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A Mössbauer Investigation of the Formation and Surface Composition of Tin–Antimony Oxide Catalysts

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The formation and surface composition of catalytically active tin–antimony oxides prepared by the calcination of precipitates have been investigated by Mössbauer spectroscopy. The initial amorphous white gel containing Sn(IV) and Sb(V) is dehydrated by calcination in air at 600°C to give blue poorly crystalline solids in which some Sb(V) is reduced to Sb(III). The occupation by these species of similar octahedral oxygen environments is associated with thermally induced lattice reconstruction and an electron charge transfer process. Prolonged heating at 600°C and higher-temperature calcination induce the incorporation of antimony into tin(IV) oxide and the segregation of a superficial antimony oxide phase. Calcination at 1000°C in air is accompanied by oxygen evolution and antimony migration which results in the formation of a rutile-type solid solution of Sb(V) in tin (IV) oxide with a surface enriched in Sb(III). No evidence is found for solid solution formation at low temperatures. Charge balance within the solid solution is achieved by the delocalisation of electrons into conduction bands. The potential relevance of tin–antimony interactions and of Sn(IV) and Sb(III) surface species is discussed in terms of the catalytic properties of tin–antimony oxides for the oxidation of olefins.

INTRODUCTION

Tin–antimony oxide catalysts for the selective oxidation and ammoxidation of olefins have often been prepared by the calcination of precipitates at ca. 600°C. Earlier Mössbauer investigations examined the nature of such materials (*1*, *2*) but two independent groups have recently studied the structural properties of tin–antimony oxides calcined over a range of temperatures (*3*, *4*). Although both groups have associated the formation of a separate antimony oxide phase with high-temperature calcination (*5*, *6*) no agreement has been reached as to the limit of antimony solubility in tin(IV) oxide and the conditions under which a solid solution may be formed. There is a similar lack of unanimity within the literature concerning the nature of the cationic oxidation states in the solid solution and the importance of this and other related phases to the catalytic performance (*3*, *4*, *6–12*). It is not surprising therefore that the active sites in the catalytic material are ill defined. Given the necessity of calcination for the formation of catalytic properties in tin–antimony oxides and the sensitivity of Mössbauer spectroscopy to changes in the chemical environment and the oxidation states of the cations, a study has been conducted to monitor the changes which occur during the thermal treatment and the conditions under which solid solutions are formed. Since significant importance has been attributed to the catalytic properties of the solid solution (*8*, *12*), special attention has been given to the nature of the cationic species and their environments within the bulk and at the surface of this phase and to the mechanism of charge balance. An attempt has also been made to elucidate the likely role of the cationic species in the catalytic process.

EXPERIMENTAL

Tin–antimony oxides of composition $Sn_{1-x}Sb_xO_2$ were prepared by methods reported earlier (*1*, *2*) and after drying at 120°C were heated according to the conditions described in Tables 1 and 2.

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^{119}Sn and ^{121}Sb Mössbauer spectra were recorded and computed as previously described (*1, 2*).

ESR spectra were recorded with a Hilger and Watts X-band spectrometer operating at 9.4 GHz. The spectra were recorded at 298 K and g values were measured relative to DPPH (diphenylpicrylhydrazyl, g = 2.0036).

RESULTS AND DISCUSSION

Structural and chemical aspects of calcination and the formation of solid solutions

The ^{119}Sn and ^{121}Sb Mössbauer spectra of the white precipitate containing 10% Sb and dried in air at room temperature show broad single peaks characteristic of Sn(IV) and Sb(V) and are similar to those reported for hydrolysed tin(IV) chloride (*13*) and antimony(V) chloride (*14*). The results are consistent with an amorphous (*3*) precipitate containing a random assembly of hydrogen-bonded Sn(IV)– and Sb(V)–hydroxyl octahedra.

The ^{119}Sn and ^{121}Sb Mössbauer parameters for the calcined tin–antimony oxides are recorded in Tables 1 and 2.

White tin–antimony oxides calcined at 300°C give quadrupole-split ^{119}Sn Mössbauer spectra which are independent ($\delta \sim 0.05$ mm s^{-1}; $\Delta \sim 0.72$ mm s^{-1}) of antimony concentration. The larger quadrupole splittings compared with that of a tin(IV) hydroxide gel dehydrated at 300°C indicate an increase in the electric field gradient at the tin nuclei arising from the presence of antimony cations. The ^{121}Sb Mössbauer spectrum of the material containing 4% antimony shows only an Sb(V) resonance whilst the solid containing 20% Sb contains some Sb(III) which presumably results from the reduction of Sb(V) as occurs during the dehydration of an antimony(V) hydroxide gel (*14*). Dehydration in these materials is incomplete (*3*) at 300°C and studies by X-ray photoelectron spectros-

TABLE 1

Tin-119 Mössbauer Parameters for Tin–Antimony Oxides ($Sn_{1-x}Sb_xO_2$)

x	Calcined 300°C for 16 h		Calcined 600°C for 16 h[b]		Calcined 800°C for 16 h	
	$\delta^a \pm 0.03$ (mm s^{-1})	$\Delta \pm 0.03$ (mm s^{-1})	$\delta^a \pm 0.03$ (mm s^{-1})	$\Delta \pm 0.03$ (mm s^{-1})	$\delta^a \pm 0.03$ (mm s^{-1})	$\Delta \pm 0.03$ (mm s^{-1})
0.00	0.00	0.65	0.00	0.56	0.00	0.57
0.01	0.05	0.71	0.07	0.66	0.02	0.61
0.02			0.05	0.66	0.01	0.64
0.03	0.04	0.72	0.05	0.67	0.06	0.63
0.04	0.04	0.71	0.08	0.68	0.01	0.59
0.05	0.06	0.70	0.08	0.67	0.06	0.60
0.06			0.10	0.69	0.02	0.65
0.07	0.04	0.72	0.10	0.68	0.04	0.63
0.08			0.11	0.67	0.01	0.65
0.09	0.04	0.72			0.03	0.64
0.18			0.13	0.73		
0.20	0.06	0.73			0.08	0.62
0.30	0.03	0.74	0.13	0.75	0.06	0.64
0.50	0.04	0.75	0.12	0.74	0.01	0.60
0.75	0.08	0.73	0.08	0.75		

[a] δ relative to SnO_2.

[b] Previously depicted as a function of antimony concentration in Ref. (*1*).

TABLE 2

Antimony-121 Mössbauer Parameters for Tin–Antimony Oxides ($Sn_{1-x}Sb_xO_2$)

x	Calcination treatment	Temperature (K)	Sb(V)		Sb(III)			Area ratio Sb(III) : Sb(V)	Ref.
			$\delta^a \pm 0.1$ (mm s^{-1})	Γ (mm s^{-1})	$\delta^a \pm 0.1$ (mm s^{-1})	$e^2qQ \pm 0.05$ (mm s^{-1})	Γ (mm s^{-1})		
0.03	20 d, 1000°C, sealed tube	77	8.23	3.24					(*2*)
0.04	16 h, 300°C	4.2	8.66	3.98					(*15*)
0.04	16 h, 800°C	4.2	8.16	3.07	−7.04		4.77	0.04	(*15*)
0.10	5 d, 25°C	4.2	8.98	3.99					(*15*)
0.10	14 d, 600°C, sealed tube	77	8.35	3.16					(*2*)
0.10	16 h, 800°C	4.2	8.41	3.60	−5.38		5.40	0.16	(*15*)
0.20	16 h, 300°C	4.2	8.65	3.96	−4.58		4.65	0.13	(*15*)
0.20	16 h, 600°C	77	8.46	3.55	−4.50		5.17	0.14	(*2*)
0.20	14 d, 600°C, sealed tube	77	8.44	3.96					(*2*)
0.20	14 d, 1000°C	4.2	8.68	3.66	−6.41	17.80	3.48	0.95	(*15*)
0.40	16 h, 600°C	77	8.38	4.39	−5.18		5.99	0.16	(*2*)
0.40	14 d, 1000°C	4.2	8.84	4.50	−6.48	18.11	4.34	1.35	(*15*)
0.50	16 h, 800°C	4.2	8.74	4.64	−6.04	16.84	4.13	0.86	(*15*)
0.65	16 h, 600°C	77	8.65	3.94	−5.06		5.72	0.27	(*2*)
0.65	16 h, 900°C	77	8.86	3.48	−5.44	13.70	2.87	0.87	(*2*)

[a] δ relative to InSb.

copy (*5, 6*) show the surface antimony composition to resemble the nominal bulk value. Mild calcination therefore gives partially dehydrated amorphous materials containing random arrays of Sn(IV), Sb(V), and Sb(III) species in approximately octahedral oxygen–hydroxyl environments.

The first significant variation in Mössbauer data occurs in the completely dehydrated blue tin–antimony oxides calcined in air at 600°C (*1, 2*). The ^{119}Sn Mössbauer parameters steadily increase as the antimony concentration is increased to ca. 10% but give no evidence for the formation of tin(II). The ^{121}Sb Mössbauer spectra show that further addition of antimony gives materials containing both Sb(V) and Sb(III). The Mössbauer data and the slightly broadened linewidths are consistent with poorly crystalline solids (*3*) containing random arrays of cations in separate but similar octahedral oxygen environments (*13, 14,16–18*). Such structural properties could readily facilitate an Sb(V) : Sb(III) charge transfer process (*19*) and give rise to the blue colour which resembles that found in the mixed-valence alkali metal antimony halides (*20*). X-Ray photoelectron spectroscopy (*5, 6*) has shown little difference between the surface and bulk compositions and it seems that calcination induces lattice reconstruction similar to that associated with the dehydration of tin(IV) hydroxide (*13*) and the pyrolysis of antimonic acid (*14*). The changes which occur when tin–antimony oxides in which $x > 0.25$ are heated for long periods at 600°C have been related (*2, 3*) to the formation of biphasic materials containing rutile and antimony oxide phases.

The ^{119}Sn Mössbauer parameters for tin–antimony oxides calcined at 800°C are very similar ($\delta \sim 0.05$ mm s^{-1}; $\Delta \sim 0.60$ mm s^{-1}) over the whole range of antimony compositions with smaller quadrupole splittings than samples heated at lower temperatures. Materials calcined at 1000°C for 14 days in air give similar Mössbauer spectra ($\delta \sim 0.04$ mm s^{-1}; $\Delta \sim 0.61$ mm s^{-1}) irrespective of the initial antimony concentration. The attenuation of the electric field gradient at the tin nuclei may be attributed to a diminished antimony concentration in a rutile-type tin(IV) oxide phase as a result of the thermally induced aggregation of SnO_2 octahedra and countermigration of antimony (*3*) to the surface (*5, 6*). Furthermore, the quadrupole splittings are only slightly larger than those of tin(IV) oxide (*13*) ($\delta = 0.00$ mm s^{-1}; $\Delta = 0.56$ mm s^{-1}) and indicate that the replacement of tin atoms by antimony in the formation of a solid solution causes only a slight increase in the valence contribution to the electric field gradient at the neighbouring tin nuclei and only a slight increase in the distortion of the SnO_2 lattice. The ^{119}Sn Mössbauer parameters are therefore indicative of the incorporation of a small amount of antimony in the tin(IV) oxide lattice with the superficially segregated antimony forming a separate oxide phase. The ^{121}Sb Mössbauer data are consistent with this model. The spectra show the presence of both Sb(V) and Sb(III) in materials heated in air with the concentration of Sb(III) increasing at higher temperatures. Indeed, materials with a high antimony content at 800 or 900°C, i.e., below the temperature at which Sb_2O_4 is volatilised, give ^{121}Sb Mössbauer spectra for which the peak area ratio suggests the dominance of Sb_2O_4 and are illustrative of the sensitivity of the technique to the formation of small quantities of this material at the surface of the rutile phase. The Mössbauer data clearly dispute the contention (*8, 9*) that calcination enhances the solubility of antimony in tin (IV) oxide.

The similarity between the ^{119}Sn Mössbauer parameters for materials calcined at 600°C in which $x >$ ca. 0.10 and those for materials heated at 300°C is indicative of the barriers to bulk equilibrium. At 600°C the higher antimony content mitigates against SnO_2 aggregation, crystal growth, and antimony migration. However, the Mössbauer parameters of materials containing a low concentration of antimony calcined at 600°C do not resemble those of solids heated at higher temperatures which appear to be approaching bulk equilibrium. Hence the Mössbauer spectra suggest that materials containing up to 30% antimony need not be best described (*9*, *12*) as solid solutions and that the Sb(V) resonance in materials heated at 500°C (*4*) may not necessarily result from Sb(V) within the solid solution. It is quite reasonable that the Sb(V) resonance should be indicative of the co-existence of both Sb(V) and Sn(IV) oxygen octahedra within a homogeneous highly disordered matrix, and that the presence of Sb(III) in these materials in which $x > 0.10$ reflects reduction of Sb(V) as occurs during the pyrolysis of antimonic acid (*14*) rather than a charge-balancing process (*4*). The Mössbauer data are consistent with the model proposed by Pyke *et al.* (3) in which calcination induces structural changes in an initially homogeneous precipitated material and the segregation of excess antimony to the surface so as to occupy adjacent sites and form a separate Sb_2O_4 phase. Hence, calcination at 1000°C in air which causes volatilisation of the Sb_2O_4 phase would be expected to produce the authentic equilibrated rutile-type solid solution containing (*3*) ca. 4% antimony in the bulk with a surface enriched (*5*, *6*) to ca. 25% with antimony. Although there is no unanimity as to the exact solubility of antimony in tin(IV) oxide, and indeed another recent report (*21*) has proposed a limit of ca. 6–7% at 750°C, it does seem that the range of antimony concentrations which may lead to solid solution formation is much less than has previously been supposed.

The cationic states in the solid solutions. Although Sn(IV) is the only tin species in the solid solution, the presence of both Sb(V) and Sb(III) must be considered in terms of the antimony within the bulk and that which enriches the surfaces.

The tin–antimony oxide containing 4% antimony corresponds to the solid solution limit of antimony in tin(IV) oxide. The ^{121}Sb Mössbauer spectrum of the material calcined at 300°C in which bulk and surface compositions are comparable (*5*, *6*) shows only the presence of Sb(V) whereas calcination at 800°C in air during which surface enrichment occurs gives a material showing the presence of both Sb(V) and Sb(III). Equilibrated tin–antimony oxides formed by air calcination at 1000°C of precipitates with initially higher antimony compositions give the solid solutions showing a larger Sb(III) : Sb(V) ratio than the materials heated at lower temperatures and, although such data must be interpreted with care when an accurate structural description of the rutile-type solid solution has yet to appear, it is significant that the Sb(III) concentration in these equilibrated materials exceeds that of any other sample. Similarly, whilst recognising that the Sb(III) chemical isomer shifts are close to those of Sb_2O_4 and that considerable caution must be exercised when considering small differences in δ, especially when only some of the data are amenable to fitting according to a quadrupole-split model, it does appear that the Sb(III) chemical isomer shifts for materials calcined at high temperatures are more negative and the linewidths larger than those for Sb(III) in Sb_2O_4 and other tin–antimony oxides. The observation is quite reasonable given that Sb_2O_4 volatilises at such high temperatures and it is significant that these materials give Sb(III) resonances which are amenable to fitting according to a quadrupole-split model and that the materials calcined at 1000°C give the largest values for e^2qQ. The Mössbauer parameters therefore correspond to a higher s-electron density at the antimony nucleus, which might reflect excess p character in the lone pair, and the occupation of more asymmetric sites than those in antimony oxides (*14*, *16*). The reluctance (*22*) of Sb(III) with a lone pair of electrons to adopt octahedral coordination and the reported similarity (*3*) in lattice parameters between tin–antimony oxides and pure SnO_2 do not suggest that Sb(III) is readily accommodated within the tin(IV) oxide lattice. The formation of Sb(III) appears therefore to result from high-temperature crystallisation of the tin(IV) oxide lattice and the migration of antimony to the surface. Since Sb_2O_4 volatilises at 1000°C and given that X-ray diffraction (*3*), X-ray photoelectron spectroscopy (*5*), and the Mössbauer data reported here have been unable to identify any Sb_2O_4 in materials calcined at 1000°C, it seems unlikely that the Sb(III) signals arise from the presence of a discrete Sb_2O_4 phase. The Mössbauer data are more consistent with the occupation by Sb(III) of an asymmetric surface site in which the principal contribution to the electric field gradient arises from neighbouring Sn(IV) species.

The formation of superficial Sb(III) in these tin–antimony oxides may be associated with the loss of oxygen which accompanies high-temperature calcination (*3*). In this respect it is interesting that, although the ESR spectra of tin–antimony oxides containing large concentrations of antimony are consistent with electron conductors, the signals from materials containing small quantities of antimony have been attributed (*23*) to the trapping at anionic vacancies of electrons created by the substitution of low concentrations of Sb(V) into tin(IV) oxide. The loss of each molecule of oxygen could be envisaged as creating two O^{2-} vacancies and four electrons which reduce two Sb(V) species to Sb(III). The process is consistent with the failure of tin–antimony oxides in which $x < 0.20$ to give an ESR signal and show any Sb(III) in the Mössbauer spectrum following calcination in sealed tubes for long periods at 600°C or at higher temperatures. Given the observed sensitivity of the technique to low concentrations of Sb(III) in the material containing only 4% antimony, it seems that calcination in sealed tubes establishes a suitable pressure of oxygen to cause readsorption at the $O2^-$ vacancy and thereby preclude the formation of Sb(III). The effect resembles that recorded in the ESR spectra of ZnO (*24, 25*) and MgO (*26, 27*) upon adsorption of oxygen. The sensitivity of the equilibrium surface composition to the gas-phase oxygen pressure resembles effects observed in cobalt–iron oxides (*28, 29*).

Charge balance in the solid solution. The preservation of electrical neutrality in the solid solution phase might reasonably be expected to involve either the replacement of two Sn(IV) units by an Sb(V) and an Sb(III) or the replacement of three Sn(IV) units by two Sb(V) and one Sn(II). However, the Mössbauer spectra of the solid solutions formed in sealed tubes show only the presence of Sn(IV) and Sb(V). Close examination of the Sb(V) chemical isomer shift data show them to fall at the most negative end of the range normally expected for Sb(V) in oxide environments (*14, 16–18*) and correspond with higher *s*-electron densities at the Sb(V) nucleus. The ^{119}Sn Mössbauer chemical isomer shifts for these materials are slightly more positive than those for tin(IV) oxide and are also indicative of increasing *s*-electron density at the Sn(IV) nuclei.

The Mössbauer data therefore show an accumulation of electrons by the cations without reduction to Sb(III) or Sn(II) and are consistent with the maintenance of charge balance by the delocalisation of electrons into a low-energy conduction band. The mechanism is consistent with increasing *n*-type semiconductivity in these materials as compared with SnO_2 (*10, 21, 30, 31*) and resembles that which has been used to account for the ^{119}Sn Mössbauer chemical isomer shifts and conduction properties in caesium tin(II) bromides (*32–35*).

The active sites in the catalytic material. Although there is little unanimity concerning the nature of the active sites (*36, 37*) there appears to be a general belief that calcination is necessary to produce a catalyst with a high selectivity in oxidation reactions. Although this has frequently been associated with the formation of solid solutions (*8–12*) more recent studies (*6, 7*) have related the increasing specific activity for the oxidative dehydrogenation of butene to butadiene to the high concentration of antimony in the catalyst surface.

The Mössbauer evidence for the presence of Sn(IV), Sb(V), and Sb(III) may therefore be considered in terms of the likely nature of the active sites in the catalytic phase. Although, Sb_2O_4 itself is relatively inactive (*7, 8, 10, 12, 36*) it has been reported that volatilisation of the oxide at 1000°C gives materials with a high catalytic performance (*7*). The Mössbauer data are consistent with a model in which the active sites in the antimony-enriched surface are characterised by an isolated Sb(III) species surrounded entirely by Sn(IV) cations in nearest neighbour sites as would be formed in the solid solution at high temperature (*3*). It is interesting that such species have been designated as active sites with acid–base properties in mechanisms for the selective oxidation of olefins (*38*). Furthermore, a recent ^{13}C NMR study of the adsorption and isomerization of *n*-butenes on tin–antimony oxide (*39*) has suggested a model whereby an adsorbed cyclic complex-like intermediate, which is formed by proton rearrangement, is associated with adjacent acid–base sites on the catalyst surface as would be provided by neighbouring Sn(IV) and Sb(III) species. Although antimony has been observed (*5, 6*) at the surface of these catalysts, the Mössbauer data constitute the first evidence for the specific formation of Sb(III) at the surface and thereby provide support for the mechanisms cited. It is also interesting that materials calcined in oxygen give ESR signals, $g \sim 1.89$, which are similar to those observed (*23*) in the tin–antimony oxides calcined in air and which have been attributed to electrons trapped at anionic vacancies. Interestingly these materials show a high Sb(III) content which suggests that tin–antimony oxides calcined in oxygen continue to lose oxygen as occurs during the calcination of mixed vanadium–titanium oxides (*40*) and supports the contention that lattice oxygen is the participating species during hydrocarbon oxidation (*41–43*).

Although the Mössbauer spectra show that the solid solution contains Sn(IV) : Sb(III) pairs with the capacity to act as active sites it is also clear that these species may exist in the disordered relatively homogeneous noncrystalline solids containing larger amounts of antimony and formed at lower temperatures. However, these materials give smaller Sb(III) contributions to the Mössbauer spectra and, even in materials containing appropriate nominal concentrations of antimony, fail to enjoy as high a proporiton of superficial antimony ions as is achieved in the solid solution (*5, 6*). Interestingly there appears to be little evidence to support the catalytic superiority of these materials.

Finally, it must be acknowledged that the Mössbauer spectra do show that tin–antimony oxides calcined over a range of temperatures may accommodate other electron charge transfer processes such as Sb(V) : Sb(III) which could be relevant to the catalytic reaction. However, Sb_2O_4, which contains both Sb(V) and Sb(III), and the structurally related Sb_2O_4/TiO_2 system do not exhibit similar catalytic properties. Hence the Sn(IV) : Sb(III) interaction appears to be most significant. In this respect it is interesting that recent studies (*4, 6*) have proposed that surface segregation of antimony at temperatures below that of the volatility of Sb_2O_4 produces a catalyst composed of an Sb_2O_4 phase lying at the surface of a solid solution of Sb(V) in tin(IV) oxide and which, presumably, derives its catalytic potential from the interaction of the surface phase with the solid solution. Although the Mössbauer spectra do not give further illumination to this proposal the failure of mixtures of SnO_2 and Sb_2O_4 to produce active catalysts, together with the Mössbauer data reported here and the importance which others have recently attributed to a high surface concentration of antimony (*3, 5, 7*) in the catalyst, does suggest that a tin–antimony interaction is significant in the catalytic reaction. It also seems that tin assumes a fundamental role in the catalyst as well as functioning as a component in a matrix which is capable of supporting high concentrations of antimony in the necessary oxidation states and geometry.

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