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Designing new amine functionalized metal-organic frameworks for carbon dioxide/methane separation

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ABSTRACT

Amine functionalized materials have drawn researcher's increasing attention to carbon dioxide/methane separation. The kinds or modification densities of amine groups have significant impacts on the adsorption and separation efficiency of carbon dioxide/methane system. In this work, grand canonical Monte Carlo (GCMC) simulations were employed to study the adsorption and separation of carbon dioxide/methane 50:50 mixture by five different metal-organic frameworks (MOFs), the unmodified MIL 53(Al) and four amine functionalized (—NH_2, —$(NH_2)_4$, —NHCO, —CH_2CONH_2) MIL-53(Al) MOFs. It was found that although original MIL 53 had the best adsorption amount, its separation efficiency is not very high. The carbon dioxide/methane separation factor of —$(NH_2)_4$ amine functionalized MIL-53 is the best in five MOFs. Moreover, the predicted separation performance of —NH_2 and —NHCO functionalized MIL-53 also surpass that of the original one. However, the predicted separation performance of —CH_2CONH_2 modified MIL-53 is not so good, both its carbon dioxide/methane separation factor and adsorption amount are lower than those of the original one. The geometric effect and energetic effect are analyzed to explain the difference of separation efficiency. This work shows that a rational design of functionalized MOF is a feasible way to improve the carbon dioxide/methane separation efficiency and to provide helpful information for future MOF preparation and applications.

1. Introduction

Natural gas is mainly composed of methane, carbon dioxide, nitrogen and some heavy paraffin hydrocarbon. Separation of carbon dioxide from methane is an important issue in the processing of low-quality natural gas. Natural gas are thought of as one kind of clean energies, but the existence of carbon dioxide in natural gas decreases remarkably its heat value [1]. Moreover in a moist environment, carbon dioxide can react with water to produce carbonic acid, which will corrode not only the equipment but also the pipes during the transportation [2]. Usually, carbon dioxide content must be reduced to below 2–3% before natural gas transport in pipes [2,3]. In addition, carbon dioxide reduction also attracted a lot of attention in the production of biomethane [4]. To get pure methane, it is also necessary to separate carbon dioxide from methane. Currently, numbers of approaches such as cryogenic distillation, chemical adsorption, membrane purification and solid adsorption are used to remove carbon dioxide form methane [5,6]. Membrane purification and solid adsorption are thought of as promising methods because of their advantages, such as easy operation, low cost and high energy efficiency [7–9]. In order to improve the adsorption separation technology, it is necessary to understand theoretically and experimentally the adsorption separation mechanism. Different methods were employed to describe the adsorption behavior, such as molecular simulations [10–13], density functional theories (DFT) and theoretical adsorption models [14].

Over the past decades, metal-organic framework (MOF) materials have attracted considerable attention because they have potential applications in hydrogen storage [15–17], carbon dioxide capture [18,19], catalysis [20], gas separation and purification [21–23], liquid separation [24] and drug delivery [25]. MOFs are composed of metal ligand complexes acting as vertices of the framework, which are connected with organic linkers [26]. Their pore size and shape can be easily tuned by varying either organic linkers or metal ligands. The structures of MOFs are usually rigid, but some of them show extraordinary flexibility [27,28]. A typical example is the series of metal terephthalates MIL-53 [29,30]. The quadrupole moment of the adsorbing carbon dioxide molecules in MIL-53 results in its strong interactions with the corner-sharing hydroxyl groups of the MIL-53 framework, which in turn induces a contraction of the framework and reduces the free pore diameter. This phenomenon also happens for the adsorption of water

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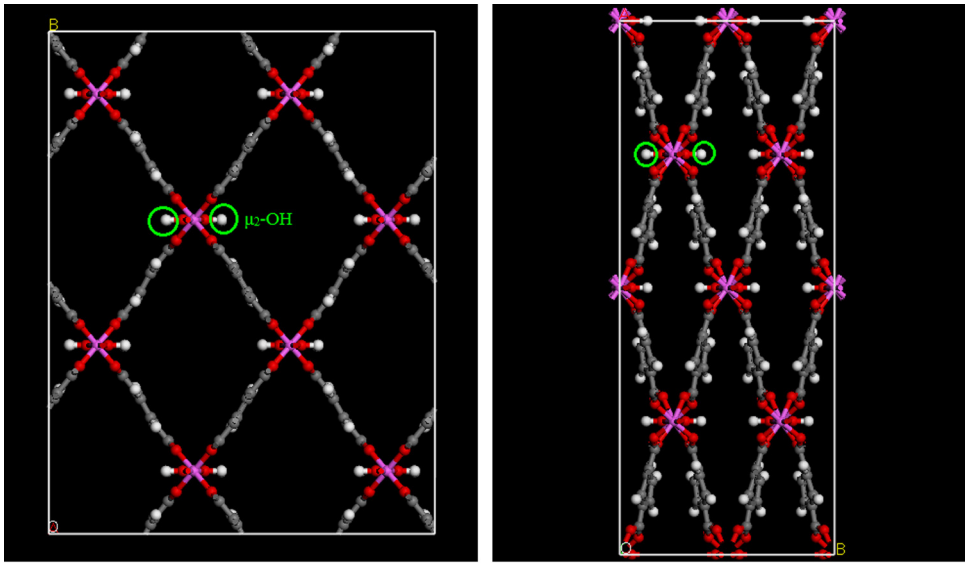

(a) (b)

Fig. 1. Lp and np structures (a, lp; b, np) of MIL-53(Al), μ_2-OH groups are labeled by circles.

molecules but not for methane. Though MIL-53 was reported as having large carbon dioxide adsorption capacities [18], because of the relatively weak interaction between carbon dioxide and pure MIL-53, designing new MIL-53 with high carbon dioxide selectivity is still a great challenge.

Grafting amine functional groups in MOFs is found to be an effective strategy to improve the adsorption and separation of carbon dioxide molecules. To date, several types of amine functionalized MOFs have been described in literatures [31–34]. Vaidhyanathan et al. [35] reported the crystallographic resolution of amine-functionalized MOFs and their binding domains with carbon dioxide molecules. Their analysis showed that the low-pressure binding and large uptake of carbon dioxide in MOF materials are influenced by three factors, i.e., strongly interacting amine functional groups, suitable pore size and the cooperative binding of carbon dioxide molecules. The requirement of researches on amine-functionalized MOF materials is extremely urgent and it will greatly speed up the industrialization process of MOFs for methane purification and carbon dioxide capture. In this work, we design four new amine functionalized MIL-53(Al) MOFs and determine the most suitable amine functional groups for enhancing carbon dioxide selectivity in natural gas purification.

2. Simulation methods and details

The GCMC simulation method was often used to study the adsorption of fluids. It is especially suitable for simulations of mixtures and inhomogeneous systems, such as fluids at interfaces and micropores [36]. The simulations were carried out using MuSiC package [37] to design and find the most appropriate amine functional groups in MIL-53 to increase carbon dioxide separation efficiency. We calculated large pore (lp) and narrow pore (np) original MIL-53(Al) and four amine (—NH_2, —$(NH_2)_4$, —NHCO, —CH_2CONH_2) modified materials. The structures of pure lp and np MIL-53 are shown in Fig. 1, which were constructed according to their experimental single-crystal X-ray diffraction data [38]. The unit cell of lp is a = 6.6085 Å, b = 16.6750 Å and c = 12.813 Å; while for that of np MIL-53 box size, it is a = 19.513 Å, b = 7.612 Å and c = 6.576 Å. For the simulation boxes, we replicate the unit cells of lp by 4 × 2 × 2 and that of np by 2 × 4 × 4 during the simulations. We find that lp form of MIL-53 has almost rectangular pores; while np form has almost trapezoidal pores after the adsorption of carbon dioxide. The unit cell volume of the np form is 40% lower than that of the lp form [29]. As the carbon dioxide loading increases, the structure switches back from the np form to the lp form. Moreover the μ_2-OH group, which is shown in Fig. 1 using the circular signs, is thought to form special interactions with carbon dioxide [39].

Table 1
LJ parameters for the original and four amine modified MIL-53(Al) MOFs.

Atoms	C	O	H	N	Al
σ (Å)	3.473	3.033	2.846	3.263	3.910
ε/k_B (K)	47.86	48.16	7.650	38.977	156.03

In previous works, various amine functional groups were used to modify MOF materials. Couck et al. [32] demonstrated that functionalized MIL-53(Al) with amino group (—NH_2) increased its selectivity in CO_2/CH_4 separations while maintaining a very high CO_2 adsorption capacity. Wang et al. [40] found two new MOFs that have 1,4-benzenedicarboxylic acid (BDC) structures modified by —NH_2 and —NHCOR. In this work, four amine (—NH_2, —$(NH_2)_4$, —NHCO, —CH_2CONH_2) groups were grafted on the BDC moiety of MOF materials. During simulations, all frameworks of the amine functionalized MOFs were kept rigid at their DFT optimized geometries [41]. We used types A, B, C and D to represent different amine modifications, as shown in Fig. 2.

The Lennard–Jones (LJ) parameters for original and amine functionalized MIL-53(Al) are from the Dreiding force field [42] and the Universal Force Field (UFF) [43], as shown in Table 1. The cutoff distance was chosen as 12 Å. The electrostatic interactions between adsorbate/adsorbent and adsorbate/adsorbate, were calculated by the Ewald summation technique [44]. The partial charges of atoms on the original and four amine functionalized MIL-53(Al) frameworks were estimated by using the DFT with the B3LYP method and LANL2DZ basis set [45] in Gaussian 09 software [46]; the Mulliken method was employed to calculate partial charges. In this work, the LJ parameters for methane were given by Goodbody et al. [47] (see Table 2). For carbon dioxide, LJ parameters refer to the work of Maurin et al. [48] (also see Table 2), in which carbon atom charge is +0.72 e and oxygen atom charge is −0.36 e. The Lorentz–Berthelot combining rules were employed to calculate fluid-framework cross interaction parameters.