Tin–Molybdenum Oxides. A Study by *X*-Ray Diffraction, Mössbauer Spectroscopy, and Electron Spin Resonance

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The formation of tin–molybdenum oxides by the calcination of precipitates involves the initial dehydration of amorphous gels to give, at low temperatures, highly-disordered rutile-type solids capable of accommodating high concentrations of molybdenum. Excess molybdenum segregates, under the influence of moderate thermal treatment, from the crystallising rutile-type phase to form macroscopically distinguishable molybdenum(VI) oxide which volatilises at higher temperatures. Prolonged calcination at high temperature gives materials which may be described as solid solutions containing low concentrations of molybdenum(V) in the tin(IV) oxide rutile-type lattice.

Although some chemical and structural features of tin–molybdenum oxides prepared by the calcination of precipitates have been observed during investigations of their catalytic activity[1,2] the fundamental solid-state properties of the materials have not been subjected to detailed examination. In particular, the conditions under which solid solution formation occurs and the nature of such solid solutions remains a matter of considerable uncertainty. We have therefore prepared some tin–molybdenum oxides by precipitation techniques and have attempted to characterise the phases which may be formed following calcination at different temperatures.

Experimental

Tin–molybdenum oxides, with various cationic concentrations, were prepared by precipitation methods. Ammonia was added in 1-cm^3 aliquots to aqueous solutions of the required proportions of tin(IV) chloride at 70 °C until cloudy suspensions persisted. The addition of aqueous ammonium molybdate solutions containing the required amounts of molybdenum gave white precipitates which were removed by centrifugation, dried at room temperature, and calcined at temperatures between 100 and 1 000 °C for 24 h in air.

X-Ray diffraction photographs were obtained with a Debye–Scherrer camera using the Straumanis method of film loading and powder *X*-ray diffraction data were recorded with a Philips vertical goniometer (PW 1050/70) using Cu-K_α radiation. Mössbauer spectra were recorded at 298 K with a Cryophysics microprocessor controlled Mössbauer spectrometer using a calcium stannate (Ca^{119m}SnO$_3$) source and absorbers containing *ca.* 10 mg tin per cm^2. The drive velocity was calibrated with a cobalt-57–rhodium source and a natural iron-foil absorber. All spectra were computer fitted. E.s.r. spectra were recorded at 298 K with a Hilger and Watts instrument operating at 9.4 GHz.

Scanning electron micrographs were obtained with a Philips EM 500 instrument. Molybdenum concentrations in materials calcined at high temperatures were determined with a Philips EM 400T electron microscope operating in the STEM mode and interfaced with an EDAX energy dispersive *X*-ray analysis system.

Results and Discussion

Structural Properties.—The *X*-ray diffraction patterns recorded from the initial white precipitates dried at 25 °C in air were indicative of amorphous gels which gave broad single-peaked ^{119}Sn Mössbauer spectra similar to those reported[3] for the precipitate formed by alkaline hydrolysis of tin(IV) chloride. It would seem reasonable to envisage these amorphous precipitates as being composed of random arrays of isolated tin(IV) and molybdenum(VI) species in separate hydroxyl octahedra.

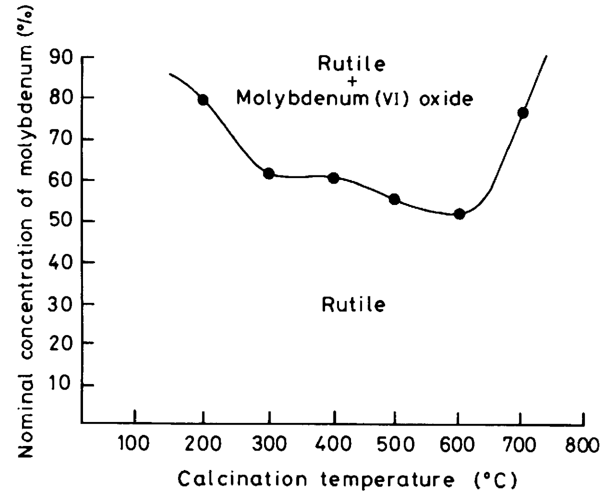

Figure 1. Schematic representation of the phases formed upon calcination of precipitates for 24 h

The precipitates lost weight on heating to give light grey or green-grey solids which were shown by powder *X*-ray diffraction to be either monophasic materials with a rutile-related structure or biphasic materials composed of the rutile-type phase and molybdenum(VI) oxide. The phases identified by *X*-ray diffraction after 24-h heat treatments are summarised in Figure 1.

Materials containing less than *ca.* 60% molybdenum and calcined at the lower temperatures of 300 and 400 °C gave broad-line *X*-ray diffraction patterns which were indicative of very poorly crystalline rutile-related materials. The ^{119}Sn Mössbauer spectra from these, and other tin–molybdenum oxides calcined at higher temperatures, were best fitted to two lines characteristic of quadrupole split tin(IV) absorptions. The quadrupole splittings of the poorly crystalline solids prepared at 300 °C (Δ = 0.54—0.61 mm s^{-1}) were independent of the nominal molybdenum contents and, given the small amount of amorphous material identified by electron microscopy, indicate that high concentrations of molybdenum may be accommodated in the disordered poorly crystalline rutile-type phase without any significant influence being exerted on the electric-field gradient at the tin nuclei. The *X*-ray diffraction patterns from materials with molybdenum concentrations greater than *ca.* 60% contained additional peaks characteristic of the presence of molybdenum(VI) oxide which presumably results from the dehydration of excess hydrolysed molybdenum in the molybdenum-rich precipitates.

Although the *X*-ray diffraction data recorded from materials containing less than *ca.* 50% molybdenum and calcined at 600 °C remained indicative of generally poorly ordered rutile-related phases the patterns were, especially those from samples containing less than *ca.* 20% molybdenum, consistent with a higher degree of crystallinity than was observed in the materials formed at lower temperatures. The ^{119}Sn Mössbauer quadrupole splitting data recorded from these samples containing lower concentrations of molybdenum were similar to that of pure tin(IV) oxide, $\Delta = 0.55$ mm s^{-1}, prepared at 600 °C by identical methods. The mixed oxides formed at 600 °C from precipitates containing molybdenum in concentrations exceeding *ca.* 50% were shown by *X*-ray diffraction to be biphasic. Although the development of the molybdenum(VI) oxide phase may be partly associated with the dehydration of the hydrolysed molybdenum species in the molybdenum-rich precipitates it is interesting to note the identification, by scanning electron microscopy and electron microprobe analysis, of outgrowths of needle-like crystals (Figure 2) of molybdenum(VI) oxide. The observations may be interpreted in terms of the thermally induced aggregation of SnO_2 octahedral units which gives rise to the development of the tin(IV) oxide-type lattice and is accompanied by a counter migration of the molybdenum, which cannot be accommodated within the rutile-related structure, to the surface to form outgrowths of crystalline molybdenum(VI) oxide.

Given that the rutile-type phase becomes more crystalline at higher temperatures when further phase separation occurs it would seem that the partial crystallisation which is achieved at temperatures around 600 °C does not correspond to the attainment of bulk equilibrium and, in contrast to the earlier reports,[1,2] we have found no evidence to describe the materials as solid solutions or as novel compounds containing tin and molybdenum. The results of this work suggest that the presence of only peaks corresponding to a rutile-type tin(IV) oxide phase in the *X*-ray diffraction patterns recorded from tin–molybdenum oxides formed at *ca.* 600 °C is not unequivocal evidence of solid solution formation. Indeed our results are more consistent with the conclusions of a recent study[4] of rutile-type tin–antimony oxides which described the solids formed by the calcination of precipitates at 600 °C as highly disordered materials. Hence we propose that the calcination of tin–molybdenum oxides at moderate temperatures gives rise to poorly crystalline rutile-related matrices capable of accommodating high concentrations of both tin and molybdenum cations.

The *X*-ray diffraction patterns recorded from materials heated at 700 °C showed an increase in the extent of the rutile-related solids, indicating the volatilisation of the molybdenum(VI) oxide which segregates from the increasingly crystalline rutile-related phase at this higher temperature. This evaporation of molybdenum(VI) oxide, which begins at temperatures below its melting point,[5,6] continues with further calcination such that all materials prepared at temperatures exceeding *ca.* 800 °C were shown by *X*-ray diffraction to be monophasic crystalline rutile-type solids from which all segregated molybdenum(VI) oxide had volatilised. The Mössbauer quadrupole splittings, $\Delta = ca.\ 0.55$ mm s^{-1}, were independent of the nominal composition of the initial precipitate and were indistinguishable from that of tin(IV) oxide prepared at the same temperature.

All the tin–molybdenum oxides prepared by calcination in air at 1 000 °C for 14 d gave well defined narrow-lined *X*-ray diffraction patterns indicative of the most crystalline tin–molybdenum oxides which may be formed by the calcination of precipitates. The small Mössbauer quadrupole splittings, $\Delta = ca.\ 0.53$ mm s^{-1}, are consistent with the *X*-ray diffraction data, suggesting that prolonged calcination at high temperature induces the segregation of any molybdenum which cannot be tolerated within the rutile-type tin(IV) oxide structure to form molybdenum(VI) oxide which is lost by volatilisation. Indeed, examination of these solids by electron microprobe analysis revealed molybdenum contents of *ca.* 2 ± 0.2% irrespective of the nominal molybdenum concentration of the initial precipitates. It would seem that of all the materials investigated in this work these samples correspond most closely to those which may be described as solid solutions of molybdenum in tin(IV) oxide.

The lattice parameters, determined from *X*-ray powder diffraction photography, of two tin–molybdenum oxides and tin(IV) oxide prepared by prolonged calcination at 1 000 °C were all within the experimental error of ±0.001 Å ($a = b = 4.738$, $c = 3.187$ Å) and in good agreement with those reported[7] for crystalline SnO_2 ($a = b = 4.738$, $c = 3.1865$ Å). The results show that the incorporation of small concentrations of molybdenum in the tin(IV) oxide lattice gives rise to negligible distortion of the rutile-type structure.

The Cationic Oxidation States.—The Mössbauer chemical isomer shift data from all the tin–molybdenum oxides, $\delta = ca.\ 0.01 \pm 0.02$ mm s^{-1} relative to tin(IV) oxide, were characteristic of tin(IV) in oxygen environments and independent of the nominal molybdenum concentration and calcination treatment.

The room temperature e.s.r. spectra recorded from the tin–molybdenum oxides calcined at 1 000 °C and containing *ca.* 2% molybdenum showed sharp signals with well resolved hyperfine structure. The signals were very similar to those previously attributed[8] to molybdenum(V) in substitutional sites in tin(IV) oxide which have been recorded from samples prepared by impregnation techniques. Hence the tin–molybdenum oxides which are formed by prolonged calcination at high temperatures and which have been described here as solid solutions would appear to consist of low concentrations of molybdenum(V) in the tin(IV) oxide lattice.

It is also pertinent to note that the poorly resolved e.s.r. signals recorded from several tin–molybdenum oxides heated at temperatures below 900 °C resembled other spectra which, in the past,[9–12] have been assigned to molybdenum(V). The resolution of the hyperfine structure in these materials, which decreased with increasing molybdenum concentration, may be associated with increasing interactions between larger concentrations of paramagnetic molybdenum(V) species[13] and/or electron-exchange phenomena similar to that recently reported[14] in tellurium–molybdenum oxides containing molybdenum(V) and involving vestigial molybdenum(VI) from the initial precipitate. Although we acknowledge that the detection of molybdenum(IV) and molybdenum(III) by e.s.r. is difficult,[15–17] it is relevant to note that preliminary examination[18] of these tin–molybdenum oxides by *X*-ray photoelectron spectroscopy has failed to show evidence for the presence of either of these molybdenum species.

Acknowledgements

We thank Courtaulds Ltd. for financial support.

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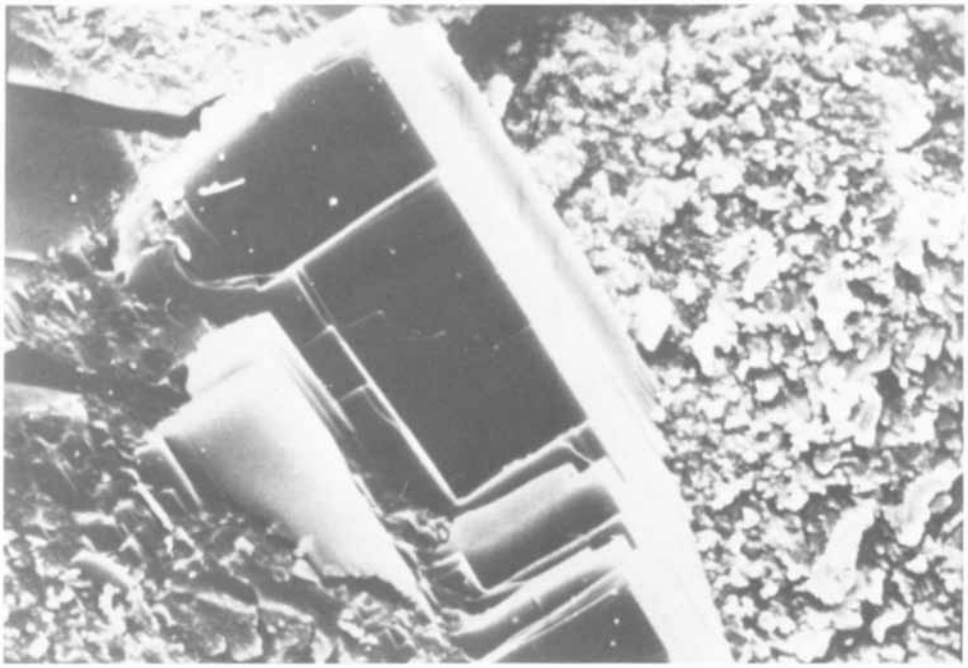

Figure 2. Outgrowth of molybdenum(VI) oxide from a tin–molybdenum oxide calcined at 600 °C; scale 1 cm = 4 μm

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Received 17*th May* 1984; *Paper* 4/809