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Hydrogen Transfer Reaction between Alcohols and Acetone

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It was found in the previous paper¹⁾ that hydrogen transfer reaction between alcohol and aldehyde was involved in the butadiene formation from ethanol over $\text{SiO}_2 \cdot \text{MgO}$. 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 $\text{SiO}_2 \cdot \text{MgO}$ 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 $\text{SiO}_2 \cdot \text{MgO}$ 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 conventional 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 $\text{SiO}_2 \cdot \text{MgO}$ (85 mol% MgO) catalyst.

It was shown in the previous paper⁶⁾ 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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