

EPR study of highly stable methyl radicals trapped in synthetic H-rho zeolite

Marek Danilczuk,
Jarosław Sadło,
Anders Lund,
Hirohisa Yamada,
Jacek Michalik

Abstract Methyl radicals generated by γ -irradiation in the proton form of synthetic rho zeolite exposed to CH_4 have been investigated by electron paramagnetic resonance (EPR) in the temperature range 110–370 K. Depending on the methane adsorption temperature two EPR spectra of $\cdot\text{CH}_3$ radicals were recorded. The isotropic quartet observed after CH_4 adsorption at room temperature was assigned to $\cdot\text{CH}_3$ radicals freely rotating in the middle of octagonal prism. After adsorption at 413 K, the isotropic quartet is overlapped with the second signal characterized with anisotropy of hyperfine splitting and g-value. It is postulated that anisotropic signal represents the $\cdot\text{CH}_3$ radicals located in α -cages and strongly interacting with silicaalumina framework. The mechanisms of radiolytic formation of methyl radicals and the possible stabilization sites are also discussed.

Key words methyl radicals • zeolite rho • EPR • radiolysis

M. Danilczuk
Institute of Nuclear Chemistry and Technology,
16 Dorodna Str., 03-195 Warsaw, Poland
and Department of Physics and Measurements
Technology, Linköping University,
S-581 83 Linköping, Sweden

J. Sadło, J. Michalik[✉]
Institute of Nuclear Chemistry and Technology,
16 Dorodna Str., 03-195 Warsaw, Poland,
Tel.: +48 22-8112347, Fax: +48 22-8111532,
E-mail: esrlab@orange.ichtj.waw.pl

A. Lund
Department of Physics and Measurements Technology,
Linköping University,
S-581 83 Linköping, Sweden

H. Yamada
National Institute for Material Science
and Technology (AIST),
1-1 Namiki, Tskuba, Ibaraki 305 0044, Japan

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Introduction

The hydrocarbon radicals are among the most fundamental and important reactive intermediates which are of wide interest in chemistry. A number of EPR investigations have been carried out concerning hydrocarbon radicals isolated in low temperature matrices of halocarbons [14, 17, 21], noble gases [5, 8, 9, 12], organic crystals [11] as well as adsorbed on porous surfaces [7, 15]. However, the studies of radicals stabilized in inert gas matrices are limited to the narrow temperature range which makes impossible investigations of temperature dependent effects, as for example molecular dynamics of radicals. In contrast, on the solid surfaces radicals can be stabilized in a much wider temperature range and easily identified by EPR spectra with specific asymmetric line profiles.

Due to their many applications zeolites are very attractive technological materials especially as heterogeneous catalysts in petrochemical processes. The reactive intermediates formed in zeolite cages are affected by the geometry and electrostatic field of zeolite lattice which is able to modify the reaction path [4, 18, 22, 23]. Thus, the zeolites offer new possibilities to study the reactivity of short-lived species and to control catalytic reactions. The EPR spectroscopy is very useful to identify the paramagnetic intermediates of catalysis with zeolite active centers and their interactions. Owing to that the transformation of adsorbed molecules can be followed.

From chemical point of view it is important to understand the mechanism of methane conversion to liquid hydrocarbons. As a prototype reaction of catalytic conversion of hydrocarbons in zeolites, hydrogen

exchange reaction of methane with proton of zeolite Brönsted sites have been investigated. It has been proved experimentally and theoretically that methane molecules after adsorption on zeolite form a transition complex with Brönsted acid sites or exchangeable cations [1, 20]. The most stable configuration of adsorbed CH_4 is achieved via two hydrogen bonds with lattice OH groups. The mechanism of proton exchange in zeolites has been studied intensely during recent years, but the nature of the transition complex is still not fully understood [10].

The EPR spectra of methyl radicals trapped in frozen matrices of liquid hydrocarbons are well known. They are characterized by isotropic hyperfine parameters and binomial line intensity distribution. In contrast, radicals adsorbed on solid surfaces have an asymmetric line profile and usually give axially symmetric spin Hamiltonian parameters. A deviation from binomial line intensity distribution has also been observed for surface radicals [15].

The present paper reports an EPR study on methyl radicals generated radiolytically at 77 K in synthetic rho zeolite exposed to methane before γ -irradiation.

Experimental

Sodium-cesium form of zeolite rho, NaCs-rho, was synthesized by the modified method described by Robson *et al.* [13]. The purity and crystallinity of the product were monitored by powder X-ray diffraction (XRD) method with $\text{CuK}\alpha$ radiation (RIGAKU: RINT2200) and the XRD pattern was compared with that given by van Ballmoos [19]. After synthesis, NaCs-rho was exchanged three times with 20% solution of NH_4NO_3 followed by calcination at 573 K in air for 20 h to give the protonic form. The D-rho zeolite was obtained after exchange of the protonic form with D_2O at room temperature for 24 h. The exchange procedure was repeated three times.

The samples of rho zeolite were placed into suprasil EPR tubes and dehydrated *in vacuo* whilst gradually raising temperature to 473 K. Oxidation with static O_2 at 573 K was then carried out for 2 h. Thereafter, oxygen was pumped off at the same temperature for the next 2 h. The adsorption of methane was carried out at room temperature and at 413 K under a pressure of 0.4 kPa and 8 kPa for 24 h. Then, the zeolite samples were irradiated in a ^{60}Co -source at liquid nitrogen temperature (77 K) with a dose of 5 kGy. The EPR spectra were measured with an X-band Bruker ESP-300E spectrometer equipped with a Bruker ER 4111 VT variable temperature unit operating in the temperature range 110–370 K. The g-value was determined using a DPPH specimen for field calibration.

Results and discussion

The structure of rho zeolite (Fig. 1) consists of α -cages connected by octagonal prisms forming a body-centered cubic unit cell comprising two α -cages and six octagonal prisms. The α -cages, which are composed of eight-, six-

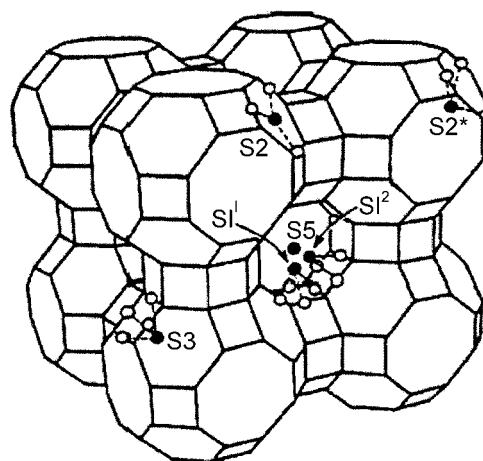


Fig. 1. The framework structure of zeolite rho showing preferential cation sites.

and four rings are the same 26-hedra that exist in zeolite A. However, in zeolite A each α -cage is connected to six neighboring β -cages by the so-called single eight-membered rings, whereas in zeolite rho the α -cages are joined by double eight rings (octagonal prism). The arrangement of α -cages in zeolite rho leads to two identical but intertwined systems of channels connecting the α -cages via an octagonal prism with a free diameter of 0.51 nm. This makes zeolite rho catalytically attractive because all cation sites are equally accessible for adsorbate molecules.

The EPR spectrum at 110 K of γ -irradiated H-rho zeolite exposed to 0.4 kPa methane shows an asymmetric singlet at $g = 2.0008$ of radiation-induced paramagnetic center in the zeolite framework similar to the signal observed in irradiated H-rho zeolites without any adsorbate. As the sample is heated up to 150 K, an isotropic quartet appears with binomial line intensity distribution 1:3:3:1, $A_{\text{iso}} = 2.3$ mT and $g_{\text{iso}} = 2.0026$ characteristic of methyl radical $\cdot\text{CH}_3$. The EPR spectra of $\cdot\text{CH}_3$ and $\cdot\text{CD}_3$ radicals measured at 210 K when the line intensities are the highest are shown in Fig. 2. The EPR signals for the methyl radicals are surprisingly stable and are still observed at 310 K.

The highly symmetric shape of the observed quartet with narrow lines and $A_{\text{iso}} = 2.3$ mT identical with the hyperfine splitting of methyl radicals observed in liquid methane and a frozen krypton matrix [2, 6, 11] prompted us to conclude that $\cdot\text{CH}_3$ radicals observed in that experiment are not adsorbed on the silicaalumina lattice but are stabilized in the void of octagonal prisms where they are freely rotating.

When methane is adsorbed at a pressure of 8 kPa, the EPR spectrum of methyl radicals shows larger linewidth (0.6 mT) and decays above 210 K. The line broadening is attributed to weak dipolar interaction of the unpaired electron with hydrogen atoms of methane molecules in the vicinity of $\cdot\text{CH}_3$ radical. The distance between CH_4 and $\cdot\text{CH}_3$ molecules decreases at higher methane pressure which results in the EPR line broadening and faster decay of $\cdot\text{CH}_3$ at low temperatures.

In dehydrated D-rho zeolite exposed to 0.4 kPa methane at room temperature, the EPR spectrum recorded at 110 K shows only an asymmetric singlet at

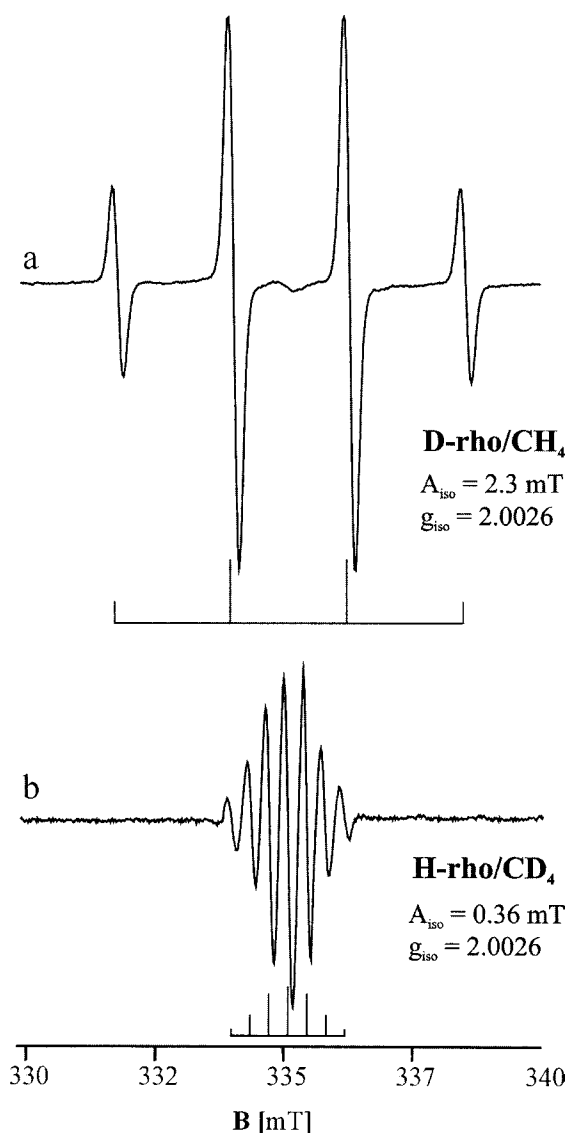
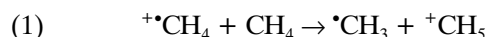


Fig. 2. EPR spectra recorded at 210 K of γ -irradiated H-rho zeolites exposed to 0.4 kPa methane. a – CH₄, b – CD₄.

$g = 2.0008$ similar to that observed in H-rho zeolite at the same temperature. During thermal annealing at 150 K an intensive isotropic quartet with binomial intensity ratio of $\cdot\text{CH}_3$ radical ($A_{\text{iso}} = 2.3$ mT, $g_{\text{iso}} = 2.0028$, $\Delta H_{\text{pp}} = 0.15$ mT) is recorded. No visible differences between EPR signals of methyl radicals in dehydrated H-rho and D-rho zeolites were observed. Thus, no proton-exchange reaction between the zeolite lattice and methane molecule or/and methyl radicals takes place. This result was confirmed in experiments with perdeuterated methane. Only isotropic septet with hyperfine splitting of 0.36 mT was observed in H-rho/CD₄ zeolite in the temperature range of 170–270 K (Fig. 2b). No contribution of $\cdot\text{CH}_3$ quartet was recorded. The observed hyperfine splitting of $\cdot\text{CD}_3$ is in agreement with the ratio of the magnetic moments of deuterium and proton.

The experimental fact that $\cdot\text{CH}_3$ radicals are observed only after sample annealing above 150 K can be explained as follows. After irradiation at 77 K, the $\cdot\text{CH}_4$ cations are formed as a result of either positive

hole transfer from the framework to CH₄ molecules or electron transfer from methane to the lattice hole center. The X-ray diffraction data of H-rho/CH₃Cl proved that methyl chloride molecules are situated preferentially in the center of octagonal prism with one hydrogen atom at the center of octagonal window [3]. By analogy we assume the same arrangement of CH₄ molecule in octagonal prism. At temperatures above 150 K, when molecules become mobile, $\cdot\text{CH}_4$ cations react with migrating methane molecules forming in octagonal prisms methyl radicals:



At temperatures over 310 K, $\cdot\text{CH}_3$ radicals start migrating from octagonal prism to the centre of supercages and the EPR signal of methyl radicals disappears.

It is well known that the adsorption capacity for similar zeolite structure depends strongly on temperature. When methane is adsorbed under the pressure of 0.4 kPa at 413 K in H-rho zeolite the EPR spectra are different than those for samples exposed to CH₄ at room temperature. At 150 K, the symmetric quartet A with EPR parameters, the same as observed in the samples exposed to CH₄ at room temperature, is recorded. However, during thermal annealing above 210 K a new EPR signal appears, an asymmetric quartet B with EPR parameters: $A_{\perp} = 2.41$ mT, $A_{\parallel} = 2.3$ mT, $g_{\perp} = 2.0033$, and $g_{\parallel} = 2.0029$ (Fig. 3) similar to methyl radicals

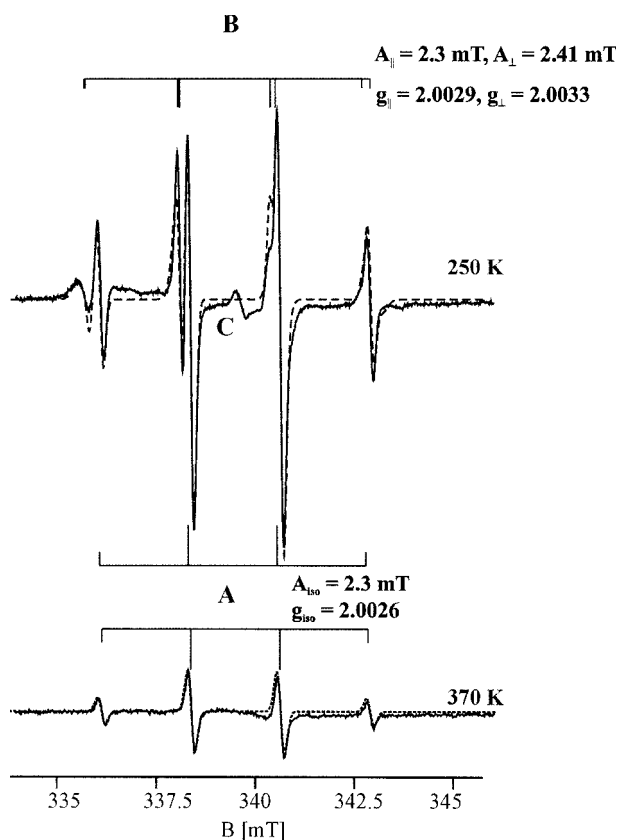


Fig. 3. EPR spectra of γ -irradiated H-rho zeolite exposed to 0.4 kPa methane at 413 K recorded at 250 K and 370 K. A – signal of freely tumbling $\cdot\text{CH}_3$ radical, B – signal of $\cdot\text{CH}_3$ radical interacted with silicalumina framework, C – signal of paramagnetic lattice center.

adsorbed on solid surfaces. Then the experimental spectrum (solid line) consists of two overlapped quartets A and B representing different types of methyl radicals and singlet C of the lattice paramagnetic centers. The simulated spectrum (dashed line) is a sum of A and B signals with Gaussian line shape, the linewidth $\Delta H_{pp} = 0.2$ mT and the EPR parameters given above.

The hyperfine coupling constant of the B methyl radical is higher than for methyl radicals in liquids (2.3 mT) and methyl radicals trapped on a solid surface (2.2 mT) [15, 16]. The anisotropy of quartet B suggests that it represents methyl radicals whose ability for rotation is limited. Thus, we assigned quartet B to $\cdot\text{CH}_3$ radicals strongly interacting with silicaalumina lattice sites which become accessible for CH_4 molecules at 413 K. The sites are probably located in α -cages because spectrum B disappears completely above 270 K in contrast to spectrum A which was still observed at 370 K.

The high stability of methyl radical A in rho zeolite might be due to the fact that the kinetic diameter of the methyl radical (2.6 Å) is very close to the diameter of octagonal prism (3.6 Å) where methyl radicals are supposed to be stabilized. Thus, the silicaalumina lattice protects $\cdot\text{CH}_3$ in octagonal prisms against the attack of reactive species whereas radicals in α -cages are vulnerable.

Conclusions

H-rho zeolite exposed to CH_4 after γ -irradiation stabilizes $\cdot\text{CH}_3$ radicals at temperatures higher than room temperature. Depending on the adsorption conditions, methyl radicals are trapped in two different sites. The first one, in the middle of octagonal prism enables free tumbling of $\cdot\text{CH}_3$ radical. The second one, close to the zeolite lattice in α -cage hinders $\cdot\text{CH}_3$ rotation. The EPR results for D-rho/ CH_4 and H-rho/ CD_4 clearly showed that proton exchange between the methane molecule and lattice protons was not involved in the mechanism of radiolytic generation of methyl radicals in zeolites.

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