

An FT-Raman Spectroscopic Study of the Conformational Properties of Chlorocyclohexane in Zeolites

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The conformational behavior of chlorocyclohexane (ClCH) adsorbed inside several representative zeolites such as completely siliceous ZSM-5, Na–Y, and siliceous Y (Si–Y) has been investigated by FT-Raman spectroscopy. The results have clearly shown that the conformational and dynamic properties of ClCH depend on the zeolitic framework structure, the presence of charge-balancing cations, as well as the Si/Al ratio. Compared to pure liquid, the population of equatorial conformation increases upon adsorption into ZSM-5. Apparently, the ZSM-5 framework stabilizes the equatorial conformation (with a larger molecular volume) via maximizing the van der Waals interactions between the host and guest. Within the ZSM-5 framework, the axial and equatorial conformers are still in dynamic equilibrium. It continues to shift toward the equatorial configuration upon lowering the temperature, and at 153 K the ClCH in ZSM-5 adopts the equatorial conformation exclusively. For the ClCH/Na–Y system, the situation is remarkably different. Upon incorporation of ClCH into Na–Y, the conformation of ClCH is immediately frozen as a result of very strong interaction with Na⁺ ions. The sorbate–cation interactions also lock the ClCH molecules into different orientations which vary from cage to cage, yielding a static disorder. However, if ClCH molecules are adsorbed in a Si–Y where the cation–sorbate interactions are lacking, the dynamic equilibrium between axial and equatorial conformation can be resumed. The relative population of equatorial conformer in Si–Y is higher than that in ZSM-5. The slightly larger equatorial concentration is attributed to the orderly packing of ClCH inside the supercage of Si–Y.

Introduction

Zeolite molecular sieves are important inorganic materials. They are microporous aluminosilicate framework materials that have well-defined cage and/or channel systems with molecular dimensions.¹ Zeolites have been extensively utilized in industry as ion-exchangers, sorbents, and particularly in petrochemical industry as catalysts. Since most applications involve initial adsorption of guest species into zeolites, it is fundamentally important to understand the behavior of guest molecules inside zeolite hosts. One particular type of the host–guest interactions in zeolitic systems is the effect of the zeolite framework on conformational properties of organic molecules adsorbed in a zeolite. Existing different conformers can significantly influence the adsorption and diffusion of the guest species and, therefore, the subsequent chemistry inside the host framework. This is due to the fact that different conformational isomers can possess different electric dipole and quadrupole moments, which interact with the zeolite framework differently.² For this reason, the conformational behavior of the guest species in several zeolitic systems has been examined.^{2–3}

In this paper, we present the results of a conformational study of chlorocyclohexane (ClCH) adsorbed inside several zeolites, including completely siliceous ZSM-5, zeolite Na–Y, and siliceous Y (Si–Y). Zeolites can be used as catalysts for dehydrohalogenation of chlorocyclohexane to produce cyclohexene, a chemical with considerable industrial importance.⁴ In recent years, adsorption of chlorinated hydrocarbons in

zeolitic materials has also been examined since zeolites can be potentially used in separation and catalytic decomposition of chlorinated halocarbons for environmental cleanups.⁵ The conformational behavior of ClCH in host materials such as thiureas were extensively investigated.⁶ The adsorption of monosubstituted cyclohexane molecules including chlorocyclohexane in several zeolites was also studied by high-resolution solid-state ¹³C NMR, and surprisingly the results suggested that zeolite frameworks did not impose any major constraints upon conformational properties of the adsorbed chlorocyclohexane.⁷ However, our recent work on methylcyclohexane, *trans*-1,4-dimethylcyclohexane,^{3a} and *trans*-1,4-dichlorocyclohexane^{3b} (all of which are structurally related to chlorocyclohexane) has shown that the conformational behavior of these molecules do depend on the zeolite framework structure, Si/Al ratio, and charge-balancing cations.

The experimental method employed in the present study is Fourier transform (FT) Raman spectroscopy. Raman technique is a preferred approach for directly observing the guest molecules inside a zeolite framework because zeolites generally exhibit very weak Raman signals.⁸ As a result, the Raman spectra observed are mainly due to the adsorbed guest species. Raman spectroscopy is also proven to be an invaluable approach for conformational analysis.⁹ Its fast time scale allows different conformational isomers to be easily observed simultaneously at ambient temperature. Compared to conventional visible Raman, a recently developed Fourier transform Raman technique can significantly reduce the fluorescence background (a major problem associated with zeolites) due to the utilization of the 1064 nm excitation line from a near-infrared laser.

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Experimental Section

Completely siliceous ZSM-5 was prepared according to a procedure previously described.¹⁰ Na-Y (Si/Al = 2.35) and siliceous zeolite Y (Si/Al = 100) were obtained from Strem Chemicals and Degussa Chemical Co., respectively. The identity, purity and crystallinity of the zeolite samples were checked by powder X-ray diffraction (XRD). Chlorocyclohexane (>99%) was obtained from Aldrich Chemical Co. and was used without purification.

Carefully measured aliquots of chlorocyclohexane were added to accurately weighed dehydrated zeolite powders in a glass tube. The tubes were carefully sealed in a flame and then were placed in an oven for 3 h at 130 °C for ZSM-5 and 12 h at 60 °C for Na-Y and Si-Y to uniformly disperse the sorbate molecules throughout the samples. The loadings were 4 molecules/unit cell (u.c.) and 3 molecules/supercage (s.c.) for ZSM-5 and zeolite Y, respectively. To prove that all the changes observed in the Raman spectra of ClCH/zeolite complexes are indeed due to the ClCH located inside the framework and not adsorbed on the outside surface of the zeolite, a spectrum of ClCH sorbed on zeolite A (Na-A, Si/Al=1) was also examined at a loading level of 3 molecules per α cage. Since the pore size of the eight-member ring of Na-A (4.1 Å) is too small for ClCH to enter the α cages, the observed spectrum of ClCH must be due to the molecules adsorbed on the external surface of Na-A. The spectrum (not shown) looked almost identical to the liquid spectrum, confirming that the spectra of ClCH/zeolite complexes discussed in the next section (Results and Discussion) are indeed due to framework-adsorbed species rather than external surface-bound molecules.

All Raman measurements were made on a Bruker RFS 100/S spectrometer equipped with an Nd³⁺: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 carried out by using a Bruker Eurotherm 800 series temperature control unit, which regulated the sample temperature within ± 1 °C.

Powder XRD patterns were recorded on a Rigaku diffractometer equipped with a graphite monochromator using a Co K α radiation (a wavelength of 1.7902 Å).

Results and Discussion

The FT-Raman spectra of chlorocyclohexane adsorbed in completely siliceous ZSM-5, Na-Y, and Si-Y were measured as a function of temperature. To assist in the interpretation of the data, the Raman spectra of chlorocyclohexane in carbon disulfide and pure liquid were also recorded at room temperature. Assignments of the Raman bands of chlorocyclohexane were based on those previously reported.¹¹

Chlorocyclohexane itself is a classical example of conformational analysis and its conformational properties in solution, liquid, and solids have been extensively examined by vibrational¹² and NMR spectroscopy.¹³ These studies have shown that a chlorocyclohexane molecule can adopt either axial (ax) or equatorial (eq) conformers. For the pure liquid or solution at room temperature, two conformers are in dynamic equilibrium. The equatorial conformer, however, is the more favored.¹²⁻¹³ At 113 K, ClCH becomes a solid and the molecules adopt the equatorial conformers exclusively.^{12b}

In the literature, the intensities of the C-Cl stretching mode have been widely used for quantitative conformational analysis of chlorocyclohexane^{12a,12c-f,13a} because, unlike other bands involving C-H motions, the C-Cl stretching modes due to different conformers are well resolved and not intensively

coupled to other vibrations. Therefore, they can be considered as relatively "pure vibrations". For the same reason, in the present work, we have also used the integrated intensities of the C-Cl stretching bands for semiquantitative analysis. Both equatorial and axial conformers possess C_s point group symmetry, and each conformer exhibits a single C-Cl stretching band in the Raman spectrum of pure liquid, appearing at 730 and 685 cm⁻¹ for equatorial and axial conformers, respectively. The intensity of a Raman mode, I_j , for a conformer j is usually given by

$$I_j = \sigma_j C_j \quad (1)$$

where σ_j and C_j are the scattering cross section and concentration of the j conformer, respectively. For the conformational equilibrium, axial \rightleftharpoons equatorial, the equilibrium constant K can be expressed by

$$K = C_{eq}/C_{ax} = (I_{eq}/I_{ax})(\sigma_{ax}/\sigma_{eq}) \quad (2)$$

Because the σ_j is usually unknown and difficult to determine experimentally, the equilibrium constant K normally cannot be directly calculated from measured intensities. Fortunately, the free energy change, ΔG° (for axial \rightleftharpoons equatorial), in a CS₂ solution at 298 K was carefully determined from a variable temperature proton NMR study to be -0.64 kcal/mol.^{13a} We prepared a solution of the same concentration and acquired the Raman spectrum at 298 K (not shown). From eq 2, using the equilibrium constant derived from NMR data, the Raman scattering cross section ratio, σ_{ax}/σ_{eq} , was estimated to be 0.85 at room temperature. This value was subsequently used to calculate the conformational population of ClCH adsorbed in zeolites at various temperatures, assuming that the scattering cross-section ratio in a zeolite is the same as in solution and is temperature independent.

ClCH/ZSM-5. The FT-Raman spectra of ClCH loaded inside completely siliceous ZSM-5 at selected temperatures as well as pure ClCH liquid are shown in Figure 1. The most noticeable spectral change was observed in the region where the C-Cl stretching vibrations occur. Figure 1B clearly illustrates that compared to the pure liquid, the intensity of the $\nu_{22}(\text{C-Cl})$ mode positioned at 685 cm⁻¹ assigned to the axial conformer¹¹ decreased significantly relative to its equatorial counterpart at 730 cm⁻¹ upon adsorption, which indicates that the conformational equilibrium shifted toward the equatorial configuration. As the ClCH/ZSM-5 system was cooled, the intensity of the $\nu_{22}(\text{C-Cl})$ axial mode progressively decreased relative to the $\nu_{22}(\text{C-Cl})$ equatorial band. At 153 K, the axial peak centered at 685 cm⁻¹ disappeared, suggesting that all of the ClCH molecules within the ZSM-5 framework adopt the equatorial form exclusively. Similar information can also be obtained qualitatively from the changes in Raman intensities of the ν_{21} , the ring breathing modes at 817 and 808 cm⁻¹ assigned to equatorial and axial conformers, respectively.¹¹ When ClCH is loaded into ZSM-5 at room temperature, a decrease in the intensity of the axial peak relative to the equatorial band was observed (Figure 1B). However, these bands are overlapped with the weak peaks due to the symmetric Si-O-Si stretching vibrations of the zeolitic framework. For this reason, the Raman spectra of ClCH/ZSM-5 were subtracted from the spectra of calcined (unloaded) ZSM-5 in the region 900-600 cm⁻¹. The difference spectra are shown in Figure 2, which now demonstrates unambiguously the relative intensity changes in ν_{21} modes. The decrease in the intensity of the axial peak at 808

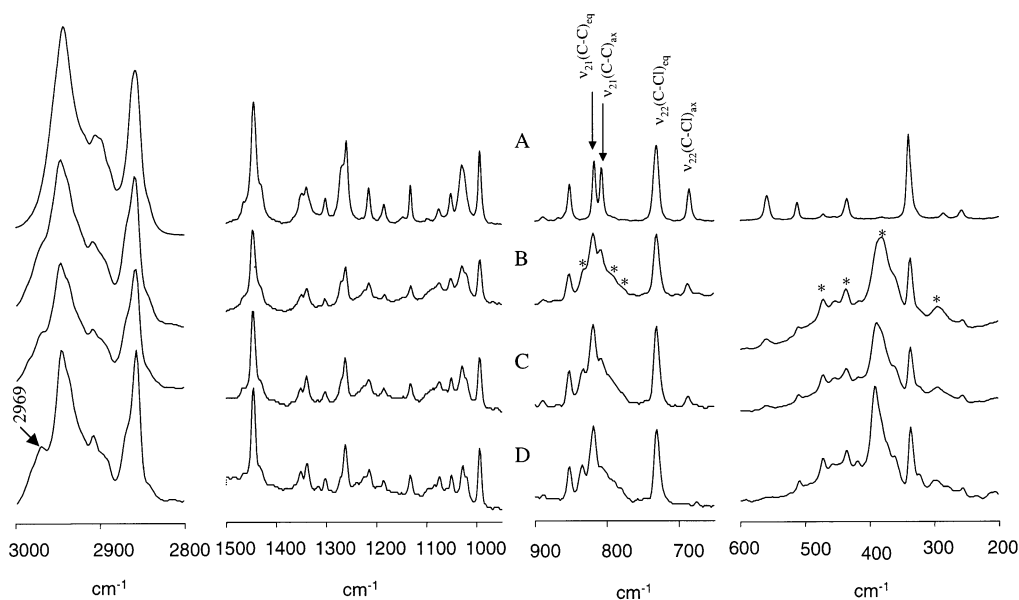


Figure 1. FT-Raman spectra (3100–200 cm^{-1}) of (A) pure ClCH liquid; ClCH adsorbed in ZSM-5 at (B) 298 K, (C) 253 K, and (D) 153 K (not to scale). The peaks labeled by (*) are due to vibrations of the zeolite framework.

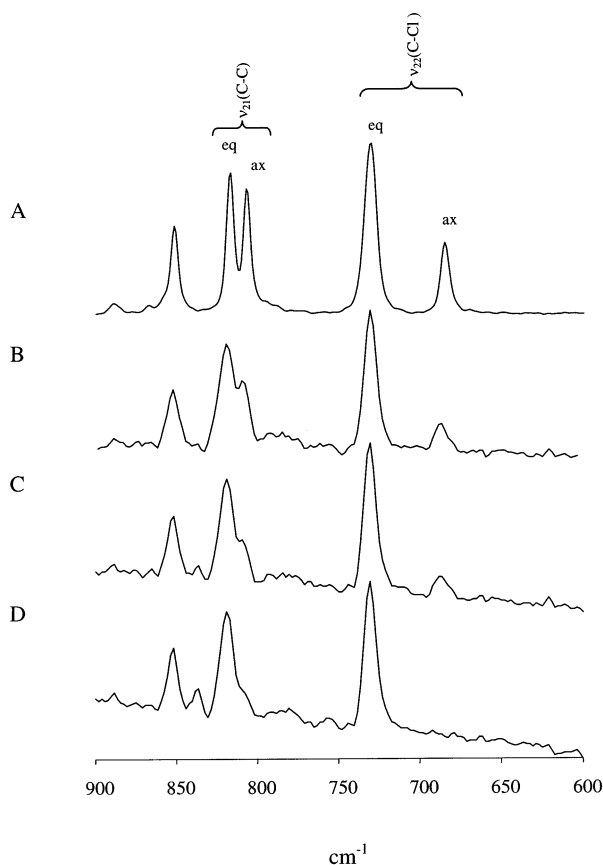


Figure 2. FT-Raman spectra (900–600 cm^{-1}) of (A) pure ClCH liquid; ClCH loaded into ZSM-5 with the zeolite background subtracted at (B) 298 K, (C) 253 K, and (D) 153 K.

cm^{-1} continues as ClCH/ZSM-5 system is cooled. At 153 K, the intensity of the axial band decreased significantly with respect to the equatorial band. However, the axial band does not disappear completely as was seen in the C–Cl stretching region, suggesting that this band must contain contributions from other vibrations. It turned out that the bands associated with ν_{21} modes can only be used qualitatively to follow the conformational change (in the absence of strong cation–sorbate

interaction) and that they are not suitable for quantitative analysis (see also discussions on ClCH/Na–Y system).

As discussed before, the integrated intensities of the Raman bands associated with the C–Cl stretching vibrations can be used to quantitatively determine the conformational population. Using the integrated intensities of the $\nu_{22}(\text{C–Cl})$ bands and the scattering cross section ratio derived earlier, we estimated that inside ZSM-5, 83% of the ClCH molecules exist in the equatorial form compared to 73% in the pure liquid. The population of the equatorial conformer increases with decreasing temperature. At 213 K, 94% of the ClCH molecules adopt the equatorial configuration. The temperature dependence of the conformational properties indicates that the ClCH molecules are in dynamic equilibrium within the ZSM-5 framework, interconverting between two conformational forms. The integrated intensity ratio ($I_{\text{eq}}/I_{\text{ax}}$) of the two $\nu_{22}(\text{C–Cl})$ bands at 730 and 685 cm^{-1} over the temperature range studied can also be employed to calculate the conformational enthalpy change, ΔH° , using the equation

$$\ln K = (-\Delta H^\circ/RT) + (\Delta S^\circ/R) \quad (3)$$

Since the equilibrium constant is proportional to $I_{\text{eq}}/I_{\text{ax}}$ and therefore

$$\ln(I_{\text{eq}}/I_{\text{ax}}) = (-\Delta H^\circ/RT) + \text{constant} \quad (4)$$

From the $\ln(I_{\text{eq}}/I_{\text{ax}})$ vs $1/T$ plot, the enthalpy difference can be obtained without the knowledge of the scattering cross sections. The van't Hoff plot is shown in Figure 3 and yielded a ΔH° value of -6.2 kJ/mol, compared to -1.1 kJ/mol for pure liquid.^{12a}

Our results clearly indicate that the ZSM-5 framework stabilizes the equatorial conformation. This observation may be explained by the nature of the interaction between zeolite framework and guest molecules. Completely siliceous ZSM-5 has a neutral framework without charge balancing cations. Therefore, the interaction with ClCH is van der Waals in nature. It appears that adopting the equatorial conformation with a larger molecular volume^{12a} allows ClCH to maximize the dispersion interactions with the zeolite framework.

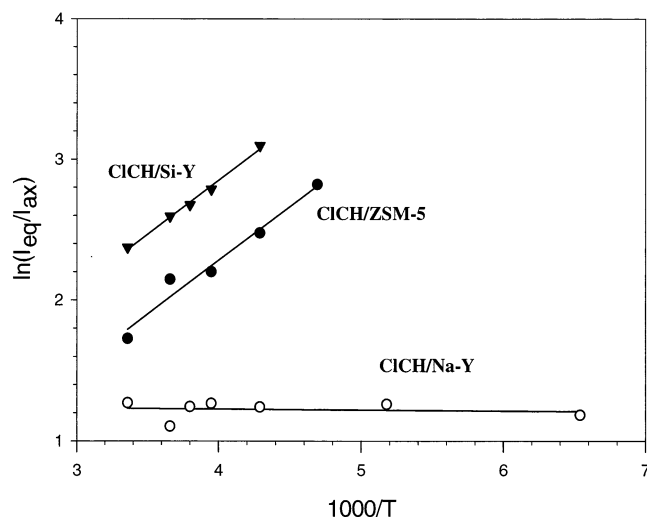


Figure 3. Plots of $\ln(I_{eq}/I_{ax})$ against temperature for ClCH adsorbed in zeolites.

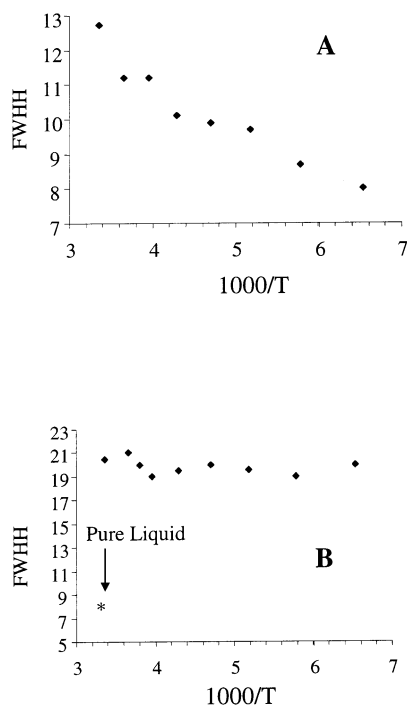


Figure 4. Plots of fwhh vs temperature of (A) CH_2 twisting mode of ClCH loaded into ZSM-5; (B) the equatorial C-Cl stretching mode ClCH loaded into Na-Y.

FT-Raman spectra can also be used to probe the dynamics of ClCH molecules within ZSM-5. It is well-known that the line width of Raman bands provides valuable information on the molecular dynamic properties.¹⁴ In general, for small organic molecules, the line width of their vibrational bands in solution or liquid are much broader than in the ordered solids because of molecular tumbling.¹⁵ In the present case, loading ClCH into ZSM-5 did not result in dramatic line narrowing of any of the Raman bands compared to the pure liquid. When the ClCH/ZSM-5 system is cooled to 153 K, several Raman peaks have steadily decreased in their full width at half-height (fwhh) relative to the room temperature spectrum. This trend is seen most notably in the CH_2 scissoring mode at 1446 cm^{-1} , which decreases its fwhh by about 6 wavenumbers (Figure 4). These changes in line width clearly indicate that at room temperature the sorbed ClCH molecules retain a substantial degree of

molecular motion within the zeolite host. As the temperature is lowered, however, the degree of molecular motion is significantly reduced.

Another noted change occurred in the CH stretching region. A free ClCH molecule with C_s symmetry should exhibit 11 ν -(CH) modes, but only three strong bands were observed at 2943, 2905, and 2857 cm^{-1} (Figure 1A). The lack of resolution is due to very subtle differences in energy and accidental degeneracy. The room-temperature Raman spectrum of ClCH/ZSM-5 shows a similar broad profile in the C-H stretching region with three intense peaks located at 2946, 2908, and 2858 cm^{-1} . However, three weak shoulders appeared at 2969, 2953, and 2868 cm^{-1} . Previous studies on structurally related guest molecules, including cyclohexane, methylcyclohexane, and *trans*-1,4-dimethylcyclohexane loaded into siliceous ZSM-5 framework, have shown that the C-H stretching vibrations are quite sensitive to the interactions with the ZSM-5 framework.^{3a} These interactions can result in the separation of accidentally degenerate modes, and in some cases are strong enough to induce a reduction in the symmetry of the sorbate molecule, resulting in the additional Raman peaks. Given the already low symmetry of the ClCH molecule, further reduction in symmetry is unlikely. Therefore, the appearance of new bands is likely the consequence of the interaction between the ZSM-5 framework and the ClCH molecules, partially removing the accidental degeneracy. As the ClCH/ZSM-5 system is cooled, a further resolution is seen in the profile of the C-H stretching region. While no new peaks are seen, the existing peaks did become slightly sharper at low temperatures. The shoulder at 2969 cm^{-1} observed at room-temperature now appears as a well-resolved peak. This peak can be assigned to ν_1 , the C-H stretching vibration of methine carbon.¹¹ A normal coordinate calculation suggested that for a free ClCH molecule, this band should appear at 2959 cm^{-1} ,¹¹ but it was not observed in the pure liquid spectrum because of the severe overlapping with the strong band at 2946 cm^{-1} . The fact that upon adsorption, this band shifted to a much higher energy suggests that there is significant interaction between the methine C-H bond and the framework because the C-H bond stretching motion of an encaged guest molecule is restricted by the framework, leading to a slight increase in force constant and therefore a high-frequency shift (an effect similar to application of external pressure to a C-H bond).¹⁶ ZSM-5 is known to have three adsorption sites: (1) the straight channels, (2) the zigzag channels, and (3) the channel intersections. There are four equivalent positions for each site. Previous work has shown that at the loading levels ≤ 4 molecules/u.c. the guest molecules such as *p*-xylene,¹⁷ naphthalene,¹⁸ *p*-dichlorobenzene,¹⁹ and *trans*-1,4-dimethylcyclohexane²⁰ all reside in the channel intersections. It is likely that the ClCH molecules are also located at the channel intersections. Since the channel sizes closely match the kinetic diameter of ClCH, to better position itself at the channel intersection, the ClCH molecule may orient itself in such a way that its C-Cl bond would extend into the straight channel of the framework, resulting in concomitantly an increase in the degree of the interaction of the axial C-H bond of methine carbon with the framework, and therefore C-H stretching frequency. Interestingly, the C-Cl stretching frequency of the adsorbed ClCH molecule did not change, implying that the equatorial C-Cl bond is more aligned along the channel axis and consequently its stretching motion is less affected by the framework.

It is well-known that the ZSM-5 framework undergoes sorbate-induced phase transitions by a large number of organic molecules.²¹ The recent XRD studies on the guest molecules

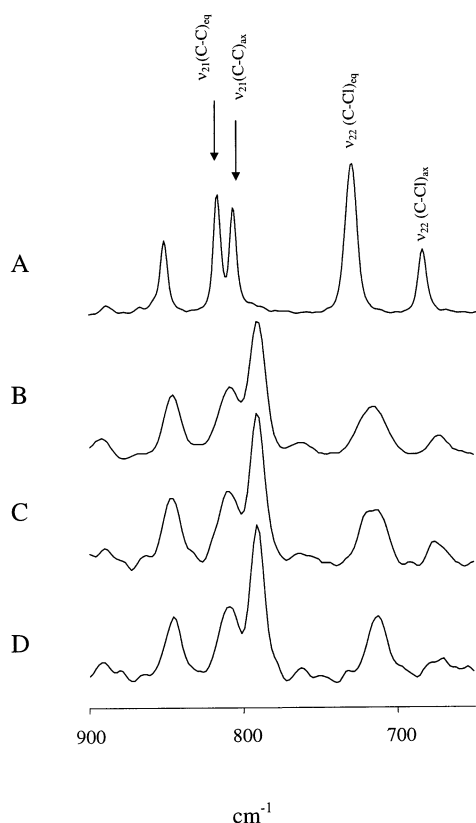


Figure 5. FT-Raman spectra (900–650 cm^{-1}) of (A) pure ClCH liquid; ClCH adsorbed in Na–Y at (B) 298 K, (C) 253 K, and (D) 153 K (not to scale).

structurally related to ClCH have shown that adsorption of *trans*-1,4-dichlorocyclohexane^{3b} and *trans*-1,4-dimethylcyclohexane²² induces a phase transformation in the ZSM-5 framework from monoclinic to orthorhombic symmetry, but no phase transition occurs when cyclohexane²³ and methylcyclohexane²² are loaded in ZSM-5. To examine the possible phase transition, we have also obtained XRD patterns of ClCH/ZSM-5 with loading levels from 1 to 4 molecules/u.c. (not shown) and they looked identical to that of calcined (empty) ZSM-5. The result suggests that similar to methylcyclohexane, adsorption of ClCH up to 4 molecules/u.c. does not cause any structure change in the ZSM-5 framework.

ClCH/Na–Y. We have examined the FT-Raman spectra of ClCH adsorbed inside Na–Y to explore the effect of a different zeolitic framework on the conformational properties of ClCH. Na–Y has faujasite (FAU) structure which contains large supercages (spherical cavities with a diameter of 12.5 Å) formed by joining the smaller sodalite cages via double six-membered ring. The guest molecule can access the cage via the 12-membered ring window with a pore diameter of 7.4 Å and the sodalite cage is normally not accessible to most organic molecules because its six-membered ring window is much too small. More importantly, the Na–Y framework has a negatively charged framework and, therefore, possesses Na^+ ions as charge-balancing cations. These cations may significantly affect both conformational and dynamic properties of ClCH in Na–Y. Indeed, examination of the $\nu_{22}(\text{C–Cl})$ stretching mode (Figure 5) does reveal some interesting behavior. Upon adsorption into Na–Y, similar to all Raman bands, the two $\nu_{22}(\text{C–Cl})$ bands become very broad. In particular, the fwhh values increased by 12 and 8 wavenumbers for equatorial and axial peaks, respectively, compared to the pure liquid. As mentioned earlier, the vibrational line width contains dynamic information and the

large fwhh values usually are indicative of significant molecular motion. However, in the present case, the substantially large line widths of the ClCH in Na–Y relative to those in pure liquid are unlikely due to dynamic processes since the degree of motion for ClCH molecules encaged in Na–Y must be reduced due to the spatial confinement imposed by the zeolitic framework. This argument is further supported by the low-temperature spectra. The Raman spectra recorded at low temperatures are similar to those measured at room temperature (Figure 5). Particularly, the two $\nu_{22}(\text{C–Cl})$ bands display little change in their integrated intensities and the van't Hoff plot (Figure 3) exhibits almost a horizontal line. These results clearly indicate that the ClCH molecules adsorbed in Na–Y are not in a dynamic conformational equilibrium and the conformational population is nearly temperature independent. The situation encountered for the ClCH molecules in Na–Y is clearly different from that in ClCH/ZSM-5 system where a progressive decrease in the population of the axial conformer with decreasing temperature was observed. It is also worth noting that the line width of the $\nu_{22}(\text{C–Cl})$ bands displayed little change upon lowering temperature (Figure 4B), which shows unambiguously that there is no significant molecular motion associated with ClCH in Na–Y. On the basis of the results presented above, we came to the conclusion that the ClCH molecules adsorbed in Na–Y are mainly in a state that is statically disordered. The disorder is apparently associated with the strong interaction of chlorine atoms of ClCH with Na^+ ions in the supercages. The existence of such interaction is clearly indicated by the fact that the frequencies of the $\nu_{22}(\text{C–Cl})$ bands shifted substantially toward the lower energies by 15 and 12 wavenumbers from 730 and 684 cm^{-1} in the spectrum of pure liquid to 715 and 672 cm^{-1} upon adsorption for the equatorial and axial C–Cl stretching bands, respectively. A strong $\text{C–Cl}\cdots\text{Na}^+$ interaction weakens the carbon–chlorine bond, resulting in a lower C–Cl stretching frequency. It appears that once entering a supercage, a ClCH molecule is locked in a particular conformation via coordination of a chlorine atom with sodium ions as indicated by the frequency shift of the $\nu_{22}(\text{C–Cl})$ bands. This coordination can occur in several docking orientations within the same supercage and may vary from cage to cage, resulting in the observed Raman spectrum being a cumulative average of all the possible orientations of the ClCH molecules in the framework. The fact that the equatorial population (78%) of ClCH in Na–Y is similar to that of pure liquid (73%) suggests that the conformation of ClCH is being frozen as soon as the molecule diffuses into the cage.

The behavior of the ν_{21} , the ring (C–C) stretching mode, is also worth discussing. As mentioned earlier, in the pure liquid, the two bands at 817 and 808 cm^{-1} were previously assigned to the ν_{21} mode mainly associated with the equatorial and axial conformers, respectively. Figure 5 shows that, upon adsorption, the intensity of the equatorial band decreased markedly relative to the axial peak. This seems to suggest that the axial population was significantly enhanced in Na–Y, which appears inconsistent with the result from the $\nu_{22}(\text{C–Cl})$ bands that the population was similar to that in pure liquid. However, a previous vibrational study concluded that the equilibrium constant ($K = C_{\text{eq}}/C_{\text{ax}}$) derived from ν_{21} bands is much smaller than that from $\nu_{22}(\text{C–Cl})$ bands.^{12e} In particular, their work showed that for ClCH in CCl_4 solution, the equilibrium constants calculated from $\nu_{22}(\text{C–Cl})$ and $\nu_{21}(\text{C–C})$ bands are 2.88 and 1.20, corresponding to an equatorial population of 74.2 and 54.5%, respectively. A comparison to literature data reveals that the K value obtained

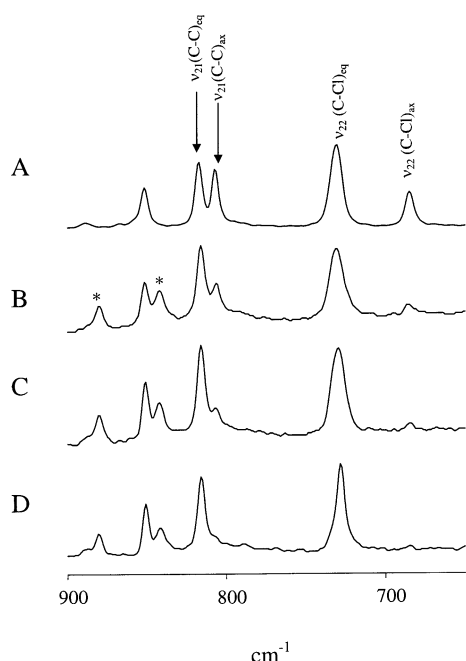


Figure 6. FT-Raman spectra (900–650 cm^{-1}) of (A) pure ClCH liquid; ClCH adsorbed in Si–Y at (B) 298 K, (C) 253 K, and (D) 173 K (not to scale). The peaks labeled by (*) are due to the vibrations of zeolite framework.

from $\nu_{22}(\text{C–Cl})$ bands is in good agreement with those obtained from many other studies utilizing different techniques such as NMR and IR (see refs in 12e). Therefore, the intensity of the axial ν_{21} band significantly overestimates the axial population. This is consistent with our observation discussed in the previous section that at 153 K, while the axial $\nu_{22}(\text{C–Cl})$ band of ClCH adsorbed in ZSM-5 disappeared completely, the axial peak of the $\nu_{21}(\text{C–C})$ mode still has significant intensity left. In ClCH/Na–Y, the peculiar behavior of the ν_{21} mode may be related to the unusually strong interaction between Na^+ and cyclohexyl ring. An inspection of the band frequency reveals that upon loading, the equatorial and axial bands shifted from 817 and 808 cm^{-1} in the pure liquid spectrum to 809 and 791 cm^{-1} , respectively. Such large low-frequency shifts suggest that the interaction is strong enough not only to affect the C–Cl bond but also to weaken the skeletal carbon backbone substantially.

ClCH/Si–Y. In the previous section, the interpretation of the Raman spectra of ClCH adsorbed inside Na–Y is largely based on the existence of very strong sorbate–cation interactions. To further confirm that the presence of Na^+ ions indeed has a profound effect on the conformational behavior of ClCH, we have also examined the Raman spectra of ClCH loaded into highly siliceous zeolite Y. The Si–Y framework is structurally identical to that of Na–Y. However, because the number of cations in Si–Y ($\text{Si/Al} = 100$) is only 3% of that in Na–Y ($\text{Si/Al} = 2.35$), the interactions between Na^+ and ClCH should be significantly reduced. Indeed, the Raman spectrum of ClCH sorbed within Si–Y at room-temperature looked more similar to that of pure liquid than that of ClCH in Na–Y. Particularly, the frequencies of the equatorial and axial peaks associated with the ν_{22} mode, C–Cl stretching, and ν_{21} mode, ring skeletal C–C stretching vibrations are identical to those of pure liquid and did not shift to lower energies at all, which directly proves that the observed frequency shifts in ClCH/Na–Y system are the result of the interactions between sorbate and cations.

Although the peaks did not move, the notable changes in the intensities of the ν_{22} and ν_{21} modes did occur (Figure 6). Upon

adsorption, both the ν_{21} and ν_{22} axial bands at 807 and 684 cm^{-1} displayed a marked decrease in intensity relative to the equatorial mode at 816 and 730 cm^{-1} , respectively. These results imply that, similar to ClCH/ZSM-5, the conformational equilibrium is displaced toward the equatorial conformation once the ClCH molecules are incorporated inside Si–Y. The calculation based on the integrated intensity ratio of $\nu_{22}(\text{C–Cl})$ mode revealed that, at room temperature, 90% of the sorbed ClCH molecules exist in equatorial form, compared to 73% in the pure liquid. Like completely siliceous ZSM-5, the Si–Y framework is also highly siliceous. Therefore, the van der Waals interaction between the sorbent and sorbate favors the equatorial conformer with a larger molecular volume, resulting in an equatorial population larger than that in pure liquid. It is also noticed that the percentage of the equatorial conformer of the ClCH adsorbed inside Si–Y is also slightly higher than that in ZSM-5 (83%). This may be attributed to that inside a supercage, three ClCH molecules pack in an orderly fashion which is more similar to that in pure ClCH solid than in liquid.

When temperature is lowered, the conformational equilibrium shifted in favor of the equatorial conformation. This is evident from the fact that the intensities of the axial ν_{21} and ν_{22} modes decrease gradually relative to their equatorial counterparts. As the temperature of the system is cooled to 233 K, the percentage of ClCH molecules in the equatorial form continues to increase up to 95%. At 173 K, the axial $\nu_{22}(\text{C–Cl})$ peak at 684 cm^{-1} almost disappeared completely. From the van't Hoff plot (Figure 4), the conformational enthalpy difference was calculated to be -6.5 kJ/mol.

Summary

In this work, we have investigated conformational properties of chlorocyclohexane adsorbed inside three zeolite hosts by variable-temperature FT-Raman spectroscopy. The results clearly demonstrate that the conformational behavior of ClCH strongly depends on the presence of charge-compensating cations and Si/Al ratio. The zeolite framework structure also affects the conformational equilibrium of the guest molecule. Compared to pure liquid, the equatorial conformation is clearly stabilized by the completely siliceous ZSM-5 framework. The increased equatorial population upon adsorption into ZSM-5 is attributed to the stronger van der Waals interaction between the siliceous framework and the equatorial conformer which has a larger molecular volume. The low-temperature spectra show that the axial and equatorial conformers are in dynamic equilibrium within the framework. The situation in the ClCH/Na–Y system is different. The ClCH molecules are in a statically disordered state without significant overall motion including the ring inversion. The disorder occurs via the strong sorbate–cation interactions, which freeze a ClCH molecule in a specific orientation as well as conformation. The dynamic conformational equilibrium can be reestablished via removing the Na^+ ions by using highly siliceous Y. In contrast to the ClCH/Na–Y system, the ClCH molecules in the supercage of Si–Y are more orderly packed.

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