

Triisopropoxysilyl-functionalized oxide nanoparticles using a di-*tert*-butyl phosphonate ester as the surface grafting agent

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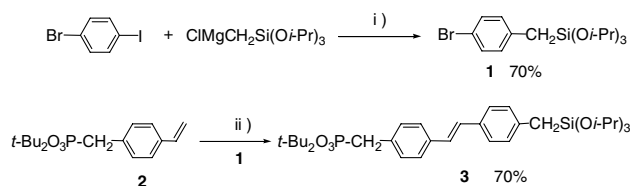
Abstract—The synthesis of a bifunctional coupling reagent possessing a triisopropoxysilyl group and a *tert*-butyl phosphonate ester is described. The *tert*-butyl phosphonate ester was used as an efficient and selective grafting reagent for the anchoring of the triisopropoxysilyl group at the surface of TiO₂ and SnO₂ nanoparticles under mild conditions. The triisopropoxysilyl group remained intact and did not react at the surface of the oxide nanoparticles. The reactivity of the triisopropoxysilyl group was then further investigated.

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The synthesis and use of nanoparticles has shown growing interest in the last decade,¹ thus methods for their surface modification are needed. In this field, the phosphonic acid group has proved very efficient for the covalent attachment of organic groups at the surface of metal oxide nanoparticles,² and the M–O–P bond has been shown to be very stable over a wide range of pH.^{2a} Application of the phosphonic acid methodology has been described in fields such as self-assembled monolayers,^{2b} modified electrodes,^{2c} electron-transfer devices,^{2d} catalysis^{2e} and biomaterials.^{2f} In this context, we were interested in the selective functionalization of metal oxide nanoparticles with a trialkoxysilane-terminated carbon chain using the phosphonic acid function as the grafting agent. Indeed trialkoxysilane-functionalized metal oxide nanoparticles have not been described to our knowledge and could be used for further reactions to prepare mineral-charged polymers or core-shell nanoparticles.¹ However, two major problems have to be solved: the acidity of the phosphonic acid is not compatible with the trialkoxysilane function stability, and the trialkoxysilane group reacts at the surface of metal oxides and is thus used for their modification.³ We present here the successful functionalization of TiO₂ and SnO₂ nanoparticles with pendant triisopropoxysilyl groups, by using the di-*tert*-butyl phosphonate ester protective group of the phosphonic acid as the grafting

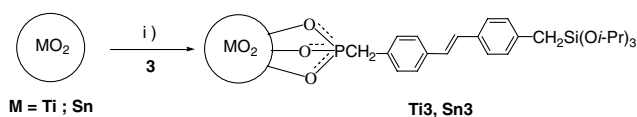
reagent. The reactivity of the trialkoxysilane-functionalized particles was also investigated.

We have recently noticed that a *tert*-butyl phosphonate ester in a silica-based hybrid material rapidly reacts with SiOH groups with formation of P–O–Si bonds and isobutene.⁴ We anticipated that this property could be used for the functionalization of the surface of metal oxides. We thus prepared the bifunctional coupling agent **3** possessing a stilbene carbon backbone, a triisopropoxysilyl group and a di-*tert*-butyl phosphonate group (Scheme 1). Compound **1** was synthesized by cross-coupling *p*-bromiodobenzene with triisopropoxysilylmethyl-magnesium chloride⁵ using NiCl₂(PPh₃)₂ as the catalyst, in 70% yield. Di-*tert*-butyl-*para*-vinylbenzyl phosphonate **2** was synthesized as already described.⁶ Compound **3** was obtained via a Heck cross-coupling reaction of **1** with **2** in 70% yield. Compound **3** (250 mg, 0.41 mmol) was then refluxed for 3 days in a



Scheme 1. Synthesis of difunctional coupling agent **3**. Reagents and conditions: (i) NiCl₂(PPh₃)₂, THF, 50 °C; (ii) 2% Pd(OAc)₂, 8% TOP, Et₃N, CH₃CN, 100 °C sealed tube.

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Scheme 2. Grafting of difunctional coupling agent **3** to TiO₂ or SnO₂. Reagents and conditions: (i) *i*-PrOH, reflux, 3 days.

suspension of TiO₂ (P25 Degussa, average particle size 21 nm, specific surface area 50 m² g⁻¹) or SnO₂ (Merck, average particle size 15–20 nm, specific surface area 15 m² g⁻¹) (750 mg) in *i*-PrOH. A large excess of phosphonate was used to ensure maximum coverage of the particle surfaces (Scheme 2).

The suspension was then filtered through Millipore, thoroughly washing with EtOH, Me₂CO and Et₂O.

Solid-state HPDEC (high power decoupling) MAS (magic angle spinning) ³¹P NMR (Fig. 1) of phosphonate **3** showed a sharp, shielded signal at 20.6 ppm indicating a well-crystallized homogeneous compound. After grafting to TiO₂ and SnO₂, the signals were slightly shifted downfield to 22.7 and 21.4 ppm, respectively, the chemical shift was in agreement with previous studies on the grafting of benzylic phosphonic acids.^{2c} An important enlargement was observed and the peak widths at half maximum were close to 10 ppm, which indicated that the phosphorus was covalently bonded to the metal oxide surface through covalent P–O–M links, with different environments because of different coordination modes and different distribution of the bonding sites at the surface. Assuming that each molecule occupies 24 Å² based on the size of the phosphonic group,^{2b} a loading of about 0.3 mmol g⁻¹ is expected for TiO₂ and 0.1 mmol g⁻¹ for SnO₂, respectively.

Microanalysis of phosphorus was 0.7% for **Ti3** and 0.35% for **Sn3**, which corresponded to a loading of 0.230 mmol g⁻¹ for TiO₂, and 0.108 mmol g⁻¹ for SnO₂ and a layer coverage of about 80% for **Ti3** and 108% for

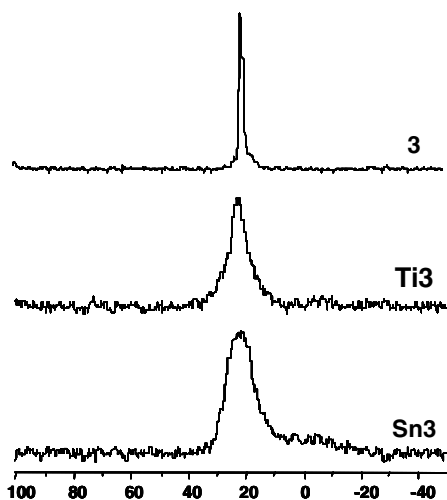


Figure 1. HPDEC MAS ³¹P NMR of **3**, grafted TiO₂ and grafted SnO₂.

Sn3, respectively. These values are close to a monolayer coverage. CP (cross-polarization) MAS ¹³C solid-state NMR showed principal signals at 133–140 ppm (stilbene), 65.7 (O–CH) and 25.4 (CH₃ isopropyl), the carbon backbone and isopropoxy groups were not affected. The *tert*-butyl groups were no longer detected, which confirmed the reactivity of the *tert*-butyl phosphonate (Fig. 2).

It was difficult to detect ²⁹Si by NMR (content of Si <1%), however CP MAS ²⁹Si solid-state NMR showed the characteristic resonance of the benzylic triisopropoxysilyl group at –55 ppm, which proved that this group did not react at the metal oxide surface. The narrow signal indicated that the trialkoxysilane groups were mobile (Fig. 3).

These data prove that the *tert*-butyl phosphonate ester of **3** reacted at the surface of metal oxide particles by forming P–O–M bonds, with formation of isobutene. Furthermore, this reaction is kinetically favored versus the anchoring of the triisopropoxy silyl group at the surface, because of the strong ability of phosphonates to coordinate to metal oxides. The nanoparticle

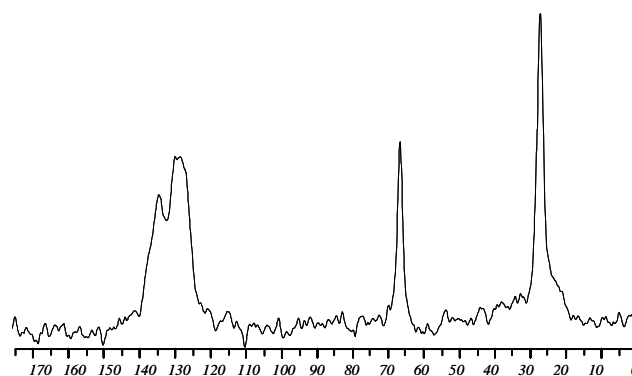


Figure 2. CP MAS ¹³C NMR of grafted TiO₂.

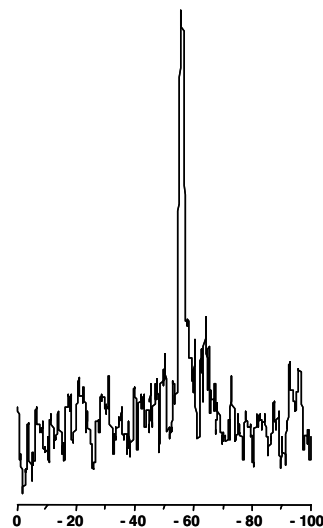


Figure 3. CP MAS ²⁹Si NMR of grafted SnO₂.

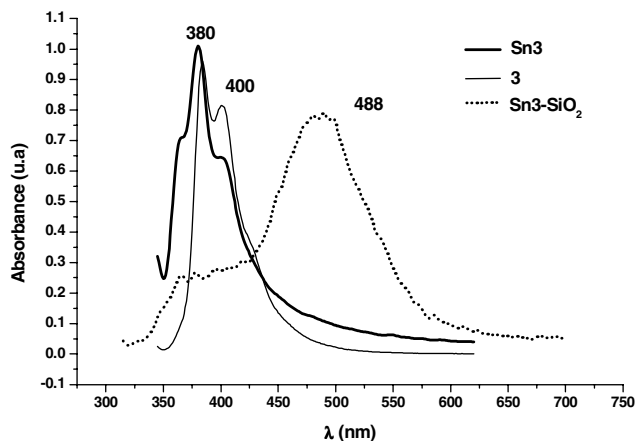


Figure 4. Fluorescence spectra of 3, Sn3, Sn3-SiO₂.

morphology was not damaged as analyzed by electron microscopy experiments.

We then carried out a preliminary experiment to investigate the accessibility and reactivity of the supported isopropoxysilyl groups. The materials **Ti3** and **Sn3** (200 mg) were reacted for 5 days with colloidal silica ludox (2.2 and 1.3 g, respectively) in MeOH, using APTS as the catalyst. The reaction was then filtered, the solids were washed with EtOH, Me₂CO and Et₂O. No modification of the ³¹P NMR signal was observed, which showed that the organic part was still grafted at the surface of the oxides, and demonstrated the stability of the P–O–M bond. ¹³C NMR showed the presence of the aromatic carbons, and the isopropyl groups were no longer detected. ²⁹Si NMR showed the Q3 and Q4 signal of silica ludox but unfortunately, we were not able to detect the T species characteristic of the condensation of the trialkoxysilyl group, because of the very low content of this species inside the solid. We then turned to fluorescence spectroscopy. **Ti3** presented no fluorescence because it was quenched by the photooxidation properties of TiO₂. Fluorescence spectra of 3, Sn3, Sn3-SiO₂ are presented in Figure 4.

The fluorescence spectra of 3 and Sn3 presented the characteristic photoluminescence of the stilbene unit with maxima at 380 and 400 nm, which showed that the organic part was not damaged after grafting. The dispersion of the organic part at the surface of SnO₂ was homogeneous, as no aggregation occurred. After reaction with ludox, a major change was observed. The photoluminescence spectrum was shifted to the red. This

red shift could be attributed to the aggregation⁷ of the stilbene units in the ground state with possible formation of excimers. Thus the organization of the stilbene units could be different after the reaction with ludox. This result suggest that condensation of the trialkoxysilyl groups has modified the conformation of the stilbene backbones by bringing them closer, and favored the orientation required for the formation of aggregates or excimers.

In conclusion, we have demonstrated that a *tert*-butyl phosphonate ester is the reagent of choice to covalently and selectively anchor a functionalized molecule at the surface of metal oxide nanoparticles. This reagent allowed the formation of a monolayer of triisopropoxysilyl groups at the particles' surface. The reactivity of the triisopropoxysilyl group was further studied with ludox under standard conditions, showing the accessibility of this group at the surface. Work is in progress to exploit the possibilities offered by this methodology.

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