

SOL-GEL SYNTHESIS AND CHARACTERIZATION OF TITANIUM OXO-ACETATE POLYMERS

S. Doeuff, M. Henry and C. Sanchez
Laboratoire de Chimie de la Matière Condensée. Université P. et M. Curie.
4, Place Jussieu. Tour 54, 5ème étage. 75252 PARIS Cedex 05. France

(Received June 21, 1990; Communicated by P. Hagenmuller)

ABSTRACT

Polymeric precipitates have been obtained from the reaction of an excess of acetic acid with titanium alkoxides. The formula $TiO(OAc)_2$ has been found from chemical analysis and has been confirmed by IR and NMR spectroscopies. All the alkoxy groups have been removed in the course of the reactions. The chemical nature of the compounds is the same whatever the alkoxide may be but the morphology of the powder is affected by the nature of the alkoxide and the experimental conditions. A structural scheme is derived from partial charge calculations relating chemistry to particles morphology.

MATERIALS INDEX : Titanium oxo-acetate - Sol-gel - Titanium alkoxides.

INTRODUCTION

Sol-gel processing appears to be a very promising method for the manufacture of glasses and ceramics (1). It uses molecular precursors, mainly metal alkoxides, as starting materials. A macromolecular oxide network is then obtained via hydroxylation-condensation reactions. The flexibility of the process comes from the reactivity of the alkoxide precursors which allows an easy control of the coordination sphere of the metal by adding various chemical reagents. New molecular precursors are then obtained for which the whole hydrolysis-condensation process is modified. Such modification leads to a better control of the process allowing for example the adjustment of rheological properties of gels. It can also change the nature and the properties of the resulting materials.

Such chemical reagents are usually nucleophilic ligands such as β -diketones or organic acids. Acetic acid is one of the chemical additives extensively used in sol-gel chemistry (2-5). Acetic acid reacts with titanium alkoxides ($Ti(OR)_4$) at the molecular level as a ligand.

It has been shown that different materials could be obtained by varying the molar ratio $R = AcOH/Ti(OR)_4$.

For $R=1$, an exothermic and stoichiometric reaction is observed which leads to the formation of a modified precursor (6,7). Titanium oxide based gels are obtained upon hydrolysis of this new

precursor (8).

For $R > 1$, all the acetic acid does not react with the alkoxide and a time evolution of the system is observed. Indeed, H_2O molecules are formed by the esterification reaction. By reacting with the modified alkoxide an hydrolysis reaction is promoted, leading to the formation of different compounds. For $R=2$, molecular crystals grow within 3 days (9,10). For $2 < R < 4$, colloids are obtained with a hydrodynamic diameter of approximately 150Å. For $R=4$ a slight precipitation is observed after a few days. When $R > 5$ a heavy white precipitate is formed in few hours.

This work describes the characterization, by various techniques, of the compounds obtained through the reaction of an excess of acetic acid with titanium alkoxides.

EXPERIMENTAL SECTION

MATERIALS

The titanium alkoxides $Ti(OR)_4$ ($OR = OEt, OPr^i, OBu^n$ respectively ethoxide, isopropoxide and n-butoxide) were purchased from FLUKA Co. $Ti(OAm^t)_4$ ($OAm^t =$ tertioamyloxide) was synthesized via alcohol exchange as previously described (11). Glacial acetic acid (PROLABO Co.) was used without further purification.

SYNTHESIS PROCEDURE

The titanium alkoxide is added drop by drop under stirring in acetic acid. A large excess of $AcOH$ is used, with a molar ratio $AcOH/Ti(OR)_4$ of 10. Since the reaction is exothermic, the solution is kept cold in a bath of ice and vigorously stirred. After 30 minutes of stirring the solution begins to be cloudy. After one day for $Ti(OEt)_4$ and $Ti(OBu^n)_4$ and three days for $Ti(OPr^i)_4$ and $Ti(OAm^t)_4$, the formation of a heavy white precipitate is observed. This precipitate is insoluble in common organic solvents, but soluble in H_2O . After filtration, the precipitate is washed 3 times with CCl_4 and dried at $60^\circ C$ for 24 hours. In the following, notation E, P, B and A will refer to precipitates obtained from $Ti(OEt)_4$, $Ti(OPr^i)_4$, $Ti(OBu^n)_4$ and $Ti(OAm^t)_4$ respectively.

RESULTS

Chemical analysis has been performed for titanium, carbon and hydrogen elements. Oxygen ratio has been calculated by difference. The titration of the acetate groups has been performed following a method already described (12).

Such analysis, leads to a ratio of about two acetate groups for each titanium atom. The valence of the titanium atom being IV (no ESR signal has been observed), we can propose for the precipitate the likely following formula: $TiO(OAc)_2$. It corresponds to a titanium oxoacetate.

The compound A has a deficit in acetate groups compensated by oxygen atoms. $Ti_{0.15}(OAc)_{1.70}$ is the proposed rough formula.

The four samples exhibit an identical diffractogram. Wide diffraction peaks are observed, corresponding to the d spacing values 14.72Å, 7.62Å, 6.06Å and 3.97Å. No identification to known compounds can be done. These results indicate that the precipitates correspond to a poorly organized phase.

The morphology of the four precipitates, as studied by scanning electronic microscopy,

reveals two different types of particles depending on the alkoxide used (Fig.1).

For E and B, compounds obtained from primary alkoxides ($\text{Ti}(\text{OEt})_4$ and $\text{Ti}(\text{OBu}^n)_4$), rodlike particules are observed (length = 40 to 70 μm , width = 8 to 12 μm). Each rodlike particle seems to be the result of the agglomeration of fibers.

On the contrary, the precipitates P and A obtained from more bulky alkoxides ($\text{Ti}(\text{OPri})_4$ and $\text{Ti}(\text{OAm}^t)_4$) exhibit more spherical particles. However, other conditions of precipitation seem to affect the precipitate morphology. When $\text{TiO}(\text{OAc})_2$ is prepared from a molar ratio $\text{AcOH}/\text{Ti}(\text{OAm}^t)_4 = 150$ without stirring after mixing, the anisotropic character of the particles can be increased. Long fibers are then observed.

As a complementary analysis the specific area of the precipitates has been mesured. This specific area has a relatively high value of 120 m^2/g averaging over all samples. (BET method). The DTA, performed under air atmosphere, has the same trace for the four precipitates. Two wide endothermic traces correspond to the removal of solvent molecules. Two exothermic traces at 300°C and 355°C corresponding to the combustion of the acetate groups, are followed by a sharp exothermic trace at 425°C. This trace could be attributed to the crystallization of TiO_2 anatase as proved by X-ray diffraction.

After the determination of the macroscopic properties of the compounds, a more detailed study using spectroscopic methods was undertaken in order to precise the local order around titanium atoms.

Several techniques have been used to characterize the obtained compounds. Since the results for the samples E, P, B are similar, the following discussion will emphasize the difference between E, P, B and A.

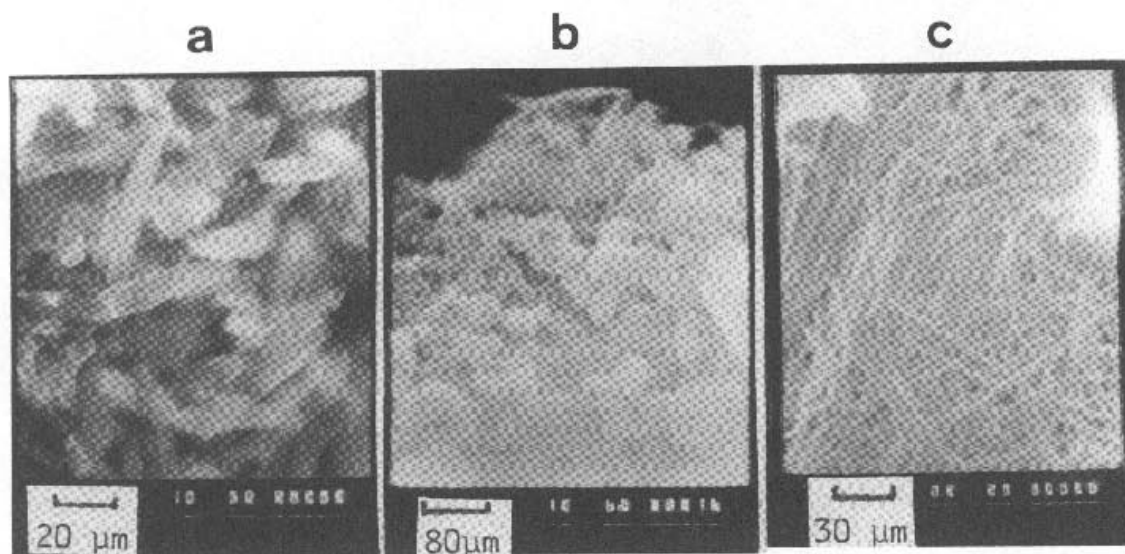


FIG. 1

SEM micrographs of the compounds E (a), D (b) and the precipitate obtained with $\text{AcOH}/\text{Ti}(\text{OAm}^t)_4 = 150$ without stirring (c).

$^{13}\text{CPMAS NMR}$

The ^{13}C NMR spectra have been recorded on a MSL-300 BRUKER spectrometer working at

75.45 MHz for ^{13}C (reference: glycine, $\delta_{\text{CH}_2/\text{TMS}} = 38.4$ ppm). The ^{13}C CPMAS (Cross polarization at the Magic Angle Spinning) spectrum of the precipitate obtained for A is shown in Fig.2. Two singlets in two different regions are observed, around 20 ppm (21.78 ppm and 23.75 ppm) and 180 ppm (183.50 ppm and 185.35 ppm). The chemical shifts around 20 ppm and 180 ppm are respectively characteristic of ^{13}C resonance of CH_3 and CO group of the acetate ligand. No signal from the residual alkoxo groups are observed.

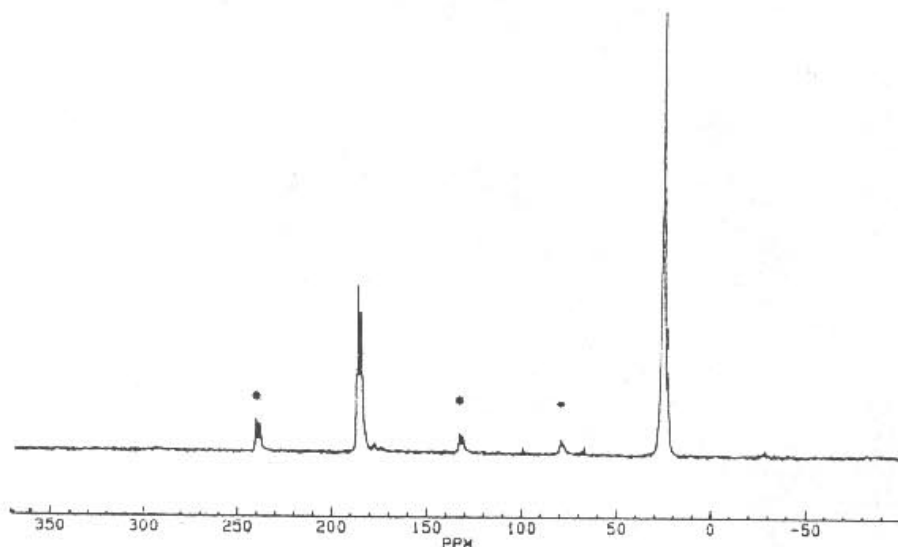


FIG. 2
 ^{13}C CPMAS of the compound A. (* Spinning bands).

INFRA-RED SPECTROSCOPY

The I-R spectra were obtained with a PERKIN-ELMER 783 spectrophotometer working in the $4000\text{-}200\text{ cm}^{-1}$ frequency range. They are displayed in Fig.3.

In both spectra, no vibration due to the alkoxo groups ($\nu_{\text{C-O-Ti}} = 1035, 1085, 1135\text{ cm}^{-1}$) is observed. Characteristic vibrations of acetate groups bonded to titanium ($\nu_{\text{sCOO}} = 1450\text{ cm}^{-1}$ and $\nu_{\text{asCOO}} = 1555\text{ cm}^{-1}, 1590\text{ cm}^{-1}$ (shoulder), 1525 cm^{-1} (shoulder)) are observed (8).

Vibrations due to acetic acid ($\nu_{\text{C=O}} = 1718\text{ cm}^{-1}$) and ester ($\nu_{\text{C=O}} = 1755\text{ cm}^{-1}$) remain, showing that a few of these molecules are still adsorbed in the precipitates.

The compounds E, P, B show well resolved bands in the low frequency region whereas the compound A exhibits a large band from $500\text{ to }300\text{ cm}^{-1}$ characteristic of the $\nu_{\text{Ti-O-Ti}}$ vibration of an oxide network.

XANES (X-ray Absorption Near-Edge Structure)

The titanium K-edge spectra were recorded at room temperature at LURE, the French synchrotron radiation facility, on the EXAFS III spectrometer.

The XANES spectra of the precipitates have been recorded on the powders placed

between two pieces of tape. All the conditions for data collection and analysis are described elsewhere (14).

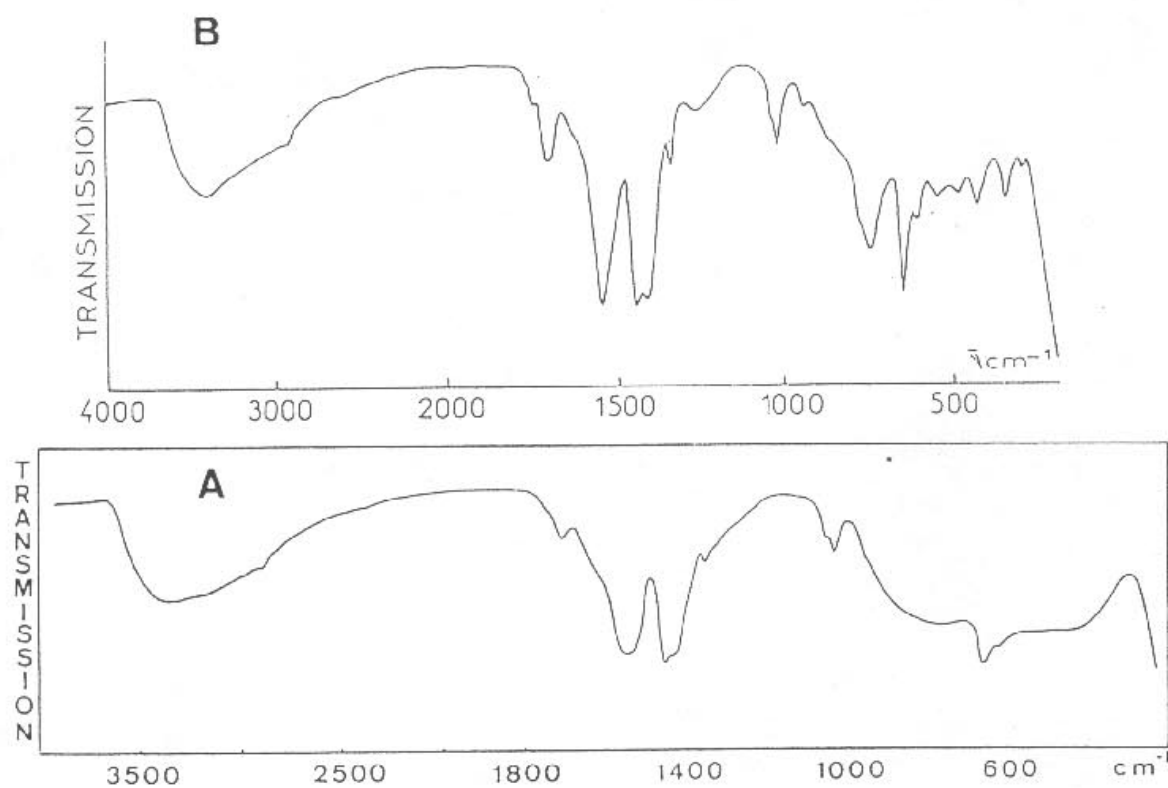


FIG. 3
IR Spectra of the compounds B and A.

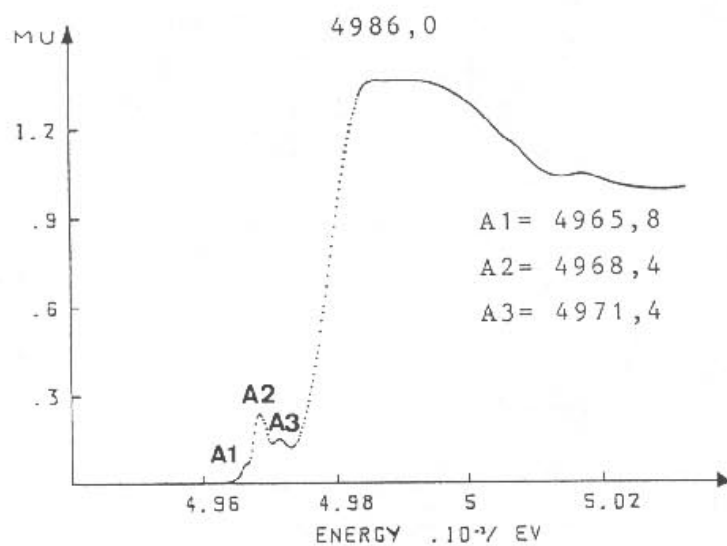


FIG. 4
Xanes spectrum of the compound A at the titanium K-edge.

The XANES study gives information about the coordination of the metallic atom. All the samples have identical spectra (Fig.4).

A well resolved triplet is observed. These pre-edge peaks are weak and located respectively at 4965.8 eV, 4968.4 eV and 4971.4 eV. The XANES spectrum of these compounds is thus characteristic of titanium atoms in octahedral symmetry (15).

EXAFS (Extended X-ray Absorption Fine Structure)

The Fourier transforms of the EXAFS experimental spectra of the four precipitates have been calculated. The filtered curve $kX(k)$ (with k , the wave vector and $kX(k) = k(\mu_0 - \mu)/\mu$, μ_0 : noise absorption and μ : absorption) of the compound B has been correctly adjusted by the simulation using two Ti-O distances and one Ti-Ti distance. The Fourier transform of the experimental EXAFS spectrum and the curve $kX(k) = f(k)$ are shown in Fig.5. The parameters so obtained are reported in Table 1.

These EXAFS results outline several points :

- the presence of a significant Ti-Ti distance (3.12 Å) confirms the polymeric nature of these materials and the well defined short range order .

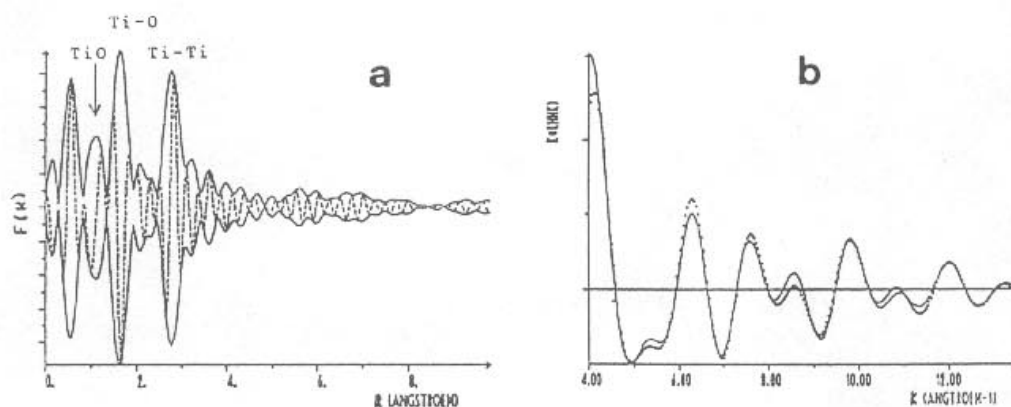


FIG. 5

EXAFS of the compound B : a- Fourier transform of the EXAFS spectrum.

b- fitting curve $kX(k) = f(k)$, experimental, ----- calculated.

TABLE 1

Fitting Results for the EXAFS Spectra of the compound B ($\text{AcOH/Ti}(\text{O}^n\text{Bu})_4$).

	N Numbers of backscattering centers	R, Å Absorbing atom- neighbors distance	σ , Å Debye-Waller factor	ρ % agreement factor
Ti-O	2.24	1.76	0.08	3.7
Ti-O	4.49	1.99	0.08	
Ti-Ti	2.01	3.12	0.06	

- the presence of two different types of Ti-O distances. A short one (Ti-O = 1.76 Å) ascribed to μ -oxo bridges. Such a distance seems short in regard of distances found in titanium dioxide. However, such a Ti-O length has been found for a μ_2 -oxo bridge when the octahedral titanium has acetate ligand in its coordination shell (10). The longest Ti-O distance (1.99 Å) is with no doubt the Ti-O bond of the acetate ligand.

DISCUSSION

Few studies on the chemical reactions between an excess of anhydride or acetic acid and titanium tetrachloride or titanium alkoxides $Ti(OR)_4$ have been reported in the literature (12,16-19). The resulting materials $Ti_2O(OAc)_6$ and $TiO(OAc)_2$ have been only studied by chemical analysis without any structural characterization.

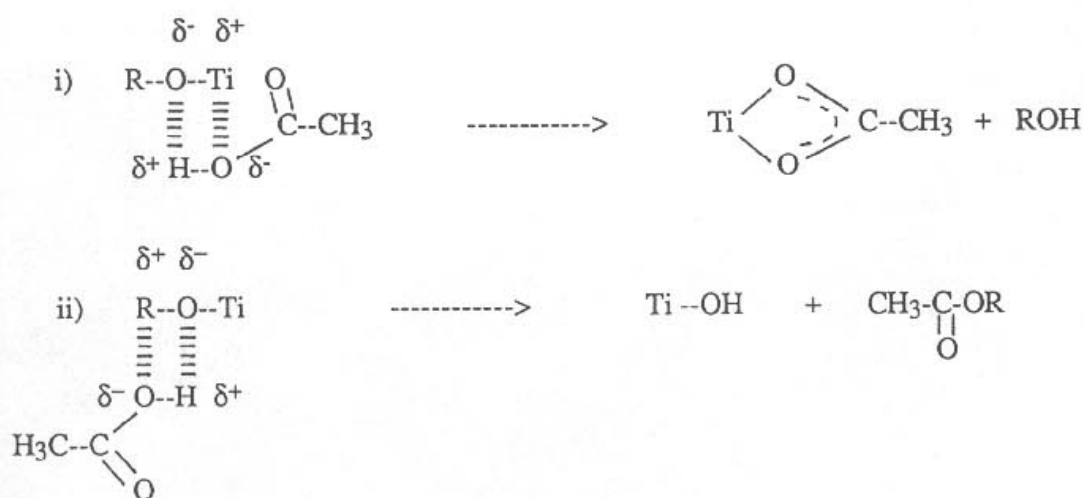
Our synthesis, at room temperature, allows us to obtain fibrous titanium oxo-acetate polymers as shown by the SEM study.

The X-ray diffraction shows that the precipitates are relatively poorly crystallized. However, they have a relatively well defined local order that has been characterized by several spectroscopic techniques (^{13}C CPMAS NMR, IR, XANES, EXAFS).

The presence of the acetate ligand in the coordination shell of the titanium atom has been shown by IR Spectroscopy and ^{13}C CPMAS NMR. The IR study, in particular, shows that the acetate ligands are bidentate towards the titanium atoms with a bridging coordination mode and/or a chelating coordination mode.

The XANES shows that the titanium atom is in octahedral coordination. The EXAFS study confirms the presence of the acetate ligand in the environment of the absorbant atom (Ti). Moreover, it clearly puts in evidence the existence of short titanium-oxygen bonds ($d = 1.76$ Å). These short Ti-O bonds correspond to μ -oxo bridges (probably μ_2 -oxo) present in this mixed network of oxide and acetate. They can no more be assigned to a terminal alkoxo ligand like those existing in the precursor $Ti(OR)_4$ since these organic groups have been totally removed in the course of the reactions, as shown by IR and ^{13}C CPMAS NMR.

From X-ray absorption, we conclude that the ratio of acetate oxygen atoms over oxo groups is two for B. Let us try to understand how such polymers could be formed, and consider the two possible mechanisms by which acetic acid could react with an alkoxo group:

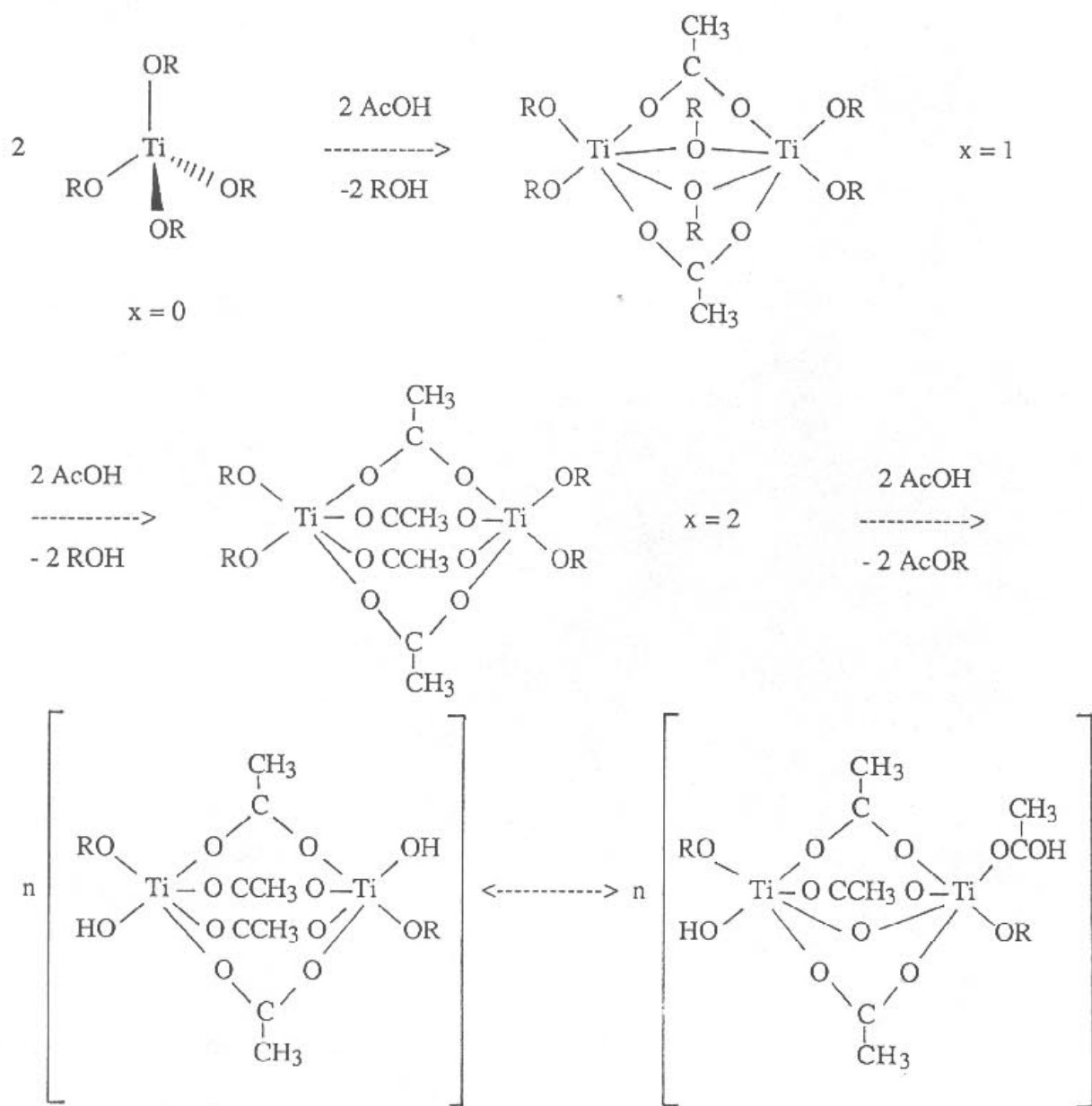


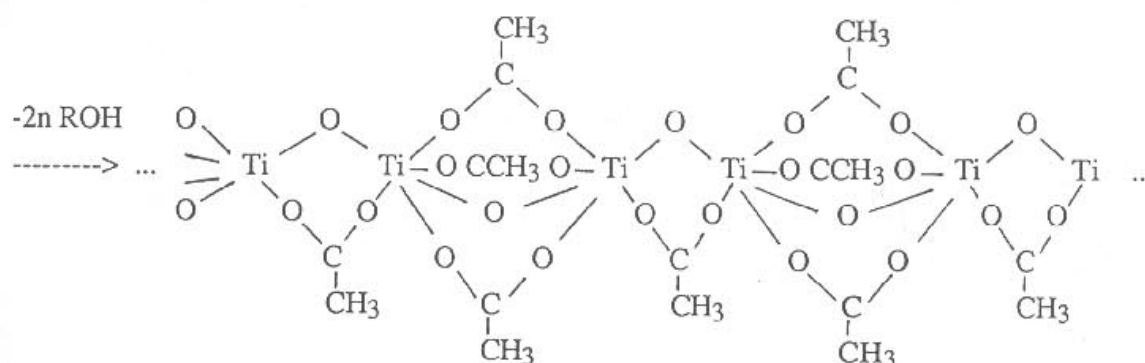
In both cases, the first step is a nucleophilic attack of a hydroxo group, which is

followed by a prototropic transfer towards the oxygen of the alkoxo group. In the first case nucleophilic attack occurs on the titanium atom leading to the elimination of an alcohol molecule and formation of a modified precursor. In the second case, nucleophilic attack occurs on the alkyl group leading to the elimination of an ester molecule and formation of an hydrolyzed precursor.

Let us try to know which center will be attacked by acetic acid, by applying the Partial Charge Model (20) to the following precursors: $\text{Ti}(\text{OPr}^i)_{4-x}(\text{OAc})_x$ ($x=0,1,2,3,4$). Owing to the previous analysis, we just have to compare partial charge beared by the Pr^i group to that beared by titanium atom. Nucleophilic attack will then always occur on the most positive charge. As shown in Fig.6, we find that chemical modification is expected if $x \leq 1$ while hydrolysis is preferred if $x > 2$.

Consequently, the following structural scheme may be proposed:





This scheme is in agreement with all our spectroscopic characterizations and may explain why fibrous polymers are readily obtained. As soon as $x=2$, chemical modification by acetic acid does not occur anymore as shown experimentally (21) and confirmed by partial charges calculations ($\delta(\text{Pr}^i) > \delta(\text{Ti})$). Hydrolysis can be performed through esterification reactions which can occur via two different mechanisms:

i/ the first one corresponds to an intramolecular esterification reaction leading to the formation of $\text{Ti}(\text{OPr}^i)(\text{OH})(\text{OAc})_2$ rather than $\text{Ti}(\text{OPr}^i)(\text{OAc})_3$.

Partial charges calculations within the hydrolyzed precursor $\text{Ti}(\text{OPr}^i)(\text{OH})(\text{OAc})_2$ shows that $\delta(\text{Pr}^i\text{OH}) = +0.68$ while $\delta(\text{AcOH}) = -0.32$. This means that only alcohol molecules could act as leaving groups. As there is only one OR group per titanium atom, this precursor is bifunctional towards alkoxylation leading to the formation of linear polymer having a stoichiometry close to $\text{TiO}(\text{OAc})_2$.

ii/ the second one corresponds to an extramolecular esterification, $\text{ROH} + \text{AcOH} \rightarrow \text{ROAc} + \text{H}_2\text{O}$ that leads to in-situ water formation. Such water could react as follow:



Partial charges calculations now show that $\delta(\text{AcOH}) = +0.02$ meaning that acetic acid could act as leaving groups. Such multifunctional precursors could then react upon each other leading to reticulated polymers mainly based on a TiO_2 network. Alternatively they could also react with linear polymers cross-linking them and leading to agglomerated fibers.

These two competitive processes could help to explain why linear polymers are clearly seen by SEM only when acetic acid is in large excess ($\text{AcOH}/\text{Ti} = 150$). When it is used as a solvent the first mechanism is highly favored. However if the ratio acetic acid/Ti decreases the second mechanism becomes a competitive process. The linear morphology of particles is then destroyed.

This structural model can also explain the reactivity of these polymers towards water. Indeed, the addition of 30 moles of water leads to the dissolution of the precipitate within 10 minutes. In another experiment, the alkoxide is added to a mixture of AcOH and H_2O ($\text{AcOH}/\text{Ti}(\text{OR})_4 = \text{H}_2\text{O}/\text{Ti}(\text{OR})_4 = 6$) and no precipitate is obtained. The solution kept limpid even after few days of stirring. An opaque white gel is obtained after 90 days. So, we observe that the precipitate can dissolve in a large excess of water and this solution yields an amorphous gel within several days. This TiO_2 gel has less than 0.2 mole of acetate per titanium. Water can break the acetate bridges in order to form small associated species that are soluble in the reactional medium. These species can finally slowly recondense by a mechanism of oxolation ($\text{Ti}-\text{OH} + \text{Ti}-\text{OH} \rightarrow \text{Ti}-\text{O}-\text{Ti} + \text{H}_2\text{O}$). During the course of these reactions, the elimination of the acetate groups occurs. This allows to form a stable network of titanium dioxide in which a small part of the acetate groups remain bonded to the titanium.

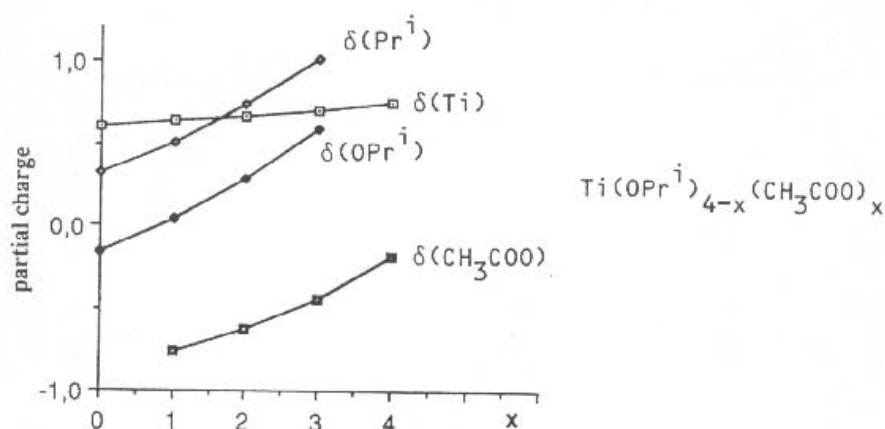


FIG. 6
Calculated partial charges as a function of x.

CONCLUSIONS

Acetic acid is a chemical reagent extensively used in sol-gel chemistry. Different materials are obtained by varying the molar ratio $R = \text{AcOH}/\text{Ti}(\text{OR})_4$.

The study of the chemical reaction between an excess of acetic acid and titanium alkoxide has shown that the so-obtained compound is a titanium oxo-acetate. The titanium coordination number is 6 and the acetate groups are all in bridging position. The compound formula is $\text{TiO}(\text{OAc})_2$. All the alkoxy groups have been removed in the course of the reaction.

The chemical nature of the resulting material do not depend on the starting alkoxide.

REFERENCES

- 1 - L. L. Hench and J. K. West, *Chem. Rev.* **90**, 33 (1990).
- 2 - B. E. Yoldas, *Amer. Ceram. Soc. Bull.*, **54**, 289 (1975).
- 3 - B. E. Yoldas, *J. Mater. Sci.*, **21**, 1080 (1986).
- 4 - S. Sakka and K. Kamiya, *J. non-Cryst. Solids*, **42**, 403 (1980).
- 5 - C. Sanchez, J. Livage, M. Henry and F. Babonneau, *J. non-Cryst. Solids*, **100**, 65 (1988).
- 6 - C. Sanchez, F. Babonneau, S. Doeuff and A. Leautic, *Ultrastructure Processing of Advanced Ceramics*, p. 77, J. Wiley and Sons Inc. publishers, New-York (1988).
- 7 - J. Livage, C. Sanchez, M. Henry and S. Doeuff, *Solid State Ionics*, **32/33**, 633 (1989).
- 8 - S. Doeuff, M. Henry, C. Sanchez and J. Livage, *J. non-Cryst. Solids*, **89**, 206 (1987).

- 9 - S. Doeuff, Y. Dromzee and C. Sanchez, *C. R. Acad. Sci. Paris*, **308** (II), 1409 (1989).
- 10 - S. Doeuff, Y. Dromzee, F. Taulelle and C. Sanchez, *Inorg. Chem.* **28**, 4439 (1989).
- 11 - D. C. Bradley, R. C. Mehrotra and W. Wardlaw, *J. Chem. Soc.* 2027 (1952).
- 12 - K. C. Pande and R. C. Mehrotra, *Zeit. Anorg. Allg. Chemie*, **290**, 95 (1957).
- 13 - K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Ed. Wiley Interscience, 3rd edition, New-York (1978).
- 14 - F. Babonneau, S. Doeuff, A. Leautic, C. Sanchez, C. Cartier and M. Verdaguer, *Inorg. Chem.* **27**, 3166 (1988).
- 15 - R. B. Greigor, F. W. Lytle, D. R. Sandstrom, J. Wong and P. Schultz, *J. non-Cryst. Solids*, **55**, 27 (1983).
- 16 - K. H. Gayer, S. F. Pavkovic and G. S. Tennenhouse, *Z. Anorg. Chem.* **354**, 74 (1967).
- 17 - N. W. Alcock, V. M. Tracy and T. C. Waddington, *J. C. S. Dalton*, 2238 (1976).
- 18 - K. C. Pande and R. C. Mehrotra, *J. Prakt. Chem.* **5**, 101 (1957).
- 19 - R. Kapoor, B. K. Batil and P. Kapoor, *Ind. J. Chem.* **25A**, 271 (1986).
- 20 - J. Livage and M. Henry, *Ultrastructure Processing of Advanced Ceramics*, p. 183, J. Wiley and Sons Inc. publishers, New-York (1988).
- 21 - R. C. Mehrotra and R. Bohra, *Metal Carboxylates*, Academic Press, London (1983).