

EPR of O_2^- Radicals in the Zeolites NH_4NaY and NH_4CaA

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Activated and non-activated states of the zeolites NH_4NaY and NH_4CaA , and their NH_4^+ forms were prepared with an $(NH_4)_2SO_4$ solution and were investigated by EPR after γ -irradiation. The formed radicals were attributed to O_2^- supposed to be trapped near a trigonally coordinated framework of ^{27}Al ($I = 5/2$). Anisotropic O_2^- spectra were observed, consisting of hyperfine structure due to the ^{27}Al framework, even at room temperature. This was attributed to the scarceness of NH_4^+ sites or trap sites because of the preparation of the NH_4^+ forms of the zeolites with an $(NH_4)_2SO_4$ solution. The crystal field splittings were found and interpreted.

Key words: EPR; Zeolites; O_2^- ; NH_4NaY ; NH_4CaA .

Introduction

Stamires and Turkevich have observed a sextet signal with a 5 G spacing, centered at $g = 2.0017$ on the activated zeolite NH_4Y irradiated in vacuum by γ -rays, and they attributed the spectrum to an electron excess center trapped by a trigonally coordinated ^{27}Al framework [1]. Some authors could not observe any hyperfine structure arising from ^{27}Al in the spectra of the samples irradiated in the presence of oxygen [2, 3]. Wang and Lunsford have observed an O_2^- spectrum that shows a recognizable hyperfine structure arising from ^{27}Al in the zeolite NH_4Y activated at 600 °C and irradiated in the presence of oxygen at 77 K [4]. They attributed the spectrum to O_2^- associated with the trigonal aluminum at an oxygen-deficient site of the framework. In addition, the same authors have observed an O_2^- spectrum consisting of a three sets of sextet lines at 77 K in the zeolite $AlHY$, irradiated by γ -rays in the presence of oxygen [5]. Vedrine and Naccache have obtained a completely different spectrum from the zeolite NH_4Y , activated in the presence of oxygen at 400 °C after γ -irradiation in vacuum at 77 K [2]. They have obtained a spectrum that has an axially symmetric g tensor, with hyperfine structure arising from the aluminum nucleus. They have

attributed the spectrum to an electron hole located in a non-bonding p orbital of a lattice oxygen next to the aluminum.

As seen, the observed EPR spectra varied markedly depending on the details of the applied process before irradiation. In many studies, NH_4^+ forms of zeolites were prepared with NH_4Cl and NH_4NO_3 solutions. In the present study we prepared the NH_4^+ forms of the zeolites with an $(NH_4)_2SO_4$ solution, and even at room temperature we could observe anisotropic O_2^- spectra with a hyperfine structure arising from the aluminum nucleus. In addition, we prepared the NH_4^+ forms of the zeolites with an NH_4Cl solution and compared these with the previous results.

Experimental

The zeolite CaA (Type 5A) was purchased from the British Drug House (BDH). Its unit cell is given in [6]. The general unit cell content of the zeolite Y is [7]



The zeolite NaY with Si/Al = 3 was obtained from Degussa.

The water in the pores of the zeolites was evaporated at 350 °C during 4 h. Then, 1 g of zeolite was placed into 50 cm³ of 0.5 M $(NH_4)_2SO_4$ solution. After stirring and storing for 24 h the solutions were

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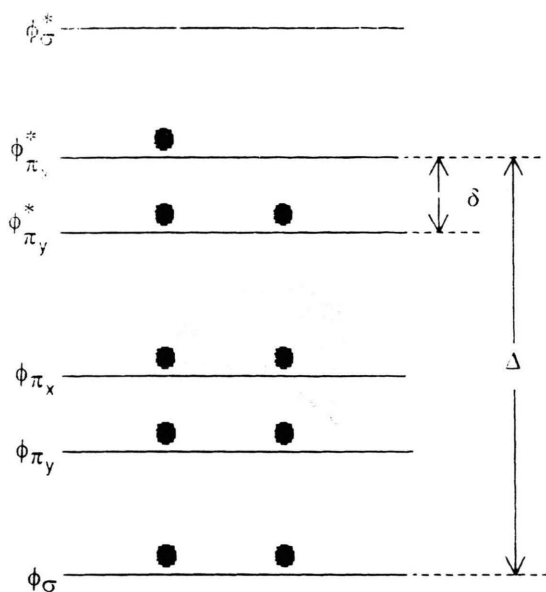


Fig. 1. The electronic energy levels of the superoxide ion O_2^- .

filtered. Then the samples were dried at room temperature. To obtain activated samples they were kept at 500 °C for 3 h. All the samples were irradiated with a γ -ray source of 0.065 Mrad/h during 24 h. The EPR spectra were recorded by an X band Varian E-109C model spectrometer equipped with a Varian temperature control unit. The g values were determined by comparison with a DPPH sample of $g = 2.0036$.

Theory

O_2^- center

The electronic energy level diagram of O_2^- is shown in Figure 1. As seen from this figure, the crystal field splitting between the levels $\phi_{\pi_x}^*$ and $\phi_{\pi_y}^*$ is δ , and the energy splitting between the levels $\phi_{\pi_x}^*$ and ϕ_{σ} is Δ . These can be used in g value calculations. Therefore, for $\Delta > \delta \gg \lambda$ g values were basically given as follows [8]:

$$g_x \cong g_e - \frac{\lambda^2}{\delta^2} + \frac{\lambda^2}{\Delta\delta},$$

$$g_y \cong g_e + \frac{2\lambda}{\Delta} + \frac{\lambda^2}{\delta^2} - \frac{\lambda^2}{\Delta\delta},$$

$$g_z \cong g_e + \frac{2\lambda}{\delta}.$$

Table 1. The g and A values of the radical O_2^- in the activated zeolites NH_4NaY and NH_4CaA . The A values are in Gauss.

Zeolite	g_x	g_y	g_z	A_x	A_y	A_z
NH_4NaY	1.995	2.009	2.025	3.25	3.75	4.00
NH_4CaA	1.991	2.009	2.029	4.00	5.00	5.50

λ is the spin orbit coupling constant, and $g_e = 2.0023$ is the free electron g value. In our calculations, $\lambda = 0.014$ eV was used.

Results and Discussion

Figure 2a shows the EPR spectra of the zeolites NH_4NaY and NH_4CaA at room temperature after the γ -irradiation, and Fig. 2b shows those of their activated states (kept at 500 °C for 3 h). As seen clearly in Fig. 2b, the spectra are anisotropic, showing three sets of sextet lines. Each set gives a different hyperfine interaction along the three axes (x, y, z), defined by the orientation of the molecule with respect to the external magnetic field. The obtained g and A values from these spectra are given in Table 1. These values are very close to the those obtained from the spectra of the activated zeolites NH_4Y and $AlHY$ at 77 K after γ -irradiation in the presence of oxygen [4, 5]. The authors attributed the spectra to O_2^- , formed by the oxygen near the lattice oxygen containing an unpaired electron. We also attribute the spectra to O_2^- formed in the present zeolites.

Some authors did not observe any hyperfine structure arising from the ^{27}Al framework [2, 3]. Even at room temperature an anisotropic O_2^- spectrum with a hyperfine structure from aluminum was not given so far. But, as seen from Fig. 2b, our spectra show the three sets of sextet lines. We attribute this hyperfine structure to the ^{27}Al ($I = 5/2$) framework. Therefore the formed O_2^- radicals in the zeolites are placed near to the framework of aluminums.

The indiscernibility of the spectra of the non-activated zeolites is caused by the interaction between the O_2^- radicals and the NH_4^+ ions in the zeolites, since the line-width ($1/T_2$), due to the spin-spin interaction increases.

The variation of the hyperfine lines with respect to one another (especially at the sextet splitting centered at $g = 2.0029$ in the low field) may depend on the mobility of the radical and on the change of the hyperfine splitting from the ^{27}Al due to the orientation of the radical with respect to the external magnetic field.

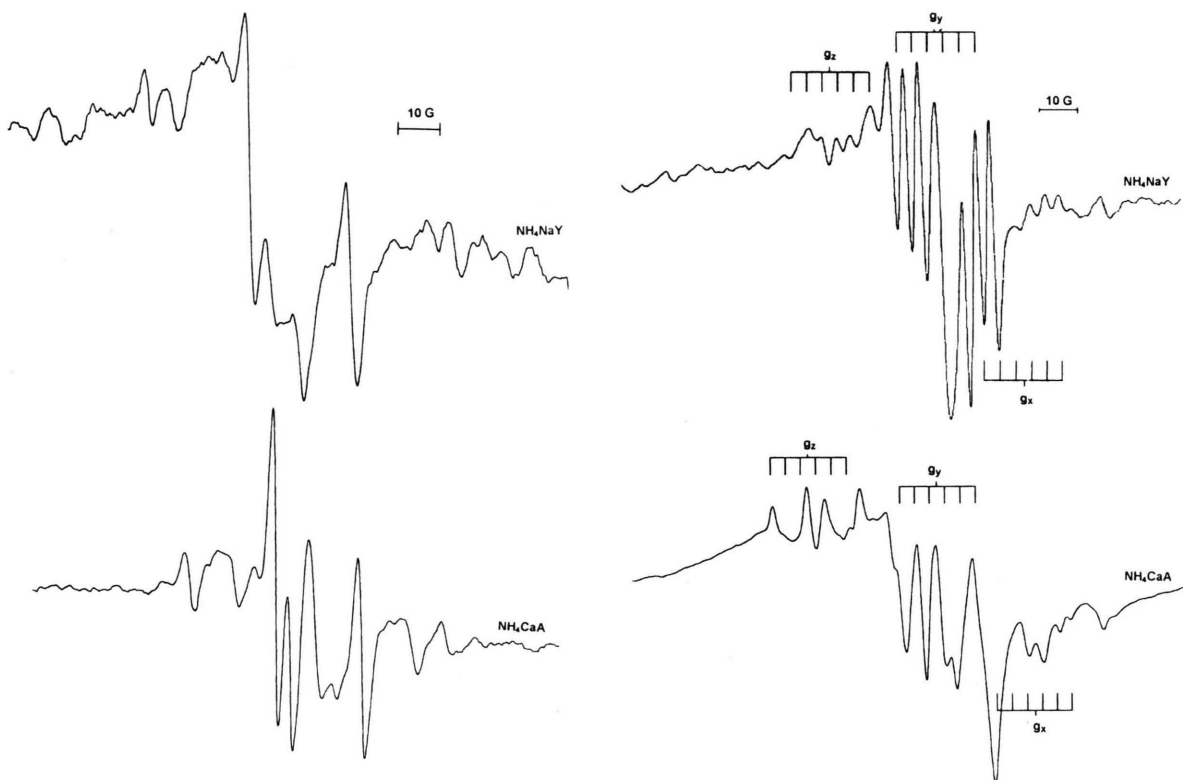
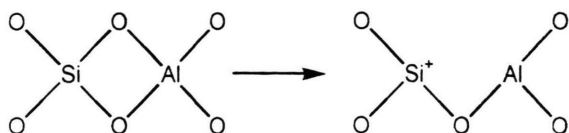


Fig. 2. The EPR spectra at room temperature of (a) the non-activated zeolites, (b) the activated zeolites.

For, when the temperature is decreased to 113 K, the lines could partly be observed.

In the EPR spectra of O_2^- , the hyperfine structure arising from aluminum can clearly be seen (Fig. 2b) in the activated zeolites NH_4NaY and NH_4CaA after they are γ -irradiated. The reason for this is the removal of the NH_4^+ ions from the zeolites. As the NH_4^+ exchanged zeolites are kept at 500 °C, the NH_4^+ ions decompose to NH_3 and H^+ . Thus sites containing H^+ , or indirectly acidic sites are formed in the zeolites. The joining of two hydrogen ions forms H_2O which also evaporates. Thus at 500 °C the three coordinated Al and Si sites deprived of oxygen are formed:



The formed O_2^- radicals are trapped next to the trigonal aluminum at the oxygen deficient sites. Therefore the formed hyperfine structure comes from the



Fig. 3. The EPR spectrum at room temperature of the activated zeolite NH_4CaA , the NH_4^+ form of which was prepared with the NH_4Cl solution.

trigonal aluminum. A similar localization was suggested for square pyramidal Cr^{5+} in the zeolites type 4A, 5A and clinoptilolite [9]. For such a spectrum, the need that the authors should irradiate in the presence of oxygen and take the spectrum at 77 K shows the

excellence of the process, before taking EPR spectra. Therefore the NH_4^+ forms of the zeolites were prepared with $(NH_4)_2SO_4$ solution. In this case, the formed NH_4^+ sites or indirectly trapped O_2^- sites, causing dipolar broadening [8, 10], become rare. Thus, the lines become narrower and can yield a good spectrum.

Figure 3 shows the EPR spectrum of the zeolite NH_4CaA , the NH_4^+ form of which was prepared with a 0.7 M NH_4Cl solution by a similar method, and irradiated after keeping at 500 °C for 3 h. As seen from this figure, the resolution of the spectrum is poor. It consists of a broad line, containing a few hyperfine lines. The non-recognizability of the spectrum can be caused by an excess of NH_4^+ sites, or of trap sites with trigonal ^{27}Al , or indirectly trapped O_2^- radicals. The zeolite NH_4NaY did not give any EPR line.

For the activated zeolites NH_4NaY and NH_4CaA , the crystal field splittings δ between the $\phi_{\pi_x}^*$ and $\phi_{\pi_y}^*$ levels in Fig. 1 are 1.233 and 1.049 eV. The splitting between the π orbits depends on the electrical charge accompanied with the cation. Therefore, for same type of zeolites, δ is expected to be two times greater for the zeolite containing Ca^{2+} than for the one containing Na^+ . But, as seen, the calculated value for the zeolite NH_4NaY is greater or about equal to that calculated for the zeolite NH_4CaA . The reason for this may be the different crystal structure of the zeolites. Therefore it can be concluded that the cations in the zeolite NaY are both more frequent and nearer than those in the zeolite CaA . This agrees with their unit cells. The values of Δ between the levels $\phi_{\pi_x}^*$ and ϕ^σ were calculated and found to be nearly the same for both zeolites, namely $\Delta \cong 4$ eV.

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