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Molecular Dynamics Simulation of CO_2 Adsorption and Diffusion in UTSA-16

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Abstract

Molecular dynamics simulation has been employed to calculate the amounts of adsorption and diffusion of CO_2 in a type of MOF named UTSA-16. The UTSA-16 has been chosen in this work due to high active water molecules coordinated in its structure which strengthen CO_2 interaction and enhances its sorption capacity. Effects of temperatures 298, 313 and 338 K and pressures up to 40 bar on the simulated adsorption properties and also on the diffusion coefficients have been elucidated. To shed light on the mechanism of microscopic phenomena, mean square displacement (MSD) and density profile analyses have been provided and discussed. It has been found that the amount of carbon dioxide adsorption increases with pressure enhancement and temperature reduction. The evaluation of density profile shows the disorder distribution of CO_2 molecules through simulation box at lower pressure and their association in the center of the box at higher pressure. The slope of the MSD value increases with increasing pressure and decreasing temperature. As a result, CO_2 diffusion coefficient decreases with temperature and increases with pressure.

Keywords: *Adsorption; CO_2; diffusion; molecular dynamics simulation; UTSA-16.*

1. Introduction

The emission of greenhouse gases (GHGs) such as CH_4, NO_2 and CO_2 from the use of coal, petroleum and natural gas resources are increasing faster than ever. Indeed, the complex natural carbon cycles are not capable to sequester the carbon which is beyond the earth's atmosphere full capacity. Therefore during recent decades, the global-warming and climate change debates has received the attention of initiatives and scientists. They endeavor to mitigate GHGs discharge to the environment and impede the adverse environmental impacts [1-2]. There are a number of options to reduce the CO_2 emissions, among them is switching to fuels with less carbon footprints, improving the energy efficiency, displacing fossil fuels with renewable and biological energy, and promoting carbon capture and utilization (CCU) [3-7]. CCU is one of the attractive options in mitigation portfolios due to its inherent potential in carbon withdrawal from the atmosphere or negative emission. Furthermore, CCU can be integrated into other energy systems without needing large amendment and can decarbonize the emission-intensive industries such as cement production by CO_2 transformation from a contaminating waste product to valuable commodities [8-9]. It could also be the opportunity for CO_2 storage at commercial-scale projects including enhanced oil and gas recovery, saline formations and CO_2 mineralization [10-11]. To put in a nutshell, capturing the large quantity of CO_2 from post-combustion gas stream and its recycling into valuable products has significant potential for growth in industrial scale. Nevertheless, high efficiency and cost of CO_2 capture membranes has been the main obstacle for the practical implementations of for CCU. Therefore, it is desirable to develop the effective materials that have thermal and physical stability, remarkable permeability and selectivity, and tolerance to contaminants.

Different technologies would be used recently for the removal of pollutants, among them are catalysis oxidation, biofiltration, absorption, condensation, membrane separation and adsorption. Adsorption is recognized as one of the promising technique in separation methods thanks to its superior features including having high removal efficiency, versatile feasibility, mechanical stability and simplicity, being environment-friendly and low cost efficiency. Adsorption is an economic and effective approach that can remove multiple contaminants at the same time using a wide variety of adsorbents including nano-sized carbon materials [12-14] and Metal Organic Frameworks (MOFs).

The outstanding features of metal organic frameworks make them a unique sorptive material for industrial CCU applications. MOFs are crystalline nanoporous materials that are constructed from inorganic and organic building units. The intrinsic crystallinity of MOFs offers the opportunity to construct membranes with the ability of separating gaseous components on the basis of differences in the molecular size and shape. The critical significance of MOFs lies in the fact that the dizzying range of them can be constructed by seemingly endless combination of building units [15]. The type of their topology is momentous for application of these outstanding materials for post-combustion CO_2 capture. Since its discovery, UTSA-16 has attracted interest for possessing highest performance in CO_2 adsorption in post-combustion emission treatment [16-17]. UTSA-16's structure constitutes of tetra-nuclear cobalt citrate clusters surrounded by four potassium ions, each of which coordinates with two structural water molecules, i.e. $[KCo_3(cit)(Hcit)(H_2O)_2]$ while $cit=C_6H_4O_7^{-4}$ and $Hcit= C_6H_5O_7^{-3}$. The structure of UTSA-16 along with cit and Hcit have been shown in Figure 1. The presence of suitable pore spaces where CO_2 molecules directly interact with water molecules enhances its sorption capacity and separation

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selectivity. The adsorption equilibrium data of carbon dioxide, methane and nitrogen on UTSA-16 has been previously published in the literature by Xiang et al. [18]. The pressure range has been limited to1 bar, but not higher pressures.

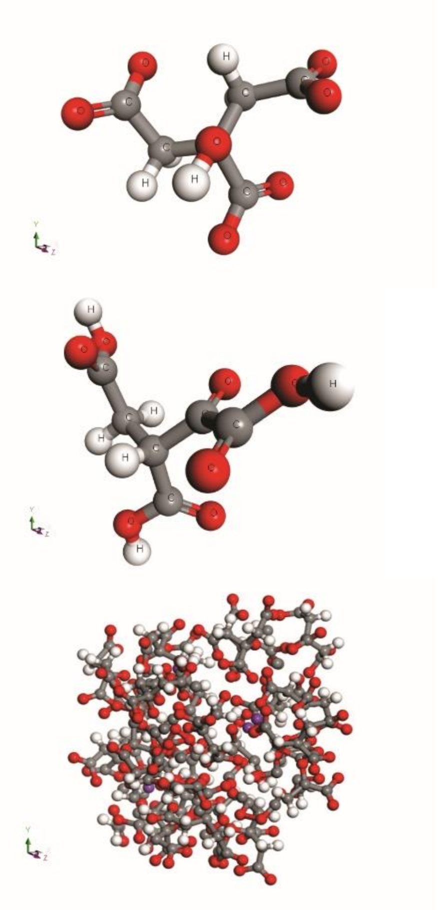

Figure 1. Atomic structure of cit (up), Hcit (middle) and UTSA-16 (down). (grey: Carbon, red: Oxygen, violet: Potassium, white: Hydrogen, blue: Cobalt).

Agueda et al. [19] synthesized UTSA-16 extrudate to measure CO_2 and other single gas diffusion through the framework. The pure adsorption equilibrium isotherms have been also measured at different temperatures (298, 313 and 338 K) and high pressures up to 40 bar for carbon dioxide. Grande et al. [20] utilized UTSA-16 for CO_2 capture from pre-combustion off-gases. They measured quaternary breakthrough curves for a typical steam-methane reformer and simulated the results using a mathematical model in order to improve the PSA unit. They also investigated a 3D printed UTSA-16 for its use within adsorption process at low pressures under a CO_2 flow [21].

The description of MOFs functionalities and explanation of their gas adsorption capacities is a challenge. The implicit knowledge of configurations and atomic or molecular interactions are required to understand the complexity of what happening inside the pores. In addition, experiment explorations on CO_2 dynamics within MOFs are limited. Molecular simulation techniques can provide the great help for researchers to screen and characterize microporous materials and to correlate the macroscopic physical properties with ones at the molecular level. While the substances' architectures are difficult to be synthesized experimentally, experimental techniques can be replaced by a rigorously designed computer simulation. Then, it is advantageous that one can save time and money by calculating properties through computational simulations. During recent years, several molecular simulation studies have been published that present Grand Canonical Monte Carlo (GCMC) and Molecular Dynamics (MD) simulations to screen different MOF structures to investigate a potential membrane candidates for a desired separation process [22-26]. They predict permeability and selectivity of MOFs and provide atomic-level insights into the design of novel materials. In this respect, Burns et al. [27] integrated industrial vacuum swing adsorption (VSA) simulator with GCMC simulations to bridge the gap between materials design and process engineering and to perform a large-scale screening of a series of MOFs, where one of them was UTSA-16, to find the best material to meet the highest CO_2 purity and recovery targets.

To the best of our knowledge, no diffusion parameter and no adsorption equilibrium data have been simulated for CO_2 in UTSA-16 at high pressures. The novelty of this work has been specified by employing MD simulation to calculate CO_2 adsorption and diffusion in UTSA-16 using Groningen Machine for Chemical Simulations (GROMACS) software. The results have been compared with those of the experiment [19]. Furthermore, to shed light on the mechanism of microscopic phenomena and even retrieving quantitative and qualitative information about the interaction between CO_2 and UTSA-16, mean square displacement and density profile analyses have been provided and discussed to elucidate the role of the adsorbent and the effect of pressure and temperature on the observed transport properties.

2. Simulation Details

GROMACS is a versatile open source software primarily designed to simulate Newtonian equations of motion in proteins and lipids, but thanks to its speed, many researchers applied it on polymers, macromolecules and MOFs. In this study, all simulation runs have been accomplished by employing the GROMACS package [28-29]. The simulation unit box is a cell which is selected sufficient large to ensure that the minimum image convention is obeyed. UTSA-16 has been considered as a rigid structure in a crystallographic unit cell (a = 6.0 nm, b = 6.0 nm and c = 6.0 nm). Each novel molecule, such as UTSA-16 adsorbent, must be parameterized individually. The conventional approach to develop a force field for description of a novel molecule is to manually assign atomic parameters. As this procedure is time-consuming and tedious, a web-based server, i.e. PRODRG, that generates force field descriptions of large molecules on the basis of GROMOS 43A1 has been developed. Here, the PRODRG server [30] has been examined to generate the force filed of UTSA-16 as it gives better agreement with the experimental isotherms [31]. In the GROMOS force field, aliphatic carbon atoms are assigned as united atoms, i.e., the carbon atom and the hydrogen atoms which have been bonded to it are treated as a single atom. This modification reduces computational effort up to a factor of 9; however the slight directional and volume effects of the presence of these hydrogens is neglected. In this force field, the parameterization is based primarily on reproducing the free enthalpies for a range of compounds. The non-bonded interactions between atoms which belong to different molecules have been described by pair wise-additive Lennard-Jones (LJ) 12-6 potentials. Cross-interactions between unlike atoms are calculated by the Jorgensen combining rules [32].

Although PRODRG is a useful tool, the input topology files used by GROMACS for small molecules (*.itp files) may be generated by the server PRODRG. However, these files must be adjusted for UTSA-16 due to the charge group adopted by PRODRG. The output topologies also contain atomic charges that are not consistent with the GROMOS force field. Knowing the defects in the PRODRG to find the partial load, quantum mechanics under the Hartree–Fock model has been used to correct the partial load. Therefore, the atomic charges for the UTSA-16 molecule have been assigned by performing the Hartree–Fock quantum mechanical calculations using Spartan software. This procedure is a common method, in the context of molecular parameterization, for dealing with adsorbents based on the GROMOS force field [33-34]. To accomplish the simulation computation, periodic boundary conditions have been taken into account for all directions of simulation box. Atom-based method has been prioritized and exerted for the computation of potential energy with a cutoff radius of 1.0 nm. The linear constraint solver (LINCS) has been applied for constraining the molecular bonds, the Leap frog algorithm [35] for integrating the equations of motion and Particle Mesh Ewald (PME) of fourth order [36] for calculating long range interactions. The MD run duration for each simulation was 400 ns with time step of 2 fs and neighbor updating of each 10 fs. All coordinates were saved for the trajectories every 20 ps. After energy minimization, the NVT (an ensemble with constant Number of particles, Volume and Temperature) and NPT (an ensemble with constant Number of particles, Pressure and Temperature) equilibrium steps were performed for 20 ns. The Berendsen thermostat and barostat [37] have been used by utilizing coupling time constants of 0.5 and 2 ps to efficiently relax the system to the target temperature and pressure.

2.1 Adsorption

The amount of adsorption has been calculated on the basis of the number of CO_2 molecules which occupy the volume between the mass center of UTSA-16 to a certain distance in three dimensions. The radius of CO_2 molecules has been also considered. According to the volume of CO_2 molecules inside the simulation box and the volume of empty space considered within and around the adsorbent, the molecules that have been placed in the pre-defined interval after system equilibration have been accounted as adsorbed molecules. Thus, the amount of adsorption is equal to the ratio of the number of CO_2 molecules in this interval to all CO_2 molecules in the simulation box.

2.4 Diffusion

Mean square displacement (MSD) is an analysis technique to investigate the diffusivity of CO_2 molecules in the simulated UTSA-16 adsorbent. It determines the gas molecules average displacement as a function of time in the limit as t approaches infinity. Then, the diffusion coefficient (D_s) can be obtained during random motion in three dimensions by using Einstein relation which is the slope of MSD over time [38,39]:

$$D_s = \frac{1}{6}\frac{d}{dt}\lim_{t\to\infty} MSD\ (t) = \frac{1}{6}\frac{d}{dt}\lim_{t\to\infty}\langle|\vec{r}(t)-\vec{r}(0)|^2\rangle \qquad (1)$$

where D_S is the self-diffusion coefficient, and $\vec{r}(0)$ the initial position vector of a molecule and $\vec{r}(t)$ the position vector of a molecule at time t.

3. Results and Discussion

The structure of UTSA-16 along with loaded CO_2 molecules has been demonstrated in Figure 2.

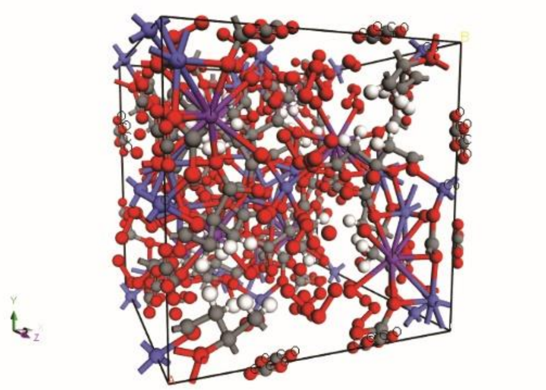

Figure 2. UTSA-16 and CO_2 molecules in simulation box. (grey: Carbon, red: Oxygen, violet: Potassium, white: Hydrogen, blue: Cobalt).

The adsorption or average loading of CO_2 in UTSA-16 has been computed at temperatures 298, 313 and 338 K and pressures up to 40 bar in order to investigate the effect of temperature and pressure on the amount of CO_2 loading. The calculated adsorption isotherms have been compared with experimental isotherms [20] and plotted in Figure 3.

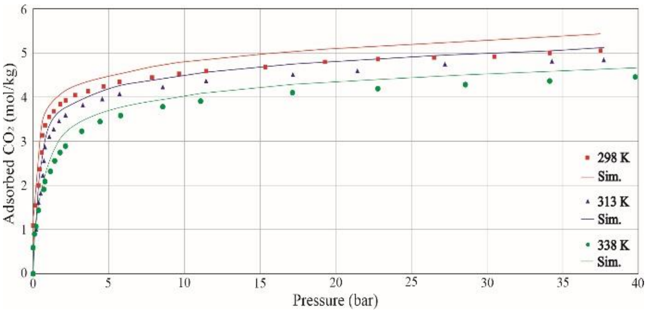

Figure 3. CO_2 adsorption isotherms and experimental data [20] at temperatures 298, 313 and 338 K.

The percentage of Average Absolute Relative Deviation (%AARD) has been calculated as below in order to show the adsorption differences quantitatively:

$$\%AARD = \frac{100}{N}\sum_{1}^{n}\frac{a_{cal}-a_{exp}}{a_{exp}} \qquad (2)$$

The values of %AARD have been obtained as %8.57, %8.52 and %8.13, respectively at temperatures 298, 313 and 338 K. The deviations show that the simulated results are in good agreement with measured data points demonstrated the validity of our computational method. It is obvious that UTSA-16 adsorbs higher amount of CO_2 at higher pressures and lower temperatures that obeys the general rule of gas capturing in porous structures. The same behavior is always observable in coal, zeolites and other porous materials [40-41]. As temperature goes up, the irregular thermal motion of CO_2 molecules become more intense, making it more difficult for the molecules to remain within the pores of MOF matrix. But a higher pressure would be favorable for the matrix to trap the CO_2 gas molecules.

To evaluate the impact of pressure on the adsorption performance of UTSA-16 more exactly, the variations of CO_2 density profile has been evaluated with respect to the distance from box center. The analysis of density profile is important to assess how the gas molecules accumulate in the simulation box. It gives an estimation of the presence of CO_2 molecules in the vicinity of the sorbents at various pressures. Density profiles have been computed considering the last 50 ns of each trajectory, using snapshots taken every 100 ps (500 frames per simulation). The exact shape of density profiles have been given in Figure 4 for six pressure points in the interval of 0.5 to 20 bar. As it is clear, numerous fluctuations in density are observed at low pressures showing the disorder distribution of CO_2 molecules through simulation box.

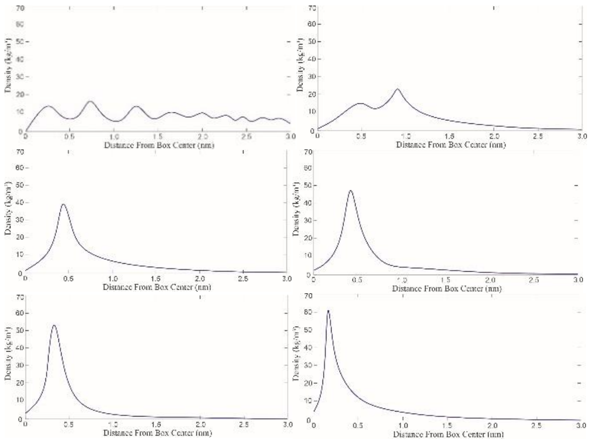

Figure 4. The diagram of density profile at 298 K and at pressures 0.5 bar (up, left), 2.5 bar (up, right), 5 bar (middle, left), 9 bar (middle, right), 14 bar (down, left) and 20 bar (down, right).

After a while and with pressure rising, the gas molecules gradually associate in the center of the box until the time when CO_2 molecules are in the nearest distance of each other and occupy most vacant pores of the sorbent. Finally, the highest value of the presence of CO_2 molecules within the canals of UTSA-16 structure is observed at the pressure 20 bar.

Knowledge of gas diffusion in nanoporous materials is vital to assess their potential over a full range of separation processes and to provide insight into molecular details of the underlying transport mechanism. Although, in contrast to the abundance of the data related to adsorption equilibrium, limited measurement data is available regarding gas transport properties in MOFs. The only information currently available on molecular gas diffusion in MOFs comes from computational simulations. Accordingly, the MD simulation has been performed in this study to obtain the CO_2 diffusion coefficient in UTSA-16 from Eq. (1). This calculation involves an Einstein relationship that measures the mean-squared displacement (MSD) of the center of mass of the adsorbed molecules. The mobility of pure CO_2 molecules or the MSD analysis have been brought in Figure 5 at temperatures 298, 313 and 338 K and at pressures 0.5, 2.5, 5, 9, 14 and 20 bar.

It is evident that the slope of the MSD increases with increasing pressure and the maximum value of MSD has been observed at the pressure 20 bar. This indicates that the increasing of the pressure makes the CO_2 molecules to move from one pore of the UTSA-16 to another one faster and easier. The variation of CO_2 diffusion with temperature and pressure has been depicted in Table 1.

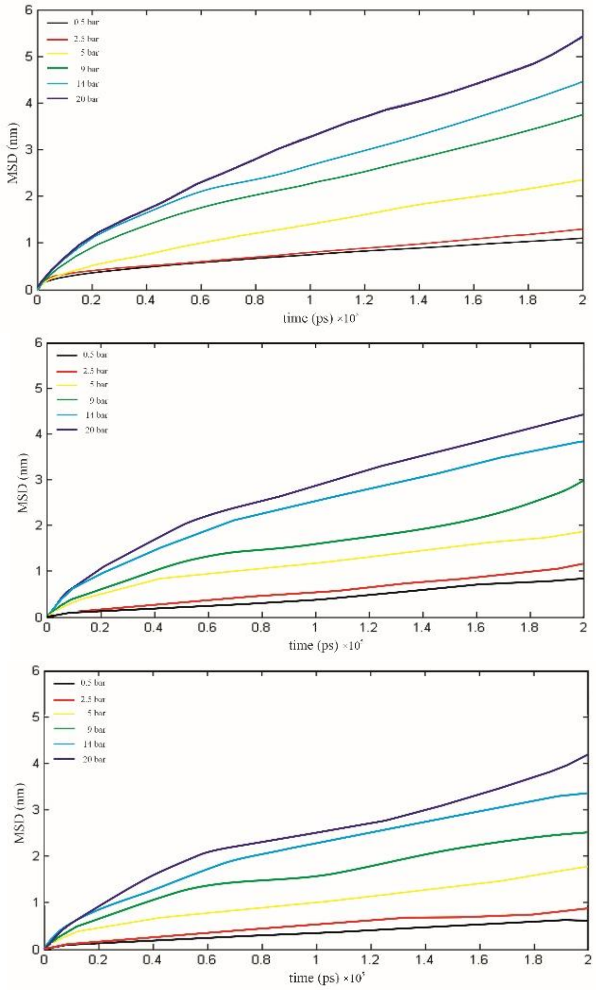

Figure 5. The MSD analysis of CO_2 molecules at 298 K (up), 313 K (middle) and 338 K (down).

Table 1. Diffusion coefficient ($\times 10^6 \frac{cm^2}{s}$) of CO_2 at different temperatures and pressures.

Pressure (bar)	298 (K)	313 (K)	338 (K)
0.5	0.57	0.56	0.56
2.5	0.71	0.64	0.61
5	0.81	0.74	0.67
9	0.92	0.81	0.73
14	1.00	0.87	0.81
20	1.04	0.96	0.88

It is also clear from Figure 5 and Table 1 that MSD value and diffusion coefficient decreases slightly with increasing temperature. As discussed in the evaluation of the amounts of adsorption, temperature enhancement increases the mobility of the gas molecules and decreases the interaction of CO_2 molecules with UTSA-16. Then, the slower translation of CO_2 molecules within the MOF matrix at higher temperatures causes the gas molecules diffusion into the media occurs in longer times which decreases the MSD value. It is useful to mention that the diffusivity of gases through zeolites can be anomalous and is dependent on the combined effect of temperature and the concentration of gas molecules inside the zeolite. According to Kärger and Pfeifer [42], five different types of concentration dependent-diffusivity can be observed as encounters between gas molecules and their interaction with different sites on zeolite walls have a pronounced influence on their mobility. Thus, some care should be taken when interpreting the results in Table 1. Assuming a type III concentration dependence [42], in addition to the decreased loading of CO_2 molecules with increasing temperature, this can lead to the decrease of the diffusion coefficient with temperature.

4. Conclusions

Molecular dynamics simulation has been employed to calculate the amounts of carbon dioxide adsorption and diffusion in a type of metal organic frameworks named UTSA-16. The presence of suitable pore spaces where CO_2 molecules directly interact with water molecules enhances its capacity for CO_2 adsorption. In addition, the interaction between UTSA-16 and CO_2 molecules affects the density profile, mobility and diffusion behavior and the way these properties is changed by temperature and pressure variations. It can be concluded that UTSA-16 adsorbs higher amount of CO_2 with pressure enhancement and temperature reduction that obeys the general rule of gas capturing in porous solids. Observing the results, it can be stated that with increasing pressure, the average distance between adsorbent and CO_2 decreases and consequently the probability of adsorption increases. Therefore, increasing the pressure on the adsorption rate shows an increasing trend. This increase is reduced at higher pressures, which indicates that the adsorbent is saturated and most of the cavities are filled by the CO_2. This claim can also be clearly seen by examining the MSD chart. On the other hand, by examining the results, it was found that with increasing temperature, the amount of CO_2 adsorption decreases somehow the optimal adsorption temperature is 298 K.

The variations of CO_2 density profile with pressure has been also evaluated to assess how the gas molecules accumulate in the simulation box. It shows the disorder distribution of CO_2 molecules through simulation box at lower pressure and their association in the center of the box at higher pressures. The MSD value and diffusion coefficient for carbon dioxide have been also studied. The slope of the MSD value increases with increasing pressure and decreasing temperature. It means that, the increasing of the pressure makes the CO_2 molecules to move faster while temperature enhancement decreases the interaction of CO_2 molecules with UTSA-16 media. As a result, CO_2 diffusion coefficient decreases with temperature and increases with pressure.

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