^{17}O MAS NMR Study of the Bonding Mode of Phosphonate Coupling Molecules in a Titanium Oxo-Alkoxo-Phosphonate and in Titania-Based Hybrid Materials

Vincent Lafond,[†] Christel Gervais,[‡] Jocelyne Maquet,[‡] Daniel Prochnow,[§]
Florence Babonneau,[‡] and P. Hubert Mutin*[,†]

*Chimie Moléculaire et Organisation du Solide, UMR CNRS 5637, Université Montpellier 2,
Place Eugène Bataillon, 34095 Montpellier, France, Laboratoire de Chimie de la Matière
Condensée, UMR CNRS 7574, Université Pierre et Marie Curie, 4, Place Jussieu,
75005 Paris, France, and Fakultät für Physik and Gewissenschaften, Universität Leipzig,
Linnéstrasse 3, 04103 Leipzig, Germany*

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^{17}O-enriched phenylphosphonic acid ($PhP^*O_3H_2$) was prepared from phosphonic acid dichloride and enriched water. This enriched phosphonic acid was used to prepare the titanium oxo-alkoxo-phosphonate $Ti_4(\mu_3\text{-}^*O)(\mu_2\text{-}OPr^i)_3(OPr^i)_5(PhP^*O_3)_3$ (**1**) as a model compound, and titanium oxide/phenylphosphonate hybrids either by sol−gel processing with $Ti(OPr^i)_4$ or by surface modification of a titania support. For comparison a gel sample was prepared using nonenriched $PhPO_3H_2$ and enriched water. The ^{17}O MAS NMR spectra of these 5 solids have been recorded at various magnetic fields (7, 9.4, and 17.6 T) and the isotropic chemical shifts and quadrupolar constants have been determined for the different oxygen sites: P═O, P−O−H, P−O−Ti, and OTi_x. These spectra give direct evidence for the presence of extensive Ti−O−P bonding in the hybrid materials.

Introduction

The elaboration of organic−inorganic hybrid materials in which the organic part is bonded to the inorganic part by a chain of covalent bonds imposes the use of coupling molecules.[1,2] Most covalent hybrid materials are based on an inorganic silica network: in this case organosilane coupling molecules such as trichloro- or trialkoxy-organosilanes are the choice coupling molecules, owing to the ease of formation and stability of Si−O−Si and Si−C bonds.[3−6] In the case of hybrids based on a metal oxide network, organophosphorus coupling molecules such as phosphonic and monoalkylphosphoric acids (or the corresponding sodium or ammonium salts) present several determining advantages over organosilanes. Indeed, M−O−P bonds (M = Ti, Zr, Al, etc.) as well as P−C bonds have a good chemical stability, as shown by the impressive number of metal phosphonate compounds reported in the literature.[7,8] P−OH (or $P{-}O^-$) groups react readily with M-OH or M-OR groups to give M−O−P bridges, allowing the synthesis of hybrid materials either by surface modification of metal oxides[9−17] or by sol−gel processing.[18−20]

Materials based on such organophosphorus coupling molecules are of great promise for applications as membranes,[21,22] heterogeneous catalysts,[20] and photovoltaic cells,[13,23,24] and in the bio-medical area.[16,25]

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* To whom correspondence should be addressed. E-mail: mutin@univ-montp2.fr.

[†] Université Montpellier.

[‡] Université Pierre et Marie Curie.

[§] Universität Leipzig.

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The bonding mode of the organophosphorus coupling molecule to the inorganic part is not easy to assess and is still open to question. FTIR spectroscopic experiments suggest that this bonding mode depends on the nature of the inorganic part and on the experimental conditions. For instance, in the case of goethite (γ-AlOOH), it was found that phosphonic acids bind to the surface as monodentate or bidentate species depending on the pH and the concentration.[26,27] In the case of hybrid solids based on titanium oxide prepared either by surface modification[9,11,15,17] or sol−gel processing,[19] the main bonding mode of phosphonic acids appeared to be tridentate ($RP(OTi)_3$ species).

^{31}P solid-state NMR spectroscopy[12,15,17,19,28,29] proved useful to distinguish between grafted phosphonate species and precipitated metal phosphonate phases, but the signals corresponding to the grafted species were not well resolved and no unequivocal assignment could be done. ^{17}O is a better probe than ^{31}P to investigate the bonding of phosphonate groups (first-neighbor effects instead of second-neighbor effects)[30] and ^{17}O solid-state NMR should provide evidence of the presence (or absence) of P−O−Ti, P═O, and P−OH bonds in the hybrid solids. Indeed, this technique has been successfully used to evidence M−O−Si bonds in metal oxide/organosilane hybrid solids[31−33] and to evidence Al−O−P bonds in porous aluminophosphates.[34]

In this work, we have used ^{17}O MAS NMR to study the bonding of phenylphosphonic acid to titania in hybrid solids prepared by sol−gel processing with $Ti(OPr^i)_4$ and by surface modification of TiO_2 anatase. The low natural abundance of ^{17}O (0.037 at. %) imposed to enrich the solids in ^{17}O. We chose to selectively enrich the oxygen sites bonded to phosphorus atoms by preparing the hybrid solids from enriched phenylphosphonic acid ($PhP^*O_3H_2$), obtained by hydrolysis of phosphonic acid dichloride with enriched water. NMR experiments on $PhP^*O_3H_2$ provided data on O═P and P−O−H sites. To obtain data on P−O−Ti sites, the titanium oxo-alkoxo-phosphonate $Ti_4(\mu_3\text{-}^*O)(\mu_2\text{-}O^iPr)_3(O^iPr)_5(PhP^*O_3)_3\cdot DMSO$ (**1**) was prepared from $PhP^*O_3H_2$ and $Ti(O^iPr)_4$. This crystalline molecular compound, characterized by single-crystal X-ray diffraction,[35] is an ideal model of a titania−phosphonate hybrid. The hybrid gel samples were prepared by a 2-step sol−gel process involving first the formation of Ti−O−P bonds by nonhydrolytic condensation of $Ti(OPr^i)_4$ with $PhPO_3H_2$, followed by the formation of the Ti−O−Ti bonds of the titanium oxide network by hydrolysis/condensation of the remaining alkoxide groups. To get information on Ti−O−P and Ti−O−Ti connectivity, two gel samples were prepared using either $PhP^*O_3H_2$ and nonenriched water or nonenriched $PhPO_3H_2$ and enriched water.

Experimental Section

Sample Preparation. Phenylphosphonic dichloride ($PhPOCl_2$, Acros) and 20 at. % ^{17}O labeled water (Isotec-France) were used as received. Titanium tetraisopropoxide ($Ti(OPr^i)_4$, Lancaster) was freshly distilled, and phenylphosphonic acid ($PhPO_3H_2$, Acros) was recrystallized in acetonitrile before use. The TiO_2 anatase support (ST 61120 NorPro) (specific surface area 145 $m^2\ g^{-1}$, total pore volume 0.38 $cm^3\ g^{-1}$, average pore diameter 10.5 nm) was calcined for 5 h at 500 °C and crushed in a mortar before use.

Synthesis of $PhP^*O_3H_2$. $PhPOCl_2$ (1.98 g, 10.2 mmol) was slowly added to enriched water (1.01 g; 55.4 mmol) in dry THF (3 mL) at −2°C. The reaction mixture was then warmed at room temperature and argon was bubbled overnight into the solution to remove dissolved hydrogen chloride. After evaporation, $PhP^*O_3H_2$ was crystallized from acetonitrile solutions. ^{31}P MAS NMR: s 21.9 ppm.

Synthesis of $Ti_4(\mu_3\text{-}^*O)(\mu_2\text{-}OPr^i)_3(OPr^i)_5(PhP^*O_3)_3\cdot DMSO$ (1). $Ti(OPr^i)_4$, (734 mg; 2.58 mmol) was added to a solution of $PhP^*O_3H_2$ (204 mg, 1.29 mmol) in DMSO (1 mL), leading to a cloudy solution. Traces of (labeled) H_2O in the reactants were sufficient for the formation of the μ_3-O bridging atom. After a few days a clear solution was obtained, from which colorless crystals of **1** grew. After 2 weeks, the crystals were isolated and dried under vacuum (10^{-1} mbar).

The structure of the labeled compound was confirmed by ^{31}P MAS NMR. The spectrum of **1** showed 3 signals in a 1:1:1 ratio at $\delta = 6.1$ ppm, $\delta A = 49.4$ ppm, $\eta = 0.45$; $\delta = 6.5$ ppm, $\delta A = 56.0$ ppm, $\eta = 0.4$; and $\delta = 7.6$ ppm, $\delta A = 52.7$ ppm, $\eta = 0.7$, where δ is the isotropic chemical shift, and δA and η are the anisotropy and asymmetry parameters, respectively.[36]

Synthesis of Hybrid Solids by Sol−Gel Processing. Two gel samples with a Ti/P ratio of 3 were prepared for this study by using a two-step sol−gel process.[19] The first sample was prepared from $Ti(OPr^i)_4$, $PhP^*O_3H_2$, and nonenriched water in order to specifically label the P−O−Ti bonds (gel and xerogel I); and the second one was made from $Ti(OPr^i)_4$, nonenriched $PhPO_3H_2$, and enriched water to label, in that case, the Ti−O−Ti bonds (gel and xerogel II). In the first step, $Ti(OPr^i)_4$ (1.12 mL, 3.79 mmol) was added under stirring to a solution of phenylphosphonic acid (200 mg, 1.26 mmol) in THF (3.5 mL), leading to a white precipitate that dissolved after 2 h. Water (0.114 mL; 6.32 mmol) diluted in THF (0.5 mL) was added very slowly over 30 min. leading to a white gel. After aging for 2 days at room temperature, the gel was washed 3× with 3 mL of THF and dried at 120 °C under vacuum (10^{-1} mbar) for 12 h.

Synthesis of Hybrid Solid by Surface Modification (TiO_2-P). $PhP^*O_3H_2$ (80.0 mg; 0.505 mmol) was added under stirring to a suspension of the titania powder (397 mg) in 500 mL of an 80:20 $MeOH/H_2O$ mixture. After stirring for 42 h at room temperature, the modified titania powder was filtered off, washed 6× with 30 mL of MeOH and dried for 12 h at 120 °C under vacuum (10^{-1} mbar).

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Table 1. Number of Scans and Recycle Delays for the Different ^{17}O MAS NMR Spectra Recorded

sample	field (T)	scan number	recycle time (s)
$PhPO_3H_2$	9.4	23632	10
	17.4	2200	2
compound **1**	9.4	44192	5
	17.4	2600	2
Xerogel I	7	91872	2.5
	9.4	24880	2.5
Xerogel II	7	10288	2.5
	9.4	9600	2.5
TiO_2-P	9.4	98224	2.5

NMR Experiments. ^{17}O MAS NMR spectra were recorded at 7.0, 9.4, and 17.6 T on Bruker MSL300 and MSL400, and Avance750 wide-bore spectrometers operating at 40.69, 54.22, and 101.69 MHz respectively, using Bruker 4-mm probes. At 7.0 and 9.4 T, all the spectra were acquired using a spin−echo $\theta-\tau-2\theta$ pulse sequence with $\theta = 90°$ (on the solid, corresponding to a 1-μs pulse length) to overcome problems of probe ringing and baseline distortions. The τ delay (80 μs) was synchronized with the spinning frequency of the rotor (12.5 kHz). At 17.6 T, the ^{17}O MAS spectra were recorded using a single-pulse excitation with a nonselective ^{17}O nutation frequency of 120 kHz because only a very short pre-acquisition delay was needed. A recycle delay between 2 and 10 s was used to ensure that quantitative spectra were produced and 2000 to 100 000 FIDs were typically accumulated to obtain a reasonable signal-to-noise ratio (Table 1). Chemical shifts were referenced to tap water ($\delta = 0$ ppm) and the resulting spectra were simulated with the DMFIT program.[37]

Results and Discussion

^{17}O solid-state NMR spectra are usually difficult to interpret due to overlapping second-order quadrupolar line shapes that can be only partially averaged by MAS.[37] To deal with this problem, the spectra were recorded at different magnetic fields. The central transition is perturbed only to second-order by the quadrupolar interaction and this perturbation scales inversely to the applied magnetic field so it is reduced at higher fields. Moreover, recording spectra at different magnetic fields greatly improves the confidence in simulations of the resonances.

MAS NMR Study of $PhP^*O_3H_2$. The ^{17}O MAS NMR spectra of $PhP^*O_3H_2$, recorded at two different magnetic fields (9.4 and 17.6 T) are displayed in Figure 1. The spectrum recorded at 9.4 T (Figure 1(a)) shows a complex signal ranging from −150 to 100 ppm where the 3 peaks corresponding to the 3 oxygen sites expected from the crystallographic structure are completely overlapping. At 17.6 T (Figure 1(b)) at least two different signals can be evidenced and the discontinuities are clear enough to distinguish two sites in the signal appearing at lower field. In solution, the proton mobility prevents a differentiation of P═O and POH sites;[30] this mobility most probably explains why both P═O and P−O−H sites are labeled in $PhP^*O_3H_2$, although this compound was prepared from nonenriched $PhPOCl_2$ (Scheme 1). Accordingly, the enrichment of $PhP^*O_3H_2$ should be only about 13 at. % ($^2/_3$ of 20 at. %). The solution ^{17}O NMR spectrum of $PhP^*O_3H_2$ in H_2O (δ 91 ppm) shows that there is no extensive oxygen exchange at room temperature between $PhP^*O_3H_2$ and H_2O.

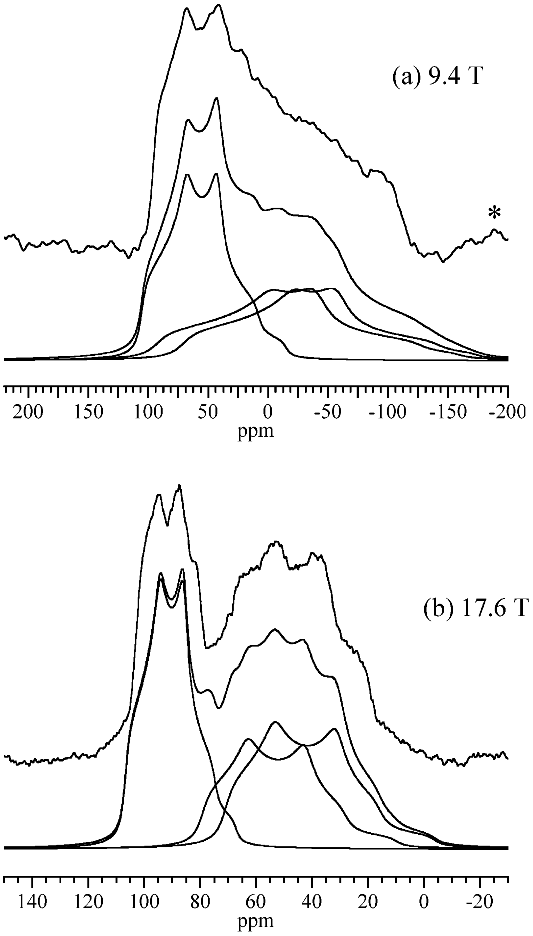
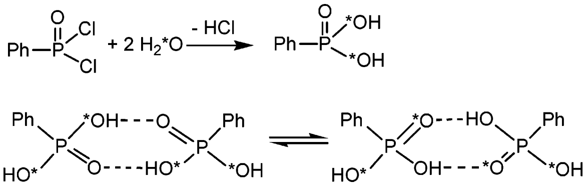


Figure 1. Experimental and simulated ^{17}O MAS NMR spectra of $PhP^*O_3H_2$ recorded at (a) 9.4 T and (b) 17.6 T (* indicates spinning sidebands).

Scheme 1



Regarding the proportions of the two main signals, the one at lower field was assigned to the P═O site, while the broader one at higher field could correspond to the two P−OH environments. Ab initio calculations were used to confirm these attributions and get an idea of the characteristic quadrupolar parameters of the different oxygen sites.[38] The spectra could then be simulated with a good agreement at both fields (Figure 1). The P═O sites are found at 106 ppm with a quadrupolar coupling constant ($C_Q = 4.8$ MHz; $\eta = 0.5$) relatively small compared to those of the OH sites ($C_Q = 7.9$ and 6.9 MHz; $\eta = 0.4$) appearing at higher field ($\delta = 91$ and 74 ppm), as observed in phenylphosphonic acid derivatives.[30]

The isotropic chemical shift values, quadrupolar coupling constants, and asymmetry parameters of each site are summarized in Table 2.

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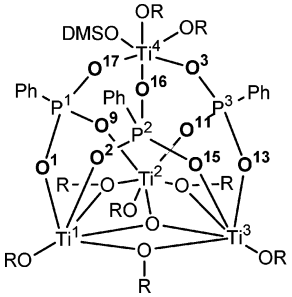

Figure 2. Schematic representation of the molecular structure of $Ti_4(\mu_3\text{-}O)(\mu_2\text{-}OPr^i)_3(OPr^i)_5(PhPO_3)_3{\cdot}DMSO$ (**1**). The O atoms in Ti−O−P bonds (boldface), the P atoms, and the Ti atoms are numbered according to ref 35.

Table 2. ^{17}O MAS NMR Parameters Extracted from the Simulations of the Spectra Recorded at 9.4 and 17.6 T

δ_{iso} (ppm) (± 1)	C_Q (MHz) (± 0.1)	η_Q (± 0.1)	assignment	% (± 2)
		$PhP^*O_3H_2$		
106.0	4.8	0.5	P=O	32
91.0	7.9	0.4	P−O−H	34
74.0	6.9	0.4	P−O−H	34
		Cluster 1		
151.0	5.2	0.15	P−O−Ti^4	11
152.5	5.2	0.15		11
177.8	8.3	0.0		10
207.0	5.2	0.1	P−O−Ti^{1-2-3}	10
210.0	5.5	0.15		10
215.0	5.3	0.15		10
219.5	5.3	0.15		10
223.0	5.2	0.1		10
240.3	5.6	0.2		10
482.2			OTi_3	8

MAS NMR Study of 1. Studies of connectivity between different metallic atoms in transition metal oxoalkoxides and oxides[39−41] and in mixed Si−O-M (M = Ti, Ta)[33,42,43] systems using ^{17}O NMR were recently reported but little work has been published on P−O−Ti containing systems, either in the liquid or solid state. Cluster **1**, therefore, appears as a good reference compound to determine the ^{17}O chemical shift and quadrupolar interaction parameters characteristic of well-defined P−O−Ti mixed bridges. Indeed, the molecular structure of **1** (Figure 2) indicates that all of the phosphonate groups are bonded to 3 different Ti atoms in tridentate $PhP(OTi)_3$ sites.

The ^{17}O MAS NMR spectrum of cluster **1** recorded at 9.4 T (Figure 3(c)) shows a sharp line around 480 ppm and broad overlapping signals ranging from 50 to 250 ppm. The narrow line can be assigned to OTi_3 sites[39,44] which shows that the μ_3-O atoms in compound **1** stem from enriched water in $PhP^*O_3H_2$. The other resonances at higher field correspond to P−O−Ti sites. Since OTi_2 sites appear at ^{17}O chemical shift values around 800 ppm and P−O−P sites have been observed between 110 and 125 ppm in pyrophosphates,[45] Ti−O−P signals can indeed be expected between 150 and 800 ppm.

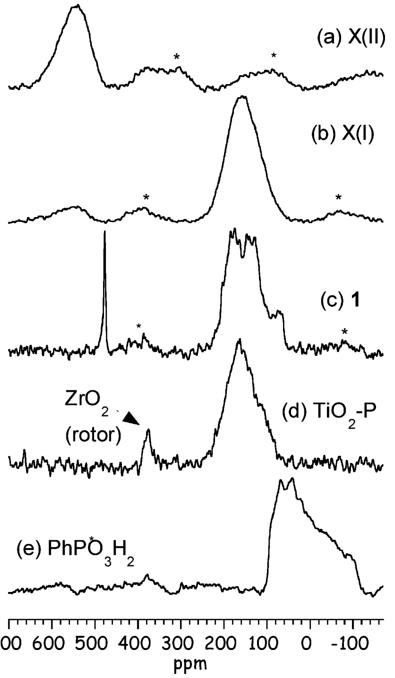

Figure 3. ^{17}O MAS NMR spectra recorded at 9.4 T of (a) xerogel I prepared from $PhPO_3H_2$, $TiOPr^i_4$, and $H_2{}^*O$; (b) xerogel II prepared from $PhP^*O_3H_2$, $TiOPr^i_4$, and H_2O; (c) $Ti_4(\mu_3\text{-}^*O)(\mu_2\text{-}O^iPr)_3(O^iPr)_5(PhP^*O_3)_3{\cdot}DMSO$ (**1**); (d) TiO_2 anatase modified by $PhP^*O_3H_2$ (TiO_2–P); and (e) $PhP^*O_3H_2$ (* indicates spinning sidebands, spinning rate 12.5 kHz).

The spectrum of **1** recorded at 17.6 T (Figure 4(b)) shows two distinct shapes in this range centered around 210 and 140 ppm, approximately in a 2:1 ratio. The crystal structure of compound **1** indicates the presence of 9 different P−O−Ti sites with different bond lengths and Ti−O−P angles (Table 3). The angles of the 6 P−O−Ti bonds linking the phosphonate groups to the 3 Ti atoms of the oxo-alkoxide base are close, in the range 123.35−126.4°. In contrast, the angles of the 3 P−O−Ti bonds to the Ti atom at the apex (Ti^4) are significantly higher and different from each other: 153.28, 159.10, and 166.96°. In zeolites, a correlation between the isotropic value of the ^{17}O chemical shift and the Si−O−Al bond angle was found.[46] Accordingly, we propose to ascribe the overlapping signals of the main shape around 210 ppm to the 6 P−O−Ti sites at the base and the signals around 140 ppm to the 3 P−O−Ti sites at the apex. This assumption was used as a basis for the simulation of the spectra using 9 signals in similar proportions with relatively close quadrupolar parameters, globally divided in a 6:3 ratio between the signals at low and high chemical shift values. A first set of parameters was obtained from the high field spectrum, which shows more distinct discontinuities, and was then refined by simulating the low field spectrum. The parameters that gave the best fits simultaneously at both fields are reported in Table 2 and the corresponding simulations are shown in Figure 4.

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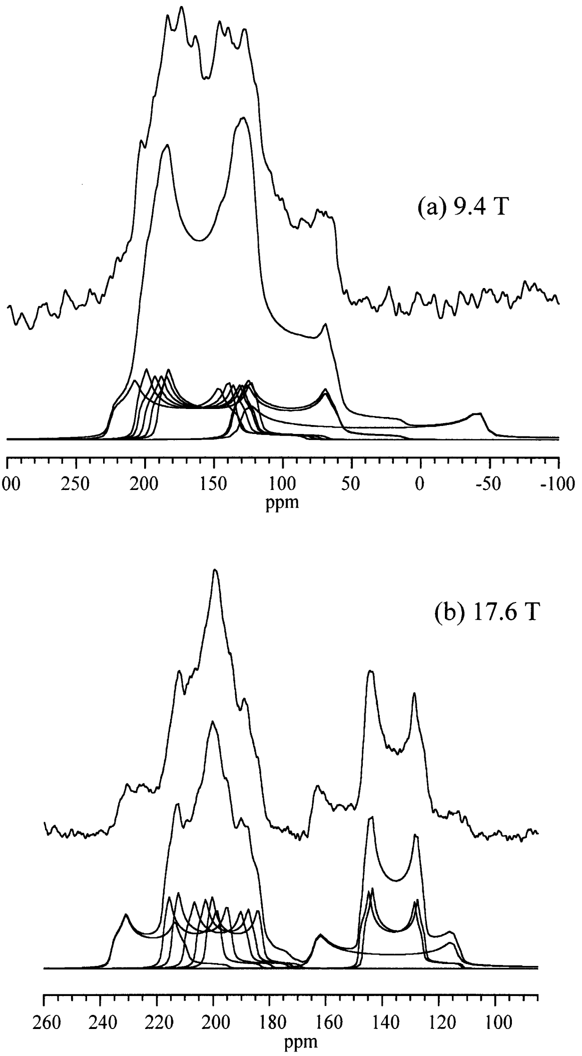

Figure 4. ^{17}O MAS NMR spectra of compound **1** at (a) 9.4 T and (b) 17.6 T (* indicates spinning sidebands) OTi_3 resonance at 482.2 ppm not shown.

Table 3. Bond Lengths and Angles for the Different P−O−Ti Sites in Compound 1[35] (O Atoms Are Numbered as In Figure 2)

O site	Ti−O bond length (Å)	P−O bond length (Å)	Ti−O−P angle (°)
O^1	1.9530(17)	1.5403(18)	126.30(11)
O^2	1.9467(17)	1.5431(19)	125.52(10)
O^9	1.9773(17)	1.5391(18)	124.60(10)
O^{11}	1.9836(18)	1.5377(19)	124.05(10)
O^{13}	1.9811(18)	1.5310(19)	123.35(11)
O^{15}	1.9761(18)	1.533(2)	126.41(11)
O^3	1.9549(17)	1.5062(19)	166.96(12)
O^{16}	2.0952(17)	1.4996(19)	153.28(11)
O^{17}	2.0399(18)	1.5078(19)	159.10(11)

Hybrid Solids. *Xerogels.* The ^{17}O MAS NMR spectrum of xerogel I prepared from $PhP^*O_3H_2$, $TiOPr^i_4$, and H_2O (Figure 3(b)) shows a major signal centered at 150 ppm. This resonance may be confidently ascribed to P−O−Ti sites, as it is in the same chemical shift range as the Ti−O−P resonances of compound **1**. There is no indication of P−O−H sites, and very few, if any, P=O sites. These findings show that most of the phosphonate groups are tridentate ($PhP(OTi)_3$ sites) as deduced previously from FTIR experiments.[18,19] Two additional minor signals around 400 and 550 ppm are assigned to OTi_4 and OTi_3 sites, respectively,[39,40] most probably originating from the presence of enriched water in $PhP^*O_3H_2$.

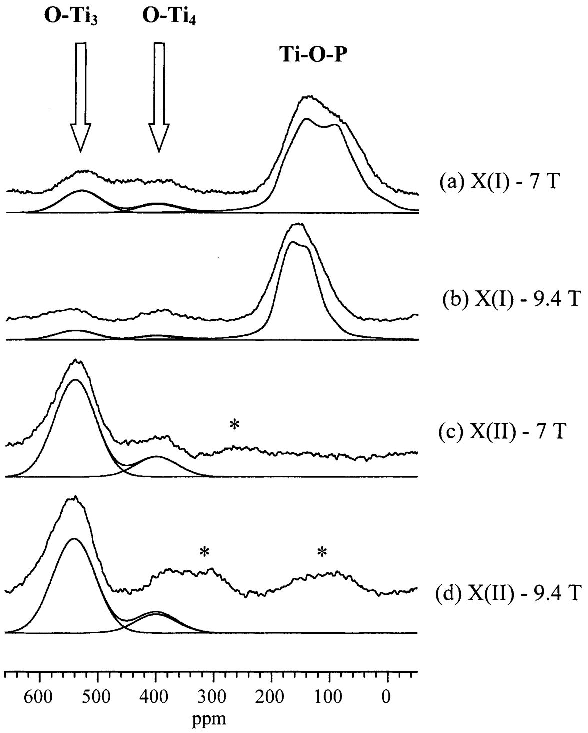

Figure 5. ^{17}O MAS NMR experimental and simulated spectra of xerogel I prepared from $PhPO_3H_2$, $TiOPr^i_4$, and $H_2{}^*O$, recorded at 7 T (a) and 9.4 T (b), xerogel II prepared from $PhP^*O_3H_2$, $TiOPr^i_4$, and H_2O, recorded at 7 T, (c) and 9.4 T (d) (* indicates spinning sidebands).

To confirm these assignments and extract the characteristic parameters of the Ti−O−P oxo-bridges, spectra were recorded at a second field, which improves the reliability of the simulations by providing additional constraints. Figure 5 shows the comparison of the ^{17}O MAS NMR spectra recorded at 7 and 9.4 T for xerogel I. The line widths in Hertz of the resonances at 400 and 540 ppm (ascribed to OTi_4 and OTi_3 environments) scale directly with the applied magnetic field, indicating that they are determined almost completely by chemical shift dispersion. These Ti−O−Ti signals were therefore simulated successfully using simple Gaussians with the same line width (in ppm) at each field. The ability to simulate such ^{17}O resonances by Gaussians neglecting second-order quadrupole effects has already been reported for TiO_2[41] nanoparticles and in sol−gel-prepared TiO_2-SiO_2 materials.[33,42]

The signal in the 250−100 ppm region assigned to Ti−O−P environments can be simulated at both fields with a pure quadrupolar line shape at $\delta_{iso} = 202$ ppm suggesting that the broadening has little chemical distribution contribution, contrary to what has been observed for Si−O−Ti signals in xerogels.[33] The NMR parameters extracted from these simulations are summarized in Table 4. The spectrum of xerogel II prepared from $PhPO_3H_2$, $TiOPr^i_4$, and $H_2{}^*O$ (Figure 3(a)) shows a major resonance at 540 ppm and a minor one at 400 ppm, assigned to OTi_3 and OTi_4 sites in good agreement with the signals observed in xerogel I. Thus, the TiO_2 network in our hybrid xerogels is similar to that of hybrid xerogels based on titania and organosilanes.[33] There is no indication of P−O−Ti sites in spectrum 3(a)

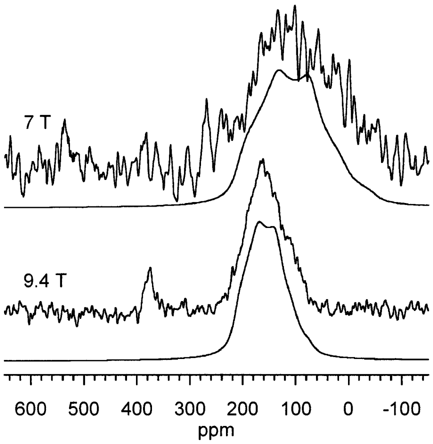

Figure 6. ^{17}O MAS NMR experimental and simulated spectra of TiO_2 modified by $PhP^*O_3H_2$, recorded at 7 T and 9.4 T.

Table 4. ^{17}O MAS NMR Parameters Extracted from the Simulations of the Spectra Recorded at 9.4 and 7 T

sample	δiso (ppm) (± 2)	C_Q (MHz) (± 0.1)	η_Q (± 0.1)	assignment
Xerogel I	202	4.7	0.4	Ti−O−P
	400			OTi_4
	540			OTi_3
Xerogel II	400			OTi_3
	540			OTi_4
TiO_2−P	210	5.3	0.5	Ti−O−P

indicating that there is no oxygen exchange around P and Ti centers during the synthesis of the xerogel. Accordingly, the use of $PhP^*O_3H_2$ or $H_2{}^*O$ permits selective labelling of Ti−O−P or Ti−O−Ti bonds, giving a detailed picture of the framework oxygen in our hybrid xerogels.

TiO_2 Modified with $PhP^*O_3H_2$. The ^{17}O MAS NMR spectrum of the hybrid solid prepared by surface modification of TiO_2 (anatase) with $PhP^*O_3H_2$ is given in Figure 3(d). The narrow resonance observed around 390 ppm can be assigned to natural abundance ^{17}O sites in the ZrO_2 rotor,[47] that are no more negligible considering the low amount of $PhP^*O_3H_2$ in our sample. The major signal, centered at 160 ppm, may be ascribed to P−O−Ti sites. As in the case of of xerogel I, there is no indication of P−O−H sites, and very few, if any, P═O sites. Figure 6 shows the comparison of the ^{17}O MAS NMR spectra recorded at 7 and 9.4 T. The signal-to-noise ratio of the spectrum recorded at 7 T is rather poor, owing to the moderate specific surface area of the support (ca 145 $m^2\ g^{-1}$). Nevertheless, both spectra can be simulated with a quadrupolar shape at 210 ppm characteristic of P−O−Ti sites (Table 4), which confirms that the bonding mode of the phenylphosphonate groups to the surface is predominantly tridentate.[9,11,15,17] A recent study using $^1H-^{31}P$ Hetcor and ^1H double-quantum MAS NMR experiments indicated the presence of residual P−OH groups for carboxyalkylphosphonic acids anchored to TiO_2.[48] This difference in bonding mode might be related to the higher acidity of phenylphosphonic acid or to the different anchoring procedures used.

As previously reported[15] for TiO_2 modified by phenylphosphonic acid, the ^{31}P MAS NMR spectrum of our sample shows a major signal at 13 ppm with shoulders around 18 and 6 ppm. Our ^{17}O NMR results suggest that these resonances should be ascribed to tridentate phosphonate species with different geometries rather than be ascribed to different bonding modes.

Conclusions

For the first time, solid state ^{17}O NMR has been used to characterize a titanium oxo-alkoxo phosphonate and hybrid solids based on TiO_2 and phosphonic acid coupling molecules. The use of enriched phosphonic acid or enriched water permits the selective labelling of Ti−O−P or Ti−O−Ti bonds, giving a detailed picture of the framework oxygen in the sol-gel derived solids. The ^{17}O NMR parameters of P═O, P−O−H, and P−O−Ti sites have been determined. These experiments unambiguously show that the bonding mode of phosphonate coupling molecules is predominantly tridentate in the hybrid solids prepared by either sol−gel processing or surface modification.

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