

## Electron Spin Resonance Study of Various Cation-Exchanged Zeolites. Adsorption of Various Species

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Adsorption of water, ammonia, benzene, cumene, cyclohexane and pyridine on dehydrated cation-exchanged zeolites have been investigated by the ESR technique in the *Q*-band. It was shown that the cations in a zeolite framework are capable of migrating and interacting with the adsorbed molecules.

Zeolites of the faujasite type are widely used as effective catalysts (1). The bulk of experimental results obtained shows that the nature and amount of exchange cations in a zeolite have a great effect on the development of various reactions (2-6). This effect might be due to direct interaction of the sorbed species with the cations. The possibility of complex formation between cations and sorbed organic molecules in zeolite supercavities has been reported (7,8). However, in dehydrated zeolites which act as catalysts the ion exchange cations often occupy sites in hexagonal prisms and sodalite cages that are inaccessible to molecules absorbed in supercavities (9). The possibility of cation migrations in a zeolite has been discussed (10). It was found that not only do the copper ions migrate in a zeolite under the action of sorbed molecules, but they can also form complexes with the latter.

This investigation was a development upon earlier research on synthetic zeolites (11,12). The possible migrations of manganese ions upon sorption of various compounds and the nature of their interaction

with the sorbed species had to be established. The changes in manganese ion positions in the framework of a prehydrated zeolite were estimated from relevant changes in ESR spectra of  $Mn^{2+}$  ions in the *Q*-band.

A classification of the ESR spectra of manganese ions in various cation-exchanged Y zeolites was given earlier (11,12). The classification and parameters of the relevant spectra obtained are listed in Table 1. It also contains the parameters of spectrum 1' obtained recently (13).

Two groups of cation-exchanged synthetic Y zeolites were compared, just as in the previous investigations. The first group consisted of zeolites with cations more hydrophilic than  $Mn^{2+}$ , i.e., those with  $Y^{3+}$ ,  $La^{3+}$ ,  $Zn^{2+}$  and  $Mg^{2+}$  cations. The second group involved cations less hydrophilic than  $Mn^{2+}$ , i.e., Ca-, Cd- and Sr-exchanged zeolites. The ESR spectrum corresponding to  $Mn^{2+}$  in the hexagonal prism was obtained for the dehydrated zeolites of the first group. Three types of spectra were run for the dehydrated zeolites of the second group: spectrum 4 due to  $Mn^{2+}$  ions in

TABLE 1  
 CLASSIFICATION OF  $Mn^{2+}$  ESR SPECTRA IN ZEOLITES

Spectrum type	Symmetry	Localization	$\Delta g$ (Oe)	$\Delta H^{3-4}$ (Oe)	$\Delta H_i^1$ (Oe)	$\Delta H_i^6$ (Oe)	$D$ (Oe)
1	Octahedral	Supercavity	$+19 \pm 1$	$96 \pm 1$	$21 \pm 1$	$22 \pm 1$	—
1'	Octahedral	Sodalite cage	$+14 \pm 1$	$94 \pm 1$	$12 \pm 1$	$12 \pm 1$	100
2	Distorted octahedral	—	—	$87 \pm 5$	$16 \pm 1$	—	—
3	Octahedral	$S_{II'}$ or $S_{IV}$	$+13 \pm 0.5$	$89 \pm 1$	$14 \pm 1$	$14 \pm 1$	100
4	Octahedral	$S_I$	$+13 \pm 0.5$	$94 \pm 2$	$12 \pm 1$	$14 \pm 1$	155
5	Tetrahedral	$S_I$ or $S_{IV}$	$+11 \pm 1$	$73 \pm 2$	—	—	—

$\Delta g$ —deviation from the DPPH  $g$ -factor.

$\Delta H^{3-4}$ —splitting between 3rd and 4th hfs components.

$\Delta H_i^1, \Delta H_i^6$ —the widths of 1st and 6th hfs components.

the hexagonal prism (site  $S_I$ ) and spectra 3 and 5 associated with  $Mn^{2+}$  in the sodalite cage (sites  $S_{II'}$  and  $S_{IV}$ ).

Certain hydrocarbons (benzene, cumene, cyclohexane), as well as water, pyridine and ammonia were used as adsorbates.

## EXPERIMENTAL METHODS

*Cation-exchanged zeolites.* They were produced from a NaY zeolite by ion exchange at room temperature. The composition of the NaY elementary unit was  $Na_{56}Si_{135}Al_{57}O_{384} \cdot 260 H_2O$ . The technique of preparing various cation-exchanged zeolites was described earlier (14). The extent of sodium ion replacement is shown by the numeral after the zeolite index.

*Hydrocarbons.* Freshly distilled benzene, cumene, cyclohexane, and pyridine were dried over a calcined NaA zeolite. The gases dissolved in hydrocarbons were removed before the experiment by repeated freeze-pump-thaw cycles.

Ammonia was dried over calcined NaA and was admitted to the vacuum system at its boiling temperature.

Adsorption was conducted under pressure of saturated hydrocarbon vapour at 25°C for 10 min with subsequent heating at 100°C for 10 min in hydrocarbon vapor. This ensured complete saturation of the zeolite supercavities with hydrocarbons,

which was estimated as 30–35 hydrocarbon molecules/elementary unit.

Water adsorption on all zeolites was apportioned in accordance with the adsorption isotherms for the temperature range of  $-47^\circ C$  to  $+25^\circ C$ .

## RESULTS AND DISCUSSION

### Water Adsorption

The sorption of water induced changes in ESR spectra of  $Mn^{2+}$  for all zeolites. With increasing water amounts there appeared all types of spectra recorded earlier in the course of the dehydration of relevant zeolites (11,12). After the whole zeolite was occupied with water only the spectrum of hydrated  $Mn^{2+}$  was observed. It means that the changes in  $Mn^{2+}$  spectra in the zeolite framework during the adsorption-desorption process are reversible.

Table 2 shows spectrum shifts from one type to another for various cation-exchanged zeolites (the amount of sorbed water is given as the number of molecules per one supercavity or sodalite cage). Certain conclusions can be made. First of all it will be noted that in CaY and CdY zeolites the shift from spectrum 5 to spectrum 3 is accompanied by higher intensity of spectrum 3. The shift occurs upon adsorption of very small water amounts (no more than 1 water molecule/cavity seems to be

TABLE 2  
CHANGES IN THE  $Mn^{2+}$  ION SPECTRA DURING  
ADSORPTION OF WATER IN VARIOUS  
CATION-EXCHANGED ZEOLITES

Zeolite	Types of $Mn^{2+}$ spectra in dehydrated zeolites-	Amount of adsorbed water molecules per cavity	Types of spectra after water adsorption
CaY-62	4, 5, 3	0.8	4, 3
		4.0	3, 1'
		20.0	1
CdY-83	4, 5, 3	0.5	4, 3
		1.0	3, 1'
		5.0	1
MgY-33	4	10	3, 1'
		12	1
		— <sup>a</sup>	1
ZnY-35	4	24	3, 1'
		— <sup>a</sup>	1
		— <sup>a</sup>	1
ZnY-81	4	10	1'
		— <sup>a</sup>	1
		— <sup>a</sup>	1
LaY-42	4	24	3, 1'
		— <sup>a</sup>	1
		— <sup>a</sup>	1
LaY-72	4	12	3, 1'
		14	1
		— <sup>a</sup>	1
YY-70	4	14	1'
		— <sup>a</sup>	1
		— <sup>a</sup>	1

<sup>a</sup> Complete saturation of zeolite cavities with water.

needed for this purpose). Increase in sorbed water to 2–4 molecules/cavity results in the appearance of another spectrum 1'. The same set of spectra 3 and 1' is observed for the MgY, ZnY, LaY zeolites, but with larger amounts of sorbed water: 8–10 molecules/cavity.

Increase in water to 12–14 molecules/cavity in these zeolites results in the appearance of spectrum 1' alone. Thus the minimum water amount needed for appearance of spectrum 1' is 2–4 molecules/cavity. It is just the number of water molecules needed for saturation of cubic octahedral cavities with water (15,16). This suggests that spectrum 1' is due to  $Mn^{2+}$  ions localized in the water-filled sodalite cage (13). Spectrum 1' appears before that of completely hydrated  $Mn^{2+}$  ions. It will be seen from Table 2 that for zeolites of the first group ( $Y^{3+}$ -,  $La^{3+}$ -,  $Mg^{2+}$ - and  $Zn^{2+}$ -exchanged zeolites) the  $Mn^{2+}$  transition to the hydrated state occurs after complete saturation of zeolite cavities with

water. In the second group of zeolites (Ca- and Cd-exchanged forms) hydrated  $Mn^{2+}$  appears even if the amount of adsorbed water in zeolite supercavities is insufficient for complete saturation. In the Cd-exchanged zeolite hydrated  $Mn^{2+}$  will form from an amount of sorbed water obviously insufficient for formation of hydrated shells of all the ions present.

The hydrated  $Mn^{2+}$  ions are so large ( $r = 4.38 \text{ \AA}$ ) that they can be in a supercavity only. Consequently, appearance of the hydrated  $Mn^{2+}$  spectrum upon water adsorption is evidence that the  $Mn^{2+}$  ions migrate from the hexagonal prisms and sodalite cages to the supercavity. Preferential interaction of water molecules with more hydrophilic ions, under conditions of water deficiency, determined the sequence of formation of hydrated ions in various zeolites. Indeed, in the CaY and CdY zeolites the more hydrophilic  $Mn^{2+}$  ions will be the first to interact with sorbed water. In zeolites containing  $Y^{3+}$ ,  $La^{3+}$ ,  $Mg^{2+}$  and  $Zn^{2+}$  ions, hydrated  $Mn^{2+}$  will form only after complete formation of hydrated shells of the ions more hydrophilic than  $Mn^{2+}$ . These results are in agreement with our concepts about water distribution in zeolites in the course of dehydration (11).

#### Ammonia Adsorption

Adsorption of ammonia on all zeolites investigated was conducted under a pressure of 50 Torr with subsequent heating in ammonia at 200°C. It was inferred from the results in Ref. (18) that under the experimental conditions used one unit cell contained 25–30 ammonia molecules. Under these conditions all spectra characteristic of dehydrated specimens disappeared almost for all zeolites, and there appeared a new spectrum with parameters:  $\Delta g = 16 \text{ Oe}$ ,  $\Delta H^{3-4} = 88 \pm 1 \text{ Oe}$ ,  $\Delta H_i^1 \approx 11 \text{ Oe}$ . The parameters of this spectrum differed from those of spectrum 3 only in the  $g$ -values. This spectrum was associated with a complex formed by the  $Mn^{2+}$  ion and ammonia molecules. For

zeolites with high sodium ion exchange (YY-70, LaY-93, ZnY-81) this spectrum appeared after more prolonged heating. Heating of CdY-83 and YY-98 even for 11 hr at 200°C did not result in complete disappearance of spectra of the initial dehydrated zeolites.

In all cation-exchanged zeolites the ammonia complex decays by heating in vacuum. As had to be expected its breakdown in a CaY zeolite is accompanied by appearance of spectrum 3 even at 50°C, while an increase in the thermal treatment temperature results in appearance of spectra 5 and 4. In other words, all spectra observed for the dehydrated CaY zeolite before interaction with ammonia reappear after the ammonia complex breakdown. Quite unexpected was the appearance of spectrum 3 after breakdown of the ammonia complex in the first group of zeolites (LaY, YY, ZnY, MgY) that displayed only spectrum 4 (site  $S_1$ ) before ammonia adsorption. Since spectrum 3 is due to  $Mn^{2+}$  coordinated to OH groups and to oxygen atoms of the zeolite network (12), its appearance could have been ascribed to traces of water in ammonia. However, the technique of ammonia drying seemed to rule out this possibility. It remained to suggest that ammonia adsorption at an elevated temperature (200°C) generated surface hydroxyl groups that interacted with  $Mn^{2+}$  after the ammonia complex breakdown. Formation of an amide group and simultaneous liberation of water during interaction of ammonia with the surface of an HY zeolite has been reported (17). Our results seem to show that such a surface reaction can occur on cation-exchanged zeolites as well. Vacuum treatment at elevated temperatures up to 450°C resulted in gradual disappearance of spectrum 3 and appearance of spectrum 4. Thus, the sequence of spectrum shifts was the same as for dehydration.

Comparison of the results obtained with those reported elsewhere can show

whether the ammonia- $Mn^{2+}$  complex forms in the supercavity or in the cubic octahedron. The interaction of ammonia with zeolites at 200°C has been found (18,19) to result in ammonia adsorption accompanied by entrance of ammonia molecules to the cubic octahedron cavities. In copper-containing Y zeolites sorbed ammonia has been found to localize in the sodalite cage (site  $S_{IV}$ ) (10,20). Thus, the entrance of ammonia to the sodalite cage can be considered as an established fact. In this case interaction of ammonia with  $Mn^{2+}$  ions localized at the sodalite cage would lead to appearance of an ESR spectrum with parameters only slightly different from those of spectrum 3, since the nearest coordination sphere of the  $Mn^{2+}$  ion consists of nitrogen, and not of oxygen atoms. Just such a spectrum was observed experimentally.

Incomplete transfer of the  $Mn^{2+}$  ions to ammonia complexes in certain zeolites with high exchange (CdY-83 and YY-98) is possibly due to occupation of  $S_{IV}$  or  $S_{II}$  by other ions that prevent penetration of ammonia into the sodalite cage.

#### *Interaction with Pyridine*

Adsorption of pyridine on LaY-72, ZnY-81, MgY-60, and NaY, that exhibit only spectrum 4 associated with  $Mn^{2+}$  localization in site  $S_1$  causes no changes in the spectrum parameters. This seems to show that the  $Mn^{2+}$  ions localized in the hexagonal prism do not interact directly with pyridine molecules.

The CaY-62 zeolite dehydrated at 450°C exhibits, along with spectrum 4, spectra 5 and 3 (the latter considerably less intensive than 5). Adsorption of pyridine at room temperature results in disappearance of spectrum 5, and after the zeolite is heated in pyridine at 100°C spectrum 3 also disappears. Spectrum 4 remains unchanged, just as for LaY, ZnY, and MgY, and its parameters are consistent with those in Table 1 (Fig. 1).

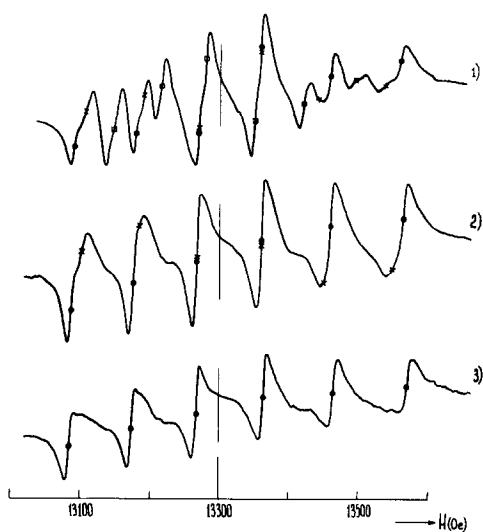


FIG. 1. The ESR spectra of  $Mn^{2+}$  ion in zeolite CaY-62 after adsorption of pyridine: (1) zeolite after dehydration at  $450^{\circ}C$ , (●) spectrum 4, (×) spectrum 3 and (□) spectrum 5; (2) after adsorption of pyridine at room temperature, (●) spectrum 4 and (×) spectrum 3; (3) after heating in pyridine vapor at  $100^{\circ}C$ , only spectrum 4.

The disappearance of spectra 3 and 5 upon pyridine adsorption shows that the  $Mn^{2+}$  ions in the sodalite cage can interact with pyridine. Complete disappearance of ESR signals might be due either to complexing of  $Mn^{2+}$  with pyridine, accompanied by charge transfer, or to a change in the spin-lattice relaxation time of  $Mn^{2+}$  in this complex. Both can induce considerable broadening of  $Mn^{2+}$  lines, and thus hinder the recording of the spectrum. Since the pyridine molecules are too large to penetrate into the sodalite cage, it remains to suggest that either the  $Mn^{2+}$  ions exhibiting spectra 3 and 5 are located in the sodalite cage close to the six-member oxygen window, where a contact between these ions and the pyridine molecules in the supercavity is possible, or these ions migrate from the sodalite cage to the supercavity to form a complex with pyridine molecules.

The CdY-81 zeolite dehydrated at  $450^{\circ}C$  also exhibits spectra 4, 5 and 3, but the changes in these spectra are different

from those for a CaY-62 zeolite. Adsorption of pyridine at room temperature induces no changes. Only after the specimen is heated in pyridine at  $175^{\circ}C$  spectrum 5 disappears. The intensity of spectrum 3 not only does not decrease, but even increases with gradual disappearance of spectrum 5. Consequently, the overall intensity of the  $Mn^{2+}$  spectra remains the same. Prolonged heating in pyridine does not result in disappearance of spectrum 3. Spectrum 4 does not change with pyridine adsorption, just as for the cation-exchanged zeolites discussed above. The only change induced by pyridine adsorption in these zeolites is that in the relative intensity of spectra 3 and 5. It might be due to migrations of  $Mn^{2+}$  ions in the sodalite cage such that the  $Mn^{2+}$  ions would occupy only the sites exhibiting spectrum 3. It follows from the above that pyridine interacts only with ions displaying ready migration from the sodalite cage to the supercavity through the six-member oxygen window, or with those that can come into direct contact with pyridine. This is the situation for zeolites in which sodium ions are replaced by calcium ions no more than by 70%. The same is observed for zeolite SrY-70. Replacement of a larger amount of sodium ions would result in occupation of sites  $S_{II}$ , and this would hinder the migration of  $Mn^{2+}$  ions to the supercavity. Such seems to be the distribution of ions in the CdY-81 zeolite. It prevents both direct contact of  $Mn^{2+}$  ions with pyridine molecules, and the interaction of  $Mn^{2+}$  with ammonia (see above).

The spectra become completely restored after pyridine is pumped off in the course of heating in vacuum.

#### *Adsorption of Benzene, Cumene, and Cyclohexane*

Adsorption of hydrocarbons induces no changes in spectrum 4. When hydrocarbons are sorbed on a CaY-62 zeolite, spectrum 5 disappears and spectrum 3 be-

comes more intensive. Its parameters coincide with those in Table 1, except in the widths of hfs components that decrease for benzene adsorption and increase for cyclohexane. These changes are observed after adsorption of hydrocarbons at room temperature. A rise of temperature results in no additional changes. Just as with pyridine adsorption, the change in relative intensity of spectra 3 and 5 in the CaY zeolite seems to be due to a change in the relative occupancy of the  $Mn^{2+}$  localization sites under the action of hydrocarbon molecules sorbed in the supercavity. Indeed, the change in the  $Mn^{2+}$  line is evidence that the hydrocarbon molecules sorbed in the cavities of a Y zeolite have an effect on the electron state of  $Mn^{2+}$ , changing the time of  $Mn^{2+}$  spin-lattice relaxation ( $T_1$ ) which is responsible for the width of a paramagnetic ion spectrum in solids.

### CONCLUSION

The cations in a zeolite framework are not stabilized, but depend on certain conditions, such as the possibility of interacting with molecules, and are capable of migration and localization at various sites of the framework. The effect of  $Mn^{2+}$  ions on complex forming molecules (water, ammonia, pyridine, benzene) seems to be accounted for both by their different sizes and by characteristics such as the donor-acceptor properties, and in certain cases by the possibility of certain adsorbate reactions.

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