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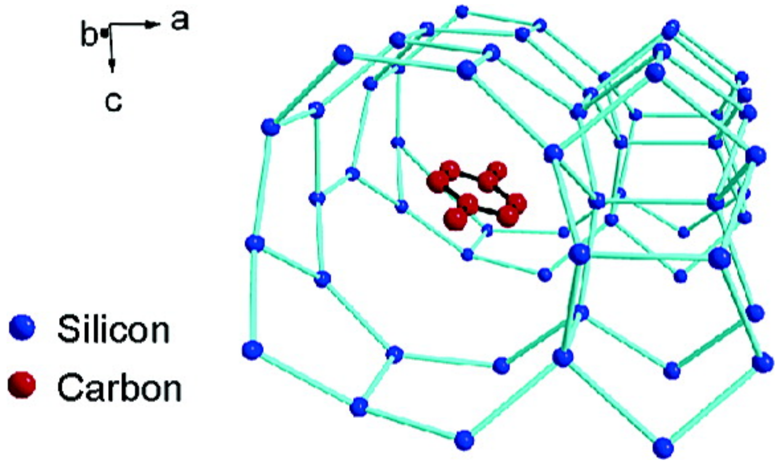

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Solid State NMR Method for the Determination of 3D Zeolite Framework/Sorbate Structures: $^1H/^{29}Si$ CP MAS NMR Study of the High-Loaded Form of *p*-Xylene in ZSM-5 and Determination of the Unknown Structure of the Low-Loaded Form

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Abstract: A general protocol is described for structure determinations of organic sorbate−zeolite complexes based on the selective, through-space, distance-dependent transfer of magnetization from protons in selectively deuterated organics to framework silicon nuclei. The method was developed using the known structure of the high-loaded ZSM-5/*p*-xylene complex containing *p*-xylene-d_6 or *p*-xylene-d_4. It was then applied to determine the unknown structure of the low-loaded ZSM-5/*p*-xylene complex using NMR alone. For the high-loaded complex improved data were obtained below 273 K, where slow motions and exchange processes of the *p*-xylene are eliminated. The general approach was validated by the exact agreement of the experimental $^1H-^{29}Si$ CPMAS spectra obtained at a specific contact time and the complete 24-line spectra simulated using $1/T_{CP}$ vs M_2 correlations from only the six clearly resolved resonances. For the low-loaded complex the ^{29}Si resonances were assigned at 267 K, and variable contact time CP experiments were carried out between 243 and 173 K using the same specifically deuterated *p*-xylenes. All possible locations and orientations of the *p*-xylene guests were sampled, and those solutions that gave acceptable linear $1/T_{CP}$ vs M_2 correlations were selected. The optimum *p*-xylene location in this temperature range was determined to be in the channel intersection with the long molecular axis parallel to [0,1,0] (ring center fractional coordinates {−0.009, 0.250, 0.541}) with the ring plane oriented at an angle of 30 ± 3° about the crystallographic *b* axis. A subsequent single-crystal X-ray study confirmed this predicted structure.

Introduction

In recent years, high-resolution solid state NMR spectroscopy has emerged as a complementary technique to X-ray diffraction methods for the investigation of the structures of molecular sieve systems.[1] In the case of low Si/Al ratio materials, the spectra give insight into the local silicon environments, the distribution of Si and Al over the T-sites, and the effects of chemical treatments, information not directly obtainable from diffraction measurements.[2] A very direct connection between the two techniques is made in the case of highly siliceous zeolites whose ^{29}Si MAS spectra show a series of very narrow resonances whose numbers and intensities reflect directly the numbers and occupancies of the crystallographically inequivalent T-sites in the asymmetric unit in the unit cell.[3] Further, the isotropic average chemical shifts of the resonances may be correlated with average structural parameters from the X-ray structure of the framework, if it is known and if the resonances can be assigned to silicons at specific T-sites.[4] Such correlations are most valid when the X-ray data are of high quality, preferably from single-crystal diffraction studies.[5]

More recently, the link between the two techniques has been further developed by the demonstration that two-dimensional COSY and INADEQUATE experiments can reliably delineate the three-dimensional bonding connectivities (Si^A-O-Si^B) within the framework.[6] In cases where the structure is known, these experiments may be used to assign the resonances in the ^{29}Si MAS spectrum to silicons at specific T-sites where this cannot be done from the relative intensities. Even complex cases can be solved, for example, the monoclinic form of ZSM-5 where there are 24 T-sites, all of which are of equal occupancy.[7] In situations where the structures are unknown or poorly

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† Deceased.

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described, the 2D NMR data may be used to propose possible topologies or space groups for refinement of powder X-ray diffraction data.[8]

Much of the interest in the structures of these materials derives from a desire to understand their molecular sieving characteristics,[9] which are critical to their use as catalysts, sorbents, and host frameworks. However, despite the importance of the problem, few sorbate−framework structures have been determined using diffraction techniques. Although the framework topologies can often be determined from refinements of powder X-ray data, these data are usually too limited to reliably determine the locations of organic guests within the frameworks. The microcrystalline nature of these materials in almost all cases precludes the use of single-crystal X-ray diffraction, an exception being the work of van Koningsveld and co-workers, who have determined the structures of several complexes of ZSM-5 where large enough single crystals can be obtained.[10,11]

In the first part of the present work we have developed a method using solid state NMR spectroscopy, specifically cross polarization (CP) MAS NMR experiments,[12] as an alternative method for determining the three-dimensional structures formed between sorbed organic molecules and molecular sieve frameworks. The CP experiment is based on the heteronuclear dipolar interaction that is through-space and dependent on the internuclear distance, making it possible to obtain three-dimensional structural data. A definite advantage to using the dipolar coupling is its inverse third-power dependence on the internuclear distance, which means that relatively accurate distances can be obtained. In the second part a computer-assisted variation of the same protocol was used to determine the (unknown) structure of the low-loaded form (2−4 molecules/unit cell) with a view to testing the validity of the approach with a subsequent single-crystal structure determination.

The system chosen for developing and validating the method was the orthorhombic form of zeolite ZSM-5 containing 8 molecules of *p*-xylene per unit cell (u.c.), as there is considerable literature data available against which to measure the viability and reliability of this approach. Most importantly, there is an excellent single-crystal X-ray diffraction derived structure by van Koningsveld and co-workers.[11] In addition, the ^{29}Si MAS NMR spectrum shows highly resolved signals, and all of them have been assigned to specific T-sites from INADEQUATE experiments.[8] Previous work has reported the ^{2}H NMR spectra of partially deuterated *p*-xylenes in ZSM-5[13a] and the ^{1}H spectra of a similar system.[13b] The ^{13}C NMR spectra of the high-loaded form have been reported to show three resonances for the CH_3 groups of the *p*-xylene molecules.[14]

There is only very limited structural information available from other methods concerning the structure of the low-loaded form of the *p*-xylene/ZSM-5 complex. The only diffraction study is the powder X-ray diffraction work of Mentzen and Vigne-Maeder,[15] who proposed that the *p*-xylene was located at the channel intersection with its long axis along the straight channel, based on a comparison of simulated and experimental powder diffraction patterns. However, two different orientations of the ring gave similar agreement. There are also solid-state NMR experiments by the same group.[16] There have also been attempts to predict the structure theoretically:[17] Reischman et al.[18] considered three possible locations for the *p*-xylene: the straight channel, the zigzag channel, and the channel intersection. From their calculations, they suggested that the lowest energy structure was that where the molecule was in the channel intersection with its long axis along the straight channel direction, but no further structural details were given. Pickett et al.[19] found several energy minima: one in the straight channel and two in the intersection with that in the straight channel being the global energy minimum. Snurr et al.[20] studied both benzene and *p*-xylene: the latter structure was not described in detail but the location was said to be the same as for benzene and was at the channel intersection. A recent review indicates a lack of more recent theoretical studies on the structure of this system.[17b] A preliminary account of some of the work presented here has been given in ref 21.

Once the reliability of the method is clearly established, the longer term goal of the present work is to extend these measurements to other zeolite/sorbate systems of unknown structure where the use of single-crystal diffraction techniques is precluded by small crystallite sizes or other effects. This could improve the understanding of the size and shape selectivity properties that are central to many of the practical applications of these materials.

In a broader context these structures represent an opportunity to investigate organic molecule/surface interactions in very well defined systems, as the vast majority of framework sites in these structures are part of internal surfaces that are perfectly ordered and have different shapes in different frameworks. These studies could also be reference points for the study of the interaction of organic molecules with similar but less ordered and less well characterized surfaces.

Materials and Methods

Sample Preparation. The highly siliceous sample of ZSM-5 was similar to those used previously for ^{29}Si MAS NMR investigations.[5−8]

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Samples containing approximately 3, 6, and 8 molecules per u.c. of *p*-xylene-d_6 and *p*-xylene-d_4 were prepared by adding an exactly measured amount of *p*-xylene-d_6 or *p*-xylene-d_4 to a weighed amount of ZSM-5 in a glass vial and then sealing and heating at 353 K for 8 h. The exact loadings were checked before and after the NMR experiments by thermogravimetric analysis (TA Instruments TG51 thermogravimetric analyzer).

Previous work on the *p*-xylene/ZSM-5 system has shown that at loadings between 2 and 4 molecules per u.c. the system is completely orthorhombic (*Pnma*) with 12 independent T-sites in the asymmetric unit, while between 6 and 8 molecules per u.c. it transforms completely to a second orthorhombic phase ($P2_12_12_1$) with 24 independent T-sites.[3b,c] Quantitative ^{29}Si MAS spectra of a sample with a loading of 4 molecules per u.c. showed the presence of only a small amount of the high-loaded form, but this makes an appreciable contribution to the spectrum when ^{1}H−^{29}Si cross polarization is used due to the polarization transfer being much more efficient in the high-loaded phase, at least at ambient temperature. To ensure that the spectral intensity came exclusively from the low-loaded form, a loading of 3.4 molecules per u.c. was used in subsequent experiments. For simplicity, this is referred to as “3 molecules” in the rest of the text.

NMR Experiments. Most experiments were carried out using a Bruker MSL 400 spectrometer equipped with a standard Bruker 7 mm MAS double-tuned probe operating at 400.13 MHz for protons and 79.6 MHz for ^{29}Si. Chemical shifts are referenced to TMS using Q_8M_8 as intermediate standard. Low-temperature ^{29}Si MAS spectra were obtained using a cooling system designed to work at low temperature for long periods of time with stable spinning rates in the range 2.5−3.5 kHz. In this arrangement the bearing gas was also the cooling gas and a pressurized 200 L liquid nitrogen Dewar was used as the cold bearing gas reservoir. This precooled bearing gas was cooled further by passing it through a coil immersed in liquid nitrogen in a 25 L Dewar. Dry nitrogen drive gas was required to avoid disruption of the sample spinning due to ice formation. The pressurized 200 L liquid nitrogen supply was also used to provide the drive gas because the Dewar has another output from which gas can be drawn off under the control of a pressure regulator. The temperature was regulated within the probe using a Bruker VT-1000 temperature control unit in conjunction with manual maintenance of the liquid nitrogen level in the 25 L Dewar. Variable-temperature, wide-line deuterium NMR spectra were obtained using a home-built probe that accommodated both 5 mm and 10 mm horizontal solenoid coils. A quadrupolar echo sequence ($90_x-\tau-90_y-\tau$-acq)[22] was used, and typical 90° pulse times were ca. 3 and 6 μs for the 5 and 10 mm coils, respectively. Low-temperature ^{2}H measurements were carried out with a flow of cold nitrogen gas and the temperature regulated using the Bruker VT-1000 temperature control unit.

Inadequate Experiments. These were performed using a standard pulse sequence[23] in which the last 90° pulse was replaced by a 135° pulse to provide quadrature detection in the double quantum frequency domain. The experiment was carried out at various temperatures, chosen for optimal spectral resolution and reliability of the CP parameters, using the experimental arrangement for working at low temperatures. The ^{29}Si 90° pulse length was 8.25 μs, and the collected data were processed and plotted using the program 2D-WINNMR.[24]

2D Spin Diffusion Measurements. A standard 2D NOESY sequence[25a] was used with a cross polarization step substituted for the initial 90° pulse.[25b] Proton decoupling was applied during both the mixing and acquisition times, and the longest mixing time was limited to 120 ms.

^{1}H/^{29}Si CP Experiments. Variable contact time experiments on the high-loaded complexes of 6 and 8 molecules of *p*-xylene-d_4 and *p*-xylene-d_6 in ZSM-5 were carried out at 293 K, 273 K, and below and those on the complexes of 3 molecules of *p*-xylene-d_6 and *p*-xylene-d_4 in ZSM-5 at 293, 243, and 233 K using the experimental arrangement for long-term operation at low temperatures described above. The experiments involved variation of the contact times up to 100 ms, and typical 90° pulse times were 11 μs (^{1}H) and 11.2 μs (^{29}Si). The number of scans accumulated for each contact time varied between 1000 and 3000.

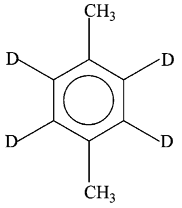
Additional experiments at 400 MHz were carried out on the low-loaded form at even lower temperatures (down to 173 K) using a DSX spectrometer courtesy of Bruker Spectrospin (see Acknowledgments). Variable contact time experiments on the complexes of 3 molecules per u.c. of *p*-xylene-d_6 in ZSM-5 were carried out at 213, 193, and 173 K, and for a low-loaded *p*-xylene-d_4 sample at 213 K.

Details of the fitting of the experimental data and the calculations done to locate the *p*-xylene molecules within the ZSM-5 framework are presented in the text.

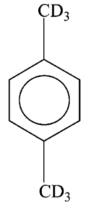
Results and Discussion

General Comments. To determine the geometric relationship between sorbed organics and the silicon atoms of the framework, experiments such as CP,[12] transferred echo double resonance (TEDOR),[26] and rotational echo double resonance (REDOR)[27] must be used, since these are based on the heteronuclear dipolar interaction between the nuclei that is a function of the through-space internuclear distance. In the present work we examine the potential of the cross polarization experiment to obtain structural information on the high- and low-loaded complexes formed between *p*-xylene and zeolite ZSM-5.

There are a number of factors that could compromise the use of the CP technique for structure determinations, and care must be taken to ensure that they are not affecting the experiments: First, the distances between the protons on the guest molecules and the silicon nuclei in the framework must be reasonably well defined. This was achieved in the present work by investigating two closely related partially deuterated systems: *p*-xylene-d_4 (**1**), where the polarization source is the protons in the methyl groups, and *p*-xylene-d_6 (**2**), where the polarization source is the four protons on the aromatic ring. Although these proton spin systems do not qualify as “isolated nuclei”, which is the optimum situation for obtaining unambiguous structural data, it was hoped that their isolation would be good enough to obtain useful structural information. However, because of their relative isolation, they may not qualify as truly abundant spin systems, the normal assumption in the interpretation of CP dynamics.



(**1**)



(**2**)

Second, the CP process can be affected by motions of the guest molecules, and these must be as well-defined as possible.

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In the present work, these were determined directly from the ^{2}H NMR solid state spectra of the complexes. A variety of molecular motions can be taken into account in the theoretical second moment calculations as long as their nature is known. However, translational motions, particularly between inequivalent sites, may possibly invalidate the structural determination, and if these are slow, they may be difficult to detect even by ^{2}H NMR. The cross polarization time constant (T_{CP}) values obtained from the fitting of the CP data can also be affected by motions; specifically, the proton relaxation time in the rotating frame $T_{1\rho(H)}$ is very sensitive to very slow molecular motions. If $T_{1\rho(H)}$ is comparable to or less than T_{CP}, the normal assumption that $T_{1\rho(H)} \gg T_{CP}$ can no longer be made, and if this is not recognized, erroneous T_{CP} values will be obtained. Last, the $T_{1\rho(H)}$ values can be affected by the amount of sorbate present, which can be varied to a certain extent without introducing structural changes of the sorbate/framework complex, and within this stability region a loading should be selected where the relaxation behaviors, particularly in terms of $T_{1\rho(H)}$, are most appropriate.

With these factors in mind, extensive studies of both the high- and low-loaded complexes were carried out. In the first part, the high-loaded complex where the structure was known is studied to develop a clear and reliable protocol that could be applied to other systems whose structures were unknown. To limit the amount of data presented, although investigations of complexes of both deuterated xylenes were carried out, in the main, only those data from the *p*-xylene-d_6 complexes that are considered more accurate are presented in the paper and in the case of the high-loaded complex, only those data from the 8 molecules per u.c. case are shown. All the other data are presented in the Supporting Information.

I: Method Development Using the High-Loaded Form of the *p*-Xylene/ZSM-5 Complex. The ^{29}Si CP MAS spectra for zeolite ZSM-5 loaded with 6, 7, and 8 molecules of *p*-xylene are almost identical and indicate that the framework structure is the same at all loadings. As previously reported, the 8 molecule per u.c. form is orthorhombic, space group $P2_12_12_1$, and has 24 T-sites in the asymmetric unit.[11] The assignment of the different resonances to the appropriate silicons shown in Figure 1b comes from previously reported INADEQUATE experiments.[7] In the spectra, the resonances corresponding to silicons 1, 3, 10, 12, 16, and 17 are reasonably well-defined, and particular attention will be paid to these in the structure determinations.

Deuterium NMR Spectra. Vega and co-workers[13] used the ^{2}H NMR spectra of various deuterated *p*-xylene/ZSM-5 systems to investigate the motions of the sorbate molecules in detail. Although the system studied was Na$^+$/ZSM-5 and is thus significantly different from that studied here, the theoretical spectra for the different molecular motions such as methyl group rotation and 180° ring "flips" provide excellent reference points for the present work and were used in the interpretation of the spectra described below.

The ^{2}H spectra of some of the present samples are shown in Figure 2. The spectrum of the *p*-xylene-d_4 intercalate at 8 molecules per u.c. (Figure 2a) shows a narrow central component, broadened by the exponential multiplication used to enhance the very broad main signal. The intensity of the major broad component in the spectrum is greatly underestimated in the quadrupolar echo experiment because of its very short T_2 value, but the splitting of 130 kHz between the central singularities clearly shows that the rings are rigid at this temperature and this loading of organic molecules. In fact, the rings appear to be static up to 333 K in this experiment. The narrow central line is indicative of completely isotropic motion, but the fraction of molecules involved is small (its concentration is estimated to be <10%) and probably reflects molecules on the exterior surfaces of the crystallites or at defect sites at this maximum loading. Similar spectra are observed for the 6 molecule complex (Supporting Information Figure S1a) with the absence of the narrow component, which lends support to the assignment proposed above.

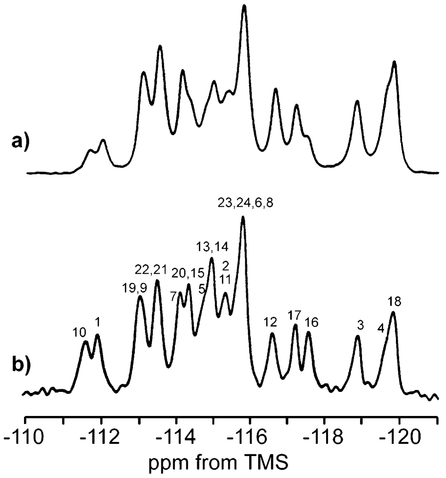


Figure 1. (a) ^{29}Si CP MAS NMR spectrum of ZSM-5 loaded with 8 molecules of *p*-xylene-d_6 per u.c., contact time 5 ms. (b) ^{29}Si MAS NMR spectrum of the same sample obtained using a recycle delay of 350 s to ensure complete relaxation of the silicon nuclei. The 90° pulse length was 13 μs. Labels refer to the T-site numbering in ref 11.

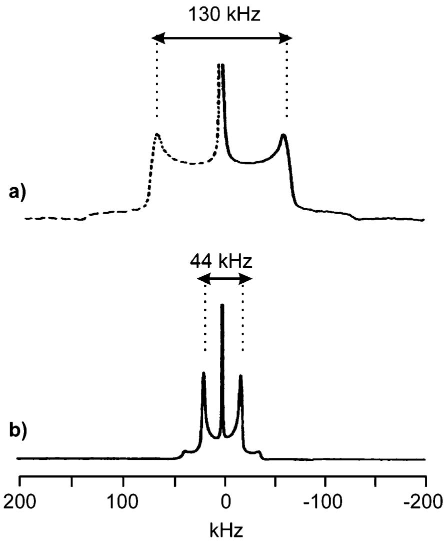


Figure 2. Room-temperature ^{2}H NMR spectra of selectively deuterated *p*-xylenes in ZSM-5 at a loading of 8 molecules per u.c. (a) *p*-Xylene-d_4: 90° pulse length 2.8 μs, echo delay 12 μs, recycle delay 6 s, 5204 scans, 2500 Hz line broadening. (b) *p*-Xylene-d_6: 90° pulse length 6 μs, echo delay 8 μs, recycle delay 1 s, 3676 scans, 200 Hz line broadening.

In the case of the *p*-xylene-d_6 intercalate (Figures 2b, SI1b), the splitting in the ^{2}H spectrum is now reduced to 44 kHz, indicating methyl group rotation, but there is no evidence of free rotation of the molecule or of large-scale diffusion. Again a small, very narrow central resonance is observed for the 8 molecule case, which is thought to be due to a small fraction of freely diffusing molecules adsorbed on the exterior surface.

Thus, on the time scales of the ^{2}H experiments, both *p*-xylene molecules have stationary rings and rotating methyl groups at room temperature, and this must be taken into account in the calculation of second moments and distances. It should be emphasized that the location of discrete atomic positions in diffraction experiments does not necessarily indicate the absence of molecular reorientations, as these are often between equivalent positions, i.e., positions of minimum potential, as in the case of 180° ring flips, and as such are not detected by diffraction experiments, which reflect the positions that most of the atoms occupy most of time. Even where diffraction experiments detect disorder, this could still be either static or dynamic in nature.[28]

Cross Polarization Experiments. The cross polarization experiments were carried out using the standard spin-lock sequence with spin temperature inversion to suppress artifacts.[12c] During the spin-locking step, there is coherence transfer from ^{1}H to ^{29}Si via the heteronuclear dipolar interaction if the two spin-locking fields $H_{1(\mathrm{H})}$ and $H_{1(\mathrm{Si})}$ satisfy the Hartmann−Hahn match condition, eq 1. In the present work the two rf fields were matched experimentally.

$$\gamma_{\mathrm{H}}H_{1(\mathrm{H})} = \gamma_{\mathrm{Si}}H_{1(\mathrm{Si})} \tag{1}$$

Quantitatively, the cross polarization process is usually described using eq 2 with the assumptions that $T_{\mathrm{CP}} \ll T_{1\rho(\mathrm{H})}$ and $T_{1\rho(\mathrm{Si})}$ is very long compared to T_{CP} and can be neglected and that the number of ^{1}H nuclei is "much larger" than the number of ^{29}Si nuclei. This latter condition is at least approximately satisfied in the present cases because of the low natural abundance of ^{29}Si (4.6%). However, in samples of this type, the protons are present at quite low concentration and there may be relatively small homonuclear dipolar couplings between protons on different molecules, so the proton reservoir may not be a strongly coupled abundant spin system. Thus, eq 2 may be expected to give only an approximate description of the behavior of the S nucleus (^{29}Si) magnetization.

$$I(t) = I_{\mathrm{o}}[1 - (T_{\mathrm{CP}}/T_{1\rho(\mathrm{H})})]^{-1}[\exp(-t/T_{1\rho(\mathrm{H})}) - \exp(-t/T_{\mathrm{CP}})] \tag{2}$$

I_{o} represents the theoretical maximum signal intensity obtainable from the polarization transfer in the absence of any loss due to relaxation processes. Of particular importance, the cross polarization time constant T_{CP} is proportional to the second moment of the dipolar line shapes (eq 3) and hence has an inverse dependence on the sixth power of the internuclear distance r.[12]

$$1/T_{\mathrm{CP}} = C(\Delta\omega^{2})_{IS}/(\Delta\omega^{2})_{II}^{\ 1/2} \tag{3}$$

C is a constant and $(\Delta\omega^{2})_{IS}$ and $(\Delta\omega^{2})_{II}$ are the heteronuclear (I,S) and homonuclear (I,I) second moments, respectively. Hence,

$$1/T_{\mathrm{CP}} \propto (\Delta\omega^{2})_{IS} \propto (\gamma_{I}^{\ 2}\gamma_{S}^{\ 2})/\sum r^{6} \tag{4}$$

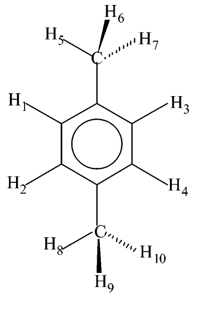
It was anticipated then that the ^{29}Si CP MAS NMR spectra of these systems would show substantial differences in the enhancements of the different signals based on their distances from the proton magnetization sources and that these effects could be used to determine the geometric relationship between the host lattice and the organic guest molecules. The effects of the distance dependence can be seen qualitatively from a comparison of the CP spectrum with that from a simple quantitative one-pulse experiment as shown in Figure 1. The structure is orthorhombic with 24 T-sites of equal occupancy. In the CP experiment, some signals are obviously enhanced compared to others. The resonances due to the silicons 1, 3, 10, 12, 16, and 17 are quite well resolved, and these were used in the initial study.

Table 1. Shortest Calculated Si−H Distances[a] from the Single-Crystal X-ray Crystal Structure for ZSM-5 Loaded with 8 Molecules per u.c. of *p*-Xylene

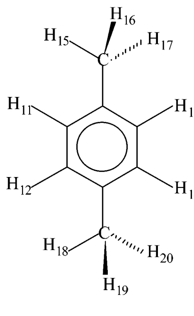
^{29}Si T-site	$\mathrm{H}_{\mathrm{arom.}}$	$r_{\mathrm{Si-H}}$ (Å)	$\mathrm{H}_{\mathrm{CH3}}$	$r_{\mathrm{Si-H}}$ (Å)
Si 1	H-13	3.963	H-19	3.566
	H-1	5.166	H-8	3.586
	H-3	5.354	H-5	4.103
Si 3	H-3	3.132	H-18	4.101
	H-4	3.619	H-19	4.408
	H-12	4.627	H-15	4.795
Si 10	H-2	4.318	H-5	3.596
	H-13	5.413	H-9	3.804
	H-1	5.889	H-8	5.858
Si 12	H-3	3.205	H-18	4.494
	H-12	3.386	H-10	4.990
	H-4	3.915	H-8	5.400
Si 16	H-1	4.344	H-5	3.508
	H-4	4.758	H-7	4.463
	H-2	5.318	H-6	5.016
Si 17	H-1	3.607	H-5	3.778
	H-13	3.572	H-19	4.089
	H-2	5.044	H-20	4.495

[a] The hydrogen atomic positions were calculated using C−H distances of 0.98 Å for the aromatic hydrogens and 1.1 Å for the methyl hydrogens, and the appropriate geometries for a planar aromatic ring and tetrahedral CH_3 group.

Since the structure is known in the present instance, it will be possible to compare calculated second moment values (calculated according to Van Vleck[29] using the internuclear distances from the X-ray structure) to the T_{CP} values deduced experimentally from fitting the CP curves to eq 2. Table 1 lists the closest Si−H distances calculated from the XRD structure.[11] The hydrogen numbering corresponds to the two different kinds of *p*-xylene molecules, XYL2 (**3**) located in the sinusoidal channels and XYL1 (**4**) located at the intersection of the sinusoidal and straight channels as shown in Figure 3. The locations of silicons 1, 3, 10, 12, 16, and 17 are highlighted in red in this figure.



XYL2 (**3**)



XYL1 (**4**)

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(28) Fyfe, C. A.; Veregin, R. P. *Trans. Am. Crystallogr. Assoc.* **1970**, 43.

(29) Van Vleck, J. H. *Phys. Rev.* **1948**, *74*, 116.

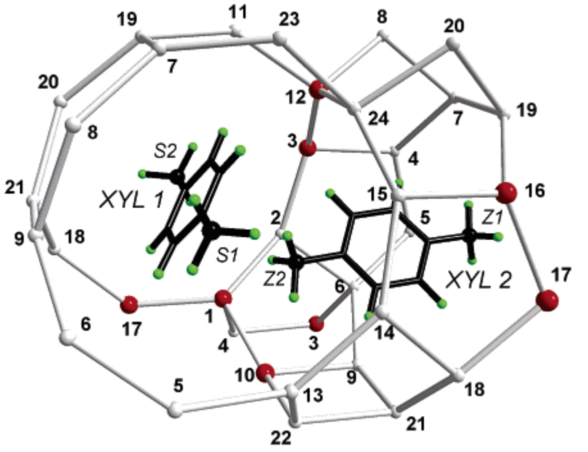

Figure 3. Structure of the high-loaded *p*-xylene/ZSM-5 framework structure viewed down the straight channel showing the locations of the *p*-xylene molecules in the sinusoidal channel (XYL2) and in the intersection of the channels (XYL1) based on the structural data of ref 11. Oxygen atoms bridging the silicons are omitted for clarity, and the locations of the silicons whose resonances are used to obtain the CP curves are highlighted in red.

^{29}Si CP/MAS spectra were obtained as a function of contact time (CT) up to a maximum of 60 ms for samples of ZSM-5 loaded with both 8 and 6 molecules of the specifically deuterated *p*-xylenes **1** and **2** at 293 K. The spectra were deconvoluted in terms of Lorentzian functions and the intensities of the reasonably well-resolved resonances of silicons 1, 3, 10, 12, 16, and 17 tabulated and fit to eq 2 using the nonlinear statistics package in Mathematica.[30] The data from these fits are given in Tables 2 and SI2 and SI3 in the Supporting Information. To conserve space, the results for both sorbates will be described, but for the most part, only data for the *p*-xylene-d_6 systems will be presented as figures; those for the *p*-xylene-d_4 systems are available in the Supporting Information.

Figure 4a shows a plot of these data for the *p*-xylene-d_6 sorbate (**1**) at a loading of 8 molecules. Qualitatively, there is agreement between the CP curves of both deuterated *p*-xylenes at both loadings and the known structure (Figure 3). Thus for *p*-xylene-d_6, at loadings of 8 molecules (Figure 4a) and 6 molecules (Figure SI4a in the Supporting Information), the curves indicate that silicons 12, 3, and 17 are much more efficiently polarized (and hence closer to the ^{1}H polarization source) than silicons 16, 10, and 1, in excellent agreement with the Si−H distances shown in Table 1. The distinction is clearest in the early part of the curves where the growth is dominated by T_{CP}. Similarly, the data for the *p*-xylene-d_4 system (Figures SI2a, SI5a) suggest that Si 1 and Si 10 are polarized more efficiently than Si 17, Si 16, Si 3, and Si 12, in agreement with the data of Table 1.

However, the fits of the curves to eq 2 are only moderately good, particularly for the two 8 molecule systems, e.g., Figure 4a. In the “conventional” case ($T_{CP} \ll T_{1\rho(H)}$), there is an exponential growth due to polarization transfer and the curve reaches a maximum value before an exponential decay dominated by $T_{1\rho(H)}$. The curves that grow fastest have the highest maxima, and the maxima in the series shift to longer contact time values as they become lower. The curves in Figure 4a do not reach clear maxima even at the maximum contact time, and the fits are relatively poor, particularly at shorter contact times.

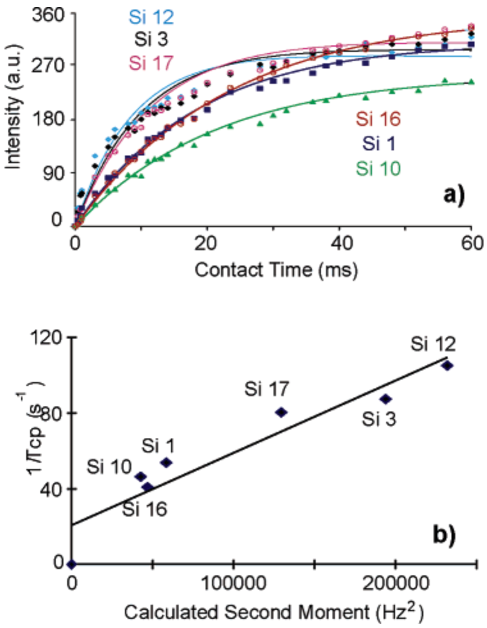

Figure 4. (a) Intensities of the ^{29}Si CP MAS NMR signals as indicated as functions of the contact time at 293 K for ZSM-5 loaded with 8 molecules of *p*-xylene-d_6 per u.c. (b) Plot of experimental $1/T_{CP}$ values vs the calculated second moments.

The two sets of data for the loadings of 6 molecules approximate better the expected behavior, with clear maxima and decays, but the fits are still not exact, particularly at shorter contact times.

The differences in behavior between the 6- and 8-molecule loadings are due mainly to differences in the $T_{1\rho(H)}$ values. At a loading of 8 molecules per u.c., the $T_{1\rho(H)}$ values are too long relative to the T_{CP} values for clear decays to be observed for the curves, and eq 2 is simplified to

$$I(t) = I_o \exp(-t/T_{CP}) \tag{5}$$

In the case of ZSM-5 loaded with 6 molecules of *p*-xylene-d_6 per u.c. (Supporting Information), a value for $T_{1\rho(H)}$ was obtained from least-squares fits to the linear decays of plots of ln(I) vs CT for Si 12 and Si 3. The average value of 12.0 ms was used in fitting all of the other curves, and an estimate of I_o = 103.7 is also obtained for these two sites. Using the above value for $T_{1\rho(H)}$ and fitting the curves using a nonlinear least-squares fit to eq 2 to obtain I_o and T_{CP} gives the data in Table SI2 (Supporting Information). The calculated curves from these fits are those shown together with the experimental data points in Figure SI4a. There is some variation in I_o (the theoretical maximum magnetization) for the different silicon sites. Although all are of equal occupancy in the structure, it is possible that I_o could vary, as there is some degree of isolation of the groups of proton spins, and different silicon sites may be in contact with different numbers of protons. Keeping I_o fixed at the value optimized for Si 12 yields a slightly different set of T_{CP} values (data not shown), but the order is unchanged.

To further probe the quality of the fits to eq 2, the resulting T_{CP} values were correlated to the heteronuclear second moments. From the known structure, these can be calculated exactly taking into account the motional characteristics observed in the ^{2}H NMR spectra and are given for the 8-molecule loading in Tables 2 and SI1.

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(30) Wolfram, S. *Mathematica: A System for Doing Mathematics by Computer*, v. 3.0; Wolfram Media: Champaign, IL, 1996.

The total second moment for the interactions of the methyl hydrogens with the silicon atoms was averaged for a rotation around the methyl C_3 axis,[31] and a static model was used in the case of interactions involving the aromatic hydrogens.[31,32] Second moments for the 6-molecule complexes were scaled by a factor $6/8 = 0.75$ to account for the incomplete occupancy of the sorbate sites.

Since T_{CP} is directly related to the $^1H/^{29}Si$ heteronuclear second moment via eq 4, a plot of $1/T_{CP}$ vs $(\Delta\omega^2)_{IS}$ should be a straight line that goes through the origin. The experimental results are shown in Figure 4b for the 8-molecule loading of *p*-xylene-d_6. A moderately good linear correlation is obtained, but the straight line deviates from the origin. This could be caused, in part, by the fact that I_o and T_{CP} are strongly correlated, but there is also a large variation within the I_o values themselves. Although, as discussed earlier, some moderate variation might be expected, the differences observed more probably reflect the poor quality of the fits to eq 2.

Similar results are obtained for the complex with 8 molecules of *p*-xylene-d_4 (**2**). There is some small variation in T_{CP} depending on whether I_o is fixed at the value found for Si 10 or used as a variable (Table SI1 in the Supporting Information). The plot of $1/T_{CP}$ vs the calculated second moments (averaged for 3-fold reorientation of the methyl groups) gives a reasonable linear correlation, but the scatter in the data is even larger than for *p*-xylene-d_6, as the dipolar interactions are considerably weaker (Figure SI2b). Again, the straight line does not intersect the origin, and there is considerable variation in I_o.

The corresponding linear correlations for the loadings of 6 molecules are considerably better (Figures SI4b, SI5b, Table SI2), although the scatter for the *p*-xylene-d_4 case is still larger and the line does not pass exactly through the origin. These improved fits are thought to be due to the curves themselves being better approximations to the CP behavior implicit in eq 2.

We suspected that the problems with the fitting of the CP data in the case of the 8-molecule loadings might be due to very slow diffusional processes of the *p*-xylene molecules occurring within the channels. Some motions might well be too slow to be detected on the time scale of the deuterium NMR experiment but could be important in the CP experiments when working with contact times as long as 60 ms. Any diffusion process could produce errors particularly in the fitting of the CP curves for the 8-molecule loadings

To investigate this, 2D-exchange CP NOESY experiments[25] were conducted on complexes of ZSM-5 with 8 molecules of *p*-xylene containing a single ^{13}C-labeled methyl group. In this experiment, the initial carbon magnetization is obtained using a CP sequence. During an evolution period (t_1) the carbon spins are proton-decoupled and are subject to chemical shift and Zeeman interactions. At the end of the evolution period, a 90° pulse is applied to the spins, which maps the ^{13}C shift information into the *z*-magnetization. If, during the interval following this pulse, which is called the mixing period, the environment changes, these ^{13}C spins show the new chemical shift modulated with the previously encoded one. After a two-dimensional Fourier transformation the presence of off-diagonal peaks indicates exchange between the correlated diagonal peaks.

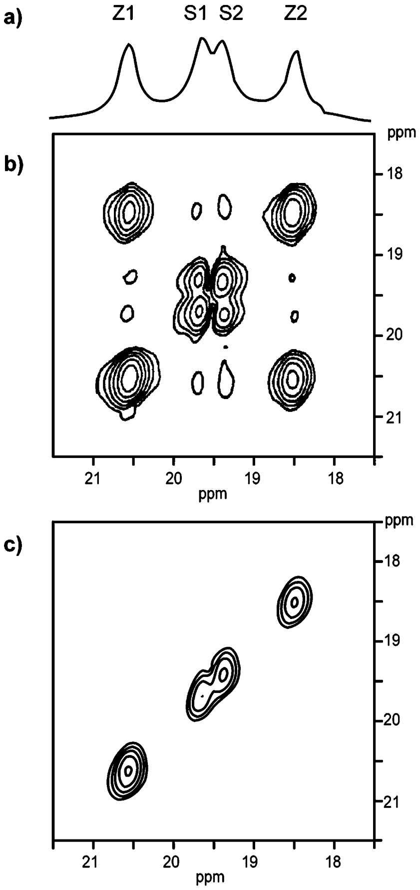

Figure 5. ^{13}C CP NOESY experiments for the complex of ZSM-5 with 8 molecules of *p*-xylene containing a single ^{13}C-labeled methyl group. (a) ^{13}C spectrum with the resonances assigned as indicated. (b) Experiment done at room temperature (293 K) with 32 experiments, 64 scans in each experiment, a sweep width of 800 Hz, and 128 data points collected during the acquisition. The mixing time was 100 ms, and a 2 ms contact time and 8 s recycle delay were used. (c) Same acquisition parameters as in (b) but at a temperature of 273 K.

In our specific system it is possible to use this technique to study the exchange process of the organic guest molecules within the zeolite channels because, for this particular and quite unique case, four different methyl groups can be resolved in the ^{13}C NMR spectrum, corresponding to *p*-xylene molecules in the straight and zigzag channels (Figure 5a). Figure 5b shows the 2D chemical exchange NOESY spectrum for the complex of 8 molecules of ^{13}C (methyl) *p*-xylene on ZSM-5 at room temperature with a mixing time of 100 ms.

The cross-peaks in the spectrum indicate the carbons that are exchanging. Using a $^1H/^{13}C/^{29}Si$ CP TEDOR experiment,[26] the four different methyl resonances can be assigned as indicated in Figure 5a, where Z1, Z2 are the methyl carbons on XYL2 in the zigzag channel and S1, S2 those on XYL1 in the straight channel (Figure 3). Full details of the assignment are given in ref 33. Thus, the 2D CP NOESY spectrum at room temperature shows that there are in fact very slow motional processes occurring in this system involving the methyl groups in both intra- and intermolecular exchange.

These motions are too slow to be detected in the deuterium NMR spectra, but could be important on the time scale of the cross polarization experiments and could affect the $T_{1\rho(H)}$ values. It should also be noted that there could also be other slow

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(31) Michel, J.; Drifford, M.; Rigny, P. *J. Chim. Phys.* **1970**, *67*, 31.
(32) Slichter, C. P. *Principles of Magnetic Resonance*; Springer-Verlag: New York, 1990; p 65.
(33) Fyfe, C. A.; Diaz, A. C. *J. Phys. Chem. B* **2002**, *106*, 226.

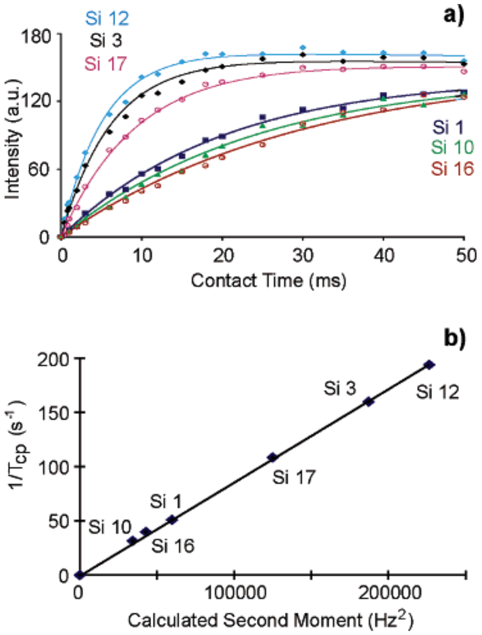


Figure 6. (a) Intensities of the ^{29}Si CP MAS NMR signals as indicated as functions of the contact time at 273 K for ZSM-5 loaded with 8 molecules of *p*-xylene-d_6 per u.c. (b) Plot of experimental $1/T_{CP}$ values vs the calculated second moments.

motions not detected by the NOESY experiment, as they do not involve chemical exchange. Figure 5c shows the 2D CP NOESY experiment of the same sample at a temperature of 273 K, which indicates that at this temperature the chemical exchange between the organic molecules is slowed to be negligible even at a mixing time of 100 ms.

Thus, the variable contact time CP experiments were repeated for the high-loaded complexes of *p*-xylene-d_4 and -d_6 in ZSM-5 at a temperature of 273 K. Figure 6a shows the CP curves for 8 molecules per u.c. of *p*-xylene-d_6 obtained at 273 K. The curves still do not show clear maxima, but are now very well defined, and the two groups are very clearly separated. The data can now be fitted very well to eq 2 (as can data obtained at lower temperatures), yielding the parameters presented in Table 2. Figure 6b shows that there is now an excellent linear correlation (which now intersects the origin) of $1/T_{CP}$ with the calculated second moments for the *p*-xylene-d_6 complex. We feel that this confirms the importance of taking into account the motional characteristics of the system for all different time scales when interpreting the cross polarization data in these structure determinations, although it should be noted that the relative order of the T_{CP} values is unchanged.

Similar results are obtained for *p*-xylene-d_4, again with a larger scatter in the data (see Supporting Information). The graph of the $1/T_{CP}$ values vs the calculated second moments (averaged for 3-fold reorientation of the methyl groups) is a straight line that goes close to the origin (Figure SI3, Table SI1), although the correlation for *p*-xylene-d_4 is not as good as for *p*-xylene-d_6, due to the motional averaging caused by the methyl rotation, which makes the second moments much smaller, and the T_{CP} values are also spread over a smaller range.

The corresponding data for loadings of 6 molecules are shown in the Supporting Information (Figures SI6, SI7 and Table SI3). The CP curves are quite similar to those obtained at 293 K, and the corresponding linear plots are of good quality.

Now that the exact linear relationship between $1/T_{CP}$ and $(\Delta\omega^2)_{IS}$ has been established for the six clearly resolved resonances, it is possible to calculate the intensities of all of the 24 silicon resonances in the spectrum, even if they are not clearly resolved. Thus, for any given contact time value, the intensity distribution of the complete spectrum can be simulated using eq 2. As an example, the calculated CP spectra are compared in Figure 7 to the experimental ones for a contact time of 5 ms, for the *p*-xylene complexes at 273 K. As can be seen, excellent agreements are obtained, giving further support to the general validity of this approach. Thus, the interpretation of the CP MAS experiments is in good agreement with the known structure of the high-loaded form ZSM-5 with *p*-xylene. To apply this method to systems of unknown structure, preliminary evaluations of the data may be made from relative distances based on the relative T_{CP} values. A trial structure may then be proposed and, following the reverse approach, the sorbate position adjusted to optimize the linear correlations between the $1/T_{CP}$ values and the calculated second moments. Then, a comparison of observed and calculated CP spectra, like those in Figure 7, should serve as an additional test.

In cases where spin-diffusion experiments cannot be done to demonstrate the absence of exchange processes involving the guest molecules (i.e., when different spin environments are not resolved for the guest molecules in the NMR spectrum), then experiments should be carried out at different temperatures until self-consistent contact time curves and T_{CP} values are obtained over a range of temperatures. Useful structural information can also be obtained from a single ^{29}Si CP MAS NMR spectrum if polarization transfer is restricted to a very short (few milliseconds) contact time. In this case, the $T_{1\rho(H)}$ relaxation processes could be considered unimportant, and a plot of the relative signal intensities ($I_{Si(x)}/I_{Si(m)}$, where x represents the different T-sites resolved in the spectrum and m the site with the maximum signal intensity) as a function of the relative second moments ($(\Delta\omega^2)_{Si(x)}/(\Delta\omega^2)_{Si(m)}$ calculated from the structure) should again yield a linear correlation.

This approach has been tested on the 273 K data from ZSM-5 loaded with 8 molecules of *p*-xylene-d_6 and *p*-xylene-d_4 at a contact time of 1 ms. The resulting correlations were of comparable quality to those presented in Figures 6 and SI3. This approach assumes that all of the I_o values are equal, and the data in Table 2 indicate that they are approximately constant in the present case, although this may not always be so. In cases where $T_{1\rho(H)}$ is too long to observe a clear signal decay, or when the CP experiment is too inefficient to do a complete variable contact time CP study in a reasonable experimental time, this method may be useful. Because the restricted volume within the channels and cavities of zeolite molecular sieves makes the sorbate−framework (^{1}H−^{29}Si) distances interdependent, the general approach is quite forgiving: a number of different approximations can be introduced and at least the approximate position of the guest molecule within the host matrix may still be efficiently determined. In addition, we have verified that other dipolar-based experiments such as REDOR[27] can also be used, which, since they depend on different relaxation times, may be the methods of choice for particular systems and in all cases where they are applicable could provide useful structural information.

Part II: Application of the Method to Determine the Structure of the Low-Loaded Form of the *p*-Xylene/ZSM-5 Complex. As in the previous study of the high-loaded *p*-xylene/ZSM-5 system, complexes of the two specifically deuterated

Table 2. Experimental and Calculated Parameters Related to the ^{1}H/^{29}Si Cross Polarization Experiments on ZSM-5 Loaded with 8 Molecules per u.c. of *p*-Xylene-d_6 at 293 and 273 K

		293 K			273 K		
^{29}Si T-site	resonance (ppm)	I_0^a (au)	T_{CP}^a (ms)	second moment (Hz^2)^b	I_0^a (au)	T_{CP}^a (ms)	second moment (Hz^2)^b
Si 1	−112.0	312 ± 15	18 ± 1	58 338	142 ± 2	20 ± 0.6	58 338
Si 3	−118.9	306 ± 4	11 ± 0.4	193 823	156 ± 1	6.2 ± 0.2	193 823
Si 10	−111.6	258 ± 13	22 ± 1	42 548	147 ± 4	26 ± 2	42 548
Si 12	−116.7	295 ± 6	9.5 ± 0.4	231 890	161 ± 2	5.2 ± 0.2	231 890
Si 16	−117.6	374 ± 16	24 ± 2	46 716	166 ± 6	22 ± 2	46 716
Si 17	−117.3	312 ± 5	12 ± 0.5	129 398	150 ± 1	9.3 ± 0.2	129 398

[a] Calculated using a nonlinear fitting program, using eq 5. [b] Calculated from the XRD data taking into account all Si−H interactions up to a distance of 8 Å.

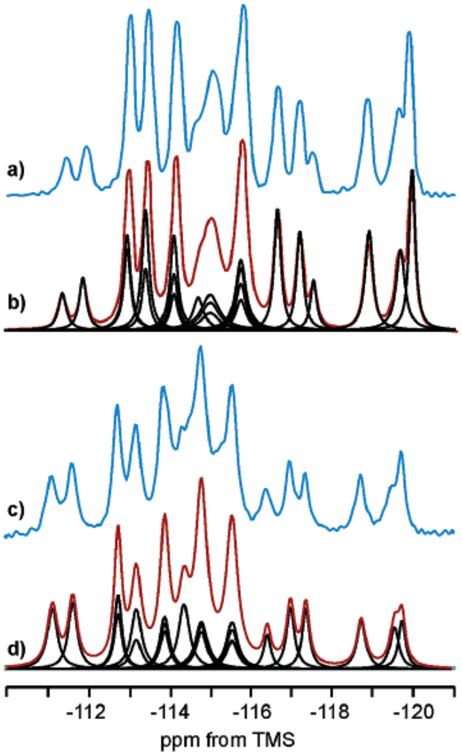


Figure 7. (a) Experimental ^{29}Si CP MAS NMR spectrum of ZSM-5 loaded with 8 molecules of *p*-xylene-d_6 per u.c. at 273 K obtained at room temperature with a contact time of 5 ms. (b) ^{29}Si CP MAS NMR spectrum calculated from the 1/T_{CP} vs second moment correlation in Figure 6b for a contact time of 5 ms. Sum of components (black) shown in red. (c) Experimental ^{29}Si CP MAS NMR spectrum of ZSM-5 loaded with 8 molecules of *p*-xylene-d_4 per u.c. at a temperature of 273 K with a contact time of 5 ms. (d) ^{29}Si CP MAS NMR spectrum calculated from the 1/T_{CP} vs second moment correlation in Figure SI3b for a contact time of 5 ms.

xylenes **1** and **2** were investigated, ensuring that a unique structure was determined from two independent experiments. Again, in the main, only the data from the *p*-xylene-d_6 complex are presented as figures; the remaining data are given in the Supporting Information. As before, the use of the specifically deuterated xylenes also makes it possible to probe their motional characteristics via ^{2}H NMR spectroscopy, at least on the spectroscopic time scale of these experiments. The quadrupolar echo ^{2}H NMR spectra of *p*-xylene-d_4 absorbed on ZSM-5 at a loading of 3 molecule per u.c. obtained at the temperatures indicated are shown in Figure 8, from which the changes in the motional states of the molecules can be deduced. By comparing the experimental spectra with the simulated spectra previously presented by Vega,[13] the following conclusions can be drawn: the spectrum of *p*-xylene-d_4 at room temperature (293 K) shows that all the *p*-xylene molecules in the sample are undergoing discrete 180° flips around the methyl−methyl (C1−C4) molecular axis on the deuterium NMR time scale. Lowering the temperature to 243 K produces a broadening of the spectrum and the appearance of a splitting of 130 kHz between the inner singularities characteristic of static (nonflipping) aromatic rings.

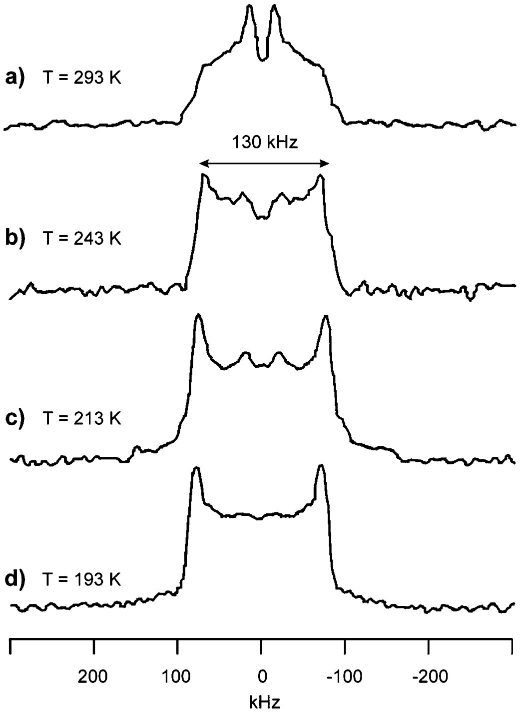


Figure 8. ^{2}H quadrupolar echo NMR spectra of *p*-xylene-d_4 in ZSM-5 at a loading of 3 molecules per u.c. at the temperatures indicated. The 90° pulse length was 3.45 μs, echo delay 30 μs, and between 1000 and 4000 scans were accumulated with a recycle delay of 20 s. The spectra were processed with a line broadening of 1000 Hz.

The spectrum indicates the presence of a distribution of molecules with stationary aromatic rings and molecules whose rings undergo 180° flips around the C1−C4 molecular axis. Reducing the temperature further increases the proportion of *p*-xylene molecules with static aromatic rings, as shown in the spectra at 213 and 193 K. In the case of the *p*-xylene-d_6 intercalate, the ^{2}H spectrum at 193 K (Supporting Information Figure SI9) shows a reduced quadrupolar line shape with a splitting of 40 kHz, indicating rotation of the methyl groups about their C_3 axes as expected, but there is no evidence for diffusional motion. Thus, in this temperature range, the *p*-xylene molecules in the low-loaded complex have freely rotating methyl groups and aromatic rings that are static or undergoing 180° flips around their methyl−methyl axes, the proportions depend-

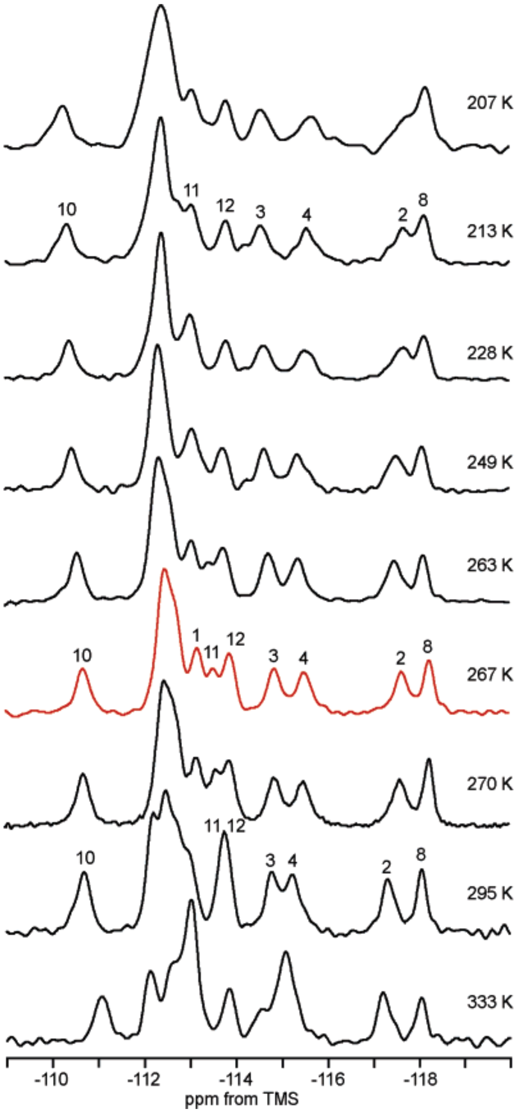


Figure 9. ^{29}Si MAS NMR spectra of the complex of ZSM-5 with 3 molecules of *p*-xylene-d_6 per u.c. at the different temperatures indicated. The numbers above selected resonances indicate the assignments to specific T-sites in the zeolite framework. The ^{29}Si 90° pulse length was 7.0 μs and between 32 and 56 scans were accumulated with a recycle delay of 12 s.

ing strongly on the temperature. These molecular motions have to be considered in the calculation of the second moments, and in general, it must be kept in mind that these conclusions are valid only in the context of the time scale of the deuterium experiments (many tens of kHz). It is anticipated that the *p*-xylene molecules must all be considered to be flipping on the time scale of the CP experiments, and it is possible that much more extensive motions might occur on this time scale at ambient temperature and above.

In the present work, the behavior of the complex was investigated over a considerable range of temperature. The ^{29}Si NMR spectra of the system ZSM-5 with 3 molecules of *p*-xylene are sensitive to changes in the temperature, and the chemical shifts of some signals are significantly affected on lowering the temperature, as seen from the series of ^{29}Si MAS NMR spectra obtained at the different temperatures shown in Figure 9. The resonances in the room-temperature spectrum have been previously assigned[5] using the INADEQUATE experiment as indicated, but because some signals can shift considerably and their shifts could possibly cross over when lowering the temperature, a new INADEQUATE experiment was done to unequivocally assign the signals for this sample at 267 K, the temperature at which the largest number of signals are clearly resolved. The analysis of the INADEQUATE spectrum (not shown) gives the assignment of the signals corresponding to Si 11 and Si 12, which were clearly resolved in the spectrum at low temperature, compared to the previously assigned room-temperature spectrum. The viability of using the cross polarization process in structural investigations of this system is demonstrated qualitatively in Figure 10, which compares the CP MAS and single pulse spectra of the low-loaded *p*-xylene-d_6 complex at 233 K. In the CP spectrum, there are clear differences in the relative intensities of the different resonances, reflecting the differences in the distances of the nuclei from the proton polarization source, namely, the aromatic ring.

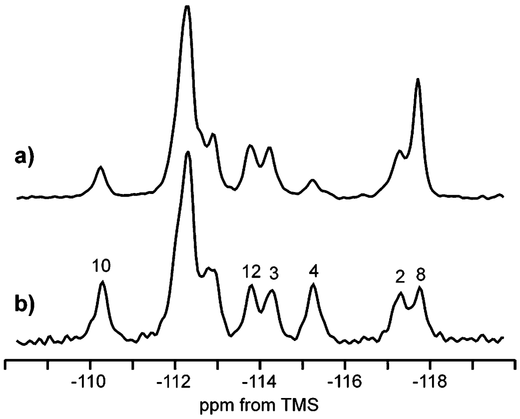


Figure 10. (a) ^{29}Si CP MAS NMR spectrum of ZSM-5 loaded with 3 molecules of *p*-xylene-d$_6$ per u.c. at 233 K, contact time 5 ms, recycle delay 2 s. (b) ^{29}Si MAS NMR spectrum of the same sample obtained using a recycle delay of 350 s to ensure complete relaxation of the silicon nuclei. The ^{29}Si 90° pulse length was 13 μs. The resonances used in the fitting are labeled with their T-site numbers.

As seen earlier, in these structure determinations by NMR, it is important that there be no effects from diffusional motions. In the study of the high-loaded complex of *p*-xylene in ZSM-5, it was important to consider not just motions on the time scale of the ^{2}H NMR spectra but also much slower motions, more on the time scale of the cross polarization experiments. In the case of the low-loaded form it is expected that similar motions could occur and that they could be of much lower energy due to the large amount of free volume available. In the high-loaded form, data collected at 273 K and below were reliable for structure determinations, but it was anticipated that considerably lower temperatures could well be needed to obtain reliable structural data on the low-loaded form.

In the high-loaded form, it was possible to probe at least some of these slow motions directly by ^{13}C 2D-chemical exchange experiments, as the four methyl groups on the two crystallographically inequivalent molecules were all inequivalent with unique chemical shifts, and this aided in the selection of an appropriate temperature for the CP experiments. However, in the present case, there is only one molecule present and variable-temperature ^{13}C CP MAS spectra (not shown) indicate that the two methyl groups are equivalent at a temperature of 233 K. Thus, complete sets of variable contact time ^{1}H/^{29}Si experiments were collected for both *p*-xylene-d_4 (**1**) and *p*-xylene-d_6 (**2**) complexes at a series of temperatures down to 233 K. For each

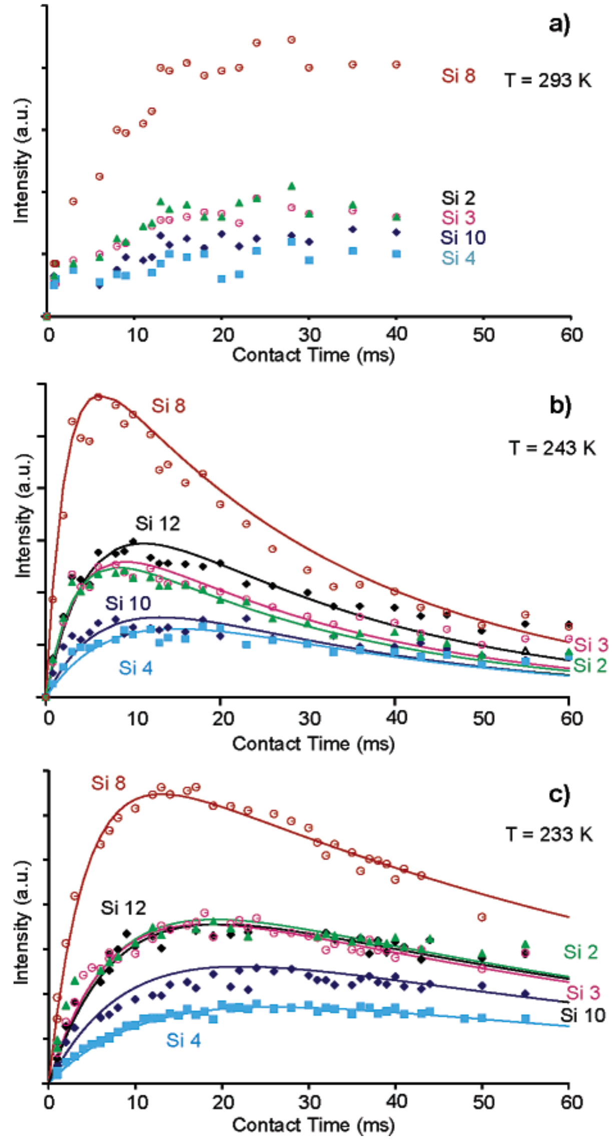


Figure 11. Intensities of the $^1H/^{29}Si$ CP MAS NMR signals as functions of the contact time for ZSM-5 with a loading of 3 molecules of *p*-xylene-d_6 per u.c. at the temperatures indicated. The lines represent the best fits calculated using eq 2 in a nonlinear least-squares fitting program with $T_{1\rho(H)}$ held constant and I_o unrestrained.

Table 3. Selected Relaxation Parameters for the ^1H and ^{29}Si Nuclei in the Specifically Deuterated *p*-Xylene/ZSM-5 Complexes at 233 K

nuclei	ca. 5 × T_1 (s)	T_2 (ms)	$T_{1\rho(H)}$ (ms)
^1H (ring)	0.8	0.04	76.9
^1H (CH_3)	0.8	0.05	59.5
^{29}Si (framework)	30	11.4−18.0	

contact time at each temperature, the spectra were deconvoluted in terms of Lorentzian curves and the areas of the resolved signals for Si 3, Si 2, Si 12, Si 8, Si 4, and Si 10 tabulated. The resulting intensity vs contact time curves are shown in Figure 11 for **2** and in the Supporting Information for **1**, respectively. These data were then tested to see how well they fit the expected cross polarization behavior. Table 3 lists some of the relaxation parameters for the ^1H and ^{29}Si nuclei in the specifically deuterated low-loaded *p*-xylene/ZSM-5 complexes at 233 K.

Table 4. Experimental and Calculated Parameters from the Least Squares Fit to the Data from the $^1H/^{29}Si$ Cross Polarization Experiments at 233 K on ZSM-5 Loaded with 3 Molecules per u.c. of *p*-Xylene-d_6

T-site	resonance (ppm)	I_o (au)[a]	T_{CP} (ms)[a]	second moment (Hz^2)[b]
Si 2	−117.7	47.1 ± 0.9	7.4 ± 0.5	15 810
Si 3	−114.6	45.1 ± 0.5	6.9 ± 0.4	14 338
Si 4	−115.5	24.0 ± 0.2	11.8 ± 0.3	3634
Si 8	−118.1	76.7 ± 0.6	4.2 ± 0.2	33 727
Si 10	−110.4	34.9 ± 0.6	9.2 ± 0.5	8522
Si 12	−113.8	46.0 ± 0.7	7.7 ± 0.4	13 883

[a] Calculated with a nonlinear fitting program using eq 2 with $T_{1\rho(H)}$ held constant at 76.9 ms. [b] Calculated for solution 58.

The CP curves in Figure 11a for the experiment carried out at room temperature cannot be fitted to eq 2. Although some signals show some enhancement compared to others, the order of the curve maxima for the different resolved silicons changes compared to that of the CP plots at lower temperatures. This behavior is a clear indication of the presence of extensive molecular motions in the system at room temperature that compromise the CP data.

In fact, at temperatures above room temperature, all the signals are enhanced to approximately the same degree, indicative of extensive diffusional averaging of the interactions. Thus, the room-temperature spectra *cannot* be used for distance and structure determinations as was claimed by Mentzen,[16] although no proper study was reported.

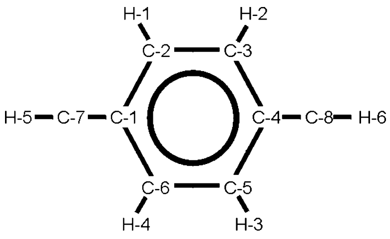
In general terms, the other data shown in Figures 11b,c for the CP data at lower temperatures approximate better the general behavior expected from eq 2, although the profiles still change with temperature, indicating possible motional effects. That is, there is an exponential growth due to polarization transfer and a decay from the loss of proton magnetization due to $T_{1\rho(H)}$. The curves that grow fastest have the highest maxima, and the maxima in the series shift to longer contact time values as they become lower. There are clear consistencies between the data sets obtained at different temperatures. Thus, in Figure 11 all the data obtained at temperatures below 243 K indicate that Si 8 is much more efficiently polarized (and hence closer to the ^1H polarization source) than the other silicons. Si 3, Si 2, and Si 12 have an intermediate enhancement, and Si 4 and Si 10 are only weakly polarized and therefore are much further away from the aromatic protons. For the *p*-xylene-d_4 system at low temperatures, Si 3 and Si 2 polarize much more efficiently than Si 8, Si 12, Si 4, and Si 10 (Supporting Information, Figure SI10).

These two sets of qualitative information preclude the *p*-xylene being in the zigzag channel system. The variable contact time cross polarization curves were then fitted to eq 2, with $T_{1p(H)}$ fixed at the value found from the clearest decay, again using the nonlinear statistics package in Mathematica.[30] The calculated curves from these fits are the solid lines shown together with the experimental data points in Figure 11.

In the case of ZSM-5 loaded with 3 molecules of *p*-xylene-d_6 per u.c., the value for $T_{1\rho(H)}$ was obtained from least-squares fits to the linear decays of plots of ln(I) vs contact time for Si 8 for each different temperature. Thus, for example, for the data carried out at 233 K, the value of 76.9 ms was used in fitting all of the other curves at that temperature. Using this value of $T_{1\rho(H)}$ and fitting the curves using nonlinear least-squares fits to eq 2 to obtain I_o and T_{CP} values yields the data in Table 4. There is some variation in I_o, which was unconstrained, for the different silicon sites in all the different data sets. Although all the silicon sites are of equal occupancy in the structure, it is possible that I_o could vary, as there is some degree of isolation of the groups of proton spins and different silicon sites may be in primary contact with different numbers of protons. The variation in I_o is thought to probably reflect, in a general sense, the quality of the fits to eq 2.

A similar approach was used for the analysis of the contact time curves for the *p*-xylene-d_4 complex (Supporting Information, Table SI4). In this case, the values for $T_{1\rho(H)}$ were obtained from least-squares fits to the linear decays of plots of ln(I) vs contact time for Si 3 at each temperature, and nonlinear least-squares fits of the curves to eq 2 yielded the I_o and T_{CP} values. For both complexes, the data obtained from the lowest temperature investigated (233 K) were used for the structure determination.

The approach taken to locate the *p*-xylene molecules in the complex was as follows: the *p*-xylene molecule was located at a specific position inside the zeolite, and all the Si−H distances between the guest molecule and the zeolite framework were calculated (the atomic positions for the silicon framework were taken from the published ZSM-5 orthorhombic structure, space group *Pnma*).[10c] The initial atomic coordinates for the *p*-xylene molecule were calculated from an origin in the center of the aromatic ring assuming the following interatomic distances: $C_{ring}-C_{ring} = 1.40$ Å, $C_{methyl}-C_{ring} = 1.47$ Å, and C−H = 0.9 Å. The labeling of the atoms is shown in **5**.



(5)

To account for the fast rotation of the methyl groups about their C_3 axes, the three hydrogens of the CH_3 were located at the center of the triangle formed by the three hydrogen atoms as indicated in **5**, where they are labeled as H-5 and H-6 (C7- -H5, C8- -H6 distances = 0.31 Å).

A computer program was written in the TURBO PASCAL language[34] to systematically apply rotation matrixes about the crystallographic *a*, *b*, and *c* axes to the starting coordinates of the *p*-xylene molecule. The new rotated coordinates (ring center {0,0,0}) were translated to the Cartesian coordinate reference system used for the reported *Pnma* structure[10c] so the *p*-xylene molecule was initially located with the long molecular axis parallel to the *b* axis and had its center on the mirror plane ({*x*, 0.25, *z*}). In this reference system, the *x* axis runs parallel to *a* (and thus approximately along the sinusoidal channels), and the *y* axis runs parallel to the straight channels (*b* axis). The program was written to systematically rotate the molecule (using 3° steps) up to 180° about *y* and up to 60° about *x* and *z* (crystallographic *c* axis). The *p*-xylene was also methodically translated (using 0.1 Å steps) from the initial position in the mirror plane along *x*, *y*, and *z*. The translations along *x* and *z* were constrained to be from 0 to 0.6 Å because the molecule clearly touches the zeolite framework for larger shifts. Translation along the *y* axis moved the molecule from the mirror plane up to 5 Å along the straight channel.

Therefore, with this program all possible viable positions and orientations of the *p*-xylene molecule in the straight channel were sampled. The calculated atomic positions for the molecule after each change were then used in a subroutine to calculate the heteronuclear second moments between the guest molecules and the silicon atoms in the zeolite framework. For the aromatic protons, motional averaging due to ring "flips" was used,[31] with the averaged Si−H second moments for the aromatic protons calculated for every solution in an independent program. The expectation that a plot of $1/T_{CP}$ vs second moments should be a straight line for an acceptable sorbate location was included as a filter in the program. A least-squares linear regression subroutine quantified (as R^2) the linearity of the plots of the calculated second moments from the atomic coordinates for every possible position and orientation of the *p*-xylene molecules vs the experimental T_{CP} values. The program output only the *p*-xylene positions and orientations with the best linear regressions: in this case a value of $R^2 > 0.95$ was chosen as the cutoff point for acceptable fits for both deuterated xylene data sets. These solutions were further reduced by considering the Si−H distances involving all 12 silicon atoms. Any solutions with Si−H distances shorter than 2.8 Å were rejected as reflecting repulsive interactions. Note that 2.8 Å is sufficient to also exclude collisions between the *p*-xylene hydrogens and the framework oxygen atoms. Despite these constraints, 106 possible solutions were found with R^2 correlation values between 0.98 and 0.995 (the highest correlation value found).

Because of the experimental error in the measurements of the T_{CP} values, it would not be valid to select the location of the *p*-xylene molecule with the best R^2 correlation value as the only criterion for best solution; in fact, the data for the *p*-xylene-d_4 case provide no information on the ring orientation. One approach would be to screen these solutions to eliminate any that were not common to both complexes, but this was not done in the present study in order to see if the data from the two complexes independently led to the same solution and a different selection procedure was used. To define the expected linear relationship between $1/T_{CP}$ and $(\Delta\omega^2)_{IS}$, only the intensities of the six best-resolved resonances were used. However, as in the case of the known high-loaded structure, if a linear relationship is established for a particular structure, it can be used to predict the intensities of all 12 resonances in the spectrum, and these can be summed to give the total spectrum for comparison with the experimental data for any given contact time. The theoretical individual Lorentzian lines for the 12 silicon sites were calculated for a contact time of 10 ms to obtain the simulated NMR spectra for each of the 106 solutions. The total areas of the theoretical spectra (obtained by adding the 12 individual Lorentzian peak lines, assuming an average value for I_o) as well as the individual Lorentzian areas for the best resolved peaks (Si 10, Si 4, and Si 3) were compared with the experimental values for both complexes. For both complexes the same three structures were found to give the best matches, further confirmation of the validity of the approach.

In general, the predicted spectra calculated as described above from these three structures agree well with the two observed ones. This is again an indication of the variation in the position

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[34] *Turbo PASCAL* version 5.0; Borland International: 4585 Scotts Valley Dr., Scotts Valley, CA 95066.

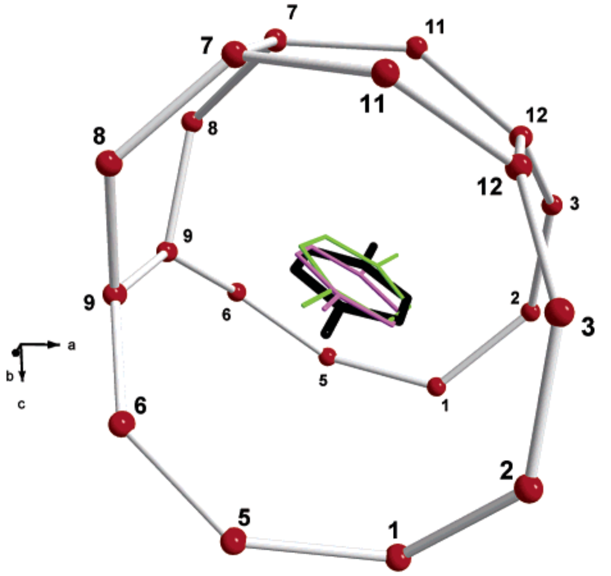

Figure 12. Predicted structures of the low-loaded form of *p*-xylene in ZSM-5, solutions 14 (green), 58 (black), and 96 (magenta). Solution 58 preserves the *Pnma* symmetry of the framework.

and orientation of the organic molecule that acceptably fit the data. These three structures (solutions 14, 58, and 96) are quite similar and are shown in Figure 12. For solution 58, shown in bold in the figure, the mirror plane of the *p*-xylene molecule coincides exactly with the crystallographic mirror plane, with the long molecular axis parallel to the *y* axis [1,0,0] and the plane of the aromatic ring oriented at an angle of 33° about the *y* axis. In solutions 14 and 96, the molecules have the aromatic rings oriented almost identically to solution 58 (with an angle of 36° along *y*), but they are shifted respectively by 0.1 and 0.3 Å from the mirror plane. Also in solutions 14 and 96, the long molecular axes of the *p*-xylene molecules are shifted respectively 9° and 12° from the [0,1,0] direction and 15° and 6° from the [0,0,1] direction. Because of the mirror plane, solutions 14 and 96 will also have mirror images, but for clarity, these are not shown in the figure. The average atomic positions for solution 96 and its mirror image are very similar to those of solution 58, as are those for solution 14's average coordinates. The maximum differences in atomic positions between solution 58 and the average solution 96 and 14 are less than 0.5 and 0.3 Å, respectively.

These structures all give acceptable fits to the observed data, and when taken together, provide an indication of the precision with which the organic molecule has been located in the framework at this temperature. The ^{13}C CP MAS NMR spectra of the low-loaded complex of [$^{13}CH_3$] *p*-xylene in ZSM-5 acquired at 293, 253, and 233 K (not shown) show only a single resonance at 19 ppm, which indicates that the chemical environments for the methyl carbons are identical on the "NMR time scale". Of the three best solutions, only solution 58 has the necessary local symmetry (long molecular axes of the *p*-xylenes perpendicular to the mirror plane in the channel intersection) to exhibit a single ^{13}C resonance and is favored on this basis.

Thus, the data from both complexes yield the same general solution for the location of *p*-xylene within the ZSM-5 framework. However, effects from slow motions cannot be ruled out. In the case of the high-loaded form, these caused the linear relationship between $1/T_{CP}$ and second moments to have a nonzero intercept, and such an effect was observed in the present work at 233 K for both complexes, as illustrated for the *p*-xylene-d_6 case in Figure 13 (Figure SI11 for the *p*-xylene-d_4 case) for solution 58. Similar effects are seen for the other cases. As previously noted, this could be due in part to the high degree of correlation between I_o and T_{CP}, but it could also be due to interfering motions including their effect on relaxation times.

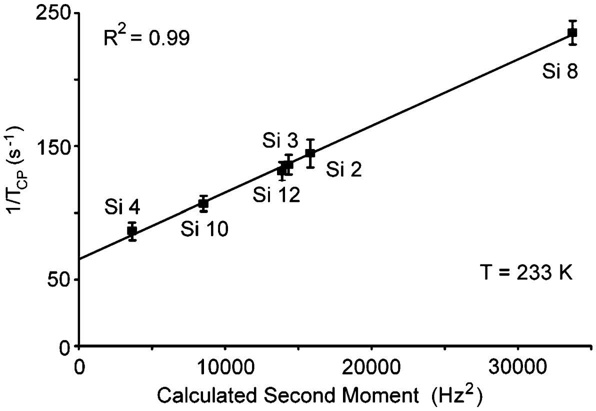

Figure 13. Plot of the experimental $1/T_{CP}$ values vs the calculated second moments (for solution 58) for ZSM-5 loaded with 3 molecules of *p*-xylene-d_6 per unit cell at 233 K.

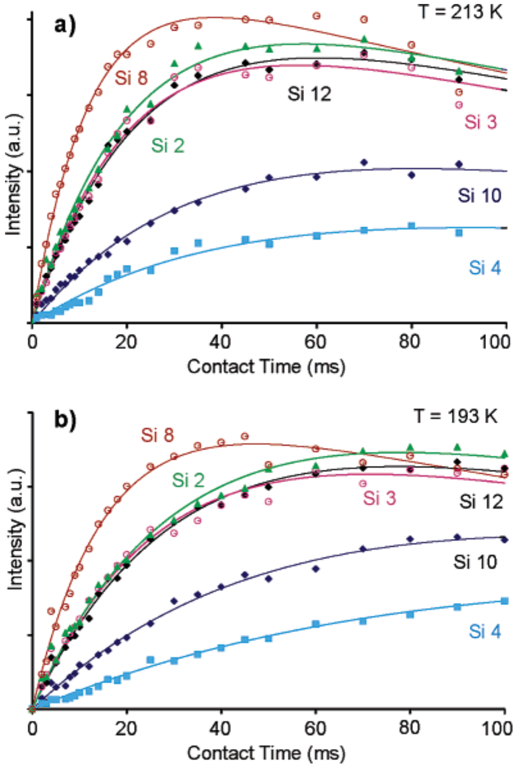

Figure 14. Intensities of the $^1H/^{29}Si$ CP MAS NMR signals as functions of the contact time for ZSM-5 with a loading of 3 molecules of *p*-xylene-d_6 per u.c. at (a) 213 K and (b) 193 K. The lines represent the best fits calculated using eq 2 in a nonlinear least-squares fitting program with $T_{1\rho(H)}$ held constant and I_o unrestrained.

To resolve this point, additional experiments were carried out on *p*-xylene-d_6 and *p*-xylene-d_4 complexes at lower temperatures with the assistance of Bruker Spectrospin, Karlsruhe. The resulting contact time curves are shown in Figure 14 for the *p*-xylene-d_6 complex. In all cases, the fits of the curves to eq 2 are improved over those at higher temperatures, and in the

Table 5. Experimental and Calculated Parameters from the Least-Squares Fits to the Data from the $^1H/^{29}Si$ CP Experiments on ZSM-5 Loaded with 3 Molecules of *p*-Xylene-d_6 per u.c. at the Temperatures Indicated

T-site	I_o (au)	T_{CP} (ms)
	213 K[a]	
Si 2	928 ± 15	21.4 ± 0.8
Si 3	854 ± 16	20.9 ± 0.9
Si 4	367 ± 20	45 ± 4
Si 8	942 ± 39	12.2 ± 0.9
Si 10	567 ± 13	36 ± 2
Si 12	894 ± 13	23.2 ± 0.8
	193 K[b]	
Si 2	916 ± 17	32±1
Si 3	819 ± 17	28 ± 1
Si 4	609 ± 43	114 ± 11
Si 8	847 ± 39	15 ± 1
Si 10	707 ± 23	58 ± 3
Si 12	865 ± 18	31.8 ± 0.9

[a] Calculated with a nonlinear fitting program using eq 2 with $T_{1\rho(H)}$ held constant at 245 ms. [b] Calculated with a nonlinear fitting program using eq 2 with $T_{1\rho(H)}$ held constant at 278 ms.

case of the *p*-xylene-d_6 complex, the data sets at 213 and 193 K are identical (an almost complete overlap of the resonances of Si 2 and Si 8 precluded the use of a data set obtained at 173 K, but the other curves at this temperature are the same as those at 213 and 193 K). The parameters from these fits are given in Table 5.

The same structure-fitting protocol described above for the data at 233 K was carried out with the automated program for the *p*-xylene-d_6 CP data at 193 K. The best solution found was almost identical to solution 58, but the plane of the aromatic ring is inclined 27° about *y* instead of 33°. This may be due to a thermal effect, as the framework structure could be somewhat different from the X-ray structure determined at higher temperature, while the NMR data reflect the actual situation at these low temperatures.

Figure 15 shows the plots of $1/T_{CP}$ vs the calculated second moments for the best solution, for the complexes of ZSM-5 loaded with 3 molecules of *p*-xylene-d_6. Data for the *p*-xylene-d_4 complex at 213 K are presented in the Supporting Information (Figure SI12a). For *p*-xylene-d_6, the intercept is zero within experimental error, suggesting that any motions now have a minimal effect on these experiments. A nonzero intercept is still found for the *p*-xylene-d_4 data at 213 K when the location and orientation found from the 193 K *p*-xylene-d_6 data are used to calculate the second moments, although the intercept is smaller than at 233 K. This could be due to the overestimation of T_{CP} from the contact time fits for silicons 4 and 10, which are quite poor due to the very low signal intensities. In addition, slow motions (especially "rocking") of the *p*-xylene molecules could have a larger effect on the locations of the methyl hydrogen nuclei than on the ring protons.

Theoretical spectra were also calculated using various protocols to assign I_o values to those silicons that are not resolved and included in the contact time curve fittings in order to assess the most appropriate method for use in future work. To this end, various possible strategies were tested for their ability to reproduce the CP curves. It was found that using the maximum I_o value or the average I_o value did not fit the curves very well but that using the empirical dependence between I_o and the second moments found in the original fits (Table 5) worked almost as well as the original curve fitting where both T_{CP} and I_o were allowed to vary. The calculated spectra for both deuterated *p*-xylenes for a contact time of 10 ms at the temperatures indicated are shown in Figure 16. There is excellent agreement for the *p*-xylene-d_6 system, and the small deviation in the *p*-xylene-d_4 case is thought to be due to the larger errors in these measurements and the more severe spectral overlap at 213 K.

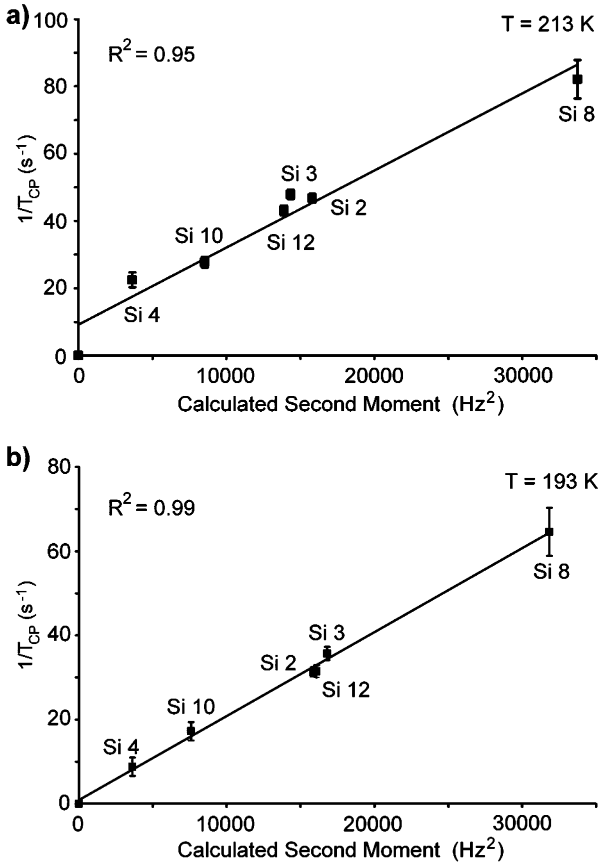

Figure 15. Plots of experimental $1/T_{CP}$ vs the calculated second moments for ZSM-5 loaded with 3 molecules per u.c. of *p*-xylene-d_6 at (a) 213 K and (b) 193 K.

The final fractional coordinates of the predicted structure of the low-loaded complex of *p*-xylene in ZSM-5 from this work are given in Table 6, and representations of the predicted structure are shown in Figure 17. Within the uncertainties involving the use of the room-temperature framework coordinates of a related (low-loaded) system,[10c] the approximations in the treatment, and the fact that the data suggest a limited distribution of acceptable orientations, we consider Figure 17 to be a reliable representation of the structure. For the best solution, the *p*-xylene molecule is located on the mirror plane in the channel intersection (fractional coordinates of the ring center are {−0.009, 0.250, 0.541}) with the long molecular axis parallel to [0,1,0] and the plane of the aromatic ring oriented at an angle of 30 ± 3° about the crystallographic *b* axis.

It is worthwhile to consider the implications of some more general aspects of the present work to NMR structure determinations of zeolite/sorbate complexes: First, the original intent was to check the correctness of the predicted structure by single-crystal X-ray diffraction. After completion of the work presented here,[35] we succeeded in obtaining and refining such single-

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(35) Diaz, A. C. Ph.D. Thesis, University of British Columbia, Canada, 1998.

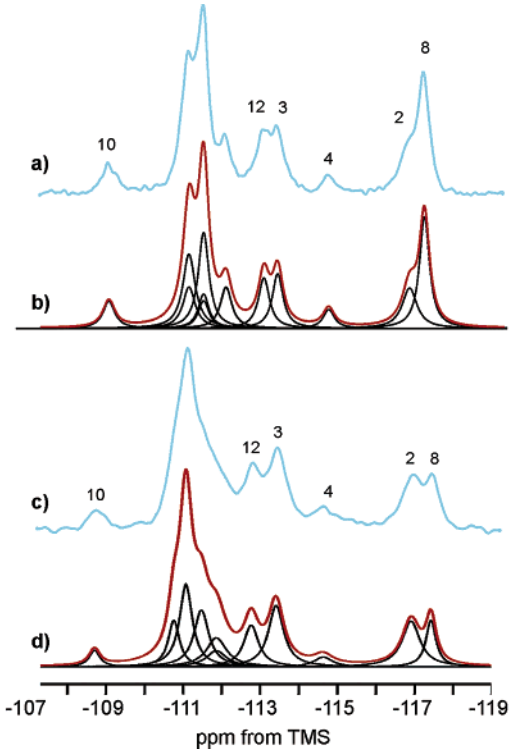

Figure 16. (a) Experimental ^{29}Si CP MAS NMR spectrum of ZSM-5 loaded with 3 molecules of *p*-xylene-d_6 per u.c. at 193 K with a contact time of 10 ms. (b) ^{29}Si CP MAS NMR spectrum calculated from the 1/T_{CP} vs second moment correlation in Figure 15b for a contact time of 10 ms. Sum of components (black) shown in red. (c) Experimental ^{29}Si CP MAS NMR spectrum of ZSM-5 loaded with 3 molecules of *p*-xylene-d_4 per u.c. at a temperature of 213 K with a contact time of 10 ms. (d) ^{29}Si CP MAS NMR spectrum calculated from the 1/T_{CP} vs second moment correlation. Sum of components (black) shown in red.

Table 6. Fractional Atomic Coordinates for the Complex of ZSM-5 Loaded with 3 Molecules per u.c. of *p*-Xylene-d_6 [a]

atom	*x*	*y*	*z*
H-1	−0.0998	0.3098	0.6104
H-2	−0.0998	0.1901	0.6104
H-3	0.0817	0.1901	0.4720
H-4	0.0817	0.3098	0.4720
H-5	−0.0090	0.4111	0.5412
H-6	−0.0090	0.0888	0.5412
C-1	−0.0090	0.3203	0.5412
C-2	−0.0624	0.2851	0.5819
C-3	−0.0624	0.2148	0.5819
C-4	−0.0090	0.1796	0.5412
C-5	0.0443	0.2148	0.5005
C-6	0.0443	0.2851	0.5005
C-7	−0.0090	0.3947	0.5412
C-8	−0.0090	0.1052	0.5412
Si 1	0.3044	0.0285	−0.2022
Si 2	0.2811	0.0629	0.0202
Si 3	0.1232	0.0640	0.0191
Si 4	0.3041	−0.1292	−0.1934
Si 5	0.1192	−0.1734	0.0217
Si 6	0.1828	−0.1725	−0.3290
Si 7	0.4230	0.0565	−0.3460
Si 8	0.0712	0.0276	−0.1923
Si 9	0.1814	0.0573	−0.3423
Si 10	0.4217	−0.1722	−0.3336
Si 11	0.2741	−0.1724	0.0250
Si 12	0.0684	−0.1301	−0.1904

[a] The *p*-xylene coordinates were calculated from the NMR data at 193 K for the best solution. The zeolite framework coordinates are those for the room-temperature orthorhombic structure reported in ref 10c. The coordinates of H-5 and H-6 are the centriods of the triangles formed by the hydrogen atoms in the (rotating) methyl groups.

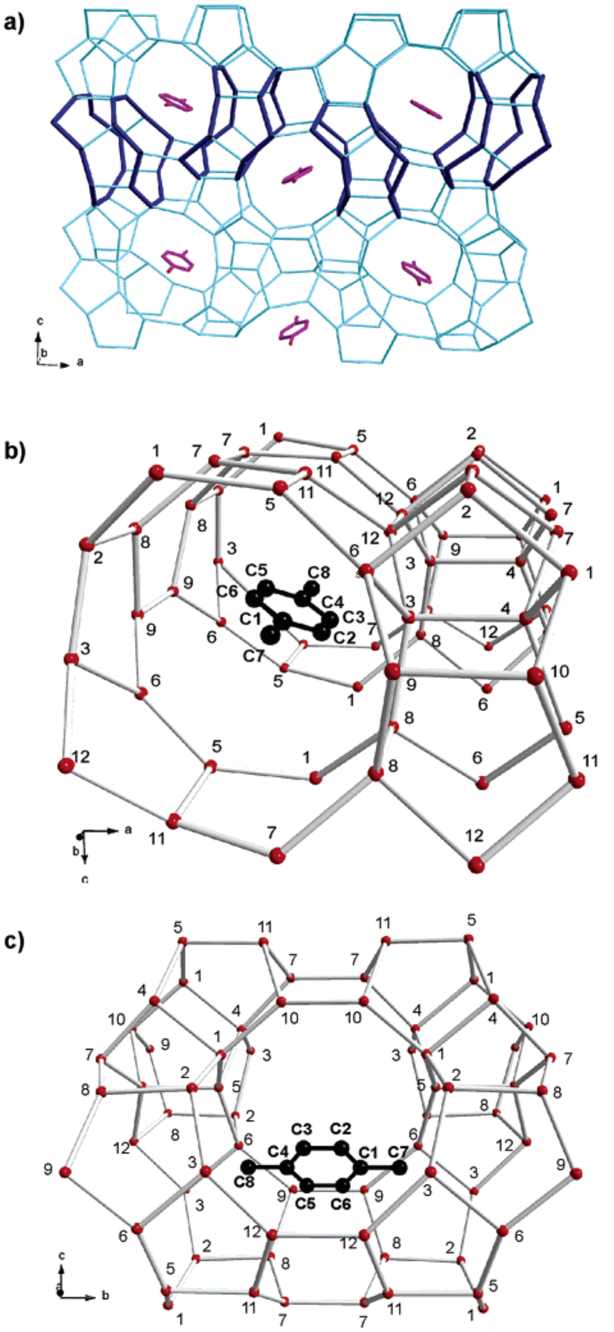

Figure 17. (a) Predicted structure (solution 58) of the low-loaded *p*-xylene/ZSM-5 complex showing the orientations of the *p*-xylene molecules (zigzag channel highlighted). (b) Channel intersection viewed along the straight channel, and (c) the zigzag channel. The silicon T-sites are labeled and oxygen atoms have been omitted for clarity.

crystal diffraction data.[36] The structure is identical in all important aspects to that obtained in the present study. The method has thus been validated in a further critical test. A second important point is that the same structure was obtained from measurements carried out over a temperature range of about 40 °C.

Although it is very important that slow motions not compromise the distance measurements, it is difficult to monitor their occurrence unless there is some symmetry-induced inequivalence involving the nuclei in the sorbate, which in general

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(36) Lewis, A. R. Ph.D. Thesis, University of British Columbia, Canada, 1998.

will not be the case. In general, the self-consistency of structures obtained at different temperatures may be the best guide.

A further implication of the present data is that some degree of slow motion can be tolerated in these distance-dependent measurements, perhaps because of the constraints imposed by the channels. Productive future research efforts will be in the development of protocols to systematize, for general application, the convergence of acceptable solutions as a function of temperature to a single limiting structure.

Conclusions

In general terms, there is good agreement between the cross polarization dynamics and the known structure of the high-loaded complex. Our data agree with the locations of the *p*-xylene molecules in the sinusoidal channels and the channel intersections. Similar results have been obtained using the REDOR pulse sequence on the same systems.[35] We feel that there is a high potential for using these techniques to investigate unknown sorbate/framework structures, provided proper precautions are taken, most importantly the avoidance of any motions of the organic sorbates that could affect the results. In the present case, the presence of chemical exchange in the high-loaded form makes the problem obvious, but in general, not all motions will involve exchange and variable-temperature studies will have to be carried out to establish experimentally the temperature where the effects of such motions have been acceptably suppressed. This temperature could well be quite low.

In the second part of the present study we have shown that the general protocol that we developed and tested on the (known) structure of the high-loaded form of *p*-xylene in ZSM-5 can be used successfully to determine an unknown structure, that of the low-loaded form. In the case of the low-loaded form of *p*-xylene in ZSM-5, completely reliable data were obtained only at 213 K and below. The same structure was determined independently from the two different specifically deuterated xylenes and from data collected over a temperature range of about 40 °C. The data also showed that although motions that interfere with the measurements must be avoided, some degree of very slow motion can be tolerated in these experiments. As long as appropriate care is taken, this general approach can be extended to other substrates and other molecular sieve frameworks. A critical test of our approach as described in the present paper will be its application to systems with unknown structures and then a check of the predicted structures by X-ray diffraction techniques. Such a study has already been carried out on the low-loaded structure of *p*-xylene in ZSM-5, and the predicted structure was identical to that found in a subsequent diffraction study.[36] Further experiments of this type are currently in progress, as are extensions and optimization of the general approach described in the present work.

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Supporting Information Available: Tables and figures for complexes of 3, 6, and 8 molecules per u.c. of *p*-xylene in ZSM-5 not presented in the text. This material (in PDF format) is available free of charge via the Internet at http://pubs.acs.org.

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