SO$_2$ Adsorption in ZSM-22: Role of Orientational Disorder in the Adsorbent

Sadique Vellamarthodika$^1$, a) and Siddharth Gautam$^2$, b)

$^1$Positron Foundation for Science and Innovation, CITTIC, Cochin University of Science and Technology, Cochin, Kerala 682022, India

$^2$School of Earth Sciences, The Ohio State University, 125 S Oval Mall, Columbus 43210 USA

Corresponding author: a) sadique@positron.foundation, b) gautam.25@osu.edu

Abstract. Here we report adsorption of SO$_2$ – an industrially and environmentally important gas – in ZSM-22, a zeolite characterized by straight channel like pores. The simple pore geometry of ZSM-22 helps us make polycrystalline models of the adsorbent with different degrees of orientational disorder. Using grand canonical Monte Carlo (GCMC) simulations, we obtain the adsorption isotherms of SO$_2$ in these models. Introducing intercrystalline space is found to enhance the adsorption capacity, with a larger intercrystalline space leading to higher adsorption. Increasing the orientational disorder of the adsorbent is found to enhance the adsorption capacity too. However, the effects of orientational disorder become weaker when the intercrystalline space is widened. This weakening of the effect of orientational disorder is a result of interplay between the width of the intercrystalline space and the strength of guest-guest interactions.

INTRODUCTION

Molecular dynamics (MD) and Monte Carlo (MC) simulations are often employed to study the behavior of confined fluids. For simplicity and ease of computation, these simulations often use ideal single crystal models of the nano-porous confining medium. In reality however, most experiments are carried out on polycrystalline samples. This difference in the models used in the simulations and the more disordered samples used in the experiments has not been addressed in much details. Recently, attempts have been made at incorporating polycrystallinity and disorder in the pore network of ZSM-5 to address the effects of intercrystalline spacing and pore connectivity on the behavior of confined fluids. Both pore connectivity and presence of intercrystalline spacing have been found to affect the behavior of confined fluid significantly. While polycrystallinity in these studies was modeled by means of inserting an intercrystalline space between crystallites with perfect ordering, the individual crystallites themselves were arranged in a perfect order with all crystallites oriented in the same direction. For systems with pores in the form of channels, the relative orientation of the crystallites can affect the behavior of the confined fluid and therefore it is imperative to systematically study the effects of orientational disorder in the polycrystalline models of nano-porous materials due to crystallites disoriented with respect to each other.

ZSM-22 is an all-silica zeolite characterized by straight parallel channel like pores of sub-nanometer size. With a simple geometry of the individual pore channels and their network, ZSM-22 provides a good model system to systematically study the effects of orientational disorder in the polycrystalline model on the behavior of confined fluid. SO$_2$ is an industrially and environmentally important gas. Given the harmful effects this atmospheric SO$_2$ might have on life in general, it is important to capture and store this gas at the source. Here we study the adsorption of SO$_2$ in polycrystalline models of ZSM-22 using grand canonical Monte Carlo (GCMC) simulations. In particular, the effect of orientational disorder of ZSM-22 on the adsorption is investigated by using models of ZSM-22 with different degrees of orientational disorder.
MATERIALS AND METHODS

Atomic coordinates provided by Kokotailo et al. were used to make models of the ZSM-22 adsorbent. To start with, a unit cell was replicated 2x1x3 times to make a single crystallite. Eight such crystallites were then arranged in a 2x2x2 lattice separated from each other by an inter-crystalline space of 4 or 8 Å to stand for small and large inter-crystalline space respectively. A vacuum equal to half the inter-crystalline gap was left on all six sides of the supercell made in this way. With periodic boundary conditions applied, this supercell thus constitutes an infinitely extended system consisting of crystallites separated from each other by a fixed and uniform inter-crystalline space in all three directions. This resulted in two polycrystalline models with different inter-crystalline spacings labeled respectively ‘small gap (SG)’ and ‘large gap (LG)’. In addition, a model was made with no inter-crystalline gap between the crystallites. This is a perfectly ordered single crystal model of ZSM-22 and is labeled ‘no gap (NG)’. To add orientational disorder to the SG and LG models, one out of eight crystallites were rotated in their position by 90 degrees at a time. A series of models with different degrees of orientational disorder (OD) were thus obtained by rotating between one to four out of eight crystallites in the LG or SG systems. The resulting models are named SG-ODn and LG-ODn respectively with n denoting the number of crystallites that are rotated about their position. In all 11 different models of ZSM-22 were made for the simulations. These are schematically shown in Figure 1.

![Figure 1](image-url)

**FIGURE 1.** (a) Simulation snapshot for the perfect crystal system ZSM-22 (NG-OD0) with SO$_2$ adsorbed at a partial gas pressure of 100 atm. (b) Simulation snapshot of SO$_2$ adsorbed in the disordered ZSM-22 system SG-OD4 at 100 atm. Individual crystallites are separated from each other by inter-crystalline spacing shown in light blue whereas channel-like pores in the crystallites are marked in light magenta. (c) Schematic representation of the pore network in some ZSM-22 models. Channel-like pores are shown as single magenta line.

In the present study we use the force field parameters of SO$_2$ employed earlier by Ribeiro. SO$_2$ molecule in this formalism is represented by a sulfur (S) atom rigidly bonded to two oxygen (O$_2$) atoms with a fixed bond length of 1.4321 Å each. O$_2$-S-O$_2$ angle is fixed at 119.5°. To model the interactions of SO$_2$ with ZSM-22 we used the CLAYFF force-field parameters to represent silicon and oxygen atoms. Cross-term parameters were calculated using the Lorentz-Berthelot mixing rules. The long-range electrostatic interactions were calculated using the Ewald sum method. We used an interaction cut-off of 14 Å. Grand canonical Monte Carlo (GCMC) simulations were carried out using DL-Monte. To start with one SO$_2$ molecule was kept at the center of the simulation cell. GCMC simulations were then carried out at a given partial pressure of SO$_2$. During the simulation, the guest molecules, i.e., SO$_2$, could be inserted/deleted, translated, or rotated with respective probabilities of 0.5, 0.25, and 0.25, while all ZSM-22 atoms were kept rigid. 2 million Monte Carlo simulation steps were used to obtain the number of SO$_2$
adsorbed in the model ZSM-22 consistent with a given gas partial pressure and temperature. Out of this the first 500000 steps were discarded for equilibration. All simulations were carried out at 300 K. In all 242 simulations were carried out. More details about the simulations can be found elsewhere.

RESULTS

In Figure 2, we show the adsorption isotherms of SO$_2$ in the 11 models of ZSM-22 investigated. The effects of inter-crystalline spacing in models with perfect orientational order is shown in Figure 2a. Introducing small crystalline gaps to NG-OD0 as in SG-OD0 enhances the adsorption capacity of ZSM-22 for SO$_2$. Moreover, as this inter-crystalline gap widens in LG-OD0, the adsorption capacity increases further. In Figure 2b and c the effects of the orientational disorder can be seen in SG-OD$n$ and LG-OD$n$ models respectively. In general, with an increase in orientational disorder, the amount of SO$_2$ adsorbed in ZSM-22 increases.

![Image of Figure 2](image_url)

**FIGURE 2.** Adsorption isotherms of SO$_2$ at 300 K in ZSM-22 models with (a) different inter-crystalline spacings and uniform orientation, (b) small inter-crystalline space and different degrees of orientational disorder and (c) large inter-crystalline space and different degrees of orientational disorder.

Comparing the adsorption amounts at a given partial pressure in different models of ZSM-22 one can assess the effects of inter-crystalline spacing and the orientational disorder on the adsorption of SO$_2$ in ZSM-22. In Figure 3, we present the number of SO$_2$ molecules adsorbed in ZSM-22 as a function of the inter-crystalline spacing and the degree of orientational disorder for 4 representative gas partial pressures. The degree of disorder is represented by $n$, with a higher value of $n$ denoting higher disorder and $n=0$ denotes a perfectly oriented model with no orientational disorder.

![Image of Figure 3](image_url)

**FIGURE 3.** (a) Effect of inter-crystalline spacing on the adsorption amounts of SO$_2$ in ZSM-22 models. The effects of orientational disorder in SG-OD$n$ and LG-OD$n$ models are shown in (b) and (c) respectively. All three sub-figures share the same legend that is included in (a).
The effect of inter-crystalline spacing is an unambiguous enhancement of adsorption amounts. Further, this effect is stronger at higher pressures. This is consistent with other studies on the effects of inter-crystalline space on fluid adsorption in ZSM-5 and Mg-MOF-74. The increase in the amount of adsorption in LG models (8 Å) compared to SG models (4 Å) is stronger than that between SG and NG models.

In SG-ODn samples, when the orientational disorder is increased from n=0 to n=4, the amount of SO₂ adsorbed increases consistently at all partial pressures of SO₂. In contrast, in the LG-ODn models, the effect of orientational disorder on adsorption is absent at low pressures; similar to that in SG-ODn models at intermediate pressures; and very weak but opposite at high pressures where an increase in the orientational disorder leads to a decrease in the amount of SO₂ adsorbed. Investigating the radial distribution of constituent atom pairs (not shown) we found that in NG-OD0, the guest-guest interactions are stronger than the guest-zeolite interactions. When inter-crystalline space is introduced, the guest interaction with the crystallite surface atoms become stronger as mentioned earlier. When some crystallites are rotated to give orientational disorder to the system, the chain of molecules running through the channel like pores of vertically stacked crystallites is disrupted. However, in SG-ODn models, the guest molecules belonging to the channel of a crystallites are still in close proximity of the guest molecules adsorbed on the surface of the crystallite below the original crystallite that has been rotated. Thus, there is a continuity in the guest-guest chains leading to a high guest density and hence stronger adsorption. In case of LG-ODn models with wider inter-crystalline space, the adsorption sites on the individual surfaces and crystallites are separated by larger distances and for this reason, the effects or orientational disorder in ZSM-22 on the amounts of SO₂ adsorbed is weaker.

Although we investigated only two different inter-crystalline spacings, the variation of adsorbed amounts with the size of inter-crystalline spacing is consistent with studies on other systems that considered larger number of inter-crystalline spacings. Thus, it can be concluded that increasing the inter-crystalline spacing in general enhances the adsorption amounts. The effects of introducing the orientational disorder is however dependent on the width of inter-crystalline spacing and gets weaker with widening of inter-crystalline spacings. The gains in adsorption of fluids due to orientational disorder in the adsorbent is therefore limited to smaller inter-crystalline spacings. These results can be used to tailor make efficient gas adsorbents for capturing and storage of gases.

CONCLUSIONS

We carried out GCMC simulations to investigate the adsorption of SO₂ in channel-like pores of ZSM-22. Effects of orientational disorder of the adsorbent was studied by selectively rotating ZSM-22 crystallites by 90 degrees, thereby introducing orientational disorder of different degrees. Orientational disorder is in general, found to enhance adsorption. However, the effects of orientational disorder on the adsorption becomes weak if the inter-crystalline spacing is increased.

REFERENCES