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Effects of incorporated oxygen and sulfur heteroatoms into ligands for CO₂/N₂ and CO₂/CH₄ separation in metal-organic frameworks: A molecular simulation study



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ABSTRACT

CO₂ separations from flue gas and natural gas are important industrial issues. As energy-efficient alternative of traditional cryogenic method, equilibrium based CO₂ separation by solid porous materials, i.e. metal organic frameworks (MOFs), has shown great potentials for CO₂ separation. In this work, CO₂/N₂ and CO₂/CH₄ separation performance in three MOFs (UiO-67, Zr-BTDC, Zr-BFDC) with various heterocyclic ligands were investigated by grand canonical Monte Carlo (GCMC) simulations using first principle derived force field parameters. CO₂/N₂ and CO₂/CH₄ mixed gas separation results show that MOFs comprising oxygen heteroatoms on ligands (Zr-BFDC) is a promising material for CO₂ separation from CO₂/N₂ and CO₂/CH₄ gas mixtures. Specifically, among the MOFs investigated, Zr-BFDC shows the highest uptake amounts of CO₂ at low pressure range owing to high CO₂ interaction affinity, while Zr-BTDC exhibits highest CO₂ uptake amounts at high pressure range due to high accessible surface area. Moreover, Zr-BTDC and Zr-BFDC also show significantly enhanced CO₂ selectivity over N₂ and CH₄ than their parent MOF, UiO-67, indicating their potential for practical CO₂ separations.

1. Introduction

Carbon dioxide (CO₂) separation from flue gas and natural gas are important industrial issues. Specifically, CO₂ separation from flue gas have a positive impact on reducing greenhouse gas emissions [1], while CO₂ separation from natural gas can improve the quantity of combustion and prevent the corrosion of transportation tubes [2]. A handful of techniques have been proposed for CO₂ capture from CO₂/N₂ and CO₂/CH₄ mixtures, such as amine absorption, cryogenic distillation, adsorption, membranes and enzymatic conversion [3–5], among which, adsorption in porous materials is energetically efficient and technically feasible.

Metal-organic frameworks (MOFs) are one kind of promising materials for gas storage and separation due to their large volume, variety structures and tunable functionality [6–9]. Many studies on CO₂ adsorption or separation from flue gas and nature gas in MOFs have been carried out in experiment and molecular simulation [10–19]. Li et al. reported an isorecticular series of cobalt-adeninate bio-MOFs, bio-MOF-11–14, and found that bio-MOF-12 exhibits a selectivity of ~52 for CO₂ over N₂ by using the ideal adsorbed solution theory (IAST) [10]. Wang et al. synthesized two UiO-67 analogues with functionalized pore

surfaces and high stability, BUT-10 and BUT-11 [11]. Their results shows that the infinite dilution selectivities of CO₂/CH₄ are 5.1 and 9.0 and those of CO₂/N₂ are 18.6 and 31.5 for BUT-10, and BUT-11, respectively.

Comparing to traditional experimental methods, simulations can provide more details of chemical phenomena in molecular level [20]. Amrouche et al. investigated the functionality impact on MOFs for CO₂ separation and suggested that the ligand dipole moment should be considered as a main criterion for quantifying the CO₂ capture performances of MOF structures [14]. Liu and Smit evaluated the separation performance of two typical ZIFs for CO₂/N₂, CO₂/CH₄, and CH₄/N₂ mixtures, and found that the electrostatic interactions produced by the frameworks are very important for achieving high adsorption separation selectivities in MOFs [15]. Babarao and Jiang simulated the storage of CO₂ in a series of MOFs at room temperature, and reported that the organic linker plays a critical role in tuning the free volume and accessible surface area and determining CO₂ uptakes at high pressures [21].

To obtain high CO₂/N₂ and CO₂/CH₄ selectivity, many strategies have been developed, such as grafting polar functional groups [14,22–24] or incorporating strong binding sites [8,25–29], to increase

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the affinity between frameworks and CO₂ molecules. Among all of the strategies, incorporating strong binding sites, such as heteroatoms, is efficient to enhance CO₂ adsorption capacity and selectivity properties [30,31]. MOFs containing N-heterocyclic ligands have been proven effective since it can incorporate Lewis basic sites into MOFs [32,33]. Recently, we reported that the incorporation of sulfur (S) or oxygen (O) heteroatoms can alter the charge distribution in the system by introducing regions of negative charge around heteroatoms, leading to enhanced affinities towards CO₂ molecules [34]. Incorporating heteroatoms on ligands shows a promising way to enhance CO₂ adsorption in MOFs, thus further understanding the role of heteroatoms on CO₂ separation from mixed gas is very important for evaluating the materials for real applications.

In this work, we investigated the CO₂/N₂ and CO₂/CH₄ separation performance in three UiO-templated MOFs (UiO-67, Zr-BTDC, Zr-BFDC) with various heterocyclic ligands by GCMC simulations. The highly porous structures and excellent stability of these types of MOFs allow them to be promising materials for the targets of CO₂ capture [35]. The force field parameters of GCMC simulations were derived from first principle calculations to guarantee the accuracy of the computations. To the best of our knowledge, this is the first study of MOFs comprising oxygen and sulfur heterocyclic ligands for CO₂/N₂ and CO₂/CH₄ mixture separation, which provides a strategy for the development of CO₂ capture materials.

2. Models and methods

2.1. MOF structures

The structures of UiO-67 and Zr-BTDC were constructed from their corresponding experimental XRD data [31,36]. The S heteroatoms of Zr-BTDC were substituted with O atoms to create Zr-BFDC. Next, periodic density functional theory optimizations were carried out with the DMol³ code [37]. The details for the DFT optimizations can be seen in our previous work [34]. These MOFs have the same primitive fcu topology with Zr₆(μ₃-O)₄(μ₃-OH)₄ core linked by different heterocyclic ligands. UiO-67 contains biphenyl-4, 40-dicarboxylate (BPDC), Zr-BTDC contains 2, 20-bithiophene-5, 50-dicarboxylic (BTDC), and Zr-BFDC contains 2, 20-bifuran-5, 50-dicarboxylic (BFDC). The guest-free crystal structures of these three MOFs are given in Fig. 1, and some details of the structures of these three MOFs are summarized in Table 1.

2.2. Force field

For describing the adsorption of pure components and mixtures of CO₂, N₂, and CH₄ molecules in the selected MOFs, the following models for the pure components were used. CO₂ was modeled as a three site rigid molecular, and its intrinsic quadrupole moment was described by a partial charge model [38]. The C-O bond length is 1.16 Å, and the partial point charges centered at each LJ site are $q_O = -0.35 e$ and $q_C = 0.70 e$. A combination of the site-site LJ and Coulombic potential was used to calculate the CO₂-CO₂ intermolecular interactions. The LJ parameters for CO₂ were taken from the TraPPE force field [38]. N₂ was mimicked by a two site model. The bond length of N-N was 1.1 Å and the LJ potential parameters for N₂ were fitted to the experimental bulk properties [39]. Furthermore, it was found that the incorporation of the quadrupole moment has an insignificant effect on N₂ adsorption [40], thus the electrostatic interaction between N₂ molecules was not considered in this work. CH₄ was represented by a united-atom model interacting with the LJ potential. The potential parameters were also adopted from the TraPPE force field [41].

For UiO-67, Zr-BTDC, and Zr-BFDC, a combination of the site-site LJ and Coulombic potentials was also used to calculate the interactions between adsorbate molecules and adsorbents. All of the LJ cross interaction parameters were determined by the Lorentz-Berthelot rules. An atomistic representation was used for the MOFs studied. The atomic

charges were taken from our previous works [34], which were calculated using density functional theory (DFT) on the basis of fragmental cluster. Dreiding force field [42], which has successfully been used to study the adsorption and separation of gases in various MOFs [17,29,43], was used to calculate the interactions between adsorbates and adsorbents. LJ parameters for Zr were taken from the universal force field (UFF) [44]. However, the N₂ and CH₄ adsorption uptakes in UiO-67 obtained by the Dreiding force field were higher than the experimental data (Fig. S1). To better represent the adsorption isotherms of pure gas in these MOFs, ab initio calculations were performed at the MP2 level of theory, scanning the gas distance from the cluster and reproducing the corresponding QM energies using these parameters. Then, the parameters of the classical potential were fitted to reproduce the quantum chemical data. All LJ parameters were provided in Tables S1–S3.

2.3. Grand canonical Monte Carlo simulation

Grand Canonical Monte Carlo (GCMC) simulations were employed to calculate the adsorption of pure components and their mixtures in the MOFs studied. The GCMC simulations were performed at pressure ranged from 0 to 3 MPa. At this pressure range, the MOFs studied in this work can be considered as rigid [45], and the flexible atoms have negligible effect on gas adsorption in these MOFs. Thus, all of the MOFs were treated as rigid frameworks, with atoms frozen at their crystallographic positions during simulations. A cutoff radius of 12.8 Å was applied to the LJ interactions, and Ewald summations were used to calculate the electrostatic interactions [46]. The equation of state (EOS) was used to convert the experimental pressures to fugacities [47,48] which were required in the GCMC simulations. In this work, the Peng-Robinson equation of state was used to convert the experimental pressures to fugacities [48]. Each GCMC simulation consisted of 1×10^7 steps to guarantee equilibration, followed by 1×10^7 steps to sample the desired thermodynamic properties. The GCMC calculations were performed using the Sorption code in Materials Studios 2017 [37]. The selectivity for component A relative to component B is defined by the following: $S = (\alpha_A/\alpha_B)(\beta_B/\beta_A)$, where α and β are the molar fractions of components A and B in the adsorbed and gas phase, respectively. The values for the isosteric heat of adsorption Q_{st} was calculated from:

$$Q_{st} = RT - \frac{\langle U_{ff}N \rangle - \langle U_{ff}N \rangle \langle N \rangle}{\langle N^2 \rangle - \langle N \rangle \langle N \rangle} - \frac{\langle U_{sf}N \rangle - \langle U_{sf}N \rangle \langle N \rangle}{\langle N^2 \rangle - \langle N \rangle \langle N \rangle} \quad (1)$$

where R is the gas constant, N is the number of molecules adsorbed, and $\langle \rangle$ indicates the ensemble average. The first and the second terms are the contributions from the molecular thermal energy and adsorbate-adsorbate interaction energy U_{ff} , respectively. The third term is the contribution from the adsorbent-adsorbate interaction energy U_{sf} .

3. Results and discussion

3.1. Validation of the force field

To confirm the reliability of the force field and the method for calculating atomic partial charges employed in this work, the adsorption isotherms of CO₂, N₂, and CH₄ were simulated and compared with available experimental data [11,31], as shown in Fig. 2. In our previous works, the reliability of using the force field parameters and atomic charges to describe the CO₂ adsorption in UiO-67 and Zr-BTDC were validated. In this work, the simulated N₂ and CH₄ adsorption isotherms of UiO-67 are also in good agreement with the available experimental data, which indicated that the force field parameters obtained by ab initio calculations at the MP2 level of theory work well for describing N₂ and CH₄ adsorption in these MOFs. Thus the LJ parameters and atomic charges are extended to study gas adsorption isotherms of Zr-

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