

Studies of Phosphonic Acids Containing a π -Conjugated Ferrocenyl Unit Grafted on Metal Oxides – Mössbauer and Electrochemical Behaviour

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The modification of metal oxide surfaces by π -conjugated ferrocene units has been performed. A phosphonic acid functionality was used to covalently anchor the π -conjugated ferrocene moiety to SnO_2 and TiO_2 particles. The covalent attachment and the monolayer coverage at the surface of the particles were confirmed by solid-state MAS ^{31}P NMR spectroscopy, microanalysis and electronic microscopy (EDX).

The properties of the ferrocene-modified oxides were analysed by cyclic voltammetry, which confirmed the electroactivity of the material, and ^{57}Fe Mössbauer spectrometry, which provided information about the oxidation state and environment of the iron atoms.

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Introduction

The syntheses of materials with ferrocene units have attracted considerable interest in the last decades.^[1] They have found increasing uses in many fields: molecular materials for non-linear optics,^[1b] polymers for electrochemical applications,^[1c] asymmetric catalysis,^[1d] amperometric biosensors for glucose oxidase,^[1e] and surfactant devices.^[1f] The covalent coverage of surface oxides by organic molecules functionalised with ferrocene is particularly important for fundamental mechanistic studies,^[2a] as well as for applications in the field of modified electrodes.^[2b–2e] Great attention has been devoted to ferrocenes possessing a grafting function, such as a mercaptan^[2c–2e] or a carboxylic acid,^[2b] in order to achieve the preparation of new electrodes. Its application as electrochemical transducers for biosensors seems promising.^[2f–2g] As the grafting of sophisticated molecules using a phosphonic acid functionality has been used for many purposes^[3,2b] and is known to be very stable,^[3c] we focused our attention to this functionality to covalently anchor ferrocene units to metal oxide particles. We have already described the preparation of phosphonic acids containing a π -conjugated ferrocenyl unit with a defined configuration of the conjugated backbone.^[4] Analyses of their

electrochemical properties in DMSO showed standard reversible redox waves assigned to the $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ couple.^[4] Here, we present our studies on the grafting of these molecules on the surface of TiO_2 and SnO_2 particles. Electrochemistry is used as a powerful tool for detecting the electroactive species at the surface. ^{57}Fe Mössbauer spectroscopy informs us about the oxidation state of the iron atoms, the symmetry of its electronic environment and the nature of the chemical bonds involved. Additional information on the structural properties is obtained from the Mössbauer effect probability and its temperature dependence.

Results and Discussion

Two types of phosphonic acids with a π -conjugated ferrocenyl unit, **1** and **2**, have been synthesised (Scheme 1), and their electronic properties characterised in solution. We have shown that a better transmission of the electronic effects is obtained with the more conjugated phenylphosphonic acid **1** than the benzylphosphonic acid **2**.^[4] The more conjugated phenylphosphonic acid **1** is a better electron-withdrawing group than the benzylphosphonic acid **2**. We then performed the grafting reaction of acids **1** and **2** (Scheme 1), in order to investigate the properties of the new hybrid organic-inorganic materials thus prepared, and particularly the modification of the electronic properties in the solid state. Three types of particle oxides were used. TiO_2 P25 Degussa (particle size of 21 nm) (**Ti**), SnO_2 synthesised by the sol-gel process^[5] and pyrolysis at 700 °C (particle size 5–10 nm) (**Ss**), and SnO_2 Merck (particle size 20 nm) (**Sc**). The surface of the TiO_2 and SnO_2 particles were modi-

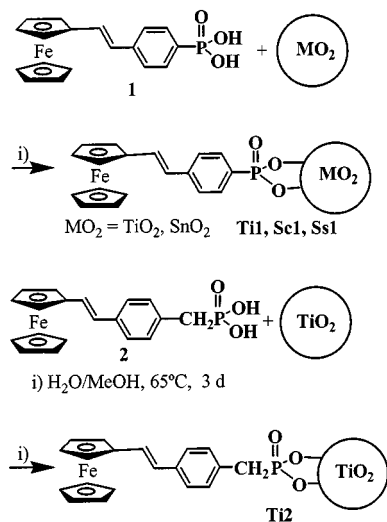
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fied by refluxing with the phosphonic acid **1** or **2** for 3 d in MeOH/H₂O (4:1) at 65 °C. This mixture of solvents was chosen because of the low solubility of the acids **1** and **2**. A large excess of acid was used to ensure the total coverage of the particle surfaces. The solids were first analysed using energy-dispersive X-ray techniques, microanalysis, and solid-state ³¹P NMR spectroscopy. Elemental analyses (Table 1) showed the presence of P and Fe in all the samples, indicating the presence of the molecules **1** and **2** at the surface of the particles. The P/Fe ratios were between 0.7 and 0.85, which confirmed that cleavage of the P–C bond did not occur. The microanalyses were corroborated by energy-dispersive X-ray analyses. Variation of the P/MO₂ ratio was not observed from one experiment to another on the same sample, which showed that the solids were homogeneous on a micrometric scale. From the low P/MO₂ ratio we have concluded that a monolayer coverage resulted at the surface of the oxide.^[3c] Note that the proportion of the organic part was higher for **Ss1** than **Sc1** because of the higher specific surface area for **Ss1** (particle size 5–10 nm for **Ss1** versus 20 nm for **Sc1**). Solid-state ³¹P NMR spectra of compounds **1** and **2** and materials **Ti1** and **Ti2** are presented in Figure 1. Phosphonic acids **1** and **2** show sharp signals at $\delta = 28.8$ and 20, respectively, which is characteristic of well-crystallised homogeneous compounds. Signals of **Ti1** and **Ti2** are shifted upfield at $\delta = 22.3$ and

13.6, respectively, which is characteristic of the formation of P–O–metal bonds. The peak width at half maximum is close to $\delta = 10$, which indicates that the phosphorus atom has different environments on the surface of the oxide because of the different coordination modes. One, two, or three P–O–metal bonds are likely to be involved in the anchoring on the surface. In the case of materials **Sc1** and **Ss1** (Figure 2), we observed the same type of behaviour with an upfield shift at $\delta = 14$ for the two materials. The signal was less symmetrical than for **Ti1** and **Ti2**, thus the



Scheme 1. Grafting of precursors **1** and **2** on TiO₂ and SnO₂

Table 1. Elemental analyses and EDX for **Ti1**, **Ti2**, **Sc1**, **Ss1**

Particles	Sample	Elemental analyses		EDX		
		% P	% Fe	P/Fe	% P	% Fe
TiO ₂ P25	Ti1	1.50	2.20	0.7	3.99	4.14
TiO ₂ P25	Ti2	1.75	2.20	0.8	4.07	3.5
SnO ₂ Merck	Sc1	0.90	1.17	0.77	2.99	3.5
SnO ₂ Synthesized	Ss1	1.40	1.65	0.85	3.5	2.8

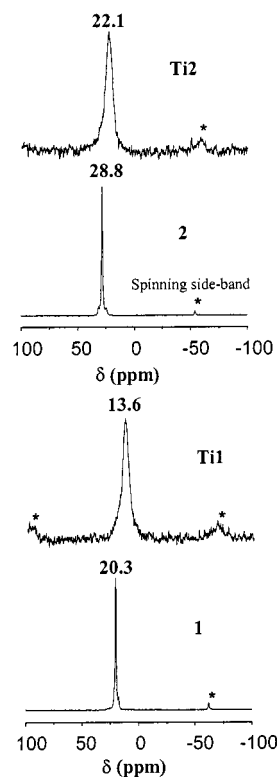


Figure 1. Solid-state hpdecmas ³¹P NMR of compounds **1**, **2**, **Ti1**, **Ti2**

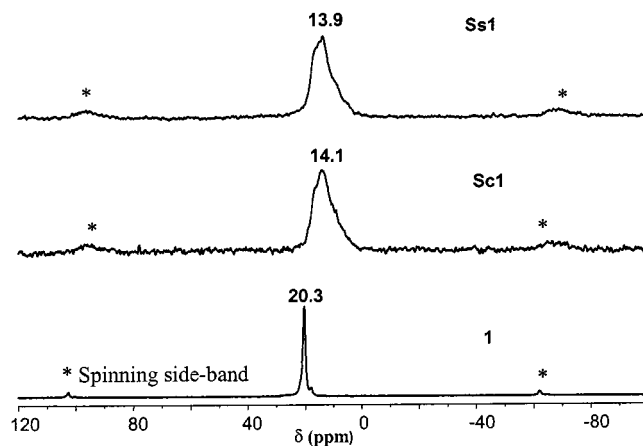


Figure 2. Solid-state hpdecmas ³¹P NMR of compounds **1**, **Ss1**, **Sc1**

surface of SnO_2 is likely to be more carved than the surface of TiO_2 .

Electrochemical Behaviour

After characterising the hybrid organic-inorganic materials, the electrochemical properties of the precursors and grafting materials were investigated by cyclic voltammetry by means of a potentiostat (E&GG model 273A). For the material powders, a modified electrode was prepared by pressing the particles on a flat pad made of stainless steel. A platinum electrode was used as the auxiliary electrode and a saturated calomel electrode was the reference, 0.1 M LiClO_4 was used as the electrolyte. The different voltammograms obtained are presented in Figures 3–5 and the half-wave potentials $E_{1/2}$ are gathered in Table 2. The electroactivity of the precursor **1** was first analysed in aqueous solution (Figure 3). We observed the quasi-reversible oxidation-reduction waves characteristic of the $\text{Fc}^{\text{II}}/\text{Fc}^{\text{III}}$ couple. The oxidation and the reduction half-wave potentials were assigned at 150 mV/SCE and 200 mV/SCE, respectively. The electrochemical analyses, in the solid state, of the acid **1** and of the grafted TiO_2 powder (**Ti1**) are presented in Figure 4a. The non-reversibility of both systems is shown. In the solid state, the diffusion and the charge transfer processes do not obey the classical laws of electrochemistry in solution. The latter are, in many cases, slower than in solution, which explains the loss of the reversibility of the systems. The electrochemical behaviour of the acid **2** and of the grafted TiO_2 powder (**Ti2**) was studied after pressing the compounds on the stainless steel felt. The systems were non-reversible (Figure 4b), which confirmed the previous results. Moreover, comparison of the voltammograms of the grafted materials **Ti1** and **Ti2** shows that the oxidation and reduction potentials are close to those of the precursors **1** and **2**, respectively (Figure 4a,b). This confirms that the π -conjugated ferrocene unit was not damaged by the grafting on the oxide. The results obtained for the material **Ti2**, which differs from **Ti1** only by the presence of a CH_2 unit between the phenyl and phosphonic groups, confirms the ferrocene elec-

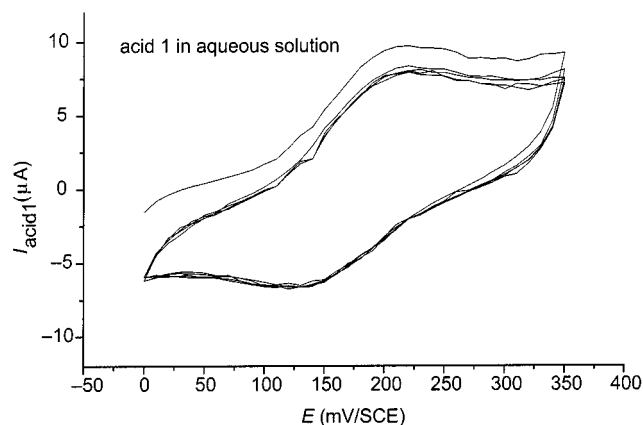


Figure 3. Cyclic voltammogram on stainless steel electrode, of acid **1** in aqueous solution (10^{-1} M LiClO_4) at 100 mVs^{-1}

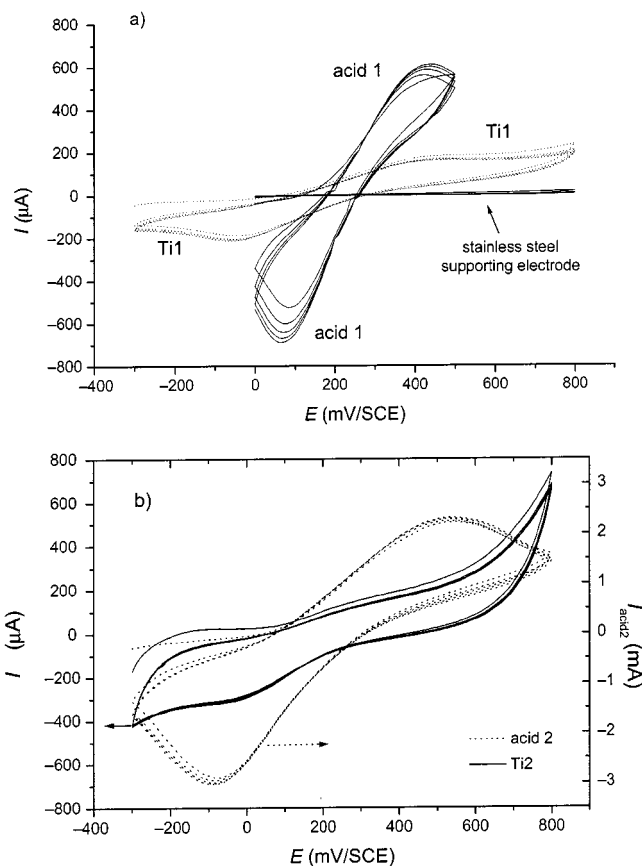


Figure 4. a) Cyclic voltammograms of **1** and **Ti1** in the solid state, stainless steel supporting electrode in aqueous solution (10^{-1} M LiClO_4) at 100 mVs^{-1} ; b) cyclic voltammograms of **2** and **Ti2** in the solid state, stainless steel supporting electrode in aqueous solution (10^{-1} M LiClO_4) at 100 mVs^{-1}

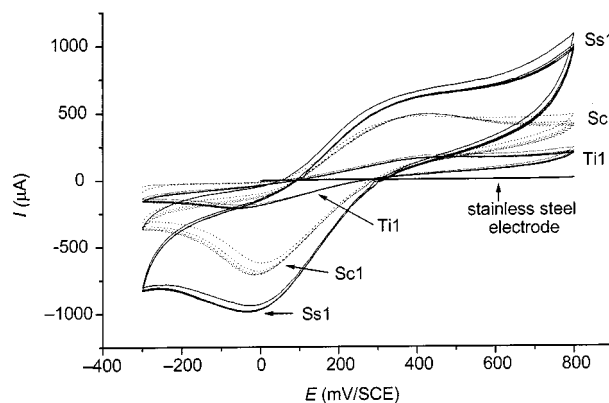


Figure 5. Cyclic voltammograms of **Ss1**, **Sc1** and **Ti1** in the solid state; stainless steel supporting electrode in aqueous solution (10^{-1} M LiClO_4) at 100 mVs^{-1}

troactivity. Furthermore, we observed the same behaviour as in a DMSO solution.^[4] It is easier to oxidise acid **2** relative to acid **1** in the solid state (Table 2), due to the presence of the CH_2 group, which reduces the withdrawing effect of the phosphonic acid substituent. This effect is less visible on the grafted powders **Ti1** and **Ti2**. In Figure 5, the elec-

Table 2. $E_{1/2}$ of **1**, **2**, **Ti1**, **Ti2**, **Sc1**, **Ss1**

	Acid 1 Solution	Solid state	Powder Ti1	Powder Sc1	Powder Ss1	Acid 2 Solid state	Powder Ti2
$E_{1/2}$ [mV]							
Oxidation	150	285	260	200	200	260	260
$E_{1/2}$ [mV]							
Reduction	200	175	110	160	160	100	100

troactivity of the ferrocene unit on both grafted SnO_2 powders **Sc1** and **Ss1** is conserved. The $E_{1/2}$ values and the intensity recorded in the cyclic voltammograms confirms that the electroactivity of the ferrocene group is to be better on the SnO_2 grafted powder than on the TiO_2 grafted powder. Note also that the SnO_2 -based system seems to be more reversible than the TiO_2 -based system ($\Delta E_{\text{Ti1}}^{\text{peak}} = 430$ mV, $\Delta E_{\text{Sc1}}^{\text{peak}} = 390$ mV).

Mössbauer Spectrometry

^{57}Fe Mössbauer experiments were performed with an EG&G constant acceleration spectrometer in transmission mode. The source of nominal activity was 10 mCi of ^{57}Co in an Rh matrix. The velocity scale was calibrated using the standard magnetic sextuplet of a high-purity iron foil absorber. The origin of the isomer shift scale was determined from the centre of the α -Fe spectrum recorded at room temperature. The absorbers were prepared from approximately 200 mg of the powders in a specific cell.

^{57}Fe Mössbauer spectroscopy has been widely used to explore the charge density and symmetry of the charge distribution around the metal atom of ferrocenyl derivatives.^[6] The Mössbauer spectra of low-spin Fe^{II} in ferrocenyl derivatives show isomer shifts δ in the range $0.45 < \delta < 0.55$ mms^{-1} and quadrupolar splittings Δ in the range $2.2 < \Delta < 2.5$ mms^{-1} . Spectra of acids **1** and **2** are presented in Figure 6. The characteristic doublet of the ferrocene units are at $\delta = 0.443$ and 0.449 mms^{-1} , respectively, and the quadrupolar splitting is at $\Delta = 2.268$ and 2.270 mms^{-1} , respectively. A secondary signal was also observed in the two spectra. The contribution of the signal to the spectra was 3.2% and 8.1%, respectively (Table 3). Isomeric shifts were in the range of the ferrocene species (0.44 and 0.49 mms^{-1} , respectively), but the quadrupole splittings are much smaller (in the range 0 to 0.38 mms^{-1}), indicating the presence of a “ferrocenium-like” low-spin Fe^{III} compound. It seems that a small fraction of ferrocene Fe^{II} has been oxidised to the Fe^{III} species. For the low-spin Fe^{II} and low-spin Fe^{III} species, the isomer shift is not very sensitive to the formal oxidation state of iron because the effective electric charges on the iron are not very different. In contrast, the quadrupole splitting of the ferrocenium ion $(\text{C}_5\text{H}_5)_2\text{Fe}^+$ decreases remarkably. For the two acids **1** and **2**, the Mössbauer parameters remain unchanged compared with unsubstituted ferrocene. The σ -bonded substituents on the

cyclopentadienyl ring do not affect the π -bonds of the ferrocene unit. After compounds **1** and **2** were grafted on TiO_2 , the materials **Ti1** and **Ti2** were analysed at room temperature (Figure 6). Major changes in the Mössbauer signals are observed, with only one broadened doublet. Respective values of the isomer shift are 0.40 and 0.38, in the range of ferrocenyl compounds. Quadrupole splitting values of about 0.6 – 0.7 mms^{-1} suggest the presence of some kind of electronic effect. The line broadening and the weak absorption are consistent with an averaged valence state of iron. This is not surprising, as TiO_2 is known to be a photo-oxidant. Sato^[6–7] has observed the same type of behaviour by adsorbing ferrocene on silica. After standing in air, the Mössbauer spectra at room temperature only showed ferrocenium. By performing the measurements at 78 K, the signal of the ferrocene Fe^{II} species appeared, together with the signal of ferrocenium Fe^{III} . Materials **Ti1** and **Ti2** were therefore analysed at low temperature. At 78 K (Figure 4c), the spectra consist of an inner- and outer-doublet which are assigned to a “ferrocenium-like” Fe^{III} and a “ferrocene-like” Fe^{II} doublet, with a ratio of about 3:1. The characteristic signal of the ferrocene unit in its Fe^{II} form is observed for both **Ti1** ($\delta = 0.51$, $\Delta = 2.26$ mms^{-1}) and **Ti2** ($\delta = 0.63$, $\Delta = 2.43$ mms^{-1}), together with the ferrocenium species for both **Ti1** ($\delta = 0.50$, $\Delta = 0.67$) and **Ti2** ($\delta = 0.49$, $\Delta = 0.65$ mms^{-1}). These last measurements show the temperature dependence of the mixed-valence state, where the valence-state changes from an averaged to a trapped valence state. This effect proves that there is an interaction between the π -electrons of the cyclopentadienyl ring of ferrocene and the metal oxides (MO_2).

Table 3. Mössbauer data for **1**, **2**, **Ti1**, **Ti2**

Compound	δ [mm s ⁻¹]	Δ [mm s ⁻¹]	Γ [mms ⁻¹]	%
1	0.443 (2)	2.268 (8)	0.30 (1)	96.8
	0.44 (4)	0	0.30 (1)	3.2
2	0.449 (3)	2.270 (8)	0.30 (1)	91.9
	0.49 (3)	0.38 (4)	0.24 (5)	8.1
Ti1 (298 K)	0.40 (3)	0.63 (4)	0.42 (6)	100
Ti1 (78 K)	0.51 (1)	2.26 (2)	0.29 (3)	34.4
	0.50 (2)	0.67 (3)	0.56 (5)	65.6
Ti2 (298 K)	0.38 (2)	0.68 (3)	0.47 (4)	100
Ti2 (78 K)	0.60 (3)	2.43 (4)	0.44 (6)	36.0
	0.49 (2)	0.65 (3)	0.56 (6)	64.0

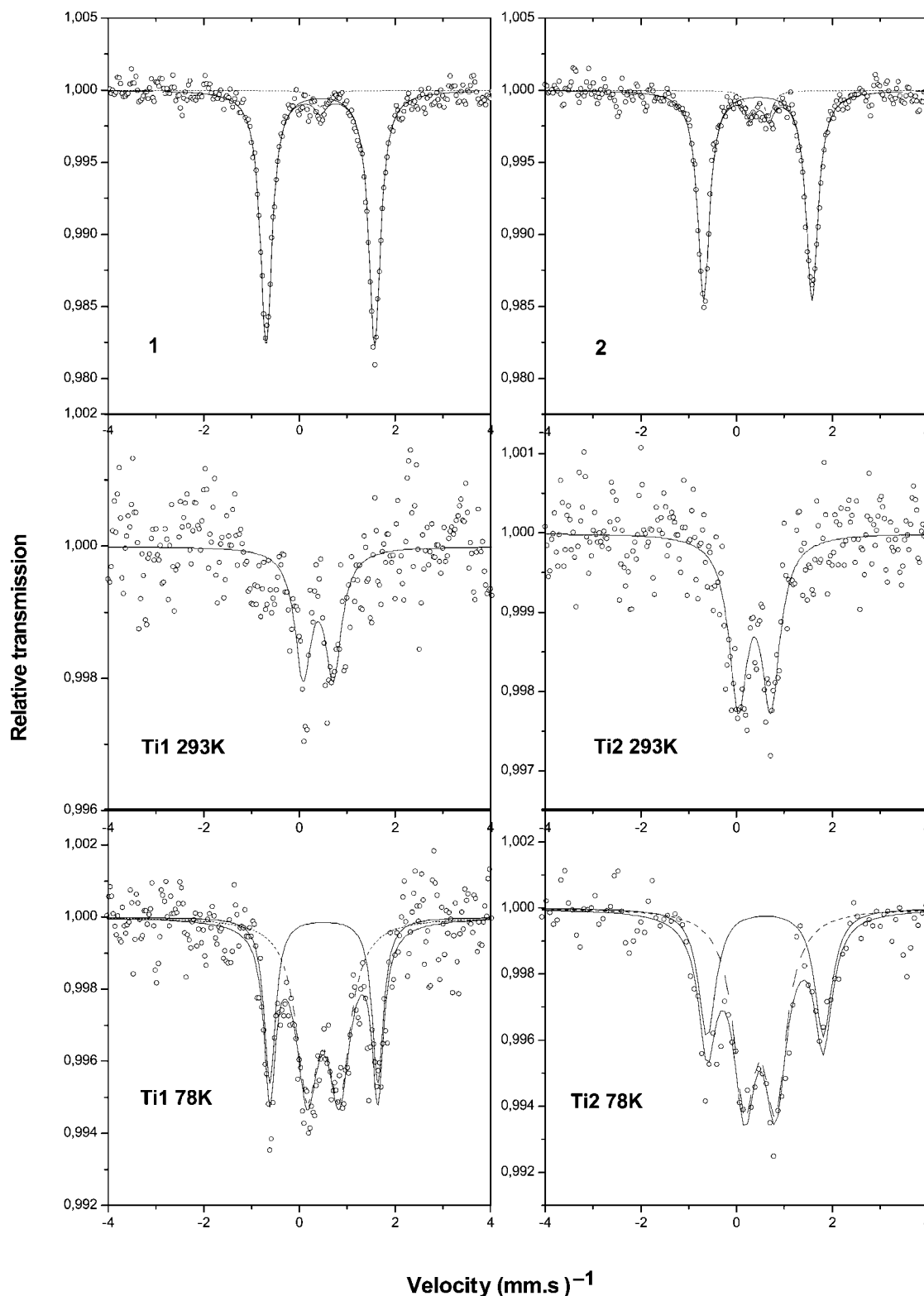


Figure 6. Mössbauer spectra of **1**, **2**, **Ti1**, **Ti2** at 293 K; **Ti1**, **Ti2**, at 78 K

Conclusion

The covalent attachment of ferrocenyl π -conjugated compounds **1** and **2** on metal oxides has been efficiently achieved by using the phosphonic acid functionality. In this

way an organic monolayer at the surface of the oxide was formed. Solid-state electrochemistry has confirmed the electroactivity of the supported ferrocene units, the electrochemical system was irreversible. Electroactivity seemed to be better with the SnO_2 grafted powders than the TiO_2

grafted powders, although coverage is higher on TiO₂ than on SnO₂. The support is effective and could be of importance for the final materials made. Mössbauer spectroscopy has shown that the ferrocene moiety was partially oxidised, and that the π -electrons of the ferrocene interact with the metal oxide. Potential applications in the field of modified electrodes and sensors are in progress.

Experimental Section

General: All reactions were performed under argon. Energy-dispersive X-ray analyses (EDX) were performed with an electronic scanning microscope Cambridge Stereoscan 360 equipped with a Link AN 10000 probe. Microanalyses were performed by the central analysis service at CNRS (Vernaison). The syntheses of the ferrocene π -conjugated phosphonic acids **1** and **2** have been described elsewhere.^[4] SnO₂ was synthesised from SnCl₄ as described.^[5] Commercial SnO₂ was purchased from Merck and TiO₂ P25 was furnished by Degussa. These oxides were functionalised by the following general procedure: The metal oxide was suspended in a mixture of MeOH (40 mL), H₂O (10 mL). Phosphonic acid **1** or **2** was added and the mixture heated at 65 °C for 3 d whilst stirring. The suspension was then cooled, filtered through a millipore membrane (0.45 μ m), washed successively with water, MeOH, EtOH, acetone, ether and dried at room temp.

Material Ti1: TiO₂ P25: 600 mg (7.51 mmol), acid **1**: 200 mg (0.524 mmol). Solid-state ³¹P NMR (hpdec, δ value): 13.6. Microanalysis (%): Fe 2.20, P 1.50, Ti 48.20; EDX (%): Fe 4.14, P 3.99.

Material Ti2: TiO₂ P25: 600 mg (7.51 mmol), acid **2**: 200 mg (0.543 mmol). Solid-state ³¹P NMR (hpdec, δ value): 22.1. Microanalysis (%): Fe 2.20, P 1.75, Ti 48.80. EDX (%): Fe 3.5, P 4.07.

Material Sc1: SnO₂ 500 mg (3.32 mmol), acid **1**: 150 mg (0.41 mmol). Solid-state ³¹P NMR (hpdec, δ value): 14.1. Microanalysis (%): Fe 1.17, P 0.90, Sn 65.45. EDX (%): Fe 3.5, P 2.99.

Material Ss1: SnO₂ 500 mg (3.32 mmol), acid **1**: 150 mg (0.41 mmol). Solid-state ³¹P NMR (hpdec, δ value): 13.9. Microanalysis (%): Fe 1.65, P 1.40, Sn 65.55. EDX (%): Fe 2.8, P 3.5.

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