ESR Study of Radiation Induced Radicals Formed on Tetrafluoroethylene Adsorbed on Mordenite Zeolites

Hidenori Yahiro, Kazumitsu Yamaji, and Masaru Shiotani*
Department of Applied Chemistry, Faculty of Engineering, Hiroshima University, Higashi-Hiroshima 739

(Received April 13, 1995)

Two radicals, hydrogen addition-type radicals (CF_2H-CF_2•), and propagating radical of polytetrafluoroethylene (R-CF_2-CF_2•), were generated by γ-irradiation of tetrafluoroethylene adsorbed on zeolites. The formation mechanisms for two radicals are discussed based on the ESR results.

It is well known that the positive holes and electrons on zeolite, which are generated by γ- or X-ray irradiation, react with organic molecules adsorbed on zeolite to form the associated radical ions.[1] In addition, since zeolites are capable of stabilizing radicals, organic radicals formed have been extensively studied by electron spin resonance (ESR) spectroscopy.[2-4] For example, one of the present authors has found three different kinds of methyl radicals formed by irradiation of methane adsorbed on zeolite-A.[3] Toriyama et al.[4] have reported that some *n*-alkane radical cations have been generated and stabilized in irradiated zeolite systems. Also, cycloalkane radical cation formation on a zeolite has been reported by Trifunac and co-workers.[5] In contrast, little is known the radicals from irradiated halogenated hydrocarbons on zeolites. In this communication, the radical formation of tetrafluoroethyelen (TFE) adsorbed on zeolite was studied by means of ESR technique combined with γ-irradiation.

Mordenite with silica-alumina molar ratio of 7.6 in a Na^+ form (represented by Na-MOR) was supplied from Tosoh Corporation. Proton-exchanged mordenite (H-MOR) was prepared as described previously.[6] The zeolite sample was placed into a quartz tube for ESR measurement and dehydrated by heating to 673-773 K in vacuum. At 77 K, tetrafluoroethylene (PCR Inc., purity > 99%) was introduced into the dehydrated zeolite. The amount of TFE adsorbed on zeolites was *ca.* 50wt% based on TG analysis. The γ-irradiation (^{60}Co source) was performed at 77 K with about 1 Mrad. ESR spectra were recorded at various temperatures between 77 K and room temperature with a Bulker ESP 300E spectrometer. Note that the TFE adsorbed zeolite sample before γ-irradiation did not exhibit any observable ESR signal at 77 K.

Three selected ESR spectra of γ-irradiated TFE on H-MOR are depicted in Figure 1. The ESR spectrum observed immediately after γ-irradiation at 77 K consists of distinct signals with a large hyperfine anisotropy due to α-fluorine nuclei, as shown in Figure 1(a). The spectral line feature is different completely from the previously reported spectra of the cation- or anion-radical of TFE,[7] but it is very similar to that of the hydrogen addition-type TFE radical stabilized in alcohol.[8] Therefore, the ESR spectrum shown in Figure 1(a) can be readily assigned to the hydrogen addition-type TFE radical (CF_2H-CF_2•). The spectrum of CF_2H-CF_2• is very close to that of CF_3-CF_2•,[8] which is characterized by the hf anisotropies of two α-fluorines and two β-fluorines. Thus, the CF_2H-CF_2• spectrum did not allow us to determine the precise hf splitting due to the β-hydrogen of CF_2H-CF_2•. Shamonia and Kotov[9] have reported an ESR spectrum similar to Figure 1(a) after γ-irradiation of TFE/zeolite-A system and assigned it to the terminal or propagating radical of polytetrafluoroethylene (PTFE), R-CF_2-CF_2•. However, this assignment is questionable since the line futures are quite different from those of γ-irradiated PTFE reported by several investigators.[10, 11]

When Na-MOR was used instead of H-MOR, the ESR signal intensity of the hydrogen addition radical was markedly decreased. This result strongly suggests that a Brønsted acid (H^+) in a zeolite can be a precursor to the hydrogen atom, similar to the case of benzene/ZSM-5 zeolite system.[2]

The ESR spectrum of CF_2H-CF_2• decayed with increasing temperature, and almost disappeared at *ca.* 200 K.

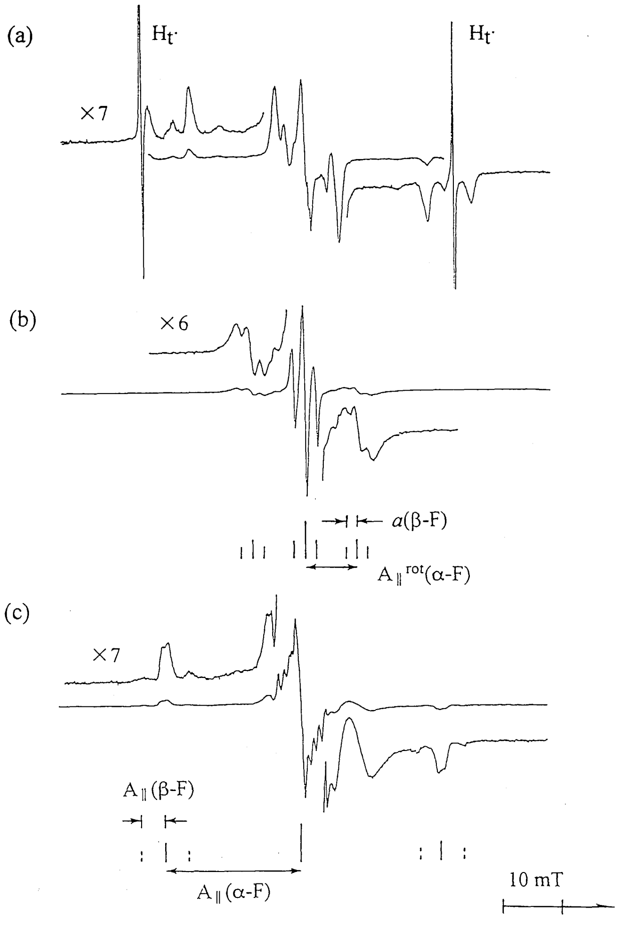

Figure 1. ESR spectra of the radical produced by γ-irradiation of tetrafluoroethylene adsorbed on mordenite zeolite. Spectra (a) and (b) were recorded at 77 K and room temperature after measuring spectrum (a), respectively, and spectrum (c) at 77 K after measuring spectrum (b). H_t• means the trapped hydrogen atom.

Simultaneously, the underlying spectrum became visible and was reversibly changed into a triple-triplet at room temperature as shown in Figure 1(b). The half hf splitting ($A_{\|}^{rot}(\alpha\text{-F})$) between the broad wing peaks was 8.7 mT, and the central triplet corresponding to $M_I = 0$ was 1.8 mT ($a(\beta\text{-F})$), suggesting the presence of two sets of two magnetically equivalent fluorines.

This radical showed temperature dependent ESR spectra. When the sample was cooled down again to 77 K, the spectrum shown in Figure 1(c) was observed. The wing peaks ($M_I = \pm 1$) due to the parallel hf component of two magnetically equivalent α-fluorines are clearly observed. The maximum splitting ($A_{\|}(\alpha\text{-F})$) estimated from the wing peaks is 22.4 mT which is in good agreement with that of the R-CF_2-CF_2• radical formed in PTFE at 77 K reported previously.[11] Thus, we can attribute the hf value to the parallel principal value of α-fluorine. The wind peaks are splitted into three additional hf lines with 4.1 mT due to two equivalent β-fluorines. The center band of the wing triplet is abnormally strong. This can be rationalized by overlapping another type of the propagating radical with non-splitted β-fluorine hf splitting: the hf splitting of β-fluorine depends strongly on the conformation of -CF_2- with respect to the unpaired electron orbital at α-carbon. A similar ESR spectrum has been already reported for the propagating radical or the terminal radical of PTFE and hyperfine coupling constants agree well with the ones reported for the γ-irradiated PTFE film.[10] Based on the above results, we conclude that the propagating radicals of PTFE were produced for the γ-irradiated TFE/zeolite system.

The formation of PTFE was confirmed as follows. The solid polymer was obtained separately from zeolite by dissolving the irradiated TFE/zeolite sample in hydrofluoric acid. Thus obtained polymer showed the IR spectrum[12] characteristic of PTFE.

The formation of the propagating radical into the cavity of Na-MOR can be supported by comparing with the results using zeolite-A. ESR spectrum for TFE/zeolite-A system, recorded at 77 K after γ-irradiation, shows a marked difference from the TFE/H-MOR system. The spectrum consists of seven lines corresponding to Na_2^+ radical without any ESR lines originating from adsorbed TFE. Since the maximum pore diameter of zeolite-A (4Å) is smaller than that of mordenite (*ca.* 7Å), it is difficult for TFE to enter into the zeolite cavity. These lead us to conclude that TFE adsorbed on extra-surface of zeolite cannot yield the propagating radicals.

The formation mechanisms for above two radicals, CF_2H-CF_2• and R-CF_2-CF_2•, are briefly discussed on the basis of the present ESR results. When the zeolite is γ-irradiated, holes and electrons are generated in zeolite. The electron reacts with proton involved in zeolite (*i. e.*, Brønsted acid) to form hydrogen atom.[2] The CF_2H-CF_2• radicals can be formed by the addition of this hydrogen atom to TFE. The hydrogen addition reaction may proceed more effectively when TFE is adsorbed at Brønsted acid site (H^+) so as to give a charge transfer type of interaction. On the other hand, the hole is transferred to TFE to yield the TFE cation radical. However, we could not observe the TFE cation at 77 K immediately after γ-irradiation. This suggests that the cation can initiate the polymerization reaction even at 77 K, probably because of its high concentration in the zeolite cavity, although we can not completely rule out a possibility that CF_2H-CF_2• is the precursor of the polymerization reaction. In fact, we have the ESR evidence showing R-CF_2-CF_2• at 77 K before annealing the sample to 200 K at which the CF_2H-CF_2• radical decayed out. The present experimental results suggest that most of the TFE molecules introduced form an aggregate state in the zeolite channel so as to yield the propagating radical even at a low temperature of 77 K after γ-irradiation. Otherwise, it would be difficult for TFE to diffuse in the zeolite to give rise to the propagating radical at 77 K. The reactions are summarized as follows:

$$\text{Zeolite} \rightsquigarrow (\text{Zeolite})^+ + e^- \tag{1}$$

$$H^+ (\text{Brønsted acid}) + e^- \longrightarrow H\bullet \tag{2}$$

$$H\bullet + CF_2{=}CF_2 \longrightarrow CF_2H\text{-}CF_2\bullet \tag{3}$$

$$(\text{Zeolite})^+ + CF_2{=}CF_2 \longrightarrow \text{Zeolite} + CF_2{=}CF_2^+ \tag{4}$$

$$CF_2{=}CF_2^+ + nCF_2{=}CF_2 \longrightarrow {}^+CF_2\text{-}(CF_2\text{-}CF_2)_n\text{-}CF_2\bullet \tag{5}$$

This study demonstrates the polymerization of TFE in the zeolite channel which is initiated by γ-irradiation. There have been reports on the formation of conducting polymer[13] in zeolites, but no attempt for PTFE/zeolite hybrids was made. The present results provide fundamental information on not only the radical formation in zeolite systems by γ-irradiation, but also a promising process for developing new organic/inorganic hybrid materials.

References and Notes

1 D. N. Stamires and J. Turkevich, *J. Am. Chem. Soc.*, **86**, 757 (1964).

2 M. Shiotani and M. Lindgren, *Molecular Eng.*, **4**, 179 (1994).

3 J. Sohma and M. Shiotani, *ACS Symposium Series*, **34**, 141 (1976); M. Shiotani, F. Yuasa, and J. Sohma, *J. Phys. Chem.*, **79**, 2669 (1975).

4 K. Toriyama, K. Nunome, and M. Iwasaki, *J. Am. Chem. Soc.*, **109**, 4496 (1987).

5 M. V. Barnabas, D. W. Werst, and A. D. Trifunac, *Chem. Phys. Lett.*, **187**, 565 (1991).

6 N. Mizuno, H. Mori, M. Tajima, S. Kagawa, H. Ueno, H. Yahiro, and M. Iwamoto, *J. Mol. Catal.*, **80**, 229 (1993).

7 A. Hasegawa and M. C. R. Symons, *J. Chem. Soc., Faraday Trans. 1*, **79**, 93 (1983); R. I. McNeil, M. Shiotani, F. Williams, and M. B. Yim, *Chem. Phys. Lett.*, **51**, 433 (1977).

8 M. Shiotani, unpublished data.

9 N. F. Shamonina and A. G. Kotov, *Vysokomol. Soedin., Ser. B*, **16**, 342 (1974).

10 S. Siegel and H. Hedgpeth, *J. Chem. Phys.*, **46**, 3904 (1967).

11 K. Toriyama and M. Iwasaki, *J. Phys. Chem.*, **73**, 482 (1968).

12 R. E. Moynihan, *J. Am. Chem. Soc.*, **81**, 1045 (1959).

13 P. Enzel and T. Bein, *J. Chem. Soc., Chem. Commun.*, **1989**, 1326; J. V. Caspar, V. Ramamurthy, D. R. Corbin, *J. Am. Chem. Soc.*, **113**, 600 (1991).