Dispersion Control of Ni Particles in Porous Silica by Solution Exchange of Wet Silica Gel

Ryoji Takahashi,* Satoshi Sato, Toshiaki Sodesawa, Masayuki Kato, and Takaaki Yoshii
Department of Materials Technology, Faculty of Engineering, Chiba University, Yayoi, Inage, Chiba 263-8522

(Received December 15, 1998; CL-980925)

Particle size of NiO in silica with well defined mesoporous structure can be controlled from 3.5 to 10 nm regardless of NiO content up to 30 wt% by solution exchange of wet silica gel derived from sol-gel process. Ni surface area of samples reduced at 500 °C can be enlarged by decreasing the NiO particle size, resulting in 30 m^2g^{-1} at 30 wt% loading. The catalysts showed superior activities for gas-phase hydrogenation of benzene.

Ni/SiO_2 catalysts prepared by ion exchange or impregnation methods have been widely investigated.[1] However, heterogeneous aggregation at interparticles of supports is considered as a disadvantage of the methods especially at higher Ni content, > 10 wt%. It has been reported that Ni particles are homogeneously dispersed in a silica gel even at higher Ni content, typically up to 30 wt% of Ni, by adopting a sol-gel method, where the catalysts are prepared from the mixed solution of silicon alkoxide and nickel salt.[2-4] However, the particle size of Ni increases with increase in Ni content, and becomes larger than 10 nm at Ni loading > 10 wt%. On the other hand, one of the authors has demonstrated that pore structure of silica gel derived from sol-gel process can be desirably controlled by a solvent exchange technique of wet gel.[5,6] For example, a silica gel dried after exchanged swelling solution with 1 mol dm^{-3} nitric acid aqueous solution shows BET surface area of ca. 600 m^2g^{-1} and average pore diameter of ca. 4 nm with sharp pore size distribution. In this work, we propose a new catalyst preparation method applying the pore size controlling technique of silica in sol-gel process to obtain a Ni/SiO_2 catalyst containing highly dispersed Ni particles.

The Ni/SiO_2 catalysts were prepared as follows. Tetraethoxysilane was mixed into an equi-volume of 1 mol dm^{-3} nitric acid aqueous solution under stirring. After the mixture had become homogeneous, it was kept in a closed container made of polystyrene at 50 °C for 20 h for the gelation. The obtained wet gel was immersed in 1 mol dm^{-3} nitric acid aqueous solution containing nickel nitrate for 1 day for exchanging the swelling solution to that containing Ni ion (denoted as N). In some cases, citric acid equimolar with Ni ion was also dissolved in the exchanging solution (denoted as CA). Typically, a wet gel piece with dimensions of about 5×4×1 cm was cut into several pieces, and was immersed in 55 cm^3 of an exchanging solution. The obtained wet gel containing Ni ion or Ni-citric acid complex was dried at 50 °C until no shrinkage was observed. After the dried gel had been crushed into powder, it was heated in air (denoted as N and CA-air) or under N_2 flow (denoted as CA-N_2) at 500 °C for 2 h to obtain a NiO/SiO_2 sample. NiO content of the NiO/SiO_2 was controlled by altering the concentration of nickel nitrate solution used for the solution exchange. As referenced catalysts, NiO/SiO_2 samples were also prepared by a usual impregnation method (denoted as IMP) and by a sol-gel method using ethylene glycol as a solvent[3] (denoted as EG).

Particle sizes of NiO were calculated from widths of X-ray diffraction (XRD) peaks.[7] Ni surface area for samples reduced with H_2 at 500 °C was calculated from H_2 chemisorption isotherm at 0 °C. The hydrogenation of benzene (Bz) to cyclohexane was performed in a standard fixed bed-flow reactor after the NiO/SiO_2 sample had been reduced with H_2 at 500 °C. The catalytic activity was evaluated in terms of the conversion of Bz, which was analyzed by TCD-GC (catalyst, 0.1 g; reaction temperature, 100 °C; feed rate of Bz, 14 mmol h^{-1}; flow rate of H_2, 120 mmol h^{-1}).

Figure 1 shows typical XRD patterns of NiO/SiO_2 samples with NiO content of 30 wt%. For dried samples, sharp diffraction peaks assigned to the nickel nitrate were observed in the N sample, whereas only a broad halo from amorphous silica gel was observed in the CA sample. For the samples heated at 500 °C, both of them showed diffraction peaks assigned to NiO while the peaks of the N sample were more intense and sharper than those of the CA sample. Further, the widths of the diffraction peaks become broader in the CA sample heated under N_2 flow. In contrast, the particle size of NiO in the N sample was not affected by the atmosphere in heat treatment. The particle sizes of NiO, estimated from integrated widths of the diffraction peaks of (111), (200) and (220) planes, were 10, 5 and 3.5 nm for N, CA-air and CA-N_2 samples, respectively, regardless of NiO content.

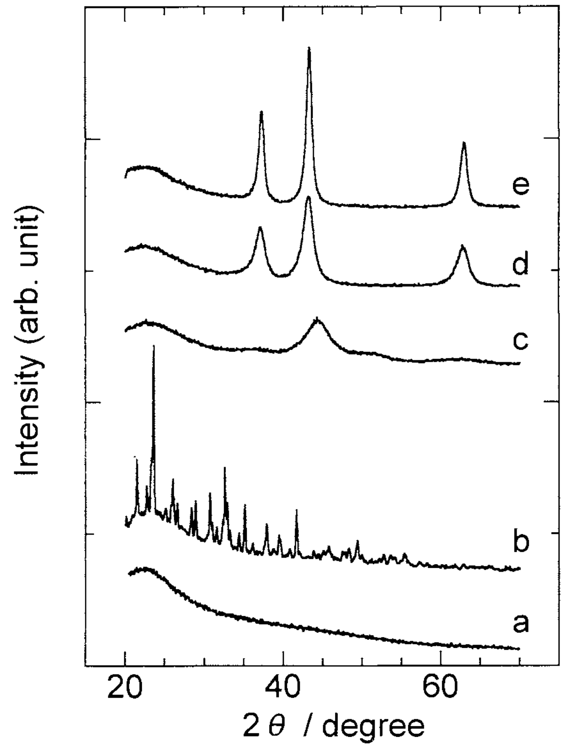

Figure 1. XRD patterns of the samples containing 30 wt% NiO with different heating temperatures. a, CA dried at 50 °C; b, N 50 °C. c, CA heated at 500 °C under N_2 flow; d, CA 500 °C in air; e, N 500 °C in air.

Copyright © 1999 The Chemical Society of Japan

The pore size distributions of the NiO/SiO$_2$ samples, which were obtained from N$_2$ adsorption isotherm at -196 °C, showed maximum at ca. 4 nm in diameter (not shown), except for the N sample containing 30 wt% NiO. This pore diameter is comparable to that of silica gel prepared without Ni species.[5,6] The wet silica gel prepared in the acidic condition is regarded as a highly branched polymeric network rather than an aggregate of particles, and has large voids.[8] The wet gel shrinks to be ca. 1/10 in volume, and the polymeric network turns to particle aggregate during drying, and pore structure of silica is formed.[5,6] It is considered that the pore formation process of silica is not affected by addition of Ni ion or citric acid. Therefore, the difference of the particle size of NiO by the preparation condition will depend on when the aggregation of Ni species occurs in the formation process of silica-gel structure. In the preparation of N samples, nickel nitrate was crystalized during drying. Because a loose network of wet silica gel allows growth and aggregation of the crystal of nickel nitrate, the NiO particle size of calcined N samples becomes larger. When citric acid is used in solution exchange, on the other hand, Ni-citric acid complex is formed.[9] The complex do not crystalize in drying, and is considered to be supported on dried silica gel in molecular scale. In the case, aggregation of the Ni species occurs after the decomposition of the complex. Because the silica gel structure becomes rigid and restricts the growth of NiO, the particle size of NiO becomes smaller. The difference in the particle size of NiO between CA-air and CA-N$_2$ samples will be attributed to the difference in the decomposition temperature of the complex.

The Ni surface area of reduced catalysts and the catalytic activity for the hydrogenation of Bz at 100 °C were shown in Figures 2 and 3, respectively. The differences in the Ni surface area and in the catalytic activity among the preparation methods are small at NiO contents lower than 10 wt%. However, in contrast to the IMP and the EG catalysts, where the increases in Ni surface area and in the catalytic activity with NiO content are small, the Ni surface area of the N series increased linearly with increasing the NiO content even at NiO content > 20 wt%. The conversion of Bz also increased as a similar manner (Figure 3). Further, the Ni surface areas of CA-N$_2$ samples became ca. three times as large as those of the N samples (Figure 2). Assume that all NiO are reduced, the dispersion of CA-N$_2$ samples can be calculated to be ca. 0.1 regardless of the NiO content. We can say that it is possible to enlarge the Ni surface area of reduced catalysts by decreasing the particle size of NiO without affecting the pore structure of silica gel. The CA-N$_2$ catalysts containing NiO > 15 wt% showed superior catalytic activities by comparing with those prepared by conventional methods (Figure 3).

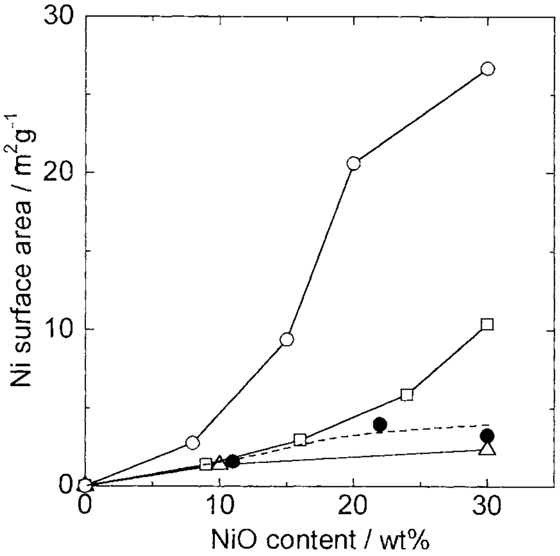

Figure 2. Variations in Ni metal surface areas with NiO content. ○, CA-N$_2$; □, N; ●, IMP; △, EG.

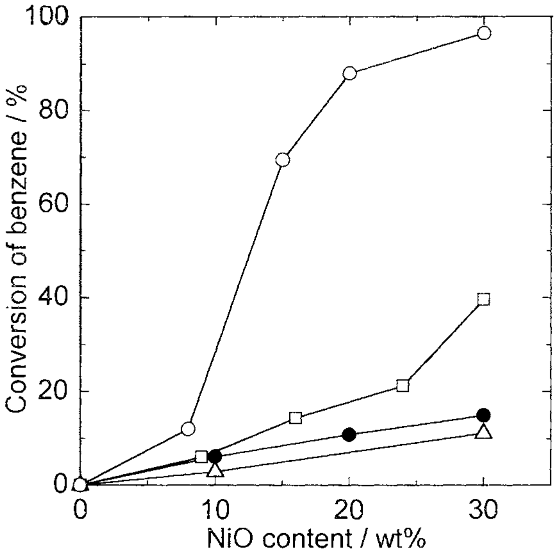

Figure3. Changes in the conversion of Bz with NiO content. ○, CA-N$_2$; □, N; ●, IMP; △, EG.

In conclusion, Ni/SiO$_2$ catalysts with controlled pore size and Ni particle size were prepared by solution exchange of wet silica gel derived from sol-gel process. The size of NiO particle in the unreduced sample can be controlled in ca. 3-4 nm regardless of the NiO content up to 30 wt% when the citric acid was used in the solution exchange. They exhibited high nickel metal surface areas and excellent catalytic activities for the hydrogenation of Bz.

References and Notes

1 K. Morikawa, T. Shirasaki, and M. Okawa, *Adv. Catal.*, **20**, 97 (1969).
2 A. Ueno, H. Suzuki, and Y. Kotera, *J. Chem. Soc., Faraday Trans.*, **79**, 127 (1983).
3 K. Tohji, Y. Udagawa, S. Tanabe, and A. Ueno, *J. Am. Chem. Soc.*, **106**, 612 (1984).
4 B. Breitscheidel, J. Zieder, and U. Scubert, *Chem. Mater.*, **3**, 559 (1991).
5 R. Takahashi, K. Nakanishi, and N. Soga, *J. Non-Cryst. Solids*, **189**, 66 (1995).
6 R. Takahashi, K. Nakanishi, and N. Soga, *Faraday Discuss.*, **101**, 249 (1995).
7 P. Scherrer, *Gottinger Nachrichten*, **2**, 98 (1918).
8 C. J. Brinker, *J. Non-Cryst. Solids*, **100**, 30 (1988).
9 T. Nakayama, N. Ichikuni, S. Sato, and F. Nozaki, *Appl. Catal. A*, **158**, 185 (1997).