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CO₂ adsorption on SBA-15: A molecular modelling

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Abstract. A study on molecular modelling of CO₂ adsorption on SBA-15 has been conducted. A model of SBA-15 with 5.6 nm pore diameter and 3.9 OH/nm² was constructed and used for the molecular studies of CO₂ adsorption. Adsorption of CO₂ molecules on SBA-15 occurred as a result of the formation of hydrogen bondings between CO₂ molecules and hydroxyl groups on the silica surface. In the presence of water molecules, the interaction between CO₂ molecules and the silica surface slightly decreased.

1. Introduction

SBA-15 (the acronym of Santa Barbara Acid 15) is one ordered mesoporous materials with a variety range of application. Due to the unique characteristics of SBA-15, this mesoporous material is applicable as catalyst [1] and adsorbent [2, 3]. SBA-15 is a mesoporous material with an ordered hexagonal structure that has a large pore size (5-30 nm), high surface areas (687-910 m².g⁻¹), large pore volumes (0.5-1.2 cm³.g⁻¹), and micro pore volumes [2, 4, 5]. The micropores increase the surface areas and surface roughness that are useful for adsorption. Furthermore, these micropores presented result in a significant higher pore volumes and surface area [5]. In comparison to MCM-41 and HMS, which have a hexagonal structure, SBA-15 is hydrothermally much more stable due to the thicker pore walls of SBA-15 (2.7 nm) [6]. It appears that SBA-15 is promising for use as a CO₂ capture agent considering the pore size and the high hydrothermal performance, even in the presence of moisture.

Over the years SBA-15 has been studied in the context of CO₂ adsorption. However, there has been a limited study of the relationship between molecular structure of SBA-15 and CO₂ diffusion within the structure on an atomistic scale. Computational chemistry, based on quantum mechanics, provides features to allow investigation of molecular structures on nanoscale and reaction mechanisms within the structures [7]. Among other computational chemistry methods, molecular modeling or molecular dynamic (MD) is a powerful tool for providing a better insight of CO₂-SBA-15 interaction, especially dynamic behaviors up to an atomistic level.

The models for SBA-15 have been proposed with different methods. Most recently, Bhattacharya, *et.al* [4] constructed the realistic model for mesoporous silica SBA-15 including the micropores in the pore walls. The initial structure for the model was a group of triblock copolymer surfactants which each surfactant consists of 11 lattice units. The surfactant was constructed to mimic the experimental surfactant P123, with 5 hydrophobic units and 3 hydrophilic units on each surfactant molecule.

In this work, a model for the structure of SBA-15 is proposed. This model is used to investigate the dynamic behaviours of partially dehydroxylated SBA-15 as opposed to fully hydroxylated SBA-15. The study also aims to study the CO₂ diffusion behaviour within SBA-15 in the presence of water molecules.

2. Materials and method

Molecular dynamic studies was conducted using Material Studio® 4.4 (Accelrys; San Diego)[8] combined with the molecular simulation program DISCOVER, FORCITE and the COMPASS as forcefield. The initial model of SBA-15 was constructed and then was subjected to further preparation



to get a good agreement with the experimental material. The study focused on evaluating the thermal stability of the hydroxyl groups on the surface of SBA-15 and the dynamic behaviour of SBA-15. SBA-15 was constructed with the similar procedure as reported by Chaffee [9]. The initial structure used for the molecular dynamic studies was generated from a three dimensional infinite lattice of α -quartz ($a=4.913$, $b=4.913$, $c=5.4052$, $\alpha=90$, $\beta=90$, $\gamma=120$). The pore diameter for the model is 5.6 nm, which corresponds to the experimental materials to allow proportional comparison. After geometry optimization, the fully hydrated material was then subjected to subsequent different temperatures, namely 373 K, 473 K, 573 K. This dehydration steps were performed via an iterative sequence of MD runs followed by water removal from Si-O-Si linkages.

The partially dehydrated model was used to investigate the CO_2 diffusion behaviour, in the presence of water molecules. Dynamic simulation was conducted by placing 15 molecules of CO_2 in arbitrary positions within the structures. Calculation of the diffusion behaviour of CO_2 in the presence of H_2O was achieved with the same procedure by adding 15 CO_2 molecules and 10 H_2O molecules. The model was subjected to dynamic simulations at 348 K at constant volume and temperature (NVT). The simulations controlled by Anderson method were carried out using 110,000 steps (110 ps) and 1 fs time steps. After which, the partially hydrated model is analysed with mean square displacement to get plots of interactions between gas and the silica surface.

3. Results and discussion

3.1. SBA-15 modeling

A model of SBA-15 has been prepared with 5.6 nm pore diameter. The initial model of α -quartz was used to construct a supercell with $a=7.36$ nm, $b=7.36$ nm, $c=0.54$ nm, $\alpha=90$, $\beta=90$, $\gamma=120$. The supercell was carved to construct a whole within the structure and was followed by hydroxylation to Si and O atoms which have less than 4 bonds and 2 bonds, respectively. The fully hydroxylated SBA-15 was subjected to geometry optimization to get a reasonable structure with the lowest energy.

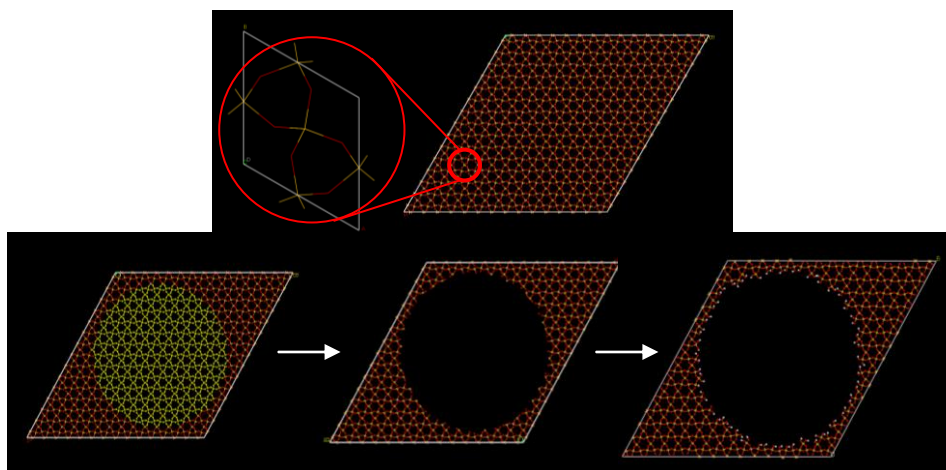


Figure 1 Construction steps of fully hydroxylated SBA-15. Three dimensional structure of α -quartz was used as initial structure. All atoms within radius 2.6 nm were selected to form a whole within the structure. The fully hydroxylated model was achieved by adding O-H or H.

Molecular dynamic simulation was conducted to determine which bonds are close enough and form hydrogen bonds. 72 sets of adjacent OH groups were edited prior to length distribution analysis. One set is the distance between O of one OH group and H of the adjacent OH group (**Figure 2**). Each set was analysed with length distribution. The result from the analysis is a plot of length distribution versus frequency, as can be seen at **Figure 3**.

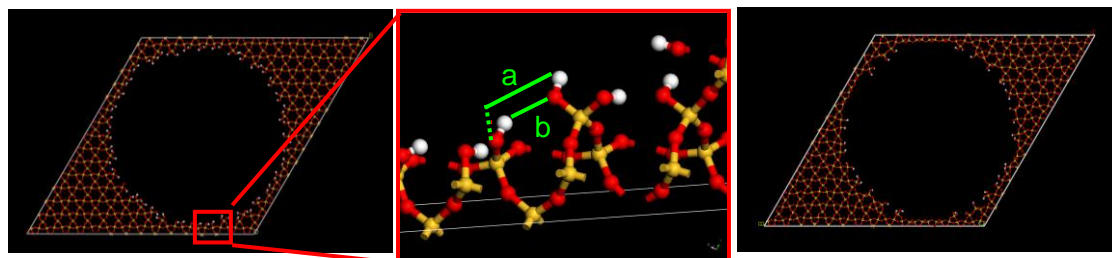


Figure 2 Selection of sets for length distribution analysis. The removal of water molecules is determined from length distribution plots resulting in partially dehydrated SBA-15.

The hydroxy pair 14 is close enough to form hydrogen bond whilst hydroxy pair 19 is not close enough to form hydrogen bond. Thus, pair 14 was chosen for dehydration by removing H₂O molecules from Si-O-Si linkages. At 373 K, there are 16 pairs of sets that are close enough to form hydrogen bonds. These all sets were dehydrated by removing water molecules. After which, the partially dehydrated model was subjected to geometry optimization with Fine quality using Smart method. Molecular dynamic simulation at higher temperature was performed followed by length distribution analysis to perform dehydration steps continuously. The iterative replication of this process, result in a reduction of silanol numbers from 8.2-3.9 OH/nm².

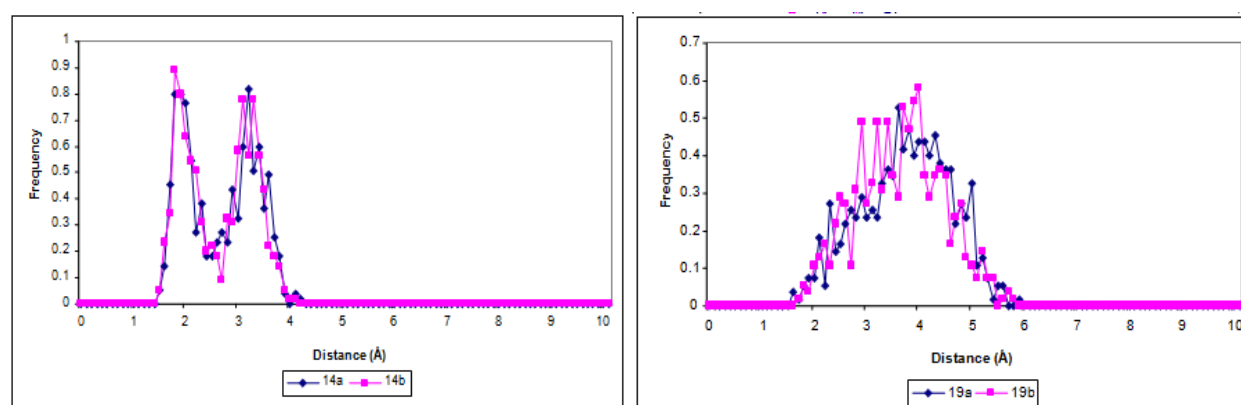


Figure 3 Length distribution plots for hydrogen bonds the hydroxy pairs 14 and 19. The maximum distance for hydrogen bond formation is 2.5 Å.

Within fully hydroxylated SBA-15, there are various types of hydroxyl groups on the silica surface, namely free (isolated) OH, vicinal (bridged) OH, geminal OH, and siloxane bridge (**Figure 4**). The dehydroxylation of silica surface occurs in several steps. Therefore, the molecular dynamic simulation was carried out at progressive temperatures. According to Voort *et.al* [6], at 373 K, below 400 K, the main dehydration occurred is the removal of physisorbed water. Yet, in the fully hydroxylated model, there is no physisorbed water molecules modeled. However, at this temperature there is a significant decrease in the amount of free hydroxyl group by 50%, from 51 to 24. At higher temperature, 473 K, the amount of free OH was constant compared to that at 373 K. Yet, the number of geminal OH and vicinal OH decline slightly to 5 and 3 pairs, respectively. Approximately 27 free OH are present on the SBA-15 surface at 573 K. The models resulted from the dynamic simulation at this temperature was chosen as a final SBA-15 structure containing 3.9 OH per nm². At higher temperature, the distance between O of one OH and H of another OH is getting further, so that it is more unlikely for both O and H to create hydrogen bond. The increase in temperature, from 373 K to 573 K, increases the amount of free OH but decreases the amount of bridged and geminal OH. Above 673 K, it is predicted that there will be only free OH left on silica surface. The results have a good

agreement compared to silica gel with pre-treatment temperature reported by Voort *et.al* [6]. Surface hydroxyl group concentration and amount of various types of OH at different temperatures are shown at **Table 1**.

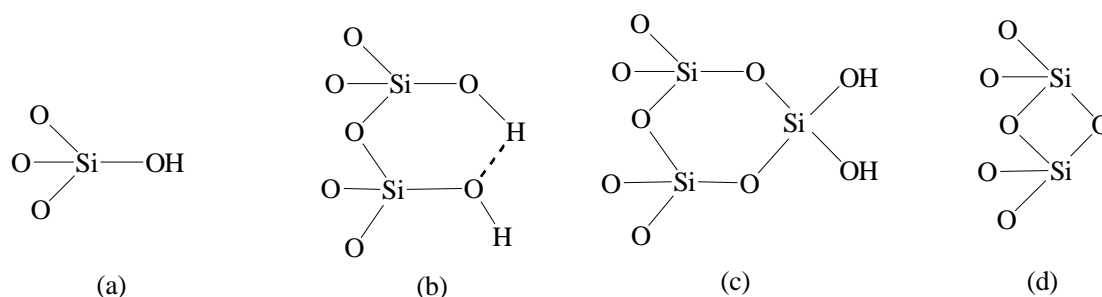


Figure 4 (a) free OH, (b) vicinal OH, (c) geminal OH, (d) siloxane bridged

Table 1 Various types of hydroxyl groups on SBA-15 models

Model	$\alpha_{\text{OH}} (\text{nm}^{-2})$	Free OH	Geminal OH (pairs)	Vicinal OH(pairs)
Fully hydrated	8.2	51	11	8
Partially dehydrated				
373 K	4.9	24	8	5
473 K	4.2	24	5	3
573 K	3.9	27	4	2

3.2. CO_2 interaction within SBA-15 structure

Interaction between CO_2 , in the presence and in the absence of water molecules, and the silica surface is mainly based on the formation of hydrogen bond. The formation of hydrogen bond between oxygen of CO_2 and hydrogen of hydroxyl group on silica surface bring CO_2 molecules move closer to silica surface. After geometry optimization, 10 out of 15 CO_2 molecules within fully hydrated model get closer to silica surface, whilst 5 other CO_2 molecules stay freely within the pore.

In partially dehydrated model, similar to fully hydrated model, there are 5 free CO_2 molecules within the pore after geometry optimization. However due to less hydroxyl groups this model possessed, it is assumed that there is a competition among CO_2 molecules to form hydrogen bonds, especially on the surface containing hydroxyl group. In the presence of water molecules, the formation of hydrogen bond is not only based on the interaction between O of CO_2 and H of hydroxyl group, but also is created from the interaction between O of CO_2 and H of H_2O , and between H of H_2O and O of hydroxyl groups.

Molecular dynamic simulation was performed after geometry optimization. The dynamic simulation was performed using FORCITE and the COMPASS as a forcefield at 75 °C and was followed by mean square displacement analysis. The dynamic simulation was achieved after running the model at 110 ps with 1 fs step. Plots of simulation time versus mean square displacement of CO_2 molecules are shown at Figure 5. Three CO_2 molecules interact stronger with hydroxyl groups on silica surface compared to other molecules. These three molecules, denoted as j,o and n, are molecules with low coefficient diffusions. Other molecules with higher coefficient diffusions interact much weaker rather than j,o, and n. These molecules inclined to interact with H_2O molecules and to move actively within the pore. It appears that the presence of water hinder interaction between CO_2 and hydroxyl groups on silica surface.

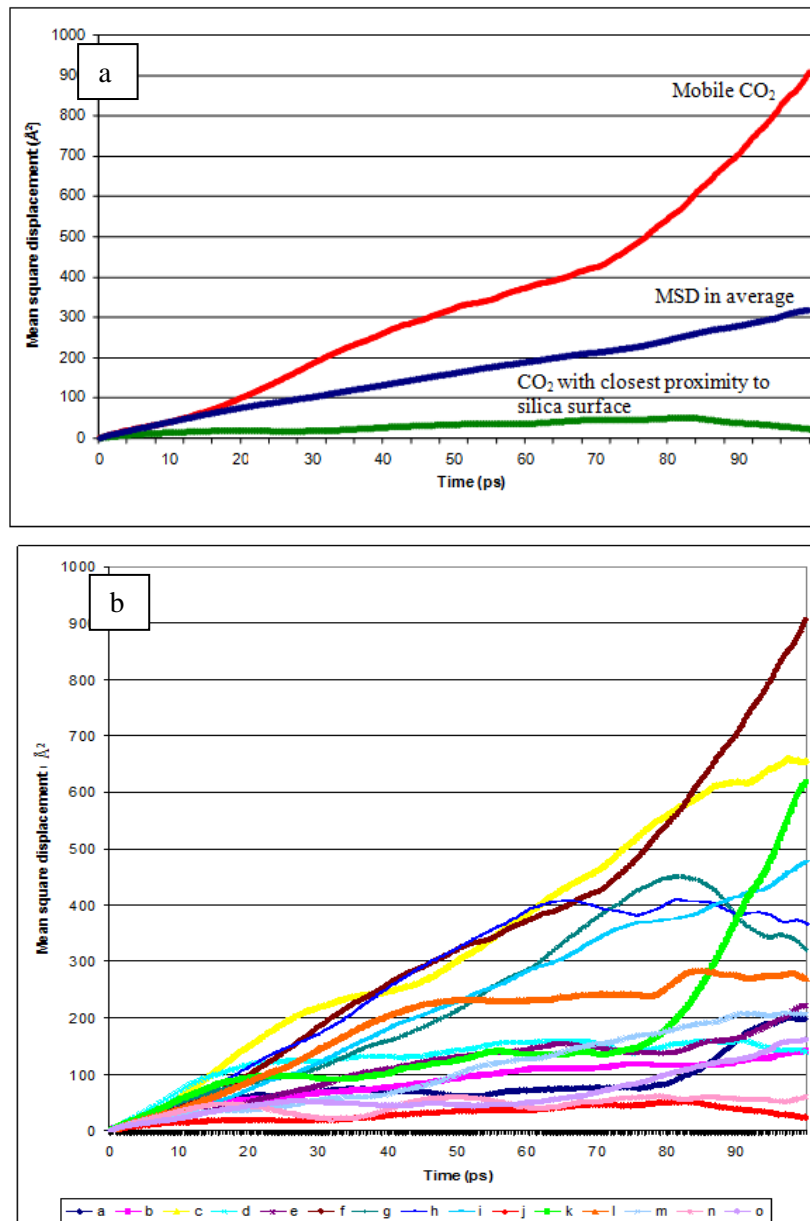


Figure 5 Mean square displacement for (a) CO₂ molecules and (b) each 15 CO₂ molecules within partially dehydrated SBA-15 in the presence of water at 75°C

Coefficient diffusion (D_α) of CO₂ molecules within three dimensional structure of partially dehydrated SBA-15 (3.9 OH/nm²) is measured by equation below:

$$D_\alpha = \frac{1}{6N_\alpha} \lim_{t \rightarrow \alpha} \frac{d}{dt} \sum_{i=1}^{N_\alpha} [(\bar{r}_i(t) - \bar{r}_i(0))^2] \quad (1)$$

which $\lim_{t \rightarrow \alpha} \frac{d}{dt} \sum_{i=1}^{N_\alpha} [(\bar{r}_i(t) - \bar{r}_i(0))^2]$ is a slope of mean square displacement plot. In Figure 6, the slope of MSD plot is 2.9618, so that the coefficient diffusion for CO₂ molecules in average within the model is 0.4936. Calculations of coefficient diffusion of each molecule were conducted by applying equation

1. However, some mean square displacement plots are not linear, so that the slopes of the graph are determined from linear trend of the graph. For instance, to calculate coefficient diffusion of CO₂ (h), the slope is determined from the linear trend in range of 0-60 ps (figure not shown). Above 60 ps the plot is not linear so it can be neglected in gradient calculation. Coefficient diffusion of each molecule is presented in Table 2.

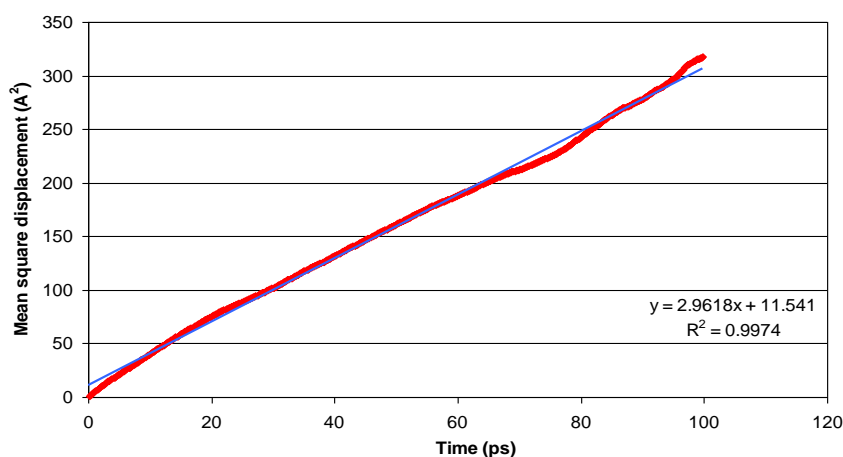
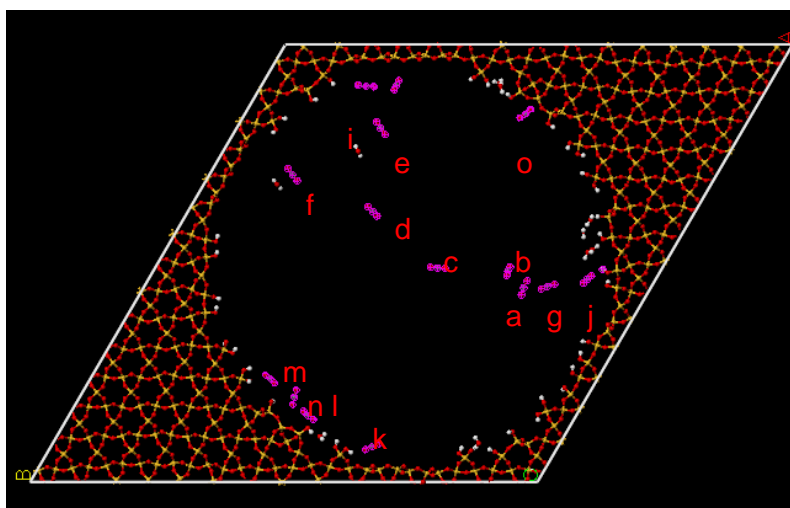


Figure 6 Mean square displacement of 15 CO₂ molecules in average

From the data presented in Table 2, it is clear that CO₂ (j), (o), and (m) are interacted stronger with silica surface compared to other CO₂ molecules. CO₂ (d) with the highest coefficient diffusion, has the greatest mobility compared to other molecules.

Table 2 Coefficient diffusion (D_a) of each molecule within partially dehydrated SBA-15 (the picture presented shows the position of each atom)



CO ₂	(D_a)
a	0.0917
b	0.1232
c	0.2264
d	0.2409
e	0.0928
f	0.2179
g	0.1304
h	0.2234
i	0.1627
j	0.0442
k	0.1649
l	0.1738
m	0.0743
n	0.1024
o	0.0687

Study of CO₂ interaction in the absence and in the presence of water within fully hydrated material is worthy for future work. However, calculation time for quantum mechanical calculation increases with the size and the complexity of the structure. In this mini project, some calculations are

still running. Thus, the data for these calculations cannot be reported. These calculations are geometry optimization for fully hydrated model with CO₂ and H₂O molecules within the structure and dynamics simulation for fully hydrated models.

Another future work required is a comparison study of CO₂ interaction within fully hydrated material and CO₂ interaction within partially hydrated material. It is projected that the formation of hydrogen bonds are more likely to occur within a model with more hydroxyl groups as opposed to a model with less hydroxyl groups. The presence of water molecules is also critical to be considered in correspondence to the selectivity of silica surface towards CO₂ and H₂O. It appears that the selectivity of silica surface will decrease in the presence of water.

4. Conclusions

A model of SBA-15 with 5.6 nm pore diameter has been constructed. The model has 3.9 OH/nm². The increase in temperature on dehydration process results in a decrease in vicinal and geminal OH, yet results in a rise in the amount of free OH and siloxane bridged. The visualisation of CO₂ interaction within the model gives a better understanding of the dynamic behaviour up to an atomistic level. CO₂ molecules have a tendency to form hydrogen bond with hydroxyl group on silica surface. However, the existence of water molecules slightly decreases the interaction between CO₂ and SBA-15.

Acknowledgments

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