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Organically modified aluminas by grafting and sol–gel processes involving phosphonate derivatives

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The surfaces of alumina particles were modified by grafting with phenylphosphonic acid and its organic-soluble ester derivatives (diethyl phenylphosphonate and bis(trimethylsilyl) phenylphosphonate). Solid-state ^{31}P NMR spectroscopy indicated that in aqueous media the formation of bulk aluminium phosphonate phases could be avoided by using phenylphosphonic acid at pH 6. The formation of such phases was detected in organic media in the presence of phenylphosphonic acid or its silyl ester. On the other hand the use of the dialkyl ester derivative in organic media allowed controlled grafting, excluding the formation of phosphonate phases even under prolonged heating. Alternatively a two-step sol–gel process was carried out, which involved first the non-hydrolytic condensation between aluminium alkoxide and phenylphosphonic acid (or the parent bis(trimethylsilyl) ester), then the hydrolysis–condensation of the remaining Al–OR groups. ^{31}P and ^{27}Al NMR spectroscopy proved the homogeneity of the solids obtained, even for P/Al ratios as high as 1.

1 Introduction

Recent works have aimed at modifying alumina surfaces with phosphonic acids, in fields such as self-assembled monolayers, ceramic membranes, chromatographic packing and adsorbents.[1–10] However the use of aqueous solutions of phosphonic acid may result in the formation of bulk phosphonate phases instead of the simple grafting depending on the conditions.[6,7] Note that aluminium hydroxide particles appear still more sensitive and accordingly may be used as a starting material in the preparation of aluminium phosphonates in the presence of stoichiometric amounts of phosphonic acid under hydrothermal conditions.[11–15]

One purpose of the present work was to experiment grafting *in non-aqueous media*, and more particularly by using alternative organic-soluble coupling agents such as bis(trimethylsilyl) phosphonate and dialkyl phosphonate. We treated Degussa C alumina, which is produced by flame hydrolysis of $AlCl_3$ and has been well characterised in the literature (it corresponds to δ-Al_2O_3 phase[16]), with phenylphosphonic acid and its derivatives chosen as model reagents. Alternatively we used a two-step sol–gel synthesis derived from the one we have previously reported for the preparation of hybrids based on TiO_2 or ZrO_2.[17,18] It involved in the first step the non-hydrolytic condensation between aluminium alkoxide and phenylphosphonic acid (or the parent bis(trimethylsilyl) ester) which leads to Al–O–P bonds, followed by the hydrolysis–condensation of the remaining Al–OR groups. Whatever the synthetic route (grafting or sol–gel), solid-state ^{31}P NMR spectroscopy was found to be a suitable tool to check the presence or not of bulk aluminium phosphonate phases.

2 Experimental

2.1 Starting materials

Phenylphosphonic acid (**PPA**) (98%) was purchased from Aldrich and it was recrystallised from acetonitrile before use. Bis(trimethylsilyl) phenylphosphonate (**BSPP**) was prepared from $PhPO(Cl)_2$ (90%, Aldrich) by reaction with dried ethanol, leading to diethyl phenylphosphonate (**DEPP**), $PhPO_3Et_2$, then reaction of the latter with Me_3SiBr in dichloromethane and distillation.[19] The manipulations with $PhPO_3(SiMe_3)_2$ were carried out under an inert atmosphere. Dichloromethane and tetrahydrofuran (THF) were distilled over appropriate drying agents. Water (HPLC grade) was purchased from Aldrich. Al_2O_3 C from Degussa (13 nm particle size; 90 $m^2\ g^{-1}$) was dried before use at 120 °C under 5×10^{-2} mbar for 5 h. $Al(OPr^i)_3$ (99.99%) was purchased from Aldrich and used without further purification.

2.2 Preparation of samples

Grafting process. A five-fold excess of grafting agent, relative to the calculated amount needed for a monolayer coverage on the particles (based on an area of 24 Å^2 per phosphonate group), was used, that is about 3 mmol of grafting agent per g of alumina.

In the case of **PPA** a suspension of 1 g of alumina C in 100 mL of deionised water was added to a solution of 0.5 g (3.11 mmol) of **PPA** in 500 mL of 3/1 methanol/water mixed solvent (the resulting concentration of **PPA** was 5.18 mmol L^{-1}). The pH was adjusted to 4 or 6 using a NaOH 1 M solution (Table 1, entries **a** and **b**). Alternatively (Table 1, entry **c**) the same procedure was carried out under

Table 1 Aluminas treated with organophosphorus derivatives: operating conditions, coefficient C in the BET equation (from N_2 adsorption–desorption isotherms), phosphorus analysis, and calculated area (Å^2/P) available for each phosphorus unit anchored on the surface.

Sample		C_{BET}	P (%)	Å^2/P
	Al_2O_3	180	0	—
a	$Al_2O_3+PhPO(OH)_2$; $MeOH/H_2O$, pH 6	57	2.1	22
b	$Al_2O_3+PhPO(OH)_2$; $MeOH/H_2O$, pH 4	60	2.4	19
c	$Al_2O_3+PhPO(OH)_2$; THF	45	1.9	24
d	$Al_2O_3+PhPO(OSiMe_3)_2$; CH_2Cl_2	45	4.5	10
e	$Al_2O_3+PhPO(OEt)_2$; CH_2Cl_2, 40 °C	80	1.0	46
f	$Al_2O_3+PhPO(OH)_2$ (f.c.)[a]	57	3.2	14

[a]Forcing conditions: the same conditions as entry b (see Experimental) except that the suspension in $MeOH/H_2O$ was refluxed for 3 days.

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non-aqueous conditions using 600 mL of tetrahydrofuran (THF). The resulting suspensions were stirred at room temperature for 3 days.

Grafting with **BSPP** and **DEPP** was performed in CH_2Cl_2, the concentration of the phosphorus agent being 77.8 mmol L^{-1}. Typically 1 g of alumina C was treated with a solution of 3.11 mmol of **BSPP** or **DEPP** in 40 mL of CH_2Cl_2; the suspensions were stirred for 24 h at room temperature (**BSPP**) or at 40 °C (**DEPP**) (Table 1, entries **d** and **e**, respectively).

The solids were filtered off, washed with 5 aliquots of methanol, then dried at 120 °C under 5×10^{-2} mbar for 5 h.

Sol–gel process. Two steps were involved. First, a solution of aluminium triisopropoxide (1, 3 or 5 equiv.; Table 2) in THF was added to a solution of **PPA** or **BSPP** in THF (1 equiv.). In all cases the concentration of aluminium alkoxide was 0.8 mol L^{-1}. After refluxing for 2 hours clear solutions were obtained. In the second step water (HPLC grade) was added dropwise over a period of 30 min, leading to white opaque gels with a waxy consistency. After 2 days at room temperature, these gels were washed successively with THF, ethanol, acetone, and diethyl ether, and the solids obtained were dried at 120 °C under 5×10^{-2} mbar for 5 h.

2.3 Characterisation

The elemental analyses were performed by the Service Central d'Analyses du CNRS (Vernaison, France). The Al/P ratios in the samples stemming from the sol–gel processing were checked by Energy Dispersive X-ray analysis (EDX) using a Link AN 1000 analyser fitted to a scanning electron microscope Cambridge Stereoscan 360. Thermogravimetric analysis was performed in dry air on a Netzsch STA409 thermobalance coupled to a Baltzers QMG421 quadrupole mass spectrometer, allowing the analysis of the gases evolved during the pyrolysis. FTIR spectra were obtained on a Perkin-Elmer 2000 spectrophotometer, either in DRIFT mode for grafted aluminas (samples diluted in KBr; spectrum of alumina in KBr as background spectrum), or in transmission mode for samples stemming from sol–gel processing (suspensions in Nujol). Solution ^{31}P NMR was performed using a Bruker AC200 spectrometer. ^{31}P solid state NMR spectra were obtained with a Bruker ASX400 or a Bruker Advance DPX300 spectrometer, using magic angle spinning (MAS; spinning rate 10 kHz) and high-power proton decoupling; the flip angle was 45° and the recycling delay 10 s. The ^{31}P chemical shifts were referenced to H_3PO_4 (85% in water). ^{27}Al solid state NMR spectra were obtained with a Bruker ASX400 spectrometer, using magic angle spinning (MAS; spinning rate 12 kHz), a flip angle of 15° and a 2 s recycling delay. The ^{27}Al chemical shifts were referenced to $Al(H_2O)_6{}^{3+}\cdot 3Cl^-$ (40% solution of $AlCl_3$ in water).

3 Results

3.1 Grafting process

Our grafting process consists of treating a suspension of alumina with a solution of the organophosphorus derivative in an organic medium (THF or CH_2Cl_2). The suspensions became stable as soon as the solution of the organophosphorus derivative was added, thus suggesting that the grafting lowered the hydrophilicity of the surface of the particles. For comparison experiments in aqueous media were carried out with phenylphosphonic acid. In the literature the point of zero charge (p.z.c.) of Degussa alumina is given as pH 8, aggregated suspensions forming between pH 6.5 and 9.5.[20] Accordingly the pH was adjusted to 4 or 6 to obtain stable aqueous suspensions. After the grafting treatment, the samples were filtered off, washed to remove physisorbed species, then dried at 120 °C under vacuum before analyses (see Experimental).

Table 2 Hybrid solids stemming from the sol–gel processing: stoichiometry of precursors, elemental analysis and specific surface areas. (**PPA** = phenylphosphonic acid; **BSPP** = bis(trimethylsilyl)phenylphosphonate)

Sample	$Al(OPr^i)_3/PPA/H_2O$ or $Al(OPr^i)_3/BSPP/H_2O$	Al/P	$S_{BET}/m^2\ g^{-1}$
Al/P 1 PPA	1/1/1.5	1.0	66
Al/P 3 PPA	3/1/3.5	2.9	472
Al/P 3 BSPP	3/1/3.5	3.5	351
Al/P 5 PPA	5/1/6.5	4.8	325

N_2 adsorption–desorption measurements gave a qualitative indication that surface modification occurred in all cases, as shown by the significant decrease of the *C* coefficient in the BET equation, indicating a decrease in the enthalpy of adsorption of dinitrogen on the surface (Table 1).

Elemental analysis gave a more accurate indication of the amount of organophosphorus units present on the surface of the particles. The resulting coverages were estimated by calculating the ratio of the specific surface area ($m^2\ g^{-1}$) over the number of phosphorus atoms per gram (Table 1). By comparison with the area of 24 Å^2/P found for layered zirconium phenylphosphonate,[21] a low coverage was obtained with $PhPO(OEt)_2$ (46 Å^2/P). With phenylphosphonic acid at pH 4 or 6, the calculated areas (19–24 Å^2/P) did not give any *a priori* evidence of coverage exceeding a monolayer. By contrast, the treatments with $PhPO(OSiMe_3)_2$ as grafting molecule, or with $PhPO(OH)_2$ under forcing conditions (entry **f**), led to calculated areas of 10–14 Å^2/P which were not consistent with monolayer coverage and strongly suggested the formation of bulk phosphonate phases.

The TG/MS analysis in air of the sample grafted with $PhPO(OH)_2$ at pH 6 (entry **a** in Table 1) indicated two weight losses. The weight loss occurring below 200 °C, which was also observed with non-treated alumina, was related to the loss of residual water and/or solvent. The weight loss occurring above 350 °C was associated with losses of H_2O and CO_2 by coupled mass spectrometry (*m*/*z* 18 and 44, respectively), and hence ascribed to the degradation of the phenyl groups. Similar thermal behaviour has been reported for phenylphosphonate groups covalently bonded to a TiO_2 matrix.[22]

The IR spectra of the samples treated with $PhPO(OH)_2$ (Fig. 1**a** and **c**) present a strong absorption near 1145 cm^{-1} typical of the P–C stretching vibration in PPh groups, and broad absorptions between 950 and 1100 cm^{-1} typical of the P–O stretching vibrations.[5,23] By comparison with the spectrum of $PhPO(OH)_2$ (Fig. 1 **PPA**), the disappearance of the phosphoryl stretching band near 1200 cm^{-1} indicates that the phosphoryl oxygen is strongly bonded to the surface. Moreover, even though the presence of weak absorptions at 900–950 cm^{-1} (the region of P–O(H) stretching bands) does not preclude the existence of some P–OH groups, the dominating bonding mode of the phosphonate groups seems to involve tridentate PO_3 units. The same conclusion may be drawn from the IR spectra of the samples treated with $PhPO(OSiMe_3)_2$ and $PhPO(OEt)_2$. Note in the former case (Fig. 1**d**) the absence of the typical Si–C stretching absorption at 851 cm^{-1}, and in the latter case (Fig. 1**e**) the absence of the typical O–CH_2 stretching absorption near 1394 cm^{-1}, which would be associated to residual $POSiMe_3$ and POEt groups, respectively.

Additional information is given by ^{31}P MAS NMR spectroscopy (Fig. 2). The spectra of the samples treated with $PhPO(OH)_2$ at pH 6 (at room temperature) and with $PhPO(OEt)_2$ in CH_2Cl_2 (at 40 °C), (Fig. 2**a** and **e**) indicate overlapping broad signals between 0 and 20 ppm which might be attributed to phosphonate groups anchored in different modes. By comparison with the chemical shifts of reported aluminium phenylphosphonates,[24–26] the upfield resonances

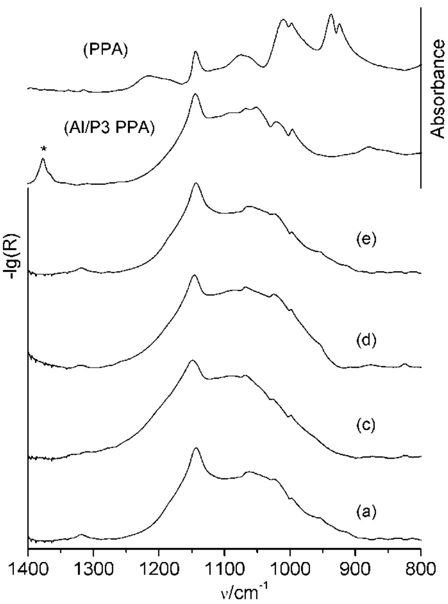


Fig. 1 DRIFT spectra of samples **a**, **c**, **d**, and **e** (after subtracting the spectrum of the initial alumina); IR spectra of phenylphosphonic acid (**PPA**) and of xerogel **Al/P 3 PPA** obtained in transmission mode (*: Nujol absorption).

between 5 and -10 ppm, which are present for the samples treated with $PhPO(OH)_2$ at pH 4, $PhPO(OH)_2$ in THF, and with $PhPO(OSiMe_3)_2$ in CH_2Cl_2 (Fig. 2**b**, **c** and **d**, respectively), may be related to the incipient formation of bulk aluminium phosphonate phases. This hypothesis is supported by the spectrum of the sample treated with $PhPO(OH)_2$ under forcing conditions (prolonged heating at pH 4) which displays signals markedly shifted at 2.9, -4.3 and -9.6 ppm (Fig. 2**f**). By contrast it is noteworthy that the prolonged heating of alumina particles in toluene in the presence of $PhPO(OEt)_2$ did not lead to any significant changes in the IR and ^{31}P NMR spectra.

3.2 Sol–gel processing

The two-step sol–gel processing we recently reported for titania-derived hybrids[22] could be extended to the preparation of alumina–phenylphosphonate hybrids. However the addition of $PhPO(OH)_2$ or $PhPO(OSiMe_3)_2$ to a solution of $Al(OPr^i)_3$ in THF led to milky and viscous suspensions; heating at 80 °C for two hours was necessary to get clear solutions. Solution ^{31}P NMR spectroscopy confirmed that both phosphorus precursors reacted with alkoxide functions, but numerous species were present at the end of this non-hydrolytic step. No major intermediate compound was formed, even after adding a small amount of water, in contrast with the case of titanium.[18]

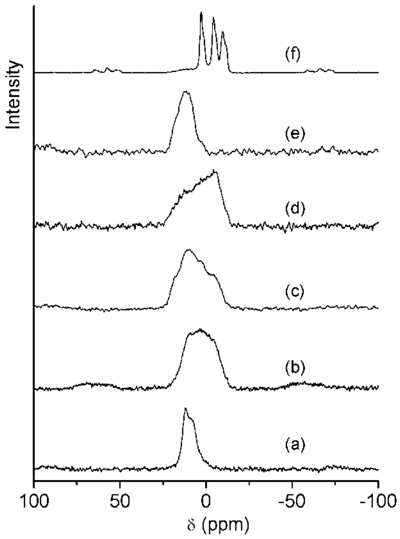


Fig. 2 Solid-state ^{31}P MAS NMR spectra of samples **a**–**f**.

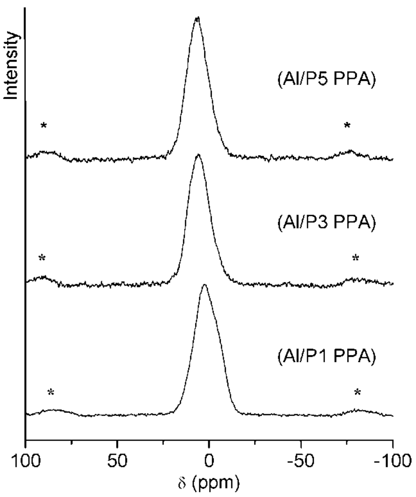


Fig. 3 Solid-state ^{31}P MAS NMR spectra of the xerogels arising from phenylphosphonic acid (**PPA**) and $Al(OPr^i)_3$ with Al/P = 1, 3 and 5 (*: spinning side band).

White opaque gels with a waxy consistence were obtained at the end of the second step (complete hydrolysis; see Experimental). After washing and drying the solids obtained were characterised (Table 2). They were found to be X-ray amorphous. EDX 10-points measurements indicated good homogeneity at the micrometer scale. The disappearance of the bands arising from P=O or P–OH groups in the IR spectra of the samples derived from $PhPO(OH)_2$ suggests the formation of tridentate PO_3 units (Fig. 2 **Al/P 3 PPA**). The features of the ^{31}P MAS NMR spectra were found to be similar whatever the Al/P ratio (a broad signal centred at about 6 ppm; Fig. 3), even though an upfield shoulder makes the signal slightly asymmetrical for Al/P 1. The ^{27}Al MAS NMR spectra (Fig. 4) showed three broad, asymmetrical signals at about 2 ppm, 25 ppm and 50 ppm, corresponding to AlO_6, AlO_5, and AlO_4 sites, respectively. The only differences in the IR spectra of the samples derived from $PhPO(OSiMe_3)_2$ were in relation to the presence of traces of residual $SiMe_3$ groups; the NMR spectra were found to be similar.

4 Discussion

The use of phosphonic acids to modify metal oxide surfaces, and more specially alumina surfaces, has been widely

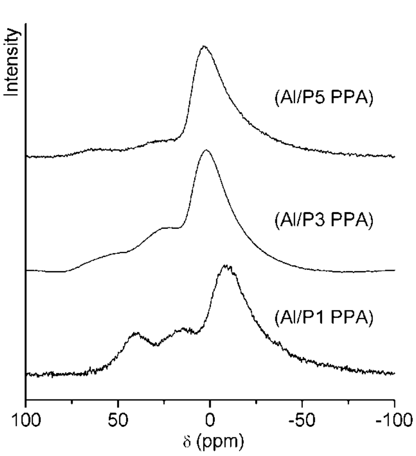
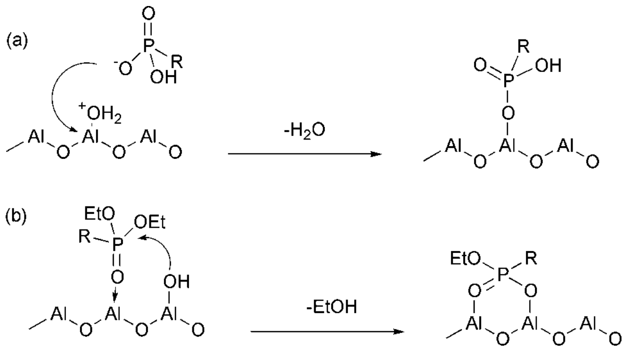
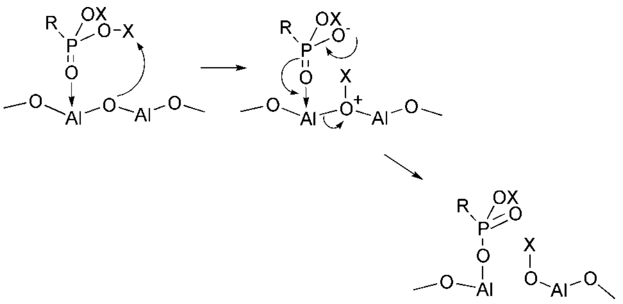


Fig. 4 Solid-state ^{27}Al MAS NMR spectra of the xerogels arising from phenylphosphonic acid (**PPA**) and $Al(OPr^i)_3$ with Al/P = 1, 3 and 5.



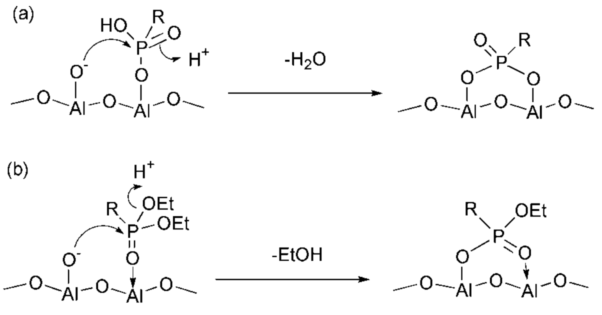
Scheme 1 Reactions with basic sites.



Scheme 3 Cleavage of Al–O–Al bonds.

reported.[1–10] The grafting involves both the coordination of the phosphoryl oxygen to Lewis acid sites, and the condensation of the P–OH functions with surface Al–OH groups, which may be either basic or acidic[27] (possible mechanisms are proposed in Schemes 1a and 2a). Accordingly the coupling agent may act as a mono-, bi- or tridentate ligand on the surface. On the other hand, to our knowledge, the use of ester derivatives as coupling agents has not been reported to date. The hydrolysis of dialkyl phosphonates involves harsh conditions, such as reflux in concentrated HCl solution. Hence the hydrolysis of $PhPO(OEt)_2$ on the surface by adsorbed water molecules can be precluded. However solid–gas reactions of dimethyl methylphosphonate on γ-alumina has been reported to occur through successive steps: the initial binding of the phosphoryl oxygen to surface acid sites, followed by the evolution of one methoxy group as methanol (this step was complete by 200 °C), then the loss of the second methoxy group at higher temperatures.[28] A similar reaction pathway, involving nucleophilic substitutions on the phosphorus centre, may be postulated here in the case of $PhPO(OEt)_2$ (Schemes 1b and 2b), but it takes place at notably lower temperatures. $PhPO(OSiMe_3)_2$ may react similarly. Nevertheless its (partial) conversion to acid by hydrolysis reaction with adsorbed water molecules cannot be precluded.

The literature dealing with the surface modification of alumina with phosphonic acids mentions the existence of a balance between grafting and the formation of bulk aluminium phosphonate phases.[6,7] As the formation of bulk aluminium phosphonate phases involves a dissolution–precipitation mechanism, the solubility of alumina (known to be low in water only within the pH range of 4.5–8.5)[29] is expected to be a determining factor. This gives an explanation for the different features of the ^{31}P NMR spectra of samples **a** and **b** in Fig. 2, which indicates the significant formation of bulk phosphonate phases at pH 4. On the other hand, grafting should be markedly favoured in organic media. However, surprisingly, the formation of bulk aluminium phosphonate phases was detected in organic media in the presence of $PhPO(OH)_2$ or $PhPO(OSiMe_3)_2$, while only grafting was observed in the presence of $PhPO(OEt)_2$. These results suggest that $PhPO(OH)_2$ or $PhPO(OSiMe_3)_2$ can cause the release of aluminium cations by cleavage of Al–O–Al bonds, unlike $PhPO(OEt)_2$. A possible reaction pathway is proposed in Scheme 3. The intermediate formation of an oxonium bridge should more likely occur through the transfer of a proton, or a trimethylsilyl group, than through the transfer of a carbocation, thus explaining that $PhPO(OEt)_2$ cannot cleave Al–O–Al bonds.



Scheme 2 Reactions with acidic sites.

The sol–gel processing allowed the preparation of modified aluminas with high phosphonate contents for which the phase separation could have been regarded as inevitable. However the reported aluminium phenylphosphonates exhibit sharp ^{31}P resonances in the range 5 to -10 ppm, and sharp ^{27}Al resonances between -13 and -21 ppm (octahedral AlO_6 sites) and around 46 ppm (tetrahedral AlO_4 sites).[24–26] It is noteworthy that such sharp signals are absent in our NMR spectra (Figures 3 and 4), which clearly indicates that no bulk aluminium phenylphosphonate phase was formed. On the other hand the broad signals observed indicate a wide distribution of sites typical of disordered solids and suggest the uniform distribution of P–O–Al and Al–O–Al bonds. Note that pseudo-boehmites arising from sol–gel processing exhibit only the typical ^{27}Al resonances of AlO_6 octahedra around 0 ppm.

5 Conclusions

The use of phenylphosphonic acid in aqueous solution at pH 6 and at room temperature favoured the grafting to the surface of alumina particles, as opposed to the formation of aluminium phosphonate phases. The solubility of alumina may explain the formation of bulk phosphonate phases under more severe conditions, that is at low pH or on heating. Surprisingly in organic media the formation of such phases was also observed with phenylphosphonic acid or its bis(trimethylsilyl) ester derivative. On the other hand it is noteworthy that the use of diethyl phenylphosphonate allowed controlled grafting of the surface, excluding the formation of bulk phases even under prolonged heating. Thus organic-soluble dialkylphosphonate derivatives may be useful coupling agent alternatives to phosphonic acids which may be difficult to solubilise.

The two-step sol–gel processing previously reported for titania–phosphonate hybrids was successfully extended to the preparation of alumina-derived hybrids. ^{31}P and ^{27}Al NMR spectroscopy proved their high homogeneity, without any hints of precipitation of aluminium phosphonate phases.

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