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The Preparation of Tin–Molybdenum Oxides

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Abstract

The characterisation of 'tin–molybdenum oxides' prepared by a variety of methods has been performed by X-ray diffraction. The results show that preparative procedures involving the calcination of precipitates or evaporates containing the two cations at high temperatures are more likely to result in solid solution formation than methods which involve the calcination of slurries or solid state reactions. However, the monophasic tin–molybdenum oxides formed by the moderate temperature calcination of precipitates or evaporates undergo further changes at elevated temperatures which indicate that bulk equilibrium is difficult to achieve in this ternary system.

Introduction

Various methods for the preparation of 'tin–molybdenum oxides' have been described in reports which have been mainly concerned with the catalytic properties of these materials [1–11]. The preparative methods appear to fall into four categories: (i) the calcination of mixtures of solid molybdenum- and tin-oxides; (ii) the calcination of slurries; (iii) the calcination of evaporated solutions containing both cationic species; (iv) the calcination of precipitates containing both cations.

However, despite the extensive interest which has been shown in the catalytic properties of these materials, the characterisation of the 'tin–molybdenum oxides' has received surprisingly little attention and there is a sparsity of data by which their fundamental solid state properties may be related to the preparative procedure. We have therefore prepared some 'tin–molybdenum oxides' according to methods representative of those summarised above and have examined the products by X-ray diffraction to elucidate the nature of the different materials and identify the methods which are best suited for the formation of compounds or solid solutions.

Experimental

The 'tin–molybdenum oxides' were prepared by procedures described below using reactant mixtures representing ranges of tin and molybdenum ratios.

Method A

Ground mixtures of molybdenum(VI) oxide and tin(IV) oxide were calcined at 600 °C (12 h) in air.

Method B

Solutions containing the required proportions of hydrated tin(IV) chloride in water (*ca.* 100 ml) were heated to 70 °C. The addition of aqueous ammonia in 1 ml aliquots gave white precipitates which initially redissolved. The addition of ammonia was continued until cloudy suspensions persisted when aqueous solutions of ammonium molybdate containing the required amounts of molybdenum were added to give white precipitates which were removed by filtration or by centrifugation. The precipitates were dried at room temperature and calcined at temperatures between 100 °C and 1000 °C for 24 hours.

Method C

Tin(IV) oxide was slurried in aqueous solutions of ammonium molybdate, the mixtures were evaporated to dryness at 120 °C (12 h) and then calcined at 600 °C (12 h) in air.

Method D

Solutions containing the required proportions of tin(II) chloride in *ca.* 4 M hydrochloric acid (*ca.* 100 ml) were added to aqueous solutions (*ca.* 100 ml) of ammonium molybdate containing the required amounts of molybdenum. The mixtures were evaporated to dryness at *ca.* 60 °C under vacuum. The residues were dried at 120 °C (12 h) and then heated at either 300 °C (24 h) or 600 °C (24 h) in air.

Method E

Solid tin(IV) oxide was thoroughly mixed with slurries of molybdic acid in water. The mixtures were evaporated to dryness at 120 °C (12 h) in air and calcined at 600 °C (12 h) in air.

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Method F

Intimately ground mixtures of molybdenum(VI) oxide and tin(IV) oxide were slurried in water and calcined at 600 °C (12 h) in air.

Method G

A sample (tin: molybdenum ratio 9:1) was prepared according to Method D and calcined at 600 °C (24 h) in air before sealing in an evacuated silica tube. An intimately ground mixture of molybdenum(VI) oxide and tin(IV) oxide (tin: molybdenum ratio 4:1) which had been dried at 600 °C (24 h) was similarly sealed in an evacuated silica tube. The samples were gradually heated (100 °C/h) to 600 °C and maintained at this temperature for 2½ days before increasing (100 °C/h) to 1000 °C (10 d). The materials were then cooled (100 °C/h) to 600 °C (18 h) and allowed to revert to room temperature.

Powder X-ray diffraction data were recorded with a Philips vertical goniometer (PW 1050/70) using Cu–K_α radiation.

Results and Discussion

The phases identified by powder X-ray diffraction in the products prepared by Methods A to F are summarised in Table I.

TABLE I. Phases Identified by Powder X-ray Diffraction in the Products prepared by Methods A to F.

Method of Preparation	Phases Identified by Powder X-ray Diffraction [12, 13]
A	Tin(IV) oxide and molybdenum(VI) oxide.
B	Tin(IV) oxide and sometimes molybdenum(VI) oxide depending on molybdenum concentration and calcination temperature.
C	Tin(IV) oxide and molybdenum(VI) oxide.
D	Tin(IV) oxide and sometimes molybdenum(VI) oxide, depending on molybdenum concentration and calcination temperature.
E	Tin(IV) oxide and molybdenum(VI) oxide.
F	Tin(IV) oxide and molybdenum(VI) oxide.

The lack of change in the reactants following treatment according to Method A suggests that solid state reactions in air are not viable at temperatures of *ca.* 600 °C and, in this respect, it is interesting that the attempted preparation of $SnMoO_4$ from tin(II) oxide and molybdenum(VI) oxide at 600 °C has also been reported to be unsuccessful [3]. Although it is known that molybdenum(VI) oxide reacts with bismuth(III) oxide to form bismuth molybdate [14] at the lower temperature of 530 °C, it is relevant to note that solid state reactions involving tin(IV) oxide frequently require elevated temperatures; for example, the formation of rare earth stannates from tin(IV) oxide and rare earth oxides occurs [15] at *ca.* 1500 °C and many other solid state reactions [16] require calcination temperatures exceeding 600 °C. Hence the resistivity to reaction between molybdenum(VI) oxide and tin(IV) oxide in open systems might reflect the relatively low calcination temperature. The volatility of molybdenum(VI) oxide [17, 18] at temperatures exceeding *ca.* 525 °C precludes the use of higher temperature reactions in air.

Slurrying mixtures of molybdenum(VI) oxide and tin(IV) oxide (molybdenum contents ranging from 5 to 20%) in water followed by calcination at 600 °C (12 h) (Method F) gave products from which powder X-ray diffraction patterns characteristic of molybdenum(VI) oxide and tin(IV) oxide were obtained. The relative intensities of the molybdenum(VI) oxide and tin(IV) oxide contributions to the diffraction patterns were similar to those observed in patterns recorded from unreacted mixtures of the oxides of corresponding compositions. Hence the lack of reactivity between reactants in the solid state appears to persist, as might be expected, when the reactants are obtained by simple evaporation of the water in which they are suspended.

Other slurries with nominal molybdenum concentrations ranging between 5 and 20% were prepared from mixtures of tin(IV) oxide with either molybdic acid and water (Method E) or aqueous solutions of ammonium molybdate (Method C). After calcination at 600 °C the products gave X-ray diffraction patterns characteristic of biphasic mixtures of tin(IV) oxide and molybdenum(VI) oxide. However, the intensities of the molybdenum(VI) oxide contributions to the X-ray diffraction patterns were lower than those observed in the patterns recorded from unreacted mixtures of the two oxides of corresponding cationic compositions. Given that no weight changes corresponding to volatilisation of molybdenum(VI) oxide were recorded during the calcination process the phenomena appear to be indicative of some chemical reaction. The lack of any changes in the intensities of the tin(IV) oxide contributions to the product patterns and the absence of any evidence for new phases suggests that the reactions give products of similar structure to tin(IV) oxide which has been shown [19] to consist of a slightly distorted octahedral array of oxygen atoms around a central tin atom and to resemble the rutile-type structure of titanium dioxide. Although the observations reported here are consistent with the formation of solid solutions by the accommodation of small amounts of molybdenum in the tin(IV) oxide structure, further evidence would be necessary to confirm that such processes do occur under these conditions. This matter is important since there is some uncertainty in the literature as to whether or not preparations involving slurries can lead to solid solution or compound formation in the tin–molybdenum–oxygen systems [4–6]. It is therefore pertinent to record that the ESR spectra recorded from these materials showed only a broad, weak signal which was different from the intense ESR spectra characteristic of molybdenum(V) recorded from the products of Methods B and D which showed a high potential for mixed oxide formation (*vide infra*). It would therefore appear that if the reactants in Methods C and E do undergo chemical reaction then the products are of a different nature to those formed at *ca.* 600 °C from Methods B and D. In this respect it may be relevant to note that the well-resolved X-ray diffraction patterns from the products of Methods C and E indicate that the rutile-type phase has a high degree of crystallinity which is more similar to that of tin(IV) oxide than that of the rutile-type products formed from Methods B and D at comparable temperatures. Whether or not the slurries containing low concentrations of molybdenum and treated according to Methods C and E give rise to chemical reaction is therefore difficult to resolve with certainty, however, even if such reactions were to be confirmed the results suggest that the extent of the reaction is severely limited.

Addition of tin(II) chloride in *ca.* 4 M hydrochloric acid to aqueous solutions of ammonium molybdate (Method D) produced blue solutions which subsequently changed to stable colours ranging between orange–brown and deep–red with increasing molybdenum concentration. During removal of the solvent under vacuum the solutions became dark grey–green and then emerald green before further evaporation gave a dark grey residue. Whilst it is acknowledged that a large number of ionic species are present in these solutions it is interesting that many of the observed phenomena can be associated with the behaviour of molybdenum species. For example, it has been reported [20] that mild reduction of acidified aqueous molybdate solutions gives a blue colouration similar to that observed in the molybdenum blue oxides. In this respect it is pertinent to note the reducing qualities of tin(II) chloride [21] and that the reduction of molybdenum(VI) in hydrochloric acid leads to the formation of chloro-oxomolybdate complexes [22], the nature and colour of which appears to depend upon the concentration of hydrochloric acid. Hence the addition of tin(II) chloride in *ca.* 4 M hydrochloric acid to aqueous solutions of ammonium molybdate seems to involve the reduction of molybdenum(VI) to give solutions with colours similar to those of the molybdenum blue oxides which are subsequently converted to species resembling the red–brown $[Cl_4OMoOMoOCl_4]^{4-}$ complex. Since evaporation might be expected to lead to an increase in the concentration of hydrochloric acid, the observed colour changes through dark grey-green to emerald green seem consistent with the reported [22] transformation of the red–brown complex to green $[MoOCl_5]^{2-}$. The residue formed on complete evaporation gave complex X-ray diffraction patterns which resisted interpretation. It would seem reasonable that such a residue could be described as a hydrolysed material which, in view of the large number of ions present in the initial reaction mixture, could contain a variety of complex species.

Evaporates were dried (120 °C) and then calcined at 300 °C. The poorly defined X-ray diffraction patterns recorded from products containing up to 20% molybdenum consisted of lines characteristic of only a rutile-type material whilst those from the products of reactions involving higher concentrations of molybdenum contained additional lines characteristic of molybdenum(VI) oxide. Other evaporates calcined at 600 °C gave more well defined X-ray diffraction patterns indicative of more crystalline materials in which only rutile-type patterns were observed from materials containing up to 15% molybdenum. The X-ray diffraction patterns from solids prepared at 600 °C which contained higher concentrations of molybdenum were characteristic of biphasic mixtures of molybdenum(VI) oxide and tin(IV) oxide. It has been shown [23] that the dehydration of tin(IV) oxide prepared by precipitation is not complete until *ca.* 600 °C and therefore the evaporates calcined at 300 °C might be envisaged as partially hydrated solids containing both tin and molybdenum cations in octahedrally coordinated oxygen/hydroxyl environments in poorly crystalline homogeneous matrices. It would seem that such materials can accommodate up to 20% molybdenum at 300 °C. Complete dehydration at 600 °C might be expected to give products which have attained a closer approximation to equilibrium and, under such conditions, a more crystalline rutile-type tin(IV) oxide phase would be expected as is reflected by the sharper X-ray diffraction patterns. It therefore seems that the thermally induced lattice construction is also associated with a concomitant segregation of molybdenum from materials in which the molybdenum concentration exceeds 15% and its separation as a discrete molybdenum(VI) oxide phase. Since concentrations of 3% molybdenum(VI) oxide were readily detectable in diffraction patterns recorded from unreacted mixtures of molybdenum(VI) oxide and tin(IV) oxide it is quite reasonable to describe the products formed at 600 °C which gave X-ray diffraction patterns characteristic of only tin(IV) oxide as monophasic. Whether such materials are solid solutions of molybdenum in tin(IV) oxide or some other type of product in which bulk equilibrium has yet to be attained will be the substance of further investigations.

Calcination of the coprecipitates prepared in Method B at 600 °C gave, when the molybdenum concentration did not exceed 50%, grey–green solids from which X-ray diffraction patterns characteristic of tin(IV) oxide were recorded. These results, like those recorded from materials containing low concentrations of molybdenum which were prepared at 600 °C according to Method D, appear to indicate a high potential for monophasic mixed oxide formation in the tin–molybdenum–oxygen system when prepared by these methods. However, the monophasic mixed oxides formed by the calcination of precipitates at 600 °C underwent phase separation when calcined at higher temperatures and gave biphasic products containing more crystalline rutile-related tin(IV) oxide-type phases and molybdenum(VI) oxide. Hence it seems that the tin-molybdenum oxides formed by the calcination of precipitates at moderately high temperatures such as *ca.* 600 °C have not achieved bulk equilibrium and that molybdenum segregates from the crystallising rutile-type phase under the influence of further calcination. It is also relevant to record that calcination at elevated temperature (*ca.* 1000 °C) causes the volatilisation of the segregated molybdenum(VI) oxide and the formation of highly crystalline rutile-type products. It is therefore quite reasonable to envisage that the thermally induced segregation of the molybdenum which cannot be accommodated in the crystalline tin(IV) oxide lattice might, at elevated temperatures, give rise to the formation of monophasic materials containing the upper limit of molybdenum which can be incorporated within the rutile-type structures and which are most accurately described as solid solutions of molybdenum in tin(IV) oxide. Given that precipitation techniques have been widely used for the preparation of catalysts [24] extensive studies of tin-molybdenum oxides of varied compositions prepared by precipitation methods and calcined over a range of temperatures are currently in progress to elucidate more clearly the conditions under which solid solution formation is achieved.

The nature of materials which were formed by the calcination of materials *in vacuo* warrant separate attention. Although a solid state reaction between tin(IV) oxide and molybdenum(VI) oxide was not detected following calcination at 600 °C in air (*vide supra*), chemical reaction between these materials at high temperatures in sealed tubes in which the loss of volatile molybdenum(VI) oxide is prevented might be expected to be more viable. Furthermore, similar high temperature treatment of materials such as the monophasic products from Method D in sealed tubes might be expected to result in further chemical and structural changes. The phase compositions of the dried reactants and products which were identified by powder X-ray diffraction are summarised in Table II.

The powder product from the ground mixture of tin(IV) oxide and molybdenum(VI) oxide gave an X-ray diffraction pattern characteristic of silica, tin(IV) oxide and molybdenum(VI) oxide. It is relevant that molybdenum(VI) oxide has been reported [27] to react with the silica in an evacuated silica tube to give a white crystalline powder shown by X-ray diffraction to be a mixture of MoO_3 and silica. Given that a light colouration was observed on the sides of the tube used here, and which was removed with the bulk product, it is likely that the crystalline silica observed in the diffraction pattern resulted from a similar process. Comparison of the intensities of the product molybdenum(VI) oxide and tin(IV) oxide contributions to the diffraction pattern with those observed in patterns from unreacted mixtures of the oxides failed to give evidence of any reaction between MoO_3 and SnO_2. It appears therefore that solid state reactions between molybdenum(VI) oxide and tin(IV) oxide are difficult even at elevated temperatures.

The powder X-ray diffraction pattern recorded from the product in the sealed tube containing the monophasic rutile-type material prepared at 600 °C according to Method D was composed of lines characteristic of tin(IV) oxide and some molybdenum(IV) oxide. The result suggests that materials prepared at 600 °C by Method D are not necessarily equilibrated solids and that the crystallisation of the host tin(IV) oxide phase at 1000 °C, as evidenced by the sharper peaks in the X-ray diffraction pattern, is accompanied by a decrease in the tolerance of the rutile-type

TABLE II. Phases Identified by Powder X-ray Diffraction in the Reactants and Products from Preparations in Sealed Tubes.

Reactants	Molybdenum Content	Phases Identified In Reactants	Phases Identified In Products
Mixture of tin(IV) oxide and molybdenum(VI) oxide, dried at 600 °C	20%	Tin(IV) oxide [12] and molybdenum(VI) oxide [13]	Silica [25], tin(IV) oxide [12] and molybdenum(VI) oxide [13]
Evaporate prepared according to Method D and calcined at 600 °C	10%	Tin(IV) oxide [12]	Tin(IV) oxide [12] and molybdenum(IV) oxide [26]

structure for molybdenum incorporation. The result suggests that the excess molybdenum segregates to form a separate phase by migration through the crystallising tin(IV) oxide matrix. This process is, in principle, not dissimilar to that observed when monophasic evaporates containing 20% molybdenum prepared by Method D at 300 °C were subsequently heated in air at 600 °C to give biphasic products. However, an important difference between the two observations is that in air at 600 °C the excess molybdenum segregates as molybdenum(VI) oxide, whereas at 1000 °C *in vacuo* molybdenum appears as the reduced oxide MoO_2. This result may imply that molybdenum in a low oxidation state within the bulk tin(IV) oxide structure migrates under the influence of heat through the crystallising lattice to form MoO_2, and that oxidation processes to give MoO_3 are prevented *in vacuo*. In this respect it seems relevant to note the high melting point [28] and thermal stability [29] of MoO_2 up to temperature of *ca.* 1100 °C and the description [6] of a tin–molybdenum oxide containing 1% molybdenum as a solid solution of molybdenum(IV) and molybdenum(V) in tin(IV) oxide.

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