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Oxidation of Propylene over the Tin-Antimony Oxide Catalysts. I. Dependency of Acrolein Formation on the Composition of Catalyst and Calcination Conditions[*1]

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For the purpose of elucidating the catalysis of the binary system consisting of Sn and Sb oxides, recommended in the patent for the oxidation of propylene to acrolein, the oxidation of propylene has been studied; in addition, the X-ray patterns of the system have been investigated. The mixtures of this binary system after sintering were different in color according to the catalyst composition and the calcination conditions. It was found that the color of the catalyst is closely connected with the formation of acrolein, and also that the blue-colored catalysts are effective in the selective production of acrolein. The pure tin oxide catalyst yielded mainly carbon dioxide and monoxide, while the pure antimony yielded scarcely any product. However, a selectivity to acrolein of more than 70% was obtained at 450°C over a catalyst with an optimal composition, for example, one with a Sn to Sb atomic ratio of 3 : 1 which had been calcined at 1000°C for 3 hr. The formation of acrolein was investigated as a function of the catalyst composition and the calcination conditions. According to the X-ray data, Sb oxide was soluble in Sn oxide, thus forming solid solutions, and the mixtures' becoming colored was attributable to the formation of the solid solutions. It was concluded that the formation of acrolein over this binary system is closely connected with the solid solutions formed between Sn and Sb oxides.

Many patents have been presented on catalysts for the oxidation of propylene to acrolein. Many of them have recommended the use of such mixed catalysts as Cu-Se oxides,[1] Mo-Bi oxides,[2] and Sn-Sb oxides.[3] Each component composing these mixed catalysts is generally inactive in the formation of acrolein by itself under the reaction conditions employed. Therefore, it is of interest to clarify the special features of the catalysis of the mixed system.

Regarding the system of Cu-Se oxides, Kominami *et al.*[4] have shown that propylene is oxidized to acrolein with SeO_2 or $CuSeO_3$ formed between CuO and SeO_2. Although several papers[5-8] have been reported on the system of Mo-Bi oxides, the mechanism remains obscure.

In this work, the oxidation of propylene has been studied over the Sn-Sb oxide binary system, the reaction mechanism of which is unknown. This paper will be concerned with the investigation of X-ray diagrams of the binary system as well as with the oxidation of propylene, hoping to confirm how far the formation of acrolein depends on the catalyst composition and on the calcination conditions.

Experimental

The oxidation of propylene was carried out in a flow-type reaction system at atmospheric pressure, using a gas mixture consisting of oxygen, propylene, and nitrogen. The partial pressure of oxygen was ketp at 0.1 atm throughout the experiments, and also that of propylene($P_{C_3H_6}$) was kept 0.1 atm except in the runs for the investigation of the effect of this partial pressure on the formation of acrolein. The total pressure was then kept at 1 atm using nitrogen.

The converter used was a Pyrex-glass tube (1.8 or 1.0 cm i. d.) with an axially-positioned thermocouple tube inside. This converter was immersed in a molten salt bath, the temperature of which was controlled within ±1°C of the desired temperature.

The reaction temperature was 450°C or 470°C. The contact time was defined as the ratio of the catalyst volume (m*l*) to the flow rate (at 25°C), which was kept at 2 m*l*/sec; the contact time was fixed at 25 sec except in the runs for the investigation of the effect of the propylene partial pressure on acrolein formation.

The catalytic activity became constant in about half an hour after the catalyst had been placed in the

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[1] Distillers, Brit. Pat. 655210 (1951).

[2] Standard Oil, U. S. Pat. 2904580 (1959).

[3] Distillers, Brit. Pat. 864666 (1961).

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

[5] R. H. Munch and E. D. Pierron, *J. Catalysis*, **3**, 406 (1964).

[6] A. C. A. M. Bleijenberg, B. C. Lippens and G. C. A. Schuit, *ibid.*, **4**, 581 (1965).

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

[8] W. M. H. Sachtler and N. H. De Boer, *Proc. 3rd Intern. Congr. Catalysis,* **1965**, 252.

current of the feed gas, and the experimental data were obtained in the stationary state.

The reactant gas and reaction products were analyzed by means of gas chromatography. Oxygen, nitrogen, and carbon monoxide were determined by a Molecular Sieve 13X column; propylene and carbon dioxide by an Acetonyl Acetone S column, and aldehydes by a DOP column.

The catalysts employed in the experiments were prepared as follows: The required amounts of finely-powdered SnO_2 and Sb_2O_5 or Sb_2O_3 were weighed and thoroughly mixed with each other. 20 mesh α-alumina granules were impregnated in water with the mixed powder thus obtained, and followed by drying on a water bath, and subsequently by heating in a muffle furnace kept at the desired temperature. The metal concentration of the catalytic material on the carrier was fixed for all the catalysts at 0.025 g atom per 100 g of α-alumina.

The X-ray investigations were carried out with a X-ray diffractometer with a Geiger-Müller counter and Ni-filtered Cu$K\alpha$ radiation.

Results and Discussion

The binary system of the Sn and Sb oxides differs in color, as Table 1 shows, ranging from white to blue according to the calcination temperature and period as well as the catalyst composition. The visible absorption spectra of the various mixtures, shown in Fig. 1, indicate that the (Sn : Sb=3 : 1, 1000°C, 3 hr) mixture is the deepest in color of all the mixtures which were calcined at 1000°C for 3 hr, though it was less deep than the (Sn : Sb=3 : 1, 1100°C, 3 hr) mixture. Here, the description of the mixture, for example, the (Sn : Sb=3 : 1, 1000°C, 3 hr) mixture, means that the Sn : Sb atomic ratio in the mixture is 3 : 1 and that the mixture has been calcined at 1000°C for 3 hr.

TABLE 1. THE COLOR OF THE CATALYSTS

Sn to Sb atomic ratio	Calcination temp., °C	Calcination period, hr	Color
SnO_2	1000	3	white
Sb_2O_5	1000	3	white
3	1000	3	blue
3	1000	1/2	light grey
3	1000	1/6	brown
3	1100	3	deep blue
3	900	3	bluish brown
3	700	3	brown
1	1000	3	grey
7	1000	3	blue
19	1000	3	light blue
97/3	1000	3	greyish white

Over the catalysts of this system, the oxidation of propylene yielded carbon dioxide, carbon monoxide, acrolein, acetaldehyde, folmaldehyde, and acids. The amount of each product varied according to the calcination conditions as well as the catalyst composition. Under the reaction conditions of this work, the pure tin oxide catalyst yielded carbon dioxide and carbon monoxide, along with small amounts of aldehydes and acids, while the pure antimony yielded scarcely any product. However, the mixed catalysts of a favorable metal composition calcined under suitable conditions produced a large amount of acrolein. The (Sn : Sb=3 : 1, 1000°C, 3 hr) catalyst, for example, consumed 29.5% of propylene fed and 40.6% of oxygen at 450°C, with a 21.3% conversion of propylene to acrolein, 2.5% to carbon dioxide, and 1.8% to carbon monoxide, while the (SnO_2 only, 1000°C, 3 hr) catalyst consumed 26.5% of propylene fed and 99.3% oxygen, with a 0.6% conversion to acrolein, 18.5% to carbon dioxide, and 4.5% to carbon monoxide.

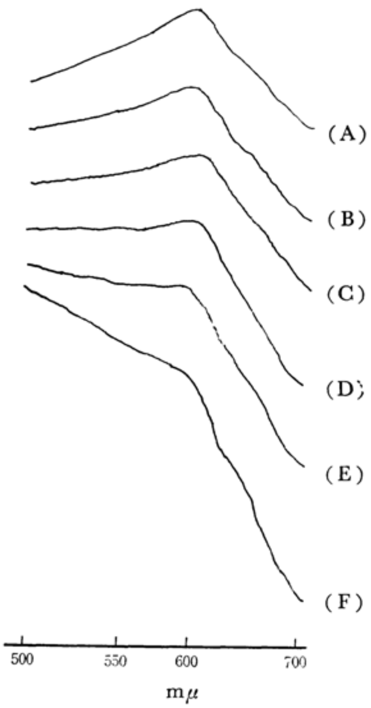


Fig. 1. The visible absorption spectra of the various mixtures.
(A) Sn : Sb=3 : 1, 1100°C, 3 hr
(B) Sn : Sb=3 : 1, 1000°C, 3 hr
(C) Sn : Sb=7 : 1, 1000°C, 3 hr
(D) Sn : Sb=1 : 3, 1000°C, 3 hr
(E) Sn : Sb=97 : 3, 1000°C, 3 hr
(F) Sn : Sb=3 : 1, 800°C, 3 hr

Figure 2 shows the effect of the initial propylene concentration on the selectivity to acrolein at 470°C over the (Sn : Sb=3 : 1, 1000°C, 3 hr) catalyst under such reaction conditions as an oxygen consumption of about 45%. With the increase in the propylene partial pressure, the selectivity of acrolein formation decreased, showing 68% at

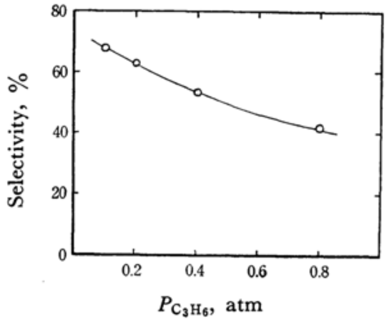


Fig. 2. The effect of the partial pressure of propylene on the selectivity to acrolein.
Catalyst: Sn : Sb=3 : 1, 1000°C, 3 hr
Reaction temperature: 470°C

0.1 atm and 42% at 0.8 atm. When employed at a high partial pressure of propylene, the catalysts were found to have turned black, showing that they had been reduced to lower oxides.

Figure 3 shows the relationship of the conversion of propylene to acrolein *vs.* the catalyst composition. Over the catalyst calcined at 800°C or 1000°C, the conversion rapidly increased upon the addition of Sb oxide to Sn oxide, while it only slightly increased over the catalysts calcined at 600°C. The maximum conversion to acrolein (25%) was obtained with the (Sn : Sb=3 : 1, 800°C, 3 hr) catalyst. In the region of Sn to Sb atomic ratios below 3 : 1, a dilution effect due to Sb oxide was observed at any calcination temperature.

Figure 4 shows the relationship of the conversion of propylene *vs.* the catalyst composition. The maximum conversion was obtained when the Sn to Sb atomic ratio of the catalysts was about 3 : 1 at each calcination temperature. However, from the rate of the decomposition of propylene investigated in the following paper, it was found that the rate decreased upon the addition of Sb oxide to Sn oxide. Accordingly, the phenomenon that the conversion of propylene decreases in a system with Sn to Sb atomic ratios above 3 : 1 is attributable to the fact that the complete oxidation occurs dominantly over catalysts with a large atomic ratio of Sn to Sb, thus causing the concentration of oxygen in the reactant gas to become very low. In the system with Sn to Sb atomic ratios below 3 : 1, a dilution effect due to Sb oxide was observed independent of the calcination temperature, as is shown in Fig. 3.

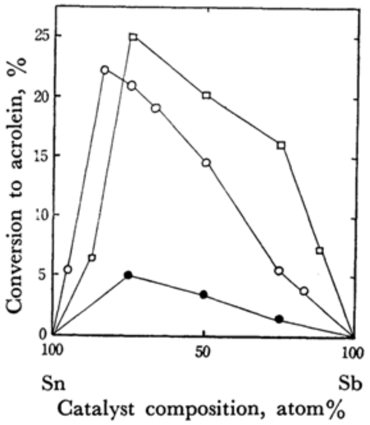


Fig. 3. The relationship of the conversion of propylene to acrolein *vs.* the catalyst composition.
Reaction temperature: 450°C
Calcination period: 3 hr
○ : Calcination temperature 1000°C
□ : Calcination temperature 800°C
● : Calcination temperature 600°C

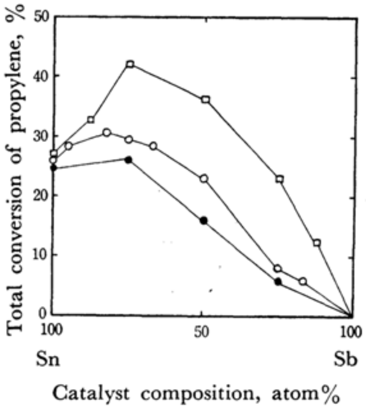


Fig. 4. The relationship of the total conversion of propylene vs the catalyst composition.
Reaction temperature: 450°C
Calcination period: 3 hr
○ : Calcination temperature 1000°C
□ : Calcination temperature 800°C
● : Calcination temperature 600°C

The selectivity to acrolein is shown in Fig. 5 as a function of the catalyst composition. The selectivity became higher when the catalyst was calcined at a higher temperature, and also the Sb

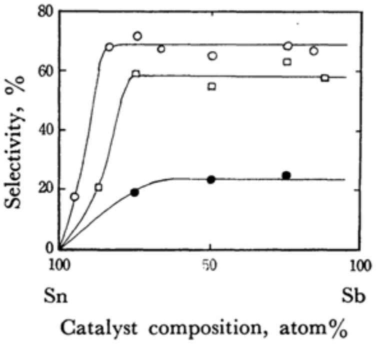


Fig. 5. The selectivity to acrolein as a function of the catalyst composition.
Reaction temperature: 450°C
Calcination period: 3 hr
○ : Calcination temperature 1000°C
□ : Calcination temperature 800°C
● : Calcination temperature 600°C

content of the catalysts increased in the range of Sn to Sb atomic ratios above 3 : 1. The catalysts with Sn to Sb atomic ratios below 3 : 1 attained a constant selectivity depending on the calcination temperature. A maximum selectivity of about 70% was obtained with the catalysts calcined at 1000°C.

Figure 6 indicates the effect of the calcination temperature on the conversion of propylene and the yield of acrolein in oxidation over catalysts with a Sn to Sb atomic ratio of 3 : 1 calcined for 3 hr. Both the conversion of propylene and the yield of acrolein were the greatest with the catalyst calcined at 900°C, showing the values of 51% and 31% respectively.

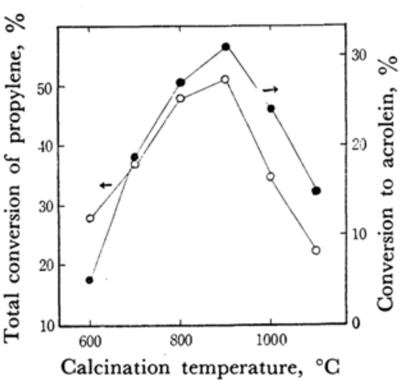


Fig. 6. The effect of the calcination temperature on the total conversion of propylene and the conversion to acrolein.
Reaction temperature: 470°C
Catalyst composition: Sn : Sb=3 : 1
Calcination period: 3 hr

Figure 7 indicates the effect of the calcination period on the conversion of propylene and the yield of acrolein in oxidation over catalysts with a Sn to Sb atomic ratio of 3 : 1 calcined at 1000°C. The maximum conversion of propylene and the yield of acrolein were observed to be 50% and 30% respectively, both the values of which were obtained with a catalyst calcined for 30 min. After the maximum, both the conversion and the yield were found to decrease as the period of calcination was prolonged.

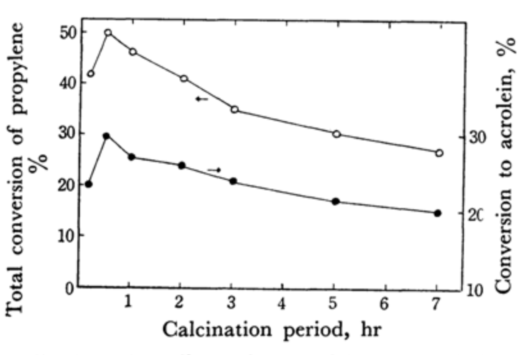


Fig. 7. The effect of the calcination period on the total conversion of propylene and the conversion to acrolein.
Reaction temperature: 470°C
Catalyst composition: Sn : Sb=3 : 1
Calcination temperature: 1000°C

As has been mentioned above, the catalytic activity of the binary system of Sn and Sb oxides is dependent upon the calcination temperature and period as well as upon the Sn to Sb atomic ratio of the catalyst, and is also related to the color of the catalyst. Therefore, it seems important, in explaining the characteristics of the catalysis of this system, to make clear why a mixture composed of Sn and Sb oxides becomes colored when subjected to calcination. These possible reasons are the following:

(1) the formation of a new compound,
(2) the formation of a solid solution, or
(3) the formation of an amorphous compound.

X-ray investigations were carried out as shown in Fig. 8. As only X-ray patterns due to Sn and Sb oxides were detected, neither a new compound nor an amorphous compound was found to be formed. The reason for this, therefore, is the formation of a solid solution. It has been examined whether or not solid solutions are formed between Sn and Sb oxides; the results are given in Table 2. As is evident from Table 2, solid solutions are certainly formed in this system. Therefore, we may be led to the conclusion that the production of acrolein on this system is related to the formation of the solid solutions. This is consistent with the finding that the catalysts produced a large amount of acrolein when calcined at a high temperature. The X-ray patterns have shown that a larger amount of Sb oxide was dissolved into Sn oxide in the (Sn : Sb= 3 : 1, 1100°C, 3 hr) mixture than in the (Sn : Sb= 3 : 1, 1000°C, 3 hr) mixture. In the system with Sn to Sb atomic ratios above 3 : 1, Sb oxide, which remains insoluble in Sn oxide, was not observed in

TABLE 2. CHANGE IN *d*-SPACINGS AND CRYSTALLITE SIZE (*D*)

Sn to Sb atomic ratio	Calicination Temp., °C	Calcination period, hr	$\Delta d/d \times 100$	*D*, Å
3	1100	3	0.16	25
3	1000	3	0.12	20
3	800	3	0.00	10

Δd: observed from the diffraction peak at $2\theta=90.86°$

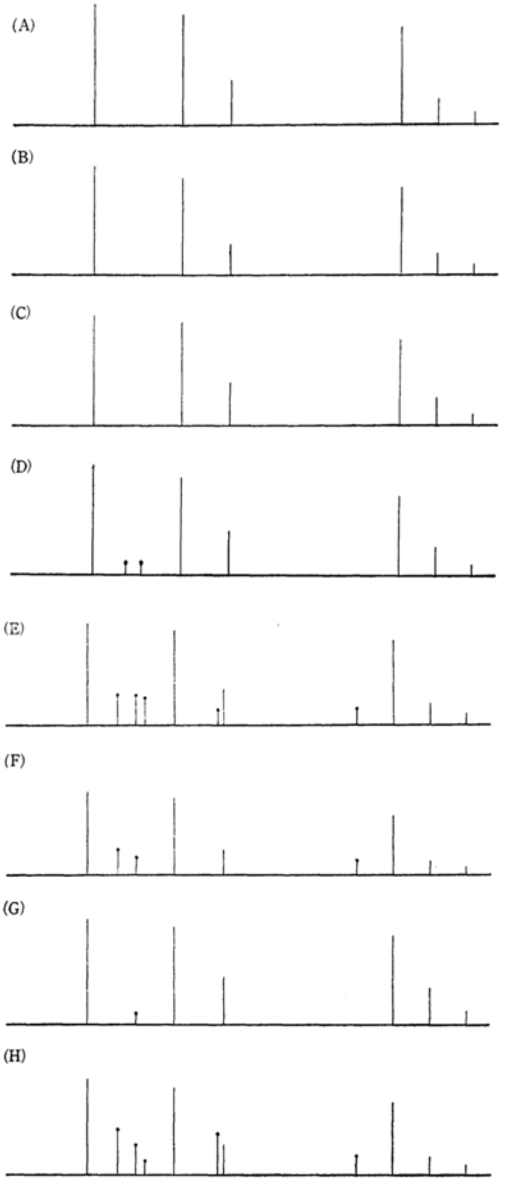
D: calculated by the following equation from the diffraction peak at $2\theta=89.76°$.

$$D=\frac{K\cdot\lambda}{\beta_{1/2}\cdot\cos\theta}$$

K: shape factor (0.9)
λ: wavelength (1.54Å)
β: half-value breadth (rad.)
θ: Bragg's angle

the diagrams. The pattern of the (Sn : Sb=3 : 1, 1000°C, 3 hr) mixture, after it had been employed in the oxidation at $P_{C_3H_6}=0.1$ atm, was quite the same as that of the fresh catalyst, in which two phases composed of a solid solution and Sb oxide were present.

When Sb oxide is dissolved into Sn oxide, the amount of dissolved Sb oxide will be larger as the temperature of calcination is higher and as the period is longer. At a Sb oxide content exceeding the limited amount of dissolution under given calcination conditions, there comes into existence a system consisting of a solid solution active for acrolein formation and Sb oxide inactive for the oxidation of propylene under such reaction conditions as in this work. These two facts explain very reasonably the dilution effect observed in Figs. 3 and 4, and the finding that the selectivities to acrolein attained the constant values in Fig. 5. However, we cannot explain why the conversion of propylene and the yield of acrolein fell off under sufficient calcination conditions. The decrease is probably due to the growth of the crystal structure, which causes a deactivation of the catalyst. Hence, the crystallite size has been calculated, the results being given in Table 2. These data show that the crystal structure grows to a larger extent at a higher calcination temperature.



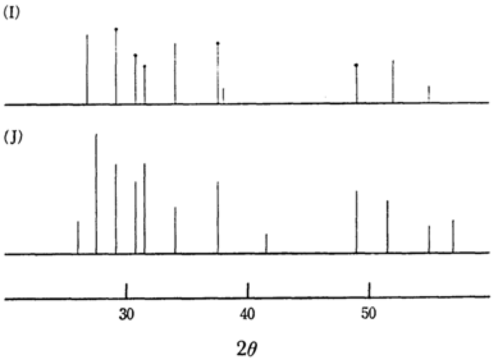


Fig. 8. X-ray patterns of the Sn and Sb oxide system. ⫯ : peak attributable to Sb oxide in the mixture. The relative intensity is based on the strongest peak of each pure oxide.
All the samples except (F) and (G) were calcined at 1000°C for 3 hr.
(A) SnO_2 (B) Sn : Sb=97 : 3,
(C) Sn : Sb=7 : 1, (D) Sn : Sb=3 : 1,
(E) The mechanical mixture of SnO_2 and Sb_2O_5 separately calcined at 1000°C for 3 hr Sn : Sb=3 : 1,
(F) Sn:Sb=3:1, calcined at 800°C for 3 hr
(G) Sn:Sb=3:1, calcined at 1100°C for 3 hr
(H) Sn : Sb=1 : 1, (I) Sn : Sb=1 : 3,
(J) Sb_2O_5

Consequently, it can be concluded that the formation of acrolein with the catalysts of this system is very dependent upon the formation of solid solutions, which requires sufficient calcination. As sufficient calcination causes the growth of the crystal structure, which is unfavorable from the point of view of activity, much attention must be taken in choosing calcination conditions. It may be due to the collapse of the solid solutions that the selectivity of the catalysts to acrolein fell off at high partial pressures of propylene.

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