An EPR Study of Mo^{5+} Introduced into NaY Zeolites by Solid-State Reactions

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By means of an EPR investigation of Mo^{5+} ions introduced into NaY zeolites by solid-state reactions, the location and coordination of Mo^{5+} in zeolites were investigated. Two different locations, free and distorted tetrahedral, were found. The molecular orbital coefficient, β^2, and the effective charge, Q, for the Mo^{5+} ions in a distorted tetrahedral structure were calculated and interpreted.

Key words: EPR; Zeolite; Mo^{5+}; NaY.

Introduction

The introduction of polyvalent ions into zeolites modifies their sorption and catalytic properties [1–3]. Molybdenum containing zeolites have many interesting catalytic properties [4–7].

Abdo and Howe have studied EPR of Mo $(CO)_6$ in NaY zeolite. On decomposition at high temperature, a signal of Mo^+ and some distinct Mo^{5+} signals were observed [8]. Minming and Howe have studied MoY zeolites prepared by aqueous ion exchange and found that the ion exchange produces a zeolite Mo^{6+}, and activation by heating in vacuum caused a reduction of up to 18% of molybdenum to Mo^{5+} [9]. They also have shown that Mo^{5+} ions occupy sites in supercages and β cages.

In the present work we have undertaken an EPR study of Mo introduced in the solid-state into the NaY zeolite to obtain information about valency states, locations and coordination of the cations.

Experimental

The zeolite NaY (zeolite Y) was purchased from Degussa. Its general unit cell content is [10]

$$Na_{56}\,[(AlO_2)_{56}\,(SiO_2)_{136}]\cdot 250\,H_2O\,.$$

The Si/Al-ratio of the zeolite NaY used in this study was 3. The solid-state reaction took place between the zeolite and 10 wt % $MoCl_5$. The zeolite and the metal chloride were crushed 1–2 mm pieces and kept at 973 K during 6 h. The EPR spectra were recorded with a Varian E-109 C model X-band EPR spectrometer, using 100 kHz modulation. The g values were determined by comparison with a DPPH sample of g=2.0036.

Theory

The splitting of the d orbitals for three structures is shown in Figure 1. When the unpaired electron occupies a d_{z^2} orbital, for a d^1 ion the spin-orbit interaction yields the ground state wave functions [11]

$$\begin{aligned} |+\rangle &= |\,d_{z^2},\ \alpha\rangle - \frac{\xi}{\Delta}\sum \langle i\,|\,\boldsymbol{L}\cdot\boldsymbol{S}\,|\,d_{z^2},\ \alpha\rangle\,|\,i\rangle\,, \\ |-\rangle &= |\,d_{z^2},\ \beta\rangle - \frac{\xi}{\Delta}\sum \langle i\,|\,\boldsymbol{L}\cdot\boldsymbol{S}\,|\,d_{z^2},\ \beta\rangle\,|\,i\rangle\,, \end{aligned} \tag{1}$$

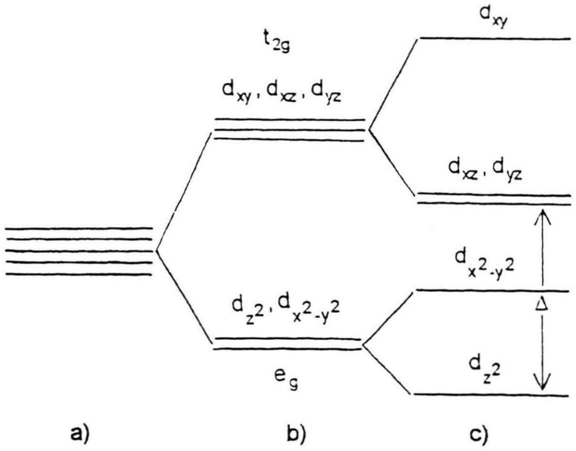

Fig. 1. Splitting of the d orbitals for a) a free ion, b) a tetrahedral and c) a distorted tetrahedral structure.

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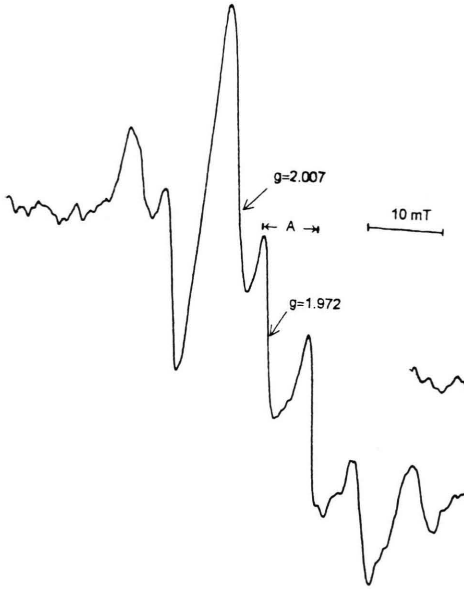

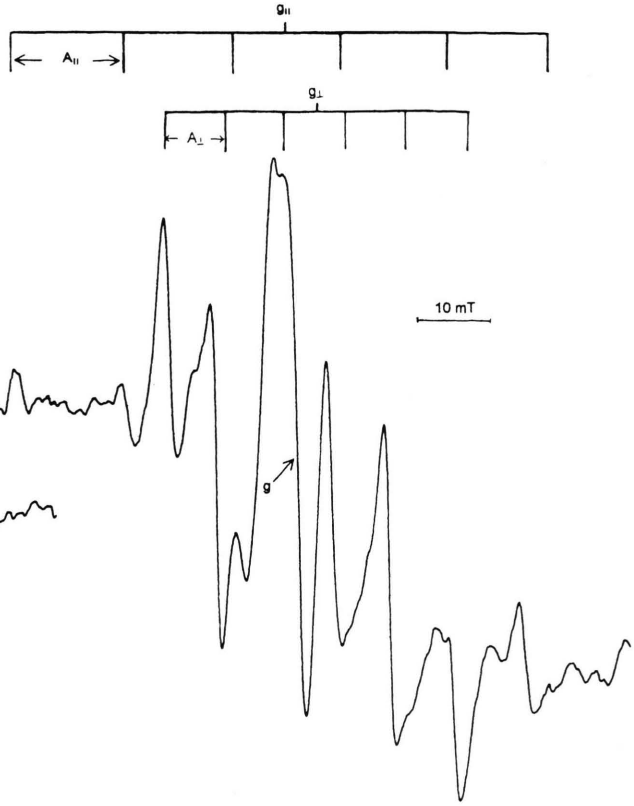

Fig. 2. EPR spectrum at room temperature of solid-state Mo^{5+} introduced into the NaY zeolite.

Fig. 3. The EPR spectrum at 143 K of solid-state Mo^{5+} introduced into the NaY zeolite.

and thus they become

$$|+\rangle = |\mathrm{d}_{z^2}, \alpha\rangle + \frac{\sqrt{3}}{2} i \frac{\xi}{\Delta} |\mathrm{d}_{yz}, \beta\rangle + \frac{\sqrt{3}}{2} \frac{\xi}{\Delta} |\mathrm{d}_{xz}, \beta\rangle, \quad |-\rangle = |\mathrm{d}_{z^2}, \beta\rangle + \frac{\sqrt{3}}{2} i \frac{\xi}{\Delta} |\mathrm{d}_{yz}, \alpha\rangle - \frac{\sqrt{3}}{2} \frac{\xi}{\Delta} |\mathrm{d}_{xz}, \alpha\rangle . \tag{2}$$

On the basis of these wave functions, the energy matrix is

$$E = \begin{array}{c|cc|} & |+\rangle & |-\rangle \\ \langle + | & \frac{1}{2} g_e \beta H_z & \frac{1}{2} \beta H_x \left(g_e - \frac{6\xi}{\Delta} \right) - \frac{1}{2} i \beta H_y \left(g_e - \frac{6\xi}{\Delta} \right) \\ \langle - | & \frac{1}{2} \beta H_x \left(g_e - \frac{6\xi}{\Delta} \right) + \frac{1}{2} i \beta H_y \left(g_e - \frac{6\xi}{\Delta} \right) & -\frac{1}{2} g_e \beta H_z \end{array} , \tag{3}$$

since the Zeeman Hamiltonian is

$$\mathcal{H} = \beta (\boldsymbol{L} + g_e \boldsymbol{S}) \cdot \boldsymbol{H} . \tag{4}$$

The matrix is diagonal when the magnetic field is along the z axis, and the difference between the energy values is $\Delta E_z = g_e \beta H$, thus

$$g_{\|} = g_e . \tag{5}$$

The matrix is non-diagonal when the magnetic field is along the x or y axis. If it is diagonalized, $\Delta E_x = \Delta E_y = (g_e - 6\,\xi/\Delta)\,\beta H$ and thus

$$g_\perp = \left(g_e - \frac{6\,\xi}{\Delta} \right). \tag{6}$$

$g_\perp < g_e$ since ξ and Δ are positive.

The ground state hyperfine constants are

$$A_\parallel = -K + P\left\{ \frac{4}{7}\beta^2 + \frac{1}{7}(2.0023 - g) \right\},$$
$$A_\perp = -K + P\left\{ -\frac{2}{7}\beta^2 + \frac{15}{14}(2.0023 - g) \right\} \tag{7}$$

when d_{z^2} is the ground state [11]. K is the Fermi contact term, β the molecular orbital coefficient for the ground state, and $P = 2\,\beta\,\gamma_N\,\beta_N\,\langle r^{-3}\rangle$. β^2 is a measure of π bonding with the ligands in the plane perpendicular to the main symmetry axis, and for d^1 configurations it can be regarded as the density of electrons on the metal ions since the ground state is always a π anti-bonding orbital. The effective charge, Q, is a measure of the ionic bonding with the ligands, and is given by

$$Q = -4 + 9\,\beta^2. \tag{8}$$

In our calculations, $P = 66.7 \times 10^{-4}\ \mathrm{cm}^{-1}$ is used [12].

Results and Discussions

Figure 2 shows the EPR spectrum at room temperature of the zeolite NaY with Mo^{5+} introduced by a solid-state reaction. As shown in the figure, there are two different locations of the Mo^{5+} ions in the NaY zeolite. The first intense peak at $g = 2.007$ belongs to adsorbed free Mo^{5+} ions, since its calculated g value is near the g value of the signal of MoO_3-NaY zeolite after having been activated in vacuum at 400 °C for 10 min [13]. The other location of Mo^{5+} gives the sextet lines. These lines belong to Mo^{95}-Mo^{97} with a nuclear spin $I = 5/2$ and about 25% natural abundance. At room temperature, the g and A values of these lines, which are isotropic, and $g = 1.972$, $A = 7.5$ mT due to the mobility of the ions. The doublet splitting of the first line at low magnetic field is caused by the presence of different isotopes. When the temperature is decreased to 143 K, of Fig. 3, the spectrum becomes axially symmetric because of the change of the crystal field symmetry. The calculated g and A values are given in Table 1. At the low temperature, the signal belonging to the absorbed free Mo^{5+} ions was observed at $g = 2.009$. The Mo^{5+} ion has an unpaired d electron, and when this electron occupies the d_{xy} orbital, the g values become $g_\parallel < g_\perp < 2$, and the ion has a distorted octahedral symmetry. As described in the theoretical part, when the unpaired electron occupies the d_{z^2} orbital, $g_\parallel = 2$ and $g_\perp < 2$, and the ion has a distorted tetrahedral symmetry. Since $g_\parallel \cong 2$ and $g_\perp < 2$, as seen from Table 1, the Mo^{5+} ion in the NaY zeolite has a distorted tetrahedral symmetry.

Table 1. The EPR parameters, at 143 K, for solid-state Mo^{5+} introduced into the NaY zeolite.

Zeolit NaY	$g_\parallel$	$g_\perp$	$A_\parallel$ (mT)	$A_\perp$ (mT)	g_{iso}	A_{iso} (mT)
	2.026	1.995	14.1	8.0	2.005	10.0

The values of β^2 and Q for Mo^{5+} having distorted tetrahedral symmetry were calculated as about 1 and 5, respectively. Since for d^1 configurations, β^2 is regarded as the electron density at the metal ion, the greater A values for Mo^{5+} in the distorted tetrahedral symmetry in zeolite NaY (this study) than the one in the distorted octahedral symmetry in MoH-Y zeolite [7] can be understood. In agreement with these statements, the greater Q value shows the more ionic character of the MoO bonding.

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