Adsorption and Separation of H₂S in HKUST-1 Metal−Organic Frameworks: A Monte Carlo Simulation Study

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Abstract. H_2S is a toxic gas and universally presents in natural gas, chemicals, and biomass syngas. It is very important to remove and separate it from gaseous mixtures. In this work, we simulated the adsorption of pure H_2S and CH_4 and their mixture on HKUST-1 under different temperatures and pressures by the grand canonical Monte Carlo (GCMC) method. The results show that the single-component adsorption capacity of H_2S and CH_4 increases with the increase of pressure, but decreases with the increase of temperature. In the low-pressure range, the adsorption of H_2S is dominated by Coulomb interaction, while Van der Waals force plays a dominant role at high pressure. HKUST-1 shows a superior selectivity for H_2S over CH_4. Its selectivity increases with the increase of both temperature and pressure. The study indicates that HKUST-1 has a good potential on the H_2S adsorption and separation.

Introduction

Metal-organic frameworks (MOFs) are a class of crystalline materials built from organic binding ligands and metal ions through self-assembly [1]. Compared with conventional inorganic porous materials, MOFs possess large specific surface areas, high porosity, and diversity of structures and functions. Thus many potential applications have been proposed in the domain of gas adsorption and separation, sensors, drug delivery, and catalysis. A large number of investigations have clearly shown that MOF materials exhibit excellent properties of adsorption and separation for CH_4, CO_2, CO, H_2, NO, and so on [2] [3].

H₂S is a harmful gas, which widely exists in natural gas, chemical fluid, and bio-syngas. Due to strong corrosivity, H_2S has a great influence on the residual life of oil pipelines, which would lead to a huge security risk. H_2S also has a serious impact on human and animal health, because a small amount of H_2S can cause suffocation. In addition, H_2S could be oxidized to form acid rain, causing serious harmful to environment. Therefore, it is important to remove and separate it from gaseous mixtures.

HKUST-1 is a kind of porous material, which is composed of $Cu_2(Ac)_4$ paddlewheel-type metal corners and BTC (1,3,5-benzenetricarboxylate) linkers. HKUST-1 has special open metal sites and three kinds of micropores, suggesting it may be a potential adsorbent for H_2S gas. In this work, we investigated the H_2S adsorption and separation properties of HKUST-1 material using a grand canonical Monte Carlo (GCMC) method.

Model and method

The HKUST-1 crystal structure was obtained from the available experimental crystallographic data (Figure 1) [4]. The Dreiding force field was used for potential parameters of the framework atoms [5]. H_2S was modeled with four-atom Lennard-Jones (LJ) interaction sites [6]. CH_4 was modeled as a rigid regular tetrahedron molecule with united-atom LJ interaction sites, and the potential parameters were taken from the TraPPE force field [7]. The atomic charges were estimated by fitting to the electrostatic potential (ESP) calculated by the density functional theory (DFT) method.

In this work, the pure H_2S, CH_4, and gas mixture adsorption isotherms were simulated using the GCMC method. All simulations were performed with the MC simulation suite of the MUSIC code [8], and periodic boundary conditions were applied in three dimensions. The framework was considered to be rigid during simulation considering the negligible influence of framework flexibility on the adsorption of gases at the low-energy conditions. The cutoff distance for truncation of the intermolecular (LJ) interactions was set to 12.8 Å, and the Ewald sum technique was used to compute the electrostatic interaction. During the simulations, the number of trial moves was 2×107. The first 10^7 moves were used for equilibration and the subsequent 10^7 moves were performed to sample the desired properties.
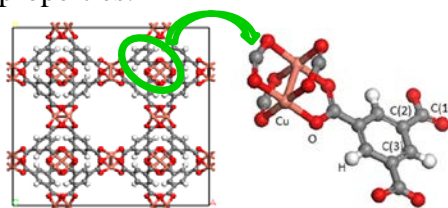

Fig.1 The structure of HKUST-1

Single-Component Adsorption

In this section, we first discuss the simulated adsorption isotherms of pure CH_4 at 298 K and compare them with the simulation data by Jagadeswara et al. [4]. As shown in Figure 2(a), the trend of the adsorption behavior was successfully predicted, which validates the force fields and models used by us.
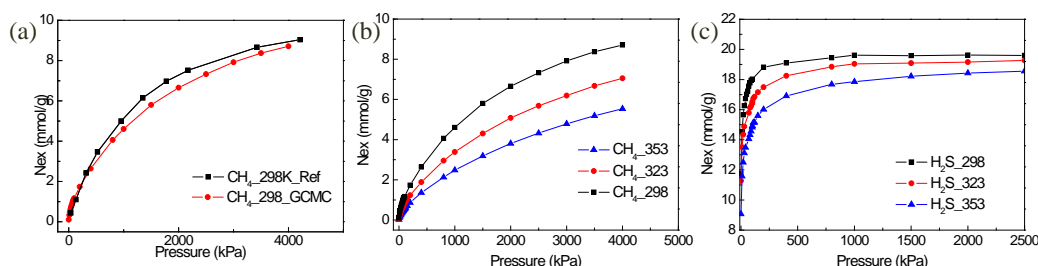

Fig.2 The simulated adsorption isotherms of CH_4 and H_2S

To predict the adsorption characteristics of HKUST-1, the single-component absolute adsorption isotherms of CH_4 and H_2S were performed at 298, 323, and 353 K (Figure 2). As shown in Figure 2, both CH_4 and H_2S uptakes are up to maximum at 298 K, followed by 323 K, and then 353 K. It is well known that the higher the temperature, the quicker the motion of molecules, which will be more difficult to be adsorbed by adsorbents. Thus, it would result in a low adsorption capacity of adsorbent at high temperatures. At 2500 kPa, the CH_4 uptake is found to decrease from 7.33 mmol/g at 298 K to 5.68 mmol/g at 353 K (by about 22.5%), while the H_2S uptake decreases from 19.60 mmol/g at 298 K to 18.55 mmol/g at 353 K (by about 5.4%), suggesting the effect of temperature on H_2S is less than that on CH_4. This is attributed to the stronger interactions between H_2S molecules and HKUST-1 frameworks than those of CH_4.

With the increase of pressure, both CH_4 and H_2S uptakes increase monotonically. Compared with gradual increase of CH_4 uptake, the H_2S uptake increases sharply at a range of 1-200 kPa, and then tends to flatten out to a constant value (19.62 mmol/g) at 2000 kPa. To further illustrate the adsorption property of H_2S at low pressures, we gave the adsorption isotherms of H_2S at the pressures of 1-200 kPa. As shown in Figure 2(c), H_2S uptake is much larger at extreme low pressures. For example, at 0.1 kPa and 298 K, the adsorption of H_2S is up to 10.38 mmol/g, much higher than that of CH_4, suggesting a good CH_4/H_2S adsorption selectivity for HKUST-1.

To illustrate the effects of Coulomb and van der Waals interactions on H_2S uptake, additional simulations were conducted by eliminating the contribution of Coulomb interaction (Figure 3(a)). The Coulomb contribution is calculated using the equation (1):

$$\omega_{Col} = \frac{N_{with} - N_{without}}{N_{with}} \times 100\% \qquad (1)$$

where N_{with} and $N_{without}$ are the H$_2$S uptake with and without Coulomb interaction, respectively. As shown in Figure 3(b), the contribution of Coulomb interaction to H$_2$S uptake decreases monotonically with the increase of pressure. For example, the Coulomb contribution is as high as 96.7% at 1 kPa, while it is only 21.9%, when the pressure is up to 2000 kPa. Overall, the adsorption of H$_2$S is dominated by the Coulomb interaction at low pressures, whereas it dominated by the van der Waals force at high pressures.
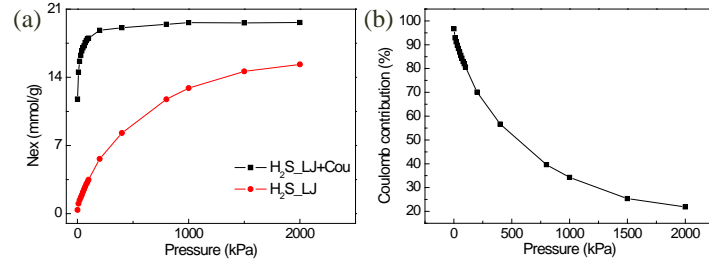

Fig.3 The Coulomb contribution for the H$_2$S adsorption

H$_2$S/CH$_4$ Mixture-Component Adsorption

It is known that the content of H$_2$S is only about 1-5% in natural gas, and about 2% in biogas. Thus, we investigated the selectivity of H$_2$S over CH$_4$ with a bulk composition of 1:99, 5:95, and 10:90 at 298, 323, and 353 K, respectively. Figure 4 shows the adsorption isotherms of H$_2$S/CH$_4$ mixture in HKUST-1. It is clear that the H$_2$S uptake is much higher than that of CH$_4$ at composition of 5:95 and 10:90. Although the adsorption of H$_2$S is less than that of CH$_4$ at composition of 1:99, the H$_2$S adsorption quantity is still much large, considering the extremely low content of H$_2$S (1%). Furthermore, at 4000 kPa and 298 K, the H$_2$S uptake is found to be 8.75, 16.90, and 19.06 mmol/g at composition of 1:99, 5:95, and 10:90, respectively, suggesting a larger increase of H$_2$S adsorption with the increase of its content in mixtures.

For all three kinds of compositions, the adsorption of CH$_4$ decreases with the increase of temperature, but it is found to be a contrary situation for H$_2$S. For example, H$_2$S uptake increases from 16.90 mmol/g at 298 K to 24.90 mmol/g at 353 K at 4000 kPa. This is caused by a combination of competitive adsorption and thermal movement. When the temperature increases, the desorption of CH$_4$ is much easier than that of H$_2$S due to a weaker interaction of CH$_4$ with framework. This would lead to larger decrease of CH$_4$ uptake than that of H$_2$S. On the other hand, the adsorption sites released by CH$_4$ favor the further adsorption of H$_2$S.
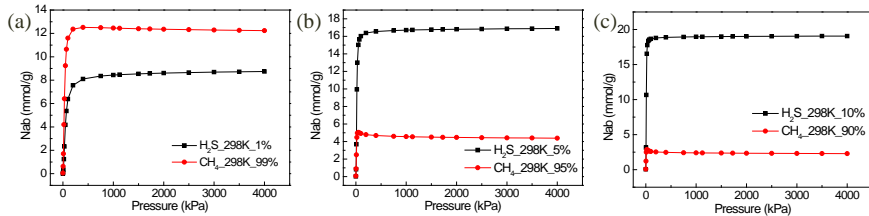

Fig.4 The adsorption isotherms of CH$_4$ and H$_2$S in CH$_4$/H$_2$S mixture

H$_2$S/CH$_4$ selectivity

Figure 5(a) shows the adsorption selectivity of H$_2$S over CH$_4$ from an equimolar H$_2$S/CH$_4$ mixture in HKUST-1 at 298K. With the increase of H$_2$S content, the selectivity of H$_2$S/CH$_4$ is found to be 70.72, 73.26, and 74.80 for the composition of 1:99, 5:95, and 10:90, respectively, suggesting a gradual increase of selectivity for H$_2$S/CH$_4$ mixture.

For the composition of 1:99 at 298 K, the H$_2$S/CH$_4$ selectivity increases sharply from 5.46 at 1 kPa to 60.54 at 200 kPa. When the pressure continues to increase, the selectivity increases slowly

and tends to flatten out to a constant value, suggesting the factor of pressure plays a main role in the H_2S/CH_4 selectivity at low pressures. As shown in Figure 5(b), at 4000 kPa, the selectivity of H_2S/CH_4 is found to be 70.72 at 298 K, 114.37 at 323 K, and 267.50 for 353 K, indicating the temperature has a large effect on the selectivity at high pressures.
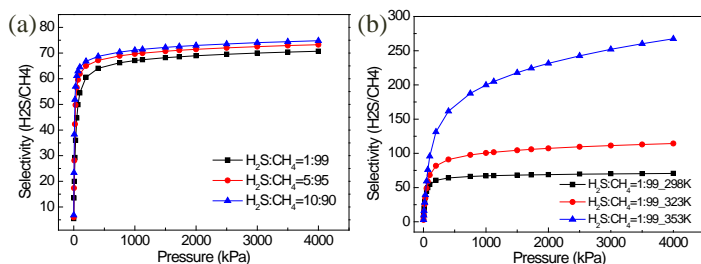

Fig.5 The H_2S selectivity in CH_4/H_2S mixtures

Conclusions

The H_2S adsorption and seperation properties of HKUST-1 material have been systematically investigated by the GCMC simulation. The results show that the adsorption capacity of H_2S is much larger than that of CH_4. For the H_2S adsorption, it is dominated by the Coulomb interaction at low pressures, while the van der Waals force plays a dominant role at high pressures. At the low H_2S content of 1-5%, HKUST-1 shows a larger H_2S selectivity for H_2S/CH_4 mixture and the selectivity coefficient increases with the increase of both temperature and pressure. All these indicate that HKUST-1 has a great potential on the adsorption and separation of H_2S gas.

Acknowledgements

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