

Surface-phase Heterogeneity in the Benzene–Silicalite System

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Variable-temperature deuterium NMR experiments of [$^2\text{H}_6$]benzene sorbed in silicalite reveal two discrete adsorption sites of differing adsorbate mobility corresponding to benzene preferentially adsorbed in mid-channel positions and molecules subsequently occupying channel intersections.

The adsorption equilibria of hydrocarbons in highly dealuminated zeolites is a relatively poorly understood area of zeolite science despite its great industrial importance. A system of particular interest is the benzene–silicalite system in which step-like transitions and hystereses in the adsorption–desorption isotherms are observed. As yet, there is no clear explanation of these phenomena, although Thamm and coworkers^{1,2} and Talu and coworkers³ have considered concepts such as ‘surface heterogeneity’ or ‘surface-phase transitions’ without being able to present direct observational evidence of these phenomena. In this work, we have studied the dynamics of benzene molecules at various loadings in the silicalite structure and we have been able to show the accessing of new sites for adsorption and increased sorbate–sorbate interaction consistent with the heat of sorption data as a function of adsorbate loading reported by Thamm.² The silicalite structure is a three-dimensional system of intersecting channels composed of near circular zig-zag (sinusoidal) channels cross-linked by elliptical, straight channels. Both channels are defined by 10-rings.⁴ Previous workers⁵ have reported the existence of two different adsorbed benzene species in ZSM-5, which is isostructural with silicalite, however, the exact nature of the adsorbed sites was not addressed. Further, recent molecular dynamic simulations^{6,7} of sorbed species in silicalite suggest that minimum-energy sites and hence preferable first sites for adsorption may be in channels or channel intersections depending on the shape of the sorbate molecule. Our work indicates that the first sites for benzene adsorption in silicalite are mid-channel positions with adsorption at the channel intersection occurring only at higher loadings, this second site for adsorption is characterized by higher adsorbate mobility than the first.

All experiments were performed on a sample of silicalite obtained from ICI with unit cell composition 95.4% SiO_2 , 0.3% Al_2O_3 and less than 0.01% M_2O where M is any alkali metal atom.⁸ The silicalite was dried at 673 K for 16 h under a vacuum of less than 10^{-3} Pa and adsorbate loadings were calculated both gravimetrically and from measured pressure changes in the calibrated adsorption system. Deuteriated benzene from Aldrich with an atom purity in excess of 99.5% was used in all the experiments. Samples at loadings of 1.3, 2.9, 4.1, 6.1 and 7.6 molecules per unit cell were prepared and sealed in glass ampoules. These loadings correspond to 0.3, 0.7, 1.0, 1.5 and 1.9 molecules per quarter unit cell or channel

intersection in the silicalite pore structure. Deuterium NMR measurements were recorded on a Bruker MSL 200 NMR spectrometer operating at 30.72 MHz using a quadrupolar echo pulse sequence with a $\pi/2$ pulse of 5 μs and a time interval of 20 μs between pulses. Deuterium lineshapes of each adsorbate loading were recorded with typically 10 000 scans at temperatures between 190 and 350 K. The temperature was stable to ± 1 K. Fig. 1 shows the deuterium lineshapes

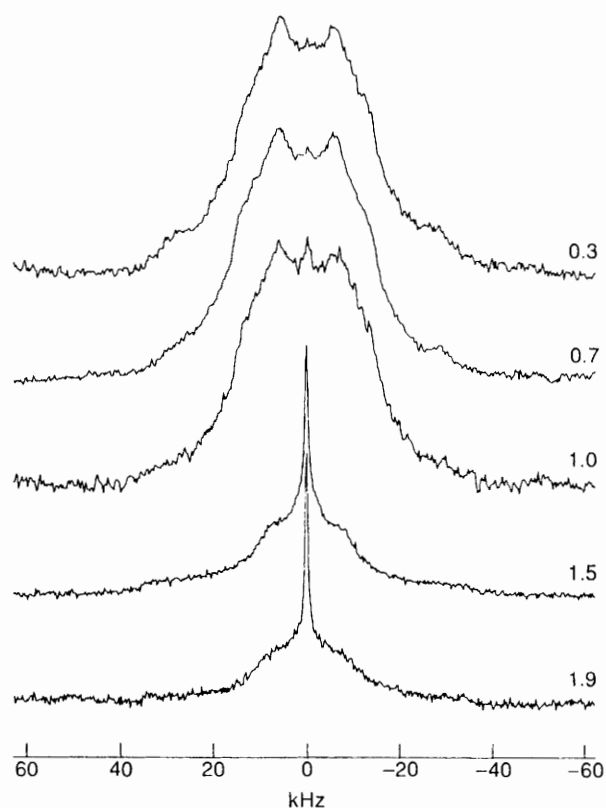


Fig. 1 Deuterium powder patterns recorded for [$^2\text{H}_6$]benzene adsorbed in silicalite at 293 K. Loadings per quarter unit cell are indicated on each spectrum. The relative intensities of all spectra are normalized to a common scale.

corresponding to benzene loadings of 0.3, 0.7, 1.0, 1.5 and 1.9 molecules per quarter unit cell. It is clearly seen that in the low-loading regime; *i.e.* 0.3 and 0.7 molecules per quarter unit cell when the heat of sorption is approximately constant, there is no significant change in the NMR lineshape consistent with no new sites for adsorption being accessed at the higher loading of 0.7 molecules per quarter unit cell. The deuterium lineshape indicates that the molecules are undergoing 180° flips about an axis in the plane of the molecule. However, at the loadings of 1.0, 1.5 and 1.9 molecules per quarter unit cell a second peak, indicative of a more mobile species undergoing rapid isotropic motion, is superimposed on the spectra acquired at the lower loadings. These changes in the nature of the lineshape are consistent with changes in the heat of sorption at the same benzene loadings as recorded by Thamm and will be discussed in future work. We suggest that the second component of the lineshape, which develops at the loading of 1.0 molecule per quarter unit cell, should be assigned to an adsorption site of high mobility and that this signal can be ascribed to benzene adsorbed at the channel intersections. The signal does not arise from benzene adsorbed on the exterior of the silicalite particle. For all loadings of greater than 1.0 molecule per quarter unit cell, two components to the lineshape were observed.

Further information, which aids the assignment of the two components to two distinct adsorption sites, is obtained by a variable temperature study at each adsorbate loading. For loadings below 1.0 molecule per quarter unit cell no significant interaction between benzene molecules is observed, which is reflected in the lack of any change in the powder pattern with decreasing temperature. This is consistent with benzene molecules adsorbed in mid-channel positions since the separation of benzene molecules within the silicalite structure would then be $\sim 12.1 \text{ \AA}^9$ compared with the longest molecular diameter of a benzene molecule of 6.9 \AA^{10} . If the first

adsorption sites to be accessed were the channel intersections, the resulting molecular separation of approximately 6.7 \AA would be expected to allow significant sorbate-sorbate interaction. In contrast, the temperature dependence of the benzene lineshape at high loadings (greater than 1.0 benzene molecule per quarter unit cell) shows significant sorbate-sorbate interactions. These interactions are manifested by a loss in mobility of the benzene molecules and a subsequent broadening of the lineshape upon cooling. The extent of sorbate-sorbate interactions is enhanced as the loading of the silicalite increases.

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