

High-Field ^{17}O MAS NMR Investigation of Phosphonic Acid Monolayers on Titania

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High-field ^{17}O MAS NMR was used to investigate the binding of self-assembled monolayers of ^{17}O -enriched phosphonic acids deposited on a titania anatase support. The spectra were recorded at two different magnetic fields (9.4 and 17.6 T), to improve the reliability of the simulations of the different resonances. The spectra recorded at 17.6 T offer an excellent resolution between the different oxygen sites, P=O, P–O–H, and P–O–Ti, thus greatly facilitating their quantification. The data reported here give direct evidence of the extensive formation of Ti–O–P bonds in the surface modification of titania by phosphonic acids. The presence of residual P=O and P–O–H sites indicates the presence of several different binding modes in phosphonic acid monolayers. The chemical shift of P–O–Ti sites is consistent with bridging (as opposed to chelating) modes.

Introduction

The functionalization of inorganic substrates by anchoring organic monolayers or self-assembled monolayers to the surface is a powerful way to tailor surface properties.¹ The best studied examples are thiol monolayers on coinage metal surfaces^{2,3} and silane monolayers on silica surfaces.^{4,5} Organophosphorus derivatives such as phosphonic acids and alkylphosphates are attracting increasing attention, as they bind strongly to a wide variety of metal^{6–9} and metal oxide substrates.^{10–14} Phosphonic acid monolayers on titanium oxide surfaces (titanium dioxide or native oxide layer on

titanium) have been particularly studied. Phosphonic acids have been used to anchor dyes to TiO₂ anatase thin films in the preparation of solar cells,^{15–18} modify TiO₂ membranes,¹⁹ improve the adhesion of thin polymer films to titanium,^{20,21} and improve bone binding to titanium dental or orthopedic implants.^{22–25} Long-chain alkylphosphonic acid form well-packed self-assembled monolayers (SAMs) on titanium oxide surfaces^{11,26,27} with excellent thermal¹⁴ and hydrolytic stability.^{28–30}

It is usually accepted that phosphonic acid molecules bind to titanium oxide surfaces via Ti–O–P bonds resulting from

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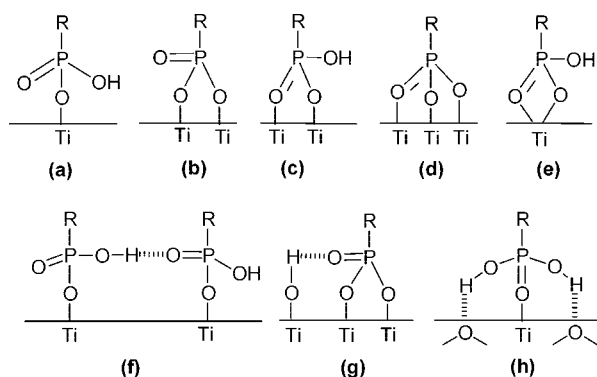
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Scheme 1. Schematic Representation of Some Possible Binding Modes: (a) Monodentate, (b, c) Bridging Bidentate, (d) Bridging Tridentate, (e) Chelating Bidentate; (f–h) Additional Hydrogen-Bonding Interactions



the condensation between P–OH and surface Ti–OH groups and from the coordination of the phosphoryl oxygen to a surface Ti atom; both bridging and chelating configurations have been envisaged,^{19,31} which leads to a variety of mono-, bi-, and tridentate binding modes (Scheme 1). In addition, remaining P–OH and P=O groups would probably be involved in hydrogen bonds with adjacent mono- or bidentate phosphonate units, or with surface hydroxyl or oxo groups.³¹ Thus, recent DFT computations³² suggested that the most stable adsorption arrangement for phosphonic acid to a titania surface would be a monodentate binding mode involving the coordination of the P=O group, stabilized by two hydrogen bonds between the remaining POH groups and surface oxo bridges (Scheme 1h). The binding of phosphonic acids to titanium oxide surfaces is not easy to assess experimentally and the few studies reported may appear contradictory. Solid-state ³¹P MAS NMR is a very useful tool, which permits to distinguish between physisorbed, chemisorbed and bulk titanium phosphonate species, but no conclusions about the binding mode can be drawn from the changes in the chemical shift.^{11,13} On the basis of FTIR spectroscopy studies, it was proposed that the surface binding mode of phenylphosphonic acid on titania was predominantly tridentate, with some bidentate binding modes.^{13,19} On the other hand, using fast magic-angle spinning (MAS) NMR experiments, Pawsey et al.³¹ detected dipolar coupled P–OH protons in carboxyalkylphosphonic acids on titania, indicating the presence of a large number of unreacted P–OH groups.

To the best of our knowledge, there is no example in the literature of ¹⁷O NMR studies on the formation of monolayers on surfaces, because of the very low natural abundance of ¹⁷O (0.037 at%) and to the lack of resolution resulting from second-order quadrupolar broadening.³³ Nevertheless, in a previous work, we showed that ¹⁷O MAS NMR could distinguish between P–OH, P=O, Ti–O–Ti, and P–O–Ti sites in ¹⁷O-enriched hybrid solids.³⁴ In addition, we presented a spectrum of titania modified by enriched phe-

nylphosphonic acid recorded at 9.4 T, giving evidence of the formation of interfacial P–O–Ti bonds in spite of the relatively low resolution. In this work, we used high-field ¹⁷O MAS NMR to investigate the binding of (self-assembled) monolayers of ¹⁷O-enriched phosphonic acids deposited on a titania anatase support. The spectra were recorded at two different magnetic fields (9.4 and 17.6 T), to improve the reliability of the simulations of the different resonances. The spectra recorded at 17.6 T offer an excellent resolution between the different oxygen sites, P=O, P–O–H, and P–O–Ti, thus greatly facilitating their quantification. The results presented here demonstrate the potential of high-field ¹⁷O MAS NMR in the characterization of monolayers and self-assembled monolayers on oxide surfaces.

Experimental Section

Synthesis of Enriched Phosphonic Acids. ¹⁷O-enriched phosphonic acids were prepared as described previously by hydrolysis of the corresponding phosphonic dichlorides with 20 at % ¹⁷O-enriched water in dry THF at 0 °C.³⁴ PhPOCl₂ was obtained from Aldrich; C₁₂H₂₅POCl₂ was prepared by reaction of C₁₂H₂₅PO₃H₂ with SOCl₂.³⁵ The ¹⁷O-enriched phosphonic acids were characterized by ³¹P NMR. C₁₂H₂₅PO₃H₂ (200 MHz, THF, ppm), 34.0; PhPO₃H₂ (200 MHz, THF, ppm), 13.9.

Surface Modification. The TiO₂–anatase support (Saint Gobain Norpro, specific surface area 120 m² g⁻¹) was dried for 12 h at 120 °C under a vacuum (1 × 10⁻¹ mbar). Phenylphosphonic acid (100 mg, 0.63 mmol) dissolved in 0.5 L of 80:20 MeOH:H₂O was reacted with TiO₂ (0.5 g) for 2 days at 20 °C.³⁴ The modified powder was washed thoroughly with MeOH, then dried for 12 h at 120 °C under a vacuum (1 × 10⁻¹ mbar). Dodecylphosphonic acid (250 mg, 1.0 mmol) was dissolved in 30 mL of toluene.³⁶ The solutions were reacted with TiO₂ (0.5 g) for 3 days at 20 °C. The modified powders were washed thoroughly with the reaction solvent, acetone, ethanol, and water, and then dried for 12 h at 120 °C under a vacuum (1 × 10⁻¹ mbar).

Solid-State NMR Experiments. ³¹P MAS NMR spectra were recorded at 7 T on a Bruker Avance300 narrow-bore spectrometer, operating at 121.496 MHz, using Bruker 4 mm probes, a spinning frequency of the rotor of 10 kHz, a flip angle of 45° and a recycle delay of 10 s. ¹⁷O MAS NMR spectra were recorded at 9.4 and 17.6 T on Bruker Avance400 and Avance750 wide-bore spectrometers operating at 54.22 and 101.69 MHz respectively, using Bruker 4 mm probes and a spinning frequency of the rotor of 12.5 kHz. At 9.4 T, the spectra were acquired using a spin–echo θ – τ – 2θ pulse sequence with $\theta = 90^\circ$ to overcome problems of probe ringing and baseline distortions. Low power pulses, selective for the central transition were used. The τ delay (80 μ s) was synchronized with the spinning frequency. At 17.6 T, the ¹⁷O MAS spectra were recorded using a single-pulse excitation with a nonselective ¹⁷O nutation frequency of 120 kHz since only a very short preacquisition delay was needed. A recycle delay between 5 and 10 s was used to ensure that fully relaxed spectra were produced. To ensure a reasonable signal-to-noise ratio, acquisition of the spectra required 1 day (for pure acids) to 3 days (for TiO₂ modified samples) at 9.4 T and 1 h (for pure acids) to 1 day (for TiO₂ modified samples) at 17.6 T. ¹⁷O and ³¹P chemical shifts were referenced to tap water and H₃PO₄, respectively ($\delta = 0$ ppm), and the resulting spectra were simulated with the DMFIT program.³⁷

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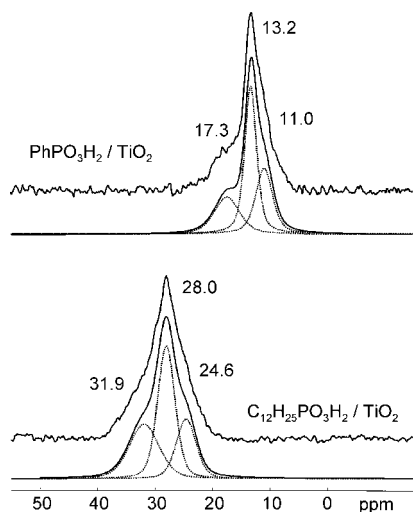


Figure 1. Experimental (full lines) and simulated (dotted lines) ³¹P MAS NMR spectra of TiO₂ modified by PhPO₃H₂ (top) and C₁₂H₂₅PO₃H₂ (bottom) recorded at 7 T.

Table 1. ³¹P MAS NMR Chemical Shifts of Selected Compounds

compd	site	δ (ppm)
PhPO ₃ H ₂	PhP(O)(OH) ₂	21.8
α-Ti(PhPO ₃) ₂	PhP(OTi) ₃	-4.0 ¹³
Ti ₃ (PhPO ₃) ₄ (O ⁱ Pr) ₈	PhP(OTi) ₃	5.8, 6.2, 7.3 ³⁸
C ₁₈ H ₃₇ PO ₃ H ₂	CP(O)(OH) ₂	31.5 ¹¹
α-Ti(C ₁₈ H ₃₇ PO ₃ H ₂) ₂	CP(OTi) ₃	7 ¹¹
C ₁₂ H ₂₅ PO ₃ H ₂	CP(O)(OH) ₂	31.9
α-Ti(C ₁₂ H ₂₅ PO ₃) ₂	CP(OTi) ₃	6.7
Ti ₃ (MePO ₃) ₄ (O ⁱ Pr) ₈	CP(OTi) ₃	14.7, 16.7, 17.6 ³⁸

Results and Discussion

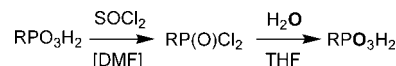
³¹P MAS NMR. The ³¹P spectra of TiO₂ anatase modified by nonenriched phenylphosphonic and dodecylphosphonic acids are displayed in Figure 1. Both spectra are qualitatively similar, but the spectrum of C₁₂H₂₅PO₃H₂/TiO₂ is broader, and the chemical shift of the main resonance is closer to that of the parent phosphonic acid (Table 1). These spectra confirm the presence of amorphous grafted phosphonate species, and the absence of bulk titanium phosphonates (α-Ti(RPO₃)₂) formed by dissolution-precipitation, which would lead to sharp resonances at -4.0 ppm (R = Ph) and 6.7 ppm (R = C₁₂H₂₅) (Table 1).^{11,13}

Simulation of the spectra with a minimum number of resonances with Gaussian-Lorentzian shapes indicates the presence in both cases of at least three sites (Figure 1, Table 2). ³¹P chemical shifts in titanium phosphates and phosphonates are sensitive to the number of titanium second-neighbors. Each condensation between P-OH and Ti-OH groups should lead to an upfield shift. Conversely, the interactions of the P=O groups with surface Lewis or Bronsted acidic sites should lead to a downfield shift.³⁹ In addition, ³¹P chemical shifts are also sensitive to variations in the O-P-O bond angles. Thus, the chemical shifts of

Table 2. Parameters Used for the Simulation of ³¹P MAS NMR Spectra

sample	δ (ppm)	width (ppm)	integration (%)
PhPO ₃ H ₂ /TiO ₂	17.3	5.2	24
	13.2	2.4	46
	11.0	3.4	30
C ₁₂ H ₂₅ PO ₃ H ₂ /TiO ₂	31.9	6.1	32
	28.0	3.6	45
	24.6	4.1	23

Scheme 2. Synthetic Scheme of the ¹⁷O-Enrichment of Phosphonic Acids with Enriched H₂O (H₂O in the Scheme)



RP(OTi)₃ sites in bulk titanium phosphonates and molecular titanium phosphonates can differ by more than 10 ppm (Table 1). Accordingly, it is not possible to unambiguously ascribe the different components^{11,13} and therefore to quantify the amount of interfacial Ti-O-P bonds.

¹⁷O MAS NMR. ¹⁷O-enrichment is required because of the poor natural abundance of ¹⁷O and the very low amount of grafted species in these organic monolayers. Assuming an average grafting density of 4 phosphonate per nm² and a specific surface area of 120 m² g⁻¹, the percentage of oxygen bound to phosphonate species in the samples would be about 4 wt % only. Enriched phosphonic acids were prepared by hydrolysis of the corresponding phosphonic acid dichlorides with enriched water (20 at %). C₁₂H₂₅PO₃Cl₂ was not commercially available and was obtained by reaction of the phosphonic acid with thionyl dichloride, catalyzed with dimethylformamide³⁵ (Scheme 2). Fast proton exchange in solution results in the labeling of both P-OH and P=O sites, with a ¹⁷O abundance of about 13 at % (2/3 of 20 at %),³⁴ thus 350 times higher than natural abundance.

The ¹⁷O MAS NMR spectra of the enriched phosphonic acids recorded at 9.4 and 17.6 T are displayed in Figure 2. The spectra recorded at 9.4 T are difficult to interpret because of overlapping quadrupolar lineshapes that are only partially averaged by MAS. Moreover, a spin-echo sequence has to

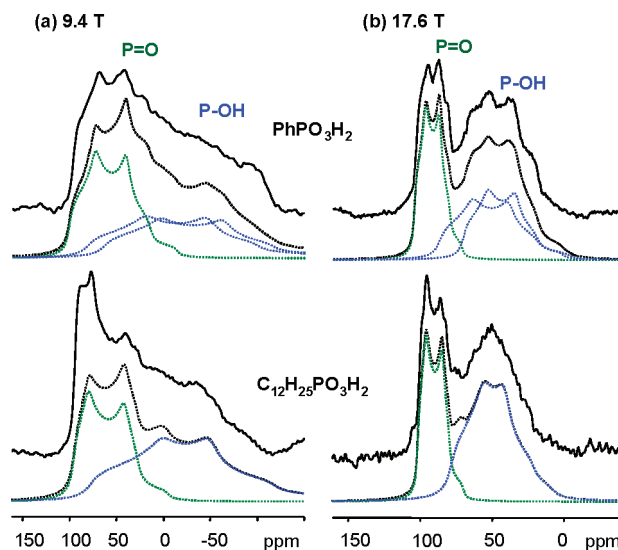


Figure 2. Experimental (full lines) and simulated (dotted lines) ¹⁷O MAS NMR spectra of PhPO₃H₂ (top) and C₁₂H₂₅PO₃H₂ (bottom) recorded at 9.4 and 17.6 T.

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Table 3. ^{17}O MAS NMR Parameters Used for the Simulation of the Spectra Recorded at 9.4 and 17.6 T of the Phosphonic Acids and of Titania Modified by the Phosphonic Acids: Isotropic Chemical Shift (δ), Quadrupolar Coupling Constant (C_Q), Asymmetry Parameter (η), and Line Broadening (LB) in Hz

sample	δ (ppm)	C_Q (MHz)	η	LB (9.4 T)	LB (17.6 T)	intensity	attribution
PhPO ₃ H ₂	106	4.8	0.4	800	600	33	P=O
	91	7.9	0.4	1000	600	35	P-OH
	74	6.9	0.4	1000	600	32	P-OH
C ₁₂ H ₂₅ PO ₃ H ₂	103	4.8	0.3	1000	600	37	P=O
	80	7.0	0.6	1000	600	63	P-OH
PhPO ₃ H ₂ /TiO ₂	185	5.4	0.3	2100	4000	80	P-O-Ti
	113	4.9	0.2	1000	900	14	P=O
	80	8.0	0.4	400	400	6	P-OH
PhPO ₃ H ₂ /TiO ₂	190	5.2	0.2	1400	1600	39	P-O-Ti
	170	5.6	0.3	1200	1400	40	P-O-Ti
	113	4.9	0.2	900	900	14	P=O
	80	8.0	0.4	400	400	7	P-OH
C ₁₂ H ₂₅ PO ₃ H ₂ /TiO ₂	185	5.2	0.3	2600	5100	65	P-O-Ti
	113	4.9	0.2	800	850	16	P=O
	85	7.3	0.4	400	400	19	P-OH
C ₁₂ H ₂₅ PO ₃ H ₂ /TiO ₂	198	5.2	0.2	1300	1600	26	P-O-Ti
	162	5.6	0.3	1100	1400	34	P-O-Ti
	113	5.0	0.2	800	1100	18	P=O
	85	7.6	0.4	400	500	22	P-OH

be applied at this field to avoid problems of probe ringing, resulting sometimes in incomplete refocusing of the signal as can be observed for the P=O site in the spectrum of dodecylphosphonic acid. 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. Indeed, the resolution is greatly improved in the spectra recorded at 17.6 T and the signal at low field arising from the P=O site⁴⁰ can be easily distinguished from the signals at higher field arising from P-OH sites. The spectra of phenylphosphonic and dodecylphosphonic acids can be satisfactorily simulated at both fields (Figure 2). Two different P-OH sites were considered in the case of phenylphosphonic acid, as expected from its crystal structure and first-principles calculations of ^{17}O NMR parameters.^{34,41} Because no crystalline structure is currently reported for dodecylphosphonic acid (preventing first-principles calculations) and because no singularities and points of inflection are found in the high field part of the spectrum, only one P-OH component was used. The isotropic chemical shift values, quadrupolar coupling constants, and asymmetry parameters of each oxygen site (Table 3) appear quite similar regardless of the nature of the organic group (alkyl or aryl) bonded to the phosphorus atom.

The spectra of TiO₂ anatase modified by the enriched phosphonic acids are reported in Figures 3 and 4. At 9.4 T, all the spectra display a major signal in the chemical shift range 200 to 0 ppm, consistent with the presence of Ti-O-P sites and some P=O sites. The spectrum of C₁₂H₂₅PO₃H₂/TiO₂ shows an additional weaker signal in the 0 to -100 ppm range, suggesting the presence of residual P-OH sites. However, the resolution is too poor to permit a reliable simulation of the spectra. On the other hand, the resolution

of the spectra recorded at 17.6 T is much better, enabling us to distinguish easily between P-O-Ti, P=O, and P-OH sites in the spectrum of C₁₂H₂₅PO₃H₂/TiO₂ (Figure 3). In the case of PhPO₃H₂/TiO₂, P-O-Ti and P=O sites are clearly visible; a weak shoulder in the high field part of the spectrum could indicate the presence of a few residual P-OH groups (Figure 4). There is no evidence of spinning side bands in the spectra: at 17.6 T, spinning side bands would fall at 120 ppm of the central line; since the main signals are observed around 185 ppm, spinning sidebands would be expected around 65 ppm (overlapping with signals ascribed to P-O-H sites) but also around 305 ppm where no signal is observed. The spectra of C₁₂H₂₅PO₃H₂/TiO₂ and PhPO₃H₂/TiO₂ were simulated using components with C_Q and η values similar to those found for the phosphonic acids (P=O and P-OH sites) and for a model molecular titanium phosphonate compound (P-O-Ti site).³⁴ Simulation of the broad resonance attributed to the Ti-O-P sites with a single pure quadrupolar shape was not consistent at both fields (see the Supporting Information). To obtain a satisfactory fit, it was necessary to use either a field-dependent line-broadening, or two (or more) P-O-Ti components, as shown in Figures 3 and 4. Both simulations likely simply indicate the presence of a distribution of surface P-O-Ti sites with different bond angles, as expected for amorphous compounds. In zeolites, it was established that the isotropic ^{17}O chemical shift decreases with increasing T-O-T angle (T = Si or Al).⁴²⁻⁴⁴ A similar trend was found for Ti₄(μ_3 -O)(μ_2 -OPrⁱ)₃(OPrⁱ)₅-(PhPO₃)₃·DMSO, where signals with isotropic ^{17}O chemical shifts between 151 and 178 ppm were ascribed to P-O-Ti sites with bond angles between 167 and 153°, and signals with isotropic ^{17}O chemical shifts between 207 and 240 ppm were ascribed to P-O-Ti sites with bond angles between 126 and 123°. The chemical shifts of P-O-Ti sites in the phosphonic acid monolayers are in the same range, suggesting the presence of P-O-Ti bond angles in the 125-165° range. Thus, the bidentate or tridentate phosphonate units in the monolayers are bridging rather than chelating. As a matter of fact, bridging phosphonate units are the rule in molecular^{38,45,46} or tridimensional^{47,48} titanium phosphonates. Unfortunately, the very low amount of surface species and their amorphous character prevents the use of elaborate NMR techniques such as MQ-MAS⁴⁹ or SATRAS.⁵⁰ MQ MAS experiments could bring information about both chemical shift values and quadrupolar

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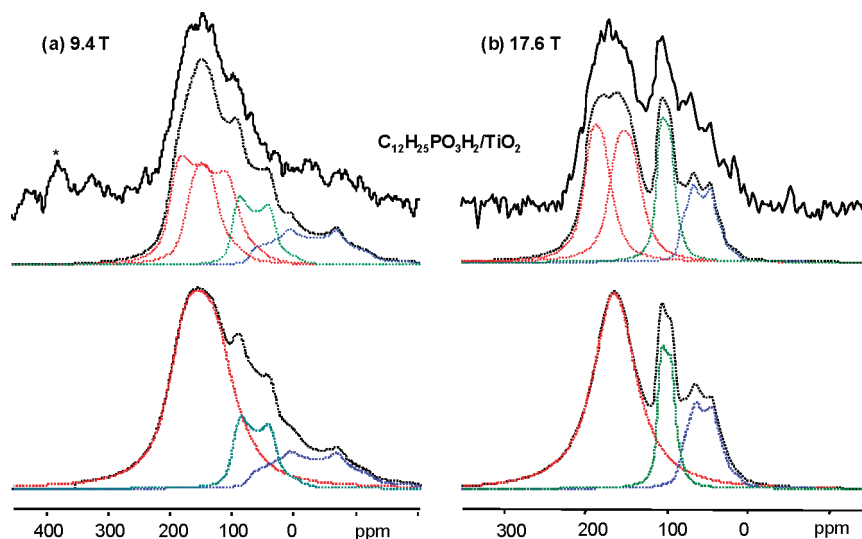


Figure 3. Experimental (full lines) ^{17}O MAS NMR spectra of $\text{C}_{12}\text{H}_{25}\text{PO}_3\text{H}_2/\text{TiO}_2$ recorded at (a) 9.4 and (b) 17.6 T and simulated spectra (dotted lines) using either one or two Ti–O–P components. The resonance around 390 ppm indicated by a star arises from natural abundance oxygen sites in the ZrO_2 rotor.

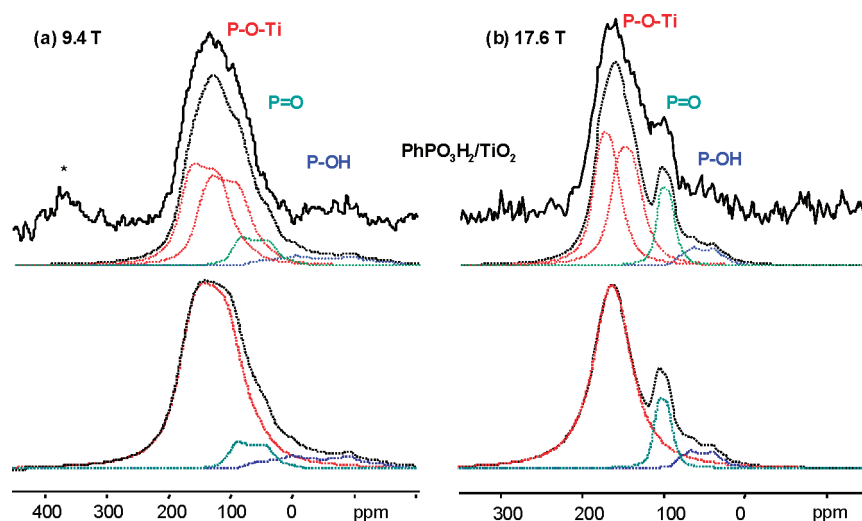


Figure 4. Experimental (full lines) and simulated (dotted lines) ^{17}O MAS NMR spectra of $\text{PhPO}_3\text{H}_2/\text{TiO}_2$ recorded at (a) 9.4 T and (b) 17.6 T using either one or two Ti–O–P components. The resonance around 390 ppm indicated by a star arises from natural abundance oxygen sites in the ZrO_2 rotor.

parameters distributions by analyzing dissymmetry in the 2D patterns.⁵¹

^{17}O NMR parameters are also sensitive to hydrogen bonding.⁵² In the case of carboxylic acids, theoretical calculations indicated that when the hydrogen bond strength increased the chemical shift of C=O sites decreased, while the chemical shift of O–H sites increased.^{53,54} A similar tendency can be found for phenylphosphonic acid by comparing the chemical shifts calculated for an isolated molecule (118.7 ppm for the P=O site, 88.2 and 46.4 ppm

for the P–OH sites) and for H-bonded molecules in the crystal (106.2 ppm for the P=O site, 90.6 and 72.4 ppm for the P–OH sites),⁴¹ where each P=O group participates in two hydrogen bonds with two P–OH groups. The position of the P=O sites in the spectra of the phosphonic acid monolayers is determined with a good precision at 17.6 T since the signal is narrow enough to be well-resolved. In the two systems, this signal is observed at about 113 ppm, supporting the presence in the monolayers of hydrogen bonds with H-bonding strengths lower than in the crystalline acids.

Similar percentages of P–O–Ti, P=O, and P–OH sites were obtained from the simulations of the spectra with three or four sites (Table 3). Whatever the phosphonic acid, the most abundant sites are P–O–Ti sites. The higher level of P–O–Ti bonding in the case of $\text{PhPO}_3\text{H}_2/\text{TiO}_2$ might be related to the higher acidity of phenylphosphonic acid compared to dodecylphosphonic acid. A similar amount of P=O groups are found in both monolayers; on the other

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hand, the amount of residual P–OH groups is much higher in the case of $C_{12}H_{25}PO_3H_2/TiO_2$.

Unfortunately, these results do not help to ascribe the different components found in the ^{31}P MAS NMR spectra. The presence of P–O–Ti, P=O and P–OH sites indicates that mono-, bi-, and tridentate surface phosphonate units (a–d in Scheme 1) can be present in these monolayers. In the case of $PhPO_3H_2/TiO_2$, there is about 80% P–O–Ti, 15% P=O, and 5% P–OH sites, consistent for instance with a mixture of 40% tridentate species d, 45% bidentate species b and 5% bidentate species c. In the case of $C_{12}H_{25}PO_3H_2/TiO_2$, there is about 60% P–O–Ti, 20% P=O, and 20% P–OH sites, consistent for instance with a mixture of 40% of each bidentate species c and d, and 20% monodentate species a. However, in each case, several compositions are possible and no correlation could be found between the ^{31}P and the ^{17}O MAS NMR spectra.

Conclusions

The present study demonstrates the potential of high-field ^{17}O solid-state NMR spectroscopy for investigating the binding of monolayers and self-assembled monolayers to inorganic surfaces. In spite of the very low amount of surface species, it is possible to obtain spectra with satisfactory signal-to-noise ratios using an enriched phosphonic acid and

a moderate-surface area support. However, the acquisition times remain quite long (ca. 24 h at 17.6 T), thus preventing the use of elaborate NMR techniques such as MQ MAS. The spectra recorded at 17.6 T offer sufficient resolution between the different oxygen sites, but it is important to record spectra at two different magnetic fields to improve the simulation and quantification of the different resonances. The data reported here give direct evidence of the extensive formation of Ti–O–P bonds in the surface modification of titania by phosphonic acids. The chemical shift of P–O–Ti sites is consistent with bridging (as opposed to chelating) modes. The presence of residual P=O and P–OH sites points to the presence of several binding modes in phosphonic acid monolayers.

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Supporting Information Available: Simulation assuming only three sites (one Ti–O–P with a LB of about 1200 Hz at both fields, one P=O, and one P–OH site) of the ^{17}O MAS NMR spectra recorded at 17.6 and 9.4 T of $PhPO_3H_2/TiO_2$ and $C_{12}H_{25}PO_3H_2/TiO_2$ (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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