Stabilization of a distorted conformation of cyclohexane adsorbed in the voids of silicalite-1

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The dimensions and topology of the voids in porous zeolites can influence the conformational geometry of guest molecules confined within it. Here we report an infrared and Raman vibrational spectroscopic study of cyclohexane confined within the voids of a medium-pore zeolite, Silicalite-1. We find that on confinement two conformers of cyclohexane are in thermal equilibrium, one of which lacks a center of inversion and is the preferred conformation at lower temperatures. Molecular modeling supports this observation; in the intersection-voids of Silicalite-1 host–guest dispersive interactions favour a distorted-chair conformer of cyclohexane with symmetry lower than D_{3d}. The results are compared with those for cyclohexane confined in the comparatively larger voids of Zeolite-Y, where it is known to exist exclusively in the chair conformer.

KEY WORDS: adsorption; cyclohexane; conformation; vibrational spectra; silicalite-1.

1. Introduction

The void spaces in zeolitic solids provide a convenient way of confining organic guests and controlling their reactivity [1–3]. The host zeolite can influence conformational properties of the included guest as well as the reactant environment. This has been widely exploited to promote one of several possible photochemical, photophysical or reaction pathways [4]. The conformation of flexible molecules in zeolites, as in other inclusion compounds, is strongly dependent on non-bonding or dispersive interactions optimized by size and shape considerations. The dimensions and topology of the void can force a confined guest molecule to adopt conformations different from what it possesses outside, either in the gaseous, liquid or solid state. Here we report a vibrational spectroscopic and molecular modeling study of the conformation of cyclohexane confined in the voids of a medium-pore zeolite, Silicalite-1.

The flexibility of a cyclohexane molecule arising from the carbon–carbon single bond network allows the ring to adopt different conformations. As pointed out by Sachse [5], as far back as the 1890s, two non-planar geometries of cyclohexane, the chair (D_{3d}) and boat (C_{2v}) conformations, may be constructed in which all carbon atoms have the tetrahedral angle and the rings free of angular strain. The absence of bond-opposition or eclipsing strain makes the chair form considerably more stable, as confirmed by electron-diffraction experiments [6]. Unfavorable eclipsing interactions in the boat form may be partially alleviated by a twist distortion. The twist-boat (D_2) and boat (C_{2v}) conformers are related by a pseudo-rotation with the former about 600 cal. below the boat, which is at a saddle-point on the pseudo-rotation path [7]. Experimental data on strained cyclohexane derivatives indicate that the twist-boat conformer lies about 5–6 kcal/mol above the chair form [8], while theoretical calculations in the range 1.31–10.6 kcal/mol [9]. The equilibrium population of the twist form at room temperature is, therefore, expected to be about 0.1%. Direct spectroscopic investigations of the twist conformer have been reported by Squillacote *et al.* [10] and Offenbach et al. [11] who obtained the matrix isolated infrared (2000–600 cm^{-1}) spectra of the twist-boat conformer by condensing hot (1200 K) cyclohexane vapor in an argon matrix. A number of new bands were observed and were attributed to the twist form of cyclohexane. Non-chair conformers of cyclohexane can, in principle, be distinguished spectroscopically from the chair conformer by the absence of inversion symmetry in the later.

Silicalite-1, the purely siliceous version of ZSM-5, is a medium-pore zeolite, the structure of which consists of a set of sinusoidal channels intersecting a set of straight channels each with 10-membered rings. The diameter of the circular sinusoidal channels is 5.4 Å and that of the elliptical straight channel is 5.7–5.1 Å, while the intersections, that are almost spherical, have a diameter of 8.7 Å. The kinetic diameter of cyclohexane, 6 Å, is comparable with that of the intersection and consequently conformational changes on confinement may be expected and indeed earlier Raman studies did suggest that the geometry could be different from the chair form [12]. The influence of zeolitic void

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topology and dimension on conformation of chlorocyclohexanes has been reported. FT-Raman studies indicate that on adsorption in ZSM-5 the equatorial conformation of these substituted cyclohexanes is stabilized as compared to the axial conformer [13,14]. Detailed grand canonical Monte–Carlo (GCMC) simulations of flexible, non-rigid cyclohexane molecules in Silicalite-1 have shown that good agreement with experimental adsorption isotherms are obtained when there is a significant enhancement in the concentration of boat conformers (2–6%) of the adsorbed cyclohexane as compared to the concentration (0.1%) in the gas phase [15]. Diffraction studies have indicated that adsorption of cyclohexane does not lead to any change in the structure of the zeolite and consequently may be considered as a rigid confining environment [16]. Here we use IR and Raman vibrational spectroscopy along with molecular mechanics and Monte–Carlo docking calculation to investigate the conformational geometry adopted by cyclohexane in the voids of Silicalite-1. We compare these results with those of cyclohexane confined in the much larger voids of Zeolite-Y. This zeolite consists of ~ 12 Å diameter supercages tetrahedrally interconnected by 12-membered ring windows with an opening of 7.4 Å. Diffraction studies as well as calculations have confirmed that cyclohexane adopts the chair conformation in Zeolite- Y [17].

2. Experimental

2.1. Vibrational Spectra

Infrared spectra were recorded on a Perkin-Elmer Spectrum-2000 FT-IR spectrometer in the diffuse reflectance mode using a DRIFT (P/N 19900 series) accessory with a cooled MCT detector. The sample chamber consisted of water-cooled stainless steel block with a zinc selenide window. Sample temperatures could be controlled between 273 and 773 K and could also be ramped at rates between 10 and 20 min for Temperature Programmed Desorption (TPD) measurements. The sample chamber was connected to a gas handling manifold and also on-line to a quadrupole mass spectrometer (SRS QMS300 series gas analyzer). The zeolite samples were activated in the infrared sample chamber by heating in a stream of Helium at 673 K for 2 h, prior to dosing with known volumes of cyclohexane. Infrared spectra were collected by co-adding 128 scans at a resolution of 2 cm^{-1}. The zeolite, activated under similar conditions as in the adsorption measurements, was used to record the background spectra. The infrared spectra reported here are, therefore, difference absorbance spectra of the zeolite with and without adsorbed cyclohexane. For variable temperature measurements the background spectra, too, was recorded at different temperatures. Raman spectra were recorded on a Bruker RFS 100/S FT-Raman spectrometer at 2 cm^{-1} resolution with an un-polarized beam. Laser power was kept at 100 mW and typically 2000 spectra were co-added to improve signal-to-noise. The zeolite samples were sealed in quartz tubes with known volumes of cyclohexane and equilibrated at 340 K.

Silicalite-1 was prepared following the procedure reported in Ref. [18]. Protonated Zeloite-Y (Si/Al = 2.4) was prepared by ion-exchanging Na ions with ammonium ions followed by calcination in air at 823 K. The amount of cyclohexane adsorbed in both infrared and Raman measurements was typically 3 μL/40 mg of Silicalite-1 and 3 μL/40 mg for Zeolite-Y. These concentrations correspond to four molecules of cyclohexane per unit cell of Silicalite-1 and 8 molecules of cyclohexane per unit cell of Zeolite-Y.

2.2. Molecular Modeling Methodology

Calculations of the location and energy minimization of flexible cyclohexane sorbate molecules in the zeolite host were implemented using software available from Molecular Simulation Inc. (MSI) [19]. The methodology involved three steps, molecular dynamics, Monte–Carlo docking and finally energy minimization. This method has been widely employed by different authors for docking flexible guest molecules in zeolites [20–22]. The procedure begins with a high-temperature molecular dynamics run for the cyclohexane molecule *in vacuo*. The resultant trajectories are sampled to produce a conformational library. The molecular dynamics calculations were carried out at 500 K using a 1 fs time step, with 10 conformations obtained by sampling every 10 fs. The molecular dynamics calculation at 500 K does not sample the entire conformational space of the cyclohexane molecule since the barrier for conversion from the chair to the twist boat is extremely high (~−10.5 kcal/mol) [8]. Consequently the molecular dynamics calculations were initiated from two different starting geometries, the chair and twist-boat conformations of cyclohexane. The molecular dynamics calculations were carried out using the consistent valence force field (CVFF) as part of the Insight II program [21, 22]. The calculated difference in energy between the twist-boat and chair conformers of cyclohexane using this force field is 9.3 kcal/mol. The docking procedure involves the random selection of positions and orientations for the cyclohexane molecule, from the conformational library generated in the molecular dynamics calculation, within the zeolite structure. These structures are screened by calculating the van der Waals energy. Only dispersive Lennard–Jones type interactions were considered; the long-range electrostatic contribution was ignored. For different conformations the process is continued until a satisfactory docked structure is achieved, with the van der Waals energy threshold being chosen to give a sterically reasonable set of structures. Finally, each candidate's docked structure is subjected to optimization by energy minimization using the CVFF force field. The cyclohexane molecule as well as the zeolite framework was allowed to relax in the final energy minimization stage.

The host–guest interaction or binding energy of cyclohexane inside the zeolite pore was taken as the minimized potential energy (E_{total}) of the host–guest ensemble minus the potential energy of each component.

$$E_{\text{interaction}} = E_{\text{total}} - E_{\text{host}} - E_{\text{guest}}.$$

These calculations were performed on a siliceous MFI zeolite lattice with unit cell values of x, y, z from –1, 0, 0 to 1, 1.5, 3. In both the docking and minimization stages, periodic boundary conditions were not applied. A cutoff of 12 Å was used for the van der Waals' term and 10,000 iterations were performed in each step of the solids docking calculation. For Zeolite-Y the calculations were carried out on a siliceous FAU lattice with unit cell values for x, y, z were from 0, 0, 0 to 2, 2, 2. The use of a siliceous Zeolite-Y circumvents the problem of dealing with a disordered distribution of protons. Similar approximations have been made in earlier calculations [17], the justification being the non-planar nature of the cyclohexane sorbate molecule. Hydrogen dummy atoms were incorporated in the Sodalite cages. Such procedures have been widely employed in the literature to avoid un-realistic insertion of guest molecules in the sodalite cages of the FAU lattice [17].

3. Results and discussions

3.1. Vibrational Spectra

The infrared and Raman spectra of cyclohexane in Silicalite-1 and Zeolite-Y are similar to that of liquid cyclohexane and consequently the assignments too (see supplementary information). There are, however, notable differences in the infrared and Raman spectra, in the methylene-stretching region, of cyclohexane adsorbed in Silicalite-1 and Zeolite-Y figure 1a and b. A comparison of the spectra shows that both the infrared and Raman spectra of cyclohexane in Silicalite show additional features (indicated by arrows in figure 1). In this region there are no contributions from the zeolite lattice and moreover, as mentioned in the experimental section, the spectra in figure 1 are difference spectra. For both Silicalite-1 and Zeolite-Y the quality of the spectra below 2000 cm^{-1} was poor and extremely noisy.

We first consider the vibrational spectra of cyclohexane in Zeolite-Y where it is known to adopt the chair conformer [17]. The assignment of the bands is straightforward since the spectra are similar to that of cyclohexane in the gas/liquid phase [23]. In the infrared spectra, the band at 2854 cm^{-1} (2862 cm^{-1}) is the CH$_2$ symmetric stretch (a$_{2u}$, e$_u$ coincidence band), the shoulder at 2912 cm^{-1} (2914 cm^{-1}) the methylene C–H antisymmetric stretch (a$_{2u}$) and the band at 2932 cm^{-1} (2933 cm^{-1}) the CH$_2$ antisymmetric stretch (e$_u$) (the figures in parenthesis are the corresponding gas phase values and the irreducible representation those of D$_{3d}$ symmetry). In the Raman spectra the band at 2853 cm^{-1} (2853 cm^{-1}) is the methylene symmetric stretch (a$_{1g}$) and the bands at 2925 cm^{-1} (2924 cm^{-1}) and 2940 cm^{-1} (2939 cm^{-1}) C–H antisymmetric stretching modes of e$_g$ and a$_{1g}$ symmetries, respectively. The fact the vibrational spectral frequencies of cyclohexane in H-Zeolite-Y are close to the gas-phase values suggests that interaction between the non-polar cyclohexane and the extra framework charge compensating protons are not significant.

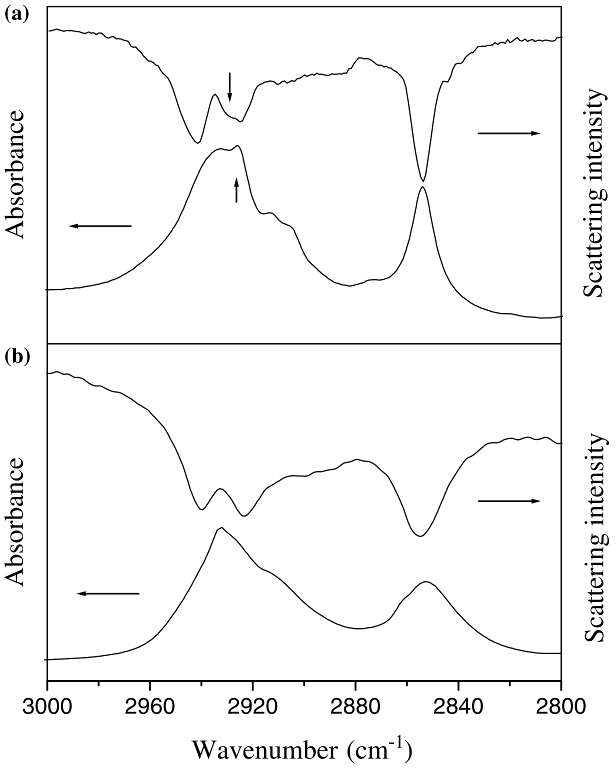


Figure 1. Infrared and Raman spectra of the C–H stretching region of cyclohexane adsorbed in (a) Silicalite-1 and (b) Zeolite-Y.

The vibrational spectra of cyclohexane in Silicalite-1, in addition to the above features, shows a sharp band at 2927 cm^{-1} in the infrared spectra and a broad shoulder at 2930 cm^{-1} in the Raman. Earlier Raman studies had observed an asymmetric broadening of the CH antisymmetric stretching (e$_g$) mode [12]. A comparison of the infrared and Raman spectra (figure 1a) shows that the additional feature at 2927 cm^{-1} in the infrared appears at the same position as an existing feature in the Raman spectra of cyclohexane in Zeolite-Y, i.e., the chair conformer (figure 1b). The additional feature in the Raman, too, has a corresponding feature in the infrared of the chair conformer. It thus appears that the infrared and Raman bands of cyclohexane that are disallowed in the chair conformer as a consequence of the mutual exclusion principle, become allowed when cyclohexane is confined within Silicalite-1. The consequence of confinement is therefore a loss of inversion symmetry; the degeneracy associated with the e_g and e_u modes of the chair form are lifted and all modes are infrared and Raman active. The vibrational spectra, therefore, indicates that on adsorption in Silicalite-1 the conformation of cyclohexane is distorted from the gas phase chair conformation. The magnitude of the distortion is likely to be small since the vibrational frequencies remain close to the gas phase values, but is, nevertheless, sufficient for the mutual exclusivity of infrared and Raman modes to be no longer valid. In the larger cavities of Zeolite-Y the chair (D_{3d}) conformation is retained. It is, unfortunately, not possible for a direct comparison of the present results (figure 1a) with the reported infrared spectra of the matrix isolated high-temperature twist conformer because the later could be recorded only in the methylene bending region [10, 11]. As mentioned earlier the quality of the spectra in the methylene bending region for cyclohexane in Silicalite-1 was poor. Nevertheless, the observations are similar in that for the infrared spectra of the matrix-isolated species, too, additional features could be assigned to infrared-disallowed modes of the chair conformer.

We have examined the temperature variation of the infrared spectra of cyclohexane in Silicalite in the temperature range 278–358 K figure 2. In this temperature range we establish from on-line TPD as well as from infrared intensity measurements that no desorption of cyclohexane occurs. The TPD of cyclohexane in Silicalite-1 shows a single desorption profile with a peak at 426 K (see supplementary information). figure 2 shows that with increasing temperature the intensity of the 2927 cm^{-1} band decreases. The behavior is reversible; on cooling the intensity of the 2927 cm^{-1} band is recovered. We interpret these results as indicating that the conformation of the confined cyclohexane is not exclusively the distorted-chair geometry but is in equilibrium with the chair form. The equilibrium population of the two conformers changes with temperature, which is reflected in the infrared spectrum. The feature at 2927 cm^{-1} is due to the distorted-chair conformer while the band at 2932 cm^{-1} has contributions from both the distorted-chair and chair conformers. On the assumption that the stretching vibrations of the chair and distorted-chair form of cyclohexane have similar absorptivities the equilibrium constant, K, can be determined from the integrated intensities of the two features. The integrated intensities at different temperatures were obtained by decomposition of the individual spectrum between 3000 and 2880 cm^{-1} as a sum of three Lorentzians centered at 2934, 2927 and 2907 cm^{-1}. In the temperature range 278–358 K the total area under the spectrum between 3000 and 2880 cm^{-1} is constant. The position and linewidth of the features at 2934 and 2907 cm^{-1}, assigned to the chair conformer, in the spectra of cyclohexane in Silicalite-1 were not floated in the decomposition procedure but were kept fixed to the values of these features in the spectra of cyclohexane in Zeolite-Y figure 1b. The

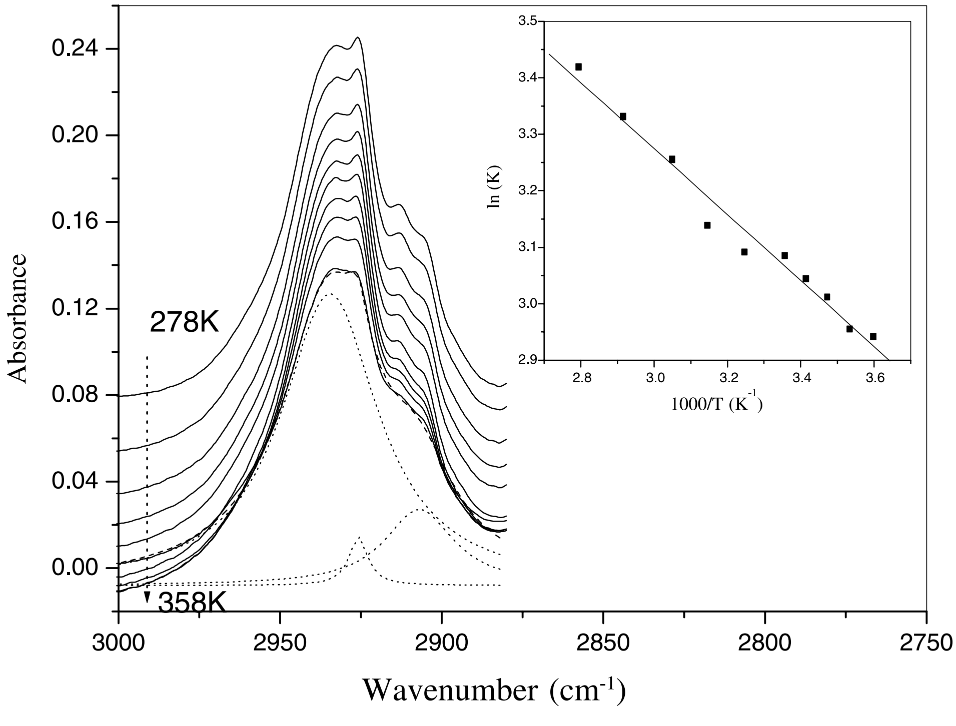


Figure 2. Infrared spectra in the methylene stretching region of cyclohexane in Silicalite-1 at different temperatures. Inset shows a van't Hoff plot, ln(K) vs [1000/T] K^{-1}. The equilibrium constant, K, was obtained from a decomposition of the spectra between 3000 and 2880 cm^{-1} as a sum of Lorentzians (see section 5). The dotted line shows the individual Lorentzians in the decomposition of the spectra at 358 K and the dashed line the overall fit.

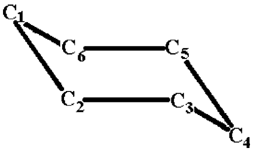
equilibrium constant so determined was found to obey the vant Hoff relation (inset of figure 2) with a ΔH (*distorted-chair* to *chair*) value of 1.1 kcal/mol. To summarize, vibrational spectroscopy indicates that when cyclohexane is confined within the voids of Silicalite-1 a conformer that lacks inversion symmetry is stabilized as compared to the chair (D_{3d}) conformer.

3.2. Molecular modeling

In order to understand the origin of the observed difference in the geometry of cyclohexane adsorbed in Silicalite-1 and Zeolite-Y a computational investigation was undertaken. The host–guest interaction energy for a flexible cyclohexane molecule inside the zeolite pores was calculated using the Monte–Carlo docking procedure for non-rigid molecules. In these calculations the first step involved the generation of a conformational library from a high temperature (500 K) molecular dynamics simulation, starting from the chair (D_{3d}) conformer of cyclohexane. Simulations were also initiated from the twist-boat (D_2) geometry of cyclohexane. The D_{3d} and D_2 geometries were the optimized geometry reported by Komornicki and McIver [24]. The generated conformers were then 'docked' within the zeolite. The interaction energy given is the lowest out of 10 possible conformations. The binding energy for calculations initiated from the twist-boat conformer were much higher (−11.9 kcal/mol) than those initiated from the chair conformer (−20.8 kcal/mol) and were, therefore, not pursued.

In Silicalite-1 the preferred location for adsorbed cyclohexane is the intersection of the straight and sinusoidal channels and the corresponding binding energy, −20.8 kcal/mol. There are four such intersections per unit cell and this observation would therefore explain why the saturated loading is four cyclohexane molecules per unit cell of Silicalite. These observations are in agreement with earlier GCMC simulations as well as ^{2}H NMR studies which indicated that the preferred location for cyclohexane molecules are the relatively large intersection voids of Silicalite-1.

Table 1
Conformational analysis of cyclohexane after Monte–Carlo docking and energy-minimization in Silicalite-1 and Zeolite-Y

	Cyclohexane / Silicalite-1	Cyclohexane / Zeolite-Y
C_1–C_2–C_3	112.30	112.40
C_2–C_3–C_4	111.88	112.21
C_3–C_4–C_5	111.83	112.20
C_4–C_5–C_6	112.15	112.23
C_5–C_6–C_1	112.29	112.25
C_6–C_1–C_2	112.65	112.44
Mean C–C–C angle	112.18	112.29
C_1–C_2–C_3–C_4	−52.77	−52.16
C_2–C_3–C_4–C_5	54.05	52.65
C_3–C_4–C_5–C_6	−53.93	−52.85
C_4–C_5–C_6–C_1	52.44	52.47
C_5–C_6–C_1–C_2	−51.17	−51.99
C_6–C_1–C_2–C_3	51.44	51.87
Mean dihedral angle	52.63	52.33
Standard deviation from mean dihedral angle	1.1	0.35

The geometry of the adsorbed cyclohexane molecule, for which the binding energy was a minimum, was examined by analyzing the dihedral C—C—C—C angles. For the optimized D_{3d} geometry of cyclohexane, from which the present simulations were initiated, all the six C—C—C—C dihedral angles are the same, 52.59°. On adsorption in Silicalite-1 the situation is altered. The six dihedral angles are no longer identical (Table 1). The mean value of the dihedral angle, 52.63, is still close to that of the chair conformer but the distribution, as characterized by the standard deviation, is large, 1.1. This suggests that the geometry of the adsorbed cyclohexane, associated with the lowest binding energy, is a distorted chair conformer with symmetry lowered from D_{3d} to probably C_1.

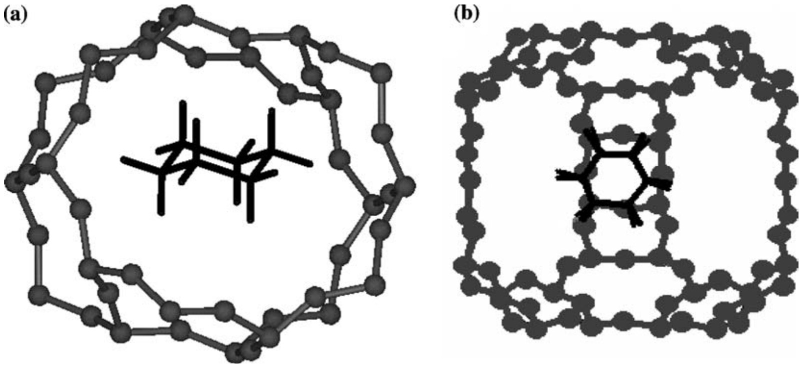


Figure 3. Molecular graphics representation of the conformation and location of cyclohexane having the minimum potential energy (a) distorted-chair conformer in the intersection voids of Silicalite-1 (as viewed looking down the straight channel) and (b) cyclohexane molecule near the 6-ring window of the supercage in Zeolite-Y.

In the FAU-Zeolite-Y lattice the preferred location is close to the six-ring window near the wall of the supercage figure 3 and the binding energy is −13.1 kcal/mol. This value is comparable to the heat of adsorption values reported in earlier calculations. The geometry of the cyclohexane molecule in Zeolite-Y (table 1) showed that although there is a change in the mean value of the dihedral angle from that of the optimized gas phase geometry the distribution of values (standard deviation = 0.35) is much smaller than that for cyclohexane in Silicalite. The D_{3d} symmetry of the gas phase is retained on adsorption in Zeolite-Y.

The results of the molecular modeling calculations are in agreement with the spectroscopic observations that had indicated that on adsorption in Silicalite-1 the cyclohexane molecule lacks inversion symmetry whereas in Zeolite-Y it is preserved. The calculations show that a distorted-chair conformer is the preferred geometry of cyclohexane in Silicalite-1.

4. Conclusions

The conformation of cyclohexane confined in the voids of a medium-pore Zeolite, Silicalite-1, has been investigated using infrared and Raman vibrational spectroscopy. The results have been compared with those for cyclohexane adsorbed in the much larger voids of Zeolite-Y, where it is known to exist exclusively in the chair conformer [17]. The infrared and Raman spectra of cyclohexane in Zeolite-Y, not surprisingly, is similar to the gas/liquid phase spectra of cyclohexane. Cyclohexane in Silicalite-1, however, shows an additional feature in the methylene-stretching region in both the room temperature infrared and Raman spectra. The additional feature in the infrared appears at the same frequency as an allowed Raman band of the chair conformer. Like-wise the additional band in the Raman corresponds to an existing feature in the infrared spectra of the chair conformer. These observations imply that in the voids of Silicalite-1, cyclohexane adopts a conformation which no longer posses inversion symmetry. On warming the additional feature in the infrared spectra decreases in intensity and the spectra gradually resembles that of cyclohexane in Zeolite-Y, i.e., the chair conformer. The intensity changes are reversible and suggest that the distorted-chair and chair conformers of cyclohexane are in thermal equilibrium in the voids of Silicalite-1. Monte–Carlo docking calculations support the above observation. Host–guest dispersive interactions favour a distorted-chair conformation of cyclohexane in the voids of Silicalite-1. In Zeolite-Y the cyclohexane molecule retains the chair conformation.

The results presented here highlight the profound influence that the topology and dimension of the zeolitic voids has on the conformation of a flexible guest molecule confined or adsorbed within it. The cyclohexane molecule in the almost spherical, ~12 Å diameter supercages of Zeolite-Y sees a nearly flat potential whereas in Silicalite-1, where the dimensions of the void (8.7 Å) and the kinetic diameter of cyclohexane (6 Å) are comparable, this is no longer true and the cyclohexane no longer adopts the stable gas phase chair conformation. In subsequent studies we show that these results have direct bearing on reactivity as well as competitive adsorption involving rigid and flexible organic molecules of similar dimensions.

5. Supplementary information

(1) Infrared and Raman spectra of cyclohexane adsorbed on Silicalite-1 and Zeolite-Y along with a table of observed band positions and assignments. (2) TPD profile of cyclohexane over Silicalite-1. (3) Details of the Lorentzian-decomposition of the spectra in figure 2.

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