

# Selective Surface Modification of SiO<sub>2</sub>–TiO<sub>2</sub> Supports with Phosphonic Acids

P. Hubert Mutin,<sup>\*,†</sup> Vincent Lafond,<sup>†</sup> Aurelian F. Popa,<sup>†</sup> Michel Granier,<sup>†</sup>  
Laurent Markey,<sup>‡</sup> and Alain Dereux<sup>‡</sup>

*Chimie Moléculaire et Organisation du Solide, UMR CNRS 5637, Université Montpellier 2, Place Eugène Bataillon, 34095 Montpellier, France, and Laboratoire de Physique de l'Université de Bourgogne, Nanosciences: Optique Submicronique and Nanocapteurs, UA CNRS 5027, 9 avenue A. Savary, F-21078 Dijon, France*

Received December 22, 2003. Revised Manuscript Received September 8, 2004

The selective surface modification by phosphonic acids of SiO<sub>2</sub>–TiO<sub>2</sub> supports at the micrometer and molecular scale was investigated. Under aqueous conditions, phosphonic acids bind to TiO<sub>2</sub> and not to SiO<sub>2</sub> surfaces. A micropatterned support was prepared by electron beam microlithography and selectivity, of the surface modification was evidenced using scanning Auger electron spectroscopy (SAES). The second support was a mesoporous SiO<sub>2</sub>–TiO<sub>2</sub> mixed oxide (10 mol % Ti) epoxidation catalyst prepared by sol–gel processing. Selectivity was deduced from the decrease of the catalytic activity upon modification and from chemical analysis; bonding modes to the surface were investigated using solid-state <sup>29</sup>Si and <sup>31</sup>P MAS NMR. The possibility to introduce different organic groups by successive treatments with a phosphonic acid and a silylating agent was illustrated in the case of the mixed oxide.

## Introduction

The tailoring of inorganic surfaces by covalent attachment of functional organic molecules finds applications in fields as diverse as adhesion, corrosion, separation, heterogeneous catalysis, sensors, or optoelectronic devices. Depending on the nature of the inorganic surface, different families of functional molecules are available. The best studied are organosilanes,<sup>1–3</sup> which are widely used to modify oxide surfaces, and alkanethiols<sup>3–5</sup> that form self-assembled monolayers (SAMs) on coinage metal surfaces. In the past 10 years, organophosphorus compounds such as phosphonates,<sup>6–14</sup>

phosphinates,<sup>14,15</sup> and alkyl phosphates<sup>16–18</sup> have attracted growing interest due to their high affinity toward metal oxide surfaces.

Selectivity of a given function for a given surface is of great importance in surface modification. Indeed, selective surface modification allows the control of the spatial repartition of the organic groups by the nature of the inorganic surface (Scheme 1), hence offering the possibility to pattern organic groups by modification of a prepatterned inorganic surface that can be easily obtained using well-established microfabrication techniques<sup>19</sup> such as photolithography or electron-beam lithography.

A spectacular example is provided by the simultaneous (“orthogonal”) selective modification of gold–metal oxide microstructures based on the high affinity of thiols for the gold areas and of carboxylic or phosphonic acid for the oxide areas.<sup>20,21</sup> Sequential bifunctionalization of Au–SiO<sub>2</sub>/Si surfaces by thiols then by organosilanes has also been reported.<sup>22,23</sup> Another example is the area-selective binding of organosilanes to

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

† Université Montpellier 2.

‡ UA CNRS 5027.

(1) Plueddemann, E. P. *Silane Coupling Agents*; Plenum Press: New York, 1991.

(2) Owen, M. J. *Adhes. Sci. Eng.* **2002**, *2*, 403.

(3) Ulman, A. *Chem. Rev.* **1996**, *96*, 1533.

(4) Gooding, J. J.; Mearns, F.; Yang, W.; Liu, J. *Electroanalysis* **2003**, *15*, 81.

(5) Ferretti, S.; Paynter, S.; Russell, D. A.; Sapsford, K. E.; Richardson, D. J. *Trends Anal. Chem.* **2000**, *19*, 530.

(6) Gao, W.; Dickinson, L.; Grozinger, C.; Morin, F. G.; Reven, L. *Langmuir* **1996**, *12*, 6429.

(7) Randon, J.; Paterson, R. J. *Membr. Sci.* **1995**, *98*, 119.

(8) Pawsey, S.; McCormick, M.; De Paul, S.; Graf, R.; Lee, Y. S.; Reven, L.; Spiess, H. W. *J. Am. Chem. Soc.* **2003**, *125*, 4174.

(9) Pechy, P.; Rotzinger, F. P.; Nazeeruddin, M. K.; Kohle, O.; Zakeeruddin, S. M.; Humphrybaker, R.; Gratzel, M. *Chem. Commun.* **1995**, 65.

(10) Will, G.; Nagaraja Rao, J. S. S.; Fitzmaurice, D. J. *Mater. Chem.* **1999**, *9*, 2297.

(11) Helmy, R.; Fadeev, A. Y. *Langmuir* **2002**, *18*, 8924.

(12) Lafond, V.; Gervais, C.; Maquet, J.; Prochnow, D.; Babonneau, F.; Mutin, P. H. *Chem. Mater.* **2003**, *15*, 4098.

(13) Zhao, B.; Moore, J. S.; Beebe, D. J. *Langmuir* **2003**, *19*, 1873.

(14) Guerrero, G.; Mutin, P. H.; Vioux, A. *Chem. Mater.* **2001**, *13*, 4367.

(15) Guerrero, G.; Chaplais, G.; Mutin, P. H.; Le Bideau, J.; Leclercq, D.; Vioux, A. *Mater. Res. Soc. Symp. Proc.* **2001**, *628*, CC6.6.1.

(16) Textor, M.; Ruiz, L.; Hofer, R.; Rossi, A.; Feldman, K.; Haehner, G.; Spencer, N. D. *Langmuir* **2000**, *16*, 3257.

(17) Hofer, R.; Textor, M.; Spencer, N. D. *Langmuir* **2001**, *17*, 4014.

(18) Tosatti, S.; Michel, R.; Textor, M.; Spencer, N. D. *Langmuir* **2002**, *18*, 3537.

(19) Madou, M. J. *Fundamentals of Microfabrication*, 2nd ed.; CRC Press: Boca Raton, FL, 2002.

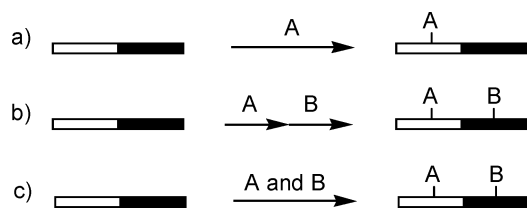
(20) Laibinis, P. E.; Hickman, J. J.; Wrighton, M. S.; Whitesides, G. M. *Science* **1989**, *245*, 845.

(21) Gardner, T. J.; Frisbie, C. D.; Wrighton, M. S. *J. Am. Chem. Soc.* **1995**, *117*, 6927.

(22) Xia, Y.; Whitesides, G. M. *Adv. Mater.* **1996**, *8*, 765.

(23) Ho, P. K. H.; Filas, R. W.; Abusch-Magder, D.; Bao, Z. *Langmuir* **2002**, *18*, 9625.

**Scheme 1. Selective Surface Modification of a Support Made of Two Different Inorganic Materials: Selective Monofunctionalization (a), Sequential (b), and Orthogonal (c) Bifunctionalization**



oxidized areas on Si(111)-H surfaces<sup>24</sup> or to the native oxide areas of a Si wafer oxidized locally in dry nitrogen.<sup>25</sup>

Selectivity between SiO<sub>2</sub> and metal oxide surfaces is more difficult to achieve and much less documented. Chloro- and alkoxy-organosilanes bind to both surfaces, and selective surface modification appears hopeless. Organophosphorus compounds are more promising; indeed, it was recently reported that alkanephosphate ammonium salts reacted selectively with the TiO<sub>2</sub> areas of prepatterned TiO<sub>2</sub>/SiO<sub>2</sub> substrates.<sup>26,27</sup> Phosphonic acids too have been used to modify a variety of metal oxide surfaces. However, surface modification of silica by phosphonic acids involving the formation of Si-O-P bonds has also been reported.<sup>28</sup> In addition, the formation of strongly bonded self-assembled monolayers on the native oxide surface of Si was recently demonstrated.<sup>29</sup>

We show here that, under aqueous conditions, phosphonic acids bind to TiO<sub>2</sub> and not to SiO<sub>2</sub> surfaces, allowing the selective surface modification of SiO<sub>2</sub>-TiO<sub>2</sub> surfaces at the micrometer and nanometer levels. The selective grafting of TiO<sub>2</sub> domains on a micropatterned support prepared by electron-beam microlithography was evidenced using scanning Auger electron spectroscopy (SAES). As an example of a SiO<sub>2</sub>-TiO<sub>2</sub> surface with (sub)nanometric TiO<sub>2</sub> domains, we used a mesoporous mixed-oxide support prepared by sol-gel processing; selectivity of the surface modification and bonding modes to the surface are deduced from solid-state NMR spectra and from the decrease of catalytic activity of the mixed oxide upon modification. The possibility to introduce different organic groups by successive treatments with a phosphonic acid and a silylating agent is illustrated in the case of the mixed oxide.

## Experimental Section

**Chemicals.** *n*-Dodecylphosphonic acid (DPA) was synthesized by Michaelis-Arbusov reaction of the *n*-dodecyl bromide and triethyl phosphite, followed by silylation with Me<sub>3</sub>SiBr and

hydrolysis. Phenylphosphonic acid (PPA) was purchased from Aldrich. Both acids were purified by crystallization from acetonitrile. <sup>31</sup>P MAS NMR (ppm): δ 31.1 (DPA), 21.4 (PPA). The oxides SiO<sub>2</sub> (Silica Gel 60A Carlo Erba, 550 m<sup>2</sup> g<sup>-1</sup>) and TiO<sub>2</sub> (P25 Degussa; 50 m<sup>2</sup> g<sup>-1</sup>; wt % Ti, 56.93; wt % P, <0.10; wt % S, <0.10; Cl, 1475 ppm) were degassed at 120 °C for 15 h under vacuum (1 mbar).

**SiO<sub>2</sub>-TiO<sub>2</sub> Micropatterned Surface.** The micropatterned SiO<sub>2</sub>-TiO<sub>2</sub> surface was fabricated by electron-beam microlithography, using BK7 glass slides covered by ca. 150 nm TiO<sub>2</sub>. The substrates were purchased at Guinchard Services (Le Mée sur Seine, France). The microfabrication process involved the following steps: (1) thin film gold coating of the substrate (for electrical conduction with the electron beam); (2) PMMA spin coating and baking; (3) electron-beam lithography; (4) nickel film deposition; (5) lift-off of the PMMA patterned structure; (6) reactive ion etching using O<sub>2</sub> for removal of gold; (7) reactive ion etching using Ar/SF<sub>6</sub> (for TiO<sub>2</sub> etching); (8) nickel stripping using diluted nitric acid; (9) reactive ion etching with O<sub>2</sub> for removal of metal residues. The final pattern consisted of an array of TiO<sub>2</sub> rounded spots about 6.5 × 7.5 μm<sup>2</sup>, separated by 3.7 mm SiO<sub>2</sub> stripes. According to atomic force microscopy (AFM) section analysis, the TiO<sub>2</sub> spots were located about 180 nm above the SiO<sub>2</sub> surface.

**Selective Modification of the Patterned Surface.** The patterned sample surface (~2.5 cm<sup>2</sup>) was first cleaned by sonicating for 3 min successively in hexane, ethanol, and water and then irradiated for 30 min under an O<sub>2</sub> stream using a two-wavelengths (185 and 254 nm) low-pressure mercury lamp to remove organic contamination. The patterned sample was then immersed in a 0.5 mM solution of DPA in HPLC grade water at 6 °C for 15 h, after which it was rinsed 3 times by sonicating for 3 min in HPLC grade water.

**SiO<sub>2</sub>-TiO<sub>2</sub> Mesoporous Mixed Oxide.** The mesoporous SiO<sub>2</sub>-TiO<sub>2</sub> mixed oxide support was prepared by nonhydrolytic sol-gel processing<sup>30</sup> as described previously. SiCl<sub>4</sub> (12.28 g, 72.28 mmol), TiCl<sub>4</sub> (1.51 g, 7.96 mmol), Pr<sub>2</sub>O (17.03 g, 166.67 mmol), and CH<sub>2</sub>Cl<sub>2</sub> (16 mL) were heated in a sealed tube at 110 °C for 4 days. The gel was then washed 3 times with 5 mL of CH<sub>2</sub>Cl<sub>2</sub>, dried at 120 °C for 15 h under vacuum (1 mbar), and calcined in air at 500 °C for 5 h. The resulting mixed oxide was characterized using elemental analysis, X-ray diffraction, N<sub>2</sub> adsorption-desorption at 77 K, and FTIR spectroscopy. The sample contained 7.7 wt % Ti (9.9 mol % TiO<sub>2</sub>) and was predominantly mesoporous, with a BET surface area of 730 m<sup>2</sup> g<sup>-1</sup>, and an average pore diameter of 3.8 nm.

**Modification of the Oxide and Mixed-Oxide Powders with Phosphonic Acids.** The (mixed) oxide powder (500 mg) was added under stirring to a solution of the phosphonic acid (2 mmol) in 500 mL of 4:1 MeOH:H<sub>2</sub>O. The MeOH:H<sub>2</sub>O solution was previously adjusted to pH 4 with NaOH. Alternatively a solution of the phosphonic acid in an organic, aprotic solvent (toluene or THF) (2 mmol in 100 mL) was used. After stirring for 15 h at room temperature, the modified powder was rinsed 8 times with 15 mL of solvent (MeOH:H<sub>2</sub>O, toluene or THF) and then dried at 120 °C for 15 h under vacuum (1 mbar).

**Grafting of Trimethylsilyl Groups.** The SiO<sub>2</sub>-TiO<sub>2</sub> mixed-oxide support was modified by trimethylsilyl groups using *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA; Avocado), a mild silylating agent.<sup>31</sup> BSTFA (1 g) was added under stirring to a suspension of the mixed-oxide powder (500 mg) in 10 mL of dry toluene. After stirring for 2 h at room temperature, the powder was rinsed 5 times with 40 mL of toluene and then dried at 120 °C for 15 h under vacuum (1 mbar).

**Catalytic Testing.** To gain information on the selectivity of the surface modification, we measured the catalytic activity of the (modified) mixed oxide in the epoxidation of cyclohexene by cumyl hydroperoxide (CHP). A 50 mg amount of catalyst

(24) Sugimura, H.; Nakagiri, N.; Ichinose, N. *Appl. Phys. Lett.* **1995**, *66*, 3686.

(25) Inoue, A.; Ishida, T.; Choi, N.; Mizutani, W.; Tokumoto, H. *Appl. Phys. Lett.* **1998**, *73*, 1976.

(26) Michel, R.; Lussi, J. W.; Csucs, G.; Reviakine, I.; Danuser, G.; Ketterer, B.; Hubbell, J. A.; Textor, M.; Spencer, N. D. *Langmuir* **2002**, *18*, 3281.

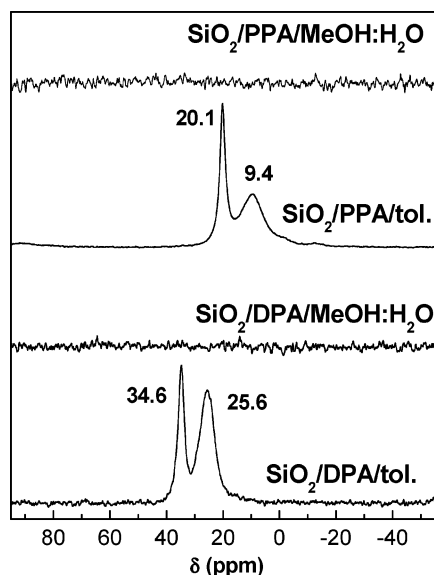
(27) Michel, R.; Reviakine, I.; Sutherland, D.; Fokas, C.; Csucs, G.; Danuser, G.; Spencer, N. D.; Textor, M. *Langmuir* **2002**, *18*, 8580.

(28) (a) Lukes, I.; Borbaruah, M.; Quin, L. D. *J. Am. Chem. Soc.* **1994**, *116*, 1737. (b) Blümel, J. *Inorg. Chem.* **1994**, *33*, 5050.

(29) Hanson, E. L.; Schwartz, J.; Nickel, B.; Koch, N.; Danisman, M. F. *J. Am. Chem. Soc.* **2003**, *125*, 16074.

(30) (a) Andrianainarivelo, M.; Corriu, R.; Leclercq, D.; Mutin, P. H.; Vioux, A. *J. Mater. Chem.* **1996**, *6*, 1665. (b) Lafond, V.; Mutin, P. H.; Vioux, A. *Chem. Mater.* **2004**, in press

(31) D'Amore, M. B.; Schwarz, S. *Chem. Commun.* **1999**, 121.



**Figure 1.**  $^{31}\text{P}$  MAS NMR spectra of silica ( $550\text{ m}^2\text{ g}^{-1}$ ) reacted with DPA or PPA in toluene or in  $\text{MeOH:H}_2\text{O}$  (1000 scans).

was added to a 50 mL two-necked round-bottom flask fitted with a condenser that had previously been evacuated and filled with argon three times. Toluene (dried and degassed; 5 mL), cyclohexene (99%, Avocado, 2.074 g, 25 mmol), and the internal standard nonane (0.2 g) were added by syringe through a septum. After equilibration at the reaction temperature ( $65\text{ }^\circ\text{C}$ ), CHP (80%, Lancaster; 0.951 g, 5 mmol) was added by syringe to the stirred solution (all reagents were previously stored on molecular sieves). The reaction mixture was kept at  $65\text{ }^\circ\text{C}$  for 155 min and then cooled, and the products were analyzed by gas chromatography (GC). The epoxide yield was related to the limiting reactant, CHP.

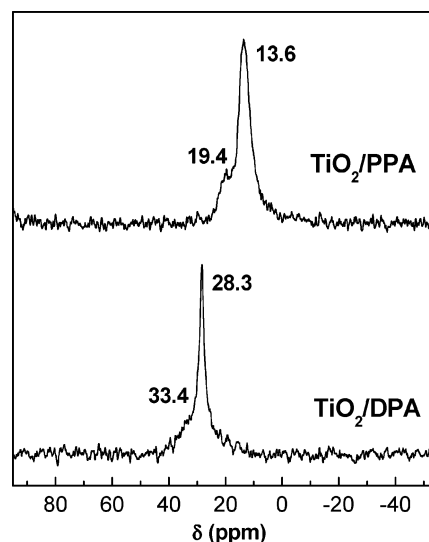
**Chemical Analysis.** Chemical analysis was performed at the "Laboratoire Central d'Analyse du CNRS", Vernaison, France. The grafting densities were calculated from the carbon content of the modified oxide powders using the specific surface area of the unmodified oxide and taking into account the weight of grafted species.

**Scanning Auger Electron Spectroscopy.** SAES was performed using a VG 310F scanning Auger electron microscope with a 10 kV primary accelerating voltage, a 3 nA beam current, and a beam diameter of 50 nm. SEM images of the analyzed areas were also collected.

**NMR Spectroscopy.**  $^{31}\text{P}$  solid-state NMR spectra were obtained with a Bruker Avance DPX300 spectrometer, using magic angle spinning (MAS; spinning rate, 10 kHz) and high-power proton decoupling; the flip angle was  $45^\circ$  and the recycling delay 10 s; the chemical shifts were referenced to  $\text{H}_3\text{PO}_4$  (85% in water).  $^{29}\text{Si}$  MAS NMR spectra were obtained on a Bruker ASX400 (spinning rate, 5 kHz) using a cross-polarization sequence with a 7 ms contact time and a 5 s recycling delay; the chemical shifts were referenced to TMS.

## Results and Discussion

**Reaction of  $\text{SiO}_2$  and  $\text{TiO}_2$  with Phosphonic Acids.** The surface modification of silica by phosphonic acids has already been reported.<sup>28</sup> Silica was reacted with phenylphosphonic acid (PPA) and dodecylphosphonic acid (DPA) in toluene, then rinsed with toluene, and dried under vacuum at  $120\text{ }^\circ\text{C}$ . In both cases the  $^{31}\text{P}$  MAS NMR spectra of the resulting powders (Figure 1) displayed two resonances. The broad, high-field resonances at 25.6 (DPA) and 9.4 ppm (PPA) may be ascribed to chemisorbed phosphonate surface species bound to silica through the formation of  $\text{Si-O-P}$  bonds.<sup>28</sup> The sharp, low-field resonances at 34.6 (DPA)



**Figure 2.**  $^{31}\text{P}$  MAS NMR spectra of  $\text{TiO}_2$  ( $50\text{ m}^2\text{ g}^{-1}$ ) reacted with DPA (bottom) and PPA (top) in  $\text{MeOH:H}_2\text{O}$ .

and 20.1 ppm (PPA) are ascribed to excess phosphonic acid not removed by the toluene rinses. According to the carbon content of the powders, the density of adsorbed phosphonate molecules was about 1 molecule/ $\text{nm}^2$ .

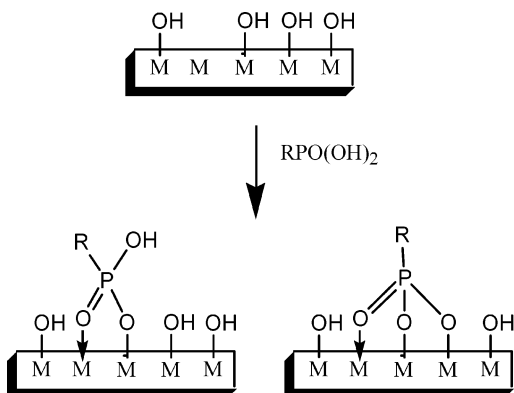
However, when silica was reacted with DPA or PPA in  $\text{MeOH:H}_2\text{O}$ , phosphonate species could no more be detected using  $^{31}\text{P}$  MAS NMR, and the grafting density was lower than 0.1 molecule/ $\text{nm}^2$  according to chemical analysis. This behavior may likely be ascribed to the sensitivity of the  $\text{Si-O-P}$  bonds to hydrolysis, illustrated by the facile hydrolysis of phosphonic acid trimethylsilyl esters,  $\text{RPO}(\text{OSiMe}_3)_2$ .<sup>32</sup> When surface modification is performed in an organic aprotic solvent such as toluene, phosphonate species may bind to the surface through hydrogen bonds and  $\text{Si-O-P}$  bonds. In addition, formation of  $\text{Si-O-P}$  bonds is favored by water removal during the drying step. On the contrary, when surface modification is performed in the presence of water, formation of  $\text{Si-O-P}$  bonds and hydrogen bonds is hindered, preventing the binding of phosphonate species to the surface.  $\text{Ti-O-P}$  bonds are much more stable toward hydrolysis than  $\text{Si-O-P}$  bonds, allowing the surface modification of  $\text{TiO}_2$  by phosphonic acids under aqueous conditions.<sup>7,14,33</sup> As a matter of fact,  $^{31}\text{P}$  MAS NMR spectra of  $\text{TiO}_2$  reacted with DPA or PPA in  $\text{MeOH:H}_2\text{O}$  (Figure 2) showed the presence of grafted phosphonate species. The binding of phosphonic acids to  $\text{TiO}_2$  surfaces results from both condensation and coordination (Scheme 2).<sup>7,14</sup> The exact bonding mode (monodentate, bidentate, or tridentate) is still much debated. In the case of PPA, a recent  $^{17}\text{O}$  MAS NMR study indicated the presence of a majority of  $\text{Ti-O-P}$  sites,<sup>12</sup> with very few residual  $\text{P=O}$  and  $\text{P-OH}$  oxygens. On the other hand, for long-chain alkylphosphonic acids  $^1\text{H-}^{31}\text{P}$  HETCOR NMR spectra indicated the presence of dipolar coupled  $\text{P-OH}$  protons.<sup>8</sup> Accordingly, the resonance at 13.6 ppm (PPA) is ascribed to tridentate  $\text{PhP}(\text{OTi})_3$  surface species, and the resonance at 28.3 ppm (DPA) is tentatively ascribed to bidentate  $\text{C}_{12}\text{H}_{25}\text{P}(\text{OTi})_2(\text{OH})$  species. The other low-field resonances could

(32) McKenna, C. E.; Schmidhauser, J. *Chem. Commun.* **1979**, 739.

(33) Randon, J.; Blanc, P.; Paterson, R. *J. Membr. Sci.* **1995**, 98, 119.



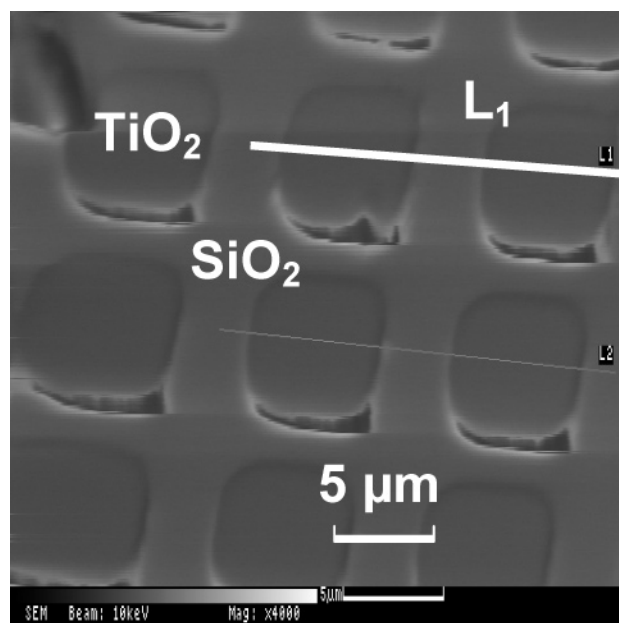
**Scheme 2. Schematic Representation of the Formation of Bidentate (left) and Tridentate Phosphonate Species by Condensation and Coordination of a Phosphonic Acids to a Metal Oxide Surface**



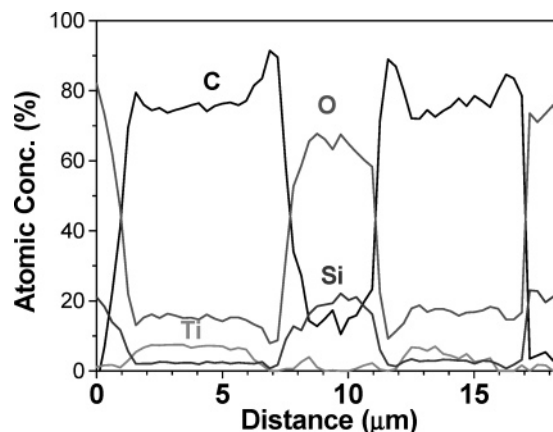
arise from phosphonate species with different bonding modes or in a distorted geometry.<sup>12</sup> From the carbon content of the modified powders, the grafting density, 2.5 DPA molecules/nm<sup>2</sup> or 3 PPA molecules/nm<sup>2</sup>, was at least 25 times higher than on SiO<sub>2</sub> reacted in MeOH/H<sub>2</sub>O, indicating that under aqueous conditions phosphonic acids react selectively with TiO<sub>2</sub> and not with SiO<sub>2</sub>.

**Surface Modification of a Model Micropatterned SiO<sub>2</sub>-TiO<sub>2</sub> Support.** To demonstrate the selective surface modification of SiO<sub>2</sub>-TiO<sub>2</sub> surfaces with DPA at the micrometer level, a micropatterned support was fabricated by electron beam microlithography. The pattern consisted in an array of TiO<sub>2</sub> rounded spots ca. 6.5 × 7.5 μm<sup>2</sup> (180 nm high), separated by ca. 3.6 μm on a SiO<sub>2</sub> surface. This micropatterned support was reacted with DPA in water, and the modified surface was characterized using SAES. The SEM image in Figure 3 shows the analyzed line L1 across the patterned surface. The concentration profiles corresponding to this SAES line scan (Figure 4) clearly showed that DPA reacts selectively with the TiO<sub>2</sub> domains.

**Surface Modification of a SiO<sub>2</sub>-TiO<sub>2</sub> Mixed-Oxide Support.** The practical resolution of our electron beam lithography apparatus was about 100 nm. To go further, that is to investigate selective surface modification at the true nanometer level, we used a mesoporous SiO<sub>2</sub>-TiO<sub>2</sub> mixed-oxide support prepared by nonhydrolytic sol-gel processing. This support,<sup>30</sup> obtained by calcination at 500 °C of a xerogel with a Ti content of 10 mol %, was amorphous to X-ray diffraction, indicating the absence of TiO<sub>2</sub> domains larger than a few nanometers. No anatase could be detected using FT-Raman spectroscopy, indicating that the anatase content was lower than 0.05 wt %. The molecular scale dispersion of the Ti was confirmed by the FTIR spectrum of this sample, which showed a prominent band at 950 cm<sup>-1</sup> ascribed to the presence of Si-O-Ti bonding.<sup>30,34</sup> For such a high titanium content, the Ti atoms in such sol-gel derived materials are not necessarily in a tetrahedral coordination. Rather, there is a mixture of 4-, 5-, and 6-fold-coordinated Ti atoms in monomeric and oligomeric titanium species, bonded to



**Figure 3.** SEM image of the modified micropatterned surface after SAES analysis. The L1 line corresponds to the concentration profiles shown in Figure 3.



**Figure 4.** Concentration profiles for carbon, oxygen, silicon, and titanium obtained by a SAES line scan across the patterned surface (L1 line in Figure 3)

the silica network by Si-O-Ti bonds.<sup>34</sup> SiO<sub>2</sub>-TiO<sub>2</sub> mixed oxides are used as heterogeneous catalysts for the epoxidation of alkenes by alkylhydroperoxides,<sup>35-37</sup> and the catalytically active species are Lewis acid Ti species, probably tetrahedral.<sup>34</sup>

Modification of a SiO<sub>2</sub>-TiO<sub>2</sub> mixed oxide by trimethylsilyl groups does not modify the coordination number of Ti atoms and therefore does not decrease their Lewis acid character (Scheme 2). Actually, it is well-known that grafting trimethylsilyl groups increases the catalytic activity of SiO<sub>2</sub>-TiO<sub>2</sub> mixed oxides.<sup>34</sup> This behavior is ascribed to the hydrophobation of the surface which favors the approach of the alkene reactant and the elimination of the more hydrophilic epoxide product. On the other hand, modification by a phosphonic acid

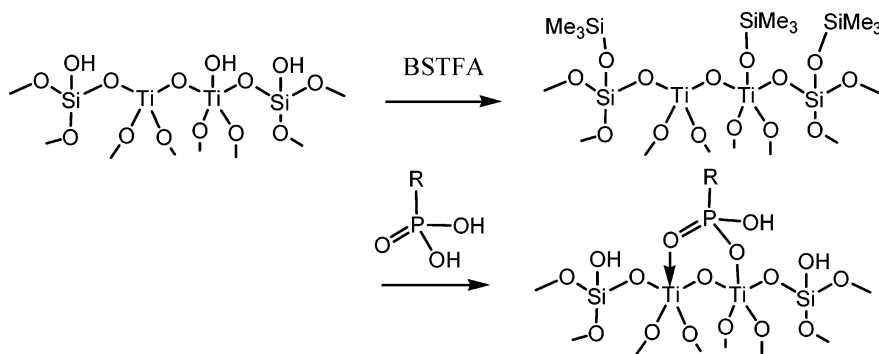
(34) Beck, C.; Mallat, T.; Bürgi, T.; Baiker, A. *J. Catal.* **2001**, *204*, 428.

(35) Hutter, R.; Mallat, T.; Dutoit, D.; Baiker, A. *Catal. Lett.* **1996**, *3*, 421.

(36) Klein, S.; Thorimbert, S.; Maier, W. F. *J. Catal.* **1996**, *163*, 476.

(37) Holland, M. A.; Pickup, D. M.; Mountjoy, G.; Tsang, E. S. C.; Wallidge, G. W.; Newport, R. J.; Smith, M. E. *J. Mater. Chem.* **2000**, *10*, 2495.

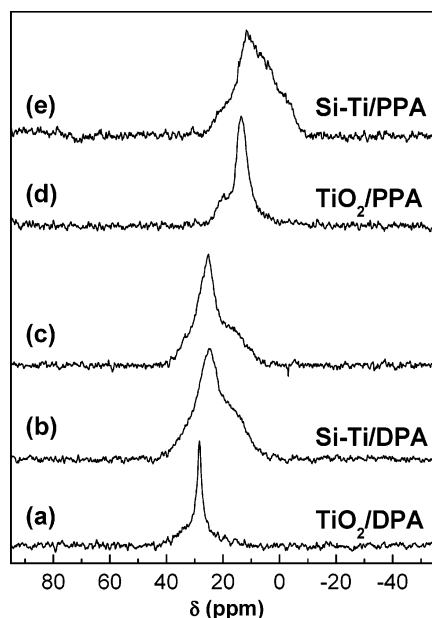
**Scheme 3. Schematic Representation of the Surface Modification of a SiO<sub>2</sub>-TiO<sub>2</sub> Mixed-Oxide Support by BSTFA (top) and by a Phosphonic Acid (bottom), Showing the Increase in Coordination Number of a Ti Site Resulting from the Coordination of the Phosphoryl Group**



**Table 1. Surface Modification of the SiO<sub>2</sub>-TiO<sub>2</sub> Mixed-Oxide Support by Trimethylsilyl and/or Phosphonate Groups: Grafting Density and Influence on the Catalytic Activity**

sample	P/nm <sup>2</sup>	Me <sub>3</sub> Si/nm <sup>2</sup>	epoxide yield <sup>d</sup> /%
Si-Ti			33
Si-Ti/TMS		1.3 <sup>a</sup>	84
Si-Ti/PPA	0.8 <sup>a</sup>		12
Si-Ti/DPA	0.6 <sup>a</sup>		10
Si-Ti/DPA/TMS	0.6 <sup>b</sup>	0.7 <sup>c</sup>	24

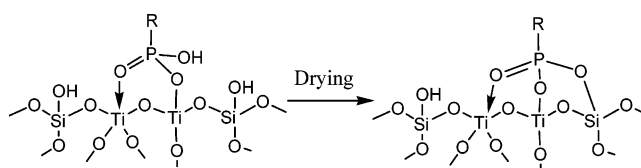
<sup>a</sup> Calculated from the carbon content using the specific surface area of the unmodified oxide and corrected for the weight of grafted species. <sup>b</sup> Assumed identical to the phosphonate grafting density before silylation. <sup>c</sup> Calculated from the carbon content assuming a grafting density of 0.6 P/nm<sup>2</sup>. <sup>d</sup> Yield of cyclohexene oxide after 155 min.



**Figure 5.** <sup>31</sup>P MAS NMR spectra of TiO<sub>2</sub> and SiO<sub>2</sub>-TiO<sub>2</sub> powders modified by phosphonic acids in MeOH:H<sub>2</sub>O: (a) TiO<sub>2</sub>/DPA; (b) Si-Ti/DPA; (c) Si-Ti/DPA re-dispersed in MeOH:H<sub>2</sub>O and dried under vacuum for 5 min at room temperature; (d) TiO<sub>2</sub>/PPA; (e) Si-Ti/PPA.

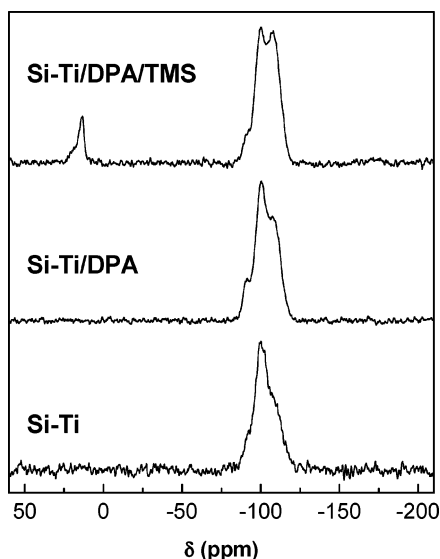
should decrease the catalytic activity of a SiO<sub>2</sub>-TiO<sub>2</sub> mixed oxide, owing to the coordination of phosphoryl groups to Ti Lewis acid sites (Scheme 3). Accordingly, comparison of the catalytic activity before and after surface modification by DPA or PPA should give information on the selectivity of the surface modification.

**Scheme 4. Formation of RP(OTi)<sub>2</sub>(OSi) Phosphonate Species on a SiO<sub>2</sub>-TiO<sub>2</sub> Mixed-Oxide Surface**



As a test reaction we chose the epoxidation of cyclohexene by cumyl hydroperoxide. We compared the catalytic activity of our SiO<sub>2</sub>-TiO<sub>2</sub> mixed oxide unmodified (Si-Ti), grafted by trimethylsilyl groups using the mild silylating agent BSTFA (Si-Ti/TMS), grafted by dodecylphosphonate and phenylphosphonic groups using DPA and PPA in MeOH:H<sub>2</sub>O (Si-Ti/DPA and Si-Ti/PPA), and modified successively by DPA and then BSTFA (Si-Ti/DPA/TMS) (Table 1). The unmodified support showed a moderate activity. The grafting of hydrophobic trimethylsilyl groups (1.3 Me<sub>3</sub>Si/nm<sup>2</sup>) increased the activity by a factor of 2.5. On the other hand, the grafting of hydrophobic dodecylphosphonate groups (0.5 DPA/nm<sup>2</sup>) or phenylphosphonate groups (0.8 PPA/nm<sup>2</sup>) strongly decreased the activity, by a factor of 3. In addition, the average grafting density was 4 times lower than the grafting density on TiO<sub>2</sub> modified under the same conditions, which corresponds to a surface coverage of about 25%. The low activity and low surface coverage of Si-Ti/PPA and Si-Ti/DPA samples point to a selective modification of the Ti species by the phosphonic acids. Further modification of Si-Ti/DPA by trimethylsilyl groups (Si-Ti/DPA/TMS sample) increased the activity, which nevertheless was more than 3 times lower than the activity of the Si-Ti/TMS sample.

The <sup>31</sup>P MAS NMR spectra of Si-Ti/PPA and Si-Ti/DPA samples (Figure 5) are much broader than those of TiO<sub>2</sub>/PPA and TiO<sub>2</sub>/DPA samples, respectively. This broadening is largely due to the presence of new high-field resonances, which points to the presence of different phosphonate surface species. Surface species bonded to Si atoms only can be excluded, as the surface modification was performed in MeOH:H<sub>2</sub>O. Accordingly, we propose to ascribe these new high-field resonances to phosphonate species bonded to both Ti and Si atoms, in RP(OTi)<sub>x</sub>(OSi)<sub>y</sub> sites for instance. The formation of Si-O-P bonds would result from condensation between Si-OH and P-OH groups, most probably during the drying treatment at 120 °C (Scheme 4). Such Si-O-P



**Figure 6.** <sup>29</sup>Si CP-MAS NMR spectra of the SiO<sub>2</sub>-TiO<sub>2</sub> mixed oxide (bottom), reacted with DPA in MeOH:H<sub>2</sub>O (middle), and reacted successively with DPA in MeOH:H<sub>2</sub>O and BSTFA in toluene (top).

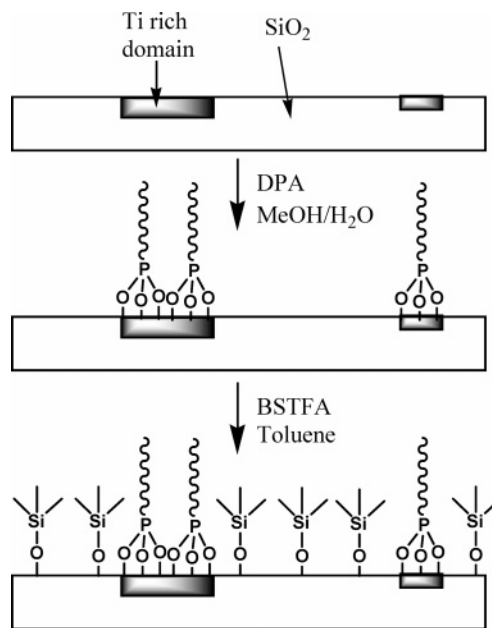
bonds are expected to be easily hydrolyzed. As a matter of fact, the spectrum of the Si-Ti/DPA sample re-dispersed in MeOH:H<sub>2</sub>O and dried briefly (5 min) at room temperature (Figure 5c) showed a significant decrease of the high-field resonance, consistent with the hydrolysis of some Si-O-P bonds.

The <sup>29</sup>Si CP-MAS NMR spectrum of the Si-Ti/DPA sample (Figure 6) shows that the binding of phosphoryl groups to surface silicon atoms can be ruled out, as no high-field resonance arising from penta- or hexa-coordinated Si atoms was detected between -120 and -220 ppm (a chemical shift of -212 ppm was previously reported for hexa-coordinated Si atoms in silicon phosphonates<sup>38</sup>). The presence of phosphonate surface species bonded to both Ti and Si atoms probably accounts for the relatively high coverage of the mixed-oxide surface (about 25%) when compared to the titanium content (10 mol %).

Further reaction of the mixed-oxide with BSTFA leads to the grafting of trimethylsilyl groups, as shown by the resonances around 14 ppm characteristic of Me<sub>3</sub>Si-OSi (M) sites in the <sup>29</sup>Si CP-MAS NMR spectrum of Si-Ti/DPA/TMS (Figure 6). Note that the <sup>31</sup>P MAS NMR spectra of Si-Ti/DPA/TMS and Si-Ti/DPA samples were identical.

Catalytic tests, chemical analysis, and NMR spectra are consistent with a selective modification of the Ti-rich domains by PPA or DPA. The significant formation of phosphonate species bonded to Ti and Si atoms is simply the consequence of the very small size (a few Ti atoms) of the surface Ti species. Modification of the Si-Ti/DPA sample by trimethylsilyl groups illustrates the possibility of sequential bifunctionalization (Scheme 5).

### Scheme 5. Schematic Representation of Selective Sequential Bifunctionalization of the SiO<sub>2</sub>-TiO<sub>2</sub> Mixed Oxide by DPA and BSTFA



Orthogonal (simultaneous) bifunctionalization appears to be much more difficult to achieve, as most silanes are readily hydrolyzable and cannot be used in aqueous media.

### Conclusions

The reaction of phosphonic acids with SiO<sub>2</sub>-TiO<sub>2</sub> surfaces in an aqueous medium leads to the selective grafting of TiO<sub>2</sub> domains, allowing the patterning of organic groups at the micrometer and nanometer level. The selectivity may be ascribed to the high affinity of phosphonic acids for metal oxide surfaces and to the sensitivity toward hydrolysis of Si-O-P bonds. Accordingly, similar selectivity is expected for other silica-metal oxide systems, such as silica-alumina or silica-ITO. Selective grafting of a micropatterned support prepared by electron-beam microlithography was evidenced directly using SAES. At the molecular level, the surface modification remained selective as shown by the loss of catalytic activity of a SiO<sub>2</sub>-TiO<sub>2</sub> heterogeneous catalyst. The extremely small size (a few Ti atoms) of the "TiO<sub>2</sub>" domains apparently led to the formation of original surface phosphonate species bonded simultaneously to Ti and Si atoms.

Successive treatments with a phosphonic acid (in an aqueous medium) and with a silylating agent of a patterned silica-metal oxide surface offers a simple, promising way to bind covalently different organic groups to oxide surfaces with a good control on their spatial repartition. Such a selective bifunctionalization has potential applications in the fields of (bio)sensors, microfluidics, and supported catalysis.

(38) Corriu, R. J. P.; Leclercq, D.; Mutin, P. H.; Sarlin, L.; Vioux, A. *J. Mater. Chem.* **1998**, *8*, 1827.