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A Solution Chemistry Study of Nonhydrolytic Sol−Gel Routes to Titania

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The etherolysis/condensation of $TiCl_4$ by diisopropyl ether ($^iPr_2O$) as well as the direct condensation between $TiCl_4$ and $Ti(O^iPr)_4$ are efficient nonhydrolytic sol−gel routes to titania. A comparison of the solution chemistry of the two routes was performed by means of NMR spectroscopy. In both cases the condensation is slow at room temperature; the true precursors are titanium chloroisopropoxides in equilibrium through fast ligand-exchange reactions. The condensation takes place at 100 °C after an induction period which drastically depends upon the O^iPr/Ti ratio in the reaction mixture. This behavior is related to the composition of the starting chloroisopropoxides mixture. The key species in the induction process appears to be $Ti(O^iPr)Cl_3$, which catalyzes the first condensation reactions.

1. Introduction

The sol−gel process, based on the hydrolysis−condensation of metal alkoxides or salts, has found increasing applications in the preparation of oxide ceramics and glasses since the past 20 years.[1] More recently, nonaqueous sol−gel approaches to oxide materials have resulted in some works which have been recently surveyed.[2] The main nonhydrolytic routes reported involve the reaction of a metal chloride with either a metal alkoxide or an organic ether, acting as oxygen donors:

$$MCl_n + M(OR)_n \rightarrow 2MO_{n/2} + nRCl \qquad \text{alkoxide route}$$

$$MCl_n + (n/2)\, ROR \rightarrow MO_{n/2} + nRCl \qquad \text{ether route}$$

In these routes, the formation of the M−O−M bridges results from the condensation between M−Cl and M−OR functions, according to:

$$\equiv M{-}Cl + \equiv M{-}O{-}R \rightarrow \equiv M{-}O{-}M\equiv + R{-}Cl \qquad \text{condensation} \quad (1)$$

In the ether route, the alkoxide functions are formed in situ by alkoxylation ("etherolysis") of M−Cl functions:

$$\equiv M{-}Cl + R{-}OR \rightarrow \equiv M{-}OR + R{-}Cl \qquad \text{alkoxylation} \quad (2)$$

These reactions are usually quite slow at room temperature; in most cases, the oxide formation requires heating between 80 and 150 °C. Actually, the main reaction that takes place at room temperature in mixtures of metal chlorides and metal alkoxides is the redistribution (ligand exchange) between the alkoxide groups and the chlorine atoms which leads to a mixture of metal chloroisopropoxides:[3−6]

$$\equiv M{-}Cl + \equiv M{-}OR \rightarrow \equiv M{-}OR\equiv + \equiv M{-}Cl \qquad \text{redistribution} \quad (3)$$

In the same way, the main reaction that takes place at room temperature between ethers and metal chlorides is the formation of a Lewis adduct, $MCl_n{\cdot}xR_2O$, such as $TiCl_4{\cdot}2Et_2O$[7] for instance.

A variety of transition metal oxides,[8] metal oxides[9] or nonmetal oxides[10] as well as multicomponent oxides[11,12] have been very recently obtained using these nonhydrolytic sol−gel routes. However, very little is known on the mechanism and kinetics of the reactions involved. Actually, prior to their use for the preparation of oxides, the condensation and alkoxylation reactions had been scarcely described.

Many studies have been devoted to the understanding of the hydrolysis and condensation reactions in aqueous sol−gel processes.[1] Such studies are lacking in the case of nonhydrolytic sol−gel processes. In this paper we report some NMR results concerning the kinetics of the condensation and alkoxylation reactions in the systems $Ti(O^iPr)_4/TiCl_4$ and $TiCl_4/^iPr_2O$. Several reasons led us to investigate the solution chemistry of these systems:

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1. First, the case of titanium well illustrates the differences between conventional and nonhydrolytic sol−gel: actually, titanium alkoxides are extremely reactive toward hydrolysis and condensation, and the use of chemical modifiers (acetic acid or acetylacetonate for instance) is necessary to obtain titanium gels. On the other hand, the nonhydrolytic condensation between Ti−Cl and Ti−OR is quite slow, and titania gels are easily obtained using either the alkoxide or the ether route.[13,14]

2. Second, we found that in nonhydrolytic sol−gel routes to titania the reaction rates as well as the structure and texture of the oxide were highly dependent on the route used and on the stoichiometry of the reactants.[14,15] For instance, the gel time at 110 °C is about 2−3 times shorter in the ether route ($^iPr_2O$) than in the alkoxide route ($Ti(O^iPr)_4$).[14]

2. Experimental Section

Titanium tetrachloride and titanium tetraisopropoxide were obtained from Aldrich and used without further purification. Diisopropyl ether was obtained from Aldrich and distilled before use over sodium. The NMR solvents (chloroform, deuterated chloroform, and deuterated toluene) were dried and distilled before use. All manipulations were carried out in an argon atmosphere.

Solutions of titanium tetrachloride and titanium tetraisopropoxide with the overall formula Ti $(O^iPr)_xCl_{4-x}$ (x between 4 and 0.5) were prepared by mixing at room temperature x moles of titanium tetraisopropoxide and $4 - x$ moles of titanium tetrachloride in chloroform or deuterated chloroform ($C = 1$ mol/L) in a Schlenk tube under dry argon. Solutions of titanium tetrachloride and two molar equivalents of diisopropyl ether in chloroform ($C = 1$ mol/L) were prepared in the same manner. ^1H and ^{13}C NMR spectra were performed after about 10 min at room temperature. For the kinetic studies of the condensation process, the solutions were immediately transferred in 5 mm NMR tubes which were then sealed under vacuum. The tubes were kept at the desired temperatures (25 or 100 °C) in a thermostated bath and withdrawn at convenient time intervals for the ^1H NMR measurements. For variable-temperature ^1H NMR, a 1/1 mixture of titanium tetrachloride and titanium tetraisopropoxide in deuterated toluene ($C = 0.4$ mol/L) was prepared and transferred into a NMR tube which was then sealed.

NMR experiments (^1H and ^{13}C) at room temperature were carried out on a 250 MHz and a 400 MHz Bruker spectrometer. Variable-temperature ^1H NMR experiments were carried out on a 250 MHz Bruker spectrometer between −70 and 30 °C. The kinetic studies were carried out on a 200 MHz Bruker spectrometer. The chemical shift reference was the tetramethylsilane.

3. Results and Discussion

3.1. Reactions in $TiCl_4/Ti(O^iPr)_4$ Solutions. ^1H NMR spectroscopy has been used to monitor the reactions that take place at room temperature and at 100 °C between $TiCl_4$ and $Ti(O^iPr)_4$.

(a) At Room Temperature. Solutions of $TiCl_4$ and $Ti(O^iPr)_4$ with overall O^iPr/Ti ratios between 0.5 and 4 were prepared in $CHCl_3$. The condensation between $Ti-O^iPr$ and Ti−Cl groups appeared very slow at room temperature: essentially no isopropyl chloride was detected after 90 h at 20 °C for a O^iPr/Ti ratio of 2. Thus, the only reaction that takes place at room temperature is the well-known redistribution of the chloride and alkoxide substituents around the titanium atoms, which leads in solution to an equilibrated mixture of $TiCl_{4-x}(O^iPr)_x$ species ($0 \leq x \leq 4$).[6]

Table 1. ^{13}C and ^1H Chemical Shifts (ppm) in $TiCl_4/Ti(O^iPr)_4$ Solutions in Chloroform as a Function of the Overall O^iPr/Ti Ratio

O^iPr/Ti	δ (CH) ^{13}C (^1H)	δ (CH_3) ^{13}C (^1H)
4	74.7 (4.41)	26.8 (1.16)
3.5	79.1 (4.62)	26.1 (1.24)
3	82.1 (4.80)	25.5 (1.26)
2.5	84.9 (4.89)	25.4 (1.37)
2	88.3 (4.88)	25.6 (1.47)
1.5	92.2 (/)	25.4 (/)
1	96.8(4.91)	25.3 (1.44)
0.5	96.7(4.91)	25.3 (1.44)

Table 2. Estimation of the Molar Percentages of $Ti(O^iPr)_iCl_{4-i}$ Species in $TiCl_4/Ti(O^iPr)_4$ Mixtures, Calculated for Different (O^iPr)/Ti Ratios Assuming $K_i = 10^{-4}$

O^iPr/Ti	1	1.7	2	2.3
% $TiCl_4$	1	1×10^{-3}	1×10^{-6}	4×10^{-10}
% $Ti(O^iPr)Cl_3$	98	30	1	2×10^{-2}
% $Ti(O^iPr)_2Cl_2$	1	70	98	70
% $Ti(O^iPr)_3Cl$	1×10^{-6}	2×10^{-2}	1	30
% $Ti(O^iPr)_4$	1×10^{-16}	4×10^{-10}	1×10^{-6}	1×10^{-3}

Weingarten and Van Wazer[6] reported that this exchange between O^iPr and Cl ligands was too fast to determine the composition of the chloroisopropoxide mixtures by ^1H NMR, using a 60 MHz spectrometer. In our experiments, although we used higher field spectrometers (250 or 400 MHz) and ^{13}C as well as ^1H, the resonances corresponding to the different $TiCl_x(O^iPr)_{4-x}$ species were still unresolved. Whatever the O^iPr/Ti ratio, our ^{13}C NMR spectra showed only two peaks arising from the CH_3 and CH groups; in the same way, the ^1H NMR spectra showed only one doublet and one septuplet corresponding to the CH_3 and CH resonances, respectively (Table 1).

Consequently, it was not possible to determine the composition of these mixtures using NMR. However, Weingarten and Van Wazer[6] found that the heats of redistribution for the $TiCl_4/Ti(O^iPr)_4$ system were strongly exothermic, indicating a large deviation from random scrambling. The three equilibrium constants of the form

$$K_i = \frac{[TiCl_{5-i}(O^iPr)_{i-1}][TiCl_{3-i}(O^iPr)_{i+1}]}{[TiCl_{4-i}(O^iPr)_i]^2} \quad \text{with } i = 1, 2, 3$$

evaluated from their data are small, $K_i \approx 10^{-4}$. A rough estimation of the relative concentrations of the $TiCl_x(O^iPr)_{4-x}$ species for different (O^iPr)/Ti is reported in Table 2.

Accordingly, in 1:1 $TiCl_4/Ti(O^iPr)_4$ mixtures (O^iPr /Ti = 2), the main precursor should be by far $Ti(O^iPr)_2Cl_2$ (note that % $Ti(O^iPr)_2Cl_2$ would be 94% with $K_i = 10^{-3}$ and 99.4% with $K_i = 10^{-5}$). The concentrations of $Ti(O^iPr)_3Cl$ and $Ti(O^iPr)Cl_3$ should be in the order of 1% and those of $TiCl_4$ and $Ti(O^iPr)_4$ should be negligible. Weingarten and Van Wazer[6] reported that $TiCl_2(O^iPr)_2$ is oligomeric in solution, whereas $TiCl_4$, $TiCl_3(O^iPr)$, and $Ti(O^iPr)_4$ are monomeric. As titanium alkoxides and

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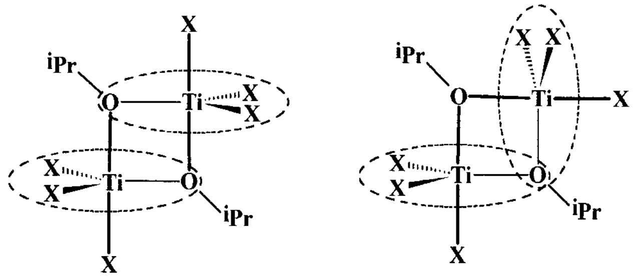
Scheme 1. Basic Structures for $TiX_3(O^iPr)$ Dimers[a]



[a] In the case of $[TiCl_2(O^iPr)_2]_2$, one of the X substituents on each Ti atom is a μ_1-O^iPr group and the others are μ_1-Cl groups.

chloroalkoxides associate by forming alkoxo bridges, at least two signals are expected in each C*H* and CH_3 region, arising from bridging and nonbridging alkoxides. However, as mentioned above, this is not the case at room temperature. Thus, we performed a variable-temperature ^{1}H NMR study for this composition (O^iPr/Ti = 2). At −70 °C, several resonances (about 10) were observed in the C*H* and CH_3 regions. This observation confirms the oligomeric nature of $Ti(O^iPr)_2Cl_2$ in solution, but also demonstrates the presence of several $[Ti(O^iPr)_2Cl_2]_n$ isomers; the simple spectrum obtained at room temperature for the composition O^iPr/Ti = 2 results from a fast exchange between such isomers. At first glance, the high number of signals may seem surprising. However, if $TiCl_2(O^iPr)_2$ was a dimer, for instance, with Ti atoms in a 5-fold coordination bonded by two μ_2-alkoxo bridges (as reported for $[Ti(OEt)_2Cl_2]_2$[16] in the solid state), there would be eight possible diastereoisomers (depending on the positions of the μ_1-O^iPr and the two μ_1-Cl ligands on each Ti atom) deriving from two different structures (Scheme 1).

(b) At 100 °C. The progress of the condensation between Ti−Cl and Ti−O^iPr at 100 °C was monitored by proton NMR for solutions of $TiCl_4$ and $Ti(O^iPr)_4$ with overall O^iPr/Ti ratios of 1, 1.7, 2, and 2.3 in chloroform. The condensation led to the formation of ^iPrCl only, confirming that only Ti−Cl/Ti−O^iPr condensation took place. For a O^iPr/Ti ratio of 2, which corresponds to the ratio used in the alkoxide route, the final condensation extent ξ (i.e., the ^iPrCl produced over the amount expected for 100% yield) was 0.95 high, corresponding to an average composition $TiO_{1.9}(O^iPr)_{0.1}Cl_{0.1}$. This composition is in good agreement with the composition (determined by elemental analysis) of titania gels prepared without solvent.[8] Thus, the presence of a solvent does not significantly modify the final condensation degree of the titania gel.

The condensation extent ξ was plotted against time in Figure 1 for the different O^iPr/Ti ratios. All the $\xi = f(t)$ curves display a quite unusual sigmoid shape; moreover, the "induction period" needed to initiate the condensation strongly depends on the initial O^iPr/Ti ratio.

This behavior has to be related to the drastic effect of the O^iPr/Ti ratio on the composition of the chloroisopropoxide mixture (Table 1), due to the low values of the equilibrium constants K_i. The decrease of the induction period, t_{ind}, observed when O^iPr/Ti increases from 1 ($t_{ind} \sim 0.2$ h) to 2.3 ($t_{ind} \sim 300$ h) cannot be accounted for by the variation of concentration in O^iPr or Cl groups. The key species appears to be $Ti(O^iPr)Cl_3$: the higher its concentration, the shorter the induction time. The extremely long induction time observed when O^iPr/Ti = 2.3 shows that $Ti(O^iPr)_2Cl_2$ and $Ti(O^iPr)_3Cl$ are practically inert toward condensation in the absence of $Ti(O^iPr)Cl_3$. Conversely, the decrease in the induction time observed when O^iPr/Ti = 2 shows that $Ti(O^iPr)_2Cl_2$ is much more reactive in the presence of a small amount of $Ti(O^iPr)Cl_3$. These results suggest that, during the induction process, the first condensations between Ti−Cl and Ti−O^iPr functions are efficiently catalyzed by $Ti(O^iPr)Cl_3$. As a matter of fact, the nonhydrolytic condensation between Si−Cl and Si−OR bonds is known to be catalyzed by Friedel−Crafts catalysts, such as $FeCl_3$ or $AlCl_3$.[17,18] $Ti(O^iPr)Cl_3$ is a strong Lewis acid, able to form 1:2 adducts with a variety of Lewis bases.[19,20] In addition, it has been shown that $Ti(O^iPr)Cl_3$ is a very active catalyst for the polymerization of olefins, whereas $Ti(O^iPr)_2Cl_2$ is inactive.[21] This behavior is possibly related to the fact that the first species is monomeric in solution, whereas the latter is oligomeric.

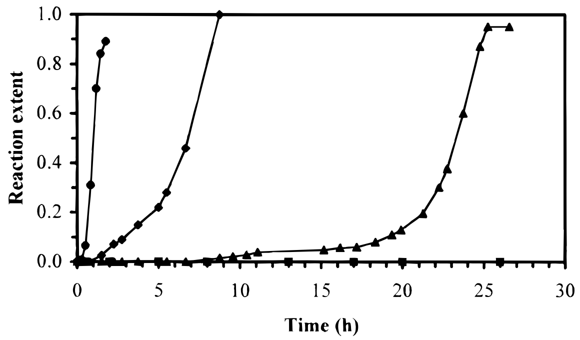


Figure 1. Condensation extent at 100 °C in mixtures of titanium tetrachloride and titanium tetraisopropoxide in chloroform of various overall O^iPr/Ti ratios: (●) O^iPr/Ti = 1; (◆) O^iPr/Ti = 1.7; (■) O^iPr/Ti = 2; (▲) O^iPr/Ti = 2.3.

The first step in the condensation of Ti−Cl and Ti−OiPr bonds is probably the formation of a μ_2-alkoxo bridge, as in the $Ti(O^iPr)_2Cl_2$ oligomers. The inertness of these oligomers in the absence of $Ti(O^iPr)Cl_3$ suggests that a weakening of the Ti−Cl bond by formation of a μ_2-Cl bridge with $Ti(O^iPr)Cl_3$ is required for the condensation to occur, for instance by a concerted elimination of ^iPrCl, as represented in Scheme 2. Although μ_2-Cl bridges are less stable than μ_2-OiPr, they were recently observed in $TiCl_4$ crystalline complexes of $Ti(O^iPr)Cl_3$ or $TiCl_4$ with 2-propanol. [22]

The sigmoid shape of the $\xi = f(t)$ curves suggests an autocatalytic process, i.e., that the condensation is catalyzed by the reaction products. To check this possibility, the condensation of $TiCl_4$ and $Ti(O^iPr)_4$ (O^iPr/Ti = 2) at 100 °C was also followed in the presence of either titania precipitate or isopropyl chloride, which

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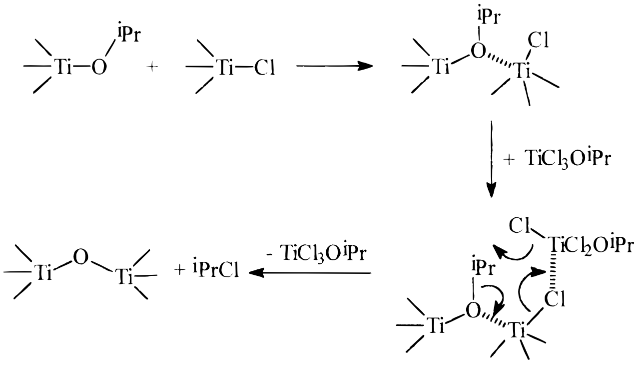
Scheme 2. Schematic Representation of the Nonhydrolytic Condensation between Ti−OiPr and Ti−Cl Functions, Catalyzed by $TiCl_3(O^iPr)$



are the final products of the condensation. The curves $\xi = f(\text{time})$ thus obtained were similar to the one obtained without titania or isopropyl chloride; in particular, the induction time was not shortened, showing that these products do not catalyze the condensation. Thus, the condensation is likely catalyzed by the intermediate condensation products (titanium oxochloroisopropoxides). As a matter of fact, titanium oxychloride, $TiOCl_2$, is an even more active catalyst for the polymerization of olefines than $Ti(O^iPr)Cl_3$.[21]

3.2. Reactions in $TiCl_4$/2 $^iPr_2O$ Solutions. The reaction of $TiCl_4$ with $^iPr_2O$ ($^iPr_2O/TiCl_4 = 2$) in sealed NMR tubes was monitored by proton NMR at room temperature and at 100 °C.

(a) At room temperature. $TiCl_4$ reacts with $^iPr_2O$ even at room temperature, leading to the formation of ^iPrCl and the consumption of $^iPr_2O$. In this case, two reactions are involved in the formation of $^iPr_2O$, the alkoxylation and the condensation reactions:

$$\equiv\text{Ti}-\text{Cl} + {}^i\text{PrO}-{}^i\text{Pr} \rightarrow \equiv\text{Ti}-\text{O}^i\text{Pr} + {}^i\text{Pr}-\text{Cl} \qquad \text{alkoxylation}$$

$$\equiv\text{TiO}-{}^i\text{Pr} + \equiv\text{Ti}-\text{Cl} \rightarrow \equiv\text{TiO}-\text{Ti}\equiv + {}^i\text{Pr}-\text{Cl} \qquad \text{condensation}$$

The amount of ^iPrCl formed by alkoxylation, $^iPrCl_{alk}$, is equal to the amount of $^iPr_2O$ consumed (obtained by integration of the $^iPr_2O$ signal). The amount of ^iPrCl formed by condensation, $^iPrCl_{cond}$, obtained by difference between the total amount of ^iPrCl formed, $^iPrCl_{tot}$ (obtained by integration of the ^iPrCl signal), and $^iPrCl_{alk}$.

Figure 2 displays the extent of alkoxylation and condensation reactions, ξ_{alk} and ξ_{cond}, as a function of time at room temperature. The alkoxylation proceeds in two steps. The first alkoxylation is quite fast and is virtually completed after 20 min only ($\xi_{alk} = 0.49$, which corresponds to the composition $Ti(O^iPr)_{0.98}Cl_{3.02}$). This finding is in good agreement with the results of Hamilton et al.[7] who reported that the addition compound of $TiCl_4$ with diisopropyl ether was not stable at room temperature (in contrast with other ethers, such as dimethyl, diethyl, or di-*n*-butyl ethers or dioxane), but readily decomposed to $Ti(O^iPr)Cl_3$ and ^iPrCl. The second alkoxylation step is about 100 times slower: ξ_{alk} increases to 0.71 after 5.5 h and 0.78 after 28 h. The condensation reaction was not detected at this stage. However, after 94 h at room temperature ξ_{cond} was 0.14 high (not shown in Figure 2) whereas it was less than 0.03 high for a 1:1 mixture of $TiCl_4$ and $Ti(O^iPr)_4$ in the same conditions.

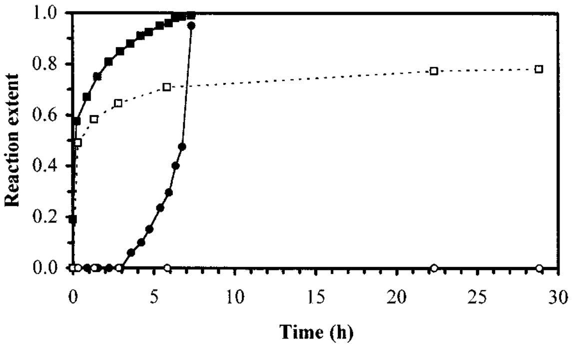


Figure 2. Alkoxylation and condensation extent at 20 °C (dotted lines) and 100 °C (full lines) in $TiCl_4$/2 $^iPr_2O$ solutions in chloroform: (□) alkoxylation at 20 °C; (○) condensation at 20 °C; (■) alkoxylation at 100 °C; (●) condensation at 100 °C.

(b) At 100 °C. The extents of alkoxylation and condensation reactions at 100 °C are reported in Figure 2. The condensation started after about 3 h, when the alkoxylation was completed at about 85%, which corresponds to the average bulk composition $Ti(O^iPr)_{1.7}Cl_{2.3}$. The curve obtained by plotting ξ_{cond} against time still shows a sigmoid shape. However, the induction period is clearly much shorter than for the 1:1 mixture of $TiCl_4$ and $Ti(O^iPr)_4$. The precipitation occurred when ξ_{cond} was 0.2 only (average bulk composition $TiO_{0.4}(O^iPr)_{1.4}Cl_{1.8}$). After 7.5 h at 100 °C, the alkoxylation reaction was virtually complete (99%) and the condensation extent was 0.95 high which corresponds to an average composition $TiO_{1.9}(O^iPr)_{0.08}Cl_{0.12}$.

The large difference in induction period observed between the alkoxide ($O^iPr/Ti = 2$) and the ether routes may be explained considering the difference in composition of the starting chloroalkoxide mixtures. When the condensation starts in the ether route, the alkoxylation is not completed. Thus, the O^iPr/Ti ratio in the chloroisopropoxide mixture is lower than 2, and the amount of $Ti(O^iPr)Cl_3$ is higher than in the alkoxide route ($O^iPr/Ti = 2$), which accounts for the shorter induction time. Actually, the second alkoxylation step is much slower than the first one (Figure 2) and one might expect an even shorter induction time in the ether route, intermediate between those observed for the O^iPr/Ti ratios 1 and 1.7 in the alkoxide route. However, in the ether route the chloroisopropoxide species are diluted by the ^iPrCl (arising from the alkoxylation) and the unreacted $^iPr_2O$, whereas there is no solvent in the alkoxide route. In addition, a proportion of the $Ti(O^iPr)Cl_3$ molecules is probably complexed by the unreacted $^iPr_2O$,[19,20] which should decrease their catalytic activity.

4. Conclusions

The redistribution of O^iPr groups and Cl atoms plays a critical part in the nonhydrolytic sol−gel processes discussed here. Redistribution is by far the fastest reaction involved in these processes; accordingly, the true molecular precursors consist of a mixture of titanium chloroisopropoxides in equilibrium. In addition, due to the nonrandom nature of this redistribution, the concentration of the various chloroisopropoxides species is highly sensitive to the mean composition (O^iPr/Ti ratio) of the chloroisopropoxide mixture.

The nonhydrolytic condensation between Ti−Cl and Ti−O^{i}Pr groups is very slow at room temperature in both routes. At 100 °C, the initial rate of the reaction is low; after an induction time the condensation rate increases quickly, indicating an autocatalysis of the condensation, presumably by the intermediate oxochloroisopropoxides.

In the $TiCl_4$/Ti(O^{i}Pr)$_4$ system, the induction time mainly depends on the concentration of Ti(O^{i}Pr)Cl_3 (which in turn depends on the O^{i}Pr/Ti ratio) which suggests that this species catalyzes the first condensation steps. As a consequence, chloroisoproxide mixtures with a O^{i}Pr/Ti ratio larger than 2 are fairly stable at 100 °C, due to the extremely low level of Ti(O^{i}Pr)Cl_3 in these mixtures.

In the ether route, the alkoxylation reaction rapidly leads to the formation of Ti(O^{i}Pr)Cl_3; the second alkoxylation step is much slower and is not completed when the condensation starts. Therefore, the concentration of Ti(O^{i}Pr)Cl_3 is higher than in the alkoxide route, which leads to a shorter induction time, and thus to a shorter gel time.

Finally, the nonhydrolytic condensation between Ti−O^{i}Pr and Ti−Cl functions strongly depends on such factors as the composition of the chloroisopropoxide mixture, the molecular complexity of each chloroisopropoxide species, and their Lewis acid character. Accordingly, a great variety of mechanisms and reaction rates may be expected for nonhydrolytic sol−gel routes to a given metal oxide, depending on the nature of the oxygen donor (alkoxide, ether, alcohol, ...), of the alkyl group and of the halogen atom.

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