Importance of Surface Hydroxyl Groups to the Dispersion of Nickel Impregnated on Silica Gels

The state of metal dispersion of supported metal catalysts depends on the physicochemical properties of support materials as described in many monographs (1). It is therefore of importance to clarify among these the key properties that allow us to control metal dispersion for desired catalytic performance. Metal dispersion is also affected by the method of metal deposition (1) and that is a current subject for the cases of wet impregnation with platinum and nickel on the supports of carbon (2–4), alumina (5–7), and silica (8–10).

Recently we have showed the influence of surface hydroxyl groups of silica for dispersing nickel and platinum over its surface by wet impregnation from experimental works using various silica gels prepared by dehydrating and rehydrating a porous silica gel under various conditions (8–10). One of the noteworthy results obtained is that the density of surface hydroxyl groups per unit surface area of support correlates with the degree of metal dispersion for 5 wt% nickel catalysts and the nickel dispersion attains a maximum at a certain density of those functional groups (9). This result has promoted the present work using a number of catalysts with changing amounts of nickel loaded on variously dehydrated (calcined) silica gels. The present paper reports further information about the relation between the dispersion of nickel and the surface hydroxyl groups of support.

Silica gel used was a powdered porous Silbead-N supplied by Mizusawa Industrial Chemicals, Ltd., which included alumina in 2 wt% and had a surface area of 560 $m^2 \cdot g^{-1}$, an average pore diameter of 2.4 nm, and a total pore volume of 0.24 $ml \cdot g^{-1}$. It was dehydrated by calcining in nitrogen at constant temperatures below 850°C for 3 h. The calcined silcia gels will hereinafter be expressed as, for example, SI(500) for one calcined at 500°C and the untreated silica gel with SI(un). Their surface hydroxyl groups were examined by thermogravimetry (TG) and Fourier transform infrared spectroscopy (FTIR, JEOL JIR-100) (9, 10). Nickel was deposited on those calcined silica gels by wet impregnation from aqueous solution of nickel nitrate. The silica gel was immersed overnight in the impregnating solution of a constant pH 5 at room temperature and the solvent was evaporated at about 50°C at reduced pressure within 1 h. After vacuum drying at 110°C, the silica gels with the nickel precursor were reduced by flowing hydrogen at 350°C for 16 h. The average diameter of nickel particles, d, was measured by X-ray diffraction line broadening (XRD, Shimadzu XD-D1w) using CuKα radiation (11). The degree of nickel dispersion is hereinafter expressed by reciprocal particle diameter, $1/d$, in nm^{-1} (12). For some selected catalysts, the amount of nickel loaded was measured by atomic absorption spectrophotometry after nitric acid extraction. The amounts measured were in good agreement with the nominal values with errors smaller than 10%, and the nominal values are therefore used in the following.

Figure 1 shows the degree of metal dispersion on silica gels calcined at various temperatures for 5.0, 7.3, and 10.0 wt% nickel loading. The calcination of support enhances the nickel dispersion and this effect is maximal at calcination temperatures de-
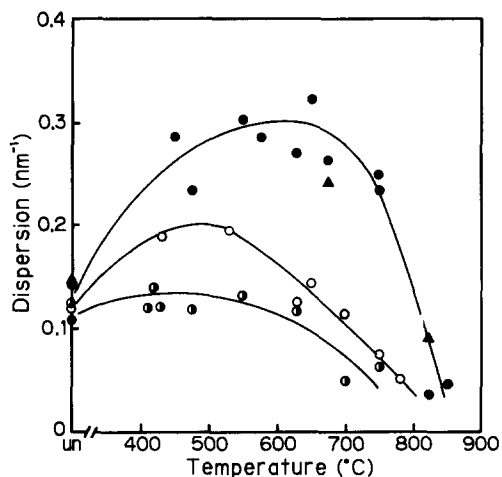
FIG. 1. The degree of metal dispersion for 5.0 (●,▲), 7.3 (○), and 10.0 wt% (◐) nickel/silica catalysts as a function of temperature of support calcination. (●, ○, ◐) XRD; (▲) TEM.
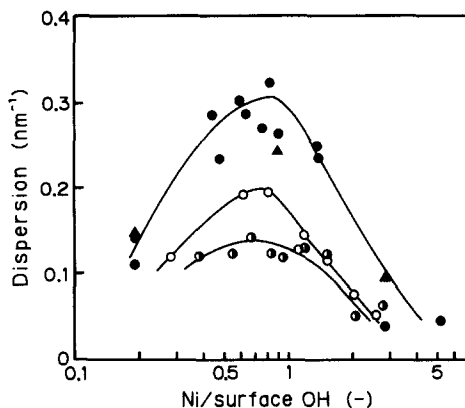

FIG. 2. The plot of the degree of metal dispersion (the same data given in Fig. 1) against the number ratio of nickel atoms loaded to surface hydroxyl groups of support used for catalysts on various calcined silica gels including 5.0 (●), 7.3 (○), and 10.0 wt% nickel (◐).

pending on the loading. The maximum of dispersion achieved shifts to smaller values and lower calcination temperatures for increasing metal loading. The calcination was found to merely decrease the number of surface hydroxyl groups of the support on either unit weight or unit surface area basis from TG and FTIR measurements (9). The densities of these groups are approximately 1.5, 2.0, and 2.4 hydroxyl groups nm^{-2} at maximum of dispersion for 5.0, 7.3, and 10.0 wt% catalysts, respectively.

In Fig. 2 the degree of nickel dispersion shown in Fig. 1 is plotted against the ratio of the number of nickel atoms mounted to that of surface hydroxyl groups of the support, Ni/OH, before metal deposition. It is interesting to note that the metal dispersion varies with the Ni/OH ratio and attains maximum at around Ni/OH = 0.7 in similar manners for different metal loadings.

To further examine the relation shown in Fig. 2, metal deposition on SI(550) and SI(un) was performed in the range of 1.0 to 10.0 wt% nickel. For SI(550) the degree of nickel dispersion was found to increase, reach a maximum at about 5 wt%, and then decrease with the increasing metal weight

loading. For SI(un), in contrast, the nickel dispersion changed only slightly with the metal weight loading. Figure 3 shows the plot of nickel dispersion against the Ni/OH ratio for those catalysts. For the catalyst on SI(550), one can also see a similar relation in which the maximum nickel dispersion appears at about Ni/OH = 0.7. Although cata-
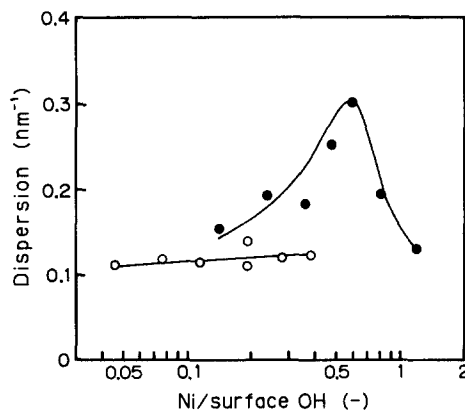

FIG. 3. The plot of the degree of metal dispersion against the number ratio of nickel atoms loaded to surface hydroxyl groups of support used for catalysts on SI(550) (●) and SI(un) (○). For each silica gel, nickel loading is varied in 1–10 wt%.

lysts on SI(un) with larger amounts of nickel were prepared, the uniformity of nickel deposition over the silica granules was poor and so these were not subjected to the XRD measurement.

For carbon support, Prado-Burguete *et al.* have recently correlated the platinum dispersion with its surface oxygen-containing groups of a particular type, which was characterized by species desorbing from these groups during temperature-programmed desorption (2).

The above-mentioned results demonstrate that surface hydroxyl groups of silica gels are of importance for dispersing nickel on them by wet impregnation and the nickel dispersion does not follow a monotonic dependence on the amount of those surface groups. When the nickel dispersion is plotted against the Ni/OH ratio, it attains maximum at about Ni/OH = 0.7, as shown in Figs. 2 and 3. Although this dependence cannot clearly be explained at present, this suggests the occurrence of some transition in the mode of nickel deposition at around Ni/OH = 0.7. The number of nickel particles deposited would increase with the Ni/OH ratio below that critical value, resulting in an increase of nickel dispersion, while it would little change at larger Ni/OH ratio, leading to a decrease of nickel dispersion. A previous transmission electron microscopy study on unreduced catalysts showed that surface hydroxyl groups of silica gels influenced the deposition of nickel precursor and that a higher degree of precursor dispersion resulted in a higher degree of nickel dispersion after reduction (9). It seems that similar transition in the mode of nickel deposition is present for alumina supports from the previous results of Huang and Schwarz (6) and Bartholomew and Farrauto (13) both of whom examined the dependence of nickel dispersion on metal weight loading.

For the calcination of Ni/OH ratio, we used the amounts of surface hydroxyl groups that were measured for dried silica gels before nickel deposition. There is a possibility that the surface of these gels would be rehydrated during the course of nickel deposition by wet impregnation. Previously we examined the rehydration of silica gels by immersion in water and found that the rehydration did not occur at room temperature while it occurred readily at 70°C (9). It is probable, therefore, that silica gels were not rehydrated when they were immersed overnight in the aqueous solution of nickel nitrate at room temperature. For a selected sample, SI(700), additional FTIR measurement has indicated that the immersion in water at 50°C for 1 h increases the amount of surface hydroxyl groups by about 30% from the comparison of integrated IR absorbance at 3600–2800 cm^{-1}. Most of the nickel precursor is deposited onto silica gels during the evaporation of the solvent at 50°C (9), and one can assume that the deposition of the precursor and the rehydration of silica gels concurrently take place during that stage of metal impregnation. Further study is needed on such concurrent processes, including the examination of the influence of the initial state of surface hydroxyl groups of support, for elucidating the mechanism of metal deposition by wet impregnation.

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