

Probing the Locations of Benzene Molecules Inside Completely Siliceous ZSM-5 by FT–Raman Spectroscopy

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The locations of benzene molecules inside completely siliceous ZSM-5 at various loading levels were determined from FT–Raman spectra of benzene adsorbed in ZSM-5. In the low loading range (1–4 molecules/u.c.), all of the guest molecules reside at the channel intersections. In the intermediate loading range (5 and 6 molecules/u.c.), four benzene molecules are located at the intersections, while the remaining guest molecules access the zigzag channel segments. In the high loading range (7 and 8 molecules/u.c.), four guest molecules remain at the intersections and the rest of the benzene molecules move to the midsections of the straight channels. The changes in the Raman spectra of both sorbate and sorbent clearly indicate that the host framework undergoes two successive phase transitions at the loadings of 5 and 7 molecules/u.c., respectively. The zeolitic framework vibrations also indicate that there are very strong interactions between the guest molecules and the host framework in the high loaded phase.

Introduction

Zeolites are microporous materials that are widely used in industry as catalysts and sorbents.¹ Many zeolites undergo structural changes upon adsorption of certain organic molecules.² Phase transitions of this type are very important in the application of these materials as sorbents and catalysts. During the past 15 years, X-ray diffraction (XRD) and ²⁹Si MAS NMR have been employed to study the structural changes induced by sorbate molecules.^{2,3} These techniques are mainly focused on the framework itself. Recently, we have shown that FT–Raman spectroscopy is a very useful method for the investigation of sorbate-induced phase transitions in zeolitic systems via monitoring the guest molecules.⁴ The FT–Raman method can provide information uniquely complementary to that obtained from X-ray diffraction since the former is sensitive to the short range ordering and local geometry around the guest molecule and the latter detects the long range ordering in the host framework. The use of the 1064 nm excitation from a near-infrared Nd:YAG laser significantly reduces the fluorescence background, a major problem frequently associated with zeolites. We have demonstrated that the spectral parameters of the guest molecules such as the band frequency, line width, and splitting are sensitive to structural changes in the host framework. The viability and reliability of the new Raman approach have been verified by examination of the *p*-xylene/ZSM-5^{4a} and *p*-dichlorobenzene/ZSM-5 complexes^{4b} whose exact structures are known from single-crystal XRD studies. We are now in a position to use this technique to investigate unknown or poorly described sorbate-framework systems. The benzene/ZSM-5 system is one of such systems. Fyfe and co-workers first reported that the adsorption of benzene induces remarkable changes in the powder XRD and ²⁹Si MAS spectra of ZSM-5.^{2b} Although this system has been examined by several techniques including powder XRD,⁵ neutron scattering,⁶ ²⁹Si MAS⁷ and ²H wide-line NMR⁸ along with diffusional,⁹ and calorimetric studies,¹⁰ the exact structures of benzene/ZSM-5

complexes are still unknown since to date there are no single-crystal X-ray diffraction data available. There are still unanswered questions remaining. The locations of the benzene molecules inside the ZSM-5 framework have been particularly controversial. ²H NMR studies indicated that at low loadings (less than 4 molecules/unit cell) the benzene molecules reside in the midsections of the straight channels. At higher loadings, benzene molecules enter the channel intersections.^{8b} Powder XRD results, on the other hand, suggested that at a loading of 4 molecules/u.c., benzene molecules first occupy the channel intersections while both straight and zigzag channels remain empty.⁵ The benzene/ZSM-5 complex with a loading of 6 molecules/u.c. has two independent guest molecules; one located at the channel intersections and one in the zigzag channels. At the maximum loading (8 molecules/u.c.) there are also two different types of benzene molecules, but they are at the intersections and the midsections of the straight channels. A sorption kinetic study indicated that the initial adsorption of benzene occurs in the straight channels and at the channel intersections, until the loading level reaches 4 molecules/u.c.¹¹ At higher loadings, benzene molecules are forced to enter zigzag channels. Recently, there has been increasing effort to understand the adsorption of benzene in ZSM-5 on theoretical grounds.¹² Again, there is discrepancy in the locations of benzene molecules. For example, the lattice model predicts that the straight channel sites fill first,^{12a} while atomistic simulations indicate that the channel intersections fill first.^{12b} Obviously, new experimental evidence on the locations of benzene molecules inside ZSM-5 will help solve the problem.

Since the FT–Raman technique is particularly sensitive to the local environment around the guest molecules, we carried out a thorough FT–Raman study on the benzene/ZSM-5 system with particular attention being paid to the locations of the benzene molecules in the zeolitic framework. There was a report of an FT–Raman study (4 cm^{−1} resolution) on the benzene/ZSM-5 system with limited loadings (2, 4, 6, and 8 molecules/u.c.).¹³ The only changes observed in the Raman spectra in that study were the appearance of a shoulder in the C–H stretching

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TABLE 1: Raman Frequencies (cm⁻¹) of Benzene Adsorbed in ZSM-5

liquid benzene	4 molecules/u.c.	6 molecules/u.c.	8 molecules/u.c.	assignment ^a
3059	3067	3083 3067	3078 3067	ν_2 , C–H stretching (a_{1g})
3047	3052	3060 3050	3058 3050	ν_7 , C–H stretching (e_{2g})
1605	1605	1614 1607	1612 1606	$\nu_1 + \nu_6$, in Fermi resonance with ν_8
1585	1586	1595 1589	1592 1588	ν_8 , C–C stretching (e_{2g})
1176	1176	1176	1176	ν_9 , C–H deformation (e_{2g})
991	991	996 991	996 991	ν_1 , ring breathing (a_{1g})
607	607	612 606	611 607	ν_6 , ring deformation (e_{2g})

^a Reference 16c.

region at a loading of 6 molecules/u.c. and slight line broadening for the ring breathing mode upon increasing loading from 4 to 6 molecules/u.c. Our experience in FT–Raman spectroscopic studies of other sorbate/ZSM-5 systems has shown that the band splitting in the Raman spectra of sorbates is often less than 4 cm⁻¹. This is because the adsorption of organic molecules only induces very subtle changes in the framework symmetry by shearing of the TO₄ layers (T = Si or Al).¹⁴ Therefore, to observe the small changes in the spectra of the guest species and accurately interpret the spectra, a higher resolution (at least 2 cm⁻¹) must be used.

Experimental Section

Completely siliceous ZSM-5 (silicalite-1) was prepared according to a procedure described in the literature with slight modification.¹⁵ The crystallinity and purity of the sample were checked by powder X-ray diffraction.

Benzene (>99%) was obtained from Caledon Laboratories Ltd. and used without further purification.

Accurately weighed aliquots of freshly calcined ZSM-5 were loaded with precisely measured amounts of benzene. The samples were placed in glass vials which were then sealed and placed in an oven for 3 h at 73 °C. This allowed the sorbate molecules to disperse uniformly throughout the sample.

All Raman spectra were recorded at room temperature on a Bruker RFS-100 FT–Raman spectrometer equipped with a Nd³⁺:YAG laser operating at a wavelength of 1064.1 nm and a liquid nitrogen cooled Ge detector. The laser power was typically 80 mW at the sample. A resolution of 2 cm⁻¹ was employed. The number of scans for each spectrum varied from 600 to 1600, depending on the loading level. For selected loadings (8 and 6 molecules/u.c.), a one-wavenumber resolution was also used. The spectra were almost identical to those recorded with a resolution of 2 cm⁻¹.

Powder X-ray diffraction measurements were made on a Rigaku diffractometer equipped with a graphite monochromator using Co K α radiation (a wavelength of 1.7902 Å).

Results and Discussion

The FT–Raman spectra of benzene adsorbed on ZSM-5 were measured as a function of loading from 1.5 to 8 molecules/u.c. The frequencies of the Raman bands at the selected loadings together with their assignments are given in Table 1.

(i) Low Loadings (1–4 molecules/u.c.). A free benzene molecule in liquid has seven Raman active bands ($2a_{1g} + 4e_{2g} + e_{1g}$). All the fundamentals of benzene adsorbed in the zeolitic

framework (except the e_{1g} mode which is extremely weak even in the spectrum of pure liquid), as well as several combinations and overtones, were clearly observed. Within the loading range of 1.5–4 molecules/u.c., the Raman spectra of benzene adsorbed in ZSM-5 were independent of the loading, suggesting that the additional benzene molecules access the same adsorption sites inside the framework. It also indicates that the framework of ZSM-5 remains unchanged throughout this loading range. The spectra of benzene adsorbed in ZSM-5 in this loading range exhibited little difference from that of the pure liquid, i.e., no new bands appeared and no splitting occurred upon adsorption. The only noticeable changes in the spectra occurred in the C–H stretching region. The Raman spectrum of pure liquid benzene (Figure 1) shows a strong band at 3059 cm⁻¹ (a_{1g}) with a well defined shoulder at 3047 cm⁻¹ (e_{2g}) in the C–H stretching region. Upon adsorption, these bands shift by 8 and 5 wavenumbers to 3067 and 3052 cm⁻¹, respectively. The observed frequency shift toward higher energies is due to the close match between the channel size (~ 5.5 Å)¹⁷ and molecular dimension (kinetic diameter of benzene is ~ 5.85 Å).¹⁸ The effect of the restriction of the C–H stretching motions from the surrounding framework is similar to compression of the C–H bonds,¹⁹ which results in a small increase in the effective force constants, leading to the frequency shift toward higher energies. This interpretation is also consistent with the fact that the a_{1g} mode exhibited a larger shift than did the e_{2g} since the former involves a slightly larger increase in volume during the stretching vibrations than the latter. The reason that the C–H stretching modes of benzene are more sensitive to the adsorption is because the C–H bonds are located on the outside of the molecule and therefore the stretching motions are affected the most by the changes in the surrounding environment.

ZSM-5 is known to have three possible adsorption sites: the intersections between the straight and zigzag channels, and the midsections of either the straight channels or zigzag channel segments. The zigzag channels have slightly smaller dimensions than the straight channels.¹⁷ There are four equivalent positions for each site per unit cell. We suggest that at low coverages, benzene molecules reside in the channel intersections. This conclusion is based on the fact that the Raman spectra of benzene adsorbed in ZSM-5 at this loading range exhibited the smallest changes, i.e., benzene molecules undergo the smallest vibrational perturbation from the surrounding framework, compared to those obtained at higher loadings [see further discussion in sections (ii) and (iii)] because among the three adsorption sites, the channel intersections have the largest

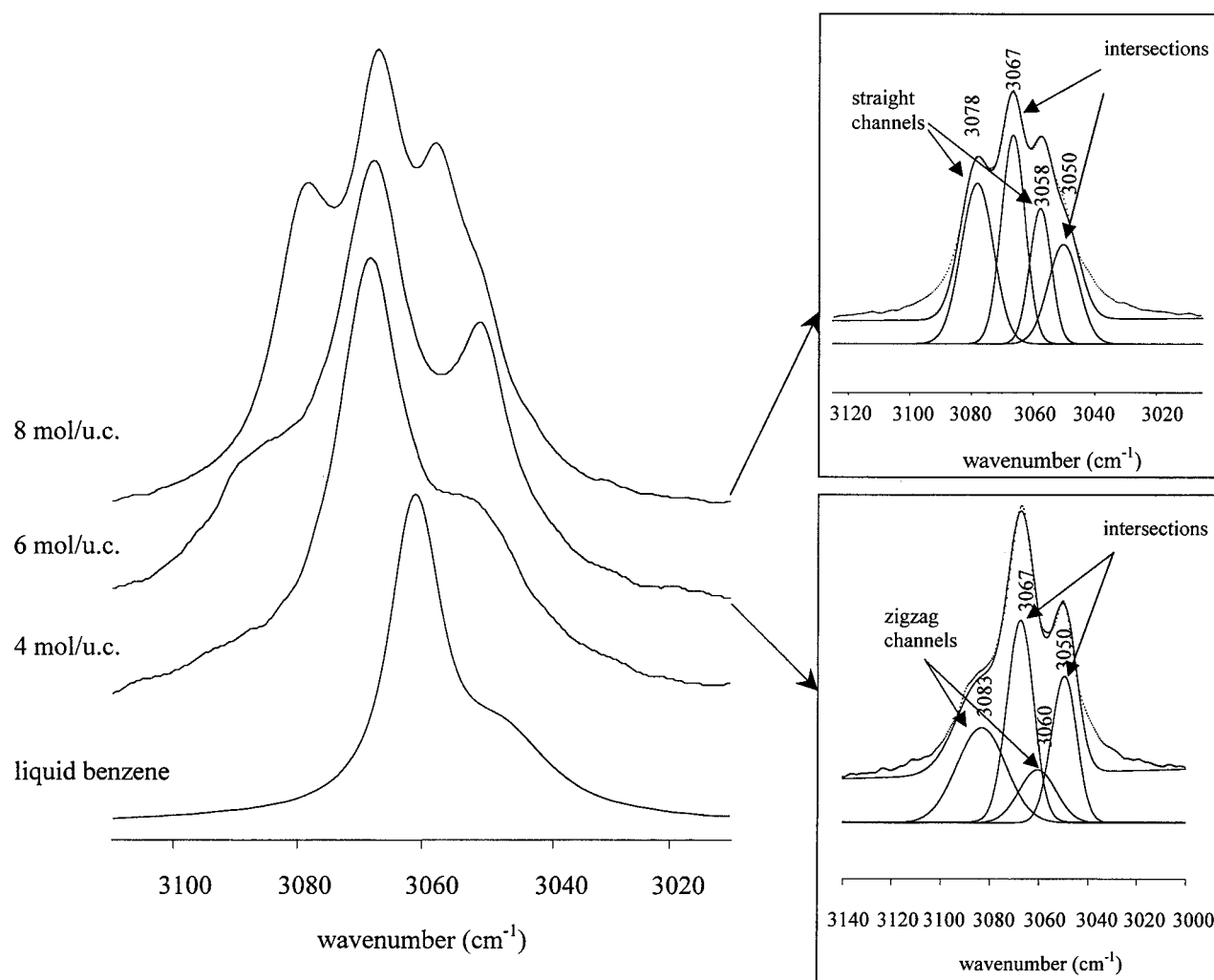


Figure 1. FT-Raman spectra of benzene/ZSM-5 complexes in the C-H stretching region at selected loadings. Top right is the deconvoluted spectrum of the 8 mol (molecules)/u.c. complex. Bottom right is the deconvoluted spectrum of the 6 molecules/u.c. complex.

amounts of free space (a near spherical "cavity" with a diameter of about 8.7 Å) for guest molecules.²⁰ Single-crystal X-ray diffraction studies have shown unambiguously that for the low-loaded *p*-xylene/ZSM-5,²¹ *p*-dichlorobenzene/ZSM-5,²² and naphthalene/ZSM-5,²³ the guest molecules are also located at the channel intersections.

(ii) Intermediate Loadings (5 and 6 molecules/u.c.). When the loading was increased to 5 molecules/u.c. the spectrum of adsorbed benzene started showing changes that became more distinct at a coverage of 6 molecules/u.c. (Figures 1 and 2). In particular, all of the fundamentals split into two components with the only exception being ν_9 at 1176 cm^{-1} . For an ordered solid, the factors such as site effect and correlation coupling usually cause the splitting in vibrational spectra. However, wide-line ^2H NMR studies have shown that at room temperature the sorbed benzene molecules are orientationally disordered.⁸ The molecular motions should effectively eliminate the above-mentioned splittings. We believe that the observed splitting actually results from the existence of two crystallographically nonequivalent benzene molecules in the framework. In the $\nu(\text{C-H})$ region (Figure 1), the deconvoluted spectrum of benzene/ZSM-5 (6 molecules/u.c.) clearly shows that there are four bands positioned at 3083, 3067, 3060, and 3050 cm^{-1} . The 3067 and 3050 cm^{-1} bands are identified as the a_{1g} and e_{2g} modes of the benzene molecules (benzene I) located at the channel intersections since their frequencies are almost identical to those of the corresponding modes observed in the spectra of benzene/ZSM-5

at the low coverages (4 molecules/u.c. or less). The 3083 and 3060 cm^{-1} bands can be assigned to the a_{1g} and e_{2g} modes originating from the second type of benzene molecule (benzene II) located in an adsorption site different from the channel intersections. The intensity ratios of both I_{3067}/I_{3083} and I_{3050}/I_{3060} estimated from the deconvoluted spectrum of benzene/ZSM-5 at a loading of 6 molecules/u.c. are approximately 2:1, implying four benzene molecules being at the intersections (benzene I) and two additional molecules (benzene II) sitting at a different adsorption site. The frequencies of benzene II are shifted to higher energies by 16 and 10 wavenumbers relative to those of benzene I located at the channel intersections for the a_{1g} and e_{2g} modes, respectively. Similarly, the bands at 607, 991, 1585, and 1605 cm^{-1} corresponding to the ring deformation, ring breathing, C-C stretching, and a combination (in Fermi resonance with the fundamental at 1585 cm^{-1}) modes, respectively, appear as singlets in the spectra of benzene/ZSM-5 at the low coverage (≤ 4 molecules/u.c.), but split into doublets at higher loadings (Figure 2). These changes were not reported in a previous Raman study.¹³ For each of these doublets, the low-frequency component is assigned to benzene I since its frequency is almost identical to that of the corresponding mode in the spectra of the samples with low loadings (Table 1). The high-frequency component which is about 6 wavenumbers higher in energy is due to benzene II. The Raman data suggest that compared to benzene I, the overall environment for the benzene II is much more restricted and constricted. Since the

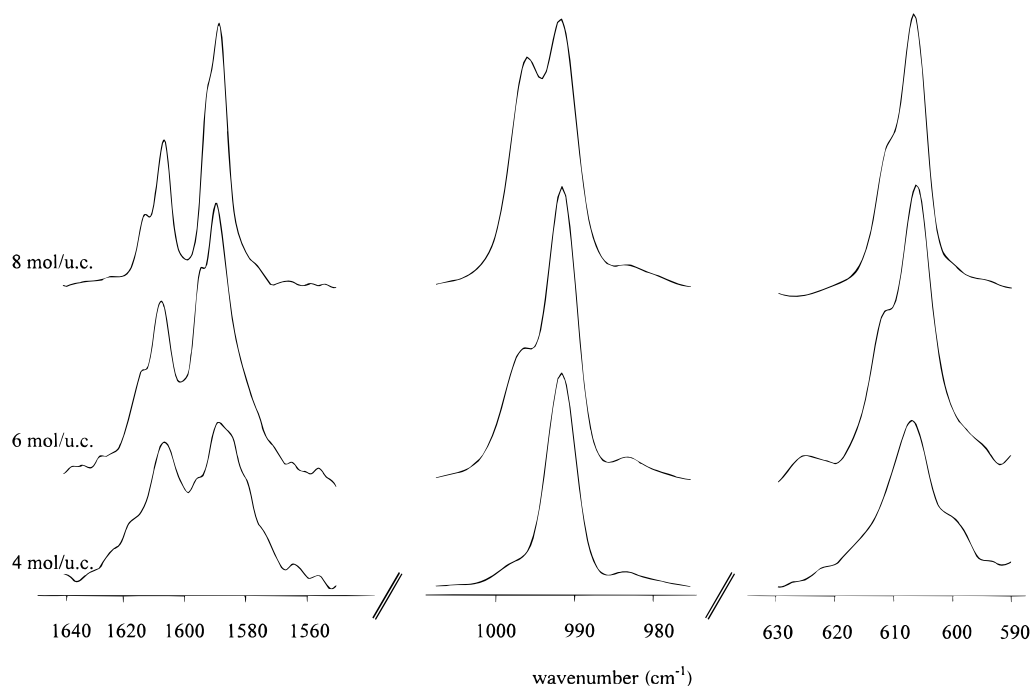


Figure 2. FT-Raman spectra of benzene/ZSM-5 at selected loadings in the C–C stretching, ring breathing and ring deformation regions.

adsorption sites at the intersections are already occupied, benzene II must be at the midsections of either the straight or zigzag channels, both of which are less accommodating than the channel intersections,²⁰ leading to the higher Raman frequencies. However, it is not clear at this point at which channel benzene II molecules are actually located.

(iii) High Loadings (7, 7.5, and 8 molecules/u.c.). The general appearance of the spectra of the samples with high loadings is similar to those of the samples with intermediate loadings (Figures 1 and 2). However, careful inspection of the spectra reveals some subtle differences. For each doublet, the relative intensity of the high frequency component increased as the loading was increased, which is particularly evident for the C–H stretching modes (3078 and 3058 cm^{-1}) and a ring breathing mode (996 cm^{-1}). This indicates an increase in the population of the second type of benzene molecule, confirming that the nature of the band splitting is indeed due to the existence of two different guest molecules. Another small but important difference is the change in the bond stretching frequencies of benzene II molecules. For instance, in the $\nu(\text{C–H})$ region, the frequencies of the a_{1g} and e_{2g} modes due to benzene I remained unchanged upon increasing the loading from 6 to 7 molecules/u.c., suggesting they are still located at the intersections. However, the positions of the a_{1g} and e_{2g} modes of benzene II shifted slightly toward lower energies from 3083 and 3060 cm^{-1} to 3078 and 3058 cm^{-1} , respectively. A similar situation was also observed for ν_8 , a C–C stretching mode. At a loading of 4 molecules/u.c., this mode appeared as a singlet at 1586 cm^{-1} . When the loading was increased to 5 molecules/u.c., a new peak began to appear at 1595 cm^{-1} due to the benzene II molecules (Figure 2). At a loading of 7 molecules/u.c., the position of this new band shifted from 1595 to 1592 cm^{-1} . We have repeated the experiments several times and found that although these observed shifts are small, they are reproducible. The implication of this finding is that at high loading levels, benzene II molecules have moved to a new adsorption site. This new site has slightly larger free space to accommodate the guest molecules, resulting in a small low-frequency shift.

On the basis of the observed changes in the Raman spectra, it is now possible to deduce the locations of benzene molecules inside the framework at various loadings. At low coverage (4 molecules/u.c. or less), there is only one type of benzene molecule (benzene I) in the unit cell. They occupy the channel intersections which have the largest free space. At the intermediate loadings (5 and 6 molecules/u.c.), there are two crystallographically nonequivalent benzene molecules. Four molecules (benzene I) remain at the intersections and additional molecules (benzene II) access the midsections of the zigzag channels which have the smallest dimensions. At high coverage (7–8 molecules/u.c.), there are also two independent benzene molecules: four molecules residing at the channel intersections, and the rest of the sorbate molecules being located in the midsections of the straight channels whose dimensions are between those of the intersections and zigzag channels. Comparing our finding with several postulations on the locations of benzene molecules in ZSM-5 available in the literature, our conclusions independently confirm those proposed by Mentzen et al. based on the powder XRD data.⁵

(iv) Possible Phase Transitions. We have shown that adsorption of benzene in three different loading ranges results in three different sets of Raman spectra. To correlate these different Raman spectra with the possible phase transitions reported in the literature, the powder XRD patterns of benzene/ZSM-5 complexes were also recorded. The powder XRD profiles of benzene/ZSM-5 with the loadings of 1.5, 2, 3, and 4 molecules/u.c. are identical and very similar to that of calcined (unloaded) ZSM-5 (Figure 3) whose exact structure is known to be monoclinic ($P2_1/n$) from a single-crystal XRD study.²⁴ The similarity in powder XRD profiles between unloaded and low loaded benzene/ZSM-5 complexes suggests that adsorption of benzene does not induce any phase transition in the zeolite within the loading range mentioned above, which is in agreement with the Raman results discussed earlier. The XRD profiles of benzene/ZSM-5 complexes with a loading of 5 and 6 molecules/u.c. are exactly the same, but they differed distinctly from that of unloaded ZSM-5 (Figure 3). For example, in the

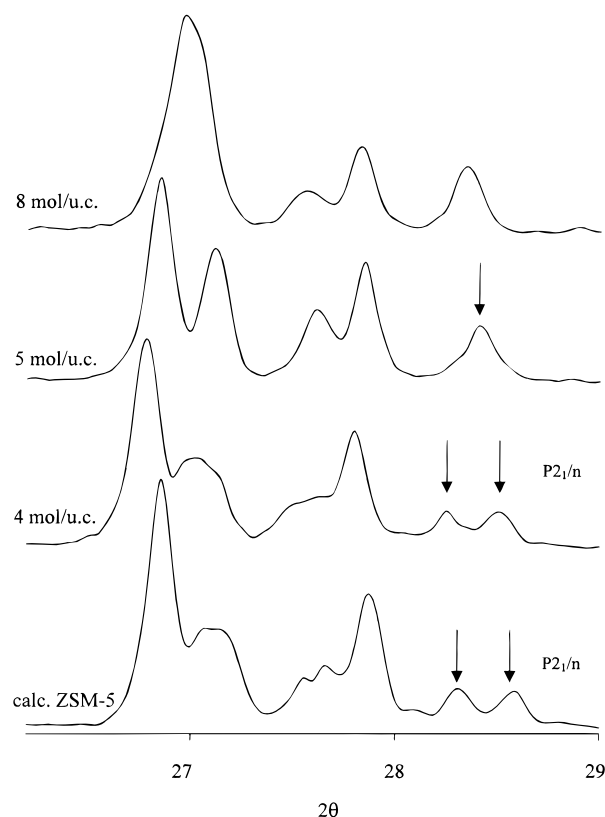


Figure 3. Powder X-ray diffraction profiles of various benzene/ZSM-5 complexes in the 26° – 29° 2θ region. \downarrow indicates the change in symmetry from monoclinic to orthorhombic, (see text).

XRD pattern of unloaded ZSM-5, a doublet was observed in the 2θ region 28° – 29° (Figure 3). It remains unchanged in the XRD patterns of the samples loaded with benzene up to 4 molecules/u.c. However, this doublet suddenly emerged as a singlet when the loading level was increased from 4 to 5 molecules/u.c. The loss of the doublet at $\sim 28.5^{\circ}$ has been widely accepted as the indication of a phase transformation in the framework of ZSM-5 from monoclinic to orthorhombic symmetry.^{2b,3a–c,6,25} Thus, the XRD results suggest that the zeolite framework starts undergoing a sorbate-induced phase transition from monoclinic to orthorhombic symmetry as soon as the fifth benzene molecule enters the unit cell (the zigzag channel). Our data confirm the powder XRD results of Mentzen et al. (who suggested that the space group of the benzene/ZSM-5 complex at a loading of 6 molecules/u.c. is $P2_12_12_1$).⁵

A second phase transition in ZSM-5 occurs at a loading of 7 molecules/u.c. as evidenced from the changes in the XRD pattern (Figure 3). Increasing loading to 7.5 and 8 molecules/u.c. did not induce any further changes in the XRD profiles, implying that the new phase is stable within the loading range of 7–8 molecules/u.c. Mentzen et al. proposed that the space group symmetry of the benzene/ZSM-5 complex with a loading of 8 molecules/u.c. to be $Pnma$.⁵ To verify their finding, we also measured the XRD patterns of *p*-dichlorobenzene/ZSM-5 and *p*-xylene/ZSM-5, both of which have a loading of 3 molecules/u.c. (not shown). These particular systems were chosen as references because the exact structures of these complexes have been identified unambiguously from single-crystal X-ray diffraction measurements to be $Pnma$.^{21,22} The fact that the powder XRD pattern of benzene/ZSM-5 looks very similar to those of *p*-dichlorobenzene/ZSM-5 and *p*-xylene/ZSM-5 indicates that the space group of the second orthorhombic phase may indeed be $Pnma$. Comparison of the powder XRD

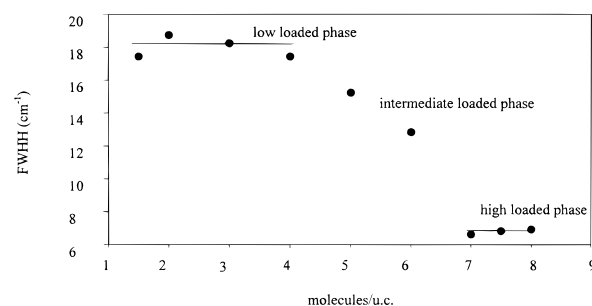


Figure 4. Plot of the full width at half-height (fwhh) of the C–H deformation mode of benzene as a function of the loading.

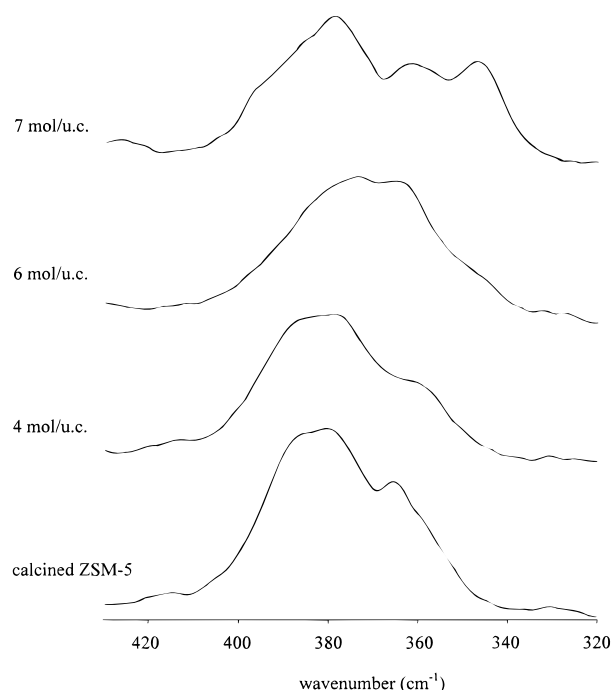


Figure 5. FT-Raman spectra of ZSM-5 framework in the $\nu_s(\text{Si–O–Si})$ region at selected loadings.

and Raman data suggests that the three sets of Raman spectra observed over three different loading ranges correspond to three different phases of ZSM-5.

The phase transition behavior can also be followed by the changes in the line width of a Raman band (ν_9) of benzene sorbed in ZSM-5. This band remained as a singlet throughout the entire loading range (1–8 molecules/u.c.), but its width is quite sensitive to the phase changes in the framework (Figure 4). The line width of vibrational modes contains the information about the dynamics of the molecule. The significant decrease in the line width clearly indicates that the degree of molecular motion was significantly reduced in the high-loaded phase.

The three phases of ZSM-5 can also be clearly identified from the zeolitic framework vibrations. Figure 5 shows the Raman spectra of ZSM-5 in the region 400 – 350 cm^{-1} where the most intense Raman bands of the zeolite framework appear. The vibrations in this region are assigned to the $\nu_s(\text{Si–O–Si})$ modes, involving the motion of oxygen atom in the plane along the direction bisecting the Si–O–Si angle.²⁶ In the unloaded ZSM-5, a rather broad profile centered approximately at 382 cm^{-1} with a resolved shoulder at 365 cm^{-1} was observed. The unit cell of completely siliceous ZSM-5 framework has a large number of atoms (288 Bravais cell atoms from $96\cdot\text{SiO}_2$), resulting in 432 Raman active modes as predicted by the factor group analysis.²⁷ Obviously, the observed broad Raman band

envelope in the region 400–350 cm^{-1} contains many closely lying unresolvable $\nu_s(\text{Si}-\text{O}-\text{Si})$ vibrations corresponding to the contributions from all the Si–O–Si bonds. The spectra of benzene/ZSM-5 in the loading range of 1–4 molecules/u.c. are independent of the coverage and look quite similar to that of unloaded ZSM-5 (Figure 5), implying that the structure of the framework remains monoclinic and this phase is stable up to a loading of 4 molecules/u.c. The result also suggests that the interactions between the host and guest are relatively small. At a loading of 5 molecules/u.c., corresponding to the phase transition from monoclinic to orthorhombic symmetry, the broad profile shifted slightly toward the lower energies (the center of the envelope moved from 382 to 374 cm^{-1}) and the distinct shoulder at 365 cm^{-1} in the spectra of the monoclinic phase almost disappeared. The frequencies of the $\nu_s(\text{T}-\text{O}-\text{T})$ modes of zeolites are very sensitive to the average T–O–T angle.^{26a,28} It is widely accepted that the frequency of the $\nu_s(\text{T}-\text{O}-\text{T})$ mode has an inverse dependence on the average T–O–T angle, which means qualitatively that a higher $\nu_s(\text{T}-\text{O}-\text{T})$ frequency corresponds to a smaller T–O–T angle. Thus, we suggest that the average Si–O–Si angle in the monoclinic phase is slightly larger than that in the first orthorhombic (intermediate loaded) phase. The overall widths of the $\nu_s(\text{Si}-\text{O}-\text{Si})$ profiles for both unloaded zeolite and the ZSM-5 loaded with 4 benzene molecules/u.c. were similar, indicating that the distribution ranges of the Si–O–Si angles in the two phases are similar.

When seven benzene molecules were incorporated into the framework, the dramatic changes in the $\nu_s(\text{Si}-\text{O}-\text{Si})$ region were observed (Figure 5). These changes imply the occurrence of the second phase transition. The spectrum of the third phase (high-loaded phase) contains at least three broad overlapping bands (at 347, 361, and 379 cm^{-1}) together with an obvious shoulder at about 394 cm^{-1} . The remarkable changes indicated that in the high-loaded phase there are very strong interactions between benzene molecules and the ZSM-5 framework and that the pores and channels undergo significant distortions. The overall width ($\sim 53 \text{ cm}^{-1}$) of the profile is much larger than that in the intermediate phase ($\sim 36 \text{ cm}^{-1}$), implying that there is a fairly large distribution in the Si–O–Si angles in the high loaded phase.

Summary

The locations of benzene molecules inside ZSM-5 at various loading levels were determined from Raman spectra of benzene adsorbed in ZSM-5. In the low loading range (1–4 molecules/u.c.), all of the guest molecules reside at the channel intersections. In the intermediate loading range (5 and 6 molecules/u.c.), four benzene molecules are located at the intersections, while the remaining guest molecules access the zigzag channel segments. In the high loading range (7 and 8 molecules/u.c.), four guest molecules remain at the intersections and the rest of the benzene molecules move to the midsections of the straight channels. The changes in the Raman spectra of both sorbate and sorbent clearly indicate that the host framework undergoes two successive phase transitions at the loadings of 5 and 7 molecules/u.c., respectively. The zeolitic framework vibrations also indicate that there are very strong interactions between the guest molecules and the host framework in the high loaded phase.

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References and Notes

- (1) *Introduction to Zeolite Science and Practice*; van Bekkum, H., Flanigen, E. M., Jansen, J. C., Eds.; Elsevier: Amsterdam, 1991.
- (2) (a) Fyfe, C. A.; Diaz, A. C.; Lewis, A. R.; Chezeau, J. M.; Grondy, H.; Kokotailo, G. T. In *Solid State NMR Spectroscopy of Inorganic Materials*; Fitzgerald, J. J., Ed., ACS Symposium Series 717; The American Chemical Society: Washington, DC, 1999, and references therein. (b) Fyfe, C. A.; Kennedy, G. J.; De Schutter, C. T.; and Kokotailo, G. T. *J. Chem. Soc., Chem. Commun.* **1984**, 541. (c) Gies, H. In *Advanced Zeolite Science and Applications*; Jansen, J. C., Stocker, M., Karge, H. G., Weitkamp, J., Eds.; Elsevier: Amsterdam, 1994; p 295 and references therein.
- (3) (a) Rohrbach, W. J.; Wu, E. L. In *Characterization and Catalyst Development*, Bradley, S. A., Gattuso, M. J., Bertolacini, R. J., Eds.; ACS Symposium Series 411, 280, The American Chemical Society: Washington, DC, 1989, and references therein. (b) Wu, E. L.; Lawton, S. L.; Olson, D. H.; Rohman, A. C., Jr.; Kokotailo, G. T. *J. Phys. Chem.* **1979**, 83, 2777. (c) Mentzen, B. F. *Zeolite News Letter* (Jpn. Assoc. Zeolite), **1993**, 10, 77 and references therein. (d) Fyfe, C. A.; Grondy, H.; Diaz, A. C.; Kokotailo, G. T.; Feng, Y.; Huang, Y.; Wong-Moon, K. C.; Mueller, K. T.; Strobl, H.; Lewis, A. R. In *Zeolites: A Refined Tool for Designing Catalytic Sites*; Bonnevot, L., Kaliaguine, S., Eds., Elsevier: Amsterdam, 1995, and references therein.
- (4) (a) Huang, Y. *J. Am. Chem. Soc.* **1996**, 118, 7233. (b) Huang, Y.; Qiu, P. *Langmuir* **1999**, 15, 1591. (c) Huang, Y.; Qiu, P. *Proceedings of the 12th International Zeolite Conference*, Vol IV; Treacy, M. M. J., Marcus, B., Higgins, J. B., Bisher, M. E., Eds., Materials Research Society: Warrendale, PA, 1999, 2431. (d) Huang, Y.; Havenga, E. A. *Langmuir* **1999**, 15, 6605.
- (5) Mentzen, B. F.; Lefebvre, F. *Mater. Res. Bull.* **1997**, 32, 813.
- (6) (a) Taylor, J. C. *Zeolites* **1987**, 7, 311. (b) Jobic, H.; Bee, M.; Dianoux, A. J. *J. Chem. Soc., Faraday Trans. 1* **1989**, 85, 2525.
- (7) (a) West, G. W. *Aust. J. Chem.* **1984**, 37, 457. (b) Strobl, H. J., Ph.D. Thesis, University of Guelph, 1989.
- (8) (a) Kustanovich, I.; Vieth, H. M.; Luz, Z.; Vega, S. *J. Phys. Chem.* **1989**, 93, 7427. (b) Portsmouth, R. L.; Duer, M. J.; Gladden, L. F. *J. Chem. Soc., Faraday Trans. 1995*, 91, 559. (c) Zibrowius, B.; Caro, J. *J. Chem. Soc., Faraday Trans. 1* **1988**, 84, 2357.
- (9) Zikanova, A.; Bulow, M.; Schlodder, H. *Zeolites* **1987**, 115.
- (10) Thamm, H. *J. Phys. Chem.* **1987**, 91, 8.
- (11) Shah, D. B.; Guo, C.-J.; Hayhurst, D. T. *J. Chem. Soc., Faraday Trans. 1995*, 91, 1143.
- (12) (a) Lee, C.-K.; Chiang, A. S. T.; Wu, F. Y. *AIChE J.* **1992**, 38, 128. (b) Snurr, R. Q.; Bell, A. T.; Theodorou, D. N. *J. Phys. Chem.* **1993**, 97, 13742. (c) Snurr, R. Q.; Bell, A. T.; Theodorou, D. N. *J. Phys. Chem.* **1994**, 98, 11948. (d) Forester, T. R.; Smith, W. J. *J. Chem. Soc., Faraday Trans. 1997*, 93, 3248.
- (13) Ashtekar, S.; Hastings, J. J.; Gladden, L. F. *J. Chem. Soc., Faraday Trans. 1998*, 94, 1157.
- (14) van Koningsveld, H. *J. Mol. Catal. A: Chem.* **1998**, 134, 89.
- (15) Collection of Verified Zeolite Synthesis; Robson, H., Ed., *Microporous Mesoporous Mater.* **1998**, 22, 628.
- (16) (a) Herzfeld, N.; Ingold, C. K.; Poole, H. G. *J. Chem. Soc.* **1946**, 316. (b) Pitzer, K. S.; Scott, D. W. *J. Am. Chem. Soc.* **1943**, 65, 803. (c) Wilson, E. B., Jr.; *Phys. Rev.* **1934**, 45, 706.
- (17) Meier, W. M.; Olson, D. H.; Baerlocher, C. *Atlas of Zeolite Structure Types*, 4th ed.; Elsevier: Amsterdam, 1996.
- (18) Bhatia, S. *Zeolite Catalysis: Principles and Applications*, CRC Press: Boca Raton, FL, 1989.
- (19) Dutta, P. K.; Shieh, D. C.; DelBarco, B. *Chem. Phys. Lett.* **1986**, 127, 200.
- (20) Xiao, J.; Wei, J. *Chem. Eng. Sci.* **1992**, 47, 1123.
- (21) Lewis, A. R., Ph.D. Thesis, University of British Columbia, 1998.
- (22) van Koningsveld, H.; Jansen, J. C.; de Man, A. J. M. *Acta Crystallogr.* **1996**, B52, 131.
- (23) van Koningsveld, H.; Jansen, J. C. *Microporous Mater.* **1996**, 6, 159.
- (24) van Koningsveld, H.; Jansen, J. C.; van Bekkum, H. *Zeolites* **1990**, 10, 235.
- (25) (a) Muller, J. A.; Conner, W. C. *J. Phys. Chem.* **1993**, 1451. (b) Lopez, A.; Soular, M.; Guth, J. L. *Zeolites* **1990**, 10, 134.
- (26) (a) Dutta, P. K.; Shieh, D. C.; Puri, M. *Zeolites* **1988**, 8, 306. (b) McMillan, P. *Am. Mineral.* **1984**, 69, 622.
- (27) (a) Bremard, C.; Laureys, J. *J. Raman Spectrosc.* **1996**, 27, 439. (b) Maroni, V. A. *Appl. Spectrosc.* **1988**, 42, 487.
- (28) (a) Creighton, J. A.; Deckman, H. W.; Newsam, J. M. *J. Phys. Chem.* **1991**, 95, 2099. (b) Dutta, P. K.; Rao, K. M.; Park, J. Y. *J. Phys. Chem.* **1991**, 95, 6654.