

The Interaction of Sorbates with Acid Sites in Zeolite Catalysts: A Powder Neutron Diffraction and ^2H NMR Study of Benzene in H-SAPO-37

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Abstract: The structure of perdeuterobenzene adsorbed in zeolitic H-SAPO-37 has been studied by powder neutron diffraction and ^2H NMR. Low temperature (5 K) diffraction measurements reveal that benzene is located both above the six-ring window and in the plane of the 12-ring window and that protons are found only at O(2) where a facial interaction with adsorbed benzene can occur. The results indicate that the acid sites are redistributed under the influence of the sorbate in order to enhance the proton-benzene interactions at the six-ring site. Variable temperature ^2H spin-lattice relaxation measurements show that the diffusion of benzene in H-SAPO-37 is intermediate between those in Na-Y (Si/Al = 1.7) and siliceous Y but is very similar to those in H-Y and US-Y. We may also infer from the ^2H NMR data that the benzene participates in a facial interaction with the protons at O(2) at low temperatures.

1. Introduction

The behavior of benzene in faujasite-type zeolites has been investigated previously by a variety of techniques in order to provide an understanding of the interactions that take place between microporous framework materials and aromatic molecules. Neutron diffraction studies¹ provided the first direct experimental evidence of an adsorption site in Na-Y above the SII cation in the supercage (s.c.), where the benzene molecule is facially coordinated to the cation (Figure 1). IR studies are consistent with this model.² Low temperature NMR investigations³ have identified a C₆ reorientation of the sorbate in which the benzene is rapidly rotating in its plane while being coordinated to the SII cation. The stability of this site is believed to be due to a quadrupolar, rather than a π -type, interaction, and it is further stabilized by dispersion interactions between the sorbate and the framework. A second adsorption site in Na-Y has been identified at the center of the 12-ring window (Figure 1); this is occupied at higher concentrations of benzene in Na-Y (2.6 molecules per supercage) and also when different cations are exchanged for sodium.⁴ ^2H NMR is unable to distinguish between this site and the site above the six-ring window, but IR spectroscopy does provide indirect evidence for its existence.² The 12-ring window adsorption site is thought to be stabilized by weak hydrogen bonding type interactions between the protons of the sorbate and the oxygen ions of the window.

The acid forms of faujasite zeolites also interact with benzene. Comprehensive IR investigations of H-Y⁵ and the isostructural silicoaluminophosphate, H-SAPO-37,⁶ have shown that, de-

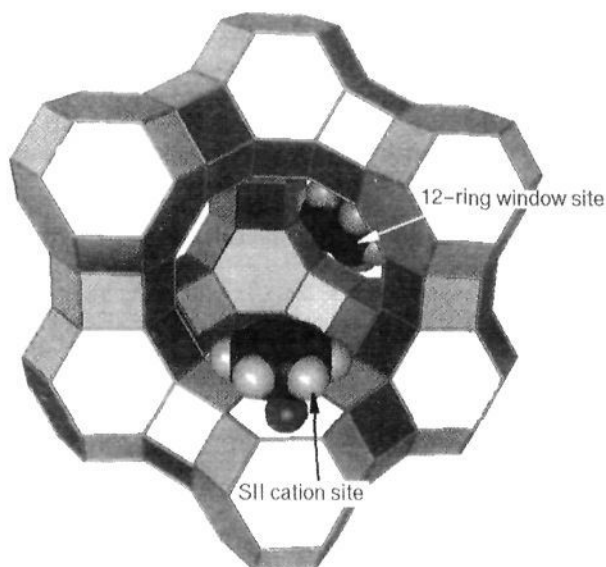


Figure 1. The adsorption sites for benzene in Na-Y as observed from neutron diffraction¹ above the SII cation and in the plane of the 12-ring window.

pending upon the pretreatment temperature, benzene interacts with protons in the α - and β -cages and that adsorption occurs at two sites that are similar in nature to those observed in Na-Y.⁷ Adsorption studies⁸ have shown, however, that the interaction between benzene and the acidic zeolites is weaker than that in Na-Y. It has been proposed that protons interact through a hydrogen bond with the π cloud of the aromatic molecule.⁶ Neutron diffraction studies of the H-Y⁹ and H-SAPO-37¹⁰ materials have recently shown that acid sites are located

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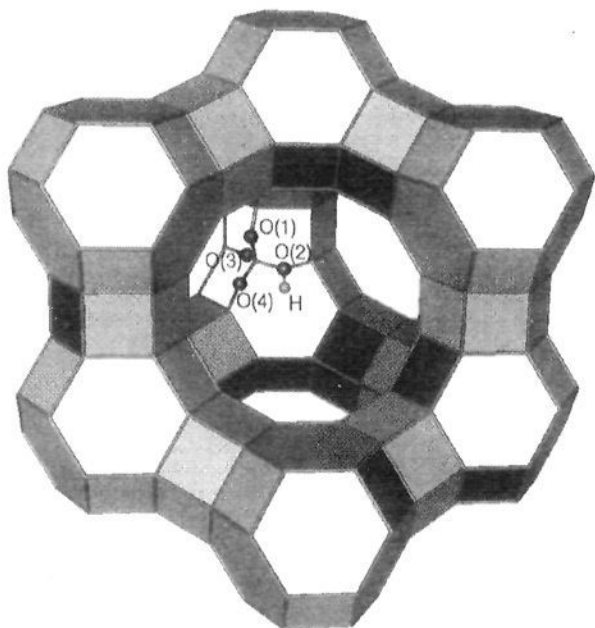


Figure 2. The faujasite structure showing the positions of the four oxygens sites that may be protonated and the observed location of the proton at O(2).

primarily at O(1) in the α -cage but also at O(2) close to the Si^{I} cation site and at O(3) near to the Si^{II} cation site in the β -cage (Figure 2). This is consistent with infrared studies⁶ and would suggest that the protons at O(1) and O(2), which are accessible in the supercage, are responsible for the observed acidity. However, this deduction is not necessarily correct because the protons with the highest occupancies, as determined by neutron diffraction, should be the most stable sites and hence the least acidic. In the present work we address this paradox by using neutron diffraction and ^2H NMR to study the behavior of benzene in H-SAPO-37. This combined approach has enabled us to probe the interaction between adsorbed benzene and acid sites in this prototypic acid catalyst.

2. Experimental Section

Na-Y (Si:Al = 1.7) was purchased from Ventron Chemicals, and $\text{NH}_4\text{-Y}$ (Si/Al = 2.5) and $\text{NH}_4\text{-SAPO-37}$ ($(\text{NH}_4)_{0.31}(\text{Al}_{1.0}\text{Si}_{0.31}\text{P}_{0.69})\text{O}_4$) were kindly provided by Dr. Don Hopkins of Amoco Oil Company. The acid forms were prepared by careful calcination of the parent materials at 525 °C under dry oxygen (since the crystallinity of the samples is rapidly lost in the presence of moisture¹¹). A commercial sample of ultrastabilized-Y (US-Y), which was obtained from Shell, Amsterdam, was also studied. Na-Y and US-Y were dehydrated under vacuum at 500 °C for at least 12 h. Known concentrations of deuterated benzene (approximately one molecule per cavity) were added gravimetrically in a glovebox. The sample for neutron diffraction was packed into a thin-walled vanadium can (~5 cm long and ~1 cm wide) and screw-sealed using indium wire. NMR samples were prepared in Pyrex ampoules (5–10 mm o.d.) which, once loaded, were evacuated, keeping the zeolite at liquid N_2 temperature, and then sealed. All samples were then heated at 80 °C for at least 4 h to attain a homogeneous distribution of sorbate within the sample.

Neutron diffraction data were obtained at 5 K from H-SAPO-37 with adsorbed benzene on the powder diffractometer, DUALSPEC, at Chalk River Laboratories, Canada. The data, in two frames, were collected at $\lambda = 1.505$ Å, between 10° and 80° and 43° and 120° 2θ ,

in steps of 0.05°. The high and low angle data sets were used jointly in a Rietveld refinement,¹² using the GSAS suite of programs.¹³ The neutron scattering lengths ($\times 10^{-14}$ m²) used in the refinement were as follows: $b_{\text{Al}} = 0.3449$, $b_{\text{Si}} = 0.4149$, $b_{\text{P}} = 0.513$, $b_{\text{H}} = -0.374$, $b_{\text{D}} = 0.6674$, $b_{\text{O}} = 0.5805$, $b_{\text{C}} = 0.665$. The model of the H-SAPO-37 parent material¹⁰ was used as the starting point for the framework refinement, but discrepancies in the low angle peak intensities indicated that benzene was contributing to the diffraction pattern. Si/P and Al occupancies were fixed according to the chemical composition. Constraints on the framework bond lengths were applied prior to inserting deuterobenzene into the refinement at positions found for benzene adsorbed in Na-Y, i.e., above the 6 ring window and in the plane of the 12-ring window. Protons were placed geometrically at each oxygen, as described in ref 10. Two orientations of the benzene at the 6-ring window site were used, one rotated 30° with respect to the other. The fractional occupancies of the benzene molecules and protons were refined, assuming that the temperature factors were the same as those found for the protons in H-Y.⁹ The sorbate positions were partially refined by allowing freedom along the 3-fold axis. The proton positions were not refined.

Deuterium NMR spectra were collected on Bruker MSL 300 and 400 spectrometers at frequencies of 46.05 and 61.4 MHz. Spin-lattice relaxation rates were measured using the inversion recovery method followed by the quadrupole echo sequence¹⁴ for observation of the signal, i.e., $180^\circ\text{-delay-}90^\circ_x\text{-}\tau\text{-}90^\circ_y\text{-}\tau\text{-echo}$. The 90° pulse was typically 3 μs and the spin-echo delay, τ , 30 μs . Spectra were recorded as a function of temperature, allowing at least 30 min for the sample to reach equilibrium. Temperatures were estimated to be accurate within ± 2 K and were stable to ± 0.5 K. A full description of the data analysis used to obtain activation energies, reduced quadrupole coupling constants (QCCs), correlation times, and diffusion coefficients has been given in an earlier paper.¹⁵

3. Results

The observed and calculated neutron diffraction profiles for perdeuterated benzene adsorbed in H-SAPO-37 (~1 mol/s.c.) are shown in Figure 3. Refinement details and atomic parameters are given in Tables 1 and 2, respectively. Benzene was found to be located both above the 6-ring window (where the two orientations suggest some rotational disorder) and in the plane of the 12-ring window, with occupancies of 12% and 22%, respectively, but protons could be found only at O(2) with an occupancy of 16% (Figure 2). The number of protons that we have detected falls well short of the expected proton content. However, ^1H MAS-NMR of perdeuterated benzene adsorbed on H-SAPO-37 showed that partial proton/deuterium exchange between the deuterons on the benzene ring and protons on the framework does occur at 80 °C. This could account for the low proton content in the host material because the substitution of D ($b_{\text{D}} = 0.667 \times 10^{-14}$ m) for H ($b_{\text{H}} = -0.374 \times 10^{-14}$ m) will diminish the scattering from the proton sites. This, however, does not alter our overall conclusion that protons redistribute to O(2), as all oxygen sites will be equally affected by the exchange provided that no preferential deuteration occurs at a particular site. The neutron diffraction refinement is relatively insensitive to the partial proton exchange into the benzene ring because the fractional occupancies of the deuterons were fixed to be the same as the carbons to which they are bonded, and the scattering from the carbon will dominate.

The ^2H NMR line shapes of benzene adsorbed in Na-Y, H-Y, US-Y, and H-SAPO-37 (~1 mol/s.c.) as a function of temperature are compared in Figure 4. At 155 K, all the samples show

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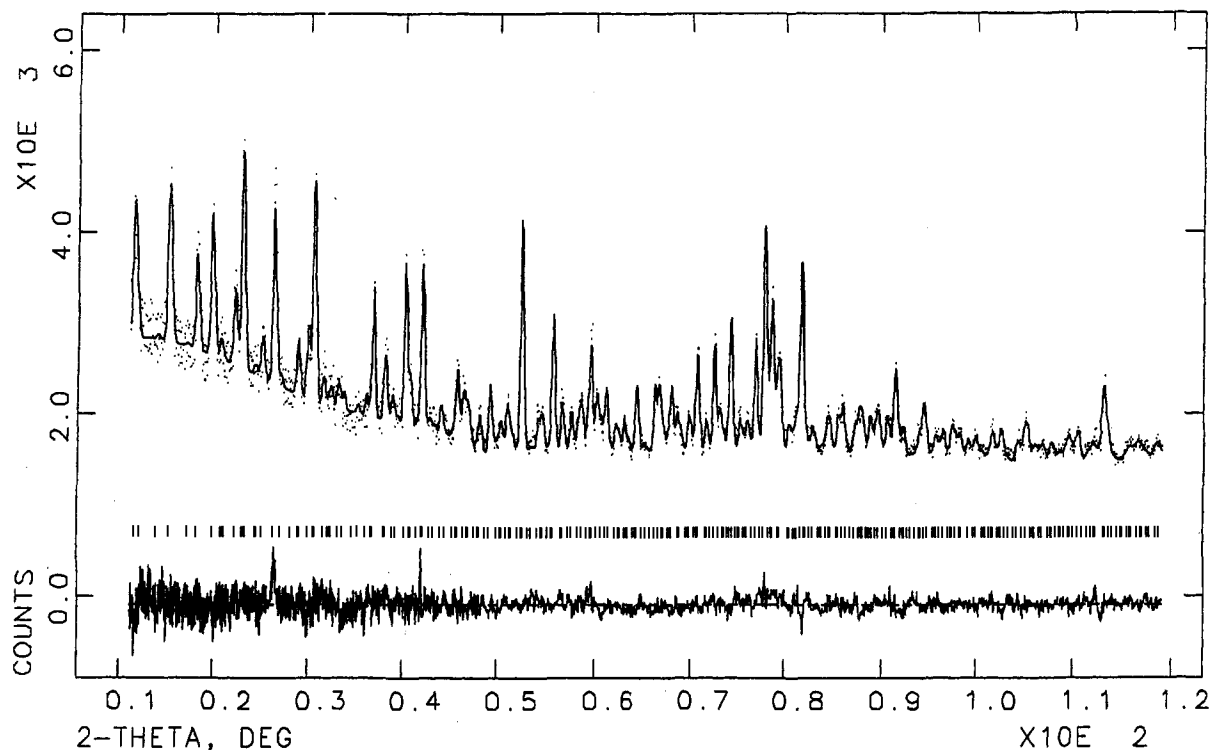


Figure 3. Experimental, calculated, and difference neutron diffraction profiles of H-SAPO-37 with adsorbed benzene. The high and low angle data sets have only been merged for the purpose of the figure.

Table 1. Details of the Neutron Diffraction Refinement

	overall	low angle data	high angle data
temp (K)	5		
wavelength (Å)	1.5050		
space group	<i>Fd3</i>		
<i>a</i> (Å)	24.790(7)		
2θ range (deg)		11–50	43–120
no. data points		780	1540
no. of reflcns		126	1042
zeropoint error		4.8(1.5)	7.8(3.2)
scale factor		2255(32)	1932(21)
<i>R_p</i> %	0.0326	0.0369	0.0286
<i>R_{wp}</i> %	0.0402	0.0443	0.0360
<i>R_F</i> %		0.0979	0.0637
χ^2	3.9		

an axially symmetric anisotropic powder pattern with a splitting between the singularities of ~ 66 kHz. This is typical of a rapid rotation of benzene around its 6-fold axis, which produces an effective quadrupole coupling constant with half the magnitude of that in the static molecule.¹⁶ As the temperature is raised, the intensity at the center of the spectrum associated with pseudoisotropic motion, involving jumps between sets of sites where the orientations of the benzene 6-fold axis are related by tetrahedral or higher symmetry, gradually dominates. Diffusion coefficients and the associated activation energies for benzene adsorbed in H-SAPO-37 were measured from ²H NMR T₁ experiments, and the results are compared in Figure 5 with the diffusion data for H-Y, US-Y, H-SAPO-37, Na-Y, and a sample of siliceous Y.¹⁵

4. Discussion

The model obtained from the diffraction data for benzene adsorbed in H-SAPO-37 shows that the protons are sited only at O(2), and the sorbate is located both in the plane of the 12-

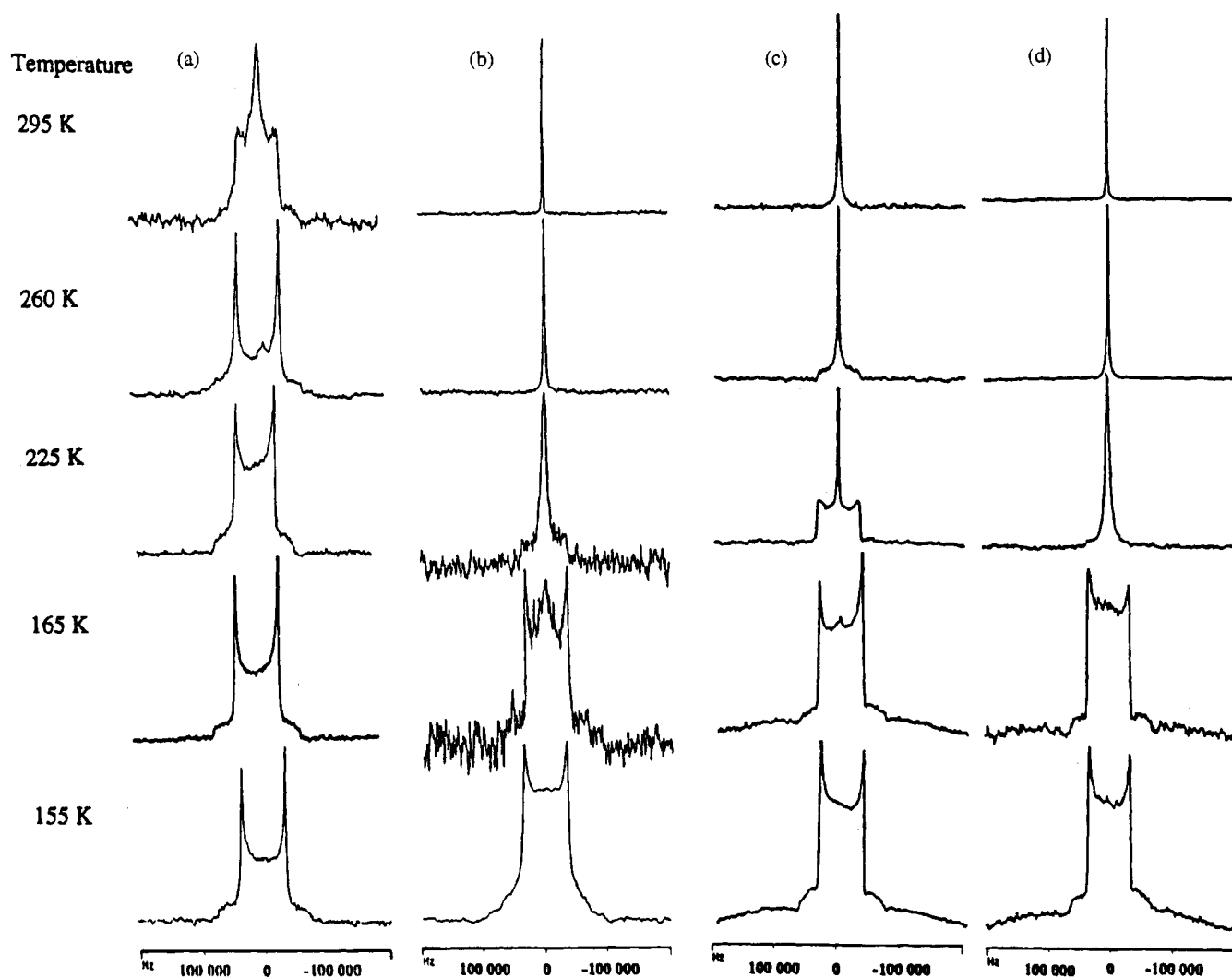
ring window and above the six-ring window, as seen in Figure 1. These adsorption sites are similar to those observed for benzene adsorbed in Na-Y at a loading level of 2.6 molecules per supercage. The low temperature ²H NMR line shape of benzene adsorbed in H-SAPO-37 is also similar to that observed in Na-Y, indicating that the sorbate is undergoing a C₆ rotation as if it were coordinated to a SII cation. In order to explain the diffraction and NMR results on H-SAPO-37, we conclude that benzene detected at the six-ring window site in the low temperature neutron experiment is participating in a facial interaction with the proton on O(2), whose location resembles that of the SII cation in Na-Y. A broadly similar model has been suggested previously based on the observation of a low frequency shift of the CH out-of-plane IR bending vibration of the benzene, which indicates a polarization of the π -electron cloud of the sorbate.⁶ Our diffraction results also confirm that the sorbate is located in the plane of the 12-ring window in H-SAPO-37. Unfortunately, the two distinct types of benzene cannot be distinguished in the ²H NMR spectra since the molecule must be undergoing rapid in-plane motional averaging at both adsorption sites. If the activation barriers to these motions were significantly different at the two sites, then upon lowering the temperature, the motion at one of the sites may slow before the other, which would result in a spectrum with a superposition of two powder patterns with different line widths. At higher temperatures the pseudoisotropic averaging appears to affect all molecules in the same way, indicating that exchange is occurring between six-ring sites as well as between six- and 12-ring sites.

The earlier diffraction study of the parent H-SAPO-37 material revealed protons at O(1), O(2), and O(3) with occupancies of 20%, 6%, and 4%, respectively, whereas protons are observed only at O(2) (16%) upon adsorption of benzene. Our inability to detect any protons at O(1), together with the increased concentration at O(2), indicate that the protons are redistributing themselves among the oxygen sites in order to interact more favorably with the sorbate. This conclusion is

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Table 2. Fractional Atomic Coordinates, Isotropic Temperature Factors, and Fractional Occupancy Numbers (Benzene in H-SAPO-37)

atom	site	x/a	y/a	z/a	B (\AA^2)	occupancy
Si(1)	96g	-0.0542(4)	0.0374(5)	0.1243(4)	0.256(18)	0.31
P(1)	96g	-0.0542(4)	0.0374(5)	0.1243(4)	0.256(18)	0.69
Al(1)	96g	-0.0545(4)	0.1257(5)	0.0345(5)	0.256(18)	1.00
O(1)	96g	-0.0037(5)	-0.1094(4)	0.1048(4)	0.732(10)	1.00
O(2)	96g	-0.0069(4)	-0.0001(4)	0.14077(13)	0.732(10)	1.00
O(3)	96g	0.1772(4)	0.1736(4)	-0.03524(26)	0.732(10)	1.00
O(4)	96g	0.1799(4)	0.1745(5)	0.32162(32)	0.732(10)	1.00
H(2)	96g	-0.002495	0.013950	0.176640	3.4	0.16(3)
C(1)	96g	0.2560(14)	0.3358(14)	0.2959(14)	3.4	0.059(6)
C(2)	96g	0.2560(14)	0.2959(14)	0.3358(14)	3.4	0.059(6)
D(1)	96g	0.3666(14)	0.2252(14)	0.2959(14)	3.4	0.059(6)
D(2)	96g	0.2252(14)	0.3666(14)	0.2959(14)	3.4	0.059(6)
C(10)	96g	0.2417(13)	0.3107(13)	0.3107(13)	3.4	0.063(6)
C(11)	96g	0.2648(13)	0.3338(13)	0.2648(13)	3.4	0.063(6)
D(10)	96g	0.3703(13)	0.2466(13)	0.2466(13)	3.4	0.063(6)
D(11)	96g	0.3288(13)	0.2051(13)	0.3288(13)	3.4	0.063(6)
C(20)	96g	0.5581(17)	0.5251(15)	0.4596(17)	3.4	0.22(1)
D(20)	96g	0.5970(14)	0.6151(17)	0.4447(15)	3.4	0.22(1)

**Figure 4.** Temperature dependence of the ^2H NMR spectra of C_6D_6 adsorbed in: (a) Na-Y (Si/Al = 1.7), (b) H-SAPO-37, (c) H-Y (Si/Al = 2.5), and (d) US-Y.

consistent with IR measurements which show that the OH stretching band associated with protons in the α -cage is shifted to lower frequencies on adsorption of benzene.⁶ We would argue that the OH species associated with O(1) are the ones in the α -cage and that the OH stretching frequency is lowered when these protons move to O(2) in order to bind to the benzene at the location above the 6-ring (Figure 2); the O-H bonding is presumably slightly weakened by the proton-benzene interac-

tion. It is interesting to note that this type of proton-benzene interaction has been observed in organic molecular crystals¹⁷ and proteins.¹⁸

Figure 5 shows that the diffusivity of benzene adsorbed in H-SAPO-37 is intermediate between that of benzene in Na-

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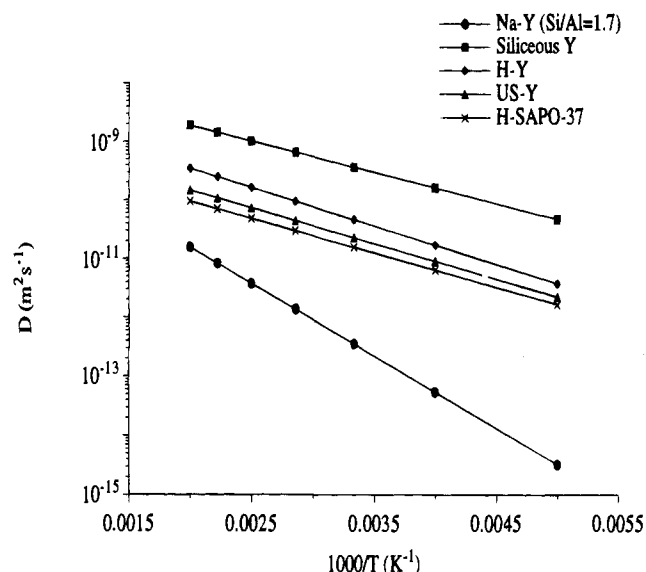


Figure 5. A comparison of the diffusion coefficients determined from ^2H T₁ NMR experiments for benzene adsorbed in siliceous Y, Na-Y (Si/Al = 1.7), H-SAPO-37, H-Y, and US-Y. The activation energies (kJ mol⁻¹) were found to be 10.2(0.8), 23.5(0.9), 11.2(0.3), 12.5(0.8), and 11.6(0.7), respectively.

Y(Si/Al = 1.7) and Sil-Y, confirming the importance of protons in stabilizing the adsorption site, but also indicating that the interaction between the sorbate and the protons is weaker than it is with alkali metal cations. This result is in agreement with previous heat of adsorption measurements (67 kJ mol⁻¹ in H-, Na-Y and 79 kJ mol⁻¹ in Na-Y⁸). Further evidence for the weaker proton/sorbate interaction at the SII site may be drawn from the fact that both the 12- and six-ring adsorption sites are occupied by benzene in H-SAPO-37 at low loadings (1 mol/s.c.); this is in contrast to that observed in Na-Y, where only the 6-ring site is occupied. This conclusion is also consistent with the onset of isotropic motion at a lower temperature in H-SAPO-37 than in Na-Y, as observed from ^2H NMR.

The conclusions reached in the previous paragraphs raise the question as to whether proton redistribution upon adsorption of benzene is unique to H-SAPO-37. Based upon the observed similarity of the diffusion of benzene in H-Y, H-SAPO-37, and

Table 3. Selected Bond Lengths (Å) and Angles (deg) in H-SAPO-37 with Adsorbed Perdeuterated Benzene

Si/P-O(1)	1.551(3)	Al-O(1)	1.739(3)
Si/P-O(2)	1.549(3)	Al-O(2)	1.738(3)
Si/P-O(3)	1.551(2)	Al-O(3)	1.739(3)
Si/P-O(4)	1.547(2)	Al-O(4)	1.737(3)
O(1)-Si/P-O(2)	110.7(1.0)	O(1)-Al-O(2)	110.5(7)
O(1)-Si/P-O(3)	111.5(8)	O(1)-Al-O(3)	108.3(7)
O(1)-Si/P-O(4)	104.4(8)	O(1)-Al-O(4)	111.0(8)
O(2)-Si/P-O(3)	108.2(8)	O(2)-Al-O(3)	107.5(6)
O(2)-Si/P-O(4)	108.2(7)	O(2)-Al-O(4)	111.8(7)
O(3)-Si/P-O(4)	113.8(9)	O(3)-Al-O(4)	107.5(6)
Si/P-O(1)-Al	136.2(5)	Si/P-O(3)-Al	143.3(5)
Si/P-O(2)-Al	148.9(3)	Si/P-O(4)-Al	143.9(6)
O(2)-H(2)	0.96(fixed)		
H(2)-center of benzene (C(1), C(2), D(1), D(2))			3.19
H(2)-center of benzene (C(10), C(11), D(10), D(11))			3.48

US-Y and the close analogies between their structures, it seems very likely that proton migration to the O(2) site occurs in all of these systems and quite possibly with other classes of sorbate, too. This would imply that the Brønsted acidity of a catalyst is determined to some extent by the chemistry of the reactant (= sorbate) and whether favorable interactions can be formed between the reactant and the acid sites. Qualitative observations that support this view have been obtained in catalytic studies.¹⁹ Conversely, many studies have used model probe molecules to determine the relative acidities of zeolite catalysts and have then extrapolated these results to more complex, catalytically-relevant systems. The use of this strategy, and also that of molecular orbital calculations on isolated acid sites, to predict the catalytic activity of a material, is obviously limited if the distribution of the active sites is dependent upon the presence and identity of the sorbate.

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