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EXTRA COUPLING OF AN ETHYL RADICAL ADSORBED ON THE ZEOLITES

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New ESR spectra were obtained from the irradiated ethane adsorbed on zeolites. The simulation method and an analysis indicate that the new spectra are those from ethyl radical having additional coupling with an extra proton.

The purpose of this letter is to report both interesting spectra obtained from the ethyl radicals adsorbed on the zeolite and interpretations of the spectra which give information on the trapping of the ethyl radicals on the zeolite surface.

The zeolites used in the experiments is 13-X supplied by Union-Carbide Corp. in U. S. A.. The zeolites were heat-treated under a vacuum either for five hours at 550°C (the high-temperature treated zeolite) or three hours at 150°C (the low-temperature treated zeolite). Ethane of 99.7% purity obtained from Takachiho Chemical Co. was introduced to the zeolite in a Spectrosil ESR sample-tube at 77°K and adsorbed on the zeolites. Radicals were produced at 77°K by γ-irradiation to the zeolites adsorbing ethane.

ESR spectrum observed from γ-irradiated zeolites without adsorbing ethane was found to be broad, asymmetric one. ESR spectra, which were observed from the γ-irradiated zeolites adsorbing ethane, showed clear multiplets which were believed to be the spectra from the radicals produced from the adsorbed ethane. An example of the spectra is shown as Fig. 1-a. This spectrum was obtained at 148°K from the irradiated ethane adsorbed on the low-temperature treated zeolite. The spectrum is definitely different from the spectrum of the ethyl radical either in liquid phase[1], or in a glassy state[2], or in adsorbed state on silica-gel.[3]

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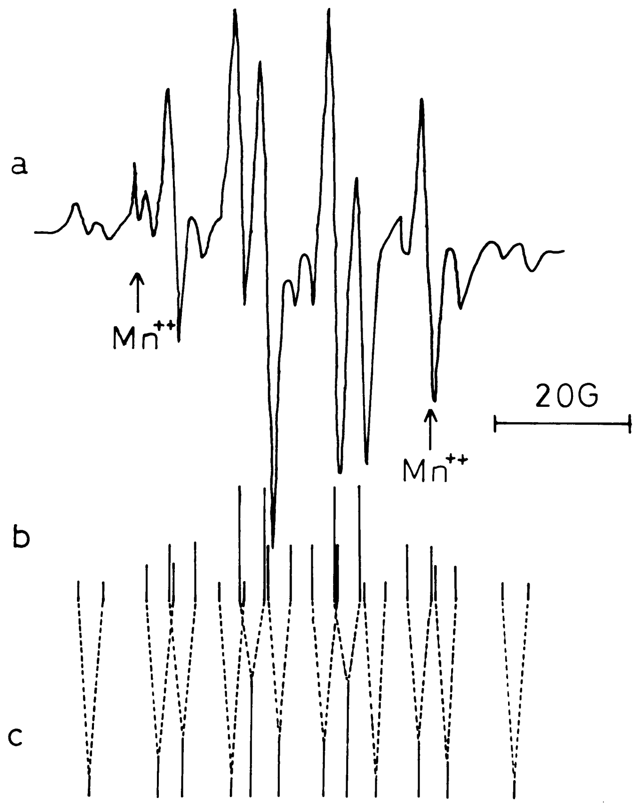

Fig. 1 a: spectrum observed at 148°K from the irradiated ethane adsorbed on the low-temperature treated zeolite. b: stick spectrum of the ethyl radical having extra doublet. c: normal spectrum of ethyl radical.[1)]

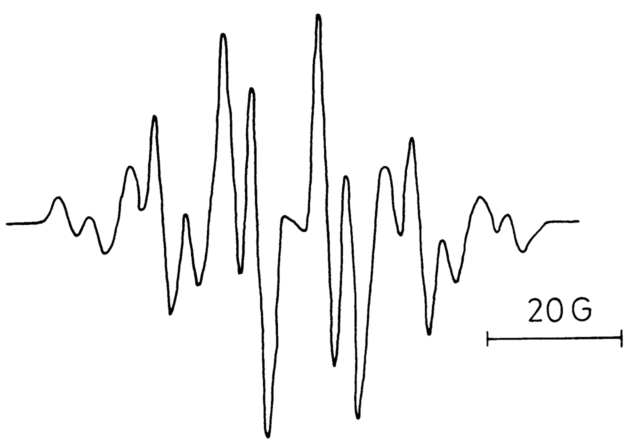

Fig. 2 simulated spectrum.

The main features of the spectrum agree with that obtained by assuming that each line of the spectrum (Fig. 1-c) of ethyl radical is split into a doublet, as shown in Fig. 1-b. The spectrum, shown in Fig. 2, was simulated spectrum based on the assumption that the couplings of 28.7 Gauss and 21.4 Gauss were taken for the three β protons and the two α protons, respectively, in the ethyl radical, and 8.0 Gauss for the separation of the extra doublet and 7.0 Gauss for the line width. The above assumed values for the couplings of both β and α protons in the ethyl radical are nearly equal to 26.9 Gauss and 22.4 Gauss, respectively, which are the experimental values[1)] of the β and α protons in the ethyl radical. In this simulation the asymmetric spectrum resulted from the irradiated zeolite was superposed with the relative weight of about 0.2 to the total spectrum. From the good similarity between the observed spectrum and the simulated one it is concluded that the observed spectrum is the spectrum of the extraordinary type of ethyl radical showing the additional doublet. Although appearance of the spectrum observed from the irradiated ethane adsorbed on the high-temperature treated zeolites was different from that observed from the ethyl radical adsorbed on the low-temperature treated zeolite, it was found that the observed spectrum was nicely simulated only by changing the coupling constant of the extra doublet from 8.0 Gauss to 12.0 Gauss in this case, too. This fact indicates that the trapping mechanism is similar for the two type of zeolites, which were heat-treated in different ways.

There are three plausible mechanisms to give such a extra-doublet: i) Spin flip transitions,[4),5)] ii) Additional lines due to the forbidden transition caused by the second order effect,[6)] iii) A coupling with an additional proton. Although the first mechanism, the spin flipping, gives the satellite lines appearing as a doublet, such satellites are always accompanied with the main lines at the center of the doublets and much more smaller than the main lines. No main central-line was observed in this case and therefore one can rule out this spin-flipping mechanism. The forbidden lines caused by the second-order effect may appear as intense as the allowed lines in the special case[6)] of that $\log\left(\frac{2g_I\beta_I H}{A_{zz}}\right)$ is nearly equal to 0.2, where g_I and β_I are the nuclear g factor and the Bohr magnetons of proton respectively, H is the static magnetic field along the Z axis and A_{zz} is a component of the coupling tensor corresponding to the coupling between the Z components of both electron and nuclear spins. However, the static magnetic field H which resonates the Lamor frequency of the X-band does not satisfy the above condition for the observed A_{zz}. Thus, one can discard this second-order effect. Above arguments convinced us that the most reasonable mechanism giving the extra-doublet is the extracoupling of the ethyl radical with an additional proton. It is interesting to note that such doublet-splitting due to the extra proton was reported on the methyl radical trapped on the silica-gels.[5)] In order to check the origin of this extra-proton, the hydrogens in the surface of the zeolite were replaced with deuterium by soaking the heat-treated zeolite in heavy water for several days within the vacuum line followed by the usual low-temperature treatment. It was found that ESR spectra observed from the ethyl radicals adsorbed on such deuterated zeolite was identical to those observed from the radicals adsorbed on the ordinary zeolite. This result strongly suggests that the extra proton giving the additional doublet is not a silanol proton but the proton which may originate from a mother molecule, ethane, and be trapped on the specific site of the zeolite.

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