X-Ray Photoelectron Spectroscopy and Mössbauer Spectroscopy Study of Iron(III) and Antimony(V) Oxides Grafted onto a Silica Gel Surface

Edilson V. Benvenutti,[a] Yoshitaka Gushikem,*[a] Adalberto Vasquez,[b] Sandra C. de Castro[c] and Gunther A. P. Zaldivar[a]

[a] Instituto de Química, UNICAMP, CP 6154, 13081 Campinas, SP, Brazil
[b] Instituto de Fisica, UFRGS, CP 15051, 91500 Porto Alegre, RS, Brazil
[c] Instituto de Fisica Gleb Wataghin, UNICAMP, CP 6151, 13081 Campinas, SP, Brazil

Pronounced antimony surface enrichment on a silica gel surface grafted with Sb_2O_5 is evident after adsorption of Fe^{3+}, and the surface new phase, presumably $FeSbO_4$, is thermally very stable.

Preparation methods for catalytic, active metal oxides highly dispersed on the surface of solids such as SiO_2, TiO_2 and Al_2O_3 have been an area of growing interest in recent years. Experimental procedures aiming to produce monolayers with thermal stability of the coating metal oxides, have been designed.[1-3]

In recent work, the preparation of an antimony(v) oxide monolayer grafted onto a silica gel surface was described.[4] This material was shown to adsorb Fe^{3+} from an acidic solution. The iron–antimony catalysts produced by mixing antimony(v) oxide and iron(III) calcinated in air at high temperature are known to be very active in the allylic oxidation of alkenes.[5,6] This work describes, for the first time, the preparation and characterization (by X-ray photoelectron spectroscopy (XPS) and Mössbauer spectroscopy) of Fe^{III}–Sb^V oxides grafted onto a silica gel surface.
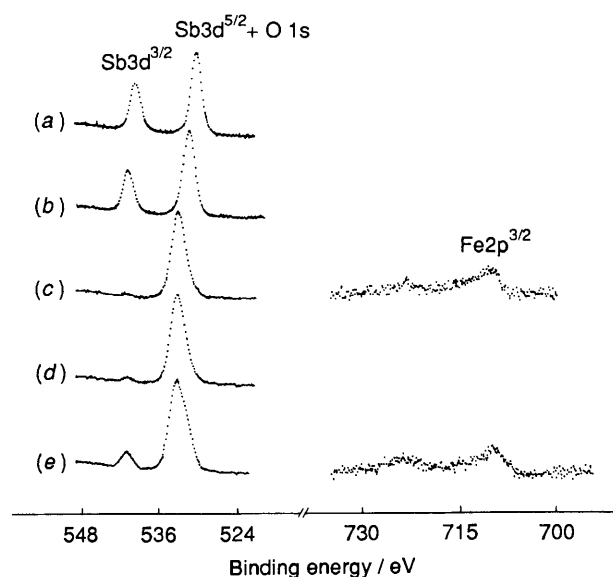
Silica gel with an average diameter pore of 60 Å and particle size between 0.2–0.5 mm was previously activated at 150 °C under vacuum (10^{-1} Pa) before use. Purified $SbCl_5$ (ca. 10 ml) was dissolved in dry CCl_4 (150 ml), and activated silica (50 g) was added. The mixture was stirred for 20 h under nitrogen at solvent reflux temperature. The resulting modified silica was filtered under nitrogen in a Schlenk apparatus, washed with pure CCl_4 to eliminate all unreacted $SbCl_5$ and trapped gaseous HCl, and finally submitted to vacuum for 5 h at 150 °C. The hydrolysis of the grafted $SbCl_5$, i.e. ($\equiv SiO)_n$-$SbCl_{5-n}$, was carried out under a flux of wet air for 20 h, then washed with twice-distilled water and finally dried for 5 h under vacuum at 150 °C.

Approximately 25 g of antimony(v) oxide grafted onto the silica gel surface, (Sb/SiO_2), was immersed in 100 ml of 0.05 mol dm^{-3} acidified $FeCl_3$ aqueous solution (pH ~ 1) and allowed to stand for 24 h at room temperature. The solid was then filtered off, washed with an acidified aqueous solution and allowed to stand for 24 h immersed in pure twice-distilled water. The resulting solid, $SbFe/SiO_2$, was filtered off and dried for 5 h at 150 °C under vacuum.
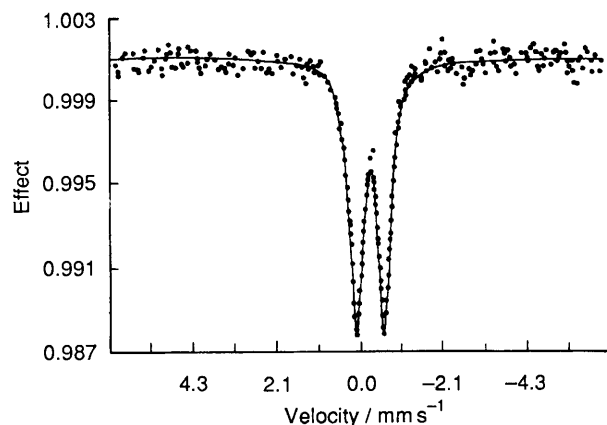

Fig. 1 X-Ray photoelectron spectra: (a) Sb_2O_3; (b) Sb_2O_5; (c) physical mixture; (d) Sb/SiO_2; (e) $SbFe/SiO_2$

Fig. 2 Mössbauer spectrum of $SbFe/SiO_2$ (treated at 150 °C) obtained at room temperature

1325

Table 1 Mössbauer and XPS parameters

Material	T/°C[b]	IS[c]	QS[d]	Sb/Si	Fe/Si	Sb 3d$^{3/2}$[e]	FWHM[f]	Fe 2p$^{3/2}$[g]	FWHM
Sb$_2$O$_3$						539.5	2.0		
Sb$_2$O$_5$						540.5	2.0		
Sb/SiO$_2$	150			0.03		540.6	2.0		
SbFe/SiO$_2$	150	0.37	0.71	0.10	0.02	540.5	2.0	711.8	4.1
	300	0.38	0.73	0.08	0.03	540.6	1.9	712.0	5.3
	500	0.37	0.77	0.09	0.03	540.6	1.9	711.8	4.7
	800	0.38	0.82	0.09	0.03	540.8	2.0	711.6	5.1
Phys. mixture				0.014		541.0	1.9	711.3	3.3

Column header: Mössbauer analyses at 25 °C (mm/s)[a]; Atomic ratio; XPS analyses binding energy/eV

[a] Deviation = ± 0.02 mm s^{-1}. [b] Calcination temperature. [c] IS = Isomer shift in relation to metallic iron. [d] QS = Quadrupole splitting. [e] Deviation = ± 0.2 eV. [f] FWHM = Full width at half maximum (eV). [g] Deviation = ± 0.3 eV.

Table 2 Elemental analyses

Material	XPS	AAS
Sb/SiO$_2$	1.2% of Sb	4.5% of Sb
SbFe/SO$_2$	3.5% of Sb	4.5% of Sb
	1.0% of Fe	1.0% of Fe

The Sb and Fe analyses were carried out after leaching the metals from the surface, decomposing the solid with boiling concentrated HCl. Atomic absorption spectra were recorded using a Perkin-Elmer 5000 AAS. The Mössbauer spectra of the SbFe/SiO$_2$ samples calcinated at 150, 300, 500 and 800 °C were measured in a conventional spectrometer operating in the constant acceleration mode. ^{57}Co in a rhodium matrix was used as the radioactive source. The velocity scale and the magnetic field were calibrated using metallic iron. The X-ray photoelectron spectra (XPS) of these samples were obtained using Al-Kα excitation source. The base pressure was lower than 10^{-5} Pa, (ESCA-36 McPherson photoelectron spectrometer). The charging of insulating samples was corrected assuming the values of 103.4 eV for the binding energy of the Si 2p line, and/or 284.6 eV for the 1s peak of adventitious carbon.

The XPS spectra obtained for Sb/SiO$_2$ and SbFe/SiO$_2$ materials are shown in Fig. 1, Sb$_2$O$_3$ and Sb$_2$O$_5$ are also displayed, together with the physical mixture of Sb$_2$O$_5$, Fe$_2$O$_3$ and SiO$_2$ in the same proportion as the SbFe/SiO$_2$ material. The results obtained for the two oxides, presented in Table 1, are in good agreement with published data on the same compounds.[7,8] The observation of the Sb 3d$^{3/2}$ binding energy values (Table 1) and the invariance of its width, points to Sb^V as being the most likely oxide present on the surface. The same kind of assignment is difficult to make for iron, based on the XPS data alone owing to the weakness of the iron signal. Nevertheless, the observed binding energy is compatible with an iron(iii) species. The binding energies of SbFe/SiO$_2$ calcinated at various temperatures did not show any significant change from 150 to 800 °C (see Table 1).

The Mössbauer spectrum of SbFe/SiO$_2$, treated at 150 °C, is shown in Fig. 2. No change in the spectra was observed even when the samples were calcinated at higher temperatures. The results are listed in Table 1. The isomer shift (IS) and the quadrupole splitting (QS) values are an indication that only Fe^{III} is present, and are comparable with those of octahedral high-spin Fe^{3+} in FeSbO$_4$.[6,9] The spectrum of the material calcinated at 800 °C, obtained at −196 °C did not show any magnetic order, although the spectrum obtained at liquid helium temperature showed a hyperfine magnetic field of 462 ± 10 kOe (Fig. 3), suggesting the formation of iron–antimonate on the surface,[10] which is different from the 531 kOe
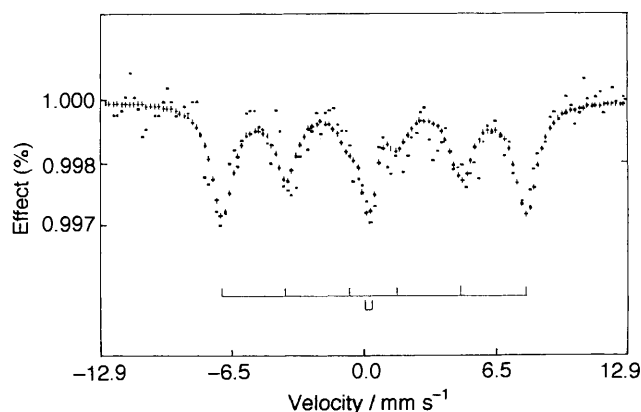
Fig. 3 Mössbauer spectrum of SbFe/SiO$_2$ obtained at helium liquid temperature

value obtained for Fe^{III} oxide dispersed onto a silica gel surface.[11]

The amount of Sb obtained by XPS for the Sb/SiO$_2$ material, is lower than the one given by AAS (Table 2), suggesting that the antimony oxide is present in the form of clusters on the surface. The adsorption of Fe^{3+} on Sb/SiO$_2$ increased the Sb/Si ratio by three times (see Table 1), much above the error margin of atomic concentration determined by XPS (20–30%). This antimony enrichment on the surface, which is clearly shown in Fig. 1, where the peak of Sb 3d$^{3/2}$ of SbFe/SiO$_2$ is intensified in relation with that of Sb/SiO$_2$, might be explained by a decrease in size of antimony(v) oxide particle dispersed on SbFe/SiO$_2$,[12] resulting in a higher covering of the silica gel surface. This effect is an indication of a strong interaction between Fe^{3+} and antimony(v) oxide dispersed on the silica gel surface, because, in the mechanically mixed oxides, the ratio Sb/Si is 0.014, and therefore, lower than that observed for SbFe/SiO$_2$ and Sb/SiO$_2$.

A noteworthy stability of the chemical species formed on the surface is observed since the ratios Fe/Si and Sb/Si remain unchanged at all calcination temperatures, in contrast with that observed for Fe$_2$O$_3$ dispersed on SiO$_2$, which exhibited considerable mobility at higher temperatures.[13]

The antimony surface enrichment has been observed by others,[14,15] for materials obtained by the coprecipitation method, where the species on the surface was due to the formation of FeSb$^{III}_{0.5}$Sb$^V_{1.5}$O$_6$ and Sb$_2$O$_3$. However, species containing Sb^{III} were not detectable in this work.

The XPS and Mössbauer, therefore, suggest that Fe^{3+} interacts with Sb$_2$O$_5$ dispersed on a silica gel surface forming the species FeSbO$_4$, which are very stable at various calcination temperatures.

Received, 3rd April 1991; Com. 1/01549D

References

1 G. C. Bond, S. Flamerz and R. Shukri, *Faraday Discuss. Chem. Soc.*, 1989, **87**, 65.
2 E. E. Getty and R. S. Drago, *Inorg. Chem.*, 1990, **29**, 1186.
3 L. T. Kubota, Y. Gushikem, S. C. de Castro and J. C. Moreira, *Colloids Surf.*, 1991, **57**, 11.
4 E. V. Benvenutti, Y. Gushikem, *Proceedings of 13th Annual Meeting of Brazilian Chem. Soc.*, Caxambu, MG, Brazil, 1989.
5 I. Aso, S. Furukawa, N. Yamazoe and T. Seiyama, *J. Catal.*, 1980, **64**, 29.
6 N. Burriesci, F. Garbassi, M. Petrera and G. Petrini, *J. Chem. Soc., Faraday Trans. 1*, 1982, **78**, 817.
7 T. Birchall, J. A. Connor and I. H. Hillier, *J. Chem. Soc., Dalton Trans.*, 1975, 2003.
8 F. Garbassi, *Surf. Interface Anal.*, 1980, **2**, 165.
9 G. M. Bartenev, R. R. Zakirov and A. D. Tsyganov, *Sov. Phys. Solid State*, 1975, **16**, 2409.
10 F. J. Berry, A. Labarta, X. Obradors, R. Rodriguez, M. I. Sarson and J. Tejada, *Hyperfine Interactions*, 1988, **41**, 463.
11 W. Kündig and H. Bömmel, *Phys. Rev.* 1966, **142**, 327.
12 R. B. Quincy, M. Houalla, D. M. Hercules, *J. Catal.*, 1987, **106**, 85.
13 J. Lee, M. Lee and P. Tseng, *Appl. Catal.*, 1989, **52**, 193.
14 I. Aso, T. Amamoto, N. Yamazoe and T. Seiyama, *Chem. Lett.*, 1980, 365.
15 P. A. Cox, R. G. Egdell, C. Harding, W. R. Patterson and P. J. Tavener, *Surf. Sci.*, 1982, **123**, 179.