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REDISPERSION OF COBALT METAL PARTICLES IN Co/TiO_2 CATALYST AND ITS EFFECTS ON PROPENE HYDROGENATION

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The rate of propene hydrogenation on Co/TiO_2 catalyst, prepared by an alkoxide technique, was significantly enhanced when the catalyst was reduced by hydrogen at 700°C. However, over the catalyst prepared by an usual impregnation method, the enhancement of the rate was not observed at any reduction temperatures. The effects of reduction temperatures on the rate of propene hydrogenation were elucidated by redispersion of metallic cobalt particles.

The catalytic properties of supported metal catalysts are often affected by the reduction temperature, since it is one of the effective factors to control the dispersion states of metals. In general, the dispersion of a metal decrease with increasing the temperature of reduction.1) Recently, Baker et al.2,3) investigated the interaction between platinum and TiO_2. They found that the mean particle size of Pt increased with the elevation of temperature for reduction up to 500°C, while at 600°C platinum particles decomposed to the smaller ones. This indicates that the redispersion of the Pt particles occurred when the catalyst was heated at 600°C in hydrogen stream. Dumestic et al. also observed the redispersion phenomenon on iron supported TiO_2 catalyst when it was reduced by hydrogen at 600°C. The redispersion of platinum was attributed to the reduction of TiO_2 to $Ti_4O_7$2) and that of iron was explained by the migration of iron atoms into the partially reduced bulk TiO_2,4) respectivelly. However, the mechanism of the redispersion and its effects on the catalytic properties are still ambiguous.

In this work, two kinds of 4.0wt% Co/TiO_2catalyst were used. Catalyst A was prepared by the alkoxide technique mentioned in the previous paper.5) The precipitates obtained by the hydrolysis of a mixed solution of titanium isopropoxide and cobalt nitrate dissolved in ethylene glycol were calcined at 500°C in an oven and then reduced by hydrogen at various temperatures. Catalyst I was prepared by an usual impregnation method using an aqueous solution of cobalt nitrate and TiO_2 powder. Catalyst I was calcined and reduced under the same conditions employed for Catalyst A.

About 1.0g of the catalyst thus prepared was packed in a quartz reactor connected to a closed circulating system to measure the rate of propene hydrogenation to propane at 50, 100, and 150°C. Both the initial pressures of propene and H_2 were 100mmHg and gases were analyzed by a gas chromatography using a column packed with Polapak Q. The rates per mass of cobalt obtained on Catalyst A were plotted against the reduction temperatures(Fig.1). The rate on Catalyst A decreased with increase in the reduction temperatures, but it was extremely enhanced when the catalyst was reduced at 700°C. In order to understand this enhancement, the morphology of metallic cobalt particles was studied by a transmission electron microscope(Hitachi H-300) operated at an accelerating voltage of 75kV with an instrumental magnification of x100,000. By measuring about 500 particles in each photograph, the particle size distribution was obtained(Fig.2). From these results the mean particle size was calculated by the equation of $\bar{d}=\Sigma n_i d_i/\Sigma n_i$. The results calculated were shown against the reduction temperatures(Fig.3). It was found that the cobalt particles in the Catalyst A became large with elevation of the reduction temperature up to 600°C, but they redispersed when the catalyst was reduced at 700°C.

The change in the crystalline size of metallic cobalt in Catalyst A was obtained from an X-ray diffraction peak assigned to the (111) planes of cobalt crystallites and the results were also given in Fig.3. The X-ray diffractometer (Geigerflex, Rigakudenki Co.) was operated at 40kV with a filament current of 15mA using Zr filter for Mo$K\alpha$ radiation. For the X-ray measurement a part of the catalyst was dipped into a collodion solution(5% pyroxylin in diethyl ether) immediately after the reduction by hydrogen$^{6)}$, so that the catalyst would be protected from the exposure to air. As could be seen in Fig.3 the redispersion of cobalt particles would be the decomposition of particles to the individual crystallites, since the mean particle size of cobalt was same to the size of cobalt crystallite when the catalyst was reduced at 700°C.

Over Catalyst I no redispersion of cobalt particles was observed even when the catalyst was reduced at 700°C(see Fig.2), hence no enhancement of the hydrogenation rate was observed. Accordingly, the enhancement of the hydrogenation rate on

Catalyst A may be caused by this redispersion of cobalt particles. The redispersion of cobalt particles resulted in the increase in the fraction of cobalt atoms located on the edge or corner of the crystallite.[7)]

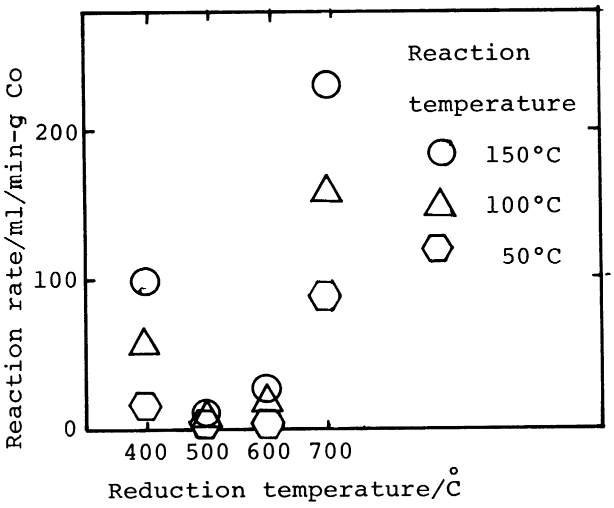

Fig.1 Relation between reduction temperature and reaction rate of propene hydrogenation per mass of cobalt on Catalyst A.

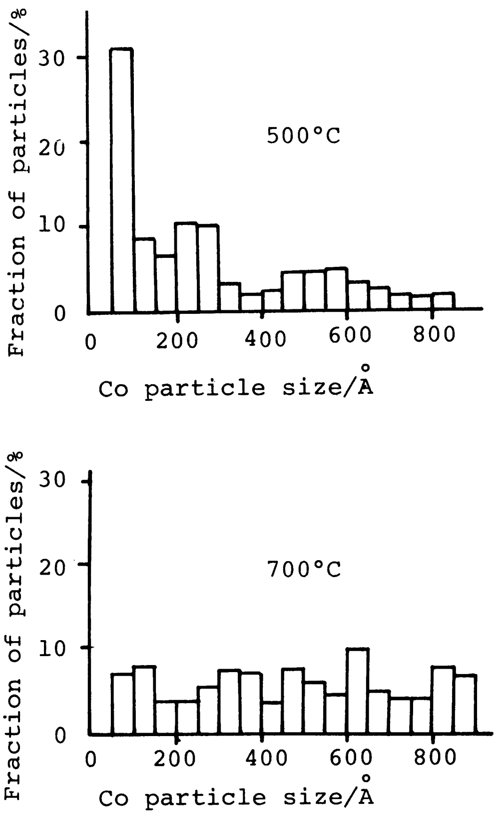

Fig.2a Cobalt particle size distributions in Co/TiO_2 catalyst I reduced at 500 and 700°C by hydrogen.

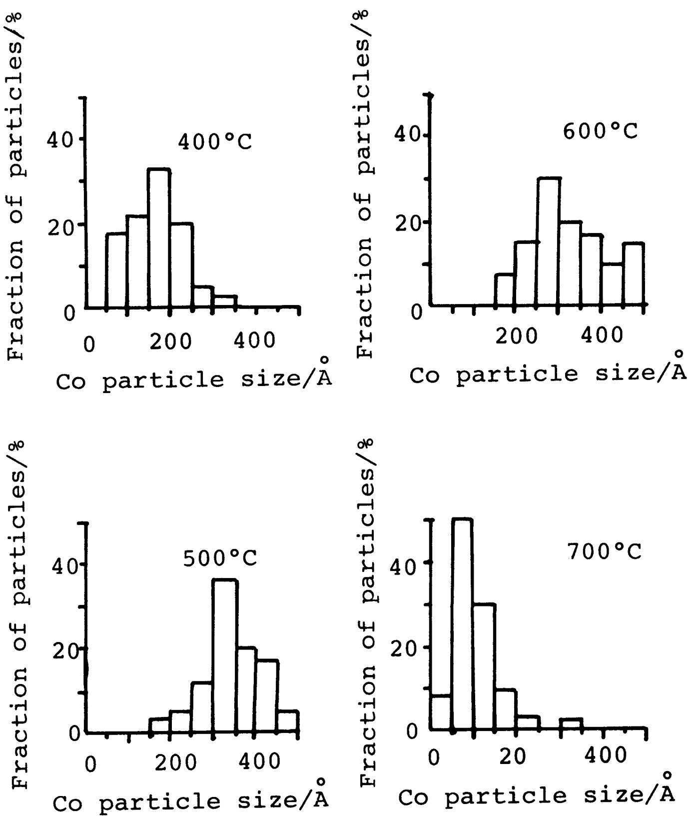

Fig.2b Cobalt particle size distributions in Co/TiO_2 catalyst A reduced at various temperatures.

Although the increase in this fraction is too small to be attributed to the enhancement of the hydrogenation rate observed, we might tentatively conclude that the hydrogenation takes place on the edge or corner atoms of the crystallites.

It must be mentioned that the phase transformation of TiO_2 occurred from anatase to rutile form, when the catalyst was reduced at700°C, where redispersion of cobalt particles was observed on Catalyst A. The redispersion was not observed on Catalyst I, even though the pase transformation of TiO_2 occurred at 700°C. This difference would be explained by the idea that the metal particles on Catalyst A were bounded to oxygen atoms in the support by forming chemical bonds.$^{5)}$ Consequently, the phase transformation of TiO_2 in Catalyst A will cause the redispersion of cobalt particles. While on Catalyst I, cobalt particles were on the support merely with van der Waals interaction.

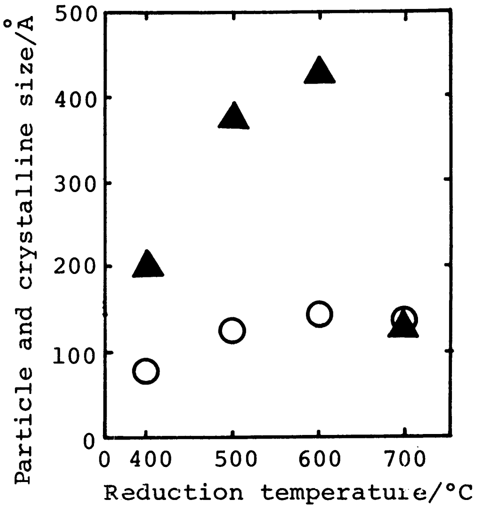

Fig.3 Changes in mean particle size of metallic cobalt(▲) and its crystalline size (○) with reduction temperatures.

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