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A Structural Study of Tin–Antimony Oxide Catalysts by High-Resolution Electron Microscopy

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Tin–antimony oxide catalysts prepared by the calcination of precipitates have been investigated by high-resolution electron microscopy. The exposure of the catalysts prepared at low temperatures to gaseous atmospheres containing hydrocabon and oxygen results in a segregation of antimony from the poorly crystalline rutile-type solids and the development of an amorphous material. The catalysts containing low concentrations of antimony are also partially converted to a non-rutile-type crystalline phase. Prolonged calcination in air of the used catalysts at high temperatures leads to the attainment of bulk equilibrium and the formation of solid solutions of antimony in tin(IV) oxide. Treatment of the equilibrated crystalline catalysts prepared at high temperatures in the hydrocarbon and oxygen gas stream gives rise to disorder within the catalyst structure which is resistant to further change at high temperatures.

INTRODUCTION

Although the catalytic properties of tin–antimony oxides for the selective oxidation and ammoxidation of hydrocarbons have been known for many years (*1*) it is only recently that their fundamental solid state properties have been subjected to substantial examination. For example, X-ray diffraction has revealed (*2, 3*) that materials prepared at high temperatures have a low tolerance for antimony incorporation within the rutile-type tin(IV) oxide lattice whilst X-ray photoelectron spectroscopy (XPS) (*4–6*) has shown that such materials are enriched at the surface in antimony. Other studies by Mössbauer spectroscopy (*7–9*) have demonstrated that the tin(IV) oxide contains antimony(V) within the bulk lattice whilst antimony(III) is located at surface sites. Despite these recent investigations there is a sparsity of information concerning the structural changes which occur in the catalysts during the catalytic reaction and recent attempts (*2–4, 10–14*) to relate solid state properties to catalytic performance, which have often involved investigations by X-ray diffraction, have been inhibited by the poor crystallinity and small particle size of the materials prepared at moderate temperatures.

Electron microscopy is an alternative technique for the structural study of these catalysts (*2, 13*) although the results of these investigations have not been unequivocal in their interpretation (*2*). However, some recent investigations of tin–antimony oxides by high-resolution electron microscopy (HREM) (*15*) using an instrument with a directly interpretable image resolution approaching 2 Å (*16*) have illustrated the potential power of this particular technique for the elucidation of fundamental structural properties in solid mixed oxides. We have therefore conducted some further investigations of tin–antimony oxides to identify the changes which are induced by treatment in gaseous atmospheres which are characteristic of the working environment of mixed oxide oxidation catalysts. We have also attempted to monitor the effect of subsequent calcination of the used catalysts in air. The results of these investigations are reported here.

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TABLE 1

Treatment of Tin–Antimony Oxides and Summary of Observations

Sample	Percentage antimony	Treatment	Description
A	2	600°C, 16 h	Small rutile-type crystals, sometimes twinned, disordered, and defective
B	2	600°C, 16 h/used as catalyst	Small irregular shaped rutile-type crystals, twinned; significant amounts of amorphous material; beam-sensitive non-rutile-type crystals
C	2	600°C, 16 h/used as catalyst/600°C, 16 h	Small rutile-type crystals; significant amounts of amorphous material
D	2	600°C, 16 h/used as catalyst/1000°C, 14 d[a]	Larger rutile-type crystals, less disordered; amorphous material
E	4	600°C, 16 h/1000°C, 17 d/used as catalyst	Medium-sized irregular-shaped rutile-type crystals, considerable disorder
F	4	600°C, 16 h/1000°C, 17 d/used as catalyst/ 1000°C, 12 d	Medium-sized irregular-shaped rutile-type crystals, considerable disorder
G	20	600°C, 16 h	Small rutile-type crystals; amorphous material
H	20	600°C, 16 h/used as catalyst	Small facetted rutile-type crystals; substantial amounts of amorphous material
I	20	600°C, 16 h/used as catalyst/600°C, 16 h	Small rutile-type crystals; substantial amounts of amorphous and poorly crystalline material
J	20	600°C, 16 h/used as catalyst/1000°C, 14 d	Small and large rutile-type crystals; sometimes twinned; large beam-sensitive non-rutile-type crystals; amorphous solid
K	20	600°C, 16 h/1000°C, 14 d/used as catalyst	Large disordered rutile-type and non-rutile-type crystals
L	20	600°C, 16 h/1000°C, 14 d/used as catalyst/ 1000°C, 12 d	Large disordered rutile-type and non-rutile type crystals Some highly beam-sensitive material

[a] d = days.

EXPERIMENTAL

Tin–antimony oxides containing 2, 4, and 20% antimony were prepared by the simultaneous addition of the appropriate proportions of antimony(V) chloride and tin(IV) chloride to ammonium hydroxide solution. The white precipitates were filtered, washed with water, dried at 120°C, and calcined at 600°C for 16 h. Some samples were subjected to further calcination as described in Table 1. Samples which were used as catalysts were supported on glass beads and packed to a depth of 10 cm within a quartz-glass microreactor of 5 mm internal diameter and supported in a Carbolite 2.67. 1077 oven. The catalysts were treated with a butene–oxygen–nitrogen (5 : 10 : 85) gas mixture at 400°C and the occurrence of oxidative dehydrogenation to butadiene and other products was confirmed by GLC.

Samples for examination by electron microscopy were prepared (*15*) by grinding the materials in an agate pestle and mortar under ethanol and allowing a drop of the resulting suspension to dry on a holey carbon film. Observations were made with the

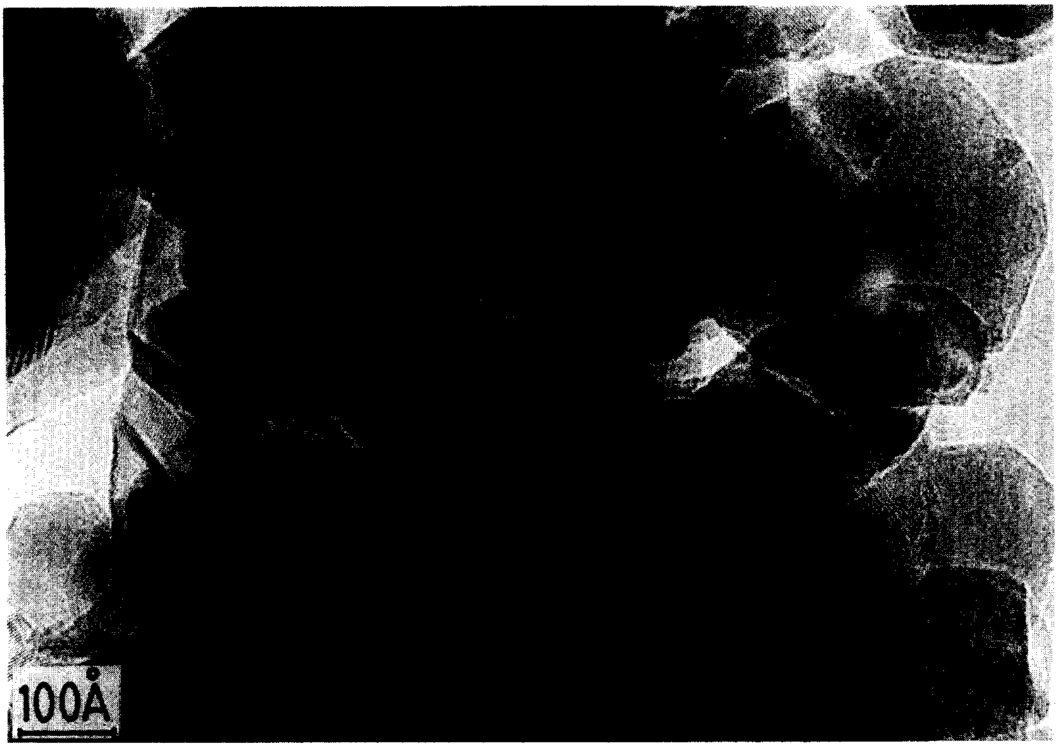

FIG. 1. Tin–antimony oxide A showing small particles of tin(IV) oxide. Coarse-spacing moiré fringes (M) due to crystal overlap along beam direction.

Cambridge University HREM (*16*) operated at 500 kV with micrographs typically being recorded at magnifications of ca. 2.5 × 10^5. A standard optical bench was normally used to measure the lattice spacings observed in the high-resolution images.

RESULTS

The results are summarised in Table 1.

Tin–Antimony Oxide A

This sample, which had been studied previously (*15*), provided the starting material for samples B, C, and D. Examination in the electron microscope showed the presence of small irregular-shaped crystals of ca. 100–800 Å diameter (Fig. 1) often containing planar faults which could sometimes be identified as twin boundaries. The broad continuous ring-type electron diffraction patterns (Fig. 2) were characteristic of small tin(IV) oxide particles with a rutile-type structure and were consistent with direct measurements of the lattice fringes and observations performed on the optical bench. The high-resolution images and the electron diffraction patterns recorded from this material gave no evidence for the presence of an antimony oxide phase.

Tin–Antimony Oxide B

The mixed oxide, which had been used in the catalytic reaction, consisted mainly of small irregular-shaped tin(IV) oxide-type crystals containing planar faults (Fig. 3). The material differed from sample A in that the high-resolution images revealed significant amounts of amorphous material (Fig. 4) and the electron diffraction patterns sometimes showed spots away from the tin(IV) oxide ring positions (Fig. 5). The identification of the origin of these reflections was hindered by their rapid disappearance during microscopic observation, even

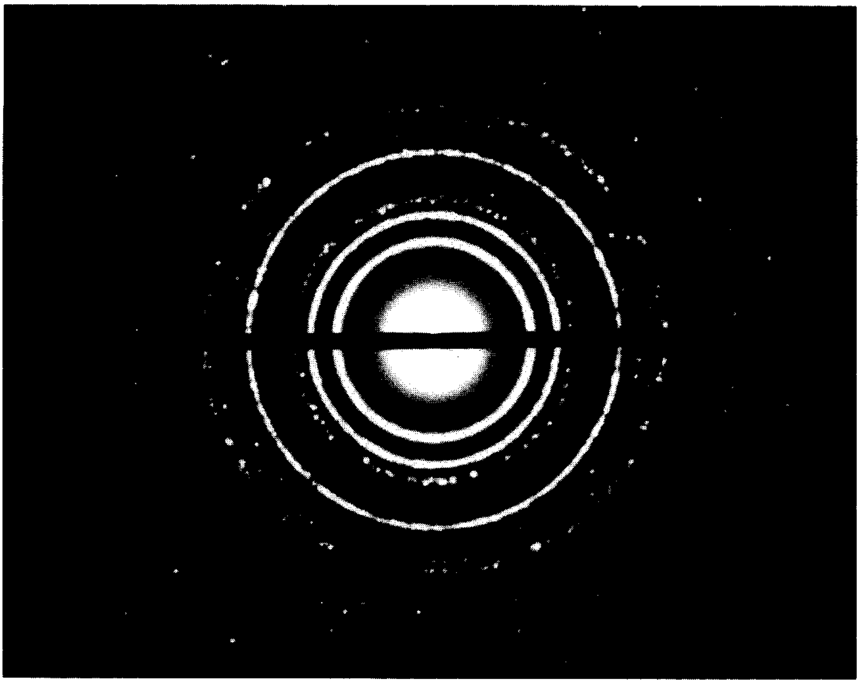

FIG. 2. Typical electron diffraction pattern from sample A: ring diameters correspond to tin(IV) oxide lattice spacings only.

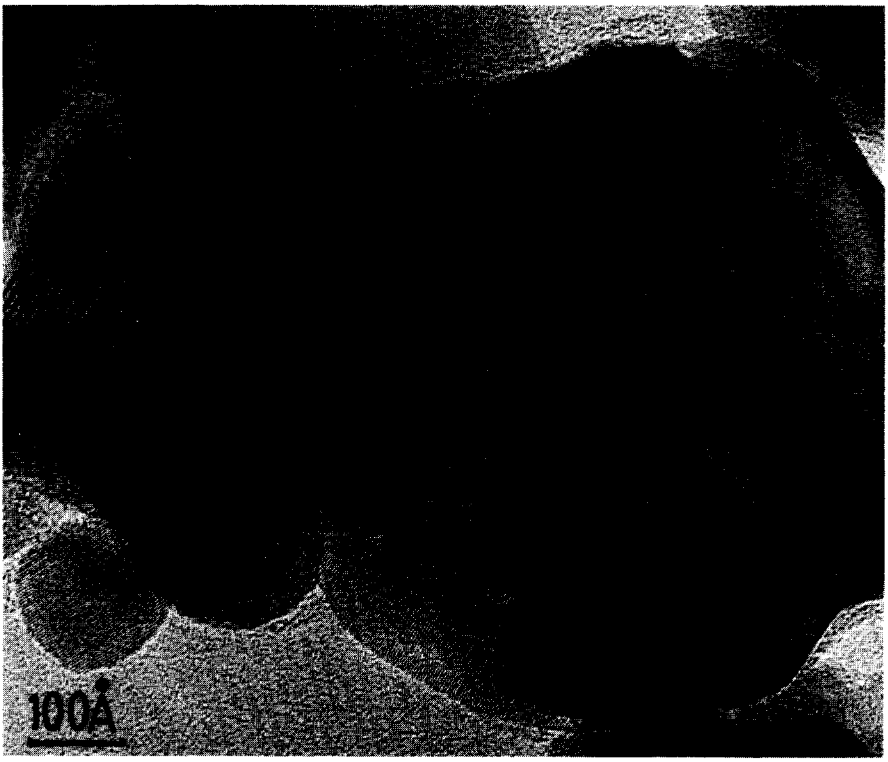

FIG. 3. Crystals of the rutile-type phase of various sizes from sample B shown here overlapping with the carbon support film. The coarse fringes (marked M) arise from moiré interference effects in regions where crystals overlap. An apparent twin boundary (marked T) and areas of disordered planar defects (arrowed) are visible in the large crystal.

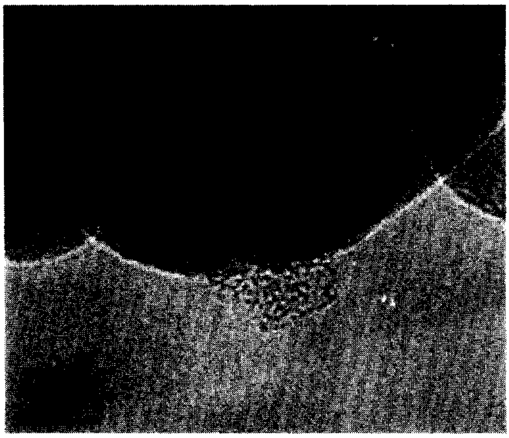

FIG. 4. A small amorphous region located on a tin(IV) oxide-type crystal from sample B.

at low beam current levels, but comparison with other diffraction patterns failed to reveal a correspondence with any known tin- or antimony oxides.

Tin–Antimony Oxide C

Following calcination at 600°C in air, the used catalyst was found to contain crystals of the rutile-type phase of the same general morphology as those observed in both the original material and the used catalyst. Furthermore, the amorphous material which was first observed after use of the catalyst in the catalytic reactor persisted in this sample. Electron diffraction, however, gave no evidence for the presence of the beam-sensitive non-rutile-type crystalline phase which had resulted from the exposure of the material to catalytic conditions.

Tin–Antimony Oxide D

This sample was characterised by the presence of larger crystals with diameters typically between 4000 Å and 1 μm and with morphologies which varied from well-rounded particles to irregular-shaped fragments (Fig. 6). Although the sample was generally less disordered than that observed when the used catalyst was calcined at lower temperatures, regions of substantially disordered and amorphous material could be identified (Fig. 7). The electron diffraction patterns were composed of rings of sparsely populated spots consistent with the presence of larger rutile-type tin(IV) oxide crystals.

Tin–Antimony Oxide E

This material, containing 4% antimony and used as a catalyst after high temperature calcination, contained irregular-shaped tin(IV) oxide-type crystals of ca. 0.1 to 4 μm diameter containing regions of considerable disorder as shown in Fig. 8.

Tin–Antimony Oxide F

Calcination of the used catalyst E at 1000°C produced a material consisting of irregular-shaped heavily disordered crystals which were very similar to the material E.

Tin–Antimony Oxide G

The sample containing 20% antimony and prepared at 600°C provided the starting material for samples H, I, J, K, and L. The crystals were smaller, ca. 20–100 Å diameter, than those observed in the material containing 2% antimony which had been subjected to similar thermal treatment (sample A) and were surrounded by substantial amounts of amorphous material

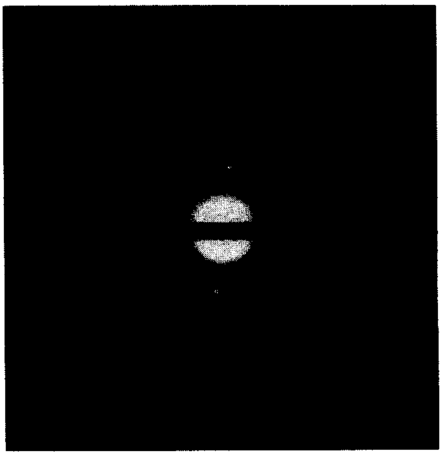

FIG. 5. Electron diffraction pattern from sample B showing short-lived spots corresponding to lattice spacings of 3.65 and 4.10 Å.

FIG. 6. Typical region of tin–antimony oxide D showing general particle morphology as well as regions of considerable disorder (arrowed).

(Fig. 9). Measurement of the lattice fringes and the ring diameters in the electron diffraction patterns showed the crystalline phase to be of the rutile tin(IV) oxide-type structure. No evidence was found for the presence of any discrete crystalline antimony oxide phases.

Tin–Antimony Oxide H

The material, which had been subjected to treatment under catalytic conditions, was somewhat similar to that of the untreated sample in that it contained small, often facetted microcrystallites. However, these were embedded in a significantly larger amount of amorphous or disordered material (Fig. 10). The broad ring-type electron diffraction patterns were characteristic of the tin(IV) oxide-type structure of the crystalline phase. No evidence was found for the presence of a separate antimony oxide phase.

Tin–Antimony Oxide I

The sample showed no noticeable changes as a result of calcination in air at 600°C and remained as a particulate material with substantial amounts of amorphous and poorly crystalline material.

Tin–Antimony Oxide J

After heating to 1000°C in air this catalyst contained three types of crystalline mate-

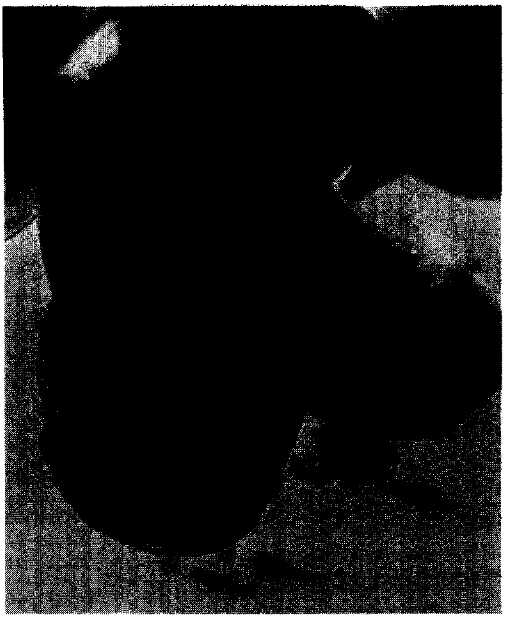

FIG. 7. Region of sample D showing disorder (D) and some amorphous material (arrowed).

rial: small crystals (ca. 100 Å diameter) which gave electron diffraction patterns characteristic of rutile-type tin(IV) oxide; larger rutile-type crystals (ca. 500–2000 Å diameter) which were sometimes twinned; and very large beam-sensitive crystals (several micrometers in diameter) of a non-rutile-type structure which were previously observed (*15*) in samples of this composition and preparation and which have not yet been characterised. Small amounts of amorphous and disordered material were also observed.

Tin–Antimony Oxide K

The tin–antimony oxide, formed at high temperature and used as a catalyst, was composed of large crystals of both tin(IV) oxide character and of non-rutile-type nature together with areas of disordered material. The electron diffraction patterns from

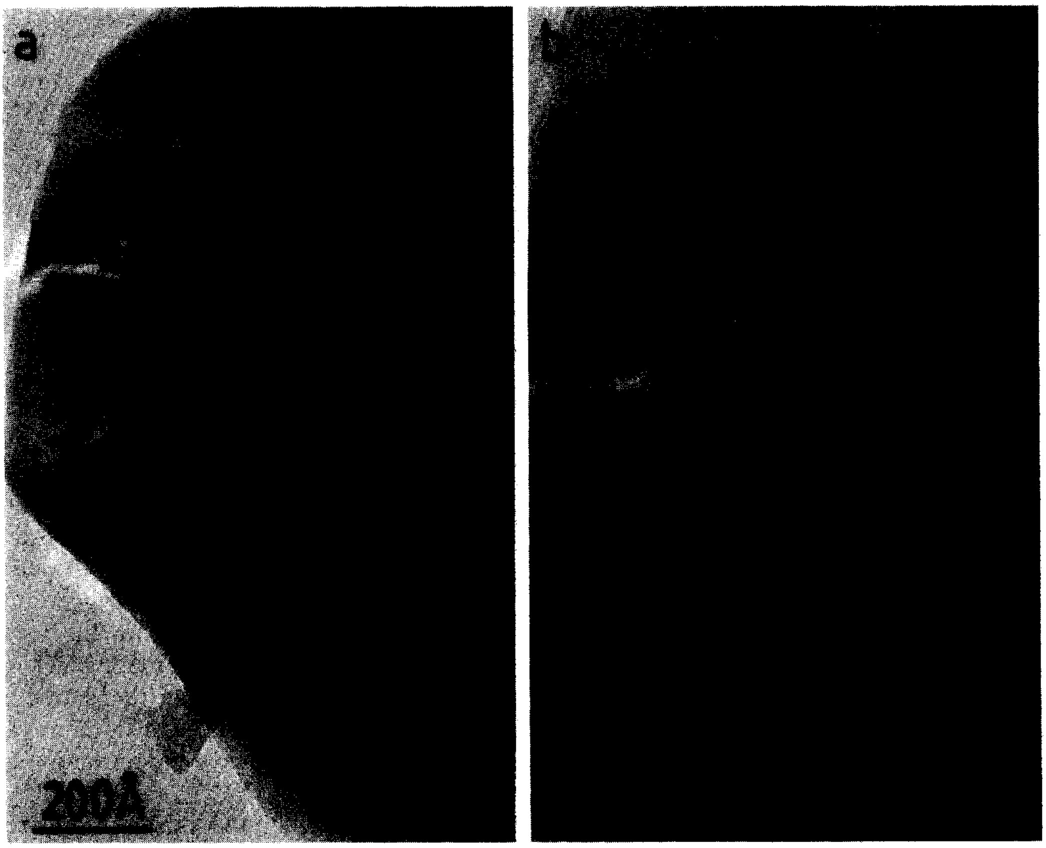

FIG. 8. (a) Disordered tin(IV) oxide-type crystal visible in sample E. (b) Enlargement from part of (a) clearly showing distortion of lattice structure.

FIG. 9. Typical region of tin–antimony oxide G showing amorphous material and tin(IV) oxide-type microcrystallites.

the non-rutile-type phase were similar to those observed in the electron diffraction patterns from sample J.

Tin–Antimony Oxide L

The used catalyst which had been heated at 1000°C consisted predominantly of rounded tin(IV) oxide-type crystals (ca. 0.2–1.0 μm diameter). Some disorder remained in the material and some large non-rutile-type crystals were observed which were also similar to those found in sample J. Some very short-lived spots were seen in the electron diffraction pattern but their origin could not be determined.

DISCUSSION

Catalysts Calcined at 600°C

The white precipitate formed by the simultaneous addition of tin(IV) chloride and antimony(V) chloride to ammonium hydroxide has been described as an amorphous material (*2*) containing tin(IV) and antimony(V) in separate octahedral hydroxyl environments (*9*). Studies of the catalytic character of tin–antimony oxide have demonstrated that calcination of this precipitate leads to the formation of a selective oxidation catalyst. Our studies of the mixed oxides formed at 600°C by high-resolution electron microscopy (*15*) have shown them to consist of small disordered crystals of a rutile-type solid and, depending on antimony concentration, varying amounts of amorphous material. Although the rutile-type phase formed at these temperatures has in the past been described as a solid solution of antimony in tin(IV) oxide and associated with the catalytic properties (*17–22*), our studies by high-resolution electron microscopy (*15*), like recent investigations by X-ray diffraction by other workers (*2*), have suggested that the low temperature calcination fails to induce large scale aggregation of the tin(IV) oxide units and that it is unreasonable to envisage such materials as equilibrated solids. It is also pertinent to record that we have been unable to identify any evidence for the presence of a separate antimony oxide phase in these materials even though the dehydration of antimonic acid at similar temperatures is known (*23*) to give the formation of Sb_6O_{13}.

The detection, in the observations reported here, of significant amounts of amor-

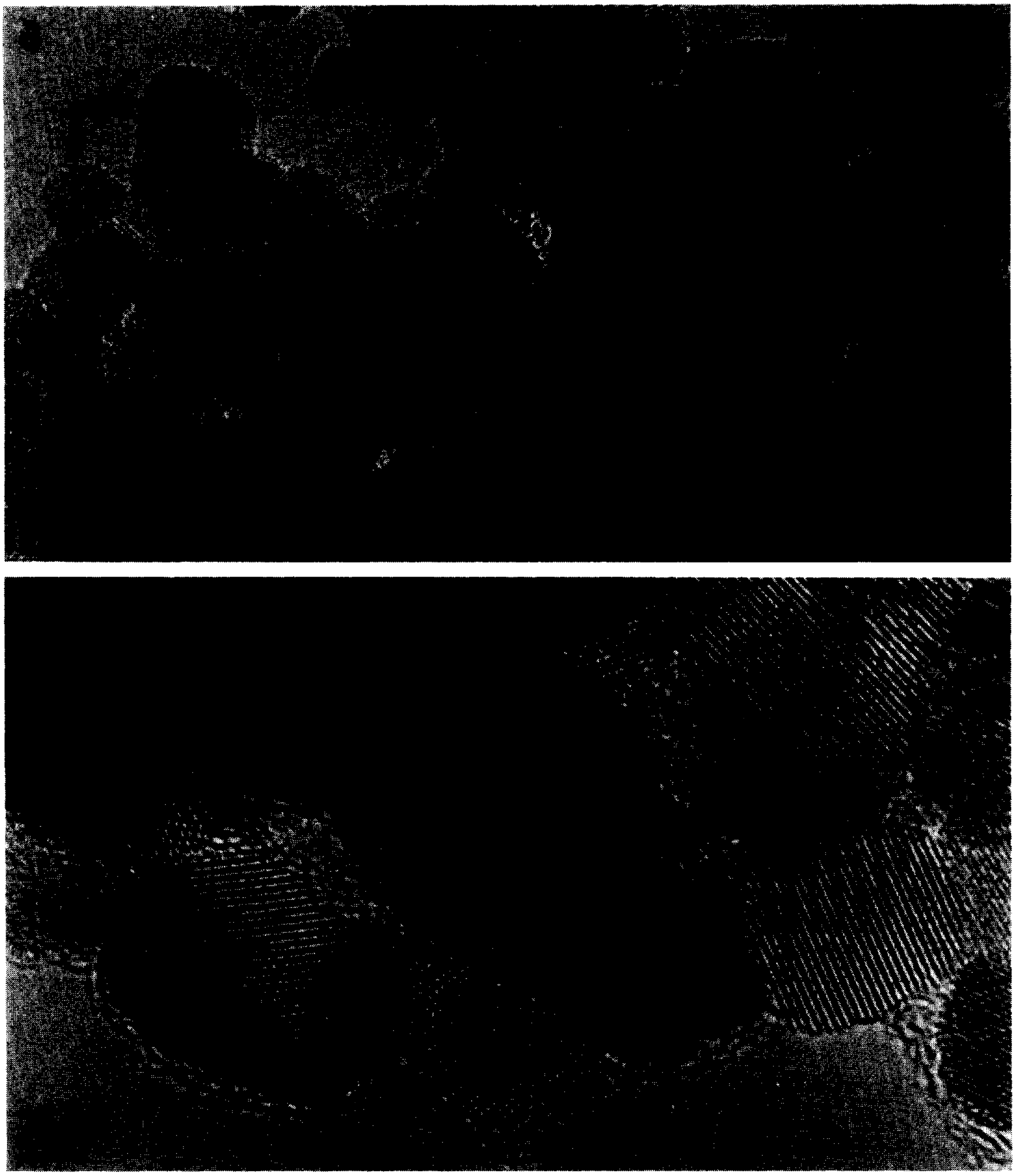

FIG. 10. (a) Region of sample H showing amorphous or poorly crystallised material (arrowed). (b) Well-facetted microcrystallites seen in sample H.

phous material following the treatment of the tin–antimony oxide containing 2% antimony and prepared at 600°C in a gaseous atmosphere containing hydrocarbon and oxygen suggests that some changes are induced in the solid during the catalytic reaction. In this respect it is relevant that our previous study of tin–antimony oxides (*15*) showed that materials containing larger concentrations of antimony gave high-resolution images revealing large amounts of amorphous antimony-containing material and which were very similar to those recorded from the used catalyst containing

2% antimony. The results recorded in this work therefore suggest that exposure of the low-antimony content catalyst formed at 600°C to hydrocarbon and oxygen gives rise to the segregation of antimony from the disordered rutile-type phase of the catalyst which does not nucleate and develop into a crystalline antimony oxide phase. It is also relevant to note that this noncrystalline antimony-bearing phase was shown by high-resolution electron microscopy to be unchanged by subsequent calcination in air at 600°C and therefore to be of quite persistent nature. The non-rutile-type crystalline solid which is also formed during the catalytic reaction was found to be highly sensitive to the electron beam and therefore not amenable to characterisation by electron microscopy. Whether or not this material is a crystalline antimony-containing material has yet to be established; however, the absence of this non-rutile-type phase from the used catalyst calcined in air suggests that the solid undergoes facile conversion under relatively mild conditions.

The tin–antimony oxide containing 20% antimony and prepared at 600°C contained (*15*) smaller crystals of the rutile-type phase and appreciable amounts of the antimony-bearing amorphous material. These properties reflect the higher concentration of antimony which, at such low temperatures, inhibits the development of the crystalline rutile-type solid. The poorly crystalline nature of these materials calcined at 600°C has also been recorded during X-ray diffraction studies (*2*) and it would seem reasonable to envisage that these highly disordered solids support a high concentration of randomly distributed tin and antimony cations. The increase in the concentration of the amorphous phase following the use of this tin–antimony oxide under catalytic conditions and which is unchanged by subsequent calcination at 600°C is consistent with the observations recorded from the catalyst containing 2% antimony.

In assessing the changes which are induced in the catalysts during the catalytic reaction it is relevant to note that Mössbauer spectroscopy (*7*) has shown that treatment of tin–antimony oxides of comparable compositions in atmospheres of butene and oxygen is accompanied by reduction of antimony(V) to antimony(III). Given the description of these tin–antimony oxides prepared at 600°C as poorly crystalline solids which have not attained bulk equilibrium (*2, 15*) it may be envisaged that the changes which are induced in the catalysts by treatment in the hydrocarbon and oxygen gas flow are associated with the reduction of antimony and its segregation from the highly disordered poorly crystalline matrix and the formation of an amorphous solid which is unchanged by subsequent low temperature calcination in air. However, it is significant that the calcination of both the used catalysts at 1000°C in air for a prolonged period of time gave materials with similar morphologies to those observed in the high-resolution study of pure tin–antimony oxides of comparable antimony contents and thermal histories (*15*). The results suggest that the high temperature conditions which are necessary (*2, 15*) for the attainment of bulk equilibrium dominate any previous structural or morphological properties which are induced by chemical processes at lower temperatures.

It is interesting that, in contrast to the tin–antimony oxide containing 2% antimony formed at 600°C and used in the catalytic reaction, no evidence was found in the used catalyst containing 20% antimony for the presence of any uncharacterised crystalline non-rutile-type phase except after it had been heated at 1000°C. In this respect it is pertinent to note that antimony oxides (*2*) and other unidentified phases (*2, 15*) have been observed in samples with initially high antimony contents.

Catalysts Calcined at 1000°C

Recent studies (*2–15*) of pure tin–antimony oxides have focused attention on the changes which are induced by calcination at high temperature. Indeed, latest structural studies (*2, 15*) have indicated that solid solutions of antimony within the rutile-type tin(IV) oxide lattice are only achieved by prolonged calcination of the dehydrated precipitates at 1000°C. The formation of these equilibriated solid solutions has been described (*2–5*) in terms of the thermally induced aggregation of the tin(IV) oxide octahedra and the countermigration of antimony to the surface to produce a solid solution and a surface antimony oxide phase. This antimony oxide is volatilised at high temperatures (*2–5*) to leave the crystalline rutile-type solid solution containing ca. 4% antimony in tin(IV) oxide (*2*) but with a surface antimony composition of ca. 25% (*5*). Hence, in contrast with earlier proposals (*21, 22*) that antimony solubility in tin(IV) oxide is enhanced at higher temperatures, more recent evidence suggests that antimony migrates from the rutile-type phase under such conditions. In this respect it is relevant that recent studies have tended to correlate the catalytic properties with the thermally induced enrichment of the surface with antimony (*2–5, 9–12*), in particular the high selectivity for the formation of butadiene from butene has recently been associated with the tin–antimony oxide solid solutions which are formed by long period calcination of the precipitates at 1000°C (*10*).

Two precipitates, containing 4 and 20% antimony, were calcined for long periods of time to give solid solutions for use in the investigations reported here. The catalytic properties of these, and the other samples investigated, in terms of the spectrum of organic products after identical treatment in the butene–oxygen–nitrogen gas flow, resembled those reported for materials prepared by similar methods and evaluated by more sophisticated techniques. The tin–antimony oxide containing 4% antimony, which corresponds to the limit of antimony solubility in tin(IV) oxide (*2*), was shown by our previous high-resolution electron microscope study (*15*) to be composed of large rutile-type tin(IV) oxide crystals which were frequently twinned and contained only a sparse quantity of amorphous material. Furthermore, our results, as well as those of the most recent surface study of tin–antimony oxide (*6*) by XPS, UPS, and HREELS, have failed to identify any discrete crystalline antimony oxide phase at the surface of the solid solution as has been described by other workers (*4*). Hence, the thermally induced enrichment of the solid solution surface by antimony which has been associated with the superior catalytic performance for the selective oxidation of butene (*10, 12*) and propene (*4*) may, from high-resolution electron microscopy and other surface sensitive techniques, be associated with a high concentration of antimony, possibly completely surrounded by tin (*5*), at the surface of the rutile-type tin(IV) oxide matrix and which does not involve the formation of a discrete crystalline superficial antimony oxide phase.

Our observations have also shown (*15*) that precipitates containing higher antimony concentrations give, when heated at 1000°C for prolonged periods, the rutile-type solid solutions, some non-rutile-type crystalline material, and substantial quantities of amorphous antimony-containing material. This is well illustrated by the high-resolution image of a tin–antimony oxide solid solution formed by heating a precipitate containing 20% antimony (*15*). The amorphous phase originates from the antimony which is not accommodated in the solid solution and which does not nucleate to form antimony tetroxide which is volatilised at high temperatures.

Hence, the larger concentrations of disordered material observed in the high-resolution images recorded from both the tin–antimony oxide solid solutions investigated here after their exposure to the catalytic reaction and which remains unchanged by subsequent calcination at moderate temperature resembles the results recorded from the poorly crystalline catalysts prepared at

600°C. However, the disordered material was resistant to change when heated to high temperatures and the high-resolution electron microscopy observations suggest that the solid solutions are less amenable to the incorporation of antimony-containing materials generated during the catalytic reaction than the highly disordered nonequilibriated catalysts formed at low temperature. Given that oxidation of the hydrocarbon has been associated (*24–26*) with oxygen from the lattice of the mixed oxide catalyst it seems likely that the reduction of the tin–antimony oxide solid solution is also accompanied by the segregation of antimony.

It is unclear why the solid solution prepared from a precipitate containing 4% antimony failed to give a crystalline non-rutile-type phase after treatment under catalytic conditions as was observed in the catalyst containing 2% antimony and heated at 600°C. Furthermore, the different, as yet uncharacterised, crystalline non-rutile-type phase identified in the catalyst prepared from a precipitate containing 20% antimony and calcined at 1000°C (*15*) was unchanged by exposure to the catalytic reaction. The influence of this phase on the catalytic performance of the tin–antimony oxide must await subsequent investigation. Further studies of samples with high antimony content are also planned since previous workers (*2*) have only identified pure antimony oxides in such materials. These studies will also examine the stability of these oxides in the electron beam.

ACKNOWLEDGMENT

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