

# UV/VIS DIFFUSE REFLECTANCE SPECTROSCOPIC (DRS) STUDY OF COBALT-CONTAINING Y ZEOLITES DEHYDRATED AT ELEVATED TEMPERATURES

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**Abstract**—The coordination changes of  $\text{Co}^{2+}$  in Y-zeolite prepared by ion-exchange and dehydrated at various temperatures, have been investigated by UV/VIS diffuse reflectance spectroscopy. Fully hydrated zeolites show an octahedral coordination of  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  in the supercage with some interaction with the framework. During dehydration at high temperatures,  $\text{Co}^{2+}$  in Y-zeolite changes its coordination, first from a symmetric to distorted tetrahedral and, successively, to an octahedral coordination. Fully hydrated sample of impregnated cobalt nitrate in Y-zeolite shows an octahedral coordination of  $\text{Co}(\text{H}_2\text{O})_6(\text{NO}_3)_2$ . During dehydration at high temperature, the cobaltous nitrate decomposes to the cobalt oxide. However, the small amount of cobalt ions in cobalt nitrate are ion-exchanged simultaneously.

## INTRODUCTION

In the large cavities of the zeolite framework, transition metal cations can form complexes with simple molecules as a ligand [1-3]. In such complexes the transition metal ions are generally linked to the framework varying the coordination, position and valence number of the transition metal ions. The location and coordination of charge-balancing cations in synthetic zeolites are attracting increasing attention in recent years in order to get some information concerning their role in catalytic processes [4-8]. A number of physical techniques have been used to investigate the location and coordination of cations in zeolites, each one itself being unable to provide a total picture. UV/VIS spectra may give good information regarding the electronic state of transition metal cations under a given set of conditions.

Egerton et al. [5] studied the magnetic properties of NaY and NaA containing cobalt ions and provided an outline of the changes in site occupancy of  $\text{Co}^{2+}$  when NaA and NaY were dehydrated. They proposed that most cobalt ions are octahedrally coordinated to six water molecules in supercage in fully hydrated state and that the majority of cobalt ions is in pseudotetrahedral coordination in partially dehydrated (25%

dehydration) state. The cobalt ions in site II, II' and I' could migrate to the hexagonal prism in fully dehydrated state. Gallezot and Imelik presented X-ray powder diffraction data which indicates that Co ions prefer hexagonal prism in dehydrated zeolites [9]. Han and Woo [10] estimated the portion of cobalt ion sites by TPR (temperature programmed reduction). When 5CoNaY (cobalt ion-exchanged NaY containing 5 wt% cobalt) was dehydrated completely, 13 of 15 cobalt ions were accommodated in site I and the other 2 cobalt ions probably occupy site I'. In this work we investigated the changes in the coordination and site transformation of  $\text{Co}^{2+}$  ions in Y-zeolite containing various amount of cobalt ions during dehydration at various temperatures. The DRS spectra of cobalt-containing Y-zeolites prepared by impregnation of aqueous cobalt nitrate solution (Co/NaY) were compared with those of CoNaY.

## EXPERIMENTAL

For preparation of catalysts, the sodium form zeolite Y of Strem Chemicals, Inc. (10779-S) was used. It was pretreated with 0.1 N sodium chloride aqueous solution to remove the sodium deficiency in NaY. The chloride was washed out from the zeolite structure with deionized water until no chloride was detected with silver nitrate in the filtrate. Cobalt ion-exchanged

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catalysts (CoNaY) were prepared by ion-exchanging pretreated NaY with 0.05 N  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  aqueous solution (pH=5) at 363 K for 12h. Catalysts were filtered and washed with flowing deionized water after ion-exchange until unused cobalt ion was removed, then dried at 383 K in air. The amount of cobalt ions exchanged was measured by atomic absorption analysis. Impregnated catalysts (Co/NaY) were prepared by impregnating aqueous  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , prepared by dissolving appropriate weight of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in 5 ml of deionized water, into 5 g of pretreated NaY at room temperature. The loading of cobalt was indicated by the number in front of abbreviation, i.e., 5CoNaY (5 wt% cobalt loading at wet basis). These catalysts were stored in a desiccator saturated with ammonium chloride solution.

Diffuse reflectance spectroscopy (DRS) spectra were obtained using a quartz vacuum cell fitted with an optical window. The cell was closed with a vacuum stopcock when the cell was removed from the vacuum line for spectral measurements. Spectra were recorded in the range between 190 and 850 nm using a Shimadzu 240 spectrometer referenced with standard  $\text{MgO}$  powder. Percent reflectance was measured by operating UV/VIS spectrometer in transmittance mode and this percent reflectance gives the percentage of the UV/VIS light diffusely reflected from the sample relative to the  $\text{MgO}$  reference.

## RESULTS AND DISCUSSION

The spectra of the fully hydrated samples of 2CoNaY, 4CoNaY, 5.5CoNaY, 5Co/NaY and 10Co/NaY are shown in Fig. 1. The pink coloured samples of hydrated CoNaY's have an absorption band at about 520 nm, which is typical of the hexa-aquo-cobalt ion complex arising from the ligand-field transition of rhombic distorted octahedral cobalt ion complex. The intensity of 520 nm band increases with the increase in the cobalt loading without any appearance of new band indicating that only octahedral hexa-aquo-cobalt ions present even at higher cobalt loadings. In agreement with Klier [11] and Egerton [5], cobalt ions remain in the supercage and are octahedrally coordinated by six water molecules in hydrated CoNaY regardless of cobalt loading. A shoulder at about 680 nm arises from the ligand-field transition of tetragonal octahedral aquo-cobalt ion complex [12].

The reddish pink coloured samples of hydrated Co/NaY's after drying at 383 K have absorption bands at about 520 and 465 nm, which are typical of the hexa-aquo-cobalt ion complex,  $\text{Co}(\text{H}_2\text{O})_6(\text{NO}_3)_2$ , arising

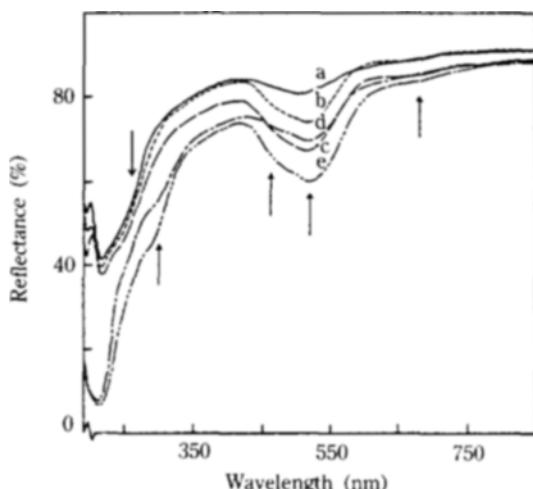


Fig. 1. DRS spectra of fully hydrated samples: (a) 2CoNaY, (b) 4CoNaY, (c) 5.5CoNaY, (d) 5Co/NaY, (e) 10Co/NaY.

from the ligand-field transition of octahedral cobalt aquo-complex [13]. Ashley and Mitchell [14] reported that the electronic transitions of  $\text{CoO}$  and  $\text{Co}_2\text{O}_4$  supported on alumina are represented by the bands at 227, 285 and 381 nm, and at 220, 270 and 370 nm, respectively. The adsorption band at about 300 nm observed in the DRS spectra of 5Co/NaY and 10Co/NaY might be ascribed to the charge-transfer transition of cobalt oxides. Unsupported cobaltous nitrate hexahydrate melts at 328 K to red liquid which becomes green and decomposes to the oxide above 347 K [15]. Therefore, it can be suggested that cobaltous nitrate hexahydrate impregnated in NaY after drying at 383 K in air does not decompose and remains in the supercage or on the exterior surface of zeolite due to the stabilizing effect of zeolite structure. However, DRS result suggests that part of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  decomposes to cobalt oxide species.

The spectra of 5.5CoNaY dehydrated at various temperatures are shown in Fig. 2. After dehydration of 5.5CoNaY at 383 K, a DRS spectrum [Fig. 2(b)] shows the presence of tetrahedral  $\text{Co}^{2+}$  indicated by absorption bands at 611, 575 and 530 nm. After dehydration at 473 K, the absorption band at 611 is shifted to 660 nm. This shift is attributed to the change of the ligand in  $\text{Co}^{2+}$  ions. In agreement with Egerton [5], the shifts in absorption bands observed during dehydration between 383 K and 473 K can be attributed to the transformation of  $\text{Co}(\text{H}_2\text{O})_6$  into  $\text{Co}(\text{Ox})_3\text{H}_2\text{O}$  species in which Ox denotes lattice oxygen. According to Egerton, tetrahedral coordination of  $\text{Co}^{2+}$  can be occurred

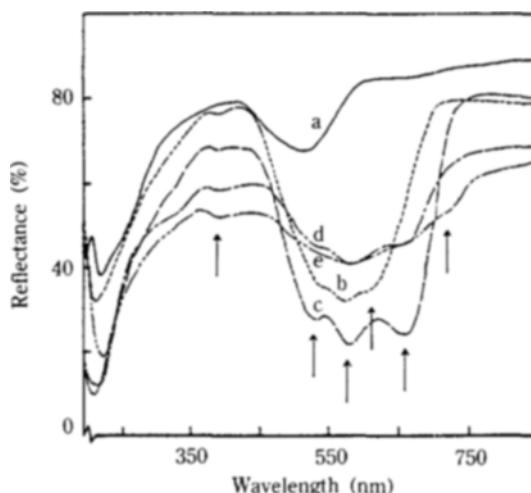


Fig. 2. DRS spectra of 5.5CoNaY dehydrated at  $1 \times 10^{-6}$  torr: (a) fully hydrated sample, (b) dehydration for 1 h at 383 K, (c) at 473 K, (d) at 673 K, (e) at 873 K.

on the face of sodalite cages, where  $\text{Co}^{2+}$  shows a threefold coordination with the lattice oxygen and with  $\text{H}_2\text{O}$  as a fourth ligand [5]. Another explanation for the shifts might come from the changes in the  $T_d$  symmetry of  $\text{Co}(\text{H}_2\text{O})_4$  to  $C_{\infty}$  symmetry of  $\text{Co}(\text{Ox})_3\text{H}_2\text{O}$  [12].

During dehydration at 673 K, the bands at 660, 575 and 530 nm appeared after dehydration at 473 K are not shifted. However, the intensities of these bands decreased significantly. This decrease in intensity of the absorption in the 670-520 nm region, may be attributed to a decrease in the amount of  $\text{Co}^{2+}$  in tetrahedral coordination due to the migration of  $\text{Co}^{2+}$  ions from site II' or I' to site I. After dehydration at 873 K, a new band appeared at 720 nm and the bands arising from tetrahedral coordination of  $\text{Co}^{2+}$  are unresolved. It is proposed that the band at 720 nm is due to  $\text{Co}^{2+}$  ions migrated into the hexagonal prism where they experience a distorted octahedral environment [16].

The changes of the band locations and intensities of tetrahedral and octahedral cobalt ion complexes in the UV/VIS absorption spectra as shown in Fig. 2 can be explained as follows. For tetrahedral complexes, the visible spectrum corresponding to the highest energy transition between the nondegenerate ground state  $^1\text{A}_g(\text{F})$  and the triply degenerated excited state  $^1\text{T}_1(\text{P})$  is split into three symmetrically spaced peak. This splitting has been attributed to a dynamic Jahn-Teller effect [17]. For tetrahedral complexes there is also a transition of  $^4\text{A}_2 \rightarrow ^4\text{T}_1(\text{F})$  in the near-infrared region around 1400 nm, as well as one of quite low

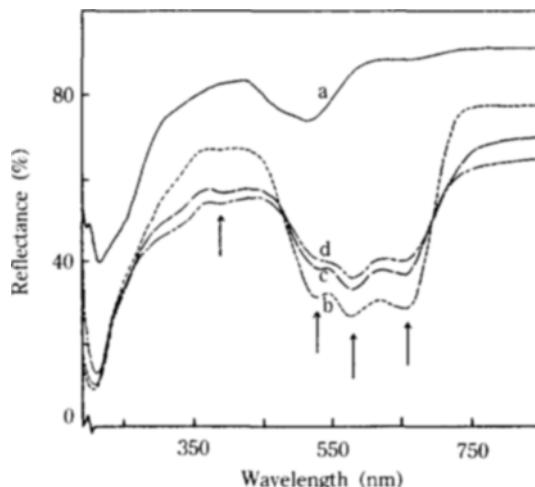


Fig. 3. DRS spectra of 4CoNaY dehydrated at  $1 \times 10^{-6}$  torr: (a) fully hydrated sample, (b) dehydration for 1 h at 473 K, (c) at 673 K, (d) at 873 K.

energy [ $^4\text{A}_2 \rightarrow ^4\text{T}_2(\text{F})$ ], which is seldom observed because it is in an inconvenient region around 2500 nm of the spectrum, and it is orbitally forbidden [18, 19]. For octahedral complexes the visible spectrum is dominated by the highest energy transition,  $^4\text{T}_1(\text{F}) \rightarrow ^4\text{T}_1(\text{P})$ , but the  $^4\text{A}_{2g}$  level is usually close to the  $^4\text{T}_1(\text{P})$  level and the transitions to these two levels are close together [19]. Since the  $^4\text{A}_{2g}$  state is derived from a  $t_{2g}^3 e_g^1$  electron configuration, and the  $^4\text{T}_1(\text{F})$  ground state is derived mainly from a  $t_{2g}^5 e_g^2$  configuration, the  $^4\text{T}_1(\text{F}) \rightarrow ^4\text{A}_{2g}$  transition is essentially a two-electron process; thus the intensity of crystal field transition absorptions for octahedral cobalt is 100 times lower than that of tetrahedral cobalt [19]. For octahedral complexes, there is one more spin-allowed transition of  $^4\text{T}_1(\text{F}) \rightarrow ^4\text{T}_2$  which generally occurs in the near-infrared region which is not detected in our spectral range [19].

There is a weak band at 390 nm. Pure oxide ( $\text{CoO}$ ) and many mixed oxides of cobalt exhibit absorption at 400-370 nm [14]. The nature of this absorption is not clear, but one possible interpretation is charge transfer between  $\text{Co}^{2+}$ - $\text{O}^{2-}$  or  $\text{Co}^{2+}$ - $\text{Co}^{3+}$ . Cobalt hydroxide formed during the ion-exchange might be transformed to cobalt oxide species during dehydration at 873 K. The weak band at 390 nm might be attributed to  $\text{Co}^{2+}$  located in a trigonal planar environment of the oxygen six-membered ring (site II in Y-zeolite) similar to the previous study by Klier et al. [18].

The spectra of 4CoNaY and 2CoNaY dehydrated at various temperatures are shown in Fig. 3 and Fig. 4.

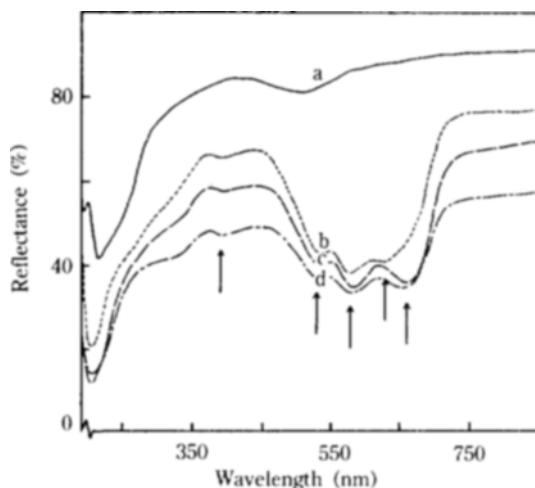


Fig. 4. DRS spectra of 2CoNaY dehydrated at  $1 \times 10^{-6}$  torr: (a) fully hydrated sample, (b) dehydration for 1 h at 473 K, (c) at 673 K, (d) at 873 K.

respectively. Comparing the spectrum of 5.5CoNaY with those of 4CoNaY and 2CoNaY after dehydration at 473 K, the intensities of absorption band between 670 and 520 nm decreased with decrease in cobalt loading. This is attributed to a decrease in the amount of  $\text{Co}^{2+}$  in tetrahedral coordination. For 4CoNaY, during dehydration at 673 K and 873 K, no changes in the spectral shape occurs, but the intensity decreases as shown in Figs. 3(c) and (d). This decrease in intensity of the absorption band between 670 and 520 nm, may be attributed to a decrease in the amount of  $\text{Co}^{2+}$  in tetrahedral coordination due to the  $\text{Co}^{2+}$  ions migration from site II' or I' to site I of octahedral coordination. However, the band arising from  $\text{Co}^{2+}$  in octahedral coordination does not appear because of very weak intensity. After dehydration of 2CoNaY at 473 K, the spectrum [Fig. 4(b)] shows absorption maxima at 625, 575 and 530 nm. The location of this band indicates that  $\text{Co}(\text{H}_2\text{O})_4$  complex still exists after dehydration at 473 K, while  $\text{Co}(\text{Ox})_3\text{H}_2\text{O}$  complex is formed from  $\text{Co}(\text{H}_2\text{O})_4$  after dehydration at 473 K for 4CoNaY and 5.5CoNaY. This indicates that the dehydration of  $\text{Co}(\text{H}_2\text{O})_4$  is more difficult for 2CoNaY than for 4CoNaY and 5.5CoNaY, because the concentration of  $\text{Co}(\text{H}_2\text{O})_4$  in site II is smaller for 2CoNaY than for 4CoNaY and 5.5CoNaY. If cobalt loading is high, there exists plenty of  $\text{Co}(\text{H}_2\text{O})_4$ , which can be converted to  $\text{Co}(\text{H}_2\text{O})_4$ , then further converted to  $\text{Co}(\text{Ox})_3\text{H}_2\text{O}$  at low temperatures. However, if cobalt loading is small, it needs a higher temperature to migrate  $\text{Co}(\text{H}_2\text{O})_4$  in site II to site II' or I' inside sodalite cage to form  $\text{Co}(\text{Ox})_3\text{H}_2\text{O}$ .

The spectra of impregnated sample 5Co/NaY dehy-

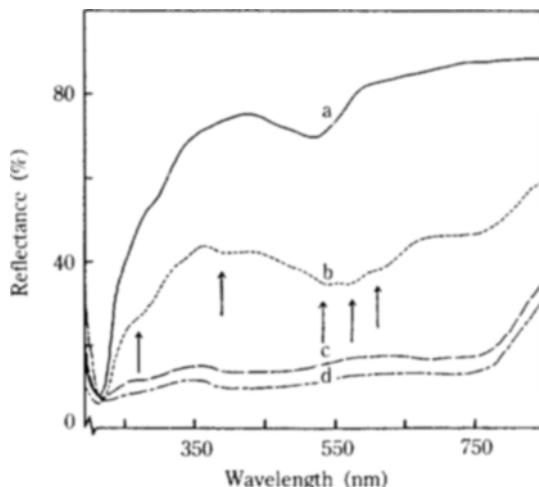


Fig. 5. DRS spectra of 5Co/NaY dehydrated at  $1 \times 10^{-6}$  torr: (a) fully hydrated sample, (b) dehydration for 1 h at 473 K, (c) at 673 K, (d) at 873 K.

drated at various temperatures are shown in Fig. 5. The colour of 5Co/NaY changed for reddish pink to black after dehydration at 673 K. After dehydration at 473 K the spectrum shows weak absorption bands at 611, 575 and 530 nm, which indicates the presence of tetrahedral  $\text{Co}^{2+}$  ions. It is evident that significant amount of  $\text{Co}^{2+}$  in concentrate  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  solution during impregnation of 5 min is ion-exchanged to form tetrahedral  $\text{Co}^{2+}$  ions after dehydration at 473 K. The bands at 390 and 270 nm [Fig. 5(b)] are attributed to the cobalt oxide species resulting from the decomposition of cobaltous nitrate [14]. The colour of the sample is too dark to observe these bands after dehydration at higher temperatures of 673 K and 873 K. However according to the literature [10, 14],  $\text{Co}_3\text{O}_4$  might be formed.

## CONCLUSIONS

The DRS spectra of 2CoNaY, 4CoNaY and 5.5CoNaY in fully hydrated state indicate that  $\text{Co}(\text{H}_2\text{O})_4^{2+}$  exists and that the amount of  $\text{Co}(\text{H}_2\text{O})_4^{2+}$  increases with increasing cobalt loading. Not any tetrahedral cobalt complexes are present even in 2CoNaY. Regardless of cobalt loadings,  $\text{Co}(\text{H}_2\text{O})_4^{2+}$  is converted to  $\text{Co}(\text{H}_2\text{O})_4^{2+}$  and further converted to  $\text{Co}(\text{Ox})_3\text{H}_2\text{O}$  after dehydration below 673 K. After dehydration at 873 K, most of  $\text{Co}(\text{Ox})_3\text{H}_2\text{O}$  are further dehydrated and migrated to hexagonal prism. The dehydration temperature for 2CoNaY required to convert  $\text{Co}(\text{H}_2\text{O})_4^{2+}$  to  $\text{Co}(\text{Ox})_3\text{H}_2\text{O}$  is higher than those for 4CoNaY and 5.5CoNaY. The DRS spectra of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  impregnated NaY(5

Co/NaY and 10Co/NaY) dehydrated at elevated temperatures indicates that significant ion-exchange was occurred during very short impregnation period.

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### REFERENCES

1. Gallezot, P., Ben Taarit, Y. and Imelik, B.: *J. Catal.*, **26**, 295 (1972).
2. Klier, K.: *Adv. Chem. Ser.*, **101**, 480 (1971).
3. Rabo, J. A.: "Zeolite Chemistry and Catalysis", ACS monograph vol. 171 (1976).
4. Kim, J. C. and Woo, S. I.: *Appl. Catal.*, **39**, 107 (1988).
5. Egerton, T. A., Hagan, A., Stone, F. S. and Vicker- man, J. C.: *J. Chem. Soc. Faraday Trans. I*, **68**, 723 (1972).
6. Zhang, Z., Wong, T. T. and Sachtler, W. M. H.: *J. Catal.*, **128**, 13 (1991).
7. Egerton, T. A. and Stone, F. S.: *J. Chem. Soc. Faraday Trans. I*, **69**, 22 (1973).
8. Gallezot, P., Ben Taarit, Y. and Imelik, B.: *J. Catal.*, **26**, 481 (1972).
9. Gallezot, P. and Imelik, B.: *J. Chim. Phys.*, **71**, 155 (1974).
10. Han, J. D. and Woo, S. I.: to be published in *J. Chem. Soc. Faraday Trans.* (1991).
11. Klier, K.: *Catalysis Rev.*, **1**(2), 207 (1967).
12. Diegruber, H. and Plath, P. J.: "Metal Microstructures in Zeolites", Jacobs, P. A., Ed., Elsevier, p. 23 (1982).
13. Hathaway, B. J. and Lewis, C. E.: *J. Chem. Soc. A*, 1183 (1969).
14. Ashley, J. H. and Mitchell, P. C. H.: *J. Chem. Soc. A*, 2821 (1968).
15. Budavari, S. and O'Neil, M. J., Eds.: "The Merck Index", 11th ed., Merck & Co., Inc., Rahway, (1989).
16. Hutta, P. J. and Lunsford, J. H.: *J. Chem. Phys.*, **66**, 10, 4716 (1977).
17. Cotton, F. A., Goodgame, D. M. L. and Goodgame, M.: *J. Am. Chem. Soc.*, **83**, 4690 (1961).
18. Klier, K., Kellerman, R. and Hutta, P. J.: *J. Chem. Phys.*, **61**, 4224 (1974).
19. Cotton, F. A. and Wilkinson, G.: "Advanced Inorganic Chemistry", 4th ed., John Wiley & Sons, New York, p. 766 (1980).