Characterization of Silica-Supported Nickel Catalysts by the Temperature-Programed Desorption of Hydrogen Adsorbed at Various Temperatures

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The temperature-programed desorption (TPD) of hydrogen adsorbed at various temperatures and at nearly saturated coverage has been used to characterize the surface of nickel particles dispersed on silica gel. The TPD spectra have two major peaks, the first and second peaks, at about 375 and 560 K. The second peak has a strong functional relation with the nickel weight loading and the heat-treatment temperature. It decreases with decreasing metal loading and increasing treatment temperature. As the adsorption temperature is increased the amount of hydrogen desorbing in the second peak is mainly increased; this is more remarkable for smaller metal loading. The two observed major peaks suggest the presence of two types of adsorption sites on nickel particles. The adsorption of hydrogen can easily occur on sites for the first peak, while it should go over some energy barrier on sites for the second one. It is assumed that these two types depend on the surface morphology of nickel particles, which is affected by their size and thermal history.

Temperature-programed desorption (TPD) is one of the useful techniques for characterizing the surfaces of solid materials, and has been applied to supported metal catalysts, as reviewed by Falconer and Schwarz.[1] Hydrogen has often been used as a probe adsorbate, since it is involved in many catalytic reactions. For silica-supported nickel catalysts, several TPD studies have been reported in the literature.[2—5] Weatherbee and Bartholomew performed TPD of the hydrogen adsorbed at temperatures below 550 K and at low and moderate coverage.[2] The obtained TPD spectra had a single peak that appeared at a certain temperature depending on the adsorption temperature. Lee and Schwarz also observed similar spectra with a single peak for the TPD of hydrogen adsorbed at high coverage up to unity and at 295 K.[3] Those TPD spectra for silica-supported samples[2,3] were very similar to those observed for unsupported nickel samples in the form of powder[2] and single crystals.[6—8] When hydrogen was adsorbed at a higher temperature of 773 K and at a nearly saturated coverage, however, Konvalinka et al. obtained more complex TPD spectra for silica-supported nickel samples.[4] The spectrum indicated several peaks, suggesting the presence of different adsorption states; it was influenced by nickel weight loading. From those studies, the TPD of hydrogen using a wider range of adsorption conditions is expected to give additional useful information concerning the surfaces of supported nickel particles.

When we are concerned with the characterization of the entire surface of supported metal particles, TPD should be performed at higher coverage close to the saturated values. In addition, the adsorption temperature should be varied, since the surfaces of the particles are not usually homogeneous, and saturated coverage may depend on the adsorption temperature. In the present work, the TPD of hydrogen under those adsorption conditions has been applied to silica-supported nickel particles. The nickel/silica samples used take on various metal dispersions upon varying the metal weight loading from 0.5 to 30% and subjecting them to heat treatments at various temperatures below 1073 K. The TPD spectra obtained upon changing the adsorption temperatures indicate the presence of two types of hydrogen adsorption sites, one of which is not activated, and the other of which is activated. The population of these sites is a strong function of the metal loading and heat-treatment temperature. The TPD data were correlated to the state of nickel dispersion, which has also been characterized by other techniques, including X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS).

Experimental

Sample preparation. A silica gel, Silbead-N (Mizusawa Industrial Chemicals, Ltd.) including alumina in 2 wt%, was used as a starting support material. It was powdered to 32—60 mesh size, washed with distilled water, dried in vacuum, and then calcined in air at 973 K for 3 h. The obtained silica gel had a nitrogen BET surface area of 370 $m^2 g^{-1}$. Nickel was deposited onto the silica by wet impregnation with an aqueous solution of nickel nitrate.[9,10] The silica powder was kept immersed overnight in the solution at room temperature and the solvent was evaporated under reduced pressure at about 323 K within 1 h. The silica powder impregnated with the nickel precursor was vacuum dried at 383 K for 2 h and then reduced by flowing hydrogen at 673 K for 10 h. The nickel weight loading ranged from 0.5 to 30 wt% (weight of metallic nickel to weight of silica gel). For a few selected samples with 5 wt% nickel, the amounts of nickel loaded were examined by atomic absorption spectrometry after extraction with nitric acid. The measured amounts were in agreement with the nominal value with errors smaller than 10%. The nominal values are hereinafter used for the nickel loading.

An unsupported nickel sample was also prepared from the same source as for the silica-supported sample. The nickel nitrate granules were ground in a mortar and reduced by hydrogen at 673 K for 10 h. Since the reduced sample comprised aggregated granules, it was ground again; a powder

of 60—150 mesh size was used for TPD. The nitrogen BET surface area of the obtained sample was 0.8 $m^2 g^{-1}$.

TPD of Hydrogen. The experiment involving TPD was performed with the same apparatus and procedure as used previously.[5] A nickel/silica sample (0.15 g) was reduced by hydrogen at 673 K for 30 min and cooled to room temperature. The sample was heated in flowing argon up to the adsorption temperature from 303 to 623 K. After the sample reached the desired temperature, argon was switched to hydrogen flowing at 30 ml min^{-1}; that temperature was maintained for 4 min, after which the sample was cooled to 303 K. It took about 5 min for this cooling. The sample was then exposed to flowing hydrogen totally for 10 min, at the desired temperature for 4 min and at decreasing temperatures for 6 min. This maximum temperature is merely called the adsorption temperature in the following sections. After hydrogen adsorption for 10 min, argon was passed through the sample in order to sweep hydrogen for about 20 min. The sample was then heated at 30 K min^{-1} and at an argon flow rate of 30 ml min^{-1}. The heating was limited to the temperature range up to 723 K in order to avoid any thermal effects on the sample. The hydrogen TPD was monitored by thermal conductivity detector. The TPD was repeated a few times for the same sample in order to obtain reproducible spectra. Under the present conditions, the initial coverage of hydrogen was close to unity at each adsorption temperature, based on a comparison of the total amount of desorbing hydrogen with those for longer adsorption times of up to 90 min.

For unsupported nickel powder, the same volume as that of a 0.15 g supported sample was used for its TPD measurement.

XRD and XPS. The nickel/silica samples were also characterized by other methods. The size of nickel particles was examined by Shimadzu XD-D1w XRD using Cu Kα radiation.[11] From the particle diameter measured, d, in nm, the degree of nickel dispersion was approximately evaluated by $0.9/d$.[12] A Shimadzu ESCA-750 was used to examine the state of surfaces of nickel particles. XPS spectra were collected after sputtering with Ar^+ and the data regarding the Ni $2p_{3/2}$ binding energy were charge-referenced to a C 1s binding energy of 285 eV.[13]

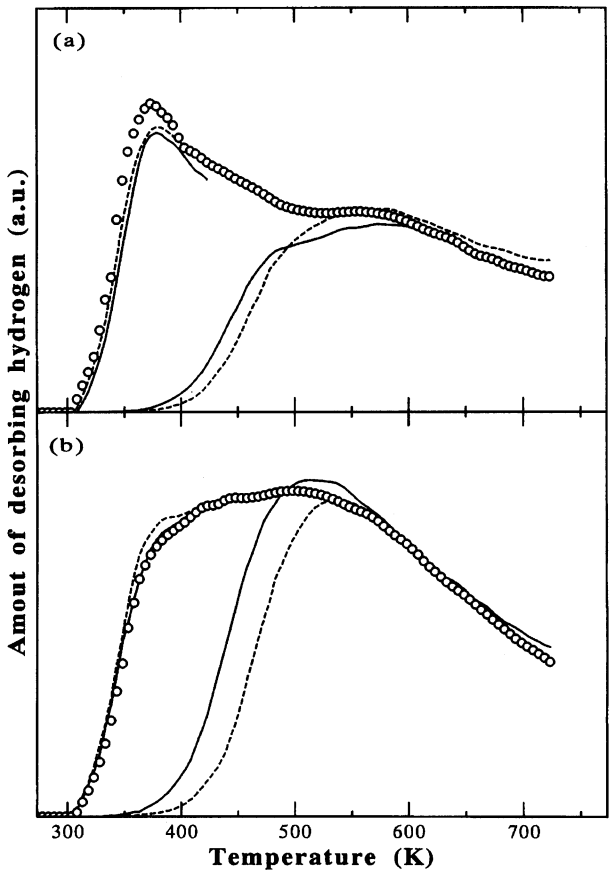

Fig. 1. TPD spectra of hyrogen adsorbed at (a) 303 K and (b) 623 K on a 5 wt% nickel/silica sample. Open circles indicate spectra collected with a standard heating schedule of 30 K min^{-1}. Lines indicate the spectra with interrupted heating schedules, as described in the text. Lines also indicate spectra for the first and second TPD: The solid and broken lines are for the cases in which the sample was kept at 303 and 393 K, respectively, after the interruption of the first TPD.

Results

Typical TPD Spectra. Figure 1 shows the typical TPD spectra (circles) of hydrogen adsorbed at 303 and 623 K for a 5 wt% nickel/silica sample. The former spectrum has two peaks at about 375 and 560 K, which will hereinafter be referred to as the first and second peaks, respectively. In contrast, the latter is very broad, showing larger amount of hydrogen desorbing in the second peak, compared with the former. The solid and broken lines are spectra for the so-called interrupted TPD,[14] in which first TPD was performed up to 423 K, cooled to 303 or 393 K, maintained at this temperature for 10 min, and cooled to room temperature; TPD was then again conducted up to 723 K. The first and second TPD spectra are separated from one another at either of the adsorption temperatures examined. These results show that hydrogen desorbing at higher temperatures hardly moves, during the interrupted period at 303 and 393 K, from the original adsorption sites to other sites that adsorb hydrogen desorbing at lower temperatures below 423 K. Since the source of support would often have a significant effect, another 5 wt% nickel sample has also been prepared using a silica gel (Davisil grade 646 from Aldrich Chemical Co., Inc.). It was calcined at 873 K, the BET area being 240 $m^2 g^{-1}$ after calcination, and loaded with nickel in the same manner as for Silbead-N. At an adsorption temperature of 303 K, the prepared sample has shown a TPD spectrum that has two major peaks that are similar to those shown in Fig. 1a.

The following sections describe the results obtained for samples of nickel on Silbead-N silica gel.

Effect of Metal Loading. Figure 2 gives the TPD spectra of hydrogen adsorbed at different temperatures for 0.5, 2.0, and 7.0 wt% nickel/silica samples. The

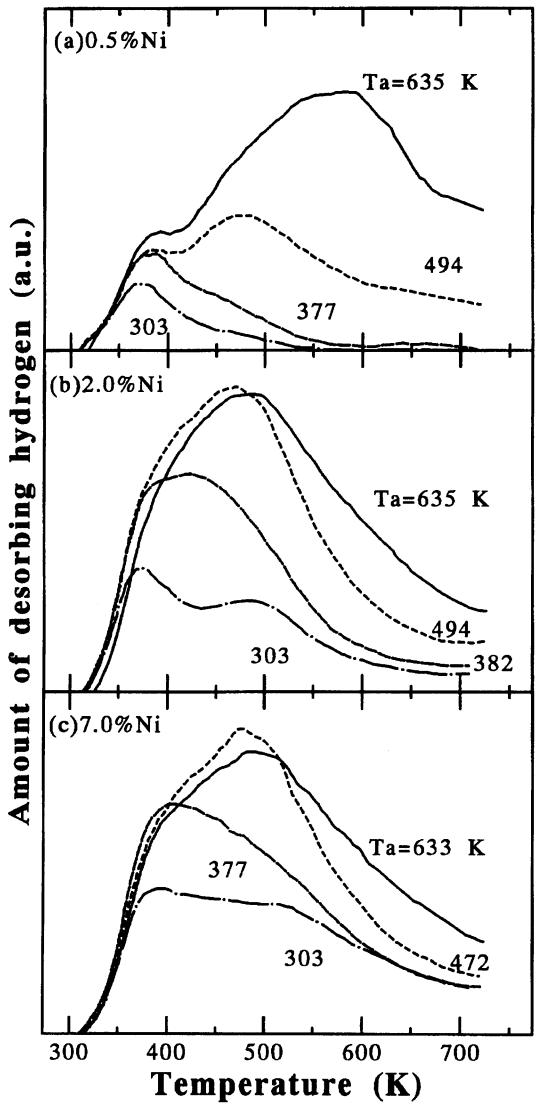

Fig. 2. TPD spectra of hydrogen adsorbed at different adsorption temperatures on (a) 0.5 wt%, (b) 2.0 wt%, and (c) 7.0 wt% nickel/silica samples.

metal loading mainly affects the second peak, which is absent for 0.5 wt%, is clearly seen for 2.0 wt%, and is included in a broad peak with the first one for the 7.0 wt% sample at an adsorption temperature of 303 K. As the temperature is increased, the amount of hydrogen desorbing up to 723 K is also increased and the temperature for the peak maximum tends to increase for these samples. The 0.5 wt% sample is different from the others in that the peak maximum appears at a higher temperature.

Figure 3 shows the influence of the adsorption temperature on the total amount of hydrogen desorbed up to 723 K, which is expressed by the relative value to that at 303 K for each sample. The effect of the adsorption temperature is larger for smaller metal weight loading; at an adsorption temperature of 623 K, the amount of desorbing hydrogen increases by factors of 8.5 and 2 for

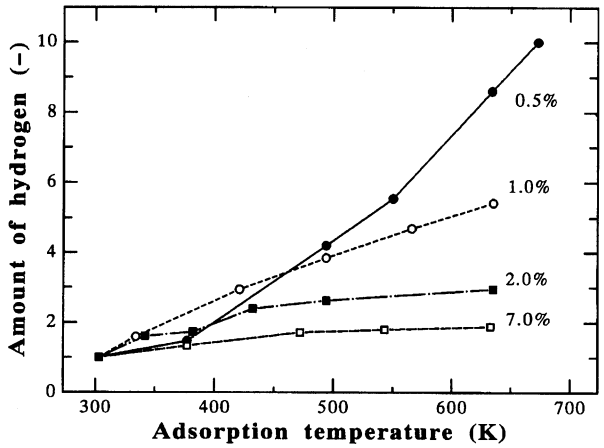

Fig. 3. Influence of the adsorption temperature on the total amount of hydrogen desorbing up to 723 K for nickel/silica samples with different metal loadings (as given).

0.5 and 7.0 wt% samples, respectively.

In Fig. 4, the degree of nickel dispersion from TPD as well as XRD is plotted against the nickel weight loading. It has been estimated from the total amount of desorbing hydrogen with a stoichiometry of one adsorbed hydrogen atom to one surface nickel atom. The TPD data at adsorption temperatures of 303 and 623 K are used in this estimation and the estimates are very different at small metal loadings. On the basis of the TPD data at 303 K, the degree of metal dispersion has a maximum at a nickel loading of around 4 wt%; based on the data at 623 K, however, it simply increases with decreasing metal weight loading, being in accordance with the trend observed for the XRD data.

Effect of Heat Treatment. The influence of heat treatments on TPD is illustrated in Fig. 5 for a selected

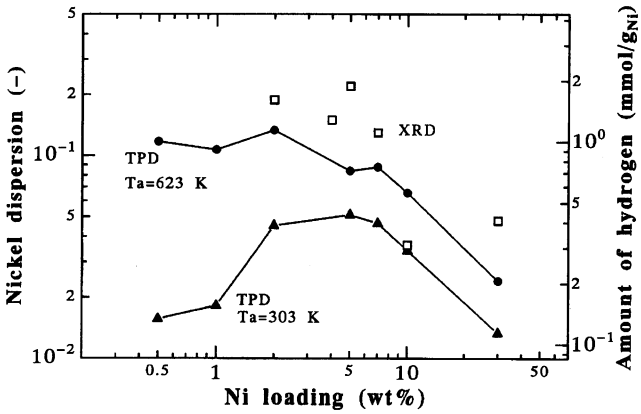

Fig. 4. Degree of nickel dispersion in nickel/silica samples as a function of nickel weight loading. The metal dispersion was measured by the total amounts of hydrogen desorbing up to 723 K; adsorption temperatures, T_a, are 303 K (closed triangles) and 623 (closed circles). The metal dispersion was also measured by XRD (open marks).

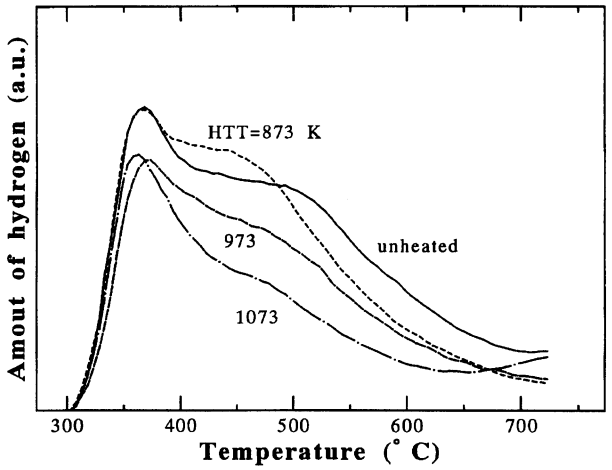

Fig. 5. Influence of heat treatments on the TPD of hydrogen adsorbed on a 5 wt% nickel/silica sample at 303 K. HTT is the heat-treatment temperature.

sample, 5 wt% nickel/silica. The effect significantly appears with treatments at 973 K or above, and it dose mainly on the second peak. The spectrum changes to that with the first peak only by a treatment at 1073 K. The total amount of desorbing hydrogen is 0.44 and 0.28 mmol g_{Ni}^{-1} before and after the treatment at 1073 K, respectively; this treatment causes a decrease by about 35%. Similar effects have also been observed for other samples that indicate two TPD peaks before a heat treatment.

Figure 6 shows TPD spectra of hydrogen adsorbed at 303 and 623 K for 0.5 and 5.0 wt% nickel/silica samples before and after a heat treatment at 1073 K. The treatment effect is small for the former sample, which adsorbs 1.0 and 0.87 mmol g_{Ni}^{-1} of hydrogen at an adsorption temperature of 623 K before and after the treatment, respectively. In contrast, the effect is significant for the 5 wt% sample, for which the treatment decreases the amount of desorbing hydrogen adsorbed at 623 K from 0.72 to 0.38 mmol g_{Ni}^{-1}, by about 50%, and the amount at 303 K from 0.44 to 0.28 mmol g_{Ni}^{-1}, by about 35 %. After the treatment, the amount of hydrogen adsorbed at 623 K is comparable to that adsorbed at 303 K.

For the 5 wt% nickel/silica sample, XRD shows the average diameter of metal particles to be 5.0 and 6.9 nm before and after a heat treatment at 1073 K, respectively, corresponding to dispersions of 0.18 and 0.13. This particle growth may be partly responsible for the above-mentioned decrease in the amount of desorbing hydrogen with the treatment.

TPD for Unsupported Nickel. For a comparison, TPD spectra have been collected for an unsupported nickel powder. Figure 7 shows the spectra of hydrogen adsorbed at 303 and 623 K. The spectrum at 303 K has a single peak at about 360 K, being similar to the first peaks for supported nickel/silica samples. The

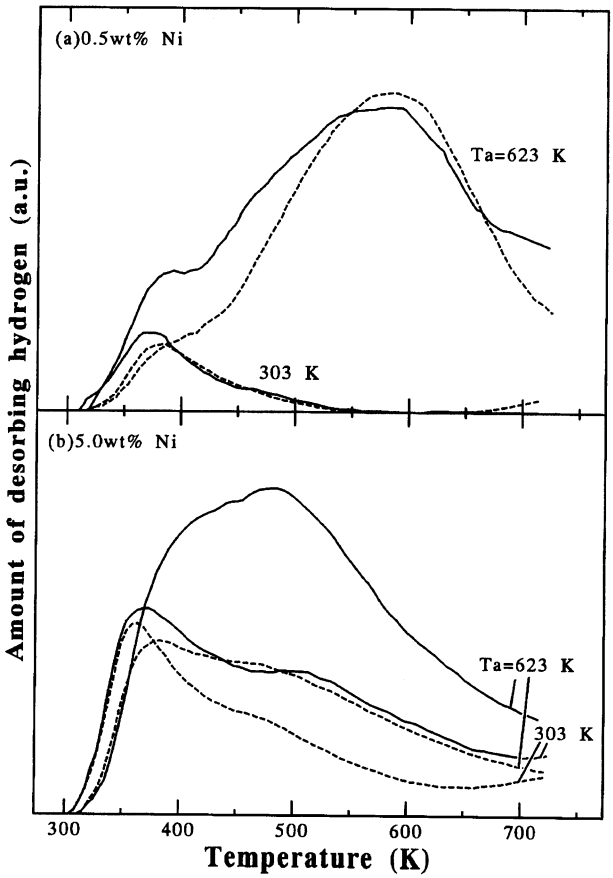

Fig. 6. TPD spectra of hydrogen adsorbed at 303 and 623 K on 0.5 and 5.0 wt% nickel/silica samples before (solid lines) and after (broken lines) heat treatment at 1073 K. T_a is adsorption temperature.

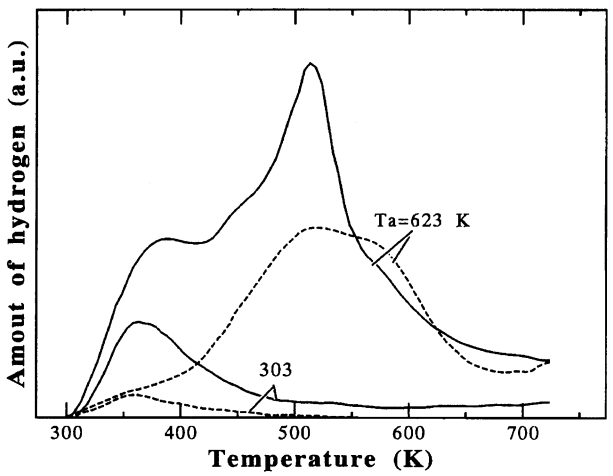

Fig. 7. TPD spectra of hydrogen adsorbed at 303 and 623 K on a sample of unsupported nickel powder before (solid lines) and after (broken lines) a heat treatment at 873 K. T_a is adsorption temperature.

adsorption at 623 K increases that peak and further gives other larger desorption peaks at higher temperatures. A heat treatment at 873 K decreases the amount

of desorbing hydrogen, probably due to sintering. The spectra at high desorption temperatures are somewhat different from those for supported samples, suggesting that the situation of hydrogen adsorption is different between unsupported bulk metal and supported fine particles as a result of size and support effects.

XPS. Figure 8 shows XPS results for supported and unsupported nickel samples. There is little difference in the binding energy of Ni $2p_{3/2}$ between 0.5 wt% and 5.0 wt% nickel/silica samples, and the energies are not influenced by a heat treatment at 1073 K. These XPS data are not correlative to the above-mentioned TPD data that show marked effects of metal loading and heat treatment. The binding energies of Ni $2p_{3/2}$ for supported samples are higher by about 2 eV compared with those for unsupported samples, suggesting some size and/or support effects. It was previously reported that dispersed small metal particles indicated larger binding energies compared with bulk metal for palladium on silica.[15,16]

Discussion

The obtained TPD spectra show that silica-supported nickel samples have different sites for hydrogen adsorption, being in agreement with the previous results of Konvalinka et al.[4] In addition, the present data at changing adsorption temperatures clearly show that both nonactivated and activated adsorption sites are present and that the population of these sites is a strong function of the metal weight loading and heat-treatment temperature. Previously, Weatherbee and Bartholomew observed only a single peak for TPD at adsorption temperatures below 520 K, and indicated that hydrogen adsorption was not activated for their silica-supported nickel samples.[2] This is not in accord with the present results, probably due to differences in the sample-preparation variables. The thermal history of samples is of significance regarding the TPD spectra, as described above.

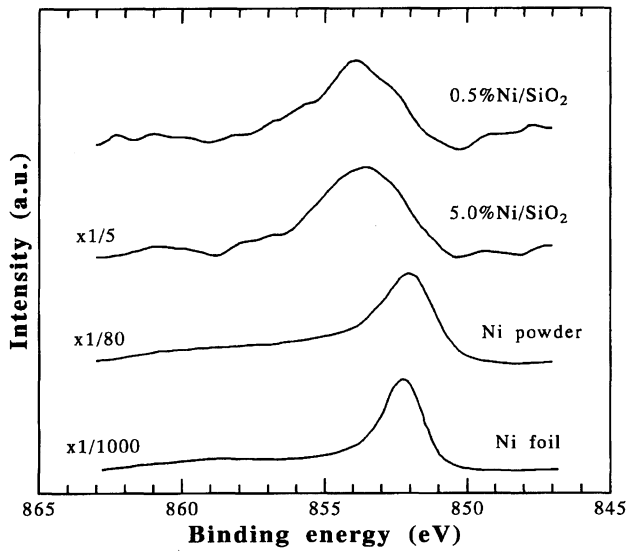

Fig. 8. XPS spectra of Ni $2p_{3/2}$ for silica-supported and unsupported nickel samples.

The present data have demonstrated that the TPD spectra of hydrogen adsorbed on the prepared nickel/silica samples have two major peaks appearing at about 375 and 560 K, indicating the presence of two types of adsorption sites. These two sites are tentatively referred to as A and B sites, corresponding to the first and second peaks, respectively. The two sites may be present on the surface of nickel particles, since the metal dispersion based on TPD data approximately agrees with that based on XRD data (Fig. 4); further, two or more TPD peaks have also appeared for nickel powder at a high adsorption temperature of 623 K. The first peak occurs over a range of desorption temperatures that is similar to a single peak observed for hydrogen adsorbed on single crystal planes of low Miller indices, the state of the adsorbed hydrogen being called β_2 or β.[6—8] It is therefore assumed that the A sites are such low-Miller-index planes and the B sites are some defects and high-Miller-index planes. The adsorption can easily take place for the former sites, while it should go over some energy barrier for the latter.

The number of A and B sites may depend on the size and thermal history of nickel particles. Metal atoms on the surface of a small particle would be highly coordinately unsaturated, having a large fraction of B sites on its surface. Such small particles are probably abundant in samples with low metal loading; these particles result in the second peak for TPD at high adsorption temperatures. A few larger particles are also present and give a single peak, the first peak, for TPD at low adsorption temperatures. Increasing the particle size would increase the fraction of A sites; large particles have both A and B sites on their surfaces. These large particles are abundantly present in samples with larger metal loadings. Hydrogen adsorbed on A sites of a particle would easily move to B sites of the same particle; the two peaks have been observed on TPD, even at an adsorption temperature of 303 K for larger nickel loading. Smaller particles are also present and can adsorb more hydrogen at higher temperatures, giving increased amounts of hydrogen desorbing at temperatures around the second peak.

The surface morphology of metal particles will change with the heat treatment. They would cause a reconstruction of the surface metal atoms, leading to a disappearance of defects and high-Miller-index planes, while causing the particle growth due to sintering. For a silica-supported nickel catalyst, such a morphological change with heat treatments was reported by Lee et al.[17] Of the present heat treatments conducted, those at 973 K or above have a significant effect. As a result of those treatments, although the B sites change into A sites the total number of A and B sites decreases. This idea can explain the changes in the TPD

spectra observed for samples with larger metal loading. For smaller nickel loading, 0.5 wt% for example, heat treatments have only slightly affected the TPD spectra of hydrogen adsorbed at the temperatures examined (Fig. 6a). It therefore seems that any change in the surface morphology with the heat treatment is inhibited for small particles in this sample, probably due to some support effects.

For hydrogen desorbing in the second peak, there is another possibility that it is adsorbed on the surface of the support through the so-called spillover.[18] Silica supports can be acceptors for spiltover hydrogen, as was clearly demonstrated by Cevallos-Candau and Conner.[19] In the present cases at high adsorption temperatures, spillover may be possible and hydrogen adsorbed on the support would desorb at temperatures in the second peak; the A sites are present on nickel particles and the B sites on the support. This will be examined by further work using infrared spectroscopy,[19] electron paramagnetic resonance,[20] and other methods.

For titania- and carbon-supported cobalt catalysts, Zowtiak and Bartholomew indicated the presence of some different adsorption sites from multiple TPD peaks of hydrogen.[21] They suggested that this was a result of metal-support interactions. The TPD data for the present nickel/silica catalysts may be correlated to the morphology of nickel particles without invoking such interactions, except that the support may inhibit morphological changes of small particles with heat treatments, as described above.

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