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ESR Study of Various Synthetic Cation-Exchanged Zeolites

Dehydration Under Vacuum

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Dehydration of cation-exchanged zeolites of the Y type have been investigated by the ESR technique. The exchange of sodium ions with Y^{3+}, La^{3+}, Zn^{2+}, Mg^{2+}, Cd^{2+}, and Ca^{2+} ions ranged from 4 to 70%.

The spectra were recorded in the Q band. A model of the behaviour of Mn^{2+} ions during dehydration of various cation-exchanged zeolites was proposed.

INTRODUCTION

This paper deals with the second stage of ESR studies on various cation-exchanged zeolites. The first was concerned with hydrated forms of these zeolites (*1*), the second with ESR spectra of Mn^{2+} ions obtained in the course of dehydration under vacuum.

As zeolites contain no paramagnetic ions, the latter had to be incorporated. Cr^{3+} (*2*), Cu^{2+} (*3–5*) and Mn^{2+} (*6–9*) were used as the paramagnetic ions. The ESR spectra of Mn^{2+} in solids, including powders, are very complex and difficult to interpret. Their complexity is due to several reasons: superposition of spectra with different parameters exhibited by Mn^{2+} ions occupying nonequivalent sites, distortion caused by zero magnetic field splitting of energy levels, appearance of additional lines due to transitions with $\Delta m \neq 0$ (the so-called forbidden transitions), etc. (*10*, *11*). Such spectra can be interpreted by comparison with those calculated theoretically, taking into account the line shapes (*12*). Incomplete analysis of all factors responsible for the spectrum shape can lead to wrong interpretation of such spectra. As shown in (*7*, *12*), analysis of experimental Mn^{2+} spectra is easier when higher frequencies are used.

EXPERIMENTAL

Various cation-exchanged zeolites were prepared from a Na-exchanged zeolite type Y at room temperature. The unit cell of the starting zeolite contained $Na_{56}Si_{135}Al_{57}O_{384}260H_2O$. The exchange of Na with cations such as Y^{3+}, La^{3+}, Zn^{2+}, Mg^{2+}, Ca^{2+}, Cd^{2+} varied within 4–70%. Specimens with a high extent of Na exchange were obtained by repeated cation exchange after heating to 550°C (*13*). The paramagnetic Mn^{2+} ions were also incorporated by cation exchange. The content of Mn^{2+} was approximately one ion per 12.5 unit cells, or per ~100 supercavities. [For composition of the zeolites studied see Table 1 of the preceding paper (*1*).]

The dehydration of zeolites was conducted by gradual calcination under vacuum. The temperature was raised by 50°C intervals from room up to 450°C. A specimen was kept at each temperature for 1–2 hr under a vacuum of 10^{-3} to 10^{-4} Torr. The Mn^{2+} ESR spectra in the Q-band were obtained at room temperature using a spectrometer described in (*1, 5, 7, 9*).

Results and Discussion

The gradually varied amount of exchanged cations permits distinguishing ESR spectra with different parameters, thus making easier the analysis of the often superimposed experimental spectra.

Five types of spectra with different hyperfine constants (A) and individual component line widths (ΔH_i) were observed in the course of dehydration. The parameters of the identified spectra are shown in Table 1. Table 2 lists the types of spectra obtained for each zeolite. Parameter D was determined by comparison of experimental and theoretical spectra (*12*). The Mn^{2+} spectra of hydrated cation-exchanged zeolites (Type 1) have been discussed in (*1*).

Type 2 Spectrum

The Mn^{2+} spectrum in an octahedral field with axial distortion (doublet splitting of the HFS component). The Type 2 spectrum is observed only for zeolites with low Na exchange (5–18%), i.e., for those in which the immediate environment of Mn^{2+} in the supercavity consists almost completely of Na ions (Fig. 1-1). Consequently, the parameters of this spectrum will coincide with those of a similar spectrum observed for a zeolite of type NaY (*14*). The causes of doublet splitting of HFS components have been discussed in (*12, 14*). The splitting was found to be accounted for by axial distortion of the octahedral electric field of the ion and by the effect of the zero field level splitting (in the spin hamiltonian $D \neq 0$). As consistent with theory, the shape of this spectrum is a function of the microwave frequency used. For instance, when from Q-band spectra one goes to the K-band, the spectrum amplitude decreases and the HFS components become broader, the doublet splitting being retained. In the X-band region the broadening is still greater and the amplitude keeps decreasing, thus making the spectrum inobservable. The exhibiting of such a spectrum by zeolites dehydrated at relatively low temperatures (100–200°C) and its appearance upon repeated adsorption of water provide evidence that the spectrum is due to Mn^{2+} ions surrounded by an axially distorted hydration shell. Naturally, such ions could occupy only the supercage of the zeolite network.

TABLE 1
Spectrum Types and Their Parameters in the Q-Band

Spectrum type	Parameters of spectra				Notes
	A,Oe	$\Delta H_{(1)}$Oe	$\Delta H_{(6)}$Oe	D,Oe	
1. Spectrum of hydrated Mn ion	96	20	22	—	Average parameters for all cation forms
2. Mn ion spectrum in an octahedral field with axial distortion (doublet splitting of HFS component)	87	50	55	~240	The average parameters are determined for the cationic forms for which each spectrum type is recorded as single
3. Mn ion spectrum in an octahedral field with axial distortion	89	12	12	≤100	
4. Mn ion spectrum in an octahedral field	95	13	13	≤100	
5. Mn ion spectrum in a tetrahedral field	73	—	—	—	

TABLE 2

Types of Spectra

Cationic forms	Temperature °C 100	150	200	250	300	350	400	450
Yttrium								
YY-4	2, 3	2, 3	2, 3, 4	3, 4	4	4	4	4
YY-11	2, 3	2, 3, 4	3, 4	3, 4	4	4	4	4
YY-70	—	4	4	4	4	4	4	4
YY-98	4	4	4	4	4	4	4	4
Lanthanum								
LaY-4	2	2	2, 3	2, 3, 4	3, 4	4	4	4
LaY-11	2, 3	2, 3	2, 3	3, 4	4	4	4	4
LaY-42	3, 4	3, 4	3, 4	4	4	4	4	4
LaY-72	—	4	4	4	4	4	4	4
LaY-93	4	4	4	4	4	4	4	4
Zinc								
ZnY-15	2, 3, 4	2, 3, 4	3, 4	4	4	4	4	4
ZnY-35	3, 4	3, 4	4	4	4	4	4	4
ZnY-81	4	4	4	4	4	4	4	4
Magnesium								
MgY-14	2, 3	3	3, 4	3, 4	4	4	4	4
MgY-33	3, 4	3, 4	4	4	4	4	4	4
MgY-60	4	4	4	4	4	4	4	4
Cadmium								
CdY-18	2, 3	2, 3	3, 4	3, 4	4	4	4	4
CdY-44	3, 4	3, 4	3, 4	3, 4	4	4	4	4
CdY-83	3	3	3, 4	3, 4	3, 4	3, 4, 5	3, 4, 5	3, 4, 5
Calcium								
CaY-14	2, 3	2, 3	2, 3, 4	3, 4	4	4	4	4
CaY-35	3	3	3, 4	3, 4	4	4	4	4
CaY-65	3	3	3	3, 4	3, 4, 5	3, 4, 5	3, 4, 5	4, 5

Type 3 Spectrum

Type 3 spectrum with $A = 89$ Oe. The formation conditions of this spectrum depend on the nature and concentration of the cations incorporated in the zeolites. The spectrum is observed for all cation-exchanged zeolites dehydrated at 100–300°C, when the extent of exchange does not exceed 40%, i.e., when the Mn^{2+} ions in the unit cell are surrounded mostly by sodium ions. (This applies to cation-exchanged zeolites with cations more hydrophilic than manganese.) This spectrum arises during heating, after that with doublet splitting (Type 2). Its intensity varies with increasing dehydration temperature and passes through a maximum at about 200°C, to drop with further temperature rise, and at 300°C the spectrum disappears.

For samples with a high content of Ca^{2+} and Cd^{2+} ions (these ions are less hydrophilic than Mn^{2+}) Spectrum 3 persists at higher heating temperatures as well. For example, with the CaY-65 zeolite it is observed up to 400°C (Table 2).

When the exchange of Na with ions more hydrophilic than Mn^{2+}, such as Y^{3+}, La^{3+}, Zn^{2+}, Mg^{2+} exceeds 40%, Spectrum 3 is not observed even at the lowest calcination temperatures.

Thus, Spectrum 3 obviously appears when the water deficiency in the zeolite framework is higher than that under conditions of Spectrum 2 appearance. It is

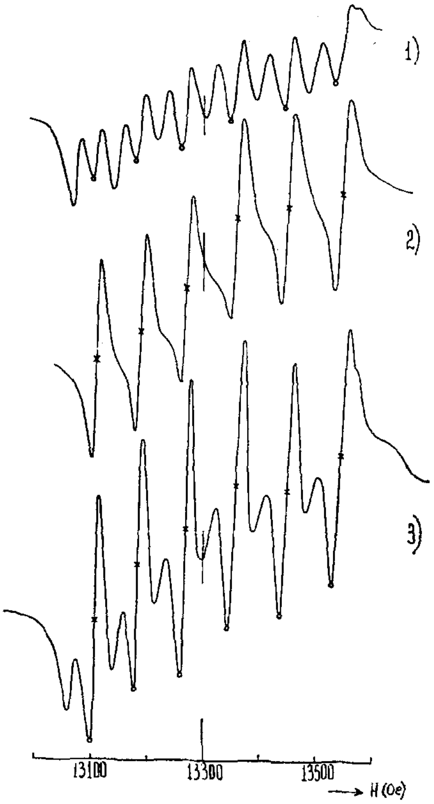


FIG. 1. ESR spectra of Mn^{2+} ions obtained in the course of thermal dehydration of zeolites: (1) Type 2 spectrum (see Table 1), zeolite LaY-4, 150°C, (2) Type 3 spectrum (see Table 1), zeolite CaY-65, 200°C, (3) superposition of spectra Types 2 and 3, zeolite LaY-4, 200°C. The signs "○" and "×" denote the conditional position of HFS components of spectra Type 2 and 3, respectively. The vertical line refers to the DPPH position.

observed only for zeolites in which the Mn^{2+} hydration shell is not completely destroyed, and is absent when the shell is destroyed. The destruction of this shell in zeolites containing ions less hydrophilic than Mn^{2+} can be achieved only at high calcination temperatures, and with zeolites containing more hydrophilic ions—even at very low temperatures.

As seen from Table 2, Spectrum 3 is often observed together with Spectrum 2. An experimental spectrum in the Q-band representing superposition of the spectrum with $A = 89$ Oe on the doublet splitting spectrum of a LaY-4 zeolite calcined at 200°C is shown as an example in Fig. 1-3. When this spectrum is observed without superposition, as for the CaY-65 zeolite, it can be recorded in the X band.

Type 4 Spectrum

The Mn^{2+} spectrum in an octahedral field with $A = 95$ Oe. The Type 4 spectrum is recorded in all zeolites dehydrated at 200°C and higher temperatures. In zeolites with low and moderate Na exchange this spectrum is observed along with those abovementioned, in the same way as for the NaY zeolite. The intensity of the spectrum with $A = 95$ Oe is maximum for

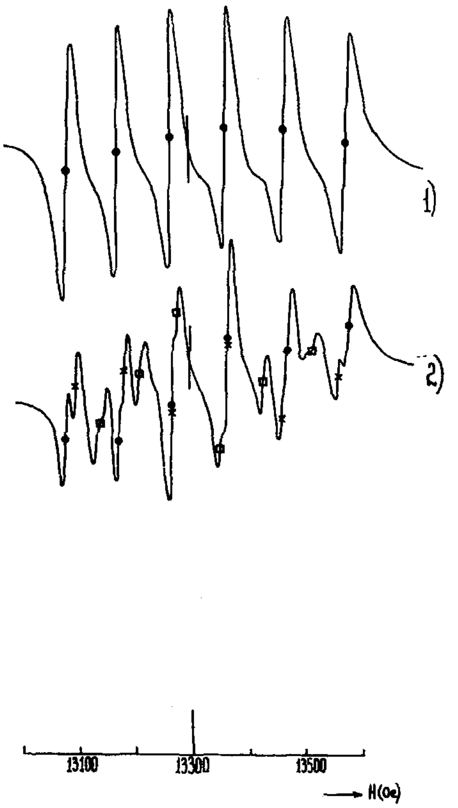


FIG. 2. ESR spectra of Mn ions obtained in the course of thermal dehydration of zeolites: (1) Type 4 spectrum (see Table 1), zeolite LaY-4, 400°C, (2) superposition of spectra Types 3-5 (see Table 1), zeolite CdY-83, 350°C. The signs "×", "●" and "□" denote the conditional position of HFS components of Spectra 3-5, respectively. The vertical line refers to the DPPH position.

samples dehydrated at 300–450°C and the spectrum looks like a single one (Fig. 2-1). Due to the relatively low value of D and the small width of the HFS components the X-band spectrum may also be observed.

When the content of ions with a hydration energy higher than that of Mn^{2+} (Y^{3+}, La^{3+}, Zn^{2+}, Mg^{2+}) is great, the spectrum with $A = 95$ Oe is observed even for specimens dehydrated at room temperature (*1*).

The HFS constant value (95 Oe) characteristic of the octahedral Mn^{2+} environment (*10*) and the smaller width of the HFS components compared to that in the Mn spectrum in a hydrated zeolite permit suggesting that Spectrum 4 is due to Mn^{2+} occupying the hexagonal prism of the zeolite network, i.e., site S_1, where the octahedral coordination of Mn^{2+} is but slightly distorted.

Type 5 Spectrum

The Mn^{2+} spectrum with $A = 73$ Oe in a tetrahedral field. The type 5 spectrum is exhibited by dehydrated zeolites with a high content of Ca^{2+}, Cd^{2+} above calcination temperatures of 300°C and higher. It is observed after the appearance of Spectrum 4 ($A = 95$ Oe), as the intensity of Spectrum 3 ($A = 89$ Oe) becomes weaker. The spectrum intensity is greatest for the cation-exchanged zeolites calcined at 350°C (Fig. 2-2), and decreases at higher dehydration temperatures.

The spectrum with $A = 73$ Oe has been observed earlier for a dehydrated zeolite of type NaA (*9*).

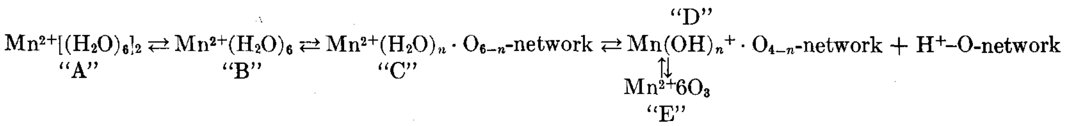
The transition from octahedral to tetrahedral coordination is known to be accompanied by a ~20% decrease in A (*15, 16*). It has been suggested (*9*) that the Mn^{2+} spectrum with a lower A value is due to tetrahedrally coordinated Mn^{2+}, and this may be the case when the Mn^{2+} ion is coordinated to three oxygen atoms of the zeolite network and to an oxygen atom of a water molecule or of its fragment. In X and Y zeolites dehydrated at 400°C at least one water molecule is retained in the sodalite cage (*17, 18*). Consequently, it is quite possible that the same spectrum in a Y zeolite may be due to tetrahedrally coordinated Mn^{2+} in the sodalite cage. The low A value suggests an essentially covalent nature of the Mn–O bond in this coordination.

CONCLUSION

It has been suggested (*1*) that the whole amount of water in cavities of an Y zeolite forms hydration shells of no more than two molecular layers around the incorporated cations. This is confirmed by the evidence (*19, 20*) that the 1640 cm^{-1} band in ir spectra, corresponding to the water physically adsorbed by the zeolite, depends upon the cation nature. When the zeolite contains ions of different hydration energies, water will be redistributed, owing to its deficiency, among the ions and will be associated mainly with the most hydrophilic ions. The most energetically advantageous sites for nonhydrated ions will then be those with the highest coordination number. Consequently, in highly Y^{3+}-, La^{3+}-, Mg^{2+}- or Zn^{2+}-exchanged zeolites the Mn^{2+} ions will then be dehydrated and shifted to the S_1 sites (to the hexagonal prisms) at the earliest dehydration stages before the hydration shells of other ions are destructed and these ions migrate to the S_1 sites (*1*). The ESR spectrum characteristic of Mn^{2+} ions in an octahedral field with weak axial distortion remains unchanged in the course of dehydration up to 450°C.

The water molecules in the cavities of Cd- and Ca-exchanged zeolites coordinate predominantly to the Mn^{2+} ions, since the hydration energy of Mn^{2+} is higher than those of Cd^{2+} and Ca^{2+} ions. Consequently, the variation in Mn^{2+} localization in the course of dehydration can best be followed just in these forms of the Y zeolite.

The following scheme of variations in Mn^{2+} coordination in the course of gradual dehydration of Ca- and Cd-exchanged zeolites can be proposed on the basis of ir spectra of zeolites and of the radiospectroscopic investigations carried out by the authors:



$$\underset{\text{“A”}}{Mn^{2+}[(H_2O)_6]_2} \rightleftarrows \underset{\text{“B”}}{Mn^{2+}(H_2O)_6} \rightleftarrows \underset{\text{“C”}}{Mn^{2+}(H_2O)_n \cdot O_{6-n}}\text{-network} \rightleftarrows \overset{\text{“D”}}{\underset{\substack{\uparrow\downarrow \\ Mn^{2+}6O_3 \\ \text{“E”}}}{Mn(OH)_n^+}} \cdot O_{4-n}\text{-network} + H^+\text{-O-network}$$

Form “A” corresponds to the completely hydrated Mn^{2+} ion with a hydration shell of no less than two coordinated molecular layers of water. The relevant ESR spectrum has been discussed elsewhere (*1*). In the course of dehydration, water is gradually removed. Form “B” sets in when only one molecular layer of water remains around the Mn^{2+} ion. The interaction of water molecules with the zeolite surface through hydrogen bonds gives rise to a strongly distorted axial electric field. The spectrum with doublet splitting (Type 2) corresponds to this state.

Further dehydration results in a decreasing amount of water molecules contacting Mn^{2+} in the first coordination sphere. As the Mn^{2+} ion tends to a high coordination number, it migrates to the sodalite cage, where high coordination can be realized both by the remaining water molecules and by the oxygen atoms of the network. This is the “C” form and it corresponds to Spectrum 3 (A = 89 Oe). The appearance of this spectrum for zeolites dehydrated at temperatures below 250°C is consistent with the interpretation of ir spectra (*20*) implying that small amounts of physically bonded water are retained in cation-exchanged zeolites within this temperature range. According to the same results (*20*) traces of physically adsorbed water are observed for zeolites with sodium to calcium exchange even at 400°C. It will be seen from Table 2 that with a CaY-65 zeolite Spectrum 3 also persists up to 400°C.

The next step of the hydration shell destruction is the dissociation of water molecules under the action of the electric field of the ion and formation of hydroxyl groups of two types: showing ~3550 cm^{-1} and ~3640 cm^{-1} absorption bands, respectively (*19*, *21*). Such a process has been found to take place in the case of bivalent ions Mg^{2+}, Ca^{2+}, and Sr^{2+} (*20*). For these ions water dissociation begins at 230°C, i.e., within the temperature range corresponding to the decrease in Spectrum 3 intensity for the zeolites studied here. Thus, the ESR results seem to show that dissociation of the water molecule bonded with Mn^{2+} takes place at certain dehydration temperatures.

Dehydroxylation at the OH groups associated to the cation begins at 350°C and terminates at 600–700°C (*22*). This confirms the suggestion that Spectrum 5 (A = 73 Oe) is due to Mn^{2+} occupying the sodalite cage and associated with the hydroxyl group. As expected from the ir data, the intensity of the ESR spectrum is maximum for samples calcined at 350°C. Calcination at higher temperatures results in a lower intensity of this spectrum. The ESR spectrum shows that the Mn^{2+} symmetry in such a coordination is tetrahedral.

Dehydroxylated Mn^{2+} migrates to a hexagonal prism, since it is the most energetically advantageous site (“E” in the above scheme). The penetration of Mn^{2+} into hexagonal prisms will depend on the degree of occupancy of the latter. As long as the prisms are not completely occupied by other ions, equilibrium of the “D” ⇄ “E” process is shifted to the right, and Spectrum 5 corresponding to the form “D” is virtually unobservable. The experimental conditions used in this research preclude the detection of fast processes, and consequently ESR study can give only the “C” → “E” transition (form “E” corresponds to Spectrum 4). This is possible for zeolites with the number of Ca^{2+} (or Cd^{2+}) ions in the unit cell less than that of the S_1 sites, i.e., for CaY-14, CaY-35, CdY-18 and CdY-44. The form “D” corresponding to Spectrum 5 can occur only after all the hexagonal prisms are occupied by other ions (i.e., by Ca^{2+} or Cd^{2+}). Indeed, Spectrum 5 is observed, along with Spectrum 4, for the zeolite CaY-65 in which almost all sites of the hexagonal prisms are occupied by Ca^{2+} ions in the course of dehydration (*23*). The coincidence of ESR spectra for Ca- and Cd-exchanged zeolites seems to show that Cd^{2+} ions in CdY-83 occupy mostly the same S_1 sites as the Ca^{2+} ions in CaY-65.

The results discussed in this paper show that when the concentration of impurity ions (the paramagnetic Mn^{2+} ion in our case) is so low that the probability of penetration of two such ions into one unit cell may be neglected, appropriate choice of the thermal treatment of the zeolite would ensure localization of impurity ions at identical sites of the unit cells in which they are contained. Consequently, variations in the localization of paramagnetic impurity ions with different thermal treatment can be followed by the ESR technique. Analysis of the results obtained shows that the position of exchanged cations in the framework of zeolite Y is a function of the amount of water associated with the cation.

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