Antimony-121 Mössbauer Investigations of Tin–Antimony Oxides

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Catalytically active tin–antimony oxides have been investigated by ^{121}Sb Mössbauer spectroscopy. Materials prepared by coprecipitation and dehydrated at 600 °C for 16 h give single-phased blue solids containing both Sb^{III} and Sb^{V} in oxygen environments. Materials containing more than 20% antimony and heated for longer periods or at higher temperatures give the segregation of an additional antimony oxide phase. Samples with an antimony concentration of less than *ca.* 10% contain Sb^{V} within the tin(IV) oxide rutile lattice. Although the Mössbauer spectra provide evidence for an increase in *s*-electron density at both tin and antimony nuclei, the data give no indication of any reduction processes leading to the formation of either Sn^{II} or Sb^{III}. A mechanism for charge compensation is proposed which involves the delocalization of electrons into a conduction band. The reaction of the tin–antimony oxides with hydrogen and the use of the material in the catalytic oxidation of olefins is accompanied by the reduction of Sb^{V} to Sb^{III}.

ALTHOUGH tin–antimony oxides have been commercially developed as catalysts for the selective oxidation and ammoxidation (reaction with NH_3 and O_2) of olefins, surprisingly little has been established about the nature of the materials, and the mechanisms of the catalytic process. Similar uncertainty is associated with the relationship between the physical and chemical properties of the catalyst and the catalytic character.

The importance of Mössbauer spectroscopy to the investigations of this catalyst is vested in the amenability of both tin and antimony to Mössbauer examination and the ability of the technique to probe features of catalytic relevance such as the phase composition, the cationic oxidation states, the environments of the cations, the charge-compensation mechanism, and the distortion of the host tin(IV) oxide lattice by the dopant antimony atoms. Although a few Mössbauer studies [1-3] of rutile-type materials have included tin–antimony oxides, the inconsistencies in data reflect the need for systematic investigations of materials of known compositions when prepared by well defined methods under controlled conditions. It was for these reasons that an initial tin-119 Mössbauer investigation of a series of tin–antimony oxides prepared by coprecipitation techniques and calcined at 600 °C was carried out in 1978.[4] The results showed that materials containing less than *ca.* 10% antimony formed solid solutions for which the Mössbauer parameters steadily departed from those of tin(IV) oxide. However, the replacement of tin by antimony in the slightly distorted rutile-type lattice gave no evidence for the reduction of tin(IV). Materials containing larger amounts of antimony appeared to contain an additional phase.

Since this work was reported some other investigations by *X*-ray diffraction,[5] optical and electron microscopy,[5] and *X*-ray photoelectron spectroscopy [6,7] have provided more detailed descriptions of the crystal chemistry, bulk structure, and surface compositions of tin–antimony oxides prepared by similar methods. However, the oxidation states of antimony, the environments of the cationic species, and the mechanism by which charge balance is maintained are still matters of considerable uncertainty. It was therefore considered appropriate that the tin–antimony oxide system should be examined by antimony-121 Mössbauer spectroscopy and the results considered in the light of the new information.

EXPERIMENTAL

Tin–antimony oxides of the type $Sn_{1-x}Sb_xO_2$ (x = 0.02—0.65) were prepared by coprecipitation from the simultaneous addition of anhydrous tin(IV) chloride and antimony(V) chloride to ammonium hydroxide solution. The white precipitates were filtered off, washed, and dried at 120 °C. They were then ground to constant particle size and heated according to the conditions in Table 1. The composition of the oxides was determined by wet chemical techniques and by *X*-ray fluorescence spectroscopy.

Samples in which $x = 0.20$ were treated with a hydrogen–nitrogen (10 : 90) gas mixture at 480 °C. The changes in weight showed the extent of reduction to depend on the period of reaction and to give materials reduced by 5.4, 10.3, and 30.2%. Samples in which $x = 0.02$ or 0.20 were also treated with a butene–oxygen–nitrogen (5 : 10 : 85) gas mixture at 400 °C.

Transmission-mode antimony-121 Mössbauer spectra were recorded with a constant-acceleration, 256-channel, microprocessor-controlled spectrometer [8] using a 1-mCi $Ca^{121}SnO_3$ source with both source and absorber at 77 K. The samples containing *ca.* 10 mg cm^{-2} of natural antimony were mixed with powdered Polythene and compressed into discs (diameter 1.6 cm, thickness 0.3 cm). All the spectra were least-squares fitted to two Lorentzian peaks to account for the possible presence of both antimony(V) and antimony(III) species. In some cases the data could be fitted to only one antimony(V) peak. All the data were subsequently fitted to sets of eight lines as would be produced by quadrupole splitting in the $\frac{7}{2}\rightarrow\frac{5}{2}$ nuclear transition of antimony-121. The asymmetry parameter was taken as zero [9] and a ratio of 1.34 : 1 was adopted for the quadrupole moments of the excited and ground states.[10] These assumptions produced acceptable fitting of the data and the possibility of a large asymmetry parameter was discounted. Only in some cases did the data show an improvement in χ^2 and other Mössbauer parameters when fitted according to the quadrupole-split model and in these cases the appropriate parameters are recorded in Tables 1 and 2. Typical spectra are depicted in the Figure.

RESULTS AND DISCUSSION

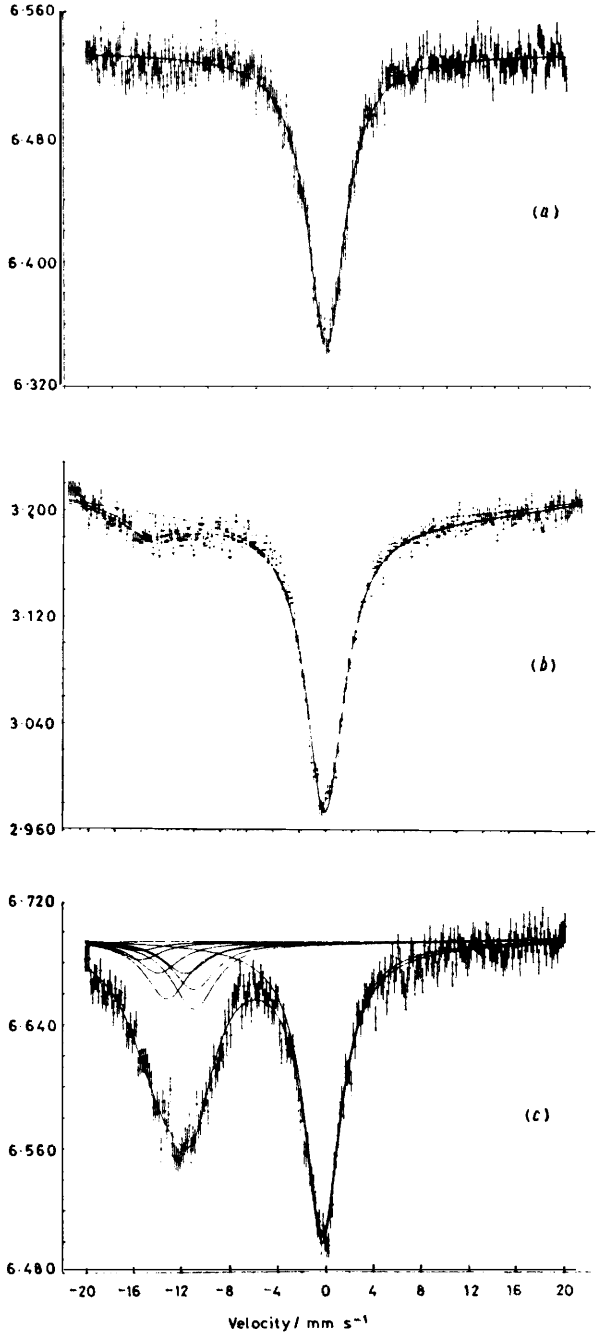
(*i*) *Tin–Antimony Oxides.*—The ^{121}Sb Mössbauer parameters of tin–antimony oxides are characteristic of antimony-(v) and -(III) species in oxide environments. The chemical isomer-shift data for antimony(v) are more negative than the values observed for Sb_2O_4 [11,12] and show a general resemblance to those recorded [13,14] for other antimony compounds with a rutile-type structure and which contain Sb^VO_6 octahedral units. The antimony(III) isomer shifts are more similar to that observed for Sb_2O_4 than other antimony oxides containing both antimony-(III) and -(v) species.[11,12]

The linewidths of the resonance peaks, especially those for materials calcined at 600 °C for 16 h, are broader ($\Gamma > 3.55$ mm s^{-1}) than expected for thin single-line antimony absorbers. The general resistance of the data to improvement when fitted to sets of eight lines suggests that short-period calcination at 600 °C produces dehydrated materials containing antimony-(III) and -(v) species in a heterogeneity of surroundings which differ only in the nature of the immediate oxygen environment. The $Sb^{III} : Sb^V$ peak-area ratio decreases with decreasing antimony concentration.

Oxides in which x = 0.20—0.65. *X*-Ray diffraction investigations [6] have shown that materials calcined at 600 °C for 16 h give single-phase rutile-type materials which, when $x > 0.20$ and heated for longer periods or at higher temperatures, give the separation of a second phase.

Materials in which $x = 0.65$ and calcined either at 600 °C for 14 d or 900 °C for 16 h are the only pure mixed oxides to give a significant improvement in χ^2 when the antimony(III) data are fitted to eight lines. The peak-area ratio for the sample calcined at higher temperature suggests that the spectrally dominating additional phase is Sb_2O_4 whilst that formed by prolonged heating at 600 °C is more characteristic of Sb_6O_{13}. The sample containing 65% antimony which was subjected to calcination at 600 °C for only 16 h gave a peak-area ratio which was more similar to that of Sb_6O_{13} than Sb_2O_4. Samples in which $x = 0.40$, despite different calcination conditions, give similar Mössbauer spectra which suggest the occupation by antimony of similar environments. It seems that the additional antimony oxide phase in these materials is insufficient to dominate the spectra. The Mössbauer parameters of materials in which $x = 0.20$ show that calcination for 16 h produces both antinomy-(III) and -(v) species in a ratio similar to the material containing 40% antimony, whereas longer calcination gives a sample showing only an antimony(v) contribution.

The Mössbauer parameters for materials containing between 20 and 65% antimony may be related to the preparative procedure. The white precipitates formed in alkaline media, which have been shown by earlier Mössbauer studies [12,15] to contain hydrated tin(IV) and antimony(v) species, are dehydrated when heated to 600 °C for 16 h and form blue solids. The Mössbauer spectra are consistent with the dehydration process causing reduction of antimony(v) as is observed during the pyrolysis of antimonic acid [12] and the transformation of tin(IV) hydroxide gel to tin(IV) oxide.[15] The coexistence of random arrays of such units in a non-



Antimony-121 Mössbauer spectra of $Sn_{0.80}Sb_{0.20}O_2$: (*a*) calcined for 14 d at 600 °C in a sealed tube; (*b*) calcined for 16 h at 600 °C; and (*c*) reacted with hydrogen–nitrogen (10 : 90) gas mixture at 480 °C crystalline solid is compatible with their description [6] as poorly crystalline, highly defective, rutile solids.

Despite the confusion in the literature [16-18] over materials in which tin and antimony are in roughly equal proportions, there is little evidence for compound formation below 900 °C and the Mössbauer data confirm that bulk equilibrium is difficult to establish by short-period calcination at low temperatures. The second phase formed by prolonged heating at 600 °C or short-period calcination at higher temperatures has the characteristics of an antimony oxide containing both antimony-(III) and -(V).

The blue colour of tin–antimony oxides heated at 600 °C resembles that observed in the alkali-metal antimony halides which has been attributed [19] to a Sb^{3+}–Sb^{5+} charge-transfer process. The close co-existence of these species in similar sites as is suggested by the Mössbauer data could readily be achieved in tin–antimony oxides with the compositions described above when heated at 600 °C for 16 h. Although some coloured oxide phases containing tin have been reported, there is an apparent absence [20] of any dark blue solids for which a Sn^{2+}–Sn^{4+} mechanism has been proposed.

TABLE 1

Antimony-121 Mössbauer parameters of tin-antimony oxides ($Sn_{1-x}Sb_xO_2$)

		Sb^V		Sb^{III}			
x	Treatment	δ/mm s^{-1}	Γ/mm s^{-1}	δ/mm s^{-1}	Γ/mm s^{-1}	e^2qQ/ mm s^{-1}	Area ratio Sb^{III} : Sb^V
0.03	20 d, 1 000 °C	8.228(116)	3.24(44)				
0.10	16 h, 600 °C	8.240(60)	3.92(24)				
	14 d, 600 °C, sealed tube	8.351(60)	3.16(30)				
0.20	16 h, 600 °C	8.464(34)	3.55(14)	−4.50(50)	5.17(140)		0.14(3)
	14 d, 600 °C, sealed tube	8.440(52)	3.96(22)				
0.40	16 h, 600 °C	8.384(56)	4.39(20)	−5.18(54)	5.99(140)		0.16(3)
	14 d, 600 °C, sealed tube	8.564(40)	3.93(16)	−5.38(22)	4.80(70)		0.15(2)
0.65	16 h, 600 °C	8.655(34)	3.94(14)	−5.06(76)	5.72(76)		0.27(2)
	14 d, 600 °C, sealed tube	8.704(32)	3.74(12)	−5.76(180)	2.62(64)	14.1(50)	0.21(2)
	16 h, 900 °C	8.860(54)	3.48(22)	−5.44(10)	2.87(34)	13.7(3)	0.87(5)

δ is relative to InSb; the standard deviations are in units of the last decimal place and correspond to 95% confidence limits.

Oxides in which $x < 0.20$. The ^{121}Sb Mössbauer parameters for materials within this range of compositions show only an antimony(V) contribution to the spectra and when subjected to prolonged or high-temperature calcination give linewidths which are smaller ($\Gamma < 3.24$ mm s^{-1}) than those reported for antimony compounds with a lead antimonate structure.[13] Such Mössbauer parameters might be expected from single-phased rutile-type materials in which the antimony(V) species occupies a unique site within an octahedral array of oxygen atoms.

Given that the metal–oxygen distances in SnO_2, Sb_6O_{13}, and Sb_2O_4 are all similar [12,21] it might reasonably be expected that any replacement of tin atoms in the tin(IV) oxide rutile lattice by antimony would be most likely to occur in materials containing a low concentration of antimony. Although the upper limit of antimony solubility has been defined as high as 20%,[18] other descriptions [16,22] have suggested a lower limit and the ^{121}Sb Mössbauer data reported here are consistent with the recent X-ray diffraction [6] and ^{119}Sn Mössbauer evidence for a limit of *ca.* 10%. Within this composition range charge balance could be achieved by either the reduction of tin(IV) or antimony(V). Since ^{119}Sn Mössbauer spectroscopy [4] has shown no evidence for the replacement of three tin(IV) atoms by two antimony(V) and one tin(II) it might reasonably be expected that the process involves the replacement of two tin(IV) atoms by one antimony(V) and one antimony(III). It might also be envisaged that the replacement would involve either substitution into the lattice or the occupation of interstitial octahedral sites. It is known however that antimony(III) like tin(II) has a lone pair of electrons and rarely adopts octahedral co-ordination.[23] In this respect it is significant that the lattice parameters of antimony-doped tin(IV) oxides are similar to those of pure tin(IV) oxide [5] and are therefore inconsistent with the accommodation of species with lone pairs of electrons within the lattice. Although the surface segregation of antimony at high temperatures could in principle provide more favourable antimony(III) sites without affecting the lattice parameters, the X-ray photoelectron investigations [6,7] have not identified such superficial species. The ^{121}Sb Mössbauer parameters of monophasic rutile-type tin–antimony oxides containing low concentrations of antimony and calcined for long periods at temperatures exceeding 600 °C do not provide evidence for the accommodation of antimony(III) within the lattice, at the surface or at crystal defects, and are therefore unable to confirm the expected reduction of antimony(III).

The Mössbauer parameters must therefore be considered in terms of the formation of the mixed oxide without reduction of either antimony(V) or tin(IV). Closer examination of the antimony(V) chemical isomer shifts, especially those of materials calcined for long periods or at high temperatures, shows that they decrease relative to the value reported for Sb_2O_4 (δ *ca.* 8.7 mm s^{-1}) [11,12] as the antimony concentration in the tin–antimony oxide decreases. It appears therefore that the *s*-electron density at the antimony nucleus is highest when the antimony concentration is between 3 and 10% and thereby complements the ^{119}Sn Mössbauer data[4] which showed the gradual accumulation of electron density over the tin-containing species as the antimony content approached *ca.* 10%. It therefore seems that the formation of monophasic materials containing antimony within the tin(IV) oxide lattice is restricted to those materials in which the antimony content is less than *ca.* 10% and when heated at temperatures exceeding 600 °C for long periods. It also appears that within this composition range charge balance is maintained by the delocalization of electrons into a low-energy conduction band composed largely of 5*s* orbitals by a similar mechanism to that which has been used to account for the low ^{119}Sn Mössbauer chemical isomer shifts and conduction properties in coloured caesium tin(II) bromides.[24–27] Such a process conforms with the band structure[28–30] of tin(IV) oxide which has been used[31] to account for the increasing[16,22] *n*-type semiconductivity of the material which reaches a reported maximum on addition of 3% antimony.[22]

TABLE 2

Tin-119 and ^{121}Sb Mössbauer parameters of tin-antimony oxides ($Sn_{1-x}Sb_xO_2$) following reaction with hydrogen and olefins

		Sn		Sb^{V}		Sb^{III}			
x	Treatment	δ[a] ± 0.03 mm s^{-1}	$\Delta \pm 0.03$ mm s^{-1}	δ/[b] mm s^{-1}	Γ/ mm s^{-1}	δ/[b] mm s^{-1}	Γ/ mm s^{-1}	e^2qQ/ mm s^{-1}	Area ratio Sb^{III} : Sb^{V}
0.20	14 d, 600 °C, sealed tube	0.15	0.75	8.440(52)	3.96(22)				
	Reduced by 5.4% by H_2	0.18	0.72	8.195(52)	3.64(20)	−4.11(40)	3.52(88)	16.2(12)	0.51(6)
	Reduced by 10.3% by H_2	0.18	0.69	8.261(56)	3.68(22)	−4.01(20)	4.37(54)	15.1(6)	1.28(6)
	Reduced by 30.2% by H_2	0.11	0.66	8.093(96)	4.00(40)	−3.20(46)	2.97(40)	6.0(12)	1.39(8)
	Treated with butene and O_2	0.04	0.67	8.577(15)	3.60(60)	−4.73(40)	3.90(40)	15.70(40)	0.38(2)
0.03	20 d, 1 000 °C	0.05	0.66	8.228(116)	3.24(44)				
0.02	Treated with butene and O_2	−0.05	0.56	8.10(70)	3.85(30)				

Standard deviations as in Table 1.

[a] Relative to SnO_2. [b] Relative to InSb.

The sample containing 3% antimony and calcined at 1 000 °C for 20 d gives the most negative antimony(V) chemical isomer shift (δ 8.228 mm s^{-1}) and corresponds with the highest *s*-electron density at the antimony(V) nucleus. The optimized specific activity for butadiene formation[32] of this equilibrated rutile-type material has been linked with the maximum surface enrichment of antimony ions which occurs without the separation of free Sb_2O_4. It is possible that the deep blue colour change in these materials at 400 °C which has been correlated[6] with the beginning of surface enrichment is connected with the delocalization of electrons into the conductance band and the formation of solid solutions.

(*ii*) *Reactions of Tin–Antimony Oxides with Hydrogen and Olefins*.—The ^{121}Sb Mössbauer spectra (Table 2) show that the reaction of tin–antimony oxides with hydrogen involves the reduction of antimony(V) to antimony(III). It is interesting that ^{119}Sn Mössbauer measurements give no evidence for the formation of tin(II). The decrease in ^{119}Sn quadrupole splitting with increased reduction is consistent with the reduction of antimony causing an attenuation of the electric field gradient at the tin nuclei.

The Mössbauer spectra of the two-phase tin–antimony oxide containing 20% antimony following its use as a catalyst for the oxidation of butene show that antimony(V) is reduced to antimony(III). Hence the reaction may be associated with either the reduction of antimony in the rutile phase or the reduction of Sb_6O_{13} or Sb_2O_4 to antimony(III) oxide. The material containing 2% antimony is quite different since it represents a monophasic substance containing antimony in the tin(IV) oxide lattice. The ^{119}Sn Mössbauer parameters of this material following its use in the catalytic process decrease to values which resemble those of pure tin(IV) oxide and are, by analogy with the materials treated with hydrogen, consistent with the reduction of antimony(V) within the rutile lattice to antimony(III). The ^{121}Sb Mössbauer spectra give no evidence for the formation of antimony(III) but this absence may reflect the low sensitivity of the technique to the detection of such a low concentration of the species.

The problem remains however as to where the antimony(III) species could be accommodated. It is interesting in this respect that microscopic investigations of antimony-doped tin(IV) oxide[5] have found evidence for the presence of twin boundaries. Since twinning is a means of slightly changing the anion to cation stoicheiometry of a crystal and providing sites with different co-ordination, it is possible that the small concentrations of antimony(III) formed by reduction of antimony(V) could segregate to the twin boundaries and thereby enjoy more favourable sites.

The failure of Mössbauer spectroscopy to identify any reduction of tin(IV) to tin(II) and the proposed reduction of antimony(V) to antimony(III) during the catalytic reaction may be correlated with mechanisms which have been proposed for chemisorption and catalytic reactions of olefins on tin–antimony oxides which have involved partial reduction of antimony(V) to antimony(III) and the formation of a π-allyl intermediate species.[16,33]

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