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A molecular dynamic study of CO_2 adsorption in fluoridised cations and non-fluoridised HKUST-1

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Abstract: Carbon dioxide (CO_2) is the major greenhouse gases exhausted from the combustion of fossil fuels (coal, oil and natural gas). CO_2 capture, separation and sequestration technology is increasingly critical to reduce CO_2 emissions. In present study, Monte Carlo and Molecular Dynamics simulations have been used to examine CO_2 adsorption in fluoridised and non-fluoridised HKSUT-1. Fluoridised HKUST-1 shows a remarkable CO_2 performance at low pressure. Radial Distribution Function and Mean Square Displacement analysis have been employed to explore the adsorption site of CO_2 and it binding strength within MOFs that CO_2 molecules in HKSUT-1 are more likely to diffuse into the Cu metal sites. However, the adsorbed CO_2 in HKUST-1F are bound closely to fluoride atoms, reducing their mobility.

Keywords: fluoridised HKUST-1, CO_2 adsorption and diffusion, computational simulations

1. INTRODUCTION

The global energy consumptions have been surging for decades due to the population blooming and urbanization[1]. The combustion of fossil fuels (e.g. coal, natural gas and oil) assuredly contributes to the greenhouse gases emissions[2]. Carbon dioxide (CO_2), one of the primary exhaust streams play a critical role in global warming which makes our human beings endangered and the entire planet impaired[3-5].

The rising level of carbon dioxide density in the atmosphere is one of the greatest environmental concerns facing our civilization today [6, 7]. Therefore, this presents an urgent need for carbon dioxide emissions being mitigated from the thermoelectric power plants and other industrial manufactures[8, 9]. Materials including amine solvents, zeolites, hydrotalcite-like compounds (HTLCs), carbon adsorbents as well as metal-organic frameworks (MOFs) for carbon dioxide capture and storage (CCS) technologies have been probed and developed to achieve an effective and efficient means in removing CO_2 from exhaust gases[10-14].

MOFs, emerging as a new type of porous solid adsorbents, have attracted many research interests in the past two decades. They are microporous crystalline substances with controllable and tailorable pore size [15, 16]. MOFs are three-dimensional coordination networks and consist of inorganic nodes (metal-based single or clusters) and organic ligands. MOFs have excellent physical and chemical properties for gas separation, molecular sequestration and catalysis (e.g. flexibility of porous size/shape, geometries and functionalities) [16-20]. MOFs usually have a surface area of over 1,000 m^2/g, high thermal stability, regenerability and potential scalability [21-23]. There are over 20,000 distinct MOFs being synthesized and reported for gas adsorption and control of carbon dioxide emission [24-27].

HKUST-1, named after it was synthesized by Chui at Hong Kong University of Science and Technology in 1999, it is also known as Cu-BTC (BTC=1, 3, 5-benzenetricarboxylate), HKUST-1 is one of the most conventional and well investigated MOFs [28-30]. The adsorption performances of HKUST-1 have been extensively probed experimentally and computationally for carbon dioxide capture and separation, which demonstrates that HKUST-1 is an excellent candidate for CO_2 emission reduction. Ye et.al reported that its adsorption capacity is 7.19mmol/g at 303 K and 10 bar[31]. In addition, Yan and coworkers demonstrated that a simple chemical treatment of HKUST-1 could significantly improve its CO_2 adsorption performance for up to 11.6mmol/g at 273 K and 1 bar , which was 61% higher compared with its pristine structure [32]. The Grand Canonical Monte Carlo (GCMC) method is the most effective numerical approach to predict gas uptake of MOFs. The GCMC adsorption isotherm of CO_2 in HKUST-1 was reported to be agreed with that of and CO_2 experimental data at low pressures. However, it was overestimated at higher pressures which probably occurs due to the additional Coulombic interactions in the simulations[33]. Zhao and co-workers calculated the adsorption isotherms of CO_2 in rigid and flexible frameworks, suggesting that the framework flexibility of Cu-BTC is unnoticeable for carbon dioxide uptake[34].

Among various numerical methods, molecular dynamics (MD) simulation has been widely implemented to examine CO_2 diffusion in MOFs. Yang et.al studied the effect of CO_2 adsorption on Cu-BTC by GCMC and MD simulations. It unfolded that the self-diffusivity of CO_2 decreases with pressure rise because the increase in CO_2 load restricts their movement. The interaction strength between Cu-BTC and CO_2 plays a major role for CO_2 uptake at a low pressure[35]. Yet, in particular, work has been made to fluoride treated of HKUST-1 due to the difficulty in synthesis, the study interest on CO_2 adsorption sites, strength and effect of the fluoride modified HKUST-1 was also scarce. The present work examines HKUST-1 and its fluoride modified structure to probe their adsorption performance for CO_2 and identify binding sites for carbon dioxides and adsorption energy via a combined GCMC&MD.

2. METHODOGY

2.1 Model construction

The model of HKSUT-1 is from the Crystallography Open Database (No.2300380). This structure was reported by Yakevenko and co-workers in 2013[36], and consists of paddlewheel-coordinated copper clusters and surrounded by 1, 3, 5-benzenetricarboxylate (BTC) organic linkers. Each metal node is composed of two copper atoms connected to the oxygens of four BTC ligands (Figure 1a). For fluoridised model (HKUST-1-F), the hydrogen atoms of BTC linkers are replaced by fluoride (Figure 1b) using the module of Materials Studio Visualizer.

2.2 Atomic Partial Charge and Force Field Calculations

Prior to adsorption simulation, geometry optimization was performed on the structure of both frameworks as well as carbon dioxide molecule. All calculations were performed by Materials Studio software. Universal force field (UFF) was employed to calculate the interactions in the frameworks. The atomic partial charges of the frameworks were obtained by the charge equilibration (QEq) method, and maintained in the following calculations. The Ewald simulation was employed to calculate the electrostatic interactions. Atom based method with a cut-off distance of 15.5 Å was used in the calculations of Van Der Waals (vdW) interactions. Similar approach was performed on CO_2 except for Atom based method for electrostatic interactions.

2.3 GCMC simulation

GCMC simulation is extensively employed to probe the adsorption capacity of porous materials. In present work, the structures of MOFs and CO_2 are flexible during the simulations. The adsorption isotherms of HKUST-1 and the HKUST-1F were performed at 298 K by Sorption modules in Materials Studio with the pressure from 0.1 to 5 bars, and equilibration process of 1×10^6 steps equilibration followed production process by 1×10^7 steps with a cut-off radius of 18.5 Å.

2.4 MD simulation

MD simulation is based on the Newton's second law of motion, which is widely employed to investigate the structure and dynamic properties of adsorbate molecules in porous materials. In present work, all MD simulations of HKUST-1 and HKUST-1F with adsorbed CO_2 were performed at 298.0 K, and the structures are flexible during the simulations. The NPT ensemble was used g, a cut-off distance of 15.5 Å was performed for the vdW interactions, and the Ewald summation method was used for the Columbic interactions. The time step was 1 fs and the total running time was 500 ps to assure the system to reach its equilibration and the average parameters of ensembles could be evaluated. Also, the binding sites of CO_2 molecules were examined by radial distribution function

(RDF), and the CO_2 diffusivity was calculated by the mean squared displacement (MSD). The adsorption energy (Ep) between MOFs and CO_2 were achieve from the average value of CO_2 adsorbed MOFs equilibrium frames, i.e. 6 frames from 400 to 500 ps,

$Ep=E_{total}-E_{MOF}-E_{CO2}$,

Where E_{total}, E_{MOF} and E_{CO2} are the energy of CO_2 adsorbed MOF, extracted MOF and extracted CO_2 molecules, respectively.

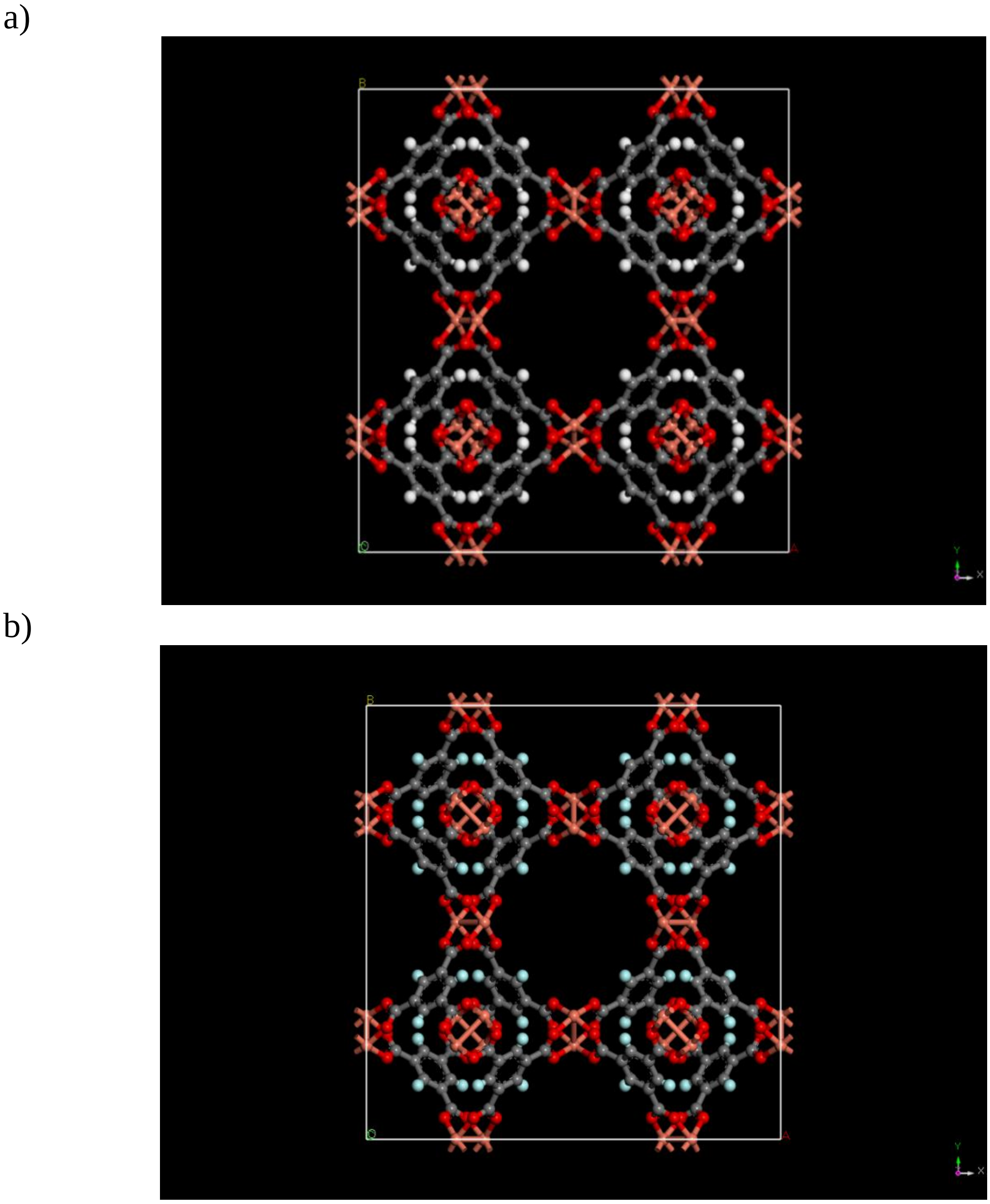

Figure 1 Unit cell of HKUST-1 (a) and HKUST-1F (b), Colour: Copper in orange, oxygens in red, carbons in grey, hydrogen in white and fluorides are light blue.

3 RESULTS AND DISCUSSION

3.1 Adsorption isotherms of CO_2 in MOFs

The adsorption isotherms of CO_2 in HKUST-1 and HKUST-1F are shown in Figure 2, which demonstrates that the adsorption capacity of the fluoridised HKUST-1F is much higher than that of non-fluoridised HKUST-1. For example, the adsorbed CO_2 in HKUST-1F unit cell is 176 at 0.1 bar compared with 62 in HKUST-1 unit cell. At 1 bar, HKUST-1F adsorbs 194 carbon dioxide molecules, which is almost the double of the HKUST-1. In addition, the uptake of CO_2 in HKUST-1 increases significantly with the pressure from 62 at 0.1 bar to 136 at 5 bars. Yet, HKUST-1F reaches the saturated adsorption equilibrium at a relatively low pressure (approximately between 0.5-1bar). The comparison of adsorption isotherms for CO_2 in both MOFs under different condition are shown in Table 1. The results show that the both HKUST-1 and HKUST-1F have a high adsorption capacity. In particular, fluoridised HKUST-1F gas a much high adsorption capacity than that of non-fluoridised HKUST-1, which may be attributed to the strong electrostatic interactions between fluoride and CO_2.

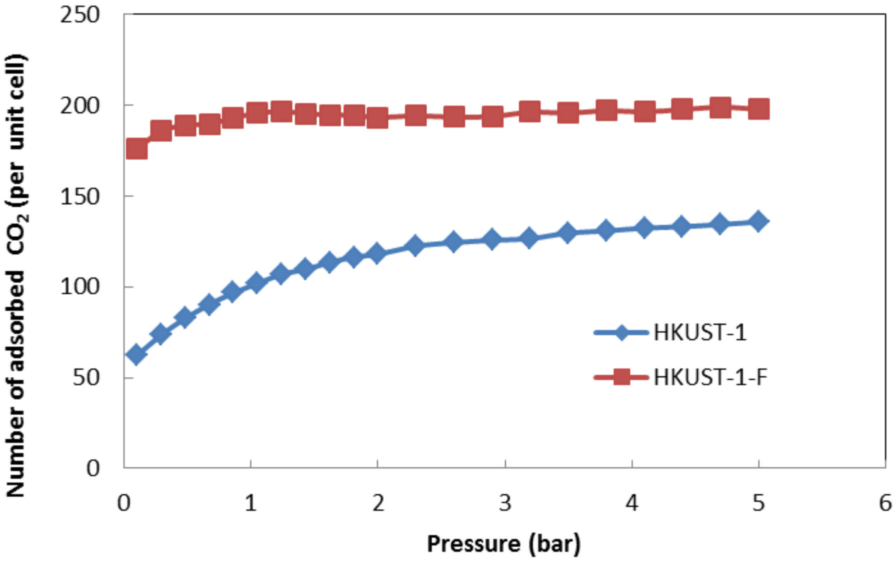

Figure 2 Adsorption isotherm of CO_2 in HKUST-1 and HKUST-1F at 298K under the pressure of from 0.1 to 5bar

Table 1 CO_2 adsorption capacity of MOFs under different conditions

MOFs	Pressure(bar)	Temperature(K)	Adsorption capacity(mmol/g)	Adsorption capacity (wt %)
HKUST-1	1	298	10.5	46.3
HKUST-1	5	298	14	61.7
HKUST-1F	1	298	17.2	75.5
HKUST-1F	5	298	17.3	76.3
HKUST-1[a] [31]	10	327	7.19	31.6
HKUST-1[a] (Ethanol+NH_4Cl) [32]	1	273	11.6	51
HKUST-1[b] [34]	10	298	11.9	52.4

a-Experiment, b-GCMC simulation

3.2 Adsorption sites of CO_2 in MOFs

The radial distribution function (RDF) is a pair correlation function which describes how atoms or particles in a system are radically packed around each other. It could provide an effective way to describe the overall structure properties of disordered molecular systems. The peaks indicate the most possible locations of an atom from the reference atom at a specific radius. In present study, RDF is used to probe the sites of CO_2 in MOFs. The RDF of HKUST-1 and CO_2 under different pressure are shown in Figure 3. The atomic pairs are Cu (MOF)-C (CO_2), O (MOF) - C (CO_2), and H (MOF) - C (CO_2).

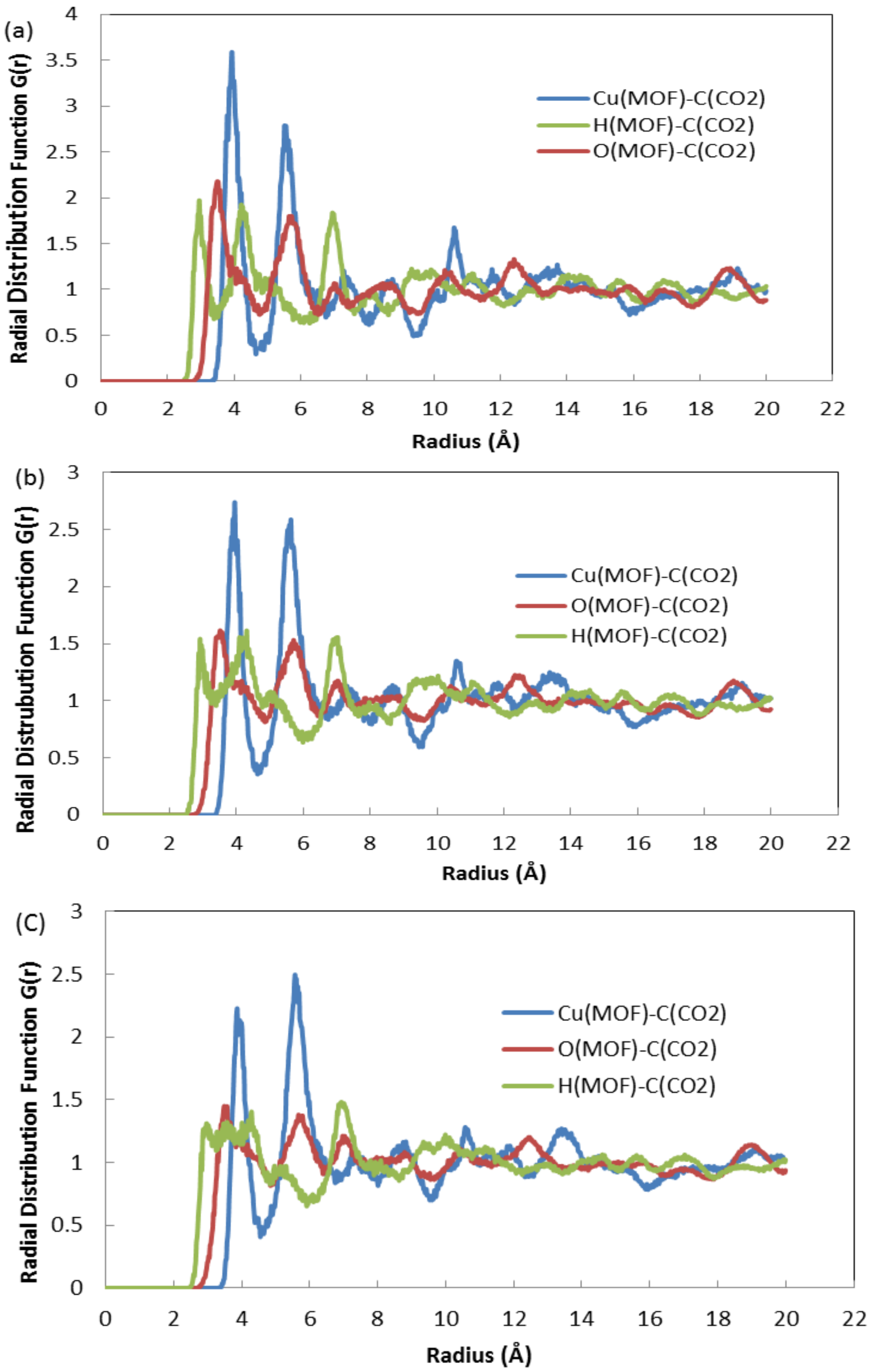

Figure 3 The radial distribution function of atomic pairs from HKUST-1 and CO_2 at 298 K and different pressure: (a) 0.1 bar, (b) 1bar, and (c) 5bar, respectively.

Figure 3a displays the shortest distance (first peak) is around 2.91 Å between H of HKUST-1 and C of CO_2, revealing the orientation of CO_2 with C atoms toward H atoms of HKUST-1. The next peak is located at 3.49 Å for O atoms of HKUST-1 and C atoms of CO_2, followed by sharp and narrow peak at 3.93 Å for Cu atoms of HKUST-1 and C atoms of CO_2. We could predict that the CO_2 molecules are more close to H atom (BTC linker) of HKSUT-1 at the pressure of 0.1 bar.

With the pressure rise (Figure 3b and 3c), we found that the first peak of Cu- C pair is still situated at around 3.9 Å, and the peak of the O-C pair is at about 3.49 Å. However, the peak of H-C pair becomes flat and broad, indicating majority of additional CO_2 adsorbed move toward Cu sites.

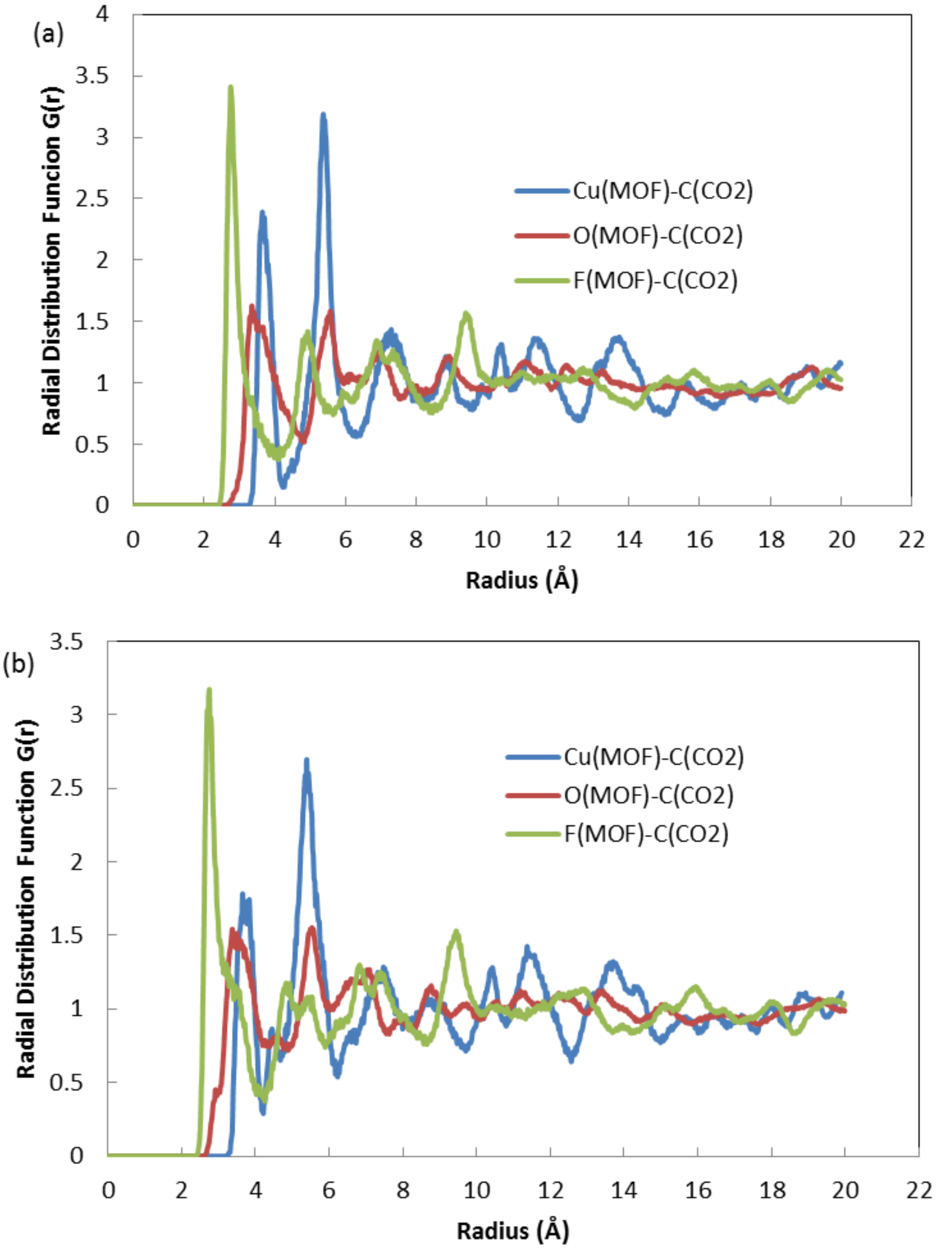

Figure 4 The radial distribution function of atomic pairs from HKUST-1F and CO_2 at 298 K and the pressure of: (a) 0.1 bar, and (b) 5bar.

Similar RDF analyses are shown for HKUST-1F in Figure 4. The atomic pairs are Cu (MOF)-C (CO_2), O (MOF)-C (CO_2) and F-C (CO_2). The results of HKUST-1F (Figure 4) indicate that there is a stronger interaction between F atoms of HKUST-1F and the C atoms of CO_2, reflected from the strong and sharp first peak at 2.75 Å. The distance of the peaks are located at the same with the pressure rising to 5bar, but become slightly wide for F-C atomic pair, demonstrating CO_2 molecules are bound tightly to F atoms. The peak of Cu-C atomic pair has a slight decrease due to the amount of the carbon dioxide adsorbed increases and CO_2 are more close to F sites.

3.3 Self-diffusivity of CO_2 in MOFs

To further probe the mobility and diffusivity of adsorbed CO_2 in MOFs. The mean squared displacement (MSD) is employed to calculate the diffusivity of CO_2 in HKUST-1 and HKUST-1F by taking the slope of the MSD curves over time (Figure 5). The results indicate the self-diffusion of CO_2 molecules in HKUST-1 and HKUST-1F declines with pressure increase. This is an expected result and can be explained by the increase in adsorbed CO_2 and then the steric hindrance of movement for adsorbed CO_2 molecules within MOFs' structures. Note that the diffusivity of CO_2 in HKUST-1F is much lower than that of non-fluoridised HKUST-1, suggesting adsorbed CO_2 is attached firmly.

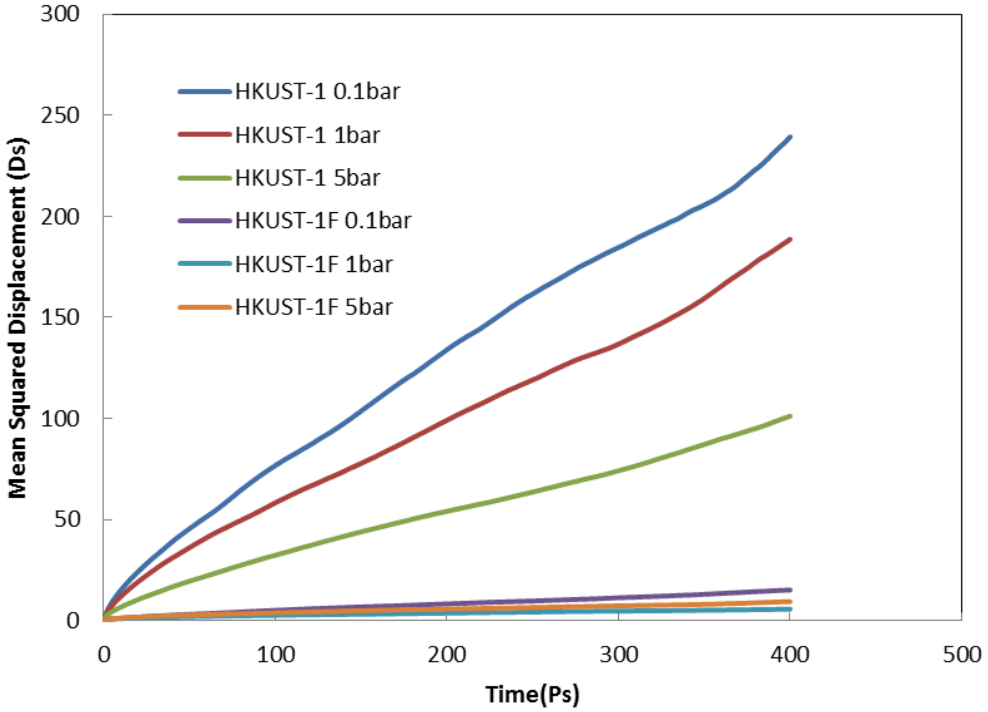

Figure 5.The mean squared displacement over time of CO_2 in HKUST-1and HKUST-1F

3.4 Interaction strength between CO_2 and MOFs

To obtain insight of the interaction strength between CO_2 and MOFs, we calculated potential energies for MOFs with adsorbed CO_2. We extracted the structures of MOFs and adsorbed CO_2 molecules, respectively, and then calculated the interaction energy (Ep) (Tables 2 and 3). The results indicate that interaction strength between MOF and CO_2 increase with pressure (i.e. CO_2 loading). Moreover, the interaction is attractive in nature of CO_2 due to the negative potential energy. The Ep of HKUST-1F is higher than HKUST-1, reflected to the increased loading number of CO_2 (adsorption capacity). The potential energy of extracted CO_2 in HKUST-1 reduced significantly from positive (repulsion) to negative (attraction), suggesting the distance between CO_2 increases (i.e. loosely adsorbed). For HKUST-1F, potential energy of CO_2 is relatively low, which indicates CO_2 molecules are stable and could hardly move.

Table 2 Interaction potential energies of CO_2 adsorbed HKUST-1

Pressure (bar)	Loading (number per unit cell)	Total Energy (Kcal/mol)	Energy of MOF (Kcal/mol)	Energy of CO_2 (Kcal/mol)	Interaction energy (Kcal/mol)
0.1	62	7974.9	8505.1	49.1	-579.3
0.5	83	7863.9	8527.5	36.4	-700
1	99	7739.7	8520.3	13.8	-794.3
3	126	7557.9	8519.9	-29.1	-932.9
5	136	7488	8520.9	-54.2	-978.7

Table 3 Interaction potential energies of CO_2 adsorbed HKUST-1F

Pressure (bar)	Loading (number per unit cell)	Total Energy (Kcal/mol)	Energy of MOF (Kcal/mol)	Energy of CO_2 (Kcal/mol)	Interaction energy (Kcal/mol)
0.1	176	-1469.3	919	7.94	-2396.6
0.5	189	-1526.5	956.3	3.1	-2486
1	194	-1538.6	975.2	2.13	-2515.9
3	195	-1558.6	961.9	2.08	-2522.9
5	198	-1549.2	994.9	2.09	-2546.3

4. CONCLUSION

Molecular dynamics simulation has been performed to investigate the adsorption location and binding strength of CO_2 in fluoridised and non-fluoridised HKUST-1. The results demonstrate that fluoridised HKUST-1F has an excellent adsorption capacity for CO_2, practically at low pressure. Moreover, adsorbed CO_2 molecules are bound closely to fluoride atoms of BTC linkers in HKUST-1F which can hinder their diffusion to metal sites.

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