

A Study of Binary Adsorption of Aromatics in Completely Siliceous Zeolite ZSM-5 by FT-Raman Spectroscopy

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In the present work, binary adsorption of *p*-xylene and toluene in completely siliceous zeolite ZSM-5 was examined by FT-Raman spectroscopy in combination with powder X-ray diffraction. The results indicate that at total loadings of ≤ 4 molecules per unit cell (u.c.) both *p*-xylene and toluene molecules prefer to reside at the intersections of straight and zigzag channels. The structure of the sorbate/sorbent complexes likely belongs to orthorhombic. At high loadings of 7 and 8 molecules/u.c., the framework of the zeolite transforms to another orthorhombic phase. In this high-loaded phase, toluene molecules are distributed evenly in both the channel intersection and the midsection of straight channel. Although *p*-xylene has access to both the channel intersection and the zigzag channel, it does show a slight preference for the channel intersection. The adsorptive behavior of these aromatics at intermediate total loadings of 5 and 6 molecules/u.c. is more complicated because the zeolitic framework is a mixture of two different orthorhombic phases.

Introduction

Zeolites are framework aluminosilicates containing three-dimensional open framework structure with molecular dimension. These materials have been widely used in industry as ion exchangers, sorbents, and catalysts. All the applications involve incorporation of the guest species into the framework of a zeolite. Therefore, it is extremely important to understand the behavior of guest molecules inside zeolitic hosts. Over the past few years, there has been interest in the single component adsorption of aromatic molecules within the framework structure of zeolite ZSM-5. The examples include *p*-xylene,¹ *p*-dichlorobenzene,² benzene,³ *p*-nitroaniline,⁴ toluene,⁵ naphthalene,⁶ biphenyl benzene,⁷ and 1,3-dimethylcyclopentenyl cation.⁸ In the previous work, we showed that FT-Raman spectroscopy can be used to help in obtaining information on the locations of sorbate molecules within the framework, especially for the systems where accurate single-crystal X-ray diffraction (XRD) data are not available.^{9,3e} The approach was then extended to include the binary adsorption in zeolites.¹⁰

Zeolite ZSM-5 can be used to separate *p*-xylene (the key material for polyester manufacture) from its isomers and other alkyl benzene derivatives. In the present work, we examined coadsorption of *p*-xylene and toluene in completely siliceous zeolite ZSM-5 using the FT-Raman method. Particular attention was paid to the locations of *p*-xylene and toluene within the ZSM-5 framework. Single component adsorption of *p*-xylene and toluene has been studied extensively by many experimental techniques.^{1,5} Recently, this binary system has been investigated by molecular modeling.¹¹

Experimental Section

Completely siliceous ZSM-5 was prepared according to a procedure described in the literature.¹² The crystals were calcined at 550 °C to remove the template ions. The sample crystallinity and purity were checked by powder X-ray diffrac-

tion. *p*-Xylene (anhydrous 99+%) and *d*₈-toluene (D, 99.5%) were obtained from Aldrich and Cambridge Isotope Laboratories, Inc., respectively. They were used as received without further purification. Accurately weighed aliquots of freshly calcined ZSM-5 were loaded with precisely measured amounts of organic sorbates. The samples were placed in glass vials, which were then carefully sealed and placed in an oven for 3–6 h at 120 °C to uniformly disperse the sorbate molecules throughout the sample. The true loading was checked by thermogravimetric analysis. All Raman spectra were recorded at room temperature on a Bruker FTS-100 FT-Raman spectrometer equipped with an Nd³⁺:YAG laser operating at the wavelength 1064.1 nm and a liquid nitrogen cooled Ge detector. The laser power was typically 80 mW at the sample. The resolution used was 2 cm⁻¹. Powder X-ray diffraction measurements were performed on a Rigaku diffractometer with graphite-monochromated Co K α radiation with the wavelength 1.7902 Å.

Results and Discussion

The FT-Raman spectra of coadsorbed *p*-xylene and *d*₈-toluene in ZSM-5 were measured at various loading levels for each component. The total loading level of both components summed together ranged from 2 to 8 molecules/u.c. Deuterated toluene was used in this study so that overlap of certain vibrational bands of the two sorbates would not occur. As well, FT-Raman spectra of single component adsorption of *p*-xylene and *d*₈-toluene in ZSM-5 were measured over a loading range 1–8 molecules/u.c. to assist in interpreting the data. The mixture composition will be indicated by (X + Y), where X and Y represent the number of *p*-xylene and *d*₈-toluene molecules per unit cell (u.c.), respectively.

It is well-known that ZSM-5 has three adsorption sites: (1) the channel intersections, (2) the midsections of the straight channels, and (3) the segments of zigzag channels.¹³ Each has four equivalent positions per unit cell. For the *p*-xylene/ZSM-5 system, a single-crystal XRD study indicated that at low loadings (≤ 4 molecules/u.c.) the molecules are situated in the channel

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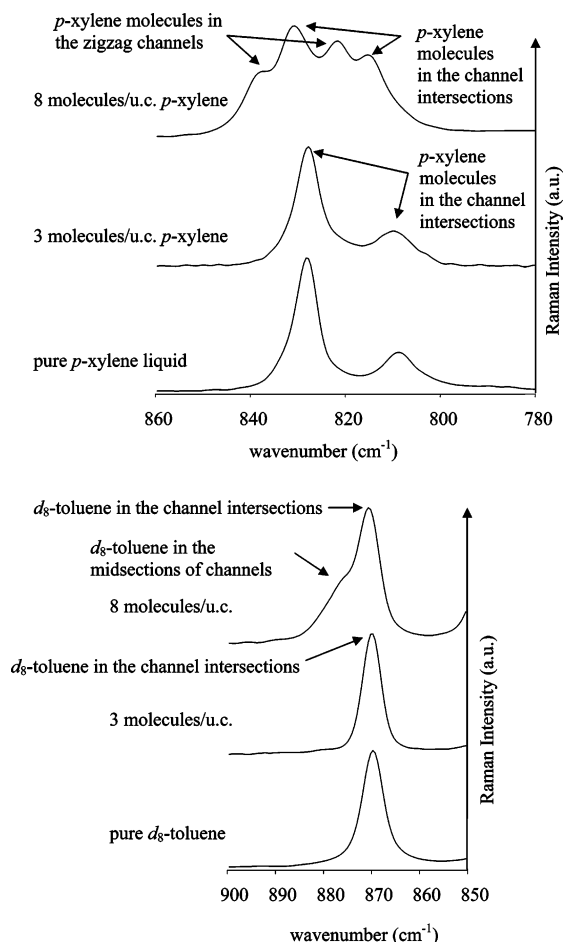


Figure 1. FT-Raman spectra of single component adsorbed *p*-xylene and *d*₈-toluene in their respective "fingerprint" regions. (Intensity not scaled).

intersections.¹⁴ At higher loadings, the molecules are then situated in both the zigzag channels and the channel intersections.^{1a} Our previous study of the single component adsorption of *p*-xylene in ZSM-5 using FT-Raman spectroscopy⁹ demonstrated that the spectra of adsorbed *p*-xylene were very sensitive to the locations of the molecules within the framework. Figure 1 illustrates the spectra of the low- and high-loaded phases of *p*-xylene in the region of 860 to 790 cm⁻¹. In the pure liquid spectrum of *p*-xylene, there are two peaks centered at 828 and 809 cm⁻¹, corresponding to ring breathing and ring C–H out-of-plane bending modes,¹⁵ respectively. These peaks are observed in the same positions in the low-loaded spectra, because *p*-xylene molecules are only situated in the channel intersections. However, in the spectrum of the high-loaded phase, there are four peaks observed in this region at 837, 831, 822, and 815 cm⁻¹. Factors such as site effect and correlation coupling usually cause the splitting in vibrational spectra in an ordered solid. However, wide-line ²H NMR studies have shown that at room-temperature sorbed *p*-xylene molecules are orientationally disordered.¹⁶ Because of the dynamic disorder in the framework, the molecular motions should effectively eliminate the above-mentioned splittings. Thus, the observed splitting actually results from the existence of two crystallographically nonequivalent *p*-xylene molecules in the framework. The dimension of the zigzag channel (~0.55 nm) is much smaller compared to the diameter of the cavity (~0.87 nm) formed by the straight and zigzag channels at their intersection. Consequently, the vibrational frequencies of the guest molecules located in the zigzag channels are higher than those of the molecules in channel

intersection. This is because the kinetic diameters of aromatic molecules (e.g., 0.585 nm for *p*-xylene) are very close to the channel dimension of ZSM-5 (0.55 nm). Consequently, the guest molecules fit into the channels very tightly. Thus, the surrounding wall of the framework restricts the stretching motions, and this effect is comparable to compression of the molecule,¹⁷ which leads to an increase in the force constant, yielding a blue-shift in frequency. For the bending modes, the stronger confinement restrictions on the encaged *p*-xylene molecules imposed by the zigzag channels cause subtle changes in the bond angles from their average values in a free molecule. This change will increase slightly the restoring potentials and, at the same time, the energies of the bending modes. Therefore, the peaks at 837 and 822 cm⁻¹ are assigned to vibrational modes of *p*-xylene located in the zigzag channels. The peaks centered at 831 and 815 cm⁻¹ are assigned to the same vibrational modes but are due to sorbate molecules located in the channel intersections. Since this region is so sensitive to the locations of *p*-xylene molecules within the framework, it will be used as a "fingerprint" to determine the location of *p*-xylene molecules within the framework of ZSM-5 in binary adsorption of *p*-xylene and *d*₈-toluene. The peak observed at 837 cm⁻¹ in the high-loaded phase is unfortunately overlapped with a peak arising from *d*₈-toluene at 840 cm⁻¹, but the other three peaks are easily distinguished in the spectra of the samples containing *p*-xylene and *d*₈-toluene.

Single component adsorption of *d*₈-toluene was also carried out to see if any peaks in the spectra could be used to determine the locations of molecules within the framework. The band centered at 870 cm⁻¹ (assigned to ν_{9b} : a C–D deformation mode)¹⁵ in the low-loaded phase split into two components at higher loadings with the higher-frequency component observed as a well-defined shoulder at 876 cm⁻¹ (Figure 1). On the basis of a previous vibrational study of single component adsorption of toluene/ZSM-5 complexes,^{5b} the band at 870 cm⁻¹ is assigned to the toluene molecules located at channel intersections, and the shoulder at 876 cm⁻¹ is due to the sorbate molecules residing in the midsection of straight channel which is a less accommodating site in the high-loaded phase. Since this peak in the *d*₈-toluene spectrum does not overlap with any peaks in the *p*-xylene spectrum and is sensitive to the loading, the behavior of this band should provide information on the locations of *d*₈-toluene molecules within the zeolite framework.

The FT-Raman spectra of adsorbed *p*-xylene and *d*₈-toluene are shown in Figure 2 in the "fingerprint" regions discussed above. When the total loading level of both components is less than or equal to 4 molecules/u.c., the peaks that arise from adsorbed *p*-xylene appear in the same positions as those observed in the low-loaded *p*-xylene spectra (828 and 809 cm⁻¹). These peak positions are observed in the spectra regardless of the number of *p*-xylene or *d*₈-toluene molecules present, as long as the total of both components remained equal to or below 4 molecules/u.c. This indicates that *p*-xylene molecules access identical sites within the framework at total loading levels ≤ 4 molecules/u.c. Since the "fingerprint" region for *p*-xylene in the spectra of low-loaded mixtures of *p*-xylene and *d*₈-toluene looks very similar to the spectra of low-loaded *p*-xylene, we conclude that *p*-xylene molecules in the mixture sample access the same sites as in single component adsorption at low loadings: the channel intersections.

A similar situation is observed for the *d*₈-toluene regions in the spectra. The peak centered at 870 cm⁻¹ remains in the same position as that observed in the low-loaded *d*₈-toluene spectrum (3 molecules/u.c.) and does not split when the total loading level

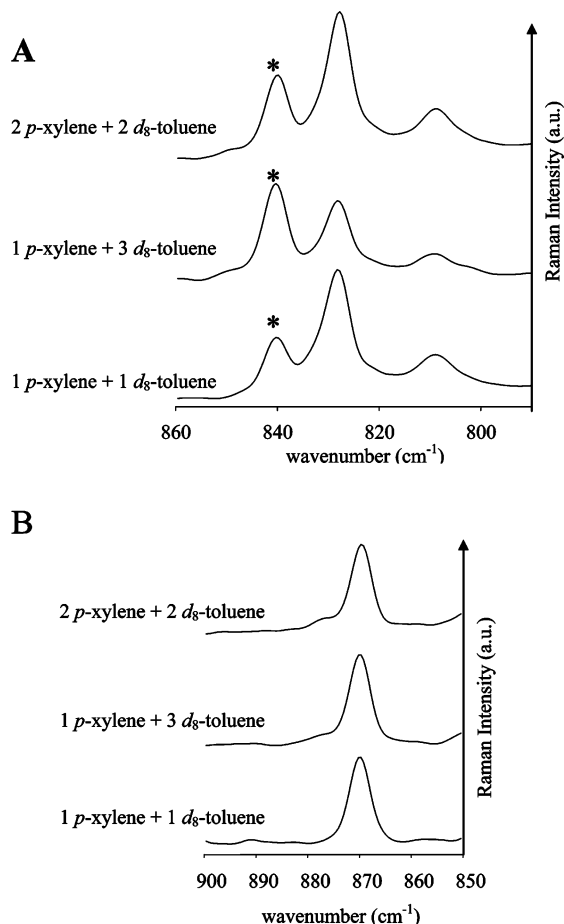


Figure 2. Selected FT-Raman spectra of binary mixtures with a total loading ≤ 4 molecules/u.c. in the (A) *p*-xylene "fingerprint" region (* indicates a *d*₈-toluene peak), (B) *d*₈-toluene "fingerprint" region. (Intensity not scaled).

of both components remains below or equal to 4 molecules/u.c. (Figure 2). This suggests that *d*₈-toluene molecules are also located in the channel intersections at low loadings.

The FT-Raman results indicate that at total mixture loadings of ≤ 4 molecules/u.c. both *p*-xylene and *d*₈-toluene molecules behave as each sorbate does in single component adsorption. Both sorbates preferentially adsorb into the channel intersections at low mixture loadings. A final look at the spectra indicates that the band positions observed in the spectra of the binary mixtures are identical to those observed in the single component adsorption spectra. This indicates that there are very little sorbate–sorbate interactions occurring within the zeolite framework.

Distinct changes in the spectra are observed once the total loading of both components exceeds 4 molecules/u.c. For binary mixtures with total loadings of > 4 molecules/u.c. and the *p*-xylene component of ≥ 2 molecules/u.c., the spectra contain two bands observed at 822 and 813 cm⁻¹ (Figure 3). This suggests that *p*-xylene molecules access the zigzag channels (indicated by 822 cm⁻¹ band) as well as the channel intersections (indicated by 813 cm⁻¹ band) at these loadings. The *d*₈-toluene "fingerprint" region exhibits the same splitting behavior in the Raman spectra (Figure 4) of samples with the total mixture loading level greater than 4 molecules/u.c. and the *d*₈-toluene component of ≥ 2 molecules/u.c. In these spectra, there are 2 peaks observed in the toluene "fingerprint" region at 876 and 870 cm⁻¹. This implies that there are some *d*₈-toluene molecules situated in the channel intersections and some *d*₈-toluene molecules situated in the midsections of the straight channels.

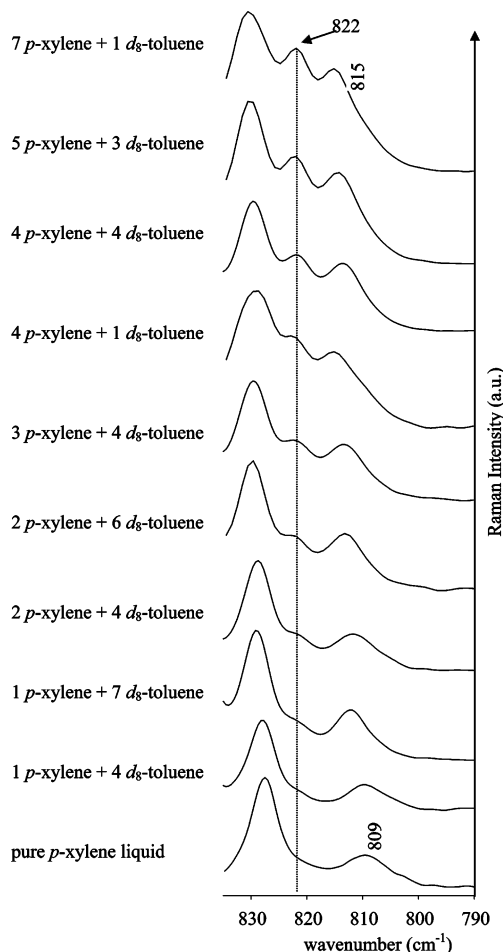


Figure 3. Selected FT-Raman spectra of binary mixtures with total loading level > 4 molecules/u.c. in *p*-xylene "fingerprint" region. (Intensity not scaled).

As the loading level of *p*-xylene increases relative to *d*₈-toluene within the framework, no other drastic changes are seen in the two "fingerprint" regions. The relative intensity of the peak centered at 822 cm⁻¹ increases as the loading of *p*-xylene increases because of the greater number of *p*-xylene molecules that are present in the zigzag channels. In the (4 + 4) spectrum, the peaks centered at 823 and 815 cm⁻¹ in the *p*-xylene "fingerprint" region are approximately equal in intensity, suggesting that the number of *p*-xylene molecules in the zigzag channels and channel intersections are roughly equal. In the *d*₈-toluene region, the intensity of the peaks centered at 877 and 871 cm⁻¹ is similar to what was observed in the single component adsorption of *d*₈-toluene in ZSM-5 with a loading of 8 molecules/u.c.

Interestingly, in the spectra of (7 + 1) and (4 + 1), the intensity of the C–D deformation mode for *d*₈-toluene in "fingerprint" region (Figure 4) looks very similar to the high-loaded single component *d*₈-toluene complex. As discussed earlier in the single component adsorption of *d*₈-toluene, the observation of a peak at 877 cm⁻¹ indicates the presence of *d*₈-toluene molecules in the midsection of straight channels. Even though statistically there is only one *d*₈-toluene molecule for every unit cell of the ZSM-5 framework, the FT-Raman results indicate that there are actually two nonequivalent *d*₈-toluene molecules. One explanation would be that some unit cells have more than one *d*₈-toluene molecule and some have none. Since this would correspond to a nonequilibrium situation, to ensure that equilibrium was reached in the samples, we repeated our experiment by preparing binary mixture samples using several

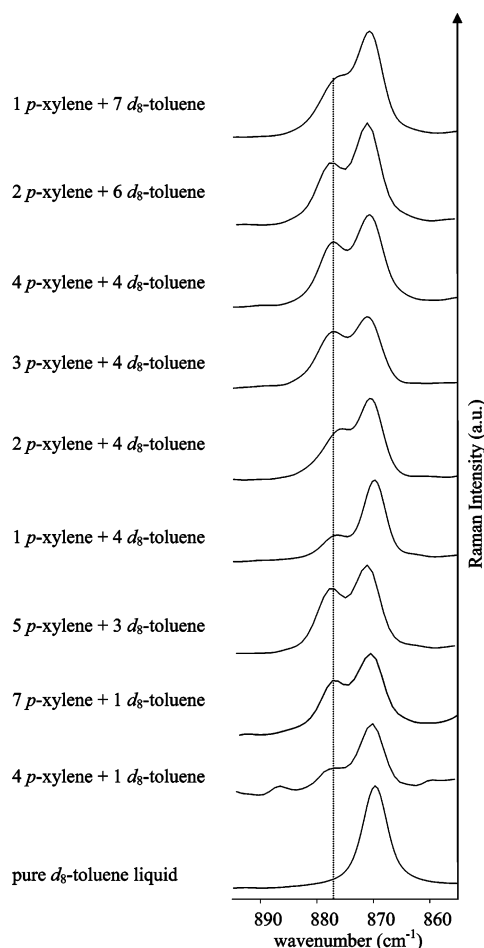


Figure 4. Selected FT-Raman spectra of binary mixtures with total loadings > 4 molecules/u.c. in the d_8 -toluene "fingerprint" region. (Intensity not scaled).

different temperatures and heating times. The resulting Raman spectra are identical, which rules out the possibility that the samples investigated did not reach equilibrium. It is more likely that, in the samples, each unit cell indeed contains only one d_8 -toluene molecule. However, for some unit cells, this molecule is located at the channel intersection, but for others, in the straight channel. The relative intensity of the (7 + 1) sample in this region (Figure 4) is very similar to that of single component adsorbed d_8 -toluene in ZSM-5 with a loading of 8 molecules/u.c., where half of the d_8 -toluene molecules reside in channel intersections and the other half are in the middle sections of the straight channel. This observation indicates that the number of unit cells where the toluene molecule resides in straight channel is roughly equal to that of the unit cells in which toluene is located in the channel intersection. It seems that, at this total loading, the toluene molecule has no preferred adsorption site. The situation for p -xylene, however, is different. The spectrum of the (1 + 7) sample in the "fingerprint" region of p -xylene (Figure 3) shows that the 822 cm^{-1} peak due to the p -xylene in the zigzag channel is barely visible, clearly implying that, for almost all the unit cells, this single p -xylene is preferentially adsorbed at the channel intersection. For the sample (1 + 4), the spectrum of toluene and p -xylene in the "fingerprint" regions indicates that, within each unit cell, the single p -xylene and 3 toluene molecules are located at channel intersections and the 4th toluene molecule is in the straight channel. Combining this and the observation mentioned earlier (that the intensity of the p -xylene peak at 822 cm^{-1} increases with increasing the loading of p -xylene) indicates that, at high loading, p -xylene exhibits a

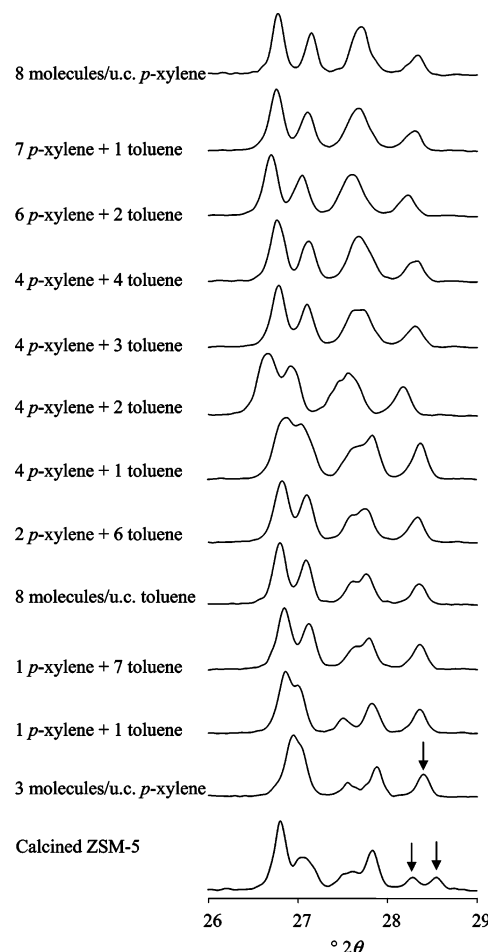


Figure 5. Selected powder X-ray diffraction profiles of binary mixtures with various loadings of p -xylene and toluene compared to the high- and low-loaded p -xylene/ZSM-5 and high-loaded toluene/ZSM-5 profiles. Nondeuterated toluene was used in the preparation of the XRD samples. \downarrow indicates the change in symmetry from monoclinic to orthorhombic (see text).

slightly higher preference for the channel intersection over the zigzag channel.

For the sample of (4 + 1), the intensity of the 877 cm^{-1} peak of toluene is much weaker compared to that of (7 + 1), suggesting that, at this particular loading, a larger number of unit cells contain a single toluene molecule residing at the channel intersection.

It is well-established that the ZSM-5 framework undergoes phase transitions upon adsorption of a wide range of organic molecules.^{1c} The phase transition behavior of the p -xylene/ZSM-5 system is well-established: It undergoes 2 successive phase transitions from $P2_1/n$ (unloaded) to $Pnma$ (stable between 1 and 4 molecules/u.c.)^{1c,14} and then at higher loadings to $P2_12_1$ (stable between 5 and 8 molecules/u.c.).¹ For toluene/ZSM-5 complexes, previous studies showed that adsorption of toluene in loadings of ≤ 4 molecules/u.c. does not induce any structure change in zeolite framework (i.e., the structure remains monoclinic).⁵ When the coverage of toluene is greater than 4 molecules/u.c., a transformation to an orthorhombic phase occurs.

To examine the effect of binary adsorption on the framework structure of ZSM-5, the powder XRD profiles were measured for a variety of mixture loading levels (Figure 5). A number of studies have established that the region of $2\theta = 26\text{--}30^\circ$ in the powder XRD profile of ZSM-5 is very sensitive to structural change in the ZSM-5 framework.^{1c,18} In Figure 5, the charac-

teristic change (2 reflections merge into 1 reflection centered at $28.5^\circ 2\theta$) in the powder pattern indicates that a change in crystal system for the zeolite framework from monoclinic (calcined ZSM-5) to orthorhombic occurred for samples with loadings of ≤ 4 molecules/u.c.^{1c,18} This orthorhombic phase is characteristic of the *Pnma* phase, since the profiles are identical to the pattern of the 3 molecules/u.c. *p*-xylene/ZSM-5 complex (whose structure was determined unambiguously by single-crystal XRD¹⁴). In single component adsorption of *p*-xylene, one adsorbed molecule of *p*-xylene in the channel system already causes the zeolite framework to adopt the phase of *Pnma*.¹⁴ In single component adsorption of toluene, there is no noticeable change in the powder pattern of ZSM-5 up to a loading of 4 molecules/u.c.^{5b} Thus, the change in the profiles of the binary samples is due mainly to the existence of *p*-xylene and not to toluene at mixture loadings of ≤ 4 molecules/u.c.

When the total mixture loading is high (7 or 8 molecules/u.c.) and the *p*-xylene loading is ≥ 4 molecules/u.c., the powder patterns are the same as that obtained for the 8 molecules/u.c. *p*-xylene/ZSM-5 phase. This similarity in powder patterns implies that the phase of the zeolite framework is $P2_12_12_1$ ^{1a} at these loadings. However, at the same total loading level of 7 or 8 molecules/u.c., but now with toluene of >4 molecules/u.c., the powder XRD pattern is very similar to that of the toluene/ZSM-5 complex with a loading of 8 molecules/u.c.^{5b} Although these two profiles are slightly different, Mentzen et al.¹⁹ suggested, using energy minimization calculations and a Rietveld refinement method, that the 8 molecules/u.c. toluene/ZSM-5 phase was $P2_12_12_1$ and therefore due to the similarity between powder patterns, and we suggest that the phase of these mixture loadings is also $P2_12_12_1$. The result is consistent with that of a recent molecular modeling study, which also suggests a phase change at the maximum loading.¹¹

In the intermediate total loading range of 5 and 6 molecules/u.c. (i.e., (4 + 2) and (4 + 1)), the powder pattern is characteristic of neither the *Pnma* phase observed for low-loaded *p*-xylene/ZSM-5 (single component) or the $P2_12_12_1$ phase observed for high-loaded *p*-xylene/ZSM-5, but is a mixture of both phases.

The zeolite framework vibrations in the $\nu_s(\text{Si-O-Si})$ region of the FT-Raman spectra also support the above findings of the powder XRD patterns. The single component adsorption study of *p*-xylene in ZSM-5 showed that the two phases of the zeolite framework have distinctly different spectra.⁹ In the low-loaded *p*-xylene phase (*Pnma*), this region exhibited a rather broad profile with peaks at 393, 385, 378, 364, and 349 cm^{-1} . The high-loaded phase of *p*-xylene/ZSM-5 ($P2_12_12_1$), however, displayed a narrower band centered at 370 cm^{-1} in this region of the spectrum. These two different profiles correspond to the two different phases of the *p*-xylene/ZSM-5 system. It was shown previously that, in the high-loaded toluene/ZSM-5 phase,^{5b} the $\nu_s(\text{Si-O-Si})$ region of the spectrum was similar to that of the high-loaded *p*-xylene/ZSM-5 phase, which is consistent with the suggestion of Mentzen et al. that the structure of high-loaded toluene/ZSM-5 is $P2_12_12_1$, the same as high-loaded *p*-xylene/ZSM-5.¹⁹ Comparing the $\nu_s(\text{Si-O-Si})$ region of the binary mixtures with that of the single component adsorption spectra might shed some light on the role each sorbate plays in the phase transitions that occur in the zeolite framework (Figure 6). With total mixture loadings of ≤ 4 molecules/u.c., the zeolite profile looks similar to the profile seen in the low-loaded *p*-xylene phase (*Pnma*). For the high-loaded mixtures of 7 and 8 molecules/u.c. (with *p*-xylene of ≥ 4 molecules/u.c.), the zeolite vibrational profile looks identical to the high-loaded

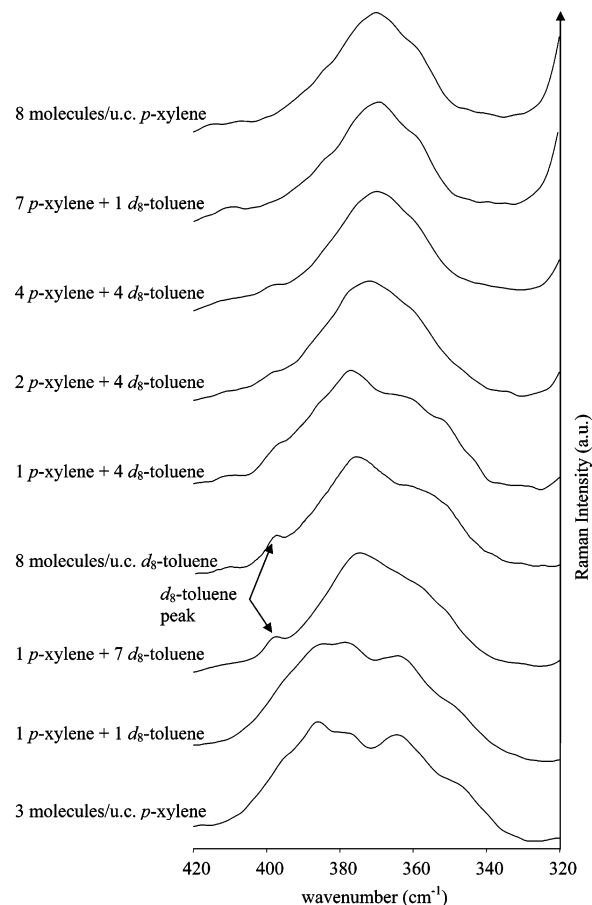


Figure 6. Selected FT-Raman spectra in the $\nu_s(\text{Si-O-Si})$ region of binary mixtures with various loadings. (Intensity not scaled).

p-xylene/ZSM-5 ($P2_12_12_1$). For the high-loaded mixtures of 7 and 8 molecules/u.c. with toluene of >4 molecules/u.c., the region looks more like the high-loaded toluene/ZSM-5 phase. Both of these phases are $P2_12_12_1$, as discussed previously. However, in the intermediate loading levels of 5 and 6 molecules/u.c., the $\nu_s(\text{Si-O-Si})$ region is not similar to either of the zeolitic vibrational profiles of low- or high-loaded *p*-xylene or toluene/ZSM-5 phases, and is a mixture of both phases. These FT-Raman results support the findings of the powder X-ray diffraction profiles.

Summary

The present study of the binary adsorption of *p*-xylene and *d*₈-toluene in ZSM-5 by FT-Raman spectroscopy and powder XRD techniques suggests that (1) at loadings of ≤ 4 molecules/u.c. the framework structure of ZSM-5 is orthorhombic with a possible space group of *Pnma*. In this low-loaded phase, both *p*-xylene and *d*₈-toluene molecules are located in the channel intersections with every unit cell being occupied. (2) At high loadings (7 or 8 molecules/u.c.), the structure of the host-guest complex apparently transforms into a different orthorhombic phase ($P2_12_12_1$). In this phase, *d*₈-toluene molecules are equally distributed at the channel intersection and in the midsection of the straight channel. *p*-Xylene accesses both the channel intersection and the zigzag channel. However, *p*-xylene seems to have a slight preference for the channel intersection as indicated by the Raman spectrum of the (1 + 7) sample. (3) At intermediate loadings of 5 and 6 molecules/u.c., the distribution of sorbate molecules within the zeolite is complicated presumably because the framework of ZSM-5 is a mixture of two different orthorhombic phases.

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