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Experimental and numerical study of CO_2 adsorption on Ni/DOBDC metal-organic framework

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HIGHLIGHTS

- Amount and heat of CO_2 adsorption were experimentally and numerically studied.
- Formation of CO_2 adsorption was revealed at molecule level.
- Selectivity of CO_2/CH_4 was sensitive to the pressure and temperature.
- Electronic interactions played leading role in the selectivity.

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ABSTRACT

Metal-organic frameworks show promising applications for carbon capture and storage. In this research, CO_2 adsorption on a Ni/DOBDC metal-organic framework was experimentally studied at a pressure range of 0 kPa–100 kPa and a temperature range of 25 °C–115 °C. The adsorption of CO_2 and selectivity for CO_2/CH_4 were also numerically examined through the grand canonical Monte Carlo method. The adsorbed amount increased significantly at the initial stage and then rose in a steady manner with increased pressure. In contrast, the isosteric heat of adsorption gradually decreased. As the temperature increased, the adsorbed amount decreased linearly, but the isosteric heat of adsorption remained nearly unchanged. The sites and density profiles of the adsorbate provided insight into the formed $Ni^{2+}\cdots O{=}C{=}O$ at the molecular level. The selectivity for CO_2/CH_4 was sensitive to pressure and temperature. The electronic contribution could reach 62.0%–68.3% in the 0 kPa–100 kPa pressure range and 40.7%–68.3% in the 25 °C –115 °C temperature range.

1. Introduction

Carbon dioxide capture and storage (CCS) is a promising technique for solving the problem of global warming [1]. Adsorption by porous materials, such as zeolites [2], active carbons [3], and modified porous media [4], is an energetic and efficient approach among the proposed CCS schemes. A novel kind of nanoporous materials called metal-organic frameworks (MOFs) have drawn considerable interest because of their large specific surface area, high selectivity, and adjustable chemical functionality. A series of MOFs have been explored in CCS [5], and they were observed to exhibit higher adsorption capacity than traditional porous materials.

Ni/DOBDC was first synthesized as a typical MOF by Dietzel et al. [6]. It consists of a hexagonal packing of helical O_5Ni chains connected by 2, 5-dihydroxyterephthalte linkers. The dimension of the 1-D parallel hexagonal channels is approximately 1.1 nm. Ni/DOBDC has high stability, large CO_2 capacity, and long-term storage capability [7]. Liu et al. [8] demonstrated that Ni/DOBDC shows high CO_2 capacity at 10 kPa and 25 °C. Dietzel et al. [9] found that the high CO_2 adsorption capacity of Ni/DOBDC is due to the unsaturated metal centers. Kizzie et al. [10] observed that Ni/DOBDC retains approximately 60% of its initial capacity under dry condition after H_2O breakthrough. In addition to experimental studies, computer simulation is also employed to explore the microscopic adsorption mechanism on MOFs. Grand canonical Monte Carlo (GCMC) simulations are extensively used for this purpose. Ding et al. [11] used GCMC to show that Ni/DOBDC tolerates the effect of SO_2 very well at 25 °C and that SO_2 increases CO_2 uptake at low percentages of SO_2 (0%–4%) and decreases CO_2 uptake at high

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Nomenclature

EC (%)	electrostatic contribution
f	fugacity (kPa)
h	Planck' constant
k	Boltzmann constant (J K^{-1})
m	molecular mass (kg)
M_a	relative molecular mass of adsorbate
M_s	the relative molecular mass of single crystal cell
N_m, N_n	number of adsorbed molecules
N_a	the number of the structure cell
N_A	Avogadro's constant
N_{ex}	excess amount (mol kg^{-1})
N_{with}	amount of adsorption with electrostatic interactions switched on (mol kg^{-1})
$N_{without}$	amount of adsorption with electrostatic interactions switched off (mol kg^{-1})
P	pressure (kPa)
p^*	acceptance probability
q	charge of the interacting atoms (e)
Q_{st}	isosteric heat of adsorption (kJ mol^{-1})
r_{ij}	the distance between atoms i and j (Å)
R	gas constant (J mol^{-1} K^{-1})
S	selectivity
T	temperature (°C)
U_{ij},U_{ff},U_{fs}	interaction energy (kJ)
U_m, U_n	the energy of the configurations n and m (kJ)
V	the volume of simulation box(m^3)
V_{free}	free volume (m^3)
x	mole fraction in adsorbed phase
y	mole fraction in bulk phase
β	the factor
μ	chemical potential (kJ mol^{-1})
ε_{ij}	LJ depth (K)
ε_0	dielectric constant (F m^{-1})
σ_{ij}, $\sigma_{Dreiding}$	LJ diameter (Å)
<>	ensemble average
Λ	thermal de Broglie wavelength
ρ	bulk density (kg m^{-3})

Superscript

+, −	insertion and deletion

Subscript

m, n	configuration m, n
Dreiding	Dreiding force field
ex	excess
ff	adsorbate–adsorbate
fs	adsorbate–adsorbent
i, j	atom i, j

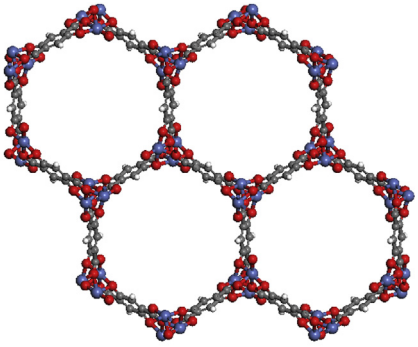
percentages. Peralta et al. [12] posited that xylene adsorption on Ni/DOBDC is enhanced by electrostatic effects; however, this is not mainly important because the geometry of the pore does not allow a close approach of the adsorbate molecules toward the metal node.

Adsorption separation is a physisorptive operation controlled by a thermodynamic equilibrium process, which is usually used to characterize the performance of a porous material. Yang et al. [13] found that geometry and pore size affect the separation characteristics of MOFs significantly. Taking MOF-5 and Cu–benzenetricarboxylate (Cu–BTC) as examples, the electrostatic interactions can enhance the separation efficiency of gas mixtures (CO_2/CH_4). Liu et al. [14] demonstrated that the electrostatic interactions can enhance the separation of CO_2/CH_4 by ZIFs at a pressure range of 0 MPa–3.0 MPa, and ZIF-69 is more beneficial in separating CO_2 from a gas mixture compared with ZIF-68 because of the presence of chlorine atoms in the former.

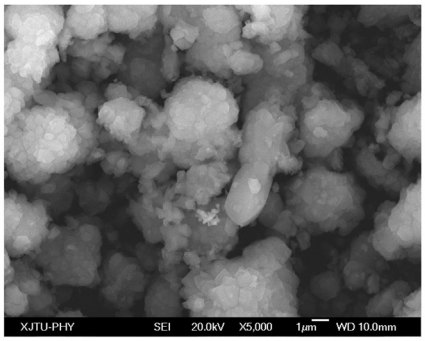
The aforementioned experimental studies mainly considered the effect of pressure at fixed-point temperature on the amount of adsorption and hardly considered the isosteric heat of adsorption and varied temperature from experiment and simulation. Thus, in the present study, the amount of adsorbed CO_2 and the corresponding isosteric heat of adsorption on Ni/DODBC were investigated by experiment and GCMC simulation by correction parameters at different pressures and temperatures. The position and density of the adsorbate were also studied to understand the process of adsorption. The effect of the electrostatic interactions on the selectivity of CO_2/CH_4 was also considered.

2. Experimental study

Ni/DOBDC was synthesized according to a procedure reported by Liu et al. [7]. The structure and as-synthesized sample are shown in Fig. 1. Fig. 2 shows a schematic diagram of the test apparatus consisting of four parts, namely, adsorption, calorimetric, gas supply, and data acquisition systems. PCTProE&E combined with Calvet calorimeter (PCT and C80, French) constituted the adsorption and calorimetric systems. The amount and heat of adsorption were synchronously determined by the PCTProE&E-Calvet calorimeter system. Based on the static volumetric measurement, the pressure, temperature, and volume measurements were recorded to



(a) Structure of Ni/DODBC. Ni atoms: blue sphere; O atoms: red sphere; C atoms: gray sphere; H atoms: white sphere



(b) SEM of Ni/DOBDC

Fig. 1. Structure and SEM of Ni/DOBDC.