An EPR Study on VO^{2+} and Mn^{2+} Ions in Some Zeolites

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The electron paramagnetic resonance (EPR) of hydrated $VOSO_4 \cdot 3H_2O$ and $MnCl_2 \cdot 2H_2O$, adsorbed on the synthetic zeolites 3A, 4A, 5A and 13X of pore diameters 0.3, 0.4, 0.5, and 1.0 nm, respectively, and the natural zeolites heulandite and clinoptilolite was investigated. The spectra indicated that the coordination structures are $VO(H_2O)_5^{2+}$ and $Mn(H_2O)_6^{2+}$, and that their EPR line widths vary with the pore diameters and the surface areas of the zeolites. The spectra of $VO(H_2O)_5^{2+}$ in natural zeolites at room temperature display an isotropic behavior and therefore indicate that the water ligands are mobile. The EPR spin Hamiltonian parameters, the molecule orbital constant β_2^{*2}, and the Fermi contact term K_{eff} were determined and are discussed. The spectra of $Mn(H_2O)_6^{2+}$ for narrow-pore zeolites indicate the existence of mobile and immobile water, whereas for wide-pore and natural zeolites they indicated the existence of only mobile water. The obtained $Mn(H_2O)_6^{2+}$ spectra are discussed.

Key words: EPR, VO^{2+}, Mn^{2+}, Zeolites, Coordination.

Introduction

It is known that the states of water molecules in porous systems can be studied by using the complexes of transition metal ions with water. Such studies give information about the coordination and the structure of the surface-adsorbed complexes and about the dynamics of the adsorbed liquids [1–4].

In our previous study we reported EPR results on $Cu(H_2O)_6^{2+}$ adsorbed on the synthetic zeolites 3A, 4A, 5A, 13X and the natural zeolites heulandite and clinoptilolite [1]. The results indicated the existence of immobile water layers in narrow-pore zeolites even at room temperature. However, the water in type 13X, heulandite and clinoptilolite behaved as being mobile.

In this study we have investigated the hydrated VO^{2+} and Mn^{2+} ion adsorbed on some zeolites to obtain information about their coordination structures, mobilities, interaction of the unpaired electron with the vanadium nucleus and the ligand field state of the Mn^{2+} ion.

Experimental

The synthetic zeolites of type 3A, 4A, 5A and 13X were purchased from the British Drug House (BDH), and the natural zeolites heulandite and clinoptilolite were obtained from the Institute of Geology, the Hacettepe University, Ankara. The unit cell constants of these zeolites were given in [1]. The samples for the EPR measurements were prepared in the following way. The zeolites were activated at 473 K for 4 h, and $4 \cdot 10^{-3}$ M $VOSO_4 \cdot 3H_2O$, and $0.8 \cdot 10^{-3}$ M $MnCl_2 \cdot 2H_2O$ aqueous solutions were prepared in distilled water. The solutions were adsorbed on the zeolites. In each adsorption, 1 g of zeolite was put into 20 cm³ of appropriate solution, stirred, and stored at room temperature for 24 h. Then, the solutions were filtered, and the zeolites were dried at room temperature.

The EPR spectra were recorded with a Varian E-109 C model X-band EPR spectrometer with 100 kHz modulation. The spectrometer is equipped with a Varian temperature control unit to perform the experiments at the desired temperatures. The g values were determined by comparison with a DPPH sample of $g = 2.0036$.

EPR Parameters of VO^{2+}

The EPR spectrum of VO^{2+} in rigid media consists of 16 hyperfine lines, 8 from the $A_{\parallel}$ and 8 from the $A_{\perp}$ components of the hyperfine tensor, since the VO^{2+} is a $3d^1$ ion and $I = 7/2$ for vanadium nucleus. The com-

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ponents of the hyperfine tensor are given by [5, 6]

$$A_{\parallel} = P\left(-\frac{4}{7}\beta_2^{*2} - K_{\text{eff}} + \Delta g_{\parallel} + \frac{3}{7}\Delta g_{\perp}\right), \quad (1)$$

$$A_{\perp} = P\left(\frac{2}{7}\beta_2^{*2} - K_{\text{eff}} + \frac{11}{14}\Delta g_{\perp}\right), \quad (2)$$

where $\Delta g_{\parallel} = g_{\parallel} - g_e$, $\Delta g_{\perp} = g_{\perp} - g_e$, K_{eff} represents the Fermi contact term, P is the electron-nucleus dipolar interaction term, and β_2^{*2} is the molecular orbital coefficient of the $3d_{xy}$ atomic orbital of the vanadium in a ligand field having C_{4v} symmetry [6].

β_2^{*2} and K_{eff} can be determined from (1) and (2) and are given as

$$\beta_2^{*2} = \frac{7}{6}\Delta g_{\parallel} - \frac{5}{12}\Delta g_{\perp} - \frac{7}{6}\frac{A_{\parallel} - A_{\perp}}{P}, \quad (3)$$

$$K_{\text{eff}} = \frac{1}{3}(\Delta g_{\parallel} + 2\Delta g_{\perp}) - \frac{A_{\parallel} + 2A_{\perp}}{3P}. \quad (4)$$

The isotropic value of the A and g tensors are $A_0 = (A_{\parallel} + 2A_{\perp})/3$ and $g_0 = (g_{\parallel} + 2g_{\perp})/3$. Using (4), the isotropic value of A can be written as

$$A_0 = -P K_{\text{eff}} - (g_e - g_0)P. \quad (5)$$

These equations are used in the following section to obtain the parameters and to interpret the experimental results.

Results and Discussion

The EPR spectra of the hydrated $VOSO_4 \cdot 3H_2O$ adsorbed on synthetic 3A, 4A, 5A and 13X zeolites are given in Figure 1. The spectra exhibit an axially symmetrical behavior. The EPR parameters are given in Table 1. For the hyperfine values in Table 1 the second order effects have been considered. The components of g and A are very close to those of the $VO(H_2O)_5^{2+}$ complex [7], and therefore, we attribute

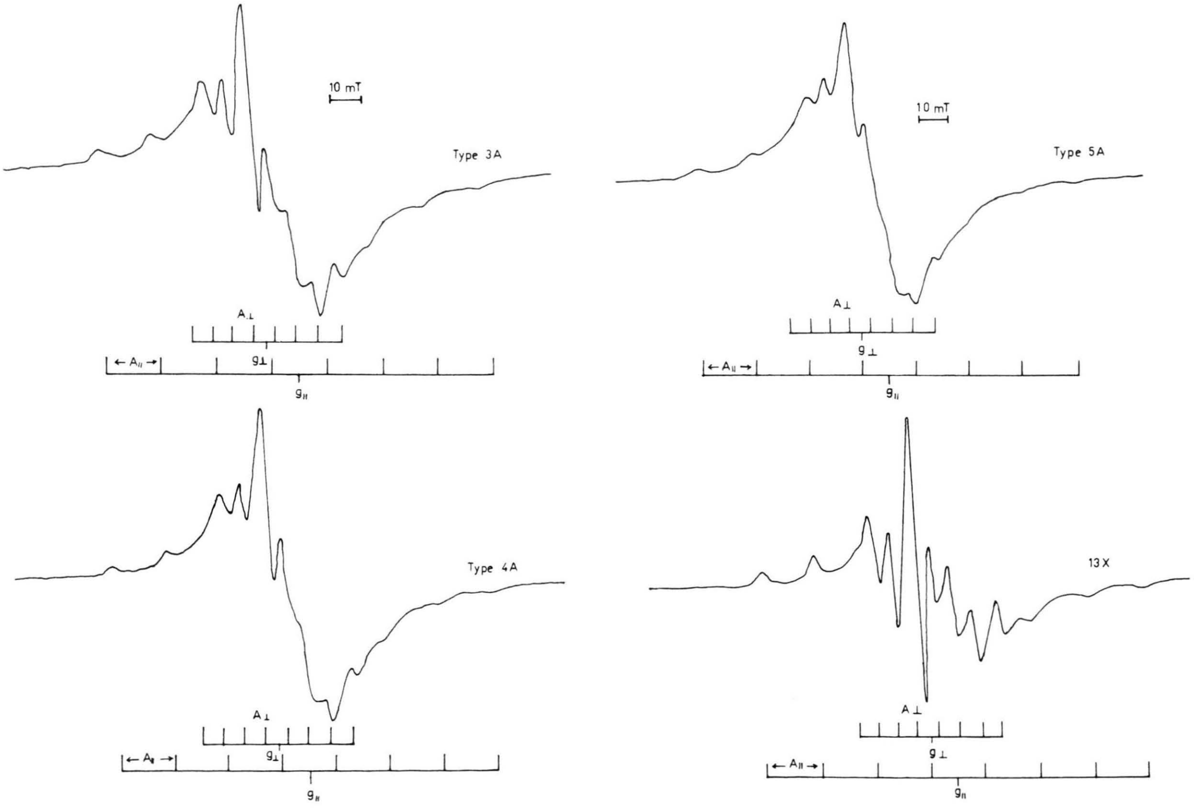

Fig. 1. The EPR spectra of the $VO(H_2O)_5^{2+}$ ions adsorbed on the synthetic types 3A, 4A, 5A, and 13X.

Table 1. The pore diameters and surface areas of the zeolites, and the EPR parameters characterizing the $VO(H_2O)_5^{2+}$ ion adsorbed on the zeolites. The A values are in mT.

Zeolit	Pore diameter (nm)	Surface Area (m^2/g)	g_0	$g_\parallel$	$g_\perp$	A_0	$A_\parallel$	$A_\perp$	β_2^{*2}	K_{eff}
Type 3A	0.3	16	1.975	1.938	1.993	11.20	19.25	7.17	0.97	0.796
Type 4A	0.4	10	1.976	1.943	1.993	11.07	18.75	7.23	0.93	0.788
Type 5A	0.5	4	1.973	1.942	1.988	10.94	18.75	7.03	0.94	0.775
13X	1.0	37	1.972	1.943	1.987	11.06	19.00	7.01	0.97	0.779
Heulandite[a]	–	67	1.973	1.939	1.990	11.90	20.00	7.85	0.97	0.846
Clinoptilolite[a]	–	20	1.973	1.937	1.991	11.99	20.00	7.99	0.96	0.853

[a] The spectra were taken at 173 K.

the EPR active structure to the $VO(H_2O)_5^{2+}$ in these synthetic zeolites. The spectra given in Fig. 1 indicate that for the A type zeolites the widths of the hyperfine lines increase as the pore diameters increase. It can be seen in Table 1 that, as the pore diameters for the A type zeolites increase, the surface areas decrease. This decrease in surface areas increases the cation numbers per unit area, and the lines broaden due to the dipolar interaction. The hyperfine lines of the 13X zeolite are the narrowest, corresponding to the largest surface area.

The spectra for the natural zeolites heulandite and clinoptilolite are given in Figure 2(a). The spectra are nearly isotropic, and $g \cong 200$. This shows that the water in these zeolites is mobile. However, when the temperature is decreased to 173 K the spectra become axially symmetrical, as shown in Figure 2(b). Therefore the coordination structure around VO^{2+} in these natural zeolites is the same as in the synthetic ones. Furthermore, all the measured components of g in Table 1 indicate that $g_\parallel < g_\perp$ and support the existence of the $VO(H_2O)_5^{2+}$ complex, that has tetragonally distorted octahedral symmetry, C_{4v}. Therefore the unpaired electron density concentrated mostly in the $3\,d_{xy}$ orbital of the vanadium ion.

All the measured and calculated parameters for the $VO(H_2O)_5^{2+}$ are given in Table 1. In the calculation of K_{eff} and β_2^{*2} from the equations of the previous section, the mostly reported value of $P = 13.6$ mT is used [8, 9]. It can be seen from this table that K_{eff} increases as the pore diameters of the synthetic 3A, 4A, and 5A zeolites decrease. This shows that, as the pore diameter decreases, the core polarization of the elec-

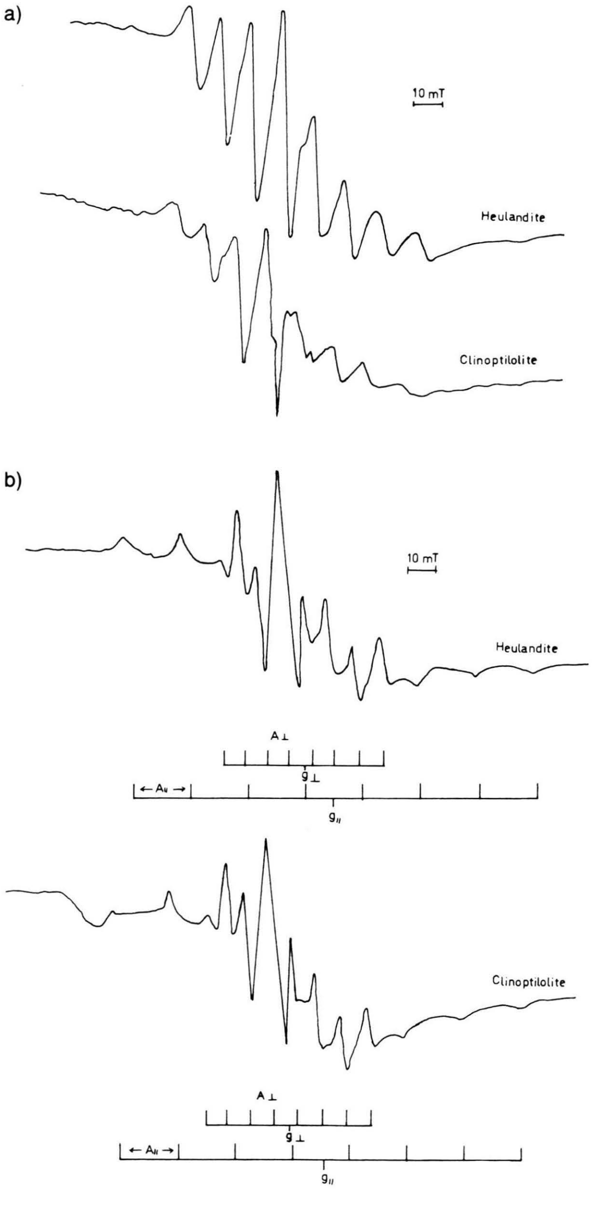

Fig. 2. The EPR spectra of the $VO(H_2O)_5^{+2}$ ions adsorbed on the natural zeolites heulandite and clinoptilolite. The spectra were recorded a) at room temperature, b) at 173 K.

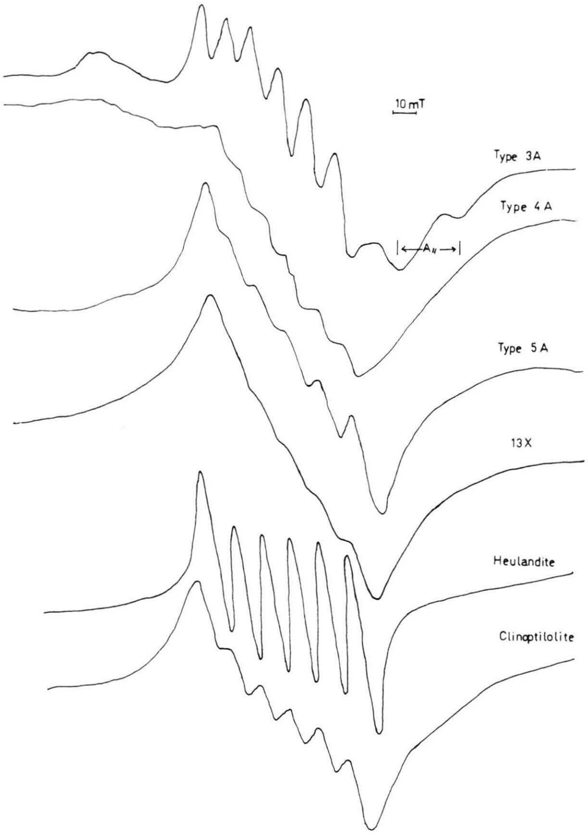

Fig. 3. The EPR spectra of the $Mn(H_2O)_6^{2+}$ ions adsorbed on the synthetic types 3A, 4A, 5A, 13X, and the natural zeolites heulandite and clinoptilolite at room temperature.

Table 2. The EPR parameters for the $Mn(H_2O)_6^{2+}$ ions for all the zeolites in this study. The A values are in mT.

Zeolit	g_0	A_0	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$	$A_{\perp}$
Type 3A	2.021	13.165	1.965	2.049	20.5	9.498
Type 4A	2.003	9.398				
Type 5A	2.005	9.098				
13X	2.040	8.898				
Heulandite	2.010	9.550				
Clinoptilolite	2.009	9.318				

tron density in the $3d_{xy}$ orbital of the vanadium increases. This may either be due to the vanadium core polarization by the electron density delocalized on other orbitals, or due to some symmetry distortions of the C_{4v} geometry, allowing the hybridization of vanadium orbitals.

The EPR spectra of the hydrated $MnCl_2 \cdot 2H_2O$ adsorbed synthetic and natural zeolites at room temperature are given in Figure 3. The spectra for the synthetic zeolites of large pore diameters and for the natural zeolites are isotropic, whereas the synthetic zeolites of pore diameters 3A, 4A display shoulders on the low-field side, and axially symmetric spectra on the high-field side. We attribute the low-field side shoulders to mobil water and the high field side spectra to immobile water. The high field side of the spectra for the 3A and 4A zeolites seem to indicate the existence of a strong ligand field and therefore, a low spin state of the Mn^{2+}. The components of the g tensor, $g_{\parallel} = 1.965$ and $g_{\perp} = 2.049$ for this state of Mn^{2+} in the zeolite of type 3A are close to the values given by Fortman and Hayes [10]. All the measured g_0 and A_0 values and the tensor components for $Mn(H_2O)_6^{2+}$ are given in Table 2.

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