Controlling Pore Shape and Size of Interpenetrated Anion-Pillared Ultramicroporous Materials Enables Molecular Sieving of CO₂ Combined with Ultrahigh Uptake Capacity

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Supporting Information

ABSTRACT: The separation of carbon dioxide (CO₂) from hydrocarbons is a critical process for the production of clean energy and high-purity chemicals. Adsorption based on molecular sieving is an energy-saving separation process; however, most of molecular sieves with narrow and straight pore channels exhibit low CO₂ uptake capacity. Here, we report that a twofold interpenetrated copper coordination network with a consecutive pocket-like pore structure, namely, SIFSIX-14-Cu-i (SIFSIX = hexafluorosilicate, 14 = 4,4′-azopyridine, i = interpenetrated) is a remarkable CO₂/CH₄ molecular sieving adsorbent which completely blocks the larger CH₄ molecule with unprecedented selectivity, whereas it has excellent CO₂ uptake (172.7 cm³/cm³) under the ambient condition. The exceptional separation performance of SIFSIX-14-Cu-i is attributed to its unique pore shape and functional pore surface, which combine a contracted pore window (3.4 Å) and a relatively large pore cavity decorated with high density of inorganic anions. Dispersion-corrected density functional theory calculation and neutron powder diffraction were performed to understand the CO₂ binding sites. The practical feasibility of SIFSIX-14-Cu-i for CO₂/CH₄ mixtures separation was validated by experimental breakthrough tests. This study not only demonstrates the great potential of SIFSIX-14-Cu-i for CO₂ separation but also provides important clues for other gas separations.

KEYWORDS: metal−organic frameworks, molecular sieving, gas adsorption, carbon dioxide, methane, separation

INTRODUCTION

The separation of carbon dioxide (CO₂) from methane and relevant hydrocarbons is a critical process for the production of clean energy and high-purity chemicals.1−3 For example, natural gas including shale gas contains methane, ethane, propane, and other impurities like CO₂, sulfur dioxide, and so on.4−5 The existence of CO₂ in natural gas will lower the calorific value and corrode the pipelines, which necessitate a CO₂ removal process.6−9 Hydrocarbons like ethane, ethylene, and propylene produced from steam cracking also inevitably mixed with a small amount of CO₂, which must be removed for purification.10−14 Physiosorption using porous materials as adsorbents is regarded as a promising method for CO₂ separation and capture owing to its low-energy consumption and mild operation condition.15−17 Up to date, a great variety of porous materials such as porous polymers,18−21 zeolites,22,23 carbon materials,24−26 metal−organic frameworks (MOFs) and/or porous coordination polymers (PCPs),15,27−36 and covalent-organic frameworks (COFs)37−41 have been investigated for CO₂ capture and separation. Among these porous materials, MOFs and/or PCPs are prominent because of their diversiform variety, high porosity, and tailorable pore size and pore functionality.42−48 Optimal porous materials for CO₂ separation through physisorption should exhibit both high uptake capacity and high selectivity toward CO₂ over other gases. However, the trade-off between uptake capacity and selectivity of porous materials has been identified as a major obstacle for efficient gas adsorptive separation.49

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Molecular sieving can reach extremely high selectivity because molecules with kinetic diameters larger than the pore will be completely excluded, whereas smaller ones can pass through. However, molecular sieving is very hard to achieve.\(^5\) It requires exquisite control on the structure of materials with intermediate pore apertures, whose size shall be just between the kinetic diameters of the separated molecules. In the system of CO\(_2\) and CH\(_4\) separation, the kinetic diameters of CH\(_4\) and CO\(_2\) are 3.8 and 3.3 Å, respectively, which are extremely close to each other. To our knowledge, only a few of porous materials can sieve CO\(_2\) over CH\(_4\) at near ambient conditions.\(^5\) For instance, Qc-5-Cu-sql-\(\beta\) with the square lattice network and narrow pore size (3.3 Å) adsorbs CO\(_2\) (72.2 cm\(^3\)/cm\(^3\)) whereas it excludes CH\(_4\) at 293 K and 1 bar. By precisely controlling the pore dimension, [Cd\(_2\)L(H\(_2\)O)\(_{\beta}\)\(_\beta\)]\(_2\)SH\(_2\)O\(_\delta\)\(_\delta\) and [Cu(bcppm)H\(_2\)O]\(_\delta\)\(_\delta\) with narrow straight pores also exhibit an obvious size-sieving effect for CO\(_2\) and CH\(_4\)/N\(_2\) with moderate CO\(_2\) capacity of 101.2 and 47.4 cm\(^3\)/bar. By precisely controlling the pore dimension, [Cd\(_2\)L(H\(_2\)O)\(_{\beta}\)\(_\beta\)]\(_2\)SH\(_2\)O\(_\delta\)\(_\delta\) and [Cu(bcppm)H\(_2\)O]\(_\delta\)\(_\delta\) with narrow straight pores also exhibit an obvious size-sieving effect for CO\(_2\) and CH\(_4\)/N\(_2\) with moderate CO\(_2\) capacity of 101.2 and 47.4 cm\(^3\)/bar. However, the CO\(_2\) uptake capacity of these materials is moderate owing to their narrow, consecutive, and straight pore channels that don’t have enough space to hold plentiful CO\(_2\). In other words, these porous materials enable the molecular sieving at the cost of reducing the uptake capacity.

Herein, we report that anion-pillared interpenetrated copper coordination network, SIFSIX-14-Cu-\(i\) (SIFSIX = hexafluoro- arsonate, \(i\) = interpenetrated, also called UTSA-200) is a remarkable CO\(_2\)/CH\(_4\) molecular sieving adsorbent which completely blocks the larger CH\(_4\) molecules, whereas it has excellent CO\(_2\) uptake (172.7 cm\(^3\)/cm\(^3\)) under the ambient condition. The exceptional molecular sieving effect of the interpenetrated porous material is attributed to its unique consecutive pocket-like channel, which has a small pore window and a relatively large pore cavity. Its pore window size of 3.4 Å is between the kinetic diameters of CO\(_2\) and CH\(_4\), so it can sieve CO\(_2\) from the CH\(_4\) with unprecedented selectivity. At the same time, SIFSIX-14-Cu-\(i\) contains high density of electronegative F group in the pore cavity that provides sufficient sites and space for gas storage and enables exceptional CO\(_2\) capacity. The single-component adsorption isotherms of CO\(_2\) and CH\(_4\) on SIFSIX-14-Cu-\(i\) were measured at different temperatures. The binding sites of CO\(_2\) within the material were investigated by simulation studies and experimental diffraction measurements. The excellent performance of SIFSIX-14-Cu-\(i\) for CO\(_2\)/CH\(_4\) separation was validated by column breakthrough experiments.

**RESULTS AND DISCUSSION**

**Structure Descriptions.** An anion-pillared copper coordination network with a doubly interpenetrated structure, SIFSIX-14-Cu-\(i\)\(_{51,62}\) was synthesized (Figure 1a). SIFSIX-14-Cu-\(i\) is a variant of the well-known SIFSIX-2-Cu-\(i\)\(_{15}\) with a smaller aperture size (3.4 Å vs 4.4 Å). We use the shorter linker 4,4’-azopyridine (azpy, 9.0 Å) to replace the 4,4’-dipyridylazacyclene (9.6 Å) with the purpose of shrinking the pore. The organic linkers and metal nodes form the two-dimensional interpenetrated nets, which were pillared by SiF\(_6\)\(^{2-}\) to generate the three-dimensional pcu frameworks. Because of the tiny pore space, the pyridine ring in the organic linker interacts with the fluorine atom in the SiF\(_6\)\(^{2-}\) pillar through C–H···F hydrogen bonding which induces the tilting of pyridine ring (Figures 1b and S1). The tilting of zigzag linker generates a contracted pore window with a size of 3.4 Å (H–H distance) (Figure 1b,c), which has the potential to sieve the molecules of CO\(_2\) and CH\(_4\).

**Figure 1.** Gas adsorption isotherms and structure description of SIFSIX-14-Cu-i. (a) Sketch of the metal node, inorganic pillar, organic linker, and the skeleton structure of SIFSIX-14-Cu-i viewed along the c-axis. (b) Diagrammatic sketch presents a pore of the pocket structure. (c) Packing diagram along the c-axis, showing the pore surfaces of 3D channels highlighted as yellow/gray (inner/outer) curved planes with pore size of 3.4 Å. (The different nets are highlighted in royal blue and gray color for clarity in (a–c); guest molecules are omitted in c for clarity. Color code: Si, yellow; F, green; Cu, blue/purple in different nets.) (d,e) Adsorption isotherms of CO\(_2\) (circle), CH\(_4\) (triangle) and N\(_2\) (square) on SIFSIX-14-Cu-i (d), SIFSIX-2-Cu-i and SIFSIX-3-Ni (e) at 273 K. (f) Comparison of CO\(_2\) and CH\(_4\) adsorption capacity in different molecular sieving materials including SIFSIX-14-Cu-i, Qc-5-Cu-sql-\(\beta\) and [Cd\(_2\)L(H\(_2\)O)\(_{\beta}\)\(_\beta\)]\(_2\)SH\(_2\)O at 293 K.
cm³/g, which is slightly lower than SIFSIX-2-Cu-i (0.31 cm³/g). In brief, SIFSIX-14-Cu-i has a consecutive pocket-like pore structure that is composed of small pore windows and relative large pore cavities (Figure 1b,c). The Brunauer–Emmett–Teller (BET) surface area and framework density of the activated SIFSIX-14-Cu-i structure are 612 m²/g and 1.4175 g/cm³, respectively. The structure and stability of SIFSIX-14-Cu-i were characterized by powder X-ray diffraction (PXRD) and thermogravimetric analysis (TGA) (Figures S2 and S3). The PXRD patterns were verified to match those calculated from single-crystal data, and the framework maintains stability to about 200 °C.

**Gas Adsorption and Separation Behaviors.** The adsorption isotherms of CO₂, CH₄, and N₂ on SIFSIX-14-Cu-i were measured at 273–333 K (Figures 1d, 4d, and S4–S6) and found to be completely reversible without hysteresis. As shown in Figure 1d, although CO₂ and CH₄ have similar kinetic diameters, they exhibit very different adsorption isotherms on SIFSIX-14-Cu-i. At 273 K and 1 bar, only very limited CH₄ (3.8 cm³/g) sorption is noticed but significant CO₂ uptake (172.7 cm³/g) is observed. At 298 K and 1 bar, SIFSIX-14-Cu-i still holds high CO₂ uptake capacity (149.6 cm³/g), which is a remarkable value for CO₂ adsorption in porous materials (Figure S9). The combination molecular sieving effect and high adsorption capacity is attributed to the unique consecutive pocket-like pore channels of SIFSIX-14-Cu-i as depicted in Figure 1b,c. The narrow adsorption pore (3.4 Å, H–H distance) of SIFSIX-14-Cu-i is smaller than the kinetic diameter of CH₄, but little larger than that of CO₂, so it allows the CO₂ molecules to get through but blocks the CH₄. On the other hand, SIFSIX-14-Cu-i has relatively large pore cavity and high density of SIF⁻² anions for gas adsorption which enable outstanding CO₂ capacity. Interestingly, the CO₂ adsorption isotherms are stepwise which imply the existence of guest-induced transition in the flexible framework. As shown in Figure S7, the transition is triggered by a certain amount (about 1 mmol/g) of the CO₂ adsorption. After transition, the framework becomes more obedient to absorb CO₂ so the CO₂ uptake increases rapidly than before which leading to a stepwise adsorption isotherm.

For comparing the separation performance of “SIFSIX” series materials, we selected two benchmark SIFSIX materials including SIFSIX-2-Cu-i and SIFSIX-3-Ni. The CO₂ and CH₄ adsorption and selectivity data are collected in Table 1 and Figures 1e and S10. As shown in Figure 1e, at 273 K and 1 bar, the CO₂ loadings on SIFSIX-14-Cu-i and SIFSIX-2-Cu-i are comparable (172.7 and 173.1 cm³/g, respectively), but the CH₄ uptake on SIFSIX-14-Cu-i (3.8 cm³/g) is significantly lower than that on SIFSIX-2-Cu-i (28.6 cm³/g). We also can see that the CH₄ uptake on SIFSIX-14-Cu-i is much lower than that on SIFSIX-3-Ni (26.5 cm³/g), whereas the CO₂ capacity of SIFSIX-14-Cu-i is nearly twice than that of SIFSIX-3-Ni (94.4 cm³/g). This can be explained by the pore structures of SIFSIX materials. SIFSIX-14-Cu-i and SIFSIX-2-Cu-i have similar pore volumes, which lead to comparable CO₂ uptakes. The pore window size of SIFSIX-14-Cu-i is much smaller than that of SIFSIX-2-Cu-i (3.4 vs 5.2 Å) and even smaller than SIFSIX-3-Ni (4.2 Å). It is small enough to block CH₄ molecules, so the CH₄ loading on SIFSIX-14-Cu-i reduces obviously. Because of the limited pore volume (0.157 cm³/g), SIFSIX-3-Ni has only about half CO₂ capacity of SIFSIX-14-Cu-i. In general, among three “SIFSIX” materials, SIFSIX-14-Cu-i exhibits the best performance with both high CO₂ uptake and high CO₂/CH₄ selectivity. Actually, CO₂ uptake of SIFSIX-14-Cu-i is among the top level of reported MOFs, including Mg-MOF-74 (101.2 cm³/g) and UTSA-16 (47.4 cm³/g) (details in Figure S6).

More importantly, comparing with other benchmark materials with the molecular sieving effect, SIFSIX-14-Cu-i is optimal both on the selectivity and capacity (detailed data see Table 1). These materials all have very low CH₄ loading, whereas CO₂ loading is different. SIFSIX-14-Cu-i has a capacity of 156.6 cm³/g at 293 K and 1 bar (Figure S11), which is much higher than that of Qc-5-Cu-sqβ (72.2 cm³/g), and [Cd₂L(H₂O)]_2·SH₂O (101.2 cm³/g, 293 K), and [Cu(bcppm)H₂O] (47.4 cm³/g, 293 K). Furthermore, comparing the amount of CO₂ adsorption per gram, the advantage of SIFSIX-14-Cu-i (110.5 cm³/g) is more obvious among the molecular sieving materials (such as Qc-5-Cu-sqβ (48.8 cm³/g) and [Cd₂L(H₂O)]_2·SH₂O (47.9 cm³/g)) depicted as in Figure 1f. It is really remarkable that SIFSIX-14-Cu-i does not lose the CO₂ adsorbing capacity while achieving the molecular sieving. It attributes to its consecutive pocket-like pore structure and plenty of anions in the pore surface.

On the basis of previous single-component adsorption data, the CO₂/CH₄ selectivity was evaluated by calculating the gas uptake ratio at 1 bar. As shown in Figure 2a and Table 1, the CO₂ uptake ratio of CO₂/CH₄ on SIFSIX-14-Cu-i at 273 and 298 K is up to 46.7 and 116.1, respectively. To the best of our knowledge, it is the highest value ever reported in porous materials and much higher than SIFSIX-3-Ni (4.3), Zeolite 13X.

### Table 1. Gas Adsorption and Selectivity Results and Comparisons

<table>
<thead>
<tr>
<th>MOFs</th>
<th>S BET (m²/g)</th>
<th>pore size (Å)</th>
<th>CO₂ (cm³/g)</th>
<th>CH₄ (cm³/g)</th>
<th>uptake ratio</th>
<th>CO₂ Qₑ (kJ/mol)</th>
<th>refs</th>
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<tr>
<td>SIFSIX-14-Cu-i</td>
<td>612</td>
<td>3.6 × 3.6</td>
<td>172.7</td>
<td>3.8</td>
<td>46.7</td>
<td>37.7</td>
<td>this work</td>
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<td>4.9 × 4.9</td>
<td>173.1</td>
<td>28.6</td>
<td>6.2</td>
<td>31.9</td>
<td>15</td>
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<tr>
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<td>368</td>
<td>4.2 × 4.2</td>
<td>94.4</td>
<td>26.5</td>
<td>3.6</td>
<td>51.0</td>
<td>63</td>
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<tr>
<td>Molecular Sieving</td>
<td></td>
<td></td>
<td>149.6</td>
<td>1.3/1.8</td>
<td>116.1/84.9</td>
<td>37.7</td>
<td>this work</td>
</tr>
<tr>
<td></td>
<td>SIFSIX-14-Cu-i</td>
<td></td>
<td>156.6</td>
<td>2.4</td>
<td>42.9</td>
<td>36.9</td>
<td>59</td>
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<tr>
<td></td>
<td>Qc-5-Cu-sqβ</td>
<td></td>
<td>72.2</td>
<td>1.9</td>
<td>37.2</td>
<td>36.0</td>
<td>50</td>
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<tr>
<td></td>
<td>[Cd₂L(H₂O)]_2·SH₂O</td>
<td>101.2</td>
<td>2.4</td>
<td>36.9</td>
<td>42.9</td>
<td>36.9</td>
<td>59</td>
</tr>
</tbody>
</table>

*BET surface area calculated from N₂ isotherms at 77 K. *Selectivity calculated by uptake ratio of CO₂/CH₄ at 1 bar. *Qₑ values of CO₂ at low surface coverage. *BET surface area calculated from CO₂ isotherms at 196 K. *At a temperature of 293 K. *The average pore size of the pocket-like pore. Measured in this work.
under similar conditions. The isosteric heat of adsorption ($Q_{st}$) of SIFSIX-14-Cu-i was derived from the isotherm data at 273 and 298 K based on the virial model (Figures 2b and S12). The $Q_{st}$ is 37.7 kJ/mol at zero loading and remains relatively constant with the increasing uptake, which indicates the homogeneous adsorption sites for CO$_2$ molecules. Comparing with SIFSIX-2-Cu-i (31.9 kJ/mol), the $Q_{st}$ value of SIFSIX-14-Cu-i has enhanced, possibly attributable to its relatively narrower pores.

Simulation Studies. To gain a deep understanding of the adsorption properties of gas within SIFSIX-14-Cu-i, molecular simulations of CO$_2$ adsorption were performed using the dispersion-corrected density functional theory (DFT-D) method. Figure 3a,b shows the optimized structure of CO$_2$ adsorption in SIFSIX-14-Cu-i as viewed along the $b$- and $c$-axes of the framework. The simulations reveal that the small window size of 3.4 Å would allow two CO$_2$ molecules to access and get adsorbed in each pore cavity. The electropositive carbon atoms in CO$_2$ molecules are attracted to the SiF$_6^{2-}$ pillaring anions, the calculated distance of O···F interaction is 2.57 Å. The DFT-D calculated binding energy ($\Delta E$) of CO$_2$ molecules on SIFSIX-14-Cu-i is 37.28 kJ/mol. Additionally, the adsorbed CO$_2$ are oriented with the torsion angle of 29.52°, which can be partially attributed to the interaction between the electronegative oxygen atom of CO$_2$ and electropositive hydrogen atom of the linkers. The shortest C=O···H hydrogen bond distance is 2.61 Å (Figure S1). In contrast, the CH$_4$ molecule (3.8 Å) is larger than the pore window (3.4 Å), so it cannot enter the modeled cavities and thereby be excluded. In view of our simulation results, the molecular sieving effect of CO$_2$ over CH$_4$ in SIFSIX-14-Cu-i is strongly supported. Furthermore, we performed experimental neutron powder diffraction measurements to confirm the DFT-D findings. The data of a CO$_2$-loaded sample were collected at 200 K. The CO$_2$ adsorption sites obtained from Rietveld refinement of the neutron powder diffraction data (Figures S13 and S14) are fully consistent with the results of DFT-D calculation. Each CO$_2$ binds at one SiF$_6^{2-}$ anion site and the experimental distance of the O···F bond is $\sim$2.50 Å.

Breakthrough Curve Measurements. To evaluate the feasibility of SIFSIX-14-Cu-i for the CO$_2$/CH$_4$ separation, real-time dynamic breakthrough tests were conducted using CO$_2$/CH$_4$ (50/50, v/v) mixtures as feed. The breakthrough curves for CO$_2$/CH$_4$ (50/50) separation at 273 K is depicted in Figure 4a (for details, see Tables S3 and S4). The curve of SIFSIX-14-Cu-i shows that CH$_4$ breaks through the column immediately, indicating the block-off effect of this material. Nevertheless, CO$_2$ breakthrough on SIFSIX-14-Cu-i occurs at 34.6 min later with the calculated adsorption capacity of 154.6 cm$^3$/cm$^3$ (equivalent to 6901 mmol/L) during $0-\tau_{break}$, correlating well with the CO$_2$ uptake capacity (158.4 cm$^3$/cm$^3$, 273 K, and 0.5 bar) from the single-component adsorption isotherm. These experimental data indicate that SIFSIX-14-Cu-i is a promising material for CO$_2$/CH$_4$ separation. Excellent cycle performance and easy regeneration of adsorbents are essential to reduce the cost of a practical process. Considering this aspect, we performed multiple column breakthrough tests with CO$_2$/CH$_4$ (50/50) mixtures as feed to verify the stable separation ability of SIFSIX-14-Cu-i. As shown in Figures 4b and S15, almost no significant decline is observed on both CO$_2$ capture capacity and breakthrough time.
during 5 cycles, indicating excellent cycle performance of SIFSIX-14-Cu-i. The PXRD also verifies that SIFSIX-14-Cu-i retains its stability after breakthrough experiments (Figure S2). The adsorbent was regenerated by purging the He flow at 10 mL/min through the column after the breakthrough test with the CO2/CH4 (50/50) mixed gas at 273 K and 1 bar. The regeneration curves depicted on Figure 4c indicate that almost all of the CH4 and CO2 are removed after 40 min. CH4 is immediately eluted by helium because it’s excluded by SIFSIX-14-Cu-i. CO2 takes a little longer to elute because of the interaction with adsorbent, but 40 min is still a short time for MOF material regeneration at 273 K. Furthermore, from Figure 4d, we can see that the CO2 adsorption isotherms of SIFSIX-14-Cu-i have strong response to the temperature increase. This is because the interactions between the framework and guests at low temperature are more stable than at high temperature, so the CO2 uptake increases more rapidly and reaches the triggering amount more easily. As shown in Figure S8, we can see that under the same CO2 triggering amount, the higher the temperature, the greater the transition pressure is. Therefore, under the same pressure, the CO2 capacity at low temperature is higher than that of at high temperature. As a result, when the temperature increases from 273 to 313 K, it resulted in 54% decrease in CO2 uptake at 0.5 bar. The decreased value even reaches to 87% when the temperature changes from 273 to 333 K. It indicates that CO2 desorption can occur under mild temperature conditions and SIFSIX-14-Cu-i is very easy to be regenerated.

## CONCLUSIONS

In summary, this work reports that an anion-pillared interpenetrated ultramicroporous material, SIFSIX-14-Cu-i, is a remarkable molecular sieve for CO2/CH4 separation with unprecedented selectivity (uptake ratio: 111.6) and excellent CO2 uptake capacity (172.7 cm³/cm³, at 273 K and 1 bar). This work also shows that precisely controlling the pore shape and size of the MOF structure to form consecutive pocket-like pore channels is an effective strategy to simultaneously achieve the size-sieving effect and high gas uptake capacity. In SIFSIX-14-Cu-i, the narrow pore window of 3.4 Å blocks off the CH4, whereas it allows CO2 to pass through the pore channels. Simultaneously, the abundant inorganic anions in relatively large pore cavity enable exceptional CO2 uptake capacity. Therefore, SIFSIX-14-Cu-i exhibits unprecedented selectivity and capacity for CO2/CH4 separation. The isosteric heat of CO2 (37.7 kJ/mol) on SIFSIX-14-Cu-i is relatively low, which enables facile regeneration conditions. The excellent separation performance of SIFSIX-14-Cu-i establishes it as a benchmark for CO2/CH4 separation and indicates that SIFSIX-14-Cu-i is a promising candidate for CO2 separation. Additionally, this study provides useful clues to simultaneously achieve molecular sieving and high uptake capacity in porous materials for other important gas separations.

## ASSOCIATED CONTENT

* Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.8b03358.

Experimental sections including the descriptions of materials needed and experimental methods such as the synthesis of SIFSIX-14-Cu-i, characterization techniques, gas adsorption measurements, calculations of isosteric heat of adsorption, density functional theory calculations, neutron diffraction experiments, and column breakthrough experiments for CO2/CH4 gas mixture (PDF)
Langmuir−Freundlich parameters fit for CO2 and CH4 in SIFSIX-14-Cu-i at 273 and 298 K; breakthrough calculations for the separation of CO2/CH4 mixture containing 50% CO2 at 273 K; schematic picture showing the DFT-D optimized CO2 adsorption configuration in SIFSIX-14-Cu-i; comparisons of PXRD patterns; TGA curves of SIFSIX-14-Cu-i; adsorption isotherms of CO2 and CH4 on “SIFSIX” materials; comparison of CO2 uptake for various MOF materials at 298 K and 1 bar; virial fit of CO2 isotherms of SIFSIX-14-Cu-i; cycling column breakthrough curves of SIFSIX-14-Cu-i for CO2/CH4 separations (50/50, v/v) at 273 K and 1 bar; schematic illustration of the apparatus for the breakthrough experiments; neutron diffraction structure of CO2/SIFSIX-14-Cu-i (CIF).

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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.

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**REFERENCES**
(22) Bae, T.-H.; Hudson, M. R.; Mason, J. A.; Queen, W. L.; Dutton, J. J.; Sumida, K.; Micklash, K. J.; Kaye, S. S.; Brown, C. M.; Long, J. R. Evaluation of Cation-Exchanged Zeolite Adsorbents for Post-
Research Article

Ligands and Exceptionally High Gas-Uptake Capacity of CO2 by Dual Functionalization of a Rht-Type Metal-Organic Framework


