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Highly selective separation of small hydrocarbons and carbon dioxide in a metal–organic framework with open copper(II) coordination sites†

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Hydrocarbons and carbon dioxide are very important raw materials for industrial products and fine chemicals. The microporous metal–organic framework ZJU-25 with high density of open metal sites, has significantly better separation potential than other MOFs, ZIFs or zeolites. It can fractionate a 5-component CH₄/C₂H₂/C₂H₄/C₂H₆/CO₂ mixture to yield individual pure components as established by the sorption isotherms and simulated breakthrough and pulse chromatographic experiments. Such separations are likely to have a significant industrial impact, resulting in significant energy savings when compared to current technologies that rely on cryogenic distillation.

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1. Introduction

Hydrocarbon mixtures can be separated into all kinds of pure component fractions for the production of fuels and chemical feedstocks. Light hydrocarbons, CH₄, C₂H₂, C₂H₄ and C₂H₆, are very important raw chemicals and energy resources. For example, methane has been considered as the most promising clean alternative fuel for future vehicle; ethane can produce ethylene during industrial scale cracking processes which can be used for manufacturing polymers such as polyethylene, polyvinyl chloride, polystyrene as well as other organic chemicals; and acetylene is a very important raw material for the petrochemical industry, electric materials and chemical and consumer products, oxy-acetylene cutting in metal fabrication.^{1–6} The increasing CO₂, which is emitted from the combustion of fossil fuels, has resulted in global warming, hence capture and sequestration of CO₂ is also very important energy and environmental issue.^{7,8} The separation of individual component from the mixture of CH₄, C₂H₂, C₂H₄, C₂H₆ and CO₂ is quite challenging and energy consuming because some of the components have comparable sizes. The dimensional size and kinetic diameter of these five gases are listed in Table 1.^{9–11} The traditional separation technology of the cryogenic distillation is very energy-intensive because these gas mixture are generated

by cracking long-chain hydrocarbons at elevated temperatures, it is thus necessary to cool down the gases to the low temperatures before distillation, which causes a substantial energy penalty. If porous materials can be applied for the efficient separation of hydrocarbon molecules and carbon dioxide at room temperatures and atmospheric pressure, tremendous energy savings could be realized.^{12–15}

A variety of microporous adsorbents have been examined for separations of these light hydrocarbons and carbon dioxide. To date, microporous metal–organic frameworks (MOFs) have offered considerable potential for usage in a variety of separations of small gas molecules based on selective adsorption.^{16–19} MOFs can be self-assembled from multifunctional organic molecules with metal ions or metal-containing clusters, resulting in a great versatility in the possible geometries and surface properties attributed to their diverse structures and topologies.^{20–43} Compared with traditional porous materials such as zeolites and activated carbon, MOFs are very unique in terms of their (1) systematically tuned micropores by choosing the different organic linkers or the diverse metal-containing secondary building units (SBUs) or by the framework

Table 1 Molecular dimensions and kinetic diameter of C₂H₂, C₂H₄, C₂H₆, CO₂ and CH₄^{9–11}

	Dimensions/Å ³	Kinetic diameter ^c /Å
C ₂ H ₂ ^a	3.32 × 3.34 × 5.70	3.3
C ₂ H ₄ ^a	3.28 × 4.18 × 4.84	4.2
C ₂ H ₆ ^b	3.80 × 4.07 × 4.82	4.4
CH ₄ ^a	3.82 × 3.94 × 4.10	3.8
CO ₂ ^a	3.18 × 3.33 × 5.36	3.3

^a Data from ref. 9. ^b Data from ref. 10. ^c Data from ref. 11.

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interpenetration, and (2) modified pore surfaces by organic and/or inorganic functional recognition sites on the pore surfaces, enabling them as very promising materials for gas separations.^{30–41} For instance, coordinatively unsaturated metal centers (UMCs), which are often produced through the removal of terminally coordinated solvent molecules to the metal centers, can enhance gas adsorption and separation properties.^{41–43} Indeed, a number of MOF materials have been reported to selectively separate methane from mixtures including hydrocarbons (ethane, ethylene, and acetylene) and carbon dioxide for the purification of natural gas, though MOF materials for simultaneous purification of the individual component of ethane, ethylene, acetylene and carbon dioxide from their mixture are still rare.^{31–38} Herein we report a metal organic framework **ZJU-25**, with open copper coordination sites and suitable pore structures, for highly selective separation of the 5-component mixture of CH₄, C₂H₂, C₂H₄, C₂H₆ and CO₂. It can fractionate the 5-component mixture into its nearly pure constituents.

2. Experimental

2.1 Gas sorption measurements

The synthesis and characterization of **ZJU-25** was reported previously in the literature.⁴⁴ A Micromeritics ASAP 2020 surface area analyzer was used to measure gas adsorption. To have a guest-free framework, **ZJU-25a**, 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 μm Hg min⁻¹ prior to measurements. The sorption measurement was maintained at 77 K with liquid nitrogen and 273 K with ice-water bath (slush), respectively. As the center-controlled air condition was set up at 23.0 °C, a water bath of 23.0 °C was used for adsorption isotherms at 296.0 K.

2.2 Single-site Langmuir model for adsorption isotherms

The experimentally measured excess isotherm loadings on pure component isotherms for C₂H₂, C₂H₄, C₂H₆, CO₂ and CH₄ at 273 K, and 296 K in **ZJU-25a** are converted to absolute loadings using

$$q^{\text{abs}} = q^{\text{excess}} + pV_{\text{pore}}/ZRT \quad (1)$$

where Z is the compressibility factor. The Peng–Robinson equation of state was used to estimate Z . The accessible pore volume within the crystals, V_{pore} , is taken to be equal to experimentally determined value of 1.183 cm³ g⁻¹.⁴⁴

The isotherm data at both temperatures are fitted with the single-site Langmuir–Freundlich model

$$q = q_{\text{sat}} bp^{\nu}/1 + bp^{\nu} \quad (2)$$

The temperature dependence of the Langmuir constant, b , is expressed as

$$b_A = b_0 \exp(E/RT) \quad (3)$$

The Langmuir–Freundlich parameters for **ZJU-25a** are provided in Table 2.

Table 2 Langmuir isotherm parameter fits for **ZJU-25a**

	q_{sat} mol kg ⁻¹	b_0 Pa ^{-ν}	E kJ mol ⁻¹	ν dimensionless
C ₂ H ₂	50	3.42×10^{-7}	13.7	0.66
C ₂ H ₄	25	2.77×10^{-7}	14.0	0.72
C ₂ H ₆	28	1.20×10^{-9}	19.4	1
CH ₄	17	3.48×10^{-9}	12.4	1
CO ₂	17	3.20×10^{-9}	16.6	1

3. Results and discussion

This framework of **ZJU-25** has three different types of pore apertures. One runs through the a axes of about 4.4×8.6 Å² (Fig. 1a) and the other two can be visualized along the c axes of about 3.6 and 5.4 Å in diameter (Fig. 1b), taking into account the van der Waals radii, respectively. The activated **ZJU-25a** displays the Brunauer–Emmett–Teller (BET) surface area of 2124 m² g⁻¹. It exhibits moderately high methane storage capacity at room temperature.⁴⁴ During our studies of this MOF for different gas sorption, we realized that it takes up quite large and different amount of C₂ hydrogen carbons, which motivated us to examine **ZJU-25a** for its potential application in gas separation, particularly for industrially important C₂/C₁/CO₂ hydrocarbon separation.

To investigate the ability of **ZJU-25a** to absorb light hydrocarbons and carbon dioxide, pure component equilibrium adsorption isotherms for methane, ethane, ethylene, acetylene and carbon dioxide are measured at 273 and 296 K. As show in Fig. 2, **ZJU-25a** exhibits different adsorption capacities to CH₄, C₂H₂, C₂H₄, C₂H₆ and CO₂. The carbon dioxide adsorption capacities, although lower than those of C₂ hydrocarbons, are considerably higher than observed for methane. It is mainly due to methane has a lower polarizability and molecular weight. Importantly, all of the isotherms are completely reversible and exhibit no hysteresis, which means that the material can be easily regenerated and re-utilised. Such different sorption enables **ZJU-25a** to be a promising material for highly selective adsorptive separation of CH₄, C₂H₂, C₂H₄, C₂H₆ and CO₂.

In order to establish the feasibility of this separation, we perform calculations using the Ideal Adsorbed Solution Theory (IAST) of Myers and Prausnitz.⁴⁵ Fig. 3 presents calculations using IAST for the component loading in the adsorbed mixture

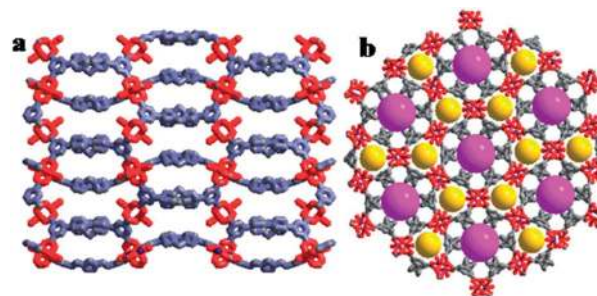


Fig. 1 X-ray single crystal structure of **ZJU-25** (a) the structure viewed along the a axes; (b) the structure viewed along the c axes.

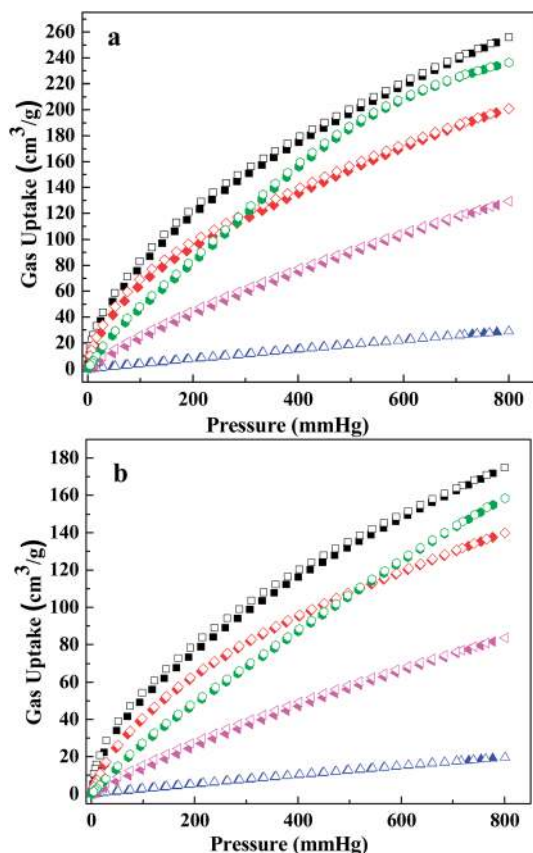


Fig. 2 CH₄ (blue), CO₂ (magenta), C₂H₆ (green) and C₂H₄ (red), C₂H₂ (black) sorption isotherms of ZJU-25 at (a) 273 K and (b) 296 K. Solid symbols: adsorption, open symbols: desorption.

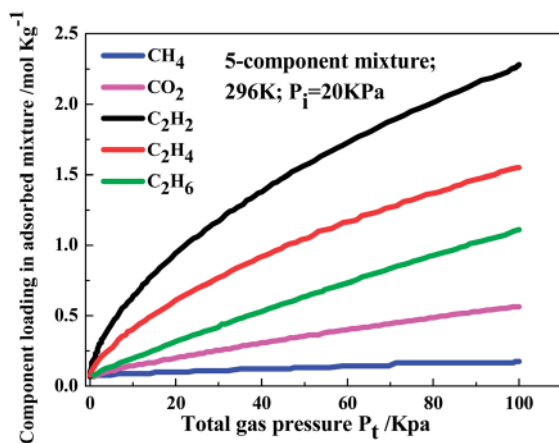


Fig. 3 IAST calculations of the component molar loadings in equilibrium with an equimolar C₂H₂/C₂H₄/C₂H₆/CH₄/CO₂ mixture at total bulk gas phase at 296 K.

in equilibrium with an equimolar 5-component C₂H₂/C₂H₄/C₂H₆/CH₄/CO₂ gas mixture at 296 K in ZJU-25a. The IAST calculations indicate that the hierarchy of adsorption strengths is C₂H₂ > C₂H₄ > C₂H₆ > CO₂ > CH₄.

We examine the separation selectivity and capacity of ZJU-25a for CO₂/CH₄, C₂H₆/CO₂, C₂H₄/C₂H₆, C₂H₂/C₂H₄ binary

mixtures at 296 K. The adsorption selectivities, S_{ads} , are defined by the following equation:

$$S_{\text{ads}} = \frac{q_1/q_2}{p_1/p_2} \quad (4)$$

in which q_1 and q_2 are the absolute component loadings of the adsorbed phase in the 5-component mixture and p_1 and p_2 are the bulk gas pressure. Fig. 4 shows the IAST calculations of the adsorption selectivity, S_{ads} , for equimolar CO₂/CH₄, C₂H₆/CO₂, C₂H₄/C₂H₆, C₂H₂/C₂H₄ mixtures at 296 K in ZJU-25a. The selectivity of C₂H₆ with respect to CO₂ is in excess of 10 for a range of pressures to 100 kPa, indicating the fairly sharp separations of this binary mixture is easy. For CO₂/CH₄ mixture, the separation selectivity is approximately 5 which displays the separation of this binary mixture can be realized. Although the adsorption selectivities of C₂H₄/C₂H₆ and C₂H₂/C₂H₄ are about 2, the separations of these binary mixtures are possible.

The isosteric heat of adsorption, Q_{st} , which represents the average binding energy of an adsorbing gas molecule at a specific surface coverage, defined as

$$Q_{\text{st}} = RT^2(\partial \ln P/\partial T)_q \quad (5)$$

is determined by using the pure component C₂H₂, C₂H₄, C₂H₆, CH₄, CO₂ isotherm fit. Fig. 5 presents the data on the isosteric heats of adsorption for C₂H₂, C₂H₄, C₂H₆, CH₄ and CO₂ in ZJU-25a. The analytic procedure used is identical to the one described in detail in the ESI† accompanying the paper by Mason *et al.*⁴⁶ These calculations are based on the use of eqn (5), along with analytic differentiation of the isotherm fits of the single-Langmuir fit parameters provided in Table 2. The isosteric heat of adsorption of CH₄ in ZJU-25a is significantly lower, and has a value of 12.4 kJ mol⁻¹, whereas the isosteric heats of adsorption of CO₂, C₂H₄, C₂H₆ and C₂H₂, in turn, are 16.6, 19.4, 19.4, 20.7 kJ mol⁻¹. It can be seen that the isosteric heats of adsorption of C₂H₄ and C₂H₆ are identical. This difference in the Q_{st} values is the prime reason for the superior performance of ZJU-25a in separating 5-component C₂H₂, C₂H₄, C₂H₆, CH₄,

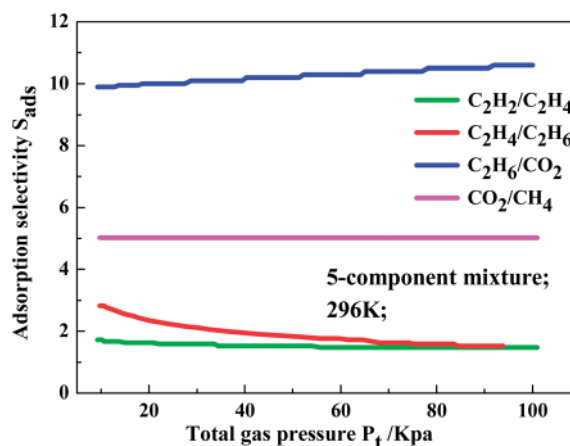


Fig. 4 Calculations using IAST for CO₂/CH₄, C₂H₆/CO₂, C₂H₄/C₂H₆, C₂H₂/C₂H₄ selectivities for equimolar 5-component C₂H₂/C₂H₄/C₂H₆/CH₄/CO₂ gas mixture at 296 K in ZJU-25a.

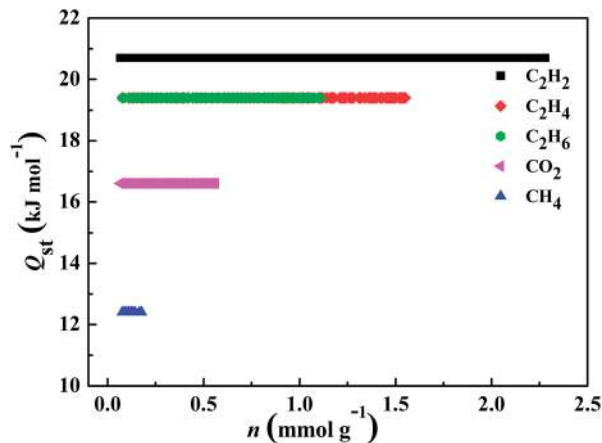


Fig. 5 The isosteric heats of adsorption of C_2H_2 , C_2H_4 , C_2H_6 , CO_2 and CH_4 on ZJU-25a.

CO_2 . The different adsorption strength of ZJU-25a to each gas is attributed to their different van der Waals interactions and some specific stronger interactions (particularly the $Cu^{2+}-C_2H_2$) with the host MOF material.^{47,48}

To further evaluate the performance of ZJU-25a for fractionating C_2H_2 , C_2H_4 , C_2H_6 , CH_4 and CO_2 into its nearly pure constituents, assuming isothermal conditions, with the adsorber maintained at 296 K, breakthrough experiments are performed in which an equimolar acetylene/ethylene/ethane/carbon dioxide/methane mixture is flowed over a packed-bed adsorber. Fig. 6 shows a schematic of a packed bed adsorber. The breakthrough characteristics are simulated using the methodology described in the work of Krishna.^{49–51} Simulated data on the gas-phase molar concentrations exiting an adsorber packed with ZJU-25a are shown in Fig. 7. The x-axis is a dimensionless time, τ , defined by dividing the actual time, t , by the characteristic time, $L\varepsilon/u$. For a given adsorbent, under chosen operating conditions, the breakthrough characteristics are uniquely defined by τ , permitting the results to be presented here to be equally appropriate for laboratory scale equipment, as well as for industrial scale adsorbers. Specifically, the calculations presented here are performed taking the following parameter values: length of packed bed, $L = 0.1$ m; fractional voidage of packed bed, $\varepsilon = 0.4$; superficial gas velocity at inlet of adsorber, $u = 0.04$ m s^{-1} . From the breakthrough curves

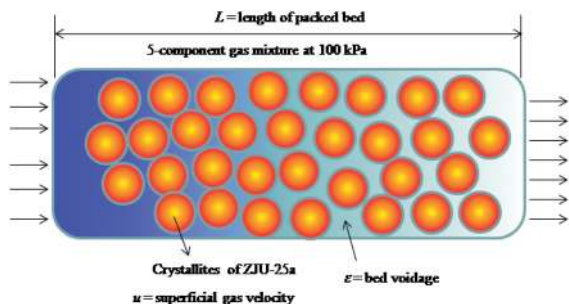


Fig. 6 Schematic of packed bed adsorber packed with ZJU-25a.

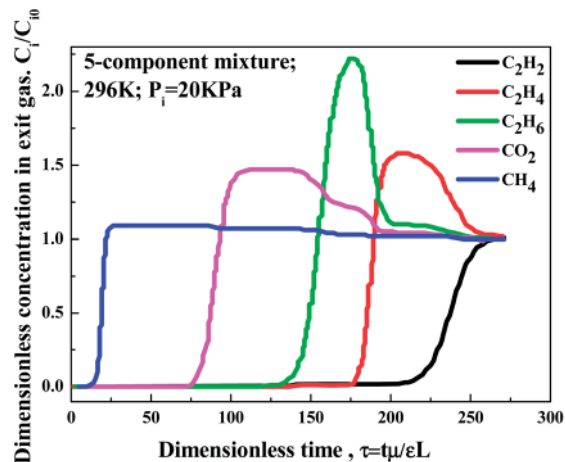


Fig. 7 Breakthrough characteristics of an adsorber packed with ZJU-25a.

presented in Fig. 7, we note that the methane which has the poorest adsorption strength “breaks through” earliest and it is possible to produce pure methane from this 5-component mixture during the adsorption cycle. Then the breakthrough times reflect the remaining relative adsorption selectivities (acetylene > ethylene > ethane > carbon dioxide) for ZJU-25a, and the curves indicate a clean, sharp breakthrough transition for each successive gas. It may be possible to recover each component in a nearly pure form for C_2H_2 , C_2H_4 , C_2H_6 and CO_2 , which is a most desirable property.

In order to further explore this property, we carry out pulse chromatographic simulations for separation of an equimolar 5-component $C_2H_2/C_2H_4/C_2H_6/CH_4/CO_2$ mixture. Fig. 8 shows the pulse chromatographic separation with ZJU-25a at 296 K. The first peak to emerge from the adsorber is that of CH_4 which means it can be used for the purification of natural gas. Following the removal of CH_4 , we see the emergence of the peak for CO_2 . The hierarchies of next set of peaks are C_2H_6 , C_2H_4 , C_2H_2 . We see that ZJU-25a is able to separate C_2 hydrocarbons

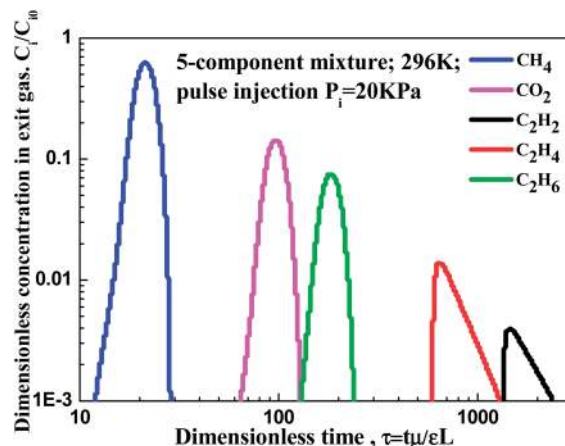


Fig. 8 Pulse chromatographic simulations for adsorber packed with ZJU-25a.

into individual components which is very rare in porous MOF materials. The result of pulse chromatographic simulations is consistent with that of the breakthrough curves.

4. Conclusions

In summary, the foregoing results demonstrate the extraordinary prospects for using the metal-organic framework **ZJU-25a** as a solid adsorbent in the separation of valuable $C_2H_2/C_2H_4/C_2H_6/CH_4/CO_2$ through simulated breakthrough and pulse chromatographic experiments. **ZJU-25** exhibits the potential for separating C_2 , C_1 hydrocarbons and carbon dioxide into individual pure components. Such unique performance of **ZJU-25** for these separations is attributed to open copper sites and suitable pore sizes and geometries. Among the reported MOFs, only MOF-74 series ones have such powerful separation capacities as well.² It is expected that this work will initiate more investigations on the emerging MOFs for such this industrially important separation.

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