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A NEW METHOD TO CONTROL NICKEL METAL PARTICLE SIZE IN Ni/SiO$_2$ CATALYST

Hideo SUZUKI, Seiji TAKASAKI, Fumio KOGA, Akifumi UENO*,
Yoshihide KOTERA, Toshio SATO° and Naoyuki TODO†

School of Materials Science, Toyohashi University of
Technology, Tempaku-cho, Toyohashi-shi, Aichi-ken 440
† National Chemical Laboratory for Industry,
Yatabe-cho, Tsukuba-gun, Ibaragi-ken 305

Techniques to control metal particle size in a supported catalyst, where metal particles may be fixed on a support by forming chemical bonds with oxygen atoms in a support, were investigated. The effect of metal particle size on a reaction selectivity was elucidated in terms of the ratio of numbers of the edge and corner atoms to those of the surface total atoms in the metal crystallites.

It is of current interest to control metal particle size in a supported catalyst. Most of this sort of works were performed by impregnation techniques with changing metal ions concentration.1~4) Metals in catalysts thus prepared were on the surface of carriers merely with physical interaction such as van der Waals force. Accordingly, the metal particles are easy to aggregate when the catalysts are treated at high temperatures. Yermakov5) and, more recently, Iwasawa6) prepared Mo-fixed catalysts from a reaction between $Mo(\pi\text{-}C_3H_5)_4$ and the surface OH groups of SiO$_2$. The control of metal particle size, often, resulted in an enhancement of a reaction selectivity.7~9) Boudart et al.10) proposed that there are two types of catalytic reactions; structure sensitive and insensitive.

In this communication, techniques to control Ni particle sizes in a silica supported catalyst, where Ni particles may be fixed by forming chemical bonds with oxygen atoms in the support, were studied. The effects of Ni particle sizes on the selectivity for alcohol formation in the reaction of propionaldehyde with H$_2$ were also investigated.

Ni-supported silica catalyst was prepared by hydrolysis of the mixed solution of ethyl silicate and Ni(OH)$_2$ dissolved in ethylene glycol at 80°C.

The precipitate thus obtained was dried at 110°C, followed by calcination at 400°C for 4~5 h in air and then reduced at 400°C in H_2 stream for 3~4 h. The samples, after the calcination in air, were submitted to an infrared analysis by KBr pellet method. As can be seen in Fig.1, three bands were observed in the region of 1200 to 700 cm^{-1}. The bands at 1100 and 810 cm^{-1} have been assigned to the lattice vibrations of SiO_2. While the band at 975 cm^{-1} may be due to the species of Si-O-Ni, since it has been reported that compounds containing Si-O-M (M represents a metal such as Ti, Zr or Fe) species have their characteristic absorption bands between 1000 and 900 cm^{-1}.[11,12] The ratio of the band intensity at 975 to that at 810 cm^{-1} was calculated with changing Ni concentration in the catalysts(Fig.2). The concentration of the species of Si-O-Ni increases with increase in Ni loading in the catalyst. These results lead us to the conclusion that Ni atoms would be fixed on the support by forming chemical bonds with oxygen atoms in SiO_2.

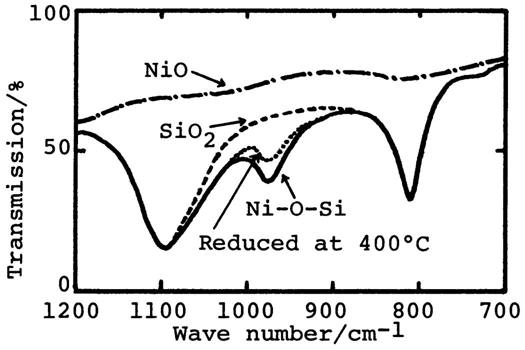


Fig.1 Infrared spectrum of Ni/SiO_2 catalyst

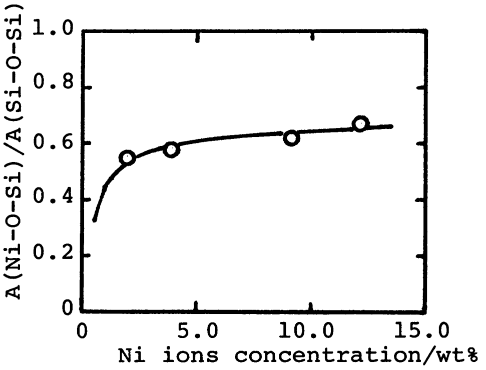
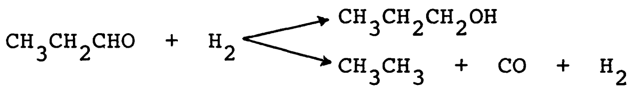


Fig.2 Absorption ratio of Ni-O-Si to Si-O-Si

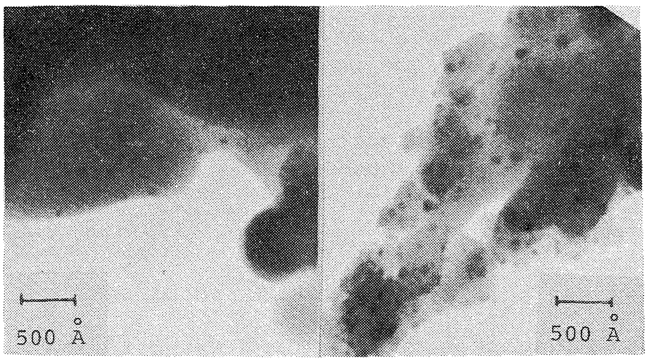
Ni particle sizes and their distributions were measured by transmission type of electron microscope (TEM) and small angle X-ray scattering (SAXS), respectively. TEM was operated at an accelerating voltage of 75 kV with an instrumental magnification of x 50,000. The micrographs obtained were enlarged by 4 times when printed. Some of the micrographs are shown in Fig.3. For the SAXS measurements, 1,2-dichloroethane was employed as a pore maskant[13], since its electron density is almost equal to that of SiO_2. The particle size distributions obtained are shown in Fig.4 and summarized in Table 1 with the results obtained by TEM.

The effects of Ni particle size on a reaction selectivity were studied for the hydrogenation of propionaldehyde at 200°C. The hydrogenation of the aldehyde accompanies the decomposition of the aldehyde as follows:



$$CH_3CH_2CHO + H_2 \begin{cases} \rightarrow CH_3CH_2CH_2OH & (1) \\ \rightarrow CH_3CH_3 + CO + H_2 & (2) \end{cases}$$

Hence, the selectivity for the hydrogenation of propionaldehyde can be obtained by the measurements of the amounts of propyl alcohol and CO (or ethane) formed during the reaction. The reaction was carried out using a conventional closed circulating reactor with ~0.5 g of the catalyst. The feed gases were usually composed of ~12 cmHg of propionadehyde and ~30 cmHg of hydrogen. The gases were analysed by gas chromatography using columns packed with molecular sives 13X and polyester FF. The typical result obtained for the reaction at 200°C was shown in Fig.5. The selectivities for the hydrogenation were measured on the Ni/SiO_2 catalysts, which contained Ni particles controlled in an even size. The selectivities were expressed in terms of the ratio of propyl alcohol formed to carbon monoxide formed in the first 15 min. of the reaction. The results calculated are shown in Fig.6.



2.2% Ni 12.6% Ni

Fig.3 Electron micrograph of Ni/SiO_2

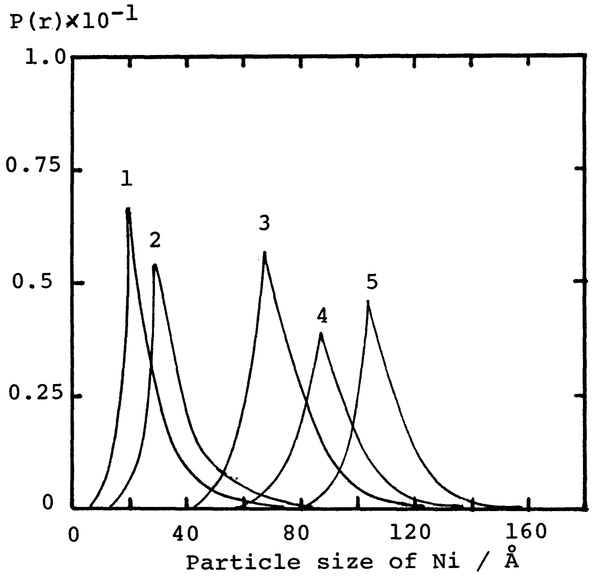


Fig.4 Particle size distribution of Ni

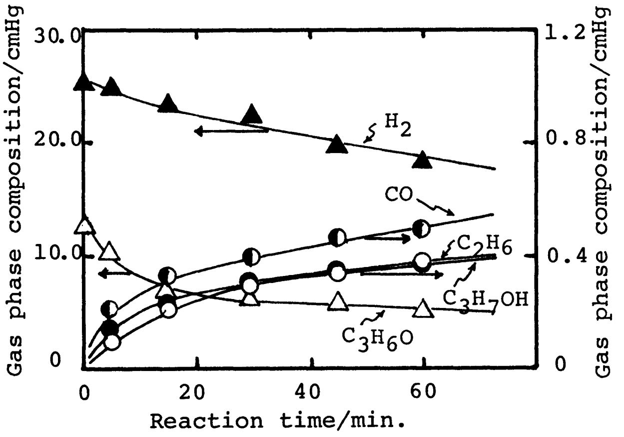


Fig.5 Hydrogenation and decomposition of Propionaldehyde at 200°C

Cat.NO.	Ni conc.	SAXS	TEM
1	2.2%	20Å	25Å
2	4.3	30	40
3	9.2	70	60
4	12.4	85	75
5	25.8	105	95

Table 1 Particle size of Ni from SAXS and TEM

The selectivity for hydrogenation was much enhanced when the particle size of Ni in the catalyst was smaller than 50 Å. This result could be explained by the calculation of the ratio of the edge and corner Ni atoms to the total Ni atoms on the surface of Ni crystallite. Hardeveld and Montfoort[14) reported that the fraction of Ni atoms located on the edge and corner of Ni crystallite (assumed f.c.c.) becomes higher when the crystalline size becomes smaller than 50 Å, just as shown in Fig.6.

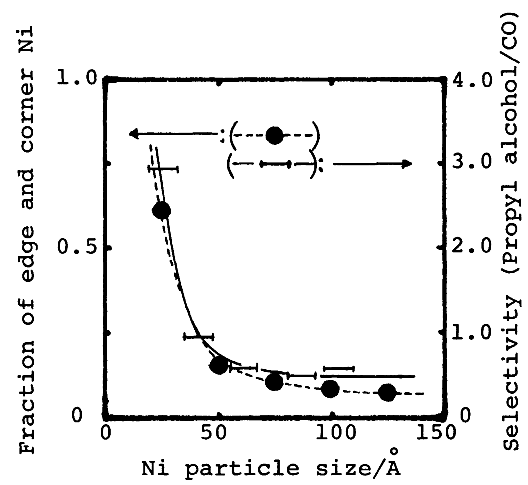


Fig.6 Selectivity for hydrogenation

Accordingly, the hydrogenation of the aldehyde might occur on Ni atoms located on the edge or the cornner of the crystallite, while the decomposition might take place on Ni atoms located on the plane surface of the crystallite.

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