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Catalyst Preparation Procedure Probed by EXAFS Spectroscopy. 1. Nickel on Silica

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Abstract: Environments of Ni atoms were probed by extended X-ray absorption fine structure (EXAFS) at every elementary step of Ni/SiO_2 catalyst preparation by two different methods. Combining the structural information obtained at the atomic level by EXAFS with the observation of the bulk by electron microscopy, detailed reaction procedures leading to different products have been revealed. The reason metal particle size distribution depends on the preparation procedure employed is ascribed to whether or not homogeneous dispersion of a small metal oxide cluster is realized before reduction.

In recent years EXAFS (extended X-ray absorption fine structure) has been recognized as an invaluable tool for the determination of the structure of matter.[1] Strong white X-rays from SR (synchrotron radiation) have made a major contribution for the advancement of EXAFS along with theoretical achievements.[2,3] At the same time, restricted machine hours available at SR stations have imposed a serious limitation on the popularity of EXAFS.

The most outstanding feature of EXAFS is the possibility of the determination of the local structure of each selected atomic species in any phase. From an analysis of EXAFS data, one can obtain information on the number and type of neighboring atoms around a selected absorbing atom, on interatomic distances, and on the root mean square deviation of the interatomic distances about the equilibrium. By making use of its advantage over the X-ray diffraction method, EXAFS has mainly been applied for the structure determination of noncrystalline solids and solutions. Besides, EXAFS is best suited to trace a procedure of synthesis through a chain of chemical reactions, because products of each elementary step can be probed regardless of the phase of the products. In spite of the potential ability of EXAFS as a probe for chemical reactions, however, it seems that there is no extensive study along this line.

It is well-known that the activity and selectivity of a metal-supported catalyst strongly depend upon the method of the catalyst preparation employed.[4] It has been anticipated that the size of metal particles on a support makes a difference in selectivity.[5] Hence, development of techniques to control the metal particle size has been desired. The conventional method of preparation called the impregnation method, however, gives a catalyst whose metal size distribution is fairly broad. One of the present authors empirically found that the hydrolysis of a mixed solution of a metal alkoxide and ethyl silicate, which is called the alkoxide method, can supply the silica-supported metal catalyst with homogeneous metal size, and the size can be controlled by the metal concentration of the starting material.[6]

The main purpose of the present report is to find out by the use of EXAFS spectroscopy why the alkoxide method has the ability to control the metal particle size on a support. The local structure around the metal is probed at every elementary stage of the preparation in both the alkoxide and the impregnation method. We conclude that the key to control the metal particle size is to disperse the metal oxide homogeneously among the support material before the reduction, which is the final step in catalyst preparation. The homogeneous metal oxide distribution is realized through the formation of a chemical bonding in the alkoxide method. The sample studied here is a silica-supported nickel catalyst that is known to be active for hydrogenation of olefins. A part of the present results has already been reported in a preliminary form.[7]

All the results reported here were obtained by a spectrometer with a conventional X-ray source. It will be clear that a small-scale EXAFS facility can supply spectra of enough quality for practical analyses and that much more work can be done by EXAFS spectroscopy in laboratories.

Table I. Preparation Procedures of Ni/SiO_2 Catalyst by the Alkoxide and the Impregnation Method

alkoxide method	impregnation method
a-1: $Ni(NO_3)_2$ dissolved in ethylene glycol; kept stirred at 80 °C for 4 h	i-1: impregnation of silica with $Ni(NO_3)_2$ aq solution followed by drying at 110 °C overnight
a-2: addition of $Si(OEt)_4$; kept stirred at 80 °C for 4 h; after hydrolysis at 80 °C for 15 h; a gel is formed	i-2: calcination in air at 450 °C for 24 h
a-3: drying at 110 °C for 24 h	i-3: reduction by H_2 at 450–500 °C for 4–10 h
a-4: calcination in air at 450 °C for 4 h	
a-5: reduction by H_2 at 450–500 °C for 4–10 h	

Experimental Section and Data Analysis

The details of the preparation of the silica-supported nickel catalyst through the alkoxide method has been reported;[6] hence only the procedures are listed in Table I as well as those of the impregnation method. The Ni concentration of the starting material is 20 wt %, but after the filtering and washing, the Ni concentration of the catalyst prepared by the alkoxide method is about 10 wt %. The Ni concentration of the catalyst prepared by the impregnation method is also 10 wt %. The liquid samples and the gel were kept between thin Mylar windows by the use of a copper spacer. The solid samples were prepared by pressing the powders into thin wafers in an IR pellet press. Boron nitride was used to dilute the sample if necessary.

The EXAFS spectrometer employed in this work is described elsewhere.[8] Basically it consists of a rotating-anode X-ray generator (Rigaku RU-200), a goniometer with a flat Ge (220) perfect crystal, slits, an SSD (Canberra 711007), an automatic sample positioner, and counting electronics, many of which are controlled by a microcomputer (SORD 223) through CAMAC bus.

Absorbance μx is obtained as $\mu x = \ln (I_0/I)$ where I and I_0 are count numbers with and without the sample and x is the sample thickness. The average data collection time was approximately 20 h and the signal count I_0 of over 2×10^6 was obtained at each data point. Measurements were made on each sample more than once, and no sample degradation was

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[*] Institute for Molecular Science.

[†] Toyohashi University of Technology.

(1) See review by: Lee, P. A.; Citrin, P. H.; Eisenberger, P.; Kincaid, B. M. *Rev. Mod. Phys.* **1981**, *53*, 769–806.

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(4) Delmon, B.; Jacobs, P. A. "Preparation of Catalyst I, II"; Poncelet, G. Ed.; Elsevier: Amsterdam, 1975, 1978.

(5) Uchijima, T.; Herrman, J. M.; Inoue, Y.; Burwell, R. L.; Buff, J. B.; Cohen, J. B. *J. Catal.* **1977**, *50*, 464–478.

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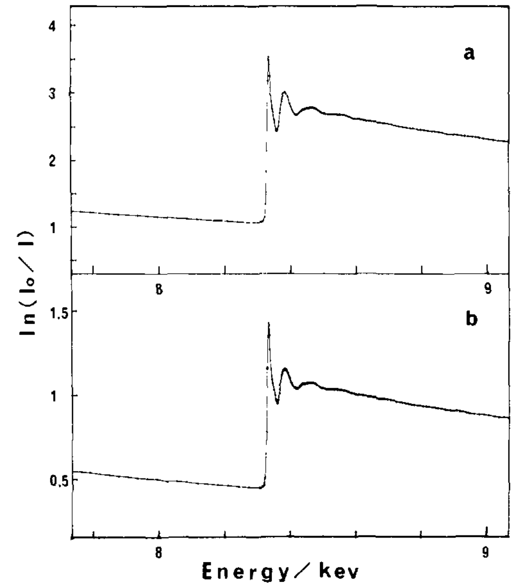

Figure 1. EXAFS spectra of (a) $Ni(NO_3)_2$ dissolved in ethylene glycol at step a-1 and (b) the gel at step a-2 of the alkoxide method of Table I.

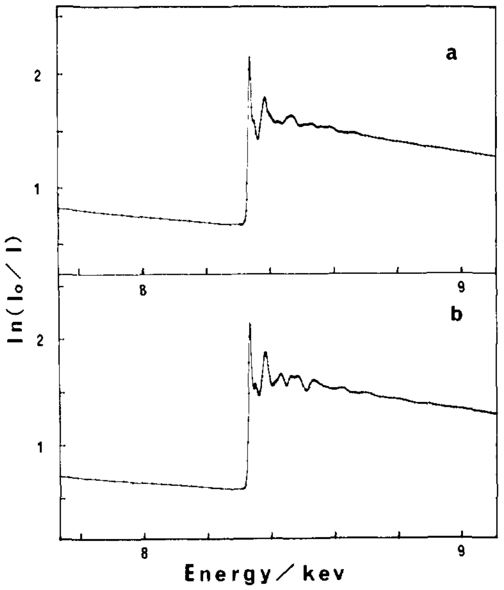

Figure 2. EXAFS spectra of (a) dried sample at step a-3 and (b) calcined sample at step a-4.

observed during the data acquisition time.

Absorption due to the atoms other than Ni was estimated by least-squares fitting Victoreen's formula[9] to the preedge absorption and was subtracted by the use of interpolation. The EXAFS function χ is defined by the equation $\chi(k) = (\mu - \mu_0)/\mu_0$ where μ and μ_0 refer to absorption by the atoms in the material of interest and in the vacuum, respectively. The smooth background μ_0 was obtained by iteratively applying the formula

$$\mu = (\mu_{i+1} + 2\mu_i + \mu_{i-1})/4 \qquad (1)$$

over the data points used for the analysis and was found to be a good approximation for μ_0. Then the extracted EXAFS oscillation was Fourier transformed into real space by employing the following formula derived by single scattering theory[2,3]

$$\chi(k) = \sum_j \frac{N_j}{kR_j^2}\exp(-2(\sigma_j^2k^2 + R_j/\lambda))F_j(\pi,k)\sin(2kR_j + \alpha_j(k)) \qquad (2)$$

where N_j is the number of atoms in the jth shell, R_j is the distance from the central absorbing atom to atoms in the jth shell, F_j is the scattering amplitude, σ_j is Debye–Waller factor, and $\alpha_j(k)$ is the phase shift. The EXAFS function was Fourier transformed by weighing k^3 to yield the radial structure function $\phi(R)$ as follows.

$$\phi(R) = (1/2)^{1/2}\int k^3\chi(k)\exp(-2\pi kR)\,dk \qquad (3)$$

The absorption edge energy E_0, which is necessary to define photoelectron wave vector k by

$$k = \sqrt{2m(E - E_0)}\Big/\hbar$$

was determined by matching the maximum of the absolute value of the Fourier transform to that of the imaginary part. The residual low-frequency oscillation due to improper background subtraction was eliminated by inverse Fourier transformation techniques. The apparent distance R_{ap} obtained from the peaks of $\phi(R)$ is known to be displaced from the true one by δ because of the phase shift on scattering. Therefore, the bond distances as well as the coordination numbers N_j were determined by curve fitting techniques. The main peaks in $\phi(R)$ were backtransformed to k space and compared with the calculated curves by the use of eq 2. The backscattering amplitudes and phase shifts reported by Teo and Lee[10] were used, and R, λ, σ, and N were varied as parameters.

Results

Observed Spectra for the Alkoxide Method. The EXAFS spectra obtained at each step of the catalyst preparation procedure with the alkoxide method are shown in Figures 1–3 and will be described in the following. The first step of the catalyst preparation by the alkoxide method is to dissolve nickel nitrate into ethylene glycol at 80 °C. In the second step ethyl silicate was added to the solution and kept stirred for 5 h at 80 °C. Then a proper amount of water was poured into the solution. After the solution is stirred for 15 h, a gel is obtained. Figure 1 depicts the EXAFS spectra of Ni dissolved in ethylene glycol and the gel. These two spectra are simple and look quite similar to each other, suggesting that only the first shell is visible by EXAFS in these samples and that the kind and number of the atoms of the first shell are the same for both samples.

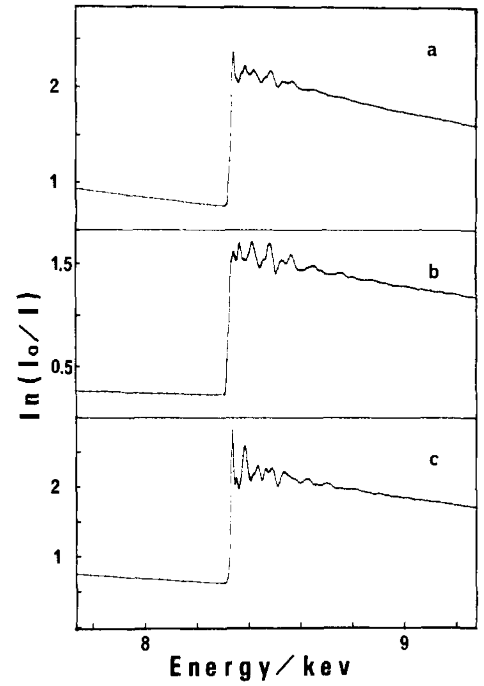

Figure 3. EXAFS spectra of (a) the catalyst at step a-5, (b) Ni foil, and (c) NiO powder.

In the third step the gel was filtered and washed with distilled water, followed by drying at 110 °C in an oven. The EXAFS spectrum of the dried sample shown in Figure 2a clearly has more structure than the previous two, indicating the appearance of more than one kind of scattering center. The fourth step of the catalyst preparation is to calcine or to heat at 450 °C for 4 h in air. The EXAFS spectrum of the calcined sample shown in Figure 2b has

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(9) "International Tables for X-ray Crystallography"; Ibers, J. A.; Hamilton, W. C., Eds.; Kynoch Press: Birmingham, England, 1974; Vol. III, p 161.

(10) Teo, B. K.; Lee, P. A. J. Am. Chem. Soc. 1979, 101, 2815–2832.

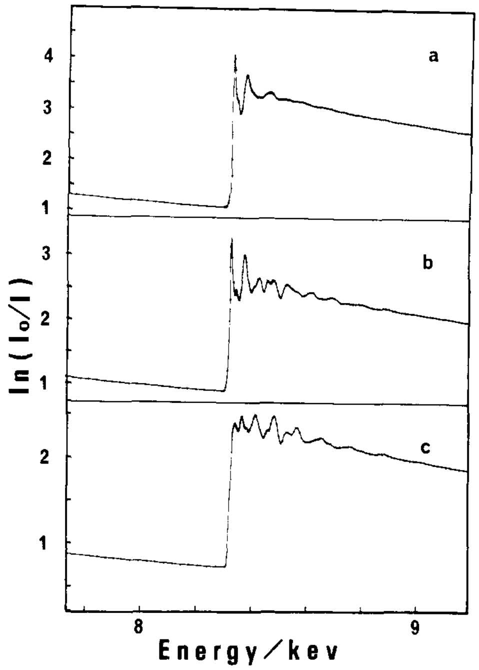


Figure 4. EXAFS spectra of (a) dried sample at step i-1, (b) calcined sample at step i-2, and (c) the catalyst at step i-3 of Table I.

much more complicated oscillation than the previous one. It looks similar to, but is not the same as, the spectrum of the reference sample NiO whose spectrum is shown in Figure 3c.

At the final stage of the preparation the calcined sample is reduced by hydrogen. The EXAFS spectrum of the reduced sample changes with reduction condition, and Figure 3a shows the one reduced at 500 °C for 7 h. For comparison the spectrum of Ni foil is shown in Figure 3b. There is a distinct difference between Figure 3a and 3b near the absorption edge. Beyond 30 eV above the edge, the region used for EXAFS analysis, however, the spectral features resemble each other. Therefore the formation of Ni metal is confirmed from raw EXAFS spectra. The difference in the near-edge structure is attributed to the existence of the sharp, strong "white line" of the NiO clusters, which still remain unreduced in Figure 3a.

Observed Spectra for the Impregnation Method. The first step of catalyst preparation by the impregnation method is to impregnate silica powder with an aqueous solution of $Ni(NO_3)_2$. The surface area of the silica powder is about 390 m^2/g. Then the sample is dried at 80 °C. The EXAFS spectrum of the dried sample is shown in Figure 4a. The oscillation is not monotonous, indicating the appearance of a second shell. The second step is to heat the sample at 400 °C for 4 h. The EXAFS spectrum of the calcined sample is shown in Figure 4b, and it coincides completely with that of NiO powder shown in Figure 3c. The final stage is the reduction, and the spectrum of the reduced sample is shown in Figure 4c. At a glance it is evident that it coincides completely with Figure 3b and that all nickel atoms exist as metal particles.

Discussion

In the present investigation the changes of local structures around Ni were probed by EXAFS spectroscopy at every elementary step of Ni/SiO_2 catalyst preparation by both the alkoxide method and the impregnation method. The information obtained by the analysis of the EXAFS spectra reflects the local structure around the Ni atom and is complementary to that of bulk structure obtained from observation by electron microscopy. Combining these two methods will lead us to a full understanding of the catalyst synthesis procedure. In the following, the implications of the EXAFS spectra are discussed, supported by the results of electron microscopy as well as those of IR and NMR spectra.

Catalyst Preparation Procedure by the Alkoxide Method. At the first step of the alkoxide method the solution shows strong acidity; therefore dissociation of ethylene glycol and subsequent coordination to nickel by oxygen atoms of ethylene glycol are anticipated. The ^{13}C NMR spectrum of this solution has two peaks, as is shown in Figure 5a. One peak coincides with that of pure ethylene glycol and the other is shifted a little. The latter is understood to be due to the carbon atoms of $(CH_2O)_2$, which coordinate to Ni atom. The coordination is confirmed, and the coordination number is estimated from the Fourier analysis of the EXAFS spectrum shown in Figure 6a. Only one strong peak is observed at 1.65 Å and is assigned to the Ni–O distance since the peak due to the Ni–O distance appears at the same position in the reference sample NiO. Curve fitting gives 2.05 Å as the bond distance, which is in agreement with the Ni–O distance of known compounds.[11] The EXAFS amplitude estimated by an inverse Fourier transform of the main peak is almost the same as that for the NiO crystal. Since the nickel atom is known to be surrounded by six oxygen atoms in NiO,[11] the same coordination number is expected for the solution prepared in the first step.

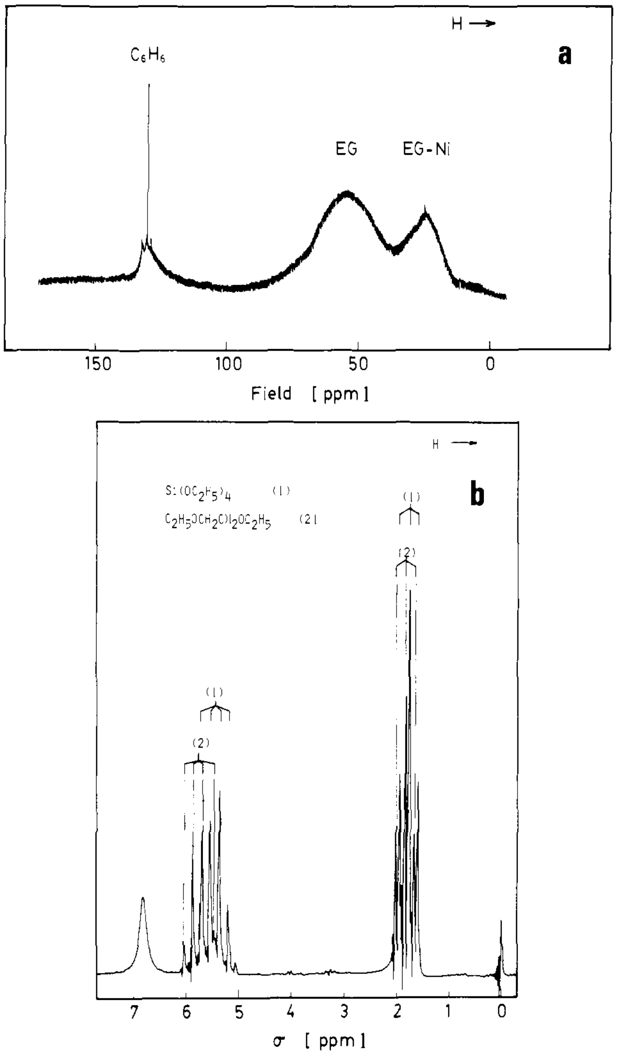
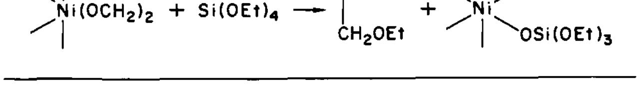


Figure 5. (a) C-13 NMR spectrum of $Ni(NO_3)_2$ of ethylene glycol obtained by a Varian FT-80 spectrometer. C_6D_6 was used as a locking material and C_6H_6 as a standard. (b) NMR spectrum of the solution of steep a-2. The spectrum coincides with that of 1,2-diethoxyethane.

In the second step a considerable amount of 1,2-diethoxyethane was detected by ^1H NMR as is shown in Figure 5b, indicating that ethyl silicate has reacted to make Ni–O–Si species as follows.



$$>Ni(OCH_2)_2 + Si(OEt)_4 \longrightarrow \begin{array}{c} CH_2OEt \\ | \\ CH_2OEt \end{array} + >Ni\begin{array}{l} OSi(OEt)_3 \\ OSi(OEt)_3 \end{array}$$

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[11] Rooksby, H. P. *Acta Crystallogr.* **1948**, *1*, 226.

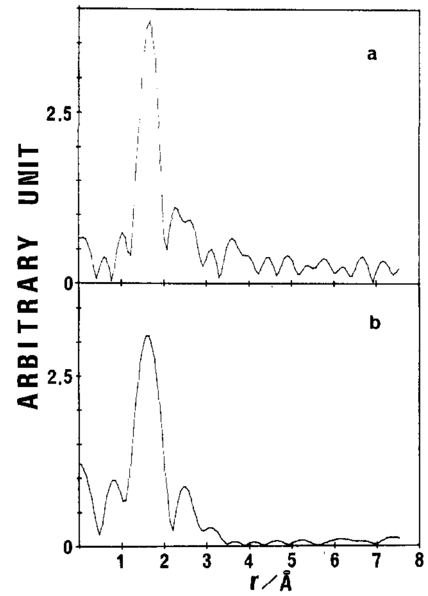

Figure 6. Fourier transform of the EXAFS spectra of (a) $Ni(NO_3)_2$ in ethylene glycol and (b) the gel shown in Figure 1.

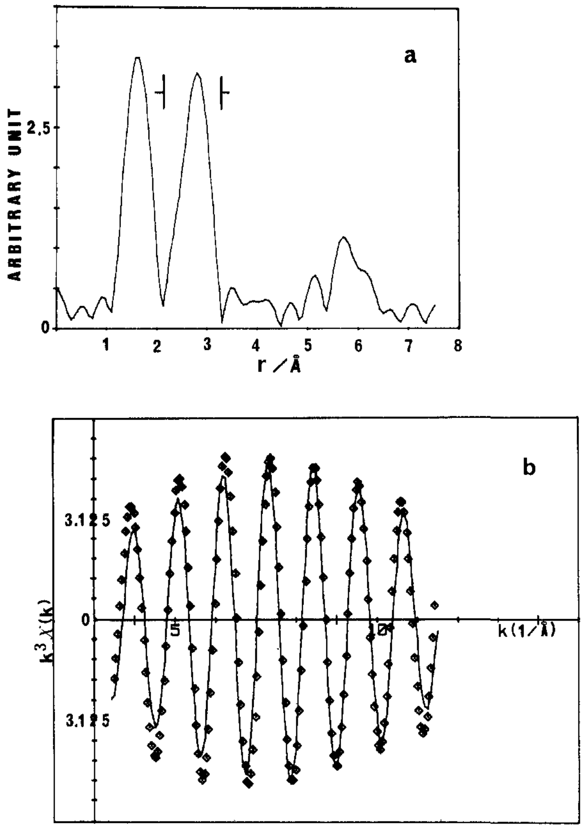

Figure 7. (a) Fourier transform of the EXAFS spectrum of the dried sample shown in Figure 2a. (b) The comparison of the inverse Fourier transform (solid line) of the second peak of (a) with the calculated $k^3\chi(k)$ curve (dots) assuming Ni–Si scattering. The range of the inverse transform is indicated in the figure.

However, only a single peak appears in the Fourier transform shown in Figure 6b, and the position is the same as that of ethylene glycol solution. This means that the first shell still consists of oxygen atoms, and the silicon atoms expected in the second shell could not be seen from EXAFS spectrum at this stage.

The Fourier transform of the EXAFS spectra of the dried sample shown in Figure 7a has two distinct peaks. The first one is located at the same position as the previous two Fourier transforms, and it is certain that this corresponds to Ni–O bonds. Since the difference between the gel and the dried sample is just dehydration, the second atoms that make the second peak in Figure 7a must still be Si. This is supported by the observation of the 975-cm^{-1} band in the IR spectrum of this compound,[6] which indicates the existence of Ni–O–Si species. In order to further confirm the nature of the nearest shells the comparison of the inverse Fourier transform of each peak with the calculated $k^3\chi(k)$ curves was made. From the comparison with the model compound NiO, it is concluded that the first shell is made of six oxygen atoms with Ni–O distance of 2.05 Å. Inverse Fourier transform of the second peak is shown in Figure 7b, as well as the "best-fit" curve calculated by employing the phase shift and the amplitude factor of Si.[10] As is readily seen the calculated curve reproduces the observed one quite well. On the other hand, calculated curves assuming Ni–Ni scattering could not reproduce the inverse FT oscillation. Therefore, in addition to the IR data, the analysis of the EXAFS spectrum gives another evidence that the second shell is made of Si atoms. From the comparison of the amplitude of the calculated curve and of the inverse Fourier transform, the Ni–Si distance is found to be 3.30 Å and the number of Si atoms around Ni was determined to be about six. The reason the second shell is clear in this sample and not seen in the previous one must be due to the uncertainty of the position of the Si atom. In the gel, the skeleton is not rigid and the rotation around Ni–O axis is possible. When dried, the sample becomes solid and the position of Si atoms relative to the Ni atom are fixed, allowing the distinct peak to appear in the EXAFS.

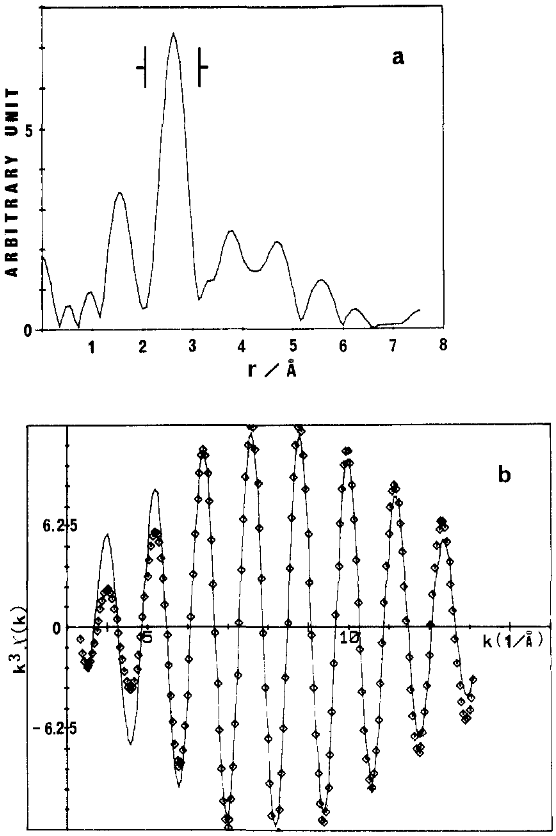

Figure 8. (a) Fourier transform of the EXAFS spectrum of the calcined sample shown in Figure 2b. (b) The comparison of the inverse Fourier transform (solid line) of the second peak of (a) with the calculated $k^3\chi(k)$ curve (dots) assuming Ni–Ni scattering. The range of the inverse transform is indicated in the figure.

The Fourier transform of the extracted oscillation of the EXAFS spectrum of the calcined sample is shown in Figure 8a. The nature of the first peak at around 1.6 Å is clear, and the first shell still consists of six oxygen atoms. The position of the second peak is close to that of the dried sample shown in Figure 7a, but as was shown previously, the spectrum resembles that of NiO, where the second shell is, of course, Ni atoms. To distinguish whether the second shell is Ni or Si, a simulation was carried out. The curve fitting using the parameters for Ni–Si could not reproduce

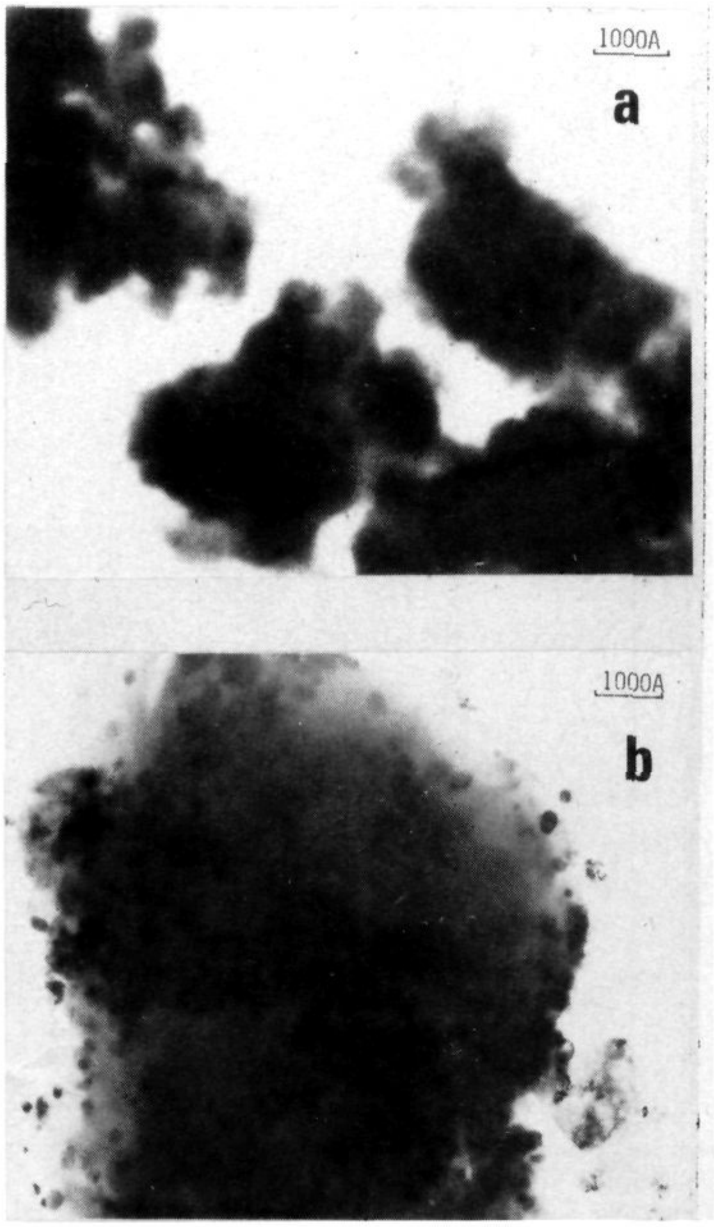

Figure 9. (a) Electron microscope photograph of the dried sample prepared by the alkoxide method. No apparent particles are observed. (b) Electron microscope photograph of the dried sample prepared by the impregnation method. Particles with various sizes are clearly visible.

the oscillation, whereas by employing the parameters for Ni–Ni reproduced the curve quite well, as is shown in Figure 8b. Indeed, the Fourier transform shows that the positions of the first and the second peaks are the same for the calcined sample and NiO powder. Therefore, it should be concluded that a rearrangement of atoms must have taken place by heating, making NiO clusters. Since silica has many polymorphic forms and the silica employed here is amorphous, a reconstruction of network must be possible by raising the temperature, leading to a rearrangment of atoms.

If compared with the Fourier transform of the EXAFS of NiO crystal shown in Figure 10c, however, the relative intensity ratio of the first and the seond peak is different and the distant peaks of the calcined sample are irregular. These features are understood to reflect that the sample does not have a long range order of unique structure around Ni atoms. IR spectra still show an absorption band at 975 cm^{-1}, indicating the existence of Ni–O–Si species.

A picture consistent with all the observations is that small NiO clusters are formed and that Ni–O–Si bonds exist at the fringe of the clusters. Therefore, although the result of curve fitting favors that the peak at 2.8 Å is due to Ni–Ni scattering, there must be some contribution from Ni–Si scattering. The size of the NiO clusters should be less than 20 Å, since no distinct structure is observed by the electron microscope with magnification of 10^5, as is shown in Figure 9a. It is expected that the distribution of these small NiO clusters is uniform inside the support material, because the sample is prepared by chemical reaction in solution.

The final stage is the reduction. It must be noted that longer hours and higher temperatures are required to reduce the sample prepared by the alkoxide method than the one by the impregnation method. It is attributed to the fact that Ni atoms are in the bulk, not on the surface of the support. The Fourier transform of the EXAFS spectrum of the reduced sample changes upon the condition of reduction, and Figure 10a shows one reduced at 500 °C for 7 h. For comparison, Fourier transforms of Ni foil and that of NiO powder are also shown in Figure 10b and 10c, respectively.

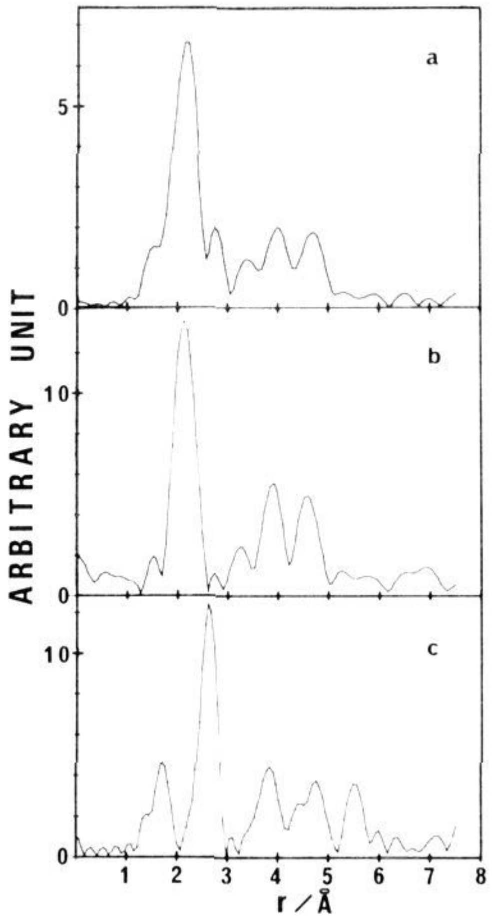

Figure 10. Fourier transform of the spectra of (a) the catalyst shown in Figure 3a, (b) Ni foil shown in Figure 3b, and (c) NiO powder shown in Figure 3c.

The main peaks in Figure 10a coincide with those of Ni foil shown in Figure 10b. Unlike the calcined sample even the distant peaks are the same as those of Ni foil, indicating that the metal particles are large enough to show bulk properties in the EXAFS spectrum. The additional peak at 2.7 Å in Figure 10a has two possibilities. One is that it is due to Ni–Ni scattering of NiO clusters, which still exist unreduced. The other, which is more attractive, is that it is due to Ni–O–Si which exists at the edge of Ni metal. The fact that it still exists under the severest reduction conditions employed favors the latter possibility but is not decisive at all. Since it is not a well-separated peak, the inverse Fourier transformation technique could not give a unique solution.

It is concluded from EXAFS spectra that nickel metal with long range order grows by reducing the uniformly distributed small NiO clusters. The conclusion is consistent with the observaion that nickel metal clusters are observed by the electron microscope at this stage. They have uniform size of 20–100 Å, depending upon the Ni concentration of the starting materials.

Catalyst Preparation Procedure by the Impregnation Method. The Fourier transform of the EXAFS spectrum of the dried sample prepared by the impregnation method is shown in Figure 11a. The existence of the Ni–O bond is evident from the comparison with the figures shown above. Coordination number of 6 is also confirmed from comparison of the amplitudes. In addition to the peak due to Ni–O, there is another peak at 2.8 Å that is exactly the same as the Ni–Si distance observed for the dried sample by the alkoxide method. The peak height is, however, about half of that in Figure 7a. Therefore it must be due to about three silicon atoms which form the second shell, and they should be Si atoms of SiO_2 on the surface. A model compatible with the observation is that Ni atoms are adsorbed on the surface of silica in the sample prepared by the impregnation method, while they are in the bulk in the sample by the alkoxide method. Three out of six oxygen atoms must be those of SiO_2, and the other three are, probably, of water coordinated around Ni. No particle was visible by the electron microscope, indicating that Ni atoms do not form big aggregates either as Ni metal or as NiO, but rather Ni atoms individually exist, probably by chemisorption, on the surface of the support.

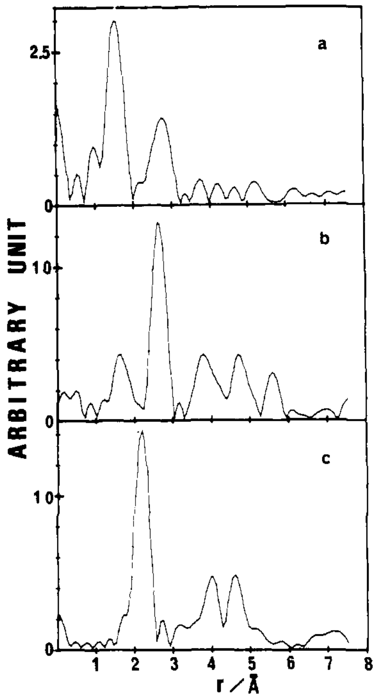

Figure 11. Fourier transform of the EXAFS spectra of (a) the dried sample of Figure 4a, (b) the calcined sample shown in Figure 4b, and (c) the catalyst shown in Figure 4c prepared by the impregnation method.

The Fourier transform of the EXAFS spectrum of the sample after the calcination procedure is shown in Figure 11b. From the comparison with Figure 10c it can be known that NiO crystallites are formed by calcination. Particles of various sizes ranging from 20 to 600 Å are observed by the electron microscope shown in Figure 9b, and EXAFS spectra clearly show that they are NiO crystallites. Therefore the rearrangements of atoms take place by calcination, as in the alkoxide method, and in the case of the impregnation method a growth of large NiO clusters occurs, i.e., the main difference between the alkoxide method and the impregnation method is concluded to be the size of NiO clusters formed by the calcination procedure. In the alkoxide method NiO clusters are too small to be observed even by the electron microscope, and uniform distribution inside the support material is expected, because the sample is prepared by chemical reaction in solution. On the other hand, big NiO clusters that are easily visible by the electron microscope are formed by the impregnation method, and the size distribution is quite broad. The size of the NiO cluster is so large that only bulk NiO is visible and no surface effect was detected by EXAFS spectra.

Greeger et al.[12] have studied the EXAFS spectra of Ni/Al_2O_3 made by the impregnation method. They reported that bulklike NiO ($N = 6$) is formed by calcination for the sample with high Ni concentration and that N reduces as the Ni content is decreased and reaches 4.8 (±20%) at 2.5% Ni loading. No prominent reduction in N was observed at the concentration studied here (10%). The concentration employed here might be too high to observe metal–support interaction, which agrees with their observations.

By reduction, which is the final step of the catalyst preparation procedure, NiO is reduced to form Ni metal. The spectrum and the Fourier transform of the reduced sample shown in Figure 11c coincide with those of Ni foil, indicating that Ni metal particles are formed and their sizes are large enough and atoms at the surface can be neglected. Electron microscopy indeed shows the existence of the particles whose size ranges to several hundred angstroms.

Conclusion

It is now clear why the alkoxide method can supply nickel-supported silica catalyst with uniform particle size while the impregnation method usually cannot. From the observations above, it is concluded that the key to control Ni particle size is to disperse small NiO clusters uniformly among the support materials. In the alkoxide method Ni–O–Si species are formed by chemical reaction in solution and as a result Ni atoms are homogeneously distributed inside the support material. By heating, rearrangements of atoms take place, making tiny NiO clusters. They are too small to be observed by the electron microscope, and the difference from NiO crystallite is clearly visible even in the EXAFS spectrum, which reflects the structure only very close to the absorbing atom. Uniform distribution of the clusters among the support is expected. At the final stage Ni atoms are formed by reduction of NiO clusters and they diffuse and coagulate to form metal particles. Since Ni atoms are equally distributed, the size of the metal particle is uniform and is controlled by Ni concentration of the starting material.

On the other hand, large NiO particles with various sizes are formed by heating in the impregnation method. Since NiO particles are already large and have a wide distribution in size, Ni metal particles obtained by reduction are not uniform in size. Since atomic adsorption is realized at the first stage of the impregnation, however, it may be possible to obtain uniform NiO distribution by finding appropriate conditions for the calcination. An effort to find an adequate condition has started.

In order to further reinforce the conclusion obtained here, preparation procedures of various kinds of supported metal catalyst are now being studied by EXAFS, and the results will be reported in the near future.

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