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Control of the Impregnation Profile of Ni in an Al_2O_3 Sphere

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Control of a radial concentration of nickel metal particles in an alumina sphere was achieved by impregnating the spheres with a solution composed of nickel nitrate dissolved in ethylene glycol, ethyl silicate, and a small amount of nitric acid. The position of the nickel narrowband from the center of the sphere was well controlled merely by the impregnating time. The nickel loading in the catalyst was intentionally varied with the nickel concentration in the impregnating solution. The external surface of the catalyst prepared was covered with thin SiO_2 films resulting from the gelling of ethyl silicate over the alumina sphere. The micropores observed in the thin SiO_2 films were sharply sized around 20 Å. © 1987 Academic Press, Inc.

INTRODUCTION

The control of the impregnation profiles of metal particles in catalyst supports was first proposed by Maatman and Prater (*1*) in an attempt to improve catalyst durability. The idea has been practically applied to the automotive catalyst (*2*) to improve catalytic performance and durability by controlled subsurface platinum and palladium on alumina supports. It is well known that there are four kinds of profiles: uniform, egg shell, egg white, and egg yolk. The first two types are easily established by control of the impregnation time (*3*) or by alteration of the starting materials of the catalyst constituents (*4*). It is also possible to prepare a catalyst with a uniform or egg shell profile by varying the ratio of the amount of impregnating solution to the pore volume of catalyst support employed (*5*). Achievement of the latter two types of profiles requires proper additions to the impregnating solution. Becker and Nuttall (*6*) reported that the impregnation profile of Pt metal in alumina spheres could be well controlled by adjusting the amount of citric acid in the impregnating solution. Besides the citric acid, oxalic acid (*7*), urea (*8*), and acetone (*9*) have often been used as additives to control the impregnation profiles.

Theoretical approaches to the control of impregnation profiles have been extensively studied. Vincent and Merrill (*10*) developed a model for the first step of the impregnation procedure by assuming one-dimensional diffusion of metal ions in micropores of a catalyst support. The model was further developed by Komiyama *et al.* (*11*) to the three-dimensional diffusion of metal ions. The thus improved model was consistent with actual impregnation profiles for both one-component ($NiCl_2$) and two-component ($NiCl_2$–HNO_3) systems (*11*). According to their theory, the one-component system should have a uniform or egg shell profile and the two-component system, an egg white or egg yolk profile. A competitive adsorption of metal ions and protons, originating from the acid added, is used to explain the subsurface profiles: egg white and egg yolk (*12*). This explanation is based on the fact that the adsorption of metal ions in an aqueous solution to solid surfaces is strongly pH dependent (*13*).

Despite these advanced techniques and theories, impregnation profiles are not always reproducible, partially because of the heterogeneity of solid surfaces and the lack of knowledge about micropore structure (*14*). An attempt to control the impregnation profiles as well as the loading of Ni

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metal in alumina spheres was successfully established in the present work. The impregnating solution employed was composed of nickel nitrate dissolved in ethylene glycol, ethyl silicate, and an appropriate amount of nitric acid. The Si–O–Ni–O–Si structures are formed merely by stirring the solution at room temperature (*15*). When the macromolecules with the Si–O–Ni–O–Si structure are larger than the micropores of the support, the macromolecules adhere, but do not penetrate, to the external surface of the support. Thus, thin SiO_2 films are produced over the external surface of alumina spheres when the catalyst is calcined in air. The Si–O–Ni–O–Si structure may disintegrate after adhering to the support surface, in which case the Ni ions will adsorb to the active sites of the support surface and compete with protons originating from nitric acid added. The Ni ions thus adsorbed may migrate into the support spheres and concentrate to form a subsurface profile during the calcination and reduction procedures. Thus, the loading of Ni ions in the catalyst is controlled by the Ni concentration in the macromolecules and, hence, the concentration of Ni in the impregnating solution. The position of the Ni narrowband with respect to the center of the support sphere can also be controlled by the impregnation time: the band moves closer to the center as the impregnation time increases.

EXPERIMENTAL

Alumina spheres. Alumina were supplied by Shokubai Kasei Kogyo Company; the surface area was 290 $m^2\ g^{-1}$ and the mean diameter, 3 mm. The alumina spheres are composed of γ-Al_2O_3 and their pore sizes are sharply distributed around 45 Å as measured by a sorption method using N_2.

Preparation of impregnating solution. The impregnating solution was prepared by addition of 30 ml of ethyl silicate to 150 ml of ethylene glycol containing 8.9 g of $Ni(NO_3)_2 \cdot 6H_2O$ at room temperature and stirring for 2 h. The pH value of the solution was about 3 and decreased to 1 when 3 ml of HNO_3 was added. The amount of $Ni(NO_3)_2 \cdot 6H_2O$ dissolved in ethylene glycol could be varied to prepare impregnating solutions with the desired Ni concentration. The pH values of all the impregnating solutions were adjusted to unity.

Impregnation procedures. Alumina spheres (5 g) were immersed in the solution for the desired time and then placed in water vapor atmosphere for 10 min to allow a gel to form on the external surface of the spheres. The water vapor was supplied with N_2 flow, passed through a water bath heated at 80°C. Impregnation time was varied from 1 min to 30 h. The alumina spheres were then dried at 110°C for 24 h in an oven, calcined at 300°C for 4 h, and reduced at 700°C for 4 h under a hydrogen stream.

Observation of impregnation profile by EPMA. The radial distributions of Ni and Si atoms in the catalyst spheres were observed with an electron probe X-ray microanalyzer (EPMA; Hitachi Model X-650) operated at an accelerating voltage of 20 kV with an energy dispersion detector. Samples were prepared by mounting the catalyst spheres in a polyester support and polishing with fine alumina powder. The alumina powder adhering to the sample was removed by ultrasonication; then platinum was evaporated over the surface of the sample to prevent the charge-up phenomenon during EPMA measurements.

Measurement of Ni loading. The catalyst calcined at 300°C for 4 h was analyzed with an X-ray fluorescence spectrometer (Rigaku Denki Co., Model 3080), operated at 50 kV with a filament current of 50 mA to generate Rh$K\alpha$ radiation. The samples were ground, mixed with the appropriate amount of $Na_2B_4O_7$, and then calcined at about 1000°C in a platinum crucible. Thus, the catalyst constituents were well dispersed in the glassy B_2O_3 disk to be subjected to spectrometric analysis.

Measurement of Ni particle size by TEM. The particle size of the Ni in the reduced catalyst was measured with a transmission electron microscope (TEM, Hitachi H-800), operated at an accelerating voltage of 200 kV with a magnification of $\times 10^5$. The sample was first ground with an agate mortar and then suspended in ethanol with the aid of supersonicant. The upper part of the suspension solution was pipetted over a microgrid for TEM measurements.

Measurement of Ni particle size by hydrogen chemisorption. The particle size of the Ni dispersed in the catalyst was also measured by hydrogen chemisorption measurements at room temperature with an absolute pressure gauge (MKS Baratoron Type 222B) in the hydrogen pressure range 5–50 mm Hg, as registered at adsorption equilibrium. The volume of hydrogen adsorbed was determined by extrapolating the linear part of the isotherm to zero pressure as proposed by Hall and Wilson (*16*). The specific surface area of Ni was estimated on the assumption that a nickel atom occupies an area of 6.8 $Å^2$, as reported by Mustard and Bartholomew (*17*). For the determination of the specific surface area of the Ni in the catalyst, the degree of reduction to Ni metal should be estimated, because not all of the Ni ions in the catalyst are completely reduced to Ni metal during the reduction procedure. The degree of reduction was obtained by measuring the saturation magnetization of the catalyst using a vibrating sample magnetometer (Toei Kogyo Co., Model VSM-2) at a magnetic field strength of 5 T (*18*).

Measurement of pore size. The micropores of the bare alumina spheres and the reduced catalysts were measured with a porosimeter (Carlo Erba, Sorptomatic 1800) using nitrogen as a sorption gas.

RESULTS

Impregnation profiles. In Fig. 1 are shown photographs of typical cross sections of the reduced catalysts, at impregnation times of 1 min, 2 h, and 15 h. The associated EPMA profiles of the Si and Ni atoms in the catalyst are also given in Fig. 1. Apparently, the Ni narrowband moved toward the center of the alumina sphere as the impregnation time increased (see Fig. 2) EPMA profiles of the Si and Ni atoms in the dried, calcined, and reduced catalysts are given in Figs. 3a, b, and c, respectively.

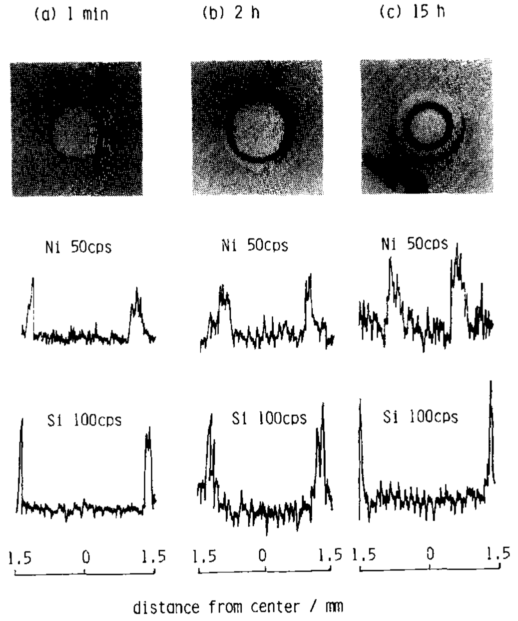


FIG. 1. Photographs of cross sections of reduced catalysts at impregnation times of 1 min (a), 2 h (b), and 15 h (c), and the corresponding EPMA profiles of Si and Ni atoms.

Ni particle size. TEM photographs of the reduced catalysts at impregnation times of 1 min, 2 h, and 15 h are shown in Fig. 4. The particles in each catalyst were relatively well controlled (at one size), and the mean particle size increased with increasing immersion time. All Ni ions in the calcined catalyst were completely reduced to Ni metal by reduction with hydrogen at 700°C, as revealed by magnetic measurements. The saturation magnetization of Ni metal is 54.39 emu/g, and NiO is an antiferromagnetic substance. The volume of hydrogen adsorbed, the specific surface area of Ni, the dispersion of Ni expressed in terms of H/M, and the mean particle size of Ni (obtained by measuring about 100 particles in photographs) were calculated and the results are summarized in Table 1.

Ni loading. The loading of Ni in the cata-

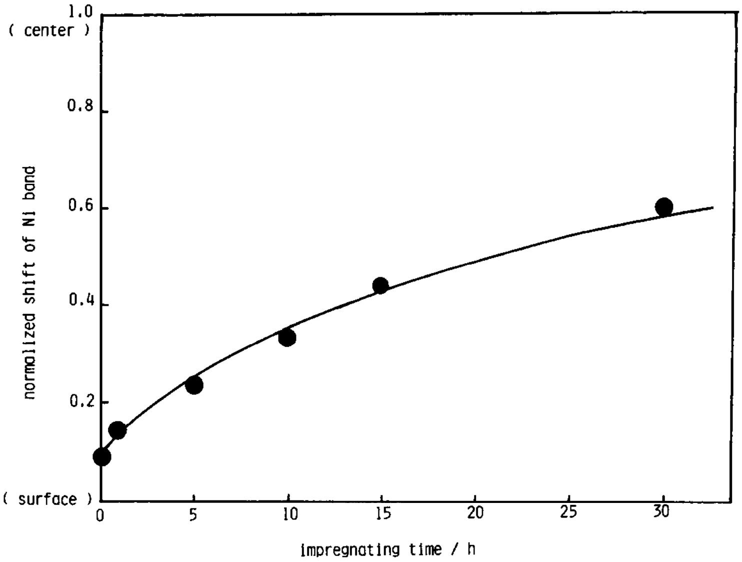


FIG. 2. Shift with impregnation time of Ni narrowband toward the centers of spheres.

lyst varied with the Ni concentration in the impregnating solution but not with the impregnation time. With an increase in the Ni concentration in the impregnating solution, the loading of Ni in the catalyst increased, as shown in Fig. 5. The impregnation time, however, did not affect the Ni loading, as also shown in Fig. 5.

Pore size distribution. The pore size distributions of the bare alumina spheres and the reduced catalysts are given in Fig. 6. Even when the impregnation time was varied from 1 min to 30 h, the pore size distributions of the reduced catalysts were almost the same. The mean pore size of the bare alumina sphere was about 45 Å, whereas that of the reduced catalyst was observed to be about 20 Å. The decrease in the pore size of the reduced catalyst was attributed to the formation of thin SiO_2 films on the external surface of the alumina spheres.

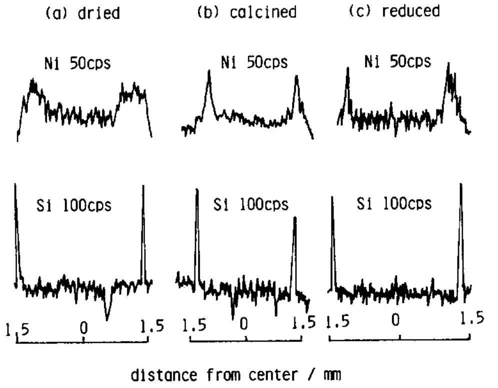


FIG. 3. EPMA profiles of Si and Ni atoms in dried (a), calcined (b), and reduced (c) catalysts. Impregnation time = 1 min.

DISCUSSION

^{13}C NMR and ^{1}H NMR measurements (*19*) previously revealed that Ni ethylene glycolate is formed during dissolution of nickel nitrate in ethylene glycol and that the Si–O–Ni–O–Si structure is constructed by the successive reaction of nickel ethylene glycolate with ethyl silicate upon addition of ethyl silicate to the solution. The reaction mechanism deduced is shown in Scheme 1. The Si–O–Ni molecules thus prepared expands three-dimensionally in the impregnating solution employed. The resulting macromolecules with Si–O–Ni–O–Si structures adhere to the entire surface of the alumina spheres when the spheres are impregnated with solution. The amount of species adhering depends on the external surface area of the alumina spheres em-

(a) 1 min (b) 2 h (c) 15 h

FIG. 4. TEM photographs of reduced catalysts at impregnation times of 1 min (a), 2 h (b), and 15 h(c).

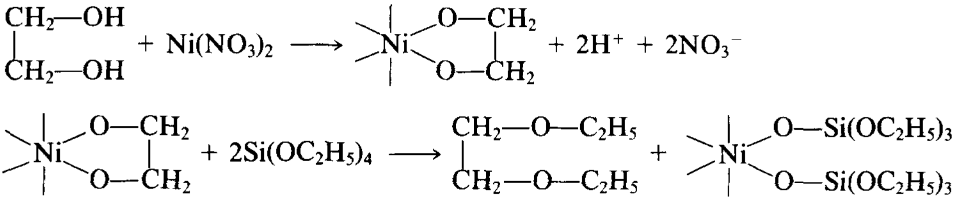
TABLE 1

Results Obtained by Hydrogen Chemisorption Experiments, and Comparison of Mean Particle Size of Ni Obtained by TEM with That Obtained by H_2 Chemisorption

Impregnation time	Volume of H_2 adsorbed (ml/g Cat.)	Specific surface area of Ni metal (m^2/g Ni)	Dispersion of Ni (H/M)	Mean particle size of Ni (Å)	
				H_2 Chem.	TEM
1 min	0.095	94.4	0.14	70	80
2 h	0.084	76.8	0.11	90	110
15 h	0.059	61.2	0.09	110	135

ployed. Consequently, the amount of Ni ion adhering depends on the Ni concentration in the corresponding impregnating solution. Thus, the Ni loading in the catalyst increased with an increase in the Ni concentration in the impregnation solution, as is obvious from Fig. 5.

When the Si-O-Ni-O-Si macromolecules were smaller than the micropores of the support, they penetrated the support, resulting in the presence of Si atoms inside the alumina spheres, as observed by EPMA. Indeed, after alumina spheres with micropores of about 100 Å were immersed in the impregnating solution, Si atoms were clearly observed inside the alumina spheres. The alumina spheres employed in the present work have micropores of about 45 Å, as shown in Fig. 6, and the Si atoms were observed to be distributed only over the external surface of the alumina spheres (see Figs. 1 and 3). This seems to suggest



SCHEME 1

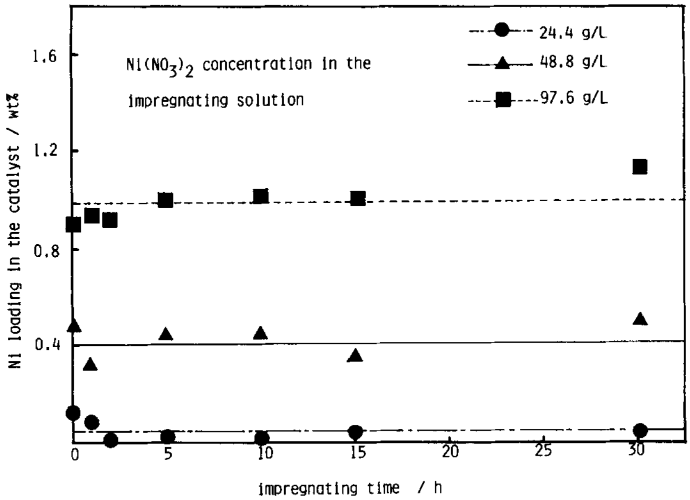


FIG. 5. Change in Ni loading with Ni concentration in the impregnation solution. The concentration of $Ni(NO_3)_2 \cdot 6H_2O$ in the impregnating solution was varied: 24.4, 48.8, and 97.6 g/liter.

that under the conditions employed in this work, the Si–O–Ni–O–Si macromolecule in solution was between 45 and 100 Å.

Since the isoelectronic pH value of Al_2O_3 is reported to be about 9 (*20*) and the pH value of the impregnating solution was set at 1, the electro-double layers around the alumina spheres should be positively charged during the impregnation. Electrochemically, this means that it is difficult for the positively charged metal ions to approach the alumina spheres through the electro-double layers. Therefore, if there are free Ni ions, not trapped in Si–O–Ni–O–Si structures, in the impregnating solution, they might not adsorb to the alumina spheres. The Si–O–Ni–O–Si structures are not charged so as to be ready to adsorb to the alumina spheres; the Ni ions in the structures adsorbed will be eliminated when they migrate into the spheres and compete with protons originating from the HNO_3 added. The protons adsorbed to alumina spheres more strongly than Ni ions and, thus, the sites available for the adsorption of Ni ions moved closer to the center of the spheres as the impregnation time increased. This seems to indicate that the radial position of the Ni narrowband is controlled by the impregnation time (see Figs. 1 and 2). When nitric acid was not added to the impregnating solution, a uniform or egg shell profile of Ni atoms was established depending upon the impregnation time. The impregnation profile of Ni atoms in the dried catalyst was rather broad, although the profiles in the calcined and reduced cat-

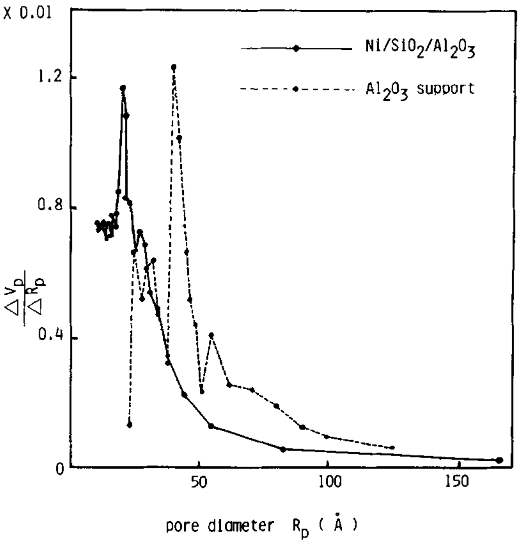


FIG. 6. Micropore size distributions of the bare alumina spheres and the reduced catalyst at an impregnation time of 2 h. The pore size distributions of the catalysts prepared in this work were almost the same as that shown in this figure.

alysts were sharp, as shown in Fig. 3. This may be due to the evaporation of water inside the alumina spheres, resulting in the enhancement of acid strength and, consequently, in the concentration of Ni atoms in a narrowband. Another feature of this impregnating technique is the formation of thin SiO_2 films on the external surface of the spheres. The average thickness of the SiO_2 film was estimated to be about 50 μm from the results shown in Figs. 1 and 3. The formation of thin SiO_2 films is attributed to gel formation over the external surface of the spheres, the gel being composed of Si–O–Ni–O–Si macromolecules. The micropores of the alumina spheres were completely covered with SiO_2 films, and the films have micropores sharply sized at about 20 Å, as clearly shown in Fig. 6. The pore volume of the reduced catalyst was 0.35 ml/g, similar to that of the bare alumina, 0.33 ml/g, indicating that the SiO_2 films merely covered the external surface of the alumina spheres but did not penetrate inside the micropores of the spheres to reduce the pore size.

When the impregnating solution was gelled by addition of the appropriate amount of water, dried, calcined at 500°C, and reduced at 500°C in a hydrogen stream, a silica-supported Ni catalyst was prepared (*21*). The catalyst thus prepared contained fine Ni metal particles of one size, owing to the atomic dispersion of Ni ions in the dried catalyst. Similarly, an atomic dispersion of Ni ions is expected for the dried catalyst prepared in the present work, since the atomic dispersion was established in the Si–O–Ni–O–Si structure. The Ni ions highly dispersed in alumina spheres may coagulate to form evenly sized NiO particles during calcination at 300°C. These tiny NiO particles were reduced by hydrogen at 700°C to produce fine Ni metal particles of one size. As shown in Fig. 4, the Ni particles in each photograph are of one size, although the size changes slightly with impregnation time, 80 Å for 1 min, 110 Å for 2 h, and 135 Å for 15 h (see the last column of Table 1). Ni particle sizes determined by hydrogen chemisorption are listed in Table 1 and are in good agreement with those observed by TEM.

Although further studies, such as determination of the pH dependence of the profile and precise estimation of the size of the Si–O–Ni–O–Si structure in the impregnating solution employed, remain to be done, the control of both the impregnation profile of Ni atoms and the Ni loading in the catalyst has been reproducibly established.

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