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Adsorptive Performance of CALF-20Metal–Organic Framework for CO_2 Capture from Flue Gas using Molecular Simulation

Mohammad Sadegh Khodadadi[1], Ahad Ghaemi*[2]

[1] PHD Resercher of Chemical Engineering, Iran University of Sceince and Technology

[2] Professor of Chemical Engineering, Iran University od Sceince and Technology

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1. ABSTRACT

Metal–organic frameworks have emerged as promising adsorbents for post-combustion carbon dioxide capture due to their high surface area, tunable pore structures, and superior adsorption performance. In this study, the adsorption behavior of CALF-20, a hydrophobic zinc-triazolate-oxalate MOF, was investigated for CO_2/N_2 separation using a combined experimental and computational approach. Grand Canonical Monte Carlo (GCMC) simulations were conducted using the RASPA package and validated against experimentally measured CO_2 adsorption data. A 3×3×3 supercell derived from the CCDC structure (No. 2084733) was employed. The Dreiding force field was used for the framework, while TraPPE parameters described the adsorbate molecules. Adsorption capacities of pure gases and binary mixtures were evaluated at 298.15 K and pressures up to 1.2 bar. The simulated CO_2 uptake reached 4.13 mmol g^{-1} at 1 bar, showing excellent agreement with the experimental value of 4.26 mmol g^{-1} with a deviation below 3%. For an 80:20 N_2/CO_2 mixture, CO_2 and N_2 adsorption capacities were 1.71 and 0.31 mmol g^{-1}, respectively. The CO_2/N_2 selectivity was calculated as 22.06 using Ideal Adsorbed Solution Theory (IAST) and 20.74 from direct mixture simulations. Four mixing rules including IAST, SIAST, EI, and SEI were evaluated. Results demonstrated that IAST-based approaches provided the most accurate predictions, while EI significantly underestimated CO_2 adsorption. The findings confirm the potential of CALF-20 as a stable and efficient adsorbent for post-combustion CO_2 capture.

Keywords: CALF-20, Metal-Organic Framework, CO_2 Capture, Mixing Rules, Molecular Simulation.

2. INTRODUCTION

The continuous increase in atmospheric carbon dioxide concentration resulting from intensive fossil-fuel consumption has intensified the need for efficient carbon capture technologies. Adsorption-based separation using porous solids has attracted considerable attention due to its lower energy demand compared with conventional absorption processes. Among advanced adsorbents, metal–organic frameworks (MOFs) have emerged as promising candidates because of their high porosity and tunable physicochemical properties.

CALF-20 is a zinc-based MOF that exhibits excellent hydrothermal stability and hydrophobicity, making it particularly suitable for flue gas treatment under humid conditions. Previous studies have mainly focused on pure-gas adsorption in CALF-20, while systematic evaluation of mixture adsorption prediction models remains limited. Reliable prediction of multicomponent adsorption from pure-component isotherms is essential for industrial process design.

* aghaemi@iust.ac.ir

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The objective of this work is to investigate the adsorption performance of CALF-20 for CO_2 capture from flue gas and to evaluate the predictive accuracy of different mixing rules, including Ideal Adsorbed Solution Theory (IAST)[1], Segregated IAST (SIAST), Explicit Isotherm (EI), and Segregated Explicit Isotherm (SEI), through comparison with direct GCMC mixture simulations using RASPA package [2] and experimental measurements.

3. MATERIALS AND METHODS

CALF-20 was synthesized using a solvothermal method from zinc oxalate dihydrate and 1,2,4-triazole precursors. Experimental CO_2 adsorption measurements were conducted in a batch adsorption system at 298.15 K and pressures ranging from 0.2 to 1.2 bar [3].

For molecular simulations, the crystal structure of CALF-20 was obtained from the Cambridge Crystallographic Data Centre (CCDC deposition number 2084733). A 3×3×3 supercell was generated and treated as a rigid framework. Grand Canonical Monte Carlo (GCMC) simulations were performed using the RASPA software package. Framework atoms were described using the Dreiding force field, while CO_2 and N_2 molecules were modeled using TraPPE parameters. Lennard–Jones and Coulombic interactions were considered, with Lorentz–Berthelot mixing rules applied for cross interactions. Long-range electrostatic interactions were calculated using the Ewald summation method.

Pure-gas adsorption isotherms were generated for CO_2 and N_2 at 298.15 K and pressures between 0.2 and 1.2 bar. Binary mixture simulations were performed for a representative flue gas composition containing 20% CO_2 and 80% N_2. Adsorption selectivity and predictive performance of different mixing rules were evaluated using Average Absolute Relative Deviation (AARD).

4. RESULTS AND DISCUSSION

The simulated pure CO_2 adsorption isotherm showed excellent agreement with experimental measurements. At 298.15 K and 1 bar, the simulated adsorption capacity was 4.13 mmol g^{-1}, compared with an experimental value of 4.26 mmol g^{-1}, corresponding to a deviation below 3%. This agreement confirms the reliability of the selected simulation methodology and force-field parameters.

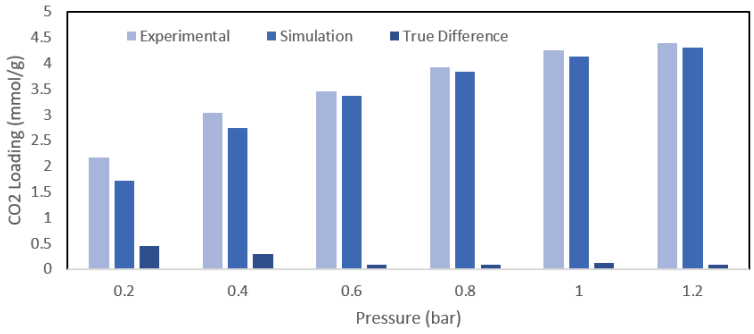

Figure 1. CO_2 Loading Experimental and Simulation Comparison

For the binary CO_2/N_2 mixture, CO_2 adsorption reached 1.71 mmol g^{-1}, whereas N_2 adsorption remained limited to 0.31 mmol g^{-1}. The resulting CO_2/N_2 selectivity was 22.06 according to IAST and 20.74 according to direct GCMC simulations, indicating strong preferential adsorption of CO_2 within the CALF-20 pores.

Comparison of mixing-rule predictions revealed that IAST and SIAST provided the highest predictive accuracy. The AARD values for CO_2 adsorption were approximately 2% and 3%, respectively, while corresponding errors for N_2 remained below 4%. SEI showed moderate accuracy with an AARD of approximately 9% for CO_2 adsorption. In contrast, EI significantly underestimated CO_2 uptake, yielding an AARD of approximately 56%.

Table 1. Average Absolute Relative Deviation (AARD) of different mixing rules relative to binary GCMC simulation results for CO_2/N_2 adsorption in CALF-20 at 298.15 K.

Mixing Rule	AARD for CO_2 (%)	AARD for N_2 (%)	Overall Performance
IAST	2	1	Excellent
SIAST	3	4	Excellent
SEI	9	1	Moderate
EI	56	3	Poor

As shown in Table 1, the IAST and SIAST models provide the most accurate predictions for both CO_2 and N_2 adsorption, with AARD values below 4%. In contrast, the EI model significantly underestimates CO_2 adsorption (AARD = 56%), indicating its limited applicability for highly selective adsorption systems such as CALF-20.

The superior performance of IAST-based methods can be attributed to their ability to account for competitive adsorption and non-ideal behavior within the adsorbed phase. These results demonstrate that CALF-20 combines favorable adsorption capacity, high selectivity, and excellent predictive consistency for flue-gas separation applications.

5. CONCLUSION

A combined experimental and molecular simulation study was conducted to evaluate CO_2 capture performance in CALF-20. The simulated adsorption behavior showed excellent agreement with experimental data, validating the adopted GCMC methodology. CALF-20 exhibited high CO_2 affinity and a CO_2/N_2 selectivity of approximately 22 under flue-gas conditions. Among the evaluated mixture prediction models, IAST and SIAST demonstrated the highest accuracy, whereas EI substantially underestimated CO_2 adsorption. The results confirm that CALF-20 is a promising and stable adsorbent for post-combustion CO_2 capture and that IAST-based models provide reliable tools for predicting multicomponent adsorption behavior in this system.

6. REFERENCES

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