Nature of the Radicals Formed on Adsorption of Unsaturated Hydrocarbons on Rare Earth-exchanged X Zeolites

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Summary Adsorption of unsaturated hydrocarbons on rare earth-exchanged zeolites affords $[RH]^{\overline{\cdot}}$ ion-radicals formed by electron transfer.

ZEOLITES are well known to be capable of stabilizing radicals.[1] When adsorbed on zeolites and irradiated with γ-, *X*-, or u.v. rays, numerous inorganic and organic substances produce radicals stable in the zeolite matrix.[2] Recently, unsaturated hydrocarbons adsorbed at low temperatures on some cation-exchanged zeolites have been found to produce radical species[3,4] with e.s.r. spectra identical with those described earlier.[2] All these spectra show hyperfine structure, are symmetric, and have an odd number of lines.

In attempts to explain the structure of these radicals, several investigators[4,5] have assumed these to be either radicals or alkyl ion-radicals formed by addition or abstraction of a hydrogen atom or proton; for example, n-butenes could yield the radicals or ion-radicals in the Scheme.

$$\begin{aligned} CH_3\text{–}CH_2CH{=}CH_2 &+ H\cdot \rightarrow CH_3\text{–}CH_2\text{–}\dot{C}H\text{–}CH_3 \\ &- H\cdot \rightarrow CH_3\text{–}\dot{C}H\text{–}CH{=}CH_2 \\ &+ H^+ \rightarrow [CH_3\text{–}CH_2\text{-}\dot{C}H\text{–}CH_3]^+ \\ &- H^+ \rightarrow [CH_3\text{-}CH\underline{\cdots}CH\underline{\cdots}CH_2]^- \end{aligned}$$

SCHEME

In agreement with the general principle that n protons present in the molecule will yield $n+1$ lines, each of the above species should produce signals with an even number of lines. However, the experimental spectra have an odd number of lines. If the structure is to remain undistorted, the odd-lines spectrum could be formed only when the number of protons in the radical species was identical with that in the original olefin molecule. This has given rise to the supposition that during the adsorption electron transfer takes place from the zeolite to the olefin adspecies. Analogous radical species were formed on adsorption of aromatic compounds, *e.g.* benzene, indicating that electron transfer was from the zeolite to the hydrocarbon with the formation of a strongly bound anion-radical. To verify this supposition, it was necessary to establish the origin of the electrons. We therefore carried out measurements on a series of Ce-, La-, and Pr-exchanged X and Y zeolites activated for 1—4 h *in vacuo* (10^{-5} Torr) at 200—600 °C in a reaction vessel enabling the kinetics of formation of the radical species to be followed directly in the cavity of the e.s.r. spectrometer (JES-ME-3X). Just at the moment of adsorption, distinct e.s.r. signals due to radicals could be observed, whose intensity rose as the temperature of activation, time of contact, and replacement of sodium for rare earth cations were increased. The signal intensity was again found to increase rapidly when activation had been carried out under oxygen (Figure 1), thus confirming the phenomenon reported earlier.[6] An even more distinct rise in intensity was observed upon preadsorption of O_2 and CO. Ion-radicals O_2^- and CO_3^- were then found, with parameters consistent with literature values.[7]

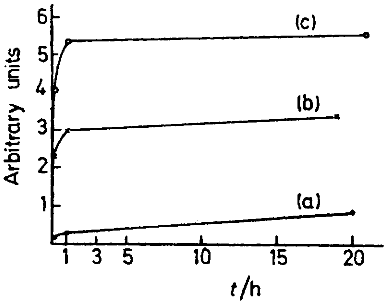

FIGURE 1. E.s.r. signal intensity of radical species *vs.* time (t) after adsorption of but-1-ene on CeX (68) zeolite: (a) activation at 500 °C; (b) activation 400 °C, addition of O_2; (c) activation 500 °C, addition of O_2.

On adsorption of monoolefins, dienes or aromatic hydrocarbons on zeolites carrying the preadsorbed ion-radicals O_2^- and CO_3^-, spectra were observed of the corresponding hydrocarbon ion-radicals, accompanied by simultaneous progressive disappearance of O_2^- and CO_3^-. In Figure 2 this process is exemplified by the adsorption of butene on a CeX (68) zeolite bearing preadsorbed O_2 and CO.

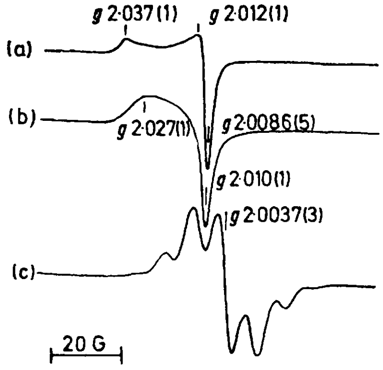

FIGURE 2. E.s.r. spectra of radical species on CeX (68) zeolite: (a) after adsorption of O_2; (b) after adsorption of O_2 then CO; (c) after addition of but-1-ene to sample (a) or (b). Figures in parentheses after *g*-values are errors in final figure.

On adsorption of benzene (Figure 3), the individual stages of the process could be followed (the spectra did not coincide).

In each case studied, after unsaturated hydrocarbons had been adsorbed on zeolites activated *in vacuo* or under O_2 or CO, the spectra of the resulting ion-radicals had identical parameters, suggesting electron transfer from electron donating centres of the zeolite to the hydrocarbon adsorbed species. Electrons may be donated by cerium cations, Ce^{3+}, or redox centres.[8] O_2^- and CO_3^- ion-radicals facilitate this process.

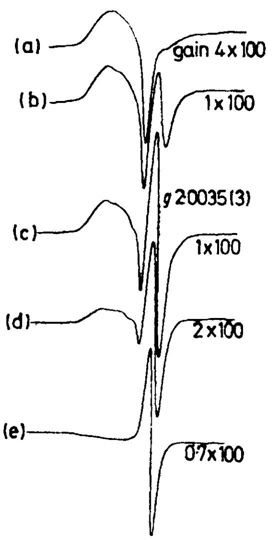

FIGURE 3. E.s.r. spectra of radical species on CeX (68) zeolite: (a) after adsorption of O_2 and then CO; (b)—(e) after adsorption of benzene (b) 4 min after; (c) 15 min; (d) 58 min; (e) 2 days.

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