Allylic Radicals from Simple Olefins Adsorbed on Hydrogen Mordenite Catalyst: Electron Spin Resonance Study

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Summary The e.s.r. spectra obtained following the adsorption of simple C_3—C_5 olefins on a hydrogen mordenite catalyst suggest the presence of adsorbed allylic radicals derived from an oligomer of the olefin.

Several authors[1] have recently reported e.s.r. spectra resulting from the adsorption of olefin molecules on a variety of cation-exchanged zeolites. No completely satisfactory description of the radical species exists, except in the few instances that the observed spectra may be attributed to the corresponding radical cation of the olefin.[1c] Spectra have now been recorded, which may be interpreted in terms of allylic radicals formed during the adsorption of a series of simple olefins on a partially dehydrated hydrogen mordenite catalyst.

Figure (a)† illustrates the spectrum obtained when 2·5 kN m^{-2} of propene is adsorbed at room temperature on a sample of Norton H-Zeolon synthetic hydrogen mordenite catalyst which had previously been outgassed in a pressure of *ca.* 2×10^{-4}N m^{-2} for 12 h at 723 K, followed by treatment in 13·5 kN m^{-2} of oxygen for 2 h at the same temperature. Identical spectra, consisting of a total of nineteen lines separated by 8·1 G, resulted from the adsorption of either but-1-ene or pent-1-ene at room temperature on a similarly treated catalyst.

A stick plot analysis, Figure (b), shows that the experimental spectrum may be satisfactorily reproduced by the following proton hyperfine coupling constants; $a_1 = 33{\cdot}6$ (triplet), $a_2 = 16{\cdot}8$ (quintet), and $a_3 = 8{\cdot}1$ G (triplet). This analysis is inconsistent with the propene radical cation, which in any case would only be formed with difficulty (ionisation potential of propene, 9·73 eV[2]). It is also incompatible with a partially charged isopropyl radical formed by hydrogen addition, as suggested by Ras,eev.[1b] A reasonable interpretation of the calculated coupling constants is in terms of an adsorbed allylic radical $RCH_2CH_2\text{-}\overbrace{CH{\dashrightarrow}CH{\dashrightarrow}CHMe}^{\cdot}$ possessing hindered rotation about the carbon–carbon bonds. Thus, taking into account the orientation dependence of the β-proton hyperfine interaction, the large triplet splitting may be attributed to interaction with one β-proton and one proton of the methyl group in a fixed orientation. The quintet splitting results from interaction with two α-protons, one β-proton, and one

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† All e.s.r. spectra were recorded using a Decca X-1 spectrometer operating at 9270 MHz with a magnetic field modulation of 100 kHz.

methyl proton while the small triplet splitting arises from interaction with the central proton of the allylic group and the remaining methyl proton.

The observation of identical spectra during the adsorption of propene, but-1-ene, and pent-1-ene suggests an initial oligomerisation of the propene molecule, followed by abstraction of a hydrogen atom leading to the formation of an allylic radical. Alternatively, proton removal from a partially charged radical cation would result in the same species. But-1-ene and pent-1-ene can be expected to behave in a similar manner and evidence exists for the oligomerisation of but-1-ene during its isomerisation over a hydrogen mordenite catalyst.[3] The regular cylindrical pore structure of the mordenite catalyst will facilitate this polymerisation and could also account for the contrasting behaviour[1d] of the faujasite-type zeolites with respect to but-1-ene adsorption.

Supporting evidence for a polymerisation process is provided by the changes which occur in the e.s.r. spectra when the catalyst is heated in the presence of adsorbed olefin. In this respect, propene, but-1-ene, and pent-1-ene again behave in a similar manner. Heating the catalyst–olefin system at 373 K for 1 h results in a decrease in the peak-to-peak separation from 8·1 to 4·3 G, indicating a delocalisation of the unpaired electron density over a longer carbon chain. In addition, this spectrum degenerates into a single line of width 14·9 G when the system is heated above 473 K, suggestive of further electron delocalisation, possibly in a polyenyl-type species. The mechanism of formation of these radical species and their role as possible catalytic intermediates is the subject of a more extensive investigation.

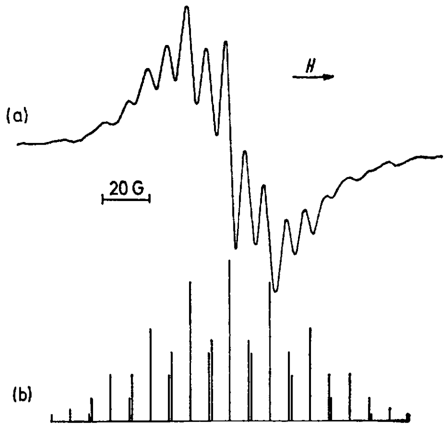

FIGURE. (a) *E.s.r. spectrum from hydrogen mordenite containing adsorbed propylene.* (b) *Reconstruction of* (a).

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