EPR Study of Cr^{5+} and Cu^{2+} in Some Zeolites Introduced by Solid- and Liquid-State Reactions

Fevzi Köksal, Fatih Ucun, and İbrahim Kartal
Physics Department, Faculty of Arts and Sciences, Ondokuz Mayıs University, Samsun, Turkey

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This study reports on the EPR of Cr^{5+} and Cu^{2+} ions, introduced by solid- and liquid-state reactions with the synthetic zeolites 3A, 4A and 5A, and the natural zeolite clinoptilolite. Cr^{3+} was oxidized to Cr^{5+} in the samples, the coordination around Cr^{5+} being square pyramidal. Superhyperfine (shf) interaction of Cr^{5+} with ^{27}Al nucleus was observed in both solid- and liquid-state-introduced 5A zeolite, whereas this shf could not be observed for the solid-state introduced 4A zeolite. The liquid-state Cr-introduced 4A zeolite needed a heat treatment at 473 K for ½ h for the appearance of shfs. Furthermore, it has been found that the coordination structure around the Cu^{2+} is square pyramidal in solid-state introduced samples, whereas it is octahedral in the liquid-state introduced ones.

Key words: EPR, Cu^{2+}, Cr^{5+}, Zeolites, Ion introduction.

Introduction

It is known that the introduction of transition metal ions into zeolites modifies their adsorption and catalytic properties. Solid-state interaction causes adsorbed ions on the outer surface to migrate to cationic positions in zeolites [1, 2]. Kucherov and Slinkin have reported the presence of at least three positions for Cr^{5+} in H-ZSM type zeolites by solid-state reaction [2]. Huang et al. have reported the presence of at least two different coordination structures around the Cr^{5+} cations in liquid-state Cr-exchanged mordenite [3]. Furthermore, many authors have reported shfs due to ^{27}Al ($I = 5/2$) in Cr-introduced NaM, NaX, and NaY zeolites [4, 5]. In the present work we have undertaken an EPR study on the solid- and liquid-state Cr and Cu introduced synthetic types 3A, 4A, 5A and clinoptilolite zeolites to obtain information about the valence state, location and coordination of the cations.

Experimental

The synthetic 3A, 4A, and 5A zeolites were purchased from the British Drug House (BDH), and the natural zeolite clinoptilolite was obtained from the Institute of Geology, The Hacettepe University, Ankara. The unit cell contents of these zeolites were given in [6]. The solid-state reactions took place between the zeolites and 10 wt.% Cr_2O_3 and CuO. The zeolites and the metal oxides mixtures were crushed in a mortar and then pressed into pellets. Then the pellets were crushed into 1–2 mm pieces and kept at 973 K during 12 h for Cr introduction, and during 6 h for Cu introduction. For the liquid-state introduction, the zeolites were activated at 673 K for 5 h, and then 1 g of zeolite was placed into either 50 cm³ of 1.4×10^{-3} M $CrCl_3 \cdot 6H_2O$, or of 1.3×10^{-3} M $CuCl_2 \cdot 2H_2O$ solutions for Cr and Cu introduction, respectively. After stirring and storing for 24 h, the solutions were filtered. Then the samples were dried at room temperature and kept at 973 K during 12 h for Cr introduction, and during 6 h for Cu introduction. The EPR spectra were recorded at room temperature with a Varian E-109 C model X-band spectrometer using 100 kHz modulation. The g values were determined by comparison with a DPPH sample of $g = 2.0036$.

Results and Discussion

1. *Cr Introduction*

The EPR spectra of liquid-state Cr-introduced samples are given in Figure 1. The spectra indicate axially symmetric behavior, obviously belonging to Cr^{5+}. This shows that Cr^{3+} is oxidized to Cr^{5+}. The components $g_{\parallel}$ and $g_{\perp}$ of the g tensor are given in Table 1.

Reprint requests to Prof. F. Köksal.

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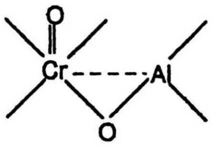
As seen in Fig. 1, shfs from ^{27}Al cannot be observed for the type 4A zeolite. However, when the liquid-state Cr-introduced 4A sample was kept at 473 K for ½ h before recording the spectrum at room temperature, then we obtained the spectrum in Figure 2. This spectrum consists of two overlapping spectra: one is without shfs, and the other with shfs. The observed shfs splitting constant due to ^{27}Al ($I = 5/2$) is $\cong 0.7$ mT and is consistent with the literature values [3–5, 7]. The components of the g tensor are given in Table 2. As seen from Tables 1 and 2, $g_{\parallel} < g_{\perp} < 2$. This indicates that the coordination around Cr^{5+} is lower than octahedral, and is either square pyramidal, or distorted tetrahedral [3]. The distorted tetrahedral coordination has a larger $\Delta g (= g_{\perp} - g_{\parallel})$ value than the square pyramidal coordination. Since our results indicate $\Delta g \cong 0.06$, the coordination should be square pyramidal. The appearance of the shfs due to ^{27}Al after heat treatment is consistent with other examples [3]. For the shfs from ^{27}Al, we think that Cr^{5+} needs a 3-coordinated Al framework nearby. Therefore the scheme [3]



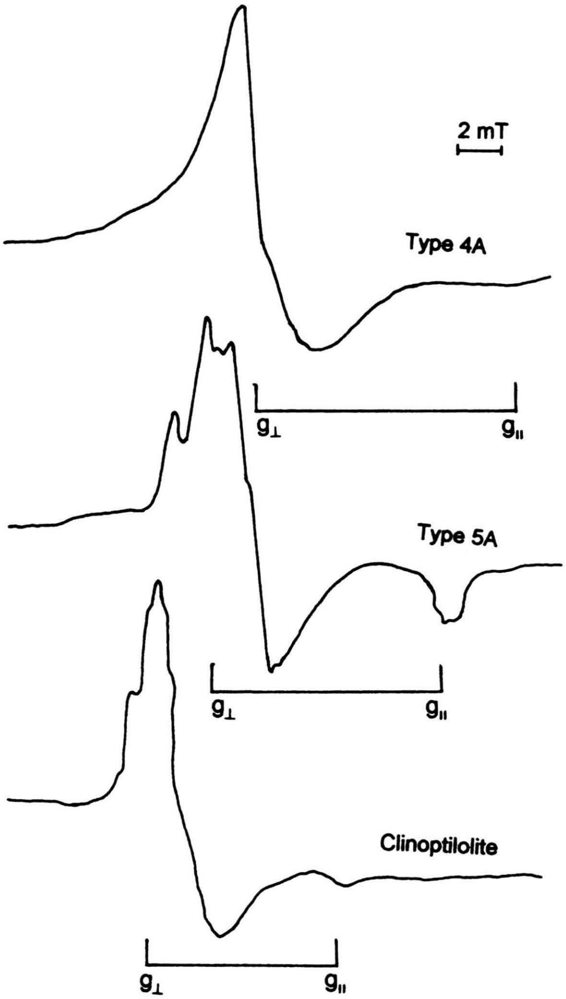


Fig. 1. The EPR spectra of the liquid-state introduced $(CrO)^{3+}$ in 4A, 5A, and clinoptilolite zeolites.

Table 1. The EPR parameters for the solid-, and the liquid-state introduced $(CrO)^{3+}$ in 4A, 5A and clinoptilolite zeolites.

Zeolite	Solid-state introduced		Liquid-state introduced	
	$g_{\parallel}$	$g_{\perp}$	$g_{\parallel}$	$g_{\perp}$
Type 4A	1.92	1.99	1.92	1.98
Type 5A	1.92	1.98	1.93	1.99
Clinoptilolite	1.92	1.98	1.94	1.99

Table 2. The EPR parameters for $(CrO)^{3+}$, introduced into 4A zeolite by liquid-state reaction, and kept at 473 K for ½ h.

$g_{\parallel}^{(1)} = 1.95$	$g_{\perp}^{(1)} = 2.00$	
$g_{xx}^{(2)} = 1.99$	$g_{yy}^{(2)} = 1.98$	$g_{zz}^{(2)} = 1.93$

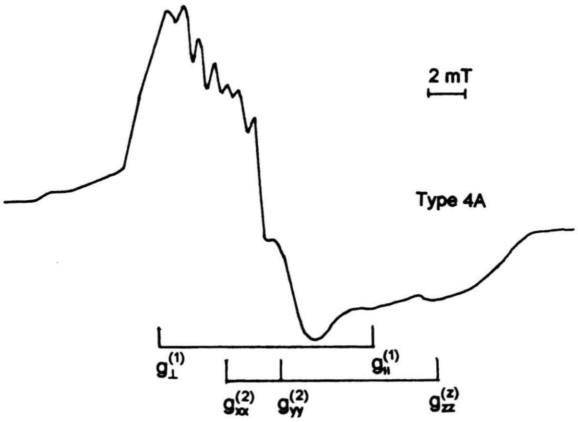
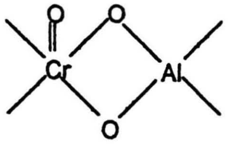


Fig. 2. The EPR spectrum of $(CrO)^{3+}$, introduced into 4A zeolite by liquid-state reaction, and kept at 473 K for ½ h.

can provide the shfs. The $(CrO)^{3+}$ spectrum without ^{27}Al shfs can be attributed to the scheme



We think that, according to this scheme, shfs on $(CrO)^{3+}$ spectra due to ^{27}Al is less probable. For the observations of this shfs the used 10% of Cr_2O_3 and 1.4×10^{-3} M aqueous solution of $CrCl_3 \cdot 6H_2O$ in preparing the samples seem to be optimal, as higher concentrations give broadened lines due to dipolar interaction and smaller concentrations do not give detectable signals.

2. *Cu Introduction*

The EPR spectra of the solid-state Cu^{2+} introduced samples in this work are given in Fig. 3, and their EPR parameters are listed in Table 3. It is thougth that the Cu^{2+} ions are coordinated to cationic positions by migrating from the outer surfaces of the zeolite crystals. The EPR spectra in Fig. 3 are consistent with this. The coordination around Cu^{2+} should be square pyramidal because this coordination of Cu^{2+} is characterized by the following parameters [8]: $g_{\parallel} = 2.33 - 2.34$ and $g_{\perp} \cong 2.07$, and $A_{\parallel} \cong 14$, $A_{\perp} \cong 1.8$ mT. As seen from Table 3, the listed parameters of the spectra are in good agreement with these values.

Table 3. The EPR parameters for the solid-, and the liquid-state introduced Cu^{2+} in 3A, 4A, 5A and clinoptilolite zeolites.

Zeolite	Solid-state introduced			Liquid-state introduced		
	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$ (mT)	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$ (mT)
Type 3A	2.34	2.075	14.0	2.40	2.07	10.5
Type 4A	2.33	2.070	14.0	2.36	2.08	11.0
Type 5A	2.33	2.070	14.0	2.35	2.08	11.5
Clinoptilolite	2.33	2.065	14.0	2.38	2.08	11.0

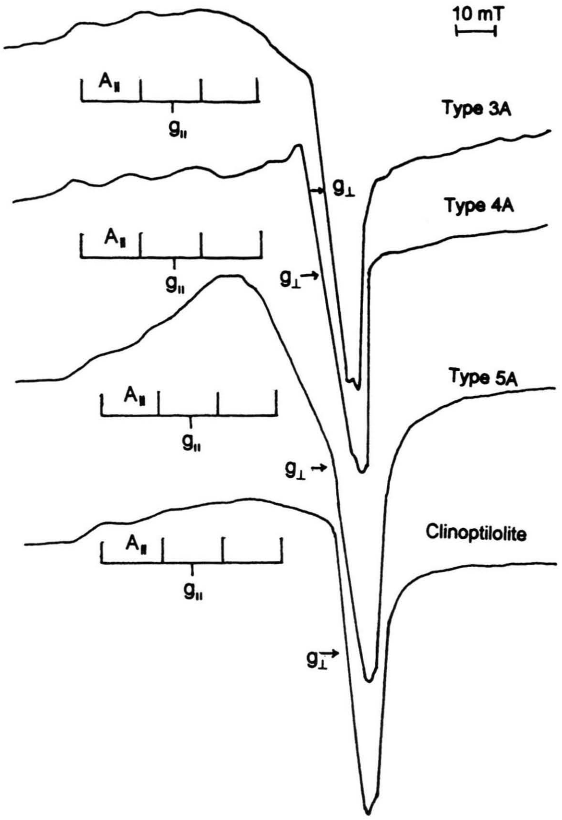


Fig. 3. The EPR spectra for the solid introduced Cu^{2+} in 3A, 4A, 5A and clinoptilolite zeolites.

The EPR parameters of the liquid-state introduced Cu^{2+} samples in this work are listed in Table 3. These values of the components of the g and the A tensors are out of the limits of square pyramidal, but they are in good agreement with the values given for an octahedral coordination [8, 9]. Therefore, the coordination around the Cu^{2+} in these samples should be octahedral. As seen from Table 3, the $A_{\parallel}$ values for Cu^{2+} in square pyramidal coordination are larger than those in octahedral. This may be due to the double bonding in the square pyramidal environment, which strengthens the hyperfine interaction of the unpaired electron with Cu^{2+}.

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