Anchoring of Phosphonate and Phosphinate Coupling Molecules on Titania Particles

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Titanium oxide particles were treated using six organophosphorus compounds chosen as model coupling molecules: phenylphosphonic and diphenylphosphinic acids, their ethyl esters, and their trimethylsilyl esters. The ability of all of these coupling molecules to modify the surface of the TiO_2 particles was demonstrated by elemental analysis, thermogravimetric analysis, and nitrogen adsorption. The bonding modes on the surface were investigated by means of diffuse reflectance IR Fourier transform (DRIFT) and ^{31}P solid-state MAS NMR spectroscopy. Upon irradiation in water, a marked trend to the photooxidative degradation of the anchored organophosphorus groups was evidenced, especially in the case of phosphinate groups.

1. Introduction

As metal–carbon bonds are generally not sufficiently stable toward hydrolysis, anchoring an organic group to a metal oxide support requires the use of coupling molecules. The usual coupling molecules are organosilanes,[1,2] organotitanates (modified titanium alkoxides),[3] and strong complexing ligands such as the ones obtained by the deprotonation of β-diketones, β-ketoesters, and carboxylic acids.[4] Organophosphorus compounds (phosphate,[5] phosphonate, or phosphinate derivatives) offer a promising alternative in the coupling of organic components to metal oxides other than silica; thus, we recently reported a novel sol–gel route to metal oxide/ phosphonate covalent hybrid solids.[6,7] Actually, the P–C bond is as stable as the Si–C one toward hydrolysis, and the versatile phosphorus chemistry gives access to a wide range of functional organic groups. The stability of P–O–M bonds is illustrated by the numerous metal phosphate and phosphonate compounds reported in the last 20 years.[8,9]

The modification of the surface of TiO_2 particles with phosphonic acids $RPO(OH)_2$ is currently attracting growing interest for numerous applications such as self- assembled monolayers,[10] ceramic membranes,[11] photo- electrochemical cells based on nanocrystalline films of TiO_2,[12,13] optical write–read–erase devices,[14] and en- zymatic catalyses.[15] Although to date few studies have dealt with the anchoring chemistry of phosphonic acids with the titanium oxide surface,[10,16] the anchoring is expected to involve both the coordination of the phos- phoryl oxygen to Lewis acid sites and the condensation of P–OH groups with surface hydroxyl groups Ti–OH.

The first aim of this work was to demonstrate that phosphonic esters (bis-trimethylsilyl and dialkyl phos- phonates) could also be used to modify the surface of titanium oxide. Anchoring by phosphinic acids and their ester derivatives, which to our knowledge has not been reported, was also investigated. The influence of the anchoring conditions (precursor, temperature, solvent, etc.) on the surface reactivity and the bonding mode was explored.

Another question was about the stability of organo- phosphorus species anchored on the surface of TiO_2, which is known to photocatalyze the oxidative degrada- tion of phosphonic acids and alkyl phosphonates.[17–20]

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Table 1. Standard Conditions of Modification of TiO₂ Particles by Organophosphorus Coupling Molecules[a]

coupling molecule	solvent (mL)	T (°C)	time (h)	dark	sample
PhPO(OH)$_2$ (PPA)	MeOH/H$_2$O[b] (600)	rt	72	no	PPA1
PhPO(OSiMe$_3$)$_2$ (PPS)	CH$_2$Cl$_2$ (40)	rt	24	no	PPS1
PhPO(OEt)$_2$ (PPE)	CH$_2$Cl$_2$ (40)	40	24	no	PPE1
Ph$_2$PO(OH) (DPPA)	MeOH/H$_2$O[b] (600)	rt	72	yes	DPPA1
				no	DPPA1′
Ph$_2$PO(OSiMe$_3$) (DPPS)	CH$_2$Cl$_2$ (40)	rt	24	no	DPPS1
Ph$_2$PO(OEt) (DPPE)	CH$_2$Cl$_2$ (40)	40	24	no	DPPE1

[a] Solvent volumes given for 1 g of TiO$_2$, 1.56 × 10^{-3} mol of coupling molecules. [b] pH adjusted to 3.5.

In the present work, we chose six organophosphorus compounds as model coupling molecules: phenylphosphonic and diphenylphosphinic (PPA and DPPA) acids, their (di)ethyl esters (PPE and DPPE), and their (bis)-trimethylsilyl esters (PPS and DPPS). The modification of the surface of titanium oxide particles (P25 Degussa), under standard and forcing conditions, was investigated by elemental analysis and ^{31}P solid-state NMR and FTIR spectroscopy. The stability of the anchoring toward photooxidation was tested.

2. Experimental Section

2.1. Starting Materials. TiO$_2$ particles (P25 Degussa) have an average particle size of 21 nm and a specific surface area of 45 ± 5 m^2 g^{-1}. They were dried (12 h, 120 °C, 10^{-2} mbar) before use. PhPO$_3$H$_2$ (PPA) (98%, Aldrich) was recrystallized from dried acetonitrile (δ ^{31}P = +21.4 (solid state)). PhPO(OEt)$_2$ (PPE) was prepared from PhPO(Cl)$_2$ (90%, Aldrich) by reaction with anhydrous ethanol, in the presence of triethylamine (δ ^{31}P = +18.3 (CH$_2$Cl$_2$/CD$_3$COCD$_3$)). PhPO-(OSiMe$_3$)$_2$ (PPS) was obtained by reaction of PhPO-(OEt)$_2$ with Me$_3$SiBr (3 equiv) in dichloromethane (δ ^{31}P = +1.4 (CH$_2$Cl$_2$/CD$_3$COCD$_3$)). Ph$_2$PO$_2$H (DPPA) (99%, Avocado) was used without further purification (δ ^{31}P = +28.7 (solid state)). Ph$_2$PO(OEt) (DPPE) was prepared from Ph$_2$PO(Cl) (98%, Avocado) by reaction with anhydrous ethanol, in the presence of triethylamine (δ ^{31}P = +29 (PhCH$_3$/CD$_3$COCD$_3$)). Ph$_2$PO(OSiMe$_3$) (DPPS) was obtained by reaction with Me$_3$SiBr (1.5 equiv) in dichloromethane (δ ^{31}P = +27.9 ppm (C$_6$D$_6$)). Dichloromethane was distilled over P$_2$O$_5$. Water (HPLC grade) was purchased from Aldrich. The manipulations with PhPO(OSiMe$_3$)$_2$ and Ph$_2$PO(OSiMe$_3$) were carried out under an inert argon atmosphere.

2.2. Preparation of the Samples. All of the samples were prepared using 1.56 × 10^{-3} mol of coupling molecules per gram of TiO$_2$, which corresponds to a 5-fold excess relative to the amount needed for a full surface coverage on the particles (assuming an area of 24 Å^2 per molecule). After modification, the anchored TiO$_2$ particles were filtered off, washed successively with methanol, acetone, and diethyl ether (to remove unreacted or physisorbed coupling molecules), and dried under vacuum (120 °C, 5 h, 10^{-2} mbar).

Standard Conditions. The "standard" conditions of modification are summarized in Table 1. Typical experiments are described below.

PPA (1.56 × 10^{-3} mol) was dissolved in a flask with 375 mL of methanol and 125 mL of water. A suspension of 1 g of TiO$_2$ in 100 mL of water was added to this solution, and the pH was adjusted to 3.5 (acid concentration 0.0028 mol L^{-1}). The resulting suspension was stirred at room temperature for 3 days, in daylight.

Table 2. Forcing Conditions of Modification of TiO₂ Particles by Organophosphorus Coupling Molecules[a]

coupling molecule	solvent (mL)	T (°C)	sample
PhPO(OH)$_2$	H$_2$O (40)	100	PPA2
PhPO(OH)$_2$	H$_2$O (15)	120[b]	PPA3
PhPO(OH)$_2$	toluene (15)	120[b]	PPA4
PhPO(OSiMe$_3$)$_2$	toluene (15)	120[b]	PPS2
PhPO(OEt)$_2$	toluene (15)	120[b]	PPE2
Ph$_2$PO(OH)	H$_2$O (40)	100	DPPA2
Ph$_2$PO(OH)	H$_2$O (15)	120[b]	DPPA3
Ph$_2$PO(OSiMe$_3$)	toluene (15)	120[b]	DPPS2
Ph$_2$PO(OEt)	toluene (15)	120[b]	DPPE2

[a] Reaction time of 24 h, in the dark (solvent volumes given for 1 g of TiO$_2$, 1.56 × 10^{-3} mol of coupling molecules). [b] Reaction performed in a sealed tube.

PPE (1.56 × 10^{-3} mol) was dissolved in CH$_2$Cl$_2$. The coupling molecule concentration was 0.042 mol L^{-1}. After addition of TiO$_2$ (1 g), the suspension was stirred for 1 day at 40 °C, in daylight.

Forcing Conditions. The "forcing" conditions of modification are summarized in Table 2. In a typical experiment, titanium dioxide (1 g), phenylphosphonic acid (1.56 × 10^{-3} mol), and water (15 mL) were placed in a 50 mL Pyrex tube which was then sealed. The coupling molecule concentration was 0.11 mol L^{-1}. The tube was heated at 120 °C in an oven for 1 day.

2.3. Stability Toward Photooxidation. These manipulations were carried out using water and toluene as solvents. Samples of TiO$_2$, anchored with phenylphosphonic or diphenylphosphinic acid (0.2 g), were placed in a PYREX Erlenmeyer containing 15 mL of solvent at room temperature and irradiated using a Rayonet photoreactor equipped with four blacklight lamps (4 W, 350 nm) for 1 day. The solids were filtered off, washed successively with ethanol, acetone, and diethyl ether, and dried in vacuo (120 °C, 5 h, 10^{-2} mbar).

2.4. Characterization. The Ti/P ratios in the solid samples were determined by elemental analysis, which was done by the "Laboratoire Central d'Analyses du CNRS" at Vernaison (France). Thermogravimetric analysis was performed in dry air (heating rate of 10 K min^{-1}) on a Netzsch STA409 thermobalance coupled to a Baltzers QMG421 quadrupole mass spectrometer, allowing the analysis of the gases evolved during the pyrolysis. The BET surface areas and the C constants of the samples were obtained from nitrogen adsorption experiments at 77 K with a Micromeritics Gemini2360 sorptometer. 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 Avance DPX300 spectrometer, using magic angle spinning (MAS) (spinning rate of 10 kHz) and high-power proton decoupling; the flip angle was 45° and the recycling delay was 10 s; the chemical shifts were

Table 3. Characteristics of the Titania Particles before and after Anchoring under Standard Conditions

sample	wt % P[a]	C_{BET}[b]	P nm^{-2} [c]	$\Delta M/M_0$ (%)[d]
TiO$_2$	0	165	0	0.2
PPA1	1.1	44	4.8	1.4
PPS1	1.1	33	4.7	1.9
PPE1	0.6	41	2.6	1.2
DPPA1	0.7	43	3.0	1.8
DPPS1	0.5	45	2.2	2.6
DPPE1	0.3	53	1.3	2.1

[a] From elemental analysis. [b] BET constant. [c] Average number of coupling molecules per nm². [d] Weight loss between 300 and 800 °C (TGA in air).

Table 4. Phosphorus Content of the Titania Particles Modified under Forcing Conditions (1 day at 120 °C)

sample	wt % P[a]	P nm^{-2} [b]
PPA2	1.3	5.6
PPA3	3.5	15.1
PPA4	2.40	10.0
PPS2	0.9	3.9
PPE2	1.1	4.7
DPPA2	0.6	2.6
DPPA3	2.9	12.5
DPPS2	0.9	3.9
DPPE2	0.4	1.7

[a] From elemental analysis. [b] Average number of coupling molecules per nm².

referenced to H$_3$PO$_4$ (85% in water). IR spectra were obtained on a Perkin-Elmer 2000 spectrophotometer, by transmission through NaCl windows in the case of liquid precursors (dialkyl and bis(trimethylsilyl)esters) or by using diffuse reflectance (DRIFT) and Kubelka–Munk units in the case of solids. A spectrum of the TiO$_2$ particles dried at 120 °C was used as the background spectrum for all the experiments with the modified samples.

3. Results and Discussion

3.1. Anchoring on the TiO₂ Particles. The surface of the TiO$_2$ particles was modified by treatment with a solution of the phosphonate or phosphinate coupling molecules in a 5-fold excess relative to the amount needed for a full surface coverage on the particles (assuming an area of 24 Å² per molecule) (Table 1). Regardless of the type of phosphorus derivative used, stable suspensions were obtained. In aqueous medium (acids), the pH was adjusted to 3.5 to be far from the point of zero charge, pzc, (5.9 for TiO$_2$), so that electrostatic repulsive forces due to charged surface sites act between the particles, giving unaggregated suspensions.[21] In organic medium (ester derivatives), the suspensions became stable as soon as the solution of the organophosphorus derivative was added, thus indicating that the anchoring lowered the hydrophilicity of the surface of oxides. After the anchoring treatment, the solutions were filtered off and the powders were thoroughly washed to remove unreacted and physisorbed species and then dried before analysis. The characteristics of the modified TiO$_2$ particles are summarized in Table 3.

Elemental analysis showed the presence of phosphorus in all the samples, indicating that all of the coupling molecules did react with the surface of the TiO$_2$ particles. The samples modified by PPA and its ester derivatives (PPE, PPS) exhibited higher P contents than those modified by DPPA and its derivatives (DPPE, DPPS), which suggests a lower cross-sectional area for phenylphosphonate than for diphenylphosphinate-anchored molecules. The lowest P contents were observed with the ethyl ester derivatives, suggesting a somewhat different reactivity. The average number of coupling molecules per nm² (P nm^{-2}) for the particles anchored under the standard conditions suggests a coverage not exceeding monolayer in all cases.

The thermogravimetric analysis (TGA) in air of the virgin TiO$_2$ powder showed one weight loss (about 2%)

from 20 to 400 °C. In contrast, TGA of the modified TiO$_2$ particles displayed two weight losses. Mass spectrometry of the evolved gases indicated that the first weight loss, below 300 °C, corresponded to the distillation of residual water and/or solvent. The second weight loss, above 300 °C, corresponded mainly to a large escape of water and carbon dioxide arising from the oxidative degradation of the phenyl groups.

Nitrogen adsorption experiments confirmed the modification of the surface; indeed, whereas the specific surface area was not significantly modified, the C constant in the BET equation was much lower for the modified powders than for the starting titania particles (Table 3). According to the BET theory, the C constant is related to the enthalpy of adsorption;[22] its decrease reflects a decrease of the interactions between the surface and the nitrogen molecules.

A second set of experiments was carried out under forcing conditions (see Experimental Section). The P content of the samples PPA3, PPA4, and DPPA3, obtained by reaction with PPA and DPPA at 120 °C in water, was very high (Table 4). They show that the reaction with the acids is no more a surface reaction but that the core of the particles is attacked, leading to the formation of bulk phases.

3.2. Infrared and ^{31}P NMR Spectroscopy. The anchoring of organophosphorus derivatives on a titania surface is expected to involve both coordination of the phosphoryl oxygen to Lewis acid sites and condensation reactions between the surface hydroxyl groups Ti–OH and the P–OX (X = H, Me$_3$Si, Et) groups. Accordingly, the possible bonding modes can be mono-, bi-, or tridentate for the phosphonate derivatives and mono- and bidentate for the phosphinate derivatives. We attempted to identify the main bonding modes for each coupling molecule, using a combination of IR and ^{31}P NMR spectroscopy.

Anchoring with Phenylphosphonic Acid and Its Derivatives. The IR spectra in the 800–1450 cm^{-1} region of the modified TiO$_2$ particles (after subtraction of the spectrum of the starting particles) and those of the precursors are displayed in Figure 1. Regardless of the type of phosphonate coupling molecule used, the IR spectra of the modified particles present close typical features, with a strong band near 1140 cm^{-1}, characteristic of P–C$_6$H$_5$ groups, and broad P–O stretching bands between 900 and 1200 cm^{-1}. A weak band at 3065 cm^{-1}, characteristic of the aromatic C–H, is also present

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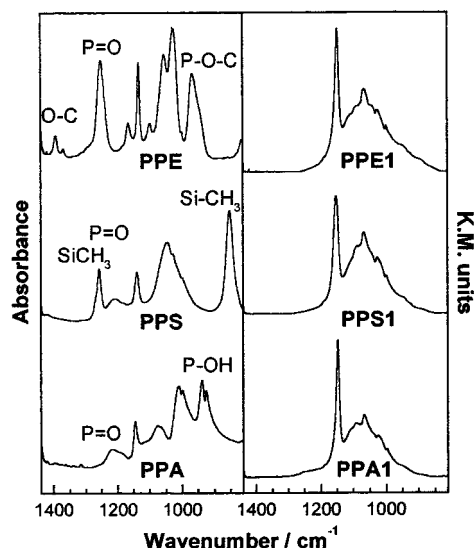
Figure 1. IR spectra of the phosphonate coupling molecules PhPO(OH)$_2$ (PPA), PhPO(OSiMe$_3$)$_2$ (PPS), and PhPO(OEt)$_2$ (PPE) (left) and of TiO$_2$ samples modified under standard conditions with these molecules (right).

for all of the samples. The O−H stretching bands at 3700 and 3500 cm^{-1}, associated with Ti−OH groups and adsorbed water, appear as negative bands in the subtracted spectra of the modified particles, which is consistent with condensations involving Ti−OH groups and with a decrease in the surface hydrophilicity. The significant decrease of the vibrations typical of P−OH, P−OSiMe$_3$, and P−OEt groups (Figure 1) suggests that the condensation of these groups with Ti−OH surface groups is practically complete, according to

$$Ti-OH + P-O-X \rightarrow Ti-O-P + X-OH$$
$$(X = H, SiMe_3, Et) \quad (1)$$
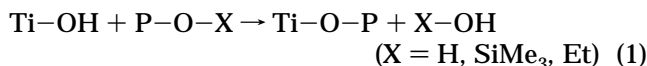
In Figure 1, note the absence of the Si−C stretching band, at 851 cm^{-1} in the spectrum of PPS1, and of the O−CH$_2$ stretching band, at 1394 cm^{-1} in the spectrum of PPE1. In the latter spectrum, the absence of C−H stretching bands at 2984, 2932, 2905, and 2871 cm^{-1} from the OEt groups confirms the complete cleavage of the P−OEt groups. However, when the samples modified with PPE were dried at room temperature instead of at 120 °C, some OEt groups could be detected, suggesting the presence of residual P−OEt groups or adsorbed EtOH. In all cases, the disappearance of the P=O stretching band near 1200−1250 cm^{-1} points to the coordination of all of the phosphoryl oxygens to surface Lewis acid sites and to the delocalization of the electrons.

Thus, regardless of the type of phosphonate coupling molecule used, the main bonding mode to the surface should involve tridentate PhP(OTi)$_3$ units, similar to those found in layered titanium phosphonates[8] and in titanium oxide−alkoxide−phosphonate complexes.[23] The formation of such surface species has already been proposed by Randon et al.[16] for the surface modification of TiO$_2$ with PPA. In addition, the presence of absorptions at 900−1000 cm^{-1} (the region of P−OH stretching

Scheme 1. Schematic Representation of the Main Bonding Modes of Diethylphosphonate Molecules on a TiO$_2$ Surface
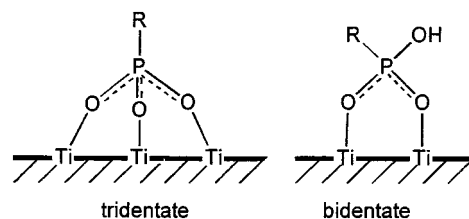
Scheme 2. Proposition of Mechanism for the Condensation of Phosphonate Coupling Molecules with Hydroxyl Surface Groups
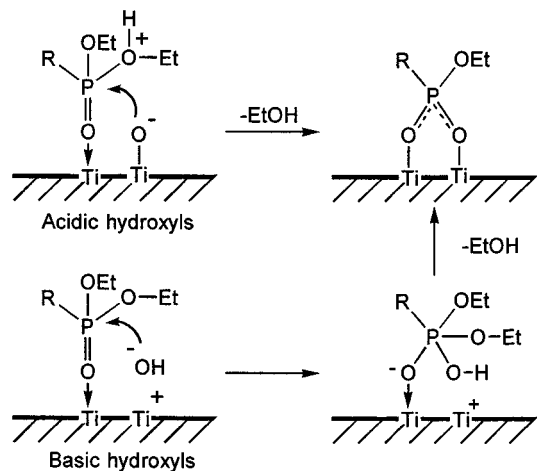

bands) suggests the presence of residual P−OH groups in bidentate PhP(OH)O$_2$ units (Scheme 1).

The surface chemistry of TiO$_2$ Degussa particles is complex: both acidic and basic Ti−OH groups as well as Lewis acid sites are present.[24] The relatively high density of grafted species observed suggests that both the acidic and basic Ti−OH groups react with the organophosphorus coupling molecules. Depending on the nature of the coupling molecule and of the Ti−OH surface groups, different mechanisms of condensation may be proposed. In the case of PPA, the easiest reaction would be the nucleophilic attack of a phosphonate anion on titanium bonded to a protonated basic OH group, with elimination of water. In all cases, the coordination of the phosphoryl oxygen on a surface Lewis acid site may assist the condensation by increasing the electrophilicity of the phosphorus atoms, thus facilitating its attack by Ti−O$^-$ (acidic Ti−OH) or OH$^-$ (basic Ti−OH) (Scheme 2).

The cleavage of P−OEt bonds on oxide surfaces has already been reported, for instance, in the case of dimethyl methylphosphonate.[25] P−OEt groups are quite stable toward hydrolysis (typical hydrolysis conditions involve refluxing overnight in 6 N HCl), and their hydrolysis by surface water prior to the interaction with the surface is most unlikely. On the other hand, P−O−SiMe$_3$ groups are much more reactive, and their hydrolysis to P−OH groups by surface water cannot be excluded.

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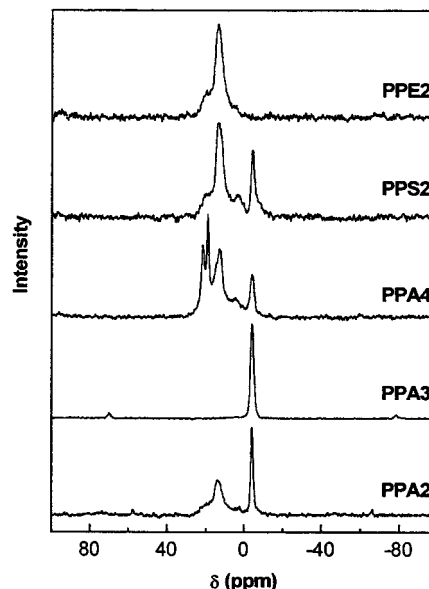
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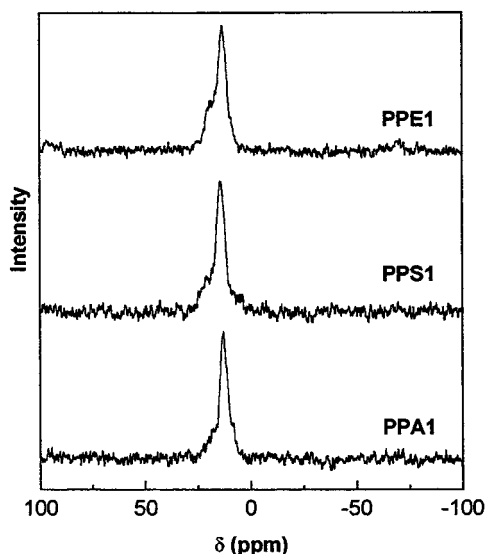
Figure 2. ^{31}P MAS NMR spectra of TiO_2 samples modified under standard conditions with $PhPO(OH)_2$ (PPA), $PhPO(OSiMe_3)_2$ (PPS), and $PhPO(OEt)_2$ (PPE).

The ^{31}P MAS NMR spectra of the particles modified under standard conditions were similar regardless of the coupling molecule (Figure 2). From the FTIR result, the major resonance at 13 ppm is ascribed to tridentate phosphonate sites $PhP(OTi)_3$. Actually, the chemical shift of this resonance is close to those found for phenylphosphonate/TiO_2 hybrids prepared by a sol–gel method.[6] The presence of an additional resonance near 19 ppm points to another bonding mode of the phosphonate groups, which is likely to be bidentate ($PhP(OTi)_2OH$ sites).

In the literature, the surface modification of TiO_2 with phosphonic acids is usually carried out in aqueous media at 100 °C.[10,16] Depending on the reaction time and the phosphonic acid concentration, significant amounts of bulk titanium phosphonate may be formed.[10] The ^{31}P MAS NMR spectrum of TiO_2 particles reacted with phosphonate coupling molecules at elevated temperatures and concentrations (forcing conditions) are displayed in Figure 3. A sharp resonance at −4 ppm, characteristic of titanium phenylphosphonate,[26] is observed in the spectra of the particles modified with PPA. Powder XRD confirmed the formation of a lamellar titanium phenylphosphonate phase. The formation of this phase accounts for the high P contents of the PPA3 and PPA4 samples. It is noteworthy that, under forcing conditions, a titanium phenylphosphonate phase is also observed in the reaction of TiO_2 particles with PPS but not with PPE. The formation of a titanium phosphonate phase probably results from a dissolution–precipitation process involving the cleavage of the oxide bonds Ti–O–Ti; Scheme 3 displays a possible reaction pathway for the cleavage of the Ti–O–Ti bonds by phosphonic acid. The Ti–O–Ti bonds have an excellent chemical stability, even under acidic conditions; thus, the coordination of the phosphoryl groups most probably assists the cleavage. The intermediate formation of an oxonium bridge would be more likely to occur through the transfer of a proton, or a trimethylsilyl group, than

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Figure 3. ^{31}P MAS NMR spectra of TiO_2 samples modified with PPA, PPE, and PPS, under forcing conditions (PPA2, 100 °C in water; PPA3, 120 °C in water; PPA4, PPS2, and PPE2, 120 °C in toluene).

Scheme 3. Proposition of Mechanism for the Cleavage of Ti–O–Ti Bonds by Phenylphosphonic Acid
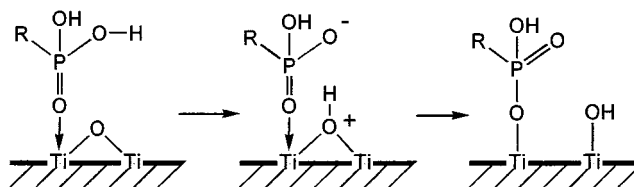

through the transfer of a carbocation in the case of a dialkylphosphonate coupling molecule, which is consistent with our observations.

Note that, depending on the coupling molecule and the anchoring conditions, the cleavage of the oxide bonds might be involved in the anchoring process as well, in addition to the condensation of surface hydroxyls Ti–OH. The low P contents found for particles modified by $Ph P(O)(OEt)_2$ (PPE) and $Ph_2P(O)(OEt)$ (DPPE) could arise from the lack of reactivity of these molecules toward the Ti–O–Ti bonds.
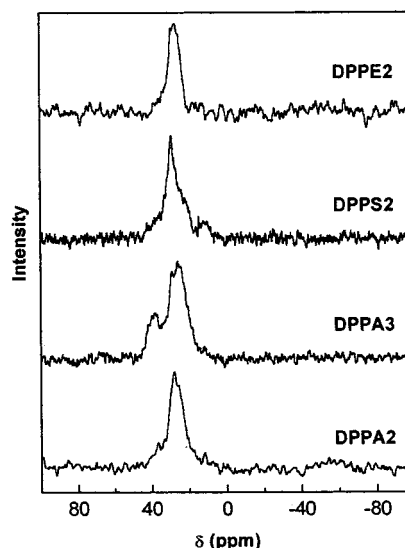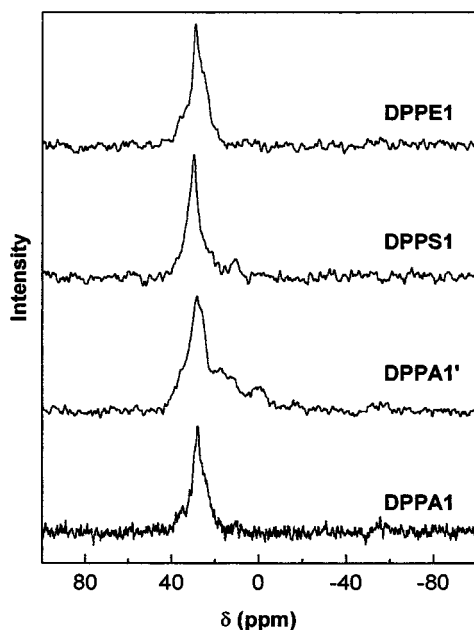
Anchoring with Diphenylphosphinic Acid and Its Derivatives. The IR spectra of all the samples modified under standard conditions by $Ph_2PO(OH)$ (DPPA), $Ph_2PO(OSiMe_3)$ (DPPS), and $Ph_2PO(OEt)$ (DPPE) were similar (Figure 4). They are dominated by the band near 1135 cm^{-1} that is characteristic of phenyl groups attached to a phosphorus atom, and P–O stretching bands are clearly identified at 1070, 1045, 1024, and 998 cm^{-1}.[27] As in the case of the phosphonate coupling molecules, the decrease of the bands that are characteristic of the functional groups (P–OH, P–OSiMe$_3$, and P–OEt) and of the P=O double bond suggests extensive condensation and coordination of the phosphoryl oxygen, leading to mainly bidentate phosphinate units. Accordingly, in the ^{31}P MAS NMR spectra (Figure 5), the major resonance around 28 ppm is tentatively ascribed to the

(27) Dahl, G. H.; Block, B. P. *Inorg. Chem.* **1967**, *6*, 1439.
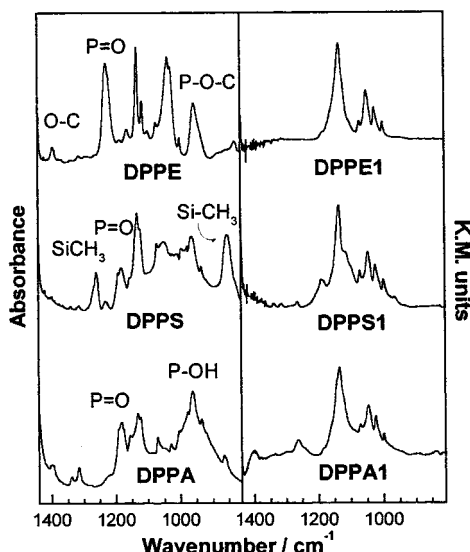
Figure 4. IR spectra of the phosphinate coupling molecules $Ph_2PO(OH)$ (DPPA), $Ph_2PO(OSiMe_3)$ (DPPS), and $Ph_2PO(OEt)$ (DPPE) (left) and of TiO_2 samples modified under standard conditions with these molecules (right).

Figure 5. ^{31}P MAS NMR spectra of TiO_2 samples modified under standard conditions with $Ph_2PO(OH)$ (DPPA), Ph_2PO-$(OSiMe_3)$ (DPPS), and $Ph_2PO(OEt)$ (DPPE).

$Ph_2P(OTi)_2$ sites; actually, a chemical shift of 33 ppm was reported for bidentate diphenylphosphinate ligands in a titanium oxide–alkoxide–phosphinate complex.[23] Note that, when the anchoring of DPPA in H_2O/MeOH was performed in daylight (sample DPPA1′, Figure 5), additional resonances were observed around 14 and 0 ppm, indicating significant photodegradation (see next paragraph). On the other hand, only minor photodegradation occurred during the anchoring of DPPS and DPPE in CH_2Cl_2.

The ^{31}P NMR spectra of the samples prepared under forcing conditions (in the dark) with the three phosphinic derivatives are displayed in Figure 6. No significant effect was observed with DPPS and DPPE in toluene. On the other hand, with DPPA in water at 120 °C (sample DPPA3), the appearance of a broad signal

Figure 6. ^{31}P MAS NMR spectra of TiO_2 samples modified with DPPA, DPPE, and DPPS, under forcing conditions (DPPA2, 100 °C in water; DPPA3, 120 °C in water; PPS2 and PPE2, 120 °C in toluene).

around 40 ppm and the high P content of the powder indicate the incipient formation of a bulk titanium phosphinate phase. However, the lack of data in the literature makes it impossible to propose any formula for such a phase.

3.3. Stability of Anchored Samples under UV Irradiation. As mentioned above, when the modification of TiO_2 with DPPA in H_2O/MeOH was performed in daylight, partial oxidation of the P–C bond occurred, as shown by the two additional resonances near 14 and 0 ppm in the ^{31}P NMR spectrum of the DDPA1′ sample (Figure 5). These resonances may be ascribed to anchored phosphonate ($PhPO_3$ sites) and phosphate (PO_4 sites) species, respectively. As a matter of fact, the ^{31}P MAS NMR spectrum of TiO_2 particles modified with phosphoric acid showed a major, dissymmetric resonance near −4 ppm (Figure 7f). It is noteworthy that, under the same conditions, P–C bond cleavage was not observed in the case of phenylphosphonic acid. This difference might be explained either by a decrease in the photocatalytic efficiency of TiO_2 particles, related to a higher coverage of the surface with tridentate phosphonate groups, or by an increased sensitivity toward oxidation of the phosphinate derivatives.

We investigated the stability of PPA1 and DPPA1 samples toward UV irradiation ($\simeq$350 nm) in water and in toluene. After irradiation in water, the ^{31}P MAS NMR spectra evidenced in both cases the extensive cleavage of the phenyl groups (parts a and c of Figure 7). The initial resonances at 13 or 28 ppm decreased and a new resonance near 0 ppm (PO_4 sites) appeared. The loss of phenyl groups was confirmed by chemical analysis of the solids after irradiation. On the other hand, the ^{31}P MAS NMR spectra of the samples irradiated in toluene were much less affected (parts b and d of Figure 7), indicating only minor oxidative degradation. Interestingly, in the presence of PPA, the phosphate species on the surface of the irradiated PPA1 sample can be exchanged by the phenylphosphonate species (Figure 7e).
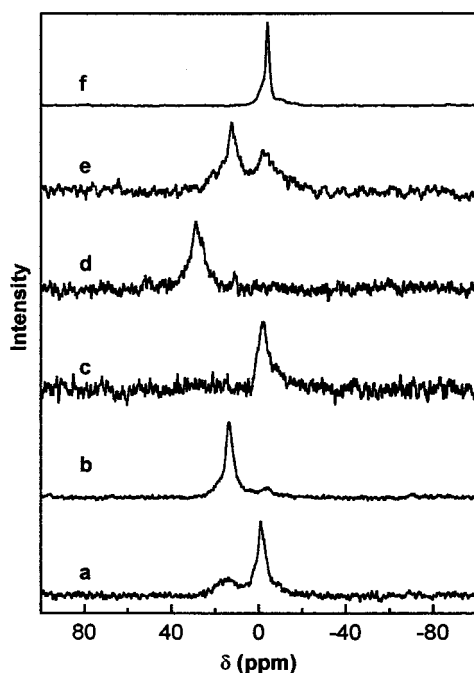
Figure 7. Stability toward irradiation (350 nm, 1 day) of PPA1 and DPPA1 samples (^{31}P MAS NMR): a, PPA1 irradiated in water; b, PPA1 irradiated in toluene; c, DPPA1 irradiated in water; d, DPPA1 irradiated in toluene; e, ^{31}P MAS NMR spectrum of sample (a) reacted with PPA (standard conditions, 48 h); f, ^{31}P MAS NMR spectrum of a TiO$_2$ sample reacted with H$_3$PO$_4$.

4. Conclusions

One important outcome of this study is the possibility of using organic-soluble phosphonic and phosphinic ester derivatives as coupling molecules, instead of the acids, which are often difficult to solubilize. When the surface modification is performed in an organic solvent, photodegradation catalyzed by TiO$_2$ remains negligible. Another advantage in using dialkyl phosphonate coupling molecules is the avoidance of the formation of bulk phases. In addition, the synthesis of the acid requires an additional hydrolysis step, which may be problematic in some cases.

An important application of TiO$_2$ is the photocatalytic oxidation of organic contaminants in water.[28] Thus, the degradation of phosphonic acids[17] and dimethyl phosphonates[17−19] on TiO$_2$ leads to phosphate species and CO$_2$. Our results indicate that the covalent anchoring to the surface of these molecules, prior to oxidation and the exchange of anchored oxidized species with unreacted molecules, should be taken into account in the reaction pathways and in the processes of deactivation/reactivation of the catalysts.

The reactivity of organophosphorus coupling molecules appears quite different from that of trialkoxysilane coupling agents.[2] In the presence of traces of water, homocondensation between trialkoxysilanes may lead to multilayers or even gel formation instead of condensation with the surface. Homocondensation of phosphonate or phosphinate coupling molecules with the formation of P−O−P bridges is unlikely, and such bridges would not be stable in the presence of water. In the case of organophosphorus coupling molecules, reaction with the surface involves not only condensation with surface hydroxyl groups but also coordination of the phosphoryl on Lewis acid sites and, depending on the anchoring conditions, cleavage of the M−O−M bonds. One drawback of phosphonic acids and silylated esters is the formation, at high temperature and concentration, of metal phosphonate bulk phases.

Their different reactivities should make alkoxysilane and organophosphorus coupling molecules quite complementary. For the surface modification of silica, for instance, alkoxysilanes are without contest the best coupling molecules; although phosphonic acids react with silica,[29] Si−O−P bonds are easily hydrolyzed. On the other hand, for the surface modification of metal oxides such as TiO$_2$, ZrO$_2$, or Al$_2$O$_3$, the absence of P−O−P bonds, the facile formation, and the stability of M−O−P bridges make organophosphorus coupling molecules highly attractive.

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