

Hydrolysis and Condensation Reactions of Transition Metal Alkoxides: Calorimetric Study and Evaluation of the Extent of Reaction

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The behavior of titanium and zirconium alkoxides towards complexation and water addition is analyzed through water titration and calorimetric experiments. A simple model is presented, which allows evaluation of the mean hydrolysis and condensation constants, K_h and K_c , of both pure and complexed transition metal alkoxides in the sol state, through the analysis of consumed water versus initial hydrolysis ratio curves. These constants allow comparison of the extents of the hydrolysis and condensation reactions for sols obtained from several alkoxide precursors. The complexation ratio only affects the condensation constant K_c , whereas the hydrolysis constant K_h remains unchanged. Analysis of the

K_h/K_c ratios has shown that in the sol state, silanol Si-OH groups are more stable than the Ti-OH or Zr-OH groups. Moreover, this study has shown that the proton concentration not only affects the kinetics, but also the final composition of the system. Calorimetric studies of the complexation and hydrolysis/condensation reactions have highlighted the role of coordination unsaturation of the transition metal alkoxides in the exothermicity of these reactions, clearly demonstrating that coordination unsaturation is the driving force behind the reactivity of these alkoxides towards nucleophilic species (e.g. water, complexing ligands, polar solvents).

Introduction

Sol-gel processes are a means of preparing dispersed materials through the growth of metal oxo-polymers in a solvent^{[1][2][3]}. Indeed, sol-gel chemistry is based on inorganic polymerization reactions. Metal oxo-polymers can be obtained through hydrolysis and condensation of molecular precursors such as metal alkoxides $\text{M}(\text{OR})_n$ (where M = Si, Ti, Zr, Al, Sn, Ce; OR is an alkoxy group, and n is the valence or the oxidation state of the metal). In the case of silicon alkoxides, these reactions are known to be equilibrium processes^[4]. The present work demonstrates, through the use of ^{17}O -NMR spectroscopy, that, in the sol state, the hydrolysis and condensation reactions of titanium alkoxides also exhibit reversible behavior. These reactions start with the nucleophilic addition of hydroxylated groups to the electrophilic metal atom M, which leads to an increase of the coordination number of the metal atom in the transition state^[3]. Consequently, the chemical reactivity of metal alkoxides toward nucleophilic reactions largely depends on the electrophilic character of the metal and its ability to increase its coordination number.

Silicon has a low electrophilicity and it remains tetra-coordinated in the $\text{Si}(\text{OR})_4$ alkoxide precursors, as well as in its oxide. Thus, silicon alkoxides are not very reactive and gelation times range from hours to several days. On the other hand, many non-silicate metal alkoxides including transition metal alkoxides, lanthanides, aluminum, tin alkoxides, etc. are coordinatively unsaturated and in most

cases the metallic center exhibits a higher electrophilicity than silicon^[5]. These alkoxides are consequently very reactive towards nucleophilic reagents. Both the higher electrophilicity and the coordination unsaturation of the metallic center can be invoked in explaining this higher reactivity of non-silicate alkoxides. However, coordination unsaturation seems to be the key parameter: titanium ($\chi = 1.32$), zirconium ($\chi = 1.29$), and cerium ($\chi = 1.17$) have electronegativities χ lower than that of silicon ($\chi = 1.74$), whereas the value for tin ($\chi = 1.89$) is higher. Thus, the difference in electrophilicities of the metal atoms does not seem to be the key parameter to account fully for the much higher reactivity of these non-silicate tetravalent alkoxides. In the work described herein, we confirm experimentally that coordination unsaturation is the main driving force behind the reactivity of transition metal alkoxides.

Hydrolysis/condensation reactions of silicon alkoxides are rather slow, and consequently they can be monitored using many analytical techniques (e.g. chromatography, infrared spectroscopy^[6]). Moreover, silicon has an isotope with a nuclear spin $I = 1/2$, so that ^{29}Si -NMR experiments offer the possibility of accurately characterizing the different species (monomers, oligomers, etc.) generated by hydrolysis and condensation^{[1][7][8][9][10]}. This accurate NMR speciation allows the determination of kinetic and thermodynamic constants for the different reactions occurring during the formation of silica-based sol-gel materials (hydrolysis, condensation, transalcoholysis, esterification).

Hydrolysis and condensation reactions of non-silicate metal alkoxides must, on the other hand, be controlled by using inhibitors such as high proton concentration^[8] or complexing ligands^[9]. However, even in the presence of inhibitors, the kinetics are too fast to be monitored by the usual techniques employed for the characterization of silicon-based systems. Moreover, many of the most interesting systems, as far as the field of material science is concerned^{[1][2][3][4][5][6][7][8][9][10][11][12]}, are not amenable to study by NMR because they are paramagnetic (Fe^{III} , $\text{Mn}^{\text{II,III}}$, Co^{II} , etc.) or because they possess a strong quadrupolar moment ($^{47}\text{Ti}^{\text{IV}}$, $^{49}\text{Ti}^{\text{IV}}$, $^{91}\text{Zr}^{\text{IV}}$, $^{93}\text{Nb}^{\text{V}}$, etc.). Since it is extremely difficult to get detailed and specific information on the hydrolysis/condensation reactions of transition metal alkoxides, an alternative approach is to collect macroscopic information and to rely upon a model to estimate the chemical composition of the polycondensates. This approach has been very successful with regard to organic polymers. Preferentially, the analysis of the polycondensates should be done in the wet state, before any drying process that can result in further condensation reactions and therefore modify the chemical composition of the system. The development of new tools could be especially helpful in classifying the behavior of metal alkoxides towards complexation, hydrolysis, and condensation reactions. A better knowledge of the extent of these reactions is of paramount importance because the structures and morphologies of the resulting networks are strongly dependent on their relative contributions. Control of the growth of transition metal oxo-polymers can be achieved through changes in the chemical reactivity of each component. The hydrolysis ratio ($H = \text{H}_2\text{O}/M$), the use of a catalyst^[8], of complexing ligands^[11], or of a templating medium^{[12][13]} are the main factors that must be mastered by the sol-gel chemist in order to achieve this control.

Taking titanium and zirconium alkoxides as examples, two main points will be discussed in this article: (i) the calorimetric behavior of transition metal alkoxides towards complexation and hydrolysis, and (ii) a model leading to an evaluation of mean hydrolysis and condensation pseudo-equilibrium (metastable equilibrium) constants of transition metal alkoxides through the analysis of water titration curves. This simple model, based on constants evaluated from a mean polymer formula, leads to a pertinent classification of the alkoxides, and allows determination of the extents of the hydrolysis and condensation reactions. However, because this model is simple, it necessarily involves certain approximations, which, of course, imply limitations. These limitations will be discussed in the context of the evolution of silica-based systems, for which hydrolysis and condensation constants have been evaluated using both the model and the speciation provided by ^{29}Si -NMR experiments.

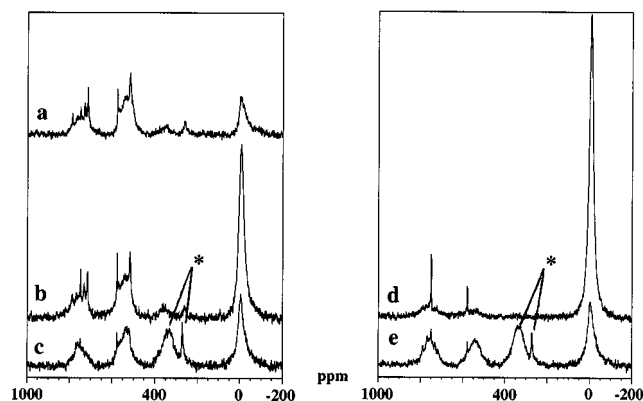
Results and Discussion

Evidence of the Reversibility of Hydrolysis/Condensation Reactions

The ^{17}O -NMR spectrum of sample ① was recorded just before the second hydrolysis (a), 5 min. after the second

hydrolysis (b), and after 24 h of ageing (c); the ^{17}O -NMR spectrum of sample ② was recorded 5 min. after the second hydrolysis (d), and after 24 h of ageing (e). The spectra obtained are presented in Figure 1.

Figure 1. (Left:) ^{17}O -NMR spectra of sample ①, just before the second hydrolysis (a), 5 min. after the second hydrolysis (b), and 24 h after (c). (Right:) ^{17}O -NMR spectra of sample ②, 5 min. after the second hydrolysis (d), and 24 h after (e).^[a]



^[a] For sample ①, the water used for the first and second hydrolyses was 5%-enriched in oxygen-17. – For sample ②, the first hydrolysis was performed with unenriched water and the second hydrolysis with 10%-enriched water. The total hydrolysis ratio of the sample was equal to 2. – The two peaks (see *) at $\delta = 273$ (enol form of free acetylacetonate) and at about $\delta = 340$ (acetylacetonate bonded to titanium) result from the isotopic ^{17}O exchange between H_2O and acacH (ketolization).

Spectrum (a) has already been described in a previous report^[28]. Five signals are observed, which can be assigned as follows:

$\delta = 800-650$	$\mu_2\text{O}$ oxo-bridges
$\delta = 600-450$	$\mu_3\text{O}$ oxo-bridges
$\delta = 400-300$	$\mu_4\text{O}$ oxo-bridges
$\delta = 300-200$	$\mu_5\text{O}$ oxo-bridges
$\delta \approx 0$	H_2O

A second addition of water to sample ① resulted, after a short time spectrum (b)], in a significant increase in the intensity of the H_2O signal ($\delta = -50$ to 50), and in a slight increase in the intensity of the signals of the $\mu_2\text{O}$ and $\mu_3\text{O}$ oxo bridges (see Table 1); the intensities of the $\mu_4\text{O}$ and $\mu_5\text{O}$ oxo bridge signals remained the same, within an experimental error of $\pm 10\%$. The ratio of residual water to oxo bridges, $\text{H}_2\text{O}/\Sigma_{\text{oxo}}$, was around 1:1. After 24 h of ageing, the intensities of the $\mu_2\text{O}$ and $\mu_3\text{O}$ oxo-bridge signals decreased slightly. The main evolution of the spectrum was seen in the $\delta = 200-400$ region, where a significant increase of the intensities was observed. In this chemical shift region, two kinds of signals can be observed:

- the signals of the $\mu_4\text{O}$ and $\mu_5\text{O}$ oxo bridges, which have been previously observed in the spectra (a) and (b);
- the signals of free and titanium-bound acac ($\delta = 273$ and $300-400$, respectively).

The chemical shift and the width of the narrow peak ($\delta = 272$, $w = 370$ Hz) correspond exactly to those of free acac, and make the assignment of this peak to the free ligand unambiguous. The signal in the range $\delta = 300-400$ can be

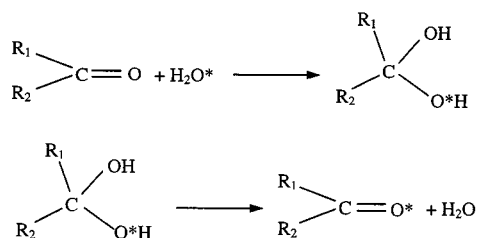
Table 1. Intensities of the peaks of the spectra of Figure 1. For sample ①, the water used for the first and second hydrolyses was 5%-enriched in oxygen-17. For sample ②, the first hydrolysis was performed with unenriched water and the second hydrolysis with 10%-enriched water. The total hydrolysis ratio of the sample was equal to 2

		$\mu_2\text{O}$ ($\delta = 800\text{--}650$)	$\mu_3\text{O}$ ($\delta = 600\text{--}400$)	$\mu_4\text{O}$ or bonded acac ($\delta = 400\text{--}300$)	$\mu_5\text{O}$ or free acac water ($\delta = 300\text{--}200$)	(δ ca. 0)	sum of the intensities ^[a]
sample ①	before the 2 nd hydro- lysis (a)	4	7	1	<1	4	16
	5 min. after (b)	5	8	1	<1	14	28
	24 hours ageing (c)	4	7	5	1	9	26
sample ②	5 min. after (d)	2	3	—	—	25	30
	24 hours ageing (e)	7	6	5	1	10	29

^[a] The sum of the intensities of the spectra of samples ① and ② after the second addition of water and after 24 hours of ageing are equal within an experimental error of $\pm 10\%$ and the sum of the intensities of sample ① before the second hydrolysis is about half of that of sample ② after the second hydrolysis, within an experimental error of $\pm 15\%$.

assigned to both $\mu_4\text{O}$ oxo bridges (which are also observed in the spectrum recorded 5 min after the second hydrolysis) and to acac bonded to titanium. However, previous studies performed on acac-complexed and uncomplexed titanium butoxide have all shown a decrease in the intensity of the signal of the $\mu_4\text{O}$ bridges with time^[28]. The significant increase of intensity observed in this chemical shift region after 24 h of ageing can therefore be mainly assigned to the enrichment of acac in oxygen-17, according to the reaction described in Scheme 1.

Scheme 1. Reaction leading to ^{17}O enrichment of the ketones



Just after the second addition of water, the spectrum of sample ② was very different to that of sample ①. In spectrum (d), the signals due to the $\mu_2\text{O}$ and $\mu_3\text{O}$ oxo-bridges are weak, and the ratio of residual water to oxo bridges, $\text{H}_2\text{O}/\Sigma_{\text{oxo}}$, is around 6:1. The evolution of the spectrum of sample ② over a period of 24 h was drastic spectrum 2, (e)]. In fact, after 24 h of ageing, it became very similar to that of sample ① (see Table 1 for the intensities of the oxo bridge signals and the water signal). One could also observe the appearance of two signals in the 200–400 region, which can be assigned to free and titanium-bonded acac, respectively.

For these two samples, when the second hydrolysis takes place, many oxo-bridges are already present following the addition of the first mole of water. The difference between these two samples is the as follows: in the case of sample ①, these pre-formed oxo-polymers are 5%-enriched in oxygen-17, whereas in the case of sample ②, these oxo-polymers are initially unenriched. The second addition of water leads to a further hydrolysis of the pre-formed oxo-polymers, which results in the formation of new oxo-bridges. This second mole of water is only partially consumed by the hydrolysis reaction and some water remains in solution.

In the case of sample ①, the enrichment of the pre-formed polymers, of the new oxo bridges, and of the residual water is the same (5% in oxygen-17), whereas in sample ②, the unenriched pre-formed polymers are, after the second hydrolysis, in the presence of 10%-enriched water. The slight increase in the intensities of the $\mu_2\text{O}$ and $\mu_3\text{O}$ signals in spectrum (b) of sample ①, as well as the two weak $\mu_2\text{O}$ and $\mu_3\text{O}$ signals observed in spectrum (d) of sample ②, can be assigned to this further hydrolysis. On the other hand, the oxo-bridges that appear in the spectrum of sample ② after 24 h of ageing cannot be assigned to such a reaction because the intensities of these two peaks are only weakly modified after 24 h of ageing in the case of sample ①. This further modification of the spectrum of sample ② can therefore be attributed to ^{17}O exchange between the enriched water and the unenriched oxo-polymers. The pre-formed oxo-core is consequently accessible to nucleophilic species, and depolymerization/repolymerization reactions can occur. The depolymerization reactions imply the nucleophilic attack of a water molecule at the metallic center, and, therefore, an increase of its coordination. A mechanism can be proposed, in which the first step is the change of coordination of the acetylacetonate group from bidentate to monodentate; the water molecule can then occupy the empty coordination site and subsequently be incorporated into the network by intramolecular rearrangements^[14].

This experiment highlights the equilibrium behavior of the hydrolysis and condensation processes. It was performed at a low hydrolysis ratio ($H = 2$) in order to avoid any quantitativity problems: at a higher initial hydrolysis ratio, part of the oxo signal is lost due to the formation of large titanium oxo-polymers that cannot be detected using solution ^{17}O -NMR^[28]. However SAXS experiments^{[15][16]} have shown that the titanium oxo-polymer sols and gels synthesized under these conditions are tenuous (the fractal dimension of the titanium oxo-polymers varies between 1.5 and 2.5, depending on the hydrolysis, complexation, or proton ratio). The fact that the structure of the oxo-polymers is non-dense indicates a high surface-to-volume ratio, which will favor the equilibria between the polymers and the water and alcohol molecules present in the solution. In the sol state, the swollen titanium oxo-polymers are not kinetically "locked-in".

Evaluation of Hydrolysis/Condensation Constants Through Water Titration Data

Curves showing the consumed water h as a function of the initial hydrolysis ratio H of the various alkoxides are shown in Figures 2–4. These curves have been fitted using Equation 5 and the values of K_h and K_c obtained are reported in Table 2 (See Experimental Section).

Figure 2. Hydrolysis of $\text{Ti}(\text{OnBu})_4$: variation of the consumed water h with the initial hydrolysis ratio H at different complexation ratios r

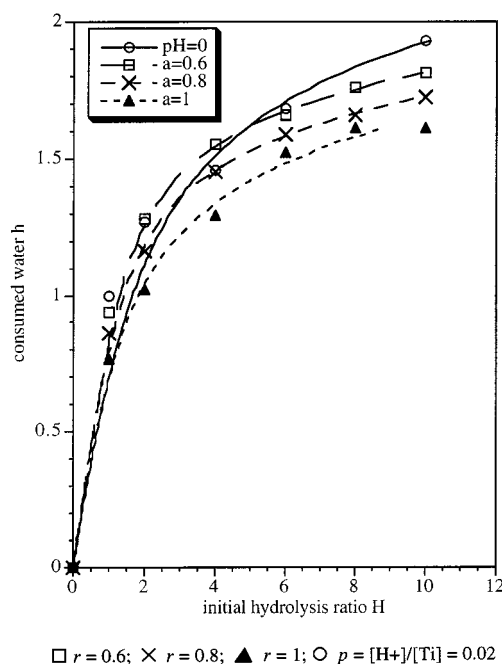
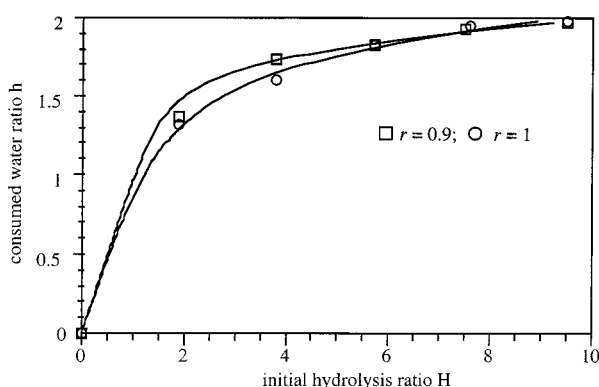


Figure 3. Hydrolysis of $\text{Zr}(\text{OnPr})_4$: variation of the consumed water h with the initial hydrolysis ratio H at different complexation ratios r



Titanium Oxide Based Sols

The curves $h = f(H)$ of $\text{Ti}(\text{OnBu})_4$ are presented in Figure 2. At low initial hydrolysis ratios ($H \leq 1$), the consumption of water is almost complete. At higher initial hydrolysis ratios, the water is only partially consumed and its consumption tends toward a limiting value that depends on the complexation ratio. The values of K_h and K_c calculated for this

Figure 4. Hydrolysis of $\text{Si}(\text{OEt})_4$: variation of the consumed water h with the initial hydrolysis ratio H at different pH values of the hydrolysis solution

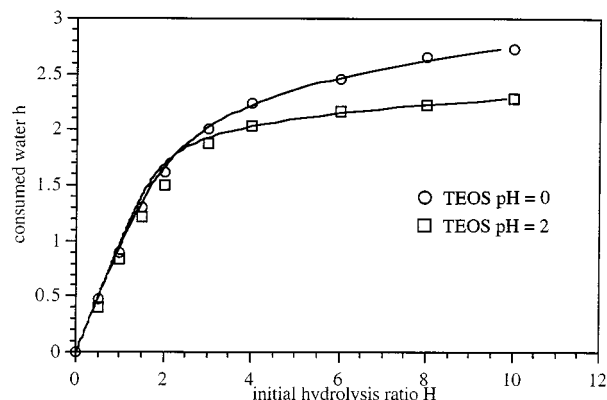


Table 2. Hydrolysis constants K_h and condensation constants K_c for reactions of $\text{Ti}(\text{OnBu})_4$, $\text{Zr}(\text{OnPr})_4$, $\text{Si}(\text{OEt})_4$, calculated using Equation 5

Sample	Hydrolysis constant K_h	Condensation constant K_c
$\text{Ti}(\text{OnBu})_4$ $r = 0.6$	0.51 ± 0.01	16 ± 2
$\text{Ti}(\text{OnBu})_4$ $r = 0.8$	0.52 ± 0.01	15 ± 1
$\text{Ti}(\text{OnBu})_4$ $r = 1$	0.52 ± 0.1	8 ± 4
$\text{Ti}(\text{OnBu})_4$ $p = [\text{H}^+]/[\text{Ti}] = 0.02$	0.55 ± 0.04	16 ± 5
$\text{Zr}(\text{OnPr})_4$ $r = 0.9$	3 ± 1	30 ± 10
$\text{Zr}(\text{OnPr})_4$ $r = 1$	1.8 ± 0.5	7 ± 3
$\text{Si}(\text{OEt})_4$ pH = 0	2.1 ± 0.2	6 ± 1
$\text{Si}(\text{OEt})_4$ pH = 2	1.2 ± 0.1	26 ± 6

alkoxide do not depend strongly on the experimental conditions: K_h is equal to 0.5 in all cases (hydrolysis of acac-modified precursors or acidic hydrolysis). However, the value of K_c seems to depend slightly on the complexation ratio, increasing marginally as the complexation ratio decreases. The ratio $K_c = K_c/K_h$ is always very high (between 16 and 32), indicating that the majority of Ti–OH groups are engaged in forming oxo bridges. It is possible to calculate the theoretical values of $k = [\text{M–O–M}]/[\text{M}(\text{OR})_4]$, h , $(h - k) = [\text{M–OH}]/[\text{M}(\text{OR})_4]$, and $(4 - r - h - k) = [\text{M–OR}]/[\text{M}(\text{OR})_4]$ from the values of K_h and K_c using Equations 5 and 6. Figure 5 shows the calculated consumed water ratio h , the condensation ratio k , the titanium hydroxyl ratio $(h - k)$ and the alkoxy ratio $(4 - r - h - k)$ as functions of the initial hydrolysis ratio H for $K_h = 0.51$ and $K_c = 16$ (i.e., for the complexation ratio $r = 0.6$). This simulation shows that the alkoxy ratio decreases very quickly: for an initial hydrolysis ratio $H = 10$, 90% of the alkoxy groups have been hydrolyzed. This simulation also shows that the Ti–OH ratio is very small at a low initial hydrolysis ratio; at higher initial hydrolysis ratios, however, the Ti–OH/Ti ratio becomes rather significant: at $H = 10$ it has a value of 0.5. This simulation is therefore an indirect proof of the presence in solution of such groups, the number of which increases with increasing initial hydrolysis ratio. The mean formula for the titanium oxo-polymers can be calculated from the fitted values of h , k , and r . As an

example, the mean formulae of the polymers obtained through hydrolysis ($0.5 < H < 10$) of one of the acac-modified samples ($r = 0.6$) are reported in Table 3. The self-consistency of this simple model can be checked by comparing the calculated Ti–OH/Ti ratio to that estimated from Karl-Fischer titrations. This estimation can be performed by carrying out the titration in two different solvents. The first one, 2-chloroethanol, is quite inert to the presence of M–OH groups, while the second one, methanol, reacts with M–OH groups to form M–O–Me groups with elimination of water. As a matter of fact, as shown in Figure 6 for the same sample (for example $r = 0.6$, $H = 2$), the measured consumption of water versus time in methanol solution is less than that measured in 2-chloroethanol. The difference between the two curves permits an evaluation of the M–OH/M ratio. This ratio was found to be 0.15, which is quite close to that calculated from the fitted K_h and K_c constants, and which leads to the following mean formula $[\text{TiO}_{1.09}\text{acac}_{0.6}(\text{OH})_{0.16}(\text{OR})_{1.06}]$.

Figure 5. Simulation of the curves h , k , $(h - k)$, $(4 - r - h - k) = f(H)$ for $K_h = 0.51$ and $K = 16$

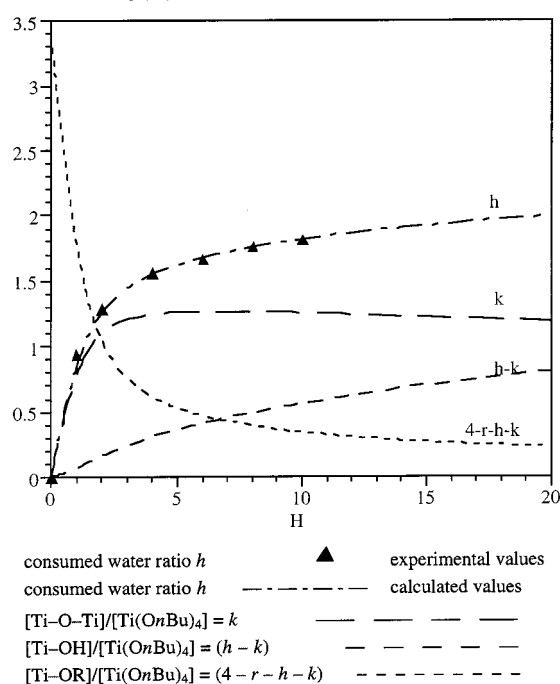
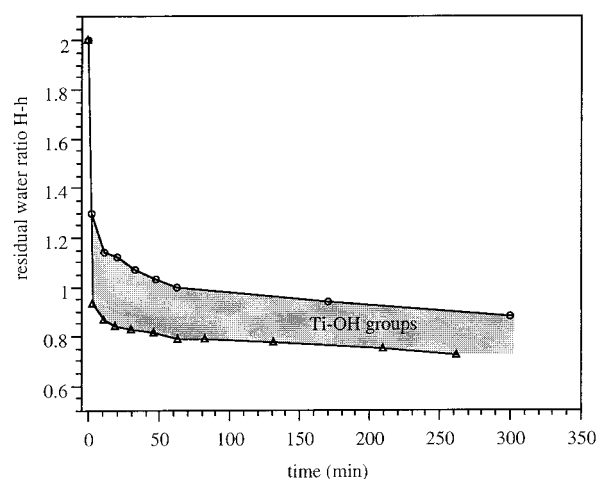


Figure 6. Comparison of the evolution of the residual water ratio $(H - h)$ versus time in two different solvents^[a]



[a] ○ methanol, Δ 2-chloroethanol/chloroform
for the system $\text{Ti}(\text{OnBu})_4$; $r = 0.6$, $H = 2$

Zirconium Oxide Based Sols

The measured values of h as a function of H for $\text{Zr}(\text{OnPr})_4$ complexed by acetylacetone ($r = 0.9$; $r = 1$) are plotted in Figure 3. The curves $h = f(H)$ have a shape similar to those for $\text{Ti}(\text{OnBu})_4$: the consumption of water increases as H increases. At a low initial hydrolysis, ratio most of the water is consumed. At higher initial hydrolysis ratios, the $h = f(H)$ curves show marked deviations from linearity; the h values are invariably below 2, even at $H = 10$. These results underline the fact that the hydrolysis/condensation reactions are incomplete. The curves have been fitted using Equation 5 and the values of K_h and K_c obtained for these systems are reported in Table 2. The hydrolysis constants of the two systems are rather similar, but the condensation constant seems, as in the case of $\text{Ti}(\text{OnBu})_4$, to increase as the complexation ratio decreases. These results allow quantification of the inhibitory effect towards condensation of complexing ligands such as acac.

Silicon Oxide Based Sols

Karl-Fischer titrations were performed for the two series of samples. The values of K_h and K_c are reported in Table 2 and the curves $h = f(H)$ are plotted in Figure 4. They are

Table 3. Mean formula of titanium oxo-polymers calculated from K_h and K_c values at different hydrolysis ratios and $r = [\text{acac}]/[\text{Ti}(\text{OnBu})_4] = 0.6$. H is the $[\text{H}_2\text{O}]/[\text{Ti}]$ ratio, h is the consumed water ratio, Ti–O–Ti is the ratio of oxo bridges per titanium, Ti–OH is the ratio of hydroxo groups per titanium, and H_2O is the ratio of unconsumed water molecules per titanium

H	h	Ti–O–Ti	Ti–OH	Ti–OR	H_2O	structural unit
0	0	0	0	3.4	0	$\text{Ti}(\text{acac})_{0.6}(\text{OR})_{3.4}$
0.5	0.45	0.42	0.02	2.52	0.05	$\text{TiO}_{0.42}(\text{acac})_{0.6}(\text{OH})_{0.02}(\text{OR})_{2.52}$
1	0.85	0.78	0.07	1.77	0.19	$\text{TiO}_{0.78}(\text{acac})_{0.6}(\text{OH})_{0.07}(\text{OR})_{1.77}$
2	1.25	1.09	0.16	1.06	0.73	$\text{TiO}_{1.09}(\text{acac})_{0.6}(\text{OH})_{0.16}(\text{OR})_{1.06}$
4	1.55	1.24	0.31	0.61	2.50	$\text{TiO}_{1.24}(\text{acac})_{0.6}(\text{OH})_{0.31}(\text{OR})_{0.61}$
6	1.67	1.26	0.41	0.47	4.29	$\text{TiO}_{1.26}(\text{acac})_{0.6}(\text{OH})_{0.41}(\text{OR})_{0.47}$
8	1.75	1.26	0.49	0.39	6.19	$\text{TiO}_{1.26}(\text{acac})_{0.6}(\text{OH})_{0.49}(\text{OR})_{0.39}$
10	1.81	1.25	0.56	0.33	8.31	$\text{TiO}_{1.25}(\text{acac})_{0.6}(\text{OH})_{0.56}(\text{OR})_{0.33}$

similar to those of the titanium and zirconium alkoxides. At low hydrolysis ratios, most of the water is consumed; at higher initial hydrolysis ratios, the consumed water ratio h remains below 3.

The curves $h = f(H)$ of $\text{Si}(\text{OEt})_4$ hydrolyzed at pH 0 and pH 2 are quite different. The two curves are in fact similar up to $H = 2$, but at higher initial hydrolysis ratios, the pH 2 curve stays below the pH 0 curve. The hydrolysis constants of these two systems are close, but the condensation constant at pH 2 is 4 times as high as that at pH 0. This result is consistent with the fact that the condensation is more complete at pH 2 than at pH 0^[1]. Protons are usually considered as catalysts for hydrolysis/condensation reactions^{[8][15]}. The above result shows that the proton concentration will also change the final composition of the system, and thus the effect of the protons is not merely kinetic. Protonation of the oxo- or hydroxo-bridges is likely to assist the redissolution-polymerization processes occurring during the formation of the transition metal oxo-polymers^[17].

For titanium and zirconium alkoxides, the only experimental value that can be measured is the consumed water h . The measurement of the condensation ratio k should however give relevant information for the determination of the hydrolysis and condensation constants. With the values of h and k , it is indeed possible to calculate K_h and K_c , for each value of H , directly from Equations 3 and 4. The condensation ratio k can be measured for silicon alkoxides by means of ^{29}Si -NMR spectroscopy, which distinguishes the silicon atoms according to their chemical environments. The chemical shifts of the species $\text{SiO}_n(\text{OR}, \text{OH})_{4-2n}$ ($0 < n < 4$) are reported in Table 4. We have used the commonly accepted notation to describe these species: a silicon Q^n is a silicon having n $-\text{OSi}$ neighbors and $(4 - n)$ $-\text{OR}$ ($-\text{OH}$) neighbors.

The NMR spectra of the systems $\{\text{Si}(\text{OEt})_4 + H \text{H}_2\text{O}, \text{pH} = 0; 0.5 < h < 10\}$ are presented in Figure 7; they have been fitted in order to derive the percentages of the atoms Q^n , as given in Table 4. The condensation ratios were calculated by using the formula:

$$k = (\%Q^1 + 2 \times \%Q^2 + 3 \times \%Q^3 + 4 \times \%Q^4) / (2 \times 100),$$

where $\%Q^n$ is the percentage of the silicon atoms Q^n .

The k values are reported in Table 5, together with the consumed water ratio measured by a Karl-Fischer titration, and the values of K_h and K_c . K_h and K_c were calculated only between $H = 1.5$ and $H = 4$; at higher values of H , the $\text{Si}-\text{OR}/\text{Si}$ ratio is too small to obtain relevant values of K_h and K_c ; on the other hand, at lower values of H , the $\text{Si}-\text{OH}/\text{Si}$ ratio is too small.

K_h and K_c values calculated for these samples using Equation 5 are reported in Table 2. The values of K_h obtained by the two methods are quite similar; however, the K_c values are different (from NMR the mean K_c is 10–12, while the mean K_c is 6–7 from water titration). These differences are especially noticeable at higher hydrolysis ratios. This discrepancy between the values of K_c obtained from ^{29}Si -NMR data and from the modelling of water titration curves, gives an indication of the limitations of the model. Such differences can have several sources:

Figure 7. ^{29}Si -NMR spectra of the systems $[\text{Si}(\text{OEt})_4 + H \text{H}_2\text{O}, \text{pH} = 0; 0.5 < H < 10]$

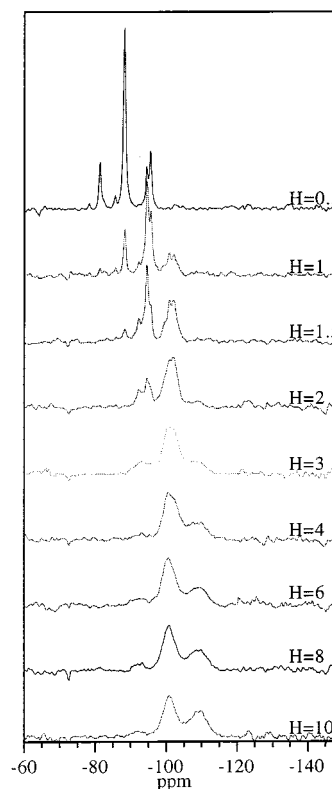


Table 4. Silicon-29 NMR chemical shifts [ppm] and percentage of Q^n species

	Q^0	Q^1	Q^2	Q^3	Q^4
chemical shift	-73 to -78	-80 to -89	-91 to -95	-99 to -103	-110 (broad)
$H = 0.5$	13	55	3		
$H = 1$		16	57	27	
$H = 1.5$		5	45	50	
$H = 2$			34	58	8
$H = 3$			17	63	21
$H = 4$			8	59	33
$H = 6$			10	57	33
$H = 8$			9	52	39
$H = 10$			8	49	44

Table 5. Values of the consumed water ratio h (Karl-Fischer titration) and the oxo bridge ratio k (^{29}Si NMR) of TEOS hydrolyzed at pH = 0, as a function of the initial water ratio H ; hydrolysis and condensation constants calculated using Eq. 3 and Eq. 4

H	h	k	K_h	K_c
0.5	0.5	0.5		
1	0.98	1		
1.5	1.37	1.2	1.9	8.7
2	1.82	1.3	1.9	6.5
3	2.14	1.5	1.7	11.1
4	2.33	1.6	2.8	24
6	2.40	1.6		
8	2.64	1.6		
10	2.99	1.7		

(i) The ^{29}Si resonances in the highly hydrolyzed samples ($H \geq 3$) are broad, indicating that some polymers have become so large that their mobility is restricted. This broadening of the NMR resonances is expected to reduce the precision of the NMR data. An accuracy of about $\pm 15\%$ in the integration of the NMR data would be sufficient to account for the differences observed between the two approaches.

(ii) some M–OH groups might have been partially titrated during Karl-Fischer titration, thus decreasing the accuracy of the estimation of the consumed water h .

Comparison of the Hydrolysis and Condensation Constants of Titanium, Zirconium, and Silicon Alkoxides

The curves $h = f(H)$ of these three alkoxides are similar: at low hydrolysis ratios, the hydrolysis reaction is almost complete, whereas at higher initial hydrolysis ratios, the consumed water tends towards a plateau. The titanium alkoxide has the lowest hydrolysis constant. The condensation constants of the titanium and zirconium species are similar. For these two alkoxides, the condensation constants are about 10 times higher than their respective hydrolysis constants. These results indicate that the condensation of M–OH groups is important and that the M–OH/M ratio is low. The influence of the complexation ratio on these two alkoxides is also the same: an increase of r results in a decrease of K_c , whereas K_h remains unchanged. The pH of the hydrolyzing solution does not seem to change K_h and K_c ; their values are very close to those of the modified precursors. For silicon alkoxides, however, the condensation constant is strongly dependent on the pH of the hydrolyzing solution: at pH = 2, K_c is high, indicating that the condensation is almost complete. At pH = 0, K_c is low, the condensation reaction is in equilibrium, and the ratio $[\text{Si–OH}]/[\text{Si}]$ is high. The silanol Si–OH groups seem to be more stable than the Ti–OH or Zr–OH groups. This result is consistent with previous ^{17}O -NMR studies: Ti–OH and Zr–OH have never been observed by liquid-state ^{17}O -NMR, whereas Si–OH groups give rise to readily detectable signals^{[16][18]}.

Calorimetric Study of the Complexation Reaction

The enthalpy of complexation of tetravalent transition metal alkoxides by acetylacetone provides a relevant insight into this reaction. Four alkoxides have been studied: three titanium alkoxides (ethoxide, butoxide, isopropoxide) and one zirconium alkoxide (*n*-propoxide). The curves of the enthalpy of complexation versus the complexation ratio $r = [\text{acac}]/[\text{M}]$ are shown in Figure 8. These curves show that the complexation reaction is always exothermic ($\Delta H < 0$), but that it reaches a plateau at $r \geq 2$ for titanium alkoxides or at $r \geq 4$ for zirconium propoxide. The complexation enthalpies of these four alkoxides are reported in Table 6.

Moreover, the entropy change associated with complexation by chelating ligands is always positive^[19], so that the free enthalpy $\Delta G = \Delta H - T\Delta S$ should be negative. Consequently, the equilibrium of complexation should be

Figure 8. Variation of the enthalpies of complexation of several metal alkoxides by acetylacetone

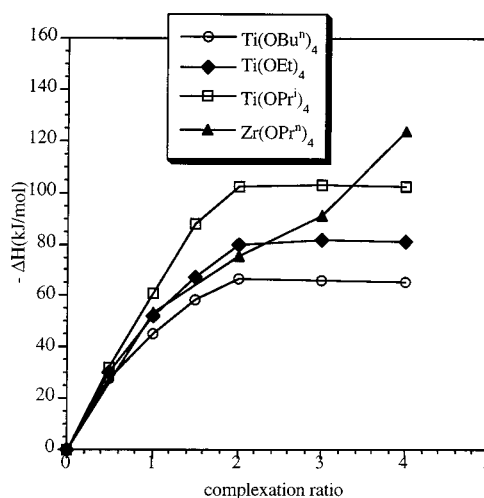


Table 6. Enthalpies ($\text{kJ}\cdot\text{mol}^{-1}$) of the complexation reactions of $\text{Ti}(\text{OnBu})_4$, $\text{Ti}(\text{OEt})_4$, $\text{Ti}(\text{OiPr})_4$, and $\text{Zr}(\text{OnPr})_4$. Gap [$\text{kJ}\cdot\text{mol}^{-1}$] is the gap of enthalpy of complexation, taking $\text{Ti}(\text{OiPr})_4$ as reference

	$\text{Ti}(\text{OnBu})_4$	$\text{Ti}(\text{OEt})_4$	$\text{Ti}(\text{OiPr})_4$	$\text{Zr}(\text{OnPr})_4$
Enthalpy of complexation	–67	–82	–102	–75 (2 acacH) –125 (4 acacH)
Energy of Ti–OR bond	–439	–422	–430	–
Gap (exp. value)	35	20	0	–
Gap (theoretical value)	18	–16	0	–

strongly shifted toward the formation of the chelated precursor up to $r = 2$ for titanium alkoxides or up to $r = 4$ for zirconium propoxide.

These results are in good agreement with previous observations, which have shown that, in the case of titanium alkoxides, substitution of the two first alkoxy groups by acetylacetone ligands occurs readily, but that the further replacement of a third alkoxy substituent by acetylacetone requires a large excess of the ligand^[5]. Zirconium alkoxides, on the other hand, react readily with four acetylacetone ligands, thus forming the $\text{Zr}(\text{acac})_4$ complex.

The complexation of the metallic center by acetylacetone results in an increase of its coordination number. For titanium, the most stable coordination number is 6; this is its usual coordination number in metallic oxides (rutile and anatase). The coordination number for titanium in the alkoxide precursor depends on the nature of the alkoxy group and on the solvent. For neat alkoxides, or in non-polar solvents such as benzene, the coordination number of titanium is 4 when the alkoxy is secondary or tertiary, or 5 with primary alkoxy groups. Primary alkoxides show a general tendency to form solvated dimers in alcoholic solution^[5]. In the bis-complexed precursor $\text{Ti}(\text{OR})_2\text{acac}_2$, however, the coordination number of the metallic center is 6. This increase in coordination number is the main reason for the exothermicity of the complexation reaction.

On the other hand, the most stable coordination numbers of zirconium are 7 and 8. Hence, zirconium propoxide can react with up to four acac ligands, forming the complex $\text{Zr}(\text{acac})_4$, in which eightfold zirconium coordination is attained^[20].

The complexation enthalpies of the various alkoxides are reported in Table 6. The enthalpies of the reactions involving $\text{Ti}(\text{OnBu})_4$ and $\text{Ti}(\text{OEt})_4$ are smaller than that with $\text{Ti}(\text{OiPr})_4$. These enthalpies can be calculated from the bond energies:

$$\Delta H[\text{Ti}(\text{OR})_4] = 2E(\text{Ti}-\text{acac}) + 2E(\text{ROH}) - 2E(\text{Ti}-\text{OR}) - 2E(\text{acacH}) \quad (1)$$

The bond energy values for the three titanium alkoxides are reported in Table 6. The energy of the $\text{RO}-\text{H}$ bond depends only slightly on the nature of the R group^[21].

Using Equation 1, we are able to calculate the gap between the enthalpies of two alkoxides. The calculated and experimental values of these gaps are also reported in Table 6. The reference point ($E = 0$) was taken as the value for $\text{Ti}(\text{OiPr})_4$. The experimental and calculated values are at variance, both for $\text{Ti}(\text{OnBu})_4$ and $\text{Ti}(\text{OEt})_4$. In order to explain these differences, we have to take into account the structure of the alkoxides in solution in their parent alcohols. $\text{Ti}(\text{OiPr})_4$ is monomeric, but $\text{Ti}(\text{OEt})_4$ and $\text{Ti}(\text{OnBu})_4$ are partially oligomerized via $\mu_2\text{-OR}$ bridges. The energies of these bridges have been previously calculated to be about $40 \text{ kJ}\cdot\text{mol}^{-1}$, both for the ethoxy bridge^[22] and for the butoxy bridge^[23]. The enthalpy of the complexation reaction is therefore:

$$\Delta H[\text{Ti}(\text{OR})_4] = 2E(\text{Ti}-\text{acac}) + 2E(\text{RO}-\text{H}) - 2E(\text{Ti}-\text{OR}) - 2E(\text{acacH}) - x \cdot E(\text{alkoxo}) \quad (2)$$

where x is the ratio bridges/titanium [$x = 0$ in the case of $\text{Ti}(\text{OiPr})_4$].

Using Equation 2, we were able to estimate the values of x for each alkoxide: $x_{\text{Ti}(\text{OnBu})_4} = 0.9$ and $x_{\text{Ti}(\text{OEt})_4} = 1.8$. Of course, these values are only approximate, but they provide an interesting way of calculating the degree of oligomerization of the primary alkoxides in solution in their parent alcohols.

Calorimetric Study of Hydrolysis/Condensation Reactions

The enthalpies of hydrolysis were determined as described in the Experimental Section. The variations of the heats of hydrolysis of $\text{Ti}(\text{OiPr})_4$, $\text{Ti}(\text{OnBu})_4$, $\text{Ti}(\text{OEt})_4$, and $\text{Zr}(\text{OnPr})_4$ with the initial hydrolysis ratio, $H = \text{H}_2\text{O}/\text{metal}$, are plotted in Figure 9. The enthalpies of hydrolysis of these four alkoxides are reported in Table 7. The hydrolysis reaction is, in all cases, exothermic, which is in line with previous observations^[5]. The curves $\Delta H = f(H)$ of the three titanium alkoxides show similar behavior: the hydrolysis reaction is exothermic up to $H = 1$ and reaches a plateau for $H > 1$. These results can be compared with those of the Karl-Fischer titrations, which show that at low initial hydrolysis ratios, the consumption of water is complete, while at higher initial hydrolysis ratios, the hydrolysis and conden-

sation reactions are incomplete. These results can also be compared with those of XANES experiments, which have indicated that at low initial hydrolysis ratios, most of the titanium atoms become hexacoordinated^[24]. We conclude from these results that the hydrolysis and condensation reactions are governed by the coordination unsaturation of the metallic center, which results in rapid reactions with any nucleophiles, and especially with water. However, the hydrolysis, oxolation, and alkoxolation reactions do not lead to an increase of coordination, since they correspond to nucleophilic substitution reactions. As a consequence, these results suggest that for transition metal alkoxides, the early stages of hydrolysis and condensation are driven by nucleophilic addition reactions. Among the two possible addition reactions, ololation (creation of hydroxy bridges) or alkoxy bridging, ololation is probably the driving force responsible for the high reactivity towards water of the transition metal alkoxides.

Figure 9. Variation of the enthalpy of hydrolysis/condensation of non-complexed alkoxides with the initial hydrolysis ratio; influence of the complexation ratio

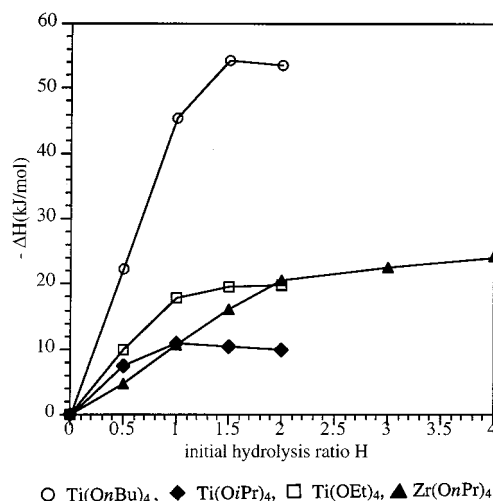


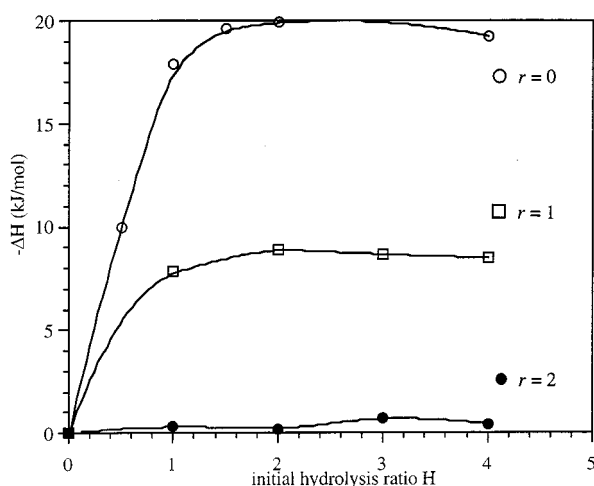
Table 7. Enthalpies of the hydrolysis reactions of: $\text{Ti}(\text{OnBu})_4$, $\text{Ti}(\text{OEt})_4$, $\text{Ti}(\text{OiPr})_4$, and $\text{Zr}(\text{OnPr})_4$

substrate	ratio	enthalpy [$\text{kJ}\cdot\text{mol}^{-1}$]
$\text{Ti}(\text{OnBu})_4$	$r = [\text{acac}]/[\text{Ti}] = 0$	-19.6
	$r = [\text{acac}]/[\text{Ti}] = 1$	-8.4
	$r = [\text{acac}]/[\text{Ti}] = 2$	-0.8
$\text{Ti}(\text{OiPr})_4$	$r = 0$	-54.3
	$r = 1$	-32.6
	$r = 2$	-0.2
$\text{Ti}(\text{OEt})_4$		-10.7
$\text{Zr}(\text{OnPr})_4$		-20.5

The hydrolysis reaction of $\text{Zr}(\text{OnPr})_4$ is exothermic until higher values of the initial hydrolysis ratio are reached ($H = 2$ and even $H = 4$). This result can be attributed to the previously mentioned fact^{[2][3][9]} that the coordination unsaturation (the coordination number of the metal in the oxide minus the metal valency) is higher for zirconium alkoxides ($8 - 4 = 4$) than for titanium alkoxides ($6 - 4 =$

2). Again, the enthalpies of reactions between nucleophilic species (e.g., organic ligands, water, hydroxy groups) and transition metal alkoxide precursors are mainly due to the increase in the coordination of the metallic center. As a consequence, the enthalpies of hydrolysis/condensation should strongly depend on the complexation ratio. Indeed, the hydrolysis reaction of the precursor solution obtained from $\text{Ti}(\text{OnBu})_4$ and acacH with a complexation ratio $r = 2$ is barely exothermic, while at lower complexation ratios, it is decidedly exothermic. Moreover, at a complexation ratio $r = 1$, the enthalpy of hydrolysis is about half of that of the non-complexed precursor (see Figure 10 and Table 7). These results confirm the importance of the coordination unsaturation in the hydrolysis/condensation reactions, since at a complexation ratio $r = 2$, the coordination of all the titanium atoms is 6. At $r = 1$, the system reacts as an equimolar mixture of non-complexed and bis-complexed precursors. The hydrolysis of acac -modified ($r = 1$; $r = 2$) $\text{Ti}(\text{O}i\text{Pr})_4$ leads to similar results (see Table 7).

Figure 10. Variation of the enthalpy of hydrolysis/condensation of pure or complexed titanium butoxide with the initial hydrolysis ratio: influence of the complexation ratio



Conclusions

This work has shown that mean hydrolysis and condensation constants calculated from water titration curves offer a useful means of quantifying the influence of parameters such as the complexation or proton ratio on the behavior of titanium alkoxides towards hydrolysis. In addition, this approach allows comparisons to be made between metal alkoxides of different metals, particularly those of transition metals, for which NMR speciation and quantitative spectroscopic analysis cannot as yet be realized.

This work has also given an indication of the limitations of the proposed model. The assumptions that were invoked to determine mean constants will benefit from further refinement. These include:

- the postulate that the polymers can all be represented by a mean structural unit;
- the assumption that the system reaches, after ageing, a metastable equilibrium state, which results in residual OR

groups. We have shown using ^{17}O -NMR spectroscopy that hydrolysis and condensation reactions are equilibrium processes. It is important to point out that another interpretation can be proposed for incomplete hydrolysis of OR groups, namely the lower reactivity of OR groups of large clusters compared to those of monomers^[17]. It is probable that both these phenomena (reversibility of hydrolysis/condensation reactions and decrease of the reactivity of OR groups with increasing cluster size) contribute to the presence of residual OR groups.

– for the acac -modified precursor, it was considered that acac was a non-hydrolyzable ligand. At high initial hydrolysis ratios and/or high acac ratios, however, some acac ligands can be partially hydrolyzed^{[28][29]}. The stability of the metal– acac bond toward hydrolysis/condensation reactions strongly depends on the nature of the metallic center. From the literature, it is known that for tetravalent metals, this stability can be classified according to the sequence $\text{Ce, Zr} > \text{Ti} \gg \text{Sn}$ ^{[3][11][25]}.

This work has also incorporated key thermodynamic data, which are consistent with the conclusions obtained. Estimates of the enthalpies for the complexation and hydrolysis/condensation reactions indicate that the increase of coordination number of the transition metal alkoxide is of paramount importance. The tendency of the metallic center to attain the coordination that it usually has in naturally-occurring crystalline oxide networks is the driving force of all the reactions of transition metal alkoxides that take place in sol-gel processes. Hydrolysis and oxolation are nucleophilic substitutions and, therefore, do not modify the coordination of the metallic center. As a consequence, it is addition reactions (e.g. oxolation and alkoxy bridging) that are responsible for the high reactivity of titanium and zirconium alkoxides. These should correspond to the consumption of the first molecules of water ($\text{H}_2\text{O}/\text{Ti} \leq 1$), for which the reaction is complete and highly exothermic. However, only a small number of M–OH groups is observed when the metastable equilibrium state is reached. This phenomenon can be explained by the high acidity of the protons of the μ_2 -OH and μ_3 -OH groups bonded to titanium atoms, which leads to deprotonation of these groups^[26].

Experimental Section

Synthesis

Titanium Oxide Based sols and gels were prepared using two different methods:

(i) *Hydrolysis of acac-Modified Precursors*: $\text{Ti}(\text{OnBu})_4$ was diluted with *n*-butanol and acetylacetone (acacH) was added dropwise under magnetic stirring, resulting in a yellow solution. Hydrolysis was performed by the dropwise addition of a solution of water in *n*-butanol. The complexation ratio $[\text{acac}]/[\text{Ti}]$ was varied from 0.6 to 1. The hydrolysis ratio $[\text{H}_2\text{O}]/[\text{Ti}]$ was varied from 1 to 10. The titanium concentration of the resulting sols was $0.4 \text{ mol}\cdot\text{l}^{-1}$.

(ii) *Hydrolysis with Water Acidified with 35% (w/w) HCl*: $\text{Ti}(\text{OnBu})_4$ was diluted with *n*-butanol as above. Hydrolysis was performed by the dropwise addition of a solution of acidified water

in *n*-butanol. The ratio $[H^+]/[Ti]$ was kept at 0.02, while the hydrolysis ratio was varied from 1 to 10. The concentration of the resulting sol was $0.18 \text{ mol}\cdot\text{l}^{-1}$.

The samples used for recording ^{17}O -NMR spectra were prepared as follows:

Sample ① was prepared following procedure (i) with both the $[acac]/[Ti]$ and $[H_2O]/[Ti]$ ratios equal to 1. The water used for this first hydrolysis was 5%-enriched with oxygen-17. After 1 h at room temperature, the sample was further hydrolyzed with a solution of 5% enriched water in *n*-butanol. The total hydrolysis ratio of the sample was thus equal to 2.

Sample ② was prepared according to the same procedure as sample ①, but the first hydrolysis was performed with unenriched water and the second hydrolysis with 10%-enriched water. Thus, after the second hydrolysis, the two systems have the same chemical composition and the same enrichment in oxygen-17.

Zirconium Oxide Based sols and gels were prepared according to a procedure analogous to (i) above: $Zr(OnPr)_4$ was first diluted with *n*-propanol, and then acetylacetone was added. The $[acac]/[Zr]$ ratio was either 0.9 or 1. Hydrolysis was performed by the dropwise addition of a solution of water in *n*-propanol. The $[H_2O]/[Zr]$ ratio was varied from 1 to 10. The concentration of the resulting sols was $0.44 \text{ mol}\cdot\text{l}^{-1}$.

Silicon Oxide Based sols and gels were prepared following procedure (ii): $Si(OEt)_4$ was first diluted with ethanol. A solution of water acidified with HCl (pH 0 or pH 2) in ethanol was then added dropwise. The hydrolysis ratio was varied from 0.5 to 10 and the concentration of the resulting sol was $0.54 \text{ mol}\cdot\text{l}^{-1}$.

Characterizations

Water Titrations were performed by the Karl-Fischer method using a 701 KF Titrino apparatus. The solvent used for the titrations was Hydranal Solvent K, rather than methanol, in order to prevent side reactions of ketones and metal hydroxyls^[27]. The reagent was Hydranal-composite 5K (Riedel-de-Haen).

The ^{29}Si -NMR spectra were recorded on a Bruker MSL 400 spectrometer operating at 79.48 MHz. The sample solution was placed in an 8 mm tube, which was placed inside a 10 mm tube containing C_6D_6 as a lock solvent. Tetramethylsilane was used as reference ($\delta = 0$).

Silicon-29 is a spin 1/2 nucleus with a natural abundance of 4.7%. A disadvantage of this nucleus is its high spin lattice relaxation time T_1 , which results in a long recycle delay. Thus, the relaxation agent chromium acetylacetonate $Cr(acac)_3$ was added in order to reduce this delay. $Cr(acac)_3$ has previously been used in similar systems, where it was shown that it does not interfere with the polymerization process^[7].

A second disadvantage of this nucleus is the presence of background Q^4 silicon units present in the silica tube, which result in a large peak at about $\delta = 110$. In order to suppress this peak, we used a $\pi_2 - \tau - \pi$ echo sequence. The experimental NMR conditions were as follows: first pulse 12.8 μs ; $\tau = 40 \text{ ms}$; second pulse 25.6 μs ; recycle delay 30 s.

The ^{17}O -NMR spectra were recorded on a Bruker MSL 400 spectrometer operating at 54.2 MHz. Again, the sample solutions were placed in an 8 mm tube, which was immersed in C_6D_6 , as a lock solvent, in a 10 mm tube. H_2O was used as reference ($\delta = 0$). The experimental NMR conditions were as follows: pulse 19.6 μs ; pre-acquisition delay (time between the end of the RF pulse and the beginning of the acquisition) 24 μs ; recycle delay 0.2 s, number of scans 1000.

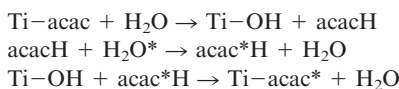
The ^{17}O spectra of ^{17}O -enriched titanium oxo-polymers have been reported previously^[28]. They are characterized by four broad bands, which can be assigned, on the basis of the published literature^{[29][30]}, as follows:

- $\delta = 650\text{--}850$: $\mu_2\text{O}$ oxo-bridges
- $\delta = 450\text{--}600$: $\mu_3\text{O}$ oxo-bridges
- $\delta = 300\text{--}400$: $\mu_4\text{O}$ oxo-bridges
- $\delta = 200\text{--}300$: $\mu_5\text{O}$ oxo-bridges
- the signal appearing at around $\delta = 0$ corresponds to the residual water.

Two additional peaks can be observed in the presence of acetylacetone^[28]:

- one broad peak at $\delta = 300\text{--}400$, attributable to acac bonded to titanium
- one narrow peak at $\delta = 273$, attributable to the enol form of free acetylacetone.

These two peaks appear a few hours after hydrolysis, and are only observed at complexation ratios higher than 1 and with a hydrolysis ratio higher than 2^[16]. They result from the isotopic ^{17}O -exchange between enriched H_2O and the free acetylacetone released by the hydrolysis of the acac ligands^[28].



(the reaction leading to enrichment of the acetylacetone in oxygen-17 is described in Scheme 1).

The recording of oxygen-17 NMR spectra necessitates a pre-acquisition delay in order to eliminate the trailing edge of the high-power pulse. This delay gives rise to a rolling baseline of $\sin x/x$ shape. A baseline correction is then performed, using a cubic splines baseline function (WinNMR 1D). The total intensity of the NMR signal has been measured for all the spectra reported herein, in order to check that this area does not vary with the ageing and the preparation of the sample solution. The areas of the spectra of all the samples after the second hydrolysis are equal, within an experimental error of $\pm 10\%$. A calibration has also been performed using a solution of 10%-enriched water in *n*-butanol, at the same concentration as in the samples of oxo-polymers. The total intensities of the spectra of the oxo-polymer samples before the second hydrolysis, after the second hydrolysis, and after 24 hours of ageing are all consistent with the intensity of the water peak of the calibration solution, within an experimental error of $\pm 10\%$. This result indicates that the formation of large polymers, which would result in the partial loss of the signal of the oxo-polymers and, therefore, in quantitativity problems, is negligible.

Calorimetric Study of the Complexation and Hydrolysis Reactions: Four alkoxides were studied: $Ti(OnBu)_4$, $Ti(OEt)_4$, $Ti(OiPr)_4$, $Zr(OnPr)_4$.

First, $m_1 \text{ g}$ of the alkoxide (or acac-modified alkoxide) was diluted with $m'_1 \text{ g}$ of its parent alcohol. This solution was placed in a Dewar vessel and its temperature T was measured. A solution of $m_2 \text{ g}$ of acetylacetone in $m'_2 \text{ g}$ of the parent alcohol (or the hydrolysis solution of water in parent alcohol) at temperature T_2 was then added. The final temperature T_f was measured about 1 min. after the addition of acetylacetone (or water). The $[acac]/[M]$ ratio of the resulting solution was varied from 0.5 to 2 [or to 4 for $Zr(OnPr)_4$]. The hydrolysis ratio was varied from 0.5 to 4. The molar enthalpy ΔH of the reaction was calculated using the equation:

$$(m_1\Delta H)/M + Cp(M_a + m_1 + m'_1)(T_f - T_1) + Cp(m_2 + m'_2)(T_f - T_2) = 0$$

(adiabatic reaction), where M is the molar mass of the alkoxide (or of the acac-modified alkoxide), $C_{p\text{alcohol}}$ is the heat capacity of the alcohol, M_a is defined as $M_d \times C_{p_d} = M_a \times C_{p\text{alcohol}}$, where C_{p_d} is the heat capacity of the Dewar vessel and M_d the mass of the Dewar vessel.

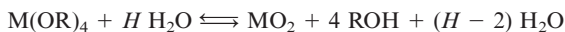
This measurement of the enthalpy is very simple, but it is only intended to give approximate data. Two assumptions are made to estimate the enthalpy of the reaction: first, we assume that the complexation occurs during the first minute after the addition of acetylacetone. This hypothesis is supported by infra-red experiments, which have shown that no free acac can be detected 1 min. after addition of the ligand^{[18][31]}. Secondly, we have assumed that all the reactants and products have the same heat capacity of the solvent, i.e. the parent alcohol. In order to minimize the error introduced by this approximation, the concentrations of reactants were kept below 5% (w/w).

Modelling of the $h = f(H)$ Water Titration Curves

Evaluation of Hydrolysis/Condensation Mean Equilibrium Constants: Hydrolysis and condensation reactions of metal alkoxides do not generally reach completion, showing reversible character in the sol state, as demonstrated by the ^{17}O -NMR experiments. Complete hydrolysis and condensation of a metal alkoxide $\text{M}(\text{OR})_n$ would result in the consumption of all the added water, up to a hydrolysis ratio $H = [\text{H}_2\text{O}]/[\text{Ti}] = n/2$, and, for hydrolysis ratios H higher than $n/2$, a plateau at $h = n/2$ (h being the consumed water ratio), according to the equation:



For a tetravalent metal alkoxide $[\text{Ti}(\text{OR})_4, \text{Si}(\text{OR})_4, \text{etc.}]$ this equation becomes:



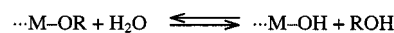
This behavior is only rarely observed. For all the alkoxides studied in the present paper, we have observed that the consumption of water does not follow this law. Two hypotheses can be made to explain this difference: the first one is that hydrolysis and condensation reactions are kinetically controlled, so that the system never reaches an equilibrium state. This hypothesis effectively rules out any possibility of evaluating the extent of reaction. The second hypothesis that can be made is that the system reaches a metastable equilibrium state, which represents a steady state where the reactants are no longer being consumed, but because of their high surface/volume ratio, the solvent-swollen oxo-polymers are still in equilibrium with free water and alcohol molecules. This steady state is not the lower minimum of the system (i.e. the crystalline oxide), but it is well known that chemical pathways can possess several minima of different depth. This second assumption is confirmed by ^{17}O -NMR experiments presented in the Results and Discussion section (vide infra). These experiments show that the hydrolysis and condensation reactions are equilibrium processes. Moreover, this hypothesis has the advantage that it allows one to study the extent of the hydrolysis and condensation reactions through to the determination of a mean chemical formula for the oxo-polymers.

The transition metal oxo-polymers that are formed by the sol-gel process are generally polydisperse in size and composition and it is therefore impossible to perform a straightforward calculation of the pseudo-equilibrium constants of each of these polymers. In order to circumvent this problem, we have defined a mean structural unit that has the mean composition of the polymers. This mean structural unit has the following approximate formula: $\text{MO}_k(\text{OH})_{h-k}(\text{OR})_{4-r-h-k}(\text{acac})_r$, where h is the consumed water

ratio, k is the ratio of oxo bridges, and r is the initial complexation ratio. Details of the calculation of the chemical composition of the mean structural unit are presented in Appendix 1.

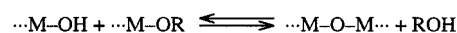
It is possible to define two constants K_h and K_c in order to describe the hydrolysis and condensation pseudo-equilibrium:

hydrolysis:



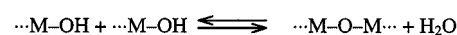
$$K_h = \frac{[\cdots\text{M}-\text{OH}]}{[\cdots\text{M}-\text{OR}][\text{H}_2\text{O}]}$$

condensation (alkoxolation):



$$K_c = \frac{[\cdots\text{M}-\text{O}-\text{M}\cdots]}{[\cdots\text{M}-\text{OH}][\cdots\text{M}-\text{OR}]}$$

condensation (oxolation):



$$K_o = \frac{[\cdots\text{M}-\text{O}-\text{M}\cdots][\text{H}_2\text{O}]}{[\cdots\text{M}-\text{OH}][\cdots\text{M}-\text{OR}]}$$

where M is a metal and R an alkyl group

The pseudo-equilibrium oxolation constant K_o can be directly deduced from K_h and K_c , as follows: $K_o = K_c/K_h$. The formula of the mean structural unit does not depend on the kind of condensation reaction (oxolation or alkoxolation) that occurs (see Appendix 1).

It is possible to express K_h and K_c as a function of k , the mean number of oxo groups, h the water effectively consumed (expressed as the ratio water/metal), r the complexation ratio, and H the initial hydrolysis ratio $H = [\text{H}_2\text{O}]/[\text{M}(\text{OR})_4]$:

$$K_h = \frac{(h-k)}{(4-r-h-k) \cdot (H-h) \cdot [\text{M}(\text{OR})_4]} \quad (3)$$

$$K_c = \frac{k}{(4-r-h-k) \cdot (H-h) \cdot [\text{M}(\text{OR})_4]} \quad (4)$$

$$H = h + \frac{4-r+K'_c(4-r-2h)^2 - (4-r-2h)\sqrt{K'_c{}^2(4-r-2h)^2 + 2K''_c(4-r)+1}}{2K'_h(4-r-h)} \quad (5)$$

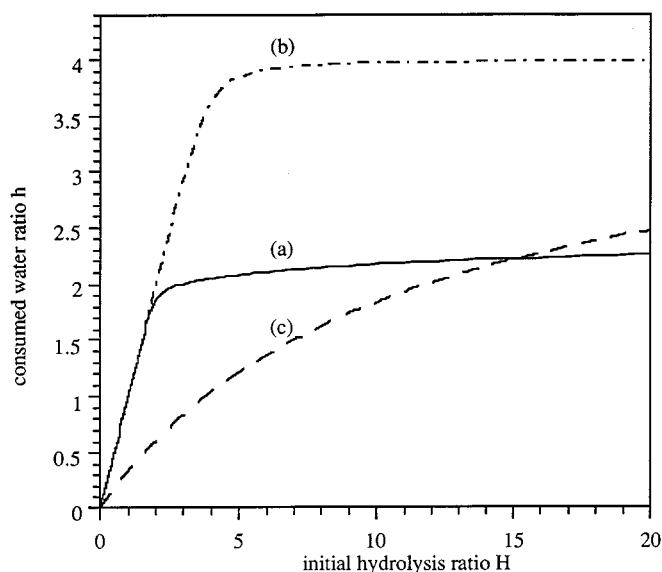
The details of the determination of this equation are presented in Appendix 2.

where $K'_c = K_c \cdot [\text{M}(\text{OR})_n]$; $K'_h = K_h \cdot [\text{M}(\text{OR})_n]$.

It is also possible to express k , the mean degree of oxo condensation, as a function of h and H :

$$k = \frac{K'_h(4-r-h)(H-h)}{K'_h(H-h)-1} \quad (6)$$

Figure 11. Examples of simulation of water titration curves: (a) $K_h = 1$, $K_c = 100$; (b) $K_h = 100$, $K_c = 1$; (c) $K_h = 0.1$; $K_c = 0.1$; K_h is the hydrolysis constant and K_c the condensation constant



The water consumed during the hydrolysis/condensation reactions was measured once the metastable equilibrium state had been reached. These measurements were performed after ageing of the sols of the various metal alkoxides for several weeks or months. The time of ageing was fixed once the consumption of water was negligible. The initial hydrolysis ratio was varied between 0.5 and 10, while the other parameters (acac/metal ratio, H^+ /metal ratio and concentration) were kept constant.

Examples of Simulation

Figure 11 depicts “extreme” behavior of the $h = f(H)$ curves:

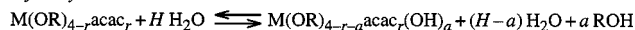
- when the condensation constant is higher than the hydrolysis constant ($K_h = 1$; $K_c = 100$; Figure 11-a), the consumption of water is complete up to $H = 2$, and for H higher than 2 it reaches a plateau. All the M–OH groups that are formed in the hydrolysis reaction are consumed in the condensation reaction, and the final composition of the system corresponds to the oxide MO_2 . The shift of the equilibria toward the formation of the oxide is due to the high value of K_c .
- When the hydrolysis constant is higher than the condensation constant ($K_h = 100$; $K_c = 1$; Figure 11-b), the consumption of water is almost complete up to $H = 4$, and then reaches a plateau at higher values of H . This limiting case corresponds to the formation of $M(OH)_4$ units, which do not polymerize.
- If the hydrolysis and condensation constants are both low ($K_h = 0.1$; $K_c = 0.1$; Figure 11-c), i.e. when both hydrolysis and condensation are incomplete, the consumption of water is not complete, even at low values of H , and the number of residual alkoxy groups is high.

Appendix 1: Determination of the formula of the mean structural unit

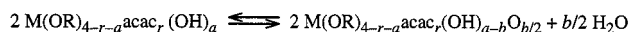
The parameters that determine the formula of the mean structural unit are:

- H the initial hydrolysis ratio
- h the consumed water ratio
- k the ratio of oxo bridges
- r the initial complexation ratio.

Hydrolysis:



considering that *oxolation* is the only condensation reaction



where b is the proportion of M–OH groups that have reacted with an M–OH group to form oxo bridges

$$\frac{n(H_2O)}{n(M)} = H - a + b/2 = H - h$$

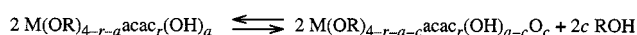
$$\frac{n(M-O-M)}{n(M)} = b/2 = k$$

mean structural unit

$$\frac{n(M-OR)}{n(M)} = 4 - r - a = 4 - r - h - k \quad M(OR)_{4-r-h-k}acac_r(OH)_{h-k}O_k$$

$$\frac{n(M-OH)}{n(M)} = a - b = h - k$$

considering that *alkoxolation* is the only condensation reaction



where c is the proportion of M–OH groups that have reacted with an M–OR group to form oxo bridges

$$\frac{n(H_2O)}{n(M)} = H - a = H - h$$

$$\frac{n(M-O-M)}{n(M)} = c = k$$

mean structural unit

$$\frac{n(M-OR)}{n(M)} = 4 - r - a - c = 4 - r - h - k \quad M(OR)_{4-r-h-k}acac_r(OH)_{h-k}O_k$$

$$\frac{n(M-OH)}{n(M)} = a - c = h - k$$

The mean structural units calculated by assuming that condensation occurs via alkoxolation or oxolation are the same.

Appendix 2: Determination of the equation of H as a function of h

$$\text{from Equation 3: } k = \frac{K'_h(4-r-h)(H-h)}{K'_h(H-h)-1} \quad (3')$$

from Eq. 4 and Eq. 3':

$$[K'_h(4-r-h)(H-h)-h][K'_h(H-h)-1] = K'_c K'_h(H-h)(2h-4+r)^2$$

this equation can be expressed as a polynomial of degree 2 in $(H-h)$:

$$(4-r-h)K'_h{}^2(H-h)^2 - K'_h\{4-r+K'_c(2h-4+r)^2\}(H-h) + h = 0$$

the discriminant of the polynomial is:

$$\Delta = K'_h{}^2(4-r-2h)[K'_h{}^2(4-r-2h)^2 + 2(4-r)K'_c + 1]$$

the root of this equation is:

$$H = h + \frac{4-r+K'_c(4-r-2h)^2 - (4-r-2h)\sqrt{K'_c{}^2(4-r-2h)^2 + 2K'_c(4-r)+1}}{2K'_h(4-r-h)} \quad (5)$$

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