

## BEHAVIOUR OF CoNaA ZEOLITES IN INTERACTION WITH WATER

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The influence of dehydration and adsorption of water on the coordination of cations, the state of adsorbed water, and stretching vibrations of CoNaA and NaA zeolites was investigated by means of electronic and infrared spectroscopy. Complexes of  $\text{Co}^{2+}$  change their symmetry from octahedral through tetrahedral to planar trigonal. The role of ligands play both skeletal oxygens and molecular water. The formation of OH groups either on the skeleton or on  $\text{Co}^{2+}$  ions was not found; the existence of these groups was assumed in the literature to explain the catalytic activity of CoNaA zeolites in the isomerization of butenes.

The catalytic activity of zeolites containing bivalent metal cations<sup>1-3</sup> in isomerization reactions of olefins is positively influenced by a small amount of water present in the zeolite (about 2 to 6 molecules per cavity). This activity has been ascribed both to the presence of bivalent cations and to acidic hydroxyl groups formed in dissociation of water. The above mentioned catalytic properties were described for zeolites containing cobalt ions, too<sup>1,2</sup>. As no detailed data on the behaviour of these complexes in the interaction with small amounts of water are available, we undertook this study with the aim to investigate in detail processes of hydration and dehydration by methods of infrared and electronic spectroscopy. These methods make it possible to investigate simultaneously water bound in the molecular form, OH groups bound to Co ions and to skeleton, the symmetry of the ligand field of the Co ion and thus — indirectly — also its position and changes of vibrations of the Si—Al—O skeleton. In order to investigate the effect of the zeolite structure and of the ratio Si/Al on these processes, we studied the zeolites CoNaX (ref.<sup>4</sup>), CoNaY (ref.<sup>5</sup>) and CoNaA; the subject of this communication is the last zeolite type.

Dehydration of CoNaA zeolites from the point of view of the  $\text{Co}^{2+}$  ion ligand field was studied by means of reflection diffusion spectroscopy<sup>6-8</sup> and by means of X-ray analysis<sup>9,10</sup>. While tetrahedral complexes of  $\text{Co}^{2+}$  ions in partially dehydrated zeolites were found by all the cited authors and their ligand field was specified, the occurrence and description of planar trigonal complexes of  $\text{Co}^{2+}$  ions in fully dehydrated zeolites is rather ambiguous.

## EXPERIMENTAL

The composition of the studied zeolites was the following: NaA:  $6 \text{ Na}_2\text{O} \cdot 6 \text{ Al}_2\text{O}_3 \cdot 12 \text{ SiO}_2 \cdot x \text{ H}_2\text{O}$ .

CoNaA:  $2 \cdot 16 \text{ CoO} \cdot 3 \cdot 84 \text{ Na}_2\text{O} \cdot 6 \text{ Al}_2\text{O}_3 \cdot 12 \text{ SiO}_2 \cdot x \text{ H}_2\text{O}$  (the weight loss after 24 h at  $400^\circ\text{C}$  and in a vacuum of  $1 \cdot 3 \cdot 10^{-4} \text{ Pa}$  was 23.75%). Cobalt forms were prepared by an exchange of Na ions of the NaA zeolite (Linde) in a  $\text{CoCl}_2$  solution under such conditions that no hydrolysis took place.

Dehydration of zeolites was carried out at temperatures  $25\text{--}600^\circ\text{C}$  in a stream of dry oxygen or under a vacuum of  $1 \cdot 3 \cdot 10^{-4} \text{ Pa}$ . Samples were first dehydrated in the stream of oxygen and then for two hours under the vacuum. Their electronic spectra did not show any difference after treating the zeolite in oxygen and after the subsequent vacuum treatment; this shows the stability of the  $\text{Co}^{2+}$  valence. Differential thermal analysis (DTA) showed that a collapse of the CoNaA structure occurs only above  $650^\circ\text{C}$ . Initial samples for hydration were zeolites dehydrated at 400 and  $600^\circ\text{C}$ . The hydration of the zeolites was carried out at  $25^\circ\text{C}$  (reflection spectra) and at  $40^\circ\text{C}$  (infrared spectra, thermostated spectrometer).

Infrared spectra were measured over the interval  $4000\text{--}350 \text{ cm}^{-1}$  on a Perkin-Elmer 621 spectrometer. Electronic spectra were recorded over the interval  $25000\text{--}14000 \text{ cm}^{-1}$  (or  $4000 \text{ cm}^{-1}$ ) using the reflection techniques  $R_{O,D}$  on an Optica Milano CF4 NI spectrometer. Details of the measuring procedures were described elsewhere<sup>4</sup>.

## RESULTS

The electronic spectra show that the original samples of the CoNaA zeolites exhibit the octahedral symmetry of the ligand field of the  $\text{Co}^{2+}$  ion (Fig. 1, bands 8200, 15500, 19800,  $21500 \text{ cm}^{-1}$ ). At the same time there are in the near infrared region clearly visible bands of upper harmonic and combination frequencies of water<sup>8</sup> ( $5200, 5600 \text{ vw}, 6900 \text{ cm}^{-1}$ ). A gradual dehydration up to  $600^\circ\text{C}$  leads to a continuous change in the positions and relative intensities of bands in the neighbourhood of  $17000$  and  $7000 \text{ cm}^{-1}$  and to a gradual increase of the  $14800 \text{ cm}^{-1}$  band which reaches a maximum at the dehydration temperature  $600^\circ\text{C}$ . For comparison, in Fig. 1 there are indicated the positions of the bands of tetrahedral  $\text{Co}^{2+}$  complexes with oxygen-containing ligands, as reported in the literature<sup>11,13,14</sup>.

The infrared spectra show that increasing the evacuation temperature is accompanied by a water desorption (Fig. 2, see also the  $1650\text{--}1630 \text{ cm}^{-1}$  band of bending vibrations of water). However, the sample contains also carbonate complexes and/or organic impurities, not removed even after 16 hours of evacuation at  $400^\circ\text{C}$  (bands at  $1620, 1590, 1430, 1340 \text{ cm}^{-1}$ ). After the treatment of the sample by oxygen and in vacuo at  $600^\circ\text{C}$  only very weak bands of water ( $3425$  and  $1663 \text{ cm}^{-1}$ ) were found in the CoNaA zeolite, corresponding to about 0.2 water molecule per unit cell (further on u.c.). Organic impurities burn up at these conditions. Changes of skeletal vibrations, measured over  $1000\text{--}350 \text{ cm}^{-1}$ , during the dehydration are only minor and concern only weak bands in the region  $850\text{--}700 \text{ cm}^{-1}$ . Up to the dehydration temperature of  $200^\circ\text{C}$  the measured spectra resembled curves 2 and 3 in Fig. 4;

above 200°C the type of the spectrum did not change (curve 1, Fig. 4). Ascribing of the bands according to Flanigen<sup>15</sup> is given in the same figure; here, T represents Si or Al, b and s indicates bending and stretching vibrations, respectively, PO is the breathing movement of windows of large cavities, *i.e.* pore opening, D4R are vibrations which reflect the presence of two- and four- membered building units of the A-type zeolite.

The hydration of the CoNaA zeolites (Figs. and 4) was studied with samples dehydrated at 600°C and containing water up to 0.2 molecules per unit cell (bands at 3430 and 1663  $\text{cm}^{-1}$  in the infrared spectrum). As early as during the first water doses the maximum shifted to 3470–3480  $\text{cm}^{-1}$ , the absorption in the region 3550–3500  $\text{cm}^{-1}$  increased, and the maximum in the region of bending vibrations of water shifted to 1650  $\text{cm}^{-1}$ . For fillings higher than 2–3 water molecules per unit cell the intensity of the 1650  $\text{cm}^{-1}$  band did not change, but a new band started to grow at 1635  $\text{cm}^{-1}$  (Fig. 3). The character of the changes is similar to those during the sorption of water on the NaA zeolite, studied in detail by Dubinin<sup>16</sup> (infrared spectra in the region of stretching and bending vibrations of water and OH, calorimetry). The authors<sup>16</sup> concluded that up to about 4 molecules of water per unit cell water interacts with  $\text{Na}^+$  ions placed in the vicinity of entrance windows of large cavities (designated by the authors as non-localized ions) prevalently *via* the

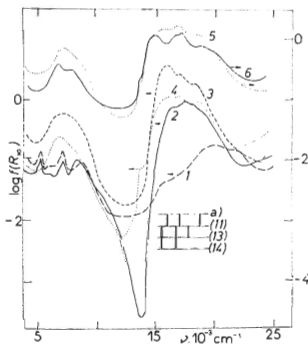


FIG. 1

Reflectance Spectra of the CoNaA Zeolite Dehydration

1 Original, 2 25°C, 3 100°C, 4 200°C, 5 400°C, 6 600°C.

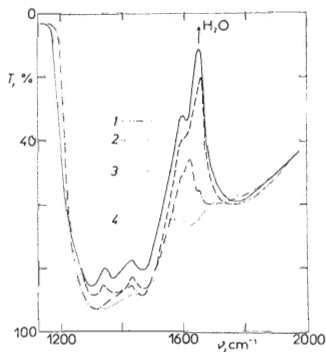


FIG. 2

IR Spectra of the CoNaA Zeolite after Dehydration

1 25°C 2 hours, 2 100°C 2 hours, 3 200°C 2 hours, 4 400°C 14 hours.

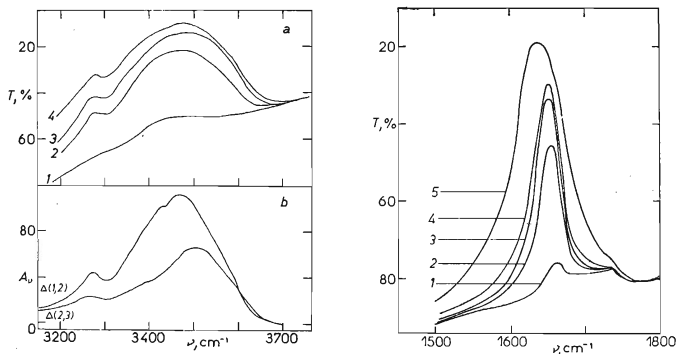


FIG. 3

IR Spectra of the CoNaA Zeolite after Water Adsorption

*a:* 1 Original spectrum after dehydration at 600° in oxygen and vacuum, 2 0.9 molecules  $\text{H}_2\text{O}/\text{u.c.}$ , 3 1.5 molecules  $\text{H}_2\text{O}/\text{u.c.}$ , 4 2 molecules  $\text{H}_2\text{O}/\text{u.c.}$  *b:* Graphical subtraction 1—2, 2—3 curves of (*a*). *c:* IR spectra of the CoNaA zeolite hydration. 1, 2, 3, 4 — see (*a*), 5  $p_{\text{H}_2\text{O}} = 4.58$  Torr.

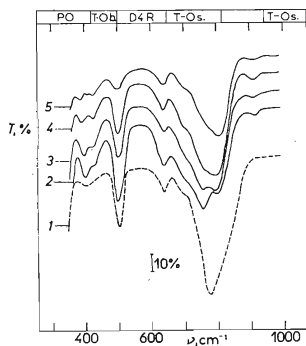


FIG. 4

IR Spectra of Skeletal Vibrations

1 NaA dehydrated at 400°C, 2 CoNaA dehydrated at 600°C in oxygen and vacuum, 3 (2) + 1.5 molecules  $\text{H}_2\text{O}/\text{u.c.}$ , 4 (2) + 2 molecules  $\text{H}_2\text{O}/\text{u.c.}$ , 5 (2) + 4.58 Torr  $\text{H}_2\text{O}$ .

ion-dipole interaction (bands at  $3440-30, 1660-65 \text{ cm}^{-1}$ ). At higher fillings besides the interaction with  $\text{Na}^+$  ions also the hydrogen bond with lattice oxygen plays a role; bands at  $3470$  and  $1650 \text{ cm}^{-1}$  appear, and the absorption at  $3550 \text{ cm}^{-1}$  increases, as could be shown by graphical subtraction. Our results on the adsorption of water on the NaA zeolite are essentially in agreement with the published data. In addition, at higher fillings the appearance of a new band of bending vibrations of water was observed at  $1630 \text{ cm}^{-1}$  whose intensity increased with hydration.

The positions of the bands of skeletal vibrations both with the NaA and the CoNaA zeolite did not change upon water adsorption, only the over-all transmittance of the sample decreased. With the CoNaA zeolites (Fig. 4) for fillings 0–2 water molecules per unit cell in addition to it the  $790 \text{ cm}^{-1}$  band decreases and a new weak band appears at  $775 \text{ cm}^{-1}$ ; this band disappears again at a higher water content. Fig. 3 shows also the initial spectrum of the NaA zeolite, for a comparison with the CoNaA zeolite.

Fig. 5 summarizes changes in the position of absorption bands in the electronic spectra in the region  $25000-14000 \text{ cm}^{-1}$  in dependence on the amount of water adsorbed on the CoNaA zeolite dehydrated at  $600^\circ\text{C}$ . As an illustration, several

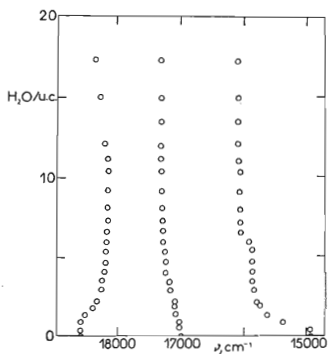


FIG. 5

Dependence of the Position of Reflectance Spectra Bands on the Hydration of the CoNaA Zeolite Dehydrated in Oxygen and Vacuum at  $600^\circ\text{C}$

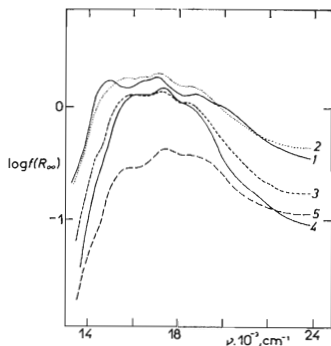


FIG. 6

Reflectance Spectra of the CoNaA Zeolite Hydration

1 CoNaA dehydrated in oxygen and vacuum at  $600^\circ\text{C}$ , 2 (1) + 2.2 molecules  $\text{H}_2\text{O}/\text{u.c.}$ , 3 (1) + 3.9 molecules  $\text{H}_2\text{O}/\text{u.c.}$ , 4 (1) + 12.1 molecules  $\text{H}_2\text{O}/\text{u.c.}$ , 5 (1) + c. 25 molecules  $\text{H}_2\text{O}/\text{u.c.}$

complete spectra are reported (Fig. 6). The adsorption band positions exhibit the largest changes in the water adsorption region about 0–3 water molecules per u.c.; in particular, the  $14800\text{ cm}^{-1}$  band shifts to  $16000\text{ cm}^{-1}$ . Also, the intensity of the entire absorption band at about  $17000\text{ cm}^{-1}$  increases with the increasing hydration. In the adsorption region 3–15 molecules of water per u.c. the electronic spectra exhibit practically no change; they correspond to tetrahedral complexes of  $\text{Co}^{2+}$  found during the zeolite dehydration. In the region of high fillings of the zeolite by water the tetrahedral symmetry of the  $\text{Co}^{2+}$  ligand field changes to octahedral symmetry. Spectra of the water adsorption on the zeolite dehydrated at  $400^\circ\text{C}$  exhibit the same changes as those on the zeolite dehydrated at  $600^\circ\text{C}$ , only with a shift of about one water molecule per u.c.

## DISCUSSION

Fully hydrated zeolites exhibit the  $O_h$  symmetry of the  $\text{Co}^{2+}$  ion ligand field which – according to the electronic spectra – does not differ from the symmetry of the  $\text{Co}^{2+}$  hexaquocomplex in aqueous solutions. However, it cannot be assessed that all the six ligands of the zeolite  $\text{Co}^{2+}$  ion are water molecules: the same role could be played by oxygens of the Si–Al–O skeleton. Riley and Seff<sup>9,10</sup> assumed on the basis of X-ray analysis the existence of  $T_d$  complexes of  $\text{Co}^{2+}$  in a hydrated single-crystal CoNaA in which one ligand is formed by a water molecule and the other three are extra-lattice oxygens formed by water fragmentation. Each of these oxygens could be bonded to a skeletal aluminium which then acquires the five-fold coordination. However, the electronic spectra did not point to the presence of these  $T_d$  complexes in the fully hydrated CoNaA zeolite (the absorption coefficients of  $T_d$  bands are in general by an order of magnitude larger than those of  $O_h$  bands).

The dehydration of CoNaA *in vacuo* leads to the formation of the  $T_d$  complexes of  $\text{Co}^{2+}$  as early as at  $25^\circ\text{C}$ . The infrared spectra in the region of stretching and bending vibrations of OH and  $\text{H}_2\text{O}$  show that during the entire dehydration process only water in its molecular form is present in the zeolite. Bands of skeletal OH or OH bound to  $\text{Co}^{2+}$  ions were not found. Therefore, molecular water forms presumably the fourth ligand in the  $T_d$  cobalt complexes of partially dehydrated zeolites; the remaining three ligands are probably oxygens in the six-membered windows (Fig. 1 and Fig. 3). The changes in the electronic spectra caused by further dehydration above  $200^\circ\text{C}$  can be explained only by the formation of complexes with a symmetry close to the trigonal planar arrangement (Fig. 1). Trigonal planar complexes of  $\text{Co}^{2+}$  (formed by three skeletal oxygens of a large window) were determined by X-ray analysis<sup>9</sup>. Also, these complexes were described by Klier and coworkers<sup>8</sup> on the basis of occurrence of the  $24000\text{ cm}^{-1}$  band in the electronic spectra. However, this band was not observed by us or by other authors<sup>6,7</sup> during the dehydration of zeolites over the temperature interval  $25\text{--}600^\circ\text{C}$ . On the other hand, changes of spectra

with the dehydration analogous to those observed by us were found by Heilbron and coworkers<sup>6</sup> for CoNaY and CoNaA, and ascribed in the case of CoNaY to the migration of  $\text{Co}^{2+}$  to  $S_1$  positions of the  $O_h$  symmetry of the ligand field, while for CoNaA they were not discussed<sup>6</sup>. The structure of the A-type zeolite does not contain a hexagonal prisma and thus it excludes the possibility of positioning  $\text{Co}^{2+}$  ions in the  $S_1$  positions of the  $O_h$  ligand symmetry. In view of the fact that during dehydration there occurs a lowering of the band intensities of the  $T_d$  complexes, a significant shift of the  $16000\text{ cm}^{-1}$  band to  $14800\text{ cm}^{-1}$ , and because the zeolites dehydrated at  $600^\circ\text{C}$  contain less than 0.2 molecules  $\text{H}_2\text{O}$  per unit cell, it is very probable that these changes reflect a transition of the tetrahedral complexes to a symmetry close to the trigonal planar symmetry in a six-membered zeolite window.

The zeolites dehydrated at  $400^\circ\text{C}$  and  $600^\circ\text{C}$  adsorb water only in its molecular form. The electronic spectra showed that in the interaction with water  $\text{Co}^{2+}$  ion take part: another ligand enters the coordination sphere of the ions with a symmetry close to the trigonal planar symmetry and the symmetry changes to the tetrahedral. This process occurs up to the filling of 2–3 water molecules per unit cell ( $2.2\text{ Co}^{2+}/\text{u.c.}$ ). It can be deduced from the position of bands in the infrared spectra that water molecules are influenced not only by the ion-dipole interaction with  $\text{Co}^{2+}$  ions, but also by the hydrogen bond with lattice oxygens. This latter type of interaction can augment an increased shift of  $\text{Co}^{2+}$  ions into the large cavity with respect to the six-membered ring plane in comparison with the situation with  $\text{Na}^+$  ions (*cf.* results of X-ray analysis<sup>9,17</sup>). An over-all lower number of  $\text{Co}^{2+}$  ions may presumably play a role, too, and thus changes with the CoNaA zeolites start at lower fillings than with the NaA zeolites. In the region of a higher hydration degree than 2–3 water molecules per unit cell the electronic spectra do not change any more; the  $T_d$  symmetry of the  $\text{Co}^{2+}$  ligand field is preserved, Co ions are presumably saturated and in the interaction of water only  $\text{Na}^+$  ions take part to a larger extent. In addition, mutual influencing of adsorbed water molecules takes place, as it follows from the infrared spectra. With the full hydration the symmetry of the  $\text{Co}^{2+}$  ligand field changes again to the  $O_h$  symmetry.

As far as the changes of skeletal vibrations are concerned, they are not significantly sensitive to the  $\text{Co}^{2+}$  ion amount in the A-type zeolites (in contrast with the X-type zeolites<sup>4</sup>), though X-ray analysis showed that changes of Si, Al—O bonds and of Si—O, Al—O angles in the skeleton take place as a result of the  $\text{Na}^+ - \text{Co}^{2+}$  exchange<sup>9,17</sup>. The presence of the  $415\text{ cm}^{-1}$  and  $795\text{ cm}^{-1}$  bands, found in CoNaA and CoNaX<sup>4</sup>, hangs together with the presence of  $\text{Co}^{2+}$ ; they were not found in the NaA forms. These bands are presumably connected with vibrations of  $\text{Co}^{2+}$  complexes and the former one is influenced by the presence of water.

As far as the positions of cations and the form of water bound in the zeolites are concerned, the processes of hydration and dehydration are reversible. During both

these processes no water dissociation was observed which would result in the formation of skeletal hydroxyls and  $\text{CoOH}^+$ ; this all despite the presence of the  $\text{Co}^{2+}$  ion electrostatic field. For these reasons the catalytic activity of the CoNaA zeolites cannot be ascribed to these types of hydroxyls. Therefore, one has to look for other relations between the catalytic activity and properties of these zeolites. It will be necessary to consider to what extent the catalytic activity is directly influenced by the  $\text{Co}^{2+}$  ion electrostatic field, by its changes in the low-hydration region, or by water bound in its molecular form to  $\text{Co}^{2+}$  ions.

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#### REFERENCES

1. Detreköy E., Kalló D.: Amer. Chem. Soc. Symposium Series, IVth Inter. Congr. on Zeolites, Chicago 1976. Molecular Sieves II, No 45, 549 (1977).
2. Hoser H., Krzyzanowski S.: J. Catal. 38, 366 (1975).
3. Lombardo E. A., Sill G. A., Hall W. K.: J. Catal. 22, 54 (1971).
4. Kubelková L., Wichterlová B.: This Journal 42, 2033 (1977).
5. Kubelková L., Wichterlová B.: Unpublished results.
6. Heilbron M. A., Vickerman J. C.: J. Catal. 33, 434 (1974).
7. Hoser H., Krzyzanowski S., Trifiró F.: J. Chem. Soc., Faraday Trans. 1 1975, 665.
8. Klier K., Kellerman R., Hutta P. J.: J. Chem. Phys. 61, 4224 (1974).
9. Riley P. E., Seff K.: J. Chem. Soc., Chem. Commun. 1972, 1287.
10. Riley P. E., Seff K.: J. Phys. Chem. 79, 1594 (1975).
11. Cotton F. A., Goodgame M. L., Goodgame M.: J. Amer. Chem. Soc. 83, 4690 (1961).
12. Wichterlová B., Beran S., Jírů P.: React. Kin. Catal. Lett. 5, 367 (1976).
13. Reinen D.: Structure and Bonding 7, 114 (1970).
14. Tarasevich Yu. I., Sivalov E. G., Golovonaya O. N.: Dokl. Akad. Nauk SSSR 233, 174 (1977).
15. Flanigen E. M., Khatami K.: Molecular Sieves Zeolites I, 201 (1971).
16. Dubnin M. M., Kisirikyan A. A., Mirzay D. I.: Izv. Akad. Nauk USSR Ser. Khim. 1974, 1699.
17. Yanagida R. Y., Amaro A. A., Seff K.: J. Phys. Chem. 77, 805 (1973).

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