

OXIDATIVE DEHYDROGENATION OF ISOPROPYL ALCOHOL ON MIXED TIN AND ANTIMONY OXIDE CATALYSTS

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Summary

From studies of the oxidative dehydrogenation of isopropyl alcohol on various compositions of mixed tin and antimony oxide catalysts, it is concluded that this mixed oxide system predominantly functions as Sb_2O_4 which is formed as a two-dimensional layer on the tin oxide matrix. At low concentrations of antimony and at low temperatures the solid solution-antimony oxide interface may be responsible for the observed activity. The participation of lattice oxygen in the process is also deduced.

1. Introduction

Mixed tin and antimony oxides are an emerging class of oxidation catalysts whose surface and phase compositions [1 - 3], acid-base [4], electrical [5] and catalytic properties [6] have been extensively investigated in recent times. There are various proposals and models for the structural properties of mixed tin and antimony oxide systems based on X-ray and Mössbauer studies [7]. Among the available models, the formation of a two-dimensional Sb_2O_4 film [7] with simultaneous segregation of antimony to the surface appears to be probable. The aim of the present paper is to provide experimental evidence for this model from both reaction and structural studies of the catalysts before and after reaction.

2. Experimental details

Mixed tin and antimony oxides containing various amounts of antimony (from 0 to 100 at.%) were prepared as follows. The required amounts of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and SbCl_3 were dissolved in a minimum amount of concentrated HCl solution and then 12.5% NH_4OH was added until pH 7 was reached. The precipitate obtained was digested in a water bath for 3 h, filtered, washed several times with distilled water until the filtrate was free from ammonium and chloride ions and then dried in an oven at 100 °C over-

night. The solid was then calcined in air at 600 °C for 16 h and subsequently calcined at 800 °C for 5 h. The surface areas of the catalysts were determined by using the Brunauer–Emmett–Teller nitrogen adsorption method. The catalytic oxidative dehydrogenation of isopropyl alcohol in the presence of gas phase oxygen (with an isopropyl alcohol to oxygen molar ratio of 2 to 1) was carried out in the temperature range 320 - 420 °C using a conventional flow-type fixed-bed reactor working at atmospheric pressure. The liquid products were analysed using gas chromatography and the gaseous products were analysed with an Orsat gas analyser. For the experiments with various molar ratios of isopropyl alcohol to oxygen, nitrogen was used as a diluent to maintain the total pressure at 1 atm. The antimony content of the mixed oxides is expressed as $\{Sb/(Sb + Sn)\} \times 100$ at.%.

3. Results and discussion

The surface areas, activation energies, phases detected using X-ray diffractograms etc. of mixed tin and antimony oxides are given in Table 1. The variation in the molar percentage of acetone formed per square metre as a function of the antimony content, shown in Fig. 1, reveals that all the mixed oxides show almost constant activity, although pure antimony oxide exhibits the highest activity. The selectivity for acetone formation is of the order of 80 - 90 mol.% for all the catalysts except for the 12 and 20 at.% Sb systems (Fig. 2). In these two cases, namely 12 and 20 at.% Sb catalysts, an increase in the temperature from 320 to 400 °C increased the selectivity for acetone formation sharply from about 50 to about 85 mol.% (Fig. 2) and decreased the selectivity for propylene formation from about 45 to about 7 mol.%. However, there is not much change in the selectivity for CO₂ formation (about 10 mol.%) with temperature. For 12 and 20 at.% Sb catalysts, an increase in the temperature from 320 to 400 °C can lead to changes in the ratio of tin to antimony on the surface. At higher temperatures there can be preferential segregation of antimony to the surface, thus accounting for the increased oxidative dehydrogenation of isopropyl alcohol.

An increase in the molar ratio of isopropyl alcohol to oxygen increases the acetone formation for the 80 at.% Sb catalyst (Fig. 3). The X-ray analysis of the samples after reaction showed specific changes for the 50 at.% Sb, 80 at.% Sb and pure Sb₂O₄ catalysts. In these three catalysts the Sb₂O₄ phase undergoes reduction to Sb₂O₃, which is re-oxidized when air is passed through at 460 °C (Table 2).

It is generally believed that antimony is soluble in the SnO₂ lattice up to about 20 at.% Sb, a two-phase system appearing at higher temperatures [7]. It is usually postulated that a two-dimensional form of Sb₂O₄ is formed on the surface of the solid, which is the active phase. If this postulate is correct, then almost all the systems containing varying amounts of antimony should show the same activity per square metre provided that a uniform layer of antimony oxide film is formed on the surface of the solid. This

TABLE 1

Properties of the mixed tin and antimony oxide catalysts

Sample	Sb (at.%)	Colour	Specific surface area (m ² g ⁻¹)	E _a for oxidative dehydrogenation (kJ mol ⁻¹)	Frequency factor (m ⁻² s ⁻¹)	Conductivity at 380 °C (Ω ⁻¹ cm ⁻¹)	E _c for conduction (eV)	Phases in fresh catalysts detected using X-rays
1	0 (SnO ₂)	Light yellow	9.2	104.8	2.9 × 10 ⁹	—	—	SnO ₂
2	5	Greyish blue	8.2	99.8	4.1 × 10 ⁸	4.6 × 10 ⁻²	0.10	SnO ₂
3	12	Greyish blue	10.5	81.9	6.7 × 10 ⁶	0.9 × 10 ⁻²	0.26	SnO ₂
4	20	Greyish blue	8.3	89.3	3.1 × 10 ⁷	0.7 × 10 ⁻²	0.24	SnO ₂
5	50	Greyish green	5.5	131.7	6.2 × 10 ¹⁰	0.7 × 10 ⁻²	0.20	SnO ₂ + Sb ₂ O ₄
6	80	Grey	3.2	92.6	5.4 × 10 ⁷	1.7 × 10 ⁻⁵	0.23	SnO ₂ + Sb ₂ O ₄
7	100 (Sb ₂ O ₄)	Yellowish white	0.4	123.1	3.1 × 10 ¹¹	4.7 × 10 ⁻¹⁰	1.71	Sb ₂ O ₄

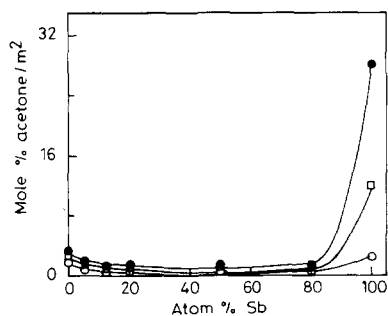


Fig. 1. The molar percentage of acetone formed per square metre *vs.* the antimony content of the mixed tin and antimony oxides (total contact time, 0.38 s): ○, 360 °C; □, 380 °C; ●, 400 °C.

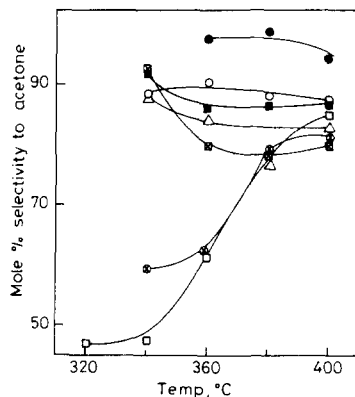


Fig. 2. The selectivity for acetone formation as a function of the temperature for the mixed tin and antimony oxides (total contact time, 0.38 s): ●, Sb_2O_4 ; ■, SnO_2 ; ○, 5 at.% Sb; □, 12 at.% Sb; ◇, 20 at.% Sb; △, 50 at.% Sb; ⬡, 80 at.% Sb.

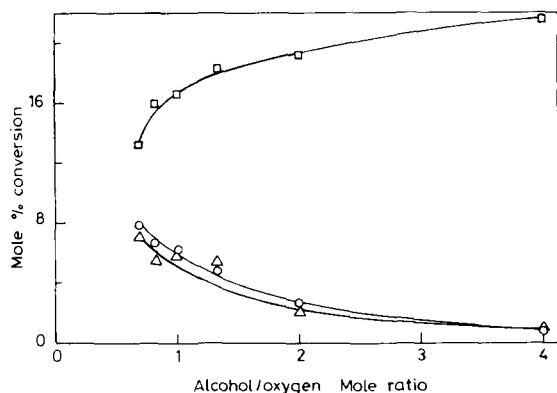


Fig. 3. Effect of the molar ratio of isopropyl alcohol to oxygen on the conversion of isopropyl alcohol into CO_2 , acetone and propylene (catalyst, 80 at.% Sb; total contact time, 0.38 s; temperature, 420 °C): ○, CO_2 ; □, acetone; △, propylene.

expectation is in accordance with the experimental observations recorded in Fig. 1. However, pure Sb_2O_4 shows a higher activity because this system is susceptible to extensive reduction to Sb_2O_3 under the reaction conditions. The lability of the lattice oxygen may be responsible for the higher selectivity observed with this system.

The surface acid-base properties of tin and antimony oxide systems have been extensively examined through the adsorption of pyridine, CO_2 , acetic acid and other probes [4]. It is generally observed that the acidity normally remains almost constant with an increase in the antimony content whereas the basicity shows changes with maxima in the composition range 40 - 70 at.% Sb. From these results it is deduced that the acidic sites are

TABLE 2

X-ray *d* spacing values for the 80 at.% Sb catalyst^a

<i>Before reaction</i>		<i>After reaction</i>	
<i>d</i> (Å)	<i>Relative intensity</i>	<i>d</i> (Å)	<i>Relative intensity</i>
4.538	10.8	6.511	8.4
3.498	40.0	4.552	12.0
3.401	30.4	4.439	10.0
3.104	100.0	3.427	34.5
2.969	43.6	3.327	44.7
2.763	10.8	3.209	34.9
2.683	39.2	3.132	50.9
2.501	10.0	3.058	100.0
2.432	19.2	2.931	35.8
2.386	8.8	2.722	12.4
2.265	7.6	2.637	45.5
1.877	22.0	2.468	14.4
1.789	21.2	2.405	14.0
1.775	16.0	2.362	10.5
1.737	22.0	1.969	14.0
1.714	10.8	1.863	16.4
1.695	10.8	1.804	13.5
1.650	13.6	1.781	22.4
1.497	11.6	1.762	20.2
1.482	10.4	1.719	20.7
1.441	11.6	1.695	12.0
1.335	7.6	1.684	16.7
		1.639	10.7
		1.618	11.5
		1.486	9.5
		1.469	10.7
		1.431	11.8

^a *d* spacing values for Sb₂O₃. (From ref. 8.)

related to the surface tin cations, which accounts for the sharp decrease in the number of acidic sites with increasing surface antimony concentration, and the basic sites are related to the surface antimony cations. According to the postulate of a two-dimensional phase formation of antimony oxide, it is natural to expect that the resulting acidity of the system should decrease significantly in the initial stages of the antimony addition to tin oxide. Furthermore, the system should exhibit considerable basicity which could be favourable for the observed catalytic activity towards the oxidative dehydrogenation of isopropyl alcohol. This conclusion is also supported by the fact that isopropyl alcohol undergoes dehydration to propylene only to the extent of 1 - 6 mol.% and selectivity to propylene remains constant (about 8 mol.%) with an increase in the antimony content.

A linear correlation was observed between the initial rate of acrolein formation from propylene and the molar percentage of acetone formed per

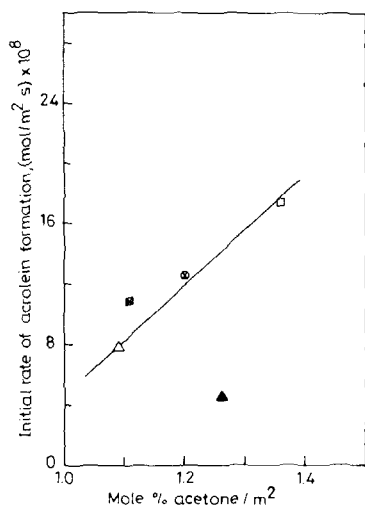


Fig. 4. Correlation between the initial rate of acrolein formation from propylene at 470 °C (from ref. 3) and the molar percentage of acetone formed per square metre from isopropyl alcohol at 400 °C for the mixed tin and antimony oxides: □, 5 at.% Sb; ⊗, 12 at.% Sb; ⊠, 20 at.% Sb; △, 50 at.% Sb; ▲, 80 at.% Sb.

square metre from isopropyl alcohol (Fig. 4), indicating that in both processes the participation of surface oxygen is involved.

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