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An X-Ray Photoelectron Spectroscopy Study of the Surface Composition of Tin and Antimony Mixed Metal Oxide Catalysts

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The surface composition of tin–antimony mixed oxide selective oxidation catalysts has been found to depend upon heat treatment, the surface becoming progressively enriched in antimony at elevated temperatures. Surface segregation of antimony has been investigated by X-ray photoelectron spectroscopy (XPS) and values obtained for the heats of segregation. The observations are discussed in the context of the nucleation and growth of antimony oxide and tin oxide phases in this system.

INTRODUCTION

Catalysts based upon mixed oxides of tin and antimony have been developed industrially in recent years (*1*, *2*) for the selective oxidation of hydrocarbons. Empirically it is observed that the catalytic performance of these materials depends critically upon the conditions of preparation and particularly upon the calcination temperature adopted. Many factors may be affected by these conditions, such as the bulk phase composition, surface area, pore size, etc. and several investigations have been reported in the literature (*3–9*). During catalytic studies of this system we have observed that the surface composition of these oxides, as determined by X-ray photoelectron spectroscopy (XPS), may vary markedly from the bulk composition. Surface enrichment in antimony occurs to an extent dependent upon bulk composition, calcination period, and calcination temperature. In this paper we report a systematic investigation of this effect.

EXPERIMENTAL

Tin antimony catalysts $Sn_{1-x}Sb_xO_2$ were prepared over the entire range $x = 0$ to 1 by coprecipitation techniques. For $x > 0.2$, anhydrous $SnCl_4$ and $SbCl_5$ were simultaneously added to ammonium hydroxide solution, maintaining the solution alkaline by the addition of more ammonia. The $SbCl_5$ component was replaced by an aqua regia solution containing the calculated quantities of dissolved antimony metal for samples with $x < 0.2$. The white precipitate formed in this reaction was thoroughly washed, filtered, and dried at 120°C. After grinding to a constant particle size the materials were then subjected to the required heat treatments. Samples over the entire composition range were calcined for 16-hr periods at 100°C intervals at temperatures up to 1000°C. In addition selected compositions were subjected to calcination for intervals varying from 1 min to 3 weeks.

The bulk composition of the oxide powders was determined by either wet

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chemical methods or X-ray fluorescence spectrometry, while the surface composition was obtained from their XPS spectra. In addition to the analysis of powder samples some experiments were also performed upon aggregates of single crystals of antimony-doped SnO_2. These varied in size up to 10 × 1 mm and were prepared by vapor phase deposition (*10*).

XPS data were obtained using an AEI ES 200B spectrometer and $MgK_{\alpha 1,2}$ ($h\nu = 1253.6$ eV) exciting radiation. Powder samples were pressed onto two-sided adhesive tape of approximate area 5 × 16 mm^2 and spectra were run *in vacua* of $\sim 10^{-8}$ Torr. In some cases it was found necessary to cool the samples (to 173 K) to avoid spectral degradation. This was generally found to be the case when samples showed a surface antimony concentration >20 atom% antimony. No changes in relative intensities of the spectral peaks were observed as a result of cooling the samples. The relative proportions of antimony and tin were derived from the peak heights of the Sb $3d_{3/2}$ and the Sn $3d_{5/2}$ signals with a reproducibility within 5%. For conversion to absolute surface concentrations we used the sensitivity factors of Wagner (*11*) and we estimate the absolute values to be correct to within ±25%.

Composition profiles for selected samples were determined by applying the argon ion etching technique. The etcher was a cold cathode ion source developed by Ion Tech Ltd which calibration experiments employing gold had shown to give a sputtering rate of $\simeq 4$ Å/min under the experimental conditions employed (5-kV argon ions and an ion current of ≈ 4 μA). Although differential sputtering of one cationic species with respect to another may occur in some systems we do not believe this to be the case for mixed oxide catalysts of tin and antimony for the following reasons:

(a) A physical mixture of the pure oxides prepared separately by the same method as the mixed oxide catalysts, and each calcined at 300°C, was etched for a total time of 30 min. Since the average diameter of the crystallites of both oxides was found by X-ray line broadening to be less than 50 Å, this etching procedure corresponded to sputtering through several crystallite diameters. At no stage was any change in the surface ratio of Sb/Sn observed, indicating no major differences in the sputtering rates of tin and antimony in oxide environments.

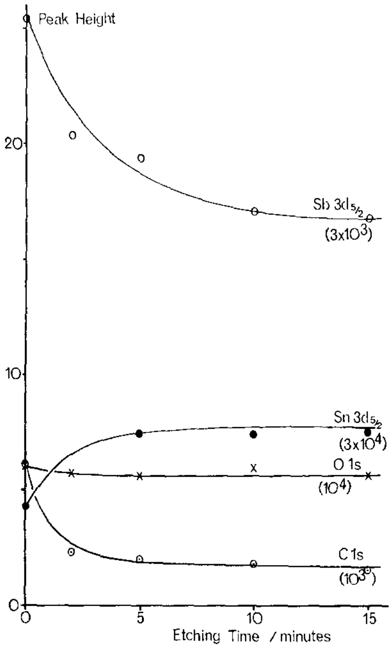

FIG. 1. Argon ion etching profile for sample $Sn_{0.8}Sb_{0.2}O_2$ calcined at 900°C for 16 hr.

(b) A sample of the mixed oxide $Sn_{0.8} \times Sb_{0.2}O_2$ dried and calcined for 16 hr at 100°C gave initial and final surface concentrations of antimony after 30 min of argon ion etching which were identical and correspond to the bulk analytical figure.

We have therefore concluded that any significant changes in composition observed for our catalysts as a result of ion etching correspond to real concentration gradients within particles of the samples.

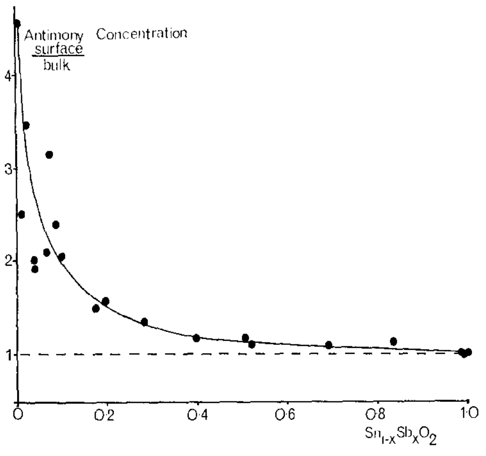

FIG. 2. Variation of the degree of surface enrichment in antimony as a function of bulk composition at constant calcination conditions (16 hr at 600°C).

As standards for the XPS work we have examined the compounds Sb_2O_3 [Sb(III)] and α-Sb_2O_4[Sb(III) + Sb(IV)]. No significant differences in the Sb $3d_{3/2}$ peak shape and half-width were observed between these two standards. This effect has recently been investigated by Orchard and Thornton (*12*) who concluded that the surface of α-Sb_2O_4 is composed of only one oxidation state of antimony, probably Sb(III). However, their deconvolution of the Sb $3d_{3/2}$ spectra from cleaned and reoxidized α-Sb_2O_4 showed a binding energy shift of 0.6 eV between Sb(III) and Sb(V). The spectra of our catalysts correspond, on the basis of peak maxima, to antimony in the oxidation state III, but this does not exclude the possibility of some Sb(V) being present.

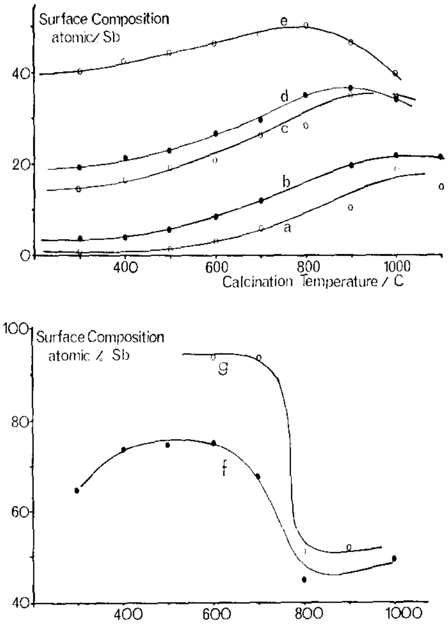

FIG. 3. Variation in surface composition with calcination temperature at constant bulk composition and constant calcination period (16 hr). (a) 0.5, (b) 4.0, (c) 12.0, (d) 17.5, (e) 39.4, (f) 68.0, (g) 83.0 atom% antimony.

OBSERVATIONS

A typical composition profile is plotted in Fig. 1 for a 20 atom% antimony sample heated for 16 hr at 900°C. Clearly the surface layer which would be exposed to catalytic reaction conditions is enriched in antimony by a factor of about 2.7 with respect to that which would be predicted from the bulk composition. This enrichment factor decreases rapidly with depth from the surface, the bulk composition being attained after bombardment equivalent to sputtering to a depth of some 50 Å. The surface enrichment factor was observed to vary with bulk composition at constant calcination temperature. Figure 2 sum-

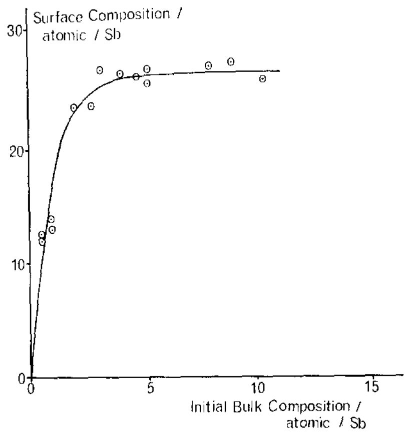

FIG. 4. Surface composition after prolonged calcination in air at 1000°C to constant weight.

marizes the data for samples calcined at 600°C for 16 hr.

Variation of the calcination temperature produced systematic changes in surface composition (Fig. 3). Catalysts containing less than 60 atom% antimony retained a constant surface composition (characteristic of the bulk) until just below 400°C. At higher temperatures the surfaces become increasingly enriched in antimony, attaining a maximum close to 1000°C, the maximum shifting slightly to lower temperatures at higher antimony concentrations. It should be noted that the temperature observed for the onset of antimony migration corresponds to that at which the color of the materials changes from white to a deep blue or green. The main feature observed for high antimony compositions was a marked decrease in surface antimony concentration at 700 to 800°C. Chemical analysis showed that the overall composition of these materials remained constant throughout these heat treatments, physical loss of antimony by vaporization of the oxide occurring only at higher temperatures (900°C for 83 atom% antimony sample; 1000°C for 40 atom% antimony sample).

Analysis of the surfaces of catalysts heated for many days in air at 1000°C gave results directly related to the bulk phase changes which have been previously reported (9). Catalysts containing more than 4 atom% antimony segregate under these conditions into two phases with rutile-like and Sb_2O_4 structures, respectively. The Sb_2O_4 is volatile at 1000°C and is slowly lost from the system so that these materials equilibrate to the rutile-like phase alone, containing about 4% antimony. Below 4% antimony no bulk phase segregation is observed. From Fig. 4 which relates the final surface composition to the *initial* bulk concentration it may be deduced that volatile Sb_2O_4 is formed only at surface compositions greater than a critical value which is close to one antimony in every four within the surface layer. Bulk compositions less than 4 atom% antimony generate surface compositions at 1000°C below this critical value and so separation of the Sb_2O_4 phase is not observed. This critical surface composition close to 25 atom% antimony was also observed for single crystals of SnO_2 doped to a total level of about 1 atom% antimony which had been prepared by deposition from a mixture of the oxides in the vapor phase at 1300°C *(10)*.

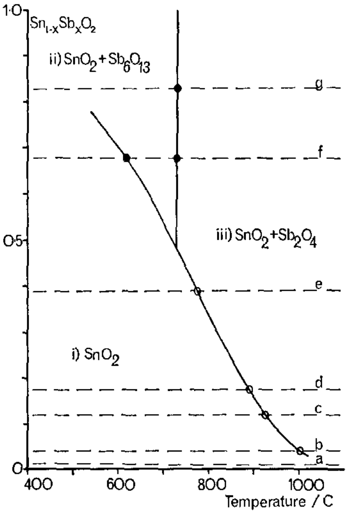

FIG. 5. The crystalline phases identified in catalysts calcined for 16-hr periods. Note: the compositions a to g correspond to Fig. 3 and the boundaries between phase regions correspond to maxima (○) or rapid changes (●) in surface composition.

DISCUSSION

Comparison of the influence of calcination temperature upon surface composition (Fig. 3) with the effect upon bulk phase composition as determined by X-ray diffraction (a) (Fig. 5) shows that three corresponding regions of temperature and composition may be distinguished: (i) a region containing only the rutile (SnO_2) phase which exhibits surface enrichment in antimony at increasing temperature,

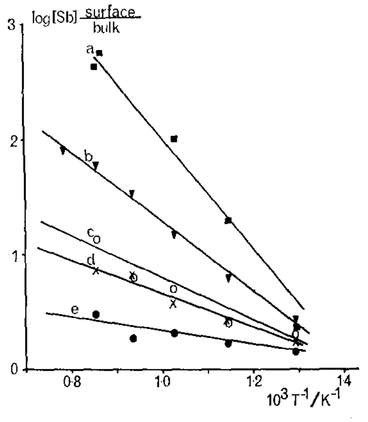

FIG. 6. Arrhenius plots for the temperature dependence of the equilibrium surface composition at constant bulk composition. (a) 0.5, (b) 4.0, (c) 12.0, (d) 17.5, (e) 39 atom% antimony.

(ii) a region with bulk antimony concentrations greater than ~60 atom% and containing only the Sb_6O_{13} and rutile-like phases in which surface composition varies little with temperature, and (iii) a region which contains the Sb_2O_4 phase which is produced at high temperatures and exhibits decreasing surface antimony composition with increasing temperature.

From the data it is apparent that the conditions of composition and temperature which delineate the rutile-like from the rutile + Sb_2O_4 region correspond to the conditions which produce maxima in the surface antimony concentration as determined by XPS.

We shall first consider the composition range $0 < x < 0.65$ which X-ray diffraction shows to contain only the rutile phase after short calcination periods at 600°C (*9*). The diffraction data indicate that material from this region is poorly crystalline, the average crystallite size increasing in the range 40 to 150 Å at decreasing antimony concentrations. Heating for 14 days at this temperature causes an additional Sb_2O_4 phase to crystallize out in the composition range $0.2 < x < 0.65$. It would therefore appear from the bulk phase analysis (*9*) that for this composition range the preparative procedure produces a homogeneous, amorphous, and hydrated material which at low temperatures loses its water of hydration and partially crystallizes into a highly defective rutile-like structure into which antimony is built. This structure is, however, metastable at compositions greater than $x = 0.2$ and Sb_2O_4 *is slowly* crystallized out.

Confirmation that surface segregation occurs in this composition region is obtained from Arrhenius plots of the equilibrium surface composition as a function of temperature (*13*). Since the observed surface composition remains constant after 16 hr heat treatments we assume that the surface is then in equilibrium with the bulk. The plots of the logarithm of the ratio of tha atomic concentration of antimony ions in the surface to that in the bulk against the reciprocal temperature fall on straight lines (Fig. 6). From the slopes of these plots the heats of segregation at each composition were calculated and found to decrease regularly at increasing bulk antimony composition (Fig. 7), tending in the limit to zero at a concentration of 100 atom% antimony.

The onset of surface enrichment in antimony at 400°C corresponds exactly to a change in color from white to a deep blue or green, indicating that antimony enrichment occurs as a result of lattice diffusion and reconstruction. The results are therefore consistent with the postulate

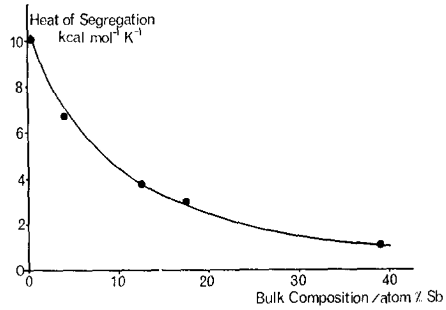

FIG. 7. The heat of segregation as a function of bulk composition.

that catalyst preparation forces antimony into an environment in which it is not particularly stable, so that at high temperatures segregation to surfaces occurs where antimony may occupy an energetically more favorable situation, probably as Sb^{3+} (*10*, *12*). Migration to surfaces would therefore be the first stage in a process resulting, if sufficient antimony is present, in the formation of a macroscopically distinguishable antimony oxide phase. The question then arises as to the definition of the stage at which nuclei of the antimony oxide phase may first be identified.

For the purpose of establishing a physical model for this system a quantitative treatment of the surface analytical data would be desirable. However, the quantitative surface analysis of oxide powders is difficult because the XPS signal is derived not only from the top monolayer of the catalyst particles but also, with increasing attenuation, from the subsurface layers. Approximately 95% of the total peak intensity is derived from the region within a distance of 3λ from the surface where λ is the escape depth. For Sn and Sb 3*d* electrons and MgK$_\alpha$ radiation $\lambda \approx 10$ to 15 Å (*14*). With very small particle sizes as are observed in this system at low calcination temperatures, a very large proportion of the material is close to a surface and variations in particle size with temperature may have a significant influence upon the apparent surface composition as determined by XPS. One possible model of this system would for example be that coprecipitation produces tiny nuclei of the rutile SnO$_2$ phase surrounded by a separate but amorphous antimony oxide phase. At increased temperatures the SnO$_2$ phase would then sinter and the proportion of tin ions close to an exposed surface would decrease relative to the concentration of antimony ions. However, we prefer the simpler model of antimony segregating as a result of heat treatment to the surface of an initially *homogeneous* coprecipitated catalyst and in which no discrete antimony oxide nuclei may be identified for the following reasons: (a) the surface composition of the dried coprecipitated catalyst corresponds to the overall bulk composition, (b) at low temperatures, the Sb$_6$O$_{13}$ phase is observed only by X-ray diffraction at high antimony composition in a region (ii) in which significant surface enrichment is *not* observed, (c) the region at high temperatures and high antimony compositions (iii) in which the Sb$_2$O$_4$ phase is observed by X-ray diffraction corresponds to that region in which a rapid fall in the apparent surface antimony composition is observed with increasing temperature. The diffraction data indicate that Sb$_2$O$_4$ rapidly sinters to form crystallites much larger than are observed for the SnO$_2$ phase, consistent with the observed decrease in the proportion of antimony cations exposed at surfaces, (d) surface enrichment in antimony is most pronounced at low antimony compositions in which free Sb$_2$O$_4$ is never observed below 900°C, even after very prolonged heat treatment (*9*), and (e) surface enrichment identical to that found for powders is observed on very large antimony-doped single crystals prepared at similar high temperatures but by a completely different vapor deposition technique.

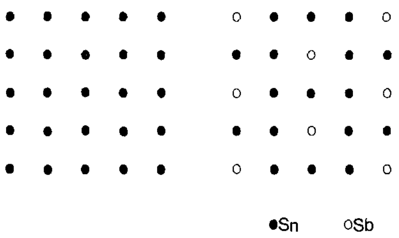

FIG. 8. Schematic representation of the (100) surface of (a) pure SnO$_2$ and (b) catalyst with 25% of the tin cations substituted by antimony.

The relationship between surface segregation of antimony and nucleation of the Sb$_2$O$_4$ phase is illustrated by the observation of a critical concentration of surface antimony below which Sb$_2$O$_4$ is not volatilized at 1000°C. Consideration of the closest packed planes of the rutile structure (Fig. 8) shows that at concentrations in the surface layer greater than one atom in four, antimony cations must reside in adjacent lattice sites. At concentrations below this, however, each antimony cation is surrounded only by tin cations provided the antimony cations are distributed at high temperatures to minimize Sb–Sb interactions. It may then be envisaged that antimony cations in adjacent lattice sites constitute a surface nucleus of Sb_2O_4 which may be lost from the surface by vaporization. Vacant surface sites would be replenished by diffusion from the bulk and vaporization of Sb_2O_4 would continue until the bulk reservoir is depleted to a level insufficient to maintain the critical surface concentration of antimony, as is observed experimentally.

In this paper we have described how the surface composition of tin and antimony mixed metal oxide catalysts is dependent upon the heat treatment employed in catalyst preparation and we have discussed possible structural relationships between surface and bulk. It may be anticipated that the catalytic properties of these materials will depend to some extent upon the structure and composition of the surfaces exposed to the reactant gases and indeed it is observed empirically that calcination temperature is an important parameter in the optimization of catalytic performance. We report the results of an investigation of the relationship between surface composition and catalytic performance in a subsequent paper (*15*).

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