^{17}O Solution NMR Characterization of the Preparation of Sol−Gel Derived SiO_2/TiO_2 and SiO_2/ZrO_2 Glasses

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^{17}O nuclear magnetic resonance was used to investigate the classical two-step procedure for the preparation of sol−gel derived SiO_2-TiO_2 or SiO_2-ZrO_2 glasses. The formation of significant amount of Si−O−M bonds (M = Ti, Zr), resulting from the reaction of silanol groups with M−OR groups, was clearly demonstrated and seems to be kinetically favored when titanium (or zirconium) alkoxide is added to a prehydrolyzed solution of tetraethoxysilane. However, under the chosen experimental conditions, the as-formed oligomeric species are unstable, leading to a partial cleavage of the Si−O−Ti bonds; this phenomenon was not observed for the SiO_2-ZrO_2 system. Two approaches have been investigated to prevent such evolution: postaddition of water to promote condensation of the highly reactive Ti−OR groups or use of chemical modifiers to slow the reactivity of the titanium (or zirconium) alkoxide.

Introduction

SiO_2/TiO_2 glasses have been largely studied for their refractory properties and their low expansion coefficients.[1] But the usual melting processing yields glasses that do not contain more than 17 wt % of TiO_2. For higher amounts, the glass becomes opaque due to crystallization of anatase or rutile. Sol−gel processing, which uses low-temperature chemical approaches, enables SiO_2/TiO_2 glasses to be prepared over a larger compositional range. The possibility of introducing more TiO_2 in the glass allows the development of applications such as catalyst supports,[2] photocatalysts for chemical properties,[3] as well as materials with variable refractive index in the field of optics.[4] This system is also considered for the preparation of protective coatings, which are chemically resistant especially in alkaline medium.[5]

The SiO_2/ZrO_2 system has been much less studied in the literature. Its applications are also in the field of materials with low expansion coefficient, as well as materials with good mechanical and chemical resistances, and this is due to the presence of zirconium.[6]

The sol−gel preparation of mixed oxides is usually quite delicate due to differences in reactivity toward hydrolysis and condensation reactions of the various precursors. Reactions occurring during sol−gel synthesis can be schematically written as follows:

$$M(OR)_n + mXOH \rightarrow [M(OR)_{n-m}(OX)_m] + mROH \quad (1)$$

with X = H (hydrolysis) or M (condensation).

The first step of the reactions is usually a nucleophilic attack of OH groups on the metal M, which provokes an increase in metal coordination. Two parameters will thus control the reaction kinetics: (i) the electronegative character of M; (ii) the ability of M to extend its coordination sphere.

These considerations justify the following classification for the reactivity of various alkoxides:

$$Si(OR)_4 \ll Ti(OR)_4 < Zr(OR)_4 \quad (2)$$

$Si(OR)_4$ are by far the less reactive alkoxides, and a catalyst such as H^+ or OH^- is used to increase their reactivity. On the contrary, the other two alkoxides are very reactive, and they usually lead to precipitation when hydrolyzed. Chelating agents have often been used in sol−gel processing to decrease their reactivity. Studies on the complexation of titanium,[7] zirconium,[8] aluminum,[9] cerium,[10] or tin[11] by carboxylates, β-diketonates, or β-ketoesters have been already published. Specific acidic conditions can also decrease the reactivity.[12]

Phase separation should be avoided for the preparation of mixed oxides such as SiO_2/TiO_2 or SiO_2/ZrO_2. The degree of homogeneity of the final materials will depend on the ability to favor co-condensation reactions between the precursors, despite their intrinsic difference in reactivity. Several strategies have been proposed in the literature to compensate the difference in reactivity of the various alkoxides. Three main examples will be given for the SiO_2/TiO_2 system.

Yoldas[13] proposed to prehydrolyze the silicon alkoxide ($H_2O/Si = 1$) under acidic conditions before addition of the titanium alkoxide. The idea is, in a first stage, to consume the water in order to create a maximum

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number of Si−OH groups:

$$\equiv\mathrm{Si{-}OR} + \mathrm{H_2O} \rightarrow \equiv\mathrm{Si{-}OH} + \mathrm{ROH} \qquad (3)$$

In a second stage, the titanium alkoxide is added and will preferentially react with the silanol groups according to

$$\equiv\mathrm{Si{-}OH} + \equiv\mathrm{Ti{-}OR'} \rightarrow \equiv\mathrm{Si{-}O{-}Ti}\equiv + \mathrm{R'OH} \qquad (4)$$

In a third stage, water is added to lead to gelation. This method is by far the most utilized one.

Sakka and Kamiya[14] proposed a one-step procedure. A solution of ethanol, water, and acetic acid is added to a mixture of silicon and titanium alkoxides. The acetic acid plays a double role: it catalyzes the hydrolysis and condensation reactions of the silicon alkoxide but also modifies the titanium alkoxide, decreasing its reactivity. This could allow the reactivities of both precursors to be adjusted. In a similar way, LaCourse and Kim[15] modified first the titanium alkoxide with acetylacetone before adding the silicon alkoxide and initiating the hydrolysis reaction.

Yamane et al.[16] tried to minimize differences in reactivities between silicon and titanium alkoxides by a proper choice of the alkoxy groups of both precursors. Reaction kinetics are very sensitive to the size of alkoxy groups due to steric effects.[17] A mixture of silicon tetramethoxide and titanium tetra(*tert*-amyl)oxide was then used to obtain homogeneous solutions.

It is, however, very difficult to judge the efficiency of these various methods, because very few analyses have been performed to characterize the species formed in solution. Basil et al.[18] and Wies et al.[19] have followed by ^{29}Si NMR in solution the preparation of SiO_2/TiO_2 gels according to the Yoldas method. But no definitive conclusions could be drawn concerning the formation of Si−O−Ti bonds. Addition of $Ti(OR)_4$ leads to the disappearance of all the resonance peaks due to Si sites containing a silanol group, but no new peak could be assigned unambiguously to species with Si−O−Ti bonds. Recently, ^{17}O NMR was proposed to characterize co-condensation reactions between various alkoxides,[20−22] using ^{17}O-enriched water as a reactant. This combines two main advantages: a great enhancement of the sensitivity of this nucleus, and a selective labeling of the hydroxyls and oxo groups formed during the hydrolysis and condensation reactions:

$$\mathrm{M{-}OR} + \mathrm{H_2}\mathit{O} \rightarrow \mathrm{M{-}}\mathit{O}\mathrm{H} + \mathrm{ROH} \qquad (5)$$

$$\mathrm{M{-}}\mathit{O}\mathrm{H} + \mathrm{RO{-}M'} \rightarrow \mathrm{M{-}}\mathit{O}\mathrm{{-}M'} + \mathrm{ROH} \qquad (6)$$

$$\mathrm{M{-}}\mathit{O}\mathrm{H} + \mathrm{H}\mathit{O}\mathrm{{-}M'} \rightarrow \mathrm{M{-}}\mathit{O}\mathrm{{-}M'} + \mathrm{H_2}\mathit{O} \qquad (7)$$

Si−O−Ti and Si−O−Zr bonds were clearly evidenced in the reaction between prehydrolyzed dimethyldiethoxysilane (DMDES) and titanium isopropoxide or zirconium *n*-propoxide.[21] Similar experiments were also performed with diphenylsilanediol and titanium isopropoxide.[23] In these various studies, instability of Si−O−Ti bonds toward hydrolysis was clearly established. In the present paper, the preparation of SiO_2-TiO_2 and SiO_2-ZrO_2 sols using the method introduced by Yoldas[13] has been investigated using ^{17}O solution NMR. First the prehydrolysis step of tetraethoxysilane (TEOS) has been characterized by ^{29}Si and ^{17}O NMR, as well as Karl Fischer titration. Addition of titanium *n*-butoxide and zirconium *n*-propoxide, modified or not by acetylacetone, to the prehydrolyzed solution of TEOS, was investigated by ^{17}O NMR to look for the formation of Si−O−Ti or Si−O−Zr bonds. The stability of such bonds during the aging process, as well as the effect of postaddition of water will be discussed.

Experimental Section

Tetraethoxysilane (TEOS), titanium *n*-butoxide ($Ti(OBu^n)_4$) and zirconium *n*-propoxide ($Zr(OPr^n)_4$, Fluka) were used as received. Modification of $Ti(OBu^n)_4$ and $Zr(OPr^n)_4$ with acetylacetone was performed by mixing the two reactants in *n*-butanol ($M/acacH/Bu^nOH$ $1/x/3$, M = Ti, Zr). Karl Fischer titrations were performed with a 701 KF Titrino apparatus from Methrom. Hydranal (Riedel-de-Haën) was used as solvent for titration. ^{29}Si and ^{17}O NMR experiments were conducted on a Bruker MSL400 spectrometer at 79.5 and 54.22 MHz, respectively. The sample was held in an 8 mm tube that was in turn placed in a 10 mm tube with C_6D_6 in the annulus as lock solvent. ^{29}Si NMR spectra were recorded with ^{1}H decoupling during acquisition, 5 μs pulse width, 10 s recycle delays, and from 96 to 144 transients. ^{17}O enriched H_2O (10 at. %, Euriso-Top, France) was used as reactant in the ^{17}O NMR experiments, which were recorded with the following parameters: 15 μs (90°) pulse width; 300 ms recycle delays; 500−6000 transients. Quadrupolar relaxation mechanism is dominant in ^{17}O NMR of siloxanes leading to short relaxation times.[24] The spectra were simulated with the WINFIT program.[25]

Results

Prehydrolysis of TEOS. The hydrolysis and condensation reactions of TEOS have been widely studied, mainly using ^{29}Si NMR,[26−28] All these studies show that the reaction kinetics strongly depends on the solution concentration, the hydrolysis ratio, and the catalyst used. In the two-step preparation of SiO_2-MO_2 (M = Ti, Zr) sols, it is important to optimize the time at which titanium or zirconium alkoxide will be added to the prehydrolyzed solution of TEOS. It should correspond to the presence of the largest amount of silanol groups

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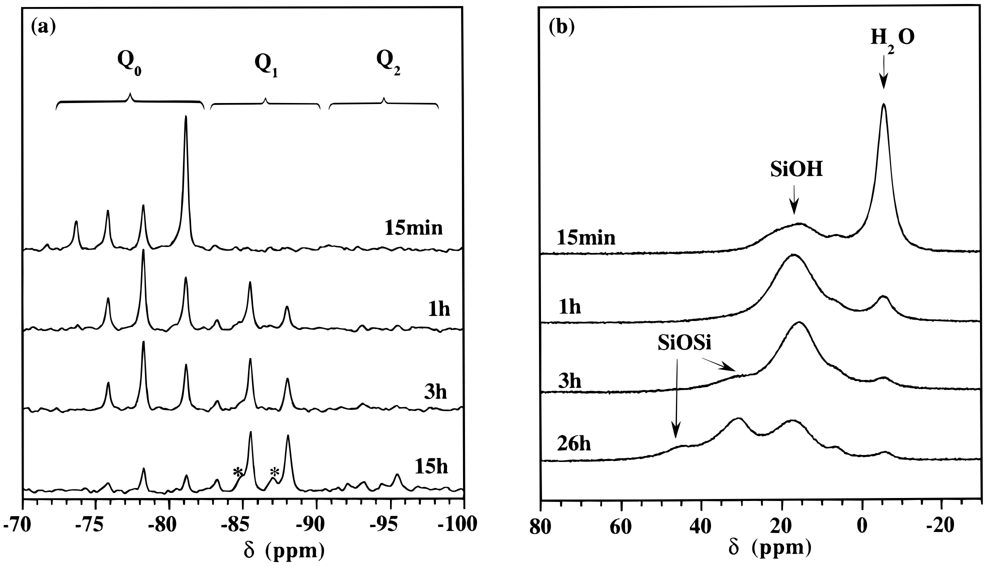

Figure 1. (a) ^{29}Si and (b) ^{17}O NMR spectra versus reaction time, of a hydrolyzed solution of TEOS (TEOS/H_2O/EtOH 1/1/4 (pH = 1.6)). (*: these signals correspond to Q_2 units in trimeric cyclic species).

and the lowest amount of residual water. Extensive formation of Si−O−Si bonds should be avoided, not to initiate phase separation in the sol. The following experimental parameters were chosen to fulfill these conditions: (i) a substoichiometric hydrolysis ratio, H_2O/Si = 1; (ii) an acidic pH (1.6) which corresponds to the longest gelation time;[29] (iii) a typical concentration ratio for sol−gel preparations, EtOH/Si = 4.

Hydrolysis and condensation reactions of the abovementioned solution (TEOS/H_2O/EtOH 1/1/4; pH = 1.6) has been investigated by ^{29}Si and ^{17}O NMR, and Karl Fischer titration, to follow quantitatively the evolution of the amount of residual water, silanol groups (Si−OH), and oxo bridges (Si−O−Si).

^{29}Si NMR: Figure 1a shows spectra at various reaction times. The peak assignments have been done according to the literature.[26,30,31] Under such experimental conditions, only short linear (dimers and trimers) and cyclic species (trimers and tetramers) are formed. From the assignments, the amount of Si−OH and Si−O−Si bridges per Si can be calculated, as well as the amount of residual water. The evolution of these various species is presented in Figures 2 and 3.

^{17}O NMR: Figure 1b presents the corresponding ^{17}O NMR spectra. The peaks were assigned by comparison with the ^{29}Si NMR spectra, as well as with published data.[22,32,33] The residual water is characterized by a rather broad peak (Δ = 250 Hz) centered at −6 ppm. The difference in chemical shift observed from tap water (δ = 0 ppm) is due to the presence of ethanol and should reflect the presence of strong hydrogen bonding between water and alcohol molecules.[24] The peak due to silanol groups is centered at ≈15 ppm. After 1 h of reaction, a signal appears at 30 ppm due to Si−O−Si bridges, which corresponds to formation of dimers according to the ^{29}Si NMR spectra. Then at longer reaction times, another signal appears around 43 ppm due to Si−O−Si bridges, certainly related to the formation of larger

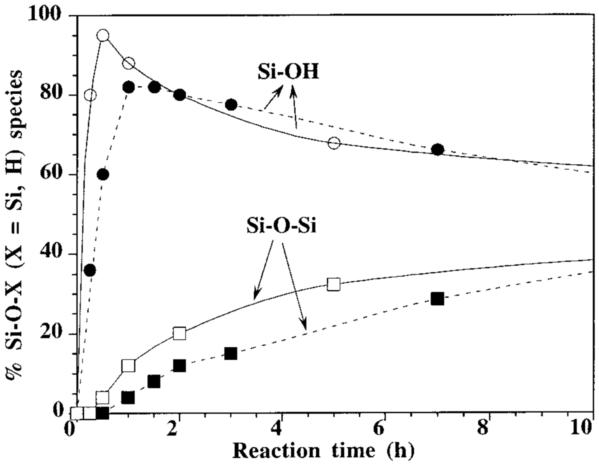

Figure 2. Evolution versus reaction time, of the amount of Si−OH and Si−O−Si groups formed in a hydrolyzed solution of TEOS (TEOS/H_2O/EtOH 1/1/4 (pH = 1.6)). Results from ^{29}Si (full lines) and ^{17}O (dashed lines) NMR experiments.

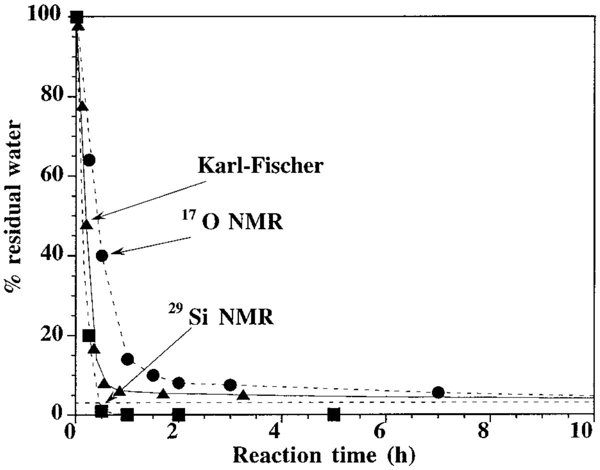

Figure 3. Evolution versus reaction time, of the amount of residual water in a hydrolyzed solution of TEOS (TEOS/H_2O/EtOH 1/1/4 (pH=1.6)). Results from ^{29}Si, ^{17}O NMR experiments and Karl Fischer titration.

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oligomers. The spectra were simulated and the evolution of the various species plotted versus reaction time (Figures 2 and 3).

Karl Fischer titration: The evolution of the water content has also been measured by the Karl Fischer technique, and the results are compared in Figure 3 with those obtained from the NMR studies.

Comparison between techniques: the evolution curves presented in Figures 2 and 3 are quite similar, considering an accuracy of ±5% on the simulations of the NMR spectra. Two distinct steps clearly appear: during the first 30 min, only hydrolysis takes place with formation of silanol groups and important consumption of water:

$$\equiv\text{Si}-\text{OEt} + \text{H}_2\text{O} \rightarrow \text{Si}-\text{OH} + \text{EtOH} \qquad (8)$$

Then a decrease in silanol groups is observed together with the formation of Si−O−Si oxo bridges. According to Assink and Kay,[28] no evidence of alcohol-producing condensation reactions for acid-catalyzed TEOS systems can be found for such low hydrolysis ratios, and so we can assume that the condensation reaction occurs according to eq 9:

$$\equiv\text{Si}-\text{OH} + \text{HO}-\text{Si}\equiv \rightarrow \text{Si}-\text{O}-\text{Si} + \text{H}_2\text{O} \qquad (9)$$

The generated water should be used back immediately for hydrolysis reactions, since no increase in the water content was observed by ^{17}O NMR under such experimental conditions. 90% of the total water is consumed within the first 30 min and then 5−10% of residual water is detected.

The two NMR techniques have their own advantages: ^{17}O NMR allows a direct detection of the species or groups of interest, H_2O, Si−OH, and Si−O−Si groups, while ^{29}Si NMR can give a precise description of all the various oligomeric species present in solution.

Reaction between Ti(OBu^n)$_4$ and a Prehydrolyzed Solution of TEOS. In the two-step preparation of the SiO_2−TiO_2 system, it is very important to optimize the time for the addition of water: it should correspond to a minimum amount of residual water, a maximum amount of silanol groups, and a minimum amount of Si−O−Si groups. The previous NMR study is of great help to optimize this time, and particularly, the ^{17}O NMR study that directly probes the quantity of these various species. In our experiments, we have chosen a time of 4 h, but any time between 2 and 4 h should be fine, since it corresponds to the end of the water consumption with an optimal quantity of silanol groups.

^{29}Si NMR study: The spectrum of a prehydrolyzed solution of TEOS aged for 4 h is presented in Figure 4a. The peaks were assigned according to the literature and the species are listed in Table 1. Monomers and dimers are mainly present in solution; the amount of Q_2 sites is less than 2%.

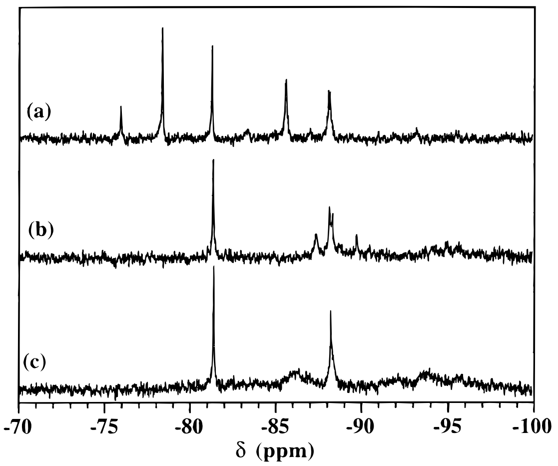

Figure 4. ^{29}Si NMR spectra of a prehydrolyzed solution of TEOS aged during 4 h, (a) before and (b,c) after addition of Ti(OBu^n)$_4$ and Zr(OPr^n)$_4$ (TEOS/H_2O/EtOH 1/1/4 (pH = 1.6); Ti(Zr)/Si = 1).

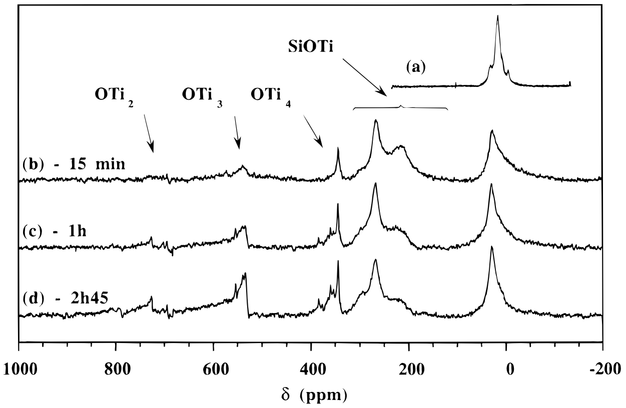

Figure 5. ^{17}O NMR spectra of a prehydrolyzed solution of TEOS aged during 4 h, (a) before and (b−d) after addition of Ti(OBu^n)$_4$: (b) 15 min, (c) 1 h, and (d) 2.75 h. (TEOS/H_2O/EtOH 1/1/4 (pH = 1.6); Ti/Si = 1).

Table 1. Species Present in a Prehydrolyzed Solution of TEOS, Aged for 4 h (TEOS/H_2O/EtOH 1/1/4 (pH = 1.6))

species	chemical shift (ppm)	%
$Si(OEt)_4$	−81.3	7
$Si(OEt)_3(OH)$	−78.4	23
$Si(OEt)_3(OH)_2$	−76.0	20
$-O-Si(OR)_3$	−88.1	4
$-O-Si(OR)_2(OH)$	−85.6	22
$-O-Si(OR)(OH)_2$	−83.4	24

After addition of Ti(OBu^n)$_4$ (Ti/Si = 1), the spectrum is strongly modified. Two main peaks remain at −81.4 and −88.3 ppm, which correspond to Q_0 and Q_1 sites with no Si−OH groups. All the other peaks have disappeared, which should correspond to a reaction of the silanol groups with the titanium alkoxide. New peaks are present at −87.3 and −89.1 ppm, certainly related to the formation of new species that cannot be precisely identified. Similar results have already been reported.[19] These results clearly emphasize the limits of this technique because of a lack of reference compounds to assign the various peaks.

^{17}O NMR Study: The ^{17}O NMR spectrum of the prehydrolyzed solution of TEOS before addition of titanium butoxide is presented in Figure 5a. The enriched species that are detected represent 75% of Si−*O*H groups, 18% of Si−*O*−Si bonds, and 7% of residual water. Immediately after addition of Ti(OBu^n)$_4$ (Figure 5b), the spectrum is strongly modified. One broad signal around 30 ppm remains, whose assignment is difficult. If one considers the loss of all Si−OH groups according to the ^{29}Si NMR study, this peak can be assigned to Si−O−Si bonds. New resonance signals are now present: a broad one in the 200−300 ppm range, in which at least two major components can be distinguished at 225 and 265 ppm. It can be safely assigned to Si−*O*−Ti bridges: the ^{17}O NMR spectrum of Ti[OSi(Me)$_3$]$_4$ (ABCR,

Karlsruhe, Germany) presents a resonance peak at 289 ppm and the chemical shifts for Si−O−Ti bridges in hydrolyzed solutions of $Me_2Si(OEt)_2/Ti(OPr^i)_4$ mixtures was found at 295 ppm.[20] However, it is difficult to give more precise assignments for the individual components. Other signals are present, one sharper at 345 ppm and one broader of low intensity at 530 ppm. These two last signals correspond to chemical shifts found for μ_4-*O* and μ_3-*O* oxo bridges (O atom bonded to respectively four and three Ti atoms).[34]

The various signals have been integrated to extract the relative amounts of the ^{17}O-containing species. Due to the line width of the peaks, this quantitative analysis as well as the following should not be considered as highly accurate (±5%). The percentages will be related to the total amount of ^{17}O and thus to the initial amount of water; but since the $Si/Ti/H_2O$ molar ratio is 1/1/1, these values correspond also to the amount of ^{17}O-enriched species per Si or Ti atom. The spectrum presented in Figure 5b gives 31%, 17%, and 52% for Si−*O*−Si, Ti−*O*−Ti and Si−*O*−Ti bonds, respectively. The starting composition of the hydrolyzed TEOS solution was 7% H_2O, 75% Si−*O*H and 18% Si−*O*−Si. Reaction 4 has thus occurred to a large extent to form Si−O−Ti bonds. Similar observations have already been pointed out for the $Me_2Si(OEt)_2/Ti(OPr^i)_4$ system.[20] The residual water is certainly responsible for the formation of Ti−O−Ti bonds according to

$$\text{Ti−OR} + H_2O \rightarrow \text{Ti−}O\text{H} + \text{ROH} \qquad (10)$$

$$\text{Ti−}O\text{H} + \text{Ti−OR} \rightarrow \text{Ti−}O\text{−Ti} + \text{ROH} \qquad (11)$$

However, the number of Si−O−Ti bonds is lower than expected, while the amounts of Si−O−Si and Ti−O−Ti bonds are higher. Reaction 4 should have led to the formation of 75% of Ti−O−Si and reactions 10 and 11 to 7% of Ti−O−Ti bonds. This could suggest redistribution reactions between Ti−O−Si and Ti−O−Ti and Si−O−Si bonds, such as, formally

$$2\text{Si−}O\text{−Ti} \rightarrow \text{Ti−}O\text{−Ti} + \text{Si−}O\text{−Si} \qquad (12)$$

But no detailed mechanism can be proposed. The increase in the amount of Si−O−Si bonds could also be related to a catalytic effect that $Ti(OBu^n)_4$ could play in the condensation of Si−O−Si bonds and already reported in the chemistry of silicones.[35]

We should note that Ti−OH groups might also be present, even if their high reactivity should push them to condense according to reaction 11. Until now, no NMR signal assigned to Ti−OH groups has ever been observed in solution[36] or even, in solid state[37,38] on TiO_2 or $SiO_2−TiO_2$ systems. As recently quoted in the literature,[39] these groups may be difficult to detect by this technique.

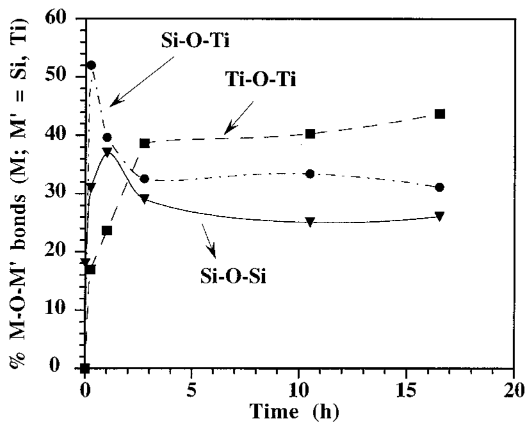

Figure 6. Evolution of the number of Si−O−Si, Si−O−Ti, and Ti−O−Ti groups after addition of $Ti(OBu^n)_4$ to a prehydrolyzed solution of TEOS aged for 4 h. ($TEOS/H_2O/EtOH$ 1/1/4 (pH = 1.6); Ti/Si = 1). Results based on the integration of the ^{17}O NMR spectra (see Figure 5).

The aging of the system was followed by recording the ^{17}O NMR spectrum, over a 17 h time period. Characteristic spectra are presented in Figure 5. Progressive changes occur during the first 3 h, and then the system seems to reach an equilibrium state. The intensity of the signal due to Si−O−Ti decreases, while new peaks are now clearly visible due to μ_2-*O* (700−900 ppm) μ_3-*O* (450−700 ppm) and μ_4-*O* (300−400 ppm) oxo bridges between Ti atoms. They are quite sharp, especially those due to μ_4-*O* species and can be related to the formation of Ti-based clusters, which have been extensively described in the literature.[40,41] Evolution of the various ^{17}O-containing groups during aging is presented in Figure 6. Integration of the total intensity of the NMR signal shows no loss during the aging period. The decrease in Si−*O*−Ti bonds corresponds mainly to an increase of the number of Ti−*O*−Ti bonds, while the number of Si−*O*−Si bonds remains almost constant. This seems to indicate that redistribution reactions occur, with a cleavage of the Si−*O* bond. Reaction mechanisms are currently unknown, but these reactions can be favored by the molecular character of the species that are formed, as schematically represented in Figure 7. The prehydrolysis step with H_2O/Si = 1, leads to species (monomers and dimers) with an average of 1 Si−OH per Si (indeed, the experimental ratio is 0.75). In Figure 7, the as-formed species was schematically represented as one unique average species, $Si(OEt)_3(OH)$ **(I)**. Then, $Ti(OBu^n)_4$ is added (Ti/Si = 1). $Ti(OBu^n)_4$ is oligomeric, and can be considered mainly as dimeric in alcohol solutions **(II)**.[36] $Ti−OBu^n$ and Si−OEt groups can undergo exchange reactions,[42] and after this step, Ti−OEt and $Si−OBu^n$ groups can be present in solution. Due to the larger number of Ti−OR groups compared to Si−OH groups, reaction 4 will lead to the formation of species such as **III,** which are small oligomers, containing a large number of residual Ti−OR and Si−OR groups. Exchange reactions certainly exist between terminal and bridging Ti−OR groups, as well as between various types of oligomers, built on various kinds of Ti and/or Si moieties. Such

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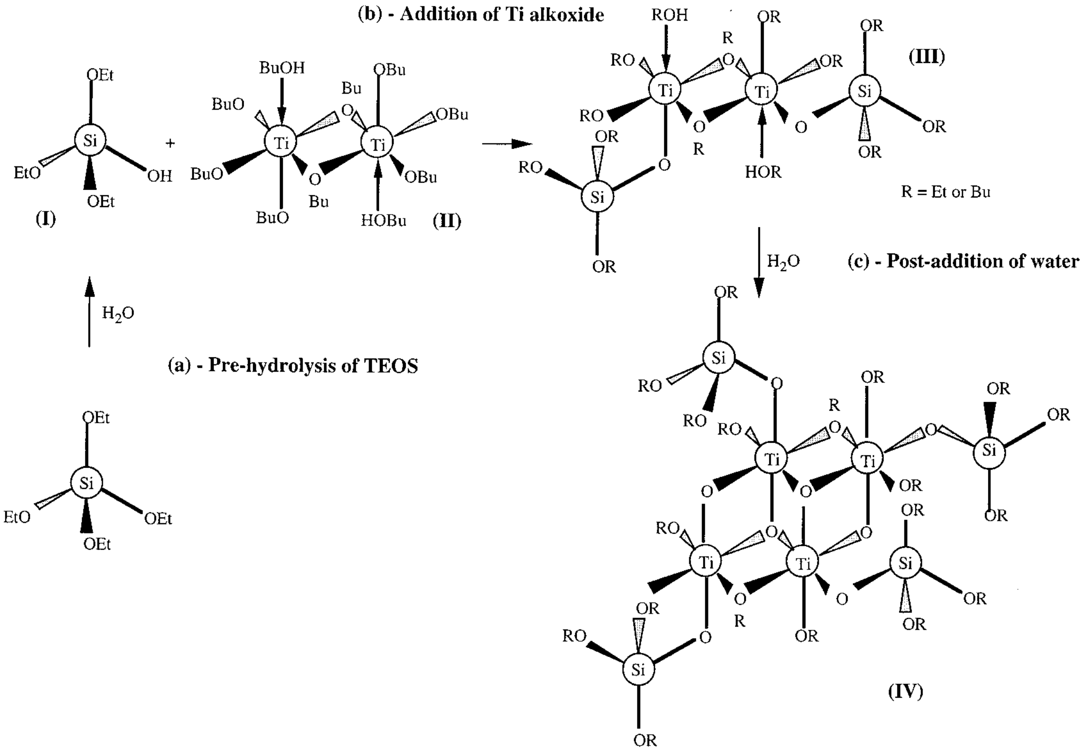

Figure 7. Schematic representation of the various stages of the synthetic procedure used for the system TEOS/Ti(OBu^n)$_4$.

equilibrium reactions could contribute to the broadening of the ^{17}O NMR lines.

These ^{17}O NMR experiments suggest that the formation of the Si−O−Ti bonds is kinetically favored when Ti(OR)$_4$ is added to a Si−OH-rich solution, but under our experimental conditions (low hydrolysis ratio and high Ti/Si ratio) which generates rather small oligomeric species, the system evolves toward a more thermodynamically stable state, favoring phase separation between Ti and Si rich species.

Effect of postaddition of water: If the large number of residual Ti−OR groups is responsible for the low stability of Si−O−Ti bonds during aging, one can think to add water in order to form Ti−O−Ti bonds and to extend the oxo-based network. One mole of ^{17}O-enriched water per Ti was thus added, 30 min after the addition of Ti(OBu^n)$_4$ to the prehydrolyzed solution of TEOS. So now the molar ratios are Si/Ti/H_2O 1/1/2. It should be noted that the amount of water is still substoichiometric compared to what is needed to totally condense the Si and Ti precursors (Si/Ti/H_2O 1/1/4).

As expected, immediately after addition of water, the ^{17}O NMR spectrum (Figure 8) shows additional broad signals around 350, 550 and 750 ppm that can be clearly assigned respectively to μ_4-*O*, μ_3-*O*, and μ_2-*O* oxo bridges. The total intensity of the Ti−O−Ti bonds represents 60% of the ^{17}O-containing species, compared to 10% in the initial solution (the percentages refer to the total amount of water). This clearly indicates that the additional water is selectively used to hydrolyze Ti−OR groups, and to form Ti−*O*−Ti bonds. The amount of Si−*O*−Si (15%) and Si−*O*−Ti (25%) bonds remains constant, suggesting that no hydrolysis of residual Si−OEt groups occur, as well as no reaction between Si−OR and Ti−OH groups to form Si−O−Ti bonds. The effect of water is thus to extend the titania-based oxo-polymer network, rejecting the Si-containing species at the surface, such as in **IV** (Figure 7). Interestingly, with such species, the relative amounts of the various oxo bridges do not vary over 20 h (Figure 8). The postaddition of water thus contributes to the stabilization of the Si−O−Ti bonds during the aging period.

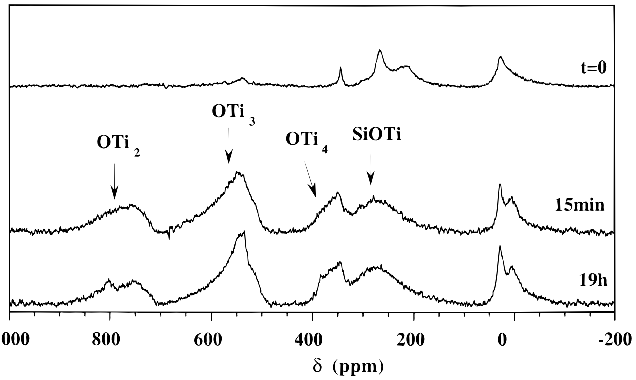

Figure 8. ^{17}O NMR spectra after addition of water (H_2O/Ti = 1) to a prehydrolyzed solution of TEOS reacted with Ti(OBu^n)$_4$ (TEOS/H_2O/EtOH 1/1/4 (pH = 1.6); Ti/Si = 1).

Effect of the Use of acac-Modified Ti(OBu^n)$_4$. Chelating ligands such as acetylacetone (acaH) are often used to decrease the reactivity of titanium alkoxide.[43] The idea is to replace the reactive alkoxy ligands by less hydrolyzable ones and also to increase the titanium coordinance.

The structure of titanium alkoxides modified by acacH has been investigated.[7,36] For Ti(OBu^n)$_4$, two species can be formed depending on x = acacH/Ti, Ti(OBu^n)$_3$(acac) **(V)**, and Ti(OBu^n)$_2$(acac)$_2$ **(VI)**.[36] Up to $x = 0.6$, only **(V)** is observed, while from 0.8 to 1.4, a mixture of **(V)** and **(VI)** is present in solution. For $x = 2$, only species **(VI)** is found.

Ti(OBu^n)$_4$/acaH = 1/0.5. As previously, prehydrolysis of a solution of TEOS is performed during 4 h (TEOS/

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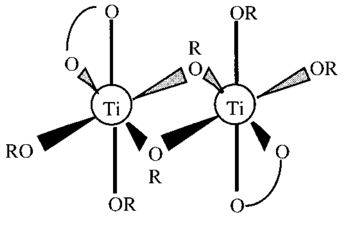
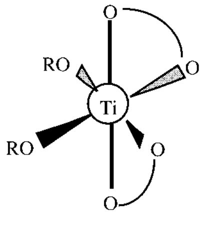


(V)



(VI)

H_2O/EtOH 1/1/4). Then the solution of modified alkoxide in *n*-butanol is added. For $x = 0.5$, the solution contains an equal mixture of $Ti(OBu^n)_4$ and **V**. An ^{17}O NMR study was done as previously and shows very similar results, with the formation of Si−O−Ti bonds which are not stable during the aging process. Quantitative analysis of the spectra over a 24 h period gives also identical evolution.

The effect of postaddition of water, 30 min after the addition of the modified alkoxide, was also followed by ^{17}O NMR. Very similar behavior is again observed compared to the system with $Ti(OBu^n)_4$, with an important formation of μ_2-O and μ_3-O bridges between Ti atoms (from 10% before to 45% after) and no change in the amount of Si−O−Si bonds (15%). However, one main difference is that the number of Si−O−Ti also increases from 25% before water addition to 40% after. Then these relative amounts remain constant over a 24 h period.

The difference from the previous system with unmodified $Ti(OBu^n)_4$ is that the water is involved in the formation of not only Ti−O−Ti bonds but also Si−O−Ti bonds. These latter bonds can be obtained from reaction 4 but also according to

$$\text{Si−OR} + \text{HO−Ti} \rightarrow \text{Si−O−Ti} + \text{ROH} \qquad (13)$$

^{17}O NMR study[36] performed on $Ti(OBu^n)_4$/acac/H_2O 1/0.5/1 shows, 15 min after addition of water, a rapid formation of μ_2-O (40%), μ_3-O (45%), and μ_4-O (10%), while only 5% of water remains. In this system, the Ti−OR groups are thus still quite reactive, and certainly more than Si−OR groups. One might think that they will hydrolyze preferentially to give Ti−*O*H groups. When $Ti(OBu^n)_4$ was used with no modification, Ti−OH was reacting with Ti−OR groups to form exclusively Ti−*O*−Ti bonds. In the present case, Ti−*O*H seems also to react with Si−OR to give Si−*O*−Ti bonds.

$Ti(OBu^n)_4$/acaH = 1/2. Similar experiments have been performed with $x = 2$. Reaction between $Ti(OBu^n)_4$ and acaH, in *n*-butanol leads exclusively to the formation of **VI** as confirmed by ^1H NMR. This solution was added to a prehydrolyzed solution of TEOS, as previously described. The ^{17}O NMR spectra are completely different from the two previous systems (Figure 9). No signal due to the formation of Ti−*O*−Ti bonds is present. One signal is found around 0−50 ppm which is more defined than for the previous systems. It can be assigned to Si−*O*−Si bonds as well as possible residual Si−*O*H bonds and water. Then a composite signal is present between 250 and 350 ppm due to Si−*O*−Ti bonds. Two peaks can be clearly distinguished, one intense at 277 ppm and one less intense at 308 ppm. The peaks are interestingly much sharper than in the previous systems. This could be due to the formation of smaller oligomeric species, such as schematically represented in Figure 10. **VI** is monomeric, in opposition with $Ti(OBu^n)_4$ **II** or **V**: thus once it reacts with the prehydrolyzed solution of TEOS, species such as **VII** can be formed preferentially. Si−O−Ti bonds represent 50% of the ^{17}O-containing species, which is the highest amount obtained in the three studied systems. The absence of any Ti−O−Ti bonds, despite the presence of residual water (<10%), has to be related to the low hydrolytic reactivity of Ti−OR groups in **(VI)**, as clearly demonstrated by a ^{17}O NMR study.[36] After hydrolysis (H_2O/Ti = 1), only one type of μ_2-O bridges is formed corresponding to the $[Ti(acac)_2O]_2$ dimeric species, with 70% of water remaining even after 6 days. The Ti−OR groups in $Ti(OBu^n)_2(acac)_2$ in which Ti is hexacoordinated, are clearly much less reactive than in $Ti(OBu^n)_4$ or even in **(V)**. This could also be related to the high stability of the as-formed Si−O−Ti bonds during aging (Figure 9).

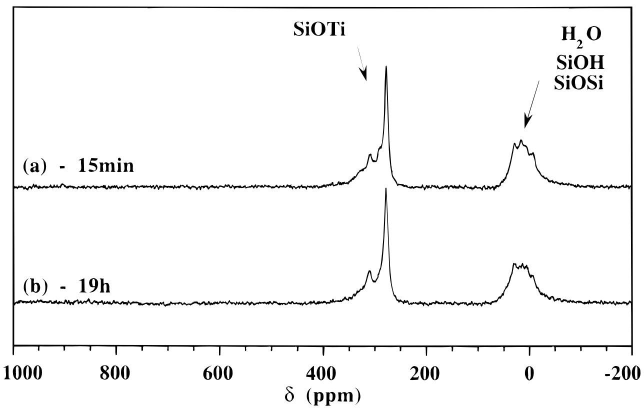


Figure 9. ^{17}O NMR spectra of a prehydrolyzed solution of TEOS aged during 4 h reacted with $Ti(OBu^n)_2(acac)_2$: (a) 15 min and (b) 19 h (TEOS/H_2O/EtOH 1/1/4 (pH = 1.6); Ti/Si = 1).

As previously, water was added 30 min after addition of the titanium precursor (H_2O/Ti = 1). The observed behavior in the ^{17}O NMR spectra is completely different from the previous systems with $x = 0$ and 0.5 but in total agreement, once again, with the low reactivity of the Ti−OR groups (Figure 11). After 15 min, no signal due to any Ti−*O*−Ti bonds is observed; the signals observed before water addition due to Si−OX (X = H, Si) and Si−O−Ti bonds are unchanged, but the peak due to the added H_2O is clearly present at −6 ppm. It corresponds to 35% of the total intensity of the spectrum, which means that only 30% of the additional water has been consumed at that time, and mainly to form Si−O−Ti bonds (the signal intensity increases from 25% to 45%). It is difficult to tell if they are formed from reaction 4 or 10, since in this system, Si−OR and Ti−OR groups may compete for hydrolysis.

The water content decreases quite slowly versus time, indicating again a slow reactivity of the residual alkoxy groups. After 1 h, only 45% of the water has reacted. At longer time, the only change in the spectra seems to be the decrease of the water signal; however, a quantitative analysis shows that the total intensity of the signals decreases by 20% after 3 h and by 40% after 20 h. This clearly indicates that species are no longer detected. This phenomenon was not observed in the previous experiments. The loss of signal could be related to the growth of species with low mobility, which will be characterized by short relaxation times. The

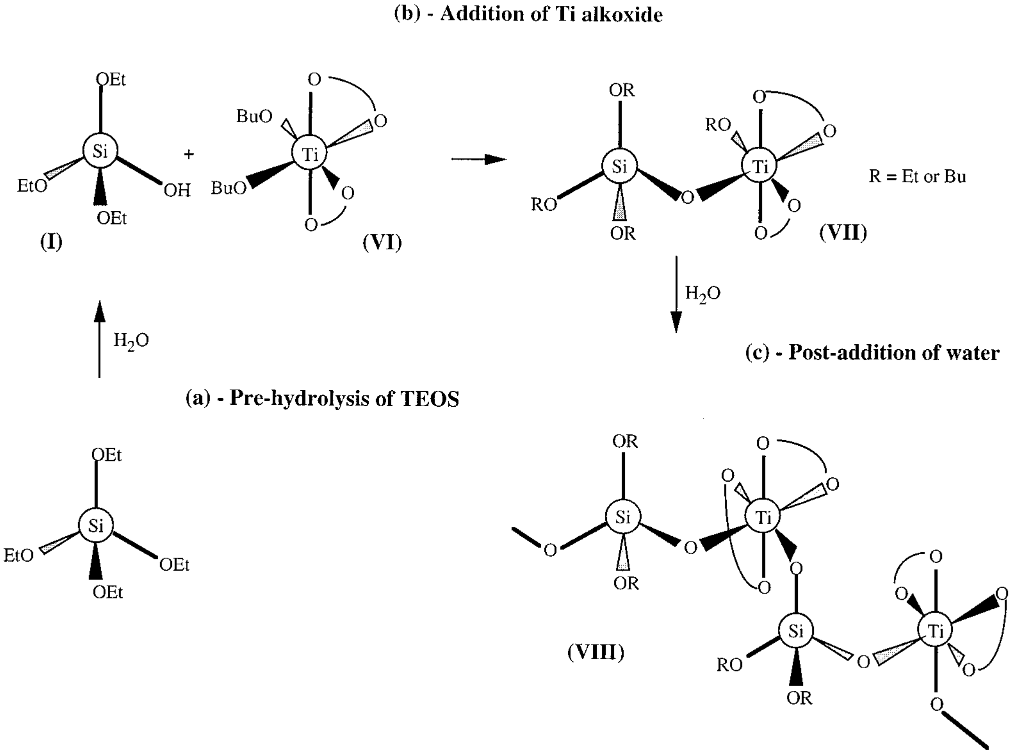


Figure 10. Schematic representation of the various stages of the synthetic procedure used for the system TEOS/Ti(OBu^n)$_2$(acac)$_2$.

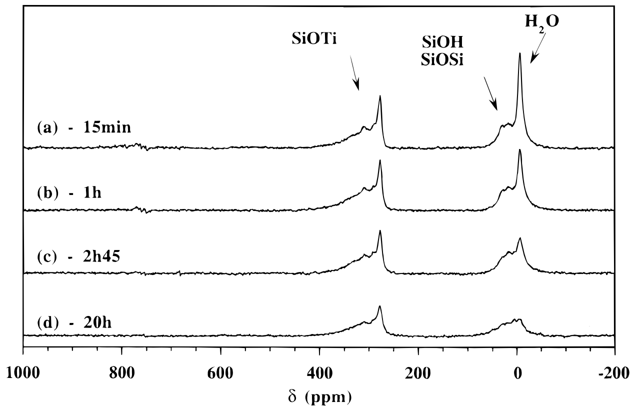


Figure 11. ^{17}O NMR spectra after addition of water (H_2O/Ti = 1) to a prehydrolyzed solution of TEOS reacted with Ti(OBu^n)$_2$(acac)$_2$ (TEOS/H_2O/EtOH 1/1/4 (pH = 1.6); Ti/Si = 1).

main difference between this experiment and the previous ones could be the way the oxo-polymers are growing, as schematically represented in Figure 10. The main difference in this system, compared to that with Ti(OBu^n)$_4$ (Figure 7), is the reactions that occur with the postaddition of water. In the first case, water is added to species such as **III** that contains a large number of reactive Ti−OR groups, leading to an exclusive formation of Ti−O−Ti bonds. In the present case, the species present in solution when water is added (such as **VII**), contain a smaller amount of much less reactive Ti−OR groups, thus favoring the formation of Si−O−Ti bonds, and thus of linear species such as **VIII**. Long polymers could thus be developed, which might not be detected any longer.

The use of acac seems to play a major role in the way the oxo-polymeric species develop, and in the way the Si and Ti sites are distributed within the polymeric network. The use of Ti-modified alkoxide should lead to a better homogeneity of the growing species.

Reaction between Zr(OPr^n)$_4$ and a Prehydrolyzed Solution of TEOS. The previous study has been reproduced with zirconium *n*-propoxide, Zr(OPr^n)$_4$, which presents a similar behavior toward sol−gel reactions, compared to Ti(OBu^n)$_4$. Similar experimental procedures have been followed, but only one acac/Zr ratio was studied; for higher values, Zr(acac)$_4$ precipitated under our experimental conditions.

^{29}Si NMR. The ^{29}Si NMR spectra of the prehydrolyzed solution of TEOS before and after addition of Zr(OPr^n)$_4$ are presented in Figure 4. The changes are quite similar to those observed after addition of Ti(OBu^n)$_4$. All the Si units with silanol groups have disappeared; the two sharp peaks correspond to Si(OEt)$_4$ and (EtO)$_3$SiO− species. Broad components are also present around −86 and −94 ppm that might be related to the formation of new species containing Si−O−Zr bonds, but no definite assignment can be made.

^{17}O NMR. The ^{17}O NMR spectra recorded before and after addition of Zr(OPr^n)$_4$ are reported in Figure 12. The changes occur immediately after Zr addition, with the appearance of a broad intense peak at 156 ppm and a sharp and low intense peak at 326 ppm. The first peak is due to Si−O−Zr bonds, in agreement with ^{17}O NMR results obtained in solution on the DMDES/Zr(OPr^n)$_4$ system[20] or in solid on SiO_2−ZrO_2 gels.[44] μ_3-O and μ_4-O bridges between Zr atoms are found around 400 and 300 ppm, respectively, in either zirconia gels[45] or crystalline monoclinic zirconia.[46] The small peak at 326 ppm is thus assigned to μ_4-O bridges. At higher

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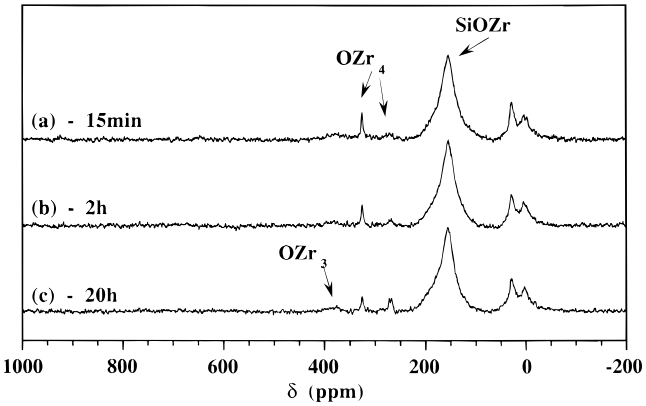

Figure 12. ^{17}O NMR spectra of a prehydrolyzed solution of TEOS aged during 4 h, after addition of $Zr(OPr^n)_4$: (a) 15 min, (b) 2 h, and (c) 20 h (TEOS/H_2O/EtOH 1/1/4 (pH = 1.6); Zr/Si = 1).

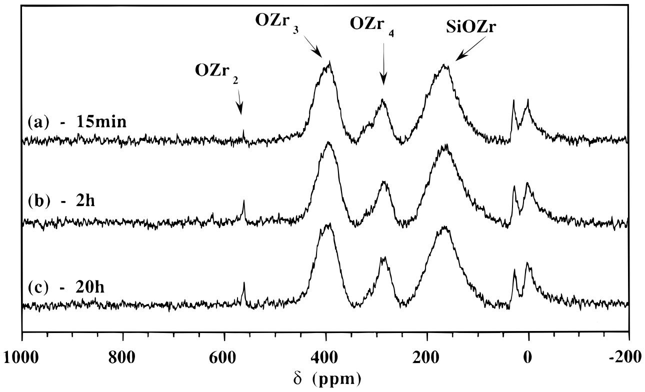

Figure 13. ^{17}O NMR spectra after addition of water (H_2O/Ti = 1) to a prehydrolyzed solution of TEOS reacted with $Zr(OPr^n)_4$ (TEOS/H_2O/EtOH 1/1/4 (pH = 1.6); Zr/Si = 1).

field, two peaks remain at 2 and 28 ppm. The latter can be assigned to Si−O−Si bonds, while the first one could be due to residual water.

The results of the addition of $Zr(OPr^n)_4$ are very similar to those observed with $Ti(OBu^n)_4$: Zr−OR groups react preferentially with silanols to form Si−O−Zr bonds:

$$\text{Si}-\mathit{O}\text{H} + \text{RO}-\text{Zr} \rightarrow \text{Si}-\mathit{O}-\text{Zr} + \text{ROH} \qquad (14)$$

But the amount of bonds is higher (65% instead of 52% of Si−O−Ti for the $Ti(OBu^n)_4$-based system), and moreover, the relative amount of the various species is almost constant over 20 h, indicating a good stability of such bridges.

Postaddition of water (H_2O/Zr = 1), 30 min after mixing $Zr(OPr^n)_4$ with the prehydrolyzed solution of TEOS, leads to the formation of a small amount of precipitate, a phenomenon that has never been observed for $Ti(OBu^n)_4$. This strongly suggests the presence in solution of unreacted zirconium alkoxide.

The ^{17}O NMR spectra presents broad signals centered at 280 and 390 ppm, respectively assigned to μ_4-O and μ_3-O bridges (Figure 13). The signal due to Si−O−Zr bonds (δ 165 ppm) largely broadens. The spectrum is not modified with time, except for a small peak, due to μ_2-O groups, which grows at 560 ppm. Quantitative analysis of the spectra is difficult because of the precipitate that forms upon water addition and results in only a partial detection of the species.

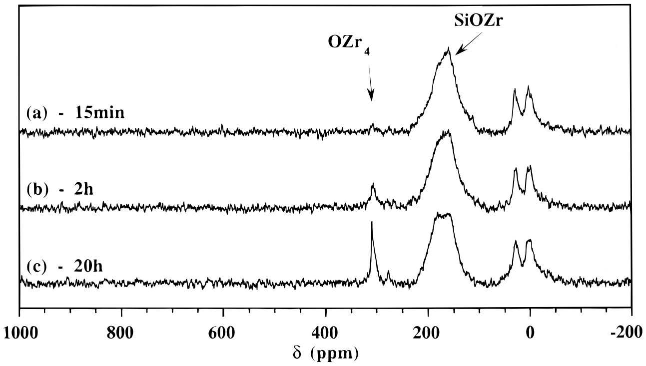

Figure 14. ^{17}O NMR spectra of a prehydrolyzed solution of TEOS aged during 4 h and reacted with $Zr(OPr^n)_{3.5}(acac)_{0.5}$: (a) 15 min, (b) 2 h, and (c) 20 h (TEOS/H_2O/EtOH 1/1/4 (pH = 1.6); Zr/Si = 1).

Effect of the Use of acac-Modified $Zr(OPr^n)_4$. As for titanium alkoxide, acacH was used to decrease the reactivity of $Zr(OPr^n)_4$ The ^{17}O NMR spectra obtained when $Zr(OPr^n)_4$ is modified with 0.5 acac groups are quite similar to those obtained with unmodified $Zr(OPr^n)_4$ (Figure 14). After 15 min, the spectrum presents a main peak due to Si−O−Zr bonds (72%) at 156 ppm and broader than in the previous case.

During aging, a component is growing at low field around 180 ppm, while the total intensity of the signal slightly decreases to 60% after 20 h of aging. Simultaneously, a sharp peak at 309 ppm is growing due to μ_4-O species: the uniqueness of this peak suggests the formation of a cluster such as that obtained by hydrolyzing acac-modified $Zr(OPr^n)_4$ (acac/Zr = 1), $[Zr_4(\mu_4\text{-}O)(\mu_2\text{-}OPr^n)_6(OPr^n)_4(acac)_4]$.[47] The intensity of this peak represents 10% after 20 h. With a modification ratio of 0.5, some redistribution reactions occur during aging, but to a lower extent than in the case of the Ti-containing system.

Postaddition of water generates also a rather large number of μ_3-O (9%) and μ_4-O (17%) species, while the number of Si−O−Zr bonds represent 50%. Similarly to the Ti-containing system, water has been involved in the formation of Zr−O−Zr as well as Si−O−Zr bonds. Interestingly, the use of acac has prevented the formation of any precipitate, in agreement with the role of inhibitor of this complexing agent.

Conclusion

The classical two-step procedure for the preparation of SiO_2-TiO_2 or SiO_2-ZrO_2 sol−gel derived glasses has been investigated by ^{17}O NMR, using ^{17}O-enriched water. This technique allowed us, besides an important enhancement of the signal sensitivity, to specifically label the oxo bridges formed at the various preparation steps. The chemical shift differences between Si−O−Si, M−O−M, and Si−O−M (M = Ti, Zr) are large enough to clearly distinguish between these various bonds and make this technique very powerful to investigate the growth of oxo-based oligomers and polymers via hydrolysis−condensation reactions.

The formation of Si−O−M bonds, by reacting Si−OH groups with M−OR groups seems kinetically favored, and the addition of titanium (or zirconium) alkoxide to

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a prehydrolyzed solution of TEOS can lead immediately to a significant formation of such bonds. The amount of bonds is directly related to the amount of Si−OH groups. A quantitative analysis of the prehydrolysis step of TEOS is thus quite important, to optimize the time for addition of titanium (or zirconium) alkoxide that should correspond to the maximum amount of silanol groups present in solution.

An important result of this study is that under the chosen experimental conditions that will generate small oligomeric species, with a large number of residual Ti−OR groups (low hydrolysis ratio and high Ti/Si ratio), the Si−O−Ti bonds formed when using $Ti(OBu^n)_4$ are not stable in solution during aging. The system will evolve toward a more thermodynamically stable state, with the formation of Ti and Si rich species, which can produce a possible phase separation in the final gel. Interestingly, the use of $Zr(OPr^n)_4$ does not lead to the same phenomenon, and the Si−O−Zr bonds are stable during aging. This different behavior is not clearly understood. The stability of the Si−O−Ti bonds can be greatly enhanced by postaddition of water, which will selectively hydrolyze the Ti−OR groups, leading to titania-based oligomeric and/or polymeric species, with Si-containing species at the surface. In such systems, the various reactions that occur in solution could cause possible phase separation in the final gels.

acac-modified titanium alkoxides can be used, and especially $Ti(OBu^n)_2(acac)_2$, in order to increase the amount of Si−O−Ti bonds and their stability. The low reactivity of the Ti−OR groups in such precursors compared to $Ti(OBu^n)_4$ seems to prevent any Si−O−Ti bond cleavage during aging. Moreover, post addition of water is used mainly to form Si−O−Ti bonds. In that case, a good distribution of Si and Ti sites within the growing network can be expected.

This paper clearly demonstrates the strength of ^{17}O NMR to investigate sol−gel reactions in SiO_2-TiO_2 and SiO_2-ZrO_2 systems. The effect of various experimental parameters can be easily investigated in order to get a better control on the chemical homogeneity of the final gels.

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