

## SOME REFLECTIONS ON MIXED TIN AND ANTIMONY OXIDE CATALYSTS

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### Summary

The characteristics of selective oxidation on mixed tin and antimony oxide catalysts with special reference to the solubility limit, the role of the matrix, the nature of the active sites and the role of acid-base sites are evaluated from an analysis of data reported in the literature. The catalytic properties of these systems are also briefly reviewed.

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### 1. Introduction

Studies on various types of multicomponent oxides used as oxidation catalysts have led to many postulates which have considered both macroscopic and microscopic parameters as the cause for the observed selectivity. In this paper it is our intention to examine briefly the applicability of some of these correlations in terms of catalytic functions with respect to mixed tin and antimony oxide oxidation catalysts. However, for an exhaustive and comprehensive treatment of this system the reader is referred to an excellent recent review by Berry [1].

It has been shown recently that solid solution formation in the mixed tin and antimony oxide system is restricted to a limited range of compositions (in most of the reports a value of about 3 at.% Sb is given although values as high as 6 - 7 at.% Sb have also been claimed [2, 3]) and requires heating at higher temperatures. Earlier studies, however, frequently suggested that high concentrations of antimony (about 20 at.%) could be accommodated in the tin dioxide lattice at lower temperatures (about 600 °C) [1]. At all other compositions, multiphase compositions were found to exist, consisting principally of rutile-type tin dioxide and oxides of antimony, mainly  $Sb_2O_4$  and  $Sb_6O_{13}$  [4]. The reported existence of an unidentified phase at lower temperatures in the antimony-rich region, however, needs further investigation to establish its structural identity and catalytic reactivity [4]. In spite of these studies on mixed tin and antimony oxide systems there are various aspects on which no unified information has so far emerged, and the following questions arise.

(1) In the substitutional solid solutions, what is the mechanism of charge balance and how does this affect the electrical properties of the resultant system?

(2) If antimony were to be enriched on the surface, what is the driving force for this? Does this result in changes in the surface energy? Can segregation also occur as a result of catalytic reaction?

(3) It is usually implied that the resultant acid–base properties of the systems are responsible for the observed catalytic activity. This implication gives rise to the following questions.

(a) What is the actual active oxidation state of the ions?

(b) What is the geometry or coordination of the active ions?

(c) How is the concentration of these sites altered as a result of surface enrichment?

(d) What is the nature of the actual active site from the following postulates? (i) Isolated antimony(III) cations are surrounded entirely by tin(IV) cations in nearest-neighbour positions [5]. (ii) Tin ions are surrounded entirely by antimony ions. (iii) Antimony ions are surrounded by four or fewer tin ions. (iv) Antimony(III) and antimony(V) [6] ions occur in small particles of  $\text{Sb}_2\text{O}_4$ .

(e) What are the implications of phase segregation and the presence of interfaces on the observed catalytic performance?

(f) Is it true that the role of the tin oxide component is to provide a matrix which is capable of supporting high concentrations of antimony in a proper oxidation state and configuration?

The present article is based on an analysis of data reported in the literature in an attempt to obtain some answers to these questions.

## 2. Method of preparation

A whole range of catalysts with varying compositions of mixed tin and antimony oxides have been prepared by coprecipitating tin(IV) and antimony(V) chlorides as hydroxides and calcining them at various temperatures in the range 400 - 1050 °C [1]. The catalysts thus obtained are expected to be a more intimate mixture of oxides of tin and antimony, and so this method is preferred to the solid state reactions between the respective oxides [2, 7].

## 3. Solubility limit of antimony in tin dioxide

There appear to be some open questions on the actual range over which a substitutional solid solution is possible. This situation arises because substitutional solid solution formation should result in a balance in charge in the system and the possible lower oxidation state of antimony, antimony(III), may not be accommodated in the octahedral positions available in the rutile

phase. From an analysis of the dependence of the electrical conductivity of the catalysts on their composition, Lemberanskii *et al.* [8] have concluded that a solid solution of antimony in tin dioxide is possible up to a maximum antimony concentration of 10 at.%. This is not in agreement with the results of the X-ray investigation by Pyke *et al.* [6]. On addition of antimony to tin dioxide an increase in the lattice parameters  $a$  and  $c$  of tin dioxide has been reported [9]. However, an increase in the antimony content beyond 5 at.% had no effect on the lattice parameters of tin dioxide. This indicates that a maximum of 5 at.% Sb is soluble in tin dioxide after calcination at 1150 °C. The conductivity maximum observed around 3 at.% Sb is substantiated by recent photoelectron spectroscopy measurements which showed that at this level of substitution the profile for the density of states approximates well to that predicted by free-electron theory [10]. It should be remembered that this is the composition (namely 3 at.% Sb) where maximum activity for the oxidation of propylene has been observed [11]; furthermore, the Mössbauer spectrum obtained for this composition corresponds to a high electron density at the antimony nuclei [12]. From observations of the appearance of antimony(V) resonance, Berry [13] has concluded that an equilibrated rutile-type solid solution containing about 4 at.% Sb in the bulk with a surface enriched to about 25 at.% Sb can be obtained.

The solubility of antimony in tin dioxide is further confirmed by the observation that the Mössbauer spectrum of the material containing 4 at.% Sb shows only antimony(V) resonance [13]. The  $^{121}\text{Sb}$  Mössbauer spectrum of completely dehydrated mixed tin and antimony oxides (calcined around 600 °C) with an antimony content greater than 10 at.% showed the presence of both antimony(V) and antimony(III) (the antimony(III) content increasing with increases in the calcination temperature). However, although the  $^{119}\text{Sn}$  Mössbauer parameters increase with increasing antimony concentration, they do not show the presence of tin(II) [13]. In fact, the mixed tin and antimony oxide systems calcined at temperatures lower than that at which  $\text{Sb}_2\text{O}_4$  is volatilized showed  $^{121}\text{Sb}$  Mössbauer spectra which are indicative of the dominance of  $\text{Sb}_2\text{O}_4$ . On the basis of the Mössbauer spectral data Berry [13] agrees with the conclusions of Pyke *et al.* [6] that calcination induces structural changes in an initially homogeneously precipitated material and leads to the segregation of excess antimony to the surface to form a separate  $\text{Sb}_2\text{O}_4$  phase.

All these studies show that the solubility of antimony in tin dioxide is restricted to a limited extent, of the order of 5 at.%.

#### 4. Active sites in mixed tin and antimony oxides

There are various postulates regarding the nature of the active sites in the mixed tin and antimony oxide systems. The observation that these systems in their active phases lead to the segregation of antimony to the

surface suggests that the active sites should involve antimony ions in a geometrical configuration surrounded by next-neighbour tin ions. The available evidence for this postulate is as follows.

(1) The pure  $\text{Sb}_2\text{O}_4$  phase is relatively inactive for the oxidation reaction [3, 11, 14 - 16].

(2) The absence of reduction of tin(IV) and the observation of the presence of antimony(III) by means of Mössbauer spectroscopy [11] showed that easy oxygen loss is possible as a result of the reduction of antimony(V) ions to antimony(III) species.

(3) Since active catalysts are often calcined compounds it has been deduced that the antimony ions segregate and assume asymmetric sites surrounded entirely by tin(IV) cations in nearest-neighbour positions and that they are the active sites with acid-base properties required for the selective oxidation of olefins [17].

(4) The acid and base sites of the catalyst surface, formed by neighbouring tin(IV) and antimony(III) species respectively, have been shown to be the sites for cyclic complex formation by proton rearrangement in the adsorption and isomerization of *n*-butenes [18].

(5) The observed electron spin resonance signal at  $g \approx 1.89$  is associated with electrons trapped in anionic vacancies, and these systems show high antimony(III) contents [19].

(6) The observation that the yield of  $\text{CO}_2$  decreased rapidly with decreasing tin concentration at the surface indicates that tin cations surrounded by other tin ions are favourable sites for the complete combustion reaction [20].

Although there is overwhelming evidence for the enrichment of antimony at the surface (this enrichment being a function of the antimony concentration as well as of the calcination temperature (Table 1)) it appears that an active catalyst cannot contain a complete layer of  $\text{Sb}_2\text{O}_4$  on the surface. This is evident from the fact that  $\text{Sb}_2\text{O}_4$  as such is inactive, and selective chemical dissolution of the inactive  $\text{Sb}_2\text{O}_4$  phase in hydrochloric acid causes an increase in the activity of the system [21]. These results have been taken to mean that surface antimony species which experience no direct or near-neighbour Sb-Sb interactions are the active sites. In this configuration it may mean that antimony ions surrounded by four or fewer tin ions alone can function as selective oxidation catalyst sites. There has been considerable doubt whether the matrix is the solid solution of antimony in tin(IV) oxide or pure tin oxide itself [6]. This aspect can be easily resolved as the active phase is usually calcined around 900 °C wherein the solid solution formation is facile and hence should form the supporting matrix for  $\text{Sb}_2\text{O}_4$ . This is also deduced from a calculation of the antimony content in the bulk of various mixed tin and antimony catalysts calcined at 950 °C. These results, deduced from data reported in the literature, are given in Table 2.

The possibility of localization and strong binding of electrons with antimony atoms available at the surface, rather than with tin atoms, has

TABLE 1

Effect of the calcination temperature of mixed tin and antimony oxide catalysts on the surface enrichment of antimony and the catalytic activity [5]

<i>Sb content</i> (at.%)	<i>Calcination</i> <i>temperature</i> (°C)	<i>Surface Sb</i> <i>content</i> (at.%)	<i>Specific activity</i> <i>for butadiene</i> <i>formation</i> ( $\mu\text{mol m}^{-2} \text{min}^{-1}$ )
4	400	3	0.3
	500	4	0.5
	600	7	0.7
	700	11	1.2
	800	15	1.3
	900	20	1.5
	1000	22	3.3
20	400	22	0.2
	500	23	0.3
	600	26	0.6
	700	30	0.8
	800	34	2.2
	900	37	3.5
	1000	36	3.2
40	400	32	0.5
	500	34	0.6
	600	36	1.0
	700	37	1.4
	800	36	1.5
	900	45	2.3
	1000	30	2.1
68	400	68	0.3
	500	68	0.3
	600	68	0.6
	700	62	1.5
	800	40	2.4
	900	49	0.8
	1000	46	1.3
83	600	93	0.2
	700	92	0.3
	800	50	3.7
	900	54	1.3

been considered to provide the thermodynamic driving force for the surface enrichment of antimony [22]. However, no conclusive statement based on firm experimental evidence is possible at present.

Although Pyke *et al.* [6] have carried out detailed X-ray and electron microscopy investigations to determine the structure of the mixed tin and antimony oxide catalysts, they finally conclude that the role of tin is rather obscure, as is evident from their statement that tin may simply provide a disordered matrix which can support high concentrations of the active species or alternatively it may have a more fundamental role in promoting

TABLE 2

Calculated atomic per cent of antimony remaining in the bulk of the mixed tin and antimony oxide catalysts

Amount of Sb (at.%)	Specific surface area <sup>a</sup> (m <sup>2</sup> g <sup>-1</sup> )	Number of layers assumed to represent the surface	Amount of Sb at the surface as determined by XPS <sup>a,b</sup> (at.%)	Calculated amount of Sb remaining in the bulk (at.%)
1.5	3.6	5	11.1	2.0
5	11	10	17.6	1.9
10	5	20	31.8	5.2
20	4.8	40	35.0	12.0

<sup>a</sup> Taken from ref. 11.

<sup>b</sup> XPS, X-ray photoelectron spectroscopy.

the catalytic oxidation reactions. However, they doubt the validity of this postulate because of the assumption that there are no significant structural changes taking place in the oxides during the catalytic reaction.

There are other postulates for active sites in the mixed tin and antimony oxide systems which include the following.

(a) Gem Sb<sup>5+</sup>=O groups are responsible for the observed oxidative dehydrogenation properties and the second metal ion adsorbs the gaseous oxygen to reoxidize the reduced antimony ions [23].

(b) Boudeville *et al.* [11] have postulated that the catalytic phase responsible for selective oxidation is the Sb<sub>2</sub>O<sub>4</sub> phase lying at the surface of a solid solution of antimony in tin dioxide.

(c) According to Godin *et al.* [24] the active sites for selective oxidation of propylene consist of octahedrally coordinated antimony(V) ions dissolved in the tin dioxide lattice.

The validity of each of these postulates has not yet been unambiguously established.

## 5. Acid-base properties

In general, acidic products are optimally formed over catalysts of high acidity and basic products are favoured over catalysts of high surface basicity. However, excessive acidity leads to complete oxidation, whereas excessive basicity lowers the activity [25]. Mixed oxides of tin and antimony have been shown to exhibit acidic activity in the propene-D<sub>2</sub>O exchange reaction [26]. For high activity in partial oxidation reactions the presence of acid and base sites of optimum strength is required [17, 20]. Pure antimony oxide, for example, which has only basic sites, is relatively inactive for partial oxidation reactions. A correlation has been obtained between the formation of CO<sub>2</sub> in the oxidation reaction and the surface acidity [20]. Initial addition

of antimony (up to 10 at.%) to tin dioxide leads to a decrease in both the acidity and the basicity of the catalyst. However, in propylene oxidation the maximum activity is around 3 at.% Sb. This indicates that the optimum strength of acidic and basic sites is necessary for propylene oxidation. In the oxidation of butene the maximum activity observed by McAteer [20] of around 33 at.% Sb is attributed to the high basicity of the catalyst. However, Irving and Taylor [27] and Sala and Trifiro [14] have observed two maxima in the activity pattern of butene oxidation, one at around 25 at.% Sb and the other at around 75 at.% Sb. Irving and Taylor [27] have measured the Brønsted acidity of mixed tin and antimony oxides by (i) isomerization of 3,3-dimethylbut-1-ene and (ii) dehydration of isopropyl alcohol. They have observed two maxima in the Brønsted acidity of the mixed oxides at around the same atomic per cent antimony and hence they concluded that the Brønsted acidity can be correlated with the activity for 1-butene oxidation (Fig. 1, curves 2 and 3). However, the maximum Brønsted acidity is found to occur in a composition range which is different from that at which the maximum activity is observed for the selective oxidation of propene to acrolein.

These studies have not established that acid-base properties are exclusively involved in the oxidation reaction. Even if they are involved it is

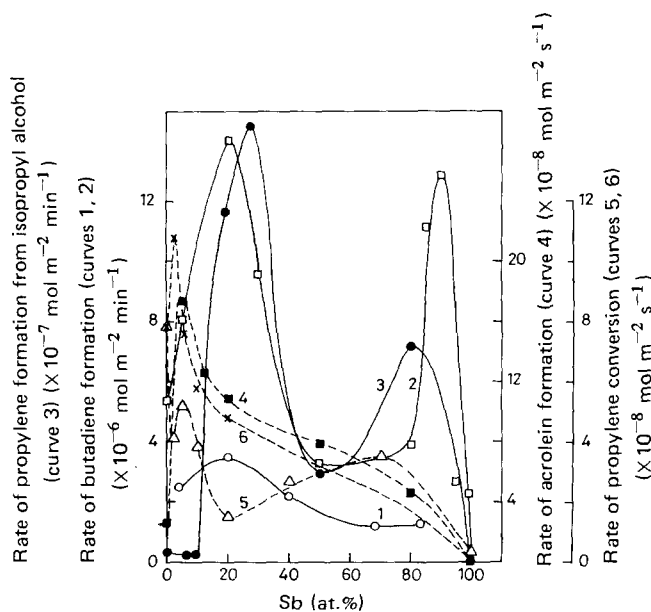


Fig. 1. Catalytic activity of the mixed tin and antimony oxide catalysts as a function of the antimony content: curves 1, 2, rate of butadiene formation in the oxidation of 1-butene (data from refs. 5 and 14 respectively); curve 3, rate of propylene formation from isopropyl alcohol (data from ref. 27); curve 4, rate of acrolein formation in the oxidation of propylene (data from ref. 15); curves 5, 6, rate of propylene conversion (data from refs. 3 and 11 respectively).

not yet clear what is the actual strength of these sites necessary to promote preferential partial or total oxidation. If a range of centres is available with varying acidic or basic strengths, the expected variation in activity and/or selectivity has not yet been established. Without this information these concepts may not be useful for catalyst selection.

## 6. Catalytic properties

The mixed tin and antimony oxides have been exploited extensively as oxidation catalysts [28 - 32]. The physicochemical characteristics of the mixed tin and antimony oxide catalysts are given in Table 3 and the details of reaction types in which this series of oxide catalysts has been used are given in Table 4. It is observed that the activity for propylene conversion passes through a maximum at about 3 at.% Sb (Fig. 1) while the selectivity for acrolein in propylene oxidation increases initially up to about 20 at.% Sb and then remains steady with further additions of antimony (Fig. 2). It has been shown that the active sites for this selective behaviour are in the  $\text{Sb}_2\text{O}_4$  phase segregated to the surface with a matrix containing a solution of antimony in tin dioxide or excess tin dioxide. The presence of antimony ions in close proximity to tin ions therefore constitutes the active sites, which can arise as a result of disordered material with a relatively homogeneous non-crystalline solid phase which can exist over a wide stoichiometric range of tin to antimony. In the initial periods of olefin oxidation on oxide catalysts, a decrease in the total activity and an increase in the selectivity for selective oxidation are usually observed, which are attributed (1) to the depletion of

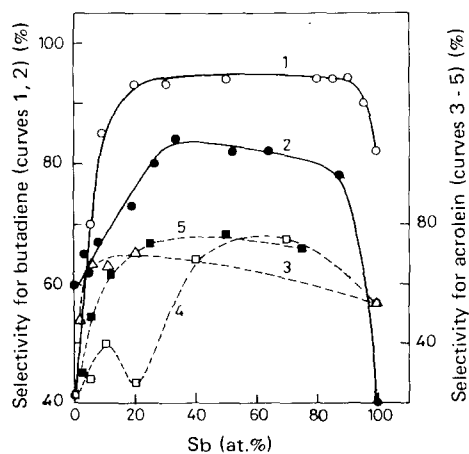


Fig. 2. Variation in the selectivity for butadiene and acrolein in mixed tin and antimony oxide catalysts as a function of the antimony content: curves 1, 2, percentage selectivity for butadiene in the oxidation of 1-butene (data from refs. 14 and 20 respectively); curves 3, 4, 5, percentage selectivity for acrolein in the oxidation of propylene (data from refs. 11, 3 and 15 respectively).



TABLE 3

Physicochemical characteristics of the mixed tin and antimony oxide catalysts

<i>Sb content</i> (at.%)	<i>Calcination</i> <i>temperature</i> (°C)	<i>Specific</i> <i>surface</i> <i>area</i> (m <sup>2</sup> g <sup>-1</sup> )	<i>Electrical</i> <i>conduc-</i> <i>tivity</i> (Ω <sup>-1</sup> cm <sup>-1</sup> )	<i>E<sub>c</sub> for</i> <i>conduction</i>	<i>E<sub>a</sub> for oxidative</i> <i>dehydrogenation</i> <i>of 1-butene or</i> <i>isopropyl alcohol</i> (kJ mol <sup>-1</sup> )	<i>Refer-</i> <i>ence</i>
<i>At 435 °C</i>						
0 (SnO <sub>2</sub> )	500	25	4.9 × 10 <sup>-5</sup>	113 kJ mol <sup>-1</sup>		[3]
1.5		31.5	1.2 × 10 <sup>-2</sup>	50 kJ mol <sup>-1</sup>		
5		43.5	5.7 × 10 <sup>-2</sup>	8.4 kJ mol <sup>-1</sup>		
10		63	5.8 × 10 <sup>-2</sup>	4.2 kJ mol <sup>-1</sup>		
20		92	2.5 × 10 <sup>-2</sup>	4.2 kJ mol <sup>-1</sup>		
40		100	1.0 × 10 <sup>-2</sup>	0		
70		15	9.4 × 10 <sup>-6</sup>	56.5 kJ mol <sup>-1</sup>		
100		2.7	2.0 × 10 <sup>-10</sup>	134 kJ mol <sup>-1</sup>		
<i>1-Butene</i>						
0 (SnO <sub>2</sub> )	600	16			142	[20]
5.9		40			103	
7.3		34			78	
26.5		48			64	
33.1		56			57	
51.9		55			59	
100		44			45	
<i>At 380 °C</i>						
<i>Isopropyl alcohol</i>						
0 (SnO <sub>2</sub> )	800	9.2	—	—	104.8	[33]
5		8.2	4.6 × 10 <sup>-2</sup>	0.10 eV	99.8	
12		10.5	0.9 × 10 <sup>-2</sup>	0.26 eV	81.9	
20		8.3	1.4 × 10 <sup>-2</sup>	0.25 eV	89.3	
50		5.5	0.7 × 10 <sup>-2</sup>	0.20 eV	131.7	
80		3.2	1.7 × 10 <sup>-5</sup>	0.23 eV	92.6	
100		0.4	4.7 × 10 <sup>-10</sup>	1.71 eV	123.1	

loosely held surface oxygen [43], (2) to the changes in the valence state of the cations in the catalyst [24] and (3) to the coverage of the active centres with irreversibly adsorbed hydrocarbons [44]. In an attempt to elucidate this aspect through the study of isobutylene oxidation over mixed tin and antimony oxide catalysts Rostevanov *et al.* [35] have shown that the complete combustion product (CO<sub>2</sub>) is formed (i) directly from isobutylene and (ii) through the combustion of condensation products deposited onto the surface. This study is particularly interesting in the sense that the mixed tin and antimony oxide catalysts like any other oxidation catalysts [45] promote the complete combustion reaction both by consecutive and by direct reaction pathways. In addition, this study establishes the poisoning effect due to adsorption of condensation products, mainly intermediates of hydrocarbon oxidation. This aspect can also be applicable to other selective oxidation catalysts and needs careful examination.

TABLE 4  
Summary of the types of reactions studied on mixed tin and antimony oxide catalysts

Catalyst composition	Calcination temperature (°C)	Reaction	Product	Observations	Reference
0 - 40 at.% Sb	500 - 950	Propylene oxidation	Acrolein	The maximum activity occurs at around 1.5 at.% Sb while the maximum selectivity for acrolein is obtained with 20 at.% Sb; the selectivity for acrolein is related to the surface Sb content	[11]
0 - 100 at.% Sb	1000	Propylene oxidation	Acrolein	The maximum activity is obtained with 5 at.% Sb and the maximum selectivity for acrolein is observed for all catalysts containing more than 25 at.% Sb	[15]
0 - 100 at.% Sb	500, 950	Propylene oxidation	Acrolein	For low Sb concentrations (less than 40 at.%) calcination at 950 °C leads to surface segregation while calcination at the same temperature for high Sb concentrations (greater than 40 at.%) leads to migration of Sb from the surface towards the bulk	[34]
Sn-Sb-O	—	Isobutylene oxidation	Methacrolein	CO <sub>2</sub> is formed in three ways	[35]
Sn-Sb-O with Al <sub>2</sub> O <sub>3</sub> (Sn:Sb, 1:1)	—	Isobutylene oxidation	Methacrolein	50% - 60% activity and 60% - 70% methacrolein selectivity; the solid solutions of the mixed tin and antimony oxides are the active components of the catalysts	[36]
0 - 100 at.% Sb	400 - 1000	Butene oxidation	Butadiene	The formation of butadiene is related to the concentration of Sb cations at the surface	[5]
80 at.% Sb	900	Butene oxidation	Butadiene	Two gem Sb <sup>5+</sup> =O groups are responsible for the activity while the role of the second metal cation is to adsorb gaseous O <sub>2</sub> to reoxidize the reduced Sb ions	[23]
Sn-Sb-O (Sn:Sb, 2:1)	—	Butene oxidation	Butadiene	Catalyst oxygen participates in the catalytic process; the reaction proceeds on a partially reduced surface of the catalyst by means of alternate reduction and oxidation	[37]

(continued)

TABLE 4 (continued)

Catalyst composition	Calcination temperature (°C)	Reaction	Product	Observations	Reference
80 at.% Sb	540	<i>o</i> -Xylene oxidation	Tolualdehyde and CO <sub>2</sub>	At 370 °C the selectivities for tolualdehyde and CO <sub>2</sub> are 45.5% and 45.9% respectively	[38]
Sn-Sb-O doped with Ga, In or Tl (Sn:Sb, 1:1)	—	Propylene ammoxidation	Acrylonitrile	Dopants such as Ga <sub>2</sub> O <sub>3</sub> and Tl <sub>2</sub> O <sub>3</sub> improve the selectivity for acrylonitrile; doping is confined to the surface layers of the catalyst	[39]
Sn-Sb-O	500	<i>o</i> -Xylene oxidation	Tolualdehyde	The yield of tolualdehyde increases with an increase in the Sb content; an increase in the calcination temperature leads to a decrease in the selectivity for the partial oxidation product	[40]
Sn-Sb-O	—	Naphthalene oxidation	Oxides of carbon	—	[41]
80 at.% Sb	800	Decomposition of isopropyl alcohol in the absence of O <sub>2</sub>	Acetone and H <sub>2</sub>	SnO <sub>2</sub> undergoes irreversible reduction to metallic Sn while Sb <sub>2</sub> O <sub>4</sub> undergoes reversible reduction to Sb <sub>2</sub> O <sub>3</sub> ; both simple dehydrogenation and oxidative dehydrogenation occur	[42]
0 - 100 at.% Sb	800	Decomposition of isopropyl alcohol in the presence of O <sub>2</sub>	Acetone	All compositions of the catalysts have the same activity and nearly the same selectivity (80%) for acetone; Sb <sub>2</sub> O <sub>4</sub> , formed as a two-dimensional layer on the tin oxide matrix, is the active phase for this reaction	[33]

From detailed X-ray photoelectron spectroscopy (XPS) studies Vedrine [34] has concluded that the selective mixed tin and antimony oxide catalyst is composed of an  $\text{Sb}_2\text{O}_4$  phase lying on a solid solution of antimony(V) in tin dioxide and that the observed catalytic activity is directly related to the surface concentration of antimony as determined by XPS. The data supporting the latter conclusion have been taken from ref. 5 and are presented in Table 1.

In the decomposition of isopropyl alcohol in the absence of gas phase oxygen over mixed tin and antimony oxide, with 80 at.% Sb, both dehydrogenation and oxidative dehydrogenation are found to occur. During the reaction tin dioxide is found to undergo irreversible reduction to metallic tin while  $\text{Sb}_2\text{O}_4$  is found to undergo reversible reduction to  $\text{Sb}_2\text{O}_3$  [42]. In the presence of gas phase oxygen, isopropyl alcohol undergoes only oxidative dehydrogenation over mixed tin and antimony oxides and all compositions of the catalyst (5 - 80 at.% Sb) have the same oxidative dehydrogenation activity and nearly the same selectivity (80%) for acetone. In the presence of gas phase oxygen, product acetone is found to undergo complete combustion to  $\text{CO}_2$  at a faster rate than the reactant isopropyl alcohol. It is concluded that the active phase for the oxidative dehydrogenation of isopropyl alcohol in the presence of gas phase oxygen is the  $\text{Sb}_2\text{O}_4$  phase formed as a two-dimensional layer on the tin dioxide matrix [33]. Portefaix *et al.* [46] have also stated that the actual mixed tin and antimony oxide catalyst consists of an oriented film of a two-dimensional  $\text{Sb}_2\text{O}_4$  layer supported by an antimony(V)-tin dioxide solid solution. A linear correlation has been established between the initial rate of acrolein formation from propylene and the mole per cent of acetone obtained per square metre by oxidative dehydrogenation of isopropyl alcohol over the mixed tin and antimony oxides [33].

Examination of scanning electron micrographs of samples of mixed tin and antimony oxides reveals that the samples possess a variable microstructure. The samples thus prepared [33] probably exhibit increased group or cluster formation with increases in the antimony content. Isolated antimony ions surrounded by tin ions may be readily obtained at low levels of antimony and, with increases in the antimony content, cluster formation probably leads to a reduction in the number of active centres available at the surface. However, the consequent variation in the microstructure of the samples has also to be taken into account to rationalize the activity patterns observed with these samples.

In conclusion, it can be stated that, although there appears to be a concurrence of the available concepts regarding the nature of the active sites, the necessary acid-base strengths of these sites and the necessity of segregation of antimony in the mixed tin and antimony oxide oxidation catalysts, the applications of newer surface analytical tools have not yet succeeded in resolving completely the requisites of a typical selective oxidation catalyst. It is gratifying to note that, although a complete rationalization of the behaviour of mixed tin and antimony oxide catalysts has not yet been achieved, some agreement has been obtained between the various postulates.

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