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Selective capture of trace sulfur gas by porous covalent-organic materials

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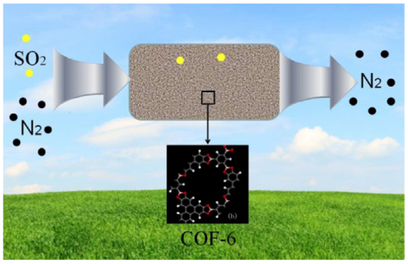
HIGHLIGHTS

- PAF-302 shows the highest excess uptake of H_2S and SO_2.
- COF-6 is an excellent material for the separation of sulfur gas.
- The modified DIH equation is suitable for the separation of trace sulfur gas mixtures.

GRAPHICAL ABSTRACT



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ABSTRACT

We have systematically investigated adsorption and separation of the sulfur gas H_2S and SO_2 in covalent-organic materials (COMs) by using molecular simulation. Results indicate that among these materials studied, PAF-302 shows the highest excess uptake of H_2S (51.94 mmol/g) and SO_2 (50.69 mmol/g) due to its large pore volume and high BET surface area. Both maximum excess uptakes of H_2S and SO_2 follow the order of PAF-302 > COF-102 > COF-10 > COF-5 > COF-8 > COF-6, which is entirely consistent with the orders of the pore volumes. For gas mixtures, the selectivity of these two-dimensional (2D) COM materials is obviously better than the three-dimensional (3D) COM materials, especially for COF-6 with smaller pore size. In short, PAF-302 is an excellent candidate for H_2S and SO_2 adsorption, while COF-6 is an excellent material for sulfur gas separation. In addition, we also find that the modified equation based on the difference of isosteric heats (i.e. DIH equation) can predict the selectivity of trace sulfur gas mixtures at zero pressure satisfactorily.

1. Introduction

As well known, sulfur dioxide (SO_2) is a major air pollutant which can lead to acid rain, urban smog and many other undesirable environmental and health problems (Jia et al., 2010). Hydrogen sulfide (H_2S) is a poisonous gas which has a great harm to human health even in very low concentrations (300 ppm) (Cosoli et al., 2008), and it also deactivates the catalysts and corrodes the equipment (Farrauto et al., 2003; Xu et al., 2005). Therefore, how to control the emissions of SO_2 and H_2S strictly and reduce sulfur content to low parts per billion (ppb) levels is still an important task for chemical engineer (Bashkova et al., 2007).

The main source of sulfur dioxide in the air is from the industrial activities, such as the generation of electricity from coal or oil that contains sulfur. Thus, it produces gas mixture of SO_2, CO_2, and N_2. One method to reduce SO_2 emission is to remove sulfur prior to burning (Peng and Cao, 2013). Another method is to remove SO_2 from flue gas using either wet or dry scrubbing (Mangun et al., 2001). H_2S is generated from natural gas processing, petroleum refining, petrochemical plants and coal gasification etc (Feng et al., 2005). Thus the gas mixtures often contain

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H_2S, CH_4, CO_2 and N_2. Aqueous solutions of alkanolamines are commonly used to remove H_2S, but they cannot reduce the sulfur content to the low levels required (Xu et al., 2005). Among the methods used to remove low concentration H_2S/SO_2 from mixture gases, adsorption by porous materials such as activated carbons (AC) (Bagreev and Bandosz, 2001; Bandosz, 1999; Guo and Lua, 2002), ammonia-treated activated carbon fibers (Mangun et al., 2001), impregnated activated carbon (Bandosz et al., 2000; Wu et al., 2007; Xiao et al., 2008), zeolites (Cosoli et al., 2008; Melo et al., 2006), metal organic frameworks (MOFs) (Hamon et al., 2009; Xiang et al., 2011), is an efficient and economical approach. For example, Cosoli et al. (2008) simulated H_2S removal from biogas by zeolites and confirmed that hydrophilic zeolites are more suitable for H_2S adsorption. Boudou et al. (2003) investigated adsorption of H_2S or SO_2 on an activated carbon cloth modified by ammonia treatment. Bagreev et al. (2002) demonstrated that quaternary and pyridinic type nitrogen significantly enhance the adsorption capacity of SO_2. Melo et al. (2006) revealed that zinox and zeolite materials could be used as H_2S adsorbents in natural gas, exceeding the capabilities of industrial compounds. Hamon et al. (2009) presented the first experimental study on hydrogen sulfide adsorption in porous MOFs, and showed that selected MOFs may be stable and easily regenerable toward H_2S sorption. However, most of MOFs possess low hydrothermal stability, which limits their application in industries. Recently, covalent organic materials (COMs) have been synthesized and widely applied in gas adsorption and separation (Xiang and Cao, 2013), because these materials are formed together by strong covalent bonds between light elements, and they therefore hold lower densities and higher thermal stability than MOFs (Côté et al., 2007; El-Kaderi et al., 2007). Furukawa and Yaghi (2009) investigated adsorption capacity of H_2, CH_4, CO_2 in covalent-organic frameworks (COFs), and found that three-dimensional (3D) COFs are good gas storage materials. Keskin (2012) used molecular simulations to calculate adsorption and diffusion of CH_4 and H_2, as well as CH_4/H_2 mixtures in three kinds of two-dimensional (2D) COFs (i.e. COF-5, COF-6, and COF-10) at room temperature, and found that the membrane selectivities of COF-5, COF-6 and COF-10 are higher than those of zeolites and similar to ZIFs and MOFs. More recently, Ben et al. successfully synthesized a new porous aromatic framework called PAF-1 (also named PAF-302) (Ben et al., 2009; Lan et al., 2010a), which not only holds a diamond-like structure and high hydrothermal stabilities, but also possesses ultrahigh BET surface area of 5600 m^2/g and high capacities for H_2 and CO_2. The previous investigations indicate that COMs could be promising materials for gas storage (Cao et al., 2009) and separation (Xiang and Cao, 2013), not only limited to H_2, CH_4 and CO_2 (Lan et al., 2010a, 2010b), but also for sulfur gases. However, to the best of our knowledge, adsorption and separation performances for H_2S and SO_2 in the COMs materials have not been investigated yet. Therefore, we selected several representative materials, including 2D materials (COF-5, COF-6, COF-8, COF-10) and 3D materials (COF-102, PAF-302) to explore the adsorption and separation of SO_2 and H_2S in COMs. The COF-5, -6, -8, and -10 were obtained through co-condensation reactions between 2,3,6,7,10,11-hexahydroxy-triphenylene (HHTP) with 1,4-benzenediboronic acid (BDBA), 1,3,5-benzene-triboronic acid (BTBA), 1,3,5-benzenetris(4-phenylboronic acid) (BTPA), and 4,4′-biphenyldiboronic acid (BPDA), respectively (Côté et al., 2005, 2007). The 2D COFs present one-dimensional channels with different pore sizes (As shown in Table 1). COF-102 is prepared by self-condensation reactions of the tetrahedral tetra(4-dihydroxyborylphenyl) methane (TBPM) (El-Kaderi et al., 2007). PAF-302 is synthesized by self-condensation of tetrakis(4-bromophenyl)methane (Ben et al., 2009). These selected materials were shown in Fig. 1 and their structural properties were listed in Table 1.

Table 1
The structure data of COMs.

Materials	Pore size (Å)	S_{BET} (m^2/g)	V_{pore} (cm^3/g)	Density (g/cm^3)	Ref.
COF-5	27	1670	1.07	0.58	Furukawa and Yaghi (2009)
COF-6	9	750	0.32	1.1	Furukawa and Yaghi (2009)
COF-8	16	1350	0.69	0.71	Furukawa and Yaghi (2009)
COF-10	32	1760	1.44	0.48	Furukawa and Yaghi (2009)
COF-102	12	3620	1.55	0.43	Furukawa and Yaghi (2009)
PAF-302	12.4	5600	2.34	0.315	Ben et al. (2009)
MIL-47(V)	10.5	1684	0.63	1.00	Zheng et al. (2009)
MIL-100(Cr)		1900	1.10	0.7	Llewellyn et al. (2008)
MIL-101(Cr)		2800	1.37	0.44	Llewellyn et al. (2008)
E-83			1.08		Molina-Sabio et al. (1995)
E-47			0.52		

2. Computational details

2.1. Potential models

In this work, CH_4 and N_2 were represented by the spherical united-atom Lennard–Jones (LJ) potential model and their potential parameters were taken from TraPPE force field (Martin and Siepmann, 1998) and Ohkubo et al. (2002), respectively. The H_2S, SO_2 and CO_2 were modeled as 3-site rigid molecules with three charged LJ interaction sites, and their potential parameters were taken from Nath (2003), Ribeiro (2006) and Potoff and Siepmann (2001), respectively. A combination of the site–site LJ and coulombic potentials was used to calculate the 3-site intermolecular interactions. The interactions between gases and solids were modeled using the LJ potential, and the Lorentz–Berthelot mixing rules were used to obtain the cross interaction parameters. Unfortunately, almost no experimental data about sulfur gases adsorption in COM materials is available. Previous simulation studies have shown that Dreiding force field leads to accurate predictions of gas adsorption in COMs (Garberoglio and Vallauri, 2008; Keskin, 2012; Yang et al., 2013). Therefore, for the adsorbents, the Dreiding force field (Mayo et al., 1990) was adopted to describe the interactions of framework atoms. During the simulations, we ignored the atomic charges of the adsorbents because there were no metal atoms in the COM materials. The adsorbents were treated as rigid materials with atoms frozen. All the size and energy parameters of gas molecules and adsorbents are shown in Table 2.

2.2. Computational methods

We used the grand canonical Monte Carlo (GCMC) simulations to study the adsorption and separation of sulfur gases in COMs. The periodic boundary conditions were applied in all three dimensions. According to their size of unit cells, we choose a simulation box containing $1 \times 1 \times 1$ for COF-102, $1 \times 1 \times 8$ for COF-5, $2 \times 2 \times 8$ for COF-6, $2 \times 2 \times 8$ for COF-8, $1 \times 1 \times 8$ for COF-10, $2 \times 2 \times 2$ for PAF-302. All the GCMC simulations were performed by using the MUSIC code (Gupta et al., 2003). The more details about the simulation can be referred to the literature (Wang et al., 2011; Yang et al., 2013).

The GCMC simulations directly give the absolute adsorption amount N_{ab}, while the experimental adsorption isotherm is often