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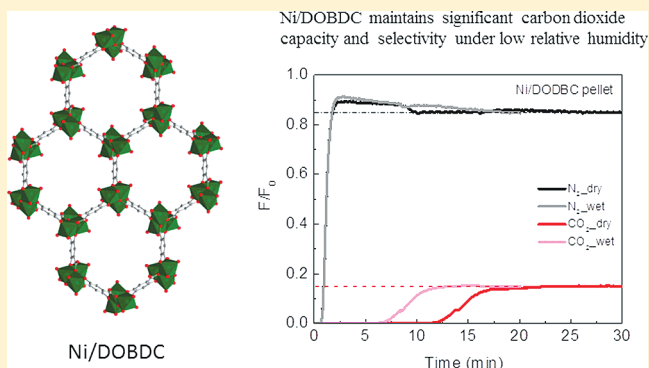
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Selective CO₂ Capture from Flue Gas Using Metal–Organic Frameworks—A Fixed Bed Study

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S Supporting Information

ABSTRACT: It is important to capture carbon dioxide from flue gas, which is considered one of to be the main cause of global warming. CO₂/N₂ separation by novel adsorbents is a promising method for reducing CO₂ emission. Meanwhile, water effects on CO₂ adsorption and CO₂/N₂ selectivity is critical to enable utilization of the adsorbents in practical applications. In this paper, Ni/DOBDC (Ni-MOF-74 or CPO-27-Ni) was synthesized through a solvothermal reaction, and the pellet sample was used in a fixed-bed CO₂/N₂ breakthrough study with and without H₂O. The Ni/DOBDC pellet has a high CO₂ capacity of 3.74 mol/kg at 0.15 bar and a high CO₂/N₂ selectivity of 38, which is much higher than those of reported metal–organic frameworks and zeolites under dry conditions. Trace amounts of water can affect CO₂ adsorption capacity as well as CO₂/N₂ selectivity for the Ni/DOBDC. However, Ni/DOBDC can retain a significant CO₂ capacity of 2.2 mol/kg and a CO₂/N₂ selectivity of 22 at 0.15 bar CO₂ with 3% RH water. These results indicate a promising future for use of the Ni/DOBDC in capturing CO₂ from flue gas.



1. INTRODUCTION

Physisorption is an economical and promising method by which to separate CO₂ from flue gases. Many adsorbents have been developed and studied for CO₂ capture, such as activated carbon, zeolites, and modified porous silica.^{1–3} The common shortcomings for these traditional adsorbents are either low CO₂ capacities or difficult regeneration processes.

Metal–organic frameworks (MOFs) or porous coordination polymers have recently been considered as novel adsorbents because of their high surface areas, large pore volumes, and easily tunable compositions. MOFs are constructed by coordinate bonds between multidentate ligands and metal atoms or small metal-containing clusters (referred to as secondary building units). A typical MOF, IRMOF-1, also known as MOF-5, is constructed with zinc atoms as metal centers and terephthalic acid molecules as ligands. The central cavity formed via the assembly of metal centers and ligands is much larger compared to other traditional adsorbents and is essential for gas storage. Tremendous choices of metal centers and organic linkers make it possible to synthesize MOFs with desired pore structures and properties for specific gas adsorption applications.^{4–6}

Many MOFs have higher saturated CO₂ capacities compared to those of the conventional adsorbents.^{7–10} However, because the CO₂ partial pressures in flue gases are usually around 0.15 bar, it is of greater importance to understand CO₂ adsorption in MOF materials in the low-pressure region than at high pressures. In addition, the major component of flue gas is the

remained N₂ after combustion. It is important to study the selectivity between CO₂ and N₂ adsorption in MOFs as well. Moreover, the existence of water in flue gas cannot be neglected because even trace amounts of water influence gas adsorption in adsorbents such as some zeolites and MOFs.^{11,12}

Some research has been conducted on selective CO₂ adsorption over N₂ using MOFs. Li et al.¹³ synthesized a robust zeolitic MOF material that selectively adsorbs CO₂ over N₂. The selective adsorption may be due to the small channels in the zeolitic MOF, which distinguish the two gases with kinetic diameters. Liu and Smit¹⁴ studied the separation performance of CO₂ over N₂ in seven MOFs using grand canonical Monte Carlo (GCMC) simulations. They found that pore size also plays an important role in the selective adsorption of CO₂ over N₂. Other researchers reported CO₂/N₂ selectivities for some MOFs, such as CuBTC,¹⁵ ZIF-68,¹⁶ and soc-MOF,¹⁷ through molecular simulations. The CO₂/N₂ selectivities of these MOFs vary between 13 and an astonishing 420, according to the simulation results. Wu et al.¹⁸ constructed a conceptual MOF by replacing all of the hydrogen atoms with O–Li groups in the aromatic rings of IRMOF-1 and found that the new Li-IRMOF-1 has a CO₂/N₂ selectivity of 395 (CO₂:N₂ = 15.6:84.4), which is 2 orders of magnitude larger than that of the original IRMOF-1 through a computational study. The high

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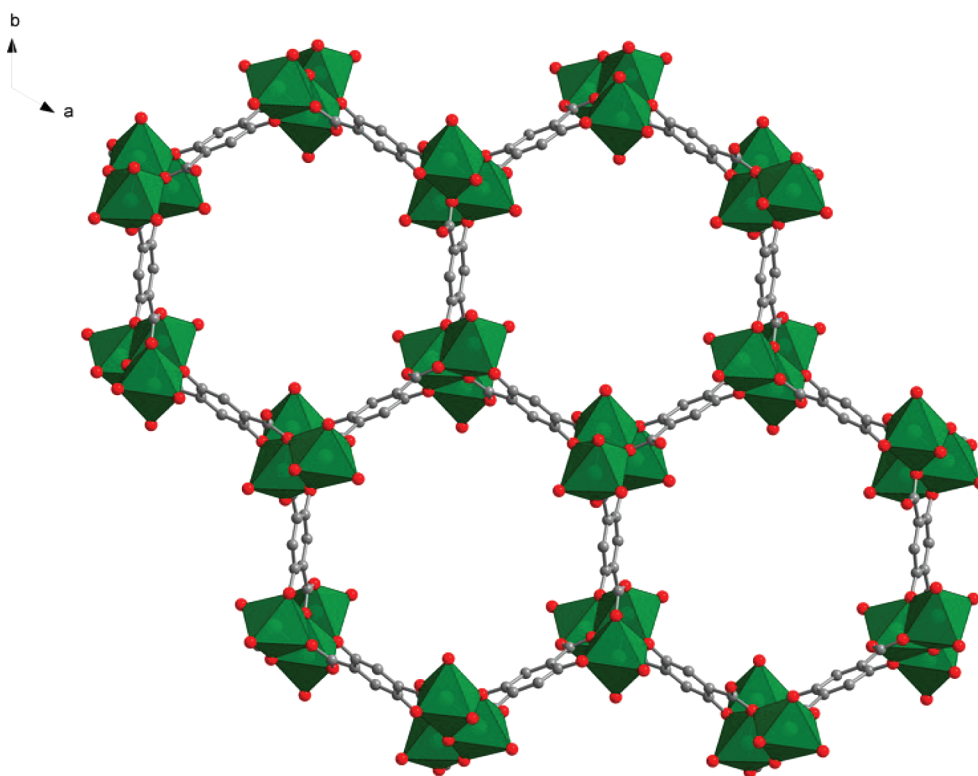


Figure 1. Ni/DOBDC crystal structure after removing solvent molecules. Ni atoms: green polyhedra; O atoms: red spheres; C atoms: gray spheres.

selectivity is due to the stronger electrostatic interactions between the framework atoms and the gas molecules induced by the introduction of lithium. However, neither the synthesis of Li-IRMOF-1 nor the high CO_2/N_2 selectivity has been verified by experiment so far. Bae et al.¹⁹ reported a way to enhance the CO_2/N_2 selectivity of a Zn-based MOF by cavity modification using a pyridine derivative. Their results showed that the modified MOF has a theoretical CO_2/N_2 selectivity of 28 at 1 bar with a mixture composed of equal mole of CO_2 and N_2 . However, the modified MOF has a much lower CO_2 capacity, which is less than 0.02 mol/kg at 0.15 bar, compared to the original MOF. Recently, Dickey et al.²⁰ reported that it is reasonable to use single-component isotherms plus the ideal adsorbed solution theory (IAST) to predict CO_2/N_2 mixtures adsorption results because the predicted results agreed well with those obtained from GCMC simulations. This study provides an alternative way to preliminarily screen MOFs for CO_2/N_2 separation based only on single-component isotherms. Nonetheless, it is necessary and critical to use experiments to study the real CO_2/N_2 mixture separation using a column breakthrough method for industrial applications.

Although simulation research has shown that it is possible to construct new MOFs or modify existing MOFs to achieve very high CO_2/N_2 selectivity, the reported experimental studies showed much lower CO_2/N_2 selectivities for many MOFs. Bastin et al.²¹ synthesized a microporous MOF-508b and obtained a CO_2/N_2 selectivity of 4 for a 50:50 mixture of CO_2 and N_2 at a total pressure of 1 bar through a fixed-bed study. Basu et al.²² mixed several MOFs, including CuBTC, ZIF-8, and MIL-53, into a polymer film and achieved a CO_2/N_2 selectivity of about 25 for a 10:90 mixture of CO_2 and N_2 . MOFs with higher CO_2 capacities and selectivities are needed to separate CO_2 from N_2 , especially in the presence of water.

The DOBDC series of MOFs has one-dimensional pores with a uniform pore size of 11 Å after the solvent molecules are removed, as shown in Figure 1. In addition, some DOBDC MOFs have unsaturated metal centers in their structures, which can enhance gas adsorption, especially under low-pressure conditions.⁵ Liu et al.¹¹ found that Ni/DOBDC has a higher CO_2 capacity at 0.1 bar than benchmark zeolites, and water does not affect CO_2 adsorption in the Ni/DOBDC as much as in NaX and 5A zeolites. In addition, Ni/DOBDC has a reasonable hydrothermal stability.¹¹ Kizzie et al.²² studied CO_2/N_2 breakthrough phenomena for the DOBDC series of MOFs. They measured saturated capacities of CO_2 for the hydrated DOBDC series of MOFs after regeneration, observing significant decreases in capacities for the Mg/DOBDC and Zn/DOBDC but much less significant decreases for the Ni/DOBDC and Co/DOBDC compared to the original samples. However, their study did not investigate the CO_2/N_2 selectivity and factors such as coexisting water that can affect the selectivity.

On the basis of previous studies, the Ni/DOBDC could not adsorb significant CO_2 when a large amount of water is preadsorbed; further, the Ni/DOBDC may lose its high CO_2 capacity after full saturation by water and repeated regeneration processes.^{11,23,24} A guard bed loaded with desiccants must be installed before the main bed loaded with the Ni/DOBDC in order to remove most of the water in flue gas and to take advantage of the high CO_2 capacity of the Ni/DOBDC at low CO_2 partial pressure and with trace amounts of water.¹¹ Therefore, it is necessary to study CO_2 adsorption in Ni/DOBDC with N_2 and minimal moisture, which may represent a practical situation for CO_2 capture from flue gas in the future.

In this work, we report on our study of CO_2/N_2 selective adsorption in the Ni/DOBDC using a fixed-bed breakthrough method. The CO_2 capacities obtained from breakthrough

experiments are compared with that obtained through a static volumetric method. The effects of trace amounts of water on CO₂ adsorption capacity and CO₂/N₂ selectivity for the Ni/DOBDC are investigated, and the ability of the Ni/DOBDC to maintain its CO₂ capacity after multiple water exposures and heat regeneration processes is also discussed. Our results can provide important and practical information for using the Ni/DOBDC as a novel adsorbent with which to separate CO₂ from flue gas.

2. EXPERIMENTAL SECTION

2.1. Material Preparation and Characterization. The Ni/DOBDC sample was synthesized following a reported solvothermal reaction procedure.²⁵ A solution of 2,5-dihydroxyterephthalic acid (1.486 g, 7.5 mmol) in THF (25 mL) and a solution of nickel(II) acetate tetrahydrate (3.733 g, 15 mmol) in water (25 mL) were combined in a Teflon-lined insert of 100 mL volume. The insert was put into an autoclave, sealed, and reacted for 3 days at 110 °C in a preheated furnace. Filtration yielded 3.107 g of a yellowish fine crystalline product that was washed three times with water (50–100 mL) and dried in air at 85 °C under vacuum.

To minimize pressure drop and prevent potential contamination to the pipelines, pellet samples were used for the breakthrough experiments. The Ni/DOBDC pellets were formed through two steps. First, a powder sample was pressed into a disk under 12 MPa for 5 min. Then, the disk was carefully broken and the fragments were sieved for 20–30 mesh (600–850 μm) pellets. The two-step procedure was repeated to make more pellets when necessary. A picture of the Ni/DOBDC pellets is shown in the Supporting Information (Figure S1).

Powder X-ray diffraction (XRD) analysis was performed on a Bruker X-ray diffractometer (D8 FOCUS, Bruker AXS Inc., Madison, WI) with a diffracted beam monochromator, and a copper target X-ray tube set to 40 kV and 150 mA. N₂ adsorption experiments at −196 °C were performed using an automatic gas sorption analyzer (Quantachrome Autosorb IQ, Quantachrome Instruments, Boynton Beach, FL). Static pure CO₂ isotherms at 25 °C were measured on a VTI HPVA-100 gas adsorption analyzer (Micromeritics, Norcross, GA). Unless otherwise specified, samples were regenerated at 250 °C under vacuum or with a He purge for 15 h before any gas adsorption.

2.2. Breakthrough Apparatus and Procedures. An intelligent gravimetric analyzer (IGA) supplied by Hiden Analytical Ltd., Warrington, U.K., was used to perform the CO₂/N₂ mixture breakthrough measurement. The IGA system has a dynamic sorption analyzer (ARBC) that can handle breakthrough adsorption experiment for multiple components.²⁶

Pellet samples with sizes from 600 to 850 μm were packed as a fixed adsorption bed for breakthrough experiments. The bed aspect ratio is about 3.12. The properties of the Ni/DOBDC pellets are listed in Table 1. The ARBC system used to measure CO₂/N₂ breakthrough curves is shown as Figure 2. Gases are introduced through the bottom inlet of the adsorption bed, and MOF pellets are held between two layers of quartz wool and two sample holders. Frit gaskets are installed at both the top and bottom of the ARBC to prevent any potential powder contamination to the main gas pipeline. The pressure drop caused by the frit gaskets is negligible.

The samples were regenerated in situ at 250 or 25 °C under He purging for 2–15 h. Before regeneration, the gas lines were

Table 1. Properties of the Ni/DOBDC Pellet

property	value
pressed pressure	12 MPa
size	600–850 μm
pellet density	0.78 g/cm ³
packing density	0.40 g/cm ³
BET surface area	1147 m ² /g
original weight	1.51 g
activated weight	1.01 g

purged with a gas mixture having the same composition and total flow rate as those in the next run. Dead volume and delay in the mass spectrometer signal were considered and deducted from measured breakthrough capacities. Activated sample weight was determined immediately after the sample was unloaded, and the ideal gas law was used to calculate the mole of gas adsorbed by MOF samples.

In a typical CO₂/N₂ breakthrough experiment, a gas mixture with a total flow rate of 35 sccm (15% CO₂ and 85% N₂) and total pressure of 1 bar flows through the adsorption bed. He with the same flow rate is used to purge the adsorption bed before and after the breakthrough experiment. In the study of water effect on CO₂/N₂ adsorption, a small amount of water vapor was premixed with N₂ and CO₂. The water concentration was determined to be about 3% RH using a mass spectrometer (see Supporting Information, Figure S2).

3. RESULTS AND DISCUSSION

3.1. Physical Properties. The Ni/DOBDC sample was characterized with XRD, and the patterns are shown in Figure 3. The Ni/DOBDC shows good crystallinity, and our results matched with those XRD patterns of the Ni/DOBDC reported in the literature.^{25,27} An N₂ isotherm at −196 °C for the Ni/DOBDC sample was obtained; the result is shown in Figure 4. It is clear that the desorption points fall directly upon the adsorption points and there is no hysteresis, which means that N₂ adsorption in Ni/DOBDC is a reversible process and the synthesized Ni/DOBDC is a microporous material. The BET surface area of the Ni/DOBDC was calculated to be 1147 m²/g using a multipoint BET model. This result is consistent with those reported in the literature.^{25,27}

3.2. Recoverable CO₂ Adsorption. A CO₂ isotherm at 25 °C obtained for the Ni/DOBDC using a static volumetric system is shown in Figure 5. The static CO₂ isotherm was used as a reference for the dynamic breakthrough measurement.

The pure CO₂ breakthrough curves for the Ni/DOBDC at 25 °C are shown in Figure 6. The Ni/DOBDC was initially activated at 250 °C for 15 h before it was subjected to the first CO₂ breakthrough measurement. After the breakthrough curve was integrated and the effect of the dead volume and mass spectrometer signal delay was deducted, the CO₂ capacity of the Ni/DOBDC was determined to be 5.37 mol/kg at 1 bar using the dynamic method. This value is close to the static CO₂ capacity of the Ni/DOBDC, which is about 5.61 mol/kg at 1 bar.

In addition to N₂ adsorption, CO₂ adsorption in the Ni/DOBDC also is reversible. Moreover, it is possible to recover most of its CO₂ capacity just by purging with He at room temperature. As shown in Figure 6, a second pure CO₂ breakthrough curve was obtained after the adsorption bed had been purged with He for 2 h. It appears that we recovered a CO₂ capacity of 5.06 mol/kg, which is more than 94% of the

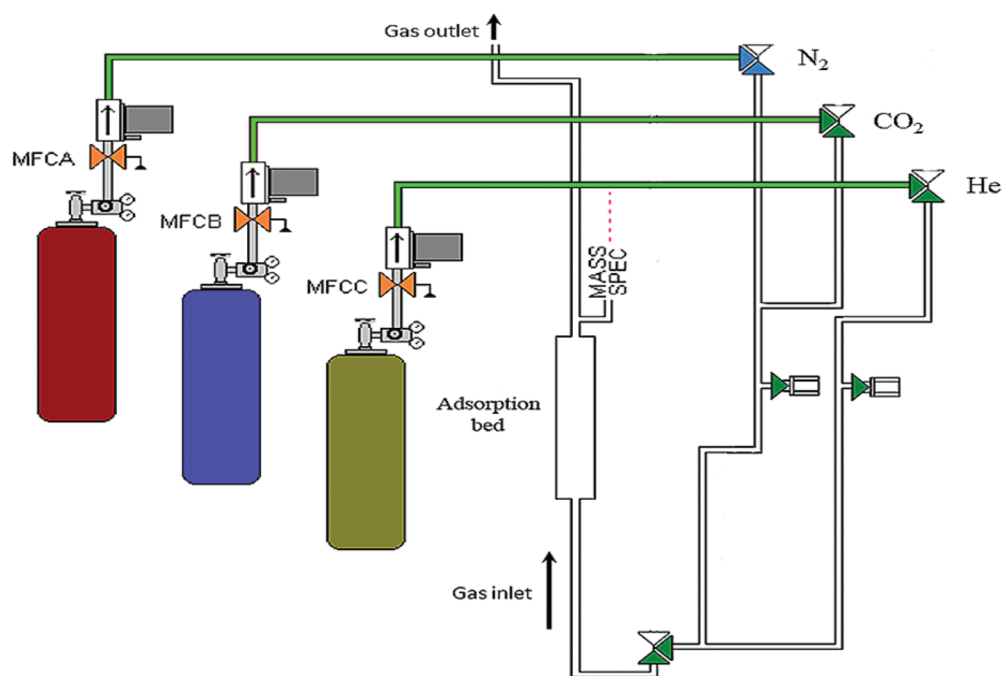


Figure 2. Apparatus for the CO_2/N_2 and $\text{CO}_2/\text{N}_2/\text{H}_2\text{O}$ mixture breakthrough experiments.

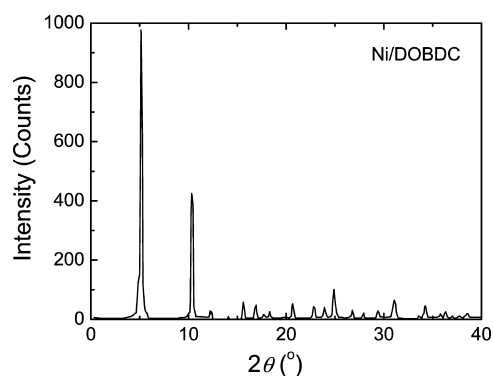


Figure 3. Powder XRD pattern for the Ni/DOBDC sample.

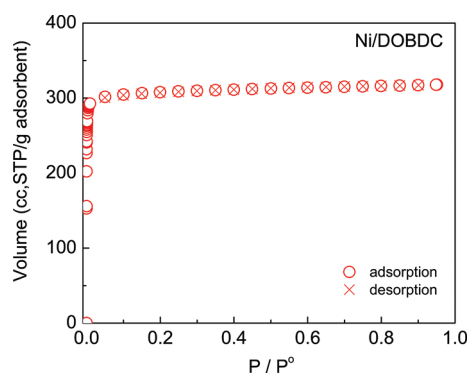


Figure 4. N_2 isotherm at $-196\text{ }^\circ\text{C}$ for the Ni/DOBDC.

original CO_2 capacity of the Ni/DOBDC, by just He purge without heating. This indicates that Ni/DOBDC is suitable for CO_2 separation in a pressure swing adsorption (PSA) application in which heat regeneration is rarely used. In addition, the 6% residual CO_2 remained in the Ni/DOBDC can be fully removed by heating at $250\text{ }^\circ\text{C}$ with He purge.

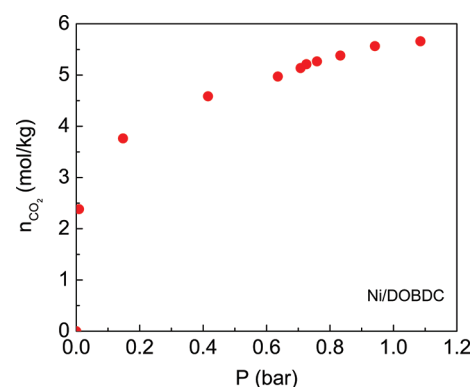


Figure 5. CO_2 isotherm at $25\text{ }^\circ\text{C}$ for the Ni/DOBDC using a static volumetric method.

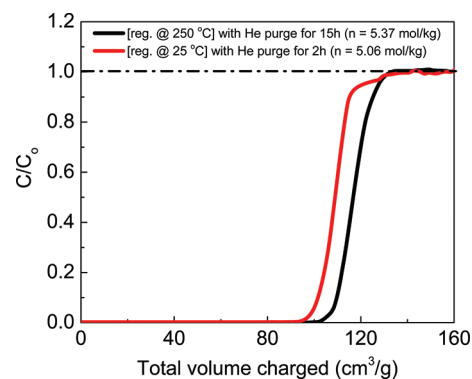


Figure 6. Pure CO_2 breakthrough curves at $25\text{ }^\circ\text{C}$ for the Ni/DOBDC regenerated at different conditions. The CO_2 flow rate is 35 sccm in both cases, and the charged volumes have been calibrated to the standard condition. "reg. @ $250\text{ }^\circ\text{C}$ " means the sample was regenerated at $250\text{ }^\circ\text{C}$.

3.3. CO₂/N₂ Breakthrough. N₂ is the major component of flue gas from power plants. Therefore, it is of great importance to study CO₂/N₂ selectivity for CO₂ capture from flue gas. The dry CO₂/N₂ breakthrough curves for the Ni/DOBDC are shown in Figure 7. The CO₂/N₂ gas mixture started flowing

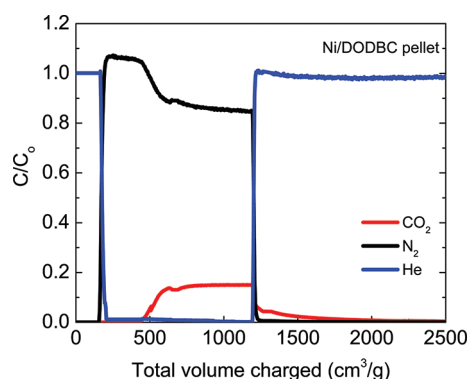


Figure 7. CO₂/N₂ (15:85) breakthrough curves at 25 °C for the Ni/DOBDC under the dry condition. The He flow rate is 35 sccm, and the flow rate of CO₂ and N₂ together is also 35 sccm. The charged volumes have been calibrated to the standard condition.

through the adsorption bed immediately after the He purge. The N₂ signal was observed almost instantly after the time delay of the mass spectrometer signal was deducted, which indicates that the Ni/DOBDC has a low N₂ capacity. In contrast, the Ni/DOBDC shows a significant CO₂ capacity even at 0.15 bar, which is as expected.^{11,23,25,27} Obviously, the Ni/DOBDC selectively adsorbs CO₂ over N₂, which can be verified by the roll-up in the N₂ breakthrough curve. Besides a partial effect from the change of volumetric flow rate, roll-up is due to the displacement of N₂ by CO₂, which has a higher affinity to the Ni/DOBDC, causing the effluent N₂ concentration to surpass its concentration in the feed. After the Ni/DOBDC is saturated with CO₂, the N₂ effluent composition decreases and matches the feed composition.²³ In addition, CO₂ can be desorbed thoroughly from the Ni/DOBDC by He purge after the breakthrough which indicates a promising potential for using it in a PSA application.

On the basis of the mass balance, the gas adsorption capacities can be determined as follows:²⁸

$$q = \frac{C_0 V t_s}{22.4W} \quad (1)$$

$$t_s = \int_0^t \left(1 - \frac{F}{F_0} \right) dt \quad (2)$$

where t_s is the stoichiometric time (min), C_0 is the feed gas concentration, F_0 and F are the inlet and outlet gas molar flow rates, respectively. q is the equilibrium adsorption capacity of gas (mmol/g), t is the adsorption time (min) which is from time zero to time when equilibrium is reached, V is the volumetric feed flow rate (cm³/min) at standard temperature and pressure (1 atm and 0 °C), and W is the weight of the activated adsorbent (g).

The CO₂ capacity for the Ni/DOBDC at 25 °C and 0.15 bar was determined to be 3.74 mol/kg using the breakthrough method. This value is more than 96% of the CO₂ capacity of the Ni/DOBDC obtained using a static method at the same partial pressure (3.86 mol/kg), as shown in Figure 5. This

result shows a good agreement between our static and dynamic measurements for CO₂ adsorption in the Ni/DOBDC. The N₂ capacity for the Ni/DOBDC at 25 °C and 0.85 bar can be determined to be 0.57 mol/kg in a similar way.

The selectivity for gas A relative to gas B is defined by the following:

$$S_{AB} = \frac{x_A/y_A}{x_B/y_B} \quad (3)$$

where x_A and x_B are the mole fractions of gases A and B in the adsorbed phase and y_A and y_B are the mole fractions of gases A and B in the bulk phase, respectively.^{28,29} On the basis of this definition, the CO₂/N₂ (15:85) selectivity for the Ni/DOBDC at 25 °C was calculated to be about 38, which is much higher than those experimental results reported in the literature for some MOFs^{21,22} and other adsorbents such as 13X zeolite³⁰ and silicalite under the same condition.³¹ The high CO₂/N₂ selectivity may be due to the unsaturated metal centers in the Ni/DOBDC strongly interacting with CO₂ molecules,^{27,32} which have larger quadrupole moments than N₂ molecules. Recently, Nakagawa et al.³³ reported a MOF CID-3 that has a CO₂ selectivity of 39, based on their breakthrough experiments using a mixture of CO₂/O₂/N₂ (1:21:78). However, the CO₂ concentration in our study is 15 times higher, so it is expected that our Ni/DOBDC should have a CO₂ selectivity much higher than 39 if the CO₂ concentration in our study also decreases to 1%. In addition, the CO₂ capacity of the CID-3 in the Nakagawa et al. study is only 3.5 mol/kg at 46 bar and 25 °C, which is insufficient for CO₂ capture from flue gas.

3.4. Water Effects on CO₂ Adsorption. As known from previous research, water can affect CO₂ adsorption in the Ni/DOBDC although not as much as in zeolites.¹¹ To evaluate the potential of using the Ni/DOBDC in practical applications of CO₂ capture from flue gas, a trace amount of water was introduced into the CO₂/N₂ mixture to simulate a scenario in which a guard bed loaded with desiccants is installed in line before the main bed loaded with the Ni/DOBDC to remove the majority of water in the flue gas. The effects of trace amounts of water on dynamic CO₂ adsorption and the CO₂/N₂ selectivity were investigated.

The CO₂/N₂ breakthrough curves for the Ni/DOBDC with a trace amount of water are shown in Figure 8. The water signal is very small due to its low concentration. Although the CO₂

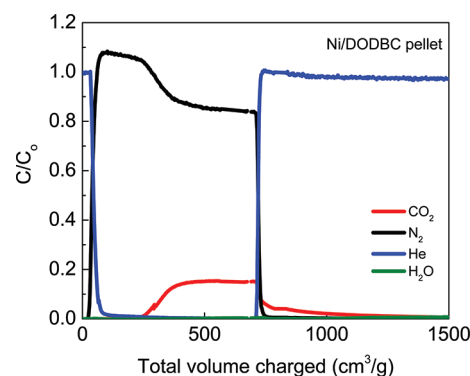


Figure 8. CO₂/N₂ (15:85) breakthrough curves at 25 °C for the Ni/DOBDC under the wet condition. The He flow rate is 35 sccm, and the flow rate of CO₂ and N₂ together is also 35 sccm. The charged volumes have been calibrated to the standard condition.

and N_2 breakthrough curves appear similar to those in the dry CO_2/N_2 breakthrough experiment, the CO_2 capacity of the Ni/DOBDC decreased significantly from 3.74 to 2.69 mol/kg even with a trace amount of water. This is because the Ni/DOBDC is very hydrophilic and can adsorb a large amount of water even at low RH, which can reduce CO_2 adsorption. This decreasing trend in CO_2 capacity is consistent with our previous work, in which water effects on static CO_2 adsorption in the Ni/DOBDC were studied.¹¹

To study the effects of a trace amount of water on CO_2/N_2 adsorption, the CO_2/N_2 breakthrough curves under dry and wet conditions were summarized in Figure 9 for comparison.

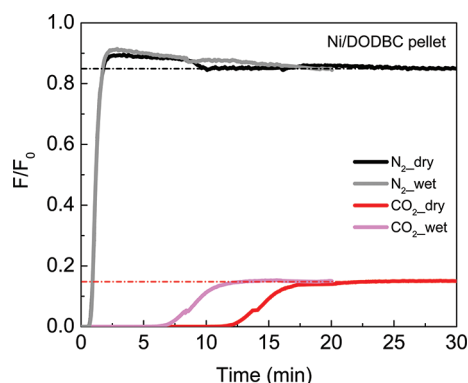


Figure 9. CO_2/N_2 (15:85) breakthrough curves at 25 °C comparison for the Ni/DOBDC under dry and wet conditions. The total molar flow rate F_0 is 1.58 mmol/min.

Although the N_2 breakthrough curves for both dry and wet conditions remained similar, CO_2 breakthrough curves changed substantially. It is obvious that the influence of water presence, reduced CO_2 adsorption from a CO_2/N_2 mixture and the CO_2 capacity of the Ni/DOBDC decreased from 3.74 to 2.69 mol/kg with 3% RH water vapor, as mentioned before. The N_2 capacity of the Ni/DOBDC under the wet condition was determined to be 0.56 mol/kg, following similar procedures reported in the literature,^{23,34} which is almost the same as the N_2 capacity of the Ni/DOBDC obtained under the dry condition. The reason could be that water molecules take up those strong adsorption sites in the Ni/DOBDC that are specific adsorption sites for CO_2 molecules. In contrast, water adsorption did not affect N_2 adsorption because N_2 is adsorbed in a less specific way in the Ni/DOBDC compared to the CO_2 adsorption. Thus, the trace amount of water affected adsorption of CO_2 but not of N_2 in the Ni/DOBDC.

Because the CO_2 capacity of the Ni/DOBDC decreased while the N_2 capacity did not, the CO_2/N_2 (15:85) selectivity decreased from 38 to 27 with 3% RH water in the CO_2/N_2 mixture. However, a CO_2/N_2 selectivity of 27 is still among the top experimental records in the literature, even without water present. This result shows that Ni/DOBDC can maintain a high CO_2/N_2 selectivity with a trace amount of water and is suitable for potential application in CO_2 capture from flue gas.

As mentioned before, heat regeneration is rarely used in a PSA application, so we took a further step to study the CO_2 adsorption from a mixture with N_2 and a trace amount of water without heat regeneration. The Ni/DOBDC sample was purged with only He between a series of three $CO_2/N_2/H_2O$ breakthrough measurements. CO_2 breakthrough curves for the Ni/DOBDC without heat regeneration are shown in Figure 10,

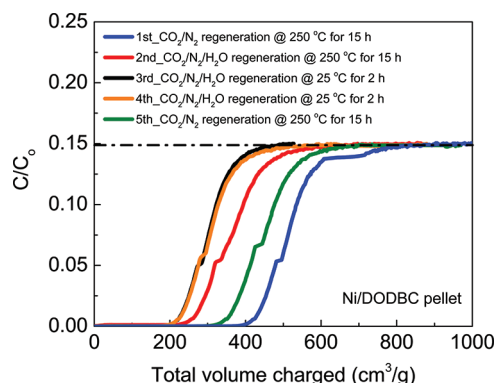


Figure 10. Comparison of 15% CO_2 breakthrough curves at 25 °C for the Ni/DOBDC. The flow rates of CO_2 and N_2 together are 35 sccm. The charged volumes have been calibrated to the standard condition.

which also includes other results for comparison. The CO_2 capacities for the Ni/DOBDC under different conditions are summarized in Table 2. The CO_2 capacity of the Ni/DOBDC

Table 2. CO_2 Capacities at 0.15 bar and 25 °C for the Ni/DOBDC Pellet under Different Conditions^a

condition	CO_2 capacity
static, regeneration at 250 °C 15 h, CO_2	3.86 mol/kg
dynamic, first_ regeneration at 250 °C 15 h, CO_2/N_2	3.74 mol/kg
dynamic, second_ regeneration at 250 °C 2 h, $CO_2/N_2/H_2O$	2.69 mol/kg
dynamic, third_ regeneration at 25 °C 2 h, $CO_2/N_2/H_2O$	2.21 mol/kg
dynamic, fourth_ regeneration at 25 °C 2 h, $CO_2/N_2/H_2O$	2.23 mol/kg
dynamic, fifth_ regeneration at 250 °C 15 h, CO_2/N_2	3.34 mol/kg

^aStatic indicates that the result was obtained using a static volumetric method; dynamic indicates that the results were obtained through a dynamic breakthrough method. The sequence of the breakthrough experiments is identified.

decreased from 2.69 to 2.21 mol/kg for the second $CO_2/N_2/H_2O$ breakthrough measurement without heat regeneration. However, the CO_2 capacity of the Ni/DOBDC did not decrease further with an additional cycle, and it remained at 2.23 mol/kg for the third $CO_2/N_2/H_2O$ breakthrough measurement. It is possible that the adsorption of H_2O was still ongoing during the first $CO_2/N_2/H_2O$ breakthrough measurement but reach equilibrium after the second and third measurements. In addition, it appears that the adsorbed water cannot be removed with only a He purge, so the CO_2 capacities did not change for the second and the third measurements. The CO_2/N_2 (15:85) selectivity decreased from 27 to 22 after H_2O adsorption reached equilibrium for the second run. Dry CO_2/N_2 breakthrough curves were measured again after the series of three $CO_2/N_2/H_2O$ breakthrough measurements. The Ni/DOBDC was fully regenerated at 250 °C for 15 h before the repeated CO_2/N_2 breakthrough experiment. The CO_2 capacity of the Ni/DOBDC recovered from 2.23 to 3.34 mol/kg. However, this result is still 11% less than the CO_2 capacity obtained for the first CO_2/N_2 breakthrough measurement. Thus, water adsorption and regeneration processes appear to have caused a permanent drop in the CO_2 capacity for the Ni/DOBDC. The drop is more significant when the water concentration is higher, as reported in the literature.²³ In addition, the CO_2/N_2 selectivity for the Ni/DOBDC decreased from 38 to 33 after it was permanently affected by the water adsorption and heat regeneration processes. However, the Ni/

DOBDC is still a promising MOF material for CO₂ capture from flue gas because it can retain high CO₂ capacity and CO₂/N₂ selectivity with a trace amount of water using only heatless regenerations.

4. CONCLUSIONS

The Ni/DOBDC MOF was synthesized through a solvothermal reaction and the pellet sample was studied for selective CO₂ adsorption in a fixed bed using a breakthrough method. Under ambient condition, the Ni/DOBDC pellet had a high CO₂ capacity of 3.74 mol/kg, which was obtained for a dry CO₂/N₂ (15:85) mixture. CO₂ adsorption in the Ni/DOBDC was found to be reversible; more than 94% of the CO₂ capacity can be recovered by just He purge regeneration at room temperature. We found that Ni/DOBDC selectively adsorbs CO₂ over N₂ as expected; it has a CO₂/N₂ selectivity of 38, which is much higher than those of some other MOFs and benchmark zeolites under dry conditions. A trace amount of water can affect CO₂ adsorption capacity as well as CO₂/N₂ selectivity in the Ni/DOBDC. The CO₂ capacity of the Ni/DOBDC cannot be fully recovered after water adsorption, even with heating. However, Ni/DOBDC can retain a CO₂ capacity of 2.2 mol/kg and a CO₂/N₂ selectivity of 22 at 0.15 bar CO₂ with 3% RH water. The impressive CO₂ adsorption performance under the wet condition, together with a reasonable stability, indicates a promising future for using the Ni/DOBDC in CO₂ capture from flue gas.

■ ASSOCIATED CONTENT

Supporting Information

Picture of the fresh Ni/DOBDC pellet (Figure S1), water concentration in the CO₂/N₂/H₂O breakthrough experiment (Figure S2), and CO₂ full breakthrough curves under dry and wet conditions in the form of molar flow rate versus time (Figure S3). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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