

ESR Spectroscopic Evidence on the Formation of NaC₆₀ and HC₆₀ in Y Zeolitic Nanocavities

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Received September 4, 2002

Key Words : C₆₀⁻, HC₆₀, NaC₆₀, Zeolites, ESR

ESR spectra of C₆₀-encapsulated zeolites have been closely analyzed to show that NaC₆₀ and HC₆₀, as well as C₆₀⁻, form in the supercage of NaY, whereas only C₆₀⁻ forms in the channel of VPI-5. The hyperfine constants of the ESR spectra indicate that 3% and 9% of the unpaired spin densities of neutral NaC₆₀ and HC₆₀ molecular species are distributed to the Na and H atoms, respectively. Both species have large g₀-values, owing to the paramagnetic contribution of H and Na atoms.

There has been a great deal of research on the physical and chemical properties of C₆₀ and on the intercalation of C₆₀ molecules in the cages and channels of zeolites.¹⁻¹⁵ The incorporation of C₆₀ molecules into the robust nanocavities of faujasite zeolites¹⁰⁻¹⁴ is more interesting than the insertion into the extra large zeolitic pores because there are no physical barriers to immobilize C₆₀ in the latter. The successful intercalation of fullerene molecules into the robust nanocavities of NaY, confirmed by ¹²⁹Xe NMR spectra,^{13,14} has led us to generate radical anions and adducts of C₆₀.

C₆₀ is easily reduced to form anionic species, owing to its great electron affinity. C₆₀ molecules often form charge transfer complexes with electron donating groups in solutions or polymeric films.¹⁶⁻¹⁸ Extensive research has focused on spectroscopic, especially ESR, studies of fullerene anions or adduct radicals generated by various techniques.¹⁹⁻²³

In the present study we show, based on the close reexamination of our recently reported ESR spectra,¹³⁻¹⁵ the formation and characterization of NaC₆₀ and HC₆₀ in NaY nanocavities.

The ESR spectra in Figure 1 show that while bare NaY and VPI-5 yield extremely weak broad ESR spectra, those introduced by C₆₀ bring in new intense sharp spectra with g₀-values of 2.0058 for NaY and 2.0034 for VPI-5. This indicates that the C₆₀ adsorbed at the wall surface of NaY and VPI-5 nanocavities gives birth to C₆₀⁻ and that the produced radical species is stable enough to exist at the ground state. All the spectra of diffuse reflectance, static and time-resolved fluorescence, and transient reflectance, as well as all the kinetics of fluorescence and transient absorption in our recently reported papers,¹³⁻¹⁵ show that a significantly large fraction of C₆₀ molecules transforms into the ground-state stable radical anions of C₆₀⁻ in the nanocavities of faujasite and VPI-5 zeolites.

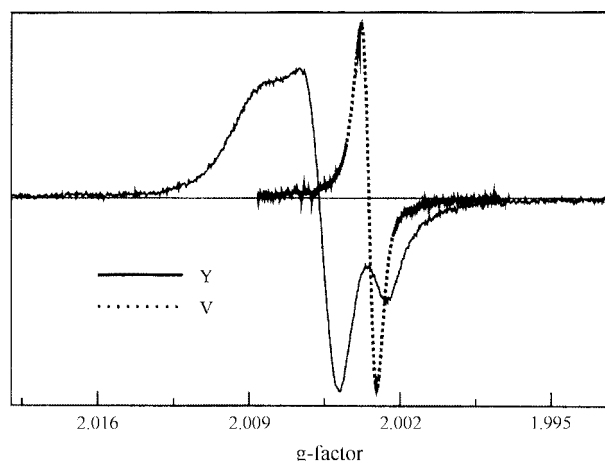


Figure 1. ESR spectra of C₆₀-introduced NaY (Y) and VPI-5 (V).

Although the g₀-values from Figure 1 are typical values for organic radicals, they are significantly larger than those (2.0006,¹⁹ 2.001,²⁰ 1.998²¹) of C₆₀⁻ in solutions. The large g₀-values are considered to arise from the polar environment.^{13-15,23,24} The earlier reported small g₀-values (~1.9994) in faujasite zeolites^{11,12} are thought to result from the anions located at the external surface rather than inside the nanocavities. The ESR spectrum of C₆₀-intercalated NaY is too multiplexed to have originated from a single species in a similar environment. The spectrum looks like a free organic radical signal superimposed with polarized organic radical signals split into multiplets by neighboring nuclear spins. We suggest that the radical anions formed in NaY nanocavities exist in different environments. Some C₆₀⁻ in NaY might have protons or sodium ions nearby. A proton is available to form a protonated species^{25,26} since dehydrated samples still contain hydrated water molecules.²⁷

The spectra in Figure 1 have been iteratively fitted with the first derivative curves of Lorentzian line-shape functions (Eq. (1)), using the parameters in Table 1 in order to understand the nature of radical species present in zeolitic nanocavities.

$$\frac{1}{\pi} \left[\sum_{m=-I}^{m=I} (4-2|m|) \right]^{-1} \sum_{m=-I}^{m=I} \left[\frac{(4-2|m|)\Delta g_{1/2}}{(g-g_0-mg_a)^2 + \Delta g_{1/2}^2} \right] \quad (1)$$

The *I* in Eq. (1) is the nuclear spin (quantum number) that

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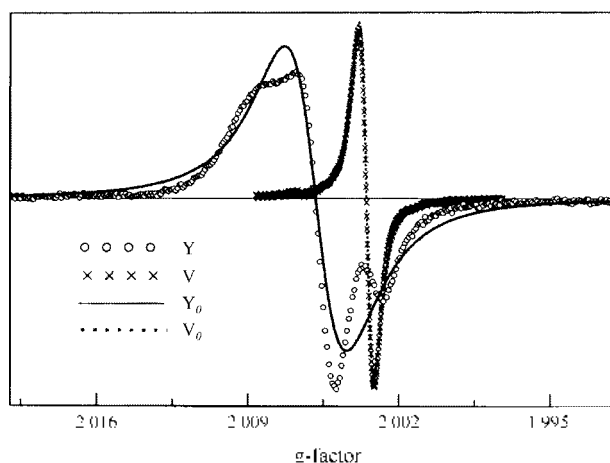


Figure 2. Single-Lorentzian curves simulated using the parameters in Table 1 to fit the spectra in Figure 1.

Table 1. Spectral parameters of the simulated curves^a in Figures 2 and 3

Figure	Curve	f ^b	I	g ₀	Δg _{1/2} ^c	ΔH _{1/2} ^c	g _a	a ^d	ρ ^e
2	Y ₀	1	0	2.0058	0.0025	0.45	-	-	-
	V ₀	1	0	2.0034	0.0007	0.12	-	-	-
3	ΣY _i	1	0	2.0058	0.0023	0.41	-	-	-
	y ₀	0.09	0	2.0033	0.0013	0.23	-	-	-
	y _{1/2}	0.32	1/2	2.0076	0.0013	0.23	0.0012	0.2	0.09
	y _{3/2}	0.59	3/2	2.0057	0.0013	0.23	0.0004	0.07	0.03

^aSimulated using the first derivatives of Eq. (1). ^bFractional abundance. ^cHalf width at the half maximum in mT converted from Δg_{1/2}. ^dHyperfine constant in mT converted from g_a. ^eCalculated using the McConnell equation ($a = Qr$) with $Q = 2.25$ mT.²⁸

gives birth to a hyperfine structure. The spectrum of C₆₀-introduced NaY hardly fits a single Lorentzian curve, whereas that of C₆₀-introduced VPI-5 does well (Figure 2). Furthermore, the fitted single Lorentzian curve, Y₀, has a very broad spectral width compared with that of V₀ (Table 1). However, the multiple Lorentzian curve of ΣY_i, composed of three different simulated curves, fits quite well into the spectrum Y (Figure 3). All of y₀, y_{1/2}, and y_{3/2} were simulated using the same hyperfine line width.

While we attribute the singlet Lorentzian curve of y₀ to C₆₀⁻ not having an associated cation, we ascribe the doublet and quartet hyperfine structures of y_{1/2} and y_{3/2} to HC₆₀ and NaC₆₀, respectively. Of special note is that the g₀-value of y₀ is very similar to that of V₀. Since the microenvironment of C₆₀⁻ in aluminophosphate VPI-5 is uniform, V without a hyperfine structure is very isotropic and narrow in line width, and it shows a low g₀-value because C₆₀⁻ in VPI-5 rarely has an associated cation. The component y₀ is found to be spectrally similar to V₀ as the microenvironment of some C₆₀⁻ in Na⁺-exchanged aluminosilicate NaY is similar to that of C₆₀⁻ in VPI-5. The C₆₀⁻ ions giving y₀ are not associated with cations directly. However, the line width of y₀, which is larger than that of V₀, suggests that NaY cages are still more heterogeneous than VPI-5 channels as known.¹¹ The hyperfine coupling strength of HC₆₀ is larger by a factor

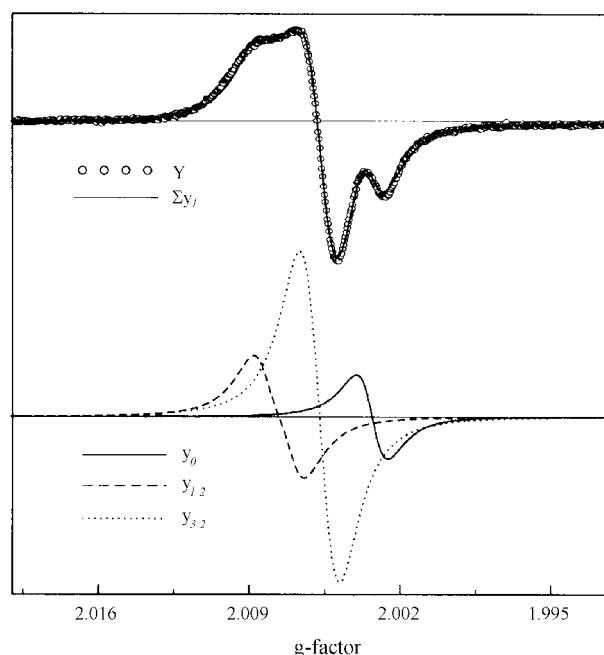


Figure 3. Multiple-Lorentzian curve (ΣY_i) composed of y₀, y_{1/2}, and y_{3/2} to fit Y. The parameters used are described in Table 1.

of 3 than that of NaC₆₀, indicating that NaC₆₀ has significantly larger ionic bond character than HC₆₀. The 9% and 3% of the unpaired spin densities of HC₆₀ and NaC₆₀ molecules are distributed to the H and Na atoms, respectively, according to the McConnell equation, using $Q = 2.25$ mT.²⁸ Of note is that the g₀-value increases as the hyperfine coupling constant increases in the order of y₀, y_{3/2}, and y_{1/2}. The negative shielding effect by the paramagnetic contribution of unoccupied orbitals is known to enhance the g₀-value. Thus, the g₀-value increment is considered to have resulted from enhanced unoccupied orbital contribution with the hyperfine constant increase. The fractional abundance in Table 1 indicates that adducted molecular species of NaC₆₀ and HC₆₀ are dominant in NaY supercages over the anionic species of C₆₀⁻. We have shown here that ground-state stable NaC₆₀ and HC₆₀, as well as C₆₀⁻, can be isolated in NaY nanocavities. The respective ESR spectra of both molecular species have been well characterized without being perturbed by the thermal motion of surrounding solvent molecules because of their isolated environment. Because reducing agents were not employed, the spectra were measured without being contaminated by undesired radical products. The ESR spectra are free from concerned dimeric species²⁹ because only one C₆₀ molecule can be intercalated into one supercage of NaY.

In summary, molecular species of NaC₆₀ and HC₆₀ have been found to exist in NaY nanocavities. Furthermore, both species show well-defined ESR spectra because of their isolated environment. The 9% and 3% of the unpaired spin densities of HC₆₀ and NaC₆₀ molecular species were found to locate at the H and Na atoms, respectively. Both species have large g₀-values, owing to the paramagnetic contribution of H and Na atoms.

Experimental Section

Highly pure NaY and VPI-5 were synthesized, dried in a vacuum, and dehydrated at 400 °C for 12 h. Dehydrated NaY with 1.0 mmol of the supercage was mixed with 25 μ mol of C₆₀ in a quartz tube. The tube was evacuated, sealed, and maintained at 650 °C for 72 h to make C₆₀ sublime and diffuse uniformly into zeolite supercages.^{13,14} 0.2 g of dehydrated VPI-5 was added to 20 mL of benzene containing 0.02 g of C₆₀ and stirred at 50 °C for 24 h. C₆₀-introduced VPI-5 was filtered off, washed thoroughly with benzene to remove any surface species, and dried in a vacuum for 24 h. X-ray diffraction confirmed that the framework structures of NaY and VPI-5 did not change during dehydration and intercalation. The successful intercalation of C₆₀ was confirmed using ¹²⁹Xe NMR spectroscopy.^{13,14} ESR derivative curves were measured at the X-band, using an ESR spectrometer (Bruker, ESP 300) with the frequency of 9.7 GHz.

Acknowledgment. The center for Molecular Catalysis and Brain Korea 21 Program supported this work.

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