Mixed Nonhydrolytic/Hydrolytic Sol−Gel Routes to Novel Metal Oxide/Phosphonate Hybrids

G. Guerrero, P. H. Mutin,* and A. Vioux

*UMR 5637, cc 007, Université Montpellier 2, Place E. Bataillon,
F34095 Montpellier Cedex 5, France*

Received August 13, 1999. Revised Manuscript Received January 31, 2000

Titanium oxide/phenylphosphonate hybrids were prepared by a two-step sol−gel processing, involving first the nonhydrolytic condensation between titanium isopropoxide and phenylphosphonic acid (or the parent bis(trimethylsilyl)ester), followed by the hydrolysis−condensation of the remaining alkoxide groups. Partial hydrolysis led to the formation of $Ti_4(\mu_3\text{-}O)(\mu_2\text{-}O^iPr)_3(O^iPr)_5(PhPO_3)_3$; the potential use of this intermediate compound as a single-source precursor was explored. The composition, thermal stability, and structure of the hybrid xerogels were investigated using EDX, TGA, XRD, FTIR, and ^{31}P,^{13}C, and ^{29}Si MAS NMR. The compositional and structural stability of the hybrids was investigated over a wide pH domain.

Introduction

During the past two decades, the development of organic−inorganic hybrid materials has been associated with the evolution of sol−gel process.[1] A wide class of hybrids involves the covalent bonding of the organic and the inorganic components through the use of coupling molecules. Organofunctional alkoxysilanes have been widely used as coupling molecules, as they lend themselves to the sol−gel copolymerization with tetraalkoxysilanes or metal alkoxides. Materials named "ormosils" (organically modified silicas) or "ormocers" (organically modified ceramics) are prepared by this method. In the case of metal alkoxides, coupling via carboxylate and β-diketonate groups has also been extensively studied.[1,2]

The aim of this work is to highlight the potentialities of phosphonate groups in the coupling of organic components to metal oxides. Actually, M−O−P and P−C bonds are quite stable toward hydrolysis and a wide range of functional phosphonates is available. Layered metal phosphates and phosphonates have attracted considerable attention these past 20 years.[3,4] However, the homogeneous incorporation of phosphonate units into metal oxide networks remains largely unexplored.[5]

For several years we have been interested in developing nonhydrolytic sol−gel routes to metal oxides and phosphonates.[6] M−O−P bridges are easily accessible by nonhydrolytic condensation of a metal alkoxide with a P−OH function:

$$\text{M−OR} + \text{P−OH} \rightarrow \text{M−O−P} + \text{ROH}$$

This reaction has been used to prepare layered metal phosphates[7,8] and phosphonates,[9] as well as molecular metal phosphates,[10,11] phosphonates,[12] and phosphinates.[12]

The nonhydrolytic condensation of a metal alkoxide with a P−OSiMe_3 function has also been proposed for the synthesis of metal phosphonates.[13]

$$\text{M−OR} + \text{P−OSiMe}_3 \rightarrow \text{M−O−P} + \text{ROSiMe}_3$$

In this context, we propose to prepare metal oxide/phosphonate hybrids by a two-step sol−gel process (Scheme 1), involving first the formation of M−O−P bonds by nonhydrolytic condensation of a metal alkoxide with a phosphonic acid (or its trimethylsilyl ester) and then the formation of the M−O−M bonds of the metal oxide network by hydrolysis/condensation of the remaining alkoxide groups.

In the present study, we prepared model phenylphosphonate/titanium oxide hybrids to explore the incorporation of phosphonate groups into metal oxides. The composition, the homogeneity, and the structure of the hybrid xerogels were investigated using EDX, TGA, XRD, FTIR, and multinuclear MAS NMR. The intermediate sols were studied by multinuclear solution NMR to gain some insight into the condensation reac-

---

[1] Judeinstein, P.; Sanchez, C. *J. Mater. Chem.* **1996**, *6*, 511−525.

[2] Schubert, U.; Husing, N.; Lorenz, A. *Chem. Mater.* **1995**, *7*, 2010−2027.

[3] Alberti, G.; Casciola, M.; Costantino, U.; Vivani, R. *Adv. Mater.* **1996**, *8*, 291−303.

[4] Clearfield, A. In *Progress in Inorganic Chemistry*; Karlin, K. D., Ed.; Wiley: New York, 1998; Vol. 47, pp 371−510.

[5] Mutin, P. H.; Delenne, C.; Medoukali, D.; Corriu, R.; Vioux, A. In *Mater. Res. Soc. Symp. Proc.*; Laine, R. M., Sanchez, C., Brinker, C. J., Giannelis, E., Eds.; Materials Research Society: Warrendale, PA, 1998; Vol. 519, pp 345−350.

[6] Vioux, A. *Chem. Mater.* **1997**, *9*, 2292−2299.

[7] Benhamza, H.; Barboux, P.; Bouhaouss, A.; Josien, F.-A.; Livage, J. *J. Mater. Chem.* **1991**, *1*, 681−684.

[8] Livage, J.; Barboux, P.; Vandenborre, M. T.; Schmutz, C.; Taulelle, F. *J. Non-Cryst. Solids* **1992**, *147/148*, 18−23.

[9] Medoukali, D.; Mutin, P. H.; Vioux, A. *J. Mater. Chem.* **1999**, *9*, 2553−2557.

[10] Lugmair, C. G.; Tilley, T. D. *Inorg. Chem.* **1998**, *37*, 1821−1826.

[11] Lugmair, C. G.; Tilley, T. D.; Rheingold, A. L. *Chem. Mater.* **1999**, *11*, 1615−1620.

[12] Guerrero, G.; Mehring, M.; Mutin, P. H.; Dahan, F.; Vioux, A. *J. Chem. Soc., Dalton Trans.* **1999**, 1537−1538.

[13] DiGiacomo, P. M.; Dines, M. D. U.S. Patent 4,299,943, 1981.

10.1021/cm991125+ CCC: $19.00

Scheme 1

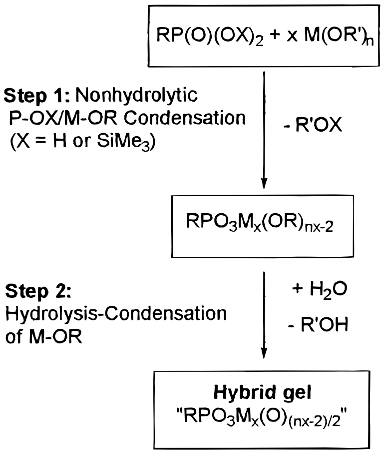

Table 1. Preparation of the Hybrid Gels from $Ti(O^iPr)_4$ and Phenylphosphonic Acid (PPA) or Phenylbis(trimethylsilyl)Phosphonate (PTMSP)

sample	$M(O^iPr)_n$: $PhPO_3X_2$:H_2O	solvent	aspect
Ti/P = 1/PPA	1:1:1	DMSO	white opaque gel
Ti/P = 3/PPA	3:1:5	DMSO	white opaque gel
Ti/P = 5/PPA	5:1:9	DMSO	white opaque gel
Ti/P = 1/PTMSP	1:1:1	CH_2Cl_2	orange transparent gel
Ti/P = 3/PTMSP	3:1:5	CH_2Cl_2	white opaque gel
Ti/P = 5/PTMSP	5:1:9	CH_2Cl_2	white opaque gel

tions involved in the two-step sol−gel process. In addition, the compositional and structural stability of the titania/phenylphosphonate hybrids was tested over a wide pH range.

Experimental Section

Chemicals. $Ti(O^iPr)_4$ (97%) was purchased from Aldrich and distilled prior to use. $PhPO(OH)_2$ (98%, Aldrich) was recrystallized from acetonitrile. $PhPO(OSiMe_3)_2$ was prepared from $PhPO(Cl)_2$ (90%, Aldrich) by reaction with anhydrous ethanol, leading to $PhPO(OEt)_2$, followed by reaction with Me_3SiBr in dichloromethane and distillation. Dimethyl sulfoxide (DMSO) was distilled over CaH_2, dichloromethane was distilled over P_2O_5. Water (HPLC grade) was purchased from Aldrich. All manipulations were carried out under an inert atmosphere.

Preparation of the Gels. Titanium oxide/phenylphosphonate hybrids with different Ti/P ratios were prepared from $Ti(O^iPr)_4$ and phenylphosphonic acid (PPA) or phenylbis(trimethylsilyl)phosphonate (PTMSP) precursors in two steps (Table 1).

In the first step, $Ti(O^iPr)_4$ was added under stirring to a solution of PPA in DMSO, or to a solution of PTMSP in CH_2Cl_2, leading to clear solutions. In all cases the concentration of the metal alkoxide was 0.8 mol L^{-1}. After the mixture was stirred for 2 h at room temperature, the water was added dropwise over a period of 30 min, leading to the formation of gels (Table 1). A gel (Ti/P = 1.33) was also prepared by slow addition (over 1 h) of water diluted in THF (50 vol %) to a solution of $Ti_4(PhPO_3)_3(\mu_3\text{-}O)(O^iPr)_5(\mu_2\text{-}O^iPr)_3 \cdot DMSO$ in THF.

For comparison, a sample of crystalline titanium phenylphosphonate, $Ti(O_3PPh)_2$, was prepared by treatment of a gel with a Ti/P ratio 0.5 (prepared from $Ti(O^iPr)_4$ and PPA) in an equimolar solution of HF in water ($F^-/Ti = 55$) at 60 °C for 2 days.

Before analysis, the samples were aged at room temperature for 2 days, and then washed successively with DMSO or CH_2Cl_2, water, ethanol, and ether, and dried in vacuo at 120 °C for 5 h.

Analytical Methods. Solution ^{31}P NMR spectra were recorded on a Bruker DPX200 spectrometer. ^{31}P solid-state NMR spectra were obtained with a Bruker ASX400 or a Bruker Avance 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 10s; the chemical shifts were referenced to H_3PO_4 (85% in water). ^{13}C and ^{29}Si MAS NMR spectra were obtained on a Bruker Avance DPX300 (spinning rate 5 kHz) using a cross-polarization sequence; the contact time was 3 and 5 ms for ^{13}C and ^{29}Si, respectively; in both cases the recycling delay was 5 s and the chemical shifts were referenced to TMS. FTIR spectra were obtained on a Perkin-Elmer Spectrum 2000 spectrophotometer using attenuated total reflectance (ATR). Thermogravimetric analysis was performed on a Netzsch STA409 thermobalance coupled to a Baltzers QMG421 quadrupole mass-spectrometer, allowing the analysis of the gases evolved during the pyrolysis. X-ray powder diffraction (XRD) was performed on a Seifert MZIV diffractometer using Cu−Kα radiation. The Ti/P and Si/P ratios in the solid samples have been determined by energy-dispersive X-ray analysis (EDX) using a Link AN 1000 analyzer fitted to a scanning electron microscope Cambridge Stereoscan 360. The analyses of the phosphorus traces in the aqueous solutions after refluxing at pH 0, 1, 9, and 10 were performed by inductively coupled plasma (ICP) at the "Service Central d'Analyses du CNRS" at Vernaison, France.

Results and Discussion

NMR Study of the $Ti(O^iPr)_4$/PPA and $Ti(O^iPr)_4$/PTMSP Sols. The reaction of $Ti(O^iPr)_4$ with $PhPO(OSiMe_3)_2$ (PTMSP) in CH_2Cl_2, or $PhPO(OH)_2$ (PPA) in DMSO (step 1) resulted in clear solutions, regardless of the Ti/P ratio. The solutions obtained for Ti/P = 3 were studied by NMR spectroscopy.

The ^{29}Si NMR spectrum of the reaction mixture $Ti(OPr^i)_4$ (3 equiv)/$PhPO(OSiMe_3)_2$ (1 equiv) in CH_2Cl_2 showed a single sharp resonance at 13.2 ppm, corresponding to $Me_3Si(O^iPr)$, which indicated complete condensation of the $P-OSiMe_3$ groups. The ^{31}P NMR spectrum (Figure 1a) displayed numerous signals between −22 and +2 ppm, probably corresponding to a complicated mixture of titanium alkoxophosphonates. The complexity of the spectrum is not surprising if one keeps in mind that phosphonate groups are potentially tridentate, and that Ti atoms are usually hexacoordinated. Thus, the Ti−O−P bridges formed by $Ti-O^iPr$/$P-OSiMe_3$ condensation and by coordination of the phosphoryl oxygen to a Ti atom may result in the formation of linear, cyclic, and polycyclic oligomers. When water (0.33 equiv) was added to this solution, the ^{31}P NMR spectrum (Figure 1b) showed one main resonance at ~7.5 ppm (accounting for about 60% of the P atoms) and resonances of minor intensity in the range of 17.4−15.9 ppm.

In the $Ti(OPr^i)_4$/PPA/DMSO system, it is not straightforward to work under rigorously anhydrous conditions, as phenylphosphonic acid and DMSO contain trace amounts of water,[14] even after careful drying. Accordingly, the ^{31}P NMR spectra of the reaction mixtures $Ti(OPr^i)_4$ (3 equiv)/$PhPO(OH)_2$ (1 equiv) in DMSO depended on the amount of adventitious water. Nevertheless, in all cases a sharp peak at ~6.8 ppm and a broad peak at ~0.3 ppm were found (Figure 1c). When

---

(14) Walawalkar, M. G.; Horchler, S.; Dietrich, S.; Chakraborty, D.; Roesky, H. W.; Schafer, M.; Schmidt, H. G.; Sheldrick, G. M.; Murugavel, R. *Organometallics* **1998**, *17*, 2865−2868.

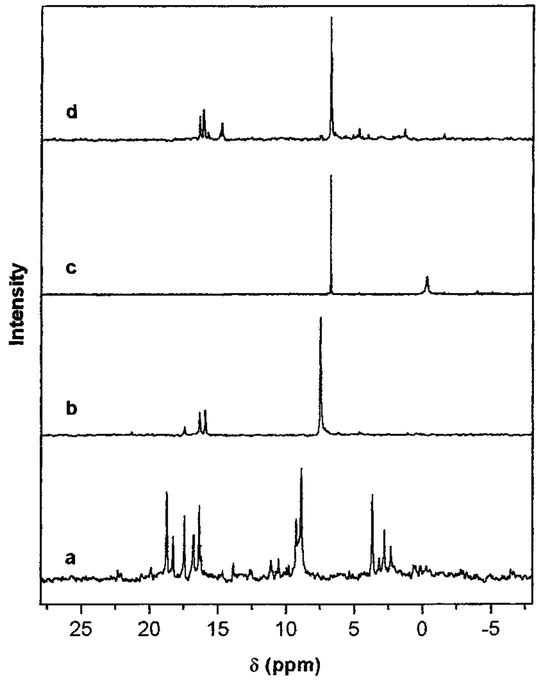

Figure 1. Solution ^{31}P MAS NMR spectra of the reaction mixtures Ti(OPr^i)$_4$/PTMSP and Ti(OPr^i)$_4$/PPA): (a) Ti(OPr^i)$_4$(3 equiv) + PTMSP (1 equiv) in CH_2Cl_2; (b) Ti(OPr^i)$_4$(3 equiv) + PTMSP (1 equiv) + H_2O (1 equiv) in CH_2Cl_2; (c) Ti(OPr^i)$_4$(3 equiv) + PPA (1 equiv) in DMSO; and (d) Ti(OPr^i)$_4$(3 equiv) + PPA (1 equiv) + H_2O (1 equiv) in DMSO.

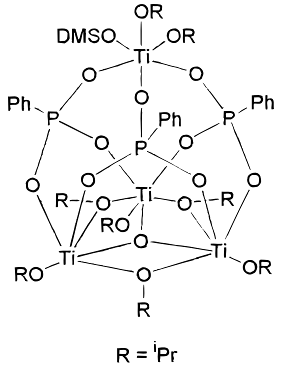

Figure 2. Molecular structure of Ti$_4$(μ_3-O)(μ_2-O^{i}Pr)$_5$(O^{i}Pr)$_3$(PhPO$_3$)$_3$·DMSO.

water (0.2 equiv) was added this latter resonance disappeared, the resonance at 6.8 ppm increased and minor peaks in the 14.7 to 16.4 ppm range formed (Figure 1d). This spectrum appears quite similar to spectrum 1b, indicating that partial hydrolysis gave the same intermediate species whatever the precursor, PPA or PTMSP.

The resonance at ~7 ppm could be attributed to a molecular titanium phosphonato oxo alkoxide. This compound was crystallized from a DMSO solution and single-crystal X-ray diffraction led to the formula Ti$_4$(μ_3-O)(μ_2-O^{i}Pr)$_3$(O^{i}Pr)$_5$(PhPO$_3$)$_3$·DMSO and to the structure displayed in Figure 2.[12]

A salient feature in this structure is that each P atom is linked to 3 different Ti atoms in Ph*P*(OTi)$_3$ tetrahedral sites, as in layered titanium phosphonates. One of the P−O−Ti bonds results from the coordination of the phosphoryl oxygen, the other ones result from the nonhydrolytic condensation between Ti−O^{i}Pr and P−OH groups. There are neither P−O−P bridges nor residual P−OH groups, which indicates that the first step (nonhydrolytic condensation) is complete. The oxo ligand that bridges three of the four Ti atoms results from the partial hydrolysis/condensation of Ti−O^{i}Pr groups.

Table 2. Elemental Analysis (EDX) and TGA Weight Losses of the Hybrid Gel Samples

sample	Ti/P (EDX)	Si/P (EDX)	$\delta m/m_0$ (%) 150−350 °C	350−1100 °C
Ti/P = 1/PPA	0.9		−10.1	−27.2
Ti/P = 3/PPA	3.1		−10.4	−17.9
Ti/P = 5 /PPA	5.5		−16.0	−14.7
Ti/P = 1/ PTMSP	1.0	0.3	−6.4	−27.8
Ti/P = 3/ PTMSP	3.1	0.3	−6.4	−16.7
Ti/P = 5/ PTMSP	5.4	0.5	−9.4	−12.2

This cluster presents two main interests: first, as an intermediate in the sol−gel process that we are developing; and second, its solubility and the presence of alkoxide groups make it a novel, single-source, sol−gel precursor to hybrid materials. Thus, hydrolysis of this cluster in THF led to a translucent gel, whose structure will be discussed in the following section.

Characterization of the Hybrid Xerogels. At the end of the hydrolytic step, gels were obtained whatever the Ti/P ratio (Table 1). The hydrolysis of Ti(O^{i}Pr)$_4$ in the absence of PPA or PTMSP under the same experimental conditions gave a white grease. Thus, PPA and PTMSP act as nucleophilic modifiers that decrease the hydrolysis−condensation rate of the metal alkoxide, as do carboxylic acids and β-diketones.[15]

EDX showed that the Ti/P ratio of the dried samples was close to the theoretical ones (Table 2). In addition, 10-point measurements indicated that the samples were homogeneous at the micrometer level. Silicon was detected in the samples derived from TPMSP, indicating the presence of residual $SiMe_3$ groups. According to XRD, all of the samples were amorphous: no peak corresponding to titania or layered titanium phenylphosphonate was detected.

The TGA curves recorded in air showed a multistep weight loss. Analysis of the evolved gases by mass spectrometry indicated that the first weight loss (from 150 to 300 °C) corresponded to the degradation of residual alkoxide groups and to the distillation of residual solvents and water. The other weight losses (from 350 to 1100 °C) corresponded to the degradation of the phenyl groups (with loss of benzene, water, and carbon dioxide).

It is noteworthy that the stability of the P−Ph bond in air (350 °C) appears comparable to the stability of the Si−Ph bond in silsesquioxane materials.

Infrared Spectroscopy. Regardless of the Ti/P ratio, the infrared spectra of the hybrid samples were practically identical in the range 1300−900 cm^{-1}, corresponding to the $PhPO_3$ tetrahedra vibration modes (Figure 3). In the spectra of the samples derived from PTMSP, a small band at 1257 cm^{-1} (symmetric CH_3 deformation) accompanied by two small bands at 852 and 760 cm^{-1} (−CH_3 rocking vibrations) confirm the presence of $SiMe_3$ groups.[16] There are no bands at 1220 cm^{-1} (P=O stretching vibration) and around 930 cm^{-1} (P−OH

---

(15) Brinker, C. J.; Scherrer, G. W. *Sol−Gel Science, the Physics and Chemistry of Sol−Gel Processing*; Academic: San Diego, CA, 1990.

(16) Smith A. L. *The Analytical Chemistry of Silicones*; Wiley: New York, 1991.

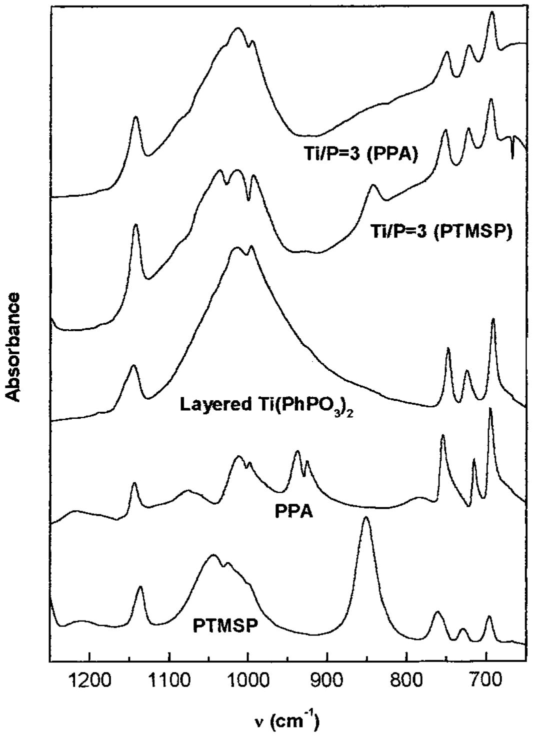

Figure 3. FTIR spectra of the hybrid xerogels prepared from PPA and PTMSP (Ti/P = 3) and FTIR spectra of layered Ti($PhPO_3$)$_2$, PPA and PTMSP.

stretching vibrations). In addition, the spectra in the range 1300−900 cm^{-1} are close to the spectra of well-crystallized, layered titanium phenylphosphonate;[17] accordingly, most of the $PhPO_3$ tetrahedra should be in the same environment, i.e., bonded to three different Ti atoms in PhP(OTi)$_3$ sites. Note that the same environment of phosphorus atoms is found in the above-mentioned titanium phosphonato oxo alkoxide (Figure 1).

Solid-State MAS NMR. Regardless of the phosphorus precursor (PPA or PTMSP) and the Ti/P ratio, the ^{31}P MAS NMR spectra of the hybrid xerogels were similar (Figure 4), showing one broad signal typical of disordered solids at about 11 ppm. An identical spectrum was obtained for the dried gel stemming from the hydrolysis of $Ti_4(PhPO_3)_3(\mu_3\text{-}O)(O^iPr)_5(\mu_2\text{-}O^iPr)_3$.DMSO (Ti/P = 1.33) in THF, which shows that the environment of P atoms in all the hybrids are similar. The ^{31}P NMR chemical shifts in amorphous titanium phosphates range between −4 to −21 ppm.[8] Accordingly, P−Ph bonds are not cleaved and all the P atoms are bonded to one Ph and three O atoms in $PhPO_3$ tetrahedral sites. Because of the sensitivity of ^{31}P chemical shifts to variations in bond angle, it is not possible to ascribe a priori the nature of phosphorus second neighbors (Ti, H, or Si) in our samples. This sensitivity is illustrated by the quite different chemical shifts found for Ph*P*(OTi)$_3$ units in molecular oxo phosphonato titanium clusters (~7 ppm) and in layered titanium phosphonate (−4.0 ppm) (Table 3).

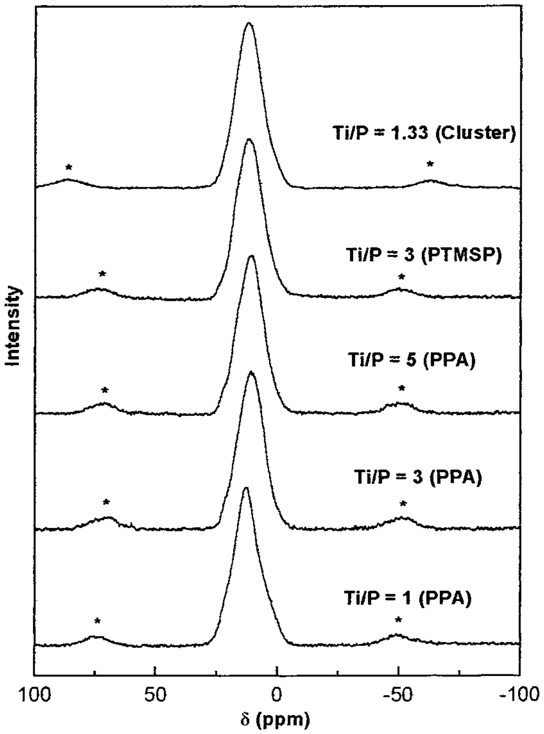

Figure 4. Solid-state ^{31}P MAS NMR spectra of the hybrid xerogels prepared from Ti(O^{i}Pr)$_4$.

Table 3. ^{31}P Solution NMR and Solid-State MAS NMR Chemical Shifts of Selected Compounds

site	sample	^{31}P chemical shift (ppm)[a]
Ph*P*O(OH)$_2$	PPA	14 (D_2O)[18] 21.4 (solid state)
Ph*P*O(OSi)$_2$	PTMSP	1.3 (CH_2Cl_2)
Ph*P*O(OSi)$_2$	PhPO(OSiMe$_2$tBu)$_2$	−0.3 ($CDCl_3$)[18]
Ph*P*O(OH)(OSi)	PhPO(OH)(OSiMe$_2$tBu)	10.4 ($CDCl_3$)[18]
Ph*P*(OTi)$_3$	layered Ti($PhPO_3$)$_2$	−4.0 (solid state)
Ph*P*(OTi)$_3$	$Ti_4(PhPO_3)_3(O)(O^iPr)_8\cdot$ DMSO	7.2 (DMSO) 7.3, 6.2, 5.8 (solid state)
Ph*P*(OTi)$_3$	(Cp*TiPhPO$_3$)$_4$(μ-O)$_2$	7.4 ($CDCl_3$)[14]

[a] 85% H_3PO_4 was used as chemical shift reference

FTIR spectroscopy indicated that most of the P atoms were in PhP(OTi)$_3$ sites, as in layered titanium phenylphosphonate. ^{31}P MAS NMR spectroscopy, in agreement with XRD, shows that our hybrid samples do not contain such a layered phase, which would lead to a sharp peak at ca. −4 ppm. Accordingly, no phase separation took place during the preparation of our hybrid samples, which may be described as a homogeneous dispersion of phenylphosphonate groups within a TiO_2 network.

The ^{13}C CP-MAS NMR spectra of the samples with Ti/P ratios of 3 showed a major signal at 131 ppm, corresponding to the aromatic carbon atoms, and two weak signals at about 75 and 18 ppm, indicating the presence of residual isopropoxy groups. In the case of samples arising from the PTMSP precursor, EDX and FTIR specroscopy showed the presence of residual SiMe$_3$ groups. Indeed, the ^{29}Si CP-MAS NMR spectra showed a sharp signal at 6.7 ppm and a broad resonance at ~14 ppm. The sharp signal is ascribed to adsorbed $Me_3SiOSiMe_3$ (arising from the hydrolysis and condensation of $Me_3Si(O^iPr)$). The broad resonance may be ascribed to Ti−OSiMe$_3$ and/or P−OSiMe$_3$ groups. However, the ^{31}P NMR spectra of the samples derived from PPA or PTMSP were identical, which suggests that most of the

---

(17) Jaimez, E.; Bortun, A.; Hix, G. B.; Garcia, J. R.; Rodriguez, J.; Slade, R. C. T. *J. Chem. Soc., Dalton Trans.* **1996**, 2285−2292.

(18) Lukes, I.; Borbaruah, M.; Quin, L. D. *J. Am. Chem. Soc.* **1994**, *116*, 1737−1741.

Table 4. Loss of Phosphorus for the Sample Ti/P = 3 /PPA after Refluxing for 12 Hours under Different pH Conditions (from the analyses of phosphorus traces in the aqueous solutions)

pH	loss of phosphorus, %
0	0.5
1	0.3
9	1.3
10	1.7

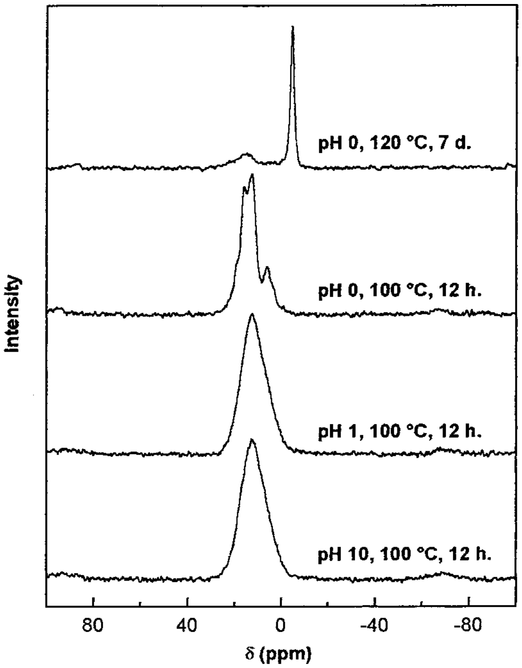

Figure 5. Solid-state ^{31}P MAS NMR spectra of the hybrid xerogel Ti/P = 3/PPA after refluxing for 12 h in solutions of pH 10, 1, and 0, and heated at 120 °C in a solution of pH 0 for 7 days.

$OSiMe_3$ groups detected by EDX and FTIR are not bonded to phosphorus. Indeed, the presence of $P-OSiMe_3$ groups would lead to a significant high-field broadening of the ^{31}P NMR peak (Table 3).

Chemical Stability of the $TiO_2/PhPO_3$ Samples. The chemical stability under acidic or basic conditions of hybrid samples with a Ti/P ratio of 3 was tested by refluxing these samples in aqueous solutions of pH 0, 1, 9, and 10 for 12 h. After separation by filtration, the solutions were analyzed for traces of phosphorus (Table 4), and the solid was characterized by ^{31}P MAS NMR (Figure 5). The compositional stability of the $TiO_2/PhPO_3$ hybrids appeared excellent: regardless of the pH, less than 2% of the P atoms are solubilized. In addition, ^{31}P MAS NMR indicated that the structure of the samples was not modified at pH 1, 9, and 10. However the spectrum of the sample treated at pH 0 indicated a beginning of structural rearrangement. To complete this rearrangement, a sample was placed in a sealed tube in a solution of pH 0 and was heated at 120 °C for 1 week. In this case, the ^{31}P MAS NMR spectrum showed a new, sharp resonance at −4.3 ppm, which shows that ~70% of the phenylphosphonate groups belong to a layered $Ti(PhPO_3)_2$ phase. EDX confirmed this phase separation: two types of particles were found, with Ti/P ratios around 0.6 and 10.

Conclusions

Phosphonate groups are highly effective for the anchoring of organic moieties to metal oxides. Original organic−inorganic hybrids exhibiting high homogeneity and stability may be obtained by a two-step sol−gel process using these “phosphonate coupling agents” and a metal alkoxide precursor.

The M−O−P bonds that connect the organic moiety to the oxide network and the M−O−M bonds that built this oxide network may be formed in two distinct steps, by independent condensation reactions. The M−O−P bonds result from the nonhydrolytic condensation between M−OR and P−OH or $P-OSiMe_3$ functions and from the coordination of the phosphoryl oxygen to titanium. It is important to note that homocondensation of the phosphonate precursors (formation of P−O−P bonds) cannot take place under the mild sol−gel conditions. The M−O−M bonds are formed by hydrolysis−condensation of the remaining alkoxide groups; the phosphonate groups act as nucleophilic modifiers that moderate the hydrolysis−condensation rate of the metal alkoxide. Partial hydrolysis leads to a molecular titanium oxo alkoxo phosphonate intermediate; the P atoms in this intermediate are bonded to three titanium atoms. Infrared spectroscopy suggests that the phosphonate groups in the phenylphosphonate/titanium oxide hybrids are predominantly in the same $PhP(OTi)_3$ environment. According to XRD and ^{31}P MAS NMR, these hybrids are monophasic; the phase separation to titanium phenylphosphonate and titanium oxide occurs only under severe conditions (hydrothermal treatment at pH 0). Accordingly, these new organic−inorganic hybrids may be described as a homogeneous distribution of phosphonate groups in an oxide network.

From a structural point of view, phosphonate/metal oxide hybrid materials appear quite different from organosilane/metal oxide hybrids, where homocondensation with formation of Si−O−Si bonds cannot be avoided. In addition phenylphosphonate/titanium oxide hybrids exhibit an excellent stability over a wide pH range.

In conclusion, phosphonate coupling agents offer a valuable alternative to conventional coupling agents for the preparation of highly homogeneous organic−inorganic hybrids. The stability and the facile formation of M−O−P bonds (M = Ti, Al, Zr, etc.) makes phosphonates particularly attractive for the coupling to metal oxides. The titanium oxo alkoxo phosphonate obtained by partial hydrolysis is soluble in organic solvents; it may be used as a model of our hybrid solids and as a single-source precursor for the preparation of nanostructured hybrid materials.

CM991125+