Dispersion of Nickel Particles Supported on Alumina and Silica in Oxygen and Hydrogen

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A transmission electron microscopic study was made to examine the behavior of Ni particles supported on amorphous Al_2O_3 and SiO_2 by thermal treatment in H_2 and O_2 atmospheres at 60 Torr. The sintering during heating in H_2 at 600°C proceeded by particle migration for Ni/Al_2O_3 but by atomic migration for Ni/SiO_2. The rate of increase in the average particle size in H_2 at 600°C was comparable to that under vacuum at the same temperature. Annular or horseshoe-shaped NiO particles spreading over the supports were formed by O_2-treatment at certain temperatures which were dependent on the support material. The formation of pitted particles was completed in a rather short period of time. By repeated heating in O_2 and in H_2 at 600°C, the particles reversibly changed their shape at the same positions. However, redispersion, the splitting of particles, occured at other sets of treating temperatures, typically oxidation at 600°C and reduction at 400°C. The treatment temperatures at which redispersion was observed differed between the two supports. The effect of the support is discussed in terms of particle–support interaction including the formation of a metal–support complex.

INTRODUCTION

Supported metal catalysts, widely used in automotive, petrochemical, and chemical industries, are always exposed to different chemical environments. The surrounding gases may affect the catalyst sintering which causes the deactivation of the catalysts (*1*).

Recently, transmission electron microscopic studies using some model catalysts have revealed the various types of the behavior of supported metal particles in gaseous environments (*2–9*). One of the interesting findings is that alternative oxidation and reduction lead to the increase of surface area of supported particles, i.e., redispersion. Ruckenstein and Chu first noted the redispersion by such a cyclic treatment for platinum dispersed on alumina and showed that the redispersion is due to either the splitting or the spreading of the particles (*2*). Baker *et al.* (*6*) and Wang and

Schmidt (*8*) observed the redispersion of platinum on titania and of rhodium on silica and alumina, respectively, under different conditions. Previously, we also showed that silica- and alumina-supported nickel particles can redisperse by a similar repeated oxidation–reduction at a particular set of treatment temperatures (*9*). These results obtained for the different systems (*2, 6, 8, 9*) suggest that there is an effective range of the treating conditions for redispersion depending on the metal–support system used.

The present study aims to elucidate the dependence of redispersion on temperatures of repeated heating in oxygen and hydrogen for nickel particles on silica and alumina films. Effective temperatures vary with the support material and this is discussed in terms of metal- and metal oxide-support interactions including the formation of a metal–support complex. In addition, an attempt is made to apply the cyclic oxidation–reduction to nickel catalysts prepared by impregnation using po-

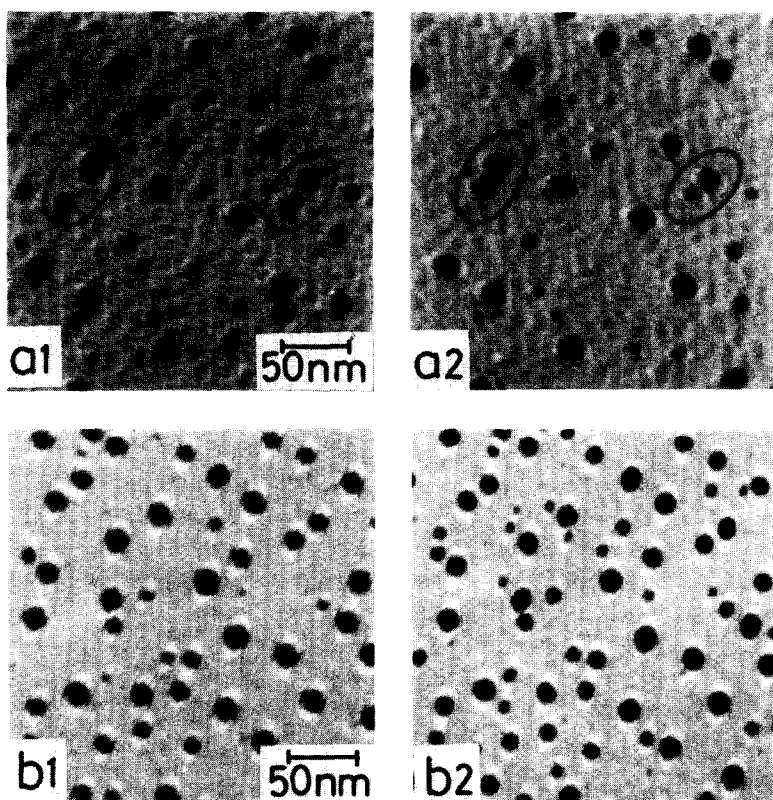[1] To whom all correspondence should be addressed.

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FIG. 1. Micrographs of Ni particles heated in H_2 at 600°C on (a) Al_2O_3 for (1) 1 and (2) 3 h; (b) SiO_2 for (1) 3 and (2) 5 h.

rous supports to see whether such treatment effects the redispersion of these catalysts.

EXPERIMENTAL

Model catalysts of nickel with a thickness of 1–2 nm on alumina and silica films were prepared by the procedure described previously (10). The Ni/Al_2O_3 and Ni/SiO_2 mounted on microscope grids were repeatedly heated in O_2 and in H_2 at 60 Torr (1 Torr = 133.3 Pa) in an electric furnace. After heat treatment for the desired period of time, the furnace was cooled to room temperature in about 1 h, and then the gas was replaced by air. The same region of a specimen was examined by a Hitachi H-300 transmission electron microscope to follow the change in size, shape, and position of each particle after each step of heating. The unidirectional diameters of 500–1000 parti-

cles of each specimen were measured to obtain the particle size distribution, and the Sauter-average size was calculated. Nickel catalysts supported on alumina and silica powders of large surface area were prepared and also subjected to the above experiment. Alumina (Neobead C) and silica (Silbead N) were obtained from Mizusawa Industrial Chemicals Ltd. Catalysts with 5 wt% nickel were prepared by impregnating the support powders (32–60 mesh) with $Ni(NO_3)_2$ aqueous solution, drying under vacuum at 100°C for 4 h, and reducing in flowing H_2 at 400 and 350°C, respectively, for 16 h.

RESULTS AND DISCUSSION

Dispersion in Hydrogen

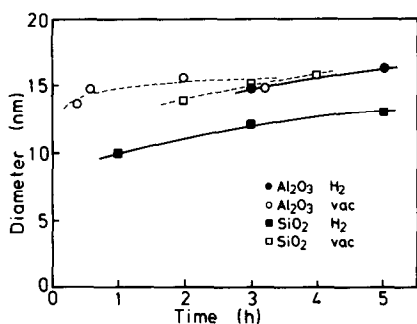Figure 1 shows micrographs of Ni/Al_2O_3 and Ni/SiO_2 specimens heated in H_2 at

FIG. 2. Sauter-average particle diameter versus heating time for (●,○) Ni/Al₂O₃ and (■,□) Ni/SiO₂ specimens at 600°C; closed and open marks indicate the results under H₂ and under vacuum, respectively.

600°C. On Al_2O_3, surface movement of Ni particles less than about 15 nm in diameter was observed as shown in ellipses; at the same time, there were a few particles which remained at the same positions and decreased in size during heating. The Ni particles on SiO_2 were mostly immobile and either grew, or contracted and disappeared. These results indicate that the prevailing sintering mechanism in H_2 at 600°C was particle migration on Al_2O_3 but atomic migration on SiO_2. Under vacuum, Ni/SiO_2 sintered by the particle migration mechanism at 600°C but similar difference in sintering mechanism between the two supports was noted at 650°C or higher (10).

The change in the Sauter-average diameter during H_2-treatment is presented in Fig. 2 including the results obtained under vacuum. For both Al_2O_3 and SiO_2, the Ni particles sintered in H_2 at a rate similar to that under vacuum.

There have been a few kinetic investigations on the sintering of Ni catalysts prepared by different procedures using porous supports (11–14). Kuo et al. showed the temperature dependence of sintering mechanism of a precipitated Ni/SiO_2 catalysts in H_2 as well as in N_2, the prevailing mechanism being particle migration at 700°C or below but atomic migration at 800°C (11, 12). Bartholomew et al. indicated a similar dependence for both an impregnated Ni/

Al_2O_3 and a controlled-pH-deposited Ni/SiO_2 in H_2 in the range of 650 to 750°C (14). The difference between the results in the literature and our results can be ascribed to the structural properties of the support used. In the case of the porous supports, their pore structure significantly influences the sintering behavior (11–14).

Judging from the sintering mechanism, the Ni–support interaction in the present Ni/SiO_2 system may be enhanced by the presence of H_2. It has been revealed that there is an unusual strong metal–support interaction in Pt/TiO_2 in H_2 atmosphere (6, 15–17). Recent studies have also given evidence for enhanced interactions in SiO_2- and Al_2O_3-supported Ni catalysts in reducing atmosphere (18–21). Praliaud and Martin indicated the formation of a Ni–Si alloy in Ni/SiO_2 by reduction of the support at about 900°C; Young et al. indicated the diffusion of Ni atoms into Al_2O_3 supports above 950°C. In these cases, strong interactions need relatively high temperatures, and therefore such H_2-treatment-induced strong interaction did not appear under the present conditions although the contribution of atomic migration to the particle growth increased by the presence of H_2 for the present Ni/SiO_2 system.

Dispersion in Oxygen

The specimens as prepared were of a continuous Ni layer on the support films. The treatment of such specimens in O_2 did not break the Ni layer. The specimens were first heated in H_2, and then, after the formation of Ni particles, were heated in O_2.

As described in the previous paper (9), when the Ni/Al_2O_3 and Ni/SiO_2 specimens were treated in O_2 at 600°C, the formation of toruslike or horseshoe-shaped NiO particles spreading over the supports was completed within 1 h and these oxidized particles showed no change upon further heating. Similar types of behavior in oxidizing atmosphere have been found by Chen and Ruckenstein for Pd/Al_2O_3 (3–5) and by Wang and Schmidt for Rh and Rh–Pt on
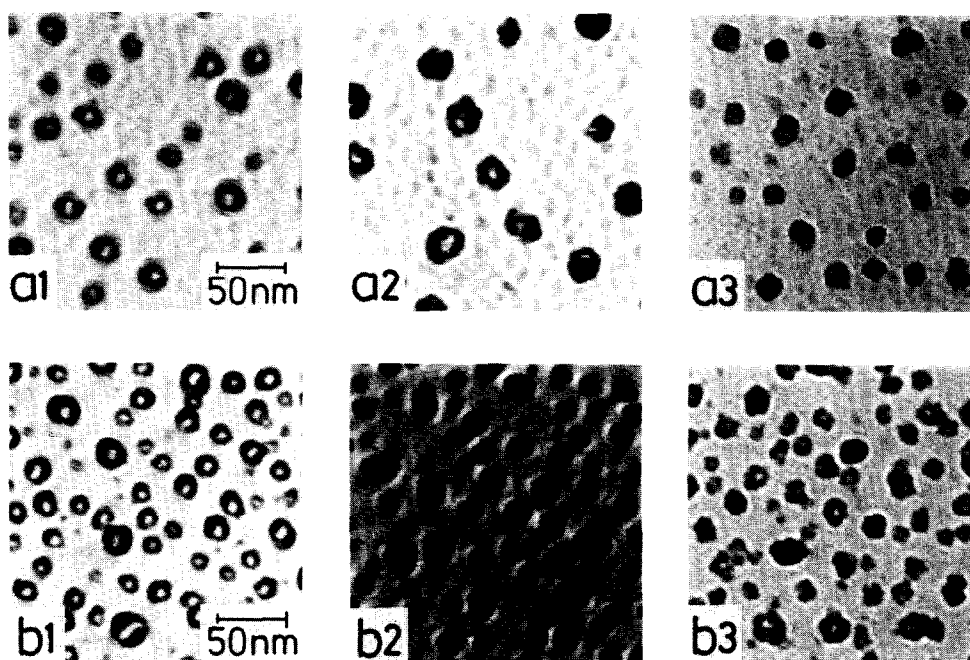
FIG. 3. Comparison of the shapes of NiO particles on (a) Al_2O_3 and (b) SiO_2 at different oxidation temperatures: Ni/Al_2O_3 and Ni/SiO_2 were treated in O_2 at (1) 400, (2) 600, (3) 700°C each for 1 h.

Al_2O_3 and SiO_2 (8). Chen and Ruckenstein suggested that such pit formation is due to the oxidation which starts at some active sites on the particle surface and to the spreading of the formed metal oxide over the nonoxidized metal; the spreading is ascribed to a difference in the interfacial energies between metal– and metal oxide–support. This is supported by our previous experiment which examined the pit formation of a Ni/Al_2O_3 specimen during a stepwise oxidation from room temperature (9). Dadyburjor has made a kinetic description based on the strain model where the pit formation and the resultant fracture of metal particles are due to the difference in the lattice parameters between the metal and the metal oxide (22). Gollob and Dadyburjor have used this model to explain the increase of the particle size in an alumina-supported Pt catalysts during heating in air at about 500°C (23). The strain model postulates only the formation of a surface layer of oxide on the metal particle and, hence,

cannot account for the spreading of the supported Pd and Ni particles. As stated by Dadyburjor (22), however, the mechanisms of the crack formation and the splitting are probably dependent on metal/support system used, oxidation temperature, oxidizing agent, particle size, and so on, although the experimental evidence is still insufficient.

In the present study, we examined the effect of oxidation temperature on the shape of NiO particles; the specimens were treated in O_2 at different temperatures for 1 h. Figure 3 shows micrographs of the specimens after O_2-treatment at 400, 600, and 700°C. On the electron micrographs, each particle is seen to have a ring around it; this is due to contamination from residual gases inside electron microscope and such a ring is artifact. In a few examinations using a liquid-nitrogen-cooled shield around the specimen, no contamination occurred. This is the same on some of the following micrographs.

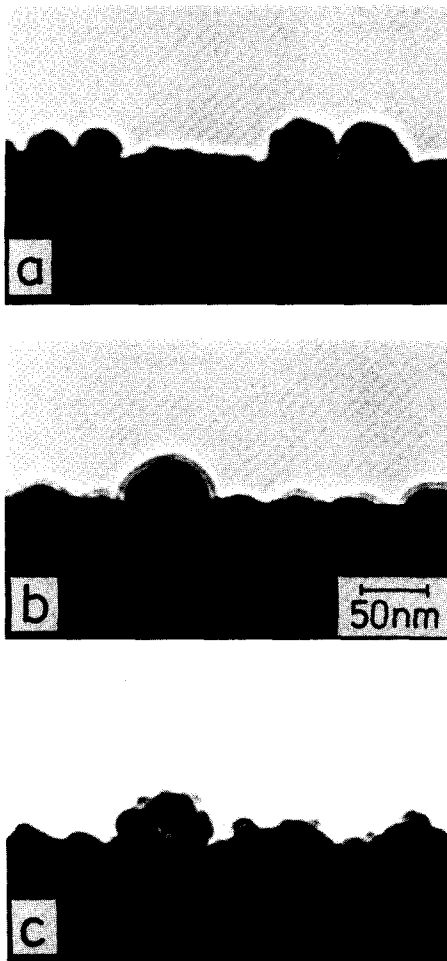On Al_2O_3, the annular shape was ob-

FIG. 4. Side views of (a,b) Ni and (c) NiO particles on SiO$_2$. The Ni/SiO$_2$ specimens were heated at 600°C for 1 h under (a) vacuum; (b) H$_2$; (c) O$_2$.

ide on nonoxidized metal should be considered. This problem will be discussed later in connection with redispersion of metal.

Figure 4 shows micrographs of the particles on the edges of folded portions of SiO$_2$ films in different atmospheres. These side views reveal the three-dimensional shape of the particles; the Ni particles are polyhedral under vacuum but hemispherical in H$_2$; the NiO particles have uneven surfaces. At present it is difficult to explain clearly the formation of these annular, uneven NiO particles on the supports.

Change in Dispersion by Cyclic Oxidation and Reduction

In Fig. 5 is presented the change in the particle size distribution of a Ni/Al$_2$O$_3$ specimen during successive treatment in O$_2$ and H$_2$. Distribution (a) that was obtained after heating in H$_2$ at 600°C for 1 h is considered as the initial state. Histograms (a)–(d) indicate that the size distribution was reversibly changed by the oxidation–reduction at 600°C. In this case, the particles varied only in shape from round to pitted particles.

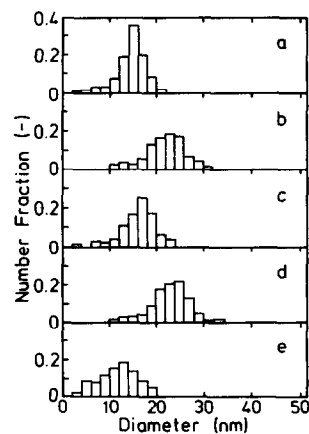When the reduction in cyclic treatment was performed at 400°C instead of 600°C,

served for almost all the particles at 400 and 600°C but not at 700°C where the outer diameter was smaller than those at lower temperatures. On the other hand, the NiO particles on SiO$_2$ were mostly of pitted shape and spread approximately to the same extent in the outer diameter at all temperatures examined, but the size of the pits tended to be smaller at higher temperature. To explain these effects of temperature and of support, thermodynamic factors, the interfacial energies of metal– and support-metal oxide, and/or kinetic factors, the rates of oxidation and diffusion of metal ox-

FIG. 5. Change in the particle size distribution of a Ni/Al$_2$O$_3$ specimen which was consecutively treated under (a) H$_2$ at 600°C for 5 h; (b) O$_2$ at 600°C for 5 h; (c) H$_2$ at 200°C for 1 h, at 400°C for 1 h, and at 600°C for 2 h; (d) O$_2$ at 600°C for 1 h; (e) alternately for 1 h each in O$_2$ at 600°C and in H$_2$ at 400°C, three times.

the fraction of small particles was increased as compared with the initial state (Fig. 5a). This indicates that there was an increase in the total surface area of Ni particles on Al_2O_3, i.e., redispersion. Similar redispersion was also noted for Ni/SiO_2 after the same treatment. The redispersion on both supports was due to the splitting of the particles, where each particle broke into two or three pieces.

The redispersion by alternative treatments in oxidizing and reducing atmospheres has been observed for other metals supported on alumina and silica. Ruckenstein and Chu have noted the redispersion of Pt on alumina and reported that several cycles of heating in O_2 and H_2 at 750°C and 1 atm were needed for Pt redispersion (2). Wang and Schmidt have also found such redispersions of Rh on silica and alumina caused by cyclic treatment where oxidation was performed in air at 600°C and reduction in H_2 at a lower temperature (8).

In addition, we sought the treatment temperatures at which the Ni particles on Al_2O_3 and SiO_2 could redisperse by splitting. In this experiment, the treatment time was fixed at 1 h and the oxidation–reduction was repeated three cycles. Table 1 summarizes the results, which indicate the dependence of redispersion on temperatures and support material. On H_2-treatment at 300°C, the reduction of NiO particles was incomplete, while at higher temperature (500°C), each reduced particle agglomerated into round shape. When the oxidation was performed at lower temperature, the spread particles shrank more easily, perhaps due to weak interaction between the particles and the supports. Redispersion may be effected by the cyclic oxidation–reduction under such conditions as the oxidation causes the sufficient spreading of the particles over the support and forms strong metal oxide–support interaction and the reduction is not so severe as to reduce and to mobilize all the Ni atoms. The strong interaction is probably due to the formation of a Ni–support complex at the particle–sup-

TABLE 1

Effects of Treatment Temperatures on Redispersion of Ni

	Oxidation	Reduction		
		300°C	400°C	500°C
Al_2O_3	400°C	X (NiO)[a]	X (Ni)	X (Ni)
	500°C	X (NiO)[s]	X (Ni)	X (Ni)
	600°C	X (NiO)[s]	O (Ni)	X (Ni)
SiO_2	400°C	X (NiO)[a]	O (Ni)	X (Ni)
	500°C	X (NiO)[s]	O (Ni)	X (Ni)
	600°C	X (NiO)[s]	O (Ni)	X (Ni)

Note. Ni/Al_2O_3 and Ni/SiO_2 specimens were repeatedly treated for 1 h each in O_2 and in H_2, three times. O, Redispersion was observed; X, not observed. "Ni" and "NiO" in parentheses indicate the state of particles examined by electron diffraction. Superscript a for NiO indicates particles agglomerated into a round shape; s means spread and/or splitted particles.

port interface and maintains the enhanced area between the particles and the support during the following reduction. When the reduction starts at a few sites on the surface of the particles, the splitting of the particles may result from the difference in density and/or in the interfacial tension between reduced and nonreduced parts of each particle.

Lo Jacono et al. reported the formation of nickel aluminate at 600°C in impregnated NiO/Al_2O_3 systems (24). There have been other investigations indicating the formation of nickel aluminate at relatively high temperatures, which, of course, are dependent on the state of the catalysts (25–30). The NiO/Al_2O_3 systems used in these works are real catalysts prepared by ordinary procedures such as coimpregnation. For Ni/SiO_2 systems, the formation of a Ni–support complex has also been evidenced (31, 32). Shalvoy et al. noted that nickel silicate is formed in coprecipitated SiO_2-supported Ni catalysts calcined at relatively low temperature of ca. 400°C (31). These results suggest that Ni–support complexes are formed in our model systems and the temperature of the formation would be
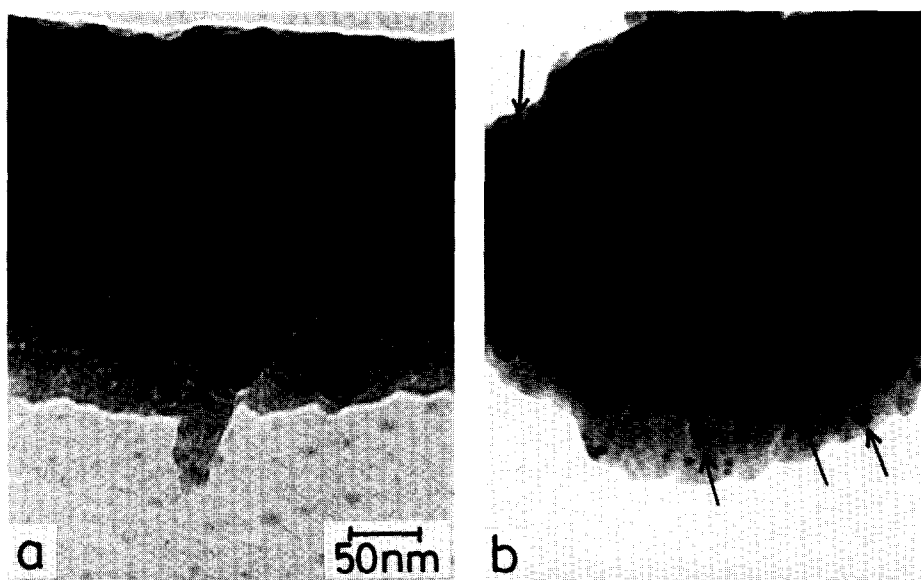
FIG. 6. Micrographs of a 5 wt% Ni/SiO$_2$ catalyst heated (a) in H$_2$ at 800°C for 3.5 h and (b) in O$_2$ at 400°C for 1 h. Arrows indicate pitted NiO particles.

lower for Ni/SiO$_2$ than for Ni/Al$_2$O$_3$. This may explain the effect of the support material on redispersion as shown in Table 1.

Previously, some authors pointed out that the reducibility of supported NiO particles is affected by the support material and the oxidation temperature (30, 31, 33–35). To examine the reducibility of our NiO on Al$_2$O$_3$ and SiO$_2$ films, the specimens, pretreated in H$_2$ to form Ni particles, were subjected to one-cycle oxidation–reduction; oxidized at 400 or 700°C for 1 h and then reduced at 250, 300, or 350°C for 1 h. For Al$_2$O$_3$, the NiO particles formed at 400°C could be reduced at 300°C, but those formed at 700°C could not be reduced unless the temperature was raised to 350°C. For SiO$_2$, however, the NiO particles formed at both 400 and 700°C could be reduced at 300°C. These results indicate that a strong NiO–Al$_2$O$_3$ interaction is formed only at high temperatures. Shalvoy et al. noted that the reduction of a coprecipitated Ni/Al$_2$O$_3$ calcined at ca. 400°C is more difficult compared with a similarly prepared Ni/SiO$_2$ (32). This agrees with our results of the model catalysts oxidized at 700°C.

Cyclic Oxidation–Reduction of Catalysts Using Porous Supports

The regeneration of deactivated catalysts has been an interesting problem not only from a laboratorial but also from an industrial point of view. As mentioned above, the redispersion of the model supported Ni catalysts can be effected by cyclic oxidation–reduction. In this work, an attempt was made to apply such a treatment to supported catalysts using porous alumina and silica. Figure 6 shows micrographs of a 5 wt% Ni/SiO$_2$ after treatment in H$_2$ at 800°C and in O$_2$ at 400°C. It should be noted that pitted particles are seen in O$_2$ although round particles are seen in the H$_2$ atmosphere. Ni (5 wt%) supported on alumina and silica were treated under conditions where redispersion of the model catalysts occurred, i.e., alternately for 1 h each in O$_2$ at 600°C and in H$_2$ at 400°C. Examination by X-ray diffraction line broadening and by temperature-programmed desorption of adsorbed H$_2$ failed to detect any increase in metal surface area. Probably, the conditions to redisperse metal particles on po-

rous supports are different from those for metal particles on flat films, and the above results (Fig. 6) suggest a possibility to achieve redispersion of Ni on porous supports if appropriate conditions are selected.

SUMMARY

The behavior of Ni supported on Al_2O_3 and SiO_2 films under 60 Torr of H_2 and of O_2 was examined by means of transmission electron microscopy. The following results were obtained.

(1) The Ni particles in H_2 at 600°C sintered mainly by particle migration for Al_2O_3 but by atomic migration for SiO_2. The rate of particle growth in H_2 was comparable to that under vacuum.

(2) Annular or horseshoe-shaped NiO particles spreading over the supports were formed by O_2-treatment at certain temperatures depending on the support material.

(3) The reduction of NiO/SiO_2 was easier than that of NiO/Al_2O_3 where the NiO particles formed at higher temperature needed higher temperature for complete reduction.

(4) Redispersion by the splitting of the particles was effected by cyclic oxidation–reduction under particular conditions, which differed between Al_2O_3 and SiO_2.

(5) The conditions for redispersion are considered as follows: on O_2-treatment, the sufficient spreading of the particles and the strong particle–support interaction are caused; on H_2-treatment, each particle is completely reduced without agglomeration into a round shape.

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