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A Study of Catalytic Partial Oxidation of Hydrocarbons. XIII. The Effect of Bi_2O_3 Content in MoO_3-Bi_2O_3-P_2O_5 Catalysts on the Dehydration of Isopropyl Alcohol

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The present authors have recently reported the effect of the Bi_2O_3 content in the MoO_3–Bi_2O_3–P_2O_5 ternary catalyst system on the oxidation of olefins, furan, and maleic anhydride.[1,2] It has been considered that, with an increase in the Bi_2O_3 content, the acidity of the catalysts changes; accordingly, the affinity, *i.e.*, the adsorptive action, of the catalysts for such basic compounds as olefins and furan, and that for such electron-acceptor-type compounds as carboxylic acid and oxygen, varies. We should measure directly the acidity of the catalyst system in order to cofirm those results. However, it is hard to measure the acidity by means of the conventional titration method, because both the acidity and the surface area are very small; moreover, the catalysts are dark—the low Bi_2O_3 content catalyst, for instance, is black. However, it is well known that there are good correlations between the acidic properties and activities of catalysts for many acid-catalyzed reactions,[3] so it seems appropriate to adopt the activity for the dehydration of alcohols as a measure reflecting the acidity of the catalyst.

In the present work, the dehydration of alcohols, especially that of isopropyl alcohol (IPA), was performed over a series of MoO_3–Bi_2O_3–P_2O_5 catalysts with various Bi/Mo ratios in order to study the dependency of the acidity on the Bi_2O_3 content and the relationship between the acidity and the activities for oxidation and isomerization reactions.

Experimental

The vapor-phase dehydration of alcohols, such as ethyl and isopropyl alcohols, was carried out over a series of MoO_3–Bi_2O_3–P_2O_5 catalysts with various Bi/Mo ratios (P/Mo=0.2 atomic ratio) in an ordinary continuous-flow-type reaction system.[4] The concentration of alcohol was about 2.2 mol% in nitrogen or air, and the flow rate was kept at 1.0 l/min (STP). The amount of the catalyst used was 20 ml (contact time=1.2 sec). The reaction temperature was varied from 160 to 300°C.

The reaction products were analyzed by gas chromatography; for propylene and ethylene: activated alumina and a 6 m column at 80°C; for alcohols and other oxygen-containing compounds: PEG20M and a 6 m column at 80°C. The other experimental procedures were similar to those employed in earlier works.[1-3]

The catalysts used in these experiments were the same as those used in previous works.[1,2] The surface area of these catalysts was $0.6 \pm 0.3\ m^2/g$, as determined by the BET method, using nitrogen at −195°C as the adsorbate, and their packing density was within the limits of 0.75—0.80 g/ml. Taking the experimental error into account, the dependence of these values upon the catalyst composition (Bi/Mo ratio) was obscure.

Results and Discussion

Dehydration of Ethyl Alcohol. Only a trace amount of ethylene was produced, even at about 300°C, over the entire range of Bi/Mo ratios. This shows that the acid strength of the catalyst is too weak to catalyze the dehydration of normal alcohol.[5]

Dehydration of Isopropyl Alconol. The effect of the reaction temperature on the conversion of isopropyl alcohol into propylene was studied over the MoO_3–Bi_2O_3–P_2O_5 catalysts in atmospheres both of nitrogen and of air. The results in nitrogen are shown in Fig. 1. Apart from propylene, only di-isopropyl ether and acetone were found in the product. The acetone formation, *i.e.*, the dehydrogenation, was very little in nitrogen—less than 1%. It was more appreciable in air, especially at high temperatures. Propylene was the main product in the dehydration above 180°C. The portion of propylene in the products decreased with a decrease in the temperature, and below 160°C, ether was predominant. The rate of propylene forma-

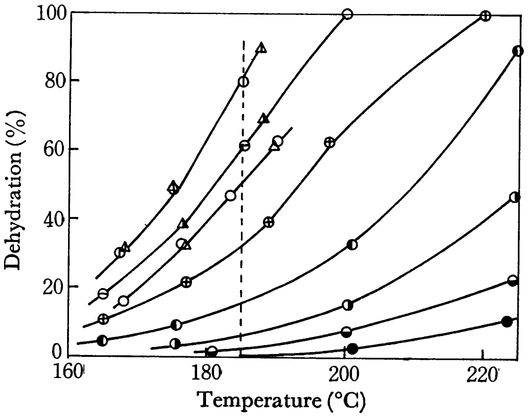

Fig. 1. Dependency of the isopropyl alcohol conversion to propylene on the reaction temperature over MoO_3–Bi_2O_3–P_2O_5 catalysts.
IPA=2.2% in N_2, contact time=1.2 sec,
○: Bi/Mo=0, △: 0.05, ⦶: 0.1, ⟁: 0.2, ⊖: 0.3, ▲: 0.4, ⊕: 0.7, ◐: 1.0, ◑: 2.0, ◒: 4, ●: ∞

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

[2] M. Ai and S. Suzuki, *J. Catal.* **26**, 202 (1972).

[3] K. Tanabe, "Solid Acids and Bases," Kodansha, Tokyo, and Academic Press, New York, London (1970), Chap. 5.

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

[5] Y. Murakami, S. Nishizawa, and H. Uchida, *Shokubai*, **13**, 108 (1971).

tion was almost of a zero order in isopropyl alcohol. No loss of activity was observed within 4—5 hr, even in the nitrogen atmosphere.

The value of the conversion to propylene at 185°C was adopted as a measure of the dehydration activity; the data are plotted as a function of the Bi_2O_3 content in Fig. 2. The value of the conversion to acetone in air at 185°C is also shown in Fig. 2. With an increase in the Bi_2O_3 content of the catalyst, the dehydration activity increases at first, passes through a maximum at the Bi/Mo atomic ratio of 0.1—0.2, and then decreases to the value of the pure Bi_2O_3 catalyst, which is extremely inactive. Although the shapes of the curves are almost the same, the activity in the air seems to be lower than that in nitrogen. Further investigation is necessary to clarify the effect of the atmosphere.

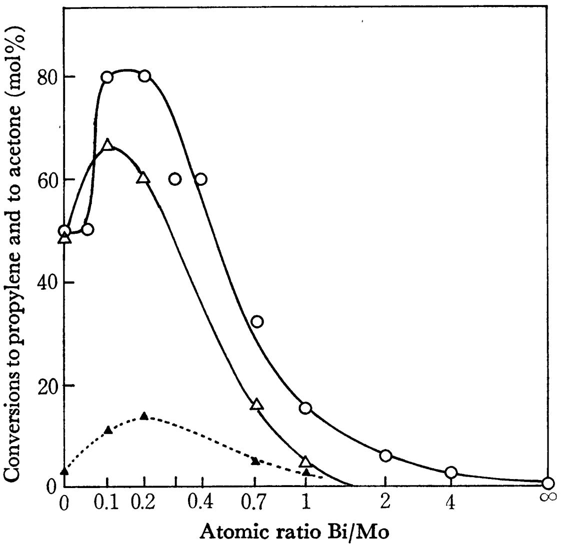

Fig. 2. Dehydration and dehydrogenation activities as a function of the Bi_2O_3 content.
temperature=185°C, IPA=2.2%, contact time=1.2 sec.
propylene---○: in nitrogen, △ : in air
acetone ---▲: in air (dotted line)

Discussion. If the dehydration activity really represents the acidity of a catalyst, it can be concluded from the results shown in Fig. 2 that a new acidic site is produced by adding Bi_2O_3 up to Bi/Mo= 0.1, that the acidity passes through a maximum at Bi/Mo=0.1—0.2, and that it then decreases sharply upon the further addition of Bi_2O_3.

If the acidity of the catalyst plays an important role in the oxidation and isomerization of olefin, a linear relation between the activities for these reactions and that for the dehydration must be obtained. The characters of the curves in Fig. 2 are quite similar to those of olefin oxidation.[1,2] Figure 3 shows the relationship between the dehydration activity for isopropyl alcohol and the oxidation and isomerization activities for butene. Both the oxidation and isomerization activities for butene increase steadily with an increase in the dehydration activity for IPA. Those results show that both the oxidation and isomerization activities are closely related to the acidities of the catalysts, which may support our explanation of the oxidation mechanism being based on the acid-base nature of the reactant and the catalyst.[1,2]

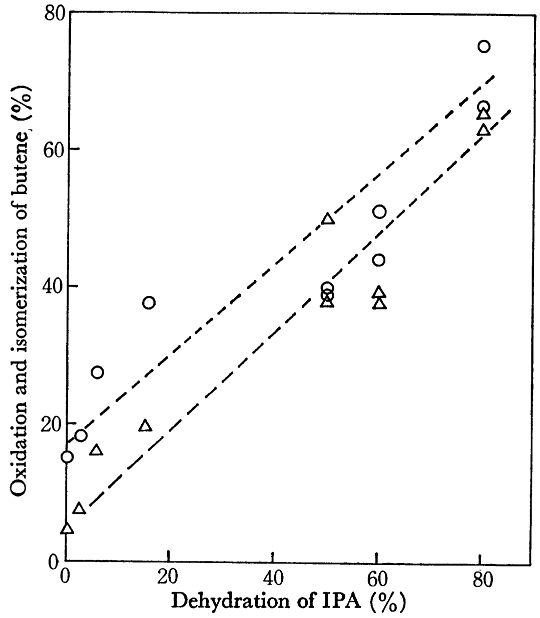

Fig. 3. Relation between the activity for IPA dehydration and the activities for oxidation and isomerization of butene.
IPA dehydration: 185°C, 2.2 mol% in nitrogen, contact time of 1.2 sec.
butene reactions: *cis*-2-C_4H_8=0.67% in air, contact time =1.6 sec.
○: over-all oxidation conversion of butene, 430°C
△: isomerization of *cis*-2-C_4H_8, 350°C:
[*trans*-2-C_4H_8+1-C_4H_8]/[*cis*-2-C_4H_8+*trans*-2-C_4H_8+ +1-C_4H_8]×100