Microporous Metal–Organic Frameworks with Hydrophilic and Hydrophobic Pores for Efficient Separation of CH₄/N₂ Mixture

Miao Chang, Yingjie Zhao, Qingyuan Yang, and Dahuan Liu*

State Key Laboratory of Organic-Inorganic Composites, Beijing University of Chemical Technology, Beijing 100029, China

Supporting Information

ABSTRACT: Highly selective removal of N₂ from unconventional natural gas is considered as a viable way to increase the heat value of CH₄ and reduce the greenhouse effect caused by the direct emission of CH₄/N₂ mixture. In this work, a three-dimensional Cu–MOF with two different types of micropores was synthesized, exhibiting a high selectivity for CH₄/N₂ (10.00–12.67) and the highest sorbent selection parameter value (65.73) among the reported materials. The CH₄ molecule interacts with the framework to form multiple van der Waals interactions both in hydrophilic and hydrophobic pores, indicated by density functional theory calculations to gain a deep insight into the adsorption binding sites. In contrast, the weak polarity feature of the hydrophobic pore and the occupied open-metal sites in the hydrophilic pore result in a very low adsorption uptake of N₂. The excellent separation performance combining the good stability and regenerability guarantees this Cu–MOF to be a promising adsorbent for an efficient separation of the CH₄/N₂ mixture.

INTRODUCTION

Nowadays, the continuous consumption of fossil fuels has raised many issues-related to energy and environment, creating an increasing demand for the development of clean energy. Natural gas (the main component is methane, CH₄) is considered as an alternative energy source due to its clean and economical features and has become one of the fastest-growing energy source in the world.^{1–6} A large amount of CH₄ is emitted from conventional natural gas and unconventional natural gas (such as landfill gas, shale gas, and coal bed methane). The latter resource with a substantial amount of CH₄ is very difficult to utilize directly because the high concentration of nitrogen (N₂) lowers the heat enthalpy. Current treatment, like direct emission, will lead to a serious greenhouse effect.² Therefore, it is of significance to efficiently separate the CH₄/N₂ mixture, which is however a great challenge because of the very similar physical properties CH₄ and N₂.^{7,8} To date, several technologies have been used, such as cryogenic distillation,⁹ membrane separation,^{10–12} and adsorption separation,¹³ where pressure swing adsorption (PSA) is regarded as an promising industrial and commercial technology,^{14,15} due to the advantages of low investment cost, simple operation, flexibility, and energy conservation.^{16,17} The key is suitable adsorbent. Different types of adsorbents have been investigated, while the separation performance is still very low so far,^{1–9} especially for the integrated consideration of selectivity and productivity simultaneously.

As a new kind of porous material, metal–organic frameworks (MOFs) have exhibited potential applications in gas separation owing to the good designability as well as structural

and chemical adjustability.^{15,18–21} Due to their unique structural and chemical features, several MOFs have been studied to separate CH₄/N₂ with better separation performances than other porous materials.^{1,7,9} However, it still needs to be further enhanced. In this work, a three-dimensional (3D) Cu–MOF was selected to separate the CH₄/N₂ mixture. The hydrophilic and hydrophobic pores endow this material with a large difference in the interaction between CH₄ and N₂ with the framework. As a result, a high selectivity for CH₄/N₂ is obtained, especially for the sorbent selection parameter (SSP)²² that can evaluate the selectivity and productivity in the mostly industrialized pressure swing adsorption (PSA) process. In addition, this MOF has good stability and regenerability, providing a great potential to separate the CH₄/N₂ mixture in practical application.

RESULTS AND DISCUSSION

Preparation and Characterization for Cu–MOF. Cu–MOF was synthesized using copper salt and H₃BTC, and the structure is given in Figure 1.²³ Copper clusters with a paddle wheel structure are connected by monomethyl BTC ester. The unique structure of Cu–MOF is due to the esterification of BTC linker during the synthesis process. Such a structure is different from the well-known Cu–BTC because the paddle wheel copper clusters are occupied by μ_2 -coordinated carboxylate O atoms of the paddle wheel unit in the adjacent

Received: June 12, 2019

Accepted: August 16, 2019

Published: August 28, 2019

Figure 1. Illustration of the crystal structure of Cu-MOF: (a) view of hydrophobic and hydrophilic pores along the *c*-axis; (b) view along the *b*-axis; and (c) coordination environment of Cu- and μ_2 -coordinated carboxylate O atoms of paddle wheel unit in the adjacent sheet (Cu, orange; O, red; C, gray; H, white).

sheet after the material is dehydrated, effecting that the Cu open-metal sites are not exposed. This change in coordination environment causes the dimensionality of the frameworks to vary from 2D to 3D with the formation of two different types of micropores.^{23,24} The hydrophilic pore is formed by the arrangement of a copper paddle wheel, and the hydrophobic pore is formed by ester groups on organic ligands. Powder X-ray diffraction (PXRD) patterns in Figure 2 agree well with the

Figure 2. Powder X-ray diffraction patterns for Cu-MOF.

simulated patterns, indicating the successful synthesis with good crystallinity. The PXRD patterns at 2θ of $10\text{--}13^\circ$ is due to the trace amount of unreacted Cu-BTC, which has also been observed in literature.²³ As indicated in literature,²³ the best yield for the esterified process reaches 100% and yields in excess of 95% could be obtained easily. With long heating times, the amount of Cu-BTC can be lower than 1% as an impurity. As shown in Figure S10a, the BET specific surface areas and the pore sizes are $110\text{ m}^2/\text{g}$ and 7 and 5 Å, respectively.

Gas Separation Performance of Cu-MOF. Single-component gas adsorption experiments of CH_4 and N_2 were first performed at 298 K, and the results are given in Figure 3. The adsorption capacity of CH_4 is about $14.17\text{ cm}^3/\text{g}$ at 298 K and 1.0 bar, while that of N_2 is relatively very low ($2.40\text{ cm}^3/\text{g}$), indicating the interaction between CH_4 and the framework is stronger than that for N_2 . To investigate the separation performance, ideal adsorbed solution theory (IAST)^{25,26} was used to calculate the selectivities using different fitting models. As shown in Figures 3b and S6 in the Supporting Information (SI), the IAST-predicted selectivities are about 10.8–11.5 (10.8 at 1.0 bar) for a dual-site Langmuir model,

10.67–12.66 (11.18 at 1.0 bar) for a single-site Langmuir–Freundlich model, 10.00–12.67 (11.14 at 1.0 bar) for the dual-site Langmuir–Freundlich model, and 10.94 for the Toth model at the range of tested pressures. Details can be found in the SI. These values are higher than most of the reported values for various porous materials, except for Co-MOF.¹ While the adsorption capacity of CH_4 in Co-MOF is about $9\text{ cm}^3/\text{g}$, it is only 64% of that in Cu-MOF in this work. In addition, the ratio of working capacity is valuable for estimating the separation performance of adsorbent in practical conditions.²⁷ For Cu-MOF, this value is about 5.90, much higher than that of all the reported materials owing to the very low adsorption capacity of N_2 .

From the practical point of view, the adsorbent should have good water stability, since the humidity usually exists in many industrial separation processes.²⁸ In fact, it is observed that the water in gas mixtures may lower the performance to separate the CH_4/N_2 mixture.²⁹ Therefore, stability test was performed by treating the MOF sample using water for three days. Experimental results demonstrate that Cu-MOF exhibits good water stability, and the adsorption capacity of CH_4 can be well-maintained as shown in Figure 3c. This may be attributed to the different coordination environments in this Cu-MOF compared to other typical MOFs with Cu open-metal sites, such as Cu-BTC. These structures can be easily destroyed by water molecules. As shown in Figure 1, the open-metal sites on copper paddle wheels are occupied by μ_2 -coordinated carboxylate O atoms of the paddle wheel unit in adjacent sheets, resulting in the framework remaining intact in the presence of water.^{23,24} Furthermore, regeneration experiment of the material was carried out at 298 K and 1.0 bar. Figure 3d shows that the adsorption capacity of CH_4 remains unchanged even after 10 cycles, indicating the excellent regenerability.

In practical separation processes, such as the typical PSA process, an excellent adsorbent should possess high selectivity and high adsorption capacity simultaneously. The former can reduce the number of cycles for the treatment of an input stream to reach a desired concentration, and the latter may lower the overall cost. In this aspect, the SSP parameter is a comprehensive indicator of the separation performance that can reflect the cyclic nature of the adsorption processes.²² One bar and 0.1 bar are used for adsorption and desorption conditions, respectively, considering the absence of the adsorption data at high pressures in literature. From Figure 4b, it is obvious that the SSP value of Cu-MOF is about 65.73

Figure 3. (a) Single-component adsorption isotherms of CH₄ and N₂ in Cu-MOF at 298 K. (b) IAST predicted selectivity of equimolar CH₄/N₂ mixture at 298 K. (c) Adsorption capacity of CH₄ after the treatment of the material using water (inset: the comparison of PXRD). (d) Results of regeneration experiment.

Figure 4. Comparison of the separation performance of CH₄/N₂: (a) selectivities as a function of the adsorption capacity of CH₄ at 298 K and 1.0 bar and (b) SSP at 298 K. The data of MIL-101-Cr were collected at 293 K.

and much higher than that of all the reported materials (Figure 4b), demonstrating that this Cu-MOF is an ideal candidate for separating the CH₄/N₂ mixture.

To confirm the application of materials in practical applications, a breakthrough experiment was performed using a mixture gas mixture of CH₄/N₂ (50/50%) with a constant flow rate of 5 mL/min at 298 K. As shown in Figure 5, N₂ was

first detected (about 2.5 min). The breakthrough of CH₄ (about 7.5 min) is obviously later than that of N₂, demonstrating that CH₄ molecules competitively adsorb in the framework over N₂. The effluent purity of N₂ is about 96%, indicating that Cu-MOF could separate the CH₄/N₂ mixture at ambient conditions.

Figure 5. Breakthrough experiment curves for the binary mixture component of CH₄ and N₂ (50/50, v/v) at a constant flow rate of 5.0 mL/min under 298 K and 1.0 bar.

To study the separation mechanism of Cu–MOF, computations were performed for CH₄ and N₂ in the framework. Geometric optimization results in Figure 6a indicate that the distances between the hydrogen atom of CH₄ and the C–H of ester groups in organic ligands in the hydrophobic pore and negative oxygen sites in the hydrophilic pore are about 2.383–2.956 and 2.900–3.205 Å on average, respectively, which are shorter than those for N₂ (about 3.378–3.648 and 3.428–3.841 Å, respectively), indicating the interaction between CH₄ and the framework is stronger than that for N₂. The calculated binding energies of 23.0 and 19.0 kJ/mol for CH₄ in different types of pores are higher than

those for N₂ (14.2 and 14.0 kJ/mol). As shown in Figure 6a, a CH₄ molecule can interact with three C–H atoms in the ester groups in the hydrophobic pore or three negative O atoms in the hydrophilic pore to form multiple van der Waals interactions.^{1,30} In contrast, Cu atoms in the paddle wheels are coordinated by μ_2 -coordinated carboxylate O atoms, resulting in a relatively weak interaction of the N₂ molecule in the hydrophilic pores. In the hydrophobic pore, the weak polarity group C–H also exhibits a weak interaction with N₂.³¹ In fact, Q_{st} of N₂ in Cu–MOF is lower than those in other porous materials.^{1,2,7,32} Therefore, the adsorption capacity of N₂ is very low, leading to the higher SSP than those in the reported materials. It should be noted that Q_{st} of CH₄ is moderate compared to the values in other materials, which can reduce the regeneration cost since the cost of energy in the regeneration process is a major factor to be considered in the practical industrial application.¹

CONCLUSIONS

In this work, a kind of Cu–MOF with hydrophilic and hydrophobic pores was synthesized, exhibiting a high selectivity and the highest SSP value among the reported values for the CH₄/N₂ mixture. The DFT calculations confirm that the CH₄ molecule interacts with the framework to form relatively stronger multiple van der Waals interactions through the H atoms of CH₄ with three C–H in the ester groups on the organic ligands in the hydrophobic pore and three negative O atoms in the hydrophilic pore. In contrast, the interaction

Figure 6. CH₄ and N₂ adsorption binding sites in the hydrophobic and hydrophilic pores of Cu–MOF by DFT calculation: (a) CH₄ and (b) N₂.

with N₂ molecule is weak due to the unique coordination environment of Cu in the paddle-wheel structure. Furthermore, this MOF has good water and thermal stabilities, as well as regenerability. These results indicate that Cu–MOF might be a potential candidate for the separation of CH₄/N₂ in practical industries.

EXPERIMENTAL SECTION

Materials. All general chemicals reagents and solvents (AR grade) are commercially available and used directly as received without further purification. Cu(NO₃)₂·3H₂O and 1,3,5-benzenetricarboxylic acid (H₃BTC) were derived from Alfa Aesar. Methanol (CH₃OH) was obtained from Sinopharm Chemical Reagent Co. Ltd.

Characterizations. Powder X-ray diffraction (PXRD) data were recorded on a D8 Advance X diffractometer equipped with a Cu sealed tube ($\lambda = 1.54178 \text{ \AA}$). The measurement of a single gas sorption isotherm and the pore structure were performed by a Quantachrome Autosorb-IQ instrument. Thermogravimetric analysis (TGA) was carried out by GA Q50 in an air atmosphere (20 mL/min, from 30 to 800 K with the rate of 5 K/min). The FT-IR spectroscopy data were obtained by the Nicolet 6700 FTIR instrument. Morphology of the material was characterized by Hitachi S-4700. For the breakthrough experiment, the concentration of the outlet gases from the column was analyzed by a gas chromatograph (Shimadzu, GC-2014C) at 298 K and 1.0 bar.

Synthesis of MOFs. The material was synthesized using the method as described in the literature.²³ Cu(NO₃)₂·3H₂O (0.991 g, 4.1 mmol) and H₃BTC (0.862 g, 4.1 mmol) were mixed with CH₃OH (10 mL) and distilled water (10 mL) in a 25 mL Teflon-lined steel autoclave. The reactor was placed in an oven and heated to 383 K for 7 days. After that, the reactor was cooled to room temperature. The obtained blue crystals were filtered and washed several times with CH₃OH solvent.

Gas Adsorption Measurement. The adsorption isotherms of CH₄ and N₂ at 273, 298, and 323 K were measured using a Quantachrome Autosorb-IQ instrument. The sample was degassed at 393 K for 12 h prior to measurement. For each gas adsorption measurement, the weight of the sample is about 600 mg.

Breakthrough Measurement. Five grams of material was packed into the column (10 × 150 mm²) with the void space filled by silica wool and purged with helium (25 mL/min) at 393 K for 6 h. After that, heating and helium purge were stopped until the device was cooled down to room temperature. Then, the mixture of CH₄ and N₂ (CH₄/N₂ = 50:50%) at the total flow rate of 5 mL/min was passed through the column. The concentration of the outlet gases from column was analyzed by a gas chromatograph (Shimadzu, GC-2014C).

Calculation of Adsorption Selectivity. The selectivity of the material was calculated by using the ideal adsorbed solution theory (IAST) based on the isotherm data of the single-component experiment.^{25,26} S_{ij} represents the ideal selectivity of the material, which can be defined as

$$S_{ij} = \frac{q_i/q_j}{y_i/y_j} \quad (1)$$

where q_i and q_j are the adsorbed quantity of the components i and j , respectively, and y_i and y_j are the gas molar fractions of components i and j , respectively.

Working capacity²² was can be defined as

$$N_i^{\text{ads}} - N_i^{\text{des}} \quad (2)$$

Sorbent selection parameter (SSP)²² can be calculated as

$$\text{SSP} = \frac{(S_{i/j}^{\text{ads}})^2}{(S_{i/j}^{\text{des}})} \times \frac{(N_i^{\text{ads}} - N_i^{\text{des}})}{(N_j^{\text{ads}} - N_j^{\text{des}})} \quad (3)$$

where $S_{i/j}^{\text{ads}}$ and $S_{i/j}^{\text{des}}$ are the selectivities of i and j components, respectively, and N_i^{ads} and N_j^{des} are the adsorption capacities of i and j components, respectively. The superscripts of “ads” and “des” represent the adsorption and desorption process, respectively.

Isosteric Heat of Adsorption. The coverage-dependent isosteric heat of adsorption is calculated using the Clausius–Clapeyron equation³³

$$Q_{\text{st}} = \frac{RT_1T_2}{T_2 - T_1} \ln \frac{P_1}{P_2} \quad (4)$$

where R is the molar gas constant (8.314 J/K/mol) and P_i and T_i are the pressure and the temperature of isotherm i , respectively.

Theoretical Calculations. Binding energy of guest molecules with MOF was calculated using the density functional theory (DFT)³⁴ method in Dmol³⁵ of Materials Studio. Generalized gradient approximation with the Perdew–Burke–Ernzerh functional was applied for the calculations, combining the double numerical plus d-functions basis set. Self-consistent field (SCF) calculations were performed, and the convergence criterion is 10^{−5} Ha in energy. To accelerate the SCF convergence, thermal smearing was used with a value of 0.005 Ha to orbital occupation.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b01740.

Calculation of the SSP; calculations of IAST and Henry's law ideal selectivity; single-component adsorption isotherms of CH₄ and N₂ in Cu–MOF at 273 and 323 K; IAST predicted the selectivity of equimolar CH₄/N₂ mixture at 273 and 323 K; N₂ adsorption–desorption isotherm at 77 K with pore size distribution; adsorption heats of CH₄ and N₂ in Cu–MOF; TGA and FT-IR spectra of Cu–MOF; selectivity and adsorption heats of CH₄ and N₂ in various materials; uptake capacity, working capacity, ratio of working capacity, and SSP values of various materials (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: liudh@mail.buct.edu.cn.

ORCID

Dahuan Liu: 0000-0003-1005-3168

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The financial support of the Natural Science Foundation of China (Nos. 21722602, 21978005 and 21576009) is greatly appreciated. We gratefully acknowledge Prof. Jinping Li and Prof. Jiangfeng Yang from Taiyuan University of Technology for the help of breakthrough measurements.

REFERENCES

- (1) Li, L. Y.; Yang, L. F.; Wang, J. W.; Zhang, Z. G.; Yang, Q. W.; Yang, Y. W.; Ren, Q. L.; Bao, Z. B. Highly Efficient Separation of Methane from Nitrogen on a Squarate-Based Metal-Organic Framework. *AIChE J.* **2018**, *64*, 3681–3689.
- (2) Ren, X. Y.; Sun, T. J.; Hu, J. L.; Wang, S. D. Highly enhanced selectivity for the separation of CH₄ over N₂ on two ultramicroporous frameworks with multiple coordination modes. *Microporous Mesoporous Mater.* **2014**, *186*, 137–145.
- (3) Niu, Z.; Cui, X. L.; Pham, T.; Lan, P. C.; Xing, H. B.; Forrest, K. A.; Wojtas, L.; Space, B.; Ma, S. Q. A Metal-Organic Framework Based Methane Nano-trap for the Capture of Coal-Mine Methane. *Angew. Chem., Int. Ed.* **2019**, *58*, 10138–10141.
- (4) Li, Q. Z.; Ruan, M. L.; Zheng, Y. N.; Mei, X. N.; Lin, B. Q. Investigation on the selective adsorption and separation properties of coal mine methane in ZIF-68 by molecular simulations. *Adsorption* **2017**, *23*, 163–174.
- (5) Liu, X. W.; Hu, J. L.; Sun, T. J.; Guo, Y.; Bennett, T. D.; Ren, X. Y.; Wang, S. D. Template-based synthesis of a formate metal-organic framework/activated carbon fibre composite for high-performance methane adsorptive separation. *Chem. - Asian J.* **2016**, *11*, 3014.
- (6) Yang, J. F.; Yu, Q. H.; Zhao, Q.; Liang, J. M.; Dong, J. X.; Li, J. P. Adsorption CO₂, CH₄ and N₂ on two different spacing flexible layer MOFs. *Microporous Mesoporous Mater.* **2012**, *161*, 154–159.
- (7) Liu, X. W.; Guo, Y.; Tao, A. D.; Fischer, M.; Sun, T. J.; Moghadam, P. Z.; Jimenez, D. F.; Wang, S. D. Explosive synthesis of metal-formate frameworks for methane capture: an experimental and computational study. *Chem. Commun.* **2017**, *53*, 11437–11440.
- (8) Guo, Y.; Hu, J. L.; Liu, X. W.; Sun, T. J.; Zhao, S. S.; Wang, S. D. Scalable solvent-free preparation of [Ni₃(HCOO)₆] frameworks for highly efficient separation of CH₄ from N₂. *Chem. Eng. J.* **2017**, *327*, 564–572.
- (9) Yao, K. X.; Chen, Y. L.; Lu, Y.; Zhao, Y. F.; Ding, Y. Ultramicroporous carbon with extremely narrow pore distribution and very high nitrogen doping for efficient methane mixture gases upgrading. *Carbon* **2017**, *122*, 258–265.
- (10) Lokhandwala, K. A.; Pinnau, L.; He, Z. J.; Amo, K. D.; DaCosta, A. R.; Wijmans, J. G.; Baker, R. W. Membrane separation of nitrogen from natural gas: A case study from membrane synthesis to commercial deployment. *J. Membr. Sci.* **2010**, *346*, 270–279.
- (11) Baker, R. W.; Lokhandwala, K. Natural Gas Processing with Membranes: An Overview. *Ind. Eng. Chem. Res.* **2008**, *47*, 2109–2121.
- (12) Luo, J. J.; Zhu, T. Y.; Song, Y. H.; Si, Z. Q. Improved permeability by incorporating polysiloxane in SBS block copolymers for CH₄/N₂ gas separation. *Polymer* **2017**, *127*, 52–65.
- (13) Jia, X. X.; Yuan, N.; Wang, L.; Yang, J. F.; Li, J. P. (CH₃)₂NH-Assisted Synthesis of High-Purity Ni-HKUST-1 for the Adsorption of CO₂, CH₄ and N₂. *Eur. J. Inorg. Chem.* **2018**, *2018*, 1047–1052.
- (14) Yang, J. F.; Li, J. M.; Wang, W.; Li, L. B.; Li, J. P. Adsorption of CO₂, CH₄ and N₂ on 8-, 10-, and 12-Membered Ring Hydrophobic Microporous High-Silica Zeolites: DDR, Silicalite-1, and Beta. *Ind. Eng. Chem. Res.* **2013**, *52*, 17856–17864.
- (15) Wang, X. Q.; Li, L. B.; Yang, J. F.; Li, J. P. CO₂/CH₄ and CH₄/N₂ separation on isomeric metal organic frameworks. *Chin. J. Chem. Eng.* **2016**, *24*, 1687–1694.
- (16) Ruthven, D. M. Past Progress and Future Challenges in Adsorption Research. *Ind. Eng. Chem. Res.* **2000**, *39*, 2127–2131.
- (17) Sircar, S. Basic Research Needs for Design of Adsorptive Gas Separation Processes. *Ind. Eng. Chem. Res.* **2006**, *45*, 5435–5448.
- (18) Mueller, U.; Schubert, M.; Teich, F.; Puetter, H.; Arndt, K. S.; Pastre, J. Metal-organic frameworks-prospective industrial applications. *J. Mater. Chem.* **2006**, *16*, 626–636.
- (19) Wang, K. K.; Li, C. F.; Liang, X. Y.; Han, T. T.; Huang, H. L.; Yang, Q. Y.; Liu, D. H.; Zhong, C. L. Rational construction of defects in a metal-organic framework for highly efficient adsorption and separation of dyes. *Chem. Eng. J.* **2016**, *289*, 486–493.
- (20) Furukawa, H.; Cordova, K. E.; Keeffe, M. O.; Yaghi, O. M. The chemistry and application of metal-organic frameworks. *Science* **2013**, *341*, 974–986.
- (21) Lu, W. G.; Wei, Z. W.; Gu, Z. Y.; Liu, T. F.; Park, J.; Park, J.; Tian, J.; Zhang, M. W.; Zhang, Q.; Gentle, T.; Bosch, M.; Zhou, H. C. Tuning the structure and function of metal-organic frameworks via linker design. *Chem. Rev.* **2014**, *43*, 5561–5593.
- (22) Tong, M. M.; Lan, Y. S.; Yang, Q. Y.; Zhong, C. L. Exploring the structure-property relationships of covalent organic frameworks for noble gas separations. *Chem. Eng. Sci.* **2017**, *168*, 456–464.
- (23) Mohideen, M. H.; Xiao, B.; Wheatley, P. S.; McKinlay, A. C.; Li, Y.; Slawin, A. Z.; Aldous, D. W.; Cessford, N. F.; Duren, T.; Zhao, X. B.; Gill, R.; Thomas, K. M.; Griffin, J. M.; Ashbrook, S. E.; Morris, R. E. Protecting group and switchable pore-discriminating adsorption properties of a hydrophilic-hydrophobic metal-organic framework. *Nat. Chem.* **2011**, *3*, 304–310.
- (24) McHugh, L. N.; McPherson, M. J.; McCormick, L. J.; Morris, S. A.; Wheatley, P. S.; Teat, S. J.; McKay, D.; Dawson, D. M.; Sansome, C. F.; Ashbrook, S. E.; Stone, C. A.; Smith, M. W.; Morris, R. E. Hydrolytic stability in hemilabile metal-organic frameworks. *Nat. Chem.* **2018**, *10*, 1096–1102.
- (25) Myers, A. L.; Prausnitz, J. M. Thermodynamics of mixed-gas adsorption. *AIChE J.* **1965**, *11*, 121–127.
- (26) Walton, K. S.; Sholl, D. S. Predicting multicomponent adsorption: 50 years of the ideal adsorbed solution theory. *AIChE J.* **2015**, *61*, 2757–2762.
- (27) Bae, Y. S.; Snurr, R. Q. Development and Evaluation of Porous Materials for Carbon Dioxide Separation and Capture. *Angew. Chem., Int. Ed.* **2011**, *50*, 11586–11596.
- (28) Kim, M. B.; Yoon, T. U.; Hong, D. Y.; Kim, S. Y.; Lee, S. J.; Kim, S. L.; Lee, S. K.; Chang, J. S.; Bae, Y. S. High SF₆/N₂ selectivity in a hydrothermally stable zirconium-based metal-organic framework. *Chem. Eng. J.* **2015**, *276*, 315–321.
- (29) Maniam, P.; Stock, N. Investigation of Porous Ni-Based Metal-Organic Frameworks Containing Paddle-Wheel Type Inorganic Building Units via High-Throughput Methods. *Inorg. Chem.* **2011**, *50*, 5085–5097.
- (30) Lin, R. B.; Wu, H.; Li, L. B.; Tang, X. L.; Li, Z. Q.; Gao, J. K.; Cui, H.; Zhou, W.; Chen, B. L. Boosting Ethane/Ethylene Separation within Isoreticular Ultramicroporous Metal-Organic Frameworks. *J. Am. Chem. Soc.* **2018**, *140*, 12940–12946.
- (31) Hu, J. L.; Sun, T. J.; Liu, X. W.; Guo, Y.; Wang, S. D. Separation of CH₄/N₂ mixtures in metal-organic frameworks with 1D microchannels. *RSC Adv.* **2016**, *6*, 64039–64046.
- (32) Nguyen, P. K.; Nguyen, H. D.; Pham, H. Q.; Kim, J.; Cordova, K. E.; Furukawa, H. Synthesis and Selective CO₂ Capture Properties of a Series of Hexatopic Linker-Based Metal-Organic Frameworks. *Inorg. Chem.* **2015**, *54*, 10065–10072.
- (33) Wang, K. K.; Huang, H. L.; Liu, D. H.; Wang, C.; Li, J. P.; Zhong, C. L. Covalent Triazine-Based Frameworks with Ultramicropores and High Nitrogen Contents for Highly Selective CO₂ Capture. *Environ. Sci. Technol.* **2016**, *50*, 4869–4876.
- (34) Barone, V.; Casarin, M.; Forrer, D.; Pavone, M.; Sami, M.; Vittadini, A. Role and Effective Treatment of Dispersive Forces in Materials: Polyethylene and Graphite Crystals as Test Cases. *J. Comput. Chem.* **2009**, *30*, 934–939.