Postprint: Effect of H2O on CO2 Capture Performance of Zeolitic Imidazolate Framework Materials

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Date: 2018-01-05T00:00:00+00:00

Abstract

Zeolitic imidazolate framework (ZIF) materials represent a novel class of adsorbents for greenhouse gas CO2. This study employs grand canonical Monte Carlo (GCMC) simulations to investigate the influence of H2O on the CO2 adsorption performance and CO2/N2 separation performance of ZIF-8 and ZIF-90. The results demonstrate that ZIF-90 exhibits superior CO2 adsorption and CO2/N2 separation performance compared to ZIF-8. In ZIF-8, the presence of H2O has negligible impact on the material’ s CO2 adsorption performance and CO2/N2 selective separation performance. H2O demonstrates a synergistic adsorption effect on CO2 adsorption in ZIF-90, and the presence of H2O significantly promotes the material’ s CO2 adsorption and CO2/N2 separation.

Full Text

The Effect of H2O on CO2 Capture in Zeolitic Imidazolate Frameworks

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Abstract

Zeolitic imidazolate frameworks (ZIFs) are novel porous materials for greenhouse gas CO2 adsorption. This work investigates the effect of H2O on CO2 adsorption and CO2/N2 separation performance in ZIF-8 and ZIF-90 using Grand Canonical Monte Carlo (GCMC) simulations. The results demonstrate that ZIF-90 exhibits superior CO2 adsorption capacity and CO2/N2 selectivity compared to ZIF-8. In ZIF-8, the presence of H2O has negligible impact on CO2 adsorption and CO2/N2 separation performance. In contrast, H2O exhibits a cooperative adsorption effect on CO2 in ZIF-90, significantly enhancing both CO2 uptake and CO2/N2 separation efficiency.

Keywords: CO2; H2O; Zeolitic Imidazolate Frameworks; Grand Canonical Monte Carlo simulations

Introduction

Increasing atmospheric CO2 concentrations and associated global warming represent a major challenge to human development. Coal-fired power plants constitute the largest source of CO2 emissions in China. Capturing CO2 from flue gas using porous adsorbents to mitigate atmospheric CO2 levels is considered one of the most effective emission reduction strategies [1]. In recent years, numerous porous materials have been investigated for post-combustion CO2 capture, among which metal-organic frameworks (MOFs) are regarded as highly promising candidates due to their excellent thermal and chemical stability, ultra-high surface area, tunable porosity, and designable structures tailored for specific applications [2].

Zeolitic imidazolate frameworks (ZIFs) are a subclass of MOFs featuring zeolite-like structures [3]. These materials consist of transition metal atoms (typically Zn or Co) connected by functionalized imidazolate (IM) organic linkers. Compared to conventional MOFs, ZIFs exhibit superior chemical and thermal stability [4]. Additionally, ZIFs demonstrate excellent CO2 capture and separation performance. Banerjee et al. [5] reported that under conditions of 273 K and 100 kPa, 1 L of ZIF-69 can store 83 L of CO2, significantly outperforming materials such as BPL carbon.

Real flue gas contains substantial amounts of water vapor in addition to CO2 and N2. Previous studies have shown that water vapor affects CO2 adsorption and CO2/N2 separation in MOFs. Kizzie et al. [6] found that small amounts of water enhance CO2 adsorption in HKUST-1, whereas the CO2 adsorption capacity of Ni-MOF-74 decreases in the presence of water. However, investigations into the effects of flue gas H2O on CO2 capture performance in ZIFs remain scarce [7]. Our previous research [7] revealed that H2O reduces CO2 adsorption capacity in ZIF-68 but improves CO2/N2 separation selectivity. To evaluate the practical potential of ZIFs for post-combustion CO2 capture, it is essential to systematically investigate the influence of flue gas H2O on their CO2 adsorption and CO2/N2 separation performance.

This study focuses on two ZIF materials with identical topological structures but different organic linkers—ZIF-8 and ZIF-90—using GCMC simulations to examine how flue gas H2O affects their CO2 adsorption and CO2/N2 separation performance. By comparing CO2 uptake and CO2/N2 selectivity in CO2/N2 and CO2/N2/H2O mixtures, we elucidate the impact of H2O on CO2 capture performance in ZIFs and analyze the underlying mechanisms. These findings provide theoretical guidance for designing ZIF materials suitable for practical operating conditions.

1.1 ZIFs Models

The atomic positions in ZIF-8 and ZIF-90 models were determined from experimental X-ray diffraction data [8, 9] to construct the simulation models, as shown in [Figure 1: see original paper]. Both ZIF-8 and ZIF-90 possess the same SOD topology, constructed from metal Zn atoms connected to different organic linkers. ZIF-8 contains methyl-imidazolate linkers, while ZIF-90 features aldehyde-imidazolate linkers. The structural properties of both materials are summarized in . The accessible surface area and total free volume were calculated using Materials Studio [10]. A probe molecule with a diameter equal to the kinetic diameter of N2 (0.28 nm) was used to calculate the accessible surface area (Sacc). The total free volume (Vfree) represents the volume not occupied by framework atoms and was determined using a probe molecule with a diameter of [MATH_PLACEHOLDER_1] nm [11].

1.2 Force Fields and Atomic Charges

The interactions between gas molecules and framework atoms were described using the Lennard-Jones 12-6 potential and Coulombic potential, with electrostatic interactions calculated using the Ewald summation method:

$$u_{ij}(r) = \sum_{\alpha \in i} \sum_{\beta \in j} \left\{ 4\varepsilon_{\alpha\beta} \left[\left(\frac{\sigma_{\alpha\beta}}{\gamma_{\alpha\beta}} \right)^{12} - \left(\frac{\sigma_{\alpha\beta}}{\gamma_{\alpha\beta}} \right)^{6} \right] + \frac{q_\alpha q_\beta}{4\pi\varepsilon_0 \gamma_{\alpha\beta}} \right\}$$

where 0 = 8.8542 × 10^-12 C^2 N^-1 m^-2 is the vacuum permittivity, and and are the collision diameter and potential well depth, respectively. Force field parameters for CO2 and N2 were taken from the TraPPE model [12]. In this model, CO2 is represented as a rigid linear molecule with a C-O bond length of 0.116 nm. To describe the quadrupole moment of CO2, the C atom carries a charge of +0.35e and each O atom carries -0.7e. N2 is modeled as a three-site rigid molecule with an N-N bond length of 0.11 nm. Each N atom has a charge of -0.482e, and a dummy atom with +0.964e is placed at the center to maintain charge neutrality. H2O was described using the TIP4P model [13], which includes three charged atoms and one Lennard-Jones center. The force field parameters for gas molecules are listed in .

Force field parameters for ZIF-8 and ZIF-90 framework atoms were taken from the UFF force field [14], which accurately describes interactions between gas molecules and framework atoms. To better describe gas adsorption behavior in ZIF-8 and ZIF-90, optimized UFF parameters were employed [15]. Framework atom force field parameters are provided in . Partial atomic charges for ZIF framework atoms were obtained from ESP charges fitted to DFT calculations [15], as shown in [Figure 2: see original paper].

1.3 GCMC Simulation Details

GCMC simulations were performed to calculate single-component gas adsorption isotherms in ZIF-8 and ZIF-90 at 298 K, as well as component adsorption and CO2/N2 selectivity from CO2/N2/H2O ternary mixtures. Framework atoms were treated as rigid and fixed at their crystallographic positions. Three-dimensional periodic boundary conditions were applied to account for the surrounding environment. To ensure computational accuracy, the simulation box consisted of 2 × 2 × 2 unit cells with a cutoff radius of 1.28 nm. The simulation comprised 2 × 10ˆ7 steps, with the first 1 × 10ˆ7 steps for equilibration and the remaining 1 × 10ˆ7 steps for statistical analysis. Simulation results are reported as absolute adsorption amounts, whereas experimental measurements yield excess adsorption amounts. The conversion between excess (nex) and absolute (nabs) adsorption is given by:

$$n_{ex} = n_{abs} - V_g \rho_g$$

where Vg is the pore volume of the adsorbent and g is the density of the bulk gas phase, which can be calculated using the Peng-Robinson equation. The separation factor S is calculated as:

$$S = \left(\frac{x_1}{x_2}\right)\left(\frac{y_2}{y_1}\right)$$

where x and y represent the mole fractions of the corresponding components in the adsorbed and gas phases, respectively.

2.1 Force Field Validation

Appropriate force field parameters are critical for reliable simulation results. The CO2 and N2 adsorption isotherms obtained from GCMC simulations for ZIF-8 and ZIF-90 were compared with experimental data, as shown in [Figure 3: see original paper]. The excellent agreement between simulation and experimental results validates the reliability of the selected force field parameters and atomic charges.

2.2 Single-Component Gas Adsorption

[Figure 4: see original paper] presents the adsorption isotherms for CO2, N2, and H2O in ZIF-8 and ZIF-90 at 298 K. The pressure ranges were 0–100 kPa for CO2, 0–100 kPa for N2, and 0–10 kPa for H2O. CO2 adsorption in both ZIF-8 and ZIF-90 is significantly higher than N2 adsorption, indicating that both materials are promising for CO2/N2 separation. H2O adsorption in ZIF-8 is very low because the -CH3 functional group is hydrophobic and hinders H2O adsorption. In contrast, due to the hydrophilic nature of the -CHO group in ZIF-90, H2O adsorption in ZIF-90 is much higher than CO2 adsorption.

2.3 Mixed-Gas Adsorption

To investigate the effect of flue gas H2O on CO2 adsorption and CO2/N2 separation performance, two gas mixtures were considered: (1) CO2/N2 and (2) CO2/N2/H2O. To simulate realistic flue gas conditions, the partial pressures were set at 15 kPa for CO2 and 5 kPa for H2O, with a total pressure of 100 kPa balanced by N2.

[Figure 5: see original paper] shows the CO2 uptake and CO2/N2 selectivity in ZIF-8 and ZIF-90 for both gas mixtures. In the CO2/N2 mixture, ZIF-90 exhibits higher CO2 adsorption capacity and selectivity than ZIF-8. This is attributed to the polar -CHO functional group in ZIF-90, whereas the -CH3 group in ZIF-8 is nonpolar. Polar functional groups enhance the interaction energy between CO2 and framework atoms more effectively than nonpolar groups [16]. Consequently, substituting with polar functional groups increases the affinity between CO2 and framework atoms, thereby improving CO2 uptake and CO2/N2 selectivity.

Furthermore, H2O has negligible effect on CO2 adsorption and CO2/N2 separation in ZIF-8 because H2O adsorption is extremely low compared to CO2 adsorption. In ZIF-90, despite substantial H2O adsorption, the presence of H2O actually promotes CO2 adsorption and CO2/N2 separation. As shown in , H2O increases the isosteric heat of adsorption for CO2 in ZIF-90, indicating a cooperative adsorption effect between H2O and CO2 that enhances CO2 uptake. This cooperative effect is absent between H2O and N2, resulting in increased CO2/N2 selectivity in the presence of H2O.

Conclusion

This study employed GCMC simulations to investigate the effects of H2O on CO2 adsorption and CO2/N2 separation performance in ZIF-8 and ZIF-90. The results demonstrate that ZIF-90 outperforms ZIF-8 in both CO2 adsorption capacity and CO2/N2 selectivity. In ZIF-8, H2O adsorption is significantly lower than CO2 adsorption, and H2O presence has no effect on CO2 adsorption or CO2/N2 separation. In ZIF-90, H2O adsorption exceeds CO2 adsorption, and a cooperative adsorption mechanism exists between H2O and CO2. The presence of H2O significantly enhances both CO2 adsorption capacity and CO2/N2 separation performance in ZIF-90.

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Note: Figure translations are in progress. See original paper for figures.