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# Properties of Nickel Cations in X-Zeolite as Studied by Electronic Spectroscopy

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Electronic spectra of Ni cations in X-zeolite were investigated. In hydrated zeolite, Ni cations are in the form of octahedral hexa-aquo complex. Upon dehydration, the coordination environment of Ni cations deviates from the octahedral one. Ammonia coordinates to Ni cations at room temperature when NiX is pretreated at 200°C, but it does not coordinate to Ni cations even at 200°C when NiX is evacuated at 500°C. This indicates that Ni cations in $S_I$ sites do not migrate to the supercage below 200°C. Adsorption of pyridine at 200°C induces the migration of the cation from $S_I$ sites to the supercage.

## INTRODUCTION

Catalytic activities of synthetic zeolites depend strongly on the nature of metal cations contained. To elucidate the properties of metal cations in zeolites, various techniques such as X-ray analysis (*1–4*), electron spin resonance (*5–10*) or infrared spectroscopy (*11–13*) have been applied. X-Ray analysis provides the information on the location of metal cations. Electron spin resonance and infrared spectroscopy also give some information on the cation sites and more importantly on the interaction of metal cations with adsorbed molecules.

In this study, we have applied the electronic spectral method to clear the interaction of the nickel cations in X-zeolite with adsorbed molecules. There have been several reports on the electronic spectra of nickel cations in zeolites (*14–15*), but their works were centered mainly on the states of nickel cations in hydrated and dehydrated zeolites and the chemical interaction of the metal cations with foreign molecules have been scarcely studied. Recently, X-ray analysis revealed the distribution of nickel cations among the cation sites of Y-zeolite and their migration upon adsorption of various molecules (*2–4*). Therefore, it was of interest to study the influence of adsorbed molecules on the local environment of nickel cations in zeolite.

## EXPERIMENTAL METHODS

The nickel form of X-zeolite (NiX) was prepared by conventional cation exchange procedures using an aqueous solution of nickel nitrate. Two samples of NiX with exchange degree of 30 and 95% are obtained and they are designated as NiX(30) and NiX(95) for further discussions. The degree of cation exchange was determined by the change in the nickel concentration of the aqueous solution.

Ammonia gas from a commercial cylinder was distilled twice and pyridine was obtained from Wako Pure Chemicals and used without further purification.

Adsorption of gases was carried out with a conventional vacuum apparatus.

The measurements of electronic spectra were carried out with a spectrophotometer Shimazu MPS-5000 in two different methods: reflectance method and transmission method. In the case of reflectance spectra, the sample powder is packed in a quartz cell of flat surfaces with 3 mm thickness and the special attachment for reflectance method for the apparatus was used. For the transmission spectra, the sample powder was pressed into a wafer, which was placed in an ordinary quartz cell. The results obtained by the two methods generally showed good agreement, though the transmission method gave more intense bands.

## RESULTS AND DISCUSSION

### *Hydrated NiX*

The hydrated NiX(95) shows the absorption maxima at 403, 680, 1180, 1460, and 1960 nm (Fig. 1a). The latter two bands in the near-infrared region are assigned to the overtone band ($2\nu_3$) and the combination band ($\nu_2 + \nu_3$) of the adsorbed water, respectively.

The position of the first three bands are close to those of $Ni(H_2O)_6^{2+}$: 395, 740, and 1180 nm (*16*). Thus, it is concluded that the nickel cations in hydrated zeolite are present as octahedral $Ni(H_2O)_6^{2+}$ complexes.

Crystal field theory provides a simple interpretation of the energy states of Ni(II) in field of $O_h$ symmetry (*17*). The triplet terms $^3F$ and $^3P$ arising from the $3d^8$ configuration of the free $Ni^{2+}$ are split as follows,

$$^3A_{2g}(F) \qquad E = -12Dq, \tag{1}$$

$$^3T_{2g}(F) \qquad E = -2Dq, \tag{2}$$

$$^3T_{1g}(F) \qquad E = 3Dq + \frac{15}{2}B - \frac{1}{2}[(15B - 6Dq)^2 + 64Dq^2]^{1/2}, \tag{3}$$

$$^3T_{1g}(P) \qquad E = 3Dq + \frac{15}{2}B + \frac{1}{2}[(15B - 6Dq)^2 + 64Dq^2]^{1/2}, \tag{4}$$

where $Dq$ is one tenth of the energy difference between $e_g$ and $t_{2g}$ orbitals, and $B$ is the Racah parameter.

Thus, the spin-allowed transitions having the following energies are expected;

$$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F) \qquad \nu_1 = 10Dq, \tag{5}$$

$$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F) \qquad \nu_2 = \frac{15}{2}B + 15Dq - \frac{1}{2}[(15B - 6Dq)^2 + 64Dq^2]^{1/2}, \tag{6}$$

$$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P) \qquad \nu_3 = \frac{15}{2}B + 15Dq + \frac{1}{2}[(15B - 6Dq)^2 + 64Dq^2]^{1/2}. \tag{7}$$

Using these equations, the values of $Dq$ and $B$ are obtained as follows,

$$Dq = \frac{1}{10}\nu_1, \tag{8}$$

$$B = \frac{1}{15}(\nu_2 + \nu_3 - 3\nu_1). \tag{9}$$

The value of Racah parameter $B$ found in complexes are always less than the value of 1041 cm$^{-1}$ found in free ion. The size of the reduction is considered to be indicative of the amount of covalent character in the bonds (*17*). The usual values of $\beta[= B(\text{complex})/B(\text{free ion})]$ fall in the interval of 0.7–0.9.

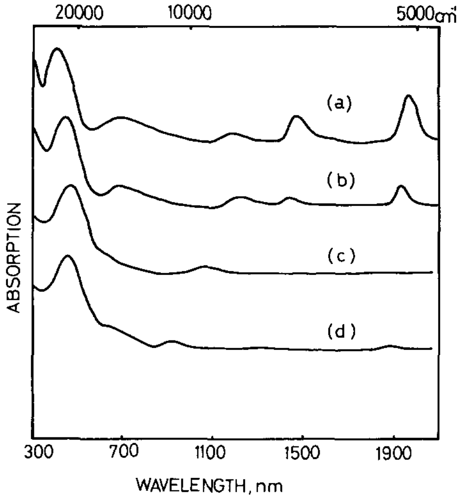

FIG. 1. Reflectance spectra of hydrated NiX(95) (a), and NiX(95) evacuated at: 100°C (b), 200°C (c), and 500°C (d).

TABLE 1
POSITIONS OF ABSORPTION MAXIMA AND SPECTRAL PARAMETERS OF ELECTRONIC SPECTRA OF NiX

| | Dehydration temp (°C) | Bands (cm$^{-1}$) 1 | 2 | 3 | $Dq$ (cm$^{-1}$ | $B$ (cm$^{-1}$) | $\beta$ |
|---|---|---|---|---|---|---|---|
| NiX(95) | Hydrated | 8450 | 14,700 | 24,800 | 845 | 943 | 0.91 |
| | 100 | 8300 | 14,600 | 22,600 | 830 | 820 | 0.79 |
| | 200 | 9500 | 15,100 | 21,700 | 950 | 553 | 0.53 |
| | 300 | 9100 | 15,900 | 22,200 | 910 | 720 | 0.69 |
| | 400 | 9100 | 15,900 | 22,500 | 910 | 740 | 0.71 |
| | 500 | 11,100 | 16,000 | 22,000 | 1110 | 313 | 0.30 |
| NiX(30) | Hydrated | 8700 | 14,900 | 25,900 | 870 | 980 | 0.94 |
| | 100 | 9100 | 15,900 | 23,600 | 910 | 813 | 0.78 |
| | 200 | 9350 | 16,100 | 21,700 | 735 | 650 | 0.62 |
| | 500 | 10,300 | 15,900 | 22,400 | 1030 | 493 | 0.47 |
| $Ni(H_2O)_6$ | | 8500 | 13,500 | 25,300 | 850 | 890 | 0.86 |

Thus, three bands in the visible region can be assigned to the $^3A_{2g}(F) \rightarrow {^3T_{2g}}(F)$ (1180 nm), $^3A_{2g}(F) \rightarrow {^3T_{1g}}(F)$ (680 nm), and $^3A_{2g}(F) \rightarrow {^3T_{1g}}(P)$ (403 nm) transitions, respectively. The calculated values of $Dq$, $B$ and $\beta$ are listed in Table 1.

Three *d–d* bands are observed at 395, 670, and 1150 nm in the case of hydrated NiX(30), and the parameters are also listed in Table 1.

### *Dehydration of NiX*

NiX(95) was evacuated at various temperatures for 3 hr and the electronic spectra was registered. The hydrated NiX exhibits light green color. The color changes into purplish pink at 200°C, into yellow at 300°C and into greenish gray at 500°C. Klier and Rolek (*14*) reported the similar color change upon dehydration of NiA, but the color change in NiA occurred at slightly lower temperatures than in NiX.

In Fig. 1, the change in the electronic spectrum of NiX(95) with dehydration temperature is illustrated. The results of the visible region of the spectra are generally in agreement with those by Garbowski *et al.* (*15*).

All three bands due to *d–d* transitions shifted upon dehydration. The values of $\nu_1$, $\nu_2$, and $\nu_3$ are listed in Table 1 for the sample at every dehydration stage, and the values of the $Dq$ and $B$ are calculated according to Eqs. (8) and (9). These values indicate that $Ni^{2+}$ in dehydrated X is in pseudooctahedral symmetry, except for the sample evacuated at 500°C. Nonsystematic shift of the absorption maxima by dehydration at temperatures between 100 and 400°C suggests that the extent of distortion from octahedral symmetry sensitively depends on the number of retained water molecules or hydroxyl groups. The unusual value of $\beta$ for the sample evacuated at 500°C indicates that $Ni^{2+}$ cations are completely in different environment from those of samples evacuated at lower temperatures. This observation is in accord with the conclusion by X-ray studies that $Ni^{2+}$ cations migrate into hexagonal prism ($S_I$ sites) on dehydration at high temperature (*3*).

The decrease in $Dq$ values upon dehydration suggests that the crystal field by the lattice oxygen is weaker than that by oxygen in water molecules, and the accompanied reduction in $\beta$ value indicates that

Ni–O bonds in dehydrated samples are more covalent in character than those in $Ni(H_2O)_6^{2+}$.

The results on NiX(30) are essentially the same as those on NiX(95).

### *Effect of Rehydration*

NiX samples evacuated at various temperatures were contacted with water vapor at room temperature.

The sample treated at 100°C showed the spectrum identical with that of hydrated NiX after 2 hr adsorption of water. When NiX treated at 200°C was contacted with water vapor for 2 hr, the absorption maximum for $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ transition was shifted from 460 nm of dehydrated sample to 412 nm. The position of this absorption was further shifted to 410 nm after 3 hr contact with water vapor and 403 nm after 4 hr which is identical to that of hydrated sample.

Samples treated at 300 and 400°C showed the band at 423 nm after 2 hr and its position returned to original 403 nm only after 18 hr contact with water. Sample treated at 500°C showed the absorption band at 423 nm after 2 hr. After 18 hr, the band showed maxima at 410 nm, not at the position of hydrated NiX(403 nm). The bands due to adsorbed water in near-infrared region were always observed after 2 hr adsorption of water.

The above results show that adsorption of water onto $Ni^{2+}$ cations is reversible, but it takes longer time to the original hydrated state when the evacuation temperature is higher. Since the portion of the $S_I$ sites occupancy by $Ni^{2+}$ cations increases with the dehydration temperature (*3*), time needed to rehydrate $Ni^{2+}$ cations may be determined by the rate of migration of Ni cations from hexagonal prism to the supercage.

### *Adsorption of Ammonia*

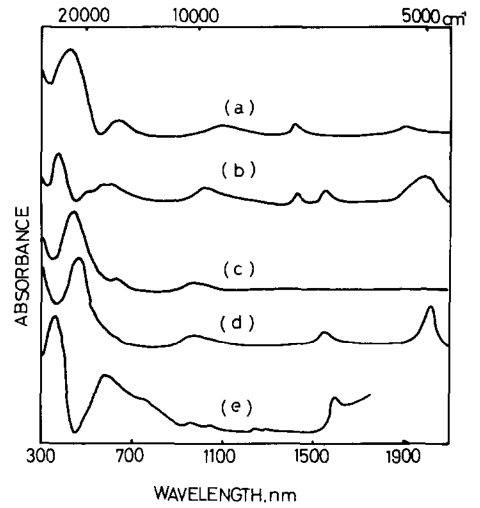

FIG. 2. Absorption spectra of NiX(30): (a) NiX(30) evacuated at 100°C, (b) after adsorption of ammonia on NiX evacuated at 100°C, (c) NiX(30) evacuated at 500°C, (d) after adsorption of ammonia on NiX evacuated at 500°C, (e) $Ni(NH_3)_6^{2+}$ in aqueous solution.

Figure 2 shows the electronic spectra of NiX samples which are in equilibrium with 250 mm Hg of ammonia vapor. NiX(30) evacuated at 100°C for 3 hr showed the absorption maxima at 395, 610, and 1030 nm (Fig. 2b). The positions of these bands are close to those of $Ni(NH_3)_6^{2+}$ in an aqueous solution (Fig. 2e). The value of $Dq$ and $\beta$ are calculated as 970 $cm^{-1}$ and 0.77, respectively, which indicate that $Ni^{2+}$ cations are in the octahedral environment. Evacuation at 100°C for 1 hr led the shift of $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ band to 420 nm, and evacuation at 200°C for 2 hr led to the almost complete recovery of the spectum of that of the dehydrated NiX.

When NiX(30) was evacuated at 500°C for 3 hr, the peaks due to *d–d* transitions do not change appreciably upon adsorption of ammonia at room temperature even after 24 hr as shown in Fig. 2c and d. The situation is the same even when adsorption is carried out at 100 or 200°C. This means that ammonia cannot coordinate to Ni cations, probably because $Ni^{2+}$ cations in $S_I$ sites do not migrate into supercage easily. This result shows the sharp contrast with that by Gallazot *et al.* (*4*) who concluded that ammonia can readily extract Ni cations from $S_I$ sites in the case of Y-zeolite.

Similar phenomena were observed also for NiX(95).

Adsorption of ammonia gave several new bands also in the near-infrared region. The bands may be assigned as follows: The 2270 nm band is a combination of the symmetric N–H deformation mode of ammonia with assymetric N–H streching mode. The 2050 nm band is a combination of the assymmetric N–H deformation mode of ammonia with the N–H stretching mode. The 1550 nm band is the first overtone of the N–H streching bands.

### *Adsorption of Pyridine*

When NiX(30) evacuated at 500°C was exposed to pyridine vapor at room temperature, a new peak due to $\pi$-$\pi^*$ transition of physisorbed pyridine appeared at 250 nm, but no change was observed in the visible region (Fig. 3a). The spectrum did not change after the system was heated to 100°C. After the system was heated at 200°C for 30 min and evacuated for 5 min, the sample showed a reddish purple color. The $\pi$–$\pi^*$ band shifted to 262 nm and the new bands appeared at 380, 480, 610, and 1070 nm (Fig. 3b). The shift of the $\pi$-$\pi^*$ band to longer wave length clearly indicates the coordination of pyridine to metal cations. The positions of three of the *d-d* transitions (380, 610, and 1070 nm) agree well with those of the known octahedral complexes (*18–20*). The band at 480 nm could be ascribed to the transition of $^3A_{2g}(F) \rightarrow {}^1T_{2g}(D)$ (*20*), but the intensity of the band seems too strong for the forbidden transition. It should be noted that the spectrum shows strong similarity to that of five coordinate nickel(II) (*21*). This seems to indicate that the nickel–pyridine complexes have a square based pyramidal streochemistry, whose sixth position is occupied by the zeolite framework at a much longer distance. It is worthy of note that the very similar spectra have been observed when various octahedral compounds were adsorbed from the aqueous solution on silica gel and the gels were dehydrated (*22*).

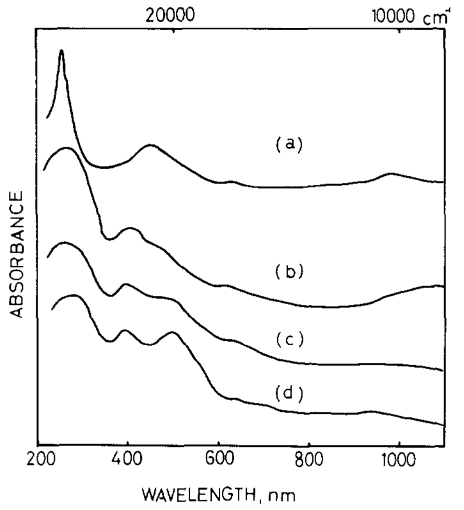

FIG. 3. Adsorption of pyridine on NiX(30): (a) after adsorption of pyridine at room temperature on NiX pretreated at 500°C, (b) after adsorption of pyridine at 200°C on NiX pretreated at 500°C, (c) after adsorption of pyridine at 100°C on NiX pretreated at 200°C, (d) adsorption of pyridine at 200°C on NiX pretreated at 200°C.

Since $Ni^{2+}$ cations in zeolites treated at 500°C are located mainly in $S_I$ sites, the coordination of pyridine indicates that the adsorption induces the migration of cations from the hexagonal prism to the supercage. Gallazot *et al.* (*4*) showed from X-ray studies that adsorption of pyridine at room temperature does not cause the migration of $Ni^{2+}$ cations of highly dehydrated Y-zeolites. But, our results show that the migration does occur if the adsorption was carried out at 200°C, indicating that the migraration process needs activation energy.

The complex formation was observed even at 100°C, when the evacuation treatment of NiX(30) was performed at 200°C, instead of 500°C (Fig. 3c). When the system was further heated at 200°C for 30 min, the complex formation was clearer on the spectrum and the absorption maxi are seen at 395, 500, 650, and 950 nm (Fig. 3d).

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