Formation of C_{60} Radical Cation in Iron(III)-Exchanged Zeolite Y

Shunichi Fukuzumi,* Tomoyoshi Suenobu, Tsutomu Urano, and Keiko Tanaka
Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadaoka, Suita, Osaka 565

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When C_{60} is introduced into the Fe^{3+}-exchanged zeolite Y sample, an intense ESR signal at g = 2.0027 is observed. The ESR signal is due to the formation of C_{60} radical cation ($C_{60}^{\bullet+}$), since the signal intensity increases with an increase in the amount of Fe^{3+} loaded in the zeolite. Addition of perylene into the $C_{60}^{\bullet+}$-zeolite system results in electron transfer from perylene to $C_{60}^{\bullet+}$ to produce perylene radical cation accompanied by the disappearance of $C_{60}^{\bullet+}$.

Since the electron transfer reduction of C_{60} yields the corresponding stable radical anion ($C_{60}^{\bullet-}$),[1] the ESR spectra of $C_{60}^{\bullet-}$ have been extensively studied.[2] In contrast, relatively little is known about C_{60} radical cation because of the difficulty in the electron transfer oxidation of C_{60} by normal oxidants as well as the instability of the radical cation in solution,[1] although the formation of C_{60} radical cation has been detected by pulse radiolysis study.[3] There have also been some reports on the ESR spectra assignable to $C_{60}^{\bullet+}$.[4-7] However, the definitive ESR detection of $C_{60}^{\bullet+}$ remains to be confirmed. In the case of C_{76} which has the lower oxidation potential than C_{60},[8] isolation of a stable salt of $C_{76}^{\bullet+}$ has recently been reported.[9]

This study reports the formation of C_{60} radical cation stabilized in Fe^{3+}-exchanged zeolite Y. Pretreatment of the Fe^{3+}-exchanged zeolite and introduction of C_{60} under high vacuum at high temperatures enables us to detect the ESR spectrum of $C_{60}^{\bullet+}$ which is stable at room temperature. The effects of the amount of Fe^{3+} loaded in the zeolite and the pretreatment temperature on the ESR intensity of $C_{60}^{\bullet+}$ are reported together with electron transfer from perylene or tetramethyltin to $C_{60}^{\bullet+}$ in the zeolite.

Zeolite NaY was activated by heating in a furnace in the air at 773 K for 6 h. The Fe^{3+}-zeolite sample (1.0 g) was prepared by suspending NaY (1.0 g) in an MeCN solution (20 mL) containing $Fe(ClO_4)_3{\bullet}6H_2O$ (46.2 - 139 mg, 1.0 x 10^{-4} - 3.0 x 10^{-4} mol) for 30 min as reported previously.[10] It was confirmed that all Fe^{3+} ions in solution were exchanged with NaY. The Fe^{3+}-zeolite was then filtered and evacuated at room temperature. An ESR tube containing the Fe^{3+}-zeolite sample (180 mg) and C_{60} (4.2 x 10^{-6} mol, 3.0 mg) was evacuated at 298 K for 12 h and sealed off. Then, the ESR tube was placed in a furnace at high temperatures (e.g., 693 K) for 3 h. After the treatment, the sample color turned brown.

Figure 1 shows the ESR spectrum of the treated sample which has an isotropic g value of 2.0027 ± 0.0002. No ESR signal at g = 2.0027 was observed without C_{60}. The g value is quite different from that of $C_{60}^{\bullet-}$ (g = 2.000).[2] The small g value of $C_{60}^{\bullet-}$ as compared to that of free electron (g = 2.0023) is expected from the singly occupied triply degenerate LUMO of C_{60}, although $C_{60}^{\bullet-}$ would be required to distort as a consequence of the Jahn-Teller distortion.[2] In contrast, a Jahn-Teller distorted molecule of $C_{60}^{\bullet+}$ is expected to have a g factor being larger than that of a free spin.[11] The g value of the ESR spectrum in Figure 1 is also different from that of the triplet C_{60} (g = 2.0014).[12] Thus, the ESR spectrum in Figure 1 may be assigned as $C_{60}^{\bullet+}$ which is oxidized by Fe^{3+} loaded into the zeolite.[13] Hwang et al. have recently reported that irradiation of a toluene solution of C_{60} affords two ESR bands with g values of 2.0013 and 2.0024, which are assigned to be the triplet C_{60} and $C_{60}^{\bullet+}$, respectively.[4] The g value of the latter and that of $C_{76}^{\bullet+}$ (2.0030)[9] agree with that in Figure 1 within experimental errors. On the other hand, the formation of $C_{60}^{\bullet-}$ (g = 1.9995) was reported for C_{60} adsorbed by activated 13 X molecular sieve which contains no oxidants.[11]

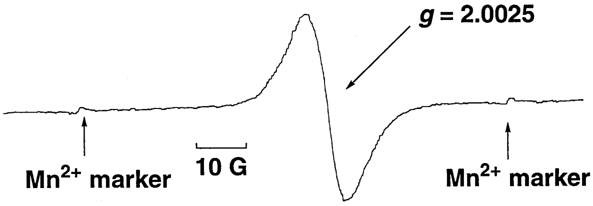

Figure 1. ESR spectrum of $C_{60}^{\bullet+}$ observed in Fe^{3+}-zeolite Y (180 mg, Fe^{3+}: 1.0 x 10^{-4} mol g^{-1}) pretreated at 873 K for 3 h and measured at 298 K.

The signal intensity (doubly integrated area) of C_{60} radical cation produced in the Fe^{3+}-exchanged zeolite with different amounts of exchanged Fe^{3+} increases drastically with an increase in the amount of exchanged Fe^{3+}, [Fe^{3+}] as shown in Figure 2a. Such a dependence of the ESR signal intensity depending on [Fe^{3+}] indicates that C_{60} is oxidized by electron transfer to Fe^{3+} to produce $C_{60}^{\bullet+}$. The g value and the linewidth are constant irrespective of [Fe^{3+}]. The ESR signal intensity also increases with an increase in the pretreatment temperature of the Fe^{3+}-zeolite sample containing C_{60} above the sublimation temperature (673 K)[14] as shown in Figure 2b. The size of C_{60} having a diameter of 7.1 Å may be small enough for C_{60} molecules to penetrate the zeolite supercage with the window diameter of 7.4 Å,[15] but the 7.4 Å openings are still too small for facile diffusion of C_{60} in the zeolite. The evaporation of C_{60} at higher temperatures may help C_{60} to squeeze into the oxidation site of Fe^{3+} inside the zeolite. Once $C_{60}^{\bullet+}$ is formed, it may be stabilized in the zeolite supercage.

When a degassed benzene solution of perylene was introduced into the Fe^{3+}-zeolite sample containing $C_{60}^{\bullet+}$ under vacuum at 298 K, the ESR signal of $C_{60}^{\bullet+}$ disappeared and instead that of perylene radical cation with the hyperfine structure was observed (g = 2.0027, a_1 = 3.0 G, a_2 = 0.6 G, a_3 = 3.8 G).[16] Since the one-electron oxidation potential of perylene (E^0_{ox} *vs.* SCE = 1.04 V)[17] is lower than the one-electron reduction potential of $C_{60}^{\bullet+}$ (E^0_{red} *vs.* SCE = 1.57 V)[8,9], electron transfer from perylene to $C_{60}^{\bullet+}$ should occur to produce perylene radical cation accompanied by disappearance of $C_{60}^{\bullet+}$. When tetramethyltin, the one-electron oxidation potential of which (Me_4Sn: E^0_{ox} *vs.* SCE = 1.56 V)[18] is just below the one-electron reduction potential of $C_{60}^{\bullet+}$, is chosen as a reductant, electron transfer from Me_4Sn to $C_{60}^{\bullet+}$ in the zeolite occurred, resulting in a drastic decrease in the ESR signal intensity of $C_{60}^{\bullet+}$. Thus, the reactivity of $C_{60}^{\bullet+}$ produced in the zeolite is consistent with that

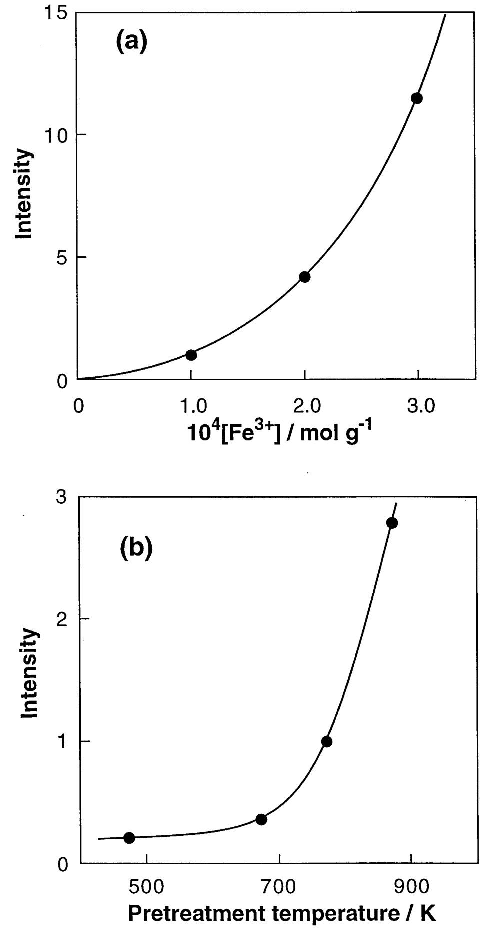

Figure 2. The doubly integrated ESR signal intensity of $C_{60}^{\bullet+}$ plotted against (a) the amount of Fe^{3+} loaded in the zeolite Y pretreated at 773 K for 3 h and (b) the pretreatment temperature with the fixed amount of Fe^{3+} loaded in the zeolite Y (1.0×10^{-4} mol g^{-1}). The doubly integrated intensity of the sample ($[Fe^{3+}] = 1.0 \times 10^{-4}$ mol g^{-1}, the pretreatment temperature = 773 K) is taken as unity.

expected from the high one-electron oxidation potential.

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