Determining the Adsorption Sites for Binary Mixtures of *p*-Xylene and *n*-Heptane in Silicalite Using FT-Raman Spectroscopy and Temperature-Programmed Desorption

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FT-Raman spectroscopy and temperature-programmed desorption (TPD) measurements have been used to gain information on the preferred adsorption sites for *p*-xylene and *n*-heptane adsorbed within silicalite. FT-Raman spectroscopy is used to probe the location of adsorbed *p*-xylene, both when pure *p*-xylene is adsorbed and for the binary mixtures. The TPD measurements in combination with the FT-Raman spectra are used to infer the location of the adsorbed *n*-heptane. The results on the preferred adsorption sites for pure adsorbates are consistent with those in the literature. The results on binary mixtures show unusual behavior at loadings of four *p*-xylene/three *n*-heptane and three *p*-xylene/four *n*-heptane molecules per unit cell. In contrast to the behavior for single component adsorption, at these loadings the *n*-heptane molecules preferentially occupy the straight channels of silicalite, forcing the *p*-xylene molecules out of their normal preferred site (the channel intersections) and into the zigzag channels. The results are of importance in understanding the performance of silicalite membranes when separating gaseous mixtures of alkanes and aromatics.

Introduction

Zeolites are used extensively in the chemical industry as catalysts and for gas separations. Both these applications rely on adsorption and diffusion of molecules within the microporous framework, and so there has been a considerable amount of experimental and theoretical work studying these processes within zeolites.[1−4] However, in many cases it is difficult to determine the location of adsorbed molecules within the internal pore structure. In particular, little is known about which adsorption sites are occupied when more than one adsorbate is present. This information is essential if the adsorption and transport properties of mixtures within zeolites are to be fully understood.

In this work, we use FT-Raman spectroscopy and temperature-programmed desorption (TPD) to study the location of adsorbed *p*-xylene and *n*-heptane in silicalite, which is the all-silica analogue of zeolite ZSM-5. The two techniques used provide different but complementary information. Results on both pure adsorbates and binary mixtures are presented. The results on binary mixtures are directly relevant to understanding membrane transport results on silicalite reported in the literature.

The first major technique used in this work is near-infrared FT-Raman spectroscopy. This enables high-quality vibrational spectra to be obtained from adsorbates in zeolites without there being significant interference from framework vibrations.[5−8] The adsorbate frequencies are affected by the adsorbate location, and any specific sorbate-framework and sorbate−sorbate interactions that may exist. An advantage of the technique over conventional IR spectroscopy is that it is straightforward to record spectra on zeolites containing known amounts of adsorbate as the sample can be prepared in sealed glass tubes; glass is a weak Raman scatterer, and so is not normally visible in FT-Raman spectra. FT-Raman spectroscopy has recently been used successfully to study sorbate-induced phase transitions and sorbate−sorbate interactions within silicalite.[8,9] Because FT-Raman spectroscopy has a very short time scale, it probes the instantaneous location of adsorbates without any complications from possible site-exchange effects.

The second major technique used in this work is temperature-programmed desorption (TPD). TPD measures the rate of desorption of species as the temperature is raised in a controlled environment. Molecules at adsorption sites which are less energetically favorable are thus expected to desorb at lower temperatures than those from more stable environments. It should be noted, however, that there will be exchange of molecules between different adsorption sites during the acquisition of TPD data, and this means that care is needed over interpretation of the results. The TPD apparatus used in this work includes a mass spectrometer, and so can measure simultaneously desorption rates for the different species present when a mixture is adsorbed in the sample. This is particularly important in determining adsorption sites for mixtures in zeolites, and is in contrast to more simple TPD equipment that records only sample mass loss (and thus cannot differentiate between the molecular species which are desorbing).

Silicalite has the MFI framework structure[10] and is composed of an intersecting channel structure of straight channels (5.4 × 5.6 Å) and zigzag channels (5.1 × 5.5 Å) (see Figure 1). This particular framework structure leads to some interesting physical chemistry when adsorbates are present. There are three possible

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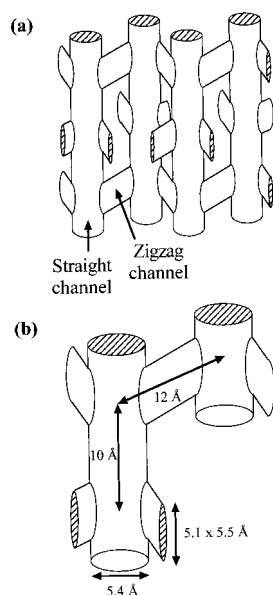
Figure 1. Schematic representations of the silicalite framework structure showing (a) the network of straight and zigzag channels and (b) the relevant channel dimensions.

adsorption sites for small and medium-sized molecules: at the channel intersections, within the straight channels, and within the zigzag channels. There are four channel intersection sites in each silicalite unit cell.

Adsorption of pure *p*-xylene in silicalite has previously been studied extensively. Adsorption isotherms indicate that silicalite can readily adsorb up to four *p*-xylene molecules per unit cell, but that higher pressures than expected are needed to reach the saturation loading of eight molecules per unit cell.[11,12] The structural reasons for this are known from single-crystal X-ray crystallographic results. When pure *p*-xylene is adsorbed within silicalite up to a loading of four molecules per unit cell, there is a structural phase change from monoclinic space group *P*2$_1$/*n* to orthorhombic space group *Pnma*, and all the *p*-xylene molecules are located at channel intersections with their methyl groups positioned in the straight channels.[13,14] At loadings higher than four molecules per unit cell up to the saturation loading of eight molecules per unit cell, there is another phase transition, this time to the orthorhombic space group *P*2$_1$2$_1$2$_1$, and the *p*-xylene molecules become located in both the channel intersections and the zigzag channels.[15] The phase transitions have also been confirmed by ^{29}Si solid-state NMR results,[16] while the existence of two *p*-xylene locations at high loadings has been detected by ^{13}C solid-state NMR spectroscopy[17] and FT-Raman spectroscopy.[8,9]

While the adsorption sites for pure *p*-xylene in silicalite have been established, those for *n*-alkanes are still far from certain principally because lack of long-range adsorbate order means that X-ray diffraction techniques are not appropriate. The adsorption isotherms for both *n*-hexane and *n*-heptane in silicalite show an anomalous inflection point at a loading corresponding to four adsorbate molecules per unit cell,[18-22] suggesting that there is preferential site adsorption as is the case for *p*-xylene. However, it has proved difficult to obtain experimental evidence on precisely which adsorption sites are occupied by *n*-hexane and *n*-heptane at low loadings. Early suggestions included adsorption in the straight channels only,[18] adsorption in the zigzag channels only,[20,22] and no preferential adsorption.[19] Thermal analysis results show that there are two desorption peaks for silicalite saturated with *n*-heptane, indicating that two adsorption states occur at high loadings, but the

assignment of the desorption peaks to specific sites remains uncertain.[23-27] There have also been a number of computer simulations of *n*-alkanes in silicalite. Initial energy minimization calculations suggested that *n*-alkanes are first adsorbed at the channel intersections, and then the straight channels at higher loadings.[28] On the other hand, more detailed recent molecular simulations using configurational-bias Monte Carlo methods suggest that, at low loadings, adsorption of *n*-hexane and *n*-heptane occurs equally in both the straight and zigzag channels, with occupation of the channel intersection sites being far less likely.[29-33] Interestingly, the molecular simulations predict the inflection point observed in the adsorption isotherms for *n*-hexane and *n*-heptane. At loadings higher than four molecules per unit cell, the simulations indicate that there is an adsorbate phase transition with commensurate "freezing" of four adsorbate molecules per unit cell into the zigzag channels only.[32,33] The cause of this is related to the fact that the length of the adsorbate molecules (10.3 Å for *n*-hexane; 11.6 Å for *n*-heptane) is comparable to the length of the silicalite channels: the length of the zigzag channels between the centers of channel intersections is 12 Å, while the length of the straight channels is 10 Å. Because of the loss of entropy at the adsorbate phase transition, higher pressures are then required in order for further adsorption, this time in the straight channels, to occur.

The major objective of this work is to gain information on the adsorbate site locations for mixtures of *p*-xylene and *n*-heptane within silicalite. Preferential adsorption of different species at different sites can have a major influence on the performance of silicalite membranes in gas separations. For instance, a recent paper reported that pure toluene permeates faster through a silicalite membrane than pure *n*-heptane.[34] In contrast to this, when both species are present in a mixture, the permeation rate of toluene is found to be significantly slower than *n*-heptane.[34] This work should help elucidate the reason for this behavior. A secondary objective of this work is to study sorbate-framework and sorbate−sorbate interactions in the *p*-xylene/*n*-heptane/silicalite system.

Experimental Section

The adsorbates were HPLC grade liquids at room temperature and had been glass distilled and filtered by the supplier (Aldrich). The silicalite sample (Si/Al = 800) was obtained from Chemie Uetikon AG (Zeocat PZ-2/900; batch number PZ-2/47 Na). The pore volume of the sample was 0.19 cm^3 g^{-1}. The silicalite samples were initially calcined overnight at 500 °C in air prior to sample preparation. Following evacuation of the sample at 10^{-6} Torr at 200 °C for 12 h, the required sorbate loading was introduced to the dry zeolite using a gravimetric technique.[9] This sealed sample tube was then kept at 65 °C for 12 h to ensure that the adsorbate was evenly distributed within the zeolite framework. Single component adsorption was studied using samples prepared with *p*-xylene loadings of two, four, six, and eight molecules per unit cell and *n*-heptane loadings from one to seven molecules per unit cell. To study the saturated binary system, samples with a total sorbate loading of seven molecules per unit cell, with varying *p*-xylene/*n*-heptane compositions, were used. Saturation capacities are known both from published isotherm data and the pore size dimensions.[19,20] For unsaturated binary mixtures, samples containing four *p*-xylene molecules per unit cell with varying *n*-heptane loadings were prepared.

The FT-Raman measurements were performed at room temperature on a Nicolet-Magna-IR 750 spectrometer equipped with a Raman module and an InGaAs detector. An Nd:YAG
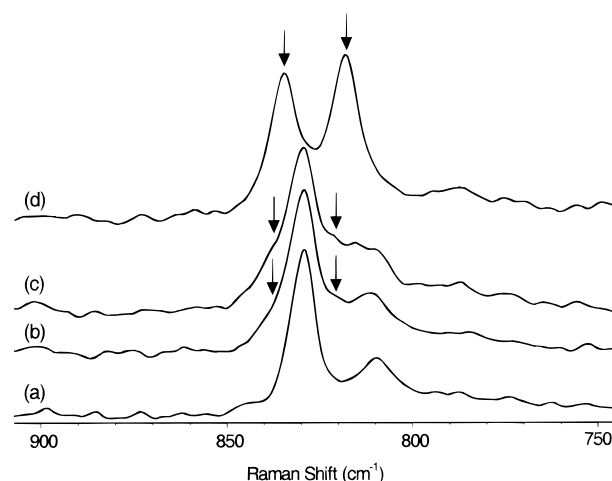
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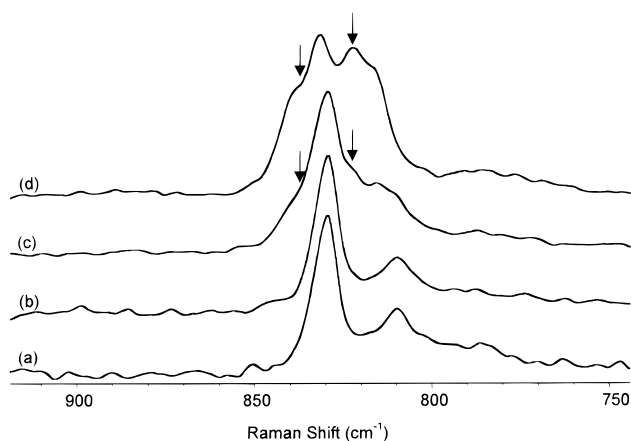
Figure 2. FT-Raman spectra (750−900 cm^{-1} region) of *p*-xylene adsorbed in silicalite at loadings of (a) two, (b) four, (c) six, and (d) eight molecules per unit cell. Arrows indicate the Raman bands at 837 and 822 cm^{-1} corresponding to *p*-xylene in the zigzag channels of silicalite.

laser was used operating at a power of 200 mW at an excitation wavelength of 1064 nm. The resolution was 4 cm^{-1}. For each spectrum, 4000 scans were added together giving a data acquisition time of approximately 2 h.

The desorption of *p*-xylene, *n*-heptane, and their binary mixtures adsorbed in silicalite were studied by TPD in a low vacuum system equipped with a quadrupole mass spectrometer (Hiden, model HAL-100). After breaking open the sealed tube, the sample was immediately placed in a narrow quartz reactor and any residual moisture removed by passing dry helium over the sample. The reactor was cooled to −50 °C and evacuated to 10^{-2} Torr. The sample was then heated at a constant rate of 5 °C min^{-1} from 0 to 350 °C and the rate of desorption of the adsorbates monitored by the mass spectrometer. Samples weighing approximately 20 mg were used for each TPD run.

Results

FT-Raman Spectroscopy. FT-Raman spectra in the range 750−900 cm^{-1} for *p*-xylene within silicalite are shown in Figure 2. At loadings of two and four *p*-xylene molecules per unit cell, the spectra show bands at 829 and 810 cm^{-1}. These bands are both within 2 cm^{-1} of those observed for pure liquid *p*-xylene, and correspond to ring breathing and ring C−H out-of-plane bending modes, respectively.[35,36] At this loading it is known from crystallographic data that the *p*-xylene molecules occupy the channel intersections.[14] At loadings of 6 and 8 *p*-xylene molecules per unit cell, two new bands are observed, at 837 and 822 cm^{-1}; these are indicated by arrows in Figure 2. These new bands are assigned to *p*-xylene molecules occupying the zigzag channels. This assignment is supported by crystallographic data.[15] It is also known that there is a framework phase transition at loadings greater than four molecules per unit cell as the space group changes from *Pnma* to *P*2$_1$2$_1$2$_1$.[15] It is apparent that the Raman bands due to *p*-xylene molecules at the intersection sites shift slightly with loading: at two and four molecules per unit cell, they appear at 829 and 810 cm^{-1}; at eight molecules per unit cell, they appear at 832 and 816 cm^{-1}. This small shift in frequency has been observed previously,[8,9] and is due to a combination of two effects which are occurring at the same time: there are some steric interactions between sorbate molecules at high loadings, and there is a small modification in local environment due to the structural phase transition. At the loading of six *p*-xylene molecules per unit


Figure 3. FT-Raman spectra (750−900 cm^{-1} *p*-xylene region) for binary mixtures containing four *p*-xylene molecules per unit cell of silicalite coadsorbed with (a) zero, (b) one, (c) two, and (d) three *n*-heptane molecules per unit cell. Arrows indicate the Raman bands at 837 and 822 cm^{-1} indicative of *p*-xylene occupying the zigzag channels of silicalite.

cell, some zigzag channels are occupied by *p*-xylene molecules while others are empty, and so peaks at both 816 and 810 cm^{-1} are detected for the molecules at the intersection sites. Minor changes in other regions of the FT-Raman spectrum are also observed as the loading is changed: these are as described in the paper by Huang.[8] In particular there are changes in the framework Si−O−Si symmetrical bending region (340−400 cm^{-1})[37] reflecting the overall phase transitions that occur.

Figure 3 shows FT-Raman spectra for silicalite containing a mixture of four molecules of *p*-xylene and between zero and three molecules of *n*-heptane per unit cell. As is the case for Figure 2, the bands in the region shown in Figure 3 are due to ring breathing and ring C−H out-of-plane bending modes for *p*-xylene. When one or two molecules of *n*-heptane are present, the spectra are little changed from those without any *n*-heptane present, indicating that the *p*-xylene molecules continue to occupy the intersection sites principally. Because there is insufficient room in the silicalite structure for *n*-heptane molecules to occupy the straight channels when the intersection sites are filled, this suggests that at these loadings the *n*-heptane molecules are located principally in the zigzag channels. The small differences between the spectra shown in Figure 3a−c reflect the fact that there may be sorbate−sorbate interactions between neighboring *p*-xylene and *n*-heptane molecules, and also that a small amount of *p*-xylene may be located in the zigzag channels (as denoted by the arrows).

However, the situation changes significantly when three molecules of *n*-heptane are present together with the four molecules of *p*-xylene. At this loading, the Raman spectrum in Figure 3d changes significantly to give just two bands at 835 and 818 cm^{-1}; these vibrational frequencies are close to those assigned to *p*-xylene in the zigzag channels when pure *p*-xylene alone is adsorbed. The relative intensity of the bands in Figure 3d has also changed compared to the other spectra in Figure 3, again supporting a change in *p*-xylene adsorption site. Thus, it appears that the presence of three molecules of *n*-heptane per unit cell forces the *p*-xylene molecules away from their preferred site (the intersections) and into the zigzag channels. This means that the *n*-heptane molecules must now be located preferentially in the straight channels.

Information supporting a change in adsorbate location at a loading of four *p*-xylene/three *n*-heptane molecules per unit cell

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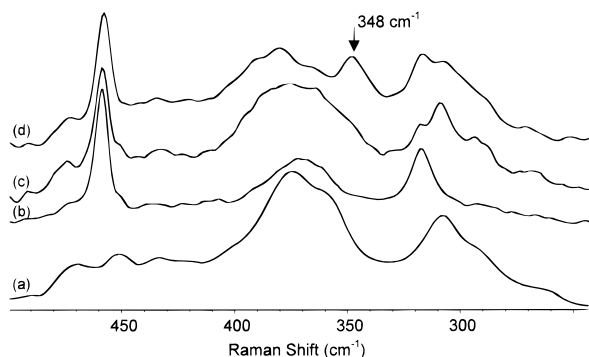
Figure 4. FT-Raman spectra (250−450 cm^{-1} region), for silicalite containing (a) seven *n*-heptane, (b) eight *p*-xylene, (c) four *p*-xylene/two *n*-heptane, and (d) four *p*-xylene/three *n*-heptane molecules per unit cell.

comes from the framework Si−O−Si symmetrical bending region of the FT-Raman spectrum (340−400 cm^{-1}).[37] A new band is observed at 348 cm^{-1} in the spectrum of silicalite containing four *p*-xylene/three *n*-heptane molecules per unit cell (Figure 4d). To confirm that the band originates from the framework rather than an adsorbate, the experiment was repeated with both deuterated *p*-xylene and deuterated *n*-heptane, and the band at 348 cm^{-1} was still observed in the spectrum at a loading of four *p*-xylene/three *n*-heptane molecules per unit cell (spectra not shown). The band is not present in the spectrum of unloaded silicalite, nor is it present for silicalite containing *n*-heptane or *p*-xylene alone (Figure 4a,b). Further, it is not present in the spectrum of silicalite containing four *p*-xylene/two *n*-heptane molecules per unit cell (Figure 4c). The existence of a new framework vibrational mode when the loading of four *p*-xylene/three *n*-heptane molecules per unit cell is reached suggests that a framework phase transition must occur at this particular loading. It should be noted that this is a different phase transition to those observed when *p*-xylene alone is present (as these do not give rise to a Raman band at 348 cm^{-1}), but it probably has the same cause: namely, the general tendency of the silicalite framework to adopt slightly different structures when aromatic molecules are present at adsorption sites within the zigzag channels.[38]

Another piece of supporting evidence for a change in adsorbate location on reaching a loading of four *p*-xylene/three *n*-heptane molecules per unit cell comes from FT-Raman spectra of the C−H methyl stretching region of *p*-xylene. The band at 2924 cm^{-1} for silicalite containing only *p*-xylene is barely affected by adsorbate loading. However, this band is shifted to 2931 cm^{-1} for silicalite containing four *p*-xylene/three deuterated *n*-heptane molecules per unit cell (spectrum not shown). This indicates a significant sorbate−sorbate interaction between the *p*-xylene methyl group and a neighboring *n*-heptane molecule; such an interaction is consistent with the proposed siting of *p*-xylene in the zigzag channels and *n*-heptane in the straight channels at this particular loading.

FT-Raman spectra were also obtained on silicalite saturated with binary mixtures of *p*-xylene and *n*-heptane (i.e. at a total loading of seven adsorbate molecules per unit cell). Spectra of the ring breathing and ring C−H out-of-plane bending modes for *p*-xylene for these mixtures are shown in Figure 5. The signal-to-noise ratio is poor at loadings of one *p*-xylene/six *n*-heptane and two *p*-xylene/five *n*-heptane molecules per unit cell, and so it is difficult to obtain adsorption site information from these spectra. At loadings of three *p*-xylene/four *n*-heptane and four *p*-xylene/three *n*-heptane molecules per unit cell, the peak maxima occur at 835 and 818 cm^{-1}. As discussed above,
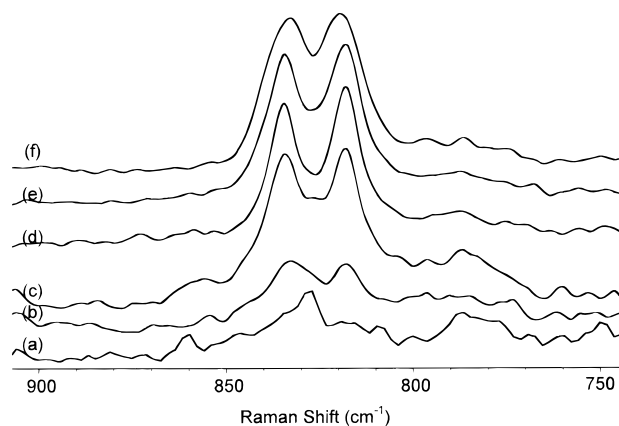
Figure 5. FT-Raman spectra (750−900 cm^{-1} *p*-xylene region) for silicalite containing (a) one *p*-xylene/six *n*-heptane, (b) two *p*-xylene/five *n*-heptane, (c) three *p*-xylene/four *n*-heptane, (d) four *p*-xylene/three *n*-heptane, (e) five *p*-xylene/two *n*-heptane, and (f) six *p*-xylene/one *n*-heptane molecules per unit cell.
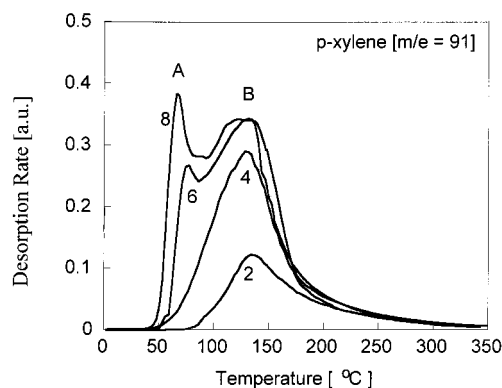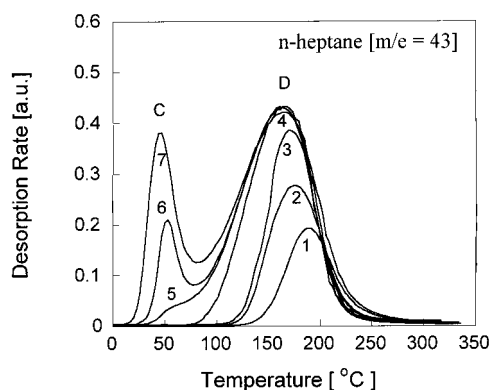

Figure 6. TPD results for *p*-xylene desorption from silicalite. The numbers indicate the initial sample loading in molecules of *p*-xylene per unit cell.

this indicates that the *p*-xylene molecules are located in the zigzag channels at these loadings. More than one type of *p*-xylene adsorption site must be occupied at loadings of five *p*-xylene/two *n*-heptane and six *p*-xylene/one *n*-heptane molecules per unit cell, and this is responsible for broadening of the Raman peaks (maxima at 833 and 820 cm^{-1}) at these loadings.

It is clear that FT-Raman spectroscopy of adsorbed *p*-xylene within silicalite provides information on the adsorption sites (including indirect information on *n*-heptane location). However, the technique is less useful at probing the location of *n*-heptane molecules directly. FT-Raman spectroscopy on pure *n*-heptane within silicalite gives complex overlapping spectra, possibly due to the mixing of different vibrational modes of the CH$_2$ and CH$_3$ groups in the *n*-alkane chain.[36] For this reason, TPD data were acquired on the same samples in order to obtain further information.

Temperature-Programmed Desorption (TPD). It is necessary to discuss first TPD results on pure *p*-xylene and pure *n*-heptane in silicalite in order to interpret the TPD results on the binary mixtures within silicalite. In Figure 6 a series of TPD data are presented for pure *p*-xylene adsorbed in silicalite at initial loadings between two molecules per unit cell up to the saturation loading of 8 molecules per unit cell. At loadings of two and four *p*-xylene molecules per unit cell, there is a single desorption peak at about 135 °C (peak B). As discussed in the FT-Raman results section above, at these loadings it is known that *p*-xylene occupies only the channel intersection sites, and

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Figure 7. TPD results for *n*-heptane desorption from silicalite. The numbers indicate the initial sample loading in molecules of *n*-heptane per unit cell.

so this peak represents desorption from this site. At higher loadings, an earlier desorption maximum is observed at 65−75 °C (peak A).

It is initially tempting to assign the desorption maximum at 65−75 °C (peak A) simply to the *p*-xylene molecules that are known to be located in the zigzag channels at these loadings. This would correspond to the conventional interpretation of desorption from a catalyst surface with two sites of different adsorption strengths. However, the actual situation in silicalite is more complicated due to the microporous channel structure: *p*-xylene molecules in silicalite may not pass one another, and it is impossible for molecules to desorb from a site in the zigzag channel without passing through the channel intersection sites. It also needs to be borne in mind that TPD is a dynamic technique, and there will be considerable exchange of molecules between the different adsorption sites as the measurement is performed. Further, there may also be a change in the preferred adsorption sites as the adsorbate loading is reduced during the TPD experiment.

The desorption peak at 65−75 °C (peak A) in fact corresponds to desorption from a state of more than four *p*-xylene molecules per unit cell (four molecules per unit cell being located in intersection sites, with the remainder being located in the zigzag channels). The actual molecules desorbing will have experienced both zigzag channel and intersection sites on the time scale of the TPD experiment. Once the loading has been reduced to a state of four molecules per unit cell, then all the molecules become preferentially located at the channel intersection sites, and their desorption results in peak B in Figure 6. The key point is that, while TPD in this case does not directly measure desorption from specific adsorption sites, it does detect the presence of different overall adsorption states. In this case, desorption from a state with *p*-xylene present in both zigzag channel environments and channel intersection sites occurs at a lower temperature than desorption from a state in which *p*-xylene is present in channel intersection sites alone. One way of envisaging this situation is that the apparent binding energy of *p*-xylene at intersection sites is reduced when there are neighboring *p*-xylene molecules in the zigzag channels.

TPD results on pure *n*-heptane adsorbed in silicalite at initial loadings between one and seven molecules per unit cell are shown in Figure 7. As was the case for pure *p*-xylene, two desorption maxima are observed at high loadings (peak C at 50 °C, and peak D at 165−190 °C). One possible explanation for this is that the binding energy of *n*-heptane in one type of channel is significantly different to that in the other type of channel (e.g., it could be envisaged that *n*-heptane in the zigzag

channels is weakly bonded, and so results in peak C, while *n*-heptane in the straight channels is strongly bonded, and so results in peak D). However, this is unlikely as computer simulations have indicated a similar affinity of *n*-heptane to both channels at low loadings.[31−33] The explanation for the two peaks may instead lie in the suggested commensurate freezing of four *n*-heptane molecules into the zigzag channels at loadings greater than four molecules per unit cell.[32] Even though the enthalpies of adsorption in the straight and zigzag sites are believed to be similar, there will be an entropic driving force toward desorption of molecules at high loadings (as there is an entropy gain when the molecules become disordered rather than being frozen in the zigzag channels). Thus, peak C originates from *n*-heptane molecules in the straight channels when the zigzag channels are fully occupied by nonmoving molecules of *n*-heptane. Once the loading reaches less than four molecules per unit cell, the *n*-heptane molecules become randomly distributed in both channels, and so a single desorption peak at higher temperature is observed (peak D). The exact temperature of this peak (165 °C at an initial loading of four molecules per unit cell, 190 °C at an initial loading of one molecule per unit cell) indicates some repulsive interactions are occurring between the adsorbed *n*-heptane molecules.

It is worth briefly commenting on the fact that TPD results can be affected by diffusional limitations. Sample equilibration will not necessarily be attained at a particular temperature at normal heating rates unless the sample crystallite size is very small, or adsorbate diffusion is very rapid. The TPD results shown here used a heating rate of 5 °C min^{-1}. We observed only small changes in the desorption maxima when a faster heating rate was applied (10 °C min^{-1}). Other workers have also observed two peak maxima for samples of silicalite saturated with *n*-heptane. These have been found at 56 and 194 °C,[23] 63 and 185 °C,[25] and 65 and 196 °C.[26] Using a rather different TPD method (slow heating in the presence of a constant partial pressure of hydrocarbon vapor), *n*-heptane desorption maxima were found at 87 and 227 °C.[27] These experiments were all performed on samples of different origins, and so they had different crystallite sizes and contained differing amounts of defects and trace aluminum impurities. The broad similarity in all reported TPD results on *n*-heptane in silicalite indicates that diffusional limitations are not playing a role in the qualitative interpretation of TPD data performed here.

As pointed out earlier, the TPD apparatus used in this work includes a mass spectrometer. In contrast to previously published work on silicalite, this allows the desorption rates of the different species present when a mixture is adsorbed to be determined. Figure 8 shows TPD results for samples containing mixtures of *p*-xylene and *n*-heptane at an initial total loading of seven molecules per unit cell. Consider first the results for the sample containing initially four *p*-xylene and three *n*-heptane molecules per unit cell. This was found by FT-Raman spectroscopy as discussed above to have the *p*-xylene molecules in the zigzag channels, and the *n*-heptane molecules in the straight channels. It can be seen that *p*-xylene desorbs most rapidly at 70 °C, though there is also a shoulder to the peak at 90 °C. On the other hand, only a small amount of *n*-heptane desorbs at a low temperature (small TPD peak at 60 °C), with most of the *n*-heptane remaining present until 170 °C. The main *p*-xylene desorption peak at 70 °C is therefore due to overall loss of *p*-xylene from the zigzag channels; this assignment is supported by the analysis of pure *p*-xylene TPD results discussed earlier. It is possible that the *p*-xylene location changes or becomes random when the loading reaches one *p*-xylene/three *n*-heptane
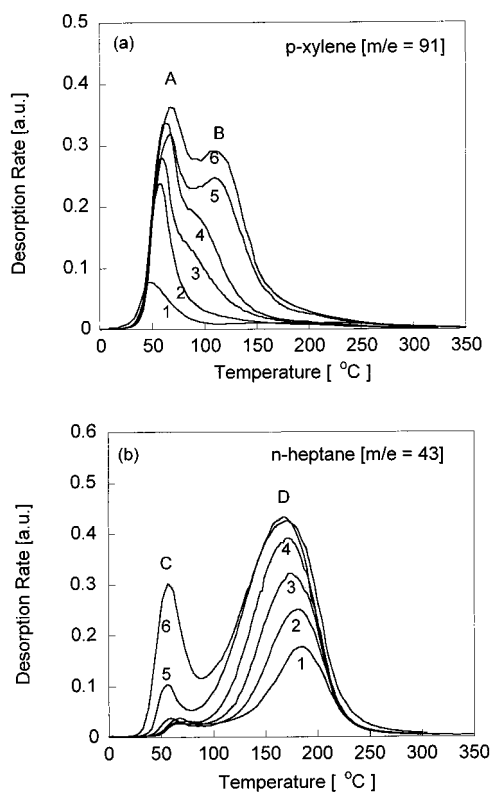
Figure 8. TPD results from silicalite initially saturated with binary mixtures of *p*-xylene and *n*-heptane. (a) *p*-xylene desorption (*m/e* = 91): the numbers indicate the initial loading of *p*-xylene in molecules per unit cell (with the loading being made up to a total of seven molecules per unit cell by *n*-heptane). (b) *n*-Heptane desorption (*m/e* = 43): the numbers indicate the initial loading of *n*-heptane in molecules per unit cell (with the loading being made up to a total of seven molecules per unit cell by *p*-xylene).

molecules per unit cell (at which point the adsorbates need not have many interactions with each other), and this may be the origin of the *p*-xylene TPD shoulder at 90 °C. After desorption of the *p*-xylene, the system becomes one containing only three molecules of *n*-heptane, and this behaves in the same way as was discussed for Figure 7, with the *n*-heptane molecules being located in both the straight and zigzag channels. It can be seen that the behavior of the sample containing three *p*-xylene/four *n*-heptane molecules per unit cell is similar to that for the one containing four *p*-xylene/three *n*-heptane. This indicates that at both these loadings the *n*-heptane has forced the *p*-xylene molecules into the zigzag channels.

Consider now the TPD results of the samples containing one *p*-xylene/six *n*-heptane and two *p*-xylene/five *n*-heptane molecules per unit cell. From the *n*-heptane TPD data, it can be seen that these samples initially lose two and one *n*-heptane molecules, respectively, at a temperature of only 50 °C. On the basis of the discussion above of the results presented in Figure 7, this suggests that at these loadings there may be four molecules of *n*-heptane nonmoving in the zigzag channels. The remaining *n*-heptane molecules must be located in the straight channels and desorb at low temperature. It is interesting that the *p*-xylene molecules also desorb at low temperature (50−60 °C) for these initial loadings. This desorption may be entropy driven (as it reduces the adsorbate loading to the point at which the remaining *n*-heptane molecules will no longer be frozen in the zigzag channels), but it is also the case that *p*-xylene at channel intersections is expected to desorb at low temperature when neighboring molecules are present in the zigzag channels (as discussed for Figure 6). Both these two samples reach the

TABLE 1: Suggested Preferred Adsorption Sites for *p*-Xylene and *n*-Heptane Molecules in Silicalite

sample loading (molecules per unit cell)	channel intersections	zigzag channels	straight channels
four *p*-xylene	four xyl		
eight *p*-xylene	four xyl	four xyl	
four *n*-heptane		two hept	two hept
five *n*-heptane		four hept	one hept
seven *n*-heptane		four hept	three hept
six *p*-xylene/ one *n*-heptane	four xyl	two xyl, one hept	
five *p*-xylene/ two *n*-heptane	four xyl	one xyl, two hept	
four *p*-xylene/ three *n*-heptane		four xyl	three hept
three *p*-xylene/ four *n*-heptane		three xyl	four hept
two *p*-xylene/ five *n*-heptane	two xyl[a]	four hept	one hept
one *p*-xylene/ six *n*-heptane	one xyl[a]	four hept	two hept

[a] *p*-Xylene assignment in this case is speculation based on knowledge of pure *p*-xylene adsorption sites; adsorption of *p*-xylene in the straight channel sites would also be consistent with the experimental results.

state of containing only four molecules of *n*-heptane after heating to ca. 80 °C, at which point the *n*-heptane molecules distribute themselves in both straight and zigzag channels as was discussed earlier for Figure 7.

Consider now the TPD results for the samples containing five *p*-xylene/two *n*-heptane and six *p*-xylene/one *n*-heptane molecules per unit cell. In this case the *p*-xylene TPD data are similar to those obtained on pure *p*-xylene, though the relative intensities of the peaks are modified by the presence of *n*-heptane (most of which does not desorb until 180 °C for these two samples). Thus, the *p*-xylene at zigzag channel sites and at channel intersections with molecules present in the zigzag channels desorbs first (peak A). After any changes in adsorbate location, the *p*-xylene at channel intersections with no neighboring molecules desorbs next (peak B), while *n*-heptane desorbs last. At the initial loadings of five *p*-xylene/two *n*-heptane and six *p*-xylene/one *n*-heptane molecules per unit cell, the presence of *p*-xylene molecules in the channel intersection sites means that the *n*-heptane molecules must be located in the zigzag channels due to the spatial restrictions of the framework.

An overall summary of the suggested preferred adsorption sites for *p*-xylene and *n*-heptane molecules in the silicalite structure on the basis of the FT-Raman and TPD results presented in this paper is given in Table 1.

Discussion

It is clear that both FT-Raman spectroscopy and TPD experiments can provide information on the location of adsorbates within zeolites. The two techniques provide different but complementary information, in part because they are measurements on very different time scales. The combination of the two techniques is particularly powerful in determining the preferential adsorption sites for *p*-xylene/*n*-heptane mixtures in silicalite. FT-Raman spectroscopy is capable of resolving the different adsorption sites for aromatic molecules within silicalite, and can also probe sorbate−sorbate interactions. TPD can probe differences in the total adsorption state as a function of loading. It is worth noting that the temperature difference between the two peak maxima in the TPD results on both pure *p*-xylene and pure *n*-heptane in silicalite is large. Thus, TPD is a sensitive measurement of the fact that two different adsorption states occur as a function of loading for these systems. This may be

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contrasted to the case of analyzing traditional equilibrium adsorption isotherms; here careful adsorption measurements are needed to identify the presence (or otherwise) of small kinks in the isotherm at particular loadings.

For the measurements on single-component adsorption, the results in this paper are consistent with those in the literature. For pure *p*-xylene adsorption, the molecules are adsorbed at channel intersection sites up to a loading of four molecules per unit cell, after which the zigzag channels become occupied as well. For pure *n*-heptane adsorption, the results are consistent with adsorption in both straight and zigzag channel sites up to a loading of four molecules per unit cell. Above this loading, there is commensurate freezing of four molecules into the zigzag channels, with the remaining *n*-heptane molecules being mobile in the straight channels.

The results obtained in this work on binary mixtures within silicalite are more interesting (Table 1). The samples containing five *p*-xylene/two *n*-heptane and six *p*-xylene/one *n*-heptane molecules per unit cell behave in a comparable way to that expected on the basis of pure *p*-xylene adsorption. Similarly, the samples containing two *p*-xylene/five *n*-heptane and one *p*-xylene/six *n*-heptane molecules per unit cell behave in a comparable way to that expected on the basis of pure *n*-heptane adsorption. However, the preferred adsorption sites at loadings of four *p*-xylene/three *n*-heptane and three *p*-xylene/four *n*-heptane molecules per unit cell are completely different, with *n*-heptane preferentially occupying the straight channels, and forcing the *p*-xylene molecules out of their normal preferred site (the channel intersections) into the zigzag channels. This particular observation is important in understanding the performance of silicalite membranes in gas separations applications. The separation selectivity of zeolite membranes is generally a function of both adsorption and diffusion properties, but it is believed that adsorption is the major factor controlling the separation of mixtures of saturated and aromatic hydrocarbons.[39] A recent paper studied hydrocarbon separations using silicalite membranes,[34] and compared the permeation rates of *n*-heptane and toluene (which might be expected to occupy the same adsorption sites as *p*-xylene). It was found that pure toluene permeated faster through a silicalite membrane than pure *n*-heptane; however, when both species are present in a mixture the permeation rate of toluene was found to be significantly slowed, while that of *n*-heptane was little affected.[34] This observation may in part be explained by the fact that the preferred adsorption sites for binary mixtures are not necessarily the same as those for pure components; this is what we observe to be the case here for the samples with loadings of four *p*-xylene/three *n*-heptane and three *p*-xylene/four *n*-heptane molecules per unit cell. The results in the current work highlight the fact that the preferred adsorption sites adopted by molecules can depend critically on sample loading, and this will complicate predictions of the performance of silicalite membranes. It also means that the optimum choice of zeolite in a membrane may itself depend on the composition of the feed (e.g., whether it is desired to remove trace species, or to separate an equimolar mixture).

References and Notes

(1) Karger, J.; Ruthven, D. M. *Diffusion in Zeolites and Other Microporous Solids*; Wiley: New York, 1992.

(2) Yang, R. T. *Gas Separation by Adsorption Processes*; Imperial College Press: London, 1997.

(3) Sirkar, K. K. *Chem. Eng. Commun.* **1997**, *157*, 145.

(4) Bates, S. P.; van Santen, R. A. *Adv. Catal.* **1998**, *42*, 1.

(5) Knops-Gerrits, P.-P.; De Vos, D. E.; Feijen, E. J. P.; Jacobs, P. A. *Microporous Mater.* **1997**, *8*, 3.

(6) Ashtekar, S.; Barrie, P. J.; Hargreaves, M.; Gladden, L. F. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 876.

(7) Ferwerda, R.; van der Maas, J. H. *J. Phys. Chem.* **1995**, *99*, 14764.

(8) Huang, Y. *J. Am. Chem. Soc.* **1996**, *118*, 7233.

(9) Ashtekar, S.; Hastings, J. J.; Gladden, L. F. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 1157.

(10) Meier, W. M.; Olson, D. H. *Atlas of Zeolite Structure Types*, Butterworth-Heinemann: London, 1992.

(11) Olson, D. H.; Kokotailo, G. T.; Lawton, S. L.; Meier, W. M. *J. Phys. Chem.* **1981**, *85*, 2238.

(12) Takaishi, T.; Tsutsumi, K.; Chubachi, K.; Matsumoto, A. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 601.

(13) van Koningsveld, H.; Jansen, J. C.; van Bekkum, H. *Zeolites* **1990**, *10*, 235.

(14) Mentzen, B. F.; Vigné-Maeder, F. *Mater. Res. Bull.* **1987**, *22*, 309.

(15) van Koningsveld, H.; Tuinstra, F.; van Bekkum, H.; Jansen, J. C. *Acta Crystallogr.* **1989**, *B45*, 423.

(16) Fyfe, C. A.; Strobl, H.; Kokotailo, G. T.; Kennedy, G. J.; Barlow, G. E. *J. Am. Chem. Soc.* **1988**, *110*, 3373.

(17) Reischman, P. T.; Schmitt, K. D.; Olson, D. H. *J. Phys. Chem.* **1988**, *92*, 5165.

(18) Jacobs, P. A.; Beyer, H. K.; Valyon, J. *Zeolites* **1981**, *1*, 161.

(19) Stach, H.; Lohse, U.; Thamm, H.; Schirmer, W. *Zeolites* **1986**, *6*, 74.

(20) Richards, R. E.; Rees, L. V. C. *Langmuir* **1987**, *3*, 335.

(21) Sun, M. S.; Talu, O.; Shah, D. B. *J. Phys. Chem.* **1996**, *100*, 17276.

(22) Eder, F.; Lercher, J. A. *Zeolites* **1997**, *18*, 75.

(23) van Well, W. J. M.; Wolthuizen, J. P.; Smit, B.; van Hooff, J. H. C.; van Santen, R. A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2543.

(24) Olson, D. H.; Reischman, P. T. *Zeolites* **1996**, *17*, 435.

(25) Long, Y.-C.; Jiang, H.-W.; Zeng, H. *Langmuir* **1997**, *13*, 4094.

(26) Yang, Y.; Rees, L. V. C. *Microporous Mater.* **1997**, *12*, 223.

(27) Millot, B.; Methivier, A.; Jobic, H. *J. Phys. Chem. B* **1998**, *102*, 3210.

(28) Titiloye, J. O.; Parker, S. C.; Stone, F. S.; Catlow, C. R. A. *J. Phys. Chem.* **1991**, *95*, 4038.

(29) June, R. L.; Bell, A. T.; Theodorou, D. N. *J. Phys. Chem.* **1990**, *94*, 1508.

(30) Maginn, E. J.; Bell, A. T.; Theodorou, D. N. *J. Phys. Chem.* **1995**, *99*, 2057.

(31) Smit, B.; Siepmann, J. I. *J. Phys. Chem.* **1994**, *98*, 8442.

(32) Smit, B.; Maesen, T. L. M. *Nature* **1995**, *374*, 42.

(33) Vlugt, T. J. H.; Krishna, R.; Smit, B. *J. Phys. Chem. B* **1999**, *103*, 1102.

(34) Funke, H. H.; Argo, A. M.; Falconer, J. L.; Noble, R. D. *Ind. Eng. Chem. Res.* **1997**, *36*, 137.

(35) Varsanyi, G. *Vibrational Spectra of Benzene Derivatives*; Academic Press: New York, 1969.

(36) Dollish, F. R.; Fateley, E. G.; Bentley, F. F. *Characteristic Raman Frequencies of Organic Compounds*; Wiley: Chichester, 1974.

(37) Dutta, P. K.; Rao, K. M.; Park, J. Y. *J. Phys. Chem.* **1991**, *95*, 6654.

(38) Mentzen, B. F. *Mater. Res. Bull.* **1992**, *27*, 831.

(39) Mizukami, F. *Stud. Surf. Sci. Catal.* **1999**, *125*, 1.