Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A

Supporting Information

Metal–Organic Frameworks with Potential for Adsorptive Separation of Methane from Carbon Dioxide, Acetylene, Ethylene, and Ethane Established by Simulated Breakthrough Experiments

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Fitting of pure component isotherms

The experimentally measured excess loadings of C_2H_2, C_2H_4, C_2H_6, CH_4, CO_2, and N_2 in **ZJU-60a**, obtained at 273 K and 296 K, were first converted to absolute loadings before data fitting. The procedure for converting excess loadings to absolute loadings is described in detail in the Supporting Information accompanying Wu et al.[1]

The isotherm data at both temperatures were fitted with the Langmuir-Freundlich model

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

with *T*-dependent parameter *b*

$$b_A = b_0 \exp\left(\frac{E}{RT}\right) \quad (2)$$

The Langmuir-Freundlich parameters for **ZJU-60a** are provided in *Tables S2*, Figure S3 presents calculations using IAST for the component loading in the adsorbed mixture in equilibrium with an equimolar 5-component $C_2H_2/C_2H_4/C_2H_6/CH_4/CO_2$ gas mixture at 296 K in ZJU-60a.

IAST calculations of Adsorption selectivity

Let us first consider the separation of CH_4 from a mixture containing C_2 hydrocarbons and CO_2. Rather than restrict our investigations to just binary CH_4/CO_2mixtures, we consider the selective adsorption of C_2 hydrocarbons and CO_2 from an equimolar 5-component $C_2H_2/C_2H_4/C_2H_6/CH_4/CO_2$ mixture. The choice of such a mixture is dictated by the fact that such mixture separations are encountered in the process oxidative coupling of methane for producing ethane.

We define the *adsorption selectivity*, defined by

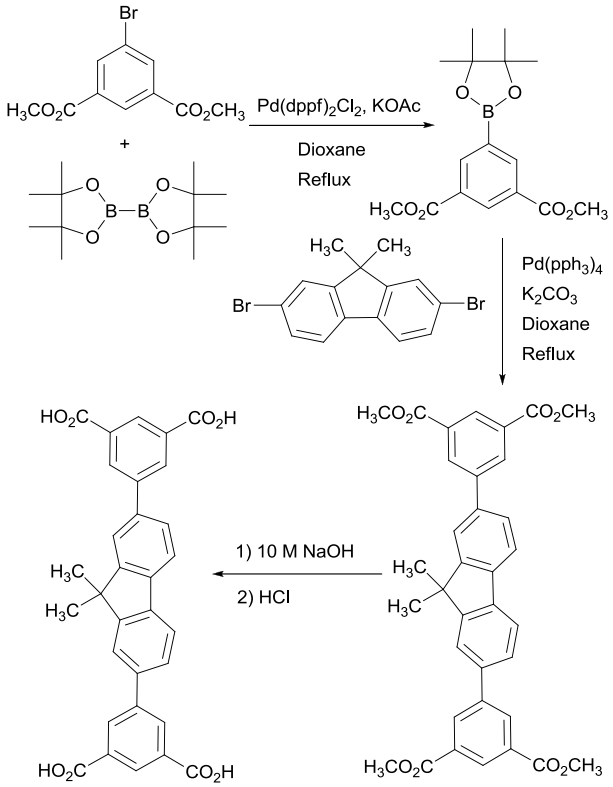
$$S_{ads} = \frac{q_1/q_2}{p_1/p_2} \qquad (3)$$

Here p_1 and p_2 are taken to be the partial pressures of CO_2 and CH_4, respectively. The q_1 and q_2 are the molar loadings in the adsorbed phase, CO_2 and CH_4, respectively, expressed in mol per kg of adsorbent material.

Breakthrough in fixed bed adsorber unit

Both selectivities and uptake capacities are important in determining the separation performance in a fixed bed adsorber. For a proper comparison we undertook breakthrough calculations. Figure S5 shows a schematic of packed bed adsorber packed with **ZJU-60a**. The methodology used in the breakthrough calculations are provided in our earlier works.[2-8] Experimental validation of the breakthrough simulation methodology is available in the published literature[1,2,9,10].

The following parameter values were used: length of packed bed, L = 0.1 m; fractional voidage of packed bed, ε = 0.4; superficial gas velocity at inlet of adsorber, u = 0.04 m/s. The inlet gas consists of an equimolar 5-component $C_2H_2/C_2H_4/C_2H_6/CH_4/CO_2$ gas mixture at 296 K and 100 kPa.



Scheme S1. Synthetic route to the organic linker used to construct **ZJU-60**.

Synthesis of the organic linekr H_4MFDI: H_4MFDI was synthesized via Suzuki coupling followed by hydrolysis and acidification as shown in *Scheme S1*.

Dimethyl (5-pinacolboryl)isopthalate was synthesized by stirring the mixture of dimethyl 5-bromo-benzene-1,3-dicarboxylate (5.4 g, 19.8 mmol), bis(pinacolato)diborane (6.0 g, 23.6 mmol), potassium acetate (5.6 g, 57.2 mmol), $Pd(dppf)_2Cl_2$ (0.2 g, 0.28 mmol), and dried 1,4-dioxane (50 mL) at 80^{o}C for 24 h and afterward extracted with ethyl acetate (20 mL). The organic layer was dried with anhydrous $MgSO_4$ and the solvent was removed in a vacuum. The crude product was purified by column chromatography (silica gel, ethylacetate/petroleum ether, 1:8 *v*/*v*). Yield: 66%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.37 (m, 12 H), 3.95 (s, 6 H), 8.64 (d, 2 H), 8.76 (s, 1H) ppm.

2, 7-dibromo-9*H*-fluorene (3.28 g, 10.0 mmol), dimethyl(5-pinacolboryl)isopthalate (9.26 g, 30.0 mmol), and K_2CO_3 (13.82 g, 100.0 mmol) were added to 1,4- dioxane (250 mL), and the mixture deaerated under Ar for 15 min. $Pd(PPh_3)_4$ (0.47 g,0.43 mmol) was added to the reaction mixture with stirring, and the mixture heated to 80 ℃ for 3 days under Ar. The resultant mixture was evaporated to dryness and taken up in

$CHCl_3$ which had been dried over $MgSO_4$. The $CHCl_3$ solution was evaporated to dryness and purified by column chromatography (silica gel, ethyl acetate/petroleum ether, 1:10 *v*/*v*). Yield: 65%. ^{1}H NMR (500 MHz, $CDCl_3$), δ = 4.00 (s, 12 H), 4.08 (s, 2H), 7.73 (d, 2 H), 7.89 (d, 2H), 7.93 (d, 2H) 8.54 (s, 4H), 8.67 (s, 2H) ppm.

Tetramethyl 5,5'-(9,9-dimethyl-9H-fluorene-2,7-diyl)diisophthalate (H_4MFDI-Me) (3.47g, 6.00mmol) was then suspended in a mixture of 1,4-dioxane (20 mL), to which 50 mL of 10 M NaOH aqueous solution was added. The mixture was stirred under reflux overnight and the THF were removed under a vacuum. Dilute HCl was added to the remaining aqueous solution until the solution was at *p*H = 2. The solid was collected by filtration, washed with water, and dried to give 5,5'-(9,9-dimethyl-9H-fluorene-2,7-diyl)diisophthalic acid (H_4MFDI) (2.87 g, 97% yield). ^{1}H NMR (500 MHz, DMSO), δ = 1.62 (s, 6 H), 7.77 (d, 2H), 8.01 (s, 2 H), 8.04 (s, 2H), 8.47(s, 6H), 13.48 (s, 4H) ppm.

Table1 S1. Crystallographic Data Collection and Refinement Results for **ZJU-60.**

	ZJU-60
Chemical formula	$C_{31}H_{22}Cu_2O_{10}$
Formula weight	681.57
Temperature (K)	293(2)
Wavelength (Å)	1.54178
Crystal system	Hexagonal
Space group	$P6_3/mmc$
a (Å)	18.4819(3)
b (Å)	18.4819(3)
c (Å)	34.4495(5)
V (Å^3)	10190.8(3)
Z	6
Density (calculated g/cm^3)	0.666
Absorbance coefficient (mm^{-1})	0.988
F(000)	2076
Crystal size(mm^3)	0.43χ0.31χ0.11
Goodness of fit on F^2	1.070
R_1, wR_2 [$I>2\sigma(I)$]	0.0599,0.1569
R_1, wR_2 (all data)	0.0721,0.1636
Largestdifference peak and hole(e/Å^3)	0.396,-0.297

Table S2. Langmuir isotherm parameter fits for **ZJU-60a**

	q_{sat} mol kg^{-1}	b_0 Pa$^{-\nu}$	E kJ mol^{-1}	dimensionless
C_2H_2	17	4.13×10^{-6}	8.9	0.66
C_2H_4	15	8.61×10^{-6}	8.5	0.72
C_2H_6	18.7	1.13×10^{-8}	14.7	1
CH_4	7.5	9.56×10^{-9}	12	1
CO_2	8.8	1.72×10^{-8}	14.2	1
N_2	4.5	8.37×10^{-9}	11.2	1

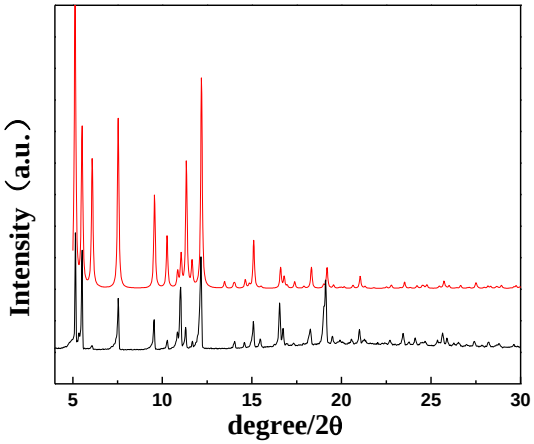


Figure S1. PXRD patterns of as-synthesized **ZJU-60** (black) and the simulated XRD pattern from the single-crystal X-ray structure (red).

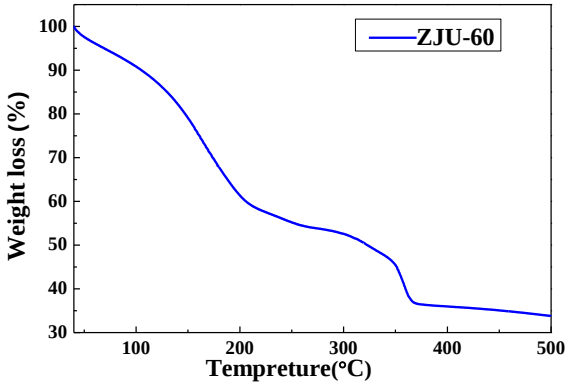


Figure S2. TG of **ZJU-60**

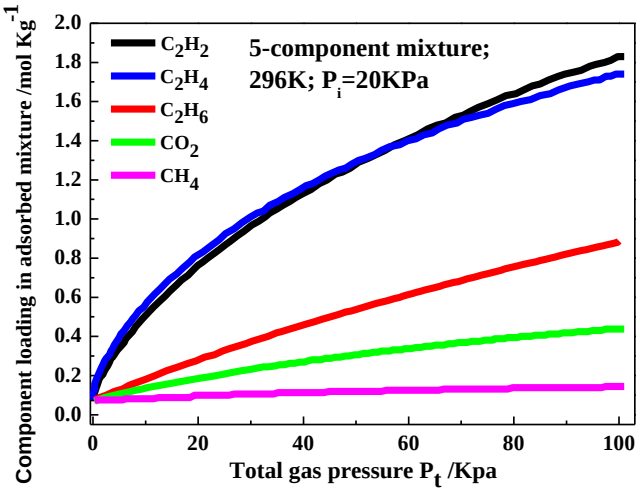


Figure S3. IAST calculations of the component molar loadings in equilibrium with an *equimolar* $C_2H_2/C_2H_4/C_2H_6/CH_4/CO_2$ mixture at total bulk gas phase at 296 K.

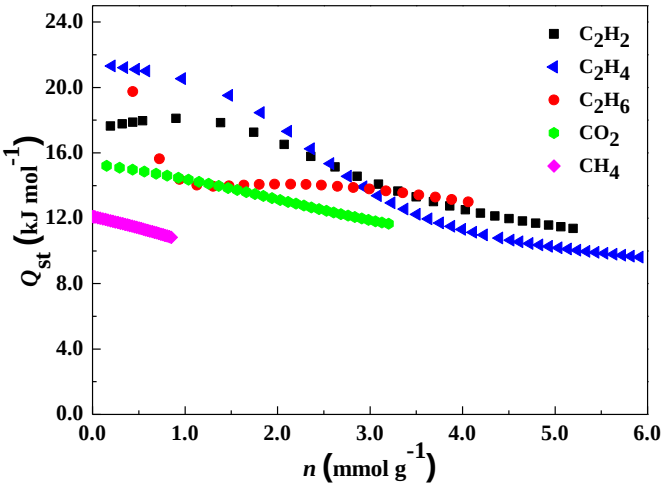


Figure S4 The isosteric heats of adsorption of C_2H_2, C_2H_4, C_2H_6, CO_2 and CH_4 on **ZJU-60a**.

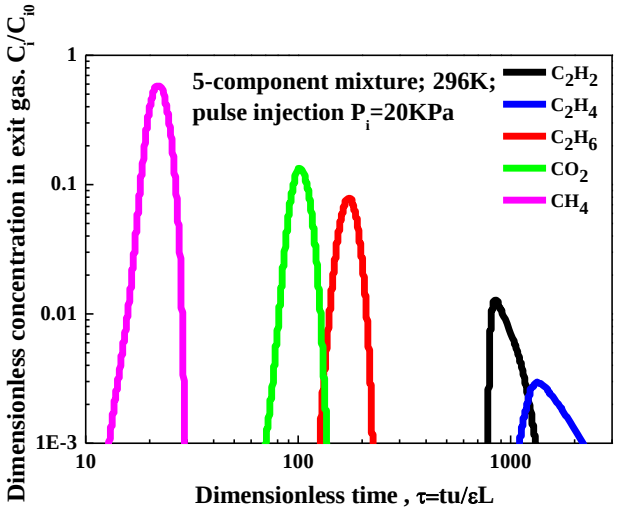


Figure S5. Pulse chromatographic simulations for adsorber packed with **ZJU-60a**. The inlet gas consists of an equimolar 5-component $C_2H_2/C_2H_4/C_2H_6/CH_4/CO_2$ gas mixture at 296 K and 100 kPa. The pulse duration is 10 s.

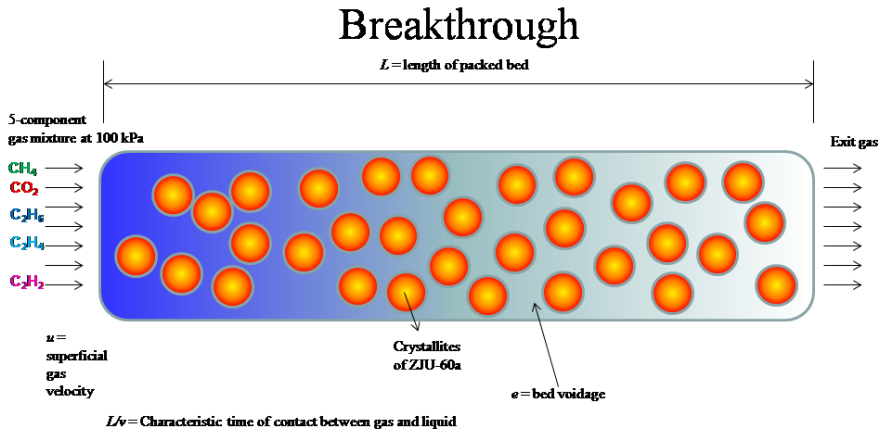


Figure S6. Schematic of packed bed adsorber packed with **ZJU-60a**.

Abbreviations

Notation

b Langmuir-Freundlich constant, $Pa^{-\nu}$

L length of packed bed adsorber, m

p_i partial pressure of species i in mixture, Pa

p_t total system pressure, Pa

q_i component molar loading of species *i*, mol kg^{-1}

q_t total molar loading in mixture, mol kg^{-1}

q_{sat} saturation loading, mol kg^{-1}

R gas constant, 8.314 J mol^{-1} K^{-1}

S_{ads} adsorption selectivity, dimensionless

t time, s

T absolute temperature, K

u superficial gas velocity in packed bed, m s^{-1}

z distance along the adsorber, m

Greek letters

ε voidage of packed bed, dimensionless

ν exponent in Langmuir-Freundlich isotherm, dimension- less

ρ framework density, kg m^{-3}

τ time, dimensionless

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