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A new metal–organic framework with potential for adsorptive separation of methane from carbon dioxide, acetylene, ethylene, and ethane established by simulated breakthrough experiments†

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A new three-dimensional microporous metal–organic framework, Cu₂(MFDI) (ZJU-60, H₄MFDI = 5,5'-(9,9-dimethyl-9H-fluorene-2,7-diyl)diisophthalic acid), was solvothermally synthesized. ZJU-60 features a three-dimensional structure with a rare sty-a type topology and has two different types of pore apertures. With open metal sites and suitable pore spaces, ZJU-60 can readily separate methane in nearly pure form from CO₂ and C₂-hydrocarbon quaternary gas mixtures at room temperature with high separation capacity and moderate selectivity. The separation feasibility has been further established by simulated breakthrough and pulse chromatographic experiments.

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1. Introduction

Natural gas often contains impurities such as CO₂, along with C₂-hydrocarbons: C₂H₂, C₂H₄ and C₂H₆. In order to meet pipeline gas specifications, these impurities need to be removed. Methane has been widely utilized as an energy source and raw material. Compared to other conventional automobile fuels such as gasoline (petrol) and diesel, methane can be considered as a cleaner energy alternative due to its clean-burning characteristics, so separation of methane from C₂-hydrocarbons (C₂s) and CO₂ is a very important industrial process.¹ The traditional cryogenic distillation separation technology, which is based on their different vapour pressures and thus boiling points, is very energy-consuming, whereas the alternative oil-absorption method is not efficient.² Adsorptive separation is one of the most promising alternative energy- and cost-efficient separation methods, so it is desirable to explore

new microporous adsorbents which can selectively separate methane from CO₂ and C₂-hydrocarbons at room temperature.

Among the diverse adsorptive separation materials, metal–organic frameworks (MOFs) have recently shown great promise for such an important application. MOFs can be self-assembled from metal ions or metal-containing clusters with multi-dentate organic linkers through coordination bonding.^{3–27} The uniqueness of porous MOFs is that their pore sizes can be systematically tuned with organic linkers of different lengths and geometries while their pore surfaces can be functionalized by the immobilization of different functional sites, such as –NH₂ and –OH, and open metal sites for their differential recognition for small molecules and thus for gas separation.^{5–15} The first examined MOF (ZIF-8) for C₂s/C₁ separation by ExxonMobil exhibits quite a low separation capacity and selectivity.²⁸ We significantly enhanced the separation capacity up to about 3.0 mol kg^{−1} and the selectivity up to 35 *via* tuning the pore and cavity sizes in the MOF UTSA-34 for C₂s/C₁ separation.²⁹ Given the fact that porous MOFs with higher separation capacity and selectivity for the C₂s/C₁ separation can significantly save the energy cost, pursuit of new porous MOF materials for this important application is highly desirable. Herein we report a new copper–organic framework, Cu₂(MFDI) (ZJU-60, ZJU = Zhejiang University, H₄MFDI = 5,5'-(9,9-dimethyl-9H-fluorene-2,7-diyl)diisophthalic acid), which can separate methane in nearly pure form from CO₂ and C₂-hydrocarbon gas mixtures at room temperature, which has been established exclusively by the sorption isotherms and simulated breakthrough and pulse chromatographic experiments.

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2. Experimental

2.1 Materials and measurements

All the chemicals were commercially available and used without further purification. ^1H NMR spectra were recorded on a Bruker Advance DMX500 spectrometer using tetramethylsilane (TMS) as an internal standard. Elemental analyses for C, H, and N were performed on an EA1112 microelement analyzer. Powder X-ray diffraction (PXRD) patterns were collected in the $2\theta = 3\text{--}30^\circ$ range on an X'Pert PRO diffractometer with Cu K_α radiation ($\lambda = 1.542 \text{ \AA}$) at room temperature. Thermogravimetric analyses (TGA) were conducted on a Netzsch TGA 209 F3 thermogravimeter with a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ in a N_2 atmosphere.

2.2 Gas sorption measurements

A Micromeritics ASAP 2020 surface area analyzer was used to measure gas adsorption. To have a guest-free framework, the fresh sample was guest-exchanged with dry acetone at least 10 times, filtered and vacuumed at room temperature for 12 h and then at 383 K until the outgas rate was $5 \text{ } \mu\text{mHg min}^{-1}$ prior to measurements. The sorption measurement was maintained at 77 K with liquid nitrogen and at 273 K with ice-water bath (slush), respectively. As the center-controlled air condition was set up at $23.0 \text{ }^\circ\text{C}$, a water bath of $23.0 \text{ }^\circ\text{C}$ was used for adsorption isotherms at 296.0 K.

2.3 X-ray collection and structure determination

Crystallographic measurements were taken on an Oxford Xcalibur Gemini Ultra diffractometer with an Atlas detector using graphite-monochromatic Cu K_α radiation ($\lambda = 1.54178 \text{ \AA}$) at 293 K for **ZJU-60**. The measurements of the unit cells and data collections for the crystals of **ZJU-60** were performed with CrysalisPro. The datasets were corrected by empirical absorption correction using spherical harmonics, implemented in the SCALE3 ABSPACK scaling algorithm.³⁰ The structure was determined by direct methods and refined by the full-matrix least-squares method with the SHELX-97 program package.³¹ All non-hydrogen atoms, including solvent molecules, were located successfully from Fourier maps and were refined anisotropically. H atoms on C atoms were generated geometrically. The solvent molecules in **ZJU-60** are highly disordered. The SQUEEZE subroutine of the PLATON software suite was used to remove the scattering from the highly disordered guest molecules.³² Crystallographic data are summarized in Table S1.†

2.4 Synthesis of ZJU-60

A mixture of H_4MDDI (1.04 mg, 0.0020 mmol) and $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ (1.949 mg, 0.0080 mmol) was dissolved in $\text{DMF-H}_2\text{O}$ (3 mL, 4 : 1, v/v) in a screw-capped vial. After HNO_3 (40 μL) (69%, aq.) was added to the mixture, the vial was capped and placed in an oven at $65 \text{ }^\circ\text{C}$ for 48 h. The resulting hexagonal flake-shaped single crystals were washed with DMF several times to give **ZJU-60**. Elemental analysis: calcd for

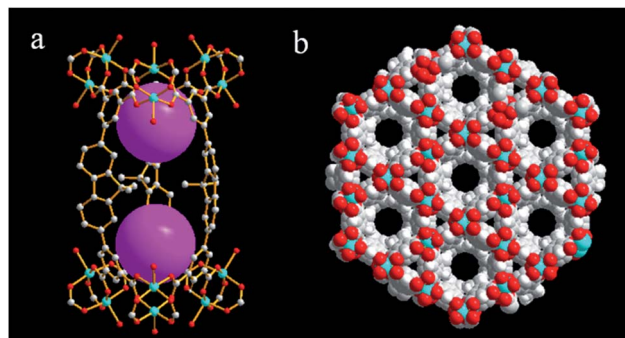


Fig. 1 X-ray single crystal structure of **ZJU-60** indicating (a) a large irregular elongated pore cage of about $4.4 \times 8.6 \text{ \AA}^2$ in diameter; and (b) the pores along the c axis with the size of about 5.4 \AA .

$[\text{Cu}_2(\text{C}_{31}\text{H}_{18}\text{O}_8)(\text{H}_2\text{O})_2](\text{DMF})_8(\text{H}_2\text{O})_{12}$: C, 44.56; H, 6.93; N, 7.56; Found: C, 44.56; H, 6.95; N: 7.56%.

3. Results and discussion

ZJU-60 was synthesized from $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ and H_4MDDI in $\text{DMF-H}_2\text{O}$ with addition of a small amount of nitric acid at $60 \text{ }^\circ\text{C}$ for 2 days as small blue cuboid block-shaped crystals. The structure of **ZJU-60** was characterized by single-crystal X-ray diffraction studies, and the phase purity of the bulk material was independently confirmed by powder X-ray diffraction (PXRD, Fig. S1†) and thermogravimetric analysis (TGA, Fig. S2†).

The single-crystal X-ray diffraction analysis reveals that **ZJU-60** crystallizes in a hexagonal space group of $P6_3/mmc$.† The framework is composed of paddle wheel dinuclear $\text{Cu}_2(\text{COO})_4$ units which are bridged by organic linkers to form a 3D rare sty-a type structure. The 3D framework of **ZJU-60** has two different types of pores. The large irregular elongated cage of about $4.4 \times 8.6 \text{ \AA}^2$ runs through the a axis (Fig. 1a). Another one along the c axis is about 5.4 \AA in diameter, taking into account the van der Waals radii (Fig. 1b).

To characterize the permanent porosity, the N_2 sorption isotherm experiments were performed at 77 K. It shows that the suitably activated **ZJU-60a** exhibits reversible Type-I sorption behaviour, characteristic of microporous materials with the saturated sorption amount of N_2 of $561 \text{ cm}^3 \text{ g}^{-1}$ (Fig. 2a). The Brunauer–Emmett–Teller (BET) and Langmuir surface areas of **ZJU-60a** are 1627 and $2394 \text{ m}^2 \text{ g}^{-1}$, respectively. As expected, these values are higher than those of MOF-505 because of the longer linker in **ZJU-60**. **ZJU-60a** has a pore volume of $0.867 \text{ cm}^3 \text{ g}^{-1}$.

Establishment of the permanent porosity of **ZJU-60a** encourages us to examine its potential application in gas storage and selective gas separation. As shown in Fig. 2b and c, **ZJU-60a** can take up moderate amounts of C_2H_2 of 178.66 and $150.57 \text{ cm}^3 \text{ g}^{-1}$ at 273 and 296 K, respectively, under 1 atm. The

† Crystal data for **ZJU-60**: $\text{C}_{31}\text{H}_{18}\text{Cu}_2\text{O}_{10}$, $M = 681.57$, $P6_3/mmc$, $a = b = 18.4819(3) \text{ \AA}$, $c = 34.4495(5) \text{ \AA}$, $V = 10\,190.8(3) \text{ \AA}^3$, $Z = 6$, $D_c = 0.666 \text{ g cm}^{-3}$, $\mu(\text{Cu-K}\alpha) = 0.988 \text{ mm}^{-1}$, $F(000) = 2076$, $\text{GoF} = 1.070$, final $R_1 = 0.0599$ for $I > 2\sigma(I)$, and $wR_2 = 0.1636$ for all data. CCDC: 969710.

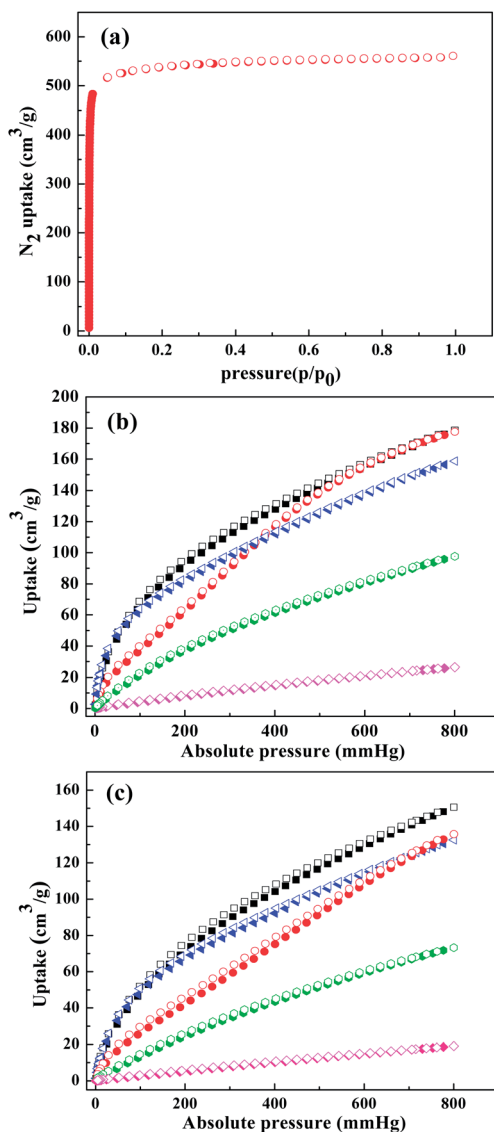


Fig. 2 (a) N₂ sorption isotherm at 77 K and CH₄ (magenta), CO₂ (green), C₂H₆ (red) and C₂H₄ (blue), C₂H₂ (black) sorption isotherms of ZJU-60a at (b) 273 K and (c) 296 K. Solid symbols: adsorption, open symbols: desorption.

amount of adsorbed C₂H₂ in ZJU-60a at 296 K is slightly higher than that in MOF-505 (148 cm³ g⁻¹).³³

ZJU-60a can take up C₂H₂ (178.67 cm³ g⁻¹), C₂H₄ (158.71 cm³ g⁻¹), C₂H₆ (177.59 cm³ g⁻¹), and CO₂ (97.69 cm³ g⁻¹) at 1 atm and 273 K, and C₂H₂ (150.57 cm³ g⁻¹), C₂H₄ (132.55 cm³ g⁻¹), C₂H₆ (135.66 cm³ g⁻¹) and CO₂ (73.3 cm³ g⁻¹) at 1 atm and 296 K, which are much higher than the amount of CH₄ (26.4 cm³ g⁻¹) at 273 K and that of CH₄ (19.06 cm³ g⁻¹) at 296 K. Such different sorption enables ZJU-60a to be a promising material for highly selective adsorptive separation of C₂-hydrocarbons and CO₂ from CH₄.

In order to establish the feasibility of these gas separations, we performed calculations using the Ideal Adsorbed Solution Theory (IAST) of Myers and Prausnitz.³⁴ Fig. S3† presents calculations using IAST for the component loading in the

adsorbed mixture in equilibrium with an equimolar 5-component C₂H₂/C₂H₄/C₂H₆/CH₄/CO₂ gas mixture at 296 K in ZJU-60a. The IAST calculations indicated that the hierarchy of adsorption strengths is C₂H₂ > C₂H₄ > C₂H₆ > CO₂ > CH₄.

The isosteric heat of adsorption, Q_{st} , defined as

$$Q_{st} = RT^2 \left(\frac{\partial \ln p}{\partial T} \right)_q$$

was determined using the pure component isotherm fits. Fig. S4† shows data on the loading dependence of Q_{st} for adsorption of CH₄, CO₂, C₂H₂, C₂H₄ and C₂H₆ on ZJU-60a. The isosteric heat of adsorption of CH₄ on ZJU-60a is 12.0 kJ mol⁻¹, whereas the isosteric heats of adsorption of C₂H₂, C₂H₄, C₂H₆ and CO₂ are 17.6, 21.4, 19.8 and 15.2 kJ mol⁻¹, respectively. The higher adsorption heats for C₂ hydrocarbons and CO₂ might be due to the comparable pore sizes and open metal sites in ZJU-60a with these small C₂ hydrocarbons and CO₂, thereby enforcing their interaction with the host framework, and thus leading to moderately high C₂-hydrocarbons/CH₄ and CO₂/CH₄ selective separation.

To obtain pure CH₄ from natural gas streams, the adsorption selectivity of CO₂ with respect to CH₄ is very important. We used two different metrics to evaluate the performance of ZJU-60a for the CO₂/CH₄ separation. The first metric is the adsorption selectivity. Fig. 3 shows the IAST adsorption selectivity, S_{ads} , for equimolar CO₂/CH₄ mixtures at 296 K in ZJU-60a. The adsorption selectivities of CO₂ with respect to CH₄ are higher than 5 for ZJU-60a for a range of pressures to 100 kPa, indicating that ZJU-60a is feasible to separate methane from CO₂ and C₂-hydrocarbons.

Besides the CO₂/CH₄ selectivity, another important metric for pressure swing adsorbers is the uptake capacity for impurities. Fig. 4 presents the IAST calculations for the uptake capacities for the total of four impurities (C₂H₂ + C₂H₄ + C₂H₆ + CO₂) in the 5-component mixture. We note that the capacity of ZJU-60a for impurity uptake reaches 3 mol L⁻¹ at 100 kPa and 296 K, which is higher than that of our recently developed UTSA-34.²⁹

In order to properly evaluate the feasibility for the practical separation, the breakthrough experiments were simulated based on the established methodology described in the work of

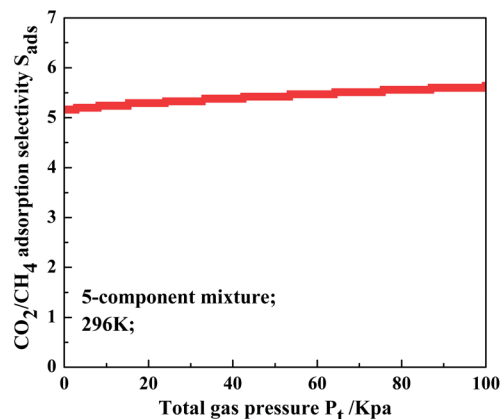


Fig. 3 IAST adsorption selectivities of CO₂/CH₄ for the equimolar C₂H₂/C₂H₄/C₂H₆/CH₄/CO₂ gas mixture in the total bulk gas phase at 296 K.

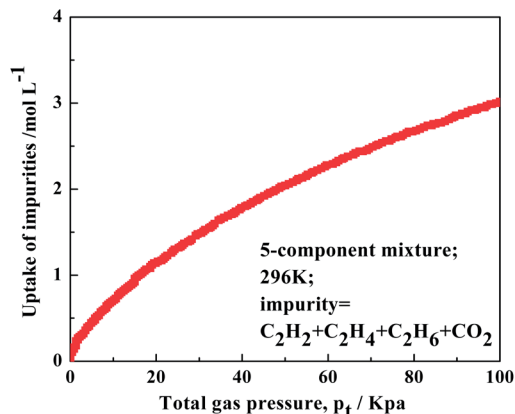


Fig. 4 IAST calculations for the uptake capacities for impurities ($\text{C}_2\text{H}_2 + \text{C}_2\text{H}_4 + \text{C}_2\text{H}_6 + \text{CH}_4 + \text{CO}_2$).

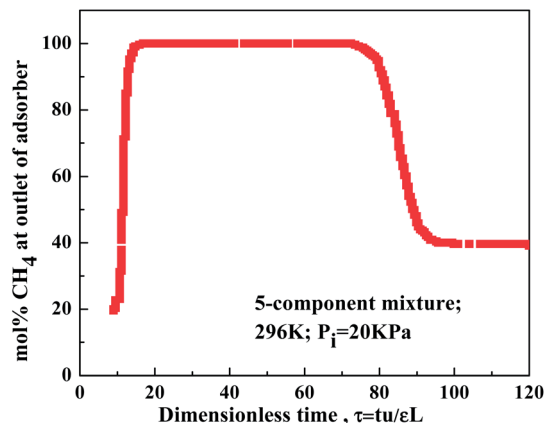


Fig. 6 The % CH_4 exiting the bed adsorber packed with ZJU-60a. The inlet gas consists of an equimolar 5-component $\text{C}_2\text{H}_2/\text{C}_2\text{H}_4/\text{C}_2\text{H}_6/\text{CH}_4/\text{CO}_2$ gas mixture at 296 K and 100 kPa.

Krishna and Long which has been exclusively confirmed by the experimental breakthrough experiments.³⁵ Fig. 5 presents data on the concentrations at the exit of the adsorber for the chosen MOFs, for illustration purposes. The x-axis in Fig. 5 is dimensionless time, τ , defined by dividing the actual time, t , by the characteristic time, $L\varepsilon/u$. We note that the sequence of breakthroughs for the MOFs is CH_4 , CO_2 , C_2H_6 , C_2H_4 , and C_2H_2 . The adsorbent has the ability to separate CH_4 in pure form from this quaternary mixture.

From the data presented in Fig. 5, we can determine the mol % CH_4 in the exit gas stream. Fig. 6 shows the % CH_4 exiting the adsorber packed with ZJU-60a. With the MOFs it is possible to recover pure CH_4 from the gas mixture in a certain interval of time. We arbitrarily set the purity requirement to be 99% CH_4 . From a material balance on the adsorbent, we can determine the amount of 99% pure CH_4 that can be produced per L of the adsorbent in the fixed bed. The productivity is 0.33 mol L^{-1} for ZJU-60a. The separation capability of ZJU-60a is also underscored in pulse chromatographic simulations (Fig. S5[†]). The breakthrough and pulse chromatographic simulations confirm

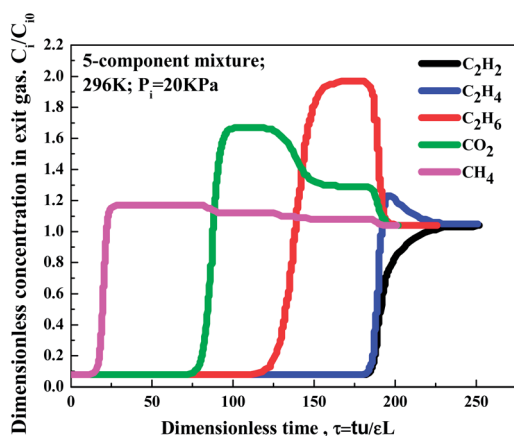


Fig. 5 Breakthrough simulation results for ZJU-60a for separation of an equimolar $\text{C}_2\text{H}_2/\text{C}_2\text{H}_4/\text{C}_2\text{H}_6/\text{CH}_4/\text{CO}_2$ mixture in a fixed bed adsorbent in the total bulk gas phase at 296 K and 100 kPa. The x-axis represents the dimensionless time, τ .

the potency of ZJU-60 for separation of CH_4 in nearly pure form from gas mixtures containing CO_2 , C_2H_2 , C_2H_4 and C_2H_6 species at room temperature.

4. Conclusions

In summary, we have synthesized a novel three-dimensional porous metal-organic framework ZJU-60 for separation of methane in nearly pure form from CO_2 and C_2 -hydrocarbon quaternary gas mixtures at room temperature with high separation capacity and moderate selectivity. The high separation capacity is attributed to the suitable pore space and open metal sites within pores of the framework to take up a large amount of hydrocarbons and CO_2 . It is expected that this work will initiate more investigations on the emerging MOFs for such industrially important separation.

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