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A Study of the Catalytic Partial Oxidation of Hydrocarbons. XVI. The Effect of the Bi_2O_3 Content in the MoO_3-Bi_2O_3-P_2O_5 Catalysts on the Oxidation of Various Olefins, Acids, and Aldehydes

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The vapor-phase oxidation of various kinds of olefins, acids, aldehydes, etc. was carried out in a flow system over a series of MoO_3–Bi_2O_3–P_2O_5 catalysts with different Bi/Mo ratios (P/Mo=0.2 atomic ratio) under fixed reaction conditions, in order to elucidate how the oxidation of these compounds is affected by the Bi_2O_3 content in the catalysts. The oxidation activity for these compounds varies in different individual manners as the Bi_2O_3 content increases. The results were interpreted successfully on the basis of the acid-base nature of the reactant and the catalyst. Then, the relationship between the character of the partial oxidations and the nature of the catalysts was discussed.

The present authors have reported in recent papers[1,2] that the MoO_3–Bi_2O_3–P_2O_5 catalyst containing a high Bi_2O_3 content, which is well-known as an excellent catalyst for such an allylic oxidation as those of *n*-butene to butadiene and of propylene to acrolein, is inadequate for the oxidation of butene, butadiene, and furan to maleic anhydride, while a low-Bi_2O_3-content catalyst (Bi/Mo=0.1 atomic ratio) is quite good for the formation of maleic anhydride. Furthermore, it has also been proved that, with in increase in the Bi_2O_3 content in the catalyst, the oxidation activities for butene, butadiene, furan, and maleic anhydride vary, that the kinetics of both butene and butadiene is of about a 0.5 order in oxygen and a 0.8 order in olefin over the low Bi_2O_3 ($Bi/Mo<0.15$) catalysts, and that it becomes almost zero-order in oxygen and first-order in olefin over a high Bi_2O_3 ($Bi/Mo>0.5$) catalyst.[2,3]

The authors have tried to interpret these results in terms of the acid-base nature of the catalyst and the reactant. With an increase in the Bi_2O_3 content, the basicity of the catalyst increases and its interaction with such electron donor-type compounds (base) as olefin decreases, while that with acids and oxygen increases.

Thus it was interesting to confirm whether or not the oxidation aspects of other organic compounds could also be interpreted by the above-mentioned acid-base conception. In the present work, the oxidation of various kinds of organic compounds, including olefins, acids, and aldehydes, over a series of MoO_3–Bi_2O_3–P_2O_5 ternary catalyst system, while varying their Bi/Mo proportions in the presence of a large excess of oxygen, was performed in order to elucidate how the oxidation of these compounds is affected by the Bi_2O_3 content in the catalyst, and to obtain more detailed information about the oxidation over catalyst systems.

Experimental

The vapor-phase oxidation of various kinds of olefins, acids, aldehydes, etc., was carried out over a series of molybdenum-bismuth-phosphorus oxide catalysts with different Bi/Mo ratios (P/Mo=0.2 atomic ratio) in an ordinary continuous-flow-type reaction system, as has been described in an earlier paper.[4]

The concentration of the reactant was in the range of 0.6—1.5 mol% in air, the flow rate was kept at 1.5 l/min (at about 20°C), and the amount of the catalyst used was 40 ml; the contact time, which was shown by the volume of the catalyst (ml) per total flow rate (ml/s), was 1.6 s. The reaction temperature was increased at intervals of 10~20 from 250°C to 650°C, and the efflux from the reactor was analysed at each temperature until the conversion be-

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[1] M. Ai and S. Suzuki, This Bulletin, **44**, 3081 (1971).

[2] M. Ai and S. Suzuki, *Nippon Kagaku Kaishi*, **1972**, 290.

[3] M. Ai and S. Suzuki, *Shokubai*, **14**, 50 (1972).

[4] M. Ai, T. Niikuni, and S. Suzuki, *Kogyo Kagaku Zasshi*, **73**, 165 (1970).

came more than 50%. Before the analysis, the feed flow was passed over the catalyst at the desired temperature for more than about 20 min in order to obtain the data under steady-state conditions. The experimental and the analytical procedures were also identical with those employed in the earlier works.[1–4)]

The catalysts used in these experiments were the same as those used in some preceding works.[2,3)] They were calcined under flowing air at 550°C for 5 hr. The surface area of these catalysts was of the order of 3 m^2/g, as determined by the BET method, and the variation in the Bi_2O_3 content had little effect on the surface area.

Results

Oxidation of Olefins. The oxidation of such olefins as *cis*-2-heptene, 2-hexene, 2-pentene, *cis*-2-butene, butadiene, propylene, and ethylene was examined over a series of MoO_3–Bi_2O_3–P_2O_5 catalysts with different Bi/Mo ratios (P/Mo=0.2 atomic ratio) under fixed reaction conditions. The relationship between the catalyst composition and the oxidation activity for such olefins as 2-heptene, 2-hexene, 2-pentene, and *cis*-2-butene is plotted in Fig. 1. The range of activity variation is so wide that it is hard to express it by a reaction rate at a constant temperature. Therefore, the value of $1000/T_{50}$ is adopted as a measure reflecting the oxidation activity, where T_{50} means the reaction temperature (K) corresponding to the reactant conversion of 50%.

The results indicate that the catalytic activity for these olefins, excluding propylene, varies similarly when the Bi_2O_3 content in the catalyst increases; the activity increases and goes through a maximum at a Bi/Mo atomic ratio of about 0.1, and then it decreases to the value of the Bi_2O_3 alone catalyst, which is extremely inactive for olefins. The higher the olefin, the higher becomes the reactivity over the whole range of Bi/Mo ratios. It is also clear that the difference in the reactivity among these olefins is relatively small in the range of low Bi_2O_3 content (Bi/Mo<0.15), but in the range of Bi/Mo=1—2, the difference becomes very significant—*i.e.*, the reactivity increases as the number of carbon atoms increases.

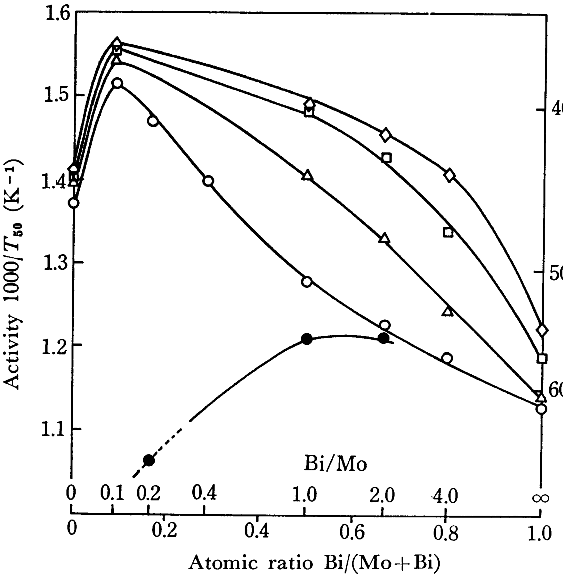

Fig. 1. Oxidation activity ($1000/T_{50}$) for olefins *vs.* the Bi_2O_3 content.
T_{50} is the temperature in K at which the conversion becomes 50%.
Olefin=0.67—1.5 mol% in air, contact time=1.6 s, ◇: *cis*-2-heptene, □: 2-hexene, △: *cis*-2-heptene, ○: *cis*-2-butene, ●: propylene.

The activity for lower olefins, including *cis*-2-butene, propylene, and ethylene, is shown as a function of the Bi_2O_3 content in Fig. 2. In the case of olefins lower than butene, the reactivity decreases markedly with a decrease in the carbon number; besides, the maximum activity is not observed at Bi/Mo=0.1. The activity for propylene passes through a maximum at about Bi/Mo=1—2. The reactivity of ethylene is too low to obtain detailed information about it, but it appears

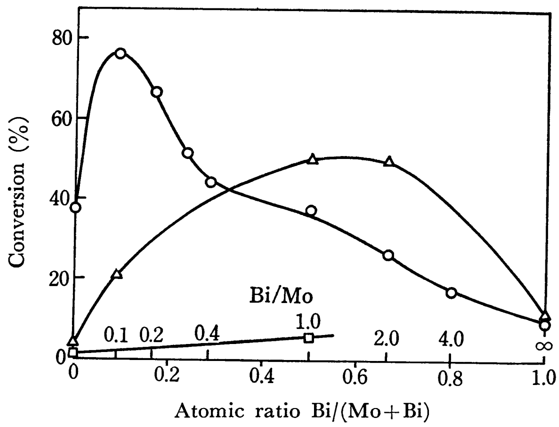

Fig. 2. Oxidation activity *vs.* the Bi_2O_3 content.
Contact time=1.6 s, olefin=0.67 mol% in air, ○: *cis*-2-butene at 430°C, △: propylene at 550°C, □: ethylene at 580°C.

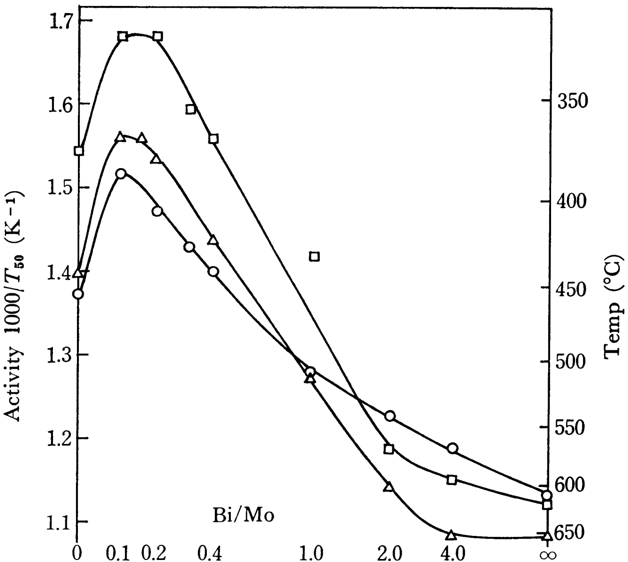

Fig. 3. Oxidation activity ($1000/T_{50}$) *vs.* the Bi_2O_3 content.
Contact time=1.6 s, reactant=0.67 mol% in air, ○: *cis*-2-butene, △: butadiene, □: furan.

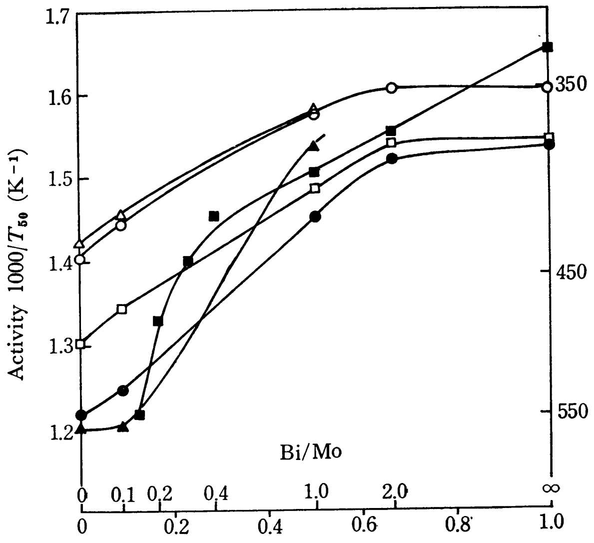

Fig. 4. Oxidation activity (1000/T_{50}) for acids *vs.* the Bi_2O_3 content.
Contact time=1.6 s, reactant=1.5 mol% in air, □: acetic acid, ○: propionic acid, △: butyric acid, ■: maleic anhydride, ●: acrylic acid, ▲: crotonic acid.

that the Bi_2O_3-rich catalyst is more active than the Bi_2O_3-poor catalyst.

The activities for unsaturated C_4 compounds, that is, *cis*-2-butene, butadiene, and furan, are compared in Fig. 3. As has been mentioned in an earlier paper,[2)] the reactivity-order of these compounds varies with an increase in the Bi_2O_3 content.

Oxidation of Acids. The oxidation of both saturated and unsaturated carboxylic acids—acetic acid, propionic acid, butyric acid, acrylic acid, crotonic acid, and maleic anhydride—is performed under fixed reaction conditions. The activities obtained are plotted as a function of the Bi_2O_3 content and compared in Fig. 4.

The results reveal:

a) the low Bi_2O_3 catalyst is very inactive for the oxidation of carboxylic acid, especially for unsaturated acid, but the high Bi_2O_3 catalyst is fairly active for the oxidation.

b) the activity for the oxidation of carboxylic acid always increases steadily with an increase in the Bi_2O_3 content.

c) acetic acid is much more stable than the higher saturated acids.

d) the reactivities of propionic acid and butyric acid are almost the same.

e) unsaturated acids are fairly stable in comparison with the corresponding saturated acids.

Oxidation of Aldehydes. Figure 5 shows the activity for the oxidation of various aldehydes, including propionaldehyde, butyraldehyde, acrolein, and crotonaldehyde, as a function of the Bi/Mo ratio. The results indicate:

a) the saturated aldehydes are much more reactive over the catalyst system than the other compounds.

b) the reactivities of propionaldehyde and butyraldehyde are almost the same.

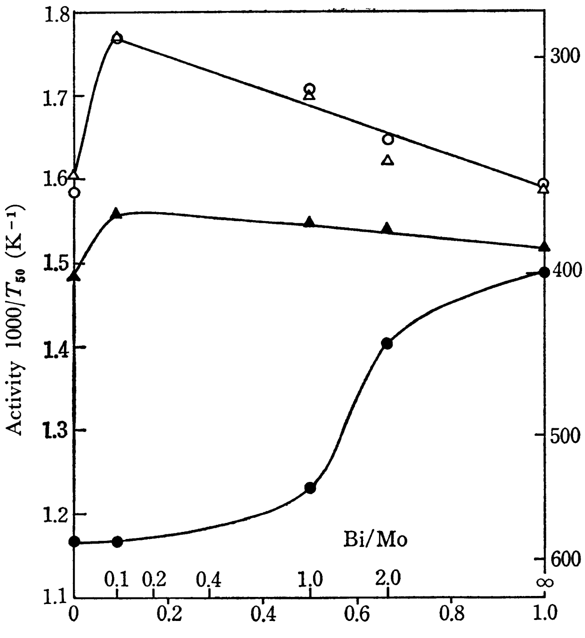

Fig. 5. Oxidation activity (1000/T_{50}) for aldehydes *vs.* the Bi_2O_3 content.
Contact time=1.6 s, reactant=1.5 mol% in air, ○: propionaldehyde, △: butyraldehyde, ●: acrolein, ▲: crotonaldehyde.

c) unsaturated aldehydes are much less reactive than the corresponding saturated aldehydes.

d) the activity-curves for propionaldehyde, butyraldehyde, and crotonaldehyde vary with the same trend as for olefins higher than propylene.

e) the activity for acrolein changes in a unique manner; at a relatively low content of Bi_2O_3(Bi/Mo$<$1), acrolein is very stable, but at a higher Bi_2O_3 content (Bi/Mo$>$ 2), it increases sharply.

Discussion

First, we attempted to discuss the oxidation aspects of these organic compounds, by supposing that the rate of contact oxidation is mainly affected by these three factors: (1) the amount of species adsorbed on the catalyst surface, which is closely related to the interaction strength between the catalyst and the reactant; (2) the reactivity or stability of the adsorbed species of the reactants, and (3) the availability of surface oxygen.

When the Bi_2O_3 content in the catalyst increases, the oxidation activities for the olefins of C_4—C_7 vary in a fashion similar to the activity for the dehydration of alcohol to olefin, which was adopted as a measure of the acidity of the catalyst, assuming that the dehydration occurs at acid sites of the catalyst.[5)] This indicates that the oxidation activities for higher olefins, as well as those for butene and butadiene,[2,3)] are intimately related to the acidity of the catalyst. According to the closeness of their ionization potential, if the amount of the adsorption is of about the same

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5) M. Ai and S. Suzuki, This Bulletin, **46**, 321 (1973).

order of magnitude in C_4—C_7 olefins, the difference in the activities for these olefins observed in the Bi_2O_3-rich composition (Bi/Mo=1—2) may be attributed to the difference in reactivity of their adsorbed species, presumably in the C–H bond-strength at the allylic position, as has been suggested by Adams *et al.*[6] In the cases of the low Bi_2O_3 content catalyst (Bi/Mo< 0.15), the difference in the oxidation rate of these olefins is not so great. Probably the rate is limited, to some extent, by the activation of oxygen because the adsorption of olefin is strong and almost reaches its saturation point, while that of oxygen is very weak.[3]

On the other hand, the activity for propylene and ethylene varies in a way different from the activity for higher olefins; this way cannot be explained directly by the adsorptive nature of the olefins. However, the fact that the interaction of the catalyst with oxygen increases with an increase in the Bi_2O_3 content[3] seems to suggest that the availability of surface oxygen increases with the Bi_2O_3 content. On this assumption, it may be considered that the lower olefins resist oxidation more strongly than the higher olefins, and that their oxidation requires more activated oxygen, that is, a higher Bi_2O_3 content catalyst.

The difference in the reactivity between butene and butadiene at various Bi/Mo ratios can be explained by the difference in their adsorption nature, that is, their basicity. As the ionization potential of butadiene (8.75—9.18 eV) is lower than that of butene (9.3—9.8 eV), the basicity of butadiene is presumably higher than that of butene. Thus, butadiene is adsorbed more strongly on the Bi_2O_3-poor catalysts and less strongly on the Bi_2O_5-rich catalysts, than is butene.

Regarding the oxidation of saturated carboxylic acids and aldehydes, it may be reasonable to consider that the carboxylic and carbonyl group play main roles in their adsorption. In the case of acid, since both acid and oxygen act as electron acceptors and since these adsorptions are promoted with an increase in the Bi_2O_3 content, the oxidation activity increases steadily with the Bi_2O_3 content. The high reactivity of the saturated aldehyde compounds may be attributed to the nature of their carbonyl group polarizing as $-C^+-O^-$, which can be attacked either by an electron-donor-type (basic) or by an electron-acceptor-type (acidic) reagent. The shapes of the curves in Fig. 5 follow the same trend as those for higher olefins. This suggests that the saturated aldehydes are, rather, basic compounds, and that they are inclined to be attacked by an electrophilic reagent.

The presence of a double bond in an aldehyde or an acid molecule increases their stability markedly. This may be, in part, due to a resonance-stabilization by their conjugated double bond, but it may be also attributed to the difference in the character of adsorption. As has been mentioned by Gorshkov *et al.*[7] some of these compounds, *e.g.*, acrolein, may be linked with the catalyst by a double bond and may thus form stable π-complexes. The stability of the adsorbed species is so great that the oxidation of acrolein may require highly activated oxygen—that is, a higher-Bi_2O_3-content catalyst.

Finally, according to the data obtained in this and past studies,[1,2,6,8,9] the relationship between the character of the partial oxidation of organic compounds and the nature of the catalyst can be generalized as follows:

a) Formation of acids from olefins and furan: an acidic catalyst (low Bi_2O_3 catalyst) is favarable, and a relatively good yield can be expected because the products is much more stable than the reactant.

b) Formation of diene from mono-olefin: the high Bi_2O_3 content catalyst has an advantage in selectivity, but the Bi_2O_3 content is limited from the point of view of the activity. Bi/Mo=1—2, therefore, is considered to be optimum.

c) Formation of acrolein from propylene: the Bi_2O_3 content of Bi/Mo=1—2 is favorable both in the activity and in the selectivity.

d) Formation of crotonaldehyde from olefin: it is difficult to get a good result, for crotonaldehyde is more reactive than olefin over every catalyst.

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[6] H. H. Voge and C. R. Adams, "Advance in Catalysis," Vol. 17, ed. by D. D. Eley, H. Pines, and P. B. Weisz, Academic Press, New York and London (1967), p. 151.

[7] A. P. Gorshkov, I. K. Kolchin, A. M. Gribov, and L. Ya. Margolis, *Kinet. Katal.*, **9**, 1086 (1967).

[8] M. Ai, *Kogyo Kagaku Zasshi*, **74**, 183 (1971).

[9] Ph. A. Batist, B. C. Lippens, and G. C. A. Schuit, *J. Catal.*, **5**, 55 (1965).