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Characterisation of sol–gel derived titanium oxopolymers: first evidence of Ti—OH groups through ^1H–^{17}O CP NMR experiments

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Titanium oxo based xerogels obtained through hydrolysis of titanium tetrabutoxide in acidic conditions have been characterised through FTIR, ^{17}O MAS and ^1H–^{17}O static CP NMR experiments. This latter technique allows the separation of the ^{17}O NMR resonances corresponding to the protonated titanium oxo sites from those of the titanium oxo unprotonated sites, by varying the ^1H to ^{17}O contact time in a cross-polarisation sequence. These experiments clearly evidence the presence of Ti—OH groups. Their characteristic ^{17}O NMR resonance, in titanium based xerogels, is located at about 200 ppm.

Sol–gel chemistry is based on the polymerisation of molecular precursors such as metal alkoxides $M(OR)_n$ (M = Si, Ti, Zr, *etc.*).[1,2] Hydrolysis and condensation of these metallic alkoxides lead to the formation of metal oxopolymers. Titanium oxopolymers and titanium oxide based gels are precursors for titania based materials, the technological importance of which has been known for a long time. Indeed, these materials can be used as pigments, as powders for catalytic or photocatalytic applications, as components for antireflective coatings, as porous membranes for ultafiltration or even as refractory fibers.[1] Titanium based gels can be obtained through the hydrolysis of $Ti(OR)_4$, but the characterisation of the resulting gels and xerogels is not an easy task.

In contrast to silica based gels, for which ^{29}Si NMR and ^1H–^{29}Si CP MAS techniques are particularly useful and relevant, sol–gel derived materials obtained through hydrolysis of transition metal alkoxides cannot be probed through NMR experiments performed on the metal nuclei because these nuclei are not easily accessible by NMR. Many of them are paramagnetic (Fe^{III}, $Mn^{II,III}$, Co^{II}, *etc.*) or possess a strong quadrupolar moment ($^{47}Ti^{IV}$, $^{49}Ti^{IV}$, $^{91}Zr^{IV}$, $^{93}Nb^{V}$, *etc.*). Another possibility, which has been more recently investigated, is to characterise transition metal oxopolymers by probing, through NMR, the oxygen atom which ensures the connectivity between the different metallic centres.

Oxygen-17 is an excellent probe for the study of the local structure of a variety of inorganic solids.[3,4] The main drawbacks of ^{17}O NMR are its poor sensitivity due to the low natural abundance and its quadrupolar moment ($I = 5/2$, 0.037% natural abundance, $Q = -2.63 \times 10^{-30}$ m^2). However, the quadrupolar interaction broadens the central transition to second order and the low natural abundance can be overcome by hydrolysing the precursors with ^{17}O-enriched water: the relative stability of the C—O bond compared to the M—O bond ensures that ^{17}O is efficiently incorporated into the growing M—O—M oxide network (and not in the released alcohol molecule). This strategy has been widely used in the study of the oxopolymers formed by sol–gel processing[5–9] and ^{17}O NMR allows the oxygen sites to be differentiated as a function of the number of titanium atoms bonded to them.[6,8–11] However, many surface driven properties (wettability, acidity, catalysis, *etc.*) of titanium oxide based materials are related to the presence of Ti—OH groups which have, until now, not been observed using NMR spectroscopy. The presence of such groups at the surface of crystalline titanium dioxide (rutile or anatase) has been evidenced by IR spectroscopy.[12] However, the intrinsic nature of sol–gel derived oxopolymers which contain remaining alkoxy groups, alcohol and adsorbed water molecules, makes straightforward spectroscopic assignment, through IR or even near IR techniques, very difficult.

^{17}O–^1H cross-polarisation is a recently explored technique because the cross-polarisation behaviour of the ^{17}O nuclei is complicated by the presence of quadrupolar interactions.[13] Cross-polarisation of the relatively insensitive oxygen-17 nucleus not only offers the possibility of large sensitivity enhancement, but also allows the selective observation of hydroxyl groups *versus* oxo bridges. It can be postulated that Ti—OH groups have never been observed using ^{17}O NMR for two main reasons: titanium based materials may exhibit a low content of such groups and/or their characteristic ^{17}O NMR resonances may be hidden by those of the titanium oxo bridges. This article describes the characterisation of titania based xerogels through chemical analysis, IR, ^{13}C CP MAS, ^{17}O MAS and ^1H–^{17}O static CP NMR experiments. This last technique allows the observation of Ti—OH groups through the selective observation of protonated oxygen using cross-polarisation.

Experimental

Sample preparation

The natural abundance of oxygen-17 is very low (0.037%), which makes it impossible to record ^{17}O solid-state spectra on naturally enriched samples. All the samples were therefore synthesised with 20% oxygen-17 enriched water.

The ^{17}O enriched portlandite sample was synthesised in order to be used as a reference compound for all the settings of the ^{17}O NMR parameters. Our titanium oxopolymer sample only contains a small amount of Ti—OH groups, resulting in a poor signal to noise ratio which makes it impossible to set the ^{17}O NMR experiments directly on the sample.

^{17}O-enriched (20%) portlandite, $Ca(OH)_2$. $CaCl_2$ (0.5 g) was dissolved in ^{17}O-enriched water (0.5 g). A solution of KOH (0.5 g) in enriched water (0.3 g) was added dropwise, resulting in the precipitation of $Ca(OH)_2$ and KCl. This precipitate was washed with a solution of water and KOH (pH = 10) in order to eliminate KCl. The resulting solid was dried at 100 °C. The powder X-ray diffractogram of the sample exhibited the characteristic features of $Ca(OH)_2$ portlandite.[14]

Titanium oxide based xerogel. Titanium *n*-butoxide $Ti(OBu^n)_4$ was diluted in *n*-butanol. Hydrolysis was performed by adding dropwise a solution of ^{17}O-enriched (20%) acidified water ($p = H^+/Ti = 0.02$) in *n*-butanol. The hydrolysis ratio,

$H=[H_2O]/[Ti]$, was 2. The protons were added to the hydrolysing solution in order to avoid the precipitation of the oxopolymers.[15] The addition of enriched water to the titanium alkoxides results in the selective enrichment of the oxo bridges of the oxopolymers according to the following:

$$\cdots Ti{-}OR + H_2O^* \rightarrow \cdots Ti{-}O^*H + ROH \quad \text{hydrolysis}$$

$$\cdots Ti{-}O^*H + \cdots Ti{-}OR \rightarrow \cdots Ti{-}O^*{-}Ti\cdots + ROH \quad \text{condensation (alcoxolation)}$$

$$\cdots Ti{-}O^*H + \cdots Ti{-}OH \rightarrow \cdots Ti{-}O^*{-}Ti\cdots + HOH \quad \text{condensation (oxolation)}$$

$$\cdots Ti{-}O^*H + \cdots (Ti{\leftarrow}S) \rightarrow \cdots Ti{-}O^*H{-}Ti\cdots + S \quad \text{condensation (olation)}$$

R is an alkyl chain and S an alcohol molecule which solvates the metallic centre. For the sake of clarity all but one of the titanium first neighbours have been omitted.

Because of this selective enrichment the ^{17}O NMR spectra of the oxopolymers exhibit only the signals of the oxo bridges and the terminal and bridging hydroxy groups. The unenriched remaining alkoxy groups are not detectable. The number of Ti—OH groups evaluated from Karl Fischer titrations performed in the sol state range between 0.05 and 0.1 OH/Ti.

The gelation of the sample occurred in a few days. The gel was then vacuum-dried at room temperature.

IR spectroscopy

The IR spectra of the sample were recorded on a Nicolet Magna-IR 550 spectrometer in the 4000–400 cm^{-1} frequency range with a resolution of 2 cm^{-1}.

^{13}C CP MAS NMR spectroscopy

The ^{13}C CP MAS spectra of the titanium oxopolymer samples were recorded on a MSL 300 spectrometer operating at 75.4 MHz. The experimental NMR conditions were: recycle delay 10 s, duration of the ^1H 90° pulse 6 μs, contact time 2000 μs, spinning frequency 5000 Hz.

Oxygen-17 NMR spectroscopy

Oxygen-17 NMR spectra were recorded on a MSL 300 spectrometer operating at 40.67 MHz.

The ^{17}O MAS or static spectra without CP were recorded using a spin-echo pulse sequence α–τ–α (α being the duration of the ^{17}O pulse and τ the delay between the first and the second pulse). This sequence was used in order to avoid the baseline distortions occasioned by the preacquisition delay (which is necessary to eliminate the trailing edge of the high-power pulse). The experimental NMR conditions were: 2.9 μs pulse ($\alpha=\pi/6$), $\tau=400$ μs, recycle delay 0.2 s. The value of τ was imposed by the spinning frequency of the rotor during the MAS experiments ($R_0=5000$ Hz): the value of τ must be a multiple of $1/R_0$ in order to avoid any distortion of the spectrum.

In the ^{17}O CP NMR experiments the cross-polarisation behaviour of quadrupolar nuclei is complicated by the presence of quadrupolar interactions. However, in the case of non-integer spin nuclei the central transition $(-\frac{1}{2}, \frac{1}{2})$ is only affected by the second-order quadrupolar interaction. For cross polarisation of the $(-\frac{1}{2}, \frac{1}{2})$ transition of ^{17}O $(I=5/2)$ the match condition predicted by the Hartmann–Hahn equation is:[13,16]

$$3\gamma_O H_{1O} = \gamma_H H_{1H}$$

With a ^1H 90° pulse of 6 μs the optimum cross-polarisation is expected for a 'solution' ^{17}O 90° pulse of 18 μs (which corresponds to a 'solid' ^{17}O 90° pulse length of 6 μs). This is only an estimated value of the duration of the 'solid' ^{17}O 90° pulse. The RF ^{17}O-channel level was then adjusted for optimal cross-polarisation by observing the resonance from ^{17}O-enriched $Ca(OH)_2$.[13] The ^{17}O CP NMR spectrum of this sample was recorded with and without using an echo sequence on the ^{17}O channel. These two sequences are schematically described in Fig. 1. The drawback of the classical CP sequence[17] [Fig. 1(a)] is that it necessitates a preacquisition delay between the end of the cross-polarisation pulses and the beginning of the acquisition of the FID signal. This delay may result in a partial loss of the signal. The CP echo sequence [Fig. 1(b)] is similar to the previous one except that, after an evolution time τ, a second pulse is performed on the ^{17}O channel. This pulse results, after a delay τ, in a refocalisation of the FID signal. The acquisition of the FID signal is then performed.

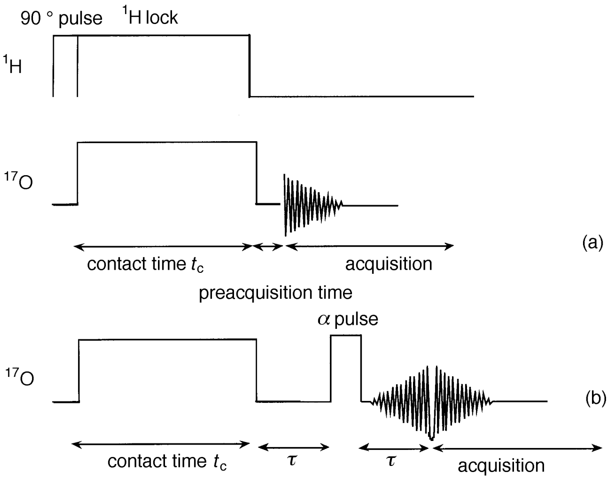

Fig. 1 Sketch of the ^{17}O CP sequence, (a) classical CP sequence, (b) with an echo pulse on the ^{17}O channel

The duration α of the ^{17}O pulse, and the delay τ between the end of the contact time and the ^{17}O pulse (see Fig. 1) were optimised on the portlandite sample.

Phase cycling was used in order to suppress the FID of the ^{17}O pulse. Chemical shifts are reported in parts per million (ppm) using an external sample of water as a 0 ppm reference.

The experimental NMR conditions were: ^1H pulse 6 μs, contact time t_c 100 or 5000 μs, delay τ 60 μs, duration of the ^{17}O pulse α 17 μs, recycling delay 5 s.

Results and Discussion

Fig. 2 represents the IR spectrum of the titanium oxopolymers sample. This spectrum can be divided into three frequency

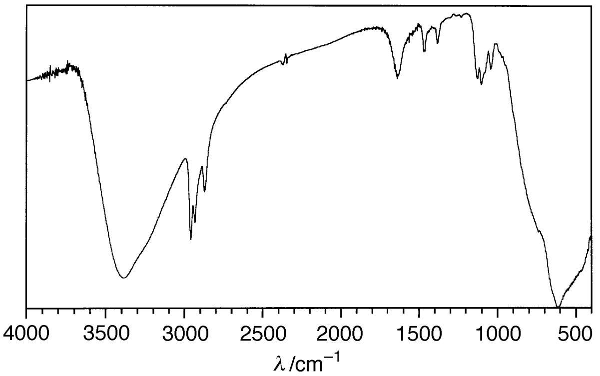

Fig. 2 IR spectrum of the titanium oxopolymers sample in the 4000–400 cm^{-1} frequency range

domains: at low wavenumbers, the broad band around 600 cm^{-1} can be assigned to the ν(Ti—O) vibrations. At intermediate wavenumbers, ranging between 900 and 1700 cm^{-1} the bands characteristic of the ν(C—O) (1150–1000 cm^{-1}) vibrations and those of δ(C—H) (1400–1200 cm^{-1}) of the butoxide chains can be observed, as well as the δ(H—O—H) (1630 cm^{-1}) of water molecules. At high wavenumbers, ranging between 2000 and 3500 cm^{-1}, a broad band characteristic of ν(O—H) vibrations, as well as the ν(C—H) vibration of the butoxy groups (2900–3000 cm^{-1}), can be observed. Therefore, the 1630 cm^{-1} band indicates the presence of adsorbed water on the oxopolymer sample, and the 1150–1000 cm^{-1}, as well as the 1400–1200 cm^{-1} and the 2900–3000 cm^{-1} bands, confirm the presence of residual alkoxy groups or residual alcohol. The presence of residual organics, titanium hydroxy groups and water molecules, lead to a blurring of the ν(O—H) band because of the presence of hydrogen bonds. This bad resolution makes the assignment of the broad ν(OH) bands difficult. Three different O—H bonds can indeed contribute to this band: the O—H bond of water, butanol and of Ti—OH groups, but the contribution of these O—H bonds can not be distinguished. IR spectroscopy can therefore not be used to evidence the presence of Ti—OH groups. The spectrum of the sample has also been recorded in the near IR range (2500–900 nm), in order to observe the 2ν(OH) and 3ν(OH) regions, but the vibrations of the O—H bonds of water, butanol and Ti—OH groups are not distinguishable either.

^{13}C CP MAS experiments performed on the titanium oxo xerogels show the presence of resonances located at $\delta_1 = 76.2$ ppm, $\delta_2 = 35.6$ ppm, $\delta_3 = 19.7$ ppm, $\delta_4 = 14.5$ ppm, respectively assigned to the carbon resonances of a butoxy chain bonded to titanium ($\mathrm{Ti{-}O{-}C^1H_2C^2H_2C^3H_2C^4H_3}$). The resonance characteristic of free butanol ($\delta_1' = 63$ ppm, $\mathrm{HO{-}C^{1\prime}H_2CH_2CH_2CH_3}$) is negligible showing that the remaining organic groups are mainly butoxy ligands.

Combining chemical analysis data and KF titrations the mean chemical formula for these titania based samples can be deduced: $\mathrm{TiO_{1.675-1.7}(OBu^n)_{0.5}(OH)_{0.05-0.01}(H_2O)_z}$.

The ^{17}O CP spectra of the portlandite sample, recorded with and without an echo pulse on the ^{17}O channel, are reported in Fig. 3. These two spectra were recorded using the sequences schematised in Fig. 1(a) and (b). The spectrum of portlandite has already been described by Walter and Oldfield.[3] It is typical of the second order quadrupolar pattern from a single oxygen site.

The echo sequence is generally used in order to avoid the distortion of the spectra which results from the preacquisition delay. This delay can also cause a partial loss of the signal. This effect can be seen in Fig. 3. The central part of spectrum 3(a), recorded without echo, is flattened compared to that of spectrum 3(b), recorded with an echo sequence. We therefore chose to use the echo sequence during the recording of the spectrum of our titanium oxopolymer samples.

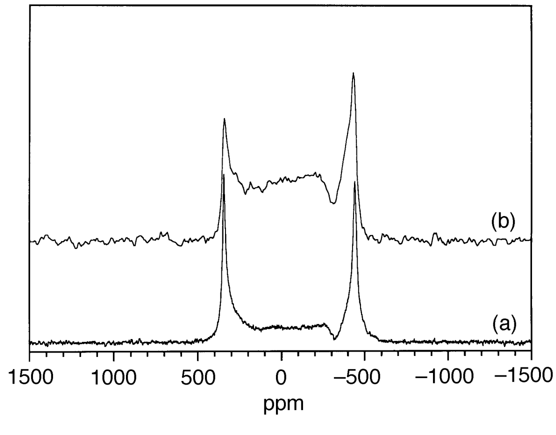

Fig. 3 ^{17}O CP spectra of the portlandite $\mathrm{Ca(OH)_2}$, (a) without a echo pulse on the ^{17}O channel; (b) with an echo pulse on the ^{17}O channel

The ^{17}O NMR spectrum recorded on the sol obtained from hydrolysis of $\mathrm{Ti(OBu^n)_4/H_2O/H^+} = 1/2/0.02$ is characterised by the presence of three broad resonances assigned to titanium oxo bridging oxygens[8] (μ_2-O at 730 ppm, μ_3-O at 520 ppm, μ_4-O at 350 ppm).

Fig. 4 represents the ^{17}O NMR spectra of the same titanium oxopolymers, after the drying of the sample. The ^{17}O static spectrum of the sample, recorded without cross-polarisation, is reported in Fig. 4(b). It is composed of two overlapping broad signals centred at 500 and 350 ppm. These resonances can be assigned to μ_3-OTi (600–400 ppm) and μ_4-OTi (350–250 ppm) according to the ^{17}O NMR solution spectra of the polymers before drying[8] and according to ^{17}O NMR solid state studies reported in the literature.[6,10] Fig. 4(a) represents the ^{17}O MAS NMR ($R_0 = 5000$ Hz) spectra of the same sample. The two main components, located at 516 and 364 ppm, corresponding respectively to μ_3-O (40%) and μ_4-O (60%) oxygen bridges are clearly observed. This feature confirms that the broadening of the signal can be partially reduced using magic angle spinning experiments. Moreover, the disappearance of the resonance due to μ_2-O oxygens observed in the wet state which transforms into μ_3-O and μ_4-O indicates that some chemical transformations occur upon drying. The presence of a large amount of μ_4-O is not compatible with the classical picture, which assumes that titanium oxopolymers produced by sol–gel synthesis are amorphous hydrated titania which should only contain μ_3-O oxo bridges. These oxopolymers should contain a large amount of polymeric species, the μ_i-O topology of which should be close to those reported in many titanium oxo clusters.

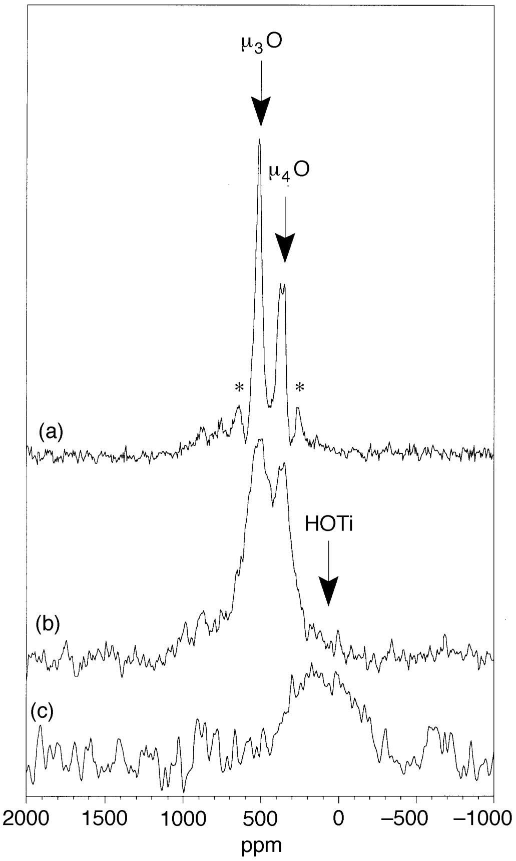

Fig. 4 (a) ^{17}O MAS NMR spectrum without CP, number of scans (N) = 12 000; (b) ^{17}O static NMR spectrum without CP, $N = 10\,000$ (* represent the spinning sidebands of the two main resonances); (c) ^{17}O static CP NMR spectrum, $N = 5000$, $t_c = 100\ \mu$s

The spectral editing of the ^{17}O NMR spectrum, *i.e.* the separation of the signals of the protonated and unprotonated sites, can be obtained by varying the ^{1}H to ^{17}O contact time t_c in the cross-polarisation sequence (the contact time is the time during which the transfer of polarisation between the protons and the oxygens takes place). The variation of the intensity as a function of t_c can be described by the following equation:

$$I(t_c)=I_{\max}(1-T_{OH}/T_{1\rho}{}^{H})^{-1}\,[\exp(-t_c/T_{1\rho}{}^{H}) - \exp(-t_c/T_{OH})]$$

where $T_{1\rho}{}^{H}$ is the spin-lattice relaxation time of the ^{1}H in the rotating frame and T_{OH} is the cross-relaxation time, the value of which is governed by the dipolar interaction between ^{17}O and ^{1}H. A short cross-relaxation time indicates a strong ^{17}O–^{1}H dipolar coupling which results from a short O—H distance. T_{OH} governs the building up of the magnetisation while $T_{1\rho}{}^{H}$ is responsible for its decay.

In this first set of experiments, the CP spectra have been recorded without magic angle sample spinning. We are currently trying to perform CP MAS experiments which should greatly reduce the linewidth of the signals. However, CP experiments with quadrupolar nuclei constitute a field of research which is just emerging and we have observed that the spinning of the sample interacts with the efficiency of the polarisation transfer, making the recording of ^{17}O CP MAS spectra difficult.

The possibility to selectively observe the protonated oxygen is demonstrated in Fig. 5 which shows the ^{17}O NMR spectra of the oxopolymers recorded with long [Fig. 5(a)] and short [Fig. 5(b)] contact times.

The ^{17}O CP NMR spectrum represented in Fig. 5(a) (t_c = 5000 μs) is composed of a broad signal centred at about 400 ppm and extending between 0 and 700 ppm. On the other hand, the spectrum represented in Fig. 5(b) (t_c = 100 μs) is composed of a less intense, broad signal centred at about 200 ppm and extending between −200 and 400 ppm.

Spectrum 5(a) is rather similar to the one represented in Fig. 4(b), *i.e.* recorded without cross-polarisation. The observed overlapping signals can therefore be assigned to μ$_3$-OTi and μ$_4$-OTi oxo bridges. These bridges are not protonated but they still can cross-polarise with the further protons located in the C—H bonds of the remaining alkoxy groups. The signals of the titanium oxo bridges are not observed in the NMR spectrum 5(b) because the contact time is lower and the cross-relaxation time of these non-protonated oxygens is too high to allow efficient cross-polarisation. The broad ^{17}O NMR resonance recorded for short contact time [spectrum 5(b)] can therefore be attributed to protonated oxygens (Ti—O*H). This signal is also present in spectrum 5(a) but it is weaker, probably because the rotating frame spin-lattice relaxation time $T_{1\rho}{}^{H}$ of the protons of the hydroxyl groups is shorter than those of the alkoxy moieties. A more accurate assignment of this resonance (*i.e.* the determination of the location of the OH groups in terminal or bridging positions) is still not straightforward because of the lack of reference compounds for these different kinds of sites.

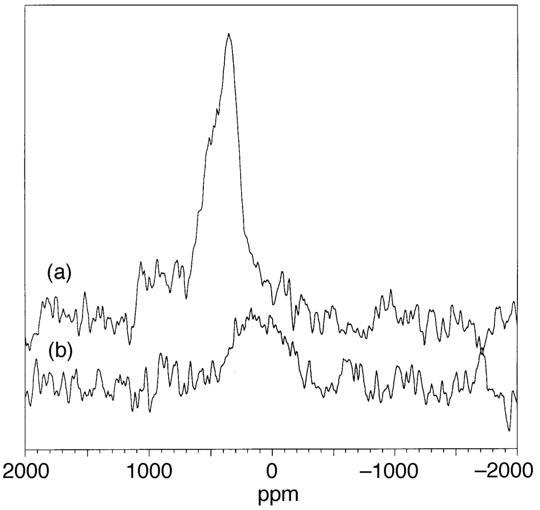

Fig. 5 (a) ^{17}O static CP NMR spectrum, N = 5000, t_c = 5000 μs; (b) ^{17}O static CP NMR spectrum, N = 100, t_c = 5000 μs

This ^{17}O NMR resonance corresponding to the remaining Ti—OH groups is not detectable in the spectrum recorded without cross-polarisation [Fig. 4(b)] because it is probably hidden by the strong signal of μ$_4$-O bridges [Fig. 4(b) and (c)]. This result indicates that the Ti—OH groups are present in this sample only in small amounts. The amount of residual Ti—OH groups depends on several parameters:[18] (i) the hydrolysis ratio: an increase of the hydrolysis ratio results in a decrease of the remaining alkoxy groups and should therefore results in an increase of the Ti—OH groups; (ii) the surface area of the sample: a high surface area may result in a high Ti—OH content. The relatively low Ti—OH content of this sample[18] (the hydroxyl to oxo ratio was estimated at 5%) could explain the small amount of Ti—OH groups observed using ^{17}O NMR; (iii) the ageing of the sample is also an important parameter which contribute to a modification of the amount of residual Ti—OH groups.

This last point is illustrated in Fig. 6 where the ^{17}O CP NMR spectra of the same sample are reported, for the same contact time (t_c = 100 μs), just after the vacuum-drying [Fig. 6(a)] and a month after drying in air [Fig. 6(b)]. The two spectra exhibit a broad resonance located at about 200 ppm and corresponding to the remaining Ti—OH groups. The main difference between the spectra is the intensity of the NMR signal. For the same number of scans and the same amount of xerogel the spectrum recorded after ageing is less intense than the one recorded just after drying: the ratio of the resonances is about 4. This result indicates that the Ti—OH groups have been partially lost upon drying even at room temperature. This loss can result either from an oxygen-17 exchange between the unenriched water of the atmosphere and the enriched hydroxy groups of the sample, or from the further condensation reactions of the hydroxy groups occurring upon ageing of the sample.

In order to shed more light on the exact nature of the Ti—OH groups and on the parameters that control their amount two main directions have to be investigated: (i) ^{17}O cross-polarisation NMR experiments are currently being carried out with samples prepared with higher hydrolysis ratios and exhibiting a high surface to volume ratio; (ii) the design

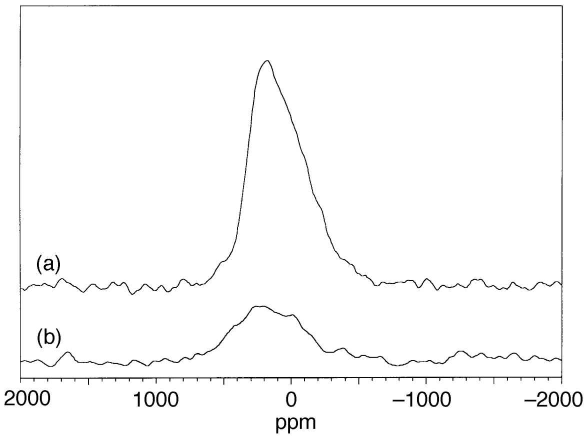

Fig. 6 ^{17}O static CP NMR spectra, N = 15360, t_c = 100 μs, (a) just after vacuum drying; (b) 1 month after vacuum drying

of a straightforward way of quantifying this kind of data is also needed.

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