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Capture of H_2S and SO_2 from trace sulfur containing gas mixture by functionalized UiO-66(Zr) materials: A molecular simulation study

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ABSTRACT

With the advantage of high selectivity, moisture stability, thermostability, acid gas resistance, high sorption capacity, and low-cost regenerability, serials of UiO-66(Zr) metal-organic frameworks (MOFs) are considered as promising materials in gas adsorption and purification applications. In this work, we carried out molecular simulations to study the adsorption and membrane separation performance of non-modified UiO-66(Zr) and its functionalized derivatives in sulfur capture from binary sulfur containing gas mixtures. Our results indicate that UiO-66-$(COOH)_2$ and UiO-66-COOH show better adsorption performance in H_2S and SO_2 capture than other functionalized derivatives. The isosteric heat of adsorption at infinite dilution and radial distribution functions display the existence of strong interactions between hydrophilic functional groups and H_2S and SO_2. The joint effect of hydrophilism and strong polarity of functional groups promotes the adsorption of H_2S and SO_2. Both UiO-66-$(COOH)_2$ and UiO-66-COOH are also expected to be ideal membrane candidates for H_2S separation because of superior permeation selectivity and permeability.

1. Introduction

With the aggravation of environmental pollution and energy crisis, effective control of air pollutant emission and the exploitation and utilization of clean energy resource become particularly critical and urgent [1]. SO_2 is a major air pollutant produced by the combustion of fossil fuels including coal and petroleum. The excessive emissions of pollution gas to the atmosphere will lead to the formation of acid rain that does not only have a serious impact on the environment, but also raises a great threat to human health. Therefore, the removal of SO_2 from flue gas becomes a key issue for protecting air environment. Biogas which serves as green energy sources is a type of combustible gas mixture which is produced by microbial fermentation and decomposition at a certain temperature, humidity, pH, and anaerobic condition and consists mostly of methane and carbon dioxide with a small amount of hydrogen sulfide, ammonia, hydrogen etc. Even in the presence of a small proportion, H_2S in biogas mixture has great harmful impact on the recovery and utilization of biogas [2]. Because of the serious corrosion of pipelines and equipments and harmful combustion products, H_2S is required to be removed before using biogas. Therefore, it is very important to explore and develop biogas desulphurization technology.

Many researches have been dedicated to SO_2 and H_2S removal from flue gas and biogas, and developed many desulphurization methods including limestone-gypsum technology, alcohol-amine technology, dual alkali scrubbing technology et al. [3–5]. The resulting mixtures often contain trace sulfur gases (ppm), and should be further treated by the adsorption technology.

Porous material was thought to be a promising adsorbent because of high selectivity and efficiency, but low operating pressure and cost. Metal-organic frameworks (MOFs), as a new family of nanoporous materials, exhibit enormous advantages over other traditional porous materials like activated carbon and zeolites because of their adjustable pore structures and chemical functionality [6,7]. Therefore, MOFs are widely applied to the fields of gas storage, separation, and purification. However, some MOFs like ZIF-90, MOF-74, Zn/Co-BTEC will undergo structural degradation when exposing in humid acid gas (like SO_2, NO_2, and H_2S etc.) [8]. Recently, a new type of MOFs called UiO-66(Zr) has drawn much attention for its good selectivity, moisture stability, thermostability,

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high working capacity, and low-cost regenerability [9–12]. Especially, the crystalline structure of UiO-66(Zr) withstands in humid acid gas conditions [13,14]. Moreover, functionalized UiO-66(Zr) materials have also been reported to possess the similar physicochemical properties of the parent framework and display better gas separation performance [15,16]. Therefore, it is reasonable to deduce the series of functionalized UiO-66(Zr) structures can be applied to the H_2S and SO_2 removal from biogas which mostly compose of CH_4 and CO_2 and flue gas which mainly consists of CO_2 and N_2.

The objective of the present work is to investigate the adsorption performance of H_2S/CH_4, H_2S/CO_2, SO_2/CO_2, SO_2/N_2 on UiO-66(Zr)-X_n (X_n = -H, -Br, -NH_2, -NO_2, -$(OH)_2$, -$(CF_3)_2$, -COOH, -$(COOH)_2$) and desulphurization adsorption mechanism by molecular simulation methods. Then we focus our studies on gas diffusion, permeability, and permeation selectivity in functionalized UiO-66(Zr) materials. The results can be applied to evaluate the performance of gas adsorption and membrane separation of functionalized UiO-66(Zr) materials.

2. Models and methods

2.1. Structure

The UiO-66(Zr)-H structure was constructed from experimental single-crystal X-ray diffraction data [9] by Material Studio software, and the structure of UiO-66(Zr)-$(COOH)_2$ derives from Yang's work [17]. Other functionalized UiO-66(Zr)-X_n (X_n = -Br, -NH_2, -NO_2, -$(OH)_2$, -$(CF_3)_2$, -COOH) structures were built by replacing the H atoms on the phenyl rings with the corresponding functional groups and selecting the lowest-energy conformation by Forcite calculation. Then, Dmol^3 periodic DFT geometry optimization calculations were carried out using Material Studio software to further relax the UiO-66(Zr)-X_n framework. The PW91 GGA function combined with DNP set were employed in these calculations. More details of geometry optimization can be found in Yang's work [16].

2.2. Force field

In this work, Lennard-Jones (LJ) and Coulombic potentials were combined to calculate the gas-gas and gas-MOFs interactions. For different guest molecules, the choices of force field of MOFs make the reference to previous studies [16–19]. For CH_4, N_2, and H_2S calculation, the LJ potential parameters of MOFs were taken from DREIDING [20] force field. For CO_2 and SO_2 calculation, UFF [21] force field was used to describe the LJ potential of MOFs. The parameters of DREIDING [20] and UFF [21] force fields were shown in Table 1. The molecular models of guest molecules were shown in Fig. S1 (supporting information) and corresponding interatomic potential parameters and atomic partial charges [22–25] were listed in Table 2. The TraPPE force field is used to model CH_4, CO_2 and N_2. CH_4 was modeled as a single Lennard-Jones (LJ) interaction site model [22]. CO_2 were treated as rigid linear molecular model with three atoms [23]. N_2 molecule was represented as a three-site model with two sites located at two N atoms and the third one located at its center of mass (COM) [23]. H_2S is modeled in a manner similar to the SPC force field for water. SO_2 is modeled as a three-site Lennard-Jones model and the partial point charges are centered at each atom [24]. A single Lennard-Jones site is used to represent sulfur, while partial charges placed at the center of the hydrogen and sulfur atoms are used to represent electrostatic interactions [25]. All relevant atomic partial charges of MOFs considered in this work were taken from Yang's work [16]. The cross interaction parameters including gas-gas and gas-MOF were determined by the Lorentz-Berthelot mixing rules and all electrostatic interactions were computed using the Ewald summation technique [26].

Table 1
LJ potential parameters for the atoms of the UiO-66(Zr) series.

Elements	DREIDING		UFF	
	σ(Å)	ε/k_B(K)	σ(Å)	ε/k_B(K)
Zr	2.783	34.724	2.783	34.724
C	3.473	47.859	3.431	52.841
O	3.033	48.161	3.118	30.195
H	2.846	7.649	2.571	22.143
N	3.263	38.951	3.261	34.724
Br	3.519	186.202	3.732	126.315
F	3.093	36.485	2.997	25.162
S	3.590	173.117	3.595	137.890

Table 2
Molecular models of guest molecules considered in this work.

Adsorbates	Geometry	Site	σ(Å)	ε/k_B(K)	q(e)	Reference
CH_4	united-atom model	CH_4	3.73	148.00	0	[22]
CO_2	dCO = 1.16 Å	C	2.80	27.0	0.70	[23]
	∠OCO = 180°	O	3.05	79.0	−0.35	
N_2	dNN = 1.10 Å	N	3.31	36.0	−0.482	[23]
		COM	0	0	0.964	
SO_2	dSO = 1.43 Å	S	3.62	145.9	0.4710	[24]
	∠OSO = 119.5°	O	3.01	57.4	−0.2355	
H_2S	dSH = 1.365 Å	S	3.72	232	−0.38	[25]
	∠HSH = 91.5°	H	0	0	0.19	

2.3. Simulation details

Grand-canonical Monte Carlo (GCMC) simulations were employed to calculate the adsorption of H_2S/CH_4 ($y_{H_2S} = 0.00333$), H_2S/CO_2 ($y_{H_2S} = 0.005$), SO_2/CO_2 ($y_{SO_2} = 0.04762$) and SO_2/N_2 ($y_{SO_2} = 0.00556$) gas mixtures on functionalized UiO-66(Zr) structures. The materials in the simulation were modeled as rigid structures, which ignores the skeleton stretching and bending vibration. The number of unit cells in the simulation box is 2 × 2 × 2 and periodic boundary conditions were applied in all directions. The LJ potential cutoff radius was chosen as $r_c = 1.40$ nm ($r \geq r_c$, $U_{LJ} = 0$). In GCMC simulations, chemical potentials obtained by Peng-Robinson equation of state were taken as inputs to calculate the gas adsorption. The total GCMC simulation consisted of 1.7×10^6 steps. The first 1×10^5 steps are for structural relaxation, the next 1×10^5 steps are for equilibrium, and the last 1.5×10^6 steps are for statistical thermodynamics calculation.

Equilibrium Molecular Dynamics (EMD) simulations in the NVT ensemble were carried out to obtain the gas diffusivity and permeability of membranes. The Nose-Hoover thermostat was chosen to keep the temperature of simulation constant and the time steps of simulation were set 1.0 fs. For each state, the total MD simulation consisted of 5×10^6 steps. 1×10^5 steps were used to relax the framework and the subsequent 2×10^5 steps for equilibration. Mean-Square Displacements (MSD) were outputted every 1000 steps and followed with calculating the self-diffusion coefficient by Einstein relation:

$$D_S^x = \frac{1}{2}\lim_{t\to\infty}\frac{d}{dt}\left\langle [x(t)-x(0)]^2 \right\rangle \qquad (1)$$

where $x(t)$ is the position vector of tracer particle along the x axis at time t and angle brackets represent the ensemble average. Similarly, we can obtain the self-diffusion coefficients on the directions of y and z axis. Therefore, the mean self-diffusion coefficient which