STUDIES OF THE STRUCTURAL STABILITY OF Sn–Sb MIXED OXIDE IN THE DECOMPOSITION OF ISOPROPYL ALCOHOL

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Summary

Typical Sn-80at.%Sb mixed oxide undergoes structural reduction during the decomposition of isopropyl alcohol in the absence of gas phase oxygen, and the active phase may contain metallic tin and Sb₂O₃. However, in the presence of oxygen the catalyst retains its structural stability and acetone is the major product together with small amounts of CO₂ and propylene. Product inhibition studies with acetone reveal that oxidation of the acetone to CO₂ occurs in preference to oxidation of isopropyl alcohol. The effect of the partial pressure of isopropyl alcohol and the partial pressure of oxygen on the decomposition of isopropyl alcohol was investigated. The presence of a large excess of oxygen favours CO₂ formation, whereas smaller amounts of oxygen favour acetone formation. A possible mechanism for the reaction in the presence of gas phase oxygen is proposed.

1. Introduction

Mixed oxides of tin and antimony are good catalysts for selective oxidation and ammoxidation of olefins [1 - 5]. Most workers [6 - 8] have stated that the formation of a solid solution of Sb⁵⁺ in SnO₂ is an important factor in the catalytic behaviour of these materials. According to the reports of Boudeville et al. [9], the selectivity for acrolein in propylene oxidation increases when the amount of antimony at the surface is increased; this occurs when the antimony concentration is enhanced or when the calcination temperature is increased. According to Boudeville et al., the active phase is Sb_2O_4 lying at the surface of a solid solution of antimony(V) in SnO_2 . The specific activity for the formation of butadiene from 1-butene has been related by Herniman et al. [10] to the concentration of antimony cations at the surface. The active sites for the formation of butadiene have been identified by Herniman et al. as isolated antimony cations surrounded entirely by tin ions as nearest neighbours. The selectivity for butadiene formation from 1-butene has been found to increase with increases in the antimony content in Sn-Sb oxide catalysts [11]. Christie et al. [12] have reported that in Sn-Sb mixed oxide catalysts the highest selectivity for acrolein in propylene oxidation has been observed with the catalyst containing 75 at.% Sb. In the light of the above observations, it was considered worthwhile to investigate the structural stability of Sn-Sb mixed oxide catalysts under catalytic reaction conditions. In the present paper the results obtained on the mixed oxides of tin and antimony containing 80 at.% Sb for a typical model catalytic reaction, namely isopropyl alcohol decomposition in the presence and in the absence of gas phase oxygen, are dealt with.

2. Experimental details

Sn-80at.%Sb mixed oxide was prepared from $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and SbCl_3 . The calculated amounts of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and SbCl_3 were dissolved in a minimum amount of concentrated HCl and then 12.5% NH₄OH was added slowly with stirring 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 overnight. The solid was then calcined in air at 600 °C for 16 h and subsequently calcined at 800 °C for 5 h. The X-ray *d* spacing values of the fresh catalyst correspond to SnO_2 and Sb_2O_4 (Fig. 1).



Fig. 1. X-ray d spacing values for catalysts under various conditions: (a) Sb_2O_3 ; (b) α -Sn; (c) Sb_2O_4 (cervantite); (d) SnO_2 (cassiterite); (e) regenerated catalyst; (f) after reaction in the absence of oxygen; (g) fresh catalyst.

The surface area of this fresh catalyst determined by using the Brunauer-Emmett-Teller nitrogen adsorption method was $3.2 \text{ m}^2 \text{ g}^{-1}$. Catalytic decomposition of isopropyl alcohol was carried out in the temperature range $360 \cdot 460 \,^{\circ}\text{C}$ using a conventional flow-type fixed-bed reactor working at atmospheric pressure. The liquid products were analysed by using gas chromatography, whereas the gaseous products were analysed with an Orsat gas analyser. In partial pressure experiments, nitrogen was used as a diluent to vary the partial pressures.

3. Results and discussion

In the absence of gas phase oxygen, Sn-80at.%Sb oxide was found to promote both the simple dehydrogenation and the oxidative dehydrogenation of isopropyl alcohol:

 $CH_3CHOHCH_3 \longrightarrow CH_3COCH_3 + H_2$

 $CH_3CHOHCH_3 + O_{catalyst} \longrightarrow CH_3COCH_3 + H_2O$

Isopropyl alcohol under the reaction conditions undergoes decomposition to give acetone with almost 100% selectivity in the absence of gas phase oxygen. However, Irving and Taylor [13] have reported that propylene is the main product in the decomposition of isopropyl alcohol over an Sn-(19.6-75)at.%Sb oxide catalyst (evacuated at 133×10^{-6} N m⁻² at 425 °C for 16 h) in a static reactor in the absence of oxygen at 135 °C with an initial pressure of isopropyl alcohol of 0.67 kN m⁻². They observed that acetone was formed in 90% yield when the concentration of antimony was less than 6.1 at.%.

 CO_2 was not formed when reactions were carried out in the absence of oxygen. However, small quantities (about 0.2 mol.%) of propylene were also found in the product. The fresh catalyst was initially highly active and the activity fell sharply up to about 16 runs and then the only reproducible results were observed when reactions were carried out in the absence of oxygen. In all these experiments the molar percentage of hydrogen obtained was always less than the molar percentage of acetone obtained (Table 1). The Arrhenius parameters calculated for the reactions are given in Table 2. The catalyst was found to undergo structural changes when the reactions were carried out in the absence of oxygen. On the basis of the X-ray diffraction patterns for the catalysts under various conditions (Fig. 1) the following deductions were made: (i) composition of the fresh catalyst, SnO₂ + Sb₂O₄; (ii) composition after reaction with isopropyl alcohol in the absence of gas phase oxygen, SnO₂ + Sn + Sb₂O₄ + Sb₂O₃; (iii) composition after regeneration with air for 5 h at 480 °C, SnO₂ + Sn + Sb₂O₄.

 Sb_2O_4 is reported to be reduced to Sb_2O_3 at about 400 °C [14] and Sb_2O_3 can be reoxidized back to Sb_2O_4 by heating in air at about the same temperature. Reduction of SnO_2 by hydrogen begins at about 170 °C but its reoxidation to SnO_2 occurs only at about 2260 °C [15]. Thus it is probable

TABLE 1

Contact time (s)	Acetone (mol.%) at the following temperatures ^a					
	400 °C	420 °C	440 °C	460 °C		
0.70	3.3 (1.8)	4.5 (2.7)	8.3 (5.9)	10.1 (6.4)		
1.02	5.3 (3.6)	7.8(5.2)	12.4(8.2)	16.4 (10.3)		
1.40	7.9(4.3)	12.8(8.9)	17.6(11.8)	22.3(14.0)		
2.36	12.3 (8.1)	16.6 (10.2)	21.8(12.8)	26.6 (16.3)		

Decomposition of isopropyl alcohol over Sn-80at.%Sb mixed oxide in the absence of gas phase oxygen

^a Values for hydrogen formation (as a molar percentage) are given in parentheses.

TABLE 2

Arrhenius parameters for the decomposition of isopropyl alcohol over Sn 80at.%Sb mixed oxide

Sample	Reaction	Activation energy (kJ mol ⁻¹)	Frequency factor $(s^{-1} m^{-2})$
1	Simple dehydrogenation in the absence of oxygen	76.7	3.3×10^5
2	Oxidative dehydrogenation in the absence of oxygen	82.7	$4.8 imes 10^5$
3	Oxidative dehydrogenation in the presence of oxygen	92.6	$5.4 imes 10^7$

that, during the reaction in the absence of oxygen, SnO_2 may be reduced to metallic tin and Sb_2O_4 may be reduced to Sb_2O_3 . However, when the catalyst is regenerated, tin is not reoxidized to SnO_2 , whereas Sb_2O_3 is reoxidized back to Sn_2O_4 . Formation of metallic tin is reported when vapours of ethyl alcohol were passed over SnO_2 at 650 °C [15]. It is also reported that ethyl alcohol vapour rapidly reduced SnO_2 to SnO at 340 °C and the reduction of SnO to metallic tin proceeded rather slowly [15]. Contrary to these observations, Fattore *et al.* [16] could not detect any structural change in SnO_2 after reduction with propylene for 10 min in the absence of oxygen at 550 °C. However, they noticed a drop in conversion from 30% to 10% in 10 min. Berry [17] did not observe the formation of any Sn^{2+} from Sn^{4+} when he reduced 80at.%Sn-20at.%Sb mixed oxide with hydrogen at 480 °C.

Since the catalyst phase was not stable in the absence of oxygen, reactions were carried out in the presence of oxygen to check the structural stability of the catalyst. In the presence of oxygen (an oxygen:(isopropyl alcohol) molar ratio of 1:2) the catalyst was found to give stabilized products from the beginning of the reaction runs. In this case also, acetone was observed to be the main product but with only about 85% selectivity

TABLE 3

Contact time (s)	Acetone (mol.%) at the following temperatures					
	360 °C	380 °C	400 °C	420 °C	440 °C	
0.37	4.4	7.8	12.8	18.6	21.0	
0.53	5.4	10.8	16.9	23.1	35.5	
0.71	6.5	12.3	21.3	33.6	42.3	
0,98	8.6	15.6	34.4	51.4	58.6	

Decomposition of isopropyl alcohol over Sn 80at% Sb mixed oxide in the presence of gas phase oxygen (oxygen:(isopropyl alcohol) molar ratio of 1:2)

(Table 3). Small amounts of propylene (about 0.3 - 3.7 mol.%) and CO_2 (about 0.1 - 2.5 mol.%) were also observed as products when the reactions were carried out in the presence of oxygen. It should be recalled here that CO_2 was not observed when the reactions were carried out in the absence of oxygen. Germain *et al.* [18] have also observed acetone as a product with about 52% selectivity when they passed a mixture of isopropyl alcohol, air and ammonia over Sn-Sb mixed oxide catalyst at 460 °C. Arrhenius parameters calculated for the reactions in the presence of oxygen are also given in Table 2.

Figure 2 shows the results obtained in terms of moles formed per hour when the reaction was carried out in the presence of various partial pressures of acetone or nitrogen. In the presence of oxygen, acetone was found



Fig. 2. Effect of acetone and nitrogen on the rate of formation of products for the decomposition of isopropyl alcohol in the presence of gas phase oxygen (temperature, 420 °C; total contact time, 0.41 s; partial pressure of oxygen, 0.4 atm (constant)): _____, CO₂ formation; --, acetone formation; \circ , \bullet , in acetone; \triangle , \blacktriangle , in nitrogen.

to undergo complete combustion as deduced from the negative values for the moles of acetone formed per hour. In order to check this, the reaction with acetone (0.6 atm) and oxygen (0.4 atm) was carried out and the rate of formation of CO_2 was found to be a maximum (Fig. 2). The number of moles of isopropyl alcohol reacted per hour in these experiments has been calculated and it is found to be always less in the presence of acetone than in the presence of nitrogen. This indicates that acetone is inhibiting the isopropyl alcohol conversion.

The effect of the partial pressure of isopropyl alcohol as well as oxygen on the conversion was also studied using nitrogen as diluent (Fig. 3). It can be seen from Fig. 3 that acetone formation increases with an increase in the partial pressure of isopropyl alcohol, whereas CO_2 formation increases with an increase in the partial pressure of oxygen. In other words, the presence of a large excess of oxygen favours complete combustion to CO_2 , whereas smaller amounts of oxygen favour acetone formation. From Fig. 3 it is also clear that with an increase in the isopropyl alcohol-to-oxygen partial pressure ratio, acetone formation increases while CO₂ formation decreases. Stroeva et al. [19] have stated that, with Sn-Sb mixed oxide catalysts, total oxidation to CO_2 is preferred to partial oxidation of hydrocarbons when the concentration of antimony is greater than 66 at.%. Rostevanov et al. [20] suggested that, when isobutylene is oxidized over Sn-Sb mixed oxide catalysts, CO_2 is formed in three different ways: (i) directly from isobutylene; (ii) via the oxidation of the product methacrolein; (iii) through the burning of the condensation products deposited onto the catalyst surface. Similarly, in isopropyl alcohol decomposition, CO_2 may be formed in two ways,



Fig. 3. Effect of the partial pressure of isopropyl alcohol (----) (constant partial pressure of oxygen, 0.4 atm) and effect of the partial pressure of oxygen (----) (constant partial pressure of isopropyl alcohol, 0.4 atm) on the conversion (in mole per cent) of isopropyl alcohol to CO_2 ($^{\circ}$) and acetone ($^{\Box}$) (temperature, 420 °C; total contact time, 0.41 s).

namely directly from isopropyl alcohol or through the oxidation of the product acetone.

The X-ray diffraction patterns for (i) the fresh catalyst, (ii) the catalyst after reaction with isopropyl alcohol in the presence of gas phase oxygen and (iii) the regenerated catalyst were found to be the same. Hence it is concluded that the catalyst does not undergo any detectable structural change when reactions were carried out with oxygen in the feed. Antimony tetroxide can be considered as $Sb^{3+}Sb^{5+}O_4$. Sb^{5+} may be the active site for the reaction and, once Sb^{5+} is reduced, it may be reoxidized through Sn^{4+} according to the following steps [19]:

 $Sb^{5+} \xrightarrow{\text{during reaction}} Sb^{3+}$ $Sb^{3+} + Sn^{4+} \longrightarrow Sb^{5+} + Sn^{2+}$ $Sn^{2+} + \frac{1}{2}O_2(g) \longrightarrow Sn^{4+} + O^{2-}$

It is concluded that in the presence of oxygen the concentration of Sb^{5+} ions is maintained constant and SnO_2 does not undergo reduction. However, in the absence of oxygen the reoxidation of Sn^{2+} formed during the reaction is not possible and hence SnO_2 undergoes reduction to metallic tin.

Acknowledgment

The authors are grateful to the University Grants Commission, New Delhi, for the award of a teacher fellowship to one of them (S.C.).

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