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Tin-119 Mössbauer and ESR Investigations of the Tin–Antimony Oxide System

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Tin–antimony oxides of the type $Sn_{1-x}Sb_xO_2$ (x = *0.01–0.10) when calcined at 873K form solid solutions in which the Mössbauer parameters steadily depart from those of stannic oxide but provide no evidence for the formation of localised tin(II). Esr measurements indicate the presence of a spin free surface species. Above* x = *0.10 a two phase region exists in which the tin rich phase shows constant* ^{119}*Sn Mössbauer parameters.*

Introduction

Although the catalytic activity of tin–antimony oxides for the oxidation of olefinic compounds has been known for several years, relatively few details of the phase diagram for the system have been established.

The thermal decompositions of tin(IV) hydroxide [1] and antimonic acid [2] have both been investigated by Mössbauer spectroscopy. Stannic oxide formed at 873K gives a small quadrupole split Mössbauer spectrum [1] reflecting the slight tetragonal distortion of the rutile type octahedral array of oxygen atoms about the tin [3]. The pyrolysis of antimonic acid [2] shows that a compound with formula Sb_2O_5 cannot be reached without reduction of antimony(V) to antimony(III). The first product which forms between 923 and 1123 K is Sb_6O_{13} which transforms at 1208 K to β-Sb_2O_4. These oxides contain both antimony(V) and antimony(III). Complete reduction to Sb_2O_3 is not achieved below 1200 K.

Since the metal–oxygen distances in all these oxides are similar [2, 3], it might reasonably be expected that some degree of mixed oxide formation may occur by the replacement of two tin(IV) atoms in the stannic oxide rutile lattice by one antimony(V) and an antimony(III). X-ray diffraction studies [4, 5] of the mixed oxide have been unable to establish the precise phase composition of the system but materials in which $x \gg 0.10$ have shown evidence of the presence of a second phase.

Experimental

Tin–antimony oxides were prepared by co-precipitation from the chlorides and were calcined for 16 hours at either 573 or 873 K to give grey or blue solids.

The ^{119}Sn Mössbauer spectra were recorded at 77 K using a conventional constant acceleration spectrometer with a $Ca^{119m}SnO_3$ source and samples containing 10 mg Sn/cm^2. The drive velocity was calibrated with a ^{57}Co/Rh source and iron foil. All the ^{119}Sn Mössbauer spectra were computer fitted to both one and two Lorentzian lines.

Results

The ^{119}Sn Mössbauer data gave superior χ^2 values and linewidths closer to that of barium stannate when fitted to two lines. No statistically significant evidence of more complex spectra could be attained.

Discussion

The infrared spectra showed the absence of hydroxyl groups in the tin–antimony oxides calcined at 873 K. Figure 1 shows the chemical isomer shifts and quadrupole splittings as a function of composition for the material calcined at 873 K.

Both Mössbauer parameters clearly increase steadily over the range 1–10% antimony and then become constant. Since $\Delta R/R$ is positive for the ^{119}Sn transition [6, 7] the larger chemical isomer shifts represent increasing *s*-electron density at the tin nucleus. It is significant that the Mössbauer spectra provide no evidence for the formation of tin(II) species which we found to be easily recognisable when present in quantities above 2 mol%. The larger quadrupole splittings indicate increasing distortion of the environment about the tin nucleus with increasing antimony concentrations.

Clearly the character of the tin–antimony oxide changes when the antimony content exceeds about 10% and it seems that up to this point the samples may be envisaged as single phases in which antimony enters the stannic oxide rutile lattice. It is significant that the catalytic activity for oxidation of propylene

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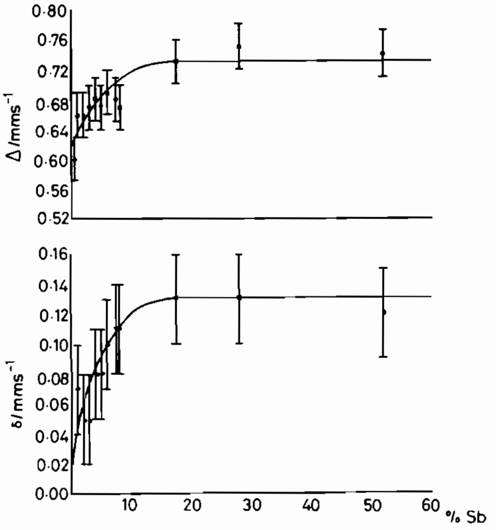

Figure 1. Tin-119 Mössbauer parameters as a function of antimony concentration.

to acrolin also increases over a similar range of antimony concentrations [8]. The ^{119}Sn Mössbauer spectra clearly show that within this range charge balance cannot be achieved by replacement of three tin(IV) units by two antimony(V) and one tin(II). Further, the small chemical isomer shift changes do not indicate the substitution of two tin(IV) atoms by antimony(V) and tin(III). The single more positive ^{119}Sn chemical isomer shifts found for the mixed oxide calcined at 873 K suggest that if charge compensation does involve the reduction of tin atoms then the extra electrons are delocalised in the tin containing phase and not localised on individual tin atoms. It is interesting to note that a model for the mixed tin–antimony oxide system involving conduction bands composed mainly of *5s* orbitals has been suggested [9] and the low ^{119}Sn Mössbauer chemical isomer shift for $CsSnBr_3$ has been explained [10, 11] in terms of delocalisation of tin *5s* electron density in a low energy conduction band.

It appears that when the mixed oxide contains a concentration of antimony in excess of 10% a two phase region begins in which the second phase, probably Sb_6O_{13}, does not contain any appreciable amount of tin.

It is also clear that the sensitivity of Mössbauer spectroscopy would be too low to reveal a spin free species such as tin(III) at typical defect concentrations. All the samples of the semiconducting tin–antimony oxide containing between 1 and 10% antimony gave an esr signal although the rather high electrical conductivity made it somewhat difficult to record. The *g* values of 1.88 and 1.90 are essentially identical to those reported for stannic oxide when reduced *in vacuo* [12–14]. The data have been interpreted in terms of interstitial sites occupied by Sn^{3+} or the presence of oxygen vacancies with one electron [12], and conduction electrons or un-ionized donor electrons [13, 14]. The absence of hyperfine interactions with ^{117}Sn or ^{119}Sn were conspicuous features of all the spectra.

The amplitude of the signal recorded during our investigations increased considerably when the samples were ground suggesting that the spectrum could be associated with surface species rather than bulk defects.

The Mössbauer and esr data are therefore compatible with a material in which charge balance in the interior of the crystals is achieved by delocalised electrons in a *5s* conduction band and at the surface by a localised spin free species. The presence of O_2^- originating from adsorbed oxygen [13] as the surface species could be important in the catalytic properties of the material.

The samples of the $Sn_{1-x}Sb_xO_2$ system (x = 0.005–0.75) calcined at 573 K gave quadrupole splittings which were quite different from that of stannic oxide (Δ 0.65 mm s^{-1}) prepared under similar conditions but which were very similar ($\delta \sim 0.05$ mm s^{-1}, $\Delta \sim 0.72$ mm s^{-1}) over the whole range of antimony concentrations and resembled those of the material calcined at 873 K in which $x > 0.08$. It seems that calcination at such a low temperature does not give a solid solution.

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