Radicals formed from Ethylbenzene Adsorption on the Zeolites H-Mordenite and H-ZSM-5

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Three types of radicals have been formed by hydrogen atom abstraction in ethylbenzene adsorption on acidic zeolites with different Al contents and structures, which also exerted an important influence on the electronic nature of the radicals.

Recently, interesting results of e.s.r. investigations of the adsorption states and transformation pathways of alkenes and some aromatics adsorbed on acidic zeolite catalysts, have been reported.[1—3] However, few studies have been carried out on the adsorption of alkylbenzenes with an alkyl group $>C_1$, such as ethyl, isopropyl, and t-butyl, which were important probe molecules for characterising the catalytic properties of solid acid catalysts. We reported earlier an α-hydrogen atom abstraction from ethylbenzene and cracking of some other alkylbenzenes at room temperature on H-mordenite.[4] The

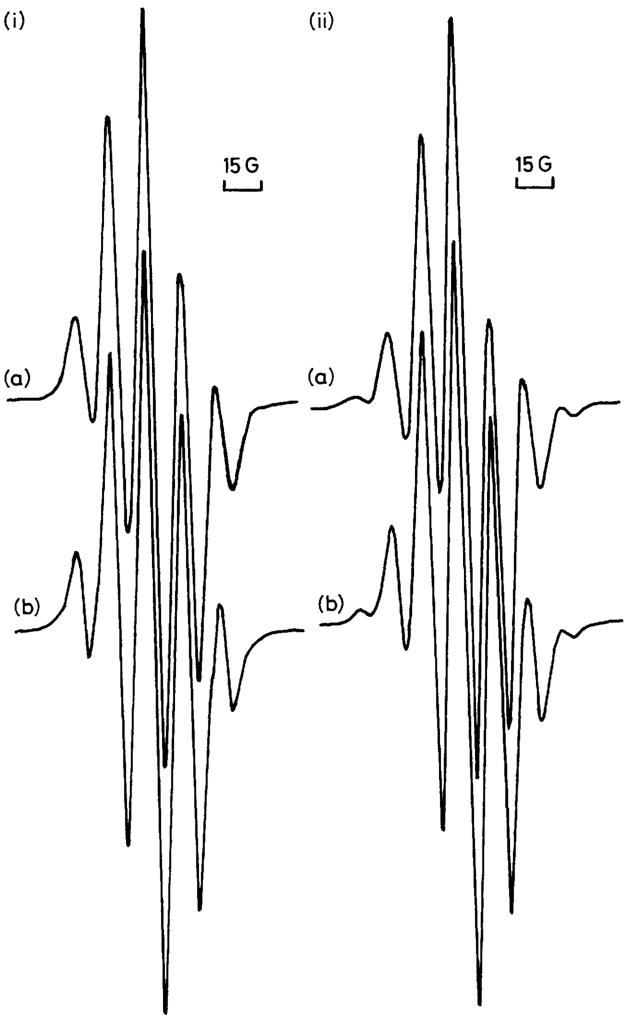

Figure 1. E.s.r. spectra: (i): (a) EB adsorbed on HM-1 at T_a, 30 min; (b) theoretical simulation of (a) due to $\mathrm{Ph\dot{C}HCH_3}$ with $a_{\alpha,\beta}$ 15.00 G and ΔH_{PP} 5.16 G. (ii) (a) EB adsorbed on HM-2 at T_a, 30 min; (b) theoretical simulation of (a) due to $\mathrm{Ph\dot{C}HCH_3}$ (I), with $a_{\alpha,\beta}$ 13.86 G and ΔH_{PP} 5.50 G, and $\mathrm{PhCH_2\dot{C}H_2}$ (II), with a_α 14.25 G, a_β 27.45 G and ΔH_{PP} 5.50 G. $\Delta g = g_I - g_{II} = 0$ and I/II = ~8.

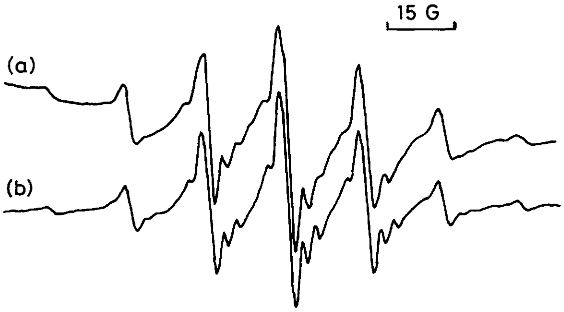

Figure 2. E.s.r. spectra: (a) EB adsorbed on H-ZSM-5 at T_a, 30 min; (b) theoretical simulation of (a) due to $\mathrm{Ph\dot{C}HCH_3}$ (I), with $a_{\alpha,\beta}$ 17.37 G and ΔH_{PP} 2.20 G, $\mathrm{PhCH_2\dot{C}H_2}$, (II), with a_α 17.78 G, a_β 34.35 G and ΔH_{PP} 2.20 G, and $\mathrm{Ph\dot{C}HCH_3}$ (III), with $a_{\alpha,\beta}$ 17.37 G, a_{ortho} 2.75 G, a_{para} 4.85 G, a_{meta} 0 G and ΔH_{PP} 1.90 G. $\Delta g = g_I - g_{II} = 0$, $\Delta g = g_I\ (g_{II}) - g_{III} = 0.0008$ and I:II:III = ~8:2.3:1.7.

present work investigates in more detail the adsorption states of ethylbenzene (EB) on zeolites with different aluminium contents and structures.

For the H-mordenite samples, HM-1 with Si/Al = 6.3 was obtained by decomposing repeatedly NH_4^+-exchanged NaM, and HM-2 with Si/Al = 20.1 was obtained by refluxing HM in concentrated HCl (6 M) for several hours. The H-ZSM-5 sample (Si/Al = 23) was prepared by template-free synthesis followed by exchange with aqueous HCl. Samples were pretreated under oxygen and degassed in an e.s.r. tube at 540 °C for H-mordenites and at 600 °C for H-ZSM-5. The adsorption was performed at room temperature at the equilibrium pressure of EB, previously purified using the freeze–thaw method. The e.s.r. spectra were recorded at room temperature on a Jeol JES-FE2XG spectrometer with 100 kHz modulation. The theoretical simulation, for which Lorentzian line shape was used, was carried out on a Jeol ES-PRIT23 ESR Data System.

Figures 1(i) and 1(ii) show the results obtained on HM-1 and HM-2. In the case of EB adsorbed on HM-1, five intense lines were observed with an approximately binomial distribution of 1:4:6:4:1, a hyperfine splitting constant (hfsc) a = 15.00 G (1G = 10^{-4} T), a central line-width ΔH_{PP} = 5.16 G, and a g value of 2.0037 [Figure 1(i) (a)]. The spectrum could be attributed to the formation of $\mathrm{Ph\dot{C}HCH_3}$ radicals by the abstraction of an α-hydrogen atom from the ethyl group, in which the unpaired electron was localised and of which the one α- and three β- hydrogen nuclei exhibited the same hfsc: theoretical simulation confirmed this [Figure 1(i) (b)].

When EB was adsorbed on HM-2, a spectrum consisting of seven quasi-equidistant lines, instead of five, was obtained. The results seemed puzzling at first; the radical $\mathrm{Ph\dot{C}HCH_3}$, even taking the different configurations resulting from its possible restricted mobility into consideration, could not give such a seven-line spectrum. Another explanation may be the formation of $\mathrm{PhCH_2\dot{C}H_2}$ by β-hydrogen atom abstraction, which could have a seven-line spectrum if the values of a_α and a_β are significantly different; however, the intensity distribution of 1:2:3:4:3:2:1 for this radical does not fit our observations. Finally, the calculated spectrum arising from the simultaneous formation of radicals by α- or β-hydrogen atom abstraction, with a relative intensity ratio of the former to the latter of about eight, conformed well to the experimental results [Figure 1(ii) (b)].

Radicals formed by the abstraction of a β-hydrogen atom are less stable than those formed by the abstraction of an α-hydrogen atom.[5] The present results suggest that the dealumination created some active sites suitable for the formation of a small quantity of the less stable radicals. Another important effect of the dealumination is that it decreased the hfsc of the major radicals from 15.00 to 13.86 G and increased the central line-width from 5.16 to 5.50 G.

The spectrum recorded after EB adsorption on H-ZSM-5 is given in Figure 2(a). Apart from the seven main lines, there appeared several other lines which were shown by a study of their saturation behaviour at different microwave powers, to arise from another new type of radical. Thus, three types of radicals were formed during EB adsorption on this zeolite. Theoretical simulation demonstrated that this new type of radical was formed by the abstraction of an α-hydrogen atom from the ethyl group with part of the unpaired electron delocalised to the benzene ring [Figure 2(b)]. The delocalisation of the unpaired electron to the benzene ring is a well known phenomenon in the case of the benzyl radical, and theoretical calculations and experimental results have shown that the *meta* hydrogen nuclei of the ring have a much smaller hfsc than the *ortho* and *para* nuclei.[6,7] However, the hfsc due to ring hydrogen nuclei of the radicals considered here are smaller (a_{ortho} 2.75, a_{para} 4.85 G, neglible for the two *meta* hydrogen nuclei) than those of benzyl radical (a_{ortho} 5.14, a_{para} 6.14, and a_{meta} 1.75 G). This may reflect the influence of the methyl group or an interaction between the radical and the zeolite active site, decreasing the electron density at the aromatic ring.

Compared with H-mordenite, H-ZSM-5 gave rise to the formation of radicals with a greater hfsc due to the alkyl hydrogen nuclei and a smaller line-width (see captions to Figures 1 and 2).

The nature of the redox centre of acidic zeolites (iron impurities, solid-state defects, surface Lewis acid sites ?) has been a subject of controversy. Lange *et al.*[1] demonstrated recently that surface Lewis acid sites were the most probable electron acceptor sites. Our results indicate the same assumption for hydrogen atom abstraction.

The proportionality between spin density, ρ, and a, $a = Q\rho$ (Q is a constant), has been long established by McConnell.[8] For the same radical in a different environment, the variation of hfsc may well reflect the different degrees of interaction between radicals and their environment. The above decreasing order of hfsc values for H-ZSM-5, HM-1, and HM-2, due to alkyl hydrogen nuclei, was therefore an indication of an increasing degree of interaction between the radicals and active sites of the different zeolites, which was related to surface Lewis acid sites. Variation of ΔH_{PP} may give supplementary information on the degree of such interaction. Thus, this work could present a sensitive method for determining the electronic nature or strength of zeolite acid sites, which is not easy to measure by other physicochemical methods.

The fact that $Ph\dot{C}HCH_3$ on H-mordenite does not exhibit any delocalisation of the unpaired electron to the benzene ring, in contrast to the benzyl radical, may now be explained by the strong interaction of the radicals with the zeolite active sites, *i.e.*, by which the unpaired electron strongly 'delocalised' to the zeolite structure. When this interaction is not strong enough, the aforementioned delocalisation can be observed, as in the case of H-ZSM-5.

Although the electron acceptor nature of the active sites of H-ZSM-5 was not so pronounced as those of H-mordenite, the relative concentration of the radicals formed by β-hydrogen atom abstraction was no lower than on the latter. This suggests that the formation of such radicals could not be indicative of the strength of corresponding active sites, and may result from a zeolite cavity or channel structure effect. The structure of the zeolite evidently has an important influence on the strength of the active sites for different types of zeolites and, perhaps, also on the structure of the radicals formed for a given zeolite.

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