October, 1983] © 1983 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 56, 2941—2944 (1983) 2941

Particle Size of Nickel in Nickel-Alumina Catalysts and Its Effects on Propene Hydrogenation

Yoriko Takai, Akifumi Ueno,* and Yoshihide Kotera
Department of Materials Science, Toyohashi University of Technology, Tempaku-cho, Toyohashi 440

(Received November 30, 1982)

The particle size of nickel in Ni/Al_2O_3 catalysts prepared by the alkoxide technique is well controlled by changing the metal concentration in the catalyst. The rate of propene hydrogenation over the catalyst increases with decrease in Ni particle size, and this phenomenon is explained on the assumption that nickel atoms located on edges and/or corners of crystallites may contribute predominantly to the hydrogenation of propene.

The relation between dispersion states and catalytic behavior of a metal has been of current interest in the field of catalysis, since it was reported that physical properties of a fine metal particle should be different from those of bulk metal when the particle size is smaller than 100 Å.[1] Boudart[2] proposed that there are two types of catalytic reactions, each called the structure sensitive reaction and the structure insensitive reaction. The hydrogenation of ethylene, cyclopropane, or benzene on Pt/Al_2O_3 is considered to be structure insensitive,[3] while the hydrocracking, isomerization, and dehydrocyclization of 2-methylpentane are likely to be structure sensitive.[4] For a structure sensitive reaction, Brunelle *et al.*[5] tried to explain the effect of metal particle size on reaction selectivity by assuming a simple geometrical arrangement of metal atoms exposed on the surface of crystallite. Otero-Schipper *et al.*[6] also applied the idea to the hydrogenation of propene or butadiene on Pt/Al_2O_3 catalyst. The idea of simple geometrical arrangement was first proposed by van Hardeveld and van Montfoort[7] and developed by Anderson.[8] On the contrary, Primet *et al.*[9] studied the influence of metal particle size on chemisorption properties of supported platinum by means of infrared spectroscopy. They discussed size effects on the basis of an idea that electronic properties of a metal would change with its particle size when it is less than 100 Å.

In the present work the hydrogenation of propene was studied on Ni/Al_2O_3 catalysts prepared by the alkoxide technique.[10] The nickel metal particle size was well controlled by adjusting the metal concentration in the catalyst. The rate of hydrogenation increased with decrease in the metal particle size and this was interpreted by an assumption that the reaction would take place preferentially on nickel atoms located on edges and/or corners of crystallites.

Experimental

Catalyst Preparation. The catalyst employed was Ni/Al_2O_3 prepared by hydrolysis of a mixed solution of aluminium isopropoxide dissolved in butyl alcohol and nickel nitrate dissolved in ethylene glycolate: The nickel nitrate was heated at 90 °C to remove water *via* $Ni(NO_3)_2 \cdot 6H_2O \longrightarrow Ni(NO_3)_2 \cdot H_2O$, and the butyl alcohol and ethylene glycolate were distilled before use; about 5.0 g of nickel nitrate was dissolved in ethylene glycolate at 80 °C. Depending upon the concentration of nickel in the designed catalyst, the corresponding amount of this solution was poured into the aluminium isopropoxide dissolved in butyl alcohol and stirred at 80 °C in an N_2 atmosphere. Water was then added to the mixed solution. The volume of water added was about 4 times the volume of aluminium isopropoxide employed. The solution was stirred at 80 °C for 4 h and then cooled to room temperature without stirring. A gel was obtained, filtered, and dried at 110 °C in an oven. The powder thus obtained was calcined at 500 °C for 4 h in air and then reduced with hydrogen at 500 °C for 4 h. The loading of Ni ions on the catalyst could be controlled by varying the concentration of nickel nitrate in the mixed solution employed. The Ni ions in the catalyst were extracted by heating the catalyst in an aqueous solution of nitric acid and the concentration of nickel ions was determined with a X-ray fluorescence spectrometer. In the present experiment the concentrations of nickel in the catalysts prepared were 0.39, 0.78, 3.96, and 13.9 wt%.

Measurement of Particle Size of Nickel Metal by Transmission Electron Micrography. The particle size of Ni in the catalyst was measured with a transmission electron microscope (TEM) operated at an accelerating voltage of 75 kV (Hitachi, H-300). The sample was first ground in an agate mortar and then suspended in water or ethyl alcohol by using supersonic waves. Some of the finest parts of the suspension was pipetted onto a microgrid covered with collodion film (400 mesh, Nisshin Film Co.). Micrographs were obtained with an instrumental magnification of ×50000 and enlarged with ×2 for print.

Measurement of Mean Particle Size by Hydrogen Chemisorption. After the reduction of catalyst samples at 500 °C, they were evacuated at the same temperature for 3 h and cooled to room temperature to be sebjected to hydrogen chemisorption measurement. The measurement was carried out by using an absolute pressure gauge (MKS Baratoron type 222B) in the hydrogen pressure range 5—50 mmHg (1 mmHg = 133.322 Pa) as registered at adsorption equilibrium. The volume adsorbed was determined by extrapolating the linear part of the isotherm to zero pressure as proposed by Hall and Wilson.[11] The specific surface area of Ni in the catalyst was estimated on the assumption that a nickel atom will occupy an area of 6.8 $Å^2$ [12] and the mean particle size was calculated by

$$d = 5/\rho S,$$

where ρ is the density of nickel metal and S is the specific surface area of nickel particle in the catalyst. In this calculation nickel particles were assumed to be in the f.c.c. packing.

Magnetic Measurement of Nickel Reduced to Metal. In order to obtain the specific surface area of nickel in a catalyst, the fraction of nickel reduced to metel should be estimated, because hydrogen adsorbs on metallic nickel but not on Ni cations in the catalyst. After the reduction of catalyst samples, they were loaded on a vibrating sample magnetometer (Toei Kogyo Co., Model VSM-2) at a vibration frequency of 80 kHz with a magnetic field strength up to 10 kOe†. The

---

† $1\ Oe = (1000/4\pi)\ A\ m^{-1}$.

TABLE 1. MEASUREMENT OF SATURATION MAGNETIZATION OF CATALYSTS AND THE FRACTIONS REDUCED TO METAL

Ni Concentration/wt%	Reduction temperature/°C	Time/h	Saturation magnetization[a] of Ni in catalyst /emu cm^3 g^{-1}	Fraction of Ni metal/%
0.39	500	2	0.0671	23.6
0.78	500	2	0.1000	31.7
3.96	500	2	0.6850	31.9
3.96	500	4	0.7250	33.7
3.96	700	4	1.250	58.2
13.9	500	2	2.370	31.4

a) Saturation magnetization of Ni: 54.39 emu cm^3 g^{-1}.

magnetization was measured at room temperature. One problem in the measurement was the exposure of the reduced catalyst to air a few minutes while being packed into the sample holder.

Particle Size Effects on Reaction Rate. As a model reaction the hydrogenation of propene was selected since Ni catalysts are often employed for the hydrogenation of olefinic hydrocarbons. The reaction was carried out at 50 °C with a closed circulating reactor, made of glass, containing about 0.5 g of catalyst. Feed gases were usually composed of propene and hydrogen each of 20 cmHg pressure. Gas products were analyzed with a gas chromatograph equiped with columns packed with molecular sieves 13X and Polapak Q. The rate of propene hydrogenation was calculated from the amount of propane produced during the initial 5 min of reaction.

Results

Particle Size of Nickel Measured by TEM and H_2 Chemisorption. Typical photographs obtained by TEM are shown in Fig. 1 for the 0.78, 3.96, and 13.9 wt% Ni/Al_2O_3 catalysts. The particle size distributions were obtained by measuring 500—1000 particles in the photographs. Unfortunately, no qualified photographs were obtained for the 0.39 wt% Ni/Al_2O_3 catalyst so as to allow the determination of particle size distribution. It must be mentioned that small nickel particles often coagulated with each other when irradiated by an electron beam from the microscope.

The mean particle size obtained by hydrogen chemisorption measurements is given in Fig. 3. The mean particle size increases with increase in the concentration of nickel in the catalyst. To obtain the mean particle size, the specific surface area of Ni was calculated by

$$S/\text{Å} = 13.6\ VN_AR^{-1},$$

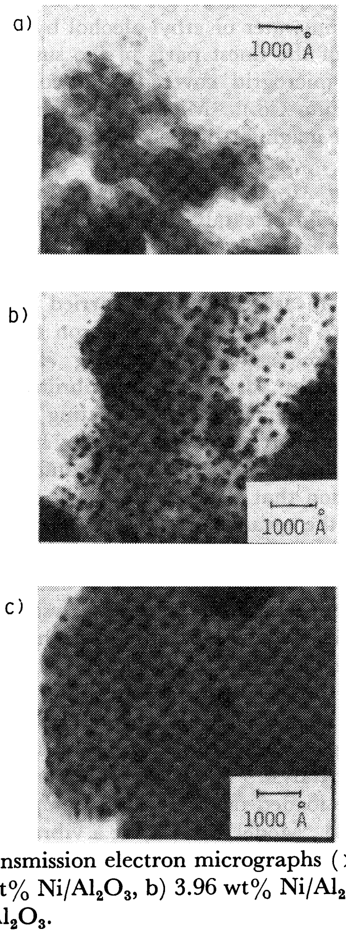


Fig. 1. Transmission electron micrographs (×10^5).
a): 0.78 wt% Ni/Al_2O_3, b) 3.96 wt% Ni/Al_2O_3, c): 13.9 wt% Ni/Al_2O_3.

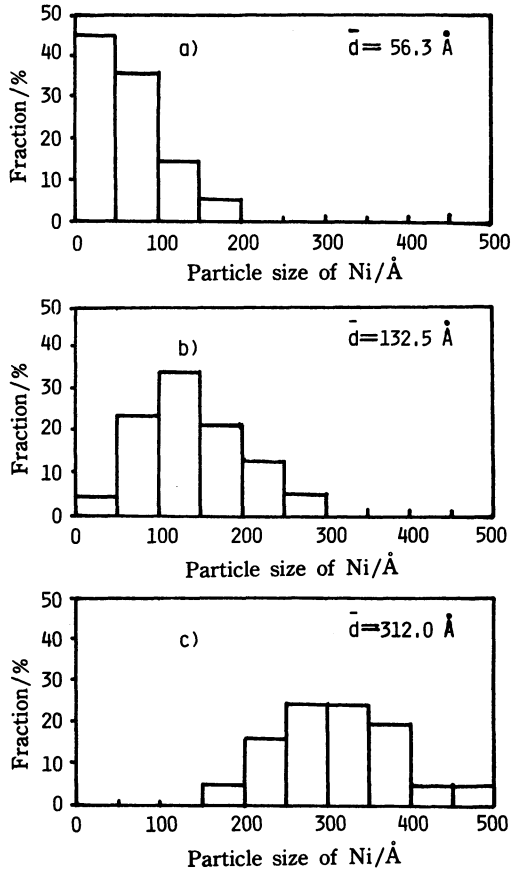


Fig. 2. Particle size distribution of Ni in Ni/Al_2O_3 catalyst.
a): 0.78% Ni/Al_2O_3, b): 3.96% Ni/Al_2O_3, c): 13.9% Ni/Al_2O_3.

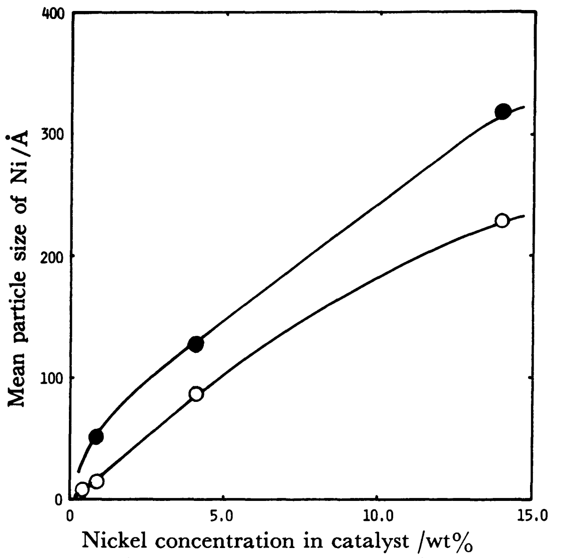


Fig. 3. Relationship between mean particle size of Ni and nickel concentration in Ni/Al_2O_3 catalyst.
—○—: Calculated from hydrogen chemisorption, —●—: measured by transmission electron micrograph.

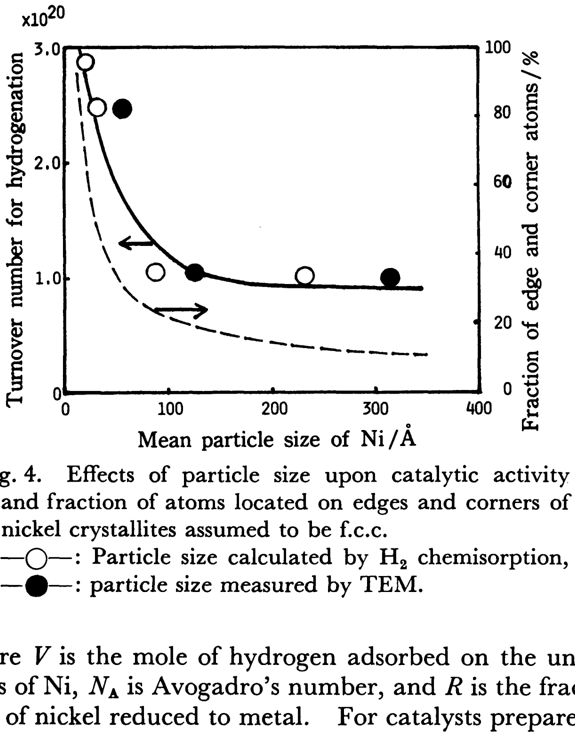


Fig. 4. Effects of particle size upon catalytic activity and fraction of atoms located on edges and corners of nickel crystallites assumed to be f.c.c.
—○—: Particle size calculated by H_2 chemisorption, —●—: particle size measured by TEM.

where V is the mole of hydrogen adsorbed on the unit mass of Ni, N_A is Avogadro's number, and R is the fraction of nickel reduced to metal. For catalysts prepared by the usual impregnation method the fraction of metal reduced is almost 1.0, while for the present catalysts it was as low as 0.3 (Table 1).

Magnetic Measurements. Measurements were made for the saturated magnetization of Ni with catalysts reduced by hydrogen at 500 and/or 700 °C (Table 1). Since the saturated magnetization of Ni is 34.59 emu $cm^3\,g^{-1}$,[13] the fraction of nickel reduced to metal was calculated from the magnetization observed, the results being given in Table 1.

Effects of Ni Particle Size on the Rate of Propene Hydrogenation. The rate obtained for the initial 5 min of reaction was expressed in terms of (the number of the molecules of propane formed per min)/(the number of the nickel atoms exposed on the surface), which is the so-called turnover number. In Fig. 4, the turnover number increased with decrease in the particle size when the size was less than 50 Å, indicating that a size effect is involved in the propene hydrogenation on Ni/Al_2O_3 catalyst.

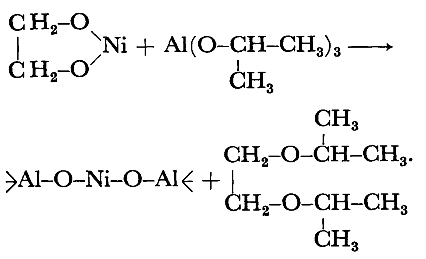
Discussion

The most important factor for studying effects of particle size on catalytic activity is that the catalyst should be free from any impurities which will affect the activity. In the present work, the catalyst was prepared by the alkoxide technique, because one of the best methods of obtaining a pure metal oxide is hydrolysis of its alkoxide in a proper solvent. It has been reported that most metals form their alkoxides by the reaction between metal chloride and sodium alkoxide in the presence of an excess of alcohol and a hydrocarbon solvent.[14] The elimination of the chlorine and sodium ions from alkoxides thus prepared is difficult. It was reported that a well dispersed Ni/Al_2O_3 catalyst was prepared by using a mixture of aluminium *s*-butylate and nickel acetate.[15]

A highly dispersed Ni/SiO_2 was prepared[10] by hydrolysis of a mixture of nickel nitrate dissolved in ethylene glycolate and ethyl silicate. In this work aluminium isopropoxide dissolved in butyl alcohol was employed in place of ethyl silicate in hope of formation of the Ni–O–Al structure in the catalyst since the Ni–O–Si structure was observed by infrared spectroscopy in Ni/SiO_2 catalyst as mentioned in the previous paper.[10] Although the Ni–O–Al structure was not identified here by infrared spectroscopy, we believe the formation of the structure in the catalyst thus prepared. This will be discussed later.

Homogeneous dispersion of metal particles is also important to investigate the relation between particle size and activity. The particle size of Ni in the catalyst thus prepared was measured by use of hydrogen chemisorption, leading to a conclusion that the mean particle size is well controllable by varying the concentration of Ni in the catalyst. At a glance over the photographs shown in Fig. 1, it is clear that the size of the Ni particles are almost the same with each other. The size distribution of nickel shown in Fig. 2 also indicates that the nickel particles are controlled so as to be in an even size level, although the mean particle sizes calculated from the results by TEM are larger than those obtained by hydrogen chemisorption. The particles of Ni in the 0.39 wt% Ni/Al_2O_3 catalyst may be too small to be observed by TEM.

The nickel ions in the catalyst prepared by the usual impregnation method are ready to be reduced by hydrogen at 500 °C, while the nickel ions in the present catalyst prepared by the alkoxide technique are hard to be reduced under the same conditions. The fraction of the nickel reduced to metal was determined by measuring the saturation magnetization of Ni in the catalyst. The magnetization would be affected by the nickel particle size,[16] but this effect was ignored here in calculating the fraction of nickel reduced. The low fraction of nickel metal in the present catalyst suggests that the nickel cations in the catalyst are strongly bound to the Al_2O_3 support. This interaction is due to formation of the Ni–O–Al structure possibly *via* the reaction between cyclic glycolate of nickel and aluminium isopropoxide



$$\begin{array}{l}\mathrm{CH_2\text{-}O} \\ |\qquad\;\rangle\mathrm{Ni} + \mathrm{Al(O\text{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}\text{-}CH_3)_3} \longrightarrow \\ \mathrm{CH_2\text{-}O} \end{array}$$

$$\rangle\mathrm{Al\text{-}O\text{-}Ni\text{-}O\text{-}Al}\langle + \begin{array}{l}\mathrm{CH_2\text{-}O\text{-}\overset{\displaystyle CH_3}{\overset{|}{C}H}\text{-}CH_3.} \\ | \\ \mathrm{CH_2\text{-}O\text{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}\text{-}CH_3}\end{array}$$

In this sense, Ni atoms may be atomically dispersed in the bulk of alumina and hence they are hardly reduced by hydrogen. The fraction of Ni reduced to metal increased gradually with increase in the reduction temperature (see Table 1).

Thus, it was confirmed that the particle size can be controlled by the concentration of Ni in the catalyst and that the particles are well dispersed in an even size level, when the catalyst is prepared by the alkoxide technique. Accordingly, a discussion on the relation between particle size and catalytic activity will be available. The hydrogenation of propene was employed as a model reaction since Ni catalysts are often used for hydrogenation processes. It is well known that catalytic hydrogenation of an olefin accompanies hydrocracking at higher temperatures, so the reaction was carried out at 50 °C where no hydrocracking takes place. The amount of propane formed is in a linear relation with reaction time during the initial 5 or 10 min of reaction. The rate of hydrogenation was estimated from the slope for the initial 5 min. The relation between the catalyst is shown in Fig. 4. It was found that the rate significantly increased when the particle size became smaller than 50 Å. Schwab(17) proposed that catalytic reactions might be divided into two groups; one consists of donor reactions in which the rate determining step involves an electron transfer from the reactant molecule to the catalyst and the other consists of acceptor reactions where the reactant must accept an electron from the catalyst. Hydrogenation belongs to the group of donor reactions so that an electron transfers to the catalyst from the reactant. Since it was reported that electrons in a metal particle will move to the carrier when the particle size is so small,(18) the observation is understandable that the rate of hydrogenation was enhanced when the size of nickel particle was less than 50 Å. Three kinds of nickel atoms may be considered to exist on the surface of particles; one is a nickel atom located on the surface plane of a crystallite and the other two are those on the edge and corner of a crystallite, respectively. The fraction of the atoms located on edges and corners of crystallites is a function of the dimension of the crystallite and the fraction is shown in Fig. 4 on an assumption that the Ni particles are f.c.c. crystallites.(7,8) The turnover number for nickel atom for the hydrogenation is also plotted against particle size in Fig. 4. Both the curves are similar to each other, suggesting that the hydrogenation might taken place over the nickel atoms located on edges and corners of crystallites. There will be a question why the atoms on edges and corners are more active for the hydrogenation. Mott and Davis(19) describe that atoms on edges and corners have two and three dangling bonds, respectively, whereas those located on surface planes have one such bond, and that the total energies (electron plus lattice) of a crystallite are lowered by the interaction of these dangling bonds: $2D^0$ $D^+ + D^-$, where D^0 is a dangling bond unperturbed, D^+ is a dangling bond from which an electron is released, and D^- is a dangling bond to which an electron has moved. In the present nickel particles, it might be possible that electrons in the dangling bonds of nickel atoms at the edges and corners will transfer to the dangling bonds of the nickel atoms located on surface planes. This will result in an enhancement of the positive character of nickel atoms located on edges and corners, hence the activity for olefin hydrogenation will also be enhanced.

The present authors would like to express their thanks to Drs. J. Tasaki, Y. Murase, and T. Mori at the Japanese Government Industrial Research Institute, Nagoya for the measurement of saturation magnetization and transmission electron micrograph.

References

1) R. Kubo, *J. Phys. Soc. Jpn.*, **17**, 975 (1962).

2) M. Boudart, *Adv. Catal.*, **20**, 153 (1960).

3) M. Boudart, *Proc. 6th Int. Congr. Catal.*, p. 1 (1976).

4) J. M. Dartigues, A. Chmbellan, and F. G. Gault, *J. Am. Chem. Soc.*, **98**, 856 (1976).

5) J. P. Brunelle, A. Sugier, and J. F. LePage, *J. Catal.*, **43**, 273 (1976).

6) P. H. Otero-Schipper, W. A. Wachter, J. B. Butt, R. L. Burwell, and J. B. Cohen, *J. Catal.*, **50**, 494 (1977).

7) R. van Hardeveld and A. van Montfoort, *Sur. Sci.*, **4**, 396 (1964).

8) J. R. Anderson, "Structure of Metallic Catalyst," Academic Press, New York (1975).

9) M. Primet, J. M. Basset, E. Garbowski, and M. V. Mathieu, *J. Am. Chem. Soc.*, **97**, 3655 (1975).

10) A. Ueno, H. Suzuki, and Y. Kotera, *J. Chem. Soc., Faraday Trans. 1*, **79**, 127 (1983); H. Suzuki, S. Takasaki, F. Koga, A. Ueno, and Y. Kotera, *Chem. Lett.*, **1982**, 127.

11) G. R. Wilson and W. K. Hall, *J. Catal.*, **17**, 190 (1970); E. Kikuchi, K. Ito, T. Ino, and Y. Morita, *J. Catal.*, **46**, 382 (1977).

12) D. G. Mustard, and C. H. Bartholomew, *J. Catal.*, **67**, 186 (1981).

13) "Kagaku Binran (Kiso-hen II)," ed by the Chemical Society of Japan, Maruzen, Tokyo (1975), p. 1233.

14) D. Bradley, R. Mehrotra, and D. Gauer, "Metal Alkoxides," Academic Press, New York (1978).

15) M. Astier, A. Bertrand, D. Bianchi, A. Chenard, G. E. E. Gardes, G. Pajonk, M. B. Taghavi, S. J. Teichner, and B. L. Villemin, "Preparation of Catalyst," ed by B. Delmon, P. A. Jacobs, and G. Poncelot, Elsevier, Brussels (1976), p. 315.

16) P. W. Selwood, *J. Phys. Chem.*, **70**, 3003 (1966).

17) G. M. Schwab, *Adv. Catal.*, **27**, 1 (1978).

18) K. Forger and J. R. Anderson, *J. Catal.*, **54**, 318 (1978).

19) N. F. Mott and E. A. Davis, "Electronic Process in Noncrystalline Materials," Clarendon Press, Oxford (1979), p. 465.