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ARTICLE TYPE

Targeted Capture and Pressure/Temperature-Responsive Separation in Flexible Metal-Organic Frameworks

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5 Based on an in-house-constructed separation apparatus, controlled and targeted CO₂ and CH₄ capture, respectively, from binary mixtures (CO₂/CH₄ or CH₄/N₂) has been realized on two flexible MOFs, [Cu(dhbc)₂(4,4'-bipy)] and [Cu(4,4'-bipy)₂(BF₄)₂], in the form of packed bed of particles. These gas mixtures were effectively separated on the flexible MOFs by using a unique two-stage separation technique. Molecular dynamic simulations have been performed to assess the atomistic interactions of
10 small molecules in flexible MOFs that directly influence the dynamic gas separation. Furthermore, structural stability and the effect of H₂O in these gas separations have been investigated, and the results suggest that the flexible MOFs show significantly improved gas separation performances.

Introduction

Gas capture and separation of mixtures are important for many
15 energy and environmental applications, such as CO₂ capture and CO₂/CH₄ or CH₄/N₂ purification.¹ CH₄, with the highest heat of combustion per mass unit (55.7 kJ/g), is poised to be one of the most important energy source candidates in the future.² However, significant quantities of natural gas and biogas cannot be used
20 efficiently because the presence of CO₂ and N₂ in these gas mixtures lowers their energy content. Thus, a prerequisite for significant advances is the generation of improved materials that can enable CO₂/CH₄ and CH₄/N₂ separations.³⁻⁵

Among the diverse adsorptive separation materials, metal-
25 organic frameworks (MOFs) have studied as promising materials for gas separation. Chemical and thermal robustness of MOFs, including structural rigidity during reversible adsorption/desorption, are key features with regard to possible industrial applications in catalysis and gas storage/separation.⁶⁻⁹

30 A so-called third generation of functional MOFs has been emerging since its conception in 1998.¹⁰ These materials exhibit a flexible (or dynamic) porous framework that can respond to pressure, temperature, or adsorption of guest molecules by changes in its structure.¹¹ Although many authors have stated that
35 flexible MOFs are good candidates for gas separation, it should be noted that such expectations have commonly been based solely on inspection of their pure-component adsorption isotherms.¹² Most direct measurements of adsorption selectivities for gaseous mixtures in flexible MOFs have related to separations

40 in the MIL-53 family of MOFs.¹³⁻¹⁷ In 2010, Kitagawa et al. studied the separation ability of CO₂ over CH₄ from CH₄/CO₂ mixture using [Cu(dhbc)₂bipy]·2CH₃COCH₃ (H₂dhbc = 4,4'-dihydroxybiphenyl-3-carboxylic acid) at a total pressure of 0.1 MPa and 273 K, but the breakthrough profiles were not
45 observed.¹⁸ In 2012, Kitagawa's group attempted CH₄/CO₂ and CH₄/C₂H₆ separation experiments on flexible ligand-base solid solution compounds designated as [Zn(5NO₂-ip)(bipy)]_n (CID-5), [Zn(5MeO-ip)(bipy)]_n (CID-6), and CID-5/6 (5NO₂-ip = 5-nitroisophthalate, 5MeO-ip = 5-methoxyisophthalate, bipy = 4,4'-
50 bipyridine), which made a contribution for study the separation ability of flexible frameworks.¹⁹

In 2009, Coudert et al. proposed the so-called osmotic framework adsorbed solution theory (OFAST) to study the evolution of gate opening in [Cu(4,4'-bipy)(dhbc)₂] (dhbc = 2,5-dihydroxybenzoic
55 acid, 4,4'-bipy = 4,4'-bipyridine) and the breathing of MIL-53 upon adsorption of CO₂/CH₄ mixtures. OFAST adequately explained the structural transitions occurring upon adsorption of a binary gaseous mixture.²⁰ Recently, molecular simulations using atomistic force fields and *ab initio* quantum mechanical
60 calculations have been extremely helpful in explaining flexibility effects, but these methods typically require prior knowledge of flexibility modes that need to be determined experimentally.²¹⁻²³ Sarkisov et al. reported a simple and computationally efficient method for predicting whether an MOF is flexible, based on
65 treating it as a system of rigid bodies connected by flexible joints, which allowed systematic prediction of large amplitude flexibility regimes.²⁴

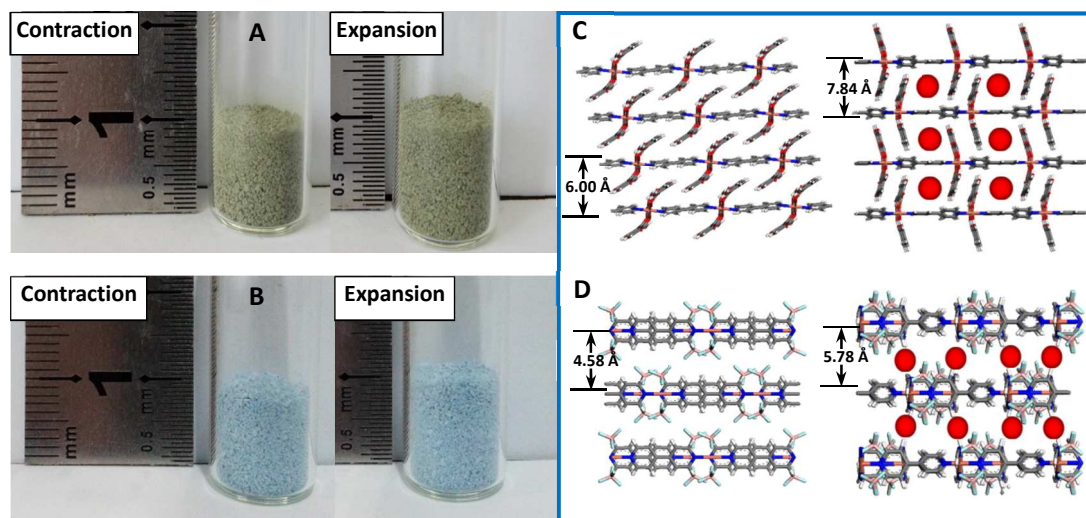


Fig. 1 Elastic structure deformations in $[\text{Cu}(\text{dhbc})_2(4,4'\text{-bipy})]$ (A,C) and $[\text{Cu}(4,4'\text{-bipy})_2(\text{BF}_4)_2]$ (B,D) in Macro and Micro Level.^{25,26}

Two flexible MOFs $[\text{Cu}(\text{dhbc})_2(4,4'\text{-bipy})]\cdot\text{H}_2\text{O}$ and $[\text{Cu}(4,4'\text{-bipy})_2(\text{BF}_4)_2]\cdot(\text{H}_2\text{O})_2$ with stacked two-dimensional (2D) frameworks were first reported by S. Kitagawa et al.²⁵ in 2003 and by P. Hubberstey²⁶ in 1997. Square-grid structures $[\text{Cu}(\text{dhbc})_2(4,4'\text{-bipy})]$ and $[\text{Cu}(4,4'\text{-bipy})_2(\text{BF}_4)_2]$ were obtained after activation at 393 K to remove the H_2O molecules. $[\text{Cu}(\text{dhbc})_2(4,4'\text{-bipy})]$ showed a gate-opening phenomenon at certain pressures of nitrogen, oxygen, or methane, corresponding to a subnetwork displacement in its structure.¹⁹ This phenomenon is restricted to systems having discrete frameworks that are not interconnected through strong chemical bonds, but interact only through weak van der Waals interactions, such that the subnets can drift, relocate, or shift with respect to one another (Figure 1C).⁴ The gate-opening phenomenon of $[\text{Cu}(4,4'\text{-bipy})_2(\text{BF}_4)_2]$ was clarified by detailed synchrotron radiation experiments on CO_2 adsorption.²⁷ After CO_2 adsorption, the interlayer distance was increased by 1.20 Å from 4.58 Å to 5.78 Å (26%), and the staggered stacked layers could slide with respect to one another, accompanied by rotation of the pyridine rings (Figure 1D).²⁸⁻³⁰ These two flexible MOFs have received a lot of attention with such potent characteristics such as gate opening, and have been mainly studied from a structural point of view, as well as with regard to their behavior upon adsorption of various guests. The most intriguing aspects relate to cases in which one guest molecule induces a structural transition or two guests work together. For example, the question arises as to how the guest-induced structural transitions during gate opening evolve upon the adsorption of gas mixtures.

To describe the dynamic separation process of binary gas mixtures in the flexible MOFs $[\text{Cu}(\text{dhbc})_2(4,4'\text{-bipy})]$ and $[\text{Cu}(4,4'\text{-bipy})_2(\text{BF}_4)_2]$, experimental data for the separation of CO_2/CH_4 and CH_4/N_2 mixtures have been collected on an in-house-constructed apparatus. The column dimensions, total pressure, temperature, and humidity have been systematically varied. In most previous studies in this field, equilibrium gas adsorption properties on MOFs have been considered. However, we surmised that studies of dynamic adsorption and diffusion processes on the MOF structures would provide more insight into the gas separation processes.^{31,32} Hence, in this work, the

adsorption and desorption kinetics of CO_2 , CH_4 , and N_2 in the gate-opening process have been investigated in detail at 0–20 bar and 195–298 K based on the two aforementioned flexible MOFs. With regard to practical application, their mechanical/chemical stabilities and separation cycle lifetimes have been compared by several quantitative and qualitative methods.³³ Furthermore, a combination of site-site Lennard–Jones (LJ) and Coulombic potentials has been employed to calculate the intermolecular interactions between adsorbate molecules as well as between adsorbate molecules and the flexible MOFs.³⁴ The results suggest that these flexible MOFs are good candidates for gas separations.

Experimental section

Materials

Syntheses of $[\text{Cu}(\text{dhbc})_2(4,4'\text{-bipy})]\cdot\text{H}_2\text{O}$ and $[\text{Cu}(4,4'\text{-bipy})_2(\text{BF}_4)_2]\cdot(\text{H}_2\text{O})_2$ were first reported by S. Kitagawa in 2003 and by P. Hubberstey in 1997,^{25,26} respectively, and the synthetic processes were subsequently improved as described in our previous work.³⁵ All chemicals were purchased in their highest available commercial purity (>98%) from Sigma–Aldrich.

Characterization

The crystallinities and phase purities of the samples were measured by powder X-ray diffraction (XRD) with a Rigaku Mini Flex II X-ray diffractometer employing $\text{Cu-K}\alpha$ radiation operated at 30 kV and 15 mA, scanning over the range 5–40° (2 θ) at a rate of 1°/min.

Single-component adsorption measurements

The purities of the carbon dioxide, methane, and nitrogen used were each 99.999%. Their adsorption isotherms were collected with an Intelligent Gravimetric Analyzer (IGA 001, Hiden, UK). Samples were activated overnight under reduced pressure at 393 K or until no further weight loss was observed.

Adsorption kinetics

Adsorption and desorption kinetic data were collected with the aforementioned Intelligent Gravimetric Analyzer (IGA 001,

Hidden, UK). The IGA system uses a gravimetric technique to accurately measure the magnitude and dynamics of gas sorption on materials under diverse operating conditions.³¹ In this work, activated $[\text{Cu}(\text{dhbc})_2(4,4\text{'-bipy})]$ and $[\text{Cu}(4,4\text{'-bipy})_2(\text{BF}_4)_2]$ samples of about 50 mg were introduced into the IGA for gas sorption measurements. The pressure controller had ranges of 0–0.1 and 0.1–2 MPa with pressure increments of 50 mbar/min and 200 mbar/min, respectively. The set pressure point was maintained by computer control throughout the course of the experiment. The unique IGA method exploits the gas behavior of the adsorption process after stabilizing the pressure and temperature. During this process, the adsorption and desorption kinetic data can be determined at each point.³⁶

Breakthrough separation experiments and procedures

The experimental set-up consisted of two fixed-bed stainless steel reactors, each with inner dimensions of $\phi 9 \times 150$ mm, connected in parallel. The horizontal reactors were placed in a temperature controlled environment, maintained at 195, 273, or 298 K. The gas flow and pressure were set and controlled at the outlet and inlet by a pressure controller valve and a mass flow meter, and a gas chromatograph continuously monitored the effluent gas from the adsorption bed. A guard tube loaded with desiccant was installed before the main bed in order to remove trace amounts of water from gaseous mixtures, or else a vapor generator was installed to simulate the effect of water on separation of the gases. When the gas mixture was adsorbed in reactor no. 1 at close to saturation, the inlet was turned off and the outlet pressure was reduced to release the gas adsorbed. At the same time, the gas flow was switched to reactor no. 2 to repeat the above step as a cyclic system.

For practical considerations, powder samples of $[\text{Cu}(\text{dhbc})_2(4,4\text{'-bipy})]$ and $[\text{Cu}(4,4\text{'-bipy})_2(\text{BF}_4)_2]$ were pelletized into particles of a certain size (220–320 μm). Details of the particle preparation process are given in the supporting information. The reactors were loaded with particles of 1 $[\text{Cu}(\text{dhbc})_2(4,4\text{'-bipy})]$ (4.1380 g) and 2 $[\text{Cu}(4,4\text{'-bipy})_2(\text{BF}_4)_2]$ (3.936 g), respectively. To ensure the homogeneous nature of the synthesized materials, samples of each batch were tested by powder X-ray diffraction and CO_2 adsorption analyses (Figure S2). More details of the pelletization procedure (Figure S1) and pre-treatment process for this apparatus are given in the supporting information.

The influence of water on the adsorption and separation of gas mixtures

Water vapor adsorption on the MOFs was determined by vapor sorption measurements on an Autosorb-iQ Quantachrome (volumetric technique) with vapor generator. The adsorption and separation of moist gases were measured on the IGA and our in-house-constructed separation apparatus.

Structural stability

Inevitably, the structural instability of MOFs has been a major deterrent to their commercial application. To examine the structural stability of $[\text{Cu}(\text{dhbc})_2(4,4\text{'-bipy})]$ and $[\text{Cu}(4,4\text{'-bipy})_2(\text{BF}_4)_2]$, samples were placed under various conditions (high temperature; with H_2O , CH_3OH , and mixtures thereof) and monitored over the course of 7 days.

Monte Carlo molecular dynamic simulation for adsorption of gas mixtures on the flexible MOFs

The potential parameters and partial charges for all of the adsorbates are shown in supporting information.^{37,38} And the MOF material studied here was modeled by the atomistic representation. The LJ potential parameters for the framework atoms of the MOFs were taken from the Dreiding force field,³⁹ and the missing parameters for Cu were taken from the universal force field (UFF),⁴⁰ as given in supporting information. The Lorentz–Berthelot mixing rules were used to determine all of the LJ cross-potential parameters of adsorbate–adsorbate and adsorbate–MOF interactions. In this work, atomic partial charges for the frameworks of the MOFs were estimated using the CBAC method developed by Zhong’s group, with slight variation to make the total charge equal to zero.^{41,42}

GCMC simulations were then performed to study the adsorption behaviors of equimolar (50:50) CO_2/CH_4 and CH_4/N_2 gas mixtures at 298 and 273 K, at pressures from 0.1 to 2.0 MPa.

Results and discussion

1. Dynamic separation of gas mixtures in flexible MOFs

The breakthrough curves of CO_2/CH_4 (50:50, v/v) and CH_4/N_2 (50:50, v/v) gas mixtures on $[\text{Cu}(\text{dhbc})_2(4,4\text{'-bipy})]$ and $[\text{Cu}(4,4\text{'-bipy})_2(\text{BF}_4)_2]$ particles were measured on the in-house-constructed separation apparatus (Figure 2) by applying purged He flows at 373 K for 2 h before cooling to room temperature.

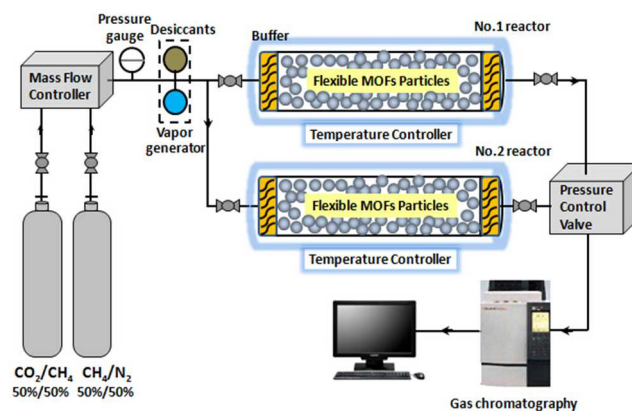


Fig.2 Breakthrough separation apparatus for flexible MOFs.

The most noteworthy observation was the volume changes in the flexible MOFs (Figure 1). However, the traditional PSA (Pressure Swing Adsorption) technique was generally not designed to handle adsorption beds that constantly undergo volume changes, and the swelling and shrinking of the pellets would lead to a significantly fluctuation of gas flows. So, it is clear that flexible MOFs adsorbent required flexible materials to support them.^{43,44} To solve this problem, two buffer zones (porous polyethylene fiber with high gas permeability and elasticity at 173–373 K) were placed on either side of the adsorbent bed to give a column of undefined dimensions, thereby allowing regular operation when volume changes occurred in the flexible MOFs (Figure 2).

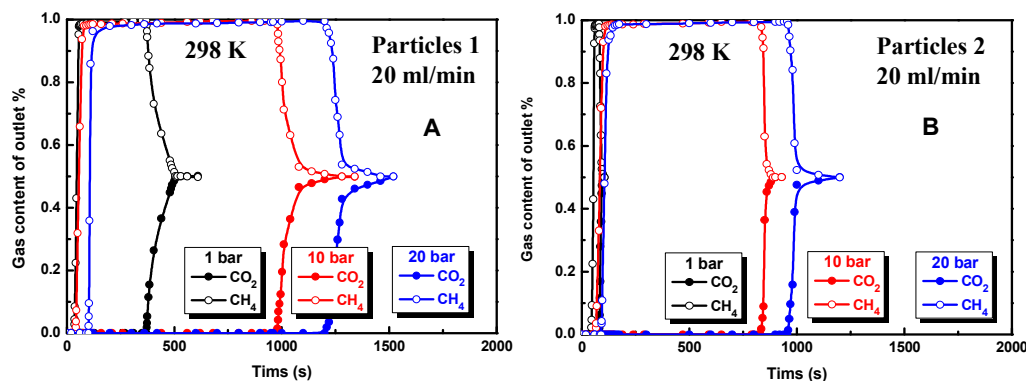


Fig.3 Breakthrough curves for binary gases separation experiments with Particles 1 versus Particles 2 using CO₂/CH₄ (50%/50%) mixtures at flow rates of 20 cm³/min and pressure of 1/10/20 bar at 298 K.

Targeted Capture of CO₂ from CO₂/CH₄ mixtures

The breakthrough profiles of CO₂/CH₄ (50%/50%) mixture are shown in Figure 3. The two flexible MOFs displayed excellent CO₂/CH₄ separation abilities in the pressure regions 1/10/20 bar at 298 K. CO₂ molecules were effectively captured from the gas mixtures. Furthermore, an obvious increase in separation capacities with increasing pressure is evident from Figure 3 A and B: for particles 1, the elution times at 20 bar were about 3.3 and 1.2 times those at 1 bar and 10 bar, respectively; for particles 2, the elution times at 20 bar were about 21.7 and 1.1 times those at 1 bar and 10 bar, respectively. Particles 2 failed to separate CO₂/CH₄ at 298 K and 1 bar, which was because the partial pressure of CO₂ was lower than the gate-opening pressure of [Cu(4,4'-bipy)₂(BF₄)₂] and hence the CO₂ molecules could not diffuse into its structure.⁴⁵⁻⁴⁷ To further study the temperature effect on separation, breakthrough experiments were conducted at 273 K and the results are shown in Figure S4. Detailed elution times and CO₂/CH₄ adsorption selectivities are given in Table 1.⁴⁶

Targeted capture of CH₄ from CH₄/N₂ mixtures

The CH₄/N₂ separation abilities of the flexible MOFs [Cu(dhbc)₂(4,4'-bipy)] and [Cu(4,4'-bipy)₂(BF₄)₂] were studied at various temperatures and pressures. Figure 4 shows the elution profiles of CH₄ and N₂ upon separation of a CH₄/N₂ (50:50) mixture at 298/195 K and 1/10/20 bar, detailed elution times and CH₄/N₂ adsorption selectivities are given in Table 2. At 298 K, both flexible MOF particles showed poor separation efficiencies for the CH₄/N₂ mixture, even when the pressure was increased to 20 bar. At 195 K, N₂ readily passed through the adsorbent bed, whereas a large amount of CH₄ was captured. In summary, CH₄ and N₂ were effectively separated by the flexible MOFs on our in-house-constructed apparatus, even though these gases have similar physicochemical properties. The separation capacities of the MOF particles were strongly affected by the temperature and pressure, since gate-opening occurred only under certain conditions for each kind of gas molecule. And detailed analysis of the breakthrough experiments, presented in section 5 of the

supporting information shows that the pure CO₂ and pure N₂ can be recovered at high productivities from CO₂/CH₄ and CH₄/N₂ mixtures.

Table 1 Dynamic separation of CO₂-CH₄ (50%/50%) mixture by particles for [Cu(dhbc)₂(4,4'-bipy)] (1) and [Cu(4,4'-bipy)₂(BF₄)₂] (2) at 298/273 K and 1/10/20 bar.

	Particles 1		Particles 2	
	Elution time (s)	S _{CO₂/CH₄}	Elution time (s)	S _{CO₂/CH₄}
298 K-1 bar	337	14.8	36	3.4
10 bar	938	28.9	768	31.0
20 bar	1110	6.4	868	17.9
273 K-1 bar	1087	53.4	1011	66.7
10 bar	1122	7.3	1042	28.2
20 bar	1030	1.2	1096	16.2

Selectivity (S) is defined as the adsorption ratio of two gases at a given temperature and pressure.⁴⁸

Table 2 Dynamic separation of CH₄-N₂ (50%/50%) mixture by particles for [Cu(dhbc)₂(4,4'-bipy)] (1) and [Cu(4,4'-bipy)₂(BF₄)₂] (2) at 298/273/195 K and 1/10/20 bar.

	Particles 1		Particles 2	
	Elution time (s)	S _{CH₄/N₂}	Elution time (s)	S _{CH₄/N₂}
298 K-1 bar	17	1.2	27	1.1
10 bar	33	1.4	26	1.3
20 bar	117	1.7	30	1.4
273 K-1 bar	16	1.4	15	1.2
10 bar	35	3.8	36	1.5
20 bar	388	5.5	43	1.7
195 K-1 bar	140	10.3	39	2.2
10 bar	436	8.6	31	5.5
20 bar	424	1.6	404	8.7

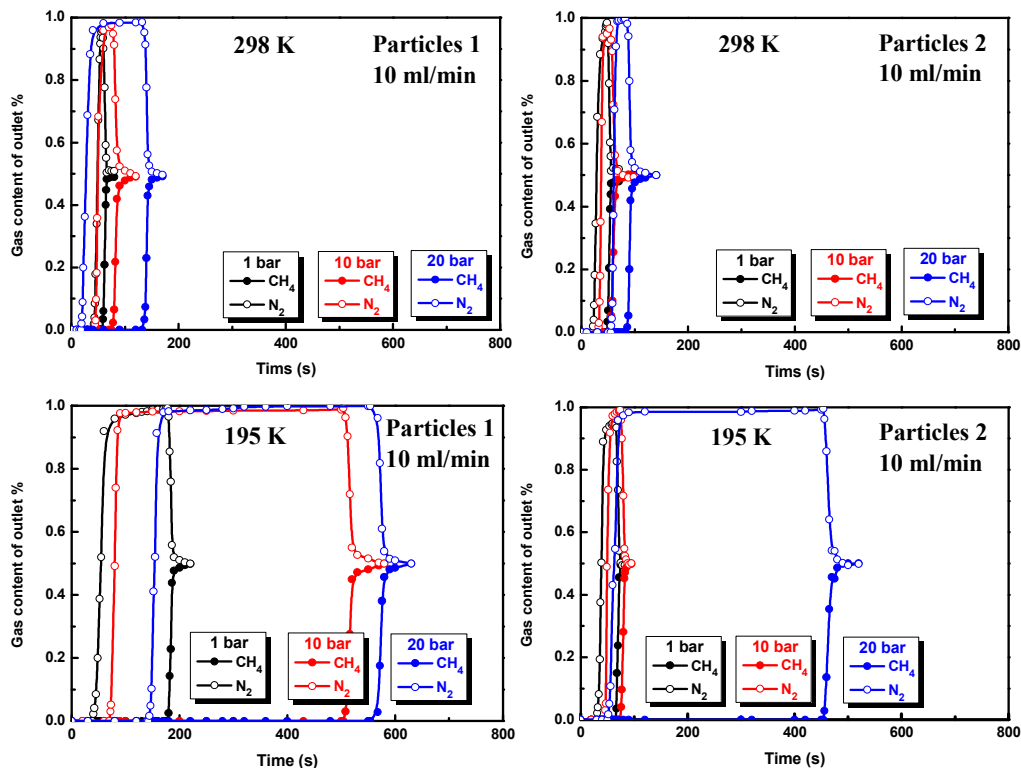
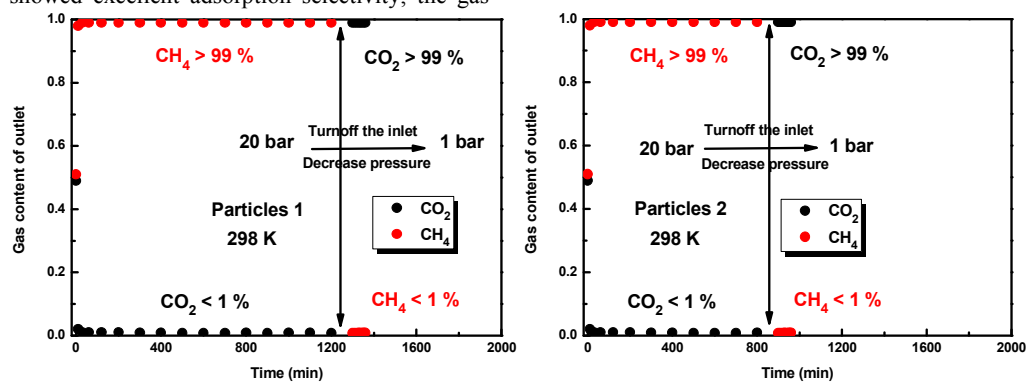


Fig.4 Breakthrough curves for CH₄/N₂ (50%/50%) separation experiments with Particles 1 versus Particles 2 at flow rates of 10 cm³/min and pressure of 1/10/20 bar at 298/195 K.

5 Two-stage pressure-responsive separation

A unique two-stage separation technique was adopted for the flexible MOFs based on their good gas separation abilities and adsorption behavior due to gate opening. As shown in Figure 5, high-pressure CO₂/CH₄ or CH₄/N₂ mixtures were passed through the adsorption beds at 298 K or 195 K, respectively. The two flexible MOFs showed excellent adsorption selectivity; the gas

mixtures were well separated, such that the concentrations of the non-retained gas at the outlet were more than 99%. When the adsorption bed was nearly saturated, the gas inlet was closed and the pressure was lowered, whereupon the adsorbed gas was slowly released from the column. By using this method, the components of the gas mixtures could be separated by controlling the pressure (Figure 5).



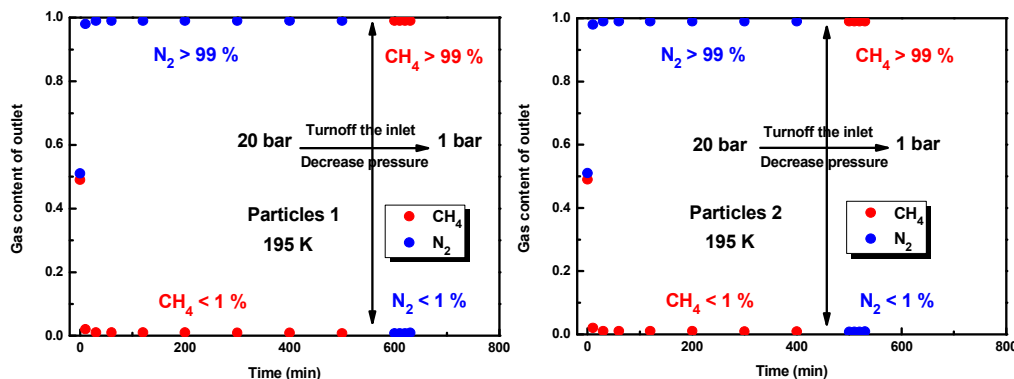


Fig.5 Schematic diagram of two staged pressure-responsive separation and breakthrough curves of CO₂/CH₄ and CH₄/N₂ on flexible MOFs particles

Cycling measurements

To ensure the regenerability of the flexible MOFs, we performed CO₂/CH₄ separation cycling experiments on particles 1 and 2 at 20 bar and 298 K (Figure S11). In the above CO₂/CH₄ separation experiments, we found that nearly all of the CH₄ and most of the CO₂ molecules were released from the adsorbent bed when the temperature and pressure were returned to normal conditions. For more accurate results, the adsorbent beds were flushed with helium for 1 h at 323 K between each cycle measurement. After three high-pressure separation cycles, the breakthrough profiles on particles 1 and 2 were clearly well retained (Figure S11). Sorption kinetics is crucial for the separation of gas mixtures.⁴⁶⁻⁴⁸ To further investigate the adsorption kinetics of the flexible MOFs, we performed dynamic sorption of CO₂, CH₄, and N₂ on the two flexible MOFs, as shown in Figure S12.

Effect of humidity on the flexible MOFs for adsorption and separation of gas mixtures

On the basis of previous studies, the gas adsorption capacities of the MOFs were expected to decrease after the pre-adsorption of a large amount of water. Indeed, some MOFs may lose their gas adsorption capacities after complete saturation by water and repeated regeneration processes. Therefore, it was necessary to study CO₂ and CH₄ adsorption in the two flexible MOFs in the presence of moisture, which may represent a future practical situation for CO₂ capture and separation from flue gases.^{49,50}

H₂O vapor adsorptions for particles 1 and 2 are depicted in Figure 8 A and B, respectively. In the low-pressure region ($P < 0.03$ bar), particles 1 showed hydrophobicity. With increasing pressure, H₂O molecules were adsorbed in the [Cu(dhbc)₂(4,4'-bipy)] structure, and a typical hysteresis phenomenon of flexible MOFs was observed in the desorption isotherm.¹⁸ A transformation from hydrophobicity to hydrophilicity triggered by pressure alone is unusual in MOFs and even in traditional materials.

At very low pressures, particles 2 showed a higher H₂O adsorption capacity than particles 1, indicating stronger interactions between the H₂O molecules and the [Cu(4,4'-bipy)₂(BF₄)₂] structure. A similar reversible rehydration process was also observed for particles 2, but a higher temperature was needed for dehydration. Such results were previously reported by Cheng et al. based on the reversible structural change of [Cu(4,4'-bipy)₂(BF₄)₂].⁵¹ Moreover, macroscopic volume changes with

gate-opening behavior were found during H₂O adsorptions on particles 1 and 2 (Figure S13). The structure expansion phenomenon was similar to that upon adsorption of CO₂ on [Cu(4,4'-bipy)₂(BF₄)₂], which was clarified by detailed synchrotron radiation experiments, as reported in the literature.²⁷

To assess the adsorption of gases in the presence of moisture, competitive adsorptions of H₂O with CO₂, CH₄, and CO₂/CH₄ mixtures were carried out. The two flexible MOF particles were first exposed to 1 bar saturated with H₂O vapor and the cell was evacuated by pumping, taking ca. 20 min to reach 20 mbar, whereupon CO₂ and CH₄ were introduced. Using the highly accurate balance of the IGA apparatus, weight changes were recorded after the introduction of gases into the cell to monitor their adsorption in the presence of pre-adsorbed H₂O (Figure 6 C and D). The results showed that CO₂ and CH₄ adsorption capacities and gate-opening behavior were not affected by residual H₂O in particles 1 after the pre-adsorption of H₂O vapor. In particles 2, however, the adsorption capacities for CO₂ and CH₄ were almost completely lost after the pre-adsorption of H₂O vapor because a large number of H₂O molecules were retained in the structure and occupied the relevant adsorption sites. This phenomenon is indicated by the H₂O vapor adsorption-desorption profiles in Figure 6 A and B.

In normal industrial environments, water vapor is inevitably present in gas mixtures. Therefore, we measured the gas separations in the presence of moisture, saturating the gas flows with H₂O vapor before entering the adsorbent bed, keeping the gas lines at constant temperature.^{52,53} CO₂/CH₄ separation experiments under humid conditions were performed in triplicate on particles 1, and the results were compared with those under dry conditions (Figure 6 E and F). The results showed that CO₂/CH₄ separation capacities at 10 bar for particles 1 were not significantly affected after conditioning with water vapor at room temperature. A possible explanation for this is that [Cu(dhbc)₂(4,4'-bipy)] showed hydrophobicity in the low-pressure region, such that H₂O molecules did not bond strongly with its structure.³⁸ In particles 2, however, the presence of water resulted in loss of its CO₂/CH₄ separation ability at 10 bar and 298 K, since a large number of H₂O molecules were quickly adsorbed at the relevant sites in its structure, consistent with the results for CO₂ and CH₄ adsorption in the presence of water.

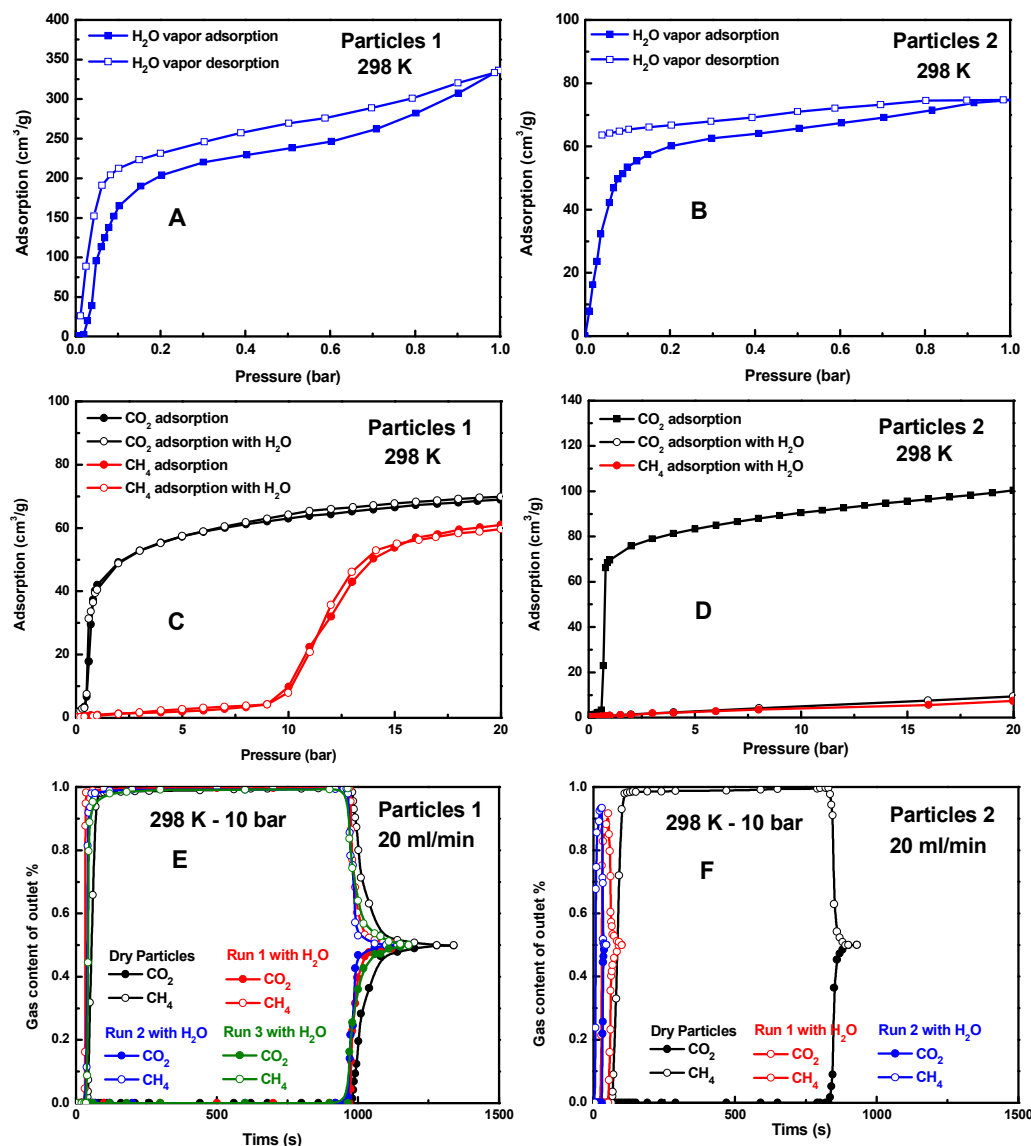


Fig.6 CO₂ and CH₄ adsorption (A, B), CO₂/CH₄ separation (C, D) were measured at 298 K for particles 1 and 2 with H₂O loadings.

Structural stability

Particles of [Cu(dhbc)₂(4,4'-bipy)] and [Cu(4,4'-bipy)₂(BF₄)₂] were placed under various conditions [high temperature; with H₂O, CH₃OH, or H₂O/CH₃OH (1:1, v/v)]. After 1, 3, and 7 days, particles were removed, activated at 393 K, and outgassed for 4 h. The final structures were analyzed by PXRD and the patterns (Figure S14) showed that both flexible MOFs retained their structural integrity under the given conditions for more than 7 days. This can be attributed to the use of H₂O/ethanol mixtures as the solvent in the synthetic process. Both flexible MOFs exhibit good structural stability towards H₂O and ethanol.

Monte Carlo molecular dynamic simulation for adsorption of gas mixtures on the flexible MOFs

In previous studies, the interpretation of isotherm measurements has been particularly challenging for gas mixtures. However, gas mixture adsorption data are required to describe the interactions between the gases and the MOF structures. The flexible structures

of the two MOFs change during the dynamic adsorption/separation process, a situation that is too complex for GCMC simulations. Hence, the “gate-opened” structures of the two flexible MOFs were used here as rigid frameworks, with atoms frozen in their crystallographic positions.

The distributions of the adsorbed CO₂, N₂, or CH₄ in equimolar mixtures in [Cu(dhbc)₂(4,4'-bipy)] and [Cu(4,4'-bipy)₂(BF₄)₂] were investigated at pressures from 0.1 to 20 bar. As shown in Figure 7, the density of CO₂ was always much higher than that of CH₄ in the co-adsorption of CO₂/CH₄ on both flexible MOFs, and the density of CH₄ was always much higher than that of N₂ in the co-adsorption of CH₄/N₂. With increasing pressure, the amount of CO₂ molecules adsorbed increased significantly, with these guest molecules occupying the inner space of the pores, as is evident from Figure 7 A and B. When the temperature was decreased to 273 K, the similar phenomenon occurred in Figure S14. In summary, the simulated results illustrate the excellent performance of the flexible MOFs for the separation of CO₂ or CH₄ from their binary mixtures.

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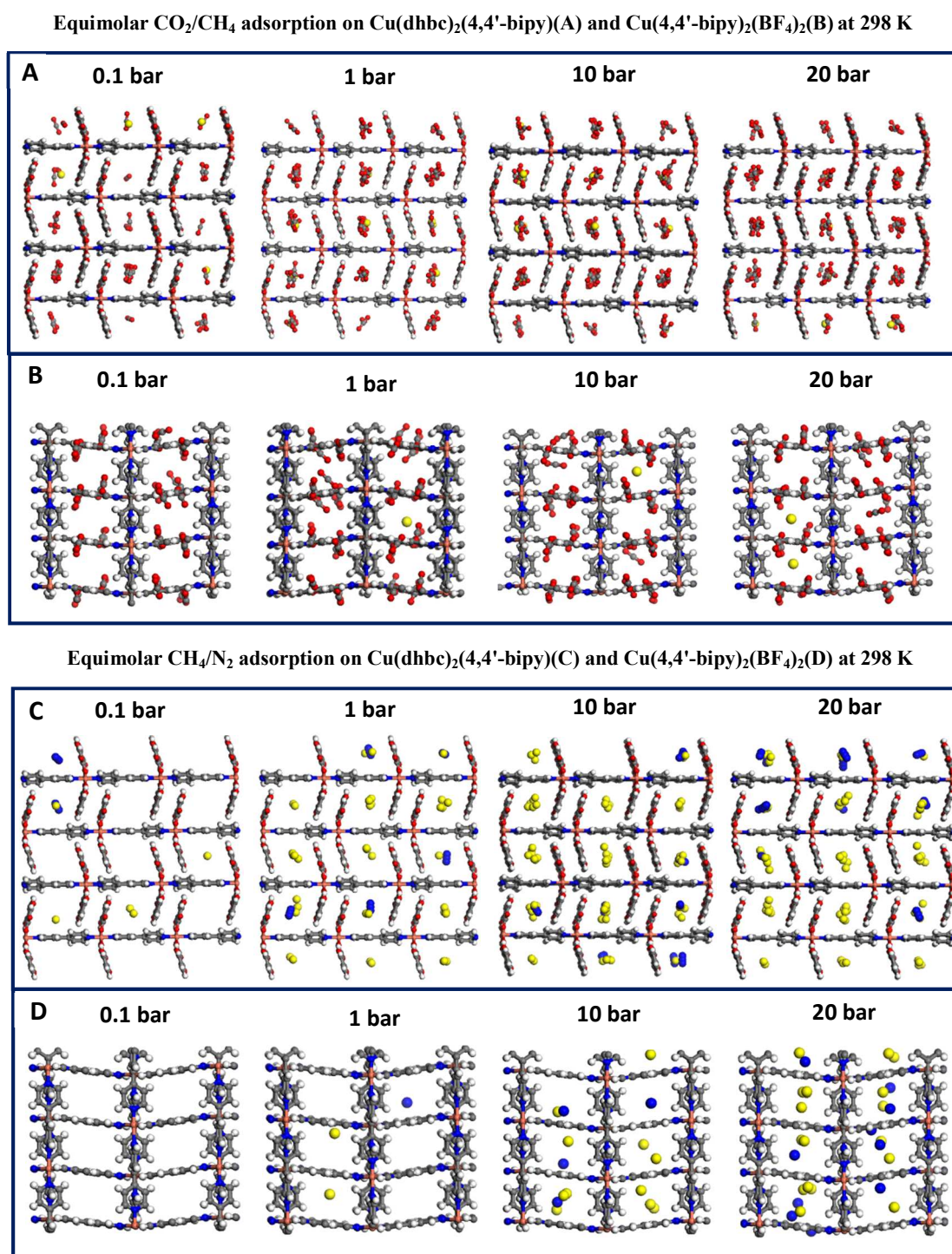


Fig.7 The distribution for an equimolar CO₂/CH₄ and CH₄/N₂ mixtures in Cu(dhbc)₂(4,4'-bipy) and Cu(4,4'-bipy)₂(BF₄)₂ at 298 K simulated by GCMC

(Cu, pink; O, red; C, gray; H, white; N, blue; CH₄, yellow).

5 Conclusion

Separation experiments on binary gas mixtures have been

performed using layered flexible MOFs of undefined dimensions. The obtained breakthrough curves could be interpreted in terms of gate-opening behavior of the MOFs. For the first time, sorption kinetics has been combined with a study of the structural transformation in flexible MOFs during the gate-opening process. Although [Cu(4,4'-bipy)₂(BF₄)₂] exhibits a good capacity for gas separations, this capacity was drastically diminished in the presence of H₂O. Under the same conditions, [Cu(dhbc)₂(4,4'-bipy)] showed hydrophobicity in the low-pressure region, and its initial capacity was maintained during the separation process. The results of GCMC simulations have indicated that the two flexible MOF structures can capture CO₂ or CH₄ from CH₄/CO₂ and CH₄/N₂ mixtures, based on the interactions between the gases and the MOFs under different conditions. In summary, we believe that the studied on flexible MOFs could be promising for practical application in the separation of gas mixtures.

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Notes and references

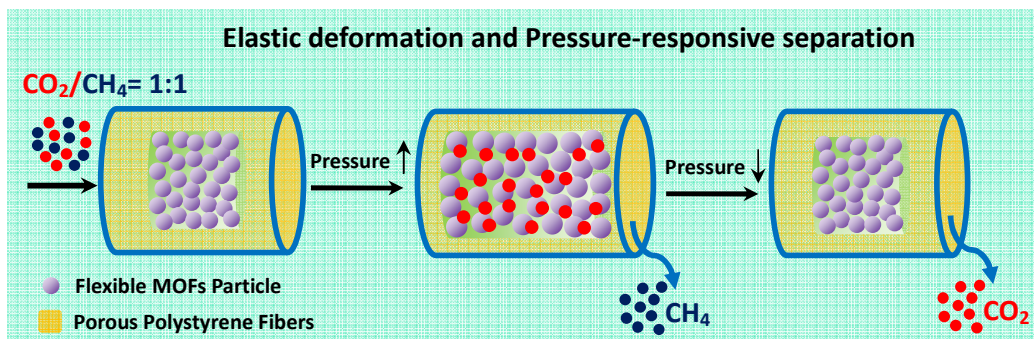
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Graphical Abstract



The pressure-responsive CO₂ and CH₄ targeted separation were studied on the flexible Metal-Organic Frameworks (MOFs) in dynamic conditions.