An FT-Raman Spectroscopic Study of the Conformational Behavior of *trans*-1,4-Dichlorocyclohexane Adsorbed in Zeolites

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We have examined the conformational properties of *trans*-1,4-dichlorocyclohexane (DCC) adsorbed in several zeolites, including completely siliceous ZSM-5, Na−Y and siliceous Y, by using FT-Raman spectroscopy. The results indicate that the conformational behavior of DCC is dependent on the zeolite framework structure, Si/Al ratio, and the charge-balancing cations. The conformational behavior of DCC in ZSM-5 differs from that in nonpolar solvents such as carbon tetrachloride in that the population of diequatorial (ee) conformer is significantly increased relative to the diaxial (aa) form upon adsorption. The ee and aa conformers are still in dynamic equilibrium as in solution, and lowering the temperature shifts the equilibrium further toward the ee configuration. The situation for DCC incorporated inside Na−Y is markedly different. Upon adsorption, the conformation of DCC is frozen by interactions with the extraframework sodium ions in the supercages of Na−Y. These interactions also lock the guest molecules into various orientations varying from cage to cage, resulting in static disorder. The dynamic conformation equilibrium can be reestablished inside the supercages of zeolite Y by removing the Na$^+$ ions by using type Y zeolites with a much higher Si content.

Introduction

Zeolites are framework materials containing pores, channels, and cavities with molecular dimensions.[1] They are extensively utilized in industry as ion-exchangers, sorbents, and catalysts. Since the applications of zeolites involve incorporating guest molecules inside zeolitic hosts, understanding host−guest interactions is of fundamental importance. One of the important aspects of host−guest interactions is the conformational behavior of guest molecules inside zeolite frameworks. Different conformers can have different electric dipole and quadrupole moments, and these molecular parameters can significantly affect the interactions between a given zeolite framework and different conformers. Consequently, the existence of different conformers can substantially influence the adsorptive and diffusive properties of guest species as well as their subsequent chemistry inside zeolites.[2]

In recent years, adsorption of chlorinated halocarbons in zeolites has attracted attention due to the environmental need for developing new separation and catalytic conversion processes involving chlorinated halocarbons.[3] In the present work, we have examined the adsorption of *trans*-1,4-dichlorocyclohexane (DCC) inside several zeolites, including completely siliceous ZSM-5, zeolite Y (Na−Y), and siliceous Y (Si−Y) by FT-Raman spectroscopy. *trans*-1,4-Dichlorocyclohexane provides a well-known example of conformational analysis for molecules with single-pair conformers.[4] Its conformational behavior in the vapor phase, solution, and solid is well understood.

Recently, Raman spectroscopy has been employed for the conformational study of organic molecules adsorbed inside zeolites.[2,5] The Raman method is a preferred technique for directly monitoring the behavior of guest species inside zeolitic hosts because zeolites are very weak Raman scatterers and thus give rise to very weak signals.[6] The weak zeolitic background allows the Raman signals from adsorbed molecules to be easily detected. Since the Raman technique has a fast time scale, different conformers can be conveniently observed simultaneously at room temperature. An often-encountered problem in the characterization of zeolites using conventional visible Raman is the strong fluorescence background. Recent advances in Fourier transform (FT) Raman instrumentation enable the measurement of Raman spectra with much reduced fluorescence background by using 1064 nm excitation from a near-infrared laser.

Experimental Section

Completely siliceous ZSM-5 was prepared according to a procedure previously described.[7] Na−Y (Si/Al = 2.35) and siliceous zeolite Y (Si/Al = 100) were obtained from Strem Chemicals and Degussa Chemical, respectively. The identity, purity, and crystallinity of the zeolite samples were checked by powder X-ray diffraction (XRD). *trans*-1,4-Dichlorocyclohexane (>99%) was obtained from TCI Chemical and used without further purification.

The loading of DCC into completely siliceous ZSM-5 was carried out using the following procedures. As-made ZSM-5 was first calcined at 550 °C for 3 h to remove the template immediately prior to adsorption. An aliquot of DCC was carefully weighed and added to a precisely weighed sample of freshly calcined ZSM-5 in a glass tube, corresponding to a loading level of 4 molecules/unit cell (u.c.). The tube was then sealed and placed in an oven at 120 °C for 6 h to uniformly disperse the sorbate molecules throughout the sample. The zeolite was only briefly exposed to air during the weighing. Since completely siliceous ZSM-5 is highly hydrophobic, the very brief exposure to air should not result in the significant adsorption of water. To check for water adsorption, we also loaded DCC under strictly controlled environments. Freshly calcined ZSM-5 was weighed and placed in an Schlenk tube.

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The zeolite sample was then heated to 400 °C under vacuum (10^{-3} Torr) for 2 h to remove possible residual water. After cooling the sample to room temperature, an accurately weighed amount of DCC was added to the Schlenk tube under nitrogen. The Schlenk tube was then evacuated (10^{-3} Torr) at room temperature for 1 h and then heated in an oven under static vacuum at 120 °C for 6 h. The DCC/ZSM-5 complex was transferred from the Schlenk tube into a melting capillary and then sealed with wax inside a glovebox. The Raman spectra of DCC/ZSM-5 prepared by the two different methods were identical. For the DCC/Na−Y complex, the loading methods described above resulted in DCC decomposition and severe fluorescence in the Raman spectra. Consequently, solution phase loading was carried out for this system. Precisely weighed samples of dehydrated Na−Y powder were placed in a flask. A 3 wt % solution of DCC in *n*-pentane was then prepared. The mass ratio of DCC to Na−Y in the pentane solution corresponded to a loading of 3 molecules/supercage (s.c.). The mixture was stirred for 24 h at room temperature. The *n*-pentane was then slowly pumped off under vacuum until all the solvent was removed. Complete removal of solvent was evident from the FT-Raman spectrum of the resulting powder, which showed no peaks due to *n*-pentane. The powder was weighed again and the mass increase indicated a loading of DCC at 3 molecules/s.c. To confirm that DCC exists as isolated molecules located inside Na−Y rather than crystallites existing outside the pore, we recorded the FT-Raman spectrum of the resulting powder at 153 K. It is well-known that the Raman spectrum of crystalline DCC exhibits extensive band splitting at low temperatures due to a solid-state effect (factor group splitting).[8] No such splitting was observed, indicating that the samples did not contain DCC crystallites. The adsorption of DCC in highly siliceous Y was conducted in the same way as described for ZSM-5.

All Raman spectra were recorded on a Bruker RFS 100/S spectrometer equipped with a Nd^{3+}:YAG laser operating at 1064.1 nm and a liquid-nitrogen cooled Ge detector. The laser power was typically 80 mW at the sample and the resolution was 2 cm^{-1}. Low-temperature measurements were achieved using a Bruker Eurotherm 800 series temperature control unit, which regulated the sample temperature within ±1 °C. Powder XRD measurements were made on a Rigaku diffractometer equipped with a graphite monochromator using Co Kα radiation (wavelength 0.17902 nm).

Results and Discussion

trans-1,4-Dichlorocyclohexane (DCC) can exist in two chair conformations: the diaxial (aa) and diequatorial (ee). Electron diffraction studies indicate that in the vapor phase, the aa and ee conformers coexist in approximately equal amounts.[9] NMR studies[10] and theoretical calculations[11] suggest that the aa conformer is actually preferred slightly in the gas phase. In nonpolar solvents, the ee and aa conformers have nearly equal populations.[8,10,12] However, in a polar medium, the conformational equilibrium is shifted in favor of the ee configuration.[8,12−13] At room temperature, pure DCC crystallizes in a disordered phase with the population of the ee conformer being ~90%.[14] The phase transition behavior of DCC and the associated changes in conformation have been studied at different temperatures and pressures.[8,15−16] In addition, the infrared and Raman spectra of DCC in gas, solid, and solution phases, and the spectral assignments of the vibrational bands to different conformers, are well established.[8,12,17−18] In the present work,
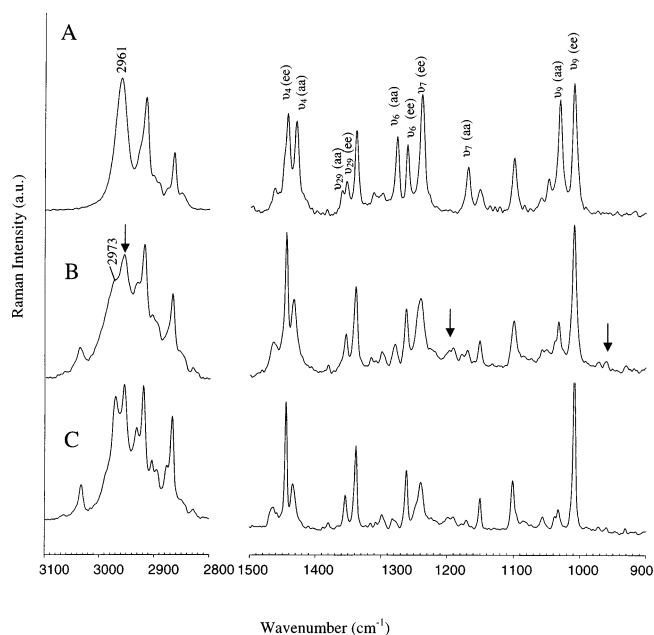

Figure 1. FT-Raman spectra of DCC (3100−900 cm^{-1}): (A) in CCl$_4$ solution; (B) adsorbed in ZSM-5 at 298 K; (C) adsorbed in ZSM-5 at 153 K (not to scale). The arrows indicate the new peaks appearing upon adsorption (see text).

the assignments of the vibrational modes of DCC were based on the assignments reported previously by Ellestad and Klaeboe.[8]

DCC/ZSM-5. FT-Raman spectra of DCC adsorbed in completely siliceous ZSM-5 at a loading level of 4 molecules/u.c. were measured as a function of temperature. To assist the interpretation of the results, the Raman spectra of pure solid DCC and DCC in CCl$_4$ solution were also recorded at room temperature. The spectra are in good agreement with those reported in the literature.[8] Figures 1 and 2 show the Raman spectra of DCC in CCl$_4$ solution and in ZSM-5 at selected temperatures.

Previous work has established that DCC exists as approximately an equal mixture of ee and aa conformers in carbon tetrachloride solution.[8,12] In the following discussion, the Raman spectrum of DCC in CCl$_4$ solution is used as a reference for discussion of the changes in spectral parameters upon adsorption into zeolites. Upon loading into ZSM-5 at room temperature, changes in the intensities of several Raman bands associated with the aa conformer relative to the corresponding ee conformer were clearly observed. In the C−Cl stretching region (Figure 2), two strong bands at 725 and 648 cm^{-1} have been assigned to the C−Cl symmetric stretching modes (ν_{11}) for the ee and aa conformers, respectively. In carbon tetrachloride solution, these peaks have almost equal intensity, which is qualitatively consistent with the ee and aa conformers having roughly equal population in CCl$_4$ solution. Upon adsorption into ZSM-5, the intensity of the 648 cm^{-1} band due to the aa conformer significantly decreased relative to the same ν_{11}(C−Cl) mode at 725 cm^{-1} of the ee conformer. Similar changes were also observed for several other vibrational modes. For example, Figures 1 and 2 show that incorporating DCC inside the ZSM-5 framework resulted in a decrease in the intensities of several aa bands at 1276 (ν_6, CH bending), 1360 (ν_{29}, CH$_2$ wagging), 1429 (ν_4, CH$_2$ scissoring), 1031 (ν_9, C−C stretching), 1170 (ν_7, CH$_2$ twisting), and 816 cm^{-1} (ν_{10}, C−C stretching) relative to their ee counterparts at 1260, 1352, 1443, 1009, 1239, and 841 cm^{-1}, respectively. These results indicate unambiguously that adsorption of DCC in ZSM-5 induces a shift in conformational
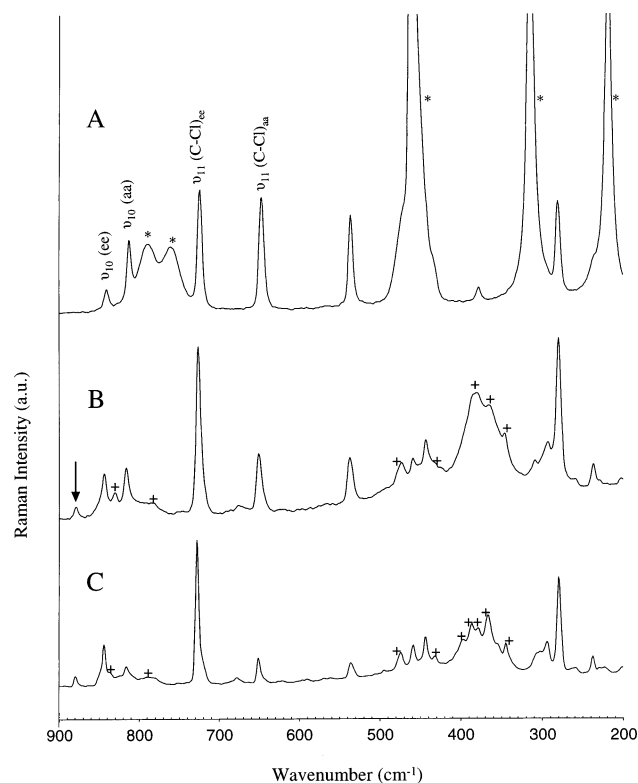
Figure 2. FT-Raman spectra of DCC (900−200 cm⁻¹): (A) in CCl₄ solution; (B) adsorbed in ZSM-5 at 298 K; (C) adsorbed in ZSM-5 at 153 K (not to scale). The arrows indicate the new peaks appearing upon adsorption (see text). The peaks labeled with * and + are due to the vibrations of CCl₄ and the zeolite framework, respectively.

Figure 3. Plots of $\ln(I_{aa}/I_{ee})$ against temperature for DCC adsorbed in zeolites.

equilibrium toward the ee conformation. To obtain conformational information at a semiquantitative level, we have further examined the integrated intensities of the C−Cl stretching modes at 725 and 648 cm⁻¹. Since the C−Cl stretching bands are considered to be "pure vibrations", i.e., well resolved and not coupled to other vibrational modes,[8] the ratio of the integrated Raman intensities of the bands due to the aa and ee conformers can be related to the ratio of their concentrations. Generally, the intensity of a Raman band, I_j, for a conformer j is given by the following equation:

$$I_j = \sigma_j C_j \tag{1}$$

where σ_j and C_j are the scattering cross section and the concentration of the j conformer, respectively. For the conformational equilibrium ee ⇆ aa, the equilibrium constant K is given by

$$K = C_{aa}/C_{ee} = (I_{aa}\sigma_{ee})/(I_{ee}\sigma_{aa}) \tag{2}$$

Since the values of σ_j are usually not known and it is extremely difficult to measure experimentally, the equilibrium constant K cannot be directly calculated from measured Raman intensities. Instead, the ratio between the equilibrium constants in zeolite (K_z) and the reference solution (K_s) can be derived from the integrated intensities of the C−Cl stretching bands,[19] assuming the scattering cross sections in the zeolite are the same as in solution.

$$K_z/K_s = (C_{aa}/C_{ee})_z/(C_{aa}/C_{ee})_s = (I_{aa}/I_{ee})_z/(I_{aa}/I_{ee})_s = f \tag{3}$$

$(I_{aa}/I_{ee})_z$ and $(I_{aa}/I_{ee})_s$ are the ratios of the integrated intensities of a given Raman mode for the aa and ee conformers in a zeolite and reference (CCl₄) solution, respectively. The value of f
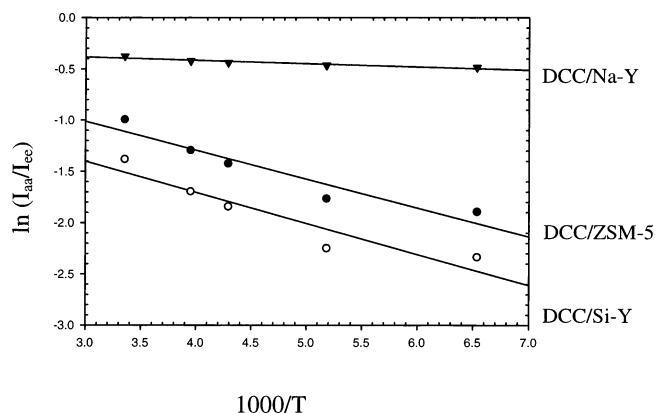
characterizes the shift in conformational equilibrium from solution to zeolite. For DCC/ZSM-5, the f has a value of 0.37 at room temperature, indicating that the aa concentration is significantly lower in ZSM-5 than in CCl₄ solution.

For DCC/ZSM-5, the intensities of the ee bands increased with respect to the corresponding aa bands (Figures 1 and 2) as the temperature was lowered. The changes in the band intensity with temperature suggests that the ee and aa conformers are in a dynamic equilibrium and lowering the temperature causes further displacement of the equilibrium toward the ee configuration. The relative intensities (I_{aa}/I_{ee}) of the two ν_{11}(C−Cl) bands at 648 and 725 cm⁻¹ over a range of temperatures were used to determine the conformational enthalpy change $\Delta H°$ using the relation

$$\ln K = (-\Delta H°/RT) + (\Delta S°/R) \tag{4}$$

As shown earlier, the equilibrium constant K is proportional to I_{aa}/I_{ee} and hence

$$\ln(I_{aa}/I_{ee}) = (-\Delta H°/RT) + \text{constant} \tag{5}$$

The plot of $\ln(I_{648}/I_{725})$ versus $1/T$ is linear (Figure 3), yielding an enthalpy difference of 2.3 kJ mol⁻¹.

From the above discussion, it appears that the ee conformation is largely stabilized by the ZSM-5 framework. The situation is different from that observed for DCC in thiourea clathrates where the equilibrium is displaced toward the aa conformation.[19] Several reasons may account for the observed preference for the diequatorial conformation in the present case. (1) Previous conformational studies have shown that DCC exhibits a solvent effect.[10,12−13] As mentioned earlier, the ee and aa conformers have about the same concentrations in nonpolar solvents, but the ee conformer has a larger population in polar solvents. Since both ee and aa conformers have zero electric dipole moment, the observed solvent effect has been interpreted in terms of the difference in electric quadrupole moment of two conformers.[11b,13] It is believed that the larger quadrupole moment of the ee conformer is more stabilized by a polar medium. Zeolites have been widely regarded as solid solvents.[20] Since the framework of completely siliceous ZSM-5 is electrically neutral (i.e., there are no extraframework charge-balancing cations), the interactions between DCC and the framework are van der Waals in nature. However, as pointed out by Hufton et al., silicalite (completely siliceous ZSM-5) cannot be considered to be completely nonpolar since surface hydroxyl groups associated with structural defects are always present to some extent.[21a] It is well established that the defects including isolated SiOH groups due to the fracture of single Si−O−Si bonds as well as

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silanol "nets" of four hydroxyls formed from the absence of a structural Si atom are not only located on the external surface, but also occur in the interior walls of both the channels and channel intersections.[21] The silanol groups on the channel and channel intersection surfaces provide a slightly polar environment, which stabilizes the larger quadrupole moment of the ee conformer. (2) Adopting the ee conformation with a slightly larger molecular volume enables DCC to maximize the dispersion interactions with the framework. (3) The orientation of DCC inside the ZSM-5 framework also contributes to the enhanced ee population. In the present study, we have measured the FT-Raman spectrum of DCC/ZSM-5 at a loading level of 1 molecule/u.c. and found it to be identical with the spectrum for DCC/ZSM-5 with a loading of 4 molecules/u.c., which implies that within the loading range 1−4 molecules/u.c., the DCC molecules occupy the identical adsorption sites inside the host framework. ZSM-5 is known to have three different adsorption sites: channel intersections and midsections of zigzag and straight channels. There are four equivalent positions for each site. Of the three adsorption sites, the channel intersection has the largest amount of free space (near a spherical "cavity" with a diameter of ∼8.7 Å) for guest molecules, whereas the dimensions of the channels are about 5.5 Å. Previous single-crystal X-ray diffraction studies have shown unambiguously that at loading levels ≤4 molecules/u.c., guest molecules such as *p*-dichlorobenzene,[22] *p*-xylene,[23] and naphthalene[24] all reside in the channel intersections. According to Magalhães et al., the kinetic diameter of *trans*-1,4-dimethylcyclohexane is greater than 9 Å.[25] Since it is well-known that methyl groups and chlorine atoms have identical steric effects,[26] it is not unreasonable to assume that DCC has a similar kinetic diameter. Taking this relatively large molecular size into consideration, we suggest that DCC is also confined in the intersection with part of the ring, presumably the methine carbon fragment, CClH, extending into the straight channels (a similar situation was also found in the *trans*-1,4-dimethylcyclohexane/ZSM-5 system[25]). This orientation certainly prefers the ee conformation because the equatorial C−Cl bonds of the ee conformer are more aligned with the channel direction compared to the aa configuration and therefore can be more easily inserted into the channels. This argument is qualitatively supported by the measured Raman frequencies of the C−Cl and C−H stretching vibrations. In the C−H stretching region, a strong peak was observed at 2961 cm^{-1} in the spectrum of DCC in CCl$_4$ solution. This peak is due largely to the C−H stretching motion of the methine groups (CH).[8] Upon loading, this peak shifts toward higher energies by 13 wavenumbers, to 2973 cm^{-1}. For the confined guest molecules in a zeolite, the blue shift in the stretching frequency may be interpreted by the argument suggested by Dutta et al. that the expansion of molecular volume during the stretching motions is resisted by the tight surrounding wall of the framework, leading to a frequency shift toward higher energies.[27] In the present case, the axial C−H bond of the methine group of the ee conformation is probably perpendicular to the channel direction and therefore its stretching vibration is more restricted by the channel. The frequencies of the ν_{11} (C−Cl) bands, on the other hand, are not affected by the adsorption at all, implying that the C−Cl bond on the same methine group is more aligned along the channel direction, and consequently the C−Cl stretching vibration is much less restricted by the framework. Further, the frequencies of the C−H stretching modes for the methylene groups remained essentially unchanged upon loading, indicating that there is little restriction of the C−H stretching motions from the surrounding framework. This suggests that

the part of the cyclohexane ring containing the methylene groups (CH$_2$) is positioned in the channel intersection, which is more accommodating. The DCC orientation inside ZSM-5 described above should prefer the ee configuration.

Another interesting finding is that upon adsorption into the ZSM-5 framework, the molecular symmetry of DCC is reduced. Inspection of the Raman spectrum of the DCC/ZSM-5 complex shows that there are several weak new peaks appearing upon adsorption at 897, 960, 1198, and 2956 cm^{-1}. These bands were not seen in the Raman spectra of either pure solid DCC (not shown) or DCC in CCl$_4$ solution at room temperature. A free DCC molecule has C$_{2h}$ point group symmetry for both conformers.[8,18] Since the molecule has a center of symmetry, the principle of mutual exclusion applies, i.e. the Raman (a$_g$ + b$_g$) and IR (a$_u$ + b$_u$) bands are noncoincident. A careful comparison of the frequencies of the new bands with those of the IR bands of DCC in solution reported by Ellestad and Klaeboe[8] reveals that these new peaks are originally IR active modes. The new bands at 1198, 897, and 2956 cm^{-1} can be assigned to ν_{42} (CH$_2$ twisting), ν_{44} (CH$_2$ rocking), and ν_{36} (C−H stretching), respectively, all of which belong to the ee conformer and are b$_u$ species. Similarly, the band at 960 cm^{-1} is due to ν_{22}, the a$_u$ mode of the aa conformer (CH bending). The fact that all of these bands, which are observed only in the solution IR spectrum, now become Raman active suggests that DCC molecules adsorbed inside ZSM-5 no longer have a center of symmetry. The results indicate that upon adsorption, the symmetry of DCC is perturbed from perfect C$_{2h}$ symmetry as a result of the interaction with the framework.

It is well established that the ZSM-5 framework undergoes phase transitions upon adsorption of a wide range of organic molecules.[28] Calcined unloaded ZSM-5 at room temperature has a monoclinic structure (space group *P*2$_1$/n).[29] A previous study has shown that the adsorption of *trans*-1,4-dimethylcyclohexane induces a monoclinic-to-orthorhombic phase change in the ZSM-5 structure.[30] Since the structure of *trans*-1,4-dimethyl-cyclohexane is very similar to DCC, we have also carried out powder X-ray diffraction (XRD) measurements for the DCC/ZSM-5 system at a loading range of 1−4 molecules per unit cell to examine possible sorbate-induced phase transitions. A number of studies have established that two regions (2θ: 26−30° and 33−35°) in the powder XRD profile of ZSM-5 are very sensitive to structural change in the ZSM-5 framework.[28a,28c,31] Figure 4 shows the powder XRD patterns of the DDC/ZSM-5 system at different loading levels as well as the calcined unloaded ZSM-5. The XRD pattern of DCC/ZSM-5 with a loading of 1 molecule/u.c. appears to be identical to that of calcined ZSM-5, indicating that incorporating only one DCC molecule per unit cell into the zeolite lattice does not induce any phase change in the framework. However, at 2 DCC molecules/u.c., the XRD pattern shows distinct changes. In particular, two doublets in the 2θ regions 26−29° and 33−35° in the XRD pattern of calcined ZSM-5 suddenly become two singlets. Since previous work has shown that the above-mentioned changes, though subtle, are characteristic of a phase transformation from monoclinic to orthorhombic symmetry,[28a,28c,31] we conclude that the adsorption of DCC into ZSM-5 induces a monoclinic-to-orthorhombic phase transition. Further increase in the loading to 4 molecules/u.c. does not cause any additional changes in the XRD profile, implying that the orthorhombic phase is stable up to the loading of 4 molecules/u.c. To maximize the van der Waals interactions and to minimize repulsive interactions, it appears that both guest and host have mutually adopted changes in their structures. In particular, the
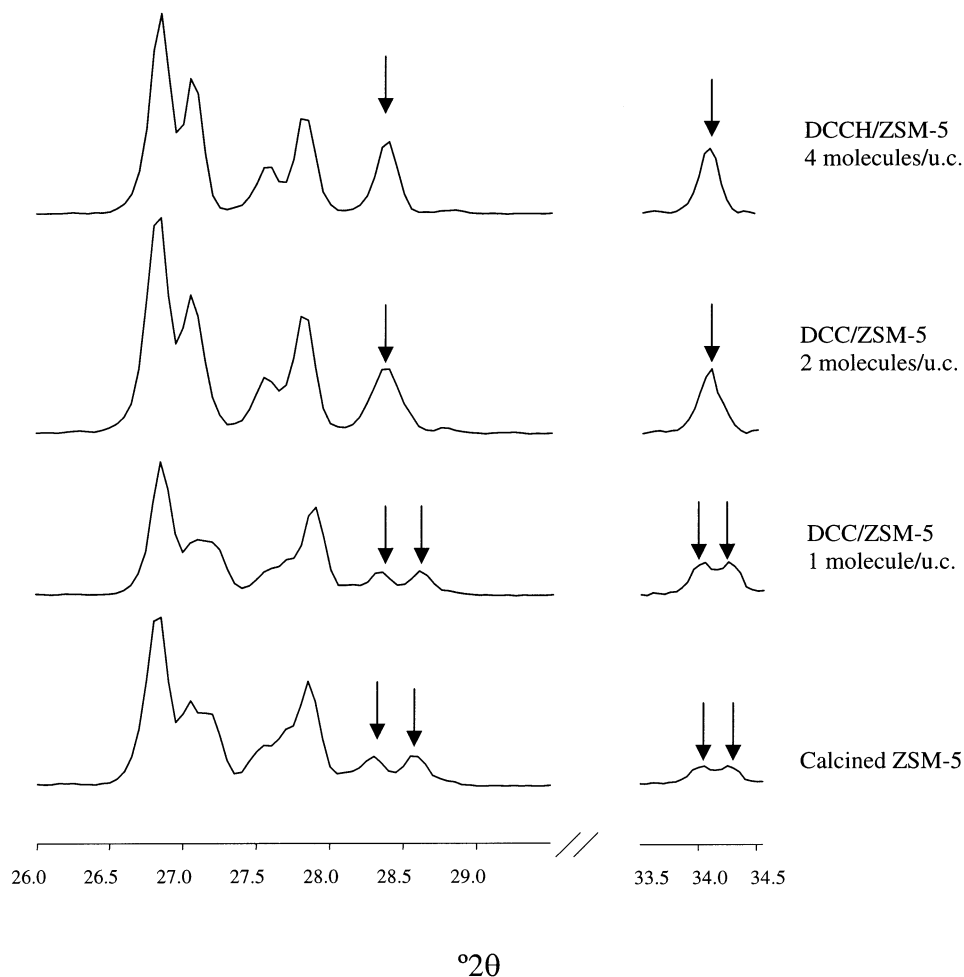
Figure 4. Powder XRD patterns of ZSM-5 in the 2θ regions of 26−30° and 33.5−34.6° with various loadings of DCC. The doublet-to-singlet changes in the two regions (see text) are indicated by the arrows (↓).

sorbate switches to the ee conformation, and sorbent transforms to a new orthorhombic phase.

The most intense Raman bands due to the ZSM-5 framework are found in the 420−320 cm^{-1} region. These peaks have been previously assigned to symmetric Si−O−Si bending vibrations.[32] At room temperature, a rather broad envelope [full width at half-height (fwhh) $\approx$ 64 cm^{-1}] consisting of several overlapping bands appears in this region (Figure 2). The broad spectral profile indicates a wide distribution of Si−O−Si angles resulting from a large number of nonequivalent Si−O−Si linkages. Upon cooling to 153 K, noticeable line narrowing was observed (Figure 2), implying that Si−O−Si linkages must undergo significant thermal motion at room temperature. However, the overall spectral width remains unchanged, indicating that the distribution of the Si−O−Si angles in the orthorhombic phase is not affected by cooling.

DCC/Na−Y. To examine the effect of different frameworks on the conformational properties of DCC, we have also recorded FT-Raman spectra of DCC adsorbed in zeolite Y. Zeolite Y has faujasite (FAU) structure containing two different types of cages. The large supercage (also called the α cage) is a nearly spherical cavity with an internal diameter of 12.5 Å. The guest molecules can enter the cage through its 12-membered ring window (diameter: 7.4 Å). The small sodalite cage (also called the β cage) is not accessible to most organic molecules because its six-membered ring pore is too small. The spectrum of DCC in Na−Y (3 molecules/s.c.) shows that, upon loading, the intensities of the ee modes increase only slightly relative to the

aa bands in comparison with the spectrum of DCC in CCl$_4$ solution (Figure 5). Using the integrated intensities of the two ν_{11}(C−Cl) modes, the value of f ($= K_z/K_s$) was calculated to be 0.67. This value is much larger than that of DCC/ZSM-5 (0.37), but less than unity, indicating that the population of the aa conformer in Na−Y is smaller than that in CCl$_4$ solution, but much greater than that in ZSM-5. It is also worth noting that the peak positions of the ν_{11}(C−Cl) modes have shifted to lower energies by 13 and 12 cm^{-1}, from 725 and 648 cm^{-1} in the spectrum of the CCl$_4$ solution to 712 and 636 cm^{-1} in the spectrum of DCC/Na−Y for the ee and aa conformers, respectively. The large low-frequency shifts clearly indicate a strong interaction between the chlorine atoms of DCC and the Na$^+$ ions inside the Na−Y supercage, because the C−Cl···Na$^+$ interaction weakens the carbon−chlorine bonds. The other unusual observation is that the line width of the two ν_{11}(C−Cl) bands increases significantly. In CCl$_4$ solutions, the full widths at half-height are 7 and 9 wavenumbers for the 725 and 648 cm^{-1} bands, respectively. Upon adsorption inside Na−Y, the line widths increase by 7 and 6 wavenumbers to 14 and 15 wavenumbers for the respective ee and aa conformers. The vibrational line width contains important information about molecular dynamics.[33] Generally, the vibrational bands of a small organic molecule in liquids are much broader than those in an ordered solid due to extensive molecular tumbling.[34] Compared to solution, the degree of motion for the DCC molecules encaged in Na−Y must be reduced due to the spatial confinement imposed by the zeolite. Therefore, the large
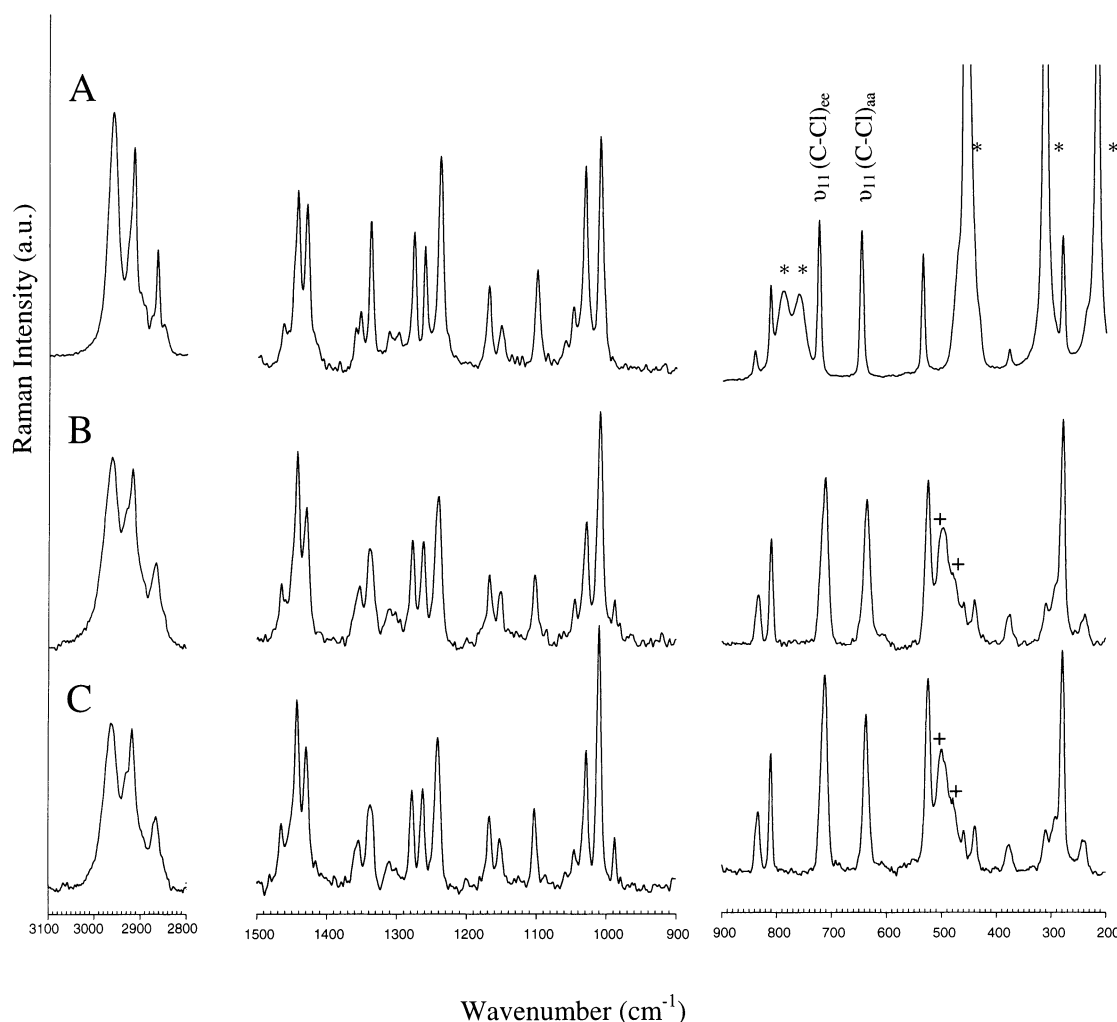
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Figure 5. FT-Raman spectra of DCC (3100−200 cm^{-1}): (A) in CCl$_4$ solution; (B) adsorbed in Na−Y at 298 K; (C) adsorbed in Na−Y at 153 K (not to scale). The peaks labeled with * and $^+$ are due to the vibrations of CCl$_4$ and the zeolite framework, respectively.

increase in line width upon adsorption is unlikely due to a dynamic process. To confirm this, we have measured the FT-Raman spectra of DCC/Na−Y in the temperature range 153 K to 298 K. Interestingly, the spectra obtained at lower temperatures and at room temperature are very similar (Figure 5). In particular, the two ν_{11}(C−Cl) bands exhibit little changes in their integrated intensities. The van't Hoff plot (Figure 3) has almost zero slope, indicating that the DCC in Na−Y is not in a dynamic conformational equilibrium. This behavior is quite different from that observed for the DCC/ZSM-5 system, which shows a progressive increase in the population of the diequatorial form upon lowering the temperature. It is also worth mentioning that the same two ν_{11} (C−Cl) bands also display little change in the line width with decreasing temperature. This observation suggests that there is no significant molecular motion associated with DCC. Apparently, the DCC molecules adsorbed in Na−Y are statically disordered. It appears that upon entering the supercages, the DCC molecules are frozen in a particular conformation through coordination of chlorine atoms with sodium ions as indicated by the frequency shifts of the ν_{11}(C−Cl) modes. This coordination can occur in several docking orientations within the same supercage, and the specific DCC orientations may vary from supercage to supercage. Consequently, the recorded Raman spectrum is a cumulative average of all possible orientations of DCC molecules within the Na−Y. The observed intensity ratio (I_{636}/I_{712}) is very similar to that in *n*-pentane solution (spectrum not shown). Apparently, the

conformation of DCC is being locked as the solvent is pumped out, resulting in a frozen population reflecting the conformational ratio in the *n*-pentane solution.

DCC/Si−Y. In the above discussion, the key element, which explains the observed Raman spectra of DCC/Na−Y, is the suggested interaction between chlorine atoms of DCC and the Na$^+$ ions of zeolite Y. To further confirm the effect of sodium ions on the behavior of DCC inside zeolite Y, we have examined the Raman spectra of DCC adsorbed in highly siliceous zeolite Y. Siliceous Y and Na−Y have the same framework (FAU) structure. Since the number of Na$^+$ ions in Si−Y (Si/Al = 100) is only 3% of that in Na−Y (Si/Al = 2.35), the possible cation−chlorine interactions are significantly minimized. The room-temperature Raman spectrum of DCC/Si−Y (Figure 6) is more similar to that of DCC/ZSM-5 than that of DCC/Na−Y. Specifically, the frequencies of the two ν_{11}(C−Cl) modes are identical to those in carbon tetrachloride solution and do not shift to lower energies at all. This result directly confirms that the frequency shift observed in the DCC/Na−Y is indeed due to the interaction with cations. For the equilibrium ee ⇆ aa, the value of *f* is 0.25 compared to 0.37 and 0.67 for DCC/ZSM-5 and DCC/Na−Y, respectively. This indicates that the aa population in Si−Y is smaller than that in ZSM-5 and Na−Y. The peak intensities of the ee modes increase with decreasing temperature, implying that the ee population of DCC in Si−Y gradually increases. From the van't Hoff plot (Figure 3), the conformational enthalpy was determined to be 2.6 kJ mol^{-1}.
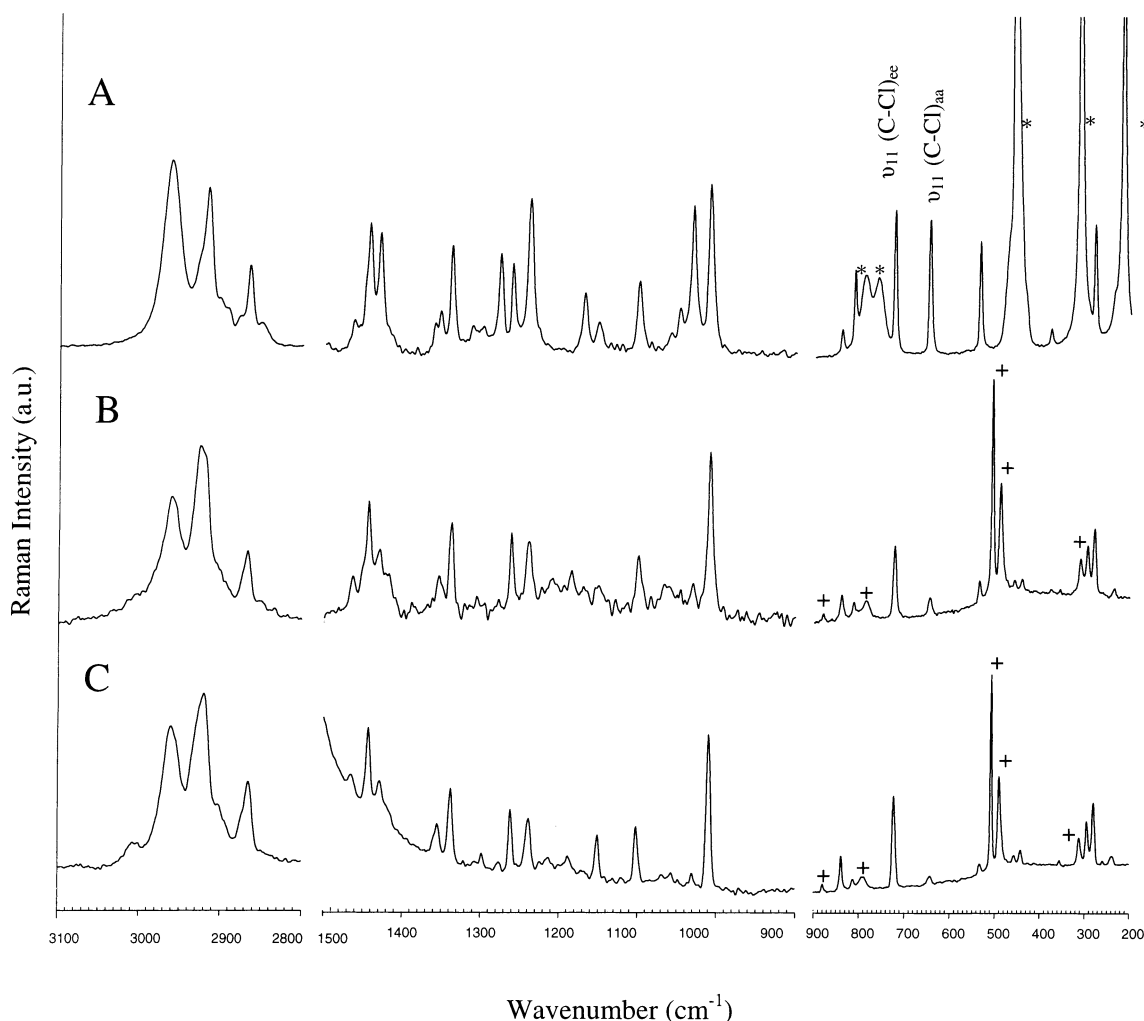
Figure 6. FT-Raman spectra of DCC (3100−200 cm^{-1}): (A) in CCl$_4$ solution; (B) adsorbed in Si−Y at 298 K; (C) adsorbed in Si−Y at 153 K (not to scale). The peaks labeled with * and + are due to the vibrations of CCl$_4$ and the zeolite framework, respectively.

Apparently, in contrast to DCC/Na−Y system, the two conformational isomers in Si−Y are in dynamic equilibrium, providing evidence that the frozen conformation observed in Na−Y is indeed related to the presence of Na$^+$ ions. The reason DCC has a higher ee population in Si−Y than in ZSM-5 is probably due to the fact that the framework of siliceous Y is slightly more polar than that of completely siliceous ZSM-5, resulting from the difference in Si/Al ratio (100 vs ∞).

Summary

In the present work, we have examined the conformational behavior of *trans*-1,4-dichlorocyclohexane adsorbed inside three zeolites. The results show that the conformational behavior of DCC is dependent on the zeolite framework structure, Si/Al ratio, and the charge-balancing cations. The ee conformation is clearly favored when DCC is adsorbed inside ZSM-5. The increased ee population upon adsorption into ZSM-5 is attributed to the slightly polar environment resulting from the silanol groups associated with the defects and the orientation of DCC in the framework. Variable temperature Raman spectra indicate that the aa and ee conformers are in dynamic equilibrium within the host framework. ZSM-5 also changes its own symmetry to maximize dispersion interaction with the guest species. In contrast to the DCC/ZSM-5 complex, disorder exists in the DCC/Na−Y system. Since lowering the temperature has little effect on the Raman spectra, the disorder observed is likely static

disorder without significant overall molecular motions, including the ring inversion, which affects the conformational equilibrium. We have discovered that the disorder occurs through the strong interactions of the chlorine atoms of DCC with the sodium ions inside the zeolite Y framework, which lock the DCC molecules into specific orientations as well as specific conformations. The dynamic conformational equilibrium can be reestablished inside zeolite Y by removing the vast majority of the Na$^+$ ions by using a highly siliceous Y.

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