



Adsorption of CO₂ by 3-D Covalent-Organic Framework Materials†

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Grand canonical Monte Carlo (GCMC) simulations using standard force fields have been carried out to model the adsorption of CO₂ gas on COF-1, COF-2 and COF-3. Our calculations indicate that the COF-3 material is the most prospective adsorbents for CO₂. The results showed that the COF-3 with -NH₂ and -CH₂OCH₂-(DHF) functionalized structures and found that the binding energy increases in the order of DHF_COF-3 < NH₂_COF-3. This implied that COF-3 with tetrahydrofuran group is responsible to high adsorption of CO₂.

Keywords: Grand canonical Monte Carlo, Covalent-organic framework, CO₂ adsorption.

INTRODUCTION

Recently, carbon dioxide adsorption has been industrially important for air purification due to concerns over green house gas emissions for global warming¹. On the other hand, CO₂ is often found as a major impurity in natural gas which has attracted more and more research interest due to the urgent demand of exploiting new and effective alternative energy sources² and its presence can reduce the energy content of natural gas. Among the diverse technologies for such separation purposes, physical adsorption by microporous materials is technically feasible, affordable and energy-efficient technology³. It has been revealed that a variety of microporous materials with channels or pores such as zeolites^{4,5}, metal organic frameworks (MOFs)^{6,7} and various carbon structures^{8,9}, are being actively investigated in gas separation and selective adsorption of organic or inorganic molecules⁵. Although these adsorbents possess relatively high CO₂ adsorption capacities, carbon structures and zeolites decline rapidly with increasing temperature and MOFs have a relatively high density because of having heavier metal elements.

The discovery of the 3D covalent-organic framework (COF) materials has attracted interests because they are constructed of strong covalent bonds and they exhibit high surface areas and extremely low densities. These characteristics have made them ideal materials for CO₂ capture.

Herein, in this paper, we first compared with the CO₂ adsorption properties on the three 3-D covalent-organic frameworks (COFs) named COF-1, COF-2 and COF-3 materials (Fig. 1) and then added the functional groups described above on the COF with the promising adsorption property to design new functional COFs and further investigate their adsorption ability of CO₂ by means of density function theory (DFT) method.

COMPUTATIONAL METHODS

Their crystalline structures of COFs were taken from experimental X-ray diffraction (XRD) data and optimized by means of the force-field method, which are shown in Fig. 1. The structural characteristics of these nanoporous materials (such as pore size, surface area, pore volume, free volume and porosity) and Henry's constant K_H for the COF-1, COF-2, COF-3 and the two functionalized COF-3¹⁰ are summarized in Table-1. These physical properties can be used to determine the small molecule storage characteristics and the strong interaction of gas molecule with adsorbent.

We used the grand canonical Monte Carlo (GCMC) method with the Dreiding force field¹¹ to simulate CO₂ adsorption isotherms in COFs and with functionalized COFs. Simulations were carried out at 298 K, in a wide range of gas pressures (1.0E-4 -50 bar) to get a complete picture about the adsorption properties and all of these materials were modeled as rigid structures. At each pressure, the GCMC simulation consisted

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of 1×10^6 steps to allow equilibration, followed by 1×10^7 steps to sample the configuration space.

The standard Lennard-Jones (LJ) parameters of Dreiding force field were used to describe the weak van der Waals (vdW) adsorption of the CO₂ molecules. We considered only dispersion and repulsion interactions, modeled using the standard Lennard-Jones equation.

$$V(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (1)$$

The interaction of CO₂ and COFs with functional groups were calculated using density function theory based computations were performed with some different methods, as implemented in Dmo¹³ and Gaussian programs^{12,13}.

RESULTS AND DISCUSSION

CO₂ adsorption isotherms with COFs by GCMC simulations: The adsorption isotherms for each component at different pressures are compared to rationalize their pressure-

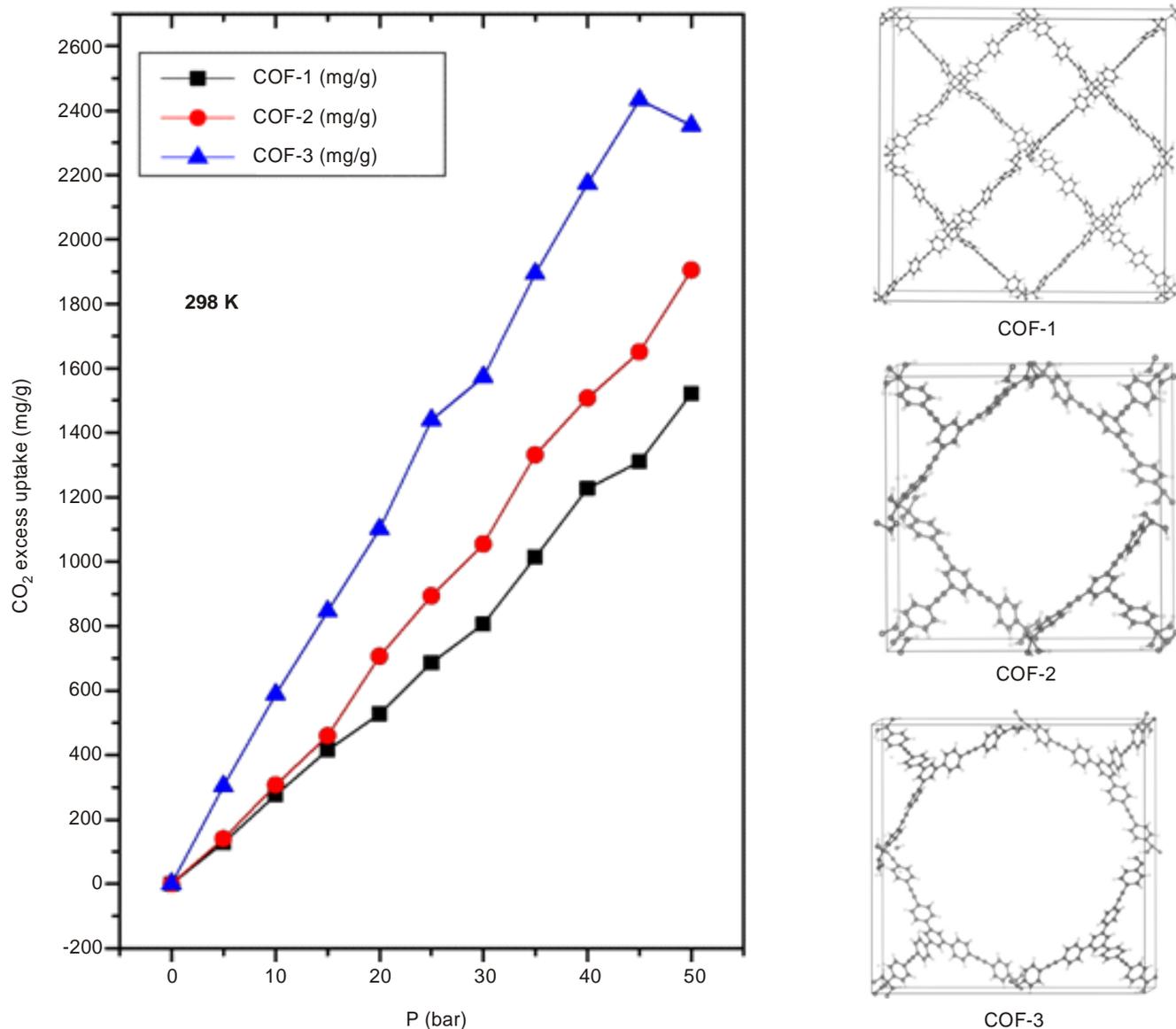


Fig. 1. (a) Simulated adsorption isotherms of CO₂ gas in the three nanoporous host materials (COF-1, COF-2 and COF-3) at 298 K; (b) Crystal structures of COFs

TABLE-1
MASS DENSITY, PORE SIZE, SURFACE AREA (S_A), PORE VOLUME (V_p), AND POROSITY WITH PER UNIT CELL AND HENRY'S CONSTANT K_H for the COF-1, COF-2, COF-3, AND THE THREE FUNCTIONALIZED COF-3

	Density (g/cm ³)	Porosity	Pore size (Å)	S_A (m ² /g)	V_p (cm ³ /g)	Free volume (Å ³)	K_H (mmol/g/kPa)
COF-1	0.06	0.90	35	8370	15.17	136817	0.097
COF-2	0.16	0.76	19	7455	4.9	15361	0.03
COF-3	0.08	0.87	26	7975	10.41	48317	0.058
NH ₂ _COF-3	0.11	0.83	25	7484	7.75	40913	0.046
DHF_COF-3	0.10	0.84	26	7286	7.98	40764	0.053

dependent adsorption capacities. Fig. 1 shows the adsorption isotherms of CO₂ in COFs at 298 K. Clearly, the shapes of the isotherms are very similar, implied a common mechanism for adsorption in the different materials. This is the result of non-specific binding with the framework atoms at high temperatures, only relatively weak physisorption between the CO₂ molecules and the sorbent. The excess uptakes of CO₂ in COF-3 are significantly higher than those for COF-1 and COF-2 in all the considered pressure range due to the larger surface area and higher isosteric heat, though slightly smaller pore volume than COF-1. It can be observed that at room temperature and pressure of 45 bar, COF-3 has the highest adsorption capacity of 2433 mm³/g, followed by COF-2 with 1651 mm³/g and COF-1 with 1310 mm³/g. Preferential adsorption of CO₂ on COF-3 indicates that the material can be used for CO₂ capture. Further, we design the COF-3 with -NH₂ and -CH₂OCH₂- (DHF) functionalized structures and investigate their adsorption ability of CO₂ by means of density function theory (DFT) method.

CO₂ interaction with model functional groups by first-principles: For accurately describing the weak interaction, we contrasted the binding energy (BE) of CO₂ and benzene by means of some different methods, such as PW91, PBE-TS along with a double numerical polarization (DNP) basis set and WB97XD, B97D, M06HF, MP2, MP2-CP (MP2 method with being corrected for basis set superposition error (BSSE) using the counterpoise (CP) technique with the large basis set of 6-311++G (2d, 2p). These results are shown in Table-2. It has been demonstrated that current DFT in general does not properly describe dispersion interactions in case of the benzene dimer, which plays a dominant role in the weak interactions. Though MP2 formally is able to account for the long-range part of the dispersion energy, but often leads to an over estimation of interaction energy. It is observed that the absolute value of binding energy obtained from a PW91/DNP method lowers 5.7 kJ/mol than that obtained from MP2-CP calculations and the binding energy of MP2 calculation over estimates 4.95 kJ/mol which is in agreement with above. In all the calculations we considered, the absolute values of WB97XD/6-311++G (2d, 2p) and PBE-TS/DNP are mostly close to the MP2-CP calculations (-10.84 and -11.42 vs. -11.66 kJ/mol). The absolute binding energy values are excessively under estimated by the other methods comparing by MP2-CP calculations. We found that CO₂ interacts with benzene mainly through the interaction

of the CO₂ quadrupole with the delocalized π electrons of the benzene ring, which is a weak dispersion-dominated interaction by PW91, PBE-TS, B97ED and M06HF calculations. Using the WB97XD, MP2 and MP2-CP methods, the stable configurations are similar and stabilized cooperatively by the O(CO₂)...H(benzene) hydrogen bond (HB)-like interaction and π ...quadrupole interaction. Therefore, in view of the binding energy value and configurations, we choose WB97XD/6-311++G (2d, 2p) method to calculate the interactions of CO₂ and the cluster models below.

To guide our molecular simulations, we study the effect on the interaction between CO₂ and the cluster models corresponding to the fragments of COF-3 unattaching or attaching various model functional groups (nitro group, tetrahydrofuran group) using WB97XD/6-311++G (2d, 2p) level of methods. Because the unit cells of these COFs are relatively large sizes, for instance COF-3 contains about 350 atoms per unit cell. Studying such systems using quantum mechanical methods is a rather difficult task, due to the large computational demand for such large systems. Hence the cluster models corresponding to the fragments in the adsorbents were adopted at high WB97XD level theory. Although in each CO₂...ligand molecular complex a variety of different energy minimum configurations were found, we only show the most stable complexes (Fig. 2).

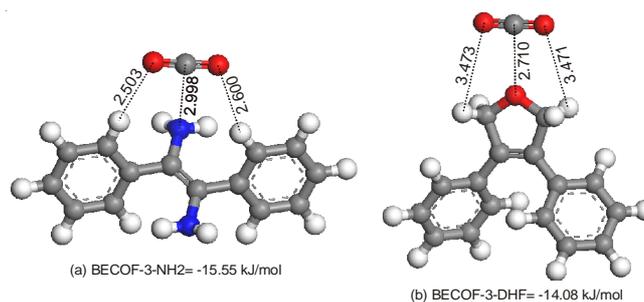


Fig. 2. Optimized conformations and binding energies (binding energy, defined as the energy of the complex minus the energy sum of CO₂ and the cluster models) of CO₂ and the cluster models of COF-3 with (a) nitro group, (b) tetrahydrofuran group, calculated at the WB97XD/6-311++G (2d, 2p) level of theory. The bond lengths are in units of angstroms. Key: C, gray; O, red; N, blue; H, white

It is found that CO₂ interacts with these functional clusters mainly through electrostatic interactions between its electro-

TABLE-2
BINDING ENERGY (BE) OF CO₂ AND BENZENE WITH SOME DIFFERENT METHODS

Method	PW91/ DNP	PBE- TS/DNP	PBE- Grimme/DNP	WB97XD/6- 311++G (2d, 2p)	B97D/6-311++G (2d, 2p)	M06HF/6-311++G (2d, 2p)	MP2/6-311++G (2d, 2p)	MP2-CP/6-311++G (2d, 2p)
BE _{C₆H₆-CO₂} (kJ/mol)	-5.96	-11.42	-2.84	-10.84	-8.43	-9.42	-16.61	-11.66

TABLE-3
PROPERTIES OF ENERGY MINIMUM CONFIGURATIONS FOR VARIOUS COMPLEXES DESCRIBED IN THIS PAPER. WE ALSO REPORT THE NATURE OF THE INTERACTIONS IN THE DIFFERENT COMPLEXES: HYDROGEN BONDING-LIKE, ELECTRON POLARIZATION BY LONE PAIR (LP) POLARIZATION, AND π ELECTRON POLARIZATION (π -INDUCTION)

Ligand	Type of interaction	BE (kJ/mol)	O-C-O angle (°)	Distances (Å)	Angles (°)
COF-3	CH...O H-bond	-13.65	178.8	CH...O 3.048	(C)H...O=C 106.2
COF-3-NH ₂	LP polarization +CH...O H-bond	-15.55	177.4	CH...O 2.503	113.2
COF-3-DHF	LP polarization +CH...O H-bond	-14.08	177.5	CH...O 3.471	99.6

positive C atom with the electronegative O or N atom of the functional groups and CH...O hydrogen bond (HB)-like interactions, but not the quadrupole- π electron interaction, with respect to pristine COF-3 cluster *via* only CH...O hydrogen bond interactions.

The binding energy has a net increase about 0.43-1.9 kJ/mol comparing to the fragment of COF-3 and the binding energy increases in the order of DHF_COF-3 < NH₂_COF-3 suggesting that the strong binding energy between CO₂ and COF-3 with tetrahydrofuran group is responsible to the ultra-high CO₂ adsorption capacities and makes it the most promising candidates for CO₂ capture.

Conclusion

As discussed above, we have identified organic linkers with adsorption sites of carbon dioxide on COFs *via* DFT methods and investigated storage of pure CO₂ in these different classes of nanostructured adsorbents by means of the grand canonical Monte Carlo method. Compared with COF-1 and COF-2, the COF-3 material is the most promising adsorbents for CO₂ capture at room temperatures. Further, it is found that the COF-3 with tetrahydrofuran group can result in evidently stronger affinity to adsorbates. These results provide useful information on modification of COFs for further improving adsorption of CO₂.

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