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Characterization of Silica-Supported Bimetallic Iron–Nickel Catalysts by EXAFS

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$Fe–Ni/SiO_2$ bimetallic catalysts with varying composition were prepared according to two procedures: alkoxide and impregnation methods. The size distribution of the metal clusters and the local structure around each kind of metal atom in the clusters are studied by TEM, XRD, and EXAFS. Fe and Ni atoms are concluded to be in small clusters with a fcc structure; that is, alloy is formed. The metal particles are not, however, uniform in composition and consist of an Ni-rich kernel covered with outer layers which contain more Fe. This tendency is more pronounced in the catalyst prepared by the alkoxide method. The reason for the evolution of such inhomogeneous clusters is examined by EXAFS through the local structure change during the preparation procedure. © 1988 Academic Press, Inc.

INTRODUCTION

Since the catalytic reaction is greatly influenced by the structure and the electronic state of metal particles in the catalyst, it is important to control them for the development of catalysts with desired properties. Bimetallic catalysts have attracted much attention in recent years (*1, 2*). The formation of an alloy is expected to induce the geometrical "ensemble effect" and the electronic "ligand effect" in the catalytic performances, leading to the appearance of novel properties which individual metals do not possess. A fundamental question to be answered first about the bimetallic catalysts is whether the very minute metal clusters in the catalyst indeed consist of both kinds of atoms or not. A more relevant question to catalytic science considers what the surface composition really is. Lytle, Sinfelt, and their collaborators (*3–8*) have extensively studied various bimetallic catalysts by extended X-ray absorption fine structure (EXAFS) spectroscopy. They showed that bimetallic clusters are formed even for combinations of metals which are not miscible in the bulk and that often the surface concentration of one of the components is greater than that of the other.

Surface species may be different even for the systems with the same bulk composition, if the preparation procedure is different. In a previous publication one of the authors proposed a preparation procedure of catalysts called the alkoxide method (*9*), by which the particle size can be controlled by adjusting the metal concentration of the starting material. The alkoxide method was applied to prepare a bimetallic catalyst $Fe–Ni/SiO_2$ and the catalyst was compared with that prepared by the conventional co-impregnation method by a transmission electron microscope (TEM) and X-ray diffraction (XRD) (*10*). As is expected from the bulk properties of iron and nickel, formation of alloys was confirmed in both cases. Recently, however, the selectivity of the catalysts for the formic acid decomposition reaction was found to be very different (*11*), which indicates the difference in surface structure.

The purpose of the present work is to characterize the $Fe–Ni/SiO_2$ prepared by

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both the methods and to determine the difference in the structures. Fe–Ni alloy catalysts have been frequently studied in relation to Fischer–Tropsch synthesis and methanation (*12–16*). The particle size distribution and the average size are estimated by TEM and XRD, and the local environments of both Fe and Ni are elaborated by EXAFS analysis with an emphasis on the surface composition. From the coordination numbers obtained and the spectral change by oxidation reaction, it is concluded that the bimetallic clusters formed are not uniform, but the surface layers are enriched in Fe, while the interiors contain more Ni. This tendency is more pronounced in the catalyst prepared by the alkoxide method.

EXPERIMENTAL

The catalyst by the alkoxide method (hereafter called catalyst A) was prepared by a hydrolysis of a mixed solution of ethyl silicate and nickel and iron ethylene glycolates; nickel and iron(III) nitrates were dissolved in ethylene glycol at 333 K, followed by addition of ethyl silicate and stirring at the same temperature in N_2 atmosphere. When the mixed solution became homogeneous, water was added to five times the number of moles of ethyl silicate, forming a gel. The gel was dried under reduced pressure and further dried in an oven at 383 K for 24 h. The powder thus obtained was calcined at 773 K for 4 h in air and then reduced with hydrogen at the desired temperature for 4 h. For comparison, the catalyst was also prepared by the conventional impregnation method (hereafter called catalyst I). The conditions employed for drying, calcination, and reduction were the same as those for catalyst A.

The particle size of metal in the catalyst was measured by a transmission electron microscope operated at an accelerating voltage of 200 kV (Hitachi H-800). The sample was first ground in an agate mortar and then suspended in ethyl alcohol by using supersonic waves. Some of the finest parts of the suspension were pipetted onto a microgrid covered with collodion film (400 mesh). Micrographs were obtained with an instrumental magnification of $\times 10^5$. The size distribution was calculated by measuring more than 500 particles in photographs.

XRD patterns were obtained with a Rigaku Geigerflex 2028 by the use of Cu$K\alpha$ radiation. The crystalline size was estimated from (111) and (200) reflections by using Scherrer's equation: $d = 0.9\lambda/\beta \cos\theta$, where λ is the wavelength of the incident X-ray and β is the width of the diffraction peak at its half-height.

The EXAFS apparatus employed is the same as the in-house spectrometer reported before (*17*), except for one modification; in order to eliminate the effect of counting loss at the characteristic lines of tungsten, the intensity of the X-ray was monitored and the filament current was adjusted to give a constant X-ray flux by a feedback system. The intensity being controlled within 5%, the tungsten L_α lines near Ni absorption edge make no distortion in the spectra (*18*). The samples used for the EXAFS experiment were kept in vacuum-tight cells, and the measurements were made without exposure to the air unless exposure was intentional, after the oxidation and/or reduction. The analysis was made according to that described previously (*19, 20*). In short, after the extraction of the oscillation and Fourier transform, back Fourier transform was made. The curve-fitting technique was subsequently employed in order to determine structural parameters such as the interatomic distance, the Debye–Waller factor, and the coordination number. The best-fit values of electron mean free path obtained for foils were used, and the backscattering amplitudes and phase shifts calculated by Teo and Lee (*21*) were employed in the calculation.

RESULTS AND DISCUSSION

Particle size of the metal is mainly deter-

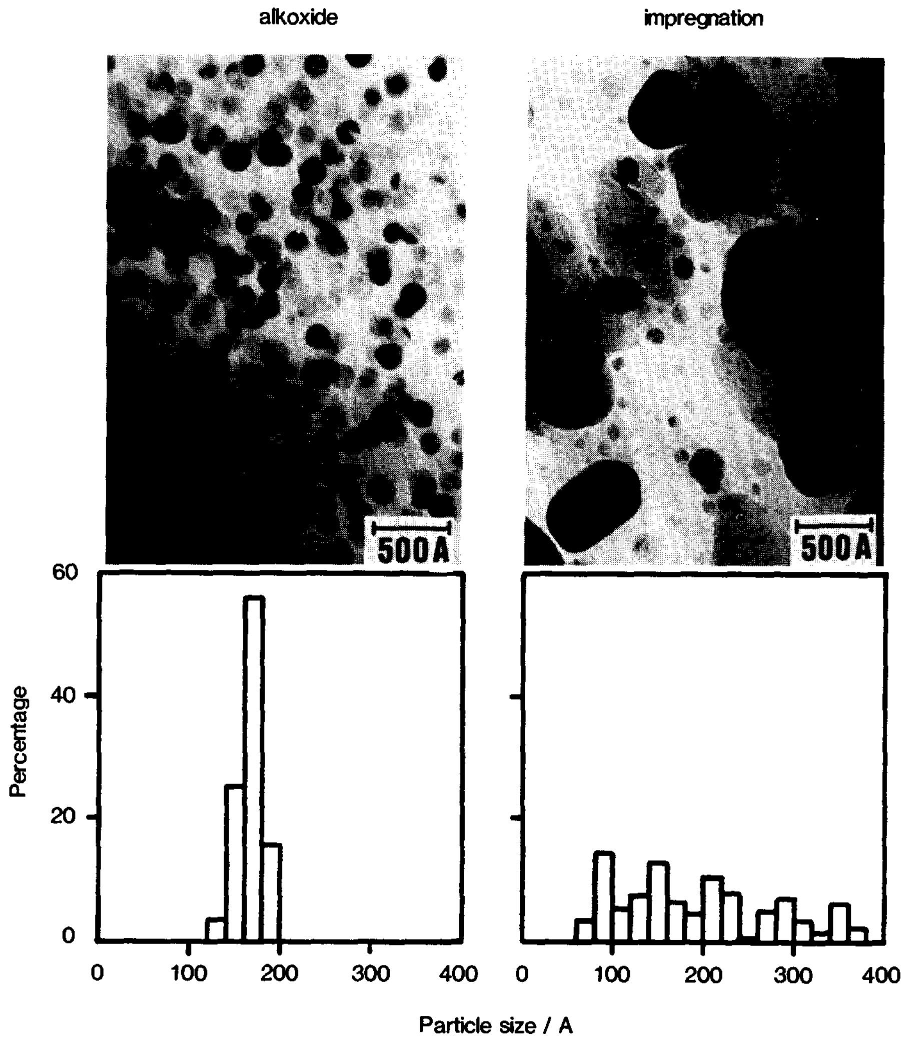

FIG. 1. Transmission electron micrographs and the particle size distributions of 20 wt% Fe–Ni/SiO_2 catalysts prepared by the alkoxide and impregnation methods. (Fe/Ni atomic ratio = 50/50.)

mined by two factors: metal concentration of the starting material and reduction temperature. A typical photograph obtained by TEM and the size distribution of metal particles are shown in Fig. 1 for the 20 wt% (total metal concentration) Fe–Ni/SiO_2 catalyst A. The catalyst was reduced at 1173 K and the atomic ratio of Fe/Ni is 50/50. The same measurements were also carried out for catalyst I, which was treated in a similar manner, and the result is shown in Fig. 1. Evidently, the metal particles in catalyst A are well controlled so that they are smaller in size and more homogeneous than those of catalyst I. It may be noted that Raupp and Delgass reported (*22*) that significantly smaller Fe–Ni particles can be prepared on silica by slow vacuum drying prior to reduction after coimpregnation. Here no such pretreatment was adopted. The mean particle size can be calculated from the TEM picture for the catalysts with varying concentrations. The results are shown in Fig. 2. As has been observed for monometallic

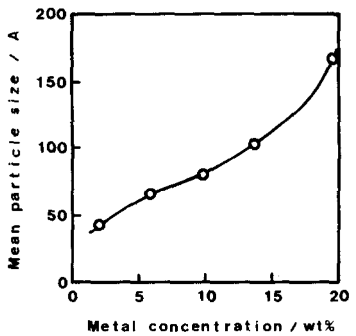

FIG. 2. Change in mean particle size of metal with varying metal concentration in Fe–Ni/SiO$_2$ catalyst prepared by the alkoxide method. (Fe/Ni atomic ratio = 50/50.)

systems (*9, 19, 20*), the mean particle size increases with the increase in the concentration of metal in the bimetallic catalysts.

Reduction temperature also has an effect on the particle size. At the highest reduction temperature employed, namely 1173 K, the mean particle size of catalyst A with 20 wt% loading is about 170 Å from the TEM picture. The mean diameter is estimated to be 140 Å from the XRD peak width, which is in fair agreement with the value by TEM. With the reduction temperature of 973 K, the size is estimated to be 85 Å from XRD and 110 Å from TEM. The XRD pattern of the catalyst reduced at 773 K becomes so diffuse that the size cannot be estimated, indicating that particles are very small. But from the TEM picture the average diameter is 105 Å. This might result because of the existence of smaller clusters which escape detection by TEM.

On the other hand, catalyst I reduced even at 773 K shows a distinct XRD pattern without broadening. The lattice spacings agree very well with those of bulk Fe–Ni alloys having the same compositions (*23*), indicating that the particles formed in catalyst I are alloys. From these observations it can also be concluded that the broadening of the XRD pattern of catalysts A originates from particle size effects and not from the effect of alloying. In passing, no diffraction peak was observed for the calcined catalysts A, while distinct peaks due to oxides were obtained with catalysts I.

EXAFS spectra of both Fe and Ni K absorption were obtained for catalyts A with varying Fe/Ni ratios. The catalysts were reduced *in situ* at 1173 K. Figures 3 and 4 show the Fe and the Ni EXAFS spectra and the associated Fourier transform of the 20 wt% catalyst with the Fe/Ni atomic ratio of 25/75. For comparison, those of the reference materials are also included. As is evident from the figures, Ni EXAFS and the associated Fourier transform are the same as those of Ni metal which has a fcc structure. On the other hand, Fe EXAFS and the associated Fourier transform are completely different from those of Fe metal which has a bcc structure, but are similar to those of Ni metal. This is an unambiguous indication of the formation of the particle of the fcc Fe–Ni alloy in the catalyst and agrees with the result from XRD analysis. Although the XRD pattern for the catalyst reduced at temperatures lower than 773 K is too diffuse to draw any conclusion about the structure, alloying is confirmed from EXAFS for those samples also.

Back Fourier transforms followed by a least-squares fit were carried out in order to obtain structural parameters, and the results are shown in Table 1. Since each atom

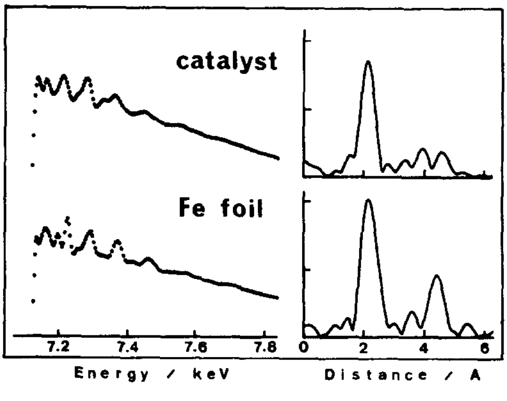

FIG. 3. Fe EXAFS and the associated Fourier transforms of 20 wt% Fe–Ni/SiO$_2$ catalyst with an Fe/Ni atomic ratio of 25/75 and an Fe foil.

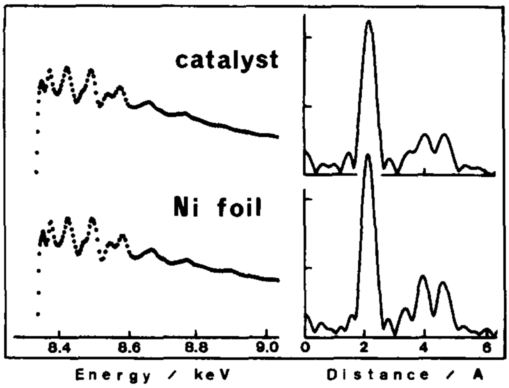

FIG. 4. Ni EXAFS and the associated Fourier transforms of 20 wt% Fe–Ni/SiO_2 catalyst with an Fe/Ni atomic ratio of 25/75 and a Ni foil.

must be surrounded by both kinds of elements, it was arbitrarily assumed in the calculation that every atom has the same ratio of nearest-neighbor Fe and Ni atoms as the bulk composition. Because of the similarity in the phase and amplitude factors of these two elements (*21*), the calculated results are not influenced much by the assumption employed. Similar results were obtained for the Fe–Ni/SiO_2 catalyst with the Fe/Ni atomic ratios of 50/50 and 75/25 and are shown in the table. EXAFS spectra were also obtained for catalysts I reduced at the same temperature. Qualitatively they are similar to the corresponding spectra of catalyst A, indicating that alloy is formed in catalyst I, too. The results of the quantitative analysis for catalyst I are included in Table 1. It is evident that the coordination number for both elements is always smaller than that expected for bulk fcc metal, which is 12. What is more, catalyst A always has smaller coordination numbers than the corresponding catalyst I and the coordination number of Fe is much smaller than that of Ni in catalyst A, while the difference is not so large in catalyst I.

The smaller coordination number is frequently observed with EXAFS analysis of tiny clusters and is well recognized to be due to the high proportion of surface atoms (*24*). Therefore the following conclusions are drawn from the above observations. First, the alloy cluster size is much smaller in catalyst A than in catalyst I, which is consistent with TEM and XRD results. Quantitatively, the coordination numbers are somewhat smaller than those expected from TEM results. This may be due to the existence of very tiny clusters which are below the detection limit of TEM. Second, iron atoms are prone to be on the surface of the alloy cluster in catalyst A. The surface

TABLE 1

Structural Parameters Obtained from the Analysis of EXAFS

		Fe K edge				Ni K edge			
	Fe/Ni	I	N	R (Å)	σ^2 (Å^2)	I	N	R (Å)	σ^2 (Å^2)
Alk.	100/0	I	6.8	2.50	0.006	I	—	—	—
	75/25	I	6.0	2.50	0.006	I	8.4	2.49	0.005
	50/50	I	5.9	2.50	0.006	I	8.1	2.48	0.006
	25/75	I	5.7	2.49	0.005	I	8.6	2.47	0.006
	0/100	I	—	—	—	I	8.8	2.45	0.005
Imp.	100/0	I	7.4	2.49	0.005	I	—	—	—
	25/75	I	7.5	2.49	0.006	I	8.6	2.48	0.006
	50/50	I	8.4	2.50	0.006	I	8.9	2.48	0.006
	75/25	I	8.9	2.48	0.006	I	8.9	2.47	0.005
	0/100	I	—	—	—	I	10.6	2.45	0.006

Note. R, interatomic distance; N, average coordination number; and σ, Debye–Waller factor.

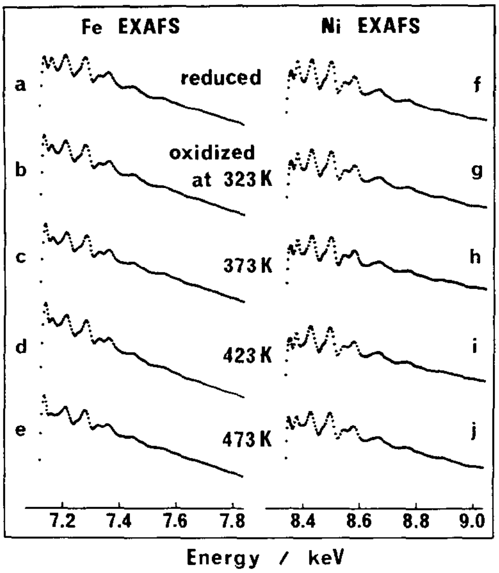

FIG. 5. EXAFS spectra of the reduced and oxidized Fe–Ni/SiO$_2$ catalysts with an Fe/Ni atomic ratio of 25/75.

of catalyst I may be Fe-rich too, because the larger cluster size may have reduced the effects of a small proportion of surface atoms.

The effect of exposing the Fe–Ni/SiO$_2$ catalyst to air provides another support related to the surface composition of the catalyst. Figure 5 shows the EXAFS spectra of the Fe/Ni = 25/75 catalyst heated successively at elevated temperatures in air after the reductions. Ni EXAFS remains almost unchanged up to 473 K, whereas a change of absorption profile near the Fe K absorption edge is evidenced even at 323 K. The first peak near the Fe edge becomes sharp and strong, and the second peak diminishes. The oscillation at the higher energy region, however, is almost unaltered. The above observations indicate that a part of the iron in the catalyst has been very easily oxidized by exposure to the air, while the rest remains metallic. This can be explained by assuming a double-layered model as the cluster structure: Ni-rich kernel and Fe-rich surface layer. Sinfelt *et al.* (*3*) have observed that only copper is oxidized in the Ru–Cu/SiO$_2$ catalyst and concluded from various evidence that copper is present at the surface. Very recently van't Blik *et al.* (*25*) reproduced a similar observation; Co K edge absorption changes after O$_2$ admission to Co–Rh/SiO$_2$ catalyst, while Rh K edge absorption is only slightly influenced. They also interpret this phenomenon by the cobalt enrichment in the surface of bimetallic particles.

On the other hand, no change was observed with catalyst I in the K absorption of both elements by exposure to air at 473 K. This does not necessarily mean that the cluster surface in catalyst I is not Fe rich, because a low dispersion may hide the effect on the surface. Indeed, Matsuyama *et al.* (*26*) reported that from the penetration depth of γ rays from ^{63}Ni the surface is Ni poor in the Fe–Ni powdered catalyst. In their case the powder was prepared from the mixed solution of nitrates without supports, and the particle size is presumed to be much larger. The difference in reactivity (*11*), however, suggests that the surface composition is somewhat different in catalysts A and I.

In order to examine the pathway of the formation of Fe–Ni alloy particles with an Fe-rich surface layer in catalyst A, EXAFS measurements were also carried out for the calcined catalyst as well as for those reduced at several temperatures. The atomic ratio was 50:50 for both catalysts. The results are shown in Fig. 6. At the calcination step, it is clear that Ni atoms in the catalyst exist as NiO, because Ni EXAFS is identical with that of NiO powder, which has already been reported (*19*). On the other hand, Fe EXAFS is not the same as that of any of the known iron oxides, FeO, Fe$_2$O$_3$, and Fe$_3$O$_4$, but a strong white line and a monotonous short oscillation suggest that the nearest neighbors of Fe are also oxygen atoms. Very small clusters of one of the oxides are the most plausible candidate responsible for this spectrum. No trace of binary oxide, that is nickel ferrite, was observed.

By reducing at 673 K, one can observe a

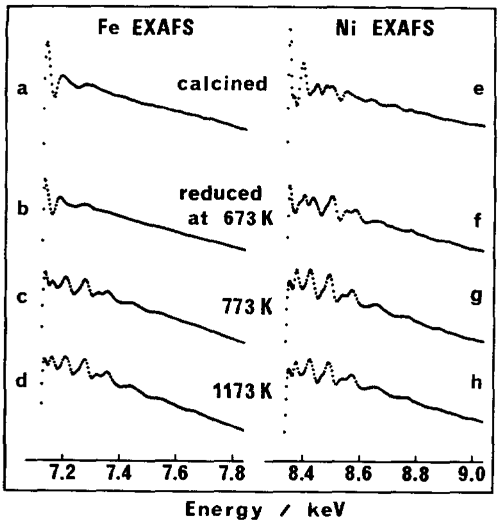

FIG. 6. EXAFS spectra of the calcined and reduced Fe–Ni/SiO$_2$ catalysts with an Fe/Ni atomic ratio of 50/50.

significant change in the local structure around nickel. Since Fig. 6f is a superposition of 6e and 6h, it is clear that a part of the NiO is reduced to metal. On the other hand, Fe EXAFS does not show any evidence of reduction at this temperature. By elevating the reduction temperature to 773 K, Ni EXAFS becomes almost completely that of metal but in the Fe EXAFS a sharp white line, which is characteristic of oxide, still remains.

The above observation leads to the following reasoning concerning why the surface of the alloy cluster is Fe rich and Ni atoms tend to be in the core. In the calcination step both elements exist as oxides. At the initial stage of reduction, Ni atoms are reduced first, forming a Ni cluster. Later, iron oxide is also reduced to coagulate with the Ni cluster to form an alloy, making the surface Fe rich. A similar scheme has been proposed by Takeuchi *et al.* (*27*) for the mechanism of copper–nickel alloy formation.

CONCLUSION

(1) As has been verified for several monometallic supported catalysts (*10, 20, 21*), the average particle size is much smaller and the size distribution is narrower in the bimetallic Fe–Ni/SiO$_2$ catalyst prepared by the alkoxide method than in that prepared by the coimpregnation method.

(2) Both elements exist in the metal particles on the support; Fe–Ni alloy is formed in catalysts prepared by both methods.

(3) The composition of the alloy is, however, not uniform but Fe is enriched on the outer layers, especially in the catalyst prepared by the alkoxide method.

(4) The reason for the surface condensation of Fe is attributed to the difference in the rates of reduction.

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