Particle-size Distribution of Nickel Dispersed on Silica and its Effects on Hydrogenation of Propionaldehyde

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Techniques to control metal particle size in a supported catalyst have been investigated. The mean particle size of nickel increases with an increase in the concentration of metal in the catalyst, varying from 2.2 to 25.8% in weight. The effects of metal particle size on reaction selectivity are explained in terms of the fraction of metal atoms located at the corners and edges in the metal crystallites. During the reaction of propionaldehyde with hydrogen on the catalyst, hydrogenation may occur on the metal atoms located at the corners or edges of the crystallites, while the decomposition of the aldehyde may take place on the metal atoms located on the plane surface of the crystallites.

It is currently of interest to elucidate the effect of particle size on the catalytic behaviour of metals since it has been reported that the physical properties of a fine metal particle should be different from those of the bulk metal when the particle size is < 100 Å.¹ Changes in the physical properties of a metal should cause changes in its activity and/or selectivity when used as a catalyst. Primet et al.² investigated the influence of metal particle size on the chemisorption properties of supported platinum by means of infrared spectroscopy. They found that the stretching frequency of NO irreversibly adsorbed on the metal is dependent on particle size, and they interpreted this in terms of back-donation to the π^* orbitals of NO⁺ on the metal. Page *et al.*³ tried to elucidate the effect of particle size on reaction selectively by assuming a simple geometric arrangement of metal atoms exposed on the surface of the crystallite. Burwell et al.⁴ also applied this idea to the hydrogenation of cyclopropane, methylcyclopropane and propene. Thus the influence of particle size on the catalytic properties of a metal can be explained by a change in the electronic structure of the metal or by the geometric structure of the metallic deposit. Not all metals exhibit changes in their catalytic properties when they are in a state of high dispersion. Boudart et al.⁵ proposed that there are two types of catalytic reactions, termed structure-sensitive and structure-insensitive. The hydrogenation of ethylene, cyclopropane or benzene on $Pt/Al_2O_3^6$ is considered to be structure-insensitive, while the hydrocracking, isomerization or dehydrocyclization of 2-methylpentane⁷ would be a structure-sensitive reaction.

In the present work techniques to control the size of nickel particles in a silica-supported catalyst were studied in order to reveal the effect of particle size on selectivity for alcohol formation in the reaction of propionaldehyde and hydrogen. Changes in selectivity are explained by the ideas proposed by Hardeveld *et al.*⁸ and Anderson⁹ on the assumption that the nickel particles are present in the form of f.c.c. crystallites.

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EXPERIMENTAL

CATALYST PREPARATION

The catalyst employed was Ni/SiO₂ and was prepared by hydrolysis of a mixed solution of ethyl silicate and nickel hydroxide dissolved in ethylene glycol. The nickel hydroxide was heated at 90 °C to remove water, *i.e.*

 $Ni(OH)_2 \cdot 6H_2O \xrightarrow{90^{\circ}C} Ni(OH)_2 \cdot H_2O$

and the ethyl silicate and ethylene glycol were distilled before use. Ca. 400 mg of the nickel hydroxide was dissolved in 150 cm³ of ethylene glycol at 90 °C. Depending upon the desired concentration of Ni in the catalyst, an appropriate amount of this solution was poured into the ethyl silicate and stirred for 3 h at 90 °C in a dry N₂ atmosphere. Water was then added to the mixed solution in the ratio 4:1 by volume to the amount of the ethyl silicate employed and stirred at 90 °C for a further 5 h. The solution was then cooled to room temperature and kept at that temperature overnight without being stirred.

The fine precipitates thus obtained were filtered and dried at 110 °C in an oven and then calcined at 450 °C in air for 4 h, followed by reduction at the same temperature for 4 h in a H_2 stream. The loading of Ni ions in the catalyst could be controlled by varying the concentration of nickel hydroxide in the mixed solution employed. The concentration of Ni ions in the catalyst was measured by X-ray fluorescence spectroscopy after the extraction of the Ni ions with hot nitric acid. In the present experiments these concentrations in the catalysts were 2.2, 4.3, 9.2, 12.4 and 25.8 wt %, respectively.

MEASUREMENTS OF NICKEL PARTICLE SIZE BY TRANSMISSION ELECTRON MICROSCOPY

The particle size of Ni in the catalyst was monitored by transmission electron microscopy (TEM) operated at an accelerating voltage of 75 kV (Hitachi). The sample was first ground in an agate mortar and then suspended in water or ethyl alcohol using a supersonic wave. Some of the finest part of the suspension was pipetted onto a microgrid covered with Collodion film (400 mesh, Nisshin Film Co). The micrographs were obtained with an instrumental magnification of \times 50000 and are enlarged 3 times as printed.

MEASUREMENTS OF THE PARTICLE-SIZE DISTRIBUTION BY SMALL-ANGLE X-RAY SCATTERING

The size of Ni particles in the catalyst and its distribution were also determined by means of the small-angle X-ray scattering (SAXS) technique. The scattering intensity was measured by a scintillation counter fitted with a line-focussed Cu X-ray tube (45 kV, 50 mA) employing a Ni filter. The scattered X-ray was mechanically scanned at a $\Delta 2\theta$ per min rate of 0.25 over the range $0.2 \leq 2\theta/^{\circ} \leq 0.5$. Scattering from micropores in the support was eliminated by the use of 1,2-dichloroethane as a pore maskant,¹⁰ since the electron density of silica is nearly equal to that of 1,2-dichloroethane. The catalyst was evacuated at 100 °C prior to adsorption of the maskant. From the intensity curves plotted as a function of diffraction angle, the Guinier radius ($R_{\rm g}$) and the Porod radius ($R_{\rm p}$) were calculated according to the equations given by Whyte *et al.*¹⁰ These parameters were used to plot the particle-size distribution curves with the assumption that the sizes are distributed log-normally.¹¹

INFRARED MEASUREMENTS

In order to determine the state of bonding of the Ni ions or metallic particles to the carrier, infrared spectroscopy (Japan Spectroscopy Co, model IR-A-3) was applied using the conventional KBr-pellet technique. Attention was mainly paid to the region 1200-700 cm⁻¹, since all the infrared absorption bands due to the present catalysts appear in this region.

Plate 1



PLATE 1.—Transmission electron micrographs of Ni particles in Ni/SiO₂ catalysts after reduction by H₂ at 450 °C for 4 h. Percentage of Ni/SiO₂ as follows: (a) 2.2, (b) 4.3, (c) 9.8, (d) 12.6, (e) 25.4.

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Plate 2



(a)



(b)

PLATE 2.—Transmission electron micrographs of Ni particles in 2.2°_{-0} Ni/SiO₂ catalyst reduced by H₂ at (a) 500 and (b) 600 °C for 4 h.

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MAGNETIC MEASUREMENT OF NICKEL REDUCED TO METAL

In order to determine the fraction of nickel reduced to metal, the catalyst was applied to a vibrating-sample magnetometer (Toei-kogyo Co, model VSM-2) at the Government Industrial Research Institute, Nagoya. The catalyst was reduced at various temperatures and then submitted to the magnetometer at a vibration frequency of 80 kHz with a magnetic field strength of up to 5 kOe. The magnetisation was measured at room temperature. One problem in making these measurements was that the reduced catalyst was exposed to air for a few moments when being packed into the sample holder.

PARTICLE-SIZE EFFECT ON REACTION SELECTIVITY

As a model reaction the hydrogenation of propionaldehyde was selected, since the catalytic hydrogenation of the aldehyde generally accompanies the decomposition of the aldehyde as follows:

$$CH_{3}CH_{2}CH_{2}OH \qquad (1)$$

$$C_2H_6 + CO + H_2.$$
 (2)

Accordingly, the selectivity for hydrogenation was calculated by measuring the amounts of propyl alcohol and carbon monoxide (or ethane) produced during the first 15 min of the reaction.

The reaction was carried out at 200 °C with a closed-circulating reactor made of glass using ca. 0.5 mg of the catalyst. The feed gases were usually composed of ca. 12 cmHg pressure of propionaldehyde and ca. 30 cmHg pressure of hydrogen.* The propionaldehyde employed was of guaranteed grade from the Nakarai Chemical Co and the hydrogen was of 99.999% purity. The gases produced were analysed by gas chromatography using columns packed with molecular sieves 13X for hydrogen, carbon monoxide, carbon dioxide and ethane, and with polyester FF for propionaldehyde and propyl alcohol.

RESULTS

PARTICLE SIZE AND SIZE DISTRIBUTION

Some of the photographs obtained by TEM are shown in plate 1. The mean particle sizes were calculated by measuring *ca.* 100 particles in the photographs for each catalyst reduced at 450 °C. The results are given in table 1 with the results obtained by SAXS. Note that the small nickel particles were often coagulated to each other by radiation from the electron beam of the microscope. Plate 2 shows photographs of the 2.2% Ni/SiO₂ catalyst reduced at 500 and 600 °C for 4 h. The particle size and size distribution of nickel metal in the catalyst were also measured by SAXS. The distribution curves calculated are given in fig. 1 and the Guinier and Porod radii are shown in table 1 with the peak width at the half-height of each distribution curve. The relation between the mean particle size obtained by SAXS and the concentration of nickel in the catalyst is shown in fig. 2.

INFRARED ANALYSIS OF THE CATALYST

The infrared spectra of the catalysts calcined at 450 °C are illustrated in fig. 3 with those of the catalysts reduced by hydrogen at 450 °C. Three absorption bands were observed in the range 700 to 1200 cm⁻¹; at 810, 975 and 1100 cm⁻¹. The bands at 810 and 1100 cm⁻¹ were due to the symmetric and antisymmetric vibrations of Si—O—Si species in SiO₂, while the band at 975 cm⁻¹ was assigned to the Si—O vibration in Si—O—Ni bonding. The ratio of the absorption intensity of the band at 975 cm⁻¹ to that at 810 cm⁻¹ was calculated for each catalyst after calcination at 450 °C in air. The relationship of this ratio to the nickel concentration in the catalyst

* 1 cmHg \equiv 13.5951 \times 980.665 \times 10⁻¹ Pa.

catalyst no.	[Ni] (%)	$2R_{\rm G}/{\rm \AA}$	$2R_{\rm P}/{\rm \AA}$	SAXS/Å result	half-width/Å	TEM/Å result
1	2.2	38	30	20	18	25
2	4.3	57	41	30	19	40
3	9.2	87	81	70	20	60
4	12.4	105	95	85	30	75
5	25.8	120	114	105	25	95

TABLE 1.—SUMMARY OF NI PARTICLE-SIZE RESULTS MEASURED BY TEM AND SAXS



FIG. 1.—Particle-size distribution of Ni in Ni/SiO₂ catalysts reduced by H₂ at 450 °C for 4 h.



FIG. 2.--Change in the mean particle size of Ni metal with Ni concentration in the catalyst.



FIG. 3.—Infrared spectra of the catalyst after calcination in air at 450 °C and after reduction by H₂ at 450 °C.



FIG. 4.—Change in the relative intensity of the band due to Ni—O—Si with Ni concentration in catalysts.

is given in fig. 4. The intensity of the absorption band at 975 cm⁻¹ decreased on raising the reduction temperature and became almost zero when the catalyst had been reduced at 800 °C for 4 h. The result obtained for 4.3% Ni/SiO₂ catalyst is shown in fig. 5.

FRACTION OF NICKEL REDUCED TO METAL

By measuring the magnetisation of nickel in 4.3% Ni/SiO₂ catalyst reduced at various temperatures, the fraction of nickel reduced to the metal was estimated. These results are also given in fig. 5, together with the results obtained by infrared analysis. An X-ray diffraction spectrum of the catalyst calcined at temperatures up to 600 °C showed that no NiO was deposited on the catalyst and that no formation of Ni₂SiO₄



FIG. 5.—Changes in the fraction of Ni reduced to metal and in the relative infrared intensity of Ni—O—Si caused by increasing the reduction temperature. Points ● and ▲ were measured after calcinations at 450 °C in air.



FIG. 6.—Hydrogenation and decomposition of propionaldehyde on the catalyst at 200 °C. ○, Hydrogen;
①, carbon monoxide; ①, ethane; ●, propyl alcohol; △, propionaldehyde.

occurred. The X-ray diffractometer (Reiger Flex, Gigakudenki Co) was operated at 30 kV with a filament current of 15 mA using a Ni filter for Cu $K\alpha$ radiation. Since our catalyst was first calcined at 450 °C and then reduced at the same temperature, neither NiO nor NiSiO₄ was present on the catalyst. Therefore some of the Ni was reduced to metal after the reduction by hydrogen at various temperatures, while the rest remained bonded to oxygen atoms in the carrier by forming Ni—O—Si bonds.

CHANGE IN REACTION SELECTIVITY WITH NICKEL PARTICLE SIZE

A typical result is shown in fig. 6 for the hydrogenation of propional dehyde on 4.3% Ni/SiO₂ catalyst at 200 °C. As can be seen in fig. 6, the amount of propyl alcohol formed reached a maximum after *ca*. 30 min of reaction and then gradually decreased,



FIG. 7.—Formation of propyl alcohol (a) and carbon monoxide (b) per unit mass of Ni in the catalysts. (Numbering of catalysts is as in table 1 and fig. 1.)

while the amounts of ethane and carbon monoxide produced continued to increase. This indicates that something happened on the surface of the catalyst during the reaction; for example, an accumulation of deposited carbon might occur on the catalyst, since the amount of carbon monoxide produced was always a little more than that of ethane. According to reaction (2), the amounts of both species produced during the reaction must be equal. In order to avoid these problems, the selectivity for hydrogenation was calculated by measuring the amounts of propyl alcohol and carbon monoxide produced in the first 15 min of the reaction. In fig. 7 the amounts of propyl alcohol and carbon monoxide formed are plotted against the reaction time using various Ni/SiO₂ catalysts reduced at 450 °C by hydrogen. The selectivities expressed in terms of (amount of propyl alcohol)/(amount of carbon monoxide) are plotted in fig. 8 as a function of the Ni particle size.

DISCUSSION

To study effect of particle size on catalytic properties attention must be paid to the following factors: the particles must be dispersed in a homogeneous size, and both the metal particles and the carrier must be free from impurities which will affect



FIG. 8.—Selectivity for hydrogenation of propionaldehyde plotted against the size of Ni metal particles in catalysts.

catalytic properties. The hydrolysis of a metal alkoxide is one of the best methods of preparing fine particles of the corresponding metal oxide. It has been reported¹² that most metals form their alkoxides by the reaction between the metal chloride and sodium alkoxide in the presence of an excess of alcohol and a hydrocarbon solvent such as benzene. It is difficult, however, to eliminate the chlorine and sodium ions from the alkoxides thus produced. Recently it was proposed that a highly dispersed nickel-on-alumina catalyst could be prepared by using aluminium s-butylate and nickel acetate.¹³

In the present work, nickel hydroxide and ethylene glycol were employed as starting materials, since it has been reported¹⁴ that metal salts react with ethylene glycol to form cyclic metal glycoxides. Thus cyclic nickel glycoxide, $(CH_2O)_2Ni$, was formed by the dissolution of nickel hydroxide into ethylene glycol at 80 °C, although the cyclic glycoxide was not isolated in this experiment. An appropriate amount of ethyl silicate was added to this glycoxide dissolved in ethylene glycol. A considerable amount of ethylene glycol diethyl ether, $C_2H_5O(CH_2)_2OC_2H_5$, was observed after 5 h of the reaction of nickel glycoxide with ethyl silicate, indicating that the Ni—O—Si bond should be formed in the following manner:

$$2(C_{2}H_{5}O)_{4}Si + (CH_{2}O)_{2}Ni \rightarrow (C_{2}H_{5}O)_{3}Si - O - Ni - O - Si(OC_{2}H_{5})_{3} + (C_{2}H_{5}OCH_{2})_{2}.$$

Details of the liquid-phase reaction between alkoxides are given elsewhere.¹⁵ Formation of the Si—O—Ni was confirmed by infrared spectroscopy. The catalyst calcined at 450 °C in air showed an infrared absorption band at 975 cm⁻¹. This band was assigned to Si—O vibrations in the Ni—O—Si group, since the absorption band characteristic of the metal—O—Si group appears in the 900-1100 cm⁻¹ region, *e.g.* 1050 cm⁻¹ for Al,¹⁶ 1018 cm⁻¹ for Zr¹⁷ and 920 cm⁻¹ for Ti.¹⁷ The relative intensity of the band at 975 cm⁻¹ increased on increasing the nickel concentration in the catalyst (fig. 4). These results seem to indicate that the nickel atoms dispersed on the silica are fixed by forming chemical bonds with oxygen atoms in the carrier. Yermakov¹⁸ and, more recently, Iwasawa¹⁹ prepared Mo-fixed catalysts by a reaction between Mo(π —C₃H₅)₄ and the surface OH groups of silica, although they did not provide infrared measurements of the Mo—O—Si bonding.

When the catalysts were heated in a hydrogen stream the relative intensity of the

band at 975 cm⁻¹ decreased on raising the reduction temperature. This was attributed to bond cleavage in Ni—O—Si resulting in the deposition of nickel metal on the carrier. For the deposition of a nickel atom, two bonds must be broken because a nickel atom is bonded to two oxygen atoms in the carrier in the manner Si—O—Ni—O—Si. This results in a higher rate of decrease in intensity of the band at 975 cm⁻¹ than the rate of increase in the fraction of nickel metal formed (see fig. 5). As mentioned elsewhere, no formation of NiO or Ni₂SiO₄ was observed in the X-ray diffraction spectrum of the catalyst calcined in air, hence no NiO and Ni₂SiO₄ particles were deposited on the surface of the catalyst. Thus we believe the particles observed by TEM after the reduction of the catalysts to be particles of metallic nickel rather than NiO and Ni₂SiO₄. The nickel metal particles thus observed by TEM are shown in plate 1. The particles in each photograph are almost homogeneous in size, varying from *ca.* 25 to *ca.* 125 Å depending upon the concentration of nickel in the catalyst. The size distribution curves measured by SAXS also show that the size of the particles can be controlled by changing the nickel loading in the catalyst (fig. 1).

During the reduction of the catalyst $(2.2\% \text{ Ni/SiO}_2)$ at 500 and/or 600 °C the nickel metal particles were briefly enlarged by sintering (plate 2). The particle size was *ca.* 25 Å when the 2.2% Ni/SiO₂ catalyst was reduced by hydrogen at 450 °C, while it reached *ca.* 30 and/or *ca.* 40 Å when reduced at 500 and/or 600 °C, respectively. Thus, the change in nickel particle size did not depend much upon the reduction temperatures employed.

As the nickel metal particles were shown to be dispersed on the carrier in a homogeneous size, the effect of particle size on the catalytic properties of the nickel could thus be investigated. As a model reaction, the hydrogenation of propionadehyde was employed. As mentioned above, hydrogenation of the aldehyde accompanies its decomposition to form carbon monoxide and ethane. The amount of carbon monoxide formed must be equal to that of ethane if the reaction occurs according to eqn (2). However, a little more carbon monoxide is formed than ethane during the reaction, indicating that a small amount of residual ethane remained on the catalyst possibly as deposited carbon. As the reaction time increases the carbon deposited accumulates on the catalyst and has an important influence on the catalytic properties of the nickel. Accordingly, the catalytic selectivity of nickel metal for hydrogenation was measured at an early stage of the reaction when the accumulation of deposited carbon is not significant.

The amounts of propyl alcohol and carbon monoxide produced per unit mass weight of nickel in the catalyst were calculated (fig. 7), and from these results the selectivity for alcohol formation was estimated (fig. 8). The selectivity was greatly increased when the metal particles were < 50 Å in dimension. This significant change has been discussed in terms of a simple geometric arrangement of the nickel atoms, with the assumption that the nickel particles are crystallized in cubes (*i.e.* f.c.c.). This idea has already been applied to supported platinum catalysts.^{3,4} According to Hardeveld⁸ and Anderson,⁹ the fraction of nickel atoms located on the edges and the corners of the nickel crystallites (f.c.c.) increases when the crystallite size becomes < 50 Å, as is shown in fig. 9.

The curves in fig. 8 and 9 are fairly in good agreement with each other, indicating that the hydrogenation of propionaldehyde occurs on nickel atoms located at the edges or corners of the crystallite, while decomposition of 'he aldehyde takes place on nickel atoms located on the plane surface of the crystallite. Note that the reaction between the aldehyde and hydrogen did not take place on the silica support alone at temperatures $< 200 \,^{\circ}C.^{20}$ (Only the condensation of the aldehyde occurred.) At temperatures $> 200 \,^{\circ}C$ slight decomposition of the aldehyde took place.

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FIG. 9.—Fraction of Ni atoms located on the edges or corners of Ni crystallite (assuming f.c.c. packing).8.9

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