The Structure and Dynamics of Benzene in Zeolite L

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Deuterium n.m.r. studies of benzene sorbed in zeolite L reveal that the molecules rotate rapidly in the molecular plane, consistent with their observed locations in 'capping' positions above channel-wall potassium cations.

Knowledge of the locations and dynamics of sorbed phases within zeolites is important in developing an understanding of their role in hydrocarbon conversion catalysis and separations.[1] Structural studies of zeolite–hydrocarbon complexes are, however, few in number, partly because of the general non-availability of suitable single crystals and partly because of the intrinsic insensitivity of *X*-ray diffraction to the parameters of lighter atoms such as hydrogen. Similarly, techniques for measuring intracrystalline diffusion[2] generally provide little information about the hydrocarbon motion on a molecular level. Developments in neutron scattering and n.m.r. techniques do, however, promise to contribute signifi-

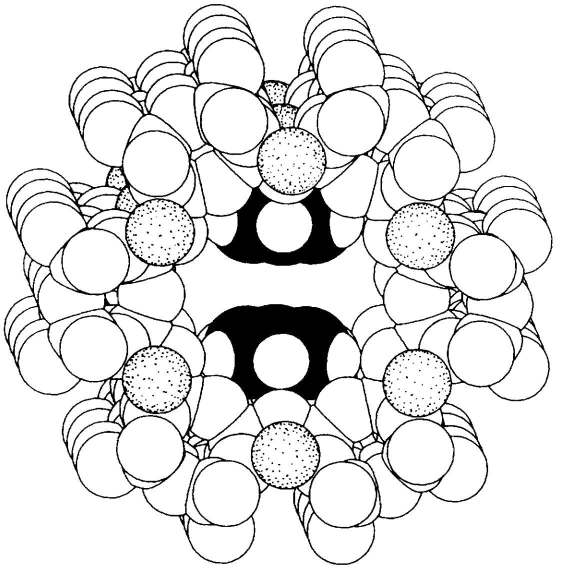

Figure 1. Representation of a portion of the structure of aluminosilicate zeolite L containing, on average, 1 molecule of perdeuteriobenzene per unit cell as determined at 78 K by p.n.d. Each channel section contains 6 equivalent benzene molecule positions in 'capping' sites above potassium cations in channel wall sites. Two of these six positions in one channel segment are shown. Half of the adjoining channel section (closer to the viewer) and the associated channel wall potassium cation sites (speckled) are also shown.

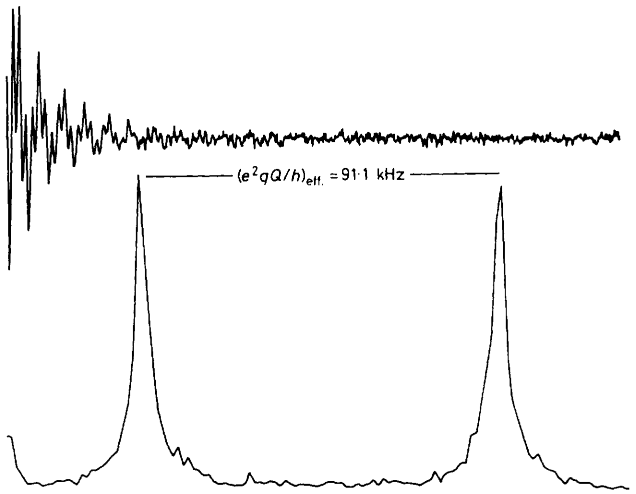

Figure 2. The ^{2}H nuclear free induction decay (upper) and its Fourier transform (lower) for C_6D_6 in zeolite L at 295 K. The splitting of 1238 p.p.m. at 55.2654 MHz corresponds to an effective quadrupolar coupling constant of 91.1 kHz (one half of the static molecular value), indicating that the molecules are rotating rapidly in the molecular plane.

cantly to these areas. The feasibility of determining the complete structures of zeolite–hydrocarbon complexes using powder neutron diffraction (p.n.d.) has been demonstrated[3] and measurements on xylenes in ZSM-5 (framework code MFI),[4] and on benzene in X-type (FAU) zeolites[5] indicate that motional narrowing effects in deuterium n.m.r. spectroscopy can provide rich information on sorbate molecular motion. We demonstrate here the combined use of these two probes in studying the behaviour of perdeuteriobenzene in zeolite L.

In preliminary experiments the structure of dehydrated potassium aluminosilicate zeolite L was determined at 298 K[6] and 78 K by p.n.d. Samples of benzene-loaded material were then prepared by injecting appropriate volumes of perdeuteriobenzene (C_6D_6; >99.96% D) into septum vials containing weighed portions of the zeolite that had been dehydrated at 400 °C. Loading levels were determined gravimetrically. The samples were allowed to equilibrate at room temperature for at least two days, with repeated agitation. They were then loaded into containers suitable for the subsequent measurements (for p.n.d., a vanadium can sealed with indium wire; for ^{2}H n.m.r., spectroscopy sealed cylindrical glass vials). The p.n.d. data from a sample with a loading level, n, of one benzene molecule per unit cell (or equivalently per channel segment) were accumulated at 78 K on the powder diffractometer of the Missouri University Research Reactor and analysed by full-matrix least-squares profile analysis.[7] Possible positions for the benzene molecules were investigated in an iterative series of profile refinements, Fourier calculations, and interactive molecular modelling. The refinement convergences were compared for different locations and orientations of the benzene molecule. In common with similar studies of pyridine in zeolite L,[8] the benzene intramolecular geometry was fixed. Nonbonded interaction energy calculations based on the naked LTL-framework indicated a benzene molecule site in the plane of the 12-ring window to be, at least, a local energy minimum. Importantly, however, in the potassium zeolite at the loading level studied here no significant occupancy of this site is observed. In the model which best reproduces the observed data (R_I = 1.78, R_P = 2.73, R_WP = 3.41, R_E = 1.35[7]) the benzene molecules lie in 'capping' sites above the K(4), type D potassium cations situated on the walls of the channels[9] (Figure 1). The mean K(4)–C distance is 3.42 Å. The mean K(4)–O(4) and K(4)–O(6) contacts are slightly increased relative to the dehydrated zeolite, presumably reflecting the interaction between the potassium cation and the π-electron density of the benzene ring.

Fourier transform ^{2}H n.m.r. spectra of perdeuteriated benzene sorbed in zeolite L were recorded at a frequency of 55.3 MHz for various loading levels for temperatures $180 \leqslant T \leqslant 300$ K. For loadings $n \leqslant 2$, the spectra are essentially temperature independent in this range (Figure 2). These spectra contain no narrow central component that would correspond to benzene molecules moving isotropically over the time scale of the measurement (10^{-6} s), such as that observed in X-type zeolites in this same composition and temperature regime.[5] The magnitude of the effective C–D quadrupolar coupling constant $(e^2qQ/h)_{\mathrm{eff.}}$ = 91.1(2) kHz, is almost exactly one half of the value of the quadrupole interaction for C_6D_6 of 183(10) kHz.[10] Molecular rotation about an axis that makes an angle β to the electric field gradient direction (that is, the direction of the C–D bond) results in a reduction in $(e^2qQ/h)_{\mathrm{eff.}}$ of $(3\cos^2\beta - 1)/2$.[11] For rotation of a benzene molecule in its molecular plane, β = 90° and a reduction factor of 0.5 is expected. The close agreement with the experimental value suggests that no other modes of molecular motion occur on a time scale $<10^{-6}$ s. This mode of molecular motion is consistent with the structural results. The interaction between the π-electron density of the benzene molecule and the type D potassium cation that is responsible for the stability of the sorption site[12] is unaffected by benzene molecule rotation about the ring normal. The size of the opening in the zeolite L channel is also such that this rotation is not greatly hindered by interaction with the framework oxygen atoms (Figure 1).

The present results demonstrate how the combined use of static and dynamic probes can provide a detailed picture of the behaviour of sorbed hydrocarbons within zeolites. Extensions of this approach to zeolites containing other sorbed hydrocarbons and hydrocarbon mixtures are in progress. Of particular current interest are hydrocarbon molecules that possess internal degrees of mechanical freedom in which the p.n.d. and n.m.r. results can be combined with complementary information on intramolecular vibrations accessible by i.r., Raman, and inelastic neutron scattering spectroscopy.

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