Antimony(v) Oxide grafted onto a Silica Gel Surface: Acidic Properties and Thermal Stability

Edilson V. Benvenutti, Yoshitaka Gushikem* and Celso U. Davanzo
Instituto de Quimica, UNICAMP, CP 6154, 13081, Campinas, SP, Brazil

Sandra C. de Castro and Iris L. Torriani
Instituto de Fisica Gleb Wataghin, UNICAMP, CP 6151, 13081, Campinas, SP, Brazil

Antimony(v) oxide grafted onto a silica gel surface was obtained in highly dispersed form, with antimony density of 0.65 atoms nm^{-2}. The material presents Brønsted and Lewis acid properties different from pyrochlore, Sb_2O_5. These sites disappear upon thermal treatment at 500 °C owing to reaction of antimony oxide with the silica surface.

In recent years, the supporting of reagents on a rigid matrix surface of metal and non-metal oxides, has become an area of growing interest aimed at obtaining highly dispersed phases.[1–7] In general, when these reagents are highly dispersed on a support their properties are not necessarily related to those of the unsupported ones. For instance, sorption properties,[3,4] and catalytic activity[5–7] were reported to be enhanced in supported materials.

Pyrochlore, antimony oxide (Sb_2O_5) is a well known material whose acidic and ion-exchange properties are very dependent upon its structure.[8,9] In this context, antimony oxide highly dispersed on another oxide surface presents an excellent opportunity for study of the changes in its properties.

In this work we report the thermal stability and the acidic properties of the Sb^V oxide grafted onto a silica gel surface. Several preparations were undertaken to establish the reproducibility of the conditions for the synthesis and the modified silica was characterized by Fourier-transform infrared (FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS) and small-angle X-ray scattering (SAXS) techniques. We show how the behaviour of grafted Sb_2O_5 is different from the pure compound.

Experimental

Silica gel (Merck), specific surface area 395 m^2 g^{-1} (BET method), average pore diameter 6 nm and average particle size 0.2–0.5 mm was activated at 150 °C under vacuum (10^{-1} Pa) before use. $SbCl_5$ (Carlo Erba) (10 cm^3), previously distilled under vacuum in a Schlenk apparatus, was dissolved in CCl_4 (Merck) (150 cm^3), dried under 0.4 nm molecular sieves. The activated silica gel (50 g) was then 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 CCl_4 to eliminate unreacted $SbCl_5$ and trapped gaseous HCl and finally submitted to vacuum for 5 h at 150 °C. The hydrolysis of the grafted $SbCl_5$, 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.[10]

In order to study the reproducibility of the preparation method, four experiments were carried out, changing the experimental conditions. The results obtained are summarized in Table 1.

The sorption of pyridine vapour by Sb/SiO_2 was studied by IR spectroscopy. Reagent-grade pyridine (Merck) was previously dried over 0.4 nm molecular sieve and submitted to various freeze–pump–thaw cycles. The cell used in this work was described elsewhere.[11] A self-supporting disk of Sb/SiO_2 having area 5 cm^2 and mass 40 mg, was prepared. The cell was connected to a greaseless vacuum line and the system pumped for 5 min at a pressure of 10 Pa at room temperature. After this treatment, pyridine was introduced into the cell at a pressure of 1.6 kPa at room temperature. The spectra of the samples were obtained at a pressure of 10^{-2} Pa after heating the disk in the cell at various temperatures. The equipment used was a Perkin-Elmer FTIR 1600, with 4 cm^{-1} resolution, and a maximum of 256 scans.

Attempts to compare the IR spectra of Sb/SiO_2 with original SiO_2 were made using KBr pellets and a diffuse-reflectance accessory with KBr as dispersing material.[4] In both procedures the concentrations used (w/w related to KBr) were 1%, 5%, 10% and 15%. Difference spectra were obtained on the Perkin-Elmer FTIR 1600.

XP spectra were obtained using an Al-Kα excitation source. The base pressure was lower than 10^{-5} Pa. The charging of insulating samples was corrected assuming the value 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 equipment used was an ESCA-36 McPherson photoelectron spectrometer.

Small-angle-scattering curves were obtained with a small-angle goniometer with slit geometry, using as X-ray source a rotating anode generator (Rotaflex RU-200) from the Rigaku Denki Co. The radiation used was monochromatized by a nickel filter. The spectra were obtained using a linear position sensitive detector (Technology for Energy Corporation, Tennessee, USA). Counting times were typically 300 s for each spectrum. Data treatment included background subtraction and absorption correction.

The BET surface areas of the materials were obtained in a Micromeritics Flow Sorb 2300 apparatus.

Table 1 Preparation of the material

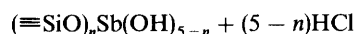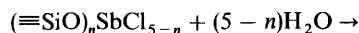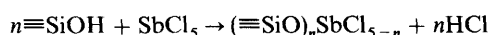| N	t^a/h	SiO_2^b/g	$SbCl_5$ (v/v)^c	Sb (% w/w)^d	Sb/mmol g^{-1}
1^e	20	50	6.7	4.5	0.37
2	24	70	9.3	5.0	0.41
3	30	70	8.0	4.7	0.39
4	32	50	6.7	4.9	0.40

^{a} Time of reaction; ^{b} mass of SiO_2 used in the preparation; ^{c} vol.% of $SbCl_5$ in 150 cm^3 of CCl_4 solvent; ^{d} based on hydrated material. The water content was *ca.* 12%; ^{e} described in detail in the Experimental section.

Results and Discussion

Characteristics of the Material

Various experimental conditions were used in this work. The representative procedures are summarized in Table 1. The amount of the attached Sb^V oxide on the silica surface was very reproducible, ranging between 0.37 and 0.41 mmol g^{-1} over the four preparations.

The equations that represent the reactions can be written as follow:

$$n{\equiv}SiOH + SbCl_5 \rightarrow ({\equiv}SiO)_nSbCl_{5-n} + nHCl$$

$$({\equiv}SiO)_nSbCl_{5-n} + (5-n)H_2O \rightarrow$$

$$({\equiv}SiO)_nSb(OH)_{5-n} + (5-n)HCl$$

where ${\equiv}SiOH$ represents the silanol group on the silica surface and $({\equiv}SiO)_nSb(OH)_{5-n}$ the antimony oxide attached to the surface, which will be denoted as Sb/SiO_2.

No peaks were observed in the X-ray diffractograms and the average Sb–Sb distance was estimated as described below.

The specific surface area, S_{BET}, in the typical preparations was 372 m^2 g^{-1}. Assuming that the grafted oxide covers the surface homogeneously, the average density, d, of antimony atoms on the surface can be estimated from:

$$d = (NN_A)/S_{BET}$$

where N is the concentration of atoms attached on the surface (mmol g^{-1}), N_A is Avogadro's constant and S_{BET} is expressed in nm^2 g^{-1}. The calculated value was $d = 0.65$ atoms nm^{-2} in a typical preparation, therefore the average interatomic distance, l, between the antimony atoms [calculated by using the equation $l = (1/d)^{1/2}$] was estimated as 1.2 nm. In the pure bulk Sb_2O_5 the Sb–Sb distance is ca. 0.3 nm.[8]

Acidic Properties

The spectra of Sb/SiO_2 submitted to 1.6 kPa of pyridine are shown in Fig. 1. The bands at 1596 and 1444 cm^{-1} [Fig. 1(a)] are due to the 8a and 19b modes, respectively, of pyridine bonded to the free silanol ${\equiv}SiOH$ groups through hydrogen bonds.[12–14] These bands were also observed in the pure silica and disappeared after heating the disk at 100 °C for 2 h under vacuum (10^{-2} Pa) [Fig. 1(b)]. The band at 1579 cm^{-1} [Fig. 1(a)] is due to the 8a mode of the physically adsorbed liquid-like pyridine.[2,13,15] The bands at 1617 and 1456 cm^{-1} that remained on the sample heated to 200 °C [Fig. 1(b) and (c)] were assigned to the 8a and 19b modes, respectively, of molecules coordinated to a Lewis acid site on the surface.[14,15] The band observed at 1490 cm^{-1} [Fig. 1(a)–1(d)] is due to the 19a mode and is always present for all kinds of pyridine adsorption. The weak band at ca. 1547 cm^{-1} [Fig. 1(a)] is due to the 19b mode of pyridinium ion,[13,14,16] i.e. pyridine adsorbed on a Brønsted acid site.

In the pyrochlore Sb_2O_5 spectrum, the band at 1547 cm^{-1} due to the pyridine molecules on a Brønsted acid site is the most intense, and the bands assigned to pyridine molecules bonded to a Lewis acid site was detected with a very weak intensity.[12] Such difference between the bulk structure and the dispersed form antimony(v) oxide is due to the absence of a crystalline lattice in Sb/SiO_2.

When the Sb/SiO_2 disk was pre-heated under 10^{-2} Pa at 300 °C and then submitted to pyridine vapour (1.6 kPa), a spectrum corresponding to the presence of liquid-like and hydrogen-bonded molecules was obtained [Fig. 2(a)]. On heating the sample to 100 °C [Fig. 2(b)], the spectrum
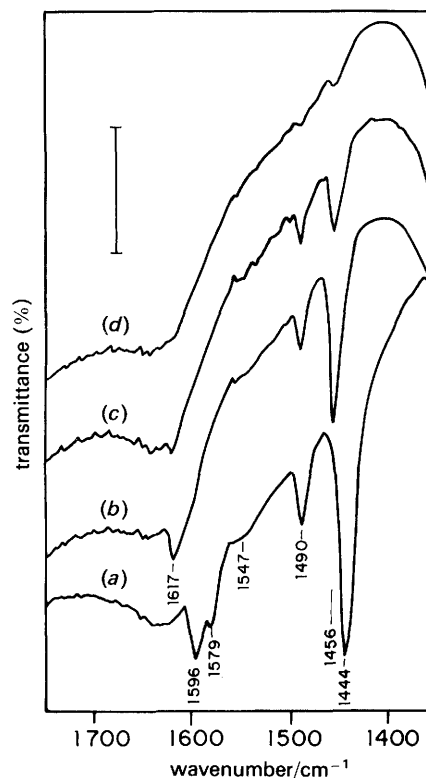

Fig. 1 IR spectra of Sb/SiO_2 (a) submitted to 1.6 kPa of pyridine at room temperature; (b) after heating for 2 h at 100 °C (10^{-2} Pa); (c) additional 2 at 200 °C (10^{-2} Pa); (d) additional 2 h at 300 °C (10^{-2} Pa). The bar value is 6% for (a) and 11% for (b)–(d)

revealed only bands assigned to pyridine molecules coordinated to Lewis acid sites, much less intense than those in Fig. 1. When a new disk was heated under vacuum (10^{-2} Pa) at 500 °C and treated as above, no pyridine bands could be observed. An explanation for the presence of acid sites and
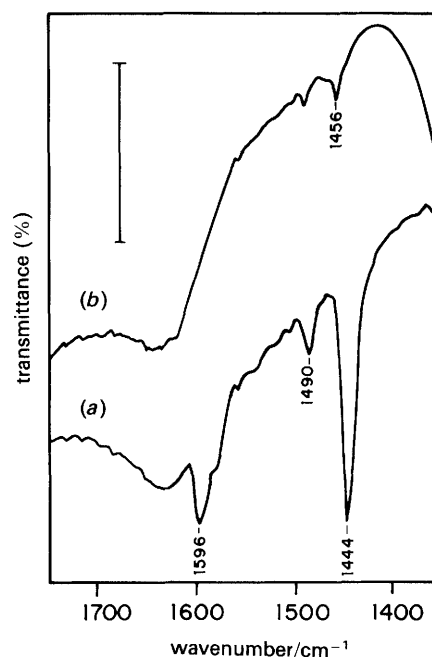

Fig. 2 IR spectra of Sb/SiO_2 previously heated at 300 °C for 2 h under vacuum (10^{-2} Pa), (a) submitted to 1.6 kPa of pyridine; (b) heated at 100 °C for 1 h under vacuum (10^{-2} Pa). The bar value is 10%

how they are deactivated by heating will be given after the next two sections.

XPS

The binding energy of Sb $3d_{3/2}$ in Sb/SiO_2 is the same as that observed for pure bulk Sb_2O_5, *i.e.* 540.5 eV.†[17,18]

It is known that in bulk Sb_2O_5 thermal treatment can promote a reduction of Sb^V to Sb^{III}.[19-22] For Sb_2O_5 heated to 1100 °C the Sb $3d_{3/2}$ binding energy is the same as that presented by Sb_2O_3. In Sb/SiO_2 such reduction was not detected (see Table 2), even on heating the sample to 1100 °C.

When the temperature rises the Sb : Si ratio remains almost unchanged for Sb/SiO_2 (Table 2). On the other hand, the Sb $3d_{3/2}$ binding energy increases suggesting the possible formation of a new phase on the surface. The practically constant Sb : Si ratio is an indication that no agglomeration of Sb^V occurs on the silica gel surface.[23,24]

SAXS

For a system of particles or pores with colloidal dimensions dispersed in a matrix with homogeneous electronic density, the variation of the average diameter of the pores can be studied by SAXS.[25,26] For the scattered intensity $I(h)$ from a dilute system of particles or pores, Guinier's law[26,27] states that $I(h)$ can be expressed by: $\ln I(h) = \ln I(0) - (R_G^2 h^2)/3$ with $h = (4\pi \sin \theta)/\lambda$, where 2θ is the angle of scattering and λ is the X-ray wavelength, 0.154 18 nm in the present case. The radius of gyration, R_G, is calculated by applying the equation: $R_G = (3p)^{1/2}$ where p is the slope of Guinier's plot, *i.e.* $\ln I(h)$ *vs.* h^2 (Fig. 3).

Assuming that the pores are spherical, the radius R_P can be calculated by applying the equation:[27] $R_P = (5/3)^{1/2} R_G$. The calculated values of the average pore diameters, D_P, for SiO_2 and Sb/SiO_2 are shown in Table 3. The slight increase of D_P in Sb/SiO_2 compared to that in SiO_2 is followed by a small decrease in the specific surface area. The increase in D_P might be explained by taking into account that the size of the pores
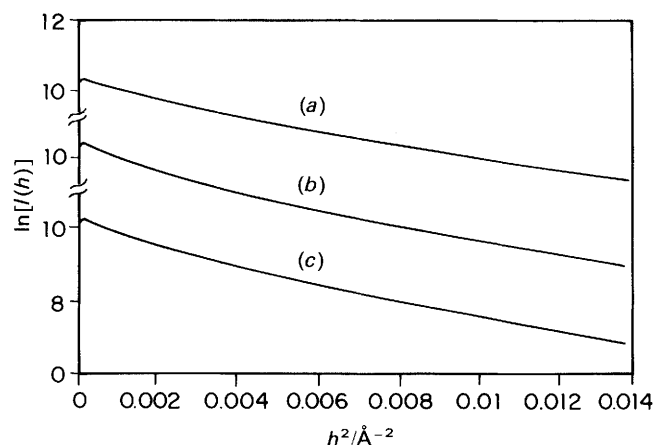

Fig. 3 Guinier's plot. (*a*) pure silica gel; (*b*) Sb/SiO_2; (*c*) Sb/SiO_2 calcinated at 800 °C for 4 h

obeys a Gaussian distribution. The smallest pores may become blocked in the grafting reaction. The population decrease of the smallest pores then shifts the distribution curve towards the larger sizes and causes a decrease in S_{BET}.

Upon calcination of Sb/SiO_2 to 800 °C, the values of D_P and S_{BET} remained unchanged.
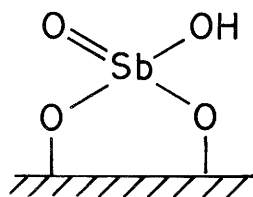
Further Considerations on the Surface Structure

In the Experimental section, attempts to compare the IR spectra of Sb/SiO_2 and SiO_2 were reported. No difference was noticed with the procedures used. Special attention was drawn to the 1000–400 cm^{-1} region where bands associated with vibrations of Sb=O and Sb—O were expected.
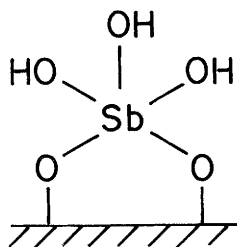
Ono *et al.*[28] studied Sb oxide on the surface of TiO_2 and observed bands at *ca.* 850 cm^{-1} and assigned them to Sb=O vibration. However, their material has a much higher quantity of Sb atoms than our sample. It can be argued that in the present case if Sb=O bonds are formed, they are below the detection limit of the IR spectrometer. Furthermore, bands that could be associated with vibrations of Sb—O bonds can be expected to be very broad due to inhomogeneity of the surface and the many types of Sb—O—Si bonds. These conditions may prevent the observation of those bands when the difference between Sb/SiO_2 and SiO_2 spectra is obtained. In conclusion, the IR study under discussion furnished no experimental evidence for the structural formulation.

There are many studies in the literature involving materials similar to that described in this paper. Based on the studies on Mo,[29-31] V[32-34] and Nb,[35] both structures in Schemes I and II could be proposed for Sb on the surface of SiO_2 (the number of Sb—OH and Sb—O—Si bonds can be altered but the following discussion will be equally valid). However, there are some indications that the structure of Scheme II would be preferred. The presence of SbO_6 octahedra in solids of the type $M^{III}SbO_4$, the absence of isolated SbO_4^{3-} species[36] and the presence of $Sb(OH)_6^-$ in aqueous solution[36] indicate that double-bond formation between Sb and oxygen occurs only in very special situations. The very few examples cited by Sala and Trifiro[37] corroborate the above observation. The study by Ono *et al.*[28] is the only example where Sb=O was observed in a material similar to Sb/SiO_2, but Sb^{III} in high concentration was detected. Our XPS results indicated quite clearly that Sb^{III} is absent.

In both Schemes I and II, Sb ions are represented as coordinatively unsaturated and this is responsible for the Lewis acidity. Brønsted acid sites were observed only in hydrated samples. This is an indication that Brønsted acid protons come from water coordinated to the above mentioned Lewis

Table 2 XPS parameters

material	$T/°C^a$	binding energy/eV^b		atomic ratio Sb/Si^e
		$3d_{3/2}^c$	FWHM^d	
Sb_2O_3		539.5	(2.0)	
Sb_2O_5		540.5	(2.0)	
	800	540.2	(2.2)	
	1100	539.6	(2.3)	
Sb/SiO_2		540.6	(2.6)	0.032
	800	541.0	(2.9)	0.036
	1100	541.1	(2.3)	0.040

^{a} Calcination temperature; ^{b} deviation = 0.2 eV; ^{c} energy reference to Si 2p line taken as 103.4 eV; ^{d} full width at half maximum (eV); ^{e} deviation = 20%.

Table 3 SAXS parameters

material	R_G (± 0.05 nm)	D_P (± 0.1 nm)	S (± 5 m^2 g^{-1})
silica gel	2.49	6.4	395
Sb/SiO_2	2.65	6.8	372
Sb/SiO_2 (800 °C)^a	2.66	6.8	372

^{a} Temperature of treatment.

† 1 eV ≈ 1.602 × 10^{-19} J.

Scheme I

Scheme II

sites, as proposed for similar materials.[38,39] The presence of Brønsted acidity similar to Sb_2O_5[12] was discounted because, unlike that material, Sb/SiO_2 has fewer Brønsted than Lewis sites.

Disappearance of Lewis acid sites upon thermal heating even at a temperature of 300 °C is due to further reticulation of antimony species with the silica surface, explaining the observed increase in the Sb $3d_{3/2}$ binding energy. This observation can be understood if antimony species on the silica gel surface are actually highly dispersed. A similar discussion would result if instead of Schemes I and II a cluster structure composed of these species were proposed.

Conclusions

From analyses of XPS and IR results we conclude that the Sb^V oxide is highly dispersed on the silica gel surface. In this situation antimony atoms are distant and thermal sintering of Sb_2O_5 in a crystalline form is inhibited. The highly dispersed material presents Lewis acid sites due to unsaturation on the coordination of Sb^V ions. These sites disappear upon thermal treatment as a consequence of a more extensive reticulation of Sb^V with the silica gel surface.

The SAXS results are consistent with those obtained by XPS and IR spectroscopy. Calcination of samples does not promote any coalescence or extensive clogging of the pores.

References

1 G. C. Bond, S. Flamerz and R. Shukri, *Faraday Discuss. Chem. Soc.*, 1989, **87**, 65.
2 G. Busca, *Langmuir*, 1986, **2**, 577.
3 Y. Gushikem, C. R. M. Peixoto and L. T. Kubota, *New Development in Ion Exchange*, ICIE, Tokyo, Japan, 1991, p. 607.
4 S. Denofre, Y. Gushikem and C. U. Davanzo, *Eur. J. Solid State Inorg. Chem.*, 1991, **28**, 1295.
5 M. Shirai, K. Asakura and Y. Iwasawa, *J. Phys. Chem.*, 1991, **95**, 499.
6 G. C. Bond and K. Brückman, *Faraday Discuss. Chem. Soc.*, 1981, **72**, 235.
7 E. C. Alyea, K. F. Brown and K. J. Fisher, *J. Mol. Catal.*, 1990, **63**, L11.
8 L. H. Baetsle and D. Huys, *J. Inorg. Nucl. Chem.*, 1968, **30**, 639.
9 W. A. England, M. G. Cross, A. Hamnett, P. J. Wiseman and J. B. Goodenough, *Solid State Ionics*, 1980, **1**, 231.
10 E. V. Benvenutti, Y. Gushikem, S. C. Castro, A. Vasquez and G. P. Zaldivar, *J. Chem. Soc., Chem. Commun.*, 1991, 1325.
11 C. C. Chu, PhD Thesis, University of East Anglia, 1983.
12 E. V. Benvenutti, Y. Gushikem and C. U. Davanzo, *Appl. Spectrosc.*, 1992, in the press.
13 P. Pichat, M. V. Mathieu and B. Imelik, *Bull. Soc. Chim. Fr.*, 1969, **8**, 2611.
14 E. P. Parry, *J. Catal.*, 1963, **2**, 371.
15 C. Morterra and G. Cerrato, *Langmuir*, 1990, **6**, 1810.
16 M. Lefrancois and G. Malbois, *J. Catal.*, 1971, **20**, 350.
17 T. Birchall, J. A. Connor and I. H. Hillier, *J. Chem. Soc., Faraday Trans. 1*, 1975, **71**, 2003.
18 F. Garbassi, *Surf. Interface Anal.*, 1980, **2**, 165.
19 C. Forano and J. P. Besse, *Eur. J. Solid State Inorg. Chem.*, 1988, **25**, 141.
20 M. Abe and K. Sudoh, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 615.
21 D. J. Stewart, O. Knop, C. Ayasse and F. W. D. Woodhams, *Can. J. Chem.*, 1972, **50**, 690.
22 C. A. Cody, L. DiCarlo and R. K. Darlington, *Inorg. Chem.*, 1979, **18**, 1572.
23 R. B. Quincy, M. Houalla and M. D. Hercules, *J. Catal.*, 1987, **106**, 85.
24 B. J. Tan, K. J. Klabunde and P. M. A. Sherwood, *J. Am. Chem. Soc.*, 1991, **113**, 855.
25 D. R. Vollet, J. C. Moreira, L. T. Kubota, J. A. Varela and Y. Gushikem, *Colloids Surf.*, 1989, **40**, 1.
26 A. Guinier and G. Fournet, *Small-Angle Scattering of X-Rays*, Wiley, New York, 1955, ch. 2.
27 O. Glatter and O. Kratky, *Small Angle X-Ray Scattering*, Academic Press, London, 1982, part II.
28 T. Ono, M. Kiryu, M. Komiyama and R. L. Kuczkowski, *J. Catal.*, 1991, **127**, 698.
29 H. M. Ismail, C. R. Theocharis, D. N. Waters, M. I. Zaki and R. B. Fahim, *J. Chem. Soc., Faraday Trans. 1*, 1987, **83**, 1601.
30 C. C. Williams, J. G. Ekerdt, J-M. Jehng, F. D. Hardcastle and I. E. Wachs, *J. Phys. Chem.*, 1991, **95**, 879.
31 A. N. Desikan, L. Huang and S. T. Oyama, *J. Phys. Chem.*, 1991, **95**, 10050.
32 S. S. Chan, I. E. Wachs, L. L. Murrell, L. Wang and W. K. Hall, *J. Phys. Chem.*, 1984, **88**, 5831.
33 T. J. Dines, C. H. Rochester and A. M. Ward, *J. Chem. Soc., Faraday Trans.*, 1991, **87**, 1611.
34 F. Hatayama, T. Ohno, T. Maruoka, T. Ono and H. Miyata, *J. Chem. Soc., Faraday Trans.*, 1991, **87**, 2629.
35 K. Asakura and Y. Iwasawa, *J. Phys. Chem.*, 1991, **95**, 1711.
36 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Wiley, New York, 4th edn., 1980, p. 481.
37 F. Sala and F. Trifiro, *J. Catal.*, 1976, **41**, 1.
38 T. Kataoka and J. A. Dumesic, *J. Catal.*, 1988, **112**, 66.
39 H. Miyata, K. Fujii and T. Ono, *J. Chem. Soc., Faraday Trans. 1*, 1988, **84**, 3121.