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VARIOUS
TECHNOLOGIES

Computer Simulation of CO_2 Separation in "SIFSIX:" A Novel Family of Metal–Organic Frameworks (MOFs)*

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Abstract—A series of MOFs with coordinately saturated metal centers and periodically arrayed hexafluorosilicate (SiF_6^{2-}) anions (SIFSIX) were constructed. The structural property, isotherm of CO_2 adsorption, isosteric heat and selectivity were calculated by molecular simulation. All of simulated results were in good agreement with the experimental ones, which made it possible to predict the adsorption and separation performance of these novel MOFs. Particularly, SIFSIX-2-Cu-i offered high adsorption capacity at relatively low pressure. Most importantly, such MOFs gave a dramatically high CO_2 selectivity versus N_2 and CH_4. Therefore, these MOFs may be relevant to CO_2 separation in the context of post-combustion (flue gas, CO_2/N_2) and natural gas upgrading (natural gas clean-up, CO_2/CH_4).

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INTRODUCTION

Greenhouse gas emission, especially leading to increased atmospheric CO_2 accumulation and global warming, is one of the most important energy and environmental issues for our earth. As a result, the effective and economical capture of CO_2 from fossil fuel-fired power plants or industries with huge CO_2 emissions is receiving widespread attention [1, 2]. Although the use of aqueous amines as chemical absorbents is currently one of the most viable means of capturing CO_2, this technology has several drawbacks [3, 4], including high degrees of corrosion and expensive regeneration of the absorbents.

The commercial adsorbents [5, 6], such as molecular sieve, zeolite, active carbon, silica-based materials have showed good performance as the candidates for CO_2 adsorption [6]. Nowadays, much novel controllable adsorbents like metal-organic frameworks (MOFs) [7] have been designed to enhance selectivity for CO_2 in the presence of other gases. The most of conventional MOFs are porous materials with unsaturated metal centers or organic amines. However, they limit the application in high moisture and also have the disadvantage of high energy regeneration [8]. A novel class of MOFs is interesting for researchers, because they consist of metals or metal clusters coordinated to multi-functional organic ligands and they possess high surface area and large pore diameter. Besides, it is amenable to crystal engineering in a manner that facilitates precise control over pore size and functionality. Burd et al. [9] addressed a framework, which have two-dimensional nets based on linked metal nodes that are pillared by SiF_6^{2-} anions (SIFSIX) in the third dimension to form three-dimensional nets with primitive cubic topology. $[Cu(4,4'\text{-bipyridine})_2(SiF_6)]_n$ (abbreviation "SIFIX-1-Cu"), the primitive cubic net for SIFIX MOFs, have one-dimensional square channels aligned by a periodic array of SIFSIX pillars. It remains one of the best adsorbents for high selectivity CO_2 vs. both CH_4 and N_2. In the following years, the SIFSIX-1-Cu with expanded and contracted pore size [10] has been designed successively. SIFSIX-2-Cu [11, 12] was successfully synthesized by reaction of 4,4'-dipyridylacetylene (abbreviation dpa) with $CuSiF_6$. It exhibits expected primitive cubic net with square channels of pore dimensions. SIFSIX-2-Cu-i [12] is its interpenetrated polymorph, which consists of double interpenetrated nets that are isostructural to the nets in SIFSIX-2-Cu.

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* The text was submitted by the author in English.

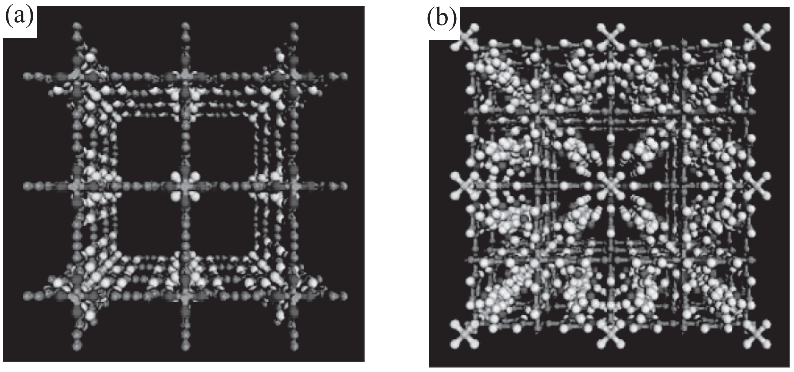

Fig. 1. Unit cells of (a) SIFSIX-2-Cu and (b) SIFSIX-2-Cu-i.

Computational chemistry is a powerful method for obtaining microscopic level insights into the studied phenomena, and it can serve as a large-scale prescreening tool. Therefore, in this work, The structural property and CO_2 adsorption performance of the SIFIX-2-Cu and SIFIX-2-Cu-i were studied by molecular simulation. Firstly, the molecular models including construction and force field parameters were established and optimized. Then, the simulated results compared the experimental ones were pointed by Monte Carlo simulation. Finally, some general rules on "SIFIX" MOFs for the CO_2 separation applications were summarized.

MODEL AND METHODOLOGY

The structure of SIFSIX-2-Cu and SIFSIX-2-Cu-i was constructed from the experimental crystal data, and the unit cell is shown in Fig. 1. SIFSIX-2-Cu and SIFSIX-2-Cu-i were a three-dimensional network, and channels exist in x, y, z direction with a size of ~12 Å and ~5 Å in diameter. The details of two molecular models were listed in Table 1.

The interaction between adsorbates and adsorbents and the interaction between the adsorbed moleculars are described by the combinations of Lennard–Jones (LJ) potential and Coulomb potential in the simulation process:

$$U_{ij} = \sum_{\substack{i,j \\ i\neq j}} \left\{ 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} \right\} \quad (1)$$

Here ε_0 equals 8.85×10^{-12} C_2 N^{-1} m^2, it is the vacuum diffusivity, σ_{ij} is the depth of the potential, r_{ij} is the length of the potential. Because of the large molecular

Table 1. Model structure and crystal data for SIFSIX-2-Cu and SIFSIX-2-Cu-i

Model name	SIFSIX-2-Cu	SIFSIX-2-Cu-i
Empirical formula	$C_{24}H_{16}CuF_6N_4Si$	$C_{26.50}H_{26}CuF_6N_4O_{2.50}Si$
Weight	566.04	646.14
Crystal system	Tetragonal	Tetragonal
Space group	P4/mmm	I4/mmm
Unit cell dimensions	a = 13.633 Å	a = 13.652 Å
	b = 13.633 Å	b = 13.652 Å
	c = 7.970 Å	c = 8.095 Å
	$\alpha = 90^{\circ}$	$\alpha = 90^{\circ}$
	$\beta = 90^{\circ}$	$\beta = 90^{\circ}$
	$\gamma = 90^{\circ}$	$\gamma = 90^{\circ}$
Volume	1481.30 Å^3	1508.72 Å^3
Density	0.624 g cm^{-3}	1.421 g cm^{-3}

quadrupole moment, CO_2 was modeled as a rigid linear triatomic molecule with three charged Lennard–Jones (LJ) interaction sites and a C–O bond length of 0.116 nm. The intrinsic quadrupole moment is approximately described by partial point charges centered at each LJ site $-0.386\bar{e}$ and $0.772\bar{e}$. The field force parameters of all adsorbates were listed in Table 2. In our simulations, all of the LJ cross-interaction parameters were determined using the Lorentz–Berthelot mixing rules:

$$\sigma_{ij} = \sqrt{\sigma_i \sigma_j}, \tag{2}$$

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}, \tag{3}$$

the universal force field (UFF) was used for the framework atoms. A number of studies in the past showed that several general purpose force fields including UFF employed in adsorption simulations of MOFs gave reasonable agreement with experiments. In order to get the partial atom charge, however, it is difficult to adopt the first principle to do the precise calculation. Throughout the paper, some useful approach and empirical findings in previously was considered. Therefore, force field parameters required for modeling adsorbate-MOF interactions were established, including repulsion, dispersion parameters and atomic partial point charges according to considerations presented previously [13–15].

In this study, a conventional grand canonical Monte Carlo (GCMC) simulation was performed to calculate the average number of adsorbates in equilibrium with the adsorbent at a given temperature and fugacity. To translate pressure to fugacity, the Peng–Robinson EOS was applied. The simulation boxes representing SIFSIX-2-Cu and SIFSIX-2-Cu-i contained 8 (2 × 2 × 2) unit cells and 1 (1 × 1 × 1) unit cell, respectively. No finite-size effects existed as verified by checking the simulations with larger boxes. The cutoff radius was set to 12.8 Å for the LJ interactions, and long-range electrostatic interactions were handled using the Ewald sum, in which, the cutoff radius was 1.28 nm and the computational precision was 0.001 kcal mol^{-1}. The total simulation steps were 3×10^7, and the first 1×10^7 steps were for equilibrium, the remaining were used for collecting the thermodynamic properties. The almost same results showed the number of GCMC steps was enough to guarantee the accuracy of simulated results. The selectivity of gas A vs. gas B in a mixture was defined as $S = x_A/x_B(y_B/y_A)$, where x_A and x_B were the molar fractions of A and B in the adsorbed phase, respectively. y_A and y_B were the molar fractions in the bulk phase.

Table 2. Force field parameters for the CO_2 model used in the molecular simulation

Atomic site	Distance, Å	σ, Å	ε, K	q, ē
C	0.000	3.304	19.618	0.772
O	1.162	0.000	0.000	–0.386
N_2	1.102	3.263	38.914	0
CH_4	1.108	0.373	148	0

RESULTS AND DISCCUSION

To understand what the influence of changing the structure of the “SIFSIX” might have on the interactions between the adsorbents and CO_2, the structural property of MOFs should be characterized compared with the theoretical one. In our simulation, Connolly surface and Connolly volume were estimated with a probe of diameter 3.3 Å, which is the kinetic diameter of CO_2. The nitrogen

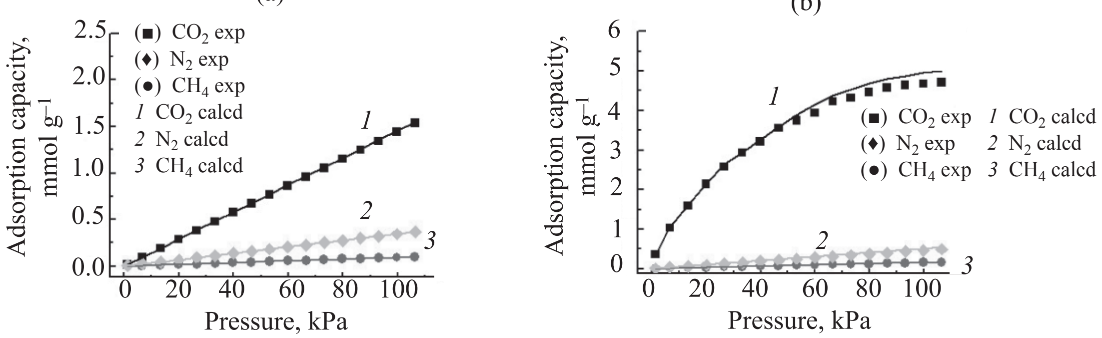

Fig. 2. Low pressure isotherms at 298 K for (a) SIFSIX-2-Cu and (b) SIFSIX-2-Cu-i.

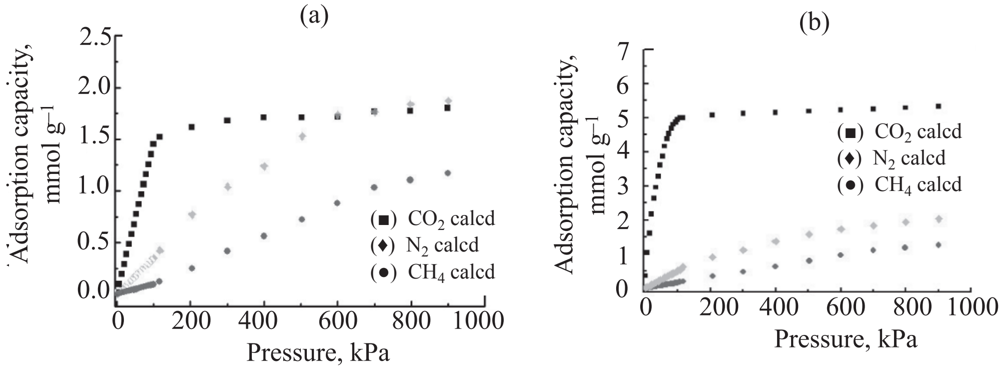

Fig. 3. High pressure isotherms at 298 K for (a) SIFSIX-2-Cu and (b) SIFSIX-2-Cu-i.

adsorption/desorption results of 3762 and 935 m^2 g^{-1} were in good agreement with 3140 (SIFSIX-2-Cu-i) and 735 m^2 g^{-1} (SIFSIX-2-Cu). Similarly, the pore volumes of two MOFs were also corresponding. This depicted that N$_2$ function have been successfully occupied in SIFSIX-2-Cu-i, and SIFSIX-2-Cu-i possessed much more active adsorptive sites than SIFSIX-2-Cu. To sum up, our two molecular models could be realistic and workable.

Figure 2 shows the simulated and experimental adsorption isotherms for CO$_2$ in MCM-41 at low pressures. Experimental data were referenced from [12]. Fairly good agreement was observed between simulation and experiment, although the simulated loading was a little higher than the experimental data of SIFSIX-2-Cu-i at relatively high pressures. This phenomenon was probably due to the deviation of model structure and interaction potential. Therefore, the simulation method could precisely predict the adsorption performance. From collected data, SIFSIX-2-Cu possessed ~1.7 mmol g^{-1} CO$_2$ adsorption, while SIFSIX-2-Cu-i exhibited higher value of ~5.02 mmol g^{-1}. These observations to a more favorable interaction between CO$_2$ and SIFSIX-2-Cu-i were attributed. Figure 3 shows the high pressure isotherms for SIFSIX-2-Cu and SIFSIX-2-Cu-i at 298 K. From the data in range of high pressure, isotherms for CO$_2$ adsorption on SIFSIX-2-Cu and SIFSIX-2-Cu-i reached a plateau at relative high pressure (about 500 kPa), however, the absorbed amount for both two structures had already reached an apparent saturation at relatively low pressures (100 kPa). In another way was that "SIFSIX" was one of the most suitable adsorbents in low pressure.

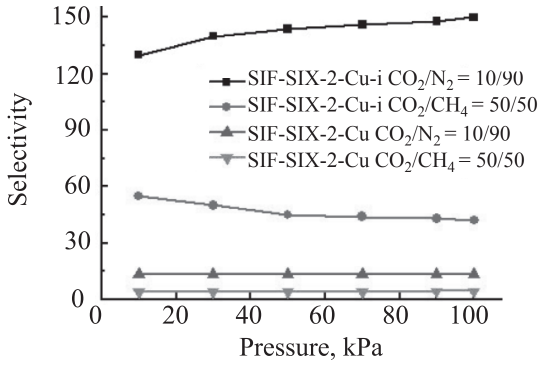

Fig. 4. Selectivity of SIFSIX-2-Cu and SIFSIX-2-Cu-i in CO$_2$/N$_2$ mixture and CO$_2$/CH$_4$ mixture simulated from low pressure at 298 K.

[Further, some real simulated CO$_2$ mixture was applied in GCMC. As shown in Fig. 4. In flue gas separation system, the selectivity of SIFSIX-2-Cu-i for CO$_2$ vs. N$_2$ was about 130, which was dramatically higher than SIFSIX-2-Cu (only about 15). Syngas containing CO$_2$ and CH$_4$ could be cleaned up via this "SIFSIX" as well. The selectivity of SIFSIX-2-Cu-i for CO$_2$ over CH$_4$ was also higher than SIFSIX-2-Cu (about 50 vs. 5). Along this result, SIFSIX-2-Cu-i is particularly suitable for CO$_2$ separation from flue gas and syngas.

The heart of pressure or temperature swing adsorption processes for CO$_2$ removal is the adsorption heat. Note that the isosteric heat is usually used to ascertain the

Table 3. Theoretical and experimental pore structure of SIFSIX-2-Cu-i and SIFSIX-2-Cu

	SIFSIX-2-Cu-i		SIFSIX-2-Cu	
	calcd.	found	calcd.	found
Pore volume, g cm^{-3}	1.12	1.15	0.23	0.26
Surface area, m^2 g	3140	3762	735	935

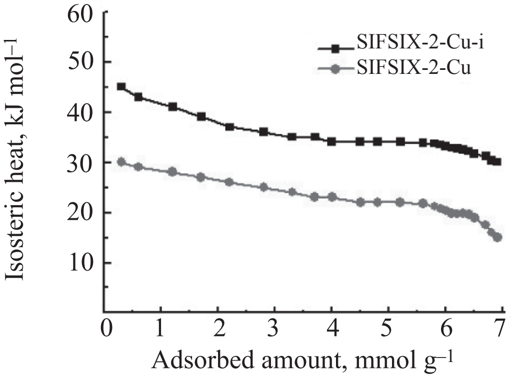

Fig. 5. Isosteric heat of SIFSIX-2-Cu and SIFSIX-2-Cu-i simulated from low pressure at 298 K.

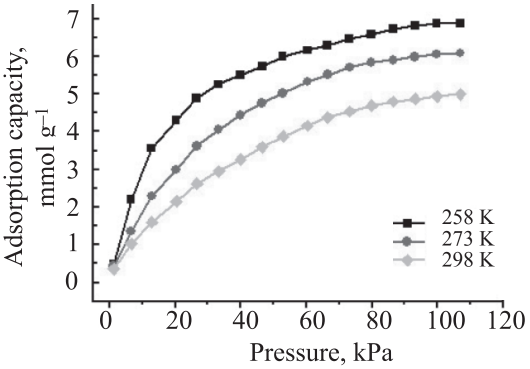

Fig. 6. CO_2 adsorption capacity of SIFSIX-2-Cu-i at different temperature

adsorption mechanism as the isosteric heat is quite sensitive to the change of adsorption energy. Within the low-pressure range in Fig. 5, the isosteric heat decreased with increasing loading. It could be expected that it would increase with further increasing pressure due to the corporative attraction between adsorbate molecules. However, it finally decreased because the space available for adsorption becomes less,and the resistance of gas transfer was much larger. Isosteric heats of CO_2 adsorption for SIFSIX-2-Cu-i and SIFSIX-2-Cu were close 35 and 25 kJ mol^{-1}, respectively. The relatively stable isosteric heat (in the range of 2–5 mmol g^{-1}) indicates homogeneous binding sites over the full range of adsorbed CO_2. They could be suitable for efficient, reversible adsorption and desorption recycle. Therefore, although the interaction between two MOFs and CO_2 were strong, the adsorption process still reversible.

Temperature plays an important role in real adsorption operation. In this paper, SIFSIX-2-Cu-i absorbed higher CO_2 amount was simulated. Figure 6 shows the adsorption capacity as a function with a total pressure at three different temperatures of 258 K, 273 K and 298 K. With the increase of pressure, the adsorption capacity was obviously increased. As increasing the temperature, however the adsorption capacity declined. The adsorption of CO_2 into pores of MOFs is an exothermic process. Accordingly, the adsorption capacity should decrease with the increase of temperature. Furthermore, temperature was a dominant factor to govern the adsorption capacity compared with pressure. Interestingly, when the temperature was decreased by only 20 K, the adsorption capacity fairly increased to about 1.4 times from 298 K to 273 K. Therefore, SIFSIX-2-Cu-i can be a potential material applied in extremely low temperature.

CONCLUSIONS

This paper, two "SIFSIX"s derived from a class MOFs of coordinately saturated metal centers and periodically arrayed hexafluorosilicate (SiF_6^{2-}) anions (called) were firstly built. Secondly, the interaction between atoms and atoms in the molecular system was optimized. Thirdly, the structural property, isotherm of CO_2 adsorption, selectivity and isosteric heat were calculated by using computer simulation. SIFSIX-2-Cu-i became a potential adsorbent for CO_2 capture. It offered high adsorption capacity at relatively low pressure. Most importantly, such MOFs gave a dramatically high CO_2 selectivity versus N_2 and CH_4. Therefore, these MOFs may be relevant to CO_2 separation in the field of post-combustion (flue gas, CO_2/N_2) and natural gas upgrading (natural gas clean-up, CO_2/CH_4).

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