Studies of the Solid State and Catalytic Properties of Tin–Molybdenum Oxides

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Some tin–molybdenum oxides, prepared by precipitation techniques and by methods described in the patent literature, have been examined by powder X-ray diffraction, ^{119}Sn Mössbauer spectroscopy and ESR. A qualitative assessment of their properties as catalysts for the oxidation of hydrocarbons indicates that catalytic activity may be associated with the tin–molybdenum oxides composed of poorly crystalline rutile-related tin(IV) oxide-type structures containing high concentrations of molybdenum. These catalytically active phases undergo partial decomposition during the catalytic reaction with a concomitant segregation of molybdenum(VI) oxide and a loss of oxygen which gives rise to the formation of anionic vacancies in which electrons are trapped.

The catalytic properties of mixed metal oxides for the oxidation and ammoxidation of hydrocarbons have been known for many years with tin–molybdenum oxides having been found to be active and selective for many reactions [1] including the partial oxidation of propene to acrolein [2], the oxidation of propene to acetone in the presence of water [3], and the oxidation of methanol to formaldehyde [4, 5]. We have recently reported [6, 7] on the influence of the preparative procedure on the nature of tin–molybdenum oxides, especially those derived from the calcination of precipitates, and have identified the segregation of molybdenum to twin boundaries in the crystalline rutile-related phases which are formed at elevated temperatures [8]. Although it would be quite reasonable to expect the catalytic performance of a solid catalyst to be related to its fundamental properties relatively few studies of such relationships have been reported. In this paper we describe some preliminary investigations of the relationship between the catalytic and solid state properties of tin–molybdenum oxides and on the changes which are induced in the mixed oxides when they are used as catalysts for the oxidation of propene.

Experimental

The tin–molybdenum oxides which were subjected to examination are described in Table I. Tin–molybdenum oxide catalysts A and B were prepared according to methods described in the patent literature [2]. Catalyst A was prepared by the calcination of a slurry of tin(IV) oxide and molybdenum(VI) oxide (Sn:Mo = 9:1) in water at 450 °C for 4 h. Catalyst B was prepared by the addition of aqueous tin(IV) chloride to a mixture of aqueous ammonia and aqueous ammonium molybdate (Sn:Mo = 1:2) to form a precipitate which was heated at 450 °C for 4 h.

Tin–molybdenum oxide catalysts C to G were obtained by the calcination of precipitates according to methods used previously [7, 8] to prepare samples for structural examination. Ammonia was added in 1 ml 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 solution containing the required amounts of molybdenum gave white precipitates which were removed by centrifugation, dried at room temperature and calcined at temperatures between 450 °C and 1000 °C for 24 h in air.

The tin–molybdenum oxides were prepared for use as catalysts by wetting with ethanol and were supported on glass beads. The catalysts were packed to a depth of 10 cm within a quartz-glass microreactor of 5 mm internal diameter, dried (70 °C, 12 h) in air, supported in a Carbolite oven and treated at 450 °C with a flowing gaseous mixture (by volume) of 4% propene, 10% oxygen, and 86% nitrogen with a gas/catalyst contact time of *ca.* 0.1 s. The products were analysed with a Pye-Unicam 104 gas-liquid chromatograph fitted with a flame ionisation detector.

Powder X-ray diffraction data were recorded with a Philips vertical goniometer (PW 1050/70) using Cu-K_α radiation. Tin-119 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/cm^2. ESR spectra were recorded at 298 K with a Hilger and Watts instrument operating at 9.4 GHz.

Results and Discussion

Initial Phase Compositions and Catalytic Activity

The phase compositions of the freshly prepared tin–molybdenum oxide catalysts were determined by powder X-ray diffraction and, together with a qualitative assessment of their catalytic activities, are described in Table I.

The X-ray diffraction pattern recorded from catalyst A, prepared by the calcination of a slurry of solid tin(IV) oxide and molybdenum(VI) oxide in water at 450 °C, showed the product to be composed of an unreacted mixture of the reactants. The result

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is consistent with previous evidence [6] that the calcination of slurries of solid reactants does not lead to chemical reaction. Catalyst B, prepared by precipitation techniques, gave an X-ray diffraction pattern containing sharp peaks characteristic of highly crystalline molybdenum(VI) oxide and broad peaks attributable to a poorly crystalline rutile-type phase. The X-ray diffraction pattern resembled those recorded from other tin–molybdenum oxides formed by the calcination at 400 °C of precipitates with similar tin and molybdenum concentrations [6, 7]. Hence catalysts A and B, prepared according to methods described in the patent literature [2], represent different types of tin–molybdenum oxides with one phase in catalyst B being amenable to description as a poorly crystalline rutile-related tin–molybdenum oxide [6, 7]. Neither catalyst would correspond to an equilibriated solid solution of molybdenum in tin(IV) oxide [7].

The poor catalytic performance of tin–molybdenum oxide catalyst A, which was manifested by the limited oxidation of propene to water and carbon dioxide, is consistent with its description as an unreacted mixture of tin(IV) oxide and molybdenum(VI) oxide which both lack catalytic potential [1]. However catalyst B, prepared by the calcination of a precipitate, showed a high activity for propene oxidation and, in a highly exothermic reaction, gave a mixture of organic products including acetic acid, acrolein, and acrylic acid, together with significant quantities of water. Although quantitative analysis of the product spectrum was not performed the results did suggest that, despite its activity, catalyst B lacked selectivity to partially oxidised hydrocarbons. Nevertheless the activity of catalyst B compared with the inactivity of catalyst A is notable and would appear to be related to the tendency of materials prepared by the calcination of precipitates at 450 °C to form the poorly crystalline rutile-related tin(IV) oxide-type phase containing high concentrations of molybdenum.

The catalytic activities of tin–molybdenum oxide catalysts C to F, which were also prepared in precipitation techniques, appeared to reflect the nominal molybdenum concentrations of the original precipitates and the subsequent thermal treatments. For example, catalyst C prepared by the calcination at 400 °C of a precipitate containing 10% molybdenum and which was shown by preliminary X-ray photoelectron spectroscopy (XPS) examination to have a similar molybdenum composition at the surface [9] was the least active material, whereas catalyst E, prepared from a similar precipitate but heated to 600 °C and in which molybdenum was shown by X-ray diffraction [7] and XPS [9] to have segregated to the surface of the rutile-type phase, was more catalytically active. It is also relevant to note that both the monophasic rutile-related catalyst D, which had been prepared by the calcination of a precipitate containing 50% molybdenum at 400 °C, and the biphasic catalyst F, formed from a precipitate containing 70% molybdenum heated at 600 °C, showed high catalytic activities. Given that the X-ray diffraction-[7] and XPS-[9] data showed that the poorly crystalline tin(IV) oxide-type phases in these catalysts were capable of holding high concentrations of molybdenum in surface sites, it seems that the molybdenum concentration in rutile-related tin–molybdenum oxide catalysts, particularly at the surface, is directly related to the catalytic properties of the materials. The inactivity of catalyst G, which may be described [7] as a solid solution of molybdenum in tin(IV) oxide and which is composed of large particles with low surface areas from which much

TABLE I. Tin–molybdenum Oxide Catalysts: Details of Preparation, their Phase Compositions and Catalytic Activity.

Catalyst	Method of Preparation (Reference)	Nominal Molybdenum Concentration in Original Precipitate (%)	Calcination Temperature (°C)	Phase Composition	Activity
A	2	10	450	Rutile + MoO_3	Almost inactive
B	2	67	450	Rutile + MoO_3	Very active
C	7	10	400	Rutile	Slightly active
D	7	50	400	Rutile	Very active
E	7	10	600	Rutile	Active
F	7	70	600	Rutile + MoO_3	Very active
G	7	5	1000	Rutile	Inactive

molybdenum volatilises under the influence of high temperature calcination, is consistent with the model.

Although no attempt was made to quantitatively assess the catalytic selectivities of these tin–molybdenum oxides, the detection of significant amounts of water in the products reflects a lack of selectivity to the partial oxidation of hydrocarbons. Whether or not this resulted from the absence of water vapour in the reactant gas mixture, as has been used [3, 10] in other catalytic evaluations of tin–molybdenum oxides, is unclear.

The Catalysts Used

The active tin–molybdenum oxide catalysts changed colour during the catalytic testing from grey to blue-green or blue black similar [11] to the colour of molybdenum blue oxides which contain molybdenum in the oxidation states of (V) and (VI). It was also interesting to note the accumulation of a white crystalline deposit, which was identified by X-ray diffraction as molybdenum(VI) oxide, on cooler regions of the apparatus below the catalyst when the active catalysts B, D, E and F were used. Although the deposition of molybdenum(VI) oxide by the effluent gases during the catalytic evaluation of biphasic catalysts B and F which contained molybdenum(VI) oxide may not be unexpected, the results from monophasic rutile-related catalysts D and E suggest that molybdenum(VI) oxide is also extracted from the molybdenum-containing tin(IV) oxide-type phases during the catalytic reaction. In this respect it is pertinent to note that the X-ray diffraction patterns recorded from the used catalysts also gave evidence of the presence of molybdenum(VI) oxide and it therefore seems that the poorly crystalline rutile-type phases in the active catalysts prepared by the calcination of precipitates undergo partial decomposition during the catalytic reaction. Whether or not this decomposition arises directly from the oxidation of propene on the catalyst surface or as a result of the reaction of product water with the molybdenum rich surfaces similar to that observed in other molybdenum-containing oxides [12], is unclear. However, it is relevant to note that the catalytic activity of the active catalysts decreased with time during the catalytic reaction, presumably as a result of the loss of molybdenum from the catalyst. Finally, it is pertinent to record that the failure by X-ray diffraction to record the segregation of molybdenum from the rutile-type phases in catalysts A, C and G may be associated with the low catalytic performance of these materials.

Given that the partial oxidation of hydrocarbons over mixed oxide catalysts often involves the loss of oxygen from the catalyst [13], it is interesting that no reduced phases were detected in the used tin–molybdenum oxides by X-ray diffraction and that the ^{119}Sn Mössbauer spectra recorded from the solids after the catalytic reaction showed no evidence for the reduction of tin(IV) to tin(II). Furthermore, all the used catalysts gave ESR spectra showing signals similar to those previously attributed to molybdenum(V) in tin(IV) oxide [7, 14] but, although consistent with the colour changes which occurred under catalytic conditions (*vide supra*), the absence of quantitative analysis of the ESR data precludes an association of the molybdenum(V) to the reduction of molybdenum(VI). However, it is relevant to record that the ESR spectra recorded from the used catalysts also displayed signals with g values of *ca.* 2.00 which were not observed in the freshly prepared mixed oxides and which disappeared when the used catalysts were annealed in air at 500 °C (12 h). The signals were similar to those which have in the past been associated with electrons trapped at anionic vacancies in tin–antimony oxides [15] and tellurium–molybdenum oxides [16]. It is also interesting to note the similar, but unexplained, signal which was detected in the ESR spectrum of a tin–molybdenum oxide following treatment in methanol and oxygen at 200 °C and *in vacuo* at 430 °C [5]. Hence the ESR signals with g-values of *ca.* 2.00 recorded from the tin–molybdenum oxides may emanate from electrons trapped at the anionic vacancies created by the loss of oxygen during the catalytic reaction. The disappearance of these ESR signals after annealing at 500 °C is consistent with the presence of such defects. Given that the Mössbauer and ESR studies showed no clear evidence for the reduction of either tin or molybdenum within the bulk of the catalysts an examination of the surfaces by a technique such as XPS is necessary to establish whether the loss of oxygen gives rise to changes in the cationic oxidation states at the catalyst surfaces.

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