

## Formation of Pitted Particles and Redispersion in Supported Nickel Catalysts during Heating in Oxygen and Hydrogen

Recent electron microscopic studies have revealed the interesting behaviors of metal particles on inorganic supports during heating in oxidizing and reducing atmospheres (1-6). Ruckenstein and his colleagues and Wang and Schmidt examined the dispersion of the platinum group of metals supported on alumina and silica. Ruckenstein and Chu first noted redispersion, the increase of metal surface area, of platinum particles on alumina either by the splitting or by the spreading of the particles through alternating treatment in O<sub>2</sub> and H<sub>2</sub> (1). When palladium particles on alumina were heated in O<sub>2</sub> at temperatures of 350 to 750°C, Ruckenstein and Chen found such phenomena as the formation of pits on the particles, the coalescence of these pits into cavities, the fragmentation of the particles into smaller ones, and the spreading of the oxidized particles over the alumina surface (2-4). Wang and Schmidt observed the similar phenomena for silica- and alumina-supported rhodium and platinum-rhodium catalysts during heating in O<sub>2</sub> and H<sub>2</sub>, and noted redispersion due to the splitting of the oxidized particles into smaller clusters in H<sub>2</sub> at 150°C (5).

In the course of our research on the sintering of supported catalysts, the similar behaviors were also observed for nickel particles on alumina and silica. In addition, we noted that the redispersion of nickel particles can be effected at a special set of treatment temperatures. The specimens of nickel (about 1 nm thick) on alumina and silica were prepared by vacuum evaporation in the same manner as described previously (7). The Ni/Al<sub>2</sub>O<sub>3</sub> and Ni/SiO<sub>2</sub> specimens on microscope grids were heated in O<sub>2</sub> and H<sub>2</sub> at 60 Torr for various durations

in an electric furnace. After each step of heating, the same region of a specimen was examined by a Hitachi H-300 transmission electron microscope. Since similar results were obtained on alumina and silica supports in each atmosphere, the results on alumina were chiefly described below.

Figure 1 shows the micrographs of a Ni/Al<sub>2</sub>O<sub>3</sub> specimen heated in O<sub>2</sub> and H<sub>2</sub>. After heating in H<sub>2</sub> at 600°C for 5 h, the Ni particles were mostly circular in shape. However, the subsequent treatment in O<sub>2</sub> at 600°C for 5 h resulted in a drastic change in morphology; almost all the particles became toruslike or horseshoe-shaped and spread over the support surface, increasing in diameter (of outmost rim, irrespective of the existence of cavities) by about 40% (Fig. 1b). These particles were ascertained to be NiO from the electron diffraction. When heated in H<sub>2</sub> again at the same temperature, all the particles contracted to the circular shape. Comparison of Figs. 1a-c indicates that the changes in shape, size, and position were almost reversible. Next, the same specimen was treated in O<sub>2</sub> at 600°C and in H<sub>2</sub> at 400°C each for 1 h. After three-times repetition of the oxidation-reduction, the Ni particles split into smaller clusters and redispersion took place (Fig. 1d).

Then we examined the effects of oxidation and reduction temperatures on redispersion of Ni/Al<sub>2</sub>O<sub>3</sub> under a fixed time of 1 h in each atmosphere. When oxidized at 600°C, redispersion was observed by the reduction only at 400°C. At the temperatures below 300°C, the reduction of NiO particles was incomplete although the particles broke into smaller clusters. At 500°C or above, the reduction was complete but the

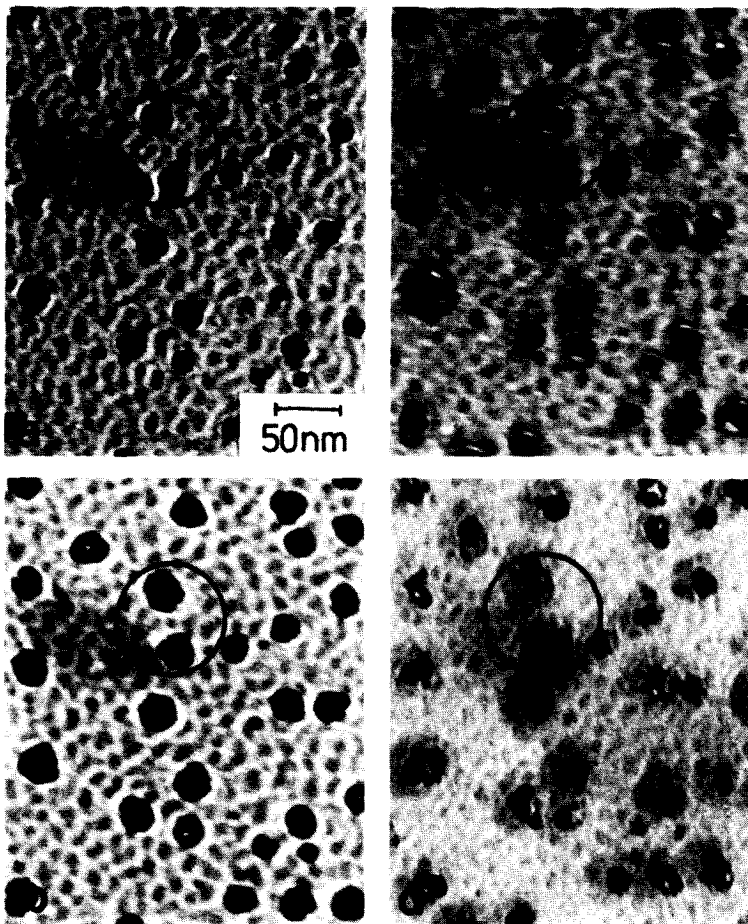


FIG. 1. Micrographs of Ni/Al<sub>2</sub>O<sub>3</sub> consecutively heated (a) in H<sub>2</sub> at 600°C for 5 h, (b) in O<sub>2</sub> at 600°C for 5 h, (c) in H<sub>2</sub> at 600°C for 1 h, and (d) alternately in O<sub>2</sub> at 600°C and in H<sub>2</sub> at 400°C each for 1 h, three times. The circles indicate the same region of the specimen.

Ni particles mostly contracted. On the other hand, when the oxidation temperature was lowered to 500°C, fixing the reduction temperature at 400°C, the particles contracted again. These results indicate that redispersion occurs under the critical conditions.

Figure 2 shows the change in surface-average of unidirectional diameters of the Ni particles on Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> supports throughout the consecutive treatment in H<sub>2</sub> and O<sub>2</sub>. Relatively long heating in H<sub>2</sub> caused a slight increase in the particle diameter due to the sintering. By replacing H<sub>2</sub> with O<sub>2</sub>, the diameter soon increased to a large extent and then changed little upon

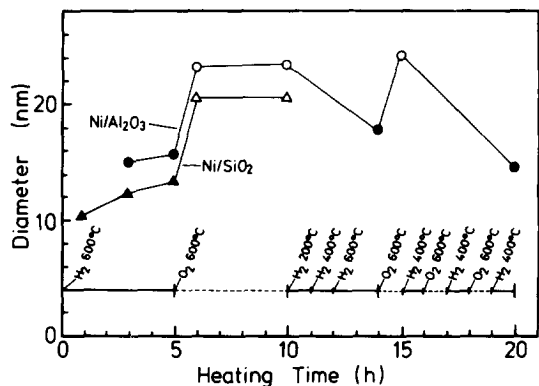


FIG. 2. Surface-average of unidirectional particle diameters as a function of cumulative heating time. The symbols ● and ▲ refer to Ni particles; ○ and △ refer to NiO particles.



FIG. 3. Micrographs of Ni/Al<sub>2</sub>O<sub>3</sub> heated in H<sub>2</sub> at 600°C for 1 h and then in O<sub>2</sub> (a) at 100°C for 12 min, (b) at 150°C for 11 min, and (c) at 200°C for 10 min. The circles indicate the same region of the specimen.

continued heating for about 4 h. However, short reduction after oxidation resulted in redispersion as previously seen in Fig. 1.

We also examined the temperature dependence of the cavity formation on the particles with the oxidation. Figure 3 shows the micrographs of a Ni/Al<sub>2</sub>O<sub>3</sub> specimen which was heated in H<sub>2</sub> at 600°C for 1 h and then in O<sub>2</sub> stepwise from room temperature. As the temperature was raised to 150°C, tiny pits were formed on the edge of the particles. At 200°C, almost all the particles were irregular in shape and the cavity formation was observed on fairly many particles.

Ruckenstein and Chen (3, 4) and Wang and Schmidt (5) pointed out that the formation of cavities on the particles and the spreading of the particles over the support surfaces relate closely to the enhanced metal-support interaction with the oxidation. Their explanation may also be valid for the present results of the Ni particles on Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> supports although detailed mechanisms are still not elucidated. Limitation of the oxidation temperature for redispersion may be related to the strength of the oxide-support interaction. Reduction at temperatures above 400°C facilitates the Ni particles to move over the support, resulting in a formation of larger particles. Precise range of temperature for redispersion would depend on the state of the specimen as well as the pressure and duration of treatment, which we are working to clarify.

The behaviors of Ni particles on SiO<sub>2</sub> were nearly the same as on Al<sub>2</sub>O<sub>3</sub>, except for the surface movement observed for the small particles only on Al<sub>2</sub>O<sub>3</sub> at the initial stage of reduction.

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