

Powder Neutron and X-ray Diffraction Studies of Benzene Adsorbed in Zeolite ZSM-5

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The whereabouts of benzene molecules adsorbed at two loadings in zeolite ZSM-5 at room temperature have been studied with powder neutron and synchrotron X-ray diffraction. The structures have been refined by the Rietveld method in space group *Pnma* by fitting simultaneously to the X-ray and neutron data. With approximately 3.4 molecules per unit cell, the best agreement is obtained with a model which has two molecules in mutually exclusive positions in the intersection of the straight and sinusoidal channels. The two positions have occupancies of 2.10(5) and 1.32(5) molecules per unit cell, respectively. At the higher benzene coverage of around 7.6 molecules per unit cell, molecules are found at three locations: in the intersection, in the sinusoidal channel, and in the straight channel. These have occupancies of 4.0, 2.45(4), and 1.15(4) molecules per unit cell, respectively. The intersection is essentially full. There appear to be favorable interactions between the molecules in the intersection and those in the sinusoidal and straight channels that help stabilize the arrangement.

Introduction

The adsorption of molecules into zeolite ZSM-5 has been studied by several theoretical and experimental techniques. At room temperature, the maximum capacity for benzene is around 8.5 molecules per unit cell. The heat of adsorption shows an unusual dependence on the extent of the filling of the pores, indicating changes in the states of the adsorbed molecules.^{1,2} Despite a number of diffraction studies, uncertainty remains as to the location of the benzene molecules.

The crystal structure of ZSM-5 has been studied by a number of workers, including van Koningsveld,³ who studied a single crystal and obtained accurate structural parameters for the framework and template molecule in the orthorhombic space group *Pnma*. Transitions have been reported in ZSM-5 to a low-temperature monoclinic form⁴ (space group *P2₁/n11*), and to another orthorhombic space group *P2₁2₁2₁* when loaded with eight *p*-xylene molecules per unit cell. The framework undergoes a distortion to accommodate the *p*-xylene molecules, which are located in the intersection of the straight and sinusoidal channels, and in the sinusoidal channel.⁵

Theoretical studies predict that benzene is favorably located at three positions in silicalite (the all-silicon analogue of ZSM-5): in the intersection, in the straight channel, and in the sinusoidal channel.⁶ Grand canonical ensemble Monte Carlo (GCMC) simulations of the progressive filling of silicalite with *p*-xylene molecules⁷ were consistent with a change in symmetry from *Pnma* to *P2₁2₁2₁* at around four *p*-xylene molecules per unit cell. A similar transition was predicted for benzene. Up to four molecules per unit cell, the molecules are adsorbed predominantly in the intersection. When these saturate, the adsorption of molecules into the straight channel triggers the

transition to *P2₁2₁2₁*, whereafter the molecules are adsorbed in the intersection and sinusoidal channels at higher loadings. Saturation occurs around eight molecules per unit cell. This picture for benzene and *p*-xylene is consistent with a number of experimental results.

The location of eight molecules of benzene per unit cell adsorbed into ZSM-5 at 77 K has been investigated by Taylor,^{8,9} using powder neutron diffraction. The arrangement of molecules is complicated, with three general locations. Two of these are in the intersection of the straight and sinusoidal channels, and the third is at the center of symmetry in the straight channel. There is considerable disorder in these positions, and six independent molecules were required to fit the powder diffraction pattern. Sacerdote-Peronnet and Mentzen¹⁰ have also used powder neutron diffraction to investigate benzene at a lower coverage, four molecules per unit cell, and see molecules adsorbed only in the intersection. Two benzene orientations are required to fit the data. Benzene in ZSM-5 has also been studied by powder X-ray diffraction, with indications of complex behavior for the molecules.¹¹

In this study, we have measured powder neutron and synchrotron X-ray diffraction patterns from ZSM-5 containing levels of adsorbed benzene of approximately 3.4 and 7.6 molecules per unit cell. For each system, a single structural model is fitted simultaneously to both data sets to obtain the best models for the location of benzene, consistent with both the neutron and X-ray data.

Experimental Section

ZSM-5 of nominal composition Na_{2.5}H_{0.1}Al_{2.6}Si_{93.4}O₁₉₂ was evacuated to a pressure of 10⁻⁵ mbar then gradually heated to 550 °C over a period of 24 h. Oxygen was passed over the sample for 4 h to remove any adsorbed hydrocarbons. After degassing and cooling, the required amount of benzene or deuteriobenzene was allowed to distill over into the sample

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chamber for a period of 24 h. The sample was sealed and allowed to equilibrate for several days before the diffraction experiment.

For the neutron diffraction study, the sample was contained in a thin-walled 16 mm diameter vanadium sample can. Diffraction patterns were measured on the instrument DIA¹² at the Institut Laue Langevin, Grenoble, at room temperature with a wavelength of 2.993 Å. Patterns were obtained from the bare dehydrated zeolite, a sample with a nominal deuteriobenzene coverage of four molecules per unit cell, and a sample with a higher nominal deuteriobenzene coverage of eight molecules per unit cell. For the X-ray studies, a second batch of samples was prepared. Two samples containing similar amounts of benzene to those above were sealed in 0.5 mm diameter glass capillary tubes. Data were collected on station 9.1¹³ at the Synchrotron Radiation Source, Daresbury, at a wavelength of 1.0361 Å.

Results

The powder diffraction patterns were analyzed by the Rietveld¹⁴ method. Using the neutron diffraction data from the bare dehydrated zeolite, the framework was refined starting with the coordinates obtained by van Koningsveld³ from a single crystal containing template molecules. The scale factor, lattice parameters, instrumental zero point, half-width parameters, Rietveld's asymmetry parameter, and two isotropic temperature factors for Si and O, respectively, were allowed to vary, along with the atomic coordinates of all the Si and O atoms, restrained by the average distances and angles observed by van Koningsveld.³ The restraints were Si–O distances of 1.587 ± 0.02 Å and O–Si–O angles of $109.5 \pm 10^\circ$. Final R -factors of $R_{\text{wp}} = 0.126$, $R_{\text{exp}} = 0.058$, and $R_1 = 0.077$ were obtained. The framework structure is very similar to that obtained from the single-crystal study, with Si–O bond distances and O–Si–O angles in the ranges 1.56(3)–1.62(4) Å and 105(2)–114(2)°, respectively. The isotropic temperature factors obtained were 3.1(2) Å² for Si and 3.43(7) Å² for O. No sodium ions could be located in the channels. A table of refined values is given in the supporting material.

For the data from the sample containing four benzene molecules per unit cell, various models for the location of benzene were investigated in space group $Pnma$, initially using only the neutron diffraction data. From the Fourier map, Figure 1, it is evident that the benzene molecules are concentrated in the intersection of the straight and sinusoidal channels, in keeping with the previous studies of Mentzen.¹⁰ It is also evident that the molecules are disordered, as a result of the plane of mirror symmetry that lies perpendicular to the straight channel at $y = 1/4$, which passes through the middle of the observed benzene density. Unless this mirror plane coincides with one of the mirror planes of the hexagonal benzene molecule, two symmetrically equivalent positions for a molecule are automatically generated.

With inclusion of the X-ray data in a joint refinement, the model which gives the best simultaneous fit to the neutron and X-ray data was developed, using the program PROFIL5.¹⁵ The patterns cannot be adequately fitted using a single benzene molecule. Two independent molecules are better, and the parameters of the most successful and efficient arrangement are given in Table 1. In the refinement, the benzene molecules were restrained to perfect hexagonal shapes, with a single refined isotropic temperature factor for both molecules. The value of the temperature factor reflects the variation in the positions of the molecules due to both static and thermal displacements, and

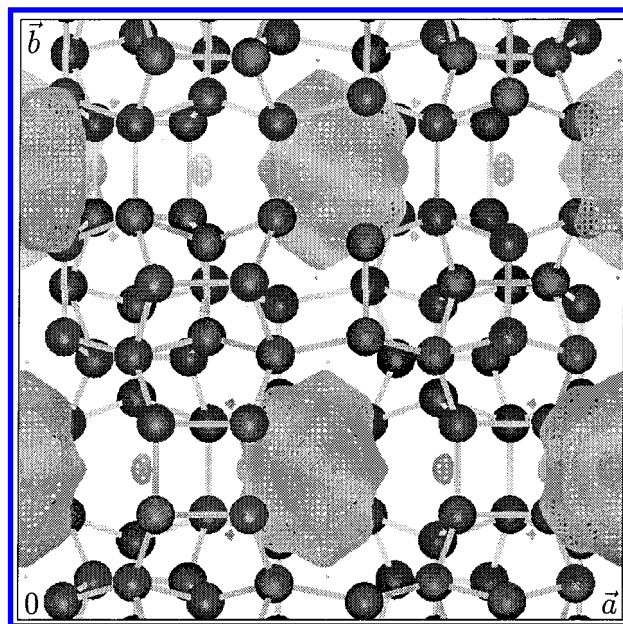


Figure 1. Difference Fourier map showing the silicon atoms of the framework and the neutron scattering density due to benzene molecules adsorbed at coverage of ~ 3.4 molecules per unit cell.

TABLE 1: Final Parameters for the Two Benzene Molecules Adsorbed in the Intersection of the Straight and Sinusoidal Channels in ZSM-5 Containing ~ 3.4 Molecules Per Unit Cell (Space Group $Pnma$)

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (iso)	<i>N</i>
Si atoms: see supporting material Table 2S				1.6(1)	
O atoms:				3.53(8)	
C(1)	−0.032(2)	0.291(2)	0.516(4)	10(2)	2.10(5)
C(2)	−0.033(2)	0.308(2)	0.617(4)	10(2)	2.10(5)
C(3)	−0.003(2)	0.266(3)	0.688(3)	10(2)	2.10(5)
C(4)	0.028(2)	0.207(2)	0.657(4)	10(2)	2.10(5)
C(5)	0.030(2)	0.189(2)	0.556(4)	10(2)	2.10(5)
C(6)	−0.001(2)	0.231(3)	0.485(3)	10(2)	2.10(5)
D(1)	−0.054(4)	0.323(3)	0.461(5)	10(2)	2.10(5)
D(2)	−0.056(3)	0.354(3)	0.641(5)	10(2)	2.10(5)
D(3)	−0.006(3)	0.278(3)	0.766(4)	10(2)	2.10(5)
D(4)	0.053(3)	0.175(3)	0.712(5)	10(2)	2.10(5)
D(5)	0.054(4)	0.143(3)	0.532(5)	10(2)	2.10(5)
D(6)	0.000(4)	0.217(4)	0.407(4)	10(2)	2.10(5)
C(7)	−0.023(4)	0.278(5)	0.586(5)	10(2)	1.32(5)
C(8)	−0.087(3)	0.255(5)	0.609(5)	10(2)	1.32(5)
C(9)	−0.107(3)	0.191(5)	0.578(5)	10(2)	1.32(5)
C(10)	−0.062(4)	0.149(5)	0.528(5)	10(2)	1.32(5)
C(11)	0.002(3)	0.172(6)	0.505(4)	10(2)	1.32(5)
C(12)	0.021(3)	0.237(7)	0.533(4)	10(2)	1.32(5)
D(7)	−0.007(6)	0.328(6)	0.609(9)	10(2)	1.32(5)
D(8)	−0.120(5)	0.286(6)	0.651(8)	10(2)	1.32(5)
D(9)	−0.157(3)	0.174(6)	0.593(7)	10(2)	1.32(5)
D(10)	−0.077(6)	0.099(5)	0.507(9)	10(2)	1.32(5)
D(11)	0.037(4)	0.140(8)	0.466(8)	10(2)	1.32(5)
D(12)	0.070(3)	0.256(8)	0.512(6)	10(2)	1.32(5)

cell constants *a*, *b*, *c* (Å): 20.1070(7), 19.9080(7), 13.3870(6)

calculated density (g cm^{−3}): 1.87

R -factors neutron: $R_{\text{wp}} = 0.112$, $R_{\text{exp}} = 0.058$, $R_1 = 0.090$

X-ray: $R_{\text{wp}} = 0.175$, $R_{\text{exp}} = 0.060$, $R_1 = 0.089$

is a simple approximation, limited by the nature of the powder diffraction data. Refinements of models with more complex temperature factors, such as separate temperature factors for each molecule or anisotropic models constrained to simulate rigid-body translational and librational motion, were less stable and tended to diverge. There is clearly significant correlation between the temperature factors and the occupancy parameters. The framework atoms were refined subject to the same restraints as for the bare zeolite. The occupancies of the two positions

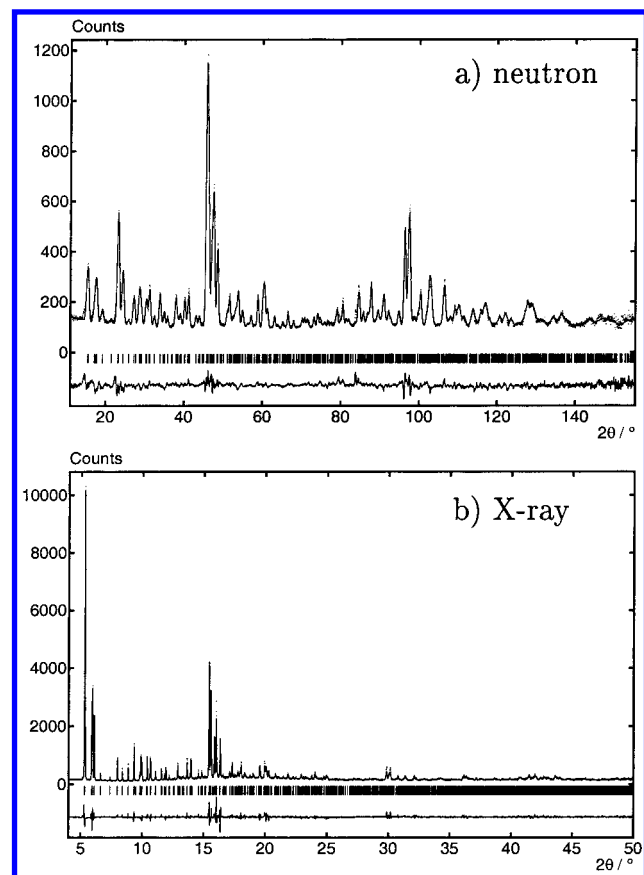


Figure 2. Observed, calculated, and difference profiles for the sample containing ~ 3.4 molecules of benzene per unit cell: (a) neutron data, (b) X-ray data.

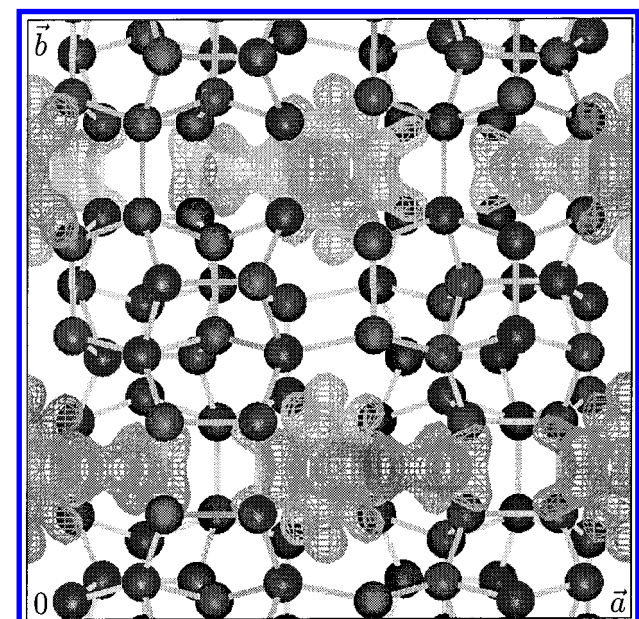


Figure 3. Difference Fourier map showing the silicon atoms of the framework and the neutron scattering density due to benzene molecules adsorbed at a coverage of ~ 7.6 molecules per unit cell.

found for benzene in the intersection refined to 2.10(5) and 1.32(5) (total of 3.4) molecules per unit cell, respectively. The observed and calculated profiles are shown in Figure 2.

For the neutron data from the sample containing eight benzene molecules per unit cell, the Fourier map, Figure 3, suggests that the molecules in the intersection are better ordered than at the lower coverage and reveals that there are molecules inside the

TABLE 2: Final Parameters for the Three Benzene Molecules Adsorbed in the Intersection and in the Straight and Sinusoidal Channels in ZSM-5 Containing ~ 7.6 Molecules Per Unit Cell (Space Group $Pnma$)

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (iso)	<i>N</i>
Si atoms: see supporting material Table 3S				4.2(2)	
O atoms:				4.87(9)	
C(1)	−0.041(1)	0.292(1)	0.510(2)	21(1)	4
C(2)	−0.081(1)	0.283(1)	0.594(2)	21(1)	4
C(3)	−0.065(1)	0.235(1)	0.666(2)	21(1)	4
C(4)	−0.008(1)	0.195(1)	0.655(2)	21(1)	4
C(5)	0.032(1)	0.203(1)	0.570(2)	21(1)	4
C(6)	0.016(1)	0.251(1)	0.498(2)	21(1)	4
D(1)	−0.052(1)	0.330(1)	0.456(2)	21(1)	4
D(2)	−0.125(1)	0.315(1)	0.604(2)	21(1)	4
D(3)	−0.096(1)	0.229(1)	0.731(2)	21(1)	4
D(4)	0.005(1)	0.159(1)	0.711(2)	21(1)	4
D(5)	0.075(1)	0.171(1)	0.560(2)	21(1)	4
D(6)	0.046(1)	0.256(1)	0.432(2)	21(1)	4
C(7)	0.083(2)	0.268(2)	0.830(3)	11(1)	2.45(4)
C(8)	0.102(2)	0.288(2)	0.925(3)	11(1)	2.45(4)
C(9)	0.166(2)	0.274(2)	0.959(3)	11(1)	2.45(4)
C(10)	0.211(2)	0.239(2)	0.898(3)	11(1)	2.45(4)
C(11)	0.192(2)	0.219(2)	0.803(3)	11(1)	2.45(4)
C(12)	0.127(2)	0.233(2)	0.768(3)	11(1)	2.45(4)
D(7)	0.033(2)	0.280(2)	0.802(3)	11(1)	2.45(4)
D(8)	0.067(2)	0.314(2)	0.973(3)	11(1)	2.45(4)
D(9)	0.182(2)	0.291(2)	1.033(3)	11(1)	2.45(4)
D(10)	0.261(2)	0.229(2)	0.924(3)	11(1)	2.45(4)
D(11)	0.226(2)	0.191(2)	0.756(3)	11(1)	2.45(4)
D(12)	0.112(2)	0.217(2)	0.695(3)	11(1)	2.45(4)
C(13)	0.034(2)	0.458(4)	0.469(4)	3(2)	1.15(4)
C(14)	0.057(2)	0.508(4)	0.404(4)	3(2)	1.15(4)
C(15)	0.043(2)	0.575(4)	0.424(4)	3(2)	1.15(4)
C(16)	0.016(2)	0.593(4)	0.516(4)	3(2)	1.15(4)
C(17)	−0.001(2)	0.544(4)	0.586(4)	3(2)	1.15(4)
C(18)	0.004(2)	0.476(4)	0.560(4)	3(2)	1.15(4)
D(13)	0.043(2)	0.405(4)	0.453(4)	3(2)	1.15(4)
D(14)	0.082(2)	0.494(4)	0.335(4)	3(2)	1.15(4)
D(15)	0.050(2)	0.612(4)	0.366(4)	3(2)	1.15(4)
D(16)	0.007(2)	0.646(4)	0.533(4)	3(2)	1.15(4)
D(17)	−0.024(2)	0.558(4)	0.655(4)	3(2)	1.15(4)
D(18)	−0.015(2)	0.438(4)	0.610(4)	3(2)	1.15(4)

cell constants *a*, *b*, *c* (Å): 20.0811(7), 19.8836(7), 13.4057(6)

calculated density (g cm^{-3}): 1.97

R-factors neutron: $R_{\text{wp}} = 0.115$, $R_{\text{exp}} = 0.064$, $R_1 = 0.092$

X-ray: $R_{\text{wp}} = 0.167$, $R_{\text{exp}} = 0.062$, $R_1 = 0.137$

sinusoidal channel. There appears to be no occupancy of sites in the straight channel, which conflicts with the predictions of theoretical calculations,⁶ but is consistent with the conclusions from the GCMC simulations,⁷ if there is a change in symmetry from $Pnma$ to $P2_12_12_1$. However, inclusion of a molecule in the straight channel¹⁶ leads to a significant improvement in the values of R_{wp} and R_1 compared to a model that has molecules restricted to the intersection and the sinusoidal channel.¹⁷ The benzene atomic parameters yielding the best simultaneous fit to the X-ray and neutron diffraction patterns in space group $Pnma$ are given in Table 2. As at low coverage, the coordinates of the framework atoms were restrained, and the molecules were restrained to perfect hexagonal shapes. The occupancy of benzene in the intersection tended to drift a little above 4 molecules per unit cell, which is the maximum possible. The occupancy was therefore fixed at 4. To aid the stability of the refinement in the final cycles, once the positions and geometry of the molecules were established, the molecules were constrained to allow only the center of mass of the molecule to move during the refinement. The final occupancies for the three benzene positions are 4.0, 2.45(4), and 1.15(4) (total of 7.6) per unit cell, for benzene(1) (in the intersection), benzene(2) (in the sinusoidal channel), and benzene(3) (in the straight

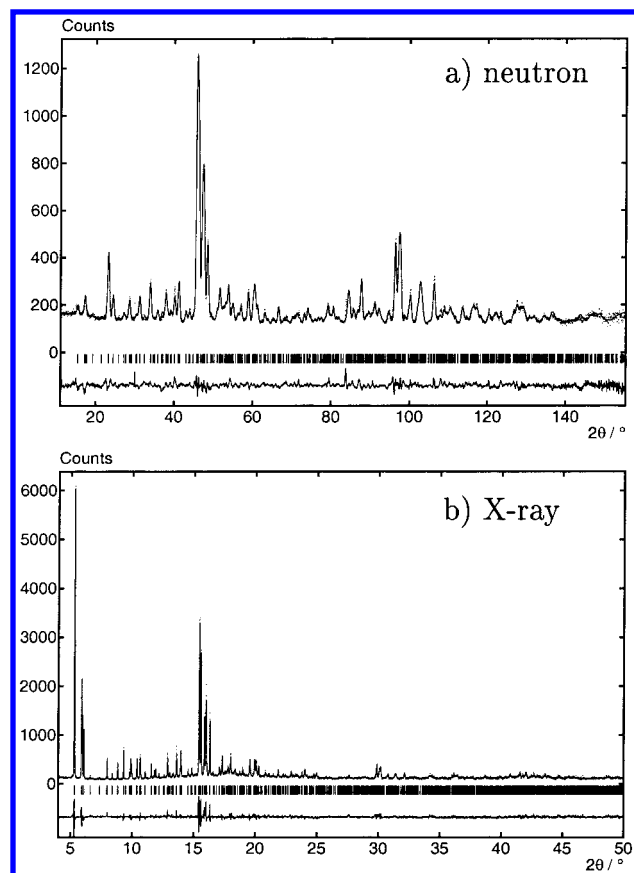


Figure 4. Observed, calculated, and difference profiles for the sample containing ~ 7.6 molecules of benzene per unit cell: (a) neutron data; (b) X-ray data.

channel), respectively. The observed and calculated profiles are shown in Figure 4.

Lower symmetry space groups are possible for the analysis.¹⁸ Each requires many more independent atomic parameters. Two were investigated. Attempts to carry out the refinement in space group $P2_12_12_1$, as found *p*-xylene for in ZSM-5,⁵ were no better than in $Pnma$. In $P2_12_12_1$, among other changes as compared to $Pnma$, the centers of symmetry in the straight channels at $(0, \frac{1}{2}, \frac{1}{2})$ and the mirror planes (at $y = \frac{1}{4}$ and $\frac{3}{4}$) which bisect the intersection and the sinusoidal channels are lost. The number of crystallographically distinct framework atoms almost doubles and the number of independent benzene molecules becomes six, as pairs of benzene molecules are no longer related by the mirror plane or the center of symmetry. Framework coordinates were taken from the single-crystal study of *p*-xylene in ZSM-5.⁵ For the adsorbed benzene, the molecules previously related by symmetry in $Pnma$ have independent coordinates and occupancies. In this case, the refinement is not stable. If the molecules are constrained to be related as if the symmetry were $Pnma$, then it is only the framework coordinates that break the $Pnma$ symmetry, and there is no significant change in the R factors. Hence it is not possible to conclude on the basis of these data whether the structure of ZSM-5 containing 7.6 molecules of benzene per unit cell is better described in space group $P2_12_12_1$. This is not really surprising. In the diffraction patterns no new peaks appear on adsorption of benzene indicating the loss of the n- or a-glide planes. Moreover, the fit in $Pnma$ is largely satisfactory. Hence, there is essentially no data to which to fit the additional parameters required in $P2_12_12_1$. Space group $Pn2_1a$ was also investigated.¹⁹ Although there was ordering for the two molecules in the straight channel, there was no significant change in R-factors. The simpler model in $Pnma$ is

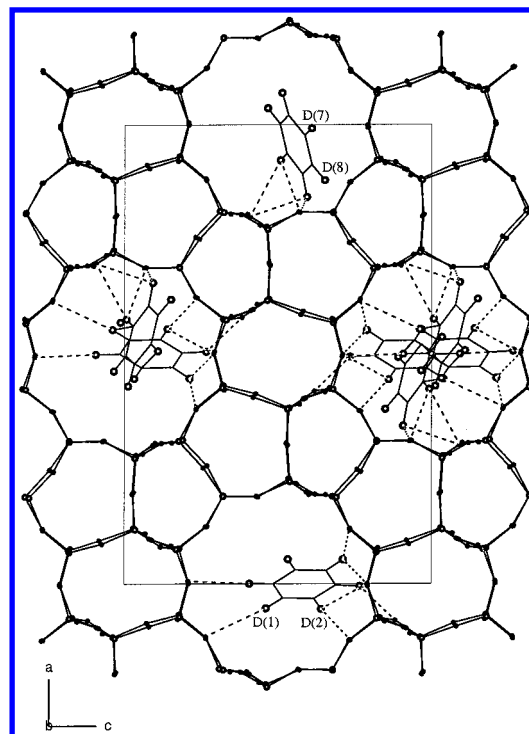


Figure 5. Projection of the two benzene positions in the intersection in ZSM-5 containing ~ 3.4 molecules per unit cell. Positions in four channels are shown: (bottom) benzene(1) molecules near the mirror plane at $y = \frac{1}{4}$; (top) benzene(2) molecules near $y = \frac{1}{4}$; (left) benzene(1) and benzene(2) molecules near $y = \frac{3}{4}$; (right) benzene(1) and benzene(2) molecules near $y = \frac{1}{4}$ and $y = \frac{3}{4}$. Framework-to-hydrogen distances of 3 Å or less are shown dotted.

therefore adopted as the basis for the discussion of the location of the molecules.

Discussion

With 3.4 molecules per unit cell, benzene is adsorbed preferentially in the intersection between the straight and sinusoidal channels. Two mutually exclusive locations have been found to fit the diffraction data most efficiently, with occupancies of 2.10(5) and 1.32(5) molecules per unit cell, respectively. The molecules are further disordered by the mirror plane that runs through the middle of the intersection, yielding four possible positions per intersection. Only one of these positions can at any time be occupied by a benzene molecule. Benzene(1) has its center 0.03 Å above the mirror plane to which it is inclined at an angle of $\sim 60^\circ$. The center of benzene(2) is 0.72 Å from the mirror plane with which its plane makes an angle of $\sim 68^\circ$. Figure 5 shows the two positions and the close approach between them. Figure 6 shows the superposition of the four benzene positions per intersection. There is a resemblance to the average neutron scattering density shown in Figure 1.

The framework is not greatly altered by adsorption of 3.4 benzene molecules. Si–O distances lie in the range 1.55(4)–1.61(3) Å, and O–Si–O angles lie between 105(2)–114(2)°. Distances between the molecules and the framework are given in Table 3. Note that caution is required in interpreting these values, because the values have high estimated standard deviations. If the six shortest hydrogen to framework oxygen distances are taken, their average is 2.87(7) Å for benzene(1) and 2.78(11) Å for benzene(2). Although the average distance seems slightly shorter for the second benzene site, Figure 5, in which the hydrogen to framework distances of less than 3.0 Å

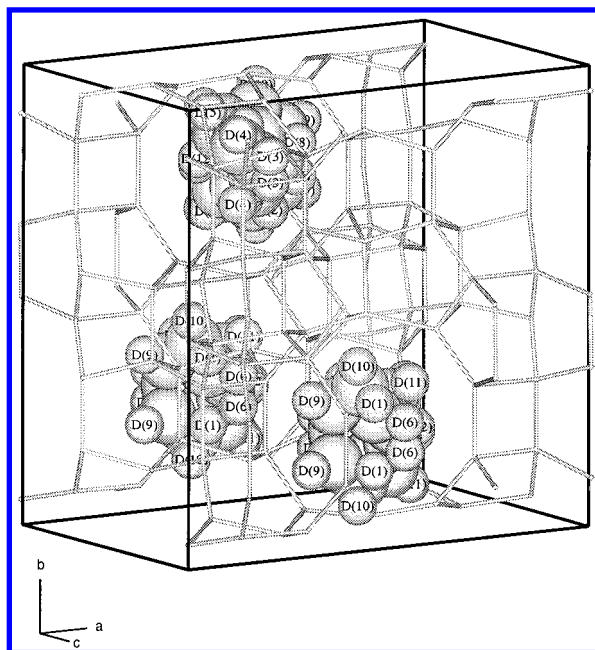


Figure 6. The superposition of the benzene(1) and benzene(2) sites in the intersection of ZSM-5, seen with a coverage of ~ 3.4 molecules per unit cell. The mirror plane passing through each intersection generates a total of four possible positions for benzene per intersection. Because of their close approach, only one of these can be occupied at any moment. Positions are shown in three intersections in the unit cell.

TABLE 3: Distances (\AA) between Benzene Molecules and Framework Atoms for the Sample Containing ~ 3.4 Molecules Per Unit Cell

D(1)	O(11)	2.93(7)	D(1)	O(20)	3.15(8)
D(2)	Si(1)	3.13(7)	D(2)	O(1)	2.65(7)
D(2)	O(21)	2.99(7)	D(3)	O(15)	2.84(7)
D(3)	O(26)	3.09(7)	D(4)	O(5)	2.73(7)
D(4)	O(21)	2.92(7)	D(5)	O(8)	3.03(8)
D(5)	O(18)	3.09(8)	D(6)	O(22)	3.00(6)
C(9)	O(2)	3.10(10)	C(10)	O(2)	3.18(9)
D(9)	Si(2)	3.18(11)	D(9)	Si(3)	3.13(10)
D(9)	O(1)	3.17(11)	D(9)	O(2)	2.39(12)
D(9)	O(20)	2.76(10)	D(10)	Si(3)	3.08(12)
D(10)	O(2)	2.55(12)	D(10)	O(20)	2.86(12)
D(11)	O(7)	3.21(10)	D(11)	O(8)	3.10(9)
D(12)	O(8)	3.17(11)	D(12)	O(25)	3.03(8)

are shown, suggests a more regular and favorable environment for benzene(1), and it is this site that has the higher occupancy. These distances can be compared to the situation for benzene adsorbed in sodium zeolite-Y.²⁰ Here, one of the two benzene molecules is located in the highly symmetric 12-ring window where it is stabilized by interactions between its hydrogen atoms and the six nearest framework oxygens at a distance of 2.73(1) \AA , and also by van der Waals attraction to the neighboring molecules attached to the SiI sodium ions in the supercage. The environment for benzene in ZSM-5 is certainly less favorable than that in zeolite-Y.

At the higher coverage, again the average framework distances and angles are not greatly altered, with Si–O distances in the range 1.54(4)–1.62(3) \AA and O–Si–O angles between 104(2)° and 117(2)°. Benzene is located at three sites with the most favored environment in the intersection, as at lower coverage, although the positions are different at the two coverages studied. The intersection is essentially full. The center of the benzene(1) molecule, in the intersection, is 0.13 \AA from the mirror plane with which it makes an angle of $\sim 47^\circ$. Benzene(2), in the sinusoidal channel, has its center 0.07 \AA from the mirror plane with which it makes a much shallower angle

TABLE 4: Distances (\AA) between Benzene Molecules and Framework Atoms for the Sample Containing ~ 7.6 Molecules Per Unit Cell

D(1)	O(11)	2.87(4)	D(11)	O(25)	2.97(5)
D(2)	O(2)	2.83(4)	D(12)	O(18)	2.56(4)
D(3)	O(15)	2.91(4)	D(12)	O(25)	2.77(5)
D(3)	O(26)	2.77(5)	C(14)	Si(2)	2.98(5)
D(4)	Si(1)	3.07(3)	C(14)	O(1)	2.51(6)
D(4)	O(5)	3.11(4)	C(14)	O(2)	2.94(6)
D(4)	O(21)	2.32(4)	C(14)	O(21)	3.02(6)
D(5)	Si(9)	3.00(3)	C(15)	O(1)	2.75(5)
D(5)	O(8)	2.90(4)	C(15)	O(2)	3.00(5)
D(5)	O(18)	2.63(4)	C(15)	O(21)	3.04(6)
D(5)	O(25)	3.08(4)	D(13)	O(7)	3.16(6)
C(8)	O(4)	2.94(5)	D(14)	Si(1)	2.58(6)
C(8)	O(17)	2.70(4)	D(14)	Si(2)	2.36(5)
C(9)	O(17)	2.82(4)	D(14)	O(1)	1.77(7)
C(11)	O(18)	3.00(4)	D(14)	O(2)	2.89(6)
D(8)	Si(4)	2.78(4)	D(14)	O(7)	3.20(8)
D(8)	Si(7)	2.84(4)	D(14)	O(13)	2.43(6)
D(8)	O(4)	2.53(5)	D(14)	O(21)	2.64(6)
D(8)	O(17)	2.03(4)	D(15)	Si(1)	2.91(6)
D(8)	O(23)	2.81(5)	D(15)	O(1)	2.36(6)
D(9)	Si(7)	3.00(4)	D(15)	O(2)	3.12(6)
D(9)	O(17)	2.29(4)	D(15)	O(21)	2.58(6)
D(9)	O(20)	2.87(4)	D(17)	O(7)	2.97(7)
D(9)	O(23)	2.75(5)	D(17)	O(14)	3.02(5)
D(10)	O(20)	2.99(4)	D(17)	O(21)	2.97(7)
D(11)	Si(6)	2.93(4)	D(17)	O(22)	2.70(7)
D(11)	Si(9)	2.96(4)	D(18)	O(1)	2.82(5)
D(11)	O(6)	2.75(5)	D(18)	O(21)	2.48(6)
D(11)	O(18)	2.27(4)			

of $\sim 29.5^\circ$. Benzene(3), in the straight channel, is positioned 0.73 \AA from the center of symmetry and makes an angle of $\sim 88.5^\circ$ with the (010) planes. Hence, it stands nearly vertically in the channel.

Benzene to framework distances are given in Table 4. Average hydrogen to oxygen distances, based on the six shortest interactions, are 2.72(4) \AA for benzene(1), 2.41(4) \AA for benzene(2), and 2.36(6) \AA for benzene(3). Some distances for benzene(2) and benzene(3) are rather short, and this no doubt reflects the limitations of our structural model, from which distances between the average positions of the framework and benzene atoms are obtained.

Benzene–benzene distances are given in Table 5 and appear generally to be sensible. Several are shorter than might be considered optimum; for benzene in sodium Y, the shortest D–D and C–D interactions are 2.56 and 2.75 \AA , respectively. Nevertheless, the distances seen in this study suggest favorable van der Waals interactions between benzene(1) and benzene(2) and between benzene(1) and benzene(3).

In Figure 7, a benzene(1) (x, y, z) molecule is shown in the intersection labeled A. This has favorable distances to a benzene(2) (x, y, z) molecule shown in the adjacent sinusoidal channel, via the D(3), D(4), and D(5) atoms of the former, and D(7) and D(12) of the latter, Table 5. A second interaction between benzene(1) and benzene(2) is possible via D(2) and D(10), as illustrated for the molecule shown in intersection B. Whereas a benzene(1) can interact with 0, 1, or 2 benzene(2) molecules depending on the local occupancy of the sinusoidal channels, each benzene(2) molecule must interact with two benzene(1) molecules, as illustrated, because the intersections are full. The molecules with the most favorable distances are shown in Figure 5. Owing to the mirror plane at $y = 1/4$, another set of interaction distances are given in Table 5, where one of the molecules is the symmetry-generated analogue of the molecule shown, (i.e., benzene(1) (x, y, z) can interact with benzene(2) ($x, 1/2 - y, z$) and with benzene(2) ($-1/2 + x, 1/2 - y, 1/2 - z$).

TABLE 5: Distances (Å) Between Benzene Molecules for the Sample Containing ~ 7.6 Molecules Per Unit Cell

benzene(1) (x, y, z)–benzene(2) (x, y, z)					
C(3)	D(7)	2.84(4)	D(4)	C(7)	3.11(4)
C(4)	D(7)	2.74(4)	D(4)	C(12)	2.97(4)
C(4)	D(12)	2.51(4)	D(4)	D(7)	2.76(4)
C(5)	D(12)	2.34(4)	D(4)	D(12)	2.45(4)
D(3)	D(7)	2.96(4)	D(5)	D(12)	2.15(4)
benzene(1) (x, y, z)–benzene(2) (x, $\frac{1}{2} - y$, z)					
benzene(2) (x, y, z)–benzene(1) (x, $\frac{1}{2} - y$, z)					
C(3)	D(7)	2.71(4)	D(3)	D(7)	2.78(4)
C(4)	C(7)	3.06(4)	D(4)	C(7)	2.65(4)
C(4)	D(7)	2.20(4)	D(4)	D(7)	1.81(4)
C(4)	D(12)	3.03(4)	D(5)	D(12)	2.96(4)
C(5)	D(12)	2.81(4)			
benzene(1) (x, y, z)–benzene(2) ($-\frac{1}{2} + x$, y, $1\frac{1}{2} - z$)					
benzene(2) (x, y, z)–benzene(1) ($\frac{1}{2} + x$, y, $1\frac{1}{2} - z$)					
D(2)	D(10)	2.88(4)			
benzene(1) (x, y, z)–benzene(2) ($-\frac{1}{2} + x$, $\frac{1}{2} - y$, $1\frac{1}{2} - z$)					
benzene(2) (x, y, z)–benzene(1) ($\frac{1}{2} + x$, $\frac{1}{2} - y$, $1\frac{1}{2} - z$)					
D(2)	D(10)	2.48(4)			
benzene(1) (x, y, z)–benzene(3) (x, y, z)					
C(1)	D(13)	2.92(7)	D(1)	D(13)	2.44(6)
C(6)	D(13)	3.17(8)	D(1)	D(18)	3.07(7)
D(1)	C(13)	3.08(7)	D(6)	D(13)	2.97(8)
benzene(1) (x, y, z)–benzene(3) (x, $\frac{1}{2} - y$, z)					
benzene(3) (x, y, z)–benzene(1) (x, $\frac{1}{2} - y$, z)					
C(4)	D(18)	2.72(8)	D(5)	C(13)	2.95(7)
C(5)	D(13)	2.67(7)	D(5)	D(13)	2.19(7)
C(5)	D(18)	3.00(8)	D(5)	D(18)	2.90(7)
C(6)	D(13)	3.21(8)	D(6)	D(13)	3.23(8)
D(4)	D(18)	2.39(7)			
benzene(1) (x, y, z)–benzene(3) ($-x$, $-\frac{1}{2} + y$, $1 - z$)					
benzene(3) (x, y, z)–benzene(1) ($-x$, $\frac{1}{2} + y$, $1 - z$)					
C(1)	D(16)	3.03(8)	C(6)	C(16)	3.21(8)
C(3)	D(15)	2.50(8)	C(6)	D(16)	2.18(8)
C(4)	C(15)	2.71(7)	D(3)	D(15)	2.82(7)
C(4)	C(16)	3.06(7)	D(4)	C(15)	2.65(7)
C(4)	D(15)	1.88(7)	D(4)	D(15)	1.79(6)
C(4)	D(16)	2.70(6)	D(5)	C(15)	3.07(6)
C(5)	C(15)	2.96(7)	D(5)	C(16)	2.61(6)
C(5)	C(16)	2.65(7)	D(5)	D(15)	2.95(6)
C(5)	D(15)	2.59(7)	D(5)	D(16)	2.13(5)
C(5)	D(16)	1.95(6)	D(6)	D(16)	2.49(7)

Figure 7 and Table 5 also show that benzene(1) can have favorable interactions with benzene(3) (x, y, z) shown in the straight channel above intersection A (via D(1), D(6) and D(13), D(18)), or to benzene(3) (x, $\frac{1}{2} - y$, z) below (via D(4), D(5) and D(13), D(18)). Benzene(1) can have either 0, 1, or 2 benzene(3) neighbors, depending on the local occupancy of the sites, whereas benzene(3) has always two benzene(1) neighbors, because the intersections are full. For the benzene(3) (x, y, z) molecule shown in Figure 7, the neighbors correspond to one of the two mirror-related positions in intersection A, (benzene(1) (x, y, z) or (x, $\frac{1}{2} - y$, z)), and one of the positions in the intersection labeled C, benzene(1) ($-x$, $\frac{1}{2} + y$, $1 - z$). Some of these distances are a little shorter than optimum. Distances to benzene(1) ($-x$, $1 - y$, $1 - z$) in C are prohibitively short and are not recorded. Simultaneous occupation of benzene(3) (x, y, z) and benzene(1) ($-x$, $1 - y$, $1 - z$) is therefore not possible, which imposes a degree of local order on the arrangement.

Benzene(1) may have up to four benzene(2) and benzene(3) neighbors, with alternative symmetry-related options. There must therefore be a degree of flexibility in the exact position of any molecule in any particular intersection. This no doubt is reflected in the large displacement parameter of 21(1) Å². Hence, the slightly short distances seen between some average benzene(3)

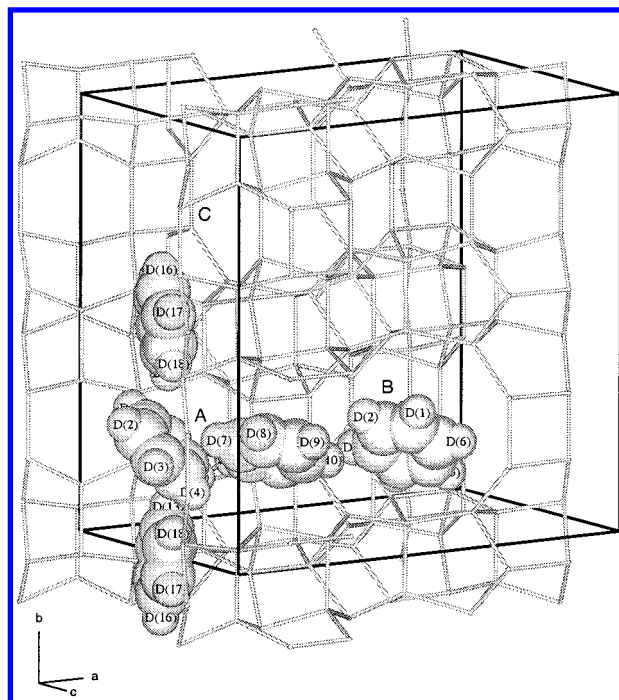


Figure 7. Some of the positions for benzene molecules are illustrated, adsorbed at a coverage of ~ 7.6 molecules per unit cell. Benzene(1) (x, y, z) and ($\frac{1}{2} + x$, y, $1\frac{1}{2} - z$) molecules are in the intersections A and B, respectively. Benzene(2) (x, y, z) is in the sinusoidal channel, and benzene(3) (x, y, z) and (x, $\frac{1}{2} - y$, z) are above and below intersection A. Important intermolecular contacts can be seen (see Table 5), e.g., benzene(1) (x, y, z)–benzene(2) (x, y, z), benzene(2) (x, y, z)–benzene(1) ($\frac{1}{2} + x$, y, $1\frac{1}{2} - z$), benzene(1) (x, y, z)–benzene(3) (x, y, z), and benzene(1) (x, y, z)–benzene(3) (x, $\frac{1}{2} - y$, z).

and benzene(1) positions noted above are not a cause of concern. Benzene(2) always has two benzene(1) neighbors, but there are two symmetry-related positions for each. Hence, the displacement parameter for benzene(2) is still substantial, but significantly less than that of benzene(1). Benzene(3) is the most constrained position, with the shortest contacts to the framework, and to the two neighboring benzene(1) positions. There is much less flexibility in the siting of this molecule, and a correspondingly small displacement parameter is obtained. Whereas the interaction distances identified in Table 5 give an overall picture of how the molecules in the channels are stabilized by intermolecular interactions, the values given have high standard deviations, and are average distances, encompassing a degree of static disorder. In themselves, they should be treated with caution. They do however indicate that the arrangement of molecules is chemically reasonable, and that there are no unavoidable intermolecular clashes that would negate the model presented here.

Conclusions

The positions found in this study are broadly in agreement with theoretical predictions⁶ and previous experimental studies, given that ZSM-5 encompasses a range of materials with different degrees of crystallinity, defects, intergrowths, and compositions. Below four molecules per unit cell, the benzene is confined to the intersection and there is considerable disorder. Two independent molecules are required to model adequately the experimental data, and further 2-fold disorder arises from the mirror plane passing through these sites. At higher coverage, the molecules are mainly located in the intersection and the sinusoidal channel, with a smaller number in the straight channel. Grand canonical ensemble Monte Carlo simulations 7

suggest that at above four molecules per unit cell there is a change in the symmetry from *Pnma* to *P2₁2₁2₁* with molecules accommodated predominantly in the intersection and sinusoidal channels. We are not able to confirm whether such a change of symmetry occurs, owing to the limited nature of our powder diffraction data. However, any deviations from *Pnma* symmetry appear to be insignificant.

The combination of X-ray and neutron diffraction has been very helpful in determining the whereabouts of benzene in ZSM-5. Because the adsorption sites are close to symmetry elements, and at low coverage there appears to be two chemically distinct sites close to each other, the observed scattering density (which is the average over all the unit cells of the sample) is highly complex and difficult to interpret. In the X-ray data, the carbon atoms dominate with hydrogen contributing only weakly, so the proximity of alternative sites means that different models, involving quite different orientations of the molecules, can fit the data comparably well. For neutrons, both carbon and deuterium atoms scatter strongly, and such a complex volume of scattering density is observed that it is again very difficult to deduce the true orientations of the molecules. However, from a combined approach, the scattering density can be unravelled, so that a model that accounts for both sets of data can be obtained, and this ought to be the best approximation to the positions of the adsorbed molecules.

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Supporting Information Available: Tables of refined Si and O atom parameters for bare ZSM-5 and for the two samples loaded with benzene. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (16) Fourier maps from powder data must be interpreted with caution, because the decomposition of the overlapping peaks into individual structure factors and calculation of the phases are dependent on the structural model. If this is in any way deficient (such as here, when there is no benzene included), the maps can be unreliable.
- (17) *R*-factors in the absence of benzene(3) are: neutron data, $R_{wp} = 0.156$, $R_1 = 0.144$; X-ray data, $R_{wp} = 0.192$, $R_1 = 0.179$.
- (18) There are four orthorhombic, nine monoclinic, and two triclinic subgroups of *Pnma*. These are *P2₁2₁2₁*, *Pn2₁a*, *P2₁ma*, *Pnm2₁*, *P2₁/n11*, *P12₁/m1*, *P112₁/a*, *Pn11*, *P1m1*, *P11a*, *P2₁11*, *P12₁1*, *P112₁*, *P1*, and *P1*.
- (19) For space group *Pn2₁a*, which has the same systematic absences as *Pnma*, a brief analysis was performed, by allowing the occupancy of the six independent molecules to refine to see if there was an arrangement that would improve the fit. In both the intersection and the sinusoidal channel, the occupancies of the two now-independent molecules stay equal within 2 combined standard deviations. For the straight channel, there is a tendency to order, with one position becoming dominant. The total occupancies of the molecules in the intersection, sinusoidal, and straight channels, and the temperature factors do not change significantly, nor is there any significant change in the *R*-factors. Given that it appears that the position in the straight channel is stabilized by interaction with the molecules in the intersection (see discussion), and the arrangement of molecules in the intersection remains essentially unaltered, this tendency to order in the straight channel was not considered important. It seems clear that in *Pnma* the refinement is on the limits of what can be extracted from the data, and the additional parameters required in the lower symmetry space group are defined by very little information. The absence of any change in *R*-factors (less than 0.1%) suggests that within the statistical precision of the data sets, the space group is *Pnma*.
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