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

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Date: 2017-11-07T00:00:00+00:00

Abstract

Zeolitic Imidazolate Frameworks (ZIFs) are a novel class of adsorbent materials for the greenhouse gas CO2. This work investigates the influence of H2O on the CO2 adsorption performance and CO2/N2 separation performance of ZIF-8 and ZIF-90 using Grand Canonical Monte Carlo (GCMC) simulations. 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 enhances the material' s CO2 adsorption and CO2/N2 separation.

Full Text

The Effect of H2O on CO2 Capture Performance of Zeolitic Imidazolate Framework Materials

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Abstract

Zeolitic imidazolate frameworks (ZIFs) are a novel class of porous materials for greenhouse gas CO2 adsorption. This work investigates the influence 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 effect on CO2 adsorption and CO2/N2 separation performance. Conversely, H2O exhibits a cooperative adsorption effect with CO2 in ZIF-90, significantly enhancing both CO2 uptake and CO2/N2 selectivity.

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

Introduction

The increasing concentration of CO2 in the atmosphere and the resulting 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 concentration is considered one of the most effective emission reduction strategies. In recent years, various 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.

Zeolitic imidazolate frameworks (ZIFs) are a subclass of MOFs featuring zeolite-like topologies. These materials are constructed by linking transition metal atoms (typically Zn or Co) with functionalized imidazolate organic linkers. Compared to conventional MOFs, ZIFs exhibit superior chemical and thermal stability. Additionally, ZIFs demonstrate excellent CO2 capture and separation performance. Banerjee et al. 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. found that small amounts of water enhance CO2 adsorption in HKUST-1, while the CO2 adsorption capacity of Ni-MOF-74 decreases in the presence of water. However, investigations into the effects of H2O in flue gas on the CO2 capture performance of ZIFs remain scarce. In our previous research, we discovered that H2O reduces the CO2 adsorption capacity of ZIF-68 but improves its CO2/N2 separation factor. To evaluate the practical potential of ZIFs for post-combustion CO2 capture, it is essential to examine the influence of flue gas H2O on both CO2 adsorption performance and CO2/N2 separation capability.

This study focuses on two ZIF materials with identical topological structures but different organic linkers—ZIF-8 and ZIF-90—and employs GCMC simulations to investigate 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 gas mixtures, we elucidate the impact of H2O on the CO2 capture performance of ZIFs and analyze the underlying mechanisms. These findings provide theoretical guidance for designing ZIF materials suitable for practical operating conditions.

1.1 ZIFs Model

The atomic positions in ZIF-8 and ZIF-90 models were determined using experimental X-ray diffraction data to construct the simulation models, as shown in [Figure 1: see original paper]. Both ZIF-8 and ZIF-90 possess the same SOD topology, consisting of metal Zn atoms connected to different organic linkers. ZIF-8 contains methyl-imidazolate linkers, while ZIF-90 is composed of 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. A probe molecule with a diameter equal to the kinetic diameter of N2 (0.28 nm) was employed 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 zero diameter.

1.2 Force Field and Atomic Charges

The Lennard-Jones 12-6 potential model and Coulombic potential model were used to describe guest-guest and guest-adsorbent interactions, with electrostatic interactions calculated using the Ewald summation method:

$$u_{ij}(r) = \sum \left\{ 4\varepsilon_{\alpha\beta} \left[\left(\frac{\sigma_{\alpha\beta}}{r} \right)^{12} - \left(\frac{\sigma_{\alpha\beta}}{r} \right)^{6} \right] + \frac{1}{4\pi\varepsilon_0} \frac{q_\alpha q_\beta}{r_{\alpha\beta}} \right\}$$

where $\varepsilon_0 = 8.8542 \times 10^{-12}\,\mathrm{C^2N^{-1}m^{-2}}$ is the vacuum permittivity, and $\sigma_{\alpha\beta}$ and $\varepsilon_{\alpha\beta}$ are the collision diameter and potential well depth, respectively.

The force field parameters for CO2 and N2 molecules were taken from the TraPPE model. 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. The N2 molecule is modeled as a three-site rigid model with an N-N bond length of 0.11 nm. N atoms have a charge of -0.482e, and a dummy atom with +0.964e is placed at the center of mass to balance the molecular charge. The H2O model was taken from TIP4P, which includes three charged atoms and one LJ center. The force field parameters for guest molecules are listed in .

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

1.3 Grand Canonical Monte Carlo Simulation Details

GCMC simulations were performed to calculate single-component gas adsorption in ZIF-8 and ZIF-90 at 298 K, as well as component-specific 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 environmental effects on CO2 adsorption. To ensure computational accuracy, the simulation box consisted of 2 × 2 × 2 unit cells with a cutoff radius of 1.28 nm. Each simulation comprised 2×10^7 steps, with the first 1×10^7 steps for equilibration and the subsequent 1×10^7 steps for statistical analysis. Simulation results yield absolute adsorption amounts, whereas experimental measurements provide excess adsorption amounts. The conversion between them follows:

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

where n_{ex} is the excess adsorption amount, n_{abs} is the absolute adsorption amount, V_g is the pore volume of the adsorbent, and ρ_g is the bulk gas density calculated using the Peng-Robinson equation. The separation factor is calculated as:

$$S = \frac{x_1/x_2}{y_1/y_2}$$

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

2 Results and Discussion

2.1 Force Field Validation

Appropriate force field parameters are crucial for reliable simulation results. The simulated CO2 and N2 adsorption isotherms 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 confirms the reliability of the selected force field parameters and atomic charges.

2.2 Single Gas Adsorption

[Figure 4: see original paper] presents the simulated adsorption isotherms for CO2, N2, and H2O on ZIF-8 and ZIF-90 at 298 K. The pressure ranges were 0-100 kPa for CO2 and N2, and 0–10 kPa for H2O. The results show that CO2 adsorption in both ZIF-8 and ZIF-90 significantly exceeds that of N2, 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 uptake. In contrast, due to the hydrophilic nature of the -CHO group in ZIF-90, H2O adsorption is substantially higher than CO2 adsorption in this material.

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 the total pressure maintained at 100 kPa using N2 as the balance gas.

[Figure 5: see original paper] shows the CO2 adsorption capacity and CO2/N2 selectivity for ZIF-8 and ZIF-90 in both gas mixtures. In the CO2/N2 mixture, ZIF-90 exhibits higher CO2 uptake and selectivity than ZIF-8. This is attributed to the polar -CHO functional group in ZIF-90, which enhances the interaction energy with CO2 compared to the nonpolar -CH3 group in ZIF-8. The polar functional group creates stronger affinity between CO2 and framework atoms, thereby increasing both CO2 adsorption capacity and CO2/N2 selectivity.

Notably, H2O has no effect on CO2 adsorption and CO2/N2 separation in ZIF-8 because H2O adsorption is extremely low compared to CO2 uptake. However, despite substantial H2O adsorption in ZIF-90, its presence actually promotes CO2 adsorption and CO2/N2 separation. As shown in , H2O increases the isosteric heat of CO2 adsorption in ZIF-90, indicating a cooperative adsorption effect between H2O and CO2 that enhances CO2 uptake. Since no such effect exists between H2O and N2, the presence of H2O improves the CO2/N2 selectivity.

Conclusion

This study employed GCMC simulations to investigate the influence of H2O on the CO2 adsorption and CO2/N2 separation performance of 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 negligible compared to CO2 uptake, and consequently, H2O has no effect on performance. In ZIF-90, however, H2O adsorption exceeds CO2 adsorption, and a cooperative adsorption mechanism between H2O and CO2 significantly enhances both CO2 uptake and CO2/N2 separation performance. These findings provide theoretical insights for designing ZIF materials suitable for practical flue gas conditions.

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