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Catalytic Properties of Silica-Alumina Prepared by Chemical Vapor Deposition

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Strong Broensted acid sites were generated on Al_2O_3 support by the chemical vapor deposition (CVD) of SiO_2 using $Si(OEt)_4$ under atmospheric pressure. The CVD silica-alumina had a maximum acid strength of Ho = -8.2 and exhibited high catalytic activities for both the dehydration of 2-butanol and the cracking of cumene.

Commercial silica-alumina is usually prepared by co-gelation or kneading method. One of the authors has recently reported that solid acids such as silica-boria,(1,2) alumina-boria(3,4) prepared by the chemical vapor deposition (CVD) technique using $B(OEt)_3$ had excellent catalytic performance for the vapor-phase Beckmann rearrangement of cyclohexanone oxime. We now attempted to prepare a different type of silica-alumina by depositing silica onto alumina surface by means of CVD, and found that thus obtained CVD SiO_2/Al_2O_3 showed higher catalytic efficiency than alumina support itself and comparable activity to commercial silica-alumina for the dehydration of 2-butanol and the cracking of cumene.

The CVD SiO_2/Al_2O_3 was prepared by bringing $Si(OEt)_4$ vapor together with air or nitrogen into contact with alumina (Dia Catalysts & Chemicals LTD., DC-2282, surface area: 203 m^2/g, pore volume: 0.72 cm^3/g, 24-60 mesh size) in a rotary CVD reactor which is made up of a Pyrex glass tube rotating in an electrical furnace inclined by 45°; the flow rates of $Si(OEt)_4$ and carrier gas were 2.7 and 400 mmol/h, respectively. The SiO_2 content of catalyst was determined by measuring the weight increase of alumina support after CVD operation. The dehydration of 2-butanol was performed at 200 °C in a flow system at a W/F of 15 g-cat.h/mol. The cracking of cumene was tested in a micropulse reactor at 468 °C over 0.1 g of catalyst using a cumene pulse size of 2 μl.

The amount of deposited SiO_2 increased with CVD temperature in the temperature range of 200 and 300 °C. Figure 1 shows the relation between the amount of deposited SiO_2 and the CVD time. When CVD operation was performed at 240 °C in N_2, the amount of SiO_2 deposited on Al_2O_3 was at most 14 wt% even at a long time (4 h) CVD operation. On the other hand, when CVD was performed at 240 °C in air, the amount of SiO_2 was linearly increased with CVD time and 0.1 g of SiO_2 could be deposited on 1 g of Al_2O_3 support every 1 h. In the CVD operation at 300 °C in N_2, however, the same deposition rate of SiO_2 as obtained at 240 °C in air was attained. Thus also in the present case, O_2 was needed for the rapid deposition of SiO_2 as indicated by Izumi et al.(1,2) in the case of deposition of B_2O_3 onto Al_2O_3. Accordingly, SiO_2 content was adjustable by the amount of feed $Si(OEt)_4$ and temperature at the CVD operation using air as carrier gas.

Figure 2 shows the catalytic performance of CVD SiO_2/Al_2O_3 catalyst prepared at 240 °C in air. CVD SiO_2/Al_2O_3 catalyst was obviously more active than Al_2O_3 support itself and the conversions of both 2-butanol and cumene increased with the increase in SiO_2 content. For the cracking of cumene, CVD SiO_2/Al_2O_3 showed the maximum conversion (62%) at a SiO_2 content of 14 wt%. In spite of its smaller surface area (177 m^2/g), the conversion level was comparable to that (68%) obtained with a commercial silica-alumina (Nikki Chemical, N631-H, 360 m^2/g). At this SiO_2 content, CVD SiO_2/Al_2O_3 catalyst was thought to have a largest number of strong Broensted acid site. On the other hand, for the dehydration of 2-butanol, the maximum conversion (91%) appeared at a SiO_2 content of 22 wt%. This conversion level was also quite comparable to that (91%) of the commercial silica-alumina catalyst. Product distribution of butene isomers obtained over CVD SiO_2/Al_2O_3 (SiO_2 22 wt%) were 1 : 4 : 4 for 1-, trans-2-, and cis-2-, respectively, which was a contrast to the cis-2-butene rich distribution over Al_2O_3 support itself. In addition, according to the measurement by use of Hammett indicators, CVD SiO_2/Al_2O_3 (SiO_2 14 wt%) also showed the maximum acid strength of Ho = -8.2 like commercial silica-alumina does. It should be noted that such a simple procedure of CVD made it possible to generate strong acid sites onto alumina support to afford a new type of silica-alumina whose catalytic efficiency is comparable to that of commercial silica-alumina.

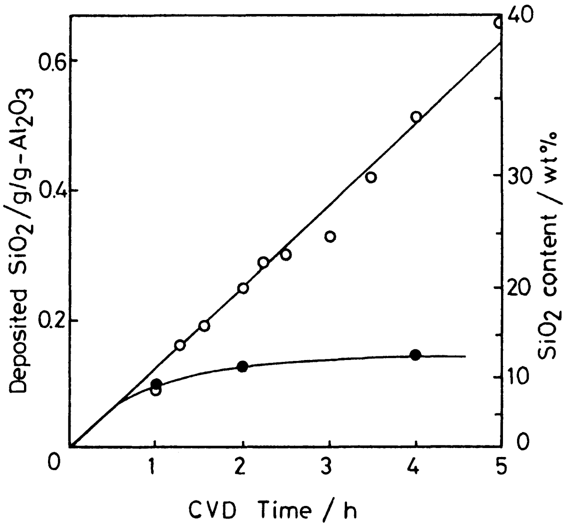

Fig. 1. Change in amount of deposited SiO_2 with CVD time.
o : CVD operation was performed at 240 °C in air, ● : at 240 °C in N_2.

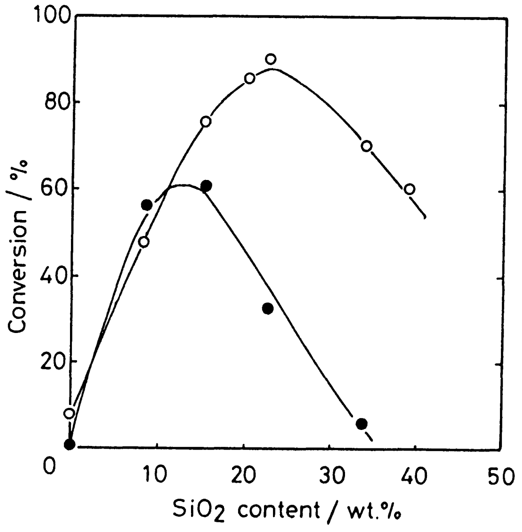

Fig. 2. Catalytic activities of CVD SiO_2/Al_2O_3 catalyst.
o : Dehydration of 2-butanol at 200 °C,
● : Cracking of cumene at 468 °C.

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