CHEMISTRY LETTERS, pp. 1089-1092, 1983.

EXAFS STUDY ON THE LOCAL STRUCTURE CHANGES AROUND Ni ATOM DURING THE COURSES OF Ni/SiO_2 CATALYST PREPARATION PROCEDURES

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The changes of local structures around Ni atom were studied by means of EXAFS spectroscopy at every elementary step of two kinds of Ni/SiO_2 catalyst preparation methods. From the analysis of EXAFS spectra, complemented by the observations by an electron microscope, differences by the structure of intermediate products by the two preparation methods have been revealed.

An activity and/or selectivity of a metal supported catalyst strongly depend upon the method of the catalyst preparation procedure employed.1) High selectivity is believed to come from uniform size of the metal particles, and high activity is from high dispersion of the catalyst metal on the support. Hence the development of the technique to control the size of metal particles on a support has been desired. One of the present authors reported2) that Ni/SiO_2 catalyst prepared by the alkoxide method has metal particles of uniform size, whereas the regular impregnation method usually gives the catalyst whose metal size distribution is fairly broad.

The main purpose of the present communication is to find out where the differences in the products by the two methods come from by pursueing the structure changes around Ni atom at every elementary stage of both preparation procedures. EXAFS is best suited for the purpose because it can probe the local structure around a selected atomic species regardless of the phase. In spite of this the work by EXAFS is still scarce, mainly because of the lack of reliable EXAFS spectrometers in laboratories and the limited access to synchrotron facilities for majority of workers. Although a lot of efforts have been made to construct laboratory EXAFS spectrometers, only two studies on catalyst by the use of them have been found in the literatures. Morrison et al.3) reported an EXAFS study on the structure of zeolite catalysts by the use of a bent crystal monochromator, and Sato et al.4) studied the structure of a Mo catalyst employing a laboratory EXAFS system with a high power X-ray generator. Recently we have constructed a laboratory EXAFS facility which features the use of an SSD.5) It is also aimed in this letter to show that the laboratory EXAFS facility is now able to supply data of enough quality for the study on substances of chemical and physical interests.

The details of the catalyst synthesis procedures employed here have been

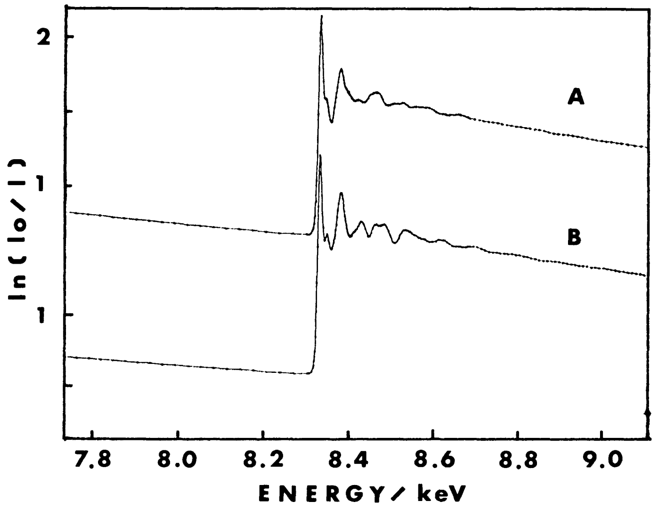


Fig.1. EXAFS spectra of (A)dried sample and (B)calcined sample prepared by the alkoxide method.

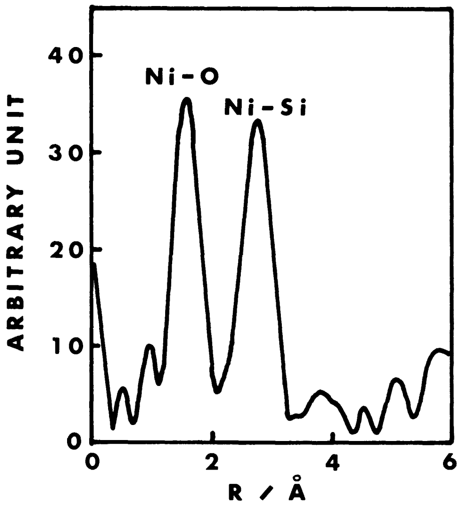


Fig.2. Fourier transform of the EXAFS spectrum shown in Fig.1(A) Phase shifts are not taken into consideration in this and the following Fourier transforms.

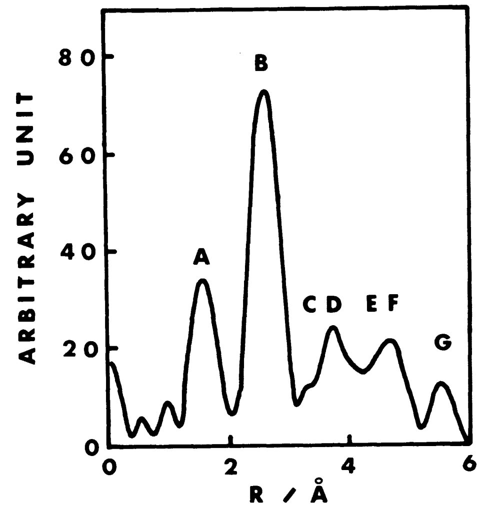
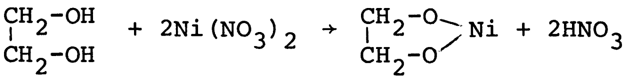
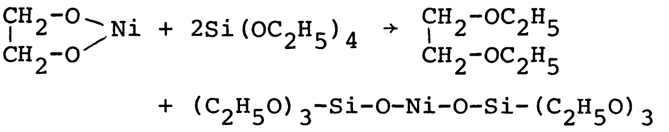


Fig.3. Fourier transform of the EXAFS spectrum whosn in Fig.1(B).

reported elsewhere.[2)] In short, the alkoxide method starts with a formation of Ni-O-Si bond by the reaction between $Ni(NO_3)_2$ and ethylene glycol, followed by a reaction with ethylsilicate, as follows;



$$\begin{array}{l}CH_2\text{-}OH\\ CH_2\text{-}OH\end{array} + 2Ni(NO_3)_2 \rightarrow \begin{array}{l}CH_2\text{-}O\\ CH_2\text{-}O\end{array}\!\!>Ni + 2HNO_3 \qquad (1).$$



$$\begin{array}{l}CH_2\text{-}O\\ CH_2\text{-}O\end{array}\!\!>Ni + 2Si(OC_2H_5)_4 \rightarrow \begin{array}{l}CH_2\text{-}OC_2H_5\\ CH_2\text{-}OC_2H_5\end{array}$$

$$+ (C_2H_5O)_3\text{-}Si\text{-}O\text{-}Ni\text{-}O\text{-}Si\text{-}(C_2H_5O)_3 \qquad (2).$$

By adding proper amount of water into the solution, a gel is obtained, suggesting a formation of long skeltal chains. The gel was filtered and washed by distilled water, followed by drying at 110°C.

An EXAFS spectrum of the dried sample is shown in Fig.1(A). The quality of the measurement can be evaluated from the figure. The formation of Ni-O-Si bonds is confirmed by the Fourier transform of the extracted oscillation weighted by k^3 shown in Fig.2. The two peaks in the figure should correspond to Ni-O and Ni-Si, respectively. It is substantiated by the comparison of the inverse Fourier transforms of the peaks with the calculated oscillations by the use of the phase shifts and scattering amplitudes proposed by Teo and Lee.[6)] Distances were varied as parameters, and R(Ni-O)=2.05 Å and R(Ni-Si)=3.30 Å gave the best fit. Coordination numbers were found to be six for both oxygen and Si.

The sample is then calcined at 450°C in air. An EXAFS spectrum of the calcined sample is shown in Fig.1(B) and a Fourier transform of the extracted oscillation is shown in Fig.3. The position of the first peak at around 1.6 Å is the same as that of Fig.2, indicating that the first shell consists of six oxygen atoms. The position of the second peak is also close to that of the dried sample shown in Fig.2, suggesting the possibility that it corresponds to Ni-Si distance. However, a Fourier transform of the EXAFS spectrum of NiO crystal shown in Fig.4 is very similar to Fig.3, implying another possibility that the local structure around Ni atom has changed to that of NiO crystal. In order to distinguish whether the second shell consists of Ni or Si, a simulation was carried out. The curves calculated by the use of the parameters for Ni-Si could not reproduce the oscillation no matter how the distance was varied. On the other hand, a calculation by employing the parameters for Ni-Ni reproduces the curve quite well as is shown in Fig.5.

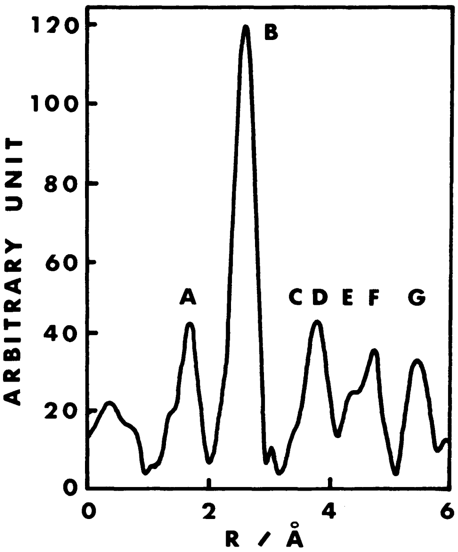


Fig.4. Fourier transform of the EXAFS spectrum of NiO crystal. Peaks indicated by A-G correspond to the following atom pairs. A:Ni-O(2.09 Å),B:Ni-Ni (2.95 Å),C:Ni-O(3.62 Å),D:Ni-Ni(4.18 Å),E:Ni-O(4.67 Å),F: Ni-Ni(5.12 Å),G:Ni-Ni(5.91 Å).

Therefore, it must be concluded that NiO clusters are formed through the calcination procedure. It is rather an unexpected result, since a rearrangement of atoms in Ni-O-Si networks by raising the temperature must be taken place. From the comparison of Fig.3 with Fig.4, it can be noticed that the widths of the peaks in Fig.3 are somewhat broader and the distant peaks are less distinct. These suggest that the structure of NiO cluster is not so rigid as that of NiO crystal and that the size of the cluster is not large enough to be distinguished as crystal by EXAFS spectra. The latter suggestion is supported by an electron microscope data. Since no particle was observed with a magnification of 10^5, the size of the cluster must be less than 20 Å.

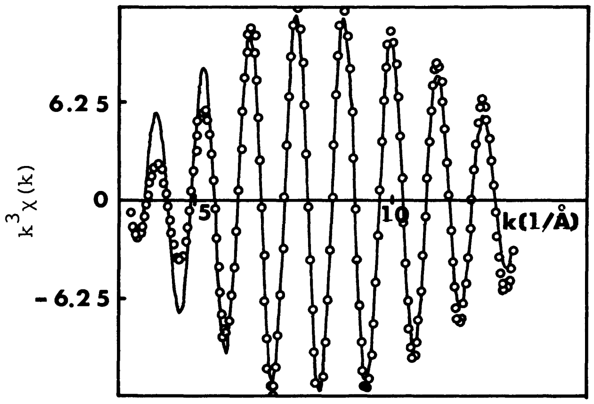


Fig.5. Calculated oscillation for Ni-Ni scattering (circles) and inverse Fourier transform of the peak denoted as B in Fig.4 (solid line).

The final step of the catalyst preparation is to reduce the calcined sample. The EXAFS spectrum of a reduced catalyst is a superposition of the spectrum of NiO crystal and that of Ni metal, and by a further reduction the features due to Ni metal grow up. As was reported previously$^{2)}$ Ni particles are dispersed homogeneously in the catalyst prepared in this manner and the particle sizes are distributed in a range between 70 and 90 Å.

On the other hand, Ni particles of Ni/SiO_2 catalyst prepared by the impregnation method have a broad size distribution, ranging from 20 to several hundreds angstrom. The EXAFS spectrum of the sample is different from the one for the catalyst by the alkoxide method and is almost the same as that of Ni metal, as is expected from the observation by the electron microscope. The EXAFS spectrum of the sample before the reduction looks, however, quite similar to that of the calcined sample by the alkoxide method. A Fourier transform of the spectrum is shown in Fig.6. It has distinct peaks up to near 6 Å and is almost the same as that of NiO crystal shown in Fig.4, indicating that NiO clusters formed at this stage by the impregnation method are much larger than those by the alkoxide method. Indeed, particles with various sizes are seen by an electron microscope.

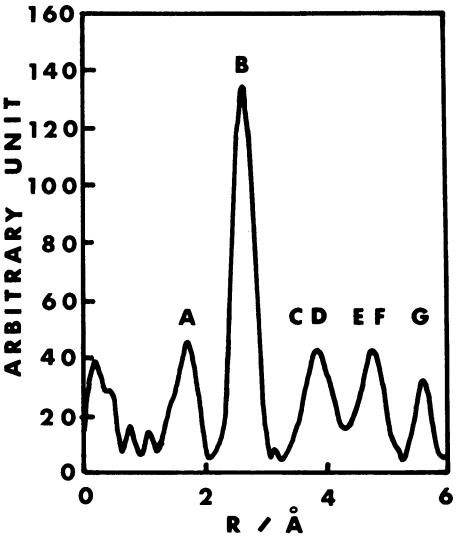


Fig.6. Fourier transform of the EXAFS spectrum of the calcined sample prepared by the impregnation method.

It is now clear where the difference between the alkoxide and the impregnation methods comes from. From the observations above, the key to control Ni particle size in the catalyst is to disperse tiny NiO clusters among the support materials at the calcination stage, which is realized by the alkoxide method. Since Ni atoms are individually adsorbed on the support at the first stage of the impregnation method as will be reported elsewhere,[7] it may be possible to obtain homogeneous distribution of NiO clusters by selecting the conditions of calcination.

In conclusion, EXAFS spectroscopy is proved to be efficient to pursue structural changes during the catalyst preparation procedures, and from the results, complemented by observations by an electron microscope, the difference between the two preparation procedures has been revealed. More details by the use of NMR and IR spectroscopic data will be reported in the near future.

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(Received May 11, 1983)