THE JOURNAL OF
PHYSICAL
CHEMISTRY A

© Copyright 2001 by the American Chemical Society VOLUME 105, NUMBER 29, JULY 26, 2001

ARTICLES

An Investigation of the Dynamic and Conformational Properties of Alkylcyclohexanes Absorbed in Siliceous Zeolite ZSM-5

Yining Huang* and James Leech

Department of Chemistry, The University of Western Ontario, London, Ontario, Canada, N6A 5B7

Received: January 4, 2001; In Final Form: April 30, 2001

The dynamic and conformational behavior of three related alkylcyclohexane molecules, cyclohexane (CH), methylcyclohexane (MCH), and *trans*-1,4-dimethylcyclohexane (DMCH), loaded within completely siliceous zeolite ZSM-5 has been investigated by variable temperature FT-Raman spectroscopy. Our results indicate that at room temperature CH molecules inside the ZSM-5 framework undergo significant reorientational motions around different axes as well as ring inversion and that the reorientational motions have ceased when the temperature is lowered to 153 K. For MCH and DMCH, in contrast, the major molecular motions are removed upon initial loading into the ZSM-5 framework. At low temperatures, the symmetry of CH inside ZSM-5 clearly deviates from the perfect D_{3d} symmetry of the free molecule. At room temperature, the conformational equilibrium of MCH guest molecules still exists in the ZSM-5 host, but at low temperatures, MCH adopts the equatorial conformation exclusively. Interestingly, for DMCH absorption into ZSM-5 results in an increase in the population of the high-energy, small-volume diaxial conformer. The low-temperature Raman spectra of the ZSM-5 framework have also shown that for CH/ZSM-5 and MCH/ZSM-5 complexes, the zeolite framework is not rigid and undergoes significant thermal motion at room temperature. For DMCH/ZSM-5, the zeolitic framework also undergoes thermal motion, but there is a larger distribution of Si−O−Si angles.

Introduction

Zeolites are microporous materials that are widely used in industry as catalysts and sorbents. For example, several decades after it was first synthesized, zeolite ZSM-5 remains one of the most commercially significant zeolites and is commonly used in the petroleum industry to convert methanol into more complex hydrocarbons.[1] Applications of zeolite materials are, in many cases, related to the interactions between the zeolite framework and an absorbed guest species. Therefore, understanding the behavior of guest molecules inside zeolite hosts is very important.

Recently, several research groups have focused on the diffusion of alkylcyclohexanes in ZSM-5, namely cyclohexane (CH), methylcyclohexane (MCH), and *trans*-1,4-dimethylcyclohexane (DMCH).[2,3] Their findings indicated that the diffusion coefficient of *trans*-1,4-dimethylcyclohexane was 2 orders of magnitude larger than the diffusion coefficients of other two sorbates. Two arguments were put forward to explain the observed difference. Chon and Park attributed the difference to the methyl groups interacting with the framework to produce a favorable orientation for channel crossing.[2] Magalhães et al. suggested that this can be related to a low-energy barrier in channel crossing for the *trans*-1,4-dimethylcyclohexane molecules.[3] Very recently, our group preformed a powder-XRD study involving the absorption of CH, MCH, and DMCH into ZSM-5.[4] The focus was on the possible phase transitions of the zeolite induced by the sorbed organic species. Our results clearly indicated that CH/ZSM-5 and MCH/ZSM-5 systems show no

---

* To whom correspondence should be addressed. E-mail: yhuang@julian.uwo.ca.

10.1021/jp010048e CCC: $20.00

evidence of a phase change, but the absorption of DMCH does induce a monoclinic to orthorhombic phase transition in the ZSM-5 framework.

We have now turned our attention to the dynamic and conformational properties of these alkylcyclohexanes incorporated inside the ZSM-5 framework. Because Raman spectroscopy has proven to be a powerful tool in the analysis of dynamic and conformational behavior of molecular systems,[5] we have carried out a systematic variable temperature FT-Raman study of these alkylcyclohexane/ZSM-5 systems. Furthermore, the FT-Raman approach is actually a preferred technique for directly monitoring the behavior of the guest species inside zeolitic hosts because the weak Raman scattering of the zeolite framework allows one to observe the signals arising from the sorbate molecules.[6]

Experimental Section

Completely siliceous ZSM-5 was prepared according to a procedure previously described, with slight modification.[7] The sample purity and crystallinity were checked by powder X-ray diffraction. Cyclohexane ($>$99.9%), methylcyclohexane (spectro-grade) and 1,4-trans dimethylcyclohexane ($>$99.9%) were obtained from Aldrich Chemical Co., Eastman Kodak, and Fluka Chemika, respectively. All chemicals were used without further purification. ZSM-5 was calcined at 550 °C for 24 h to remove the organic template. Carefully weighed aliquots were loaded with precise amounts of the organic sorbates. The loading for all samples was 4 molecules per unit cell of ZSM-5. These samples were sealed in glass vials and placed in an oven for 3 h at 10 degrees below the boiling point of the organic molecule that was loaded. All Raman spectra were recorded on a Bruker RFS 100/S spectrometer equipped with an 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.

Results and Discussion

FT-Raman spectra of CH, MCH, and DMCH absorbed in completely siliceous ZSM-5 were measured as a function of temperature. To assist in interpreting the results, the spectra of pure CH and DMCH in their respective ordered solid phases at low temperature were also obtained. The dynamics of guest species can be monitored via the changes in Raman line widths as a function of temperature. In general, the line widths for these small organic molecules in liquid phases are rather broad due to molecular tumbling, whereas in an ordered solid phase the corresponding line width usually becomes much narrower.[8] As an important spectral parameter, the vibrational line width has been extensively employed to study the molecular dynamics associated with order–disorder phase transitions in many organic solids, including cyclohexane.[9]

A comparison between pure liquid cyclohexane and cyclohexane in ZSM-5 at room temperature exhibited virtually no difference in the line width for all of the bands observed. The spectral profile and line widths of the room-temperature spectrum of CH in ZSM-5 are also very similar to those of pure CH crystallizing in a disordered phase (phase I) where extensive molecular motions occur.[10] These results suggest that the cyclohexane molecules inside the ZSM-5 framework still undergo significant motions at room temperature. Conceivably, several explanations may describe the motion of the CH molecules within the framework. The first mechanism would be isotropic tumbling similar to the motion experienced by the molecules in the liquid. However, the cyclohexane molecules are believed to reside at the intersections of the straight and sinusoidal channels within the ZSM-5 framework.[11] The channel intersections form a spherical cavity with a diameter of about 8.7 Å,[12] whereas the kinetic diameter of the CH molecule is approximately 6.0 Å.[3] The close match in diameter implies that the CH molecules are probably not experiencing isotropic tumbling within the framework and a further explanation is needed. The stable chair conformation of cyclohexane (D_{3d} symmetry) has a C_3 principal rotation axis and 3 C_2-rotation axis perpendicular to this principal axis. The reorientation of the CH molecules about one or more of its rotation axis is probably a more reasonable explanation for the observed motion of the guest molecules. Indeed, these motions were detected in the plastic phase of pure CH solid.[13] A further contribution to the dynamic behavior may also be due to the inversion of the cyclohexane backbone between equal energy chair conformations. The activation energy for this process in pure liquid CH is approximately 10 kcal/mol,[14] and does not seem to be affected significantly by loading into the ZSM-5. The overall motion is most likely a combination of a reorientation about the molecular C_3 and C_2 axes coupled with ring inversion. A ^{2}H NMR study of cyclohexane in the acidic form of ZSM-5 confirmed that restrictions imposed by the framework at room-temperature prevent isotropic motion from occurring, and that a combination of several different motions is required to reproduce the ^{2}H NMR powder pattern.[15] With cooling, the full width at half-height (fwhh) of several bands due to the CH molecules decreases significantly with decreasing temperature. For example, the fwhh of the ν(C–C) band at 1026 cm^{-1} is ~14 cm^{-1} in both the liquid and the CH/ZSM-5 system (Figure 1A). When the CH/ZSM-5 system is cooled to 153 K the fwhh of this band is reduced to ~5 cm^{-1}. The narrowing of this and other bands implies that the dynamic nature of the guest molecule has changed. A previous single-crystal X-ray study of pure CH at 150 K indicated that in the ordered crystalline phase (phase II), all motions associated with cyclohexane molecules have ceased, with the exception of ring inversion.[16] We have also obtained the Raman spectrum of crystalline cyclohexane at 153 K. The spectrum shows that the fwhh of the C–C stretching mode ν(C–C) at 1026 cm^{-1} is ~4 cm^{-1}. This is an indication that within the zeolite the reorientational motion of cyclohexane molecules has ceased at 153 K, and the only remaining dynamic process is probably ring inversion.

A different situation was observed for the MCH/ZSM-5 and DMCH/ZSM-5 complexes. These two systems showed significant band narrowing for several bands upon loading into the zeolite framework. A comparison of the line width of the same ν(C–C) mode is given in Figure 1. At room temperature, the line width of this mode decreased by 6 and 4 cm^{-1} for the MCH and DMCH systems, respectively, upon absorption. Further cooling of these systems down to 153 K, however, did not result in a significant change in line width as was observed in the CH/ZSM-5 system. This line narrowing upon absorption implies that initial loading into the zeolite results in the removal of much of the molecular motion associated with the MCH and DMCH molecules. To further confirm these findings, we have also measured the FT-Raman spectrum of pure DMCH at 153 K. At this temperature, the pure DMCH crystallizes in an ordered phase where the molecular reorientational motions have ceased. The line widths in a majority of the bands of DMCH in the ordered crystal phase are comparable to those of the same bands

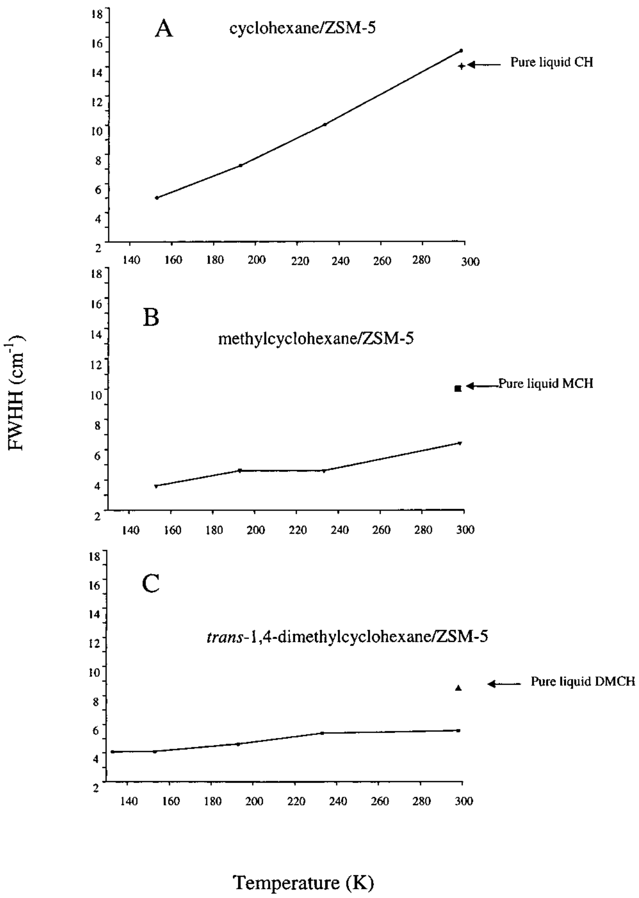

Figure 1. Temperature dependence of the full width at half-height (fwhh) in cm^{-1} for the ν(C−C) band of (A) CH, (B) MCH and (C) DMCH absorbed in ZSM-5.

of DMCH inside ZSM-5 at room temperature. For example, our data show that the line width for the ν(C−C) mode centered at 1060 cm^{-1} in the ordered crystal phase at 153 K is as narrow as ∼5 cm^{-1}. This value is the same as that of DMCH adsorbed in ZSM-5 at room temperature. These results confirm that the degree of molecular motion of the sorbed species has been limited due to confinement within the ZSM-5 framework. Other possible motions are the wobbling of the guest molecule around an axis directed along the two methyl bearing carbon atoms of the DMCH molecule, and ring inversion.

Low temperature Raman spectroscopy has also been used effectively for the conformational study of many organic molecules.[5] Therefore, it should provide valuable insight regarding the structural and conformational properties of guest molecules within the host structures. Liquid cyclohexane exists primarily in the stable chair conformer and possesses D_{3d} point group symmetry. Therefore, the Raman active modes have A_{1g} and E_g symmetry. Interestingly, when the CH/ZSM-5 complex was cooled to 153 K, all the A_{1g} modes remained as singlets, but several E_g modes split into doublets. For example, the E_g mode of CH absorbed in ZSM-5 due to the CH_2 twisting appeared as a single band positioned at 1267 cm^{-1} at room temperature. Upon cooling to 153 K, it is clearly split into two components (Figure 2). In the C−H stretching region the band centered at 2922 cm^{-1} in the spectrum of pure CH liquid has been assigned as an E_g mode due to the $\nu_{as}(CH_2)$.[17] Upon loading into the zeolite and cooling to 153 K, the line shape of this mode becomes asymmetric and a shoulder begins to develop at 2919 cm^{-1} (Figure 2). Deconvolution of this region indicates that the asymmetry of this peak is indeed due to the contribution of two separate bands, confirming that this doubly degenerate E_g mode is beginning to split (Figure 2). The observed splittings for the E_g modes of CH in ZSM-5 at 153 K are very similar to those found in the Raman spectra of ordered pure CH crystals at low temperatures, which have been reported in the literature[10] and obtained in this study. For instance, Figure 2 shows that the E_g mode at 2922 cm^{-1} is clearly split into a doublet at 148 K in the spectrum of the pure solid CH phase. A single crystal X-ray study has shown that at this temperature pure CH crystallizes in an ordered phase (phase II) and that the conformation of the CH molecules is still the chair configuration, but the symmetry is distorted significantly from D_{3d} (the site symmetry is only C_i).[16] This explains why in the corresponding Raman spectra all the doubly degenerate E_g modes are split. The similar splitting pattern for the E_g modes displayed in the spectra of pure solid CH and the CH molecules inside the zeolite at low temperature suggests that at 153 K the molecular symmetry of CH loaded inside the zeolitic framework must be lower than perfect D_{3d}, resulting in the removal of degeneracy of the E_g modes.

At room temperature, pure methylcyclohexane is known to exist in two rapid equilibrating conformations (95% with the methyl group in the equatorial position, and 5% with it in the axial position[14,18]). Bands due to the ring-breathing mode of MCH molecules appear in the Raman spectrum between 800 and 740 cm^{-1}. This region provides evidence for the existence of the two stable conformers of the molecule (Figure 3). Two peaks are observed in this region: a strong band at 770 cm^{-1} and a much weaker band at 753 cm^{-1}. They have been previously assigned unambiguously to the equatorial and axial components, respectively.[18] A previous study has shown that the axial mode observed in the spectrum of the pure liquid at room temperature disappears when cooled to 152 K, suggesting that MCH molecules in the pure liquid adopt the low-energy equatorial conformation exclusively at 152 K.[18] Upon loading MCH into the zeolite, the peak due to axial conformer, although very weak, is still visible (Figure 3), which indicates that a small portion of the MCH molecules retains the axial conformation. With cooling to 153 K, this peak disappeared, indicating that all the MCH molecules adopt the low-energy, equatorial conformation exclusively.

The conformational behavior of DMCH inside ZSM-5 is also worth mentioning. At ambient conditions, DMCH molecules in the pure liquid are known to exist primarily in the diequatorial conformation. An equilibrium does exist, however, between the diequatorial and diaxial conformers with relative populations of 99.7% and 0.3%, respectively.[14] Because of the low concentration of the diaxial conformer at ambient conditions, the room temperature Raman spectrum of pure liquid DMCH only contains the bands due to the diequatorial conformer. However, a number of vibrational studies on a series of pure dimethylcyclohexanes[19,20] and *trans*-1,4-dihalocyclohexane[21] have shown that when high external pressures are applied, the population of diaxial conformers was increased significantly due to the smaller molecular volume of the diaxial conformer (for example, the Cl−Cl distances are 5.24 and 6.32 Å for the aa and ee conformers of *trans*-1,4-dichlorocyclohexane, respectively.[21]), leading to an increased packing efficiency in the crystal.[20] In the present case, a significant increase in the population of the diaxial comformer upon loading was observed. This is evident from the change in the C−H stretching region of DMCH upon adsorption. Figure 4 shows that upon absorption, the band positioned at 2950 cm^{-1} in the spectrum of pure DMCH liquid split into a doublet and the splitting becomes more

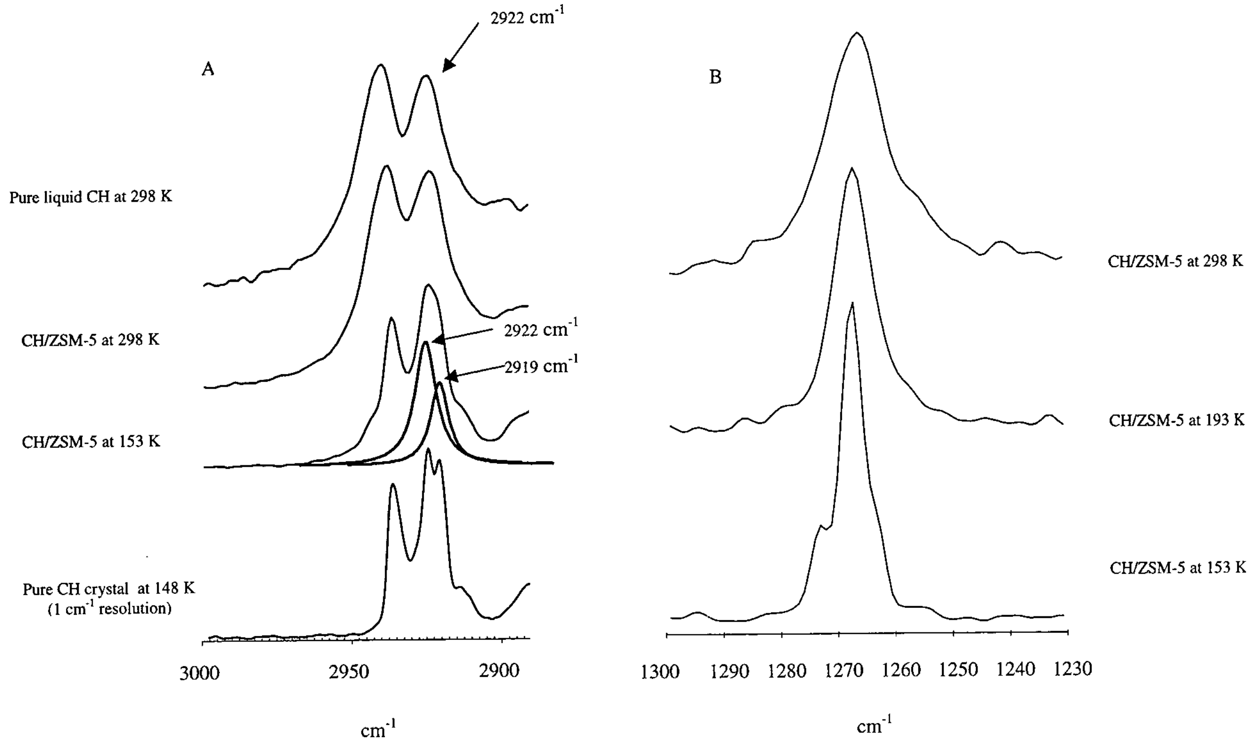

Figure 2. FT-Raman spectra of CH absorbed in ZSM-5, pure CH liquid and the ordered crystalline phase in selected spectral region at different temperatures.

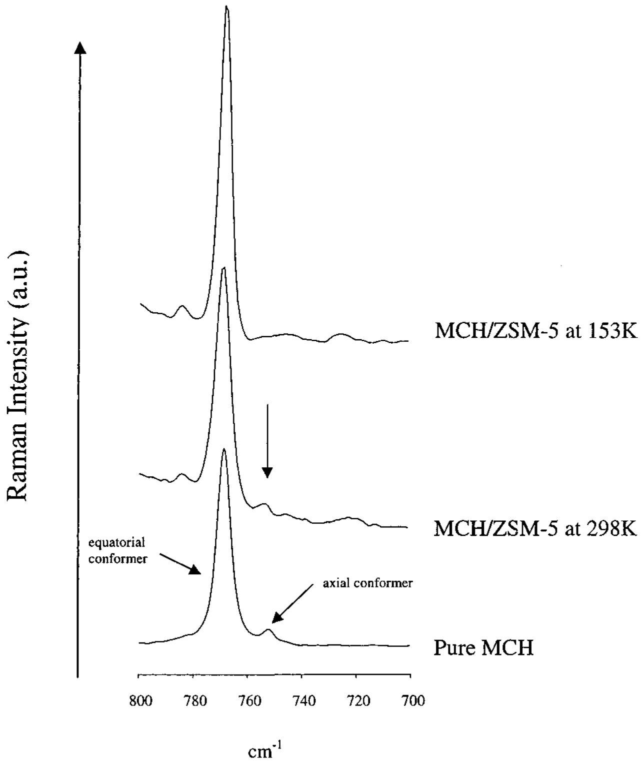

Figure 3. FT-Raman spectra of MCH sorbed in ZSM-5 at different temperatures and the pure liquid in ring breathing region.

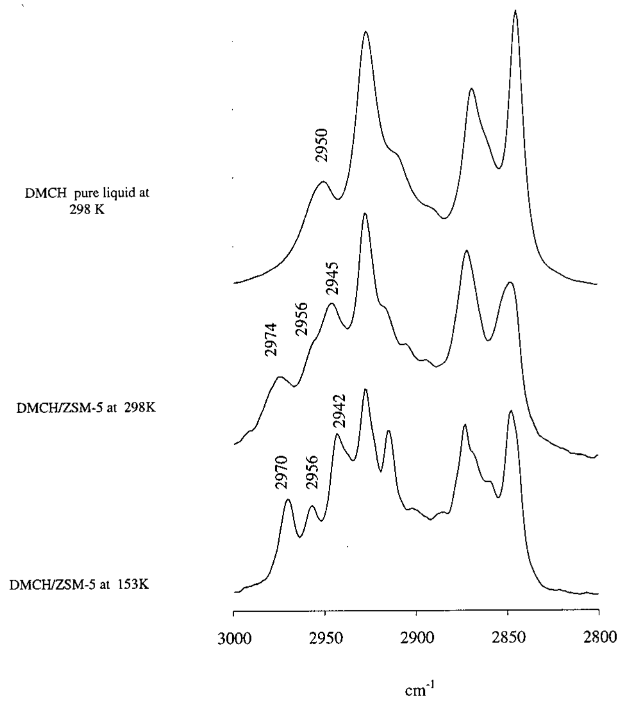

Figure 4. FT-Raman spectra of DMCH absorbed in ZSM-5 and the pure liquid at different temperatures in the C−H stretching region.

evident at low temperatures. The 2950 cm^{-1} band observed in the spectrum of pure DMCH can be assigned to the ν(CH) mode due to the methine groups and the $\nu_{as}(CH_3)$, which are accidentally degenerate.[20,21] The splitting observed upon absorption indicates that there are significant interactions between the zeolitic framework and the C−H bonds of DMCH, which affect ν(CH) and $\nu_{as}(CH_3)$ differently, resulting in the removal of the accidental degeneracy. Upon absorption, a new band appeared at higher energies at 2974 cm^{-1} (Figure 4). The frequency of this new band is much higher than those of the C−H vibrations observed at ambient conditions for pure DMCH which adopts almost exclusively the ee conformation. These observations are consistent with the conformational changes reported for *trans*-1,4-dichlororcyclohexane (which has the same C_{2h} symmetry as DMCH). An early study by Ellestad et al. showed that careful annealing can yield a solid phase of *trans*-1,4-dichlorocylohexane in which all of the molecules adopt the aa conforma-

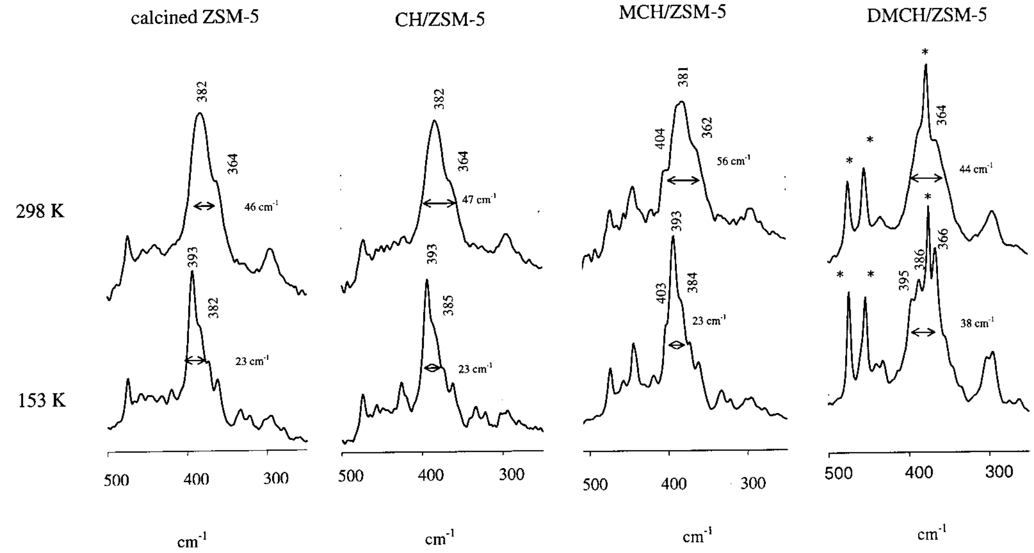

Figure 5. FT-Raman spectra of zeolitic framework vibrations of unloaded ZSM-5, CH/ZSM-5, MCH/ZSM-5, and DMCH/ZSM-5 in the Si−O−Si bending region at 298 and 153 K. The bands labeled with * are due to the sorbate molecules.

tion.[21] The formation of this "aa" phase was accompanied by the appearance of several characteristic "aa" bands, including a strong band in the high-energy side of the C−H stretching region at 2989 cm^{-1}. This band was assigned to the C−H stretching vibration due to the methine group of the aa conformer, whose frequency is much higher than that of the corresponding band for the ee conformer (2963 cm^{-1}).[21] As pointed out by Fyfe et al. there is considerable evidence from physical organic chemistry that methyl groups and chlorine atoms have identical steric effects,[22] so we assigned the new band at 2974 cm^{-1} to the DMCH with the aa conformation. Our Raman data suggest that upon loading, a significant portion of DMCH adopts the aa conformation, which has a smaller-volume. Inside ZSM-5, DMCH is located at the intersection of straight and zigzag channels.[3] As mentioned earlier, the channel intersections have a spherical cavity with a diameter of about 8.7 Å, which is very close to the kinetic diameter of DMCH (> 9 C).[3] Obviously, such a "tight fit" is the reason DMCH undergoes a conformational change from lower energy ee conformation with a larger molecular volume to higher energy aa configuration with a smaller volume. Upon lowering the temperature, the aa band at 2974 cm^{-1} becomes slightly more intense, implying that the population of aa conformer is further increased. This is because upon cooling, the unit cell of ZSM-5 shrinks slightly. Consequently, the increased constraints imposed by the zeolitic framework at low-temperature further shifts the conformational equilibrium in favor of diaxial conformer. However, the severe band overlap precludes us from determining the conformational energy change quantitatively.

The zeolitic framework vibrations also exhibited some interesting changes with temperature. The most intense Raman bands due to the ZSM-5 framework appear in the region between 450 and 250 cm^{-1} (Figure 5). The bands in this region arise from Si−O−Si bending vibrations.[23] For CH/ZSM-5 complex, the most prominent zeolitic vibrations include a relatively intense peak centered at 382 cm^{-1} and a shoulder at 364 cm^{-1}. The overall profile is rather broad at room temperature with the fwhh of ~47 cm^{-1}. This broadness may arise from one or a combination of two possibilities. First, for ZSM-5 there are a large number of nonequivalent Si−O−Si linkages within the framework.[24] This may result in a broad spectral envelope due to many closely lying unresolvable Si−O−Si bending vibrations corresponding to the contributions from all the Si−O−Si bonds. Second, the Si−O−Si linkage or Si−O−Si bond angles may undergo large-amplitude thermal motions at room temperature, which would also yield a broad profile. Low-temperature Raman measurements should shed light on the origin of this broadning. If the first explanation is correct, a decrease in temperature will not affect the distribution of nonequivalent Si−O−Si bond angles significantly and, as a result, no significant line narrowing should occur. In the second case, lowering the temperature should reduce the thermal motions of the Si−O−Si linkages, leading to substantial band narrowing. In the CH/ZSM-5 system the width of the profile decreased from ~47 cm^{-1} to ~23 cm^{-1} (Figure 5) upon decreasing temperature, which indicates that the Si−O−Si linkages in ZSM-5 have relatively large thermal motions at room temperature. Our Raman data indicate clearly that the lattice of ZSM-5 is reasonably flexible at room temperature, as proposed by Muller and Conner.[11] It is also interesting to note that at 153 K, the band at 382 cm^{-1} together with the shoulder at 364 cm^{-1} are shifted toward higher energies to 393 and 385 cm^{-1}, respectively. It has been shown previously that the frequencies of the T−O−T bending modes of zeolites (T = Si or Al) are sensitive to the average T−O−T angle. The frequency of a T−O−T bending mode has an inverse dependence on the average T−O−T angle,[23] meaning that a higher T−O−T bending frequency corresponds to a smaller average T−O−T angle. In the present case, the observed high-frequency shift suggests that the shrinkage of the ZSM-5 unit cell at low temperatures is accompanied by the reduction in the average Si−O−Si angle. It should also be pointed out that the spectral profile due to zeolitic vibrations for CH/ZSM-5 complexes and its behavior at low temperature are identical to those of unloaded (empty) ZSM-5 (Figure 5). This similar behavior is due to the fact that the framework structures of CH/ZSM-5 and unloaded ZSM-5 are both monoclinic as shown by powder XRD studies.[4,11] However, the similarity also implies that the interactions between CH and the framework are weak.

For the MCH/ZSM-5 complex, our previous study showed that the PXRD pattern of MCH/ZSM-5 is identical to those of CH/ZSM-5 and calcined (unloaded) ZSM-5, suggesting that the structure of MCH/ZSM-5 is also monoclinic.[4] Figure 5 shows the zeolitic bands of MCH/ZSM-5 at both 298 and 153 K. The overall spectral appearance at room temperature looks very similar to that of CH/ZSM-5 and unloaded ZSM-5. The framework vibrations of the MCH/ZSM-5 complex also behaved similarly to CH/ZSM-5 and unloaded ZSM-5 upon lowering the temperature. These observations are expected since the framework symmetry of all three systems is monoclinic. However, a careful inspection of the spectra reveals a subtle difference. For MCH/ZSM-5, there is a new band positioned at 404 cm^{-1} which appears as an obvious shoulder on the high-frequency side of the 381 cm^{-1} main band. The appearance of this new peak is an indication that the zeolitc framework undergoes a noticeable distortion upon absorption of MCH, implying that the interaction between MCH and the framework is stronger than that in the CH/ZSM-5 complex.

For the DMCH/ZSM-5 system, however, the situation is much different. At 153 K, instead of one broad envelope, some peak sharpening was observed in this region. The profile now clearly encompasses at least 3 well resolved zeolitic bands at 395, 386, and 366 cm^{-1}, indicating that the Si−O−Si linkages undergo thermal motion at room temperature, but the overall width of the profile remains about the same ∼40 cm^{-1} upon cooling (Figure 5). The DMCH/ZSM-5 system possesses orthorhombic symmetry,[4] which is different from the CH/ZSM-5 and MCH/ZSM-5 systems. The low-temperature Raman results indicate that in the orthorhombic phase there is a larger distribution of the Si−O−Si linkages, implying that the interactions between the DMCH and the ZSM-5 framework are much stronger.

Summary

Our variable temperature FT-Raman spectroscopic study has shown that the ZSM-5 framework has different influence on the dynamic and conformational characteristics of three related alkylcyclohexane derivatives. For the smaller CH molecules, significant motion within the ZSM-5 host seems to be retained upon loading, and only with cooling are these motions frozen out. For the larger DMCH molecules, initial loading into ZSM-5 was sufficient to limit the molecular dynamics of the DMCH molecules, and upon cooling little change was observed in the dynamic properties. The structural and conformational properties of the three alkylcyclohexanes are different. The symmetry of CH inside ZSM-5 deviates from perfect D_{3d} at low temperatures. For MCH molecules loaded at room temperature, the conformational equilibrium is similar to that found for the pure liquid MCH. At low temperatures, MCH molecules exist exclusively in the equatorial conformation. For the larger DMCH molecules at room temperature, both the diequatorial and the diaxial conformations are adopted upon initial loading, and the population of diaxial conformer seems to increase slightly with decreasing temperature. Our study also suggests that for CH/ZSM-5 and MCH/ZSM-5 complexes, the zeolite framework is not rigid and undergoes significant thermal motion at room temperature. For DMCH/ZSM-5, the framework also undergoes thermal motion and there is a larger distribution of Si−O−Si angles. The unique ability of DMCH to adopt a conformation of smaller volume and to induce a structural change in the host framework may be responsible for the unusually large diffusion coefficient of DMCH in ZSM-5 compared to CH and MCH.

Acknowledgment. Y.H. acknowledges the Natural Science and Engineering Research Council of Canada for a research grant and the award of an FT-Raman spectrometer.

References and Notes

(1) Bhatia, S. *Zeolite Catalysis: Principles and Applications*; CRC Press: Boca Raton, 1990.

(2) Chon, H.; Park, D. H. *J. Catal*. **1988**, *114*, 1.

(3) Magalhaes, F. D.; Laurence, R. L.; Conner, W. C. *J. Phys. Chem. B* **1998**, *102*, 2317.

(4) Huang, Y.; Havenga, E. A. *Langmuir* **1999**, *15*, 6605.

(5) Gardiner, D. J.; Graves, P. R. *Practical Raman Spectroscopy*. Springer-Verlag: New York, 1989, p 104.

(6) (a) Huang, Y. *J. Am. Chem. Soc.* **1996**, *118*, 7233. (b) Huang, Y.; Havenga, E. A. *J. Phys. Chem. B* **2000**, *104*, 5084. (c) Huang, Y.; Havenga, E. A. *Chem. Mater*. **2001**, *13*, 738. (d) Crawford, M. K.; Dobbs, K. D.; Smalley, R. J.; Corbin, D. R.; Maliszewskyj, N.; Udoric, T. J.; Cavanagh, R. R.; Rush, J. J.; Grey, C. P. *J. Phys. Chem. B* **1999**, *103*, 431.

(7) Robson, H. *Collection of Verified Zeolite Synthesis. Microporous Mesoporous Mater*. **1998**, *22*, 628.

(8) Sushchinskii, M. M. *Raman Spectra of Molecules and Crystals.* Israel Program for Scientific, New York, 1972.

(9) (a) Bailey, R. T. In *The Plastically Crystalline State*; John Wiley & Sons: New York, 1972 p 233. (b) Huang, Y.; Gilson, D. F. R.; Butler, I. S. *J. Phys. Chem.* **1993**, *97*, 1998. (c) Haines, J.; Gilson, D. F. R. *J. Phys. Chem*. **1989**, *93*, 6237. (d) Huang, Y.; Gilson, D. F. R.; Butler, I. S. *J. Phys. Chem.* **1992**, *96*, 1151. (e) Huang, Y.; Gilson, D. F. R.; Butler, I. S. *J. Phys. Chem.* **1991**, *95*, 5051.

(10) Ito, M. *Spectrochim. Acta* **1965**, *21*, 2063.

(11) Müller, J. A.; Conner, W. C. *J. Phys. Chem.* **1993**, *97*, 1451.

(12) Xiao, J.; Wei, J. *J. Chem. Eng. Sci.* **1992**, *47*, 1123.

(13) Andrew, E. R.; Eades, R. G. *Proc. R. Soc.* London, 1953, p 398.

(14) Eliel, E. L.; Allinger, N. L.; Angyal, S. J.; Morrison, G. A. *Conformational Analysis 3rd ed.*; John Wiley & Sons. Inc: New York, 1965, Chapter 2 and references therein.

(15) Aliev, A. E.; Harris, K. D. M. *J. Phys. Chem. A.* **1997**, *101*, 4541.

(16) Khan, R.; Fourme, R.; André, D.; Renaud, M. *Acta Crystallogr*. **1973**, *B29*, 131.

(17) Dows, D. A. *J. Mol. Spectrosc.* **1965**, *16*, 302.

(18) Hankin, S. H.; Khalil, O. S.; Goodman, L. *Chem. Phys. Lett.* **1979**, *63*, 11.

(19) Dare-Edwards, M. P.; Gardiner, D. J.; Walker, N. A. *Nature* **1985**, *316*, 614.

(20) Gardiner, D. J.; Walker, N. A.; Dare-Edwards, M. P. *Spectrochim. Acta* **1987**, *43A*, 21.

(21) Ellestad, O. H.; Klaeboe, P. *J. Mol. Struct.* **1975**, *26*, 25.

(22) Fyfe, C. A.; Strobl, H.; Gies, H.; Kokotailo, G. T. *Can. J. Chem.* **1988**, *66*, 1942.

(23) Dutta, P. K.; Shieh, D. C.; Puri, M. *Zeolites* **1988**, *8*, 306.

(24) (a) van Koningsveld, H.; van Bekkum, H.; Jansen, J. C. *Acta Cryst.* **1987**, *B43*, 127. (b) van Koningsveld, H.; Jansen, H.; van Bekkum, H. *Zeolites* **1990**, *10*, 235.