Effects of inter-crystalline space on the adsorption of ethane and CO_2 in silicalite: Implications for enhanced adsorption

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Effects of inter-crystalline space on the adsorption of ethane and CO_2 in silicalite: Implications for enhanced adsorption

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Adsorption of fluids in nanoporous materials is important for a variety of industries including catalysis and is a promising strategy for hydrogen storage and CO_2 sequestration. It has therefore been studied extensively. In a typical adsorption experiment, the sorbent sample is usually in powder form which consists of several crystallites separated by an inter-crystalline space. This inter-crystalline space may compete with the nanopores in engineered as well as natural materials for fluid adsorption. While in computer simulations that are used to complement experiments, much attention is focused on the choice of force-field parameters, the effect of inter-crystalline spaces on the properties of adsorbed fluids remains largely ignored. We attempt to study the effects of inter-crystalline space on the simulated adsorption of ethane and CO_2 modelled in TraPPE formalism in a silicalite model composed of crystallites separated by different inter-crystalline spaces. The effect of inter-crystalline space is found to be profound and differs for the two sorbates. Presence of quadrupole moment makes CO_2 adsorption in the inter-crystalline space more favorable and suggests that increasing surface area of a catalytic substrate for enhanced adsorption might be a relatively more effective strategy for adsorption of a quadrupolar molecule as compared to an apolar molecule. Also, the results imply that in experiments investigating molecules confined in porous media using powder samples, apolar molecules are less likely to give undesired bulk-like contribution from inter-crystalline spaces to the experimental data. CO_2 molecules adsorbed on the crystallite surfaces are found to exhibit a high degree of orientational ordering and exhibit a preferred orientation favorable for higher amounts of adsorption. While larger inter-crystalline spacings lead to higher adsorption, the effect of using a larger crystallite is to reduce the amount of adsorption. The mutual negation of these two effects explains the apparent agreement of the experimental data obtained on a powder sample and the simulation data obtained using a perfect crystal model. This work has implications for both simulations of adsorption isotherms in nanoporous materials and the interpretation of experimental data obtained for these systems.

1 Introduction

Adsorption of fluids in nano-porous materials is important for a variety of industrial processes. For example, adsorption in nanoporous materials has been identified as a promising strategy for hydrogen storage[1] and CO_2 sequestration[2]. Several chemical processes depend on the adsorption of fluid reactants in nanoporous materials where the latter act as catalysts[3]. A study of adsorption of fluids is therefore of importance in research. Both experimental[4]as well as simulation[5] techniques are used in these studies. Comparisons are commonly made between experiments and simulations carried out on models of the samples used in the experiments[6]. Use of periodic boundary conditions allows models of materials with a few thousand atoms to represent samples of macroscopic dimensions investigated in the experiments[6,7]. However, the models used in the simulations are often highly idealized versions of the real samples and largely ignore the imperfections of the crystalline or amorphous structure of the real sample. This is particularly relevant for the system of molecules confined in porous substrates, as the guest molecules can occupy both the pore space in the substrate as well as the space between the substrate crystallites in a powder sample. Further, in a powder sample, several crystallites make up a particle and extra inter-particle space exists between any two particles. Although inter-particle space is much larger than the inter-crytalline space the effect of both inter-crystalline as well as inter-particle spaces is to expose the surface of a crystallite for adsorption of the fluid molecules. Studying the effects of inter-crystalline space can therefore be useful to understand the role of these exposed surfaces. Recently, attempts have been made

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to incorporate inter-crystalline spaces in the simulated models by inserting empty space between perfect crystallites. For example, effect of inter-crystalline space on the diffusion of guest molecules has been reported by Thomas and Subramanian[8–10]. They found important effects of the presence of inter-crystalline space on the diffusion of n-hexane and 2,2 – dimethyl butane inside poly-crystalline (powder) models of zeolite BEA[8] and Na-Y[9]. It was found that incorporating inter-crystalline space in the simulation cell resulted in better agreement with the diffusivity data collected from ZLC experiments on powder samples of BEA zeolites with sorbates[8]. Simulations on n-hexane in Na-Y zeolite with inter-crystalline space incorporated in different dimensions also exhibited better agreement with the experimental data collected using powder samples[9]. Earlier, another study addressed the effect of inter-crystalline space on the diffusive properties of Xenon in Na-Y zeolite[10]. Despite these studies addressing the structural and dynamical aspects of guest molecules, to the best of our knowledge the effect of inter-crystalline space on the adsorption of fluids in nano-porous material has remained essentially unexplored.

Silicalite is an all-silica analogue of ZSM-5, an industrially important nano-porous catalytic material which has a network of 0.55 nm channel-like pores and has been widely studied for its adsorption properties[11–13]. We have earlier reported adsorption, structure and dynamics of ethane and CO_2 in silicalite[14,15]. With a similar molecular size, ethane and CO_2 are good candidates to study the varied effects of electrostatic interactions on adsorption properties of gas molecules[14]. As the quadrupole moment of ethane[16] is an order of magnitude smaller than that of CO_2[17], force fields, especially the ones under united atom formalism, ignore the electrostatic interactions in ethane entirely, whereas those in CO_2 are usually incorporated through partial charges assigned to the carbon and oxygen atoms. The quadrupole moment of CO_2 makes it adsorb on silica substrates preferentially and replace hydrocarbons[18–24]. Several studies of CO_2 and ethane under confinement have been undertaken[14,20–24].

Given the importance of gas adsorption in nano-porous matrices to the gas storage, recovery and catalysis industry, this study probes the effects of inter-crystalline space on the adsorption of gases in nano-porous matrices. Grand Canonical Monte Carlo (GCMC) simulations are used to assess the adsorption of ethane and CO_2 in silicalite with inter-crystalline space of different sizes (0, 3, 5, 10 and 20 Å referred to as models S0, S1, S2, S3 and S4 respectively henceforth). In the present study we use these two guest molecules to study the role of quadrupole moment in the effects of inter-crystalline space on the adsorption of gases in silicalite. We present the details of our simulations in section 2 after which we present the results obtained from the simulations in section 3. The significance and implications of the results obtained are then discussed in section 4 following which we summarize our conclusions in section 5.

2 Simulation Details

A model ZSM-5 pore network was built using the co-ordinates provided by Koningsveld et al.[25]. As stated above, this zeolite has a network of 0.55 nm channels running straight in the crys-

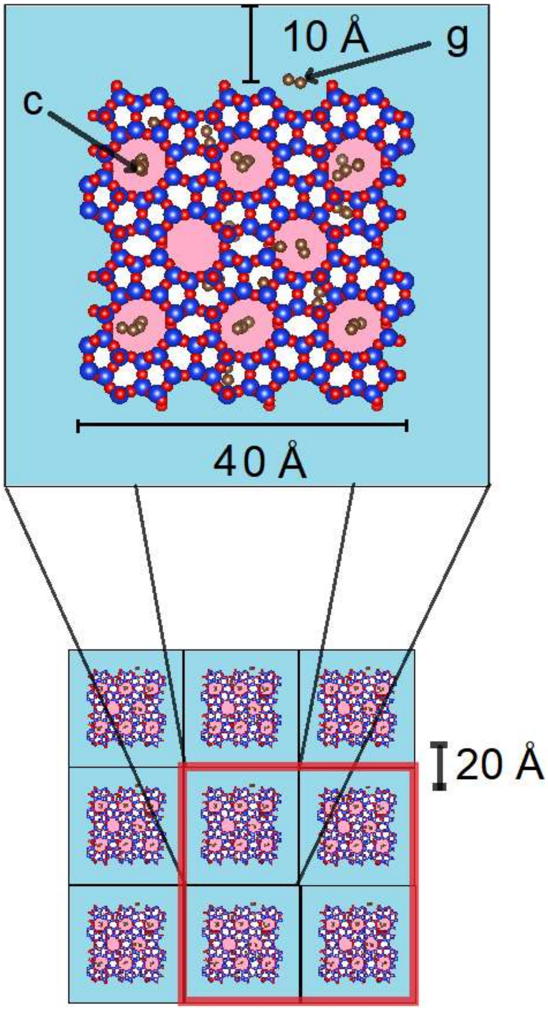

Fig. 1 Schematic illustration of the inter-crystalline space in 2D space (X-Z plane) of S4 model. The simulation cell consists of a supercell made of $2 \times 2 \times 3$ unit cells of silicalite surrounded by empty space of 10 Å shown with the color cyan in all directions. Periodic images of this simulation cell as shown at the bottom give rise to a pattern of silicalite crystallites separated by inter-crystalline spacing of 20 Å. At the bottom, eight periodic images are shown surrounding the original simulation cell while the arrows on all boundaries indicate that the pattern is repeated infinitely. Some of the crystalline pores (straight channels, running along the Y-direction) can be seen as pink regions. A guest molecules (ethane here) can be seen in the inter-crystalline space (g) marrked by an arrow at the upper right region at the top while several others occupy the crystalline pores (c) shown in pink. A larger simulation cell consisting of $2 \times 2 \times 2$ replicas of the simulation cell on the top was also simulated to investigate size effects. In 2D space this simulation cell can be seen as the red rectangle at the bottom of the figure. The results from the simulation of this larger cell and those with the smaller cell seen on top here converged well.

tallographic *b* axis and sinusoidally in the *a*-*c* plane crossing each other in slightly larger intersections. All these channels and intersections provide porosity and henceforth, we shall refer to them collectively as crystalline pores. The unit cell of ZSM-5 was then replicated in the three Cartesian directions to get a $2 \times 2 \times 3$ supercell of dimensions $40.044 \times 39.798 \times 40.149$ Å^3. This supercell constitutes a crystallite. Empty spaces ranging in size from 1.5, 2.5, 5.0 or 10.0 Å were left vacant on all sides of the supercell (see Figure 1). With periodic boundary conditions applied in all directions, this resulted in systems consisting of crystallites of silicalite separated from each other by inter-crystalline spacings of 3, 5, 10 or 20 Å and extending infinitely in all directions (models S1, S2, S3 and S4 respectively). A simulation was also carried out on a larger simulation cell by replicating the entire simulation cells in S1 - S4 (i.e. for S4, the top panel of Figure 1) $2 \times\ 2 \times 2$ in all directions. The resulting larger simulation cell is shown highlighted with a red rectangle at the bottom of Figure 1. The results obtained from this system converged with those obtained with a simulation cell consisting of just one supercell as in S1-S4. All further calculations were therefore carried out using the smaller cell of 1 supercell each. A simulation cell without any spacing was used to represent a perfect crystal without any inter-crystalline spacing (model S0). Finally, to study the effect of crystallite size, a system of $4 \times 4 \times 6$ supercell with inter-crystalline space 20 Å was simulated (i.e. the crystallite in the simulation cell at the top of Figure 1 doubled in size and eight times in volume; denoted L4). Initially, two molecules each of CO_2 or ethane were loaded in silicalite. GCMC simulations were then carried out on the simulation cell thus obtained using DL-Monte[26]. During the simulation, the guest molecules, i.e., ethane or CO_2, could be inserted/deleted, translated, or rotated with respective probabilities of 0.5, 0.25 and 0.25, while all silicalite atoms were kept rigid. All simulations were carried out using a series of gas partial pressures (up to 100 bar) at 308 K. To make a direct comparison between ethane and CO_2, both guest molecules were modeled with the TraPPE-UA force field[27], while CLAYFF force field[28] was used to model the interactions of silicalite atoms. All cross-term interactions were calculated using the Lorentz-Berthelot mixing rules[7]. To probe the effect of quadrupole moment of CO_2 the adsorption of an apolar or charge-free CO_2 was also simulated by turning off electrostatic interactions. This strategy of turning off electrostatic interactions to investigate their role in the adsorption of CO_2 has been employed earlier by Gowers et al.[29]. For ethane and CO_2, 2 million and 5 million Monte Carlo steps, respectively were sufficient to obtain statistically meaningful configurations. Of these, the first 500,000 steps for ethane and 350,000 steps for CO_2 were discarded to ensure the best values at equilibrium. Coordinates were sampled every 1000 steps. The corresponding number of steps for the charge-free CO_2 were same as those for ethane.

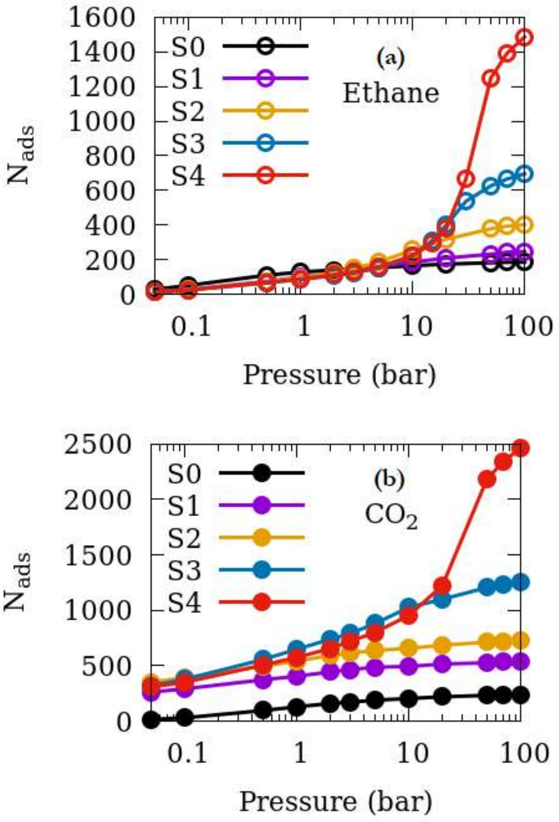

Fig. 2 Adsorption isotherms of (a) ethane and (b) CO2 in silicalite with different inter-crystalline spaces.

3 Results

3.1 Effect of inter-crystalline space on the adsorption isotherms

In Figure 2, we show the adsorption isotherms of ethane and CO_2 in silicalite models S0 - S4. For CO_2 the inter-crystalline space gives rise to higher adsorption at all pressures. For S0, both ethane and CO_2 exhibit a type I isotherm characteristic of microporous materials[30]. As the inter-crystalline space increases, the isotherms of both sorbates start to exhibit deviation from the shape of type I isotherm and take a shape that is characteristic of mesoporous materials[30]. We note that although the inter-crystalline spaces investigated are limited to 2 nm in the confinement direction, it leads to confinement along only one direction, while the inter-crystalline space is effectively infinite in other directions. This means that the inter-crystalline space represents an infinitely extended slit pore. The resulting super-crystal is thus similar to a mesoporous material. Although both ethane and CO_2 clearly exhibit an isotherm characteristic of a mesoporous material at an inter-crystalline space of 20 Å ethane starts to show a transition to this type at a smaller inter-crystalline space. Also, at low pressures the adsorbed amount of ethane is slightly lower in the models with inter-crystalline space as compared to S0. Increasing the inter-crystalline space while keeping the crystallite size the same in general results in higher amounts of sorbate being adsorbed, especially at high pressures.

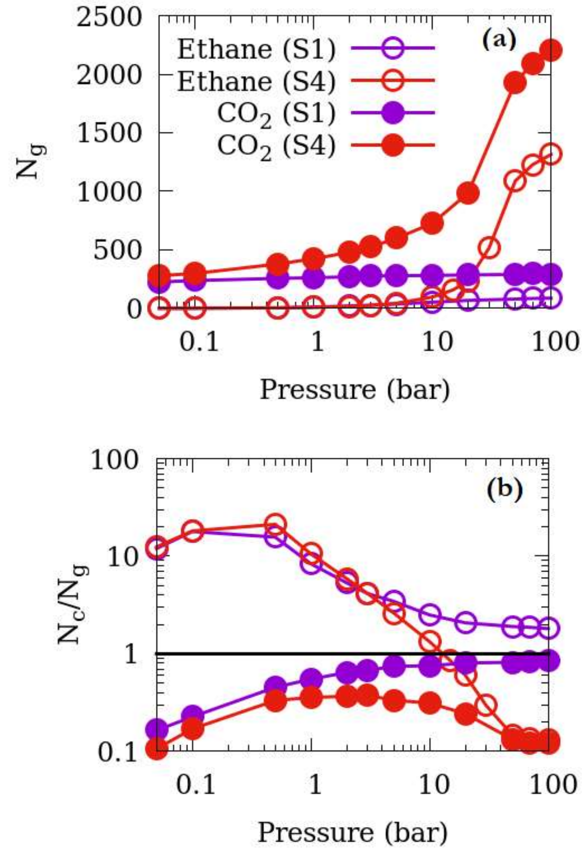

Fig. 3 (a) Sorption isotherms of ethane and CO_2 in the inter-crystalline spaces of silicalite (N_g). (b) Ratio of the number of molecules adsorbed in the crystalline pore spaces (N_c) to those adsorbed in the inter-crystalline spaces. Key to lines and symbols in (b) is same as in (a).

3.2 Preferred location of sorbed molecules

It is instructive to look at the distribution of guest molecules between the 0.55 nm pores within the crystals (N_c) and the inter-crystalline spaces (N_g). In Figure 3, we show the number of molecules adsorbed in the inter-crystalline spaces (N_g) and the ratio N_c/N_g. The ratio (N_c/N_g) is high for ethane at low pressures indicating that the ethane molecules prefer to be adsorbed in the crystalline pore spaces. At higher pressures, this ratio decreases and even becomes smaller than 1 for larger inter-crystalline spacing. Conversely, this ratio for CO_2 is smaller than 1 at all pressures indicating a larger number of CO_2 molecules occupying the inter-crystalline spaces compared to the crystalline pores. This suggests that CO_2 prefers to be adsorbed on the crystallite surface (inter-crystalline spaces).

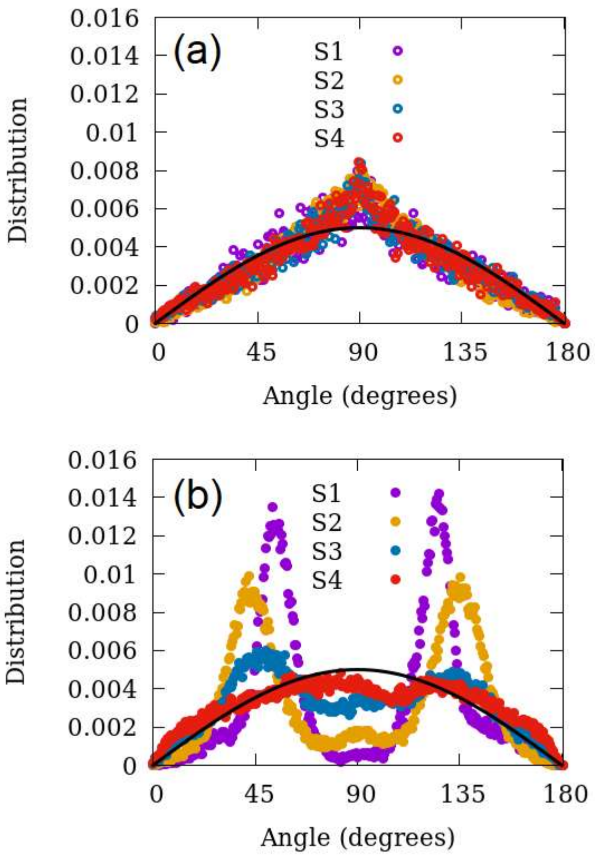

Fig. 4 Distribution of angles made by the molecules in the inter-crystalline spaces with the surface normal of the closest crystallite in (a) Ethane and (b) CO_2 at 10 bar pressure for samples with different inter-crystalline spaces. Distribution obtained for ethane and CO_2 are shown by symbols, whereas a black line represents the distribution expected for a completely isotropic system.Adsorption isotherms of (a) ethane and (b) CO_2 in silicalite with different inter-crystalline spaces.

3.3 Orientational Structure of Molecules in the Inter-crystalline Space

In Figure 4 we show the orientational distribution of ethane and CO_2 molecules that occupy the inter-crystalline spaces. Surface normal of the closest crystallite is taken as a reference and the angle made by the sorbate molecules with this direction is used to obtain the distribution. Also shown in the figure is the distribution expected for a completely isotropic system with no preferred orientation. Ethane molecules have a tendency to orient almost isotropically with a very weak preference for lying perpendicular to the surface of the closest crystallite. Further, no significant difference is observed on the orientational behavior of ethane for different inter-crystalline spacings. Conversely, CO_2 molecules in the inter-crystalline spaces show a strong preference in orientation. The two peaks observed in the distribution at $\sim$ 45 and 135 degrees demonstrate that CO_2 molecules prefer to incline on the crystallite surfaces making an angle of $\sim$ 45 degrees with the surface. This tendency of preference in orientation seems to get reduced when the inter-crystalline spacing gets larger.

3.4 Role of Electrostatic Interactions (Quadrupole moment of CO_2)

To probe the role of electrostatic interactions due to the quadrupole moment of CO_2, we removed this distinctive property and compared the simulation results to ethane. The resulting adsorption isotherms of the charge-free CO_2 and the corresponding (N_c/N_g) variation are shown in Figure 5. Clearly, the variation of quantities reported in Figure 5 for the charge-free CO_2 is more like that for ethane than CO_2 reported in Figures 2 and 3. Up to 10 bar pressure, no significant difference can be seen in the amount of adsorption for different inter-crystalline spaces, while at higher pressures (e.g. 100 bar), the amount of adsorption is about five times more in S4 (1498 molecules) compared to S0 (300 molecules).

3.5 Effect of crystallite size

We conducted additional simulations of ethane and CO_2 adsorption in a larger crystallite with an inter-crystalline spacing 20 Å (L4) keeping all other simulation details the same. The adsorption isotherms obtained from these simulations along with those from S4 for comparison are shown in Figure 6. The use of a larger crystallite results in a reduction in the amount of CO_2 adsorbed at all pressures. For ethane, this reduction in the amount of adsorption can be seen only at high pressures while at low pressures the isotherms for L4 and S4 are almost identical indicating that the same amount of ethane is adsorbed in both L4 and S4 at these pressures.

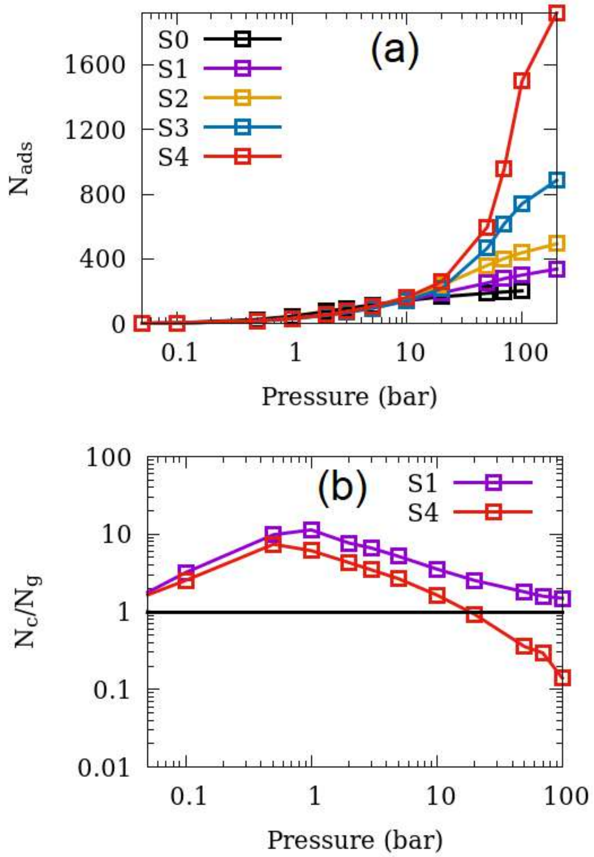

Fig. 5 Adsorption isotherms of charge-free CO_2 in silicalite. (b) (N_c/N_g) ratio for the systems S1 and S4 in (a).

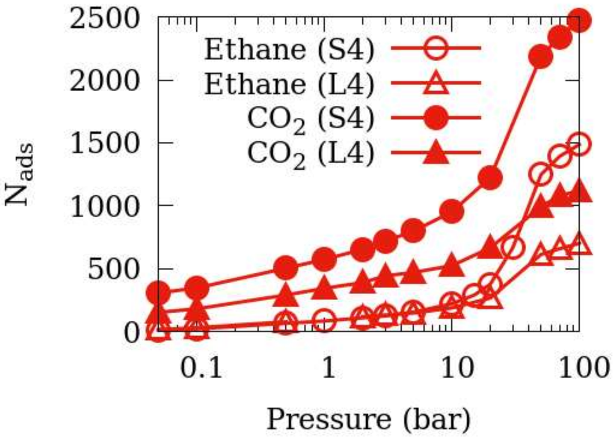

Fig. 6 Adsorption isotherms of ethane and CO_2 in silicalite with an inter-crystalline space of 20 Å and crystallites of small (S4) and large (L4) sizes.

4 Discussion

Similar to the effects of inter-crystalline space on the structure and dynamics of guest molecules as observed by Thomas and Yashonath in several systems[8–10], incorporating inter-crystalline space affects the adsorption properties profoundly. Although increasing the inter-crystalline spacing enhances the high pressure adsorption capabilities of the substrate, the effect is different for different sorbed molecules. For ethane, a preference to adsorb in the crystalline pores over the inter-crystalline spaces (large N_c/N_g) leads to a slight reduction in the adsorbed amounts at low pressures with introduction of the inter-crystalline spaces. Conversely, for CO_2 a small N_c/N_g ratio results in a higher adsorption amount even at low pressures. The preference exhibited by CO_2 to occupy the inter-crystalline spaces over the crystalline pores has important implications for experimental studies carried out on powder samples. In experiments investigating the structure and dynamics of guest molecules adsorbed in porous materials using a powder sample, some guest molecules are expected to occupy the inter-crystalline spaces. In addition empty space exists between grains and particles that are made up of several crystallites. The contribution from these to the experimental data in addition to those molecules occupying the crystalline pores is an unwanted contribution. For example, in an experiment investigating the dynamics of propane in 20 nm silica aerogel pores, it was estimated that less than 10 % of the propane fluid remained outside the aerogel pores in the sample cell due to tight packing of the sample, thereby minimizing the inter-particle spacing[18]. Note that tight packing can minimize the inter-particle spacing, but not necessarily inter-crystalline spacing. In another experiment investigating the vibrational spectra of propane in MCM-41-S pores, an absence of bulk-like peaks in the low energy spectrum of confined propane suggested that the contribution of bulk-like propane in the inter-particle and inter-crystalline spaces was negligible[31]. This is consistent with the results obtained here that show that apolar alkanes like ethane and propane are more likely to occupy the crystalline pores as compared to the inter-crystalline spaces and crystallite surfaces. Thus, even if inter-crystalline spacing can not be controlled even with tight packing of the sample, for an apolar molecule, the contribution from the fluids adsorbed in inter-crystalline spaces can be expected to be minimal. For CO_2 however, this is not the case and care should be taken to incorporate the contribution of CO_2 in the inter-crystalline space that might exhibit bulk-like behavior in the analysis of data. This is also applicable to the interpretation of adsorption isotherms obtained experimentally on powder samples for CO_2 in nanoporous silica substrates. A significant amount of CO_2 is expected to be adsorbed on the crystallite and particle surfaces in addition to the nanopores. A correct estimate of the nanopore adsorption amount would therefore require correcting for the contribution from CO_2 molecules occupying the inter-particle space.

Another important implication of the preferred adsorption of CO_2 on crystallite surfaces is for the efficiency of adsorption in a porous material. Increasing the specific surface area of a material is known to affect the adsorbing capability[32]. For example, the adsorption of bovine serum albumin (BSA) on TiO_2 has been found to be enhanced with an increase in the surface area of TiO_2[33]. While increasing the surface area is in general a good strategy for enhancing adsorption, our results indicate that increase in the surface area of a substrate might result more efficient adsorption of a quadrupolar molecule like CO_2 compared to that of an apolar molecule like ethane.

The strong quadrupole moment of CO_2 plays an important role in distinguishing its behavior from ethane. This is confirmed by turning off the electrostatic interaction in the simulation of CO_2 resulting in behavior of CO_2 very similar to that of ethane. The preferential adsorption of CO_2 on the silica surface reported in other studies[18–24] is consistent with our observation of enhanced CO_2 adsorption in the crystallite surfaces thereby occupying the inter-crystalline space even at lower pressures. In contrast ethane, devoid of strong interaction with silica prefers to adsorb in the crystalline pores rather than the crystallite surface or the inter-crystalline spaces. A stronger interaction of CO_2 with the crystallite surfaces also leads to highly ordered orientational structure of CO_2. This ordering in the orientational structure of molecules due to strong electrostatic interactions has also been observed earlier for several systems[22,34]. In fact the orientation of CO_2 molecules with respect to the surface of the crystallite is the same as that observed for CO_2 residing at the surface of a 4 nm cylindrical pore of silica[22]. At molecular dimensions the curvature of a 4nm cylindrical pore wall is very small and the surface of the pore itself can be considered planar which explains the similarity to the crystallite surface in this study. This inclined orientation of CO_2 molecules with respect to the surface is more favorable to higher amounts of adsorption as compared to an orientation parallel to the surface as the former leads to a tighter packing of the adsorbed CO_2 molecules.

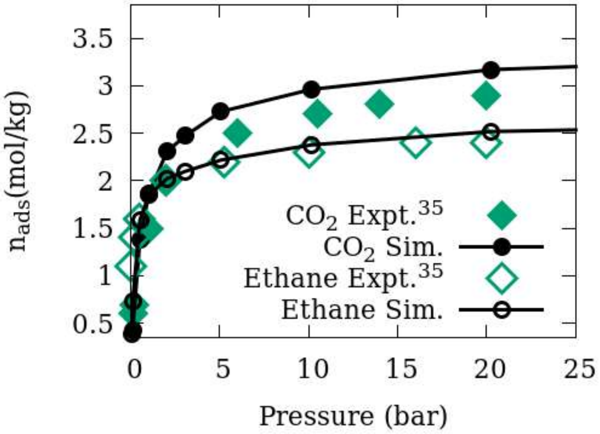

Fig. 7 Comparison of adsorption isotherms obtained here for the system S0 with the experimental data reported by Sun et al.[35]

Although the inter-crystalline spacing seems to have a significant effect on the adsorption behavior of guest molecules in silicalite as is evident from Figure 2, the isotherms obtained for a perfect crystal (S0) reported here and elsewhere[14,35] seem to agree well with the experimental isotherms obtained for powder samples. For example, we have converted the data shown in Figure 2 for the model S0 to amount of fluid in mols adsorbed per kg of silicalite and shown it in Figure 7. Only low pressure data is shown as the experimental data is limited to pressures below 25 bar. At these low pressures, although the isotherms for ethane in different models S0 - S4 are not significantly different, those for CO_2 are progressively higher for the models S1 - S4 with a significant difference between them. A good agreement between the experimental data is obtained for the models S0 for both ethane and CO_2. This means that the isotherms simulated here for models with inter-crystalline space (S1 – S4) largely overestimate the amount of the guest molecules sorbed. It is important to note here that the models S1 – S4 that account for inter-crystalline space, despite providing a model for deviation from ideal crystalline structure, have small crystallite sizes. In a real sample, the size of crystallites can be expected to be much larger and heterogenous. Thus, to get a better agreement with the experimental data, there is a need for simulating larger crystallites. Given limited computational resources, it is not possible to simulate large crystallites, but we can probe the effect of increasing the crystallite size on the adsorption isotherms. As seen in Figure 6, increasing the size of the crystallites seem to reduce the amount of molecules sorbed. The inter-crystalline space and the crystallite size thus have opposite effects on the adsorption isotherms. By balancing the size of the inter-crystalline space and the crystallites these effects can cancel each other. This means that for a large enough ratio of the crystallite size to inter-crystalline space, a poly-crystalline model would exhibit adsorption isotherms similar to a perfect crystal model. This explains the agreement observed between the simulations of adsorption isotherms in perfect crystals and the experiments carried out on powder samples.

The model simulation cell incorporating inter-crystalline space as used here and in other studies to represent a powder sample as against a crystalline sample is far from representing all the complexities present in a powder sample. A natural polycrystalline sample would have crystallites with different orientations and the individual crystallites can also be inclined to each other, making the inter-crystalline space non-uniform. However, the effects of these imperfections can be largely dominated by the effect of inter-crystalline spacing. This work is a first attempt at understanding this predominant effect and shows that just including the presence of inter-crystalline space alone can have profound effects on the simulation of adsorption isotherms.

5 Conclusions

Our simulations have shown that inter-crystalline space has a profound effect on the adsorption of guest molecules in porous materials. This effect further depends on the type of sorbate. Presence of quadrupole moment makes CO_2 adsorption in the inter-crystalline space more favorable and suggests that increasing surface area of a substrate might be a relatively more effective strategy for adsorption of a quadrupolar molecule as compared to a neutral molecule. The simulation data obtained here have important implications for experimental studies carried out on powder samples to investigate the behavior of fluids confined in porous media. While the amount of apolar fluids trapped in the inter-particle spaces, and hence giving unwanted bulk-like contribution to the experimental data can be expected to be negligible, that due to a quadrupolar fluid cannot be ignored. The result obtained here also suggest that increasing the surface area of the substrate as a strategy to enhance adsorption can be expected to work more efficiently for CO_2 compared to ethane. While larger inter-crystalline spacings lead to higher adsorption, the effect of using a larger crystallite is to reduce the adsorption amount. The mutual negation of these two effects explains the apparent agreement of the experimental data obtained on a powder sample and the simulation data obtained using a perfect crystal model. This study has important implication not only for the simulation of adsorption isotherms in porous materials, but also interpretation of the experimentally obtained adsorption isotherms.

Conflicts of Interest

The authors declare that there are no conflicts of interest.

Acknowledgements

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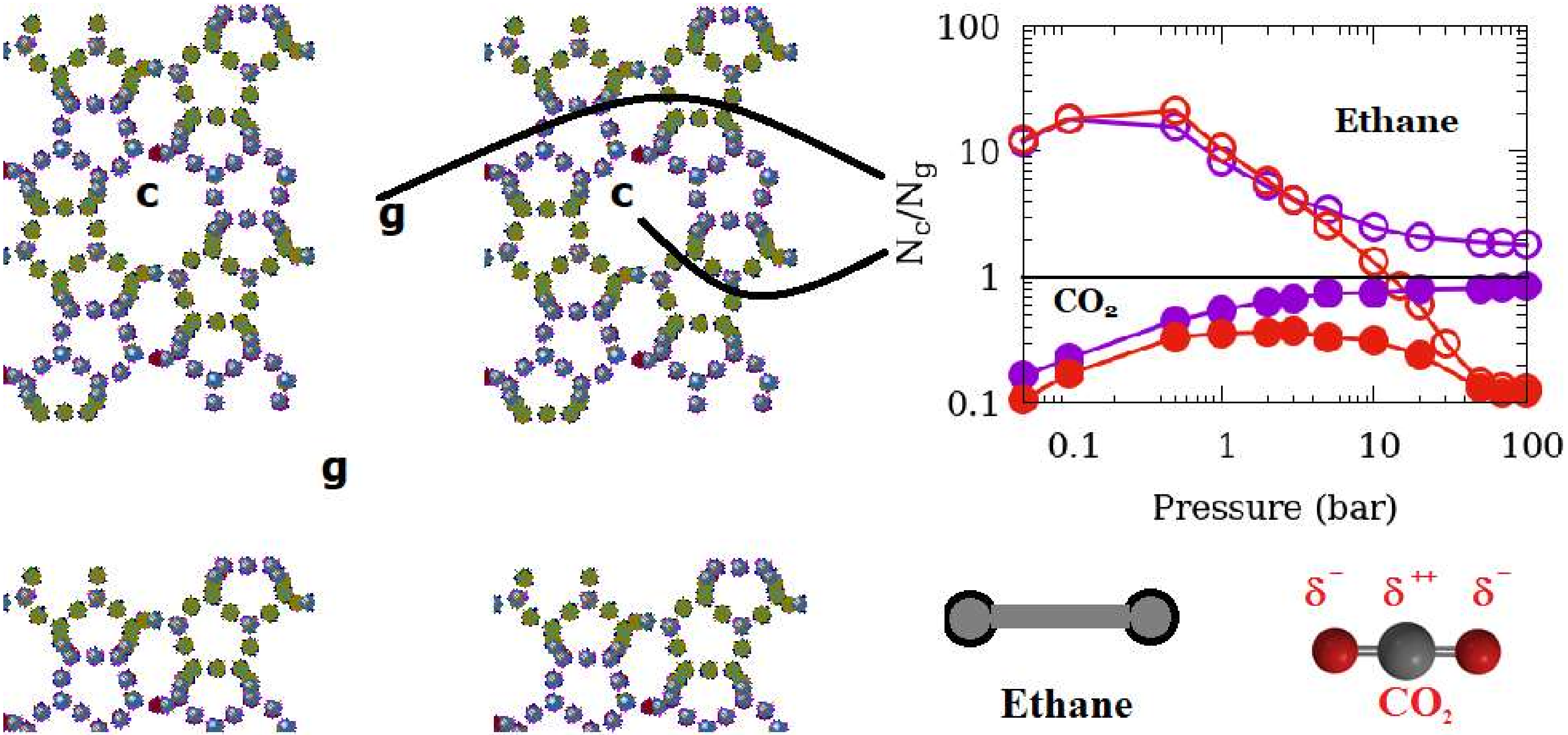

Monte Carlo simulations reveal the effects of inter-crystalline space on the adsorption of ethane and CO_2 in silicalite