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Oxidation of Propylene over the Tin-Antimony Oxide Catalysts. II. Investigations of Physicochemical Properties of the Catalysts

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The physicochemical properties of the binary system composed of Sn and Sb oxides have been investigated. The electrical conductivity increased rapidly up to 3 atom% Sb, and subsequently decreased, little by little, as the Sb oxide content in the binary system increased. The surface area also increased rapidly up to 3 atom% Sb, and in the region exceeding this content a dilution effect due to Sb oxide was observed. The behavior of the initial rate of acrolein formation as a function of the catalyst composition was fairly similar to that of the surface area. The apparent activation energies for carbon dioxide formation at first decreased, and then became nearly constant when the Sb content of the catalysts increased. On the other hand, the activation energies for acrolein formation may be considered to be always constant, independent of the catalyst composition, at about 17 kcal/mol. The activation energies for the catalyst reduction by hydrogen were 28 kcal/mol for Sn oxide, 14 for a mixture containing 25 atom% Sb, and 30 for Sb oxide. Consequently, it has been concluded from these results that it may depend on the nature of the chemisorbed oxygen which attacks propylene whether the propylene is oxidized into acrolein or into such complete combustion products as carbon dioxide.

In the studies of the binary system of Sn and Sb oxides, a former paper1) was concerned with the effect of the catalyst compositon and the calcination conditions on the formation of acrolein, and with an investigation of the X-ray patterns of the catalysts; it was confirmed that Sb oxide was dissolved into Sn oxide and that the solid solutions thus formed were active in the production of acrolein.

The present paper will deal with the physical and catalytic properties of the binary system for the purpose of elucidating why the solid solutions composed of Sn and Sb oxides are active in acrolein formation.

Many works2-6) have thus far been presented on various binary systems, though few have dealt with the correlation between the reaction activity and the physicochemical properties. Butler *et al.*,6) however, observed a correlation between the conducitivity and the apparent activation energy for the decomposition of benzene over mixed catalysts of V_2O_5 containing MoO_3 or GeO_2.

From the viewpoint of controlled-valency semiconductivity, the decomposition of N_2O7-9) and the oxidation of CO10,11) have thus far been studied,

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1) K. Wakabayashi, Y. Kamiya and N. Ohta, This Bulletin, **40**, 2172 (1967).

2) C. R. Adams and T. J. Jennings, *J. Catalysis*, **2**, 63 (1963).

3) R. H. Munch and E. D. Pierron, *ibid.*, **3**, 406 (1964).

4) Ph. A. Batist, B. C. Lippens and G. C. A. Schuit, *ibid.*, **5**, 55 (1966).

5) W. M. H. Sachtler and N. H. De Boer, *Proc. 3rd Intern. Congr. Catalysis*, 252 (1965).

6) J. D. Butler and B. G. Weston, *J. Catalysis*, **2**, 8 (1963).

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but the mechanism of the catalysis has not been completely elucidated.

Experimental

The apparatus, experimental procedures, and methods of catalyst preparation were the same as were employed in the previous work.[1)]

The samples used in the measurements of the surface area and of the electrical conductivity were prepared by heating the powder of SnO_2 and Sb_2O_5 at a desired ratio, the two ingredients being thoroughly admixed without any carrier.

The surface areas were measured with nitrogen by the BET method at $-196°C$; an area of 16.2 Å^2 was assumed for the nitrogen molecule. The dc resistance of a 2 g portion of the powdered sample was measured with Wheatstone's bridge. The apparatus was similar to that of Griffith *et al.*[12)] The electrodes were platinum disks 12 mm in diameter; two springs applied a constant pressure to the sample between the electrodes.

The reduction of the catalysts was carried out at the atmospheric pressure of hydrogen in the range from 400°C to 500°C by using a thermobalance.

Results

Figure 1 shows the electrical conductivity of the binary system composed of Sn and Sb oxides. The measurements were carried out in air at room temperature. The conductivity increased markedly up to 3 atom% Sb, and then decreased little by little in the region above 3 atom% Sb.

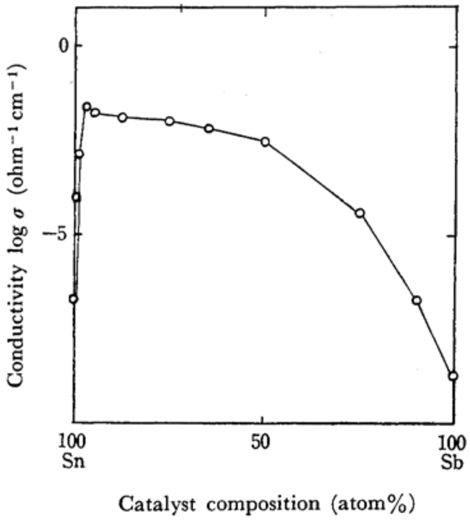

Fig. 1. The conductivity of the Sn and Sb oxide binary system.

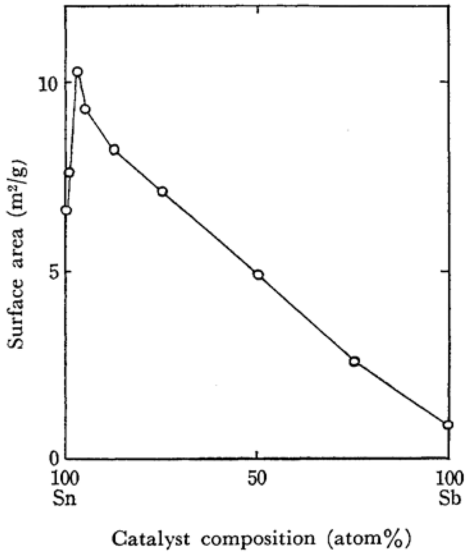

Fig. 2. The surface area of the Sn and Sb oxide binary system.

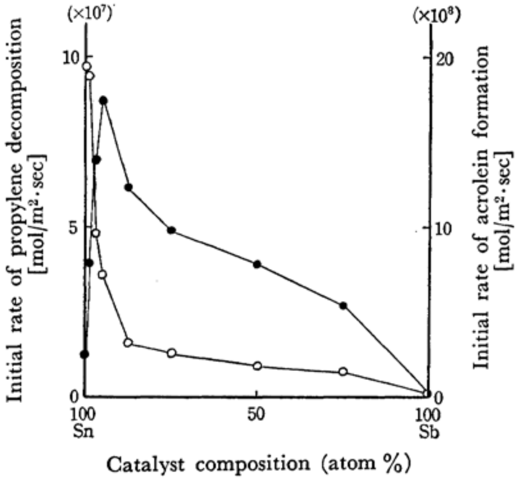

Fig. 3. Initial rate of acrolein formation and propylene decomposition.
Catalyst: calcined at 1000°C for 3 hr
Reaction temperature: 470°C
○: Propylene decomposition
●: Acrolein formation

Figure 2 shows the surface area as a function of the composition of Sn and Sb oxides. The surface area increased as markedly as may be observed in Fig. 1 up to 3 atom% Sb. However, in the region of higher Sb oxide concentrations the surface area subsequently decreased, and a dilution effect due to Sb oxide was observed.

Figure 3 shows the initial rates of acrolein formation and propylene decomposition at 470°C. A rapid increase in the initial rate of acrolein formation was caused by the addition of Sb oxide; the maximum rate was obtained at a 5 atom% Sb content. In the region of higher Sb oxide concentrations, a dilution effect seems to exist. The initial rate of propylene decomposition fell

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12) P. R. Charman, R. H. Griffith and J. D. E. Marsh, *Proc. Roy. Soc.*, **224**, 419 (1954).

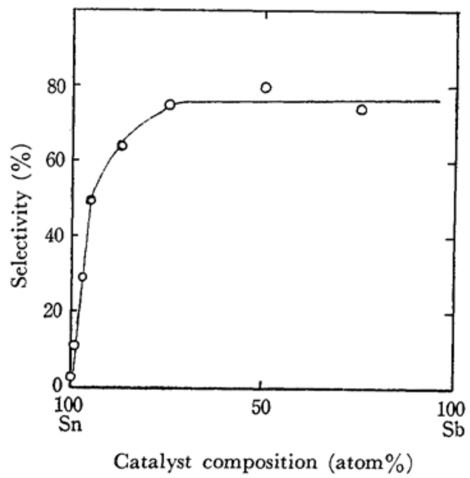

Fig. 4. Selectivity to acrolein when the consumption of propylene was about 10%.
Catalyst: calcined at 1000°C for 3 hr
Reaction temperature: 470°C

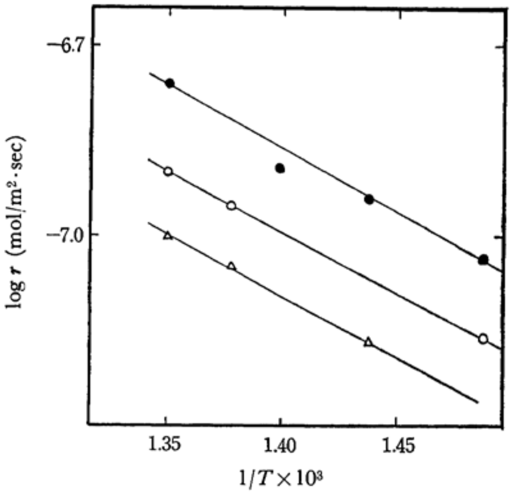

Fig. 5. Representative Arrhenius plots for acrolein formation.
Catalyst: calcined at 1000°C for 3 hr
●: Catalyst with a Sn-to-Sb atomic ratio: 95 : 5
○: Catalyst with a Sn-to-Sb atomic ratio: 7 : 1
△: Catalyst with a Sn-to-Sb atomic ratio: 7 : 1

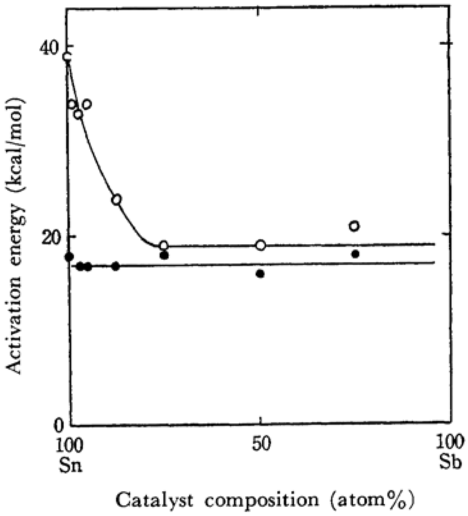

Fig. 6. Apparent activation energies for carbon dioxide formation and acrolein formation.
Catalyst: calcined at 1000°C for 3 hr
○: Carbon dioxide formation
●: Acrolein formation

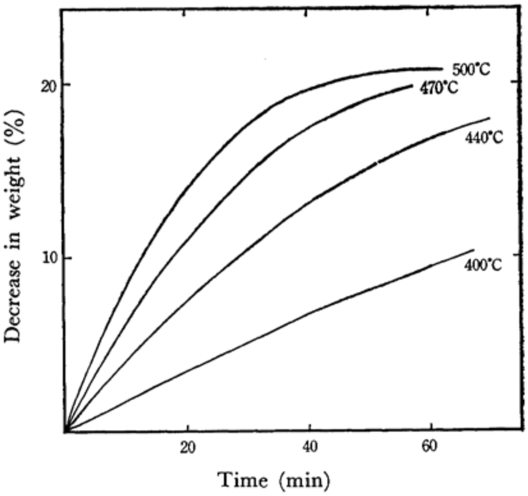

Fig. 7. Weight lost upon reduction by hydrogen.
Sample: mixture with a Sn-to-Sb atomic ratio of 3 : 1, calcined at 1000°C for 3 hr.

off rapidly as Sb oxide was added to Sn oxide. The formation of carbon dioxide was extremely depressed by the addition of Sb oxide, as is summarized in Table 1.

The selectivity to acrolein when the conversion of propylene is about 10% is shown in Fig. 4 as a function of the catalyst composition. The selectivity at first increased upon the addition of Sb oxide, and then it became almost constant in the region of Sn-to-Sb atomic ratios below 3 : 1.

The apparent activation energies for the formation of acrolein (E_{acr}) and carbon dioxide (E_{CO_2}) have been obtained from Arrhenius plots in the temperature range from 400°C to 490°C, using an initial rate, r, which is considered to be proportional to the rate constant, k. These plots of log r against $1/T$ have given a reasonably straight line for all the catalysts of various compositions. In the case of acrolein formation, representative Arrhenius plots are shown in Fig. 5. Figure 6 shows E_{acr} and E_{CO_2} as functions of the catalyst composition. E_{acr} remained constant over the entire range of compositions of the binary system. On the other hand, E_{CO_2} decreased up to 25 atom% Sb, and then became constant in the region of Sn-to-Sb atomic ratios below 3 : 1.

TABLE 1. RATE OF REACTION
Reaction temperature: 470°C

Catalyst composition (Sn/Sb)	Rate of reaction (mol/m²·sec) $d(CH_2{=}CHCHO)/dt$ ($\times 10^8$)	$d(CO_2)/dt$ ($\times 10^8$)	$-d(C_3H_6)/dt$ ($\times 10^7$)
SnO_2	2.6	252	9.9
99/1	7.8	165	9.8
97/3	14.0	59	4.9
95/5	17.4	35	3.5
7/1	12.4	9.3	1.9
3/1	9.8	3.9	1.3
1/1	7.8	1.9	0.98
1/3	5.5	1.4	0.74

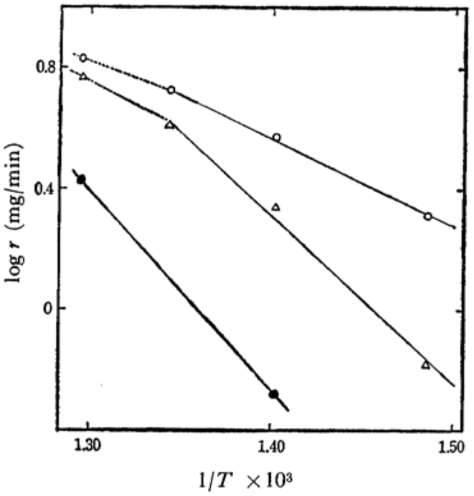

Fig. 8. Arrhenius plots for catalyst reduction by hydrogen.
○: Sample with a Sn-to-Sb atomic ratio of 3 : 1
△: SnO_2
●: Sb_2O_5
Each sample was calcined at 1000°C for 3 hr.

Figure 7 indicates the weight loss during reduction by hydrogen of a mixture with a Sn-to-Sb atomic ratio of 3 : 1. The reduction rate has been represented by the decrease in the weight of a sample between 5 and 15 min after the beginning of the reduction. Arrhenius plots for the reduction are shown in Fig. 8. The diffusion process seems to have an effect upon the reduction rate at temperatures as high as 500°C. The apparent activation energies thus obtained were 28 kcal/mol for Sn oxide, 14 for the mixture with a Sn-to-Sb atomic ratio of 3 : 1, and 30 for Sb oxide.

Discussion

As has been mentioned in the earlier paper,¹⁾ SnO_2 and Sb_2O_5 form a substitutional solid solution. The solid solution is formed as follows:

$$(1-2\delta)SnO_2 + \delta Sb_2O_5 \rightarrow$$
$$Sn_{(1-4\delta)}{}^{4+}Sn_{2\delta}{}^{3+}Sb_{2\delta}{}^{5+}O_2 + \frac{1}{2}\delta O_2 \qquad (1)$$

or

$$Sb_2O_5 \rightarrow 2Sb_{(Sn)}{}^{+} + 2\ominus + 2SnO_2 + \frac{1}{2}O_2 \qquad (2)$$

where $Sb_{(Sn)}{}^{+}$ indicates Sb^{5+} which has been substituted for Sn^{4+}. SnO_2 acts as a n-type semiconductor; accordingly Sn^{3+}, which may be called anion vacancies, or quasi-free electrons, is produced as is shown above when the lattice of SnO_2 dissolves Sb_2O_5. The Sn^{3+} content is equivalent to the amount of Sb^{5+} substituted for Sn^{4+}. The solid solutions were found, from the X-ray investigations described in the previous paper, to have a homogeneous crystal of the same structure as the original SnO_2, but the dimensions of the unit cell must be larger, as the ionic radius of Sn^{3+} is larger than that of Sn^{4+}. Hence, an expansion of the lattice by the addition of Sb_2O_5 may be expected. This has also actually been observed, as has been shown in the previous paper.

Phase Composition of Sn and Sb Oxide System. How far Sb_2O_5 is dissolved into SnO_2 is dependent upon the calcination temperature and the period. However, it is difficult to determine the solubility by measuring Δd because of the fact that the addition of Sb_2O_5 to SnO_2 does not cause much change in the *d*-spacings in X-ray patterns; also, it is difficult to ascertain whether Sb_2O_5 is completely dissolved into SnO_2 at a low Sb content because of the fact that the relative intensity of Sb_2O_5 in X-ray patterns is considerably smaller than that of SnO_2. It was shown by the X-ray investigations described in the previous paper that some Sb_2O_5 remains insoluble in SnO_2 in the case of a (Sn/Sb=3, 1000°C, 3 hr) mixture, and that a larger amount of Sb_2O_5 is dissolved into SnO_2 in a (Sn/Sb=3, 1100°C, 3 hr) mixture than in the (Sn/Sb=3, 1000°C, 3 hr) mixture. Here, the description of the (Sn/Sb=3, 1000°C, 3 hr) mixture means that the Sn-to-Sb atomic ratio in the mixture is 3 : 1 and that the mixture has been calcined at 1000°C for 3 hr. Hence, it is certain that two phases consisting of Sb_2O_5 and the solid solution are present in the (Sn/Sb=3, 1000°C, 3 hr) mixture. However, it remains uncertain whether Sb_2O_5 insoluble in SnO_2 is present in the mixture with a Sn-to-Sb atomic ratio above 3 : 1 when it is calcined at 1000°C for 3 hr, as has been shown in the X-ray patterns in the previous paper.

As quasi-free electrons equivalent to the amount of Sb dissolved into SnO_2 are produced, the conductivity increases upon the addition of Sb_2O_5 to SnO_2, showing a maximum value at a 3 atom% Sb content. It is impossible, however, to determine from the conductivity measurements how far the Sb oxide is dissolved into the Sn oxide, because the conductivity is not necessarily proportional to the concentration of the foreign ion when dissolved in great quantities. Nevertheless, it may be considered, judging from the conductivity data, that the Sb oxide is almost completely dissolved up to 3 atom% Sb. The surface area also increases rapidly upon the addition of a small amount of Sb oxide; it is largest at a 3 atom% Sb content. In the region of the oxide system containing more than 3 atom% Sb, a dilution effect due to Sb oxide has been observed. Taking into consideration the conclusion of the conductivity investigations, the increase in the surface area upon the addition of a small amount of Sb oxide can be attributed to the formation of the solid solutions. As the surface area is regarded as dependent upon the dimensions of the grain size, it seems that the grain size may become small when the lattice of Sn oxide dissolves Sb oxide.

The investigation of the initial rate of acrolein formation, if based on the conclusion drawn from the conductivity and surface area data, shows that the initial rate is mainly dependent upon the amount of the solid solutions formed on the catalyst surface. A dilution effect due to the Sb oxide added seems to be present in the region above a 5 atom% Sb content. The dilution effect in the above two cases can be attributed to the Sb oxide which remains insoluble in Sn oxide. Hence, it may be concluded that the two phases composed of Sb oxide and the solid solutions are present in the system exceeding about a 5 atom% Sb content.

Why the mixtures of Sn and Sb oxides become colored upon being calcined at a high temperature may be due to the Sn^{3+} produced when the lattice of Sn oxide dissolves Sb oxide. Accordingly, the maximum solubility may be qualitatively determined from the depth of the color of the mixtures. As was mentioned in the previous paper, the mixture with a Sn-to-Sb atomic ratio of 3 : 1 is deepest in color of all the mixtures when calcined at 1000°C for 3 hr, but it is less deep than the (Sn/Sb=3, 1100°C, 3 hr) mixture. The maximum solubility of Sb oxide into Sn oxide may, therefore, be regarded as nearly 25 atom%; this value is in good agreement with the value inferred from the measurements of the apparent activation energies for the formation of carbon dioxide and of the selectivity to acrolein. Consequently, it may be concluded that Sb oxide is completely dissolved into Sn oxide up to 3 or 5 atom% Sb when calcined at 1000°C for 3 hr, and that Sb oxide as well as the solid solution is present in the system at a higher Sb content, though the maximum solubility is nearly 25 atom%.

Formation of Acrolein and Carbon Dioxide. Many mixed catalysts, for example, CuO-SeO_2,(13) Fe_2O_3-As_2O_3,(14) Bi_2O_3-MoO_3,(15) and SnO_2-Sb_2O_5,(16) recommended for the oxidation of propylene to acrolein, contain one metal oxide which is considered to produce acrolein selectively by itself, though the rate of formation is slow. The heat of the formation of this oxide from a lower oxide or metal to a higher is relatively small, as Table 2 shows. A pure molybdenum oxide catalyst, as has been reported previously,(17) scarcely oxidizes propylene at all in such a reducing atmosphere as that in this work, nor does a pure antimony oxide catalyst. This may be because these oxides are easily reduced to lower oxides or metals, whose surface is in a reducing atmosphere with a large amount of adsorbed propylene and, accordingly, almost inactive in the oxidation of propylene as a result of the poverty of active oxygen on the surface. Kominami *et*

TABLE 2. THE HEAT OF FORMATION OF THE METAL OXIDES

Metal oxide	(kcal/mol)
SnO_2	137.4
SnO	66.0
Sb_2O_5	229.6
Sb_2O_3	164.4
Fe_2O_3	195.2
FeO	64.6
As_2O_5	219.4
As_2O_3	156.6
CuO	33.0
Cu_2O	43.0
SeO_2	63.5
Bi_2O_3	137.8
MoO_3	180.4
MoO_2	142.8
V_2O_5	437
V_2O_4	361.6
V_2O_3	302

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13) Distillers: Brit. Pat. 655210 (1951).

14) T. Ishikawa and T. Hayakawa, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **67**, 1391 (1964).

15) Standard Oil: U. S. Pat. 2904580 (1959).

16) Distillers: Brit. Pat. 864666 (1961).

17) K. Wakabayashi and Y. Kamiya, This Bulletin, **40**, 401 (1967).

al.[18] have proposed the following mechanism with respect to the CuO-SeO_2 system:

$$SeO_2 \text{ (or } CuSeO_3) + C_3H_6 \rightarrow \text{acrolen} + Se\ (CuSeO) \qquad (3)$$

$$Se\ (CuSeO) + CuO \rightarrow SeO_2\ (CuSeO_3) + Cu_2O \qquad (4)$$

$$Cu_2O + O_2 \rightarrow CuO \qquad (5)$$

This may mean that one oxide in the mixed catalysts is effective in the activation of oxygen, and another, in the activation of propylene. In the binary system composed of Sn and Sb oxides, antimony ions may be effective in the activated adsorption of propylene, as has been investigated with regard to Bi_2O_3-MoO_3[2,5] and Cu_2O[19]. In this discussion, however, only the chemisorption of oxygen will be taken into consideration.

Oxygen is adsorbed on a metal oxide as follows:

$$O_2 \rightleftarrows O_2^- \rightleftarrows O^- \rightleftarrows O^{2-} \qquad (6)$$

At a low temperature, the oxygen adsorbed on a metal oxide is considered to be converted to O_2^- or O^-, and at a high temperature, to O^- or O^{2-}. Therefore, under these reaction conditions, it may be assumed that there may be present on the catalyst surface both O^- and O^{2-} ions. The former is an oxygen ion adsorbed on the catalyst, while the latter is an oxygen ion more strongly adsorbed, one which may be of the same nature as the lattice ion.

As is shown in Fig. 6, E_{CO_2} decreases up to about 25 atom% Sb and remains nearly constant hereafter. In the V_2O_5-MoO_3 system,[20] a vanadium-oxygen bond is weakend by the addition of MoO_3. If the SnO_2-Sb_2O_5 system is analogous, a tin-oxygen bond may become weaker as the Sb oxide is dissolved into the Sn oxide. The measurements of the activation energies for the catalyst reduction indicate that a mixture with a Sn-to-Sb atomic ratio of 3 : 1 has an activation energy smaller by 14 kcal/mol than a pure tin oxide. This finding is in fairly good agreement with the difference in E_{CO_2}. Hence, the lattice oxygen is possibly connected with the formation of carbon dioxide.

On the other hand, little change in E_{acr} was observed in spite of the change in the amount of Sb oxide added. This suggests that the formation of acrolein may be dependent upon the O^- ions, according to the report that ethylene oxide is yielded by O_2^- rather than O^- ions in the oxidation of ethylene.[21]

Thus:

Formation of carbon dioxide

$$O^{2-}\text{ (lattice oxygen)} + C_3H_6 \rightarrow \text{complete combustion products} + [O_v^{2+}\cdot 2e]\text{ (oxygen defect)} \qquad (7)$$

$$\frac{1}{2}O_2 + [O_v^{2+}\cdot 2e] \rightarrow O^{2-}\text{ (lattice oxygen)} \qquad (8)$$

Formation of acrolein

$$\frac{1}{2}O_2 + Sn^{3+} \rightarrow O^- + Sn^{4+} \qquad (9)$$

$$O^- + C_3H_6 + Sn^{4+} \rightarrow \text{acrolein} + Sn^{3+} \qquad (10)$$

where Sn^{3+} indicates an anion vacancy.

This mechanism explains very reasonably the results of the kinetic measurements and the selectivities of the catalysts as well as the dilution effects. As the amount of quasi-free electrons on the catalyst surface increases when Sb oxide is added to Sn oxide, the increase in the initial rate of acrolein formation, shown in Fig. 3, is observed. On the other hand, an active lattice oxygen ion available for carbon dioxide formation is removed from the system, leaving an anion vacancy, when Sb oxide is dissolved into Sn oxide, so the rate of carbon dioxide formation falls off. That the maximum value of the rate of acrolein formation was obtained at a 5 atom% Sb content suggests that the concentration of anion vacancies avaiable on the catalyst surface is highest at this content. It is due to the more marked decrease in the rate of carbon dioxide formation that the rate of propylene decomposition decreases upon the addition of Sb oxide to Sn oxide and that the selectivity to acrolein increases above 5 atom% Sb even though the rate of acrolein formation falls off.

The selectivity to acrolein was 32% at the contact time of 0.5 sec and 17% at 2.5 sec with a (Sn/Sb= 97/3, 1000°C, 3 hr) catalyst, though it was 74% at 7.5 sec and 68% at 25 sec with a (Sn/Sb=3, 1000°C, 3 hr) catalyst, where Sb oxide is considered to dissolve into Sn oxide almost to the maximum extent of solubility. Therefore, a lattice oxygen ion may also be related to the further oxidation of acrolein.

However, detailed information on the reaction kinetics as well as on the adsorption of oxygen and propylene is necessary before a quantitative reaction scheme can be presented.

The authors wish to express their thanks to Professor Emeritus Shingo Ando for his continued advice and encouragement in this work.

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18) N. Kominami, A. Shibata and S. Minekawa, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **65**, 1510 (1962).

19) H. H. Voge, C. D. Wagner and D. P. Stevenson, *J. Catalysis*, **2**, 58 (1963).

20) K. Tarama, S. Teranishi, S. Yoshida and N. Tamura, *Proc. 3rd Intern. Congr. Catalysis*, 282 (1965).

21) G. D. Lyubarskii, *Dokl. Akad. Nauk USSR*, **110**, 112 (1956).