

## On the Catalytic Properties of Sb-Sn Mixed Oxides

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Treatment of an Sb-Sn mixed oxide, calcined at 750 °C, with dil. HCl greatly improves the mild oxidation of propene to acrolein; it has been shown that large  $\alpha$ -Sb<sub>2</sub>O<sub>4</sub> particles, formed during the high-temperature calcination, do not favour this oxidation.

Sb-Sn mixed oxide catalysts have been commercially developed for the mild oxidation of propene to acrolein, for its ammoxidation to acrylonitrile, and for the oxidative dehydrogenation of butenes to buta-1,3-dienes.<sup>1</sup> Despite extensive study,<sup>2-4</sup> reviewed recently by Berry,<sup>5</sup> the catalytic properties of these oxides and the exact nature of the active sites remain unclear and controversial. In previous papers<sup>3,6</sup> we have been the first to show unambiguously, using the x.p.s. technique, that the increased selectivity in mild oxidation observed for materials calcined at high temperatures ( $T \geq 700$  °C) is due to a migration of Sb towards the surface of the solid. An  $\alpha$ -Sb<sub>2</sub>O<sub>4</sub> phase could be detected by X-ray diffraction when the Sb content was high enough ( $\geq 20$  atom %) and we suggested that the active phase consisted of a thin layer of Sb<sub>2</sub>O<sub>4</sub> particles

lying on the surface of the solid solution of Sb/SnO<sub>2</sub> which is highly electron conducting.

To study the active sites, we thought it could be interesting to dissolve the  $\alpha$ -Sb<sub>2</sub>O<sub>4</sub> particles selectively with respect to the solid solution. Preliminary experiments on pure Sb<sub>2</sub>O<sub>4</sub> and SnO<sub>2</sub> calcined at 750 °C showed that Sb<sub>2</sub>O<sub>4</sub> totally dissolves in a 4 M HCl solution at room temperature for 1 h while SnO<sub>2</sub> does not. We used a sample calcined at 750 °C with a very high content of both Sb (70 atom %) and  $\alpha$ -Sb<sub>2</sub>O<sub>4</sub> particles, characterized by X-ray diffraction and electron microscopy. The sample was treated with 4 M HCl as described above and then heated at 500 °C and at 750 °C in air in order to follow the Sb migration.

The main data are summarized in Tables 1 and 2. Analysis

**Table 1.** Experimental characteristics of oxides after calcination/acid treatment.

Sample	Description <sup>a</sup>	Specific surface area/m <sup>2</sup> g <sup>-1</sup>			Atom % Sb/Sb + Sn		Particle size of solid solution <sup>b</sup> /Å
		Total	Solid solution	Sb <sub>2</sub> O <sub>4</sub> particles	Chemical analysis	x.p.s.	
(A)	SnO <sub>2</sub> calcined at 500 °C	20	20	—	0	0	—
(B)	Sb <sub>2</sub> O <sub>4</sub> calcined at 500 °C	3	—	3	100	100	—
(C)	Sb <sub>6</sub> O <sub>13</sub> calcined at 500 °C	50	—	—	100	100	—
(D)	Mixed oxide calcined at 750 °C	15.7	15.5	0.2	67.5	66	50 <sup>c</sup>
(E)	Oxide (D) after 1 h HCl treatment	78.4	78.3	0.1	34.2	34	45 <sup>d</sup>
(F)	Oxide (E) calcined at 500 °C	78.4	—	—	34.2	40	—
(G)	Oxide (F) calcined at 750 °C	49.8	—	—	34.2	45	62 <sup>e</sup>
(H)	Oxide (D) after 2 h HCl treatment	143	143	0	22.7	31	45
(I)	Oxide (D) after 3 h HCl treatment	145	145	0	16.9	27	43
(J)	Mechanical mixture <sup>f</sup>	5.8	5.8	0	—	—	—

<sup>a</sup> Oxide (D) = Sb/SnO<sub>2</sub> solid solution + small particles (300–3000 Å) of  $\alpha$ -Sb<sub>2</sub>O<sub>4</sub> (easily dissolved by HCl) + large particles (several  $\mu$ m) of  $\alpha$ -Sb<sub>2</sub>O<sub>4</sub>. Oxide (E) = Sb/SnO<sub>2</sub> solid solution + eroded large particles of  $\alpha$ -Sb<sub>2</sub>O<sub>4</sub>. Oxide (F) = Sb/SnO<sub>2</sub> solid solution with Sb migrating to the surface + eroded large particles of  $\alpha$ -Sb<sub>2</sub>O<sub>4</sub>. Oxide (G) = Sn/SnO<sub>2</sub> solid solution with layer of Sb<sub>6</sub>O<sub>13</sub> particles. <sup>b</sup> Particle size determined by X-ray diffraction. <sup>c</sup> Sb<sub>2</sub>O<sub>4</sub> detected (5  $\mu$ m particles). <sup>d</sup> Sb<sub>2</sub>O<sub>4</sub> detected [less than in footnote (c), 5  $\mu$ m particles with eroded shapes]. <sup>e</sup> Sb<sub>6</sub>O<sub>13</sub> (25%) detected by i.r. spectroscopy, not by X-ray diffraction. <sup>f</sup> Mechanical mixture of Sb<sub>2</sub>O<sub>4</sub> and SnO<sub>2</sub> (previously calcined at 750 °C), mixed to obtain 70% Sb content without further heat treatment.

**Table 2.** Catalytic properties at 380 °C and at low conversion (few %).<sup>a</sup>

Sample	C <sub>3</sub> H <sub>6</sub> conversion <sup>b</sup> (%)	Rate of C <sub>3</sub> H <sub>6</sub> conversion /10 <sup>-2</sup> mol s <sup>-1</sup> m <sup>-2</sup>	Rate of acrolein formation /10 <sup>-2</sup> mol s <sup>-1</sup> m <sup>-2</sup>	Selectivity for acrolein (%)
(A)	1.00	2.73	1.01	37
(B)	0.01	0.14	0.06	42
(C)	0.01	0.02	0.01	54
(D)	0.42	1.42	1.31	92
(E)	2.42	1.66	1.34	81
(F)	2.97	2.04	1.71	84
(G)	0.60	0.65	0.60	92
(H)	1.63	0.61	0.30	49
(I)	1.17	0.43	0.14	33
(J)	0.28	2.58	1.63	63

<sup>a</sup> Samples described in Table 1. C<sub>3</sub>H<sub>6</sub>:O<sub>2</sub>:N<sub>2</sub> = 1:1:5.5. <sup>b</sup> For 100 mg sample.

of the *X*-ray diffraction line-widths for the solid solution of SnO<sub>2</sub> is in excellent agreement with electron microscopy and electron microdiffraction characterization. Thus, the contribution, *S*, of both entities to the surface area may be calculated, since with spherical particles (which is true for solid solution particles) the relationship  $S \text{ (m}^2\text{/g)} = 6/(\rho d)$  can be used where *d* is the particle diameter expressed in μm and ρ is the density (5.82 g cm<sup>-3</sup> for Sb<sub>2</sub>O<sub>4</sub>, 6.95 g cm<sup>-3</sup> for SnO<sub>2</sub>). As hysteresis was not observed for any of the samples during N<sub>2</sub> adsorption-desorption cycles it can be concluded that the materials are not porous.

The results from the data reported in Tables 1 and 2, together with the electron microscopy results, may be summarized as follows.

- (i) Pure Sb<sub>2</sub>O<sub>4</sub> or Sb<sub>6</sub>O<sub>13</sub> phases are not very active or selective for acrolein formation.
- (ii) HCl treatment for 1 h dissolves all the small Sb<sub>2</sub>O<sub>4</sub> particles and partially dissolves the larger ones (eroded shapes). The propene conversion per gram is highly increased but is only slightly increased per surface area unit. However, the selectivity for acrolein decreases because of the subsequent increase in the formation of CO<sub>2</sub>.
- (iii) Heating of sample (ii) above at 500 °C causes only a small increase in catalytic properties.
- (iv) Heating of sample (iii) above again at 750 °C caused its conversion level to decrease but its selectivity to increase to its starting value (92%). Moreover, while Sb<sub>6</sub>O<sub>13</sub> was detected in large amounts (ca. 25%) by i.r. spectroscopy, electron microscopy showed that the large Sb<sub>2</sub>O<sub>4</sub> particles

had disappeared. The size of the solid solution particles increased from 45 to 62 Å. Since the Sb<sub>6</sub>O<sub>13</sub> could not be detected by *X*-ray diffraction, only by i.r. spectroscopy, the Sb<sub>6</sub>O<sub>13</sub> may lie at the surface of the solid solution particles, resulting in a decrease in propene conversion. This is in keeping with the x.p.s. measurements which show that the oxide particles are enriched in surface antimony (45 vs. 34%) (For small particles, the x.p.s. technique can probe a large part of the volume, although with an electron free path λ of 18 Å, 75% of the x.p.s. signal stems from the first layer of depth λ.)

- (v) Further acid treatment (2 h and then 3 h) results in complete dissolution of the Sb<sub>2</sub>O<sub>4</sub> particles but also in a decrease in extent and selectivity of propene conversion into acrolein. This decrease presumably arises from the loss of Sb from the surface not only as Sb<sub>2</sub>O<sub>4</sub> particles but also from the solid solution.

This work clearly shows that the catalytic performance of Sb-Sn mixed oxides may be enhanced by eliminating inactive phases such as Sb<sub>2</sub>O<sub>4</sub> or Sb<sub>6</sub>O<sub>13</sub>. A careful choice of selective chemical attack or appropriate preparation of the oxide may lead to an especially interesting catalyst. The question of the active sites in mild oxidation still remains since it is clear that while the SnO<sub>2</sub> solid solution has to be surface-enriched in Sb, an excess of Sb results in inactive Sb<sub>2</sub>O<sub>4</sub> particles. The question whether the active sites are Sb ions surrounded by four Sn atoms, as proposed by Pyke *et al.*,<sup>7</sup> or Sb ions surrounded by more or fewer Sn atoms, or Sb<sup>III</sup>-Sb<sup>V</sup> ions in very small Sb<sub>2</sub>O<sub>4</sub> surface particles, lying on an electron conducting solid solution, as suggested by one of us,<sup>3</sup> remains to be answered.

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