A Fourier Transform-Raman Investigation of the Host−Guest Interactions of *p*-Chlorotoluene, Toluene, and Chlorobenzene Sorbed on Completely Siliceous ZSM-5

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The host−guest interactions of three related sorbates including *p*-chlorotoluene, toluene, and chlorobenzene adsorbed on completely siliceous ZSM-5 have been examined by Fourier-transform (FT)-Raman spectroscopy. For *p*-chlorotoluene/ZSM-5 systems, a phase transition was detected at a loading of 4 molecules per unit cell (u.c.). Our work confirms the results of previous studies that *p*-chlorotoluene/ZSM-5 and *p*-xylene/ZSM-5 complexes exhibit similar phase-transition behavior. However, our data also show uniquely that the sorbate−sorbent interactions are significantly stronger in the *p*-chlorotoluene/ZSM-5 system. For the toluene/ZSM-5 system, a sorbate-induced phase transition in the ZSM-5 framework was also observed. Based on the information obtained from the C−H stretching region, we suggest that in the low-loaded phase, toluene molecules are located at the channel intersections, whereas in the high-loaded phase, the sorbate molecules occupy both intersections and midsections of the straight channels. In the chlorobenzene, two successive phase transitions were detected at 3 and 7 molecules/u.c. Below the coverage of 5 molecules/u.c., the guest species reside in the channel intersections. At higher loading levels, a string of sorbates is formed along the straight channels. Strong one-dimensional sorbate−sorbate interactions also occur.

Introduction

Zeolites are microporous materials that are widely used in industry as catalysts and sorbents.[1] Upon the adsorption of particular organic molecules many zeolites undergo phase transitions.[2] Understanding the nature of these transitions is crucial to their use as catalysts and sorbents. Previous studies of sorbate−sorbent systems have chiefly involved using powder X-ray diffraction and ^{29}Si magic-angle spinning NMR with emphasis on the zeolitic framework.[2,3] Recently, we have demonstrated that the Fourier transform (FT)-Raman technique is also a very useful approach for investigating sorbate-induced phase transitions, because it has the ability to detect subtle changes in the zeolitic framework by monitoring spectral features such as band splitting, line width, and frequency shift of both the guest molecules and host framework.[4] This method can provide unique information complementary to that obtained from other techniques such as powder X-ray diffraction (XRD) and solid-state NMR. We have checked the reliability and viability of this new approach by examining systems such as *p*-xylene/ZSM-5[4a] and *p*-dichlorobenzene/ZSM-5,[4b] whose exact structures are known from single-crystal XRD studies.[5,6] We presently are extending the use of this technique to investigate poorly described or unknown sorbate-framework systems. In this report, we present the results of a FT-

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Raman spectroscopic investigation of host−guest interactions in three related sorbate−sorbent systems including *p*-chlorotoluene/ZSM-5, toluene/ZSM-5, and chlorobenzene/ZSM-5 complexes. The exact structures of these complexes are unknown because no single-crystal X-ray diffraction studies have been reported on these systems.

Experimental Section

Completely siliceous ZSM-5 was prepared with a slight modification of a procedure described previously.[7] The crystallinity and purity of the sample were checked by XRD.

Toluene (99.8% HPLC Grade) and chlorobenzene (99.9% HPLC Grade) were obtained from Sigma-Aldrich Chemical Co. Inc. *p*-Chlorotoluene (⩾99% GC) was obtained from Fluka Chemika AG. All chemicals were used without further purification.

Accurately weighed aliquots of freshly calcined ZSM-5 were loaded with precisely measured amounts of each sorbate. The samples were placed in glass vials, which were then sealed and placed in an oven for 3 h at 100 °C, 120 °C, and 150 °C, respectively. This allowed the sorbate molecules to disperse uniformly throughout the samples.

All Raman spectra were recorded at room temperature on a Bruker RFS-100 FT-Raman spectrometer equipped with a Nd^{3+}:YAG laser operating at a wavelength of 1064.1 nm and a liquid nitrogen cooled Ge detector. The laser power was typically 100 mW at the sample. A resolution of 2 cm^{-1} was used. The number of scans for each spectrum varied from 600 to 1600, depending on the loading level.

XRD measurements were made on a Rigaku diffractometer equipped with a graphite monochromator using Co Kα radiation (a wavelength of 1.7902 Å).

Results and Discussion

The FT-Raman spectra and powder X-ray diffraction profiles of *p*-chlorotoluene, chlorobenzene, and toluene adsorbed on ZSM-5 were measured as a function of loading from 1.5 to 8 molecules per unit cell (u.c.). The Raman spectrum of each pure sorbate was also recorded to aid in the interpretation of the data.

***p*-Chlorotoluene/ZSM-5.** The adsorption of *p*-chlorotoluene in ZSM-5 is interesting because a single-step conversion of *p*-chlorotoluene to *p*-chlorobenzaldehyde (an intermediate in the synthesis of dyes, optical brighteners, and pharmaceuticals) can be achieved over high silica ZSM-5 incorporated with vanadium.[8] However, compared with the related systems such as *p*-xylene/ZSM-5, *p*-dichlorobenzene/ZSM-5, and benzene/ZSM-5, *p*-chlorotoluene (CT)/ZSM-5 has received much less attention. So far, there are only two reports on CT/ZSM-5 involving the use of ^{29}Si magic-angle spinning (MAS) NMR and conventional powder XRD methods in the literature.[9,10] Both were focused mainly on the structures of the framework. Little is known about the behavior of guest species inside the zeolite.

Low-Loading Range (1.5−4 molecules/u.c.). Within this loading range, the FT-Raman spectra of CT adsorbed in ZSM-5 are independent of the coverage, that is, increasing the loading level did not alter the spectra. This indicates that the first four CT molecules access identical sites within the framework structure. These results also suggest that there is no phase change occurring throughout the above-mentioned loading range, which agrees with previous NMR and powder XRD data.[9,10] The spectra of CT adsorbed on ZSM-5 within the low-loading range looked similar to those of pure CT liquid in the spectral range of 1650−100 cm^{-1}. The interesting changes occurred in the C−H stretching region. A free CT molecule under C_{2v} point symmetry should display four Raman active ring C−H stretching modes ($2a_1+2b_1$). The spectrum of pure CT in the ring ν(CH) region displays only two bands positioned at 3063 and 3029 cm^{-1}. The 3063 cm^{-1} band was previously assigned to ν_1 and ν_2 .[11,12] Both have a_1 symmetry and are accidentally degenerate. Figure 1 shows that this band has the highest relative intensity compared with all other C−H stretching vibrations. Upon adsorption, this band shifted by 11 cm^{-1} to 3074 cm^{-1} and its relative intensity was reduced remarkably. (*Note:* All the intensity changes discussed above are relative to a band positioned at 1379 cm^{-1}, a methyl C−H bending mode, which neither splits nor is broadened in the entire loading range.) These changes were also accompanied by the appearance of a new band at 3060 cm^{-1}. We assigned this new band to one of the two a_1 modes that are degenerate in the spectrum of pure CT liquid. Apparently, significant interactions occur between the zeolite framework and C−H bonds of the aromatic ring, which affect ν_1 and ν_2 differently, resulting in the removal of the accidental degeneracy. We further assigned the 3074 cm^{-1} band to the ν_1 mode and 3060 cm^{-1} band to the ν_2 mode. The assignment was based on the observed frequency shift. It had been observed previously that for many molecules closely related to CT, such as *p*-xylene, *p*-dichlorobenzene, and benzene, the ring C−H stretching vibrations experience frequency shift toward higher energies upon adsorption on ZSM-5.[4] This results from the restriction of the C−H stretching motions from the surrounding framework, because the dimensions of these molecules closely match the channel sizes of ZSM-5.[13] Because the ν_1 mode of CT involves a slightly larger increase in volume during the stretching vibration than does the ν_2 mode, a larger blue shift for the ν_1 mode is expected.

In the methyl C−H stretching region, the frequency of the $\nu_s(CH_3)$ mode centered at 2922 cm^{-1} in the spectrum of pure CT liquid increased by 7 cm^{-1} upon adsorption. The behavior of this mode is different from that of *p*-xylene adsorbed in ZSM-5. Our previous work showed that the frequency of the same $\nu_s(CH_3)$ mode remained essentially unchanged in the low-loaded phase compared with the pure-liquid spectrum.[4a] We suggested that the lack of change in frequency is due to the long axis of *p*-xylene being orientated along the channel direction; therefore, the methyl C−H stretching vibration is much less restricted by the framework. This argument has been confirmed by a recent single-crystal X-ray diffraction study of low-loaded *p*-xylene/ZSM-5

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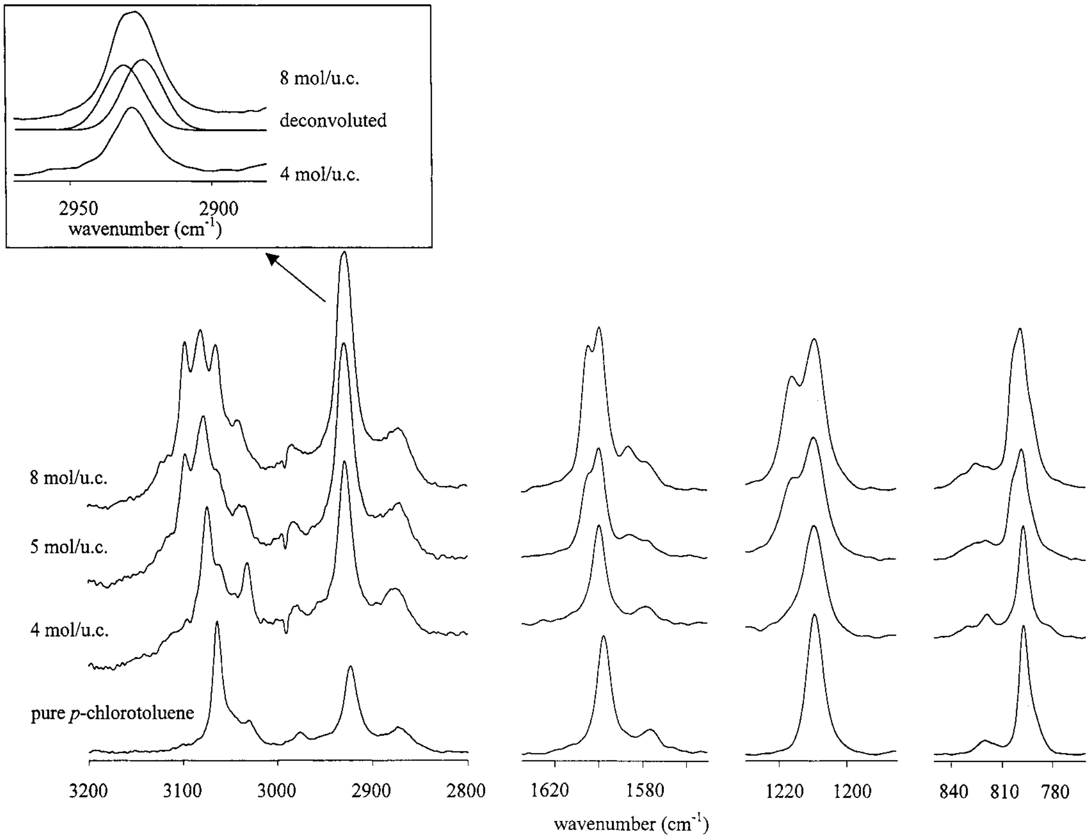

Figure 1. FT-Raman spectra of *p*-chlorotoluene/ZSM-5 complexes in several regions at selected loadings. The insert is an enlargement of the $\nu_s(CH_3)$ mode.

complex, which shows that *p*-xylene molecules are located at the channel intersections with the methyl–methyl axis being exactly along the straight-channel direction.[5a] In the present case, observation of a significant frequency shift to higher energies indicates that substantial interaction must occur between methyl hydrogens and framework oxygen atoms, resulting from the C_2 axis of the CT molecule deviating by a small angle from the straight-channel axis. Such interaction is probably due to the existence of a large permanent molecular dipole moment (2.21 D).[14]

ZSM-5 has three adsorption sites: the intersections between the straight and zigzag channels, and the midsections of either the straight channels or zigzag channel segments.[15] There are four equivalent positions for each site per unit cell. The channel intersection has the largest free space (a near spherical "cavity" with a diameter of about 8.7 Å) for guest molecules.[16] Therefore, the molecules located at this site should undergo the smallest vibrational perturbation from the surrounding framework. The sizes of the zigzag channels, on the other hand, have the smallest dimensions and are the least accommodating; therefore, the sorbate molecules in the zigzag channels are expected to exhibit the largest frequency shift toward higher energies. Based on the discussion above, we suggest that the CT molecules occupy the channel intersections, because the Raman spectra of CT adsorbed in ZSM-5 within this coverage range displayed the smallest changes, that is, the CT molecules undergo the smallest vibrational perturbation upon adsorption compared with those obtained at higher loadings.

High-Loading Range (5–8 molecules/u.c.). When the loading was increased to 5 molecules/u.c. distinct changes started occurring in most regions of the spectrum, implying the onset of a phase transition. These changes were complete as a loading level of 6 molecules/u.c. was reached, indicating the completion of the phase transition. The phase-transition behavior can be followed by shifts in frequency of several vibrational modes. Figure 2A demonstrates a sudden increase in the frequency of ν_{19}, where the phase transition at a loading of 5 molecules/u.c. is evident. This mode appeared as a single band at 300 and 309 cm^{-1} in the low- and high-loaded phases, respectively. However, both bands were present in the spectra of the samples with the loadings of 5 and 6 molecules/u.c. (Figure 2B), indicating that both low- and high-loaded phases coexist at these loading levels. At the transition, some vibrational modes undergo line broadening. Figure 3 illustrates an abrupt increase in the line width of $\nu_s(CH_3)$ at a loading of 5 molecules/u.c. The spectrum of the high-loaded phase also looked remarkably different from that of the low-loaded phase with many bands split into two components. Figure 1 shows the splitting in various spectral regions. The observed splitting indicates the existence of two crystallographically nonequivalent CT molecules. We assign the low-frequency component of each doublet to the CT molecules (CT I) residing in the channel intersections (which have the largest dimension), because the fre-

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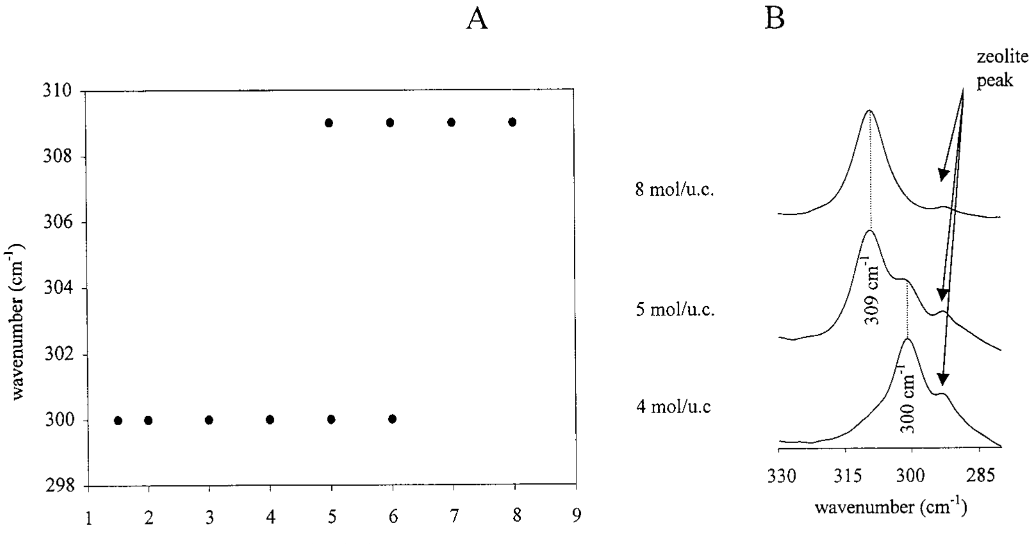

Figure 2. (A) Plot of the frequency of ν_{19} as a function of loading. (B) The corresponding FT-Raman spectra of *p*-chlorotoluene/ZSM-5 complexes are shown at selected loadings.

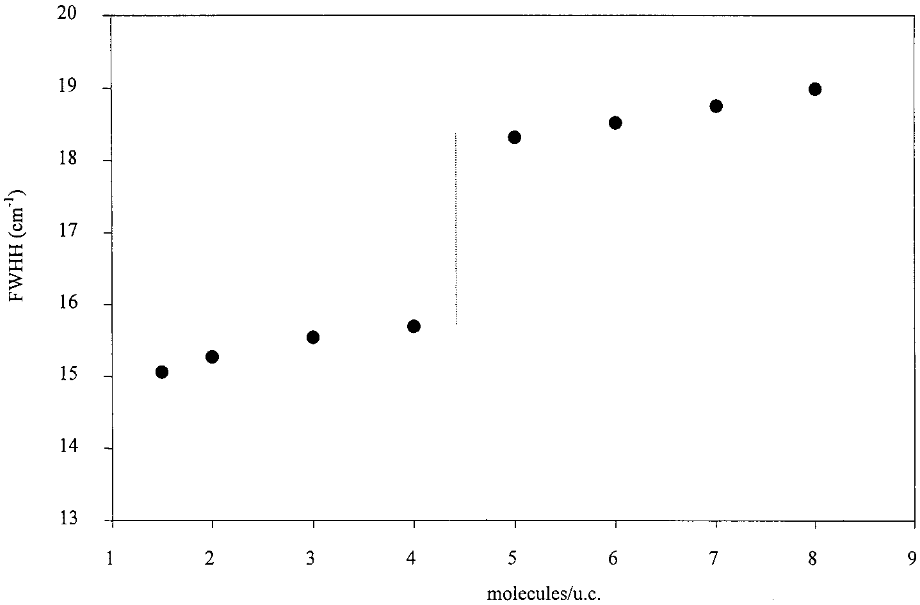

Figure 3. Plot of the full width at half-height (fwhh) of the $\nu_s(CH_3)$ mode of *p*-chlorotoluene as a function of loading.

quency of this component is identical with that of the corresponding mode in the spectra of the samples with low loadings and the high-frequency component to the guest molecules located in either the zigzag or the straight-channel segments. We further suggest that the CT molecules (CT II) are actually located in the mid-sections of the zigzag channels. This argument is based on the frequencies of the symmetric ring C−H stretching vibrations. Our previous work[4] has shown that these modes are very sensitive to the locations of the guest molecules inside the framework, because the C−H bonds are on the exterior of the molecule and, therefore, most sensitive to the changes in their environment. The frequency of the symmetric ring C−H stretching mode (3095 cm^{-1}) of CT II, ν_1, exhibited a very large shift with respect to the value of the same mode in the pure liquid spectrum (3063 cm^{-1}). This shift (32 cm^{-1}) is very similar to that (31 cm^{-1}) observed in the closely related, high-loaded *p*-dichlorobenzene/ZSM-5 system, which does consist of two types of guest species residing in the intersections and zigzag channels, respectively, as determined unambiguously by single-crystal X-ray diffraction.[6] When the sorbate molecules are in the straight channel, the corresponding shift has a smaller value (less than 10 cm^{-1}), as seen in toluene/ZSM-5 and chlorobenzene/ZSM-5 (see discussion below), because the dimensions of the straight channels are slightly larger than the zigzag channels,[13a] and the ring C−H stretching motions are therefore less restricted.

It is also interesting to compare the host−guest interactions between high-loaded CT/ZSM-5 and *p*-xylene/ZSM-5. Single-crystal X-ray diffraction studies have shown that there are two nonequivalent *p*-xylene molecules in the high-loaded ZSM-5 phase with four molecules (*p*-xylene I) at the intersections and the rest (*p*-xylene II) in the zigzag channels.[5b] As mentioned earlier, the symmetric ring C−H stretching mode of CT II has shifted by 32 wavenumbers from 3063 to 3096 cm^{-1} in the spectra of pure liquid and high-loaded phase, respectively. Such a large increase in frequency

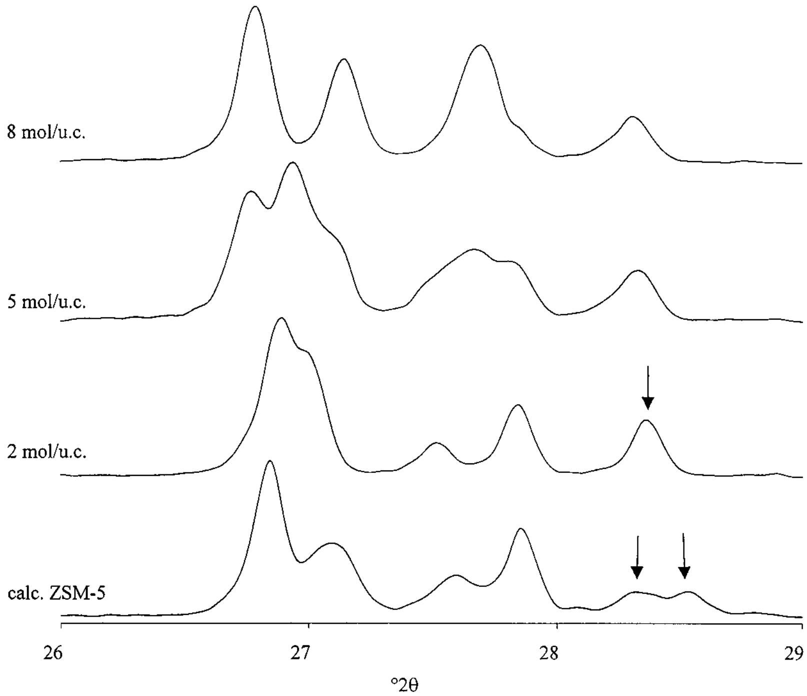

Figure 4. Powder X-ray diffraction profiles of various *p*-chlorotoluene/ZSM-5 complexes in the 26−29° 2θ region. ↓ indicates the change in symmtery from monoclinic to orthorhombic (see text).

indicates very strong host−guest interactions that induce the observed phase transition. For the *p*-xylene II, the corresponding frequency shift is smaller.[4a] The fact that the frequency shift (32 cm^{-1}) of the ring ν (C−H) mode of CT II is significantly larger than that of the same mode of *p*-xylene II (20 cm^{-1}) implies that, in the high-loaded phase, the CT molecules located in the zigzag channels interact with the framework more strongly than those of *p*-xylene. As mentioned earlier, the line width of ν_s(CH$_3$) of CT becomes much broader in the high-loaded phase. A closer look (Figure 1) reveals that the shape of this mode is asymmetric, indicating that this peak also splits into two components. The high-frequency component can be assigned to the methyl group of CT molecules located in the zigzag channels. Observation of two different methyl group suggests the interaction between the methyl group of CT II and the wall of the zigzag channel is stronger. This behavior is much different from that of *p*-xylene sorbed in ZSM-5. The methyl groups of *p*-xylene virtually have no interactions with the framework, because the frequencies of the ν_s(CH$_3$) mode in both high- and low-loaded phases are identical and exhibit little difference from that of pure liquid. Neither splitting nor line broadening occurred at the phase transition. These results imply that the host−guest interactions in the CT/ZSM-5 system are stronger than that in the *p*-xylene/ZSM-5 complexes.

We have shown that adsorption of CT in two different loading ranges results in two sets of Raman spectra. To confirm these different Raman spectra correspond to two different phases, the powder XRD patterns of CT/ZSM-5 at various loading levels were also obtained. The XRD profiles (Figure 4) of 0, 2, and 8 CT molecules/u.c. correspond to three different known phases of ZSM-5 ($P2_1/n$, $Pnma$, and $P2_12_12_1$).[10] Thus, the changes in XRD patterns are in agreement with the Raman data. The XRD pattern of the sample with a loading of 5 molecules/u.c. indicates a mixture of the two phases, which is also consistent with the Raman spectrum.

In short, our results indicate that in the low coverage (≤4 molecules/u.c.), the guest molecules occupy the channel intersections. Whereas, when the loading is increased to 5 molecules/u.c., the ZSM-5 framework undergoes a phase transition to adopt the fifth sorbate molecule. Our Raman data seem to suggest that one of the CT molecules that was sitting in the channel intersections now moves into the midsection of the zigzag channel and that the incoming fifth CT molecule replaces the vacant adsorption site at the intersection. The locations of CT molecules at high loadings (≥5 molecules/u.c.) are such that 4 molecules are located at the channel intersections and the remaining ones are sitting in the midsections of the zigzag channels.

Although the phase-transition behavior of CT/ZSM-5 seems to be similar to that of *p*-xylene/ZSM-5, the interactions between the guest species and host framework were much stronger in CT/ZSM-5 than in *p*-xylene/ZSM-5 systems. In addition, the strong interaction of the methyl group of CT with the zeolite indicates that, unlike *p*-xylene adsorbed in ZSM-5, the molecular long axis (C_2) of CT is not exactly aligned along the channel direction.

Toluene/ZSM-5. The exact structures of toluene/ZSM-5 complexes at different loadings are unknown because no single-crystal XRD data are available, although the sorption and diffusion of toluene in ZSM-5 have been studied previously by use of calorimetric methods,[17] adsorption measurements,[18] ^{2}H NMR,[19] conventional powder XRD,[20] and molecular dynamic simulations.[21] Here, we present the results of the first FT-Raman study of host−guest interactions in the toluene/ZSM-5 system.

The Raman spectra of toluene/ZSM-5 complexes were measured with respect to the loading of sorbate. The spectra of toluene adsorbed in ZSM-5 looked the same in low coverage (1−4 molecules/u.c.), implying that

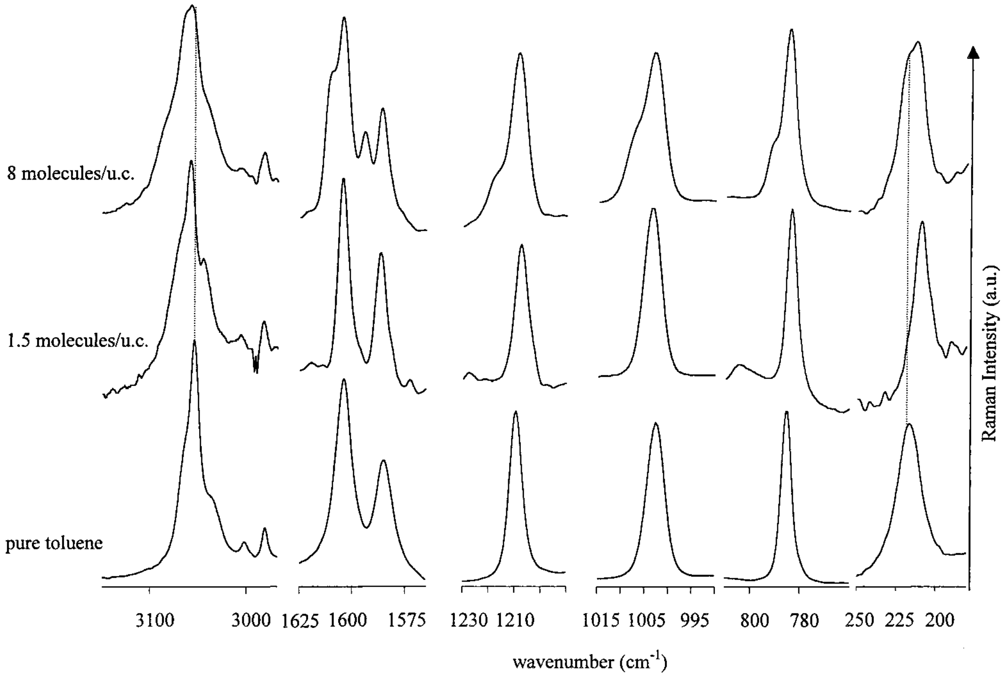

Figure 5. FT-Raman spectra of toluene adsorbed on ZSM-5 in various regions at selected loadings.

toluene is accessing the same adsorption sites up to a loading level of 4 molecules/u.c. Within the abovementioned loading range, the spectra of toluene are very similar to that of pure toluene liquid, that is, no splitting occurred and no new peaks appeared. The only noticeable change is that, upon adsorption, the ring C−H stretching modes moved from 3053 and 3037 cm^{-1} in the spectrum of pure liquid to 3058 and 3044 cm^{-1}, in toluene/ZSM-5 complexes, respectively. The methyl symmetric C−H stretching mode, $\nu_s(CH_3)$, only shifted slightly from 2918 cm^{-1} in liquid to 2922 cm^{-1} in toluene/ZSM-5 complexes. However, this shift (4 cm^{-1}) is smaller than the shift (7 cm^{-1}) observed for the same mode in CT/ZSM-5 complexes, indicating that the interaction between the methyl group and the framework is weaker in toluene/ZSM-5 than in CT/ZSM-5 and that the molecular axis of toluene is more aligned with the channel direction.

Starting from a loading of 5 molecules/u.c., several changes occurred in the spectrum of toluene, and these changes become more pronounced at the maximum loading of 8 molecules/u.c. In particular, two bands at 1604 and 1586 cm^{-1}, the C−C stretching modes[12,22] were split into two components (Figure 5). Similarly, a peak at 209 cm^{-1}, a C−CH_3 in plane-bending mode, was split into a doublet. In addition, Figure 5 shows that a prominent shoulder was also developed on the high-frequency side of the bands positioned at 1208, 1003, and 784 cm^{-1}, which are due to the C−H deformation, ring breathing, and C−C bending modes, respectively. These changes in the spectrum of the sorbate occur concomitantly with a sorbate-induced phase transition occurring at a loading of 5 molecules/u.c.

The phase transformation is also evident from the changes in the zeolitic framework vibrations. Figure 6A shows the Raman spectra of ZSM-5 in the region 425−325 cm^{-1} where the most intense Raman bands of the zeolitic framework appear. The vibrations in this spectral region are assigned to the symmetric Si−O−Si bending modes.[23] Our recent work has shown that these zeolite bands are also sensitive to the structural change in the framework.[4a,4e] In the unloaded ZSM-5, a broad envelop centered at 380 cm^{-1} together with a prominent shoulder at 365 cm^{-1} was observed. The fact that the spectra of ZSM-5 framework incorporated with 1−4 toluene molecules/u.c. are very similar to those of unloaded ZSM-5 and are independent of the loading level indicates that the framework structure of ZSM-5 remains monoclinic ($P2_1/n$), and this phase is stable up to a loading of 4 molecules/u.c. Starting from a loading level of 5 molecule/u.c., the profile of ZSM-5 framework vibrations underwent distinct changes. In the intermediate loading of 5 molecules/u.c. the overall breadth of the zeolitic profile becomes broader and consists of several overlapping peaks implying that a phase transition had occurred. As the loading level is increased to 6 molecules/u.c., the profile of zeolitic vibrations becomes less broad and contains two distinct peaks at 375 and 354 cm^{-1}. Increasing the loading level further did not induce changes in the spectra. The Raman results are confirmed by powder XRD data (Figure 6B). The powder XRD patterns of the samples with the loading less than 4 molecules/u.c. is essentially identical with that of unloaded ZSM-5, which is consistent with the Raman results. At the loadings above 4 molecules/u.c. two reflections (in the 2θ region 28−29°) in the spectrum of

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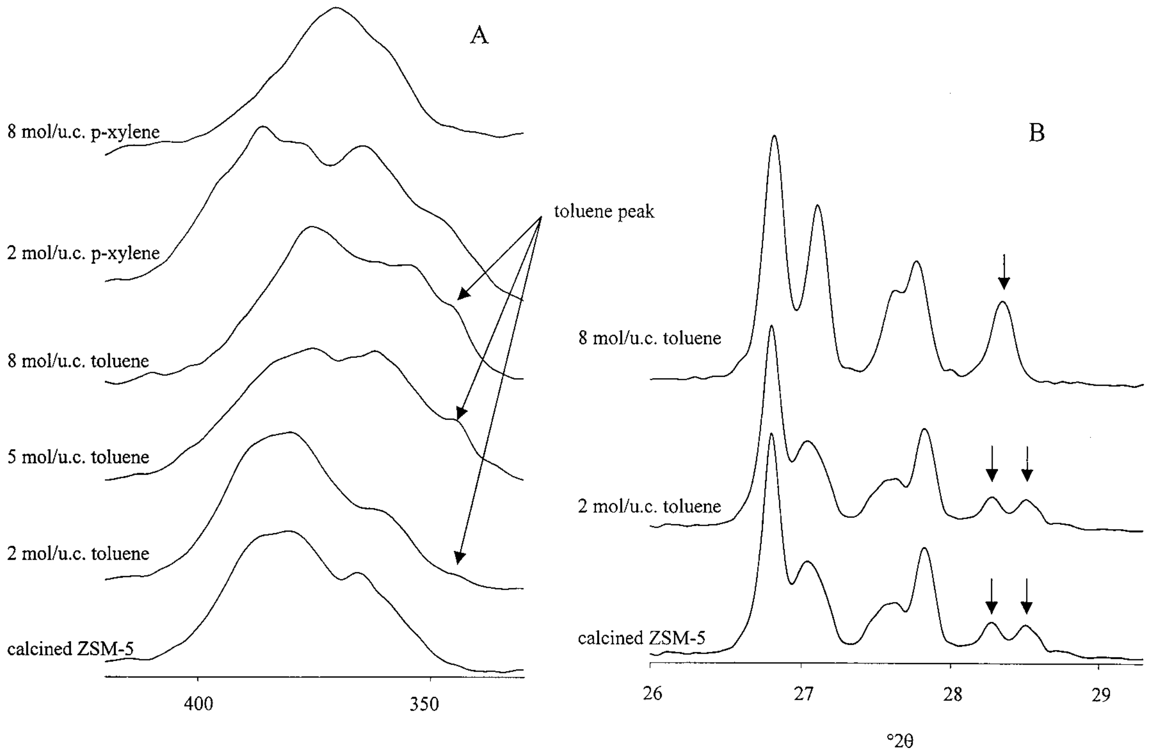

Figure 6. (A) FT-Raman spectra of ZSM-5 framework in the ν_s(Si−O−Si) region at selected toluene loadings. (B) Powder X-ray diffraction profiles of selected toluene/ZSM-5 complexes in the 26−29° 2θ region. ↓ indicates the change in symmetry from monoclinic to orthorhombic (see text).

the low-loaded phase suddenly emerged as a single reflection in the high-loaded phase, which is characteristic of a monoclinic to orthorhombic phase transition.[3]

Previous single-crystal X-ray diffraction studies of *p*-xylene/ZSM-5 and *p*-dichlorobenzene/ZSM-5 have shown that the framework of ZSM-5 can adopt two different orthorhombic forms, *Pnma* and $P2_12_12_1$, depending on the nature and the loading level of the sorbate.[5,6] A conventional powder XRD study suggested that the structure of the high-loaded phase of toluene/ZSM-5 belongs to space group $P2_12_12_1$, which is the same as that of high-loaded *p*-xylene/ZSM-5.[10] Our previous work has shown that for *p*-xylene/ZSM-5, two orthorhombic phases can be clearly distinguished from their distinct Raman spectra in framework Si−O−Si bending region. In the present case, the profile of the zeolite vibrations in the 8 molecules/u.c. spectrum looks similar to that observed in high-loaded *p*-xylene/ZSM-5 (Figure 6A). The similarity in the Raman spectra suggests that the space group symmetry of the high-loaded toluene/ZSM-5 complex may be $P2_12_12_1$. Thus, the Raman results confirm the results of powder XRD.

As discussed earlier, the frequencies of the ring C−H stretching vibrations are very sensitive to the overall environment surrounding an aromatic molecule inside ZSM-5 and therefore can be used to obtain the information on the locations of guest molecules. The strongest symmetric ring C−H stretching mode of toluene is ν_{13} [a_1 ν (C−H)$_{sym}$] positioned at 3053 cm^{-1} in the spectrum of pure liquid. In the high-loaded phase (Figure 5), the overall profile looks similar to that in pure liquid. But careful inspection reveals that this mode actually splits into a doublet centered at 3063 and 3057 cm^{-1} with approximately equal intensity. The low-frequency component can be assigned to the molecules located at the channel intersections (toluene I) because its frequency is very close to that of pure liquid. The high-frequency component can be assigned to the toluene molecules adsorbed at either the straight channels or zigzag channels (toluene II) because it experienced a slightly larger frequency shift. We suggest that toluene II resides in the straight channels. This assignment is based on the fact that the frequency difference in ν_{13} between toluene II and pure liquid is only 10 cm^{-1}, much smaller than those found in *p*-xylene and *p*-dichlorobenzene adsorbed in ZSM-5. The exact structures of *p*-xylene/ZSM-5 and *p*-dichlorobenzene/ZSM-5 loaded with 8 molecules/u.c. have been determined by single-crystal X-ray diffraction methods. In each case, 4 molecules are located in the intersections and the remaining 4 molecules reside in the zigzag channels. In the Raman spectra, the symmetric ν (CH) modes corresponding to the ν_{13} of toluene also split into two components. However, the differences in frequency between the high-frequency component representing the guest molecules in the zigzag channels and free molecule are quite large. The shifts are 20 and 30 cm^{-1} for *p*-xylene and *p*-dichlorobenzene in high-loaded ZSM-5 phases, respectively. The small shift observed in high-loaded toluene/ZSM-5 complexes indicates that toluene II molecules are likely residing in the midsections of the straight channels whose dimensions are between those of the intersections and zigzag channels.

In short, the changes in the Raman spectra of both sorbate and sorbent indicate a monoclinic to orthorhombic phase transition occurring at a loading of 5 molecules/u.c. The structure of the low-loaded phase is monoclinic. The space group symmetry of high-loaded toluene/ZSM-5 complexes may be $P2_12_12_1$. There are two types of crystallographically nonequivalent toluene molecules

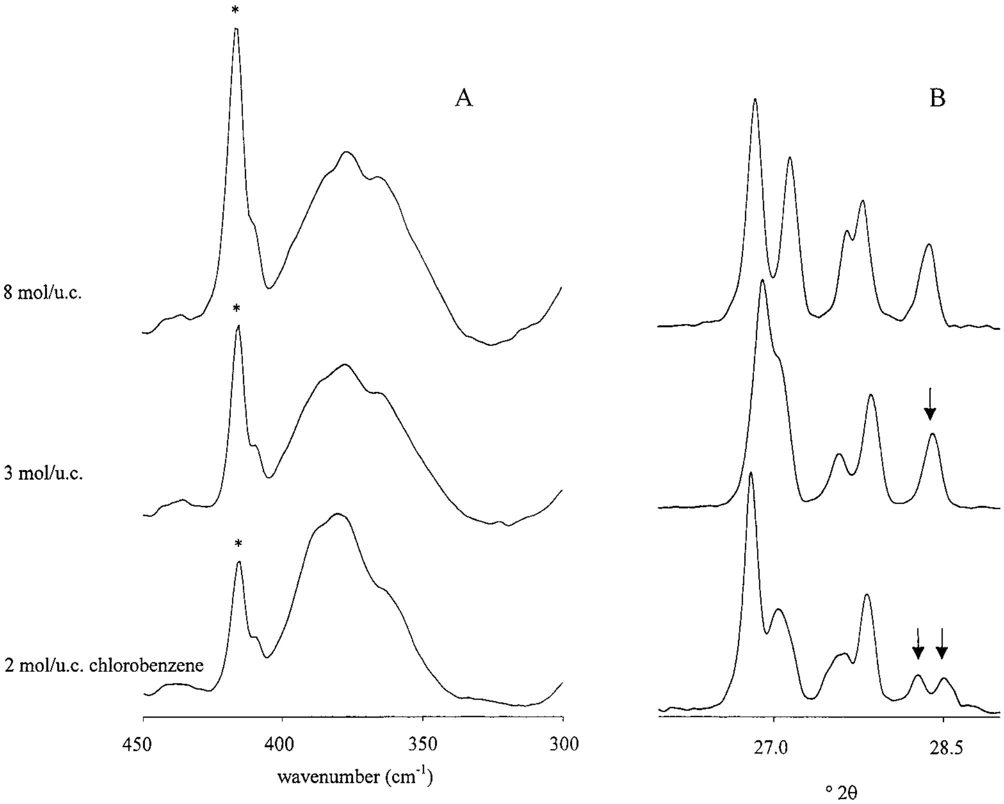

Figure 7. (A) FT-Raman spectra of ZSM-5 framework in the ν_s(Si–O–Si) region at selected chlorobenzene loadings. The peak labeled (*) is a chlorobenzene vibrational mode. (B) Powder X-ray diffraction profiles of selected chlorobenzene/ZSM-5 complexes in the 26–29° 2θ region. ↓ indicates the change in symmetry from monoclinic to orthorhombic (see text).

in the high-loaded complexes: 4 molecules residing at the channel intersections and the rest of the sorbate molecules being located in the midsections of the straight channels.

Chlorobenzene/ZSM-5. Our results show that the chlorobenzene/ZSM-5 system exhibits rather peculiar phase-transition behavior. The broad envelop of the zeolite symmetric Si–O–Si bending vibrations looks similar to that of unloaded ZSM-5 within the coverage of 1–2 molecules/u.c., inferring that the monoclinic phase is only stable up to a loading of 2 molecules/u.c. (Figure 7A). Within the intermediate loading range of 3–7 molecules/u.c., the spectral appearance of these Si–O–Si bending modes is independent of the loading, but looks distinctly different from that in the low-loading range, suggesting that the framework undergoes a phase transition at a loading of 3 molecules/u.c. (Figure 7A) The overall shape of the above-mentioned zeolitic vibrations changed again when the maximum loading (8 molecule/u.c.) was reached, indicating that there is a second phase change. To confirm these conclusions, we also measured powder XRD patterns of the samples. Figure 7B clearly shows a monoclinic to orthorhombic phase change at a loading of 3 molecules/u.c. and a second structural change at 8 molecules/u.c.

Unlike the sorbent, the FT-Raman spectra of chlorobenzene adsorbed in ZSM-5 remain identical within the loading range of 1–4 molecules/u.c. This indicates that, despite the phase transition at 3 molecules/u.c., the first 4 sorbate molecules are accessing the same adsorption sites, presumably in the intersections. This suggests that the same adsorption sites are energetically preferred by chlorobenzene in both phases and the structural difference between the two phases must be quite subtle. These spectra are also very similar to that of pure chlorobenzene liquid with the only noticeable differences occurring in the C–H stretching and C–Cl bending regions. For free chlorobenzene,[12,24] five Raman-active ν(C–H) ($3a_1+2b_1$) bands are expected. In the spectrum of pure liquid, only one C–H stretching mode at 3067 cm^{-1} was observed (Figure 8). Upon adsorption, this band becomes two peaks (a strong band at 3074 cm^{-1} with a pronounced shoulder at 3062 cm^{-1}). The splitting results from lifting the accidental degeneracy of the vibrations due to the interactions between the guest species and the host framework. We assigned the high- and low-frequency components to a_1 and b_1 ν(C–H) modes, respectively. In the spectrum of pure liquid, the C–Cl out-of-plane bending mode was observed at 195 cm^{-1}. When adsorbed in ZSM-5, this mode appeared at 187 cm^{-1}. The low-frequency shift suggests that at the low-loading levels, the sorbate–sorbate interaction is weaker than that in pure liquid. These data infer that there are noticeable sorbate–framework interactions but insignificant sorbate–sorbate interactions.

At loadings above 4 molecules/u.c., the sorbate spectra started showing some changes (Figure 8). In particular, at the loading of 5 molecules/u.c., the shape of several bands centered at 1584, 1002, 614, and 187 cm^{-1} due to the C–C stretching, C–H bending, and in-plane ring C–C–C deformation and C–Cl in-plane bending, respectively, started becoming asymmetric, and a weaker shoulder was gradually developed on the high-energy side of each band mentioned above (Figure 8). After the

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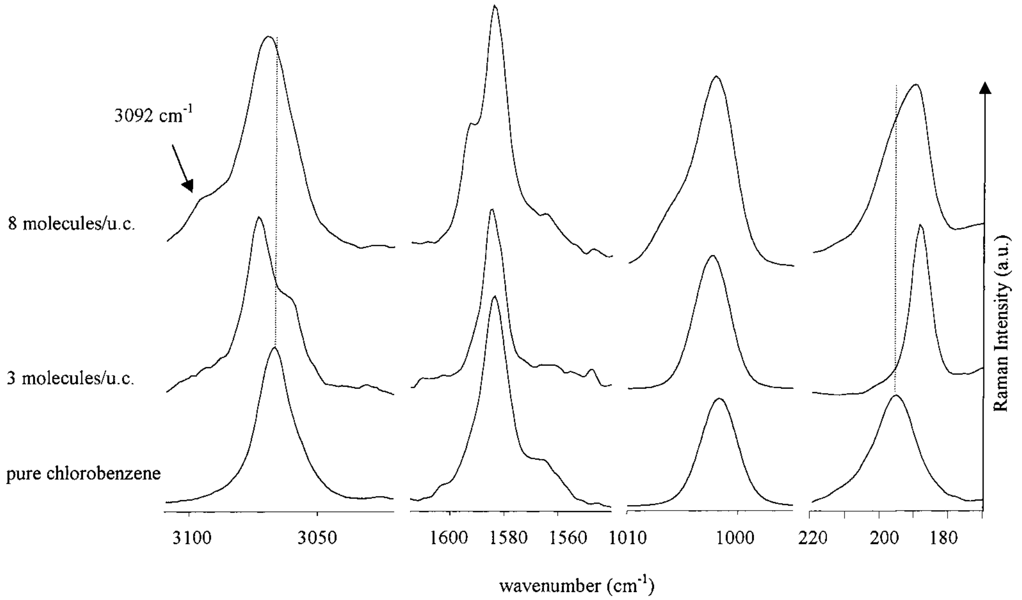

Figure 8. FT-Raman spectra of chlorobenzene/ZSM-5 complexes in various regions at selected loadings.

previous discussion, the observation of two components can be interpreted as the existence of two types of crystallographically nonequivalent sorbate molecules. The low-frequency component is due to the sorbate molecules (chlorobenzene I) located at the channel intersections, because the vibration undergoes minimum perturbation and its frequency is very close to that of pure liquid. The high-frequency component corresponds to the second type of molecules (chlorobenzene II) residing at a less accommodating site. The fact that the frequency differences (under 2 cm^{-1} resolution used) between the two types of molecules are fairly small (they never fully separate from each other) suggests that chlorobenzene II is at the midsections of the straight channels. There is no significant change in the sorbate spectra at the second framework transformation, suggesting that chlorobenzene II occupies the same sites (the midsections of straight channel) in both phases. The overall picture for the sorbate packing at loading levels higher than 4 molecules/u.c. is such that all the sorbate molecules are located in the straight channels with 4 molecules (chlorobenzene I) occupying all four channel intersections in the unit cell with the C_2 axis aligned along the straight channel direction and the remaining molecules (chlorobenzene II) at the midsections of the straight channels. At the maximum loading, a one-dimensional molecular string inside each straight channel is formed.

At the maximum loading, a weak new band emerged at about 3092 cm^{-1} (Figure 8). We assign this new band to the a_1 ν(C−H) mode originating from the C−H bond collinear with the C_2 axis of the molecule. This mode is accidentally degenerate with the other two a_1 ν(C−H) modes in pure liquid. In the high-loaded phase, there is a strong interaction between chlorobenzene I and II molecules along the straight channel direction. This one-dimensional sorbate−sorbate interaction is enhanced by the large dipole moment (1.68 D)[14] possessed by the molecule, which results in a slight increase in the effective force constant for this particular C−H bond, and therefore an increase in the bond stretching frequency. Consequently, this a_1 ν(CH) mode appears at higher frequency and is no longer degenerate with the others.

Conclusions

We have examined the host−guest interactions in three related sorbate/ZSM-5 systems by FT-Raman spectroscopy. For *p*-chlorotoluene/ZSM-5 systems, a phase transition was detected at a loading of 4 molecules/u.c. Our work confirms the results of previous studies that *p*-chlorotoluene/ZSM-5 and *p*-xylene/ZSM-5 exhibit similar phase-transition behavior. However, our Raman data show uniquely that the sorbate−sorbent interactions are much stronger in CT/ZSM-5 system. For the toluene/ZSM-5 system, a sorbate-induced phase transition in the ZSM-5 framework was also observed. The low-loaded phase was monoclinic and the high-loaded phase may have the space group symmetry of $P2_12_12_1$. Based on the information obtained from the C−H stretching region, we suggest that in the low-loaded phase, toluene molecules are located at the channel intersections, whereas in the high-loaded phase, the sorbate molecules occupy both intersections and midsections of the straight channels. In chlorobenzene, two successive phase transitions were detected at 3 and 7 molecules/u.c. Below the coverage of 5 molecules/u.c., the guest species reside in the channel intersections. At higher loading levels, a string of sorbates is formed along the straight channels. Strong one-dimensional sorbate−sorbate interactions also occur.

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