

HYDROLYSIS OF TITANIUM ALKOXIDES: MODIFICATION OF THE MOLECULAR PRECURSOR BY ACETIC ACID

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Monolithic TiO_2 gels can be reproducibly obtained when the hydrolysis of titanium alkoxides is performed in the presence of acetic acid. This carboxylic acid does not act only as an acid catalyst, but also as a ligand and changes the alkoxide precursor at a molecular level therefore modifying the whole hydrolysis condensation process. Infra-red experiments show that bidentate acetates replace OR groups and are directly bounded to the titanium. Both, chelating and bridging acetates, are observed, leading to $\text{Ti}(\text{OR})_x(\text{Ac})_y$ oligomers.

Hydrolysis of this new molecular precursor removes first (OR) groups and bridging acetates. Chelating acetates are still observed in the gel. They can only be removed upon heating above 200°C .

1. Introduction

The gel route to glasses and ceramics has attracted increasing scientific and technological interest during the last few years [1–3]. Since TiO_2 is a major constituent in many electronic devices, much attention has been focused on monodisperse TiO_2 powders prepared by hydrolysis of titanium alkoxides [4,5]. TiO_2 – SiO_2 glasses have also been prepared by the sol–gel process [6,7], such glasses are known to show very low thermal expansion [8] and high refractive index [9]. Anti-reflection layers are easily deposited on large glass panes by dip-coating [10], while TiO_2 – SiO_2 fibres have been drawn from spinnable alkoxide solutions [11].

In all the reported experiments, hydrolysis of titanium alkoxides is performed in the presence of an acid catalyst that allows experimental control of the rate and the extent of the hydrolysis reaction [12]. As for $\text{Si}(\text{OR})_4$ hydrolysis, the mechanism for this reaction should be an electrophilic substitution [3]. Depending on the authors, different acids have been used, such as HCl [13,14], HNO_3 [9,15] or CH_3COOH [8,16]. All these acids are supposed to play the same role and the influence of the counter anion Cl^- , NO_3^- or CH_3COO^- has never been studied.

In this paper we would like to show that stable monolithic TiO_2 gels can be

reproducibly prepared in the presence of acetic acid. We shall then discuss the role of the acetate anion and show that it behaves as a ligand, directly bonded to the titanium ion.

Acetic acid could then be considered as a chemical additive playing a role in some way similar to Drying Control Chemical Agents (DCCA) such as oxalic acid in the case of SiO_2 gels [17].

2. Gel formation

TiO_2 gels are obtained through hydrolysis and polycondensation of $\text{Ti}(\text{O}i\text{Bu})_4$ in an n-butanol–acetic acid–water mixture. All solutions were prepared with:

Titanium butoxide (FLUKA) (ana.: Ti 14.1%)

Acetic acid 100% (PROLABO) ($\text{H}_2\text{O}\%$: 0.0500 max)

n butanol (PROLABO) ($\text{H}_2\text{O}\%$: 0.1 max)

Our experiments showed that precipitation never occurs when acetic acid is added to the alkoxide prior to water, even in small amounts. We therefore chose the following procedure.

Glacial acetic acid is first added to pure $\text{Ti}(\text{O}i\text{Bu})_4$. An exothermic reaction takes place leading to a clear solution. Water, diluted with n-butanol is then added under vigorous stirring. After intimate mixing, the clear solution is left to stand in a closed vessel, in order to avoid alcohol evaporation. The gelation process is strongly dependent on the respective concentrations in the solution [3]. It appears that, at a given temperature (293 K), the gelation process strongly depends on the respective concentrations of titanium alkoxide, acetic acid and water. We thus tried to check the influence of each parameter separately by modifying the concentration of a single reagent while keeping all other parameters at a constant value. We also observed that the time of gelation could depend on the volume of the solution and the size of the vessel. We therefore chose to perform all the experiments in the same glass vessel and with the same total volume. Syneresis is usually observed during gelation, some liquid being released by the gel over a period of several months [18]. This effect is specially important when the duration of gelation becomes shorter. It can correspond to a total shrinkage of about 50% or even more [19,20].

The optical aspect of the gel also depends on the gelation kinetics [19,20]. Gels obtained within half an hour or less are opalescent or even opaque while those obtained after several days are either transparent or translucent. They look yellowish by reflection but exhibit a red color arising from a Tyndall effect [21] when examined by transmission.

Table 1 gives the influence of the titanium concentration. The experiments were performed with a constant amount of water (46×10^{-3} mol) (0.8 ml) and acetic acid (17.5×10^{-3} mol) (1 ml) in a total volume of 14 ml. It shows that the gelation time quickly decreases when the titanium concentration increases.

Table 1

Gelation time (T_{gel}) as a function of titanium concentration (Ti) (CH_3COOH concentration (Ac) = $1.2 \text{ mol} \cdot \text{l}^{-1}$, water concentration (H_2O) = $3.3 \text{ mol} \cdot \text{l}^{-1}$)

(Ti) ($\text{mol} \cdot \text{l}^{-1}$)	T_{gel} (min)	Aspect
0.15	900	opaque, monolithic ^{a)}
0.20	91	opaque, monolithic
0.24	30	opaque, monolithic
0.50	12	transparent, monolithic
0.71	7	transparent, monolithic
0.72	2	transparent, monolithic
0.74	1	translucent monolithic
0.78	0	translucent monolithic

^{a)} Monolithic gels obtained are cylindrical pieces (diameter of 2.5 cm and around 7 cm high).

Table 2

Gelation time (T_{gel}) as a function of the amount of water (Titanium concentration (Ti) = $0.8 \text{ mol} \cdot \text{l}^{-1}$, CH_3COOH concentration (Ac) = $1.2 \text{ mol} \cdot \text{l}^{-1}$)

(H_2O)/(Ti)	T_{gel}	Aspect
4.3	1 s	opalescent-monolithic
3.6	10 min	opaque monolithic
2.8	3 days	translucent monolithic
2.4	1 month	translucent monolithic
0.5	^{a)}	translucent colloidal solution

^{a)} No gelation after 8 months.

No gel was obtained when the titanium concentration was smaller than 0.15 mol l^{-1} .

Table 2 gives the influence of the amount of water expressed as the (H_2O)/(Ti) ratio. These experiments were performed with a constant amount of $\text{Ti}(\text{O}i\text{Bu})_4$ ($11.7 \times 10^{-3} \text{ mol}$) (4 ml) and acetic acid ($17.5 \times 10^{-3} \text{ mol}$) (1

Table 3

Gelation time (T_{gel}) as a function of the amount of acetic acid (Titanium concentration (Ti) = $0.8 \text{ mol} \cdot \text{l}^{-1}$, water concentration (H_2O) = $3.3 \text{ mol} \cdot \text{l}^{-1}$)

(Ac)/(Ti)	T_{gel}	Aspect
0.3	30 s	opaque with cracks
1.0	2 min	translucent-monolithic
1.2	5 min	translucent-monolithic
1.5	60 min	transparent-monolithic
2.2	4 days	translucent-monolithic
3.0	12 days	translucent-monolithic
4.5	1 month	opalescent-monolithic
7.5	4 months	opaque-monolithic

ml) in a total volume of 14 ml. It shows that the gelation time decreases with the amount of water, no gelation being observed below a $(\text{H}_2\text{O})/\text{Ti} = 0.5$.

Table 3 gives the influence of the amount of glacial acetic acid expressed as the $(\text{CH}_3\text{COOH})/(\text{Ti})$ ratio. These experiments were performed with a constant amount of titanium alkoxide (11.7×10^{-3} mol) (4 ml) and water (46×10^{-3} mol) (0.8 ml) in a total volume of 14 ml. They show that acetic acid has the opposite effect to titanium or water. The time of gelation increases with the acetic acid concentration.

Of course, in a given experiment these three parameters are not independent. However, we observed that transparent monolithic gels could be obtained within a short time (about half an hour) with the following experimental conditions:

$$\begin{aligned}(\text{Ti}) &\sim 0.8 \text{ mol. l}^{-1} \\ (\text{CH}_3\text{COOH})/(\text{Ti}) &\sim 1.5 \\ (\text{H}_2\text{O})/(\text{Ti}) &\sim 4.\end{aligned}$$

3. Infra-red study of gel formation

In this study we try to follow the polycondensation process by infra-red spectroscopy in order to obtain information on how the titanium coordination changes when acetic acid and water are added.

Infra-red spectra were recorded on a Perkin-Elmer 580 spectrometer in the $4000\text{--}200 \text{ cm}^{-1}$ frequency range. Molecular precursor solutions and gels were studied by putting a droplet between two KRS5 windows. Xerogels were studied as powders dispersed in a KBr pellet. Our analysis of IR data was based on the results published in the literature, especially those reported by Nakamoto et al. [22] as described in the Appendix.

3.1. Influence of CH_3COOH

Fig. 1a gives the infra-red spectrum of pure $\text{Ti}(\text{O}i\text{Bu})_4$. It exhibits sharp bands around $2960\text{--}2930\text{--}2870 \text{ cm}^{-1}$ and $1465\text{--}1375 \text{ cm}^{-1}$ corresponding respectively to the stretching and bonding vibrations of the aliphatic CH_2 and CH_3 groups. A series of three bands can also be seen on the low energy side of the spectrum, below 1125 cm^{-1} , corresponding to the $\text{Ti}\text{--O}\text{--C}$ vibrations of butoxy groups directly bonded to titanium [23].

Fig. 1b gives the infra-red spectrum of acetic acid. We see the following characteristic bands: 1770 cm^{-1} C=O stretch. (monomer), 1718 cm^{-1} C=O stretch. (dimer), 1415 cm^{-1} CH_3 asym. deformation, 1295 cm^{-1} CH_3 sym. deformation and COH bending.

Fig. 2a gives the infra-red spectrum recorded on the clear solution obtained after adding 1.5 mol. of CH_3COOH per mol. of alkoxide. We still see the

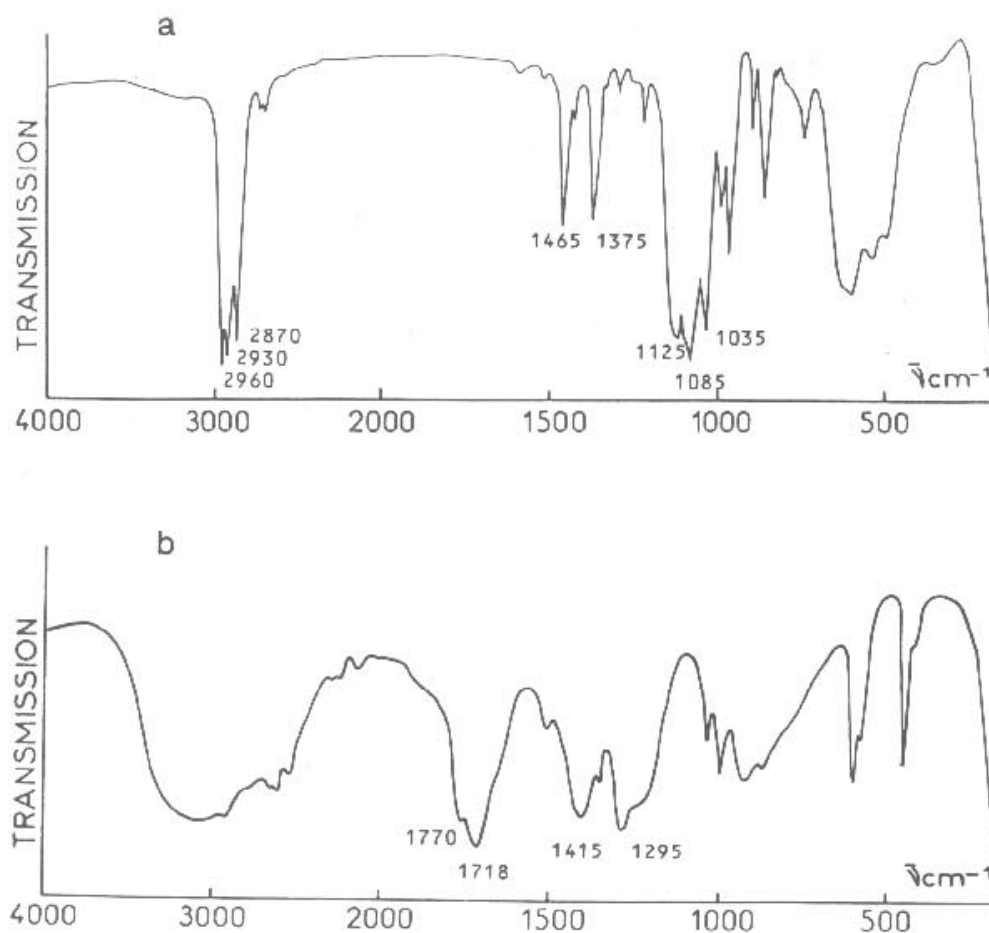
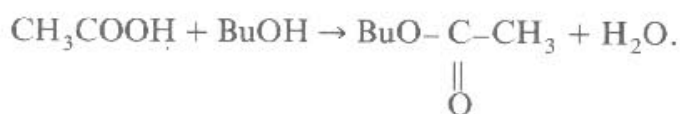


Fig. 1. Infra-red spectra of the molecular precursors: (a) pure $\text{Ti}(\text{OBu}^n)_4$, (b) acetic acid.

previous bands, typical of organic groups and Ti-OR bonds, together with new bands corresponding to free acetic acid ($1718\text{--}1412\text{ cm}^{-1}$) [24] and butyl acetate ester ($1745\text{--}1247\text{ cm}^{-1}$) formed by the reaction



It would be more interesting however, to notice a set of two bands around 1500 cm^{-1} that, according to the literature, could be due to acetate ligands [22–28]. The frequency separation ($\Delta\nu < 130\text{ cm}^{-1}$) between the $\nu_{\text{asym}}(\text{COO})$ at 1570 cm^{-1} and $\nu_{\text{sym}}(\text{COO})$ at 1440 cm^{-1} suggests that CH_3COO acts as a bidentate ligand (see Appendix). It would be difficult to say whether the acetate is a chelating (bonded to one Ti) or a bridging (bound to two Ti) [22–29] ligand, but it is obviously directly bonded to the titanium. However, the linewidth and some shoulders suggest that both coordinations should occur. These new features increase in intensity while those corresponding to the alkoxide decrease when the amount of acetic acid increases up to two CH_3COOH per $\text{Ti}(\text{OBu}^n)_4$. Beyond this limit the addition of acetic acid is no

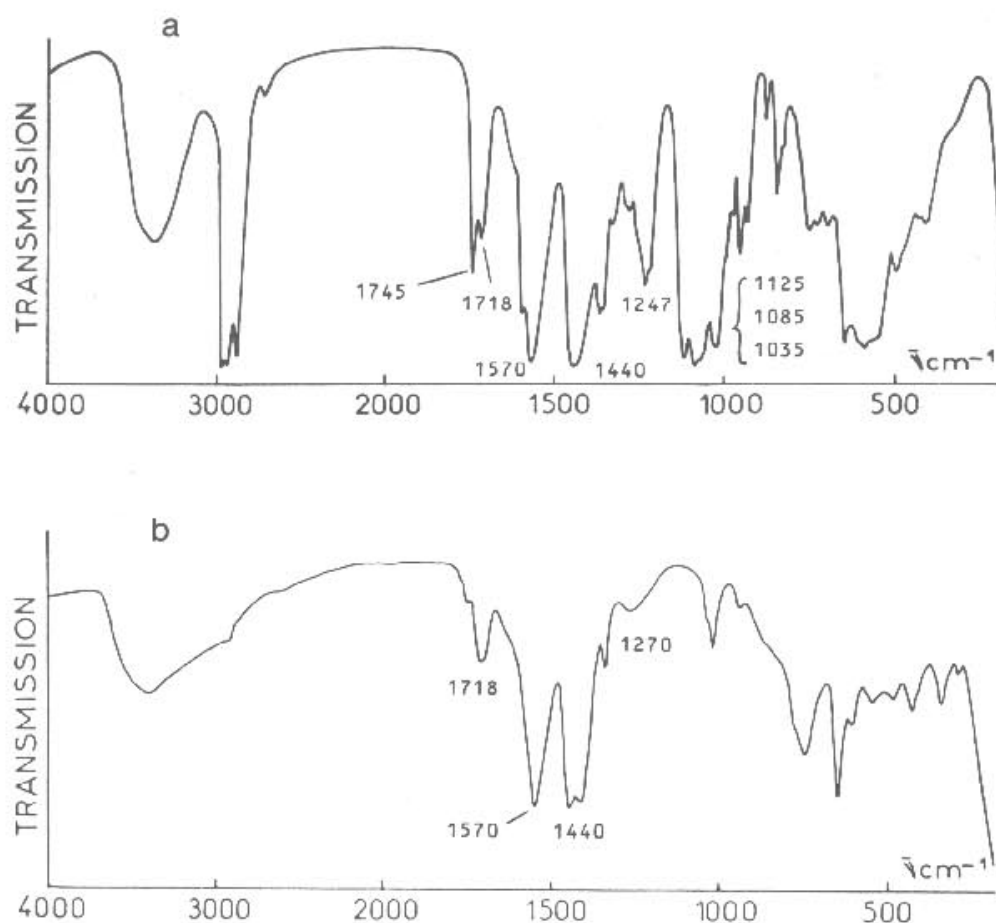


Fig. 2. Infra-red spectra after addition of acetic acid: (a) addition with a Ac/Ti ratio of 1.5, (b) addition of an excess of acetic acid (Ac/Ti = 10).

longer exothermic [30,31]. A gelatinous precipitate appears when acetic acid is added in large excess (Ac/Ti = 10). The infra-red spectrum of such a precipitate, washed with CCl_4 and dried under vacuum is shown in fig. (2b). The set of two bands, around 1500 cm^{-1} , corresponding to bidentate acetates can still be observed while two new bands around 1718 cm^{-1} and 1270 cm^{-1} appear. These bands could also be attributed to the $\nu(\text{COO})$ vibrations of an acetate ligand, but the large frequency separation ($\Delta\nu = 450 \text{ cm}^{-1}$) between the ν_{sym} (1270 cm^{-1}) and the ν_{asym} (1718 cm^{-1}) suggest an unidentate acetate ligand [21–29]. Moreover, it should be pointed out that all infra-red features typical of Ti–OR bonds have completely disappeared. This suggests that we now have a polymeric titanium acetate [30,32] from which all OR groups have been removed. The fresh precipitate is actually slightly soluble and can be dissolved into a large excess of water under vigorous stirring within a few minutes. A clear solution is then obtained where the infra-red bands characteristic of bidentate acetate ligands can still be seen ($\Delta\nu \approx 125 \text{ cm}^{-1}$). Upon ageing for about a week in a closed vessel, this solution gives rise to a translucent yellowish gel where only bidentate acetate ligands remain.

3.2. Influence of water

As reported in the preceding section, a gel is obtained when water is added to the clear solution containing titanium alkoxide and acetic acid. Fig. 3a gives the infra-red spectrum recorded on a gel obtained in the following conditions:

$$(\text{Ti}) = 0.8 \text{ mol. l}^{-1}, (\text{Ac})/(\text{Ti}) = 1.5, (\text{H}_2\text{O})/(\text{Ti}) = 4.$$

This spectrum has to be compared with fig. 1b corresponding to the $\text{Ti}(\text{OR})_4\text{-CH}_3\text{COOH}$ solution before water addition. The most interesting difference comes from a modification of the doublet around 1500 cm^{-1} that corresponds to bidentate acetate ligands linked to titanium. Its intensity decreases while the bands become sharper. The frequency separation ($\Delta\nu = 105 \text{ cm}^{-1}$) between the $\nu_{\text{sym}}(\text{COO})$ at 1455 cm^{-1} and the $\nu_{\text{asym}}(\text{COO})$ at 1560 cm^{-1} is consistent with bidentate acetate ligands [29], but its smaller value suggests chelating acetates rather than bridging acetates [22–29]. We may then think that the decrease in intensity of the doublet comes mainly from the breaking of the acetate bridges. The two bands around 1715 cm^{-1} and 1270 cm^{-1} are

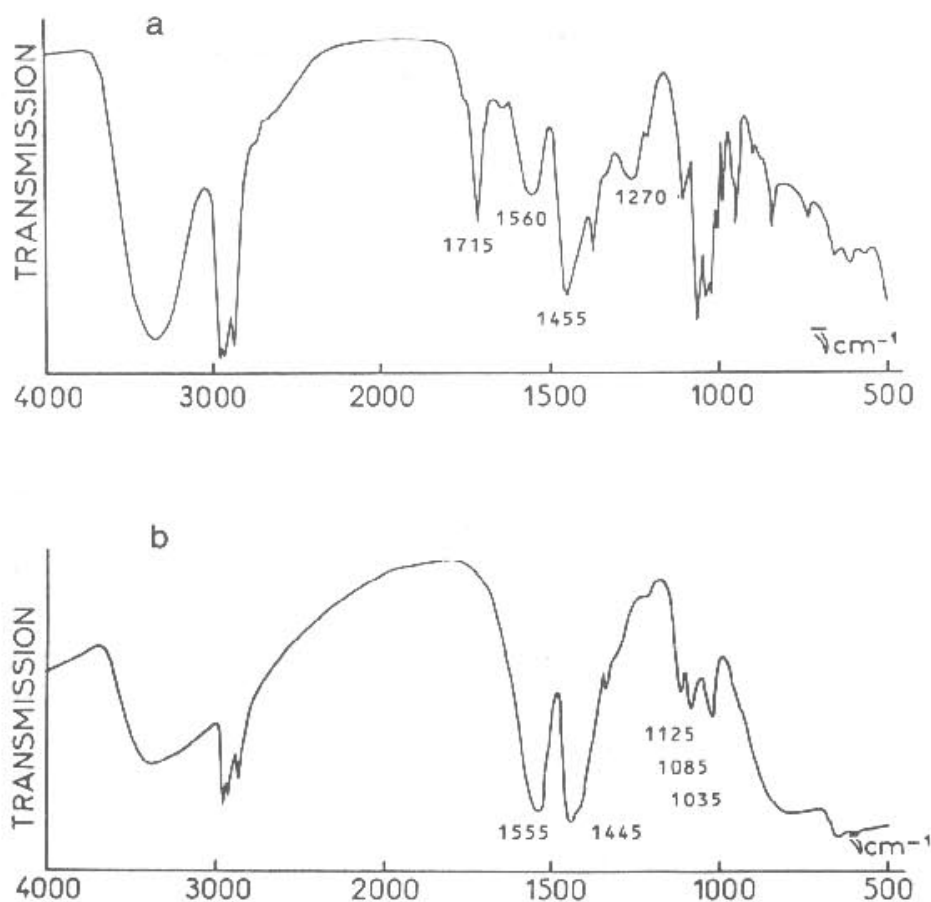


Fig. 3. Infra-red spectra after hydrolysis of the molecular precursors. (a) gel, (b) xerogel obtained upon drying for 1 h at 80°C .

still visible. They can be attributed to free acetic acid but their intensity seems to be too high to be due to CH_3COOH only. This suggests that some monodentate acetate ligands, that exhibit infra-red bands in the same region, should still be linked to the titanium.

Fig. 3b shows the infra-red spectrum recorded on a xerogel obtained after drying the previous gel for 1 h at 80°C . The two bands at 1555 cm^{-1} and 1445 cm^{-1} are still visible, suggesting the presence of chelating acetate groups. The two bands typical of monodentate acetates have completely disappeared while OR groups linked to titanium give rise to a few bands between 1100 and 1000 cm^{-1} . The low energy side of the spectrum exhibits only a broad signal that should be due to the envelope of the phonon bands of a Ti-O-Ti bond of a titanium oxide network [33].

4. Discussion

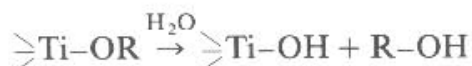
The sol-gel processing of TiO_2 is usually performed via the hydrolysis and polycondensation of titanium alkoxides in the presence of an acid catalyst. Acids are supposed to increase the lability of protonated OR groups and favor electrophilic substitutions. A survey of the literature shows that the acid can be either HCl [13,14], HNO_3 [9,15], or CH_3COOH [8,16]. The counter anion is supposed to have a negligible effect on the process.

In this paper we have shown that clear monolithic gels rather than colloidal precipitates can be easily obtained when hydrolysis is performed in the presence of acetic acid. Moreover, infra-red spectra clearly show that the acetate anion acts as a ligand and changes the precursor at a molecular level. Such a regulation of both nucleation and polymerization processes has also been performed by Matijevic et al. in order to form monodisperse colloids [34,35]. In his experiments, the release of precipitating anions was controlled by adding organometallic precursors such as acetates. It appears that they are able to promote particle uniformity, even after calcination.

Depending on the Ac/Ti ratio, different $\text{Ti}(\text{OR})_x(\text{Ac})_y$ compounds may be obtained. At the beginning of the process as long as $|\text{Ac}|/|\text{Ti}| \leq 2$ the reaction appears to be fast and highly exothermic, OR groups are replaced by chelating acetate ligands and soluble molecular species are formed. A stoichiometric compound $\text{Ti}(\text{OR})_2(\text{Ac})_2$ could be obtained when $|\text{Ac}|/|\text{Ti}| = 2$ [30,31]. Experiments are in progress in order to isolate and characterize such a compound [36].

Beyond 2 mol. of acetic acid per titanium, the reaction becomes slow and no exothermic effect is observed anymore [29-31]. The viscosity of the solution increases markedly upon ageing and bridging acetate ligands are observed by infra-red spectroscopy. We may then assume that oligomers are formed leading to a polymeric titanium acetate when an excess of acetic acid is added. This is consistent with some observations reported in the literature showing that soaps or precipitates are sometimes obtained [31,37].

Adding water to the $\text{Ti}(\text{OR})_x(\text{CH}_3\text{COO})_y$ precursor seems to have two effects. The first one, of course, would be to remove the OR groups according to



initiating therefore the condensation process.

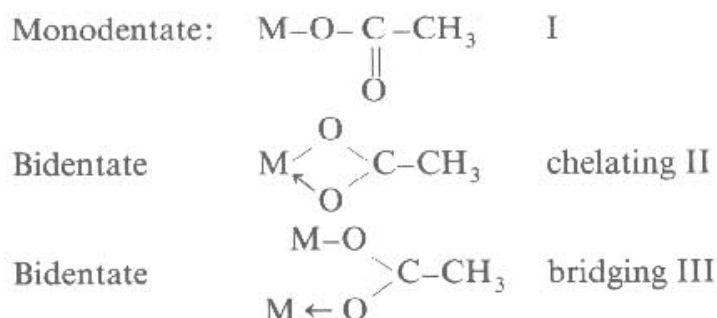
The second one seems to be the breaking of the acetate bridges giving rise to monodentate or chelating acetate ligands. Upon further hydrolysis, monodentate acetate and OR groups are removed giving rise to Ti-OH bonds. Hydrolysis of chelating acetates seems to be more difficult so that acetate groups still remain in the monolithic xerogel. They will be only removed upon heating at a temperature of about 300°C [38].

Acetate then seems to have a major role as a chelating ligand. It reacts chemically with the alkoxide giving rise to a new molecular precursor $\text{Ti}(\text{OR})_x(\text{Ac})_y$. The chelating acetates are then less easily hydrolysed than the OR groups increasing therefore the time of gelation as shown in table 3. This favors the polycondensation process, and leads to monolithic gels where high polymers rather than small colloidal particles are present.

We may think that the chelating effect of acetates is not unique. It should be observed with other carboxylic acids leading to polynuclear carboxylates [28]. We have actually performed other experiments with other organic reagents such as acrylic acid or oxalic acid. They give similar results. These observations might explain in some way the role of oxalic acid as a Drying Control Chemical Additive DCCA that lead to clear monolithic SiO_2 gels [17].

Appendix

A survey of the literature shows that extensive studies have been published about the infra-red spectra of metal carboxylates [22]. In our case the acetate anion may coordinate according to the following modes:



The stretching symmetric $\nu_{\text{sym}}(\text{COO})$ and antisymmetric $\nu_{\text{asym}}(\text{COO})$ vibrations of the free acetate ion are located at 1416 cm^{-1} and 1560 cm^{-1} respectively. Their frequency separation is $\Delta\nu = 144 \text{ cm}^{-1}$.

Table 4
Stretching vibrations of acetate ligands in different Ti(IV)-acetate complexes according to [29]

Coordination mode	$\nu_{\text{asym}}(\text{COO})$ (cm^{-1})	$\nu_{\text{sym}}(\text{COO})$ (cm^{-1})	$\Delta\nu$ (cm^{-1})
Monodentate I	1720	1295	425
Bidentate chelating II	1550	1470	80
Bidentate bridging III	1590	1430	160

For a monodentate acetate ligand (I), the $\nu(\text{C}=\text{O})$ vibration lies at higher frequencies than $\nu_{\text{asy}}(\text{COO})$ while the $\nu(\text{C}-\text{O})$ vibration lies at lower frequencies than $\nu_{\text{sym}}(\text{COO})$. Their frequency separation is therefore much larger. It usually lies around $\Delta\nu = 400 \text{ cm}^{-1}$ [22,26-29].

Such a variation is not observed when the acetate acts as a bidentate ligand (II) or (III). The frequency separation then lies between 80 cm^{-1} and 160 cm^{-1} . It is not obvious in this case to distinguish between (II) and (III) but bridging acetates usually give rise to larger $\Delta\nu$, between 120 cm^{-1} and 160 cm^{-1} [22].

Infra-red spectroscopy then appears to be a very good technique to get information about the coordination mode of acetate ligands. Monodentate and bidentate ligands can be unambiguously distinguished.

The position and splitting of the infra-red bands also depend on the nature of the metal atom. Many correlations between infra-red spectra and structural data of metallic acetates can be found in the literature [22,28,29], but the structure of Ti(IV) acetates has not yet been reported. A detailed infra-red analysis has however been published by Von Thiele and Panse [29]. Their main results are reported in table 4.

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