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Benzene Adsorption in Microporous Materials

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Abstract. The adsorption behaviour of benzene in silicalite-1, $AlPO_4$-5 and EU-1 has been investigated using gravimetric techniques and molecular simulation methods. For the one-dimensional, 12-membered ring (MR) channels of $AlPO_4$-5 and the unidirectional, 10-MR channels with 12-MR side pockets of EU-1, the isotherms of benzene show simple type I behaviour. For the three dimensional 10-MR channels of silicalite-1, an anomalous behaviour of the benzene molecules sorbed has been observed. Two steps at loadings of *ca.* 4 and 6 molecules per unit cell [m.(u.c.)$^{-1}$], respectively, and an hysteresis loop between loadings from 6 to 8 m.(u.c.)$^{-1}$ can be found in the isotherms of this system. These stepped isotherms can be classified as showing type VI isotherm behaviour but in this system the reasons behind the steps are of a new and novel nature. These abnormal adsorption properties have been ascribed to the subtle interplay of increased sorbate-sorbate interactions and decreases in the entropy of sorption due to the energetically heterogeneous surfaces which are present in silicalite-1. The composition and structure of the silicalite-1 samples also play an important role on the adsorption properties of this system.

1. Introduction

We should like to dedicate this paper to the memory of Professor W. Schirmer. One of us (LVCR) has been a personal friend of Professor Schirmer for some 30 years and it is with great sadness to hear of his recent death.

The adsorption equilibria of hydrocarbons in zeolites, which are involved in many significant industrial catalysis and separation processes, is of great importance in understanding adsorption and kinetic processes involving these sorbates and sorbents. Effect of the sorbent framework channel structures on the adsorption behaviour of hydrocarbon sorbates has been an interesting topic for many years.

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Silicalite-1 has intersecting straight and sinusoidal channels of similar dimensions which are determined by the near circular arrangements of 10 framework oxygens in the straight channels and slightly elliptical arrangements of 10 framework oxygens in the sinusoidal channels. The effective free diameters of these two channel segments are *ca.* 0.55 nm. The two types of channels intersect at intervals of *ca.* 1.0 nm to give a regular array of channel intersections.

Experimental isotherms of benzene in silicalite-1 have been measured by several research groups (Doelle et al., 1981; Wu et al., 1983; Beschmann et al., 1987; Thamm, 1987; Shah et al., 1988; Talu et al., 1989; Tsikoyiannis and Wei, 1991; Xiao and Wei, 1992; Lee and Chiang, 1996; Song and Rees, 2000; Floquet et al., 2003). The data obtained are, however, not always

consistent with one another. But one conclusion can be reached from the higher temperature isotherms which all show a Langmuir shape with a maximum adsorption capacity of 4 m.(u.c.)$^{-1}$. The isotherms of Talu et al. (1989) and Tsikoyiannis and Wei (1991) at lower temperatures display one step or kink around 4 m.(u.c.)$^{-1}$ and then rise to a final plateau at somewhat below eight molecules per unit cell. Lee and Chiang (1996) reported two inflections at *ca.* 4 and 6 m.(u.c.)$^{-1}$, respectively, in benzene isotherms at temperatures of 283, 293 and 303 K but only one inflection at 273 K. Wu and co-workers (1983), and Shah and co-workers (1988) reported isotherms with saturation values around 8 m./u.c without any step. Thamm (1987) reported an isotherm with two steps at loadings of *ca.* 4 and 6 m.(u.c.)$^{-1}$ at 303 K. In addition, a hysteresis loop was found in this isotherm between loadings of about 6 to 8 m.(u.c.)$^{-1}$. Thamm (1987) also found that the heat of adsorption of benzene in silicalite-1 showed a characteristic behaviour which was dependent on the temperature and the amount adsorbed. Tsikoyiannis and Wei (1991) reported a hysteresis loop, but only for samples with higher aluminium contents.

In order to interpret this anomalous adsorption behaviour, studies on the spatial distribution of benzene molecules within the silicalite-1 framework have been carried out using different methods (Snurr et al., 1993; Nakazaki et al., 1992; Mentzen and Lefebvre, 1997; Sacerdote et al., 1990; Bulow et al., 1989; Zibrowius et al., 1985; Xiao and Wei, 1992; Mentzen, 1987; Floquet et al., 2003; Goyal et al., 2000; Vigne-Maeder and Jobic, 1990; Inui and Nakazaki, 1991; Talu, 1991; Raksakoon and Limtrakul, 2003; Lafebvre and Mentzen, 1994). It has been generally accepted that at loadings $\leq$4 m.(u.c.)$^{-1}$, benzene molecules are localised in the intersections of the two channel networks of silicalite-1 although Talu (1991) has suggested that the straight channel segments are the preferential adsorption sites for benzene molecules. However, the packing arrangements of benzene molecules in silicalite-1 at loadings higher than 4 m.(u.c.)$^{-1}$ are still in doubt.

$AlPO_4$-5 is a zeolite-like aluminophosphate material synthesized for the first time in 1982 by Wilson et al. (1982). The channel system of $AlPO_4$-5 consist of only one-dimensional circular channels controlled by the rings of 12 framework oxygens with a diameter of 7.3 Å. The corresponding isotherms of benzene in the unidirectional channels of $ALPO_4$-5 where there are, obviously, no channel intersections are expected to be now much simpler in behaviour compared with those for silicalite-1.

EU-1 is a novel high-silica zeolite whose synthesis was first reported in 1981 (Casci et al., 1981). Its framework structure is composed of unidirectional 10-MR main channels bound by 5.8 $\times$ 4.1 Å in the [100] direction and of dead-end 12-MR side pockets of 6.8$\times$5.8 Å cross section and 8.1 Å depth.

The primary objective of this study is to compare the adsorption behaviour of benzene sorbed in the three types of channel systems mentioned above and also to give an insight into the fundamental adsorption behaviour of benzene in silicalite-1 at loadings up to the saturation capacity 8 m.(u.c.)$^{-1}$ using a gravimetric adsorption method and molecular simulation techniques. The effect of differing chemical compositions, hydroxyl nests, etc., of the zeolite samples on the adsorption properties of the systems has also been investigated.

2. Models and Computational Procedures

2.1. Solid Docking

Simulations of the configurations of benzene inside silicalite-1, combining Monte Carlo (MC), energy minimization (EM) and molecular dynamics (MD) procedures, were carried out using the Solid_Docking package of the commercial InsightII software which by rapid searches is able to locate possible low-energy binding sites/packing arrangements for guest molecules within a host lattice. The simulations, first of all, apply a Monte Carlo algorithm to insert a rigid benzene molecule into a random position within the zeolite framework structure and then calculate the interaction energy for the guest-host system. If the energy is below a certain threshold, the configuration is accepted and another attempt is then made to find a suitable site for a second molecule, and so on for successive molecules until the target number of guest molecule has been reached. The whole packing arrangement is then saved. These processes are repeated to obtain different configurations (100 frames are used in this study) so that more accurate conformations can be obtained. The converged configurations are refined using dynamical simulated annealing, which is especially essential for the conformations at high loadings, to allow the molecules to overcome potential energy barriers and to relax into more stable lower energy configurations.

The unit cell of silicalite-1 used has an orthorhombic Pnma space group with a = 20.022 Å, b = 19.899 Å, c = 13.383 Å containing 96 silicon and 192 oxygen atoms. The zeolite framework was identical for all simulations and was assumed to be rigid during all runs. The simulation box was defined as a single crystallographic unit cell to which periodic boundary conditions were applied in order to simulate the infinite zeolite structure.

The cff91_czeo forcefield, belonging to the cff91 forcefield, was used to describe the interactions in both the host framework lattice and the guest sorbate molecules. This is a forcefield developed specially for the simulation of zeolites. The van der Waals interactions were calculated using an inverse 9th-power term for the repulsive part rather than the more conventional Lennerd-Jones model. For the dynamical simulated annealing procedure, the interactions were computed using a quartic expression to make sure that at small, even zero, separations the energy is finite. Atoms can, therefore, come very close to one another without the catastrophic consequences which would normally be observed. The calculations were performed on a Silicon Graphics workstation. The focus of these simulations is on structural rather than thermodynamic properties of the sorbate molecules. These simulations are much less computationally demanding and more efficient for simulating configurations of the systems when large molecules and high loadings are involved in a zeolite framework. A similar method has been employed by George et al. (1997) for the methane/silicalite-1 system.

2.2. *Adsorption Simulations*

The configurations obtained from the above solid docking simulations were calculated at 0 K, i.e., entropy not involved. In order to take the temperature aspect into account, adsorption simulations of benzene in silicalite-1 were performed at 303 K with different loadings up to the saturated adsorption capacity of 8 m.(u.c.)$^{-1}$. using the rapid Monte Carlo statistical simulation, the canonical ensemble Monte Carlo (fixed loading) simulation in which the Metropolis scheme was used. The simulations were started by randomly choosing the initial coordinates of the sorbate molecules.

Accelrys' Cerius^2 4.2 software was used to carry out the simulations on a Silicon Graphics workstation. Initially, high-energy configurations were rejected to save computational time during the simulations. These configurations are those in which the sorbate molecules and the framework are very close together, i.e., the distance between the atoms of the sorbate and the framework is less than half their van der Waals radii. The van der Waals energies between the sorbate and the framework were calculated by summing all pair interactions within a specific volume, in which the radius is determined by a cut-off distance. The van der Waals energy term within the zeolite framework is restricted to the minimum image convention, in which an atom is considered to interact with its closest neighbour atoms in a periodic box around it. In the case of sorbate-sorbate energy, the interactions are not limited to the atoms within the minimum image border but to the molecules whose centres of mass are within it. Both the benzene molecules and the zeolite framework were treated as rigid units. The only permitted degrees of freedom are the three translational and three rotational variables associated with the sorbate molecule. Electrostatic interactions were initially considered but their contribution was found to be insignificant compared to the van der Waals energies. These interactions were, then, excluded as omitting the Coulomb energy can greatly reduce simulation times.

The unit cell of silicalite-1 used is the same as that described in Section 2.1. The simulation box was defined again as one crystallographic unit cell to which periodic boundary conditions were also applied in order to simulate the infinite zeolite structure. The various Monte Carlo step sizes for the simulations were adjusted in order to obtain a fifty percent acceptance probability. The interaction cutoff distance was fixed at 6.6 Å, which is slightly less than half the smallest parameter for the simulation cell, so it accounts for all of the necessary interactions. At least 4×10^5 simulation steps were performed and the equilibration of the system was monitored by measuring the configuration energy as a function of Monte Carlo steps, which should exhibit a small fluctuation around a central value after sufficiently long runs. For each loading and each force field used in this study, these processes are repeated to obtain different configurations (20–80 runs are applied) so that the most possible locations of the sorbed benzene molecules in silicalite-1 can be obtained for each loading.

The Sorption Demontis (Demontis et al., 1989), Burchart-Dreiding (Mayo et al., 1990) and PCFF (Hill and Sauer, 1994) Force Fields were applied in the simulations, respectively. For the Sorption Demontis forcefield, the sorbate-sorbate interactions are described us-

ing Buckingham potentials. The sorbate-zeolite interactions take into account the short-range atom-atom interactions between the benzene molecules and the oxygen atoms of the zeolite. The short range interactions with the silicon atoms are neglected because they are well shielded by the oxygen atoms of the SiO_4 framework tetrahedra. The Burchart-Dreiding forcefield combines the Burchart forcefield which prescribes the host framework and the Dreiding II forcefield which treats the guest molecule. The parameters for the framework-molecule interactions are derived from the parameters of both forcefields combined by the arithmetic combination rule. The van der Waals interactions in the Burchart forcefield are expressed by an exponential-6 term and the electrostatic interactions by partial atomic charges and a screened Coulombic term. In the Drieding II forcefield, the Lennard-Jones potential is applied to describe the van der Waals interactions and the electrostatic interactions are described by atomic monopoles and a screened Coulombic term. PCFF was developed based on CFF91 with parameterisation including the functional groups of zeolites. The van der Waals interactions in this forcefield were calculated using an inverse 9th-power term for the repulsive part rather than the more conventional Lennard-Jones model.

3. Experimental

A gravimetric balance (Sartorius) was used to measure the isotherms of benzene, by applying conventional procedures, in *ca.* 140–200 mg of the zeolite samples, which had been outgassed under a vacuum of $<10^{-3}$ Pa at 673 K for more than twenty hours prior to the sorption measurements. A more accurate, fully automated and computer controlled gravimetric system [IGA (Intelligent Gravimetric Analyzer), Hiden Analytical Ltd., Warrington, UK] was, also, employed in this study. A sensitive microbalance (resolution of 0.1 μg) is mounted in a thermostated enclosure and thus provides higher accuracies and stabilities. The sample temperature was regulated to $\pm 0.1^{\circ}$C by either a water bath or a furnace.

The IGA system has been used to carry out temperature programmable desorption (TPD) measurements for benzene sorbed in silicalite-1. In this method a sorbate gas is brought into adsorption equilibrium with the sorbent at room temperature at a specified pressure which was chosen from the isotherm to give the required loading. The system was then heated at rates of 5 to 20 K min^{-1} from room temperature to ca. 653 K. The above equilibrium pressure was maintained during the heating. The weight of the sorbent was recorded as a function of temperature from which TG (Thermal Gravimetry) and DTG data could be derived.

The zeolite samples used in this study are summarised in Table 1. Silicalite-1 (A) was synthesised by Van-Den-Begin et al. from a gel containing a TPA-water solution (20wt% TPAOH) and a Ludox solution (40 wt% colloidal SiO_2) (Van-Den-Begin et al., 1989). Silicalite-1 (B) is a commercial zeolite, RD 1051/87, produced by LAPORTE Inorganic. The $AlPO_4$-5 was kindly supplied by Dr. C. Cundy, UMIST, UK. The sample was synthesised by a microwave route using triethylamine template in a fluoride medium. The EU-1 sample was synthesized by the Na, dimethyldibenzylammonium (DMDBA)-route and was also provided by Dr. C. Cundy, UMIST, UK.

All of the samples were used for the adsorption and DTG measurements after calcination at 823 K for 10 hours in an oven. The crystals were heated in air from room temperature to 823 K at 2 K min^{-1}. X-ray diffraction patterns and SEM micrographs showed that these zeolite samples were highly crystalline.

Benzene was supplied by the National Physical Laboratory, UK, with a purity of 99+%.

Table 1. Properties of the zeolite samples used in this study.

Sample	Shape	Crystal size/μm	Si/Al ratio	No. of internal SiOH groups per gram (Van-Den-Begin et al., 1989)/10^{20}
Silicalite-1 (A)	Sphere (twinned)	14.4 (diameter)	∞	5.4
Silicalite-1 (B)	Cube	$4 \times 3 \times 4$	1338	–
EU-1	Coffin	$6.5 \times 4.5 \times 0.7$	–	–
$AlPO_4$-5	Cylinder	25(length) $\times$ 8	–	–

4. Results and Discussion

The isotherms of benzene in silicalite-1 (A) and silicalite-1 (B) at higher temperatures are shown in Fig. 1. A pronounced inflection can be seen in the isotherm in silicalite-1 (B) at 323 K at a loading of *ca.* 4 m.(u.c.)$^{-1}$, while no step is found in the isotherms of silicalite-1 (A), suggesting that the conflicting isotherms reported in the literature, as mentioned above, may result from differences in the samples used. The synthesis gel composition for silicalite-1 (A) sample had no aluminium present and, thus, the Si/Al ratio of the product should be almost infinite. The large number of internal silanol groups (cf. Table 1), measured by ^{1}H-MAS NMR (Van-Den-Begin et al., 1989), existing in the bulk phase of the silicalite-1 (A) crystals induced by the presence of TPA ions during the pentasil-type synthesis is, therefore, the most probably factor influencing the adsorptive properties (Zecchina et al., 1992). The adsorption behaviour of the system is also influenced by the Si/Al ratios of the samples (Pope, 1986; Thamm, 1987; Song and Rees, 2000). It is worth noting that the effect of different sorbent samples on the adsorption properties is far less significant for the *n*-alkanes/silicalite-1 systems than that for the aromatics in silicalite-1 zeolites. For the case of aromatics/MFI systems, the defect effect is more pronounced than that for *n*-alkanes/MFI systems due to the fact that an additional interaction between sorbate molecules and the sorbent framework will be involved in the aromatics/MFI systems compared with the simple dispersion/repulsion forces which are involved with the alkanes.

Figure 2 presents the isotherms of benzene in both silicalite-1 samples at lower temperatures. The results reported by Lee and Chiang (1996) that two steps at ca. 4 and 6 m.(u.c.)$^{-1}$, respectively, in each benzene isotherm at temperatures of 283, 293 and 303 K and only one step at 273 K were confirmed in this study

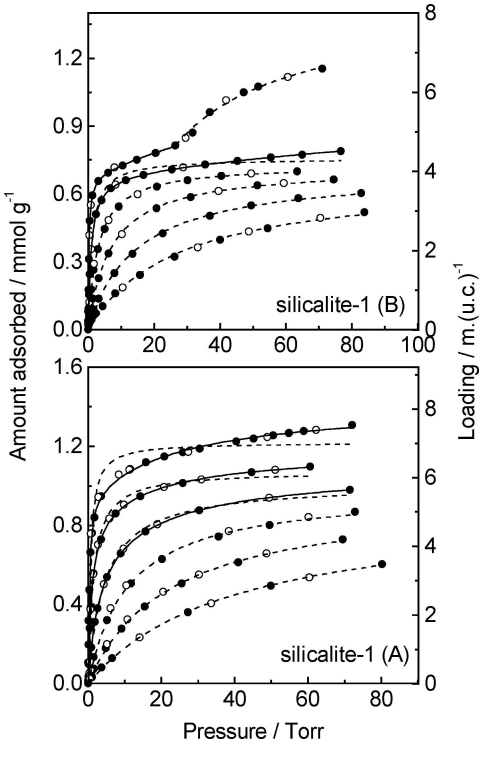

Figure 1. Adsorption (●) and desorption (◯) isotherms of benzene in silicalite-1 (A) and silicalite-1 (B) at temperatures of (from top to bottom) 323, 348, 373, 395, 415, and 435 K. Dashed lines are the fits of the Langmuir model and solid lines are the fits of the dual-site Langmuir (double Langmuir) model (Song and Rees, 1997).

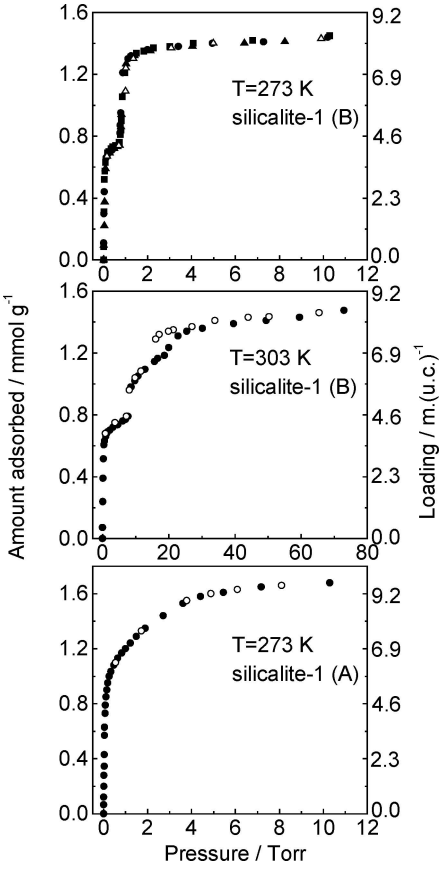

Figure 2. Adsorption (●) and desorption (◯) isotherms of benzene in silicalite-1 (A) and silicalite-1 (B) at low temperatures. The other symbols present the repeat experiment results.

using the silicalite-1 (B) sample. A hysteresis loop which appeared in the isotherm of Thamm (1987) can also be observed in the isotherm at 303 K. However, the isotherm in silicalite-1 (A) at 273 K levels off at about 9 m.(u.c.)$^{-1}$ without any inflection.

Step-like isotherms have been attribute to phase transitions occurring in the sorbent induced by sorption of the sorbate molecules (Mentzen, 1992; Snurr et al., 1993; Lee and Chiang, 1996; Ashtekar et al., 1998; Takaishi et al., 1998). This suggestion can be discarded with the following reasons. Firstly the phase transitions can also occur at loadings in the range ca. 0-2 m.(u.c.)$^{-1}$ (Mentzen, 1994; Mentzen and Gelin, 1995; Gelin et al., 1995; Lee and Chiang, 1996; Lefebvre and; Takaishi et al., 1998) where no isotherm steps are found. Secondly, the symmetry changes also occur on change of temperature. The higher the temperature, the lower the loading at which the phase transition takes place (van Koningsveld et al., 1987; Takaishi et al., 1998). However, the loadings at which the steps are found are independent of temperature in most cases. Thirdly, a phase transition of silicalite-1 from monoclinic to orthorhombic was observed when trichloroethene was sorbed at a loading of ca. 7 m.(u.c.)$^{-1}$ using an in situ neutron diffraction technique (Floquet et al., 2003), but no inflection in the isotherm was found. Finally, the transformation of silicalite-1 from monoclinic to orthorhombic symmetry involves only minor displacements of the atomic positions within the framework structure which, under appropriate conditions, are highly reversible and cause only very small changes in size and shape of the channel system (Engelhardt and Michel, 1987; Goyal et al., 2000). The fact that the structural differences between the topologically equivalent orthorhombic and monoclinic forms of MFI framework are very small is generally overlooked by many workers who ascribed the changes in the adsorptive properties simply to these phase transitions.

Neutron diffraction studies (Goyal et al., 2000; Floquet et al., 2003) suggested that the steps observed in the isotherms of benzene in silicalite-1 are not signatures of phase transitions of the sorbent structure but are related to three stages in the filling process induced by the three kinds of sites present in silicalite-1.

As mentioned in the introduction section, the intersections of the two channel systems of silicalite-1, of which there are four per unit cell, are the most preferred sorption sites for benzene, which is consistent with the fact that a step occurs in the isotherm when the loading increases above 4 m.(u.c.)$^{-1}$. Thamm (1987) has ascribed the inflections of the benzene isotherms in silicalite-1 to the redistribution and/or reorientation of benzene molecules occurring in the system at the loadings where the steps occur. These redistribution and/or reorientation processes will result in an large entropy loss in the adsorbed phase.

Figure 3 presents the isosteric heats of adsorption and the sorbed phase entropies of benzene in silicalite-1 calculated from the isotherms measured in this work using the Clausius-Clapeyron equation, which are in good agreement with Thamm's calorimetric data (1987). It can been seen that the entropy of the system does decrease with increasing loading (cf. Fig. 3(b)) but this entropy loss is balanced by the large increases in the corresponding heats of adsorption as shown in Fig. 3(a).

One can, therefore, conclude that the unusual isotherms of benzene in silicalite-1 can be attributed to energetically heterogeneous surfaces which are present in the adsorbent. These heterogeneities, arising from sorbate-sorbent and sorbate-sorbate interactions, cause spatial configuration changes as the loading increases.

It is interesting to point out that the isotherms in Figs. 1 and 2 which show one or more steps are examples of Type VI isotherms (Gregg and Sing,

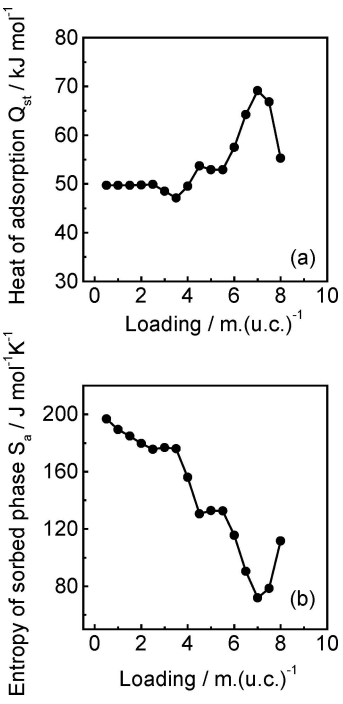

Figure 3. Isosteric heats of adsorption (a) and the sorbed phase entropies (b) of benzene in silicalite-1 (B) as a function of loading.

1982). However, these inflections are not due to the accepted mechanism for such steps, i.e. second and third layer adsorption on very homogeneous surfaces but are due to adsorption on different sets of sites where heat/entropic factors introduce distinct differences to the sorption process at well-defined adsorbate concentrations.

By applying simulation calculations the factors which cause the anomalous steps and the hysteresis loop in the isotherms can be elucidated explicitly at molecular levels. The configurations of benzene within silicalite-1 with the lowest potential energies at loadings from 4 to 8 m.(u.c.)$^{-1}$ derived from the solid docking simulation calculations mentioned above, are presented in Figs. 4 and 5. The structures displayed here were obtained by the simulations at a temperature of 0 K.

At loadings up to 4 m.(u.c.)$^{-1}$, the molecules are located in the intersections with the aromatic-ring plane normal to the x-z plane (cf. Fig. 4 (a,4) and (b,4)). The sorbate-sorbate interactions will be negligible at these loadings. The adsorption simulations at 303 K for a loading of 4 m.(u.c.)$^{-1}$ using the three force-fields mentioned above demonstrate that all the sorbed benzene molecules are still located at the intersections but now very much disordered, i.e., several orientations of the sorbed benzene molecules can be found, implying that at realistic temperatures, the intersections are still the preferential adsorption sites for benzene in silicalite-1 and that the sorbed molecules can easily rotate in these sites.

At a loading of 5 m.(u.c.)$^{-1}$, however, a dramatic change occurs in the structure of the system, as shown in Fig. 4 (a,5) and (b,5), obtained from the solid docking calculations. Four molecules are distributed in the intersection and the straight channel segments forming a cluster, or polymeric chain along the straight channel direction with those molecules in the intersections now parallel to the *x*-*z* plane. The fifth molecule which does not join the chain remains in an intersection site of an adjacent straight channel and retains the same orientation as observed at loadings $\leq$4 m.(u.c.)$^{-1}$. When entropy is concerned, i.e., at higher temperatures, the polymeric chain shown in Fig. 4 (a,5) and (b,5) cannot be obtained. As displayed in Fig. 6, the intersections are still fully occupied at 303 K with the extra sorbed benzene molecule located at either the straight channels or the sinusoidal channel segments forming dimers and/or trimers. The results obtained by using different force fields are more or less the same.

At 0 K, with the loading increasing to 6 m.(u.c.)$^{-1}$, the polymeric chain, displayed in Fig. 4 (a,5) and (b,5), remain unchanged but now there are two molecules located in the intersection sites of the adjacent straight channels as shown in Fig. 4 (a,6) and (b,6). The formation of such chains has been proposed by Sacerdote et al. (1990) by comparing X-ray powder diffraction data and calorimetrically determined differential adsorption heats, with computer simulated atom-atom interactions for this system at a loading of 8 m.(u.c.)$^{-1}$.

Similar structure can also be obtained at 303 K with the molecules sorbed in the intersections more disordered than those at 0 K as shown in Fig. 7(a). Other possible locations for benzene in silicalite-1 found by adsorption simulations at 303 K at a loading of 6 m.(u.c.)$^{-1}$ are presented in Fig. 7(b). Again, all the intersections are occupied by the sorbed molecules and the molecules in access of 4 m.(u.c.)$^{-1}$ are sorbed in the sinusoidal channel and the straight channel segments, respectively. This finding is in excellent agreement with the adsorption pattern derived from the Neutron diffraction studies (Floquet et al., 2003). These results indicate that the sorbed benzene molecules tend to form large clusters containing at least 4 benzene molecules through either one channel direction (most probably the straight channel direction) or two channel directions, leading to much stronger sorbate-sorbate interactions and higher constraint of the sorbed molecules than those for dimers and/or trimers.

The adsorption patterns presented in Figs. 5 (a,7), (6,7), (a,8) and (b,8) can also be found by the adsorption simulations at 303 K at related loadings. Another possible adsorption pattern that four benzene molecules in the intersections, two in the sinusoidal channel segments and one in the straight channel segments per unit cell can be found at a loading of 7 m.(u.c.)$^{-1}$. For a loading of 8 m.(u.c.)$^{-1}$, other possible occupancies of the intersections, the sinusoidal segments and the straight channel segments for the sorbed benzene molecules at 303 K are 4, 3 and 1 per unit cell, respectively. The occupancies of 4, 2 and 2 per unit cell for the intersections, the sinusoidal segments and the straight channel segments, respectively, are also readily obtained. These results are in agreement with those obtained from Neutron diffraction studies (Goyal et al., 2000; Floquet et al., 2003). The configuration proposed by Sacerdote et al. (1990) that the sorbed benzene molecules at a loading of 8 m.(u.c.)$^{-1}$ form infinite polymeric chains only down the straight channels cannot be, however, obtained, implying that the sorbed benzene molecules are

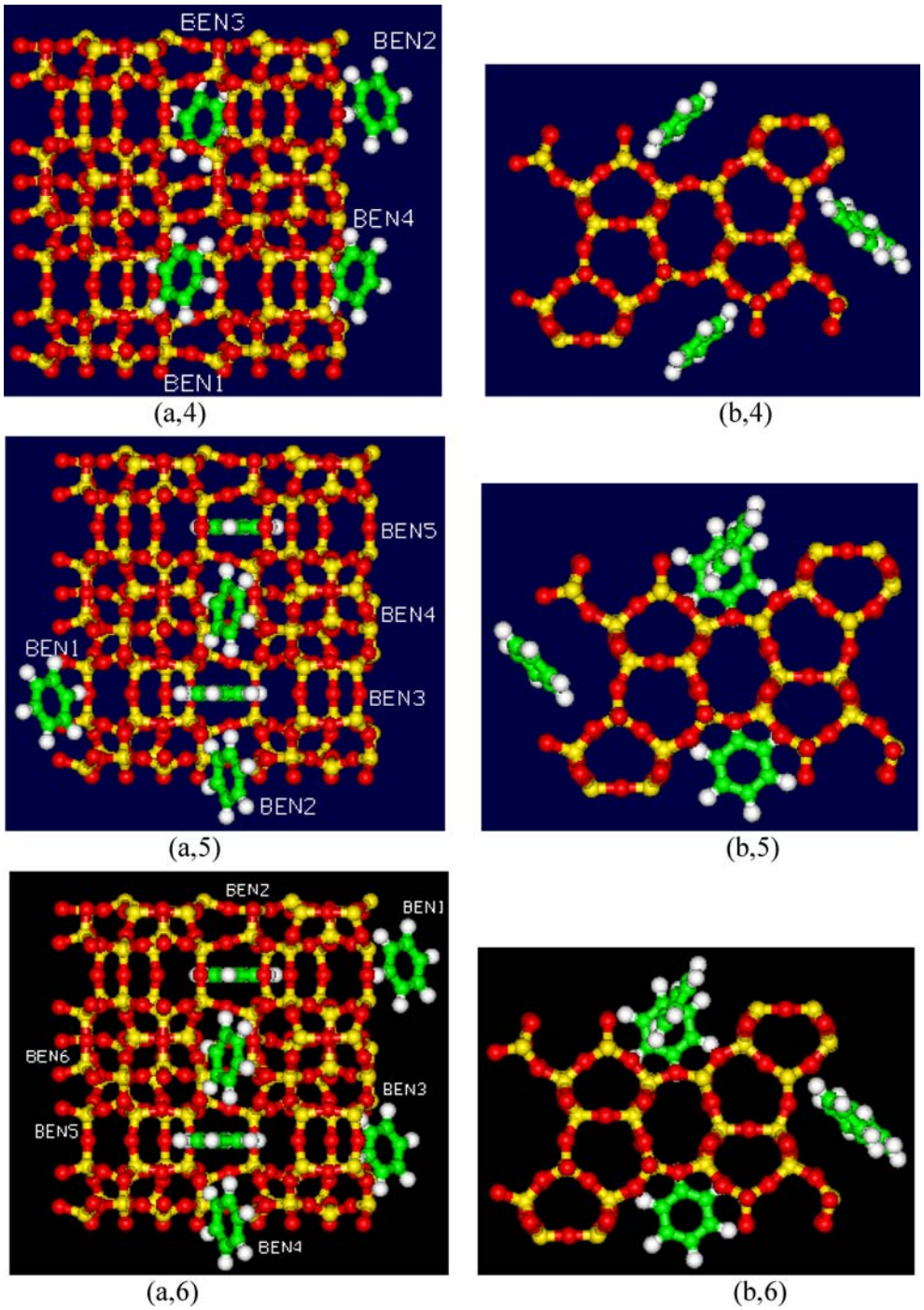

Figure 4. Configurations of the sorbed benzene molecules in silicalite-1 at different loadings, derived from the solid docking simulations, viewed down the Z axis (a) and Y axis, i.e. the straight channel direction (b). The numbers in the parentheses indicate the number of molecules per unit cell.

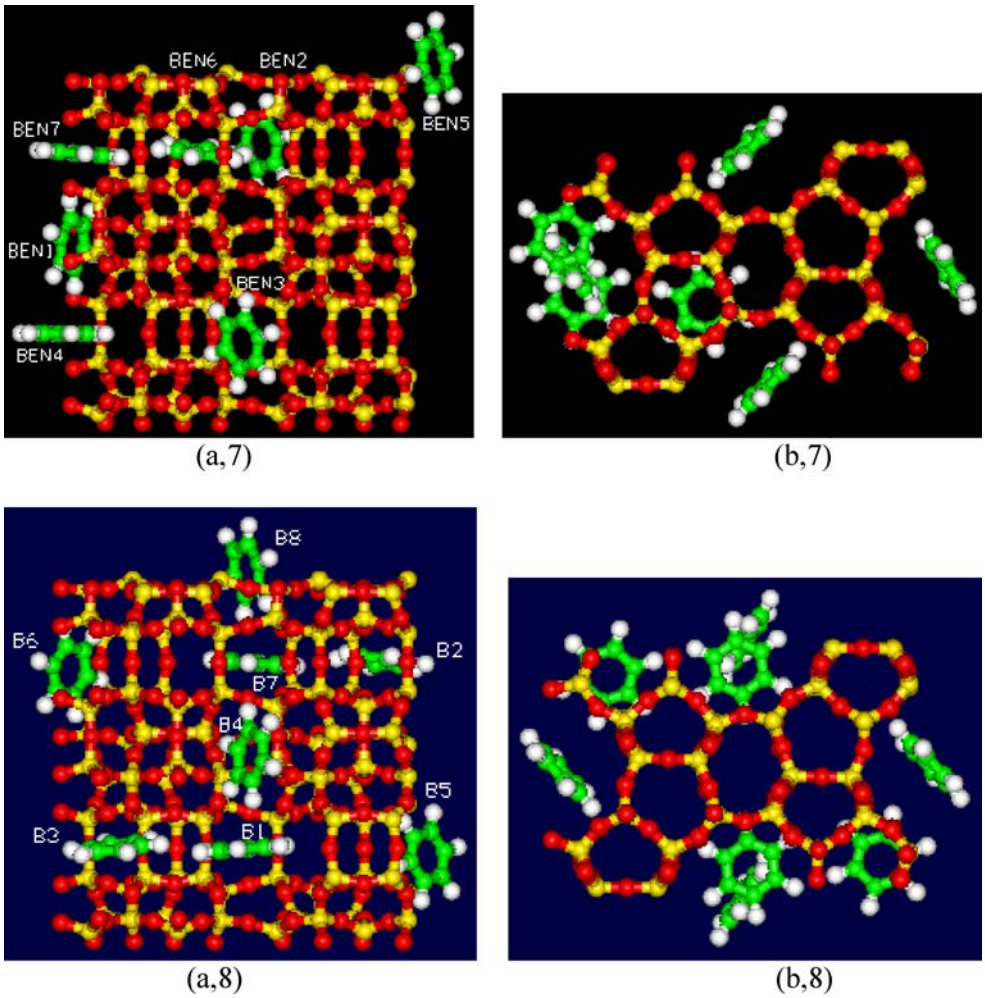

Figure 5. Configurations of the sorbed benzene molecules in silicalite-1 at different loadings, derived from the solid docking simulations, viewed down the *Z* axis (a) and *Y* axis, i.e. the straight channel direction (b). The numbers in the parentheses indicate the number of molecules per unit cell.

clustered through both sinusoidal channel and straight channel directions forming large clusters, leading to, again, a strong sorbate-sorbate interactions and a large entropy loss.

Similar simulation configurations can be derived by using different force fields listed above but the heat of adsorption calculated on applying the Burchart-Dreiding forcefield is more consistent with the experimental results (Thamm, 1987) than that obtained from the other two force fields (Song et al., 2002). The loading dependence of the isosteric adsorption heat of benzene in silicalite-1 calculated using the adsorption simulations is, however, different from that displayed in Fig. 3(b). The heat of adsorption derived from the simulations tend to be more or less a constant which may be due to the rigid restraints for both the sorbate molecules and the framework used in these calculations

It is worth noting that the steps are also influenced by the presence of internal defects in the silicalite-1 framework. Zecchina et al. (1992) have demonstrated that the presence of hydroxyl groups in silicalite-1 can lead to the absence of the inflection in the adsorption isotherm of nitrogen. The fact that no such inflection can be found in the isotherm of benzene in silicalite-1 (A) sample at 273 K (cf. Fig. 2) can, therefore, also be attributed to the large number of hydroxyl groups existing in the sample (cf. Table 1).

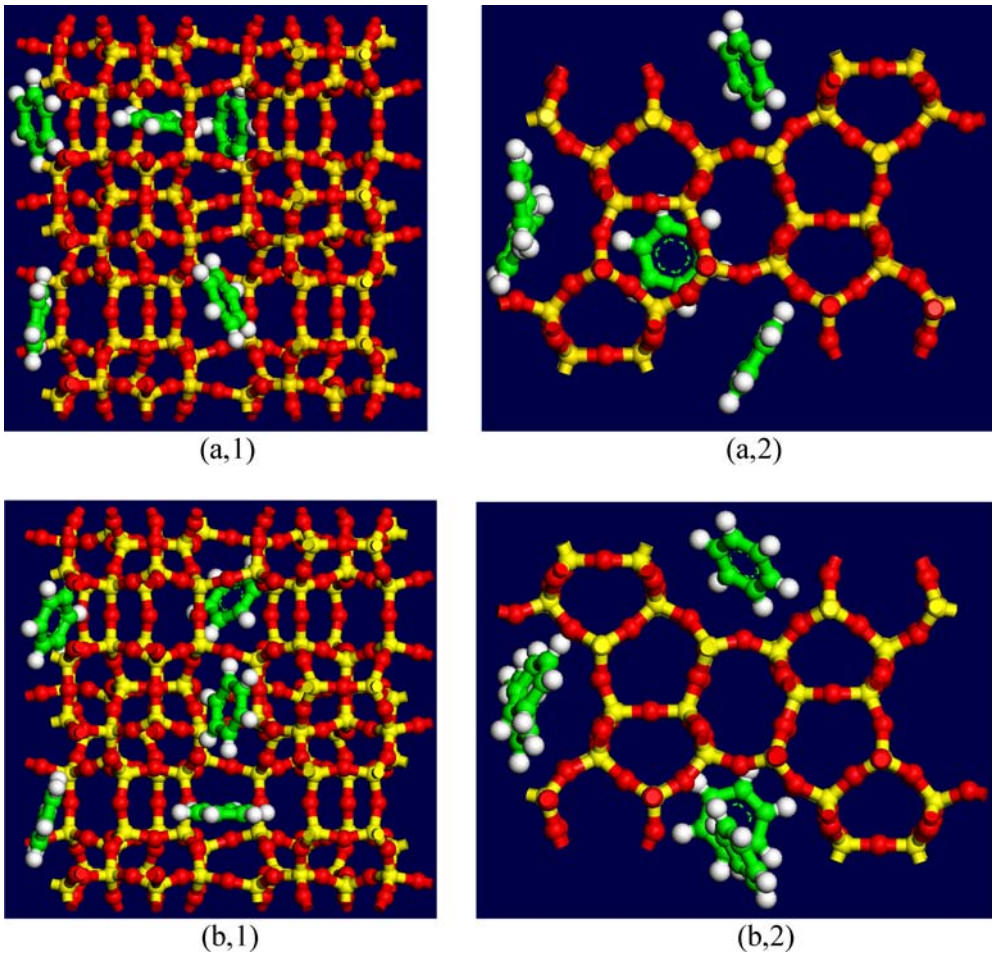

Figure 6. Possible locations of the sorbed benzene molecules in silicalite-1 at 303 K with a loading of 5 m.(u.c.)$^{-1}$, obtained from the adsorption simulations, viewed down the *Z* axis (1) and *Y* axis, i.e. the straight channel direction (2).

The saturation adsorption capacity for benzene in silicalite-1 determined experimentally (cf. Fig. 2) is *ca.* 8 m.(u.c.)$^{-1}$, which is consistent with previously reported data (Flanigen et al., 1978; Wu et al., 1983; Thamm, 1987; Guo et al., 1989). This value is much smaller than the theoretical value of 12 m.(u.c.)$^{-1}$ based on the crystallographic data for silicalite-1 and the liquid density of benzene as presented in Table 2. The spatial configuration of the sorbed benzene at a loading of 8 m.(u.c.)$^{-1}$ (cf. Fig. 5 (a,8) and (b,8)) shows that there are still two straight channel segments and two sinusoidal channel segments per unit cell left available, implying that the adsorption occurs on energetically preferred centers rather than a process of volume filling within the microporous network. As mentioned above, a large entropy loss is involved at high loadings because of the increase in the interactions of the sorbed benzene molecules with one another and both rotation and translation of benzene molecules being indubitably impeded with this increase and the shape restraint of the channel segments. This entropy decrease can, however, be balanced by the large increase in the corresponding heats of adsorption (cf. Fig. 3) (Smit and Maessen, 1995). For

Table 2. Saturation Capacities and adsorbed volumes of benzene in the zeolite samples used in this study.

Sorbent	Saturation Capacity/m.(u.c.)$^{-1}$	Adsorbed Volume/ ml g^{-1}	Theoretical Free Volumes/ml g^{-1}
Silicalite-1	8	0.13	0.19
EU-1	8.5	0.11	0.144
$AlPO_4$-5	1.8	0.11	0.145

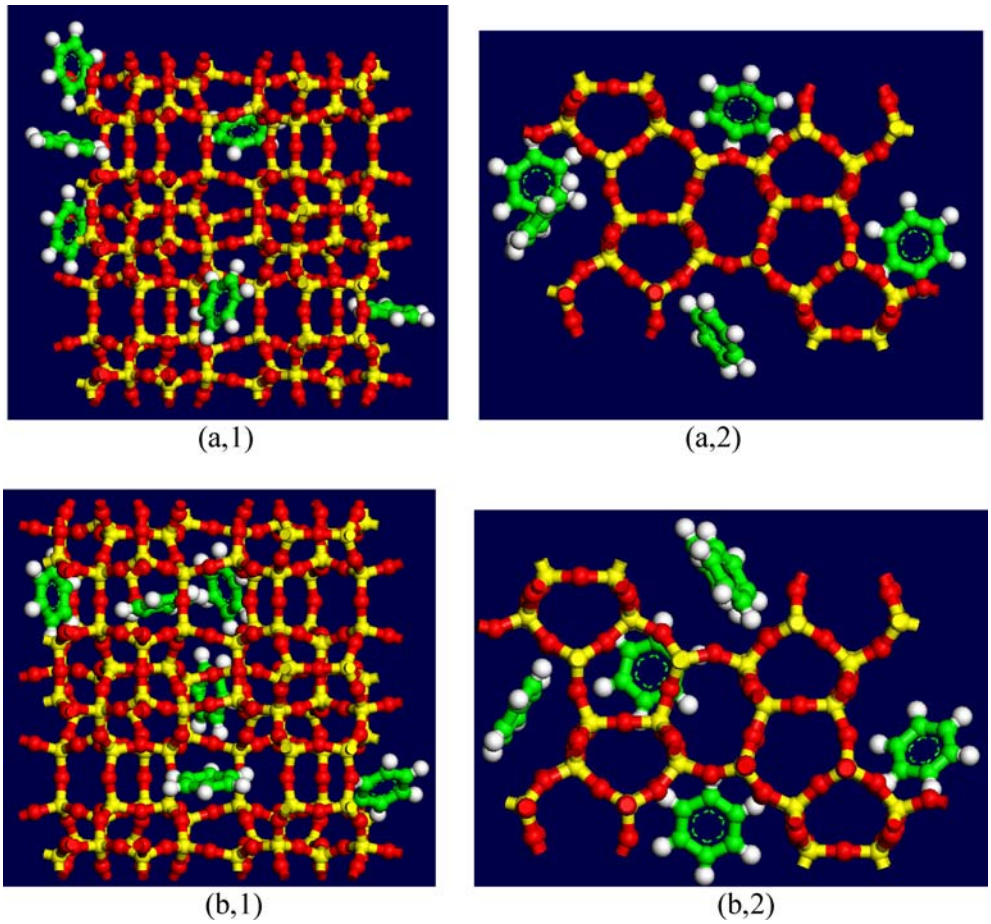

Figure 7. Possible locations of the sorbed benzene molecules in silicalite-1 at 303 K with a loading of 6 m.(u.c.)$^{-1}$, obtained from the adsorption simulations, viewed down the Z axis (1) and Y axis, i.e. the straight channel direction (2).

loadings in excess of 8 m.(u.c.)$^{-1}$, a further entropy loss would occur due to the very tight packing of the sorbed benzene molecules. The corresponding heats of adsorption will, nevertheless, decrease at very high loadings and are not able to balance the entropy decrease. The saturated adsorption capacity of ca. 8 m.(u.c.)$^{-1}$ is, therefore, controlled by both the entropy and enthalpy effects of the sorbed benzene molecules.

In the light of the simulation results, a possible interpretation of the hysteresis loop found in the isotherm of benzene in silicalite-1 (B) at 303 K is proposed. At loadings lower than 6 m.(u.c.)$^{-1}$, the sorbed molecules are associated with one another by forming only dimers or trimers via either the straight channel direction or the sinusoidal channel direction as shown in Fig. 6. In the hysteresis loop region, the sorbed benzene molecules form a large polymeric cluster through both the framework channels, leading to strong sorbate-sorbate interactions which can be seen from the heat of adsorption of this system as shown in Fig. 3. On increasing the loading some reorientation and relocation of the molecules already sorbed may occur to give clusters with maximum sorbate-sorbate interaction energy. At maximum loading the sorbed benzene molecule will form a large infinite cluster throughout the whole framework channels. On desorbing from this maximum loaded state, molecules have to be removed from this strongly bound cluster, leading to the clusters formed during the desorption process being different from those formed during the adsorption process and hysteresis occurs.

Fig. 8 displays the DTG profiles of benzene molecules sorbed in silicalite-1 derived from the temperature programmed desorption results at various adsorption loadings measured using the IGA apparatus. Only a single high temperature peak was observed in these DTG profiles when the initial adsorption

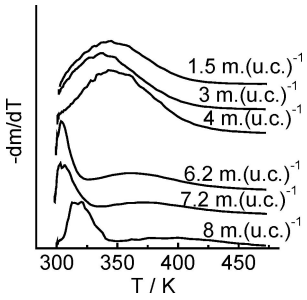

Figure 8. DTG profiles of benzene in silicalite-1 (B) at different loadings, where m is the mass of the sorbent system and T the temperature. dm/dT denotes the change of mass with temperature.

loadings were lower than 4 m.(u.c.)$^{-1}$. Whereas at higher loadings two peaks were found. The new lower temperature peak can be, therefore, associated with the desorption of molecules sorbed above a loading of 4 m.(u.c.)$^{-1}$. The results clearly demonstrate that the initial 4 m.(u.c.)$^{-1}$ sorbed in the preferred channel intersection sites require higher temperatures before desorption occurs compared to molecules sorbed in the other sites at loadings in excess of 4 m.(u.c.)$^{-1}$. As these latter molecules are sorbed with higher heats of adsorption (cf. Fig. 3), mainly from increased sorbate-sorbate interactions, the ease by which they are desorbed must be due to gains in entropy on desorption as the main driving force. In Fig. 8 the higher temperature peak in the DTG curves for molecules sorbed in the channel intersection sites increase in temperature from ∼343 K for a loading of 1.5 m.(u.c.)$^{-1}$ to about ∼403 K for a loading of 8 m.(u.c.)$^{-1}$. This increase arises from the increase in equilibrium pressure that is maintained in these DTG measurements as the loading increases (see experimental section for the conditions used in the IGA apparatus). The experimental results also showed that changing the heating rate had little or no effect on the TG and DTG profiles.

The TG and DTG profiles of the benzene molecules sorbed in silicalite-1 (B) with a initial loadings of 6 m.(u.c.)$^{-1}$ are shown in Fig. 9(a). The complete desorption of the two molecules in excess of 4 m.(u.c.)$^{-1}$ occurs over the temperature range of 298–323 K. If the initial equilibrium system is heated to 323 K the molecules in excess of 4 m.(u.c.)$^{-1}$ will, thus, be removed. Following this low temperature heating if the system is cooled to room temperature and then a second temperature programmed desorption is initiated but now using the reduced equilibrium pressure over the sorbent appropriate for a loading of 4 m.(u.c.)$^{-1}$. The resulting TG and DTG profiles, presented in Fig. 9(b),

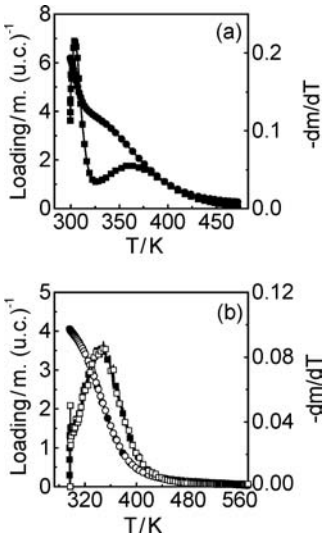

Figure 9. TG (●) and DTG (■) profiles of benzene in silicalite-1 (B) at loadings of 6 m.(u.c.)$^{-1}$ (a) and 4 m.(u.c.)$^{-1}$. (b) compared with TG (◯) and DTG (□) profiles after pretreating the system originally adsorbing 6 m.(u.c.)$^{-1}$ by increasing temperature from room temperature to that where the lower temperature peak in the DTG curves disappear, i.e., two sorbed molecules per unit cell are removed, and then cooling down to room temperature again before commencing the TG and DTG measurements.

match exactly the profiles generated previously starting with the sorbent loaded only with 4 m.(u.c.)$^{-1}$. This perfect match indicates that, when the benzene molecules sorbed in excess of 4 m.(u.c.)$^{-1}$ are removed, the remaining 4 m.(u.c.)$^{-1}$ will be redistributed back to their preferred intersection sorption sites.

The isotherms of benzene in $AlPO_4$-5 and EU-1 are shown in Fig. 10 which are consistent with similar data reported in the literature (Rao et al., 1990; Rozwadowski et al., 1999). Unlike the intricate adsorption behaviour in silicalite-1, these isotherms present only type I behaviour, implying that the surfaces of these framework channels are energetically more uniform compared to those for silicalite-1 and that simple volumetric filling processes are occurring in these systems. For the unidirectional, larger diameter, cylindrical channels of $AlPO_4$-5, however, sorbate-sorbate interactions are still occurring as seen from the deviation of some isotherms from the simple Langmuir model. These sorbate-sorbate interactions may be the reason for the very small, poorly-defined hysteresis loop in the benzene isotherms at 273 and 303 K as shown in Fig. 10. While for the smaller diameter channels of EU-1, even with large dead-end side pockets, sorbate-sorbate interactions are insignificant.

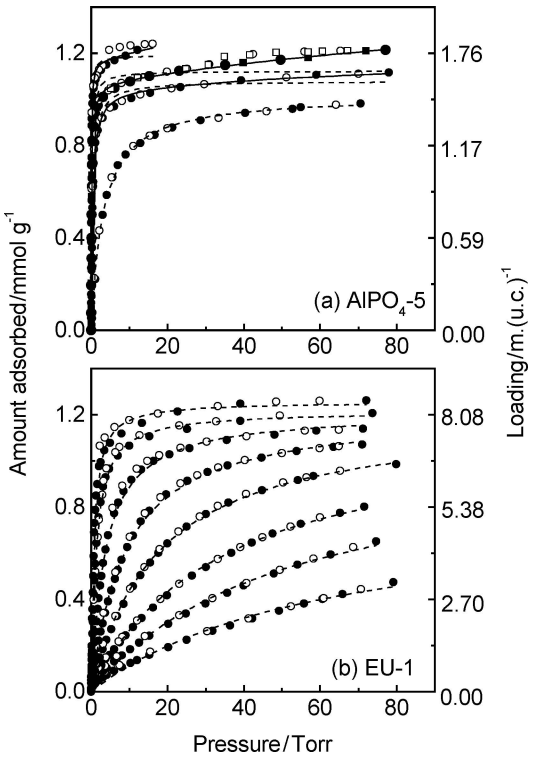

Figure 10. Adsorption (●) and desorption (◯) isotherms of benzene in $AlPO_4$-5 (a) and EU-1 (b) at temperatures of (from top to bottom) 273, 303, 323, and 373 K for (a), and of 344, 362, 383, 405, 423, 441, 461, and 481 K for (b). Dashed lines are the fits of the Langmuir model and solid lines are the fits of the dual-site Langmuir (double Langmuir) model (Song and Rees, 1997).

The saturation adsorption capacities of benzene in the three sorbents are listed in Table 2 along with the adsorbed volumes and the theoretical free volumes. The adsorbed volumes are much less than the theoretical sorption volume. The difference in the adsorbed volume and the theoretical volume may arise from differences in the cross-sectional areas of the sorbate molecules and the available cross-sectional area of the channels for $AlPO_4$-5 and EU-1. However, there is, also, the possibility that fault planes exist in the $AlPO_4$-5 and EU-1 samples used in this study which prevents molecules being adsorbed in some channel segments. Further investigations such as molecular simulations are in progress to try to get a better understanding on these systems. For silicalite-1, the adsorbed volume of benzene is controlled by both the entropy and enthalpy effects of the sorbed benzene molecules as discussed above.

Conclusions

Molecular simulations show that the intersections of the two channel networks of silicalite-1 are the energetically preferred adsorption sites for the sorbed benzene molecules. After all the intersections are fully occupied by benzene molecules, i.e. loading approaches 4 m.(u.c.)$^{-1}$, further adsorption will cause a redistribution or rearrangement of the sorbed molecules with some molecules forming polymeric chain clusters.

Sorption isotherms of benzene in silicalite-1 show two interesting steps which occurs at loadings of *ca.* 4 and 6 m.(u.c.)$^{-1}$, respectively. Such steps have been shown to occur after the first 4 m.(u.c.)$^{-1}$ to be sorbed have filled the four, energetically preferred, channel intersection sites. The steps are due to the subtle interplay of increased sorbate-sorbate interactions and decreases in the entropy of sorption when molecules, at loadings in excess of 4 m.(u.c.)$^{-1}$, have to occupy sinusoidal and straight channel segment sites. Such stepped isotherms could be classified as showing type VI isotherm behaviour but in this systems the reasons behind the steps are of a new and novel nature and not due to second and third layer adsorptions on a very homogeneous, planar surface.

The hysteresis loop found in the isotherm of benzene in silicalite-1 system results from the strong sorbate-sorbate interactions, the energetically heterogeneous surfaces of the sorbent framework and the close packing of the sorbed benzene molecules, which lead to packing differences of the sorbed molecules on adsorption and desorption branches of the isotherm.

The adsorption behaviour of benzene in silicalite-1 is affected by the chemical nature of the silicalite-1 samples. Structural defects can result in the disappearance of the steps in the isotherms.

Temperature programme desorption studies and simulation calculations, using Accelrys software, have helped greatly to elucidate the underlying features controlling the diffusion of benzene molecules sorbed in the two types of channel networks present in silicalite-1.

The sorption of benzene molecules in the one-dimensional, 12-MR channels of $AlPO_4$-5 and the unidirectional 10-MR channels with large 12-MR side pockets of EU-1 shows little or none of the complications found with silicalite-1. In $AlPO_4$-5 and EU-1, the isotherms tend to be reasonably rectangular in form but the maximum volume of sorbate sorbed is less than the theoretical volume of the channels.

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