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Cite this: *Inorg. Chem. Front.*, 2023, 10, 3015Design of a robust rod-packing scandium–organic framework for C₂H_x/CO₂ separation, CO₂ storage, and catalytic CO₂ cycloaddition†

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The exploration of efficient CO₂ capture and conversion techniques is of great importance for global sustainable development. Herein, a novel bi-microporous Sc-MOF, named [Sc₃(NTB)₂(CH₃COO)₃] (SNNU-616-Sc, NTB = nitrilotribenzoic acid), was successfully designed and utilized for CO₂ storage and catalytic conversion. The linear [Sc₃(COO)₆] trinuclear clusters were linked by triple acetate anions into 1D chains, which were further extended by NTB linkers and interleaved to produce the 3D robust rod-packing Sc-MOF with two types of open channels of about 12 Å and 3.8 Å, respectively. Notably, the bare N atom from NTB ligands can not only act as active sites to adsorb CO₂ molecules, but also provide Lewis basic sites for the CO₂ fixation reaction. Together with the high framework stability and two types of microporous open channels, SNNU-616-Sc shows high adsorption selectivity to effectively separate CO₂ from CO₂–C₂H_x binary mixtures (C₂H_x = acetylene, C₂H₂; ethylene, C₂H₄; ethane, C₂H₆), and a CO₂ storage capacity of 30 mmol g^{−1} (273 K and 29 bar), which surpasses most MOF adsorbents. Moreover, SNNU-616-Sc can also serve as an efficient recyclable catalyst for CO₂ fixation with epoxides in the presence of tetrabutylammonium bromide as a co-catalyst without any organic solvent under mild conditions. Particularly, for the catalytic reaction of CO₂ cycloaddition with epoxide bromopropane, the yields of cyclic carbonates can reach up to 97.5% with the selectivity higher than 98% and a conversion of 99%.

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Introduction

The greenhouse gas carbon dioxide is the main cause of global warming, and its excessive emissions caused by the combustion of fossil fuel can bring about a series of serious environmental issues, such as extreme weather, ocean acidification, and the greenhouse effect.^{1,2} It is extremely critical to develop efficient technologies for the mitigation of CO₂ emission to tremendously reduce the energy crisis and concurrently diminish environmental issues.^{3–5} In order to achieve this purpose, many contributions have been made by researchers in various fields in recent years.^{6,7}

On the one hand, physical capture technology for CO₂ molecules using porous solid adsorbents and the selective separation of CO₂ from the C₂-hydrocarbons produced from

industrial manufacture^{8–10} have attracted researchers' particular interest, as well as developing a series of materials for selective CO₂ capture and separation from C₂-hydrocarbons (C₂H₂, C₂H₄ and C₂H₆).^{11–18} On the other hand, to face environmental problems, converting CO₂ to value-added chemical products for CO₂ aftertreatment that can achieve a carbon-neutral energy cycle in the environment has also raised considerable concerns.^{2,19} Considering that the multifunctional applications of cyclic carbonates, such as solvents, degreasers, electrolytes in lithium-ion batteries, and precursors for the synthesis of fine chemicals and various polycarbonates,^{20,21} adding the excellent properties of stability and low toxic, the conversion of CO₂ into cyclic carbonate becoming the most promising strategies for CO₂ fixation.²² However, it is challenging to develop efficient, economical, and recyclable heterogeneous catalysts for CO₂ conversion because of the high thermodynamic energy barrier for the inert C=O bond of CO₂ molecules. Summing up the above, developing a kind of efficient CO₂ capture and conversion technique with mild operating conditions and low energy consumption would decrease the global energy demand and carbon emission.

In recent decades, metal–organic frameworks (MOFs), a kind of promising crystalline porous material constructed

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from functionally organic linkers coupled with metal ions/clusters, have drawn much attention due to their high specific surface area, excellent porosity, regular pore systems, good chemical stability, and various topologies.^{23–31} Considering the exploitation of new absorbents, MOF materials are undoubtedly used as a candidate to ease the emission of greenhouse gases due to the advantages above and play important roles in catalyzing CO₂ cycloaddition with epoxides in the CO₂ fixation reaction.^{32–34}

Given all this, a novel highly stable bi-microporous Sc-MOF (SNNU-616-Sc) with bare Lewis basic nitrogen sites was successfully synthesized to develop efficient CO₂ capture and conversion materials. Thanks to the synergistic effects of extra-stability, open N sites and bi-microporosity, SNNU-616-Sc exhibits top-level CO₂ storage capacity and efficient separation ability for the binary mixture of CO₂–C₂-hydrocarbons. Moreover, 1D channels with a size of about 12 Å in this structure can improve the mass transfer rate of the substrate during the catalytic reaction, which makes the SNNU-616-Sc material an efficient recyclable catalyst for CO₂ fixation with epoxides. And the possible reaction mechanism for the catalytic reaction of CO₂ cycloaddition was also discussed.

Experimental section

Materials and methods

Sc(NO₃)₃·9H₂O, nitrilotribenzoic acid (H₃NTB), *N,N*-dimethylformide (DMF), acetonitrile (CH₃CN), and acetic acid (CH₃COOH) were from commercial sources without further purification. Powder X-ray diffraction (PXRD) data were collected on a MiniFlex 600 X-ray diffractometer over the 2θ range of 5–50° using Cu Kα radiation at room temperature. Thermogravimetric analyses (TGA) were carried out in the range of 25–900 °C using an HCT-1 thermal analyzer with a heating rate of 2 °C min^{−1} under a N₂ atmosphere. The high pressure gas adsorption performance for CO₂ was analyzed on a BSD-PH high pressure gas sorption analyzer. Gas adsorption isotherms under 1 bar were obtained by using a 3-Flex surface-area and pore-size analyzer, and CO₂, C₂H₄, C₂H₂, C₂H₆ and N₂, and all gases used in the adsorption experiment were of 99.99% purity. Breakthrough experiments were conducted on a home-built dynamic gas breakthrough set-up.

Synthesis

Synthesis of [Sc₃(NTB)₂(CH₃COO)₃] (SNNU-616-Sc). NTB (9 mg, 0.024 mmol) and Sc(NO₃)₃·9H₂O (11 mg, 0.048 mmol) were dissolved in a mixed solution of 2 mL DMF and 2 mL CH₃CN in a 25 mL glass vial, and then 0.5 mL of CH₃COOH were added to this solution and sealed. After sonication for 10 minutes, the raw materials were completely dissolved to obtain a clear solution, and then the vial was placed into the oven and heated to 120 °C for 6 days. After the temperature dropped to room temperature, yellowish block crystals of SNNU-616-Sc were obtained and washed with fresh DMF. The crystal photo of the optical microscope is shown in Fig. S1.†

X-Ray single crystal structure determination

The diffraction data of the single crystal sample for SNNU-616-Sc were collected using a Bruker APEX-II CCD with GaKα (λ = 1.34139) radiation at 170 K. The structure was solved and refined by direct methods using the SHELXS program. All non-hydrogen atoms were refined anisotropically. The detailed crystallographic data and the structure refinement parameters of SNNU-616-Sc are summarized in Table S1.† Selected bond lengths and bond angles are given in Table S2.†

Gas adsorption

Before the measurements of gas adsorption, samples were exchanged with fresh pentane solvent and vacuum heated at 393 K for 10 h to obtain activated MOF samples. In order to evaluate the permanent porosity of SNNU-616-Sc, N₂ adsorption measurements were conducted at 77 K. Gas adsorption measurements of activated samples for single components (CO₂, C₂H₄, C₂H₂, and C₂H₆) at different temperatures (273 K, 283 K, and 298 K) were performed to evaluate the feasibility of SNNU-616-Sc MOF as an adsorbent material to separate CO₂ from the CO₂–C₂H_x mixtures. High pressure gas adsorption performance analysis for CO₂ was conducted at different temperatures to evaluate the storage ability of SNNU-616-Sc.

Breakthrough experiments

To further verify the actual binary CO₂–C₂-hydrocarbon separation performance, breakthrough column experiments were conducted for activated SNNU-616-Sc. About 500 mg of MOF samples were filled in a stainless-steel column (a length of 12 cm, an inner diameter of 0.44 cm, an external diameter of 0.6 cm), and helium was passed with the flow rate of 20 mL min^{−1} under ambient pressure at room temperature for 12 h to activate further. Subsequently, a CO₂–C₂H_x (50/50) mixture gas was passed into the column. Before each testing, a helium flow of 30 mL min^{−1} had to be maintained for 2–3 h to remove the air and residual gas molecule from the column.

Catalytic CO₂ cycloaddition

Before the catalytic trials, SNNU-616-Sc was activated at 393 K under high vacuum (10^{−6} Torr) for 10 h. The activated-MOF catalyst (20 mg), epoxide substrates (20 mmol), and *n*Bu₄NBr (32 mg, 0.1 mmol) were placed in a Teflon sample holder inside a stainless-steel reactor. Before the catalytic reactions, the system was filled with CO₂ to get rid of the residual air and then the reactor was sealed and pressurized with CO₂ until 0.8 MPa, and the reactions proceeded at 80 °C for 8 h under stirring. After the catalytic reaction, the reactor was cooled in a water bath, and then ethyl acetate was added into the reactor and the product was taken out. The as-obtained suspension was finally centrifuged to obtain the liquid supernatant and diluted with ethyl acetate. After that, the product was analysed by gas chromatography with a flame ionization detector. For the recycling tests, the supernatant liquid was carefully removed after each catalytic run, and the solid catalyst was

washed with acetone and dried to remove all volatile compounds before reusing for further catalytic cycles.

Results and discussion

Structural analysis

Single crystal X-ray diffraction analysis revealed that SNNU-616-Sc crystallizes in the trigonal system, space group $R\bar{3}$. Each Sc(III) atom connects six O atoms to form an octahedral coordination model (Fig. 1a), and adjacent three Sc(III) atoms are linked by six carboxylates from six NTB organic linkers to afford a linear $[\text{Sc}_3(\text{COO})_6]$ trinuclear cluster. As shown in Fig. 1b, each NTB ligand connects three linear trinuclear clusters. Each linear trinuclear motif is bridged by three acetate anions, generating a 1D metal-organic chain (Fig. 1d). Three neighbour 1D chains were further connected by NTB linkers (Fig. 1c) in different directions, and thus interleaved to produce the 3D architecture of SNNU-616-Sc (Fig. 1e and f). Notably, two types of 1D channels with different sizes are observed along the *c*-axis direction, which are larger hexagonal and smaller triangular channels with their sizes of about 12 Å and 3.8 Å, respectively (Fig. 1e). Furthermore, the 1D Sc-carboxylate chains can be regarded as rod-like secondary building units, which make SNNU-616-Sc a novel rod-packing metal-organic framework.

It is noted that the small pore with a size of 3.8 Å is obviously fitting for selective CO_2 adsorption (CO_2 , $3.18 \times 3.33 \times 5.36 \text{ Å}^3$; C_2H_2 , $3.32 \times 3.34 \times 5.7 \text{ Å}^3$; C_2H_4 , $3.28 \times 4.18 \times 4.84 \text{ Å}^3$; C_2H_6 , $4.08 \times 3.81 \times 4.82 \text{ Å}^3$).³⁵ Combined with the bare nitrogen atoms as efficient adsorptive sites for CO_2 molecules, SNNU-616-Sc should be a good candidate for CO_2 adsorption and separation applications under low pressure. The other pore of about 12 Å is large enough to facilitate not only high-pressure storage for CO_2 , but also rapid diffusion of molecules inside the pores, which can be expected to offer a confined

space to accelerate the mass transfer and facilitate the catalytic reaction. Clearly, SNNU-616-Sc has great potential as a tri-functional material for $\text{C}_2\text{H}_x/\text{CO}_2$ separation, CO_2 storage, and catalytic CO_2 fixation.

Stability measurements and porosity characterization

The phase purity of the as-synthesized and activated SNNU-616-Sc MOF samples was confirmed by PXRD measurements (Fig. 2a). The chemical stability was measured by the treatment of MOF samples (30 mg) in solution (10 mL) with different pH values. The PXRD patterns of the as-synthesized and treated MOF samples matched well with the simulated pattern from the data of single crystal X-ray diffraction. These results indicated that SNNU-616-Sc can keep the skeleton intact for more than 48 h in the solutions with a wide pH value range from 3 to 11. The TGA curves (Fig. S2†) showed that the main temperature points of collapse for the SNNU-616-Sc sample before and after solvent exchange were similar. At the very beginning, the weight loss for the solvent-exchanged sample was observed below 373 K because of the loss of solvent molecules. After that, the skeleton was stable up to about 720 K under a N_2 atmosphere and the framework will collapse over this temperature, which confirms the high thermal stability of SNNU-616-Sc.

N_2 adsorption-desorption isotherms at 77 K confirmed that SNNU-616-Sc has excellent textural properties and exhibits permanent microporosity, as evidenced by reversible type I adsorption isotherms (Fig. 2b). The pore size distributions (PSD) determined by non-local density functional theory (NLDFT) are presented in Fig. 2b (inset). Two main types of pore sizes are observed, which are basically in accordance with the results indicated by the single crystal structure. Moreover, the Brunauer-Emmett-Teller specific surface area calculated from N_2 adsorption isotherms is $1398 \text{ m}^2 \text{ g}^{-1}$ and the pore volume is $0.87 \text{ cm}^3 \text{ g}^{-1}$ for SNNU-616-Sc, which further indicate the great adsorption ability because the adsorption ability of the materials for CO_2 largely depends on the specific surface area and the micropore volume of the adsorbent.³⁶ In comparison to the reported MOF materials, the BET surface area of SNNU-616-Sc is less than those of MOF-177 ($4508 \text{ m}^2 \text{ g}^{-1}$),³⁷ ZJU-195a ($1722 \text{ m}^2 \text{ g}^{-1}$),³⁸ and MOF-505 ($1547 \text{ m}^2 \text{ g}^{-1}$),³⁷ and but higher than those of many famous reported MOF materials, such as MIL-53 (Cr) ($1197 \text{ m}^2 \text{ g}^{-1}$),³⁹ UPC-110

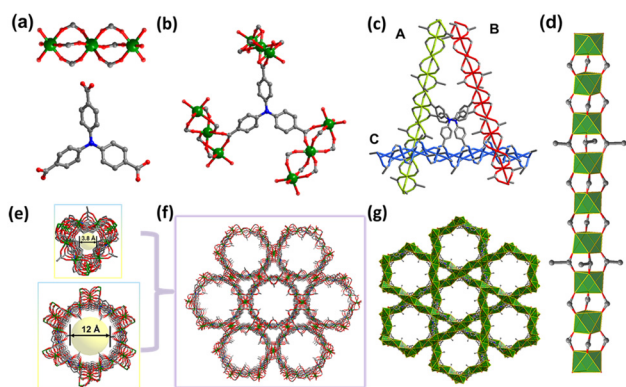


Fig. 1 The structures of SNNU-616-Sc: (a) the linear $[\text{Sc}_3(\text{COO})_6]$ trinuclear cluster; (b) the linkage between $[\text{Sc}_3]$ -clusters and the NTB ligand; (c) the distribution of three 1D chains from different directions; (d) the detailed structure of the 1D chain extended by acetate anions and $[\text{Sc}_3]$ -clusters; (e) two types of 1D open channels with different sizes; (f) and (g) the 3D framework viewed along the *c*-axis direction.

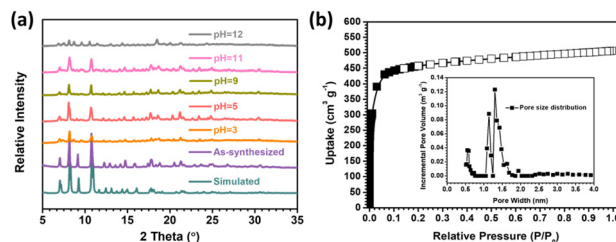


Fig. 2 (a) PXRD patterns for SNNU-616-Sc after different treatments; (b) N_2 adsorption-desorption isotherms at 77 K and the pore size distributions for SNNU-616-Sc.

(1384 m² g⁻¹),⁴⁰ SNNU-45 (1007 m² g⁻¹),⁴¹ and NKMOF-1-Ni (382 m² g⁻¹).⁴²

Gas adsorption

The single-component gas adsorption experiments for CO₂, C₂H₄, C₂H₂, and C₂H₆ were first conducted at different temperatures to explore the CO₂ adsorption and separation performance for SNNU-616-Sc. According to Fig. 3, the CO₂ uptake is 36.3 cm³ g⁻¹ at 298 K and 1.0 bar. Under the same conditions, these values for C₂H₄, C₂H₂, and C₂H₆ are 69.6, 76.3, and 77.7 cm³ g⁻¹, respectively. Obviously, SNNU-616-Sc shows much higher uptake capacity for C2-hydrocarbons than for CO₂. In addition, the steeper adsorption curves of C₂H₄, C₂H₂, and C₂H₆ in the range of low pressure were reflected in a wide range of temperatures from 273 K to 298 K, which indicate stronger interactions with the MOF skeleton and indicate great potential for the separation of CO₂ molecules from the C2-hydrocarbons.

The adsorption heat (Q_{st}) in SNNU-616-Sc was further calculated based on the virial equations (eqn (S1) and (S2)†) to evaluate the binding strength between the MOF and gas molecules. The value of adsorption heat for CO₂ at zero-coverage (20.3 kJ mol⁻¹) is much lower than the values of C₂H₄ (27 kJ mol⁻¹), C₂H₂ (28.7 kJ mol⁻¹), and C₂H₆ (27.5 kJ mol⁻¹) (Fig. 4a and S3†). These results indicate stronger interactions with the MOF skeleton for C₂H_x than CO₂ molecules, which are line with the adsorption curves under lower pressure. In addition, the $-Q_{st}$ value at zero-coverage of CO₂ is less than those of many best CO₂-uptake MOFs such as UTSA-74a (25 kJ mol⁻¹),⁴³ NKMOF-1-Ni (40.9 kJ mol⁻¹),⁴² JCM-1 (33.4 kJ mol⁻¹),⁴⁴ and JXNU-5 (25.2 kJ mol⁻¹),⁴⁵ indicating the low regenerative energy consumption of SNNU-616-Sc during the process of recycling.

The ideal adsorbed solution theory (IAST) was applied to calculate the separation performance for binary CO₂-C₂H_x mixtures. The adsorption isotherms at 298 K were fitted by the

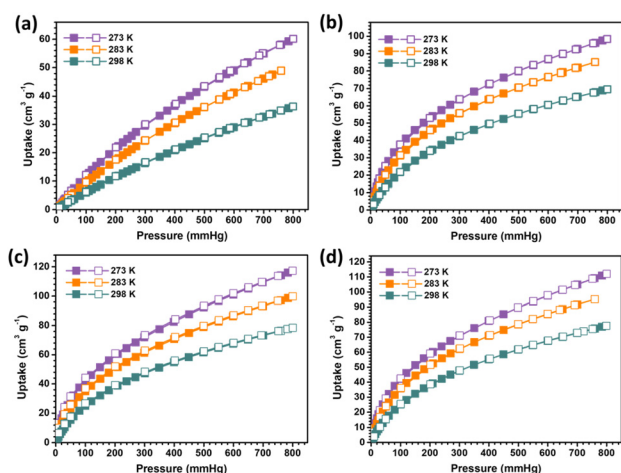


Fig. 3 The gas adsorption isotherms at different temperatures: (a) CO₂; (b) C₂H₄; (c) C₂H₂; and (d) C₂H₆.

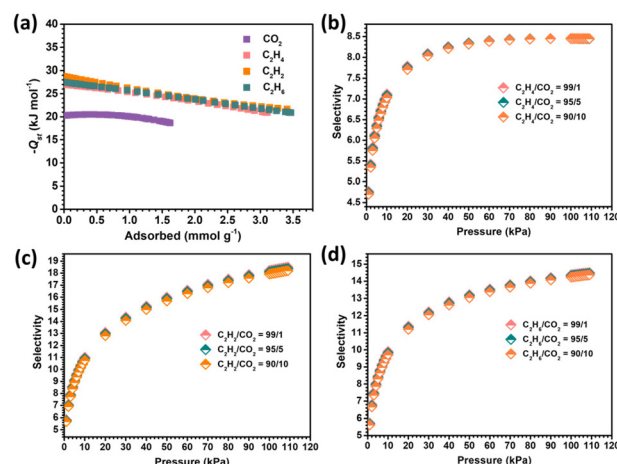


Fig. 4 The calculated adsorption enthalpy for different gases (a), and the IAST separation selectivity at 298 K in SNNU-616-Sc for C₂H₄/CO₂ (b), C₂H₂/CO₂ (c), and C₂H₆/CO₂ (d).

Langmuir-Freundlich equation (eqn (S3)†). As shown in Fig. S4,† the calculated equimolar mixed gas selectivity values of C₂H₄/CO₂, C₂H₂/CO₂, and C₂H₆/CO₂ at 298 K and 1.0 bar are 8.4, 16.5, and 13.5, respectively. The C₂H_x/CO₂ separation ability for different components at 298 K was further calculated (Fig. 4b-d), which shows that with the increase of pressure, the selectivity values increase. This can be attributed to the lateral interactions between CO₂ molecules that were enhanced as the mixture pressure increased.⁴⁶ Particularly, one percent of CO₂ in the binary mixture of C₂H_x/CO₂ still show good separation selectivity, indicating the excellent ability of removing trace CO₂ from the CO₂-C₂H_x mixtures. In general, SNNU-616-Sc has good separation potential to remove CO₂ from the binary mixture of CO₂-C2-hydrocarbons.

Breakthrough experiments

To confirm the practical separation performance of SNNU-616-Sc for the CO₂-C₂H_x mixture, breakthrough experiments were conducted. The binary mixture of CO₂-C₂H_x was injected into a packed column with a flow rate of 2.0 mL min⁻¹ at 298 K to evaluate the separation performance. As depicted in Fig. 5a, the CO₂ molecule broke through the bed quickly after feeding the gas mixture into the fixed adsorption column, while the detection time for C₂H₄, C₂H₂, and C₂H₆ is later than that of CO₂ for these three kinds of binary mixtures, showing that the component of C2-hydrocarbons can remain for a longer time in comparison to the CO₂ molecules in the breakthrough column. According to the breakthrough curves, CO₂ molecules broke through the column at a time of 14.7 min g⁻¹, whereas the time for C₂H₄, C₂H₂, and C₂H₆ was retained in the adsorption bed for 32.7, 31.6, and 34.9 min g⁻¹, respectively, which indicate the stronger interaction between C2-hydrocarbons and the skeleton of SNNU-616-Sc than that of CO₂, in line with the results of adsorption enthalpy. And the breakthrough time gaps for these three kinds of binary mixtures (C₂H₄/CO₂, C₂H₂/CO₂, C₂H₆/CO₂) are similar to each other, which indicate an

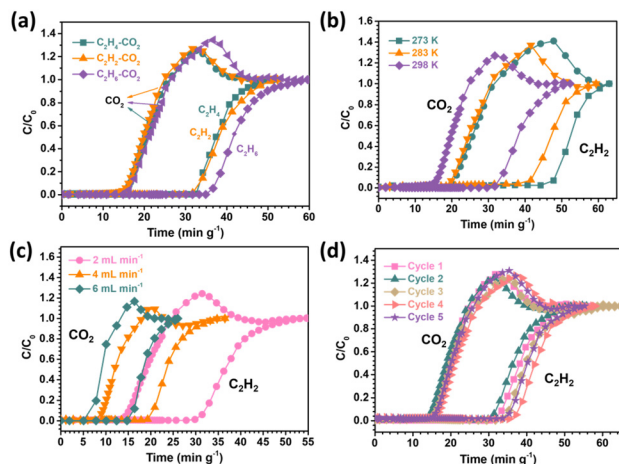


Fig. 5 Breakthrough curves of SNNU-616-Sc under 1 bar for three equimolar mixtures at 298 K with the flow rate of 2 mL min⁻¹ (a), the C₂H₂/CO₂ mixture at different temperatures with a flow rate of 2 mL min⁻¹ (b), the C₂H₂/CO₂ mixture with different flow rates at 298 K (c), and five recycling breakthrough curves for C₂H₂/CO₂ at 298 K with a flow rate of 2 mL min⁻¹ (d).

excellent separation performance based on the porous adsorbent material SNNU-616-Sc. The actual capture amount of four kinds of gases calculated from the breakthrough curves (eqn (S5) and (S6)†) was 0.89, 1.7, 1.75, and 1.9 mmol g⁻¹ for CO₂, C₂H₄, C₂H₂, and C₂H₆, respectively. And the separation factors for C₂H₄/CO₂, C₂H₂/CO₂, and C₂H₆/CO₂ were 1.91, 1.97 and 2.13. Moreover, the purity of the obtained CO₂ from the three mixtures is above 99.5%.

Moreover, the breakthrough experiments of the C₂H₂/CO₂ binary mixture under different conditions were further conducted to explore the effects of temperature and gas flow rate on the separation performance in actual application. As shown in Fig. 5b, the separation interval time of SNNU-616-Sc for C₂H₂/CO₂ is 15.8 min g⁻¹ at 298 K and 1 bar, which increases with the decreasing temperature. The separation time is shorter than that of reported materials such as JCM-1,⁴⁴ UTSA-74a,⁴⁷ and FJU-90a,⁴⁸ and comparable to the benchmark ZJUT-2a,⁴⁹ and UPC-200(Al)-F-BIM.⁵⁰ At 283 K and 273 K, the separation interval times reach 21.2 min g⁻¹ and 25.4 min g⁻¹, respectively. On the other hand, when the flow rate decreases, the separation interval time increases clearly, but when the gas flow rate increases, a shorter separation interval time and smaller transfer mass were observed (Fig. 5c). Even with a flow rate of 6 mL min⁻¹, the C₂H₂/CO₂ separation interval time still is about 10 min g⁻¹.

Ideal gas adsorbents should have good recyclability in practical industrial applications. Five successive C₂H₂/CO₂ dynamic breakthrough experiments were carried out on SNNU-616-Sc at 298 K and 1 bar with a flow rate of 2 mL min⁻¹ to evaluate the recyclability. As shown in Fig. 5d, almost constant breakthrough curves indicate its outstanding recyclability and stability. Furthermore, the breakthrough curves at different temperatures for C₂H₄/CO₂ and C₂H₆/CO₂ were also

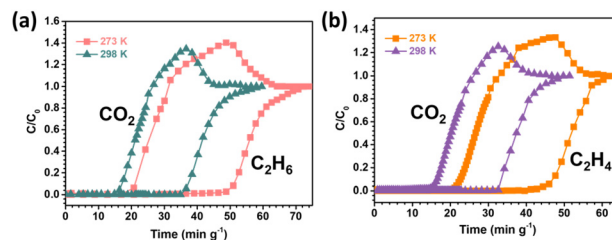


Fig. 6 The breakthrough curves at different temperatures under 1 bar with the flow rate of 2 mL min⁻¹ for C₂H₆/CO₂ (a) and C₂H₄/CO₂ (b).

evaluated and are depicted in Fig. 6. Similar to the C₂H₂/CO₂ mixture, the separation interval time increases to about 30 and 25 min g⁻¹ for C₂H₆/CO₂ and C₂H₄/CO₂ mixtures at 273 K. In our opinion, the smaller triangular channels with a size of 3.8 Å in the structure of Sc-MOF should mainly contribute to the prominent C₂H_x/CO₂ separation performance, which surpasses many famous MOF adsorbents and makes SNNU-616-Sc a great adsorbent for practical separation in industrial applications.

High-pressure CO₂ storage

The single-component CO₂ adsorption isotherm of SNNU-616-Sc has no tendency of gentle curve in comparison to the other three C2-hydrocarbon gases from 0 to 1 bar, which indicates that SNNU-616-Sc may be can adsorb much more CO₂ under higher pressure. At the same time, taking the high BET specific surface area (1398 m² g⁻¹) and larger pore size of 1D hexagonal channels (12 Å) into account, SNNU-616-Sc should be more propitious to high-pressure CO₂ storage. High-pressure CO₂ adsorption results at different temperatures for SNNU-616-Sc show that the storage capacity can reach as high as 30 mmol g⁻¹ (672.2 cm³ g⁻¹ and 48.8 wt%) at 273 K and 29 bar (Fig. 7a and Table S4†), which is slightly lower than the performance of MFM-160a (32 mmol g⁻¹, 19.8 bar) and superior to most MOFs reported at 273 K (Fig. S7†), such as MIL-125-Ti (10.761 mmol g⁻¹, 9.8 bar),⁵¹ β-Zn (8 mmol g⁻¹, 28 bar),⁵² MIX-MIL-125-Ti (7.71 mmol g⁻¹, 9.8 bar),⁵¹ MOF-74-Mg (~7 mmol g⁻¹, 30 bar),⁵³ MFC-1 (6.7 mmol g⁻¹, 30 bar),⁵³ MIL-100-Fe (0.62 mmol g⁻¹, 30 bar),⁵³ and MMC1 (~0.6 mmol g⁻¹, 30 bar).⁵³ At room temperature, SNNU-616-Sc still can take up CO₂ of 17.1 mmol g⁻¹ (384.3 cm³ g⁻¹, 29 bar), which was competitive with many famous MOFs under the same con-

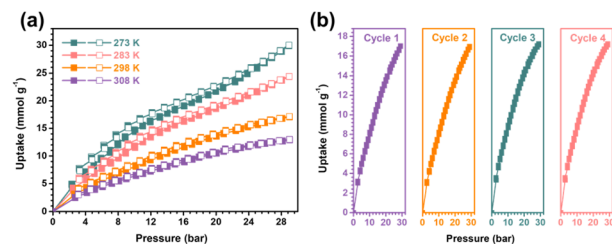


Fig. 7 The high-pressure CO₂ adsorption-desorption curves at different temperatures (a) and the recyclability results (b) at 298 K.

ditions like MOF-505 (18 mmol g⁻¹, 30 bar),³⁷ MIL-101-Cr (14.38 mmol g⁻¹, 40 bar),⁵⁴ MIL-53-Cr (10.6 mmol g⁻¹, 25 bar),³⁹ and MIL-53-Al (9.5 mmol g⁻¹, 25 bar).⁵⁵ Besides, SNNU-616-Sc displays excellent reusability for CO₂ storage under at least five regeneration conditions (Fig. 7b).

GCMC simulations

GCMC simulations were further adopted for SNNU-616-Sc to investigate the probable adsorption sites of CO₂ and C₂-hydrocarbons in the MOF skeleton. As shown in Fig. S8,† the probable sites of CO₂ molecules in SNNU-616-Sc are mainly distributed in triangular channels with a suitable pore size, and the second sites are distributed in the surroundings of the N atom sites from the NTB ligands. SNNU-616-Sc shows three same binding site distribution toward C₂H₂, C₂H₄, and C₂H₆, in which the first two adsorptive sites are the same as for CO₂ molecules. The third sites are within the larger hexagonal channels. So, the number of adsorptive sites for C₂-hydrocarbons is clearly more than those for CO₂ molecules in the structure of SNNU-616-Sc, combined with the suitable pore volume and the higher strength of the interaction between C₂ hydrocarbons and the skeleton than the CO₂ molecules, and further supports the efficient separation performance of CO₂ molecules from C₂H_x/CO₂ mixtures.

The difference in the interactions between guest molecules and the MOF skeleton in the SNNU-616-Sc may arise from the Lewis basic bare N sites. The binding sites of CO₂, C₂H₄, C₂H₂ and C₂H₆ were further evaluated by modelling studies. The distances of C–H...N for C₂-hydrocarbons (C₂H₄, C₂H₂, and C₂H₆) and O=C...N for CO₂ molecules were obtained. As given in Fig. 8, the O=C...N distance for CO₂ molecules (5.05 Å) is markedly longer than the C–H...N distances for C₂-hydrocarbons (C₂H₄, 4.4 Å; C₂H₂, 4.98 Å; C₂H₆, 4.19 Å), showing stronger interactions of C₂-hydrocarbons than CO₂, which also

offers theoretic support for the effective CO₂-C₂-hydrocarbon separation performance.

Cycloaddition of CO₂ with epoxides

The prominent CO₂ adsorption and separation performances of SNNU-616-Sc encourage us to further investigate the catalytic activity for cycloaddition of epoxides with CO₂. Accordingly, a series of epoxide substrates were examined for the synthesis of the corresponding cyclic carbonates in the presence of SNNU-616-Sc as a catalyst at 0.8 MPa CO₂ pressure and 353 K (Table 1). As for entry 1 to entry 3, epoxides with alkyl chains of different lengths were used as substrates for the reaction, and the yields of epoxyp propane, epoxyp butane, and epoxyp hexane were 95.8%, 94.2%, and 73.6%, respectively. Among them, epoxyp hexane with the longest alkyl chain showed the lowest yield, which indicated that the catalyst activity of the cycloaddition reaction declined with the increase of steric hindrance. So, the effective size of the epoxides is necessary to facilitate their entrance into the channel to close the catalytically active sites. Only 74.6% of epoxyp hexane was converted due to its difficult diffusion into the pores of the catalyst, and the difficulty of ring opening due to the large steric hindrance of the benzene ring hindering the Br⁻ attack also resulted in its low conversion. Moreover, SNNU-616-Sc exhibits highly efficient catalytic activity with a yield of 97.5% in carbonate formation after 8 h with 99% conversion and 98.6% selectivity when epoxide bromopropane was used as a reactant in the presence of *n*Bu₄NBr as a co-catalyst (Table 1, entry 5).

The blank experiment (entry 6) by only adding the cocatalyst *n*Bu₄NBr was conducted under the same conditions without SNNU-616-Sc, and the yield of cyclic carbonates is only

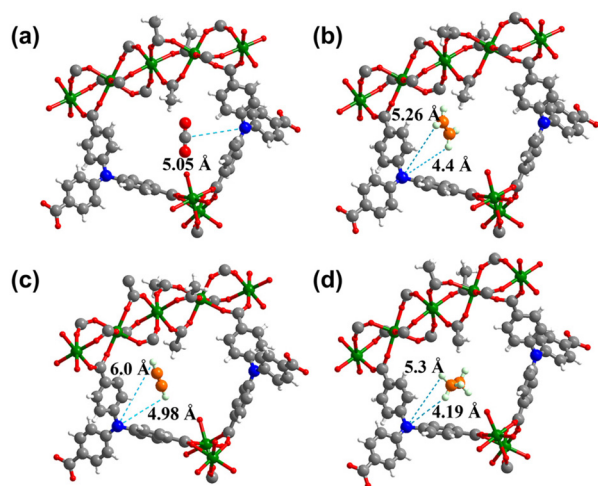


Fig. 8 The binding sites between bare N sites and CO₂ (a), C₂H₄ (b), C₂H₂ (c) and C₂H₆ (d) molecules calculated by modelling studies for SNNU-616-Sc.

Table 1 Catalytic performance of SNNU-616-Sc for the CO₂ cycloaddition reaction with different epoxides

No	Substrate	PCO ₂ (MPa)	T (°C)	t (h)	Yield (%)	Con. (%)	Select. (%)
1		0.8	80	8	95.8	97.2	95.6
2		0.8	80	8	94.2	99.9	94.3
3		0.8	80	8	73.6	74.6	94.2
4		0.8	80	8	90.2	92.3	97.7
5		0.8	80	8	97.5	99	98.6
6 ^a		0.8	80	8	52.5	47.5	98.8
7 ^b		0.8	80	8	74.0	81.9	90.4
8 ^c		0.8	80	8	37.7	36.7	99.8

Reaction conditions: epoxide = 20 mmol; catalyst = 20 mg SNNU-616-Sc; *n*Bu₄NBr = 0.1 mmol, 32 mg; semi-batch reaction; determined by GC. ^a Without a catalyst. ^b Catalyst = Sc(NO₃)₃·9H₂O. ^c Catalyst = NTB ligand.

52.5% with a low conversion rate of 47.5%, indicating that $n\text{Bu}_4\text{NBr}$ played an important role in ring opening, but it is deemed insufficient in improving the catalytic activity due to the lack of sufficient catalytic sites and mass transfer channels of the substrate. From the entries 5 and 6, $\text{Sc}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ metal salts or NTB ligands are used as catalysts added to the reaction in the presence of $n\text{Bu}_4\text{NBr}$, which shows clearly lower catalytic activity in comparison to the SNNU-616-Sc MOF catalyst. Therefore, the catalytic sites and mass transfer channels are of great significance in the catalytic reactions of CO_2 cycloaddition.

Recyclability is a critical criterion for an effective heterogeneous catalysis. The cycling experiments for epoxide bromopropane were also conducted under the same conditions (80 °C, 8 h, 0.8 MPa of CO_2 pressure) after easy separation and a simple filtration for SNNU-616-Sc, and washed several times with acetone. Fig. 9a shows that the recycled MOF catalyst can be reused up to at least five consecutive times without any considerable activity attenuation, showing an excellent recyclability. Moreover, the regenerative SNNU-616-Sc catalyst was analysed by PXRD. The PXRD patterns for the fresh MOF and recovered catalyst after 5 cycles are in full agreement with each other, further supporting the extraordinary catalytic stability of the SNNU-616-Sc catalyst (Fig. 9b).

Temperature-programmed desorption (TPD) of CO_2 and NH_3 analysis were performed to investigate the acid–base nature of the catalyst. As shown in Fig. S9,† SNNU-616-Sc shows an obvious peak at about 523 K for TPD- CO_2 , and TPD- NH_3 has very little peaks over the whole range of temperatures, indicating the presence of strong basic sites in this structure and almost no acidic sites in the catalyst. The results of TPD analyses confirmed that the SNNU-616-Sc catalyst offers strong basic sites for the CO_2 cycloaddition catalytic reactions.

Cycloaddition reaction mechanism

Based on the single crystal structure, CO_2 adsorption and catalytic CO_2 cycloaddition of SNNU-616-Sc with epoxides, a plausible catalytic reaction mechanism was proposed.⁵⁶ As shown in Fig. 10, in the first step, the bare N sites with lone pair electrons acted as Lewis basic sites to activate CO_2 molecules. In the second step, Br^- anions generated from the co-catalyst

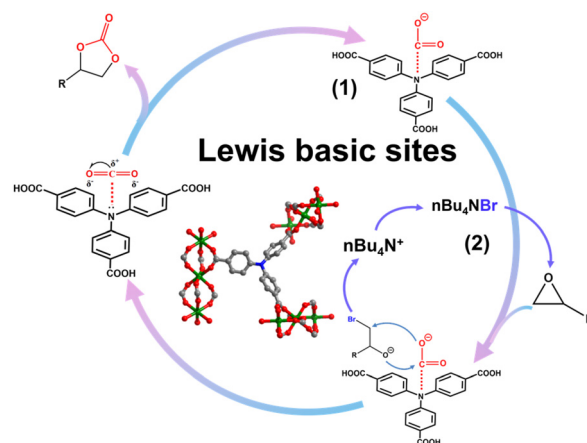


Fig. 10 The proposed catalytic mechanism of SNNU-616-Sc for CO_2 cycloaddition.

attack the less hindered C atom of the coordinated epoxides, followed by a ring-opening step. Thereafter, activated CO_2 interacts with the oxygen anion of the opened epoxy ring, forming an alkyl carbonate anion, and the corresponding cyclic carbonate is generated through ring closure with the elimination of the bromide ion. So, the good catalytic performance of SNNU-616-Sc is believed to be attributed to the synergistic effect of the basic catalytic sites and large mass transfer 1D channels in the presence of $n\text{Bu}_4\text{NBr}$.

Conclusions

In this work, a robust rod-packing Sc-MOF with two types of micropores and Lewis basic bare N atoms was synthesized and utilized for CO_2 adsorption and conversion. Benefitting from the synergistic effects of high chemical and thermal stability, bi-microporous open channels, and bare N sites, the Sc-MOF exhibits not only a prominent separation ability of CO_2 from $\text{C}_2\text{H}_x\text{-CO}_2$ binary mixtures, but also an extra-high CO_2 storage capacity. Remarkably, the Sc-MOF also can act as an excellent catalyst for CO_2 cycloaddition with epoxides with high productivity, prominent selectivity, and good recyclability. In general, we offer a helpful route to explore novel CCS materials with high CO_2 adsorption and conversion performance under mild conditions, which are critical for the global energy demand and carbon emission.

Author contributions

Hong-Juan Lv: methodology, data collection and analysis, and writing the original draft. Shu-Cong Fan: investigation and data analysis. Yu-Cheng Jiang: formal analysis. Shu-Ni Li: investigation and resources. Quan-Guo Zhai: supervision, checking & editing, and funding acquisition.

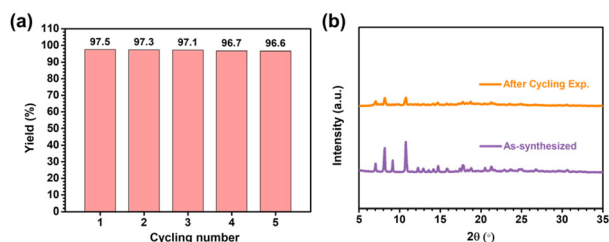


Fig. 9 (a) The yield of epoxide bromopropane for five catalytic cycles; (b) PXRD patterns for SNNU-616-Sc samples after the CO_2 cycloaddition reactions.

Conflicts of interest

There are no conflicts to declare.

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References

- 1 D. Gilfillan and G. Marland, CDIAFF: Global and National CO₂ Emissions from Fossil Fuel Combustion and Cement Manufacture: 1751–2017, *Earth Syst. Sci. Data*, 2021, **13**, 1667–1680.
- 2 S. S. A. Shah, T. Najam, M. Wen, S.-Q. Zang, A. Waseem and H.-L. Jiang, Metal–Organic Framework-Based Electrocatalysts for CO₂ Reduction, *Small Struct.*, 2022, **3**, 2100090.
- 3 J. Yu, L.-H. Xie, J.-R. Li, Y. Ma, J. M. Seminario and P. B. Balbuena, CO₂ Capture and Separations Using MOFs: Computational and Experimental Studies, *Chem. Rev.*, 2017, **117**, 9674–9754.
- 4 L. Lei, Y. Cheng, C. Chen, M. Kosari, Z. Jiang and C. He, Taming Structure and Modulating Carbon Dioxide (CO₂) Adsorption Isotherm Heat of Nickel-Based Metal Organic Framework (MOF-74(Ni)) for Remarkable CO₂ capture, *J. Colloid Interface Sci.*, 2022, **612**, 132–145.
- 5 Y. Ding, Z. Pang, K. Lan, Y. Yao, G. Panzarasa, L. Xu, M. Lo Ricco, D. R. Rammer, J. Y. Zhu, M. Hu, X. Pan, T. Li, I. Burgert and L. Hu, Emerging Engineered Wood for Building Applications, *Chem. Rev.*, 2023, **123**(5), 1843–1888.
- 6 F. A. Philip and A. Henni, Enhancement of Post-Combustion CO₂ Capture Capacity by Incorporation of Task-Specific Ionic Liquid into ZIF-8, *Microporous Mesoporous Mater.*, 2022, **330**, 111580.
- 7 D. Fu and M. E. Davis, Carbon Dioxide Capture with Zeotype Materials, *Chem. Soc. Rev.*, 2022, **51**, 9340–9370.
- 8 Y. Xie, H. Cui, H. Wu, R.-B. Lin, W. Zhou and B. Chen, Electrostatically Driven Selective Adsorption of Carbon Dioxide over Acetylene in an Ultramicroporous Material, *Angew. Chem., Int. Ed.*, 2021, **60**, 9604–9609.
- 9 Z. Zhang, S. B. Peh, R. Krishna, C. Kang, K. Chai, Y. Wang, D. Shi and D. Zhao, Optimal Pore Chemistry in an Ultramicroporous Metal–Organic Framework for Benchmark Inverse CO₂/C₂H₂ Separation, *Angew. Chem., Int. Ed.*, 2021, **60**, 17198–17204.
- 10 L. Jiao, J. Y. R. Seow, W. S. Skinner, Z. U. Wang and H.-L. Jiang, Metal–Organic Frameworks: Structures and Functional Applications, *Mater. Today*, 2019, **27**, 43–68.
- 11 Z. Zhu, J. Hu, X. Geng, B. Qin, K. Ma, Y. Wang and J. Gao, Process Design of Carbon Dioxide and Ethane Separation using Ionic Liquid by Extractive Distillation, *J. Chem. Technol. Biotechnol.*, 2018, **93**, 887–896.
- 12 H. Wang, M. Fan, Z. Zhang, J. Hao and C. Wang, Control of Cryogenic Extractive Distillation Process for Separating CO₂–C₂H₆ Azeotrope, *Comput. Chem. Eng.*, 2019, **128**, 384–391.
- 13 H. Wang, C. Wang, Z. Zhang, M. Fan, X. Yan and F. Li, Selection of State Equation and Innovative Process Design for Removing CO₂ by Azeotropic Distillation, *Chem. Eng. Technol.*, 2021, **44**, 710–722.
- 14 S. Wang, Q. Yang and C. Zhong, Adsorption and Separation of Binary Mixtures in a Metal–Organic Framework Cu-BTC: A Computational Study, *Sep. Purif. Technol.*, 2008, **60**, 30–35.
- 15 I. V. Zandvoort, E.-J. Ras, R. D. Graaf and R. Krishna, Using Transient Breakthrough Experiments for Screening of Adsorbents for Separation of C₂H₄/CO₂ Mixtures, *Sep. Purif. Technol.*, 2020, **241**, 116706.
- 16 G. Xu, Z. Meng, X. Guo, H. Zhu, K. Deng, C. Xiao and Y. Liu, Molecular Simulations on CO₂ Adsorption and Adsorptive Separation in Fullerene Impregnated MOF-177, MOF-180 and MOF-200, *Comput. Mater. Sci.*, 2019, **168**, 58–64.
- 17 H. J. Jun, D. K. Yoo and S. H. Jhung, Metal-organic Framework (MOF-808) Functionalized with Ethyleneamines: Selective Adsorbent to Capture CO₂ under Low Pressure, *J. CO₂ Util.*, 2022, **58**, 101932.
- 18 Y. Wan, Y. Miao, R. Zhong and R. Zou, High-Selective CO₂ Capture in Amine-Decorated Al-MOFs, *Nanomaterials*, 2022, **12**, 4056–4065.
- 19 L. Wang, Y. Dong, T. Yan, Z. Hu, A. A. Jelle, D. M. Meira, P. N. Duchesne, J. Y. Y. Loh, C. Qiu, E. E. Storey, Y. Xu, W. Sun, M. Ghoussoub, N. P. Kherani, A. S. Helmy and G. A. Ozin, Black Indium Oxide a Photothermal CO₂ Hydrogenation Catalyst, *Nat. Commun.*, 2020, **11**, 2432.
- 20 T. Lescouet, C. Chizallet and D. Farrusseng, The Origin of the Activity of Amine-Functionalized Metal–Organic Frameworks in the Catalytic Synthesis of Cyclic Carbonates from Epoxide and CO₂, *ChemCatChem*, 2012, **4**, 1725–1728.
- 21 R. Babu, A. C. Kathalikkattil, R. Roshan, J. Tharun, D.-W. Kim and D.-W. Park, Dual-Porous Metal Organic Framework for Room Temperature CO₂ Fixation via Cyclic Carbonate Synthesis, *Green Chem.*, 2016, **18**, 232–242.
- 22 Y. Tang, W. Chen, R. Liu, L. Wang, Y. Pan, R. Bi, X. Feng, M. He, Q. Chen and Z. Zhang, Solvent-Free CO₂ Fixation Reaction Catalyzed by MOFs Composites Containing Polycarboxylic Acid Ligands, *ChemistrySelect*, 2021, **6**, 5350–5355.
- 23 Z. J. Chen, M. R. Mian, S. J. Lee, H. Y. Chen, X. Zhang, K. O. Kirlikovali, S. Shulda, P. Melix, A. S. Rosen, P. A. Parilla, T. Gennett, R. Q. Snurr, T. Islamoglu, T. Yildirim and O. K. Farha, Fine-Tuning a Robust Metal–Organic Framework toward Enhanced Clean Energy Gas Storage, *J. Am. Chem. Soc.*, 2021, **143**, 18838–18843.

- 24 J. Pei, X.-W. Gu, C.-C. Liang, B. Chen, B. Li and G. Qian, Robust and Radiation-Resistant Hofmann-Type Metal–Organic Frameworks for Record Xenon/Krypton Separation, *J. Am. Chem. Soc.*, 2022, **144**, 3200–3209.
- 25 L. Liu, S. Du, X. Guo, Y. Xiao, Z. Yin, N. Yang, Y. Bao, X. Zhu, S. Jin, Z. Feng and F. Zhang, Water-Stable Nickel Metal–Organic Framework Nanobelts for Cocatalyst-Free Photocatalytic Water Splitting to Produce Hydrogen, *J. Am. Chem. Soc.*, 2022, **144**, 2747–2754.
- 26 J.-D. Xiao and H.-L. Jiang, Metal–Organic Frameworks for Photocatalysis and Photothermal Catalysis, *Acc. Chem. Res.*, 2019, **52**, 356–366.
- 27 Y.-Y. Xue, X.-Y. Bai, J. Zhang, Y. Wang, S.-N. Li, Y.-C. Jiang, M.-C. Hu and Q.-G. Zhai, Precise Pore Space Partitions Combined with High-Density Hydrogen-Bonding Acceptors within Metal–Organic Frameworks for Highly Efficient Acetylene Storage and Separation, *Angew. Chem., Int. Ed.*, 2021, **60**, 10122–10128.
- 28 J. Wang, Y. Zhang, Y. Su, X. Liu, P. Zhang, R.-B. Lin, S. Chen, Q. Deng, Z. Zeng, S. Deng and B. Chen, Fine Pore Engineering in a Series of Isoreticular Metal–Organic Frameworks for Efficient C₂H₂/CO₂ separation, *Nat. Commun.*, 2022, **13**, 200.
- 29 X. Zhang, R.-B. Lin, H. Wu, Y. Huang, Y. Ye, J. Duan, W. Zhou, J.-R. Li and B. Chen, Maximizing Acetylene Packing Density for Highly Efficient C₂H₂/CO₂ Separation through Immobilization of Amine Sites within a Prototype MOF, *Chem. Eng. J.*, 2022, **431**, 134184.
- 30 X.-J. Kong and J.-R. Li, An Overview of Metal–Organic Frameworks for Green Chemical Engineering, *Engineering*, 2021, **7**, 1115–1139.
- 31 J.-R. Li, J. Yu, W. Lu, L.-B. Sun, J. Sculley, P. B. Balbuena and H.-C. Zhou, Porous Materials with Pre-Designed Single-Molecule Traps for CO₂ Selective Adsorption, *Nat. Commun.*, 2013, **4**, 1538.
- 32 B. Parmar, P. Patel, R. S. Pillai, R. K. Tak, R. I. Kureshy, N.-U. H. Khan and E. Suresh, Cycloaddition of CO₂ with an Epoxide-Bearing Oxindole Scaffold by a Metal–Organic Framework-Based Heterogeneous Catalyst under Ambient Conditions, *Inorg. Chem.*, 2019, **58**, 10084–10096.
- 33 G. Yunjang, C. Youngson and P. Dae-Won, Catalytic Performance of CPM-200-In/Mg in the Cycloaddition of CO₂ and Epoxides, *Catalysts*, 2021, **11**, 430–444.
- 34 S.-C. Fan, S.-Q. Chen, J.-W. Wang, Y.-P. Li, P. Zhang, Y. Wang, W. Yuan and Q.-G. Zhai, Precise Introduction of Single Vanadium Site into Indium–Organic Framework for CO₂ Capture and Photocatalytic Fixation, *Inorg. Chem.*, 2022, **61**, 14131–14139.
- 35 W. Xie, L. Yang, J. Zhang and X. Zhao, The Adsorptive Separation of Ethylene from C₂ Hydrocarbons by Metal–Organic Frameworks, *Chem. – Eur. J.*, 2023, e202300158.
- 36 Y. Cao, Y. Zhao, Z. Lv, F. Song and Q. Zhong, Preparation and Enhanced CO₂ Adsorption Capacity of UiO-66/Graphene Oxide Composites, *J. Ind. Eng. Chem.*, 2015, **27**, 102–107.
- 37 A. R. Millward and O. M. Yaghi, Metal–Organic Frameworks with Exceptionally High Capacity for Storage of Carbon Dioxide at Room Temperature, *J. Am. Chem. Soc.*, 2005, **127**, 17998–17999.
- 38 L. Zhang, K. Jiang, Y. Li, D. Zhao, Y. Yang, Y. Cui, B. Chen and G. Qian, Microporous Metal–Organic Framework with Exposed Amino Functional Group for High Acetylene Storage and Excellent C₂H₂/CO₂ and C₂H₂/CH₄ Separations, *Cryst. Growth Des.*, 2017, **17**, 2319–2322.
- 39 X. Zhou, W. Huang, J. Liu, H. Wang and Z. Li, Quenched Breathing Effect, Enhanced CO₂ Uptake and Improved CO₂/CH₄ Selectivity of MIL-53(Cr)/Graphene Oxide Composites, *Chem. Eng. Sci.*, 2017, **167**, 98–104.
- 40 W. Fan, X. Wang, X. Liu, B. Xu, X. Zhang, W. Wang, X. Wang, Y. Wang, F. Dai, D. Yuan and D. Sun, Regulating C₂H₂ and CO₂ Storage and Separation through Pore Environment Modification in a Microporous Ni-MOF, *ACS Sustainable Chem. Eng.*, 2019, **7**, 2134–2140.
- 41 Y.-P. Li, Y. Wang, Y.-Y. Xue, H.-P. Li, Q.-G. Zhai, S.-N. Li, Y. Jiang, M.-C. Hu and X. Bu, Ultramicroporous Building Units as a Path to Bi-microporous Metal–Organic Frameworks with High Acetylene Storage and Separation Performance, *Angew. Chem., Int. Ed.*, 2019, **58**, 13590–13595.
- 42 Y.-L. Peng, T. Pham, P. Li, T. Wang, Y. Chen, K.-J. Chen, K. A. Forrest, B. Space, P. Cheng, M. J. Zaworotko and Z. Zhang, Robust Ultramicroporous Metal–Organic Frameworks with Benchmark Affinity for Acetylene, *Angew. Chem., Int. Ed.*, 2018, **57**, 10971–10975.
- 43 F. Luo, C. Yan, L. Dang, R. Krishna, W. Zhou, H. Wu, X. Dong, Y. Han, T.-L. Hu, M. O’Keeffe, L. Wang, M. Luo, R.-B. Lin and B. Chen, UTSA-74: A MOF-74 Isomer with Two Accessible Binding Sites per Metal Center for Highly Selective Gas Separation, *J. Am. Chem. Soc.*, 2016, **138**, 5678–5684.
- 44 J. Lee, C. Y. Chuah, J. Kim, Y. Kim, N. Ko, Y. Seo, K. Kim, T. H. Bae and E. Lee, Separation of Acetylene from Carbon Dioxide and Ethylene by a Water-Stable Microporous Metal–Organic Framework with Aligned Imidazolium Groups inside the Channels, *Angew. Chem., Int. Ed.*, 2018, **57**, 7869–7873.
- 45 R. Liu, Q.-Y. Liu, R. Krishna, W. Wang, C.-T. He and Y.-L. Wang, Water-Stable Europium 1,3,6,8-Tetrakis(4-carboxylphenyl)pyrene Framework for Efficient C₂H₂/CO₂ Separation, *Inorg. Chem.*, 2019, **58**, 5089–5095.
- 46 Z. Zhang, S. Xian, Q. Xia, H. Wang, Z. Li and J. Li, Enhancement of CO₂ Adsorption and CO₂/N₂ Selectivity on ZIF-8 via Postsynthetic Modification, *AIChE J.*, 2013, **59**, 2195–2206.
- 47 F. Luo, C. Yan, L. Dang, R. Krishna, W. Zhou, H. Wu, X. Dong, Y. Han, T. L. Hu, M. O’Keeffe, L. Wang, M. Luo, R. B. Lin and B. Chen, UTSA-74: A MOF-74 Isomer with Two Accessible Binding Sites per Metal Center for Highly Selective Gas Separation, *J. Am. Chem. Soc.*, 2016, **138**, 5678–5684.

- 48 Y. Ye, Z. Ma, R.-B. Lin, R. Krishna, W. Zhou, Q. Lin, Z. Zhang, S. Xiang and B. Chen, Pore Space Partition within a Metal–Organic Framework for Highly Efficient C₂H₂/CO₂ Separation, *J. Am. Chem. Soc.*, 2019, **141**, 4130–4136.
- 49 H.-M. Wen, C. Liao, L. Li, L. Yang, J. Wang, L. Huang, B. Li, B. Chen and J. Hu, Reversing C₂H₂–CO₂ Adsorption Selectivity in an Ultramicroporous Metal–Organic Framework Platform, *Chem. Commun.*, 2019, **55**, 11354–11357.
- 50 W. Fan, S. Yuan, W. Wang, L. Feng, X. Liu, X. Zhang, X. Wang, Z. Kang, F. Dai, D. Yuan, D. Sun and H.-C. Zhou, Optimizing Multivariate Metal–Organic Frameworks for Efficient C₂H₂/CO₂ Separation, *J. Am. Chem. Soc.*, 2020, **142**, 8728–8737.
- 51 Z. H. Rada, H. R. Abid, J. Shang, Y. He, P. Webley, S. Liu, H. Sun and S. Wang, Effects of Amino Functionality on Uptake of CO₂, CH₄ and Selectivity of CO₂/CH₄ on Titanium Based MOFs, *Fuel*, 2015, **160**, 318–327.
- 52 S. Galli, N. Masciocchi, G. Tagliabue, A. Sironi, J. A. R. Navarro, J. M. Salas, L. Mendez-Liñan, M. Domingo, M. Perez-Mendoza and E. Barea, Polymorphic Coordination Networks Responsive to CO₂, Moisture, and Thermal Stimuli: Porous Cobalt(II) and Zinc(II) Fluoropyrimidinolates, *Chem. – Eur. J.*, 2008, **14**, 9890–9901.
- 53 R. Ben-Mansour, N. A. A. Qasem and M. A. Habib, Adsorption Characterization and CO₂ Breakthrough of MWCNT/Mg-MOF-74 and MWCNT/MIL-100(Fe) Composites, *Int. J. Energy Environ. Eng.*, 2018, **9**, 169–185.
- 54 S. Pourebrahimi, M. Kazemeini and L. Vafajoo, Embedding Graphene Nanoplates into MIL-101(Cr) Pores: Synthesis, Characterization, and CO₂ Adsorption Studies, *Ind. Eng. Chem. Res.*, 2017, **56**, 3895–3904.
- 55 S. Pourebrahimi, M. Kazemeini, E. Ganji Babakhani and A. Taheri, Removal of the CO₂ from Flue Gas Utilizing Hybrid Composite Adsorbent MIL-53(Al)/GNP Metal–Organic Framework, *Microporous Mesoporous Mater.*, 2015, **218**, 144–152.
- 56 H.-G. Jin, F. Chen, H. Zhang, W. Xu, Y. Wang, J. Fan and Z.-S. Chao, Postmetalation of a New Porphyrin Ligand-Based Metal–Organic Framework for Catalytic Oxidative Carboxylation of Olefins, *J. Mater. Sci.*, 2020, **55**, 16184–16196.