H}_2\text{O}$  [8].

Complexing anions are those with an average electronegativity close to that of water ( $\bar{\chi}=2.49$ ). Nitrates for instance ( $\bar{\chi}=2.76$ ) exhibit a weak complexing ability. They are able to substitute two water molecules giving rise to chain polymers  $[\text{Zr}(\text{OH})_2(\text{NO}_3)(\text{OH}_2)_2]_n^+$  in which zirconium remains eight-fold coordinated [19]. It has to be pointed out however that nitrates remain terminal groups. They do not link chains together and do not behave as network formers.

The mean electronegativity of phosphates  $\text{H}_2\text{PO}_4^-$  ( $\bar{\chi}=2.50$ ) and sulfates  $\text{HSO}_4^-$  ( $\bar{\chi}=2.64$ ) is closer to that of water. These anionic species therefore exhibit a stronger complexing ability. They are thus able to substitute all coordinated water molecules leading to condensed species such as  $[\text{Zr}(\text{OH})_2\text{SO}_4]_n$  [19]. Moreover, they behave as

network formers bridging zirconium species together.

Anions with a low electronegativity such as  $\text{Cl}_{\text{aq}}^-$  are no more able to coordinate the zirconium. They are less complexing ligands than water and behave as counter ions giving the same kind of condensed species as highly electronegative anions [20].

#### 4. Discussion

Anions play an important role during the sol-gel synthesis of metal oxides. At a molecular level, they are able to coordinate the metal cation giving rise to new precursors whose chemical reactivity against hydrolysis and condensation should be different. Then once colloidal species are formed, anions change the double layer composition and the ionic strength of the solution therefore modifying the aggregation process. The first chemical step can be described as a nucleophilic substitution within the coordination sphere of the cation.

The reactivity of metal complexing towards anions depends on the positive charge of the cation. It increases when its electronegativity decreases.

The reactivity also depends on the ability of the metal atom to increase its coordination number. This ability can be estimated from the difference ( $N-Z$ ) between the maximum coordination number  $N$  and the oxidation state  $Z$ . For a given group, ( $N-Z$ ) increases with the size of the metal cation i.e. when going down to the periodic table. It has to be pointed out, however, that this parameter does not play a major role in the inorganic route where aquo-cations always exhibit their maximum coordination.

The stability of an  $M-X$  bond of course depends also on the nature of  $X$ . It increases with the complexing ability of  $X^-$ . In strongly ionizing solvents such as water, ionic bonds are not stable against ion pair formation.

Once a new molecular precursor is formed with the counter ion, three different types of behavior may be observed:

(1) The complexing ability of the new ligand is not strong enough, so that it will be more or less easily removed upon hydrolysis or by ion pair formation. The chemical modification remains therefore effective only during the first steps of the hydroxylation-condensation process. An inorganic oxide is

Table 1  
Electronegativity range of complexing anions  $X^-$  toward a  $[\text{Zr}(\text{OH})_h(\text{OH}_2)_{n-h}]^{(z-h)+}$  cationic precursors, as a function of the hydrolysis ratio  $h = \text{OH}/\text{ZR}$ :

<i>h</i>	0	1	2	3	4
$\bar{\chi}_{\text{max}}$	2.84	2.79	2.71	2.64	2.51
$\bar{\chi}_{\text{min}}$	2.55	2.45	2.35	2.24	2.06

obtained but the gelation kinetics can be modified.

(2) The new ligand is strongly complexing so that it cannot be removed upon hydrolysis. It thus ends up in the solid phase where it can act either as a network modifier or a network former. Network modifiers are obtained when the new ligand is not able to form bridges between metal atoms. This is the case of  $\text{NO}_3^-$  ions in the precipitation of zirconium, acetylacetone in the formation of  $\text{TiO}_2$  colloids [15] or methyl groups in the synthesis of ORMOSILS [21].

(3) Network formers are obtained when the ligand is able to form bridges such as  $\text{HSO}_4^-$  and  $\text{H}_2\text{PO}_4^-$  in the precipitation of zirconium basic salts or acetates in the hydrolysis of modified titanium alkoxides. Network formers can also be obtained with chemical species that are able to give rise to organic polymerization [4]. Mixed organic-inorganic gels are then obtained such as the so-called ORMOSILS [21].

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