CHARACTERIZATION OF Sn–5at.%Sb MIXED OXIDE CATALYST STUDIED BY X-RAY PHOTOELECTRON SPECTROSCOPY AND AUGER ELECTRON SPECTROSCOPY

B. VISWANATHAN, S. CHOKKALINGAM and T. K. VARADARAJAN

Department of Chemistry, Indian Institute of Technology, Madras 600036 (India)

S. BADRINARAYANAN

Physical Chemistry Division, National Chemical Laboratory, Pune 411008 (India)

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Summary

X-ray photoelectron spectroscopy and Auger electron spectroscopy analyses of an Sn–5at.%Sb mixed oxide catalyst showed that activation leads to an increase in concentration of antimony on its surface. This surface segregation is induced by the presence of oxygen in the gas phase. The active catalyst probably contains both antimony(V) and antimony(III) in addition to antimony(V) in solid solution with SnO_2.

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1. Introduction

Sn–Sb mixed oxide catalysts have received considerable attention in recent years because of their relevance to selective oxidation and ammoxidation of olefins [1 - 3]. It is generally agreed that pretreatment can lead to enrichment of antimony on the surface of the catalyst; this surface enrichment of antimony has been found to be a function of antimony content as well as of activation temperature [4, 5]. The studies of Boudeville *et al.* [4] on the identification of the nature of the antimony species present on the surface showed that at low antimony content and low activation temperature antimony(V) is present in solid solution in the SnO_2 lattice, while at high antimony content (greater than 5 at.%) and higher temperatures the presence of an Sb_2O_4 phase was also identified. Hernimann *et al.* [6] have correlated the specific activity for the formation of butadiene from 1-butene with the concentration of antimony ions on the surface and deduced that isolated antimony ions on the surface surrounded by tin ions alone constitute the active site for this reaction. In this paper we present the results of X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) studies on an Sn–5at.%Sb mixed oxide catalyst. We have attempted to obtain answers to the following specific questions.

(1) Do the activated and reacted catalysts have the same surface composition as that of the fresh catalyst?

(2) What are the probable valence states of antimony on the surface of the active catalyst?

(3) If surface segregation does occur, is it induced as a result of reaction and/or as a result of activation?

Surface segregation of antimony during oxidative dehydrogenation of isopropyl alcohol has been deduced from indirect kinetic evidence for various compositions of tin and antimony mixed oxides [7]. This prompted us to study this process, and in this paper we present the results of XPS and AES studies on an Sn–Sb mixed oxide catalyst with 5 at.% Sb, since the catalytic activity in propylene oxidation is maximum at about this composition.

2. Experimental details

The Sn–Sb oxide catalyst with 5 at.% Sb was prepared by the method reported previously [7]. The catalyst was first calcined at 870 K for 16 h and subsequently at 1070 K for 5 h. X-ray diffraction showed the formation of a single phase by this calcination procedure. The catalytic oxidation of isopropyl alcohol in the presence of gas phase oxygen ([isopropyl alcohol]: [oxygen] = 2:1) was carried out in the temperature range 320 - 400 °C using a conventional flow-type fixed-bed reactor working at atmospheric pressure.

XPS and AES recordings were made for a thin layer of the powdered sample using a VG Scientific ESCA-3 MK II spectrometer. Al Kα (1486.6 eV) radiation was used for the XPS measurements. All XP spectra were recorded under similar conditions (pass energy, 50 eV; entry slit, 4 mm; pressure, 10^{-9} Torr). The calibration was checked by determining the binding energy of Au $4f_{7/2}$ (84 eV). The instrumental resolution obtainable for the Au $4f_{7/2}$ level was 1.6 eV (full width at half-maximum).

3. Results and discussion

The physicochemical characteristics of the 5 at.% Sb system together with the values of kinetic parameters for the oxidative dehydrogenation of isopropyl alcohol in the presence of gaseous oxygen are given in Table 1, together with representative values for other compositions (12, 20, 50 and 80 at.% Sb). It is generally believed that antimony oxide is soluble in the tin oxide lattice up to 4 at.% Sb. It is postulated that the actual oxidation catalyst consists of an oriented film of Sb_2O_4 supported by an Sb^{5+}–SnO_2 solid solution [8]. Our observation that almost all systems containing varying amounts of antimony showed the same activity (Table 1) is evidence for this postulate.

TABLE 1

Physicochemical characteristics and catalytic activity of Sn–Sb mixed oxide catalyst systems

| Sb content (at.%)	Specific surface area $(m^2 g^{-1})$	Phases in fresh catalysts	Conductivity at 380 °C $(\Omega^{-1} cm^{-1})$	Rate of acetone formation at 400 °C $(\times 10^5 mol$ $min^{-1} m^{-2})$	Selectivity for acetone at 400 °C (mol.%)
5	8.2	SnO_2	4.6×10^{-2}	3.9	85.0
12	10.5	SnO_2	0.9×10^{-2}	3.5	84.8
20	8.3	SnO_2	0.7×10^{-2}	3.2	80.9
50	5.5	SnO_2 + Sb_2O_4	0.7×10^{-2}	3.2	82.5
80	3.2	SnO_2 + Sb_2O_4	1.7×10^{-5}	3.7	78.5

The XPS peaks obtained with the fresh catalyst, after reaction with isopropyl alcohol in the presence of gaseous oxygen and after activation, are shown in Fig. 1. The relative proportions of tin and antimony were derived from the XPS line intensities of the Sb $3d_{3/2}$ and Sn $3d_{5/2}$ signals (Table 2).

The shape of the Sb $3d_{3/2}$ XPS peak has been considered as indicating the nature of the antimony species on the surface. The asymmetry parameters given in Table 2 show that the observed Sb $3d_{3/2}$ peak may result from the overlap of two peaks, for binding energies of 540.2 eV and about 539.4 eV. The binding energies of antimony in Sb_2O_3 and Sb_2O_5 referenced to E(C 1s) = 285 eV are 539.4 eV and 540.3 eV respectively [9, 10]. The values of separation between the Sn $3d_{5/2}$ and Sb $3d_{3/2}$ levels, given in Table 2, show that tin does not undergo any change from SnO_2 and therefore the assignment of Sn $3d_{5/2}$ (486.5 eV) can be used as an internal reference. Boudeville et al. [4] assign the two XPS peaks to antimony(V) in the SnO_2 matrix (solid solution) and Sb_2O_4. The data given in Table 2 show that in the case of the activated catalyst the antimony content at the surface is slightly greater than that observed on both the fresh catalyst and the used catalyst.

Cox et al. [11] have made a detailed study of tin oxide doped with 3 at.% Sb (calcined at 1300 K for several days) and they concluded that antimony is enriched on the surface to the extent of 25 at.% and that this enrichment is confined to the surface layer on the basis of the intensity ratio of the 3d and 4d XPS peaks and its kinetic energy dependence. They have substantiated this result by high resolution electron energy loss spectroscopy and UV photoelectron spectroscopy measurements which showed that there is no increase in free-carrier concentration at the surface resulting from this segregation. In the present case we observed surface enrichment by a factor of about 1.5 as a result of activation, the increase not being as high as that reported by Cox et al. (who gave a factor of 8). This difference may be due
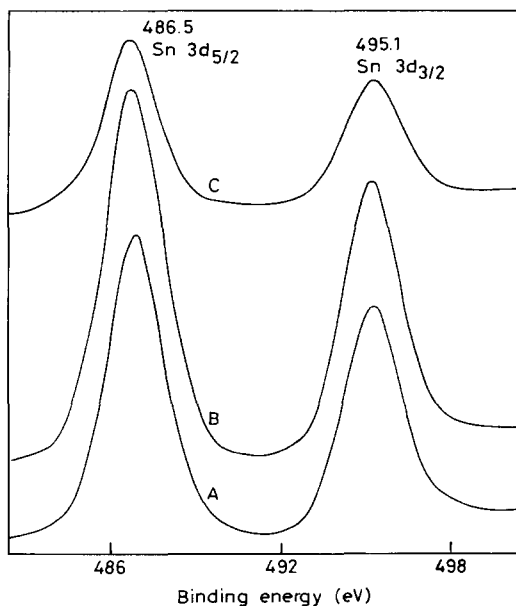
(a)
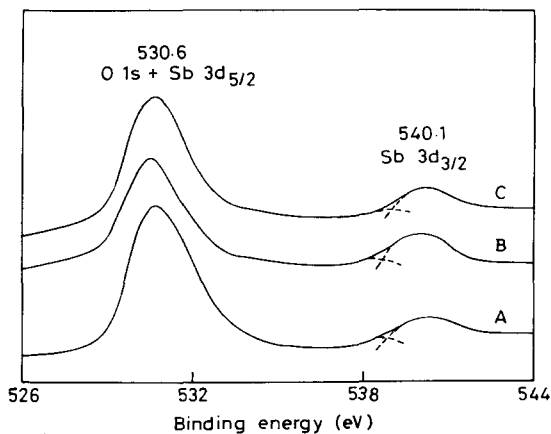
(b)

Fig. 1. X-ray photoelectron spectra of the Sn–Sb mixed oxide catalyst with 5 at.% Sb: curve A, fresh catalyst; curve B, catalyst after reaction with isopropyl alcohol at 400 °C in the presence of gaseous oxygen ([isopropyl alcohol]:[oxygen] = 2:1 (molar ratio); reaction time, 1 h); curve C, catalyst activated by passing air over it at 460 °C for 5 h.

to the high temperature of activation used by Cox *et al.* [11]. It is known that surface enrichment is dependent on the temperature of calcination [4, 5]. The surface segregation appears to be promoted by oxygen in the gas phase as well as being dependent on the nature of the antimony species. Activation with air after the catalyst had been used in reaction resulted in higher segregation compared with that obtained after calcination of the fresh catalyst.

TABLE 2

Characteristic parameters from XPS results

Sample	Sb $3d_{3/2}$ XPS peak			$E(Sb\ 3d_{3/2}) - E(Sn\ 3d_{5/2})$ (eV)	$\dfrac{[Sb]}{[Sb] + [Sn]}$ (%) [a]
	Binding energy (eV)	γ (eV)	Asymmetry		
A	540.1	2.3	1.40	53.6	3.23
B	539.9	2.2	1.09	53.4	3.34
C	540.2	2.1	1.00	53.7	4.97

γ is the linewidth at half-height and the asymmetry parameter is the ratio γ_1/γ_2 [4].
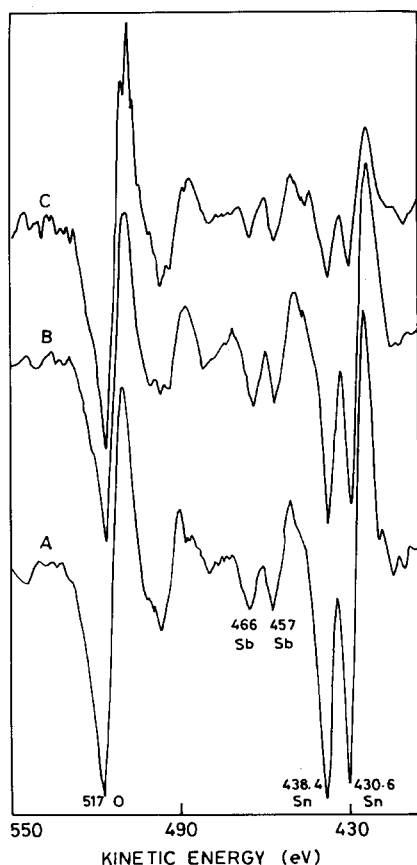[a]From the 3d lines in the X-ray photoelectron spectrum.

Fig. 2. Auger spectra of Sn–Sb mixed oxide catalyst with 5 at.% Sb. Curves A, B and C correspond to the catalysts described in the caption to Fig. 1.

Following the assignment of Boudeville *et al.* [4] the present catalyst can be assumed to contain antimony(V) in solid solution with SnO_2, in addition to the Sb_2O_4 phase. The Sb_2O_4 is presumably in a mixed valence state

compound, *i.e.* $1/2(Sb_2O_3 \cdot Sb_2O_5)$, with an overall oxidation state intermediate between antimony(III) and antimony(V). If all the antimony were present as Sb_2O_4 alone the linewidth would be about 1.7 - 1.9 eV, but when antimony(V) ions are also present the peak becomes asymmetric with a broader linewidth of up to 2.3 eV. The data given in Table 2, together with the linewidths of 2.1 - 2.3 eV, favour the formation of antimony(V) in solid solution of SnO_2 in addition to the Sb_2O_4 phase, consistent with the low (5 at.%) antimony content in the catalyst. However, this contention has to be considered with caution since the Sb $3d_{3/2}$ peak is very small and there may be considerable error in the calculation of the asymmetry factor.

The antimony $M_5N_{4,5}N_{4,5}$ and $M_4N_{4,5}N_{4,5}$ Auger spectra of the three samples have also been recorded to substantiate the above deductions. These results are shown in Fig. 2 together with those of the tin lines. From the sharper $M_4N_{4,5}N_{4,5}$ peak one can distinguish the antimony(III) species (usually at 458.7 eV) from the antimony(V) species at 457.8 eV. The fresh catalyst system seems to contain both antimony(III) and antimony(V) while the surface concentration of antimony(V) is increased in the activated catalyst, resulting in a sharper $M_4N_{4,5}N_{4,5}$ peak at lower kinetic energy (456.4 eV). However, the AES peaks due to tin do not change their position (438.4 eV and 430.6 eV), indicating that the oxidation state of the tin is not altered as a result of activation or reaction. However, the reduction in intensity of peaks due to tin species is in accord with the XPS results. The surface segregation of antimony is promoted by the catalytic reaction itself, although the effect is more pronounced as a result of activation.

Acknowledgment

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