[February, 1986] © 1986 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 59, 347—350 (1986)

Pretreatments of Porous Silica for Improving the Activity of a Nickel-Loaded Catalyst

Masahiko Arai, Yutaka Ikushima, and Yoshiyuki Nishiyama*
Chemical Research Institute of Non-Aqueous Solutions, Tohoku University, Katahira, Sendai 980

(Received July 15, 1985)

Nickel catalysts supported on porous silicas treated with water, ethanol, and 1-butanol were found to be more active than that supported on untreated silica for ethane hydrogenolysis and furan hydrogenation. To elucidate the reason for the activation, some surface properties of the treated silicas were examined. The treatments decreased the surface area and increased the volume of the macropores, the surface density of hydroxyl groups, and the heat of immersion in water per unit surface area. The state of nickel on the support was examined by temperature programed desorption(TPD) of hydrogen, X-ray diffraction(XRD), and scanning electron microscopy/X-ray microanalysis. The dispersion measured by XRD was not appreciably altered by the treatments, but the TPD showed more hydrogen desorbed above 150 °C from nickel on the treated supports. The activation of nickel by pretreatment of the support was ascribed to the increase of those nickel atoms which dispersed finely over the support by the increased number of surface hydroxyl groups. This was based on the number of hydroxyl groups per unit surface area. The nickel catalyst supported on the pretreated silicas showed greater thermal stability.

It is well established that the activities of supported metal catalysts are influenced by the surface properties of the supports, so that the choice of the support material is important for the preparation of the catalysts.[1] Therefore some surface modifications of the support can improve the activity of the catalysts loaded on it. Previously, we have reported that nickel and platinum catalysts loaded on porous silicas pretreated with water and alcohols are more active than those on untreated silicas.[2,3] As the impregnation of the active metal species was done from aqueous solutions, it was our anticipation that alcohol treatment, which would be expected to give the surface a hydrophobic nature, would lead to a lower dispersion of the active metal. Contrary to this anticipation, the catalytic activities of metals on alcohol treated silicas were found to be higher than those on untreated silica. As a follow-up of the previous work, the present study was undertaken to clarify the reason for the activation by the pretreatment of the support. In doing so, temperature programed desorption of hydrogen was extensively used to characterize the state of nickel on the support, as it seems to be more relevant to examine those metals which are active in catalysis.[2]

A number of researches on surface modifications of silica as well as other metal oxides have been reported in the literature.[4—10] Their concern of these authors, however, is more with the actions of modified surfaces as adsorbents and solid acid catalysts. There was little attempt made to use modified materials as supports for the metal catalyst.

Experimental

A porous silica material was used, Silbead-N obtained from Mizusawa Industrial Chemicals, Ltd. It was powdered to 32—60 mesh and treated with water at 280 °C, ethanol at 280 °C, and 1-butanol at 250 °C. Detailed procedures of these treatments were described previously.[2,3] The silica was characterized before and after the treatments by the following means. (i) The surface area was measured by the nitrogen BET method. (ii) The pore size distribution was determined by the Cranston-Inkley method using a nitrogen adsorption isotherm[11] and by a mercury porosimetry (Shimadzu-Micromeritics Pore Sizer 9300). (iii) FT-IR diffuse reflectance spectra were obtained using a mixture of the silica (ca. 5 wt%) and potassium bromide with a JEOL JIR-100 spectrometer. (iv) The heat of immersion in either water or hexane was measured at 22 °C using a Tokyo Riko TCC-21 calorimeter.

Using the treated and untreated silicas, supported nickel (5 wt%) catalysts were prepared by impregnation with nickel nitrate from its aqueous solution. The impregnated samples were vacuum dried and reduced in flowing hydrogen at 350 °C for 16 h. The state of the nickel dispersion was examined by temperature programed desorption (TPD) of hydrogen, X-ray diffraction line broadening (XRD), and scanning electron microscopy/X-ray microanalysis (SEM-XMA). For TPD, using a 5 mm i.d. quartz tube reactor operated at atmospheric pressure, ca. 0.3 g of the catalyst was exposed to flowing hydrogen of 48 ml min^{-1} at room temperature for 20 min. The adsorbed hydrogen was then desorbed by linear heating at 30 °C min^{-1} in an argon carrier at a flow rate of 40 ml min^{-1}. The catalytic activity was examined for ethane hydrogenolysis at 350 °C and furan hydrogenation at 110 and 200 °C with ethane and furan partial pressures of 16.0 and 27.7 kPa, respectively. The apparatus and procedures for the TPD and the activity test were described in detail previously.[2,3]

In the following sections, the water-, ethanol-, and 1-butanol-treated and untreated silicas will be referred to as SI(W), SI(E), SI(B), and SI(U), respectively.

Results

Effects of Treatments of Silica on the Surface Properties.

(1) Surface Area and Porosity. The BET surface area, pore volumes, and XRD data as well as the heat of immersion of the silicas are summarized in Table 1. The treatments caused the surface area to decrease to less than 1/5 of the initial value. The pores in SI(U) were mostly smaller than 5 nm in diameter and the treatments enlarged the pore diameter. Compared with

Table 1. Characterization of Treated and Untreated Silicas

	SI(U)	SI(W)	SI(E)	SI(B)
Surface area (m^2/g)	680.0	74.3	98.1	131.2
Pore volume (ml/g)				
diameter<5 nm	0.202	0.052	0.010	0.020
5—30 nm	0.021	0.063	0.142	0.220
XRD[a) 2θ (deg)	23.8	21.6	22.0	22.2
d (nm)	0.37	0.41	0.40	0.40
Heat of immersion				
in water (J/m^2)	0.218	0.616	0.422	0.417
in hexane (J/m^2)	0.246	0.335	0.200	0.276

a) A Cu$K\alpha$ ray was used. d is the corresponding interlayer spacing.

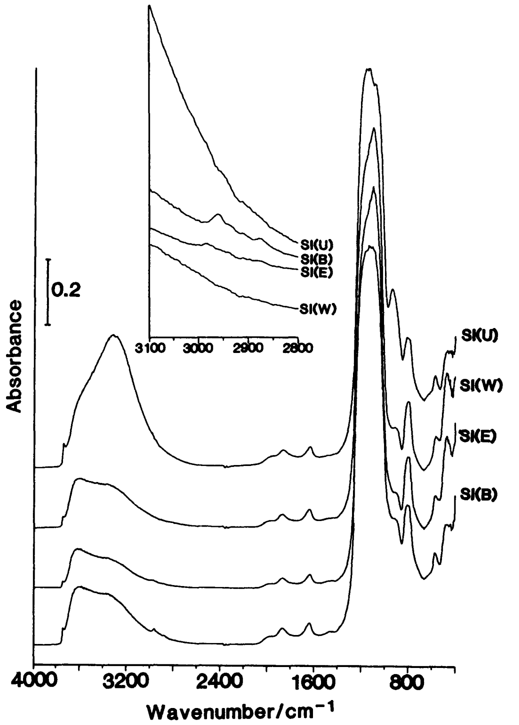

Fig. 1. FT-IR spectra for treated and untreated silicas.

SI(U), the total pore volumes of SI(W) and SI(E) were smaller by factors of 0.6—0.7 while that of SI(B) was comparable. The mercury porosimetry showed the absence of macropores larger than 30 nm even in the treated silicas. The observed maximum pore diameter was 20 nm for SI(E) and SI(B) and 30 nm for SI(W).

The XRD showed an increase in the interlayer spacing, d, with the treatments, the order of d being SI(W)>SI(E)≥SI(B)>SI(U). This suggests that the treatments caused a growth of cristobalite- and/or tridymite-like structure in the silica.

(2) Infrared Absorption Spectra. In Fig. 1, FT-IR spectra for the treated and untreated silicas are compared. The intensity of absorption of the sharp peak at 3750 cm^{-1}, of the broad band between 3600 and 2800 cm^{-1}, and of the weak band at 870 cm^{-1} was decreased by the treatments. These absorptions can be assigned to surface hydroxyl groups. Thus the number of hydroxyl groups on the treated silicas was smaller than that on the untreated silica when compared on a unit weight basis. However, as the surface area was decreased by the treatments, the number of hydroxyl groups in unit surface area increased (see Fig. 2). In addition, the spectra of SI(E) and SI(B) have absorption bands at 1450 and 2950 cm^{-1}, which can be assigned to methyl and methylene groups. These indicate the exchange of some hydroxyl groups with alkoxyl groups on the silica surface.

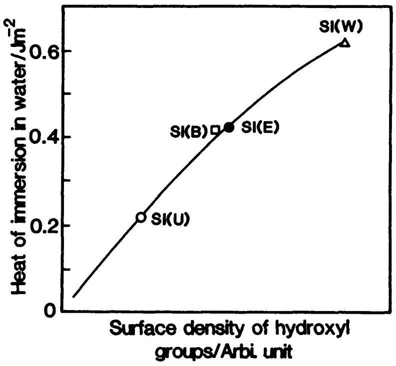

Fig. 2. A plot of heat of immersion in water versus relative surface density of hydroxyl groups.

(3) Heat of Immersion in Water and Hexane. The heat of immersion per unit surface area is presented in Table 1. The surface treatments caused the heat of immersion in water to increase by factors of about 3 and 2 for the water and alcohol treatments, respectively. Figure 2 shows a plot of the heat of immersion in water against the relative density of surface hydroxyl groups from FT-IR. The latter was obtained by graphically integrating the absorbance between 2600 to 3800 cm^{-1} in Fig.1 and then normalizing to the absorbance at 1640 cm^{-1} assigned to a silicon-oxygen overtone vibration.[12,13) The correlation indicates that the surface hydrophilicity was associated with the surface hydroxyl groups for the present silicas and that, contrary to expectation, the treatment by alcohols rendered the silica more hydrophilic nature. On the other hand, the heat of immersion in hexane per unit surface area was only slightly changed. It was increased by the water and 1-butanol treatments but it was decreased by the ethanol treatment.

Effect of Silica Pretreatments on the Catalytic Properties of Supported Nickel.

(1) Metal Dispersion. Figure 3 shows TPD spectra of hydrogen adsorbed on the nickel catalysts on SI(U), SI(W), and SI(B). In the present TPD experiment, the heating of the catalyst was restricted to below 350 °C to avoid thermal effects on the nickel dispersion during repeated measurements. It was found that the catalysts on the treated silicas could, as a whole, adsorb larger amount of hydrogen than that on SI(U). After the heat treatment in hydrogen at 500 and 700 °C, the total

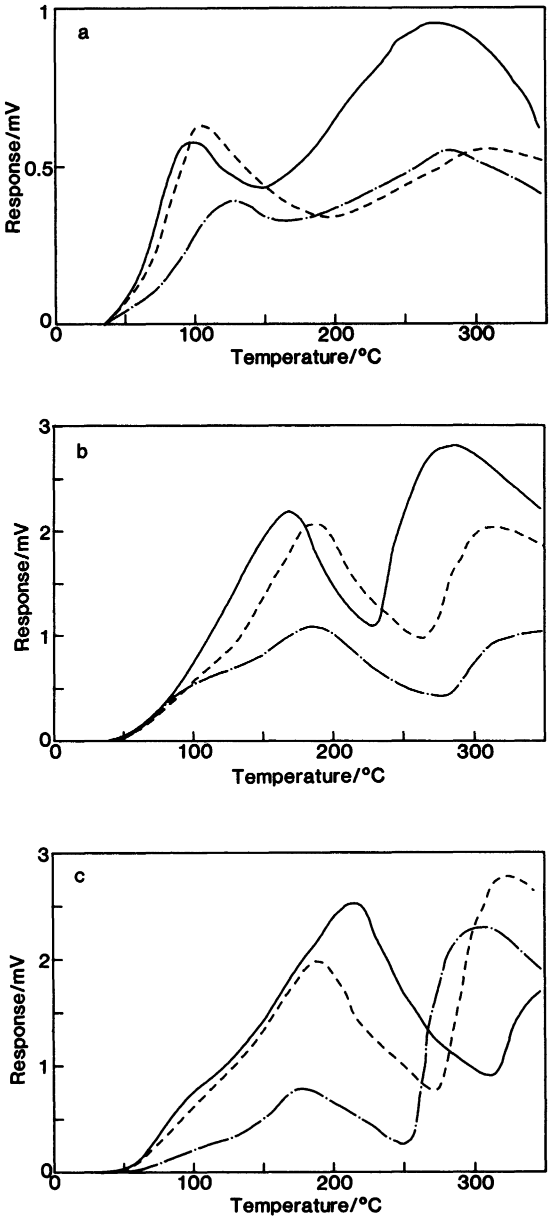

Fig. 3. TPD spectra of hydrogen adsorbed on (a) Ni/SI(U), (b) Ni/SI(W), and (c) Ni/SI(B). ——: as reduced, – – –: heated in hydrogen at 500 °C for 1 h, —·—: heated in hydrogen at 700 °C for 1 h.

amount of hydrogen desorbed in the TPD decreased for all the catalysts used. However, the amounts of hydrogen desorbed from nickel on the treated silicas were larger or, at least, comparable to that from the catalyst on SI(U) without the heat treatment although the TPD patterns were different.

Table 2. Mean Nickel Crystallite Size[a]

H.T.T.[b]	Support			
	SI(U)	SI(W)	SI(E)	SI(B)
As reduced (350 °C)	7.3	6.5	7.1	6.3
700 °C	8.8	14.8	11.3	11.2

a) Determined by an XRD line broadening, in nm. b) Heat treatment temperature. The treatment was performed in a flowing hydrogen for 1 h.

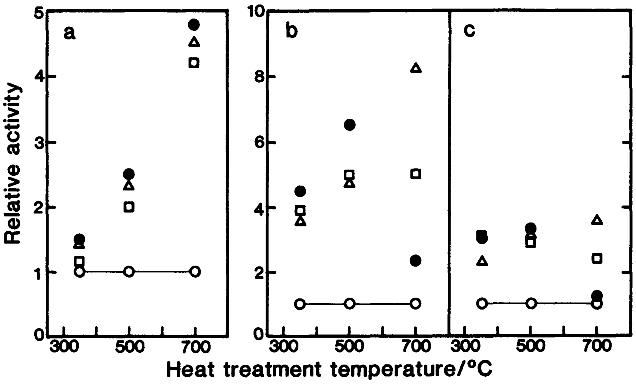

Fig. 4. Relative activities of (△) Ni/SI(W), (●) Ni/SI(E), and (□) Ni/SI(B) to (○) Ni/SI(U) for ethane hydrogenolysis at 350 °C (a) and furan hydrogenation at 110 °C (b) and at 200 °C (c).

Table 2 presents mean crystallite sizes of the supported nickel obtained by XRD, including the influence of heat treatment in hydrogen at 700 °C for 1 h. It shows that the nickel crystallites in the catalysts as prepared had similar sizes although the supports used were different in the surface area, porosity, and hydrophilicity as noted above. On heat treatment, the crystallites in all the catalysts grew but the extent of growth was larger for the treated silicas than that for SI(U).

To see whether or not the surface pretreatment of the support caused some irregular distribution of nickel at the time of impregnation, the radial distribution of nickel on the cleaved surface of a catalyst particle was examined by SEM-XMA. The nickel distribution was found to be uniform within experimental error for all the catalysts on SI(U), SI(W), SI(E), and SI(B).

(2) Catalytic Activity. Figure 4 shows the catalytic activities of nickel supported on the treated silicas in ethane hydrogenolysis and furan hydrogenation relative to those of nickel on untreated silica. For the SI(U)-supported catalyst, the heat treatment in hydrogen at 500 °C decreased the activity in ethane hydrogenolysis at 350 °C by 44% and those in furan hydrogenation at 110 and 200 °C by 35 and 22%, respectively; the treatment at 700 °C decreased it in the same order, by 80, 68, and 60%. Though the heat treatment deactivated all the catalysts examined, those on surface-modified silicas were more stable against thermal deactivation than that on SI(U) as seen in Fig. 4.

Discussion

It is noteworthy that the structure of the silica was altered by the autoclave treatments with such alcohols as ethanol and 1-butanol as well as with water. Namely, the treatments decreased the surface area by factors less than 1/5 while they increased the volume of the pores in the range of 5-30 nm in diameter. Previous workers

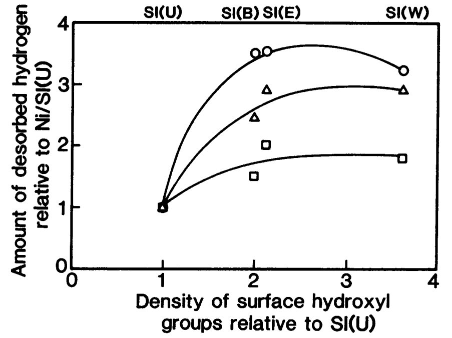

Fig. 5. Correlation between hydrogen adsorbability of supported nickel and density of surface hydroxyl groups of the supports. ○: Desorbed at 150—250 °C, △: 150—300 °C, □: 25—350 °C.

showed that the hydrothermal treatment of oxide gels including alumina and silica-alumina resulted in the change of surface area and pore structure, and it varied their catalytic properties.10,14) On our treatments, the extent of the structural change is thought to be associated with the penetrability of the treating agent into the silica gel structure. The solvents penetrated into unstable gel caused some rearrangement of its structural units, resulting in a partial crystallization as indicated by the XRD measurements, thereby reducing its surface area.

Along with the structural change, there occurred chemical change of the silica surface on the treatments. They increased the density of hydroxyl groups on the surface. The larger heat of immersion of treated silicas in water on unit surface area basis than that of untreated one is mainly due to the increased density of the surface hydroxyl groups. Some of the surface hydroxyl groups were replaced with alkoxyl groups by the alcohol treatments as expected, but their effect on the surface properties seems small.

An interesting finding is that the pretreatments of the silica enhanced the catalytic activity of supported nickel in spite of a concurrent significant decrease in the surface area of the silica. One probable explanation is that the larger density of the hydroxyl groups on the silica surface resulted in a higher dispersion of nickel, as evidenced by the TPD of hydrogen. Figure 5 shows the plot of the amount of hydrogen desorbed against the density of surface hydroxyl groups from the FT-IR spectra, both in relative values to SI(U). It suggests that the amount of hydrogen retained on the catalyst has some correlation with the surface hydroxyl groups on the support. The hydrogen adsorbability can be related with the catalytic activity in either hydrogenolysis or hydrogenation.2) Dispersion of nickel estimated from XRD gave no reasonable correlation with the catalytic activity. It is therefore inferred that well-dispersed nickel atoms play a main role in the catalysis and those in larger crystallites have small activity.

For all the catalysts examined, the heat treatment in hydrogen at 500 and 700 °C caused deactivation due to the sintering of the nickel crystallites as evidenced by the XRD measurements. At treatment temperatures of 500 and 700 °C, there is a possibility of an occurrence of strong nickel-support interaction, e. g., the formation of a nickel-support complex.15,16) Nickel atoms on the treated silicas were more stable than those on the untreated one, which suggested a stronger interaction with the treated supports.

Part of the enhanced activities of the catalysts on the pretreated supports may be ascribed to their increased pore diameter, which would favor the diffusion of reactants and products in the catalyst. The contribution of pores in activity enhancement needs further study.

The present study was done using a particular kind of silica gel, so that it is natural to ask whether the pretreatments of the support are applicable to other substances as well. An additional study using two aluminas indicated that the effectiveness of the pretreatments depended on the substance used; a catalyst with Neobead-C (Mizusawa Industrial Chemicals, Ltd.) was activated by the pretreatment of the support though the extent of the activation was less marked, whereas the other with JRC-ALO-1 (Catalysis Society of Japan) was not activated to any appreciable extent.

References

1) D. L. Trimm, "Design of Industrial Catalysts," Elsevier, Amsterdam (1980), p. 91.

2) Y. Ikushima, M. Arai, and Y. Nishiyama, *Appl. Catal.*, **11**, 305 (1984).

3) M. Arai, K. Kato, H. Saito, and Y. Nishiyama, *Nippon Kagaku Kaishi*, **1985**, 1016.

4) J. A. Hockey, *Chem. Ind. (London)*, **1956**, 57.

5) R. L. Burwell, Jr., *CHEMTECH*, **4**, 370 (1974).

6) H. Utsugi, H. Horikoshi, and T. Matsuzawa, *J. Colloid Interface Sci.*, **50**, 154 (1975).

7) N. G. Newman and W. Hertl, *J. Chromatogr.*, **65**, 467 (1972).

8) S. Okazaki and T. Kanno, *Nippon Kagaku Kaishi*, **1973**, 1285.

9) A. V. Tench, D. Giler, and J. F. J. Kibblewhite, *Trans. Faraday Soc.*, **67**, 854 (1971).

10) S. Furuyama, O. Murashita, Y. Yukumoto, and T. Morimoto, *Bull. Chem. Soc. Jpn.*, **53**, 3039 (1980).

11) R. W. Cranston and F. A. Inkley, *Adv. Catal.*, **2**, 143 (1957).

12) H. A. Benesi and A. C. Jones, *J. Phys. Chem.*, **63**, 179 (1959).

13) H. Heyne and F. C. Tompkins, *Trans. Faraday Soc.*, **63**, 1274 (1967).

14) M. Inoguchi, *SHOKUBAI*, **20**, 144 (1978).

15) R. B. Shalvoy, P. J. Reucroft, and B. H. Davis, *J. Catal.*, **56**, 336 (1979).

16) A. L. Hausberger, K. Atwood, and C. B. Knight, *Adv. Chem. Ser.*, **146**, 47 (1975).