The Structure of Nickel Oxide Clusters inside the Supercage in Y-Zeolite by XAFS#

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Synopsis. XAFS has been measured for the nickel oxide cluster in the Y-zeolite. The atomic distances in the cluster are close to those in the crystallite NiO. However, the weak intensity of Ni-fourth neighbor Ni and the coordination numbers give a model of the cluster in the supercage.

Currently, the design of nano-composite materials is intensively studied from various view-points, because the generation of new materials with novel characters of chemical, magnetic, electronic, and optical property is anticipated.[1] Because the zeolite provides us the space in the size of angstrom, it will be a candidate for the micro-manufacturing materials which contain metals, clusters, organic and inorganic substances, etc.[2]

We previously reported the structural change of the nickel oxide clusters in the cavity of Y-zeolite during the preparation,[3] and related it to the catalyst activity. Nickel oxide cluster was aggregated into small nickel oxide particles by soaking in an alkaline solution, and the activity of the oxidation of carbon monoxide was remarkably improved. However, we could not determine the structure of the nickel oxide in detail because of low intensity of our home-made XAFS instruments. We studied the magnetic behavior of the catalyst also; NiO in the Y-zeolite showed ferromagnetic behavior in compared to antiferro-magnetic property of usual NiO. The nickel Y-zeolite showed a remanent magnetization and a hysteresis loss above 40 K.[4] The purpose of the present investigation is thereby to determine the structure by XAFS, and to interpret the chemical and physical property from the view-point of structure.

X-Ray absorption measurements were carried out at BL-10B on the storage ring of Photon Factory at the National Laboratory of High Energy Physics.[5] The absorption spectra were measured in the transmission mode at room and liquid N_2 temperatures for Ni–K edge. The XAFS spectra have been analyzed by the standard procedures.[6]

Figure 1 shows Fourier transformation of the XAFS data to real space together with that of NiO crystallite as a reference. This is obtained after the correction of the phase-shift, and corresponds to a kind of radial distribution function around the nickel atom. The NiO crystallite of the reference compound gives us clearly five peaks at about 1.7, 2.6, 3.8, 4.6, and 5.4 Å, which corresponds to the distances of Ni–O, Ni–Ni, Ni–second neighbor Ni, Ni–third neighbor Ni, Ni–fourth neighbor Ni, respectively. On the other hand, Fourier transformation of the nickel in Y-zeolite (NiY) showed the XAFS function different from that of NiO; the intensity of Ni–O on the NiY is larger than on NiO, however, those of Ni–Ni on the NiY are smaller than on NiO. Since the intensity of Ni–fourth neighbor Ni at 5.8 Å is almost undiscernible, the nickel located far from the centered Ni is hard to see. We then measured the XAFS at 77 K to find the long distance interaction; however, almost the same function of radial distribution as shown above was observed.

XAFS function was analyzed by the curve-fitting method on the basis of the parameters of crystallite NiO in order to determine the structure of the nickel cluster in the zeolite, as shown in Table 1. The distance of

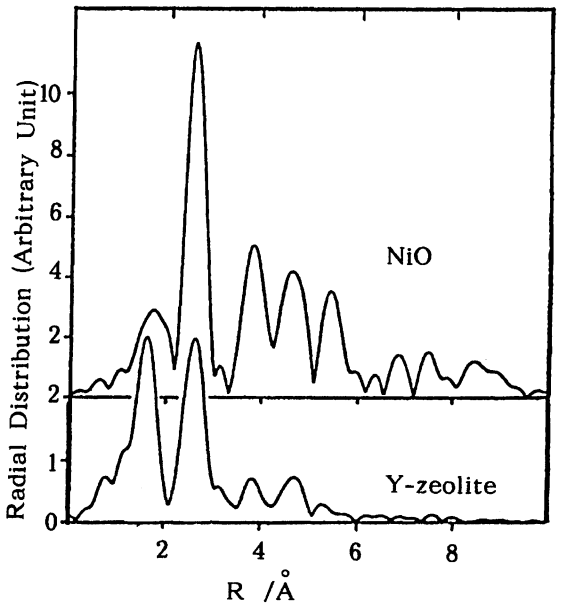

Fig. 1. Fourier transformation of the XAFS data for the nickel in the Y-zeolite and the crystallite NiO.

Table 1. Structural Result for Nickel Oxide in Y-Zeolite[a]

	Ni–O	Ni–Ni	Ni–Ni	Ni–Ni
Atomic distance (Å)	2.06 (2.084)	2.97 (2.947)	4.20 (4.168)	5.14 (5.104)
Coordination number	5.0 (6)	3.1 (12)	1.7 (6)	3.6 (24)

a) The values in the parentheses are from the crystallite NiO.

#In memory of Professor Hiroshi Kato.

Ni–Ni of NiY, 2.97 Å is close to that of the crystallite NiO, 2.91 Å. The angle of the Ni–O–Ni is calculated to be 90° from the data of lengths. The distance of Ni–second neighbor Ni, 4.20 Å is close to the calculated distance, 4.12 Å based on the assumption of straight Ni–O–Ni. The distance of Ni–third neighbor Ni, 5.14 Å is also close to the calculated distance, 5.04 Å based on the assumption of the NiO cubic crystal with 2.06 Å of the Ni–O distance. All atomic distances of the nickel oxide cluster in the zeolite are close to those of the NiO crystallite; therefore, the NiO cluster in the zeolite has the dignity of the cubic structure of the crystallite NiO. However, the weak intensity of Ni–fourth neighbor Ni, 5.4 Å suggests a limited size of the cluster.

We now propose the structure model I of the cubic morphology for the cluster as shown in Fig. 2. The model cluster includes 13 nickel atoms, and 5.5, 1.8, 3.7, and 0.9 of the Ni–Ni coordination number; these should be compared with 9.4 nickel atoms and 3.1, 1.7, 3.6, and ca. 0 of Ni–Ni interactions of the experimental value. When the cubic center nickel is removed in the model I, the number of total nickel is 12, and the coordination numbers of Ni–Ni interactions are 4, 2, 4, and 1. Then, if two more nickel atoms are removed, there are 10 nickel atoms with 3.4, 1.6, 3.2, and 0.8 of the coordination number; these parameters unambiguously coincide with the experimental values.

Alternative structure model II does not give such satisfactory values of coordination number. The modified model I of the structure is thereby the most plausible. The unit dimension of this cluster is 8.2 Å, and the diagonal distance 14.3 Å is exactly agreed with the size of the supercage of the Y-zeolite. The number of oxygen around Ni in the zeolite is calculated to be 5.0, and smaller than 6.0 of the expected value of cubic crystal.[7] The coordination unsaturated site is available for the adsorption site. Furthermore, all nickel atoms are located on the surface of the cluster, and it is easy for a reactant molecule to access. The high activity of CO oxidation and the large magnetic anisotropy are caused by the structure. The cavity of Y-zeolite stabilized the structure.

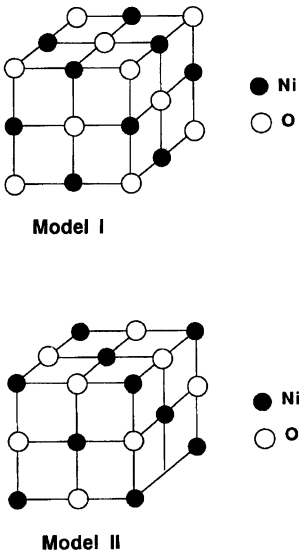

Fig. 2. The structure models for the cluster. All oxygen atoms around Ni are not pictured.

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7) XANES of the zeolite is slightly different from that of the NiO, which suggests that the electronic structures of Ni differ each other.