Journal of
Materials Chemistry A

RSCPublishing

PAPER

View Article Online
View Journal | View Issue

Cite this: *J. Mater. Chem. A*, 2013, **1**, 9916

A cationic microporous metal–organic framework for highly selective separation of small hydrocarbons at room temperature†

Hui Xu,[a] Jianfeng Cai,[a] Shengchang Xiang,[d] Zhangjing Zhang,[d] Chuande Wu,[e] Xiangtang Rao,[a] Yuanjing Cui,[a] Yu Yang,[a] Rajamani Krishna,*[c] Banglin Chen*[ab] and Guodong Qian*[a]

Received 28th May 2013
Accepted 13th June 2013

DOI: 10.1039/c3ta12086d

www.rsc.org/MaterialsA

A new three-dimensional cationic metal–organic framework $Zn_8O(EDDA)_4(ad)_4\cdot(HEDDA)_2\cdot6DMF\cdot27H_2O$ (**ZJU-48**; H_2EDDA = (*E*)-4,4′-(ethene-1,2-diyl)dibenzoic acid; ad = adenine) was solvothermally synthesized and structurally characterized. **ZJU-48** features a three-dimensional structure with a cationic skeleton and has one-dimensional pores along the *c* axis of about 9.1×9.1 Å^2. The activated **ZJU-48a** exhibits a BET surface area of 1450 m^2 g^{-1}. The structural features of the charged skeleton of **ZJU-48a** have enabled its stronger charge-induced interaction with C_2 hydrocarbons than with C_1 methane, resulting in highly selective gas sorption of C_2 hydrocarbons over CH_4 with the adsorption selectivity over 6 at 298 K. The separation feasibility has been further established by the simulated breakthrough and pulse chromatographic experiments, thus methane can be readily separated from their quaternary mixtures at room temperature.

1 Introduction

Hydrocarbons are very important raw materials for industrial products and fine chemicals, so it is important to develop materials for efficient and safe storage of hydrocarbons.[1] Furthermore, their technological development for the separation of C_2 hydrocarbons from C_1 methane will promote their efficient practical usage. For example, methane is a clean alternative to other automobile fuels whereas ethane is an important material for the production of ethylene during industrial scale cracking processes. The traditional cryogenic distillation method for small hydrocarbon separation suffers from high energy cost, while the oil-absorption method is not efficient;[2] it is thus necessary to develop and explore more efficient separation technologies and materials. The implementation of adsorbent based methodologies through pressure swing adsorption (PSA) and thermal swing adsorption (TSA) has shown promise in cost efficient separation of these small hydrocarbons. In fact, a number of microporous materials have been explored for the separation of C_2 hydrocarbons from methane over the last two decades.[3]

Microporous metal–organic framework (MOF) materials are self-assembled from organic ligands and metal ion/cluster centres through coordination bonding and have been rapidly emerging as new types of microporous adsorbents for gas storage and separation.[4–23] The pore sizes of MOFs can be systematically optimized to make the small gas molecules go through the pores while the large ones are blocked outside. Also, MOF pores can be immobilized with different functional sites such as open metal sites, $-NH_2$, $-OH$, and Lewis pyridine sites, to enhance MOF interactions with different gas molecules. Among the different strategies used, the open metal site strategy has been particularly useful for both gas storage and separation.[5–12] Ionic MOFs recently have attracted much attention. An ionic MOF skeleton can serve as an ionic host to accommodate different guests with balanced charge by electrostatic interactions and further cooperatively realize specific functions. Furthermore, some cations and anions can be utilized to tune the pore sizes to enhance gas selectivity, as demonstrated in a few examples of MOFs.[13–19]

We and others have mainly focused on immobilizing open metal sites and optimizing pore sizes to target MOF materials for the highly selective separation of small hydrocarbons.[20–26] Because C_2 hydrocarbons have quite different polarizability properties from C_1 methane, ionic frameworks might be of

---

[a] State Key Laboratory of Silicon Materials, Cyrus Tang Center for Sensor Materials and Applications, Department of Materials Science & Engineering, Zhejiang University, Hangzhou 310027, China. E-mail: gdqian@zju.edu.cn

[b] Department of Chemistry, University of Texas at San Antonio, One UTSA Circle, San Antonio, Texas 78249-0698, USA. E-mail: banglin.chen@utsa.edu; Fax: +1 210-458-7428

[c] Van't Hoff Institute for Molecule Sciences, University of Amsterdam, Science Park 904, 1098 XH Amsterdam, The Netherlands. E-mail: r.krishna@uva.nl

[d] College of Chemistry and Materials, Fujian Normal University, 3 Shangsan Road, Cangshang Region, Fuzhou, 350007, China

[e] Department of Chemistry, Zhejiang University, Hangzhou 310027, China

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c3ta12086d

interest and important as new types of MOF materials for the separation of these hydrocarbons by the enhanced adsorbent–adsorbate interactions through charge-induced forces.[17] Herein, we report the first example of cationic microporous MOFs$Zn_8O(EDDA)_4(ad)_4\cdot(HEDDA)_2\cdot6DMF\cdot27H_2O$ (**ZJU-48**; H_2EDDA = (*E*)-4,4′-(ethene-1,2-diyl)dibenzoic acid; ad = adenine) with a BET surface area of 1450 $m^2\ g^{-1}$ for highly selective separation of C_2 hydrocarbons from C_1 methane, which has been established exclusively by the sorption isotherms and simulated breakthrough and pulse chromatographic experiments.

2 Experimental

2.1 Materials and measurements

All the chemicals were commercially available and used without further purification. Elemental analyses of C, H, and N were performed on an EA1112 microelemental analyser. Powder X-ray diffraction (PXRD) patterns were collected in the $2\theta = 3$–60 °C range on an X'Pert PRO diffractometer with Cu Kα radiation ($\lambda = 1.542$ Å) at room temperature. Thermogravimetric analyses (TGAs) were conducted on a Netszch TGA 209 F3 thermogravimeter with a heating rate of 10 °C min^{-1} in an N_2 atmosphere.

2.2 Gas sorption measurements

A Micromeritics ASAP 2020 surface area analyser was used to measure gas adsorption. In order to remove guest solvent molecules in the framework, a fresh sample of **ZJU-48** was exchanged with chloroform 10 times and then activated at 273 K under high vacuum for 12 h until the outgas rate was <5 μmHg min^{-1} prior to measurements. During the sorption measurement the sample was maintained at 77 K with liquid nitrogen and 273 K with an ice-water bath (slush), respectively. As the center-controlled air condition was set at 296 K, a water bath of 296 K was used for adsorption isotherms at 296 K.

Isotherm data were analysed using the virial equation:

$$\ln(n/p) = A_0 + A_1n + A_2n^2 + \ldots$$

where *p* is the pressure, *n* is the amount adsorbed, and A_0, A_1, *etc.* are virial coefficients. The Henry's law constant (K_H) is equal to $\exp(A_0)$, and the selectivity can be obtained from the constant K_H.

2.3 Synthesis of ZJU-48

$Zn(OAc)_2\cdot2H_2O$ (0.183 mmol, 40 mg), adenine (0.074 mmol, 10 mg), H_2EDDA (0.113 mmol, 30 mg) were dissolved in a mixed solvent of DMF (13.5 ml) and H_2O (1 ml), then 0.1 ml of HNO_3 with a concentration of 62% was added, and the mixture was transferred to and sealed in a 20 ml Teflon-lined autoclave, which was heated at 125 °C for 1 day. After slow cooling to room temperature, yellow crystals of **ZJU-48** were collected by filtration. Anal. calcd for $Zn_8C_{134}N_{26}H_{174}O_{58}$: C, 44.67; H, 4.83; N, 10.11. Found: C, 44.77; H, 4.41; N: 10.12%.

Table 1 Crystallographic data collection and refinement results for **ZJU-48**

	ZJU-48
Chemical formula	$C_{116}H_{78}Zn_8N_{20}O_{25}$
Formula weight	2675.10
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Tetragonal
Space group	*P*4/*n*
a (Å)	28.7876(11)
b (Å)	28.7876(11)
c (Å)	11.1348(5)
V (Å^3)	9227.7(6)
Z	2
Density (calculated g cm^{-3})	0.767
Adsorption coefficient (mm^{-1})	1.058
F(000)	2136
Crystal size (mm^3)	0.46 × 0.36 × 0.21
Goodness of fit on F_2	1.074
R_1, wR_2 [$I > 2\sigma(I)$][a]	0.0816, 0.2139
R_1,wR_2 (all data)[a]	0.1324,0.2340

[a] $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$; $\mathrm{w}R_2 = \left[\dfrac{\sum \mathrm{w}\left(|F_o| - |F_c|^2\right)}{\sum \mathrm{w}{F_o}^2}\right]^{1/2}$.

2.4 X-Ray collection and structure determination

Single crystal diffraction data were collected on an Oxford Xcalibur Gemini Ultra diffractometer with an Atlas detector using graphite monochromatic Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293 K. The structure of **ZJU-48** was solved by direct methods and refined with full-matrix least-squares on F_2 with the SHELXL-97 program package. The H atoms on the ligand were placed in idealized positions and refined using a riding model. The H atoms on the coordinated solvent O atoms could not be located. The unit cell includes a large region of disordered solvent molecules, which could not be modelled as discrete atomic sites. We employed PLATON/SQUEEZE to calculate the diffraction contribution of the solvent molecules, thereby producing a set of solvent-free diffraction intensities. CCDC 931058. Crystallographic data are summarized in Table 1.

3 Results and discussion

ZJU-48 was synthesized by the solvothermal reaction of $Zn(OAc)_2\cdot2H_2O$, adenine and H_2EDDA in a mixture solvent of DMF–H_2O with the addition of a small amount of HNO_3 at 125 °C for 1 day as yellow prismatic single crystals. The structure 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. S3†) and thermogravimetric analysis (TGA) (Fig. S2†). The crystalline product is insoluble in most of the common organic solvents.

The X-ray single crystal structure of **ZJU-48** showed that it crystallized in the tetragonal space group *P*4/*n*. As shown in Fig. 1, **ZJU-48** is a three-dimensional (3D) framework comprising Zn–adenine rod chains, which were further linked to EDDA ligands *via* their carboxylate groups. Within the Zn–adenine rod chains, four Zn1 atoms adopt tetrahedral

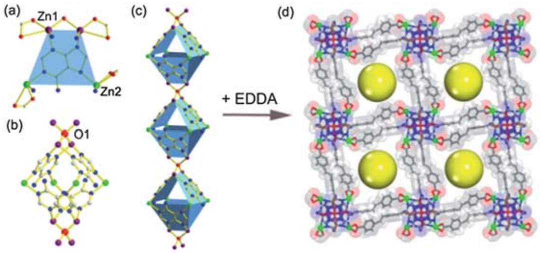

Fig. 1 View of 3D **ZJU-48**. (a) Each adenine ligand coordinated to two Zn1 and two Zn2 atoms to form walls of octahedral cages; (b) four Zn1 atoms adopt tetrahedral geometry through coordination to a μ4-oxygen atom O1 to form the Zn_4O SBU structure; (c) Zn2-adenine octahedron is linked with Zn_4O to form Zn-adenine rod chains; (d) EDDAs link Zn-adenine rod chains to give the 1D channels of 9.1 × 9.1 Å^2 extending along the *c* direction.

geometry through coordination to a μ4-oxygen atom O1 to form the Zn_4O SBU structure, which were further linked with two adenine–Zn2 octahedrons. **ZJU-48** has one-dimensional pores along the *c* axis of about 9.1 × 9.1 Å^2, which were filled with guest molecules. The void space accounts for approximately 62.3% of the whole crystal volume (4247.5 Å^3 out of the 9227.7 Å^3 per unit cell volume) by PLATON analysis. The most interesting thing is that **ZJU-48** is an ionic MOF with the cationic skeleton. The N_2 sorption isotherm at 77 K showed that **ZJU-48** displayed Type-I sorption behaviour with a BET surface area of 1450 m^2 g^{-1} (Fig. 2(a)).

Thermogravimetric analysis (TGA) of **ZJU-48** showed that approximately 25.1% weight loss occurred before 220 °C due to the release of H_2O and DMF solvent molecules, and the framework is stable up to 400 °C. PXRD studies indicate that the activated **ZJU-48a** generated at 0 °C under high vacuum for 1 day keeps the highly-crystalline feature whose pattern matches with that of the as-synthesized one, indicating that **ZJU-48** is robust. The robust properties and the permanent porosity of **ZJU-48** encouraged us to examine its potential application for storage and selective separation of small hydrocarbons. Sorption isotherms are repeatable, which means that **ZJU-48** can be easily re-utilized. As shown in Fig. 3, **ZJU-48a** can take up moderate amounts of C_2H_2 of 77.83 and 57.07 cm^3 g^{-1} at 273 and 296 K, respectively, under 1 atm. Although the amount of adsorbed C_2H_2 in **ZJU-48a** at 296 K is lower than those with high density of open metal sites such as Zn-MOF-74 (122 cm^3 g^{-1}), the C_2H_2 uptake of **ZJU-48a** at 296 K is comparable with our previously reported **UTSA-36** (57 cm^3 g^{-1}) with smaller pore sizes, and is higher than **MOF-5** (26 cm^3 g^{-1}) with larger pore sizes.

ZJU-48a systematically exhibits different adsorption capacities to CH_4 than those of C_2H_6, C_2H_4 and C_2H_2 at both 273 and 298 K. **ZJU-48a** can take up C_2H_2 (77.83 cm^3 g^{-1}), C_2H_4 (65.65 cm^3 g^{-1}), C_2H_6 (80.66 cm^3 g^{-1}) but a much lower amount of CH_4 (11.96 cm^3 g^{-1}) at 1 atm and 273 K; and C_2H_2 (57.07 cm^3 g^{-1}), C_2H_4 (39.43 cm^3 g^{-1}), C_2H_6 (43.78 cm^3 g^{-1}) and also a lower amount of CH_4 (7.82 cm^3 g^{-1}) at 1 atm and 296 K. This indicated that **ZJU-48a** is a promising material for highly selective adsorptive separation of C_2 hydrocarbons from CH_4.

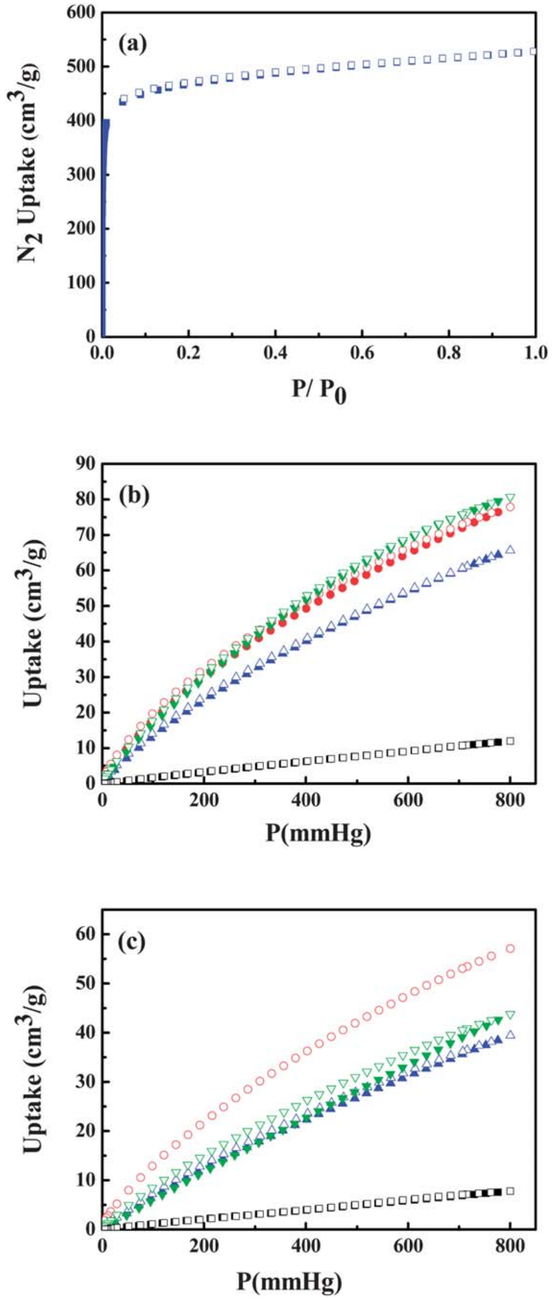

Fig. 2 (a) N_2 sorption isotherm at 77 K and CH_4 (black), C_2H_6 (green) and C_2H_4 (blue), C_2H_2 (red)sorption isotherms of **ZJU-48a** at (b) 273 K and (c) 296 K. Solid symbols: adsorption, open symbols: desorption.

In order to establish the feasibility of this separation, we performed calculations using the Ideal Adsorbed Solution Theory (IAST) of Myers and Prausnitz.[27] Fig. S4† shows IAST calculations of the component molar loadings in equilibrium with an *equimolar* CH_4–C_2H_2–C_2H_4–C_2H_6 mixture as a function of the total bulk gas phase pressure at 296 K. The IAST calculations indicated that the hierarchy of adsorption capacity is commonly $CH_4 < C_2H_6 \approx C_2H_4 < C_2H_2$, making the CH_4/C_2H_6 separation the crucial one. As shown in Fig. 3, the adsorption selectivities of C_2H_6 with respect to CH_4 are in excess of 6 for a range of pressure to 100 KPa, indicating the feasibility of this MOF for the practical application in C_2/C_1 separation, although this selectivity value is lower than those best MOFs with high

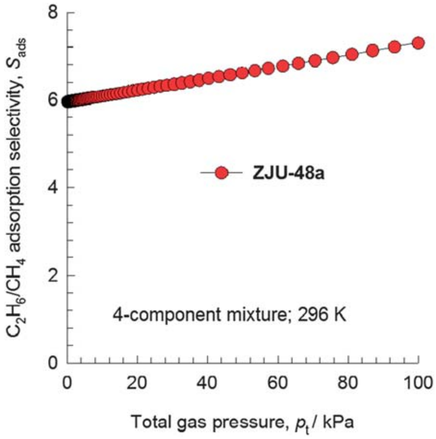

Fig. 3 IAST calculations of the C_2H_6/CH_4 adsorption selectivity for adsorption from an equimolar CH_4–C_2H_2–C_2H_4–C_2H_6 mixture at the total bulk gas phase at 296 K.

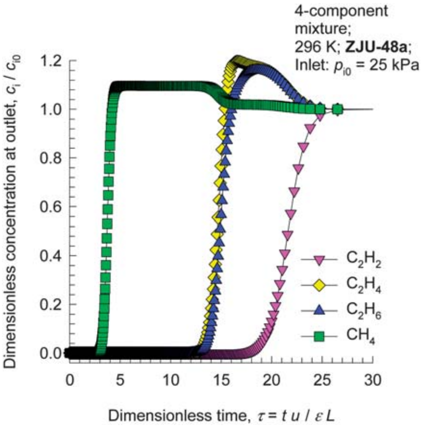

Fig. 5 Breakthrough simulation results for **ZJU-48a** for separation of an *equimolar* CH_4–C_2H_2–C_2H_4–C_2H_6 mixture in a fixed bed adsorbent at the total bulk gas phase at 296 K and 100 kPa. The *x*-axis represents the dimensionless time, τ.

density open metal sites such as Cu(BTC) (HKUST-1), Mg-MOF-74 and Co-MOF-74 for C_2/C_1 separation, with the selectivity values of about 11, 14 and 18, respectively (Fig. S5†).

To figure out why **ZJU-48a** exhibits selective separation for small hydrocarbons, 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. 4 shows data on the loading dependence of Q_{st} for adsorption of CH_4, C_2H_2, C_2H_4, and C_2H_6 on **ZJU-48a**. The isosteric heat of adsorption of CH_4 on **ZJU-48a** is 14.0 kJ mol^{-1}, whereas the isosteric heats of adsorption of C_2H_2, C_2H_4, and C_2H_6 are 15.6, 21.7 and 28.0 kJ mol^{-1}, respectively. The isosteric heat for C_2H_6 is very high, which is even comparable to that of Mg-MOF-74 (Fig. S6†). The higher adsorption heats of C_2 hydrocarbons can be attributed to the larger van der Waals interactions between the framework and C_2 hydrocarbons. The charged framework skeleton of **ZJU-48a** results in even stronger interactions with those easily polarized C_2 hydrocarbons.[17]

To further demonstrate the feasibility for the practical separation, the breakthrough experiments were simulated based on the established methodology described in the work of Krishna and Long which has been exclusively confirmed by the experimental breakthrough experiments.[25] Fig. 5 shows the data on the concentrations at the exit of the adsorber for **ZJU-48a**. The *x*-axis in Fig. 5 represents a dimensionless time, τ, defined by dividing the actual time, *t*, by the characteristic time, $L\varepsilon/u$. We note that **ZJU-48a** has the capability of separating CH_4 in pure form from this quaternary mixture. The breakthrough of C_2H_4 and C_2H_6 occurs at approximately the same time, indicating that **ZJU-48a** is not suitable for separation of C_2H_4–C_2H_6 mixtures. The separation capability of **ZJU-48a** is also underscored in pulse chromatographic simulations (Fig. S7†). The breakthrough and pulse chromatographic simulations confirm the potency of **ZJU-48** in separation of CH_4 from mixtures containing C_2H_2, C_2H_4 and C_2H_6 species.

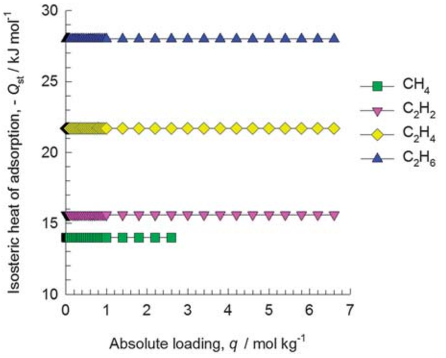

Fig. 4 The isosteric heats of adsorption of C_2H_6, C_2H_4, C_2H_2 and CH_4 on **ZJU-48a**.

4 Conclusions

In summary, we have synthesized a novel porous metal–organic framework **ZJU-48** with the cationic skeleton for the highly selective separation of C_2 hydrocarbons over methane. The cationic skeleton in **ZJU-48** enhanced the interactions by electrostatic interaction between MOF and more polarized gas molecules, leading to highly selective separation of C_2 hydrocarbons over C_1 methane. The realization of this first example of cationic microporous MOF **ZJU-48** for the highly selective separation of C_2/C_1 hydrocarbons might facilitate the extensive research endeavour to explore this ionic MOF approach, so some novel ionic MOF materials will be emerging for the separation of these industrially important hydrocarbons.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grants 51229201, 51272231 and 51010002), and Grant AX-1730 from the Welch Foundation (B.C.). We also appreciate the support from NSFC (21273033, 21203024) and the Award 'MinJiang Scholar Program' in Fujian Province, China.

Notes and references

1 R. W. Baker, *Ind. Eng. Chem. Res.*, 2002, **41**, 1393.

2 N. B. K. Magnowski, A. M. Avila, C. C. H. Lin, M. Shi and S. M. Kuznicki, *Chem. Eng. Sci.*, 2011, **66**, 1697; S. Hosseinpour, S. Fatemi, Y. Mortazavi, M. Gholamhoseini and M. T. Ravanchi, *Sep. Sci. Technol.*, 2010, **46**, 349; V. R. Choudhary and S. Mayadevi, *Zeolites*, 1996, **17**, 501; R. W. Triebe, F. H. Tezel and K. C. Khulbe, *Gas Sep. Purif.*, 1996, **10**, 81.

3 S. M. Kuznicki, V. A. Bell, S. Nair, H. W. Hillhouse, R. M. Jacubinas, C. M. Braunbarth, B. H. Toby and M. Tsapatsis, *Nature*, 2001, **412**, 720; S. M. Kuznicki, V. A. Bell, I. Petrovic and B. T. Desai, *US Pat.*, 6068682, 2000.

4 M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe and O. M. Yaghi, *Acc. Chem. Res.*, 2001, **34**, 319; S. Kitagawa, R. Kitaura and S. Noro, *Angew. Chem., Int. Ed.*, 2004, **43**, 2334; D. Bradshaw, J. B. Claridge, E. J. Cussen, T. J. Priora and M. J. Rosseinsky, *Acc. Chem. Res.*, 2005, **38**, 273; G. Ferey, *Chem. Soc. Rev.*, 2008, **37**, 191; R. E. Morris and P. S. Wheatley, *Angew. Chem., Int. Ed.*, 2008, **47**, 4966; M. P. Suh, Y. E. Cheon and E. Y. Lee, *Coord. Chem. Rev.*, 2008, **252**, 1007; D. M. D'Alessandro, B. Smit and J. R. Long, *Angew. Chem., Int. Ed.*, 2010, **49**, 6058; O. K. Farha and J. T. Hupp, *Acc. Chem. Res.*, 2010, **43**, 1166; B. Chen, S. C. Xiang and G. D. Qian, *Acc. Chem. Res.*, 2010, **43**, 1115; H. L. Jiang and Q. Xu, *Chem. Commun.*, 2011, **47**, 3351; M. P. Suh, H. J. Park, T. K. Prasad and D. W. Lim, *Chem. Rev.*, 2012, **112**, 782; K. Sumida, D. L. Rogow, J. A. Mason, T. M. Mcdonald, E. D. Bloch, Z. R. Herm, T. H. Bae and J. R. Long, *Chem. Rev.*, 2012, **112**, 724; J. R. Li, J. Sculley and H. C. Zhou, *Chem. Rev.*, 2012, **112**, 869.

5 W. Morris, B. Leung, H. Furukawa, O. K. Yaghi, N. He, H. Hayashi, Y. Houndonougbo, M. Asta, B. B. Laird and O. M. Yaghi, *J. Am. Chem. Soc.*, 2010, **132**, 11006; E. D. Bloch, D. Britt, C. J. Doonan, F. J. Uribe-Romo, H. Furukawa, J. R. Long and O. M. Yaghi, *J. Am. Chem. Soc.*, 2010, **132**, 14382; H. Deng, S. Grunder, K. E. Cordova, C. Valente, H. Furukawa, M. Hmadeh, F. Gandara, A. C. Whalley, Z. Liu, S. Asahina, H. Kazumori, M. O'Keeffe, O. Terasaki, J. F. Stoddart and O. M. Yaghi, *Science*, 2012, **336**(6084), 1018.

6 S. Ma, D. Sun, D. Yuan, X. S. Wang and H. C. Zhou, *J. Am. Chem. Soc.*, 2009, **131**, 6445; J. R. Li, J. Yu, W. Lu, J. Sculley, P. B. Balbuena and H. C. Zhou, *Nat. Commun.*, 2013, **4**, 1588.

7 P. Q. Liao, D. D. Zhou, A. X. Zhu, L. Jiang, R. B. Lin, J. P. Chen and X. M. Chen, *J. Am. Chem. Soc.*, 2012, **134**, 17380; C. T. He, J. Y. Tian, S. Y. Liu, G. F. Ouyang, J. P. Zhang and X. M. Chen, *Chem. Sci.*, 2013, **4**, 351.

8 F. Wang, Y.-X. Tan, H. Yang, Y. Kang and J. Zhang, *Chem. Commun.*, 2012, **48**, 4842.

9 K. Li, D. H. Olson, J. Seidel, T. J. Emge, H. Gong, H. Zeng and J. Li, *J. Am. Chem. Soc.*, 2009, **131**, 10368.

10 H. Wu, W. Zhou and T. Yildirim, *J. Am. Chem. Soc.*, 2009, **131**, 4995.

11 Y. Q. Lan, H. L. Jiang, S. L. Li and Q. Xu, *Adv. Mater.*, 2011, **23**, 5015.

12 S. C. Xiang, W. Zhou, J. M. Gallegos, Y. Liu and B. Chen, *J. Am. Chem. Soc.*, 2009, **131**, 12415; S. C. Xiang, W. Zhou, Z. J. Zhang, M. A. Green, Y. Liu and B. Chen, *Angew. Chem., Int. Ed.*, 2010, **49**, 4615; S. Xiang, Y. He, Z. Zhang, H. Wu, W. Zhou, R. Krishna and B. Chen, *Nat. Commun.*, 2012, **3**, 954; M. C. Das, H. Xu, Z. Wang, G. Srinivas, W. Zhou, Y.-F. Yue, V. N. Nesterov, G. Qian and B. Chen, *Chem. Commun.*, 2011, **47**, 11715; Y. He, S. Xiang and B. Chen, *J. Am. Chem. Soc.*, 2011, **133**, 14570; Y. Hu, S. Xiang, W. Zhang, Z. Zhang, L. Wang, J. Bai and B. Chen, *Chem. Commun.*, 2009, 7551; Y.-S. Xue, Y. He, S.-B. Ren, Y. Yue, L. Zhou, Y.-Z. Li, H.-B. Du, X.-Z. You and B. Chen, *J. Mater. Chem.*, 2012, **22**, 10195; Z. Zhang, S. Xiang, X. Rao, Q. Zheng, F. R. Fronczek, G. Qian and B. Chen, *Chem. Commun.*, 2010, **46**, 7205; Z. Chen, S. Xiang, H. D. Arman, J. U. Mondal, P. Li, D. Zhao and B. Chen, *Inorg. Chem.*, 2011, **50**, 3442; Z. Zhang, S. Xiang and B. Chen, *CrystEngComm*, 2011, **13**, 5983; S. Xiang, Z. Zhang, C. G. Zhao, K. Hong, X. Zhao, D. L. Ding, M. H. Xie, C. D. Wu, R. Gill, K. M. Thomas and B. Chen, *Nat. Commun.*, 2010, **2**, 204.

13 M. Dincă and J. R. Long, *J. Am. Chem. Soc.*, 2007, **129**, 11172.

14 D. F. Sava, V. C. Kravtsov, F. Nouar, L. Wojtas, J. F. Eubank and M. Eddaoudi, *J. Am. Chem. Soc.*, 2008, **130**, 3768; F. Nouar, J. Eckert, J. F. Eubank, P. Forster and M. Eddaoudi, *J. Am. Chem. Soc.*, 2009, **131**, 2864.

15 K. L. Mulfort, O. K. Farha, C. Stern, A. A. Sarjeaut and J. T. Hupp, *J. Am. Chem. Soc.*, 2009, **131**, 3866; D. Himsl, D. Wallacher and M. Hartmann, *Angew. Chem., Int. Ed.*, 2009, **48**, 4639.

16 S. Yang, X. Lin, A. J. Blake, K. M. Thomas, P. Hubberstey, N. R. Champness and M. Schroder, *Chem. Commun.*, 2008, 6108; S. Yang, X. Lin, A. J. Blake, G. Walker, P. Hubberstey, N. R. Champness and M. Schroder, *Nat. Chem.*, 2009, **1**, 487; S. Yang, X. Lin, W. Lewis, M. Suyetin, E. Bichoutskaia, J. E. Parker, C. C. Tang, D. R. Allan, P. J. Rizkallah, P. Hubberstey, N. R. Champness, K. M. Thomas, A. J. Blake and M. Schröder, *Nat. Mater.*, 2012, **11**, 710.

17 S. Chen, J. Zhang, T. Wu, P. Feng and X. Bu, *J. Am. Chem. Soc.*, 2009, **131**, 16027; Q. Zhai, Q. Lin, T. Wu, L. Wang, S. Zheng, X. Bu and P. Feng, *Chem. Mater.*, 2012, **24**, 2624; E. Quartapelle Procopio, F. Linares, C. Montoro, V. Colombo, A. Maspero, E. Barea and J. A. R. Navarro, *Angew. Chem., Int. Ed.*, 2010, **49**, 7308; D. Peralta, G. Chaplais, A. S. Masseron, K. Barthelet, C. Chizallet, A. A. Quoineaud and G. D. Pirngruber, *J. Am. Chem. Soc.*, 2012, **134**, 8115; H. J. Park and M. P. Suh, *Chem. Sci.*, 2013, **4**, 685.

18 J. An and N. L. Rosi, *J. Am. Chem. Soc.*, 2010, **132**, 5578; J. An, C. M. Shade, D. A. C. Czegan, S. Petoud and N. L. Rosi, *J. Am. Chem. Soc.*, 2011, **133**, 1220.

19 J. Yu, Y. Cui, C. Wu, Y. Yang, Z. Wang, M. O'Keeffe, B. Chen and G. Qian, *Angew. Chem., Int. Ed.*, 2012, **51**, 10542.

20 R. Krishna and J. R. Long, *J. Phys. Chem. C*, 2011, **115**, 12941–12950.

21 S. C. Reyes, J. G. Santiesteban, Z. Ni, C. S. Paur, P. Kortunov, J. Zengel and H. W. Deckman, *US Pat.*, US2009/0216059A1, 2009.

22 S. Horike, Y. Inubushi, T. Hori, T. Fukushima and S. Kitagawa, *Chem. Sci.*, 2012, **3**, 116–120.

23 E. Bloch, W. L. Queen, R. Krishna, J. M. Zadrozny, C. M. Brown and J. R. Long, *Science*, 2012, **335**, 1606.

24 Y. He, R. Krishna and B. Chen, *Energy Environ. Sci.*, 2012, **5**, 9107; Y. He, Z. Zhang, S. Xiang, F. R. Fronczek, R. Krishna and B. Chen, *Chem.–Eur. J.*, 2012, **18**, 613; Y. He, Z. Zhang, S. Xiang, H. Wu, F. R. Fronczek, W. Zhou, R. Krishna, M. O'Keeffe and B. Chen, *Chem.–Eur. J.*, 2012, **18**, 1901; M. C. Das, H. Xu, S. Xiang, Z. Zhang, H. D. Arman, G. Qian and B. Chen, *Chem.–Eur. J.*, 2011, **17**, 7817; Y. He, Z. Zhang, S. Xiang, F. R. Fronczek, R. Krishna and B. Chen, *Chem. Commun.*, 2012, **48**, 6493; Y. He, W. Zhou, R. Krishna and B. Chen, *Chem. Commun.*, 2012, **48**, 11813.

25 R. Krishna and J. R. Long, *J. Phys. Chem. C*, 2011, **115**, 12941.

26 C. Zhang, R. P. Lively, K. Zhang, J. R. Johnson, O. Karvan and W. J. Koros, *J. Phys. Chem. Lett.*, 2012, **3**, 2130.

27 A. L. Myers and J. M. Prausnitz, *AIChE J.*, 1965, **11**, 121.

Supporting Information for the manuscript

A Cationic MicroporousMetal-Organic Framework for Highly Selective Separation of Small Hydrocarbons at Room Temperature

Hui Xu[a],Jianfeng Cai[a], Shengchang Xiang[d],Zhangjing Zhang[d], Chuande Wu[e], Xiangtang Rao[a], Yuanjing Cui[a], Yu Yang[a], Rajamani Krishna*[c], Banglin Chen*[ab] and Guodong Qian*[a]

[a]*State Key Laboratory of Silicon Materials, Cyrus Tang Center for SensorMaterials and Applications, Department of Materials Science &Engineering,Zhejiang University, Hangzhou 310027, China. E-mail:gdqian@zju.edu.cn*

[b]*Department of Chemistry, University of Texas at San Antonio, OneUTSA Circle, San Antonio, Texas 78249-0698, USA. E-mail: banglin.chen@utsa.edu; Fax: (+1) 210-458-7428*

[c]*Van't Hoff Institute for Molecule Sciences, University of Amsterdam Science Park 904, 1098 XH Amsterdam (The Netherlands). E-mail: r.krishna@uva.nl*

[d]*College of Chemistry and Materials, Fujian Normal University, 3 Shangsan Road, Cangshang Region, Fuzhou, 350007, China*

[e]*Department of Chemistry, Zhejiang University, Hangzhou 310027, China*

*Corresponding Authors. E-mail:gdqian@zju.edu.cn, banglin.chen@utsa.edu, r.krishna@uva.nl

1. Fitting of pure component isotherms

The measured experimental data on pure component isotherms for **ZJU-48a**, were first converted to absolute loading using the Peng-Robinson equation of state for estimation of the fluid densities. The pure component isotherm data for CH_4, C_2H_2, C_2H_4, and C_2H_6, expressed in terms of *absolute* loadings, were fitted with the Langmuir isotherm model

$$q = q_{A,sat} \frac{b_A p}{1 + b_A p} \qquad (1)$$

with T-dependent parameter b_A

$$b_A = b_{A0} \exp\left(\frac{E_A}{RT}\right) \qquad (2)$$

The fitted parameter values are presented in Table S1. Figure S4 presents IAST calculations of the component molar loadings in equilibrium with an *equimolar* $CH_4/C_2H_2/C_2H_4/C_2H_6$ mixture as a function of the total bulk gas phase pressure at 296K.

2. Adsorption selectivity

Let us first consider the separation of CH_4 from a mixture containing C_2 hydrocarbons. Rather than restrict our investigations to just binary CH_4/C_2H_6 mixtures, we consider the selective adsorption of C_2 hydrocarbons from an equimolar 4-component $CH_4/C_2H_2/C_2H_4/C_2H_6$ 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 ethene.

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 C_2H_6 and CH_4, respectively. The q_1 and q_2 are the molar loadings in the adsorbed phase, C_2H_6 and CH_4, respectively, expressed in mol per kg of adsorbent material.

3. Isosteric heat of adsorption

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

$$Q_{st} = RT^2 \left(\frac{\partial \ln p}{\partial T} \right)_q \tag{4}$$

were determined using the pure component isotherm fits.

4. Breakthrough in fixed bed adsorber unit

In demonstrate the separation performance of a pressure swing adsorption (PSA) unit, we performed breakthrough calculations with step-input of an equimolar $CH_4/C_2H_2/C_2H_4/C_2H_6$ mixture. The x-axis in Figure 5 is a dimensionless time, τ, defined by dividing the actual time, t, by the characteristic time, $\frac{L\varepsilon}{u}$.

Table S1. Langmuir isotherm parameter fits for **ZJU-48a**

	$q_{\mathrm{A,sat}}$ mol kg^{-1}	b_{A0} Pa^{-1}	E_{A} kJ mol^{-1}
C_2H_2	6.9	9.6×10^{-9}	15.6
C_2H_4	6.9	4.87×10^{-10}	21.7
C_2H_6	9	2.91×10^{-11}	28
CH_4	3.2	4.06×10^{-9}	14

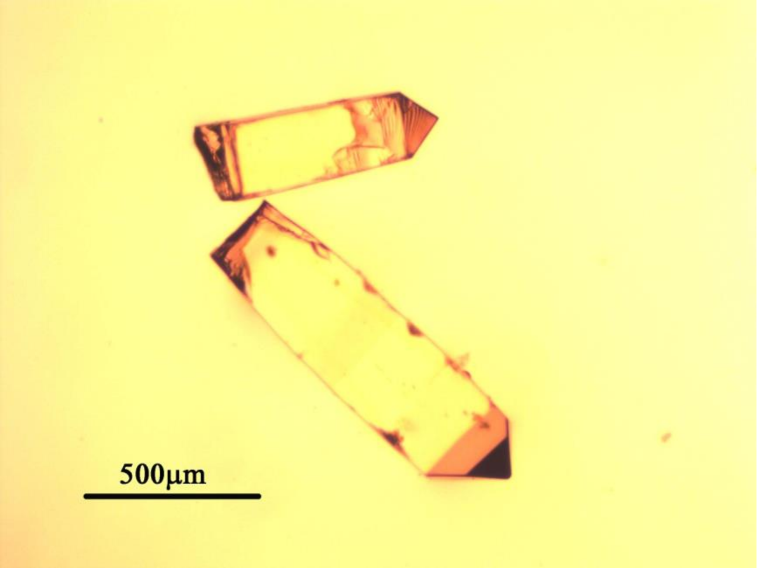

Figure S1 Fluorescent microscope images of **ZJU-48** crystals illuminated with visible light.

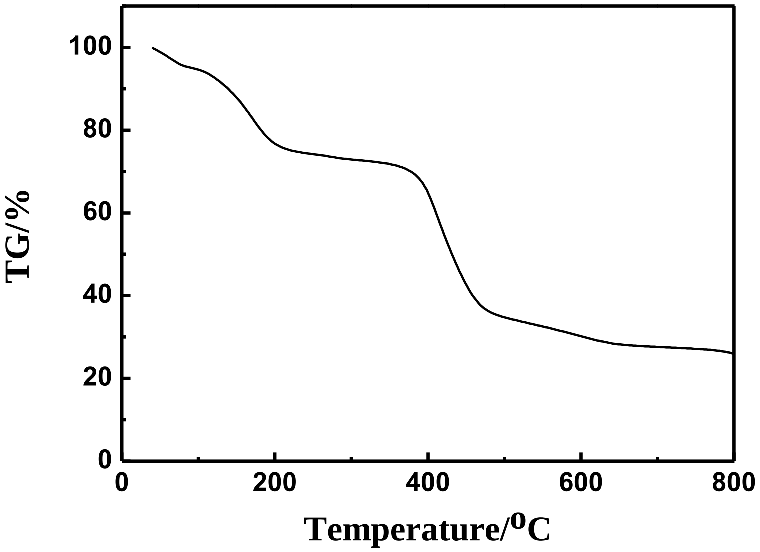

Figure S2. TG of **ZJU-48**

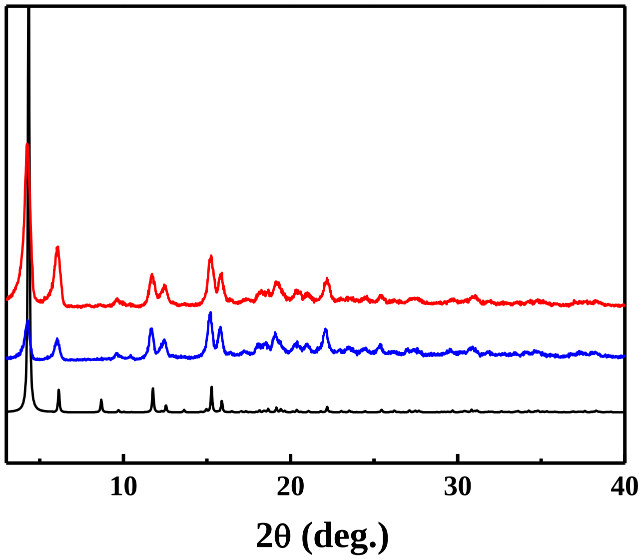

Figure S3. PXRD patterns of **ZJU-48** (simulated: black; as-synthesized: blue; activated at 0 °C in vacuum for 12h: red).

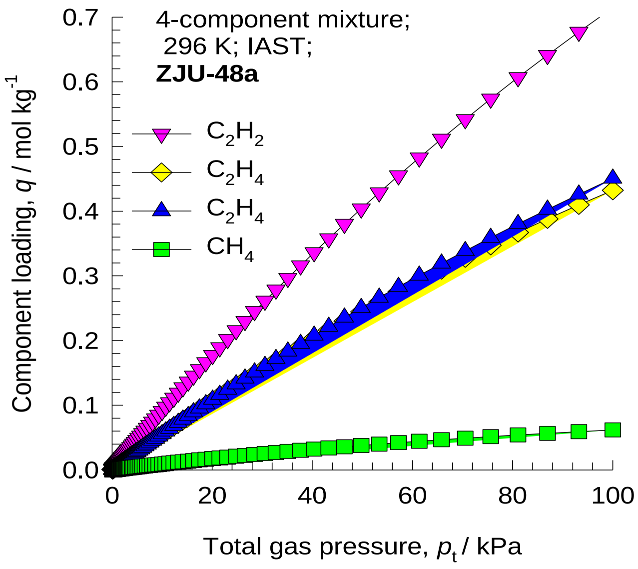

Figure S4. IAST calculations of the component molar loadings in equilibrium with an *equimolar* $CH_4/C_2H_2/C_2H_4/C_2H_6$ mixture at total bulk gas phase at 296 K.

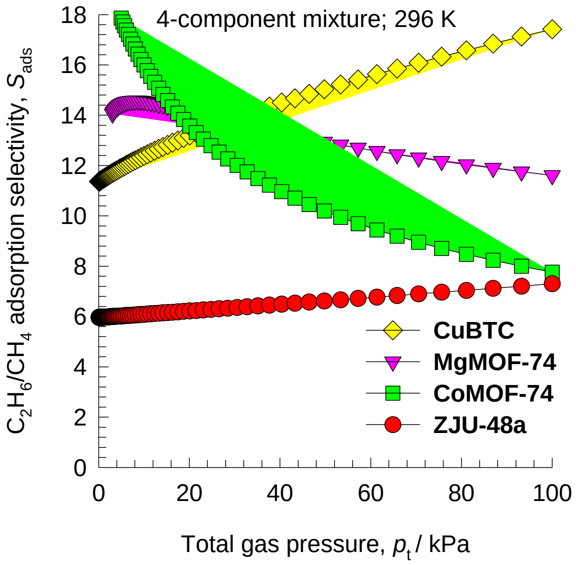

Figure S5. IAST calculations of the C_2H_6/CH_4 adsorption selectivity of four MOFs for adsorption from an equimolar $CH_4/C_2H_2/C_2H_4/C_2H_6$ mixture at total bulk gas phase at 296 K.

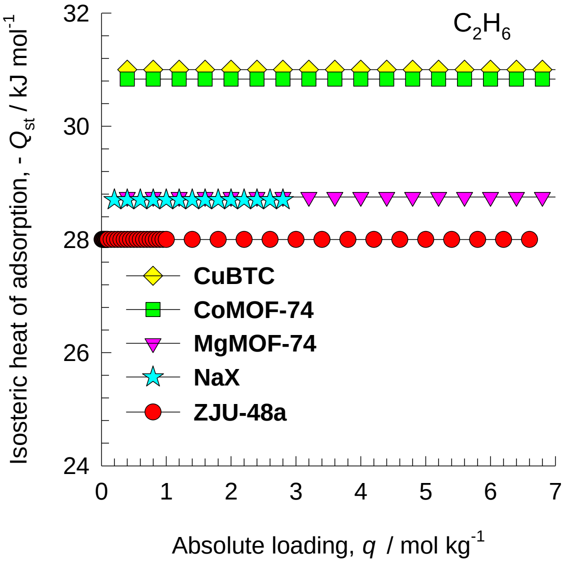

Figure S6 The isoteric heats of adsorption of different porous materials for C_2H_6.

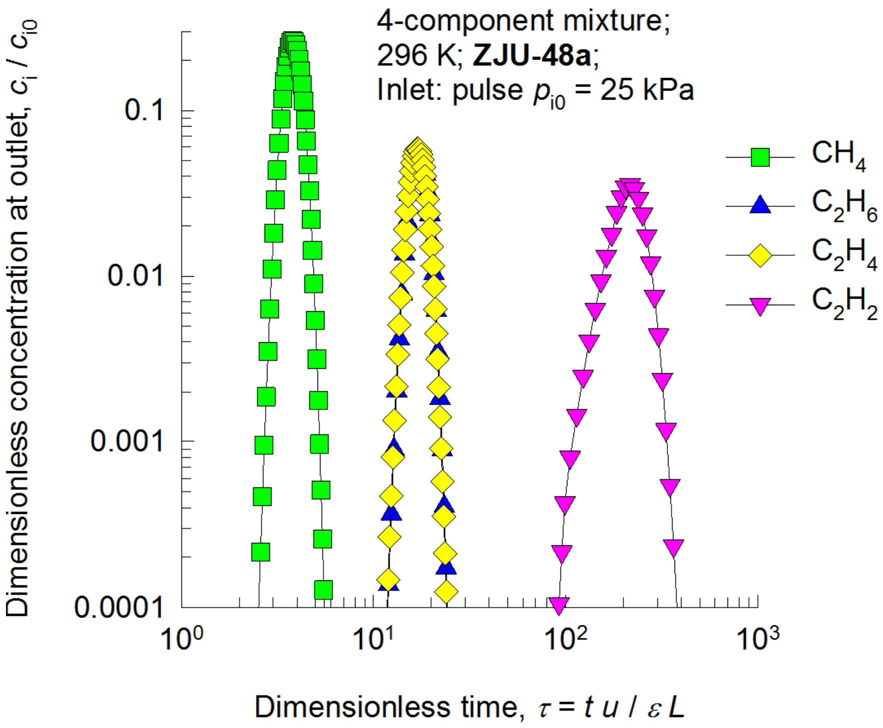

Figure S7. Pulse chromatographic simulations for separation of an *equimolar* 4-component $CH_4/C_2H_2/C_2H_4/C_2H_6$ mixture with **ZJU-48a** as adsorbent material. A pulse of the equimolar mixture is injected for 10 s at the start of the process, and subsequently the adsorbed components are desorbed by use of purge inert gas.

5. References

(1) Myers, A. L.; Prausnitz, J. M. Thermodynamics of mixed gas adsorption, *A.I.Ch.E.J.* **1965**, *11*, 121-130.