

## The Active Species of Sb-Mo-O Catalyst for the Oxidative Esterification of Ethanol

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The freshly prepared catalyst of Sb-Mo-O system was only a mixture of  $\text{MoO}_3$  and  $\text{Sb}_2\text{O}_4$ , which was not selective for the ester formation. However, in the course of the oxidation of ethanol, some reduced phases such as  $\text{Sb}_4\text{Mo}_{10}\text{O}_{31}$  were formed in the catalyst, accompanied with an increase of ester formation. It is suggested that the reduced phases were effective for the ester formation.

It is well known that ethyl acetate can be manufactured by the reversible reaction between acetic acid and ethanol in the presence of an acidic proton and usually performed in a liquid phase.<sup>1,2)</sup> And also ethyl acetate can be produced by the condensation of acetaldehyde (Tischtschenko reaction).<sup>3)</sup> Although Kunugi et al.<sup>4-6)</sup> reported that ethyl acetate was formed by the oxidative esterification of ethanol over metallic palladium on active charcoal catalyst (Pd/C), the yield of ethyl acetate was low because of the low conversion of ethanol. We reported<sup>7)</sup> that the oxidative esterification of ethanol to ethyl acetate can occur over various kinds of single and mixed oxide catalysts. In the present study, the combination of  $\text{Sb}_2\text{O}_4$  and  $\text{MoO}_3$  was found to be effective for the oxidative esterification of ethanol to ethyl acetate. The activity was discussed in relation to the structural change of the catalyst during reaction and the active species was proposed.

Catalysts were prepared by mixing the commercial powders of  $\text{MoO}_3$  and  $\text{Sb}_2\text{O}_3$  in water, followed by continuous stirring, boiling to dryness, and subsequent calcination in air at 500 °C for 5 h. Reaction was carried out in a flow system by introducing a gaseous mixture of ethanol, oxygen, and nitrogen (diluent), normally in a molar ratio of 1:1:3, to the catalyst bed. Selectivities and yields were calculated on the mole basis of ethanol. X-Ray diffraction was carried out with a Rigaku Denki 4011 diffractometer using CuK radiation equipped with a chamber in which sample was subjected to an in situ measurement at high temperatures in various gas streams. The degree of reduction with hydrogen or ethanol was estimated from the oxygen consumption for reoxidation of the reduced samples. After evacuation up to 400 °C, the reduced sample was exposed to oxygen in a closed system, and heated up to 600 °C for the completion of reoxidation. It was confirmed that the reduction degree of unreduced catalyst was very small, and the reoxidation

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of the reduced catalyst in air at room temperature was negligibly slow. Combustion products were scarcely produced during reoxidation process.

The Sb-Mo-O system was investigated by varying the composition ratio to optimize its catalytic performance for ester formation. The temperature dependences of ethyl

acetate yields over the Sb-Mo-O system are given in Fig. 1. For all these catalysts, the ethyl acetate yield increased at lower temperature, but it decreased at higher temperatures because of the consecutive oxidation to  $\text{CO}_2$ . However, the temperatures at the maximum yield were considerably lowered over the binary oxide catalysts in comparison to the single oxides. Moreover, the maximum yields were greatly enhanced by the combination of two oxides. The highest yield of ethyl acetate reached to about 30%, which has not been achieved over any other catalyst reported so far.

The results given above were obtained ca. 4 h after the reaction started, when the reaction attained the steady state. The change of catalytic activity and selectivities over the Sb-Mo-O catalysts in the course of ethanol oxidation at 300 °C is shown in Fig. 2. Ethanol conversion was almost unchanged with reaction time. As for the freshly prepared catalyst, main product was acetaldehyde. The selectivity to ethyl acetate increased gradually in the course of reaction, accompanied with a decrease of selectivity to acetaldehyde, and they approached to steady values at ca. 4 h after the reaction started. This suggests that the catalytic reaction caused a structural change of the catalyst, which is

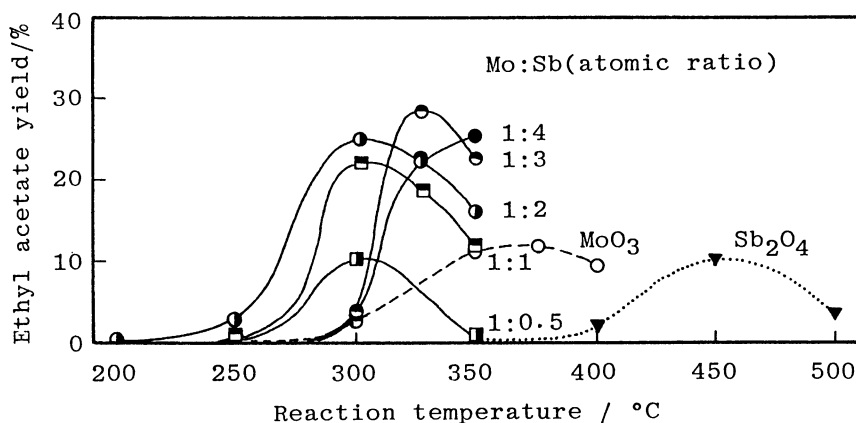


Fig.1. Temperature dependence of ethyl acetate yield over Sb-Mo-O system catalysts.

( $\text{C}_2\text{H}_5\text{OH}:\text{O}_2:\text{N}_2=1:1:3$ ,  $W/F=13.6$  g-cat·h/mol)

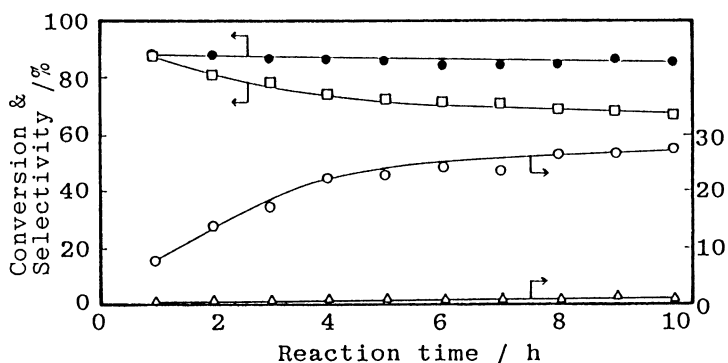


Fig.2. Reactivity change at 300 °C with reaction time over Sb-Mo-O catalyst (Mo:Sb=1:1.5).

- conversion of ethanol
- selectivity to ethyl acetate
- selectivity to acetaldehyde
- △ selectivity to  $\text{CO}$  &  $\text{CO}_2$

favorable to the oxidative esterification.

The phase diagram<sup>8)</sup> of the ternary system of Sb-Mo-O at 500 °C contains no binary oxides between  $\text{MoO}_3$  and  $\text{Sb}_2\text{O}_4$  at the highly oxidized state. When the Sb-Mo-O system is reduced with  $\text{H}_2/\text{H}_2\text{O}$  gas mixtures, three kinds of binary oxides, i.e.,  $\text{Sb}_2\text{Mo}_{10}\text{O}_{31}$ ,  $\text{Sb}_4\text{Mo}_{10}\text{O}_{31}$ , and  $\text{Sb}_2\text{MoO}_6$ , can be formed in different conditions.

In the present study, the structural changes of the Sb-Mo-O catalyst in some reducing conditions were monitored in situ by X-ray diffraction at elevated temperatures. The freshly prepared Sb-Mo oxide catalyst consisted of only a mixture of  $\text{Sb}_2\text{O}_4$  and  $\text{MoO}_3$  after the calcination in air at 500 °C, in which the diffraction lines from  $\text{Sb}_2\text{O}_4$  was very weak because of its poor crystallinity. When Sb-Mo-O catalyst was reduced at 400 °C (the reduction was extremely slow at 300 °C) with a stream of  $\text{H}_2:\text{N}_2=1:4$  (in mol), the

diffraction peaks of single oxides were much weakened and the three kinds of binary oxides mentioned above were formed gradually as shown in Fig. 3(A). However, mainly the  $\text{Sb}_4\text{Mo}_{10}\text{O}_{31}$  phase was formed as a reduced phase after the use for ethanol oxidation (ethanol: air=1:4 in mol) at 300 °C, as shown in Fig. 3(B). The  $\text{Sb}_4\text{Mo}_{10}\text{O}_{31}$  phase was also formed selectively by the reduction of the catalyst with ethanol (ethanol: $\text{N}_2=1:4$  in mol) at 300 °C. These results indicate that not only the mixing of  $\text{MoO}_3$  and  $\text{Sb}_2\text{O}_4$ , but also the reduction of the catalyst is indispensable for the enhancement of ester formation in the oxidation of the ethanol. The relation between ester selectivity in Fig. 2 and the formation of  $\text{Sb}_4\text{Mo}_{10}\text{O}_{31}$  phase suggests that this phase is most likely to bring about the high selectivity for the oxidative esterification. The  $\text{Sb}_4\text{Mo}_{10}\text{O}_{31}$  phase was always observed in the  $\text{Sb}_2\text{O}_4$ - $\text{MoO}_3$  oxide after producing high yield of ethyl acetate. The reduced phases disappeared in the reoxidation in air at 500 °C.

Since the formation process of the new phases is expected to involve the reduction of the oxides according to the phase diagram, the changes in phase and in oxidation state of the catalyst were investigated using ethanol or hydrogen as reducing reagents. Figure 4 shows reduction degrees of the catalyst, which are expressed as a percentage of the lost oxygen with an exposure of the unreduced

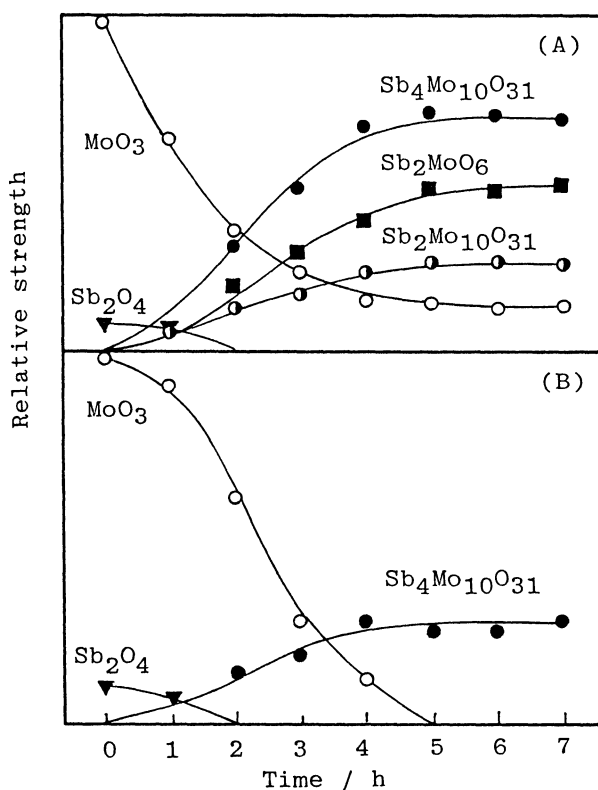


Fig.3. Structural change of the Sb-Mo-O catalyst (Mo:Sb=1:1.5).

(A) reduced at 400 °C with  $\text{H}_2:\text{N}_2=1:4$

(B) used at 300 °C with ethanol:air=1:4

sample to the reducing reagents for 4 h. It is noted that the catalyst in the working state was obviously reduced during the catalytic oxidation of ethanol, when the ester formation was enhanced. Moreover, the reduction degrees of the  $\text{MoO}_3\text{-Sb}_2\text{O}_4$  catalyst were also measured in the absence of gaseous oxygen. It was obvious from Fig. 4 that the mixture of  $\text{MoO}_3\text{-Sb}_2\text{O}_4$  was much more reducible with ethanol than with hydrogen.

Since the catalyst reduced to some extent is expected to be effective for the oxidative esterification of ethanol as mentioned above, the catalyst was pretreated with ethanol and hydrogen before reaction, respectively. The induction period of ca. 4 h for the formation of ethyl acetate as observed in Fig. 2 was

shortened to 2 h, when the catalyst was pretreated with hydrogen ( $\text{H}_2:\text{N}_2=1:4$ ) at 400 °C for 4 h. And the induction period disappeared after pretreatment of the catalyst with ethanol (ethanol:air=1:4) at 300 °C for 4 h. These results give further understandings of the relationship between the formation of the reduced phases such as  $\text{Sb}_4\text{Mo}_{10}\text{O}_{31}$  and the selectivity to ester. Acetic acid and ketones were fairly produced, however, ethyl acetate was scarcely formed by introducing a mixture of acetaldehyde and nitrogen even though the catalyst was pretreated with ethanol (the catalyst was at the favorable state to the ester formation in the oxidation of ethanol), which excludes the possibility of the condensation of acetaldehyde.

#### References

- 1) K.Othmer, "Encyclopedia of Chemical Technology," Wiley, New York (1958).
- 2) F.A.Lowenheim and M.K.Moran, "Industrial Chemicals," Wiley-Interscience, New York (1975).
- 3) Tischtschenko, Chem. Zentralbl., 77,1309(1906).
- 4) T.Kunugi, T.Matsuura, and T. Kono, Kogyo Kagaku Zasshi, 71,1517(1968).
- 5) T.Kunugi and T.Kono, Kogyo Kagaku Zasshi, 72,1282(1969).
- 6) T.Kunugi, T.Kono, T.Yanagisawa, and H.Arai, Nippon Kagaku Kaishi, 1972, 2271.
- 7) L.Wang, K.Eguchi, H.Arai, and T.Seiyama, Chem. Lett., 1986, 1173.
- 8) M.Parmentier, C.Gleitzer, and R.J.D.Tilley, J. Solid State Chem., 31,305(1980).

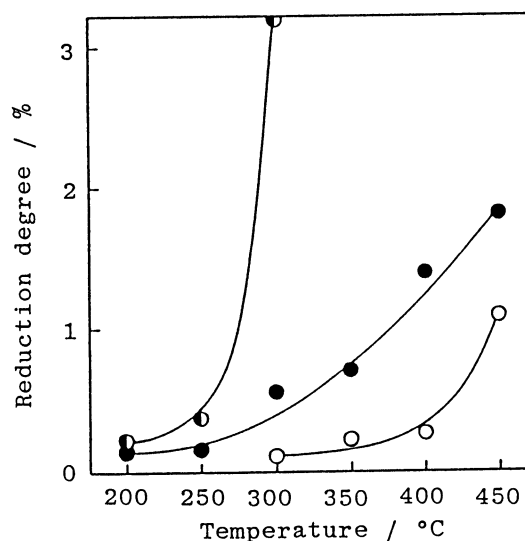


Fig.4. Dependences of reduction degree on the temperature (Mo:Sb=1:2).

● after catalytic reaction for 4 h with  $\text{C}_2\text{H}_5\text{OH}:\text{Air}=1:4$ ; after reduction for 4 h with ●  $\text{C}_2\text{H}_5\text{OH}:\text{N}_2=1:4$  or ○  $\text{H}_2:\text{N}_2=1:4$ .

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