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Hydrogen Transfer Reaction between Alcohols and Acetone

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It was found in the previous paper[1] that hydrogen transfer reaction between alcohol and aldehyde was involved in the butadiene formation from ethanol over $SiO_2 \cdot MgO$. This fact was pointed out by Quattlebaum *et al.*[2] but the mechanism postulated by them was highly improbable. They found purified SiO_2 was most active, while Jones *et al.*[3] reported it was inactive. Basic oxides such as CaO[4] and MgO[5] were also reported as active catalysts.

In this study, various kinds of $SiO_2 \cdot MgO$ having different composition and also different acidity and basicity, were used in order to make clear the roles of acidic and basic sites.

Experimental

Catalysts. SiO_2, MgO, and $SiO_2 \cdot MgO$ having different MgO contents were prepared by the method described before.[1]

Acidity and Basicity Measurements. Adsorbed amount of pyridine at 200°C and boron trifluoride at 300°C was measured by the gravimetric method described before.[1]

Reaction. A coventional flow type reactor was used. Alcohol and acetone were introduced with hydrogen as a gaseous mixture into a catalyst bed.

Results and Discussion

The reaction took place between any alcohol and ketone or aldehyde. In this study, ethanol, 1-propanol, 2-butanol, and acetone were chosen as reactants. This reaction was confirmed to be an intermolecular hydrogen transfer, because (1) the same activity was observed when helium was used as carrier gas instead of hydrogen, and (2) the hydrogenation of acetone or dehydrogenation of these alcohols did not take place under this reaction condition.

Reactivity of ethanol, 1-propanol, and 2-butanol as hydrogen donors were compared. The sequence of reactivity was, 2-butanol (1.02)$\gg$1-propanol (7.2×10^{-4})$>$ethanol (4.7×10^{-4}) herein, the values in the bracket are the reaction rates in mol/g-cat·hr at 200°C over $SiO_2 \cdot MgO$ (85 mol% MgO) catalyst.

It was shown in the previous paper[6] that release of the proton from hydroxy group was the rate determining step in the dehydrogenation of alcohols over basic sites, which gives the sequence of reactivity as follows, 2-butanol$\ll$1-propanol$<$ethanol. The reactivity sequence of alcohols in the hydrogen transfer reaction was quite different from that in the dehydrogenation reaction.

Acid-base properties and the activities of the catalysts were shown in Figs. 1 and 2. The catalytic activity in

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1) H. Niiyama, S. Morii, and E. Echigoya, This Bulletin, **45**, 655 (1972).

2) W. M. Quattlebaum, W. J. Toussaint, and J. T. Dunn, *J. Am. Chem. Soc.*, **69**, 593 (1947).

3) H. E. Jones, E. E. Stahly and B. B. Corson, *ibid.*, **71**, 1822 (1949).

4) Y. Schachter and H. Pines, *J. Catal.*, **11**, 147 (1968).

5) S. A. Bullard, H. D. Finch, and D. E. Winkler, "Advances in Catalysis," Vol. 10, Academic Press, New York and London (1959) p. 754.

6) H. Niiyama and E. Echigoya, This Bulletin **44**, 1739 (1971).

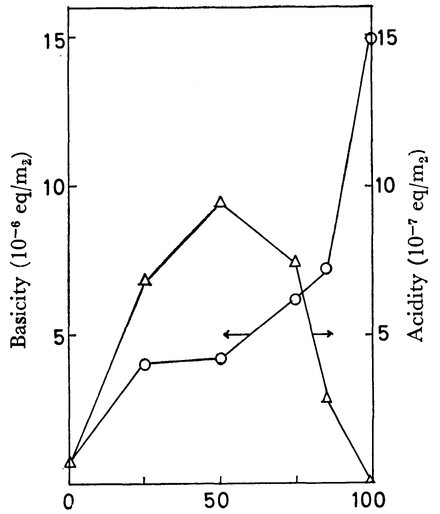


Fig. 1. The correlation between acidity or basicity and MgO contents.

—△— acidity (amount of pyridine adsorbed at 200°C)
—○— basicity (amount of BF_3 adsorbed at 300°C)

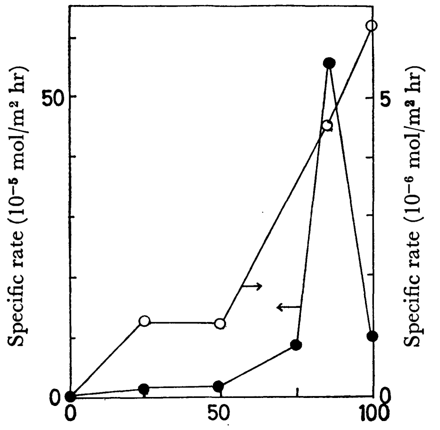
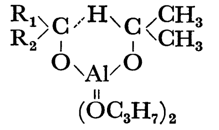


Fig. 2. The correlation between catalytic activity and MgO contents.

—○— ethanol-acetone at 200°C
—●— 2-butanol-acetone at 140°C

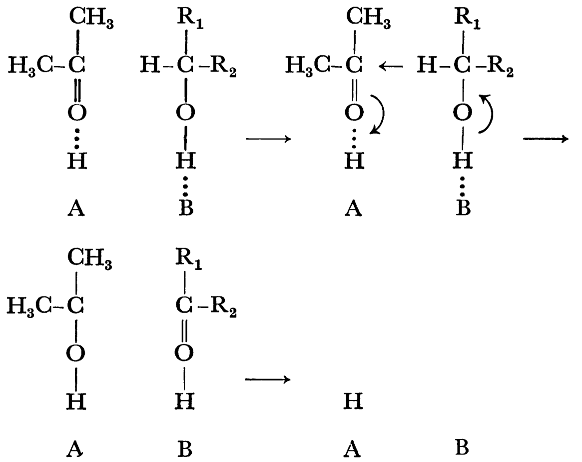
the ethanol-acetone system was well correlated with basicity. On the other hand, the profile of the activity against MgO content in the 2-butanol-acetone system was quite different from that of acidity or basicity. It is similar to that of butadiene formation from ethanol.[1] From this profile, it is expected that acidic sites also play important roles in the latter case.[7]

Reaction Mechanisms. The reduction of ketone or aldehyde by aluminum isopropoxide is known as Meerwein-Ponndorf reduction. Williams *et al.*[8] and Jackman *et al.*[9] postulated that the reaction proceeded through the following cyclic intermediate. Hydride ion



Intermediate postulated by Williams *et al.*[8]

originally attached to the carbinol carbon transferred to ketone to make another alcolate. This mechanisms will be applied in our case.



That is, electrophilicity of carbonyl carbon increases by the adsorption on acidic sites (HA) and neucleophilicity of carbinol carbon also increases by the adsorption on basic sites (B). The reactivity of alcohols is expected to depend on the number of aliphatic group attached to the carbinol carbon. Since ethanol has no secondary carbon, it has very small neucleophilicity. Then, the activation of ethanol caused by basic sites is the most important process and so the correlation between activity and basicity is established. On the other hand, 2-butanol is rich in neucleophilicity. Then the difficulty of activation of 2-butanol becomes comparable with that of acetone. Accordingly, no simple correlation with acidity or basicity was obtained, but the catalyst which had adequate acidity and basicity showed high activity.

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[7] Acidic and basic sites are cooperative in the butadiene formation reaction.

[8] E. D. Williams, K. A. Krieger, and A. R. Day, *J. Am. Chem. Soc.*, **75**, 2404 (1953).

[9] L. M. Jackman, A. K. Macketh, and J. A. Mills, *J. Chem. Soc.*, **1947**, 2641.