Electronic Supplementary Material (ESI) for CrystEngComm.

Electronic Supplementary Information

Separation of C2/C1 hydrocarbons through gate-opening effect in a microporous metal–organic framework

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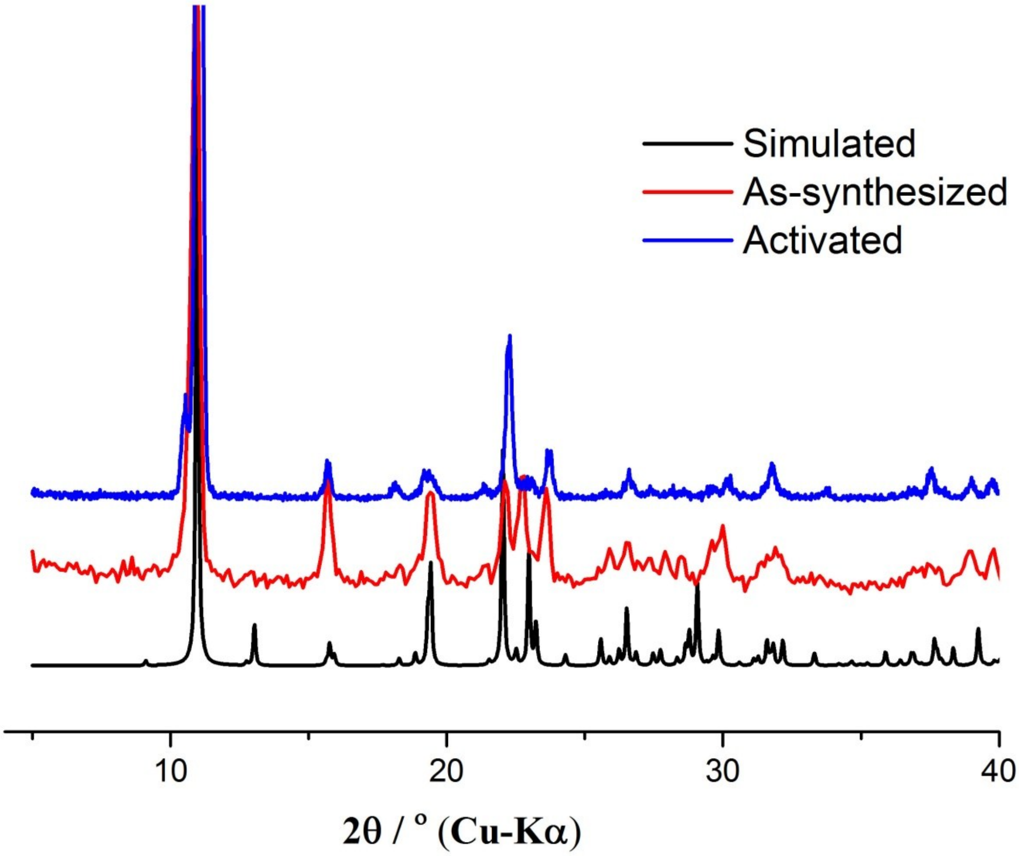

Fig. S1. PXRD patterns of as-synthesized **1** (red) and activated **1a** (blue) compared with the simulated XRD pattern from the single-crystal X-ray structure (black).

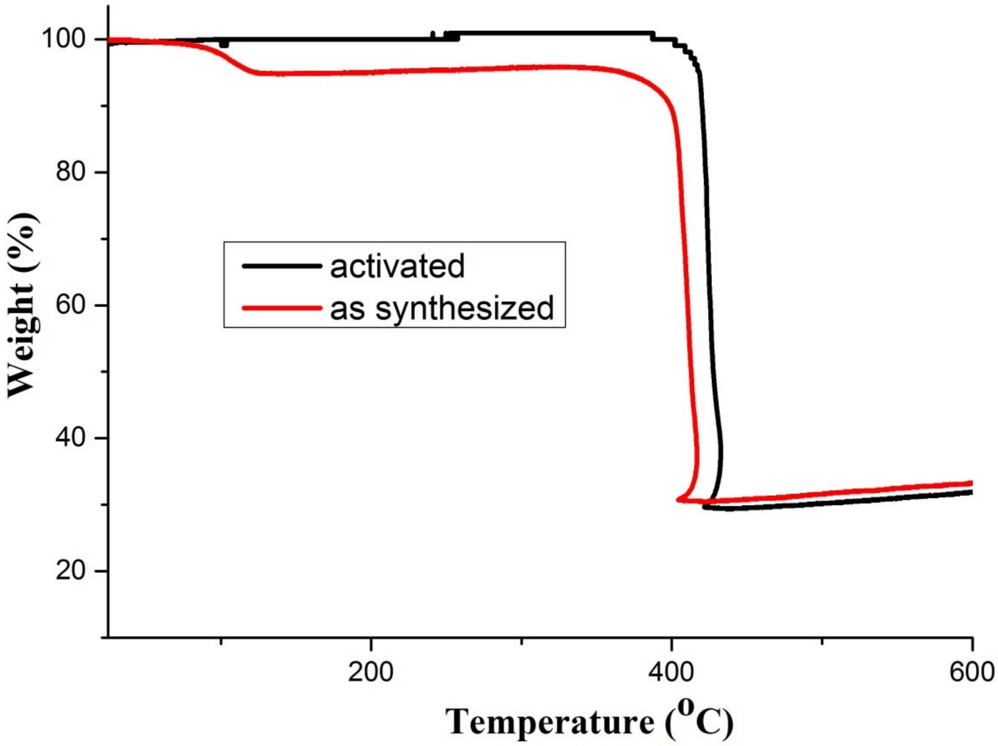

Fig. S2. TGA curves of as-sythesized **1** (red) and activated **1a** (black).

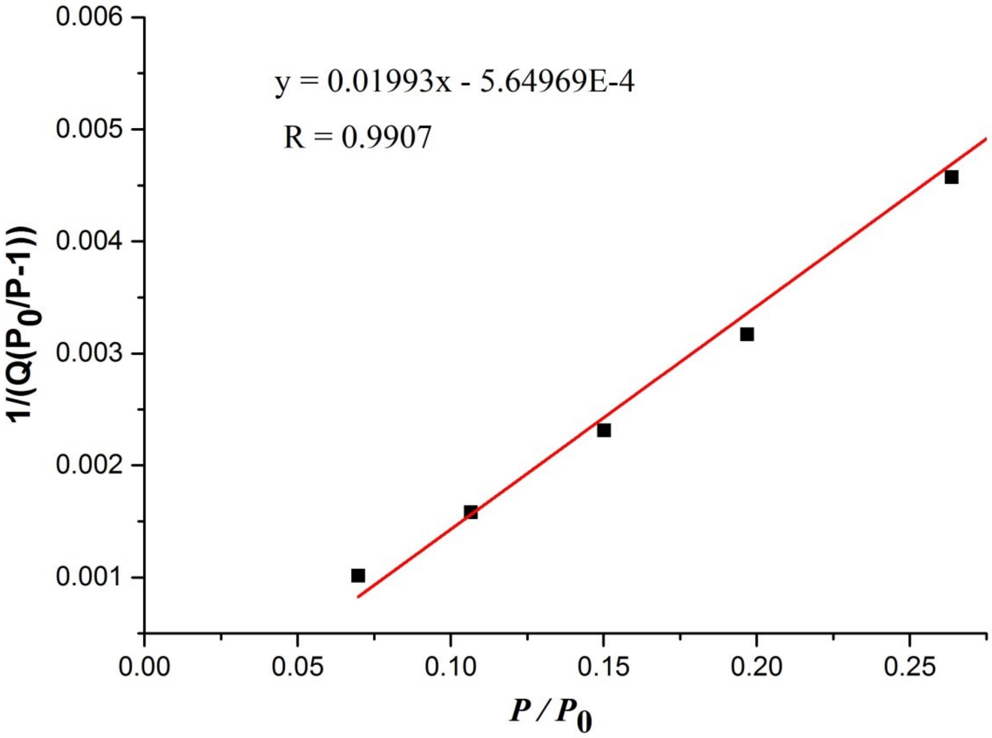

Fig. S3. The BET surface area of **1a** obtained from the CO_2 adsorption isotherm at 196 K.

$S_{BET} = 1/(0.01993 - 5.64969E-4)/22414 \times 6.023 \times 10^{23} \times 0.170 \times 10^{-18} = 236\ m^2\ g^{-1}$

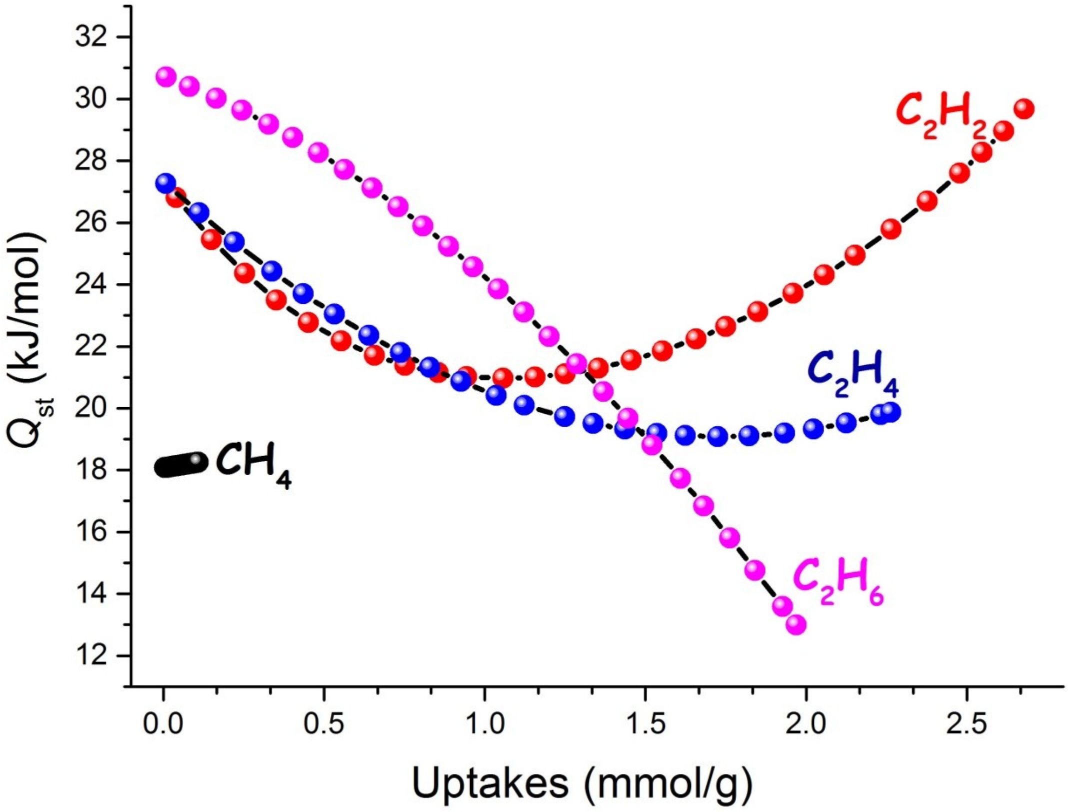

Fig. S4. Coverage dependencies of the adsorption enthalpies for **1a** calculated based on their adsorption isotherms at 273 and 298 K.

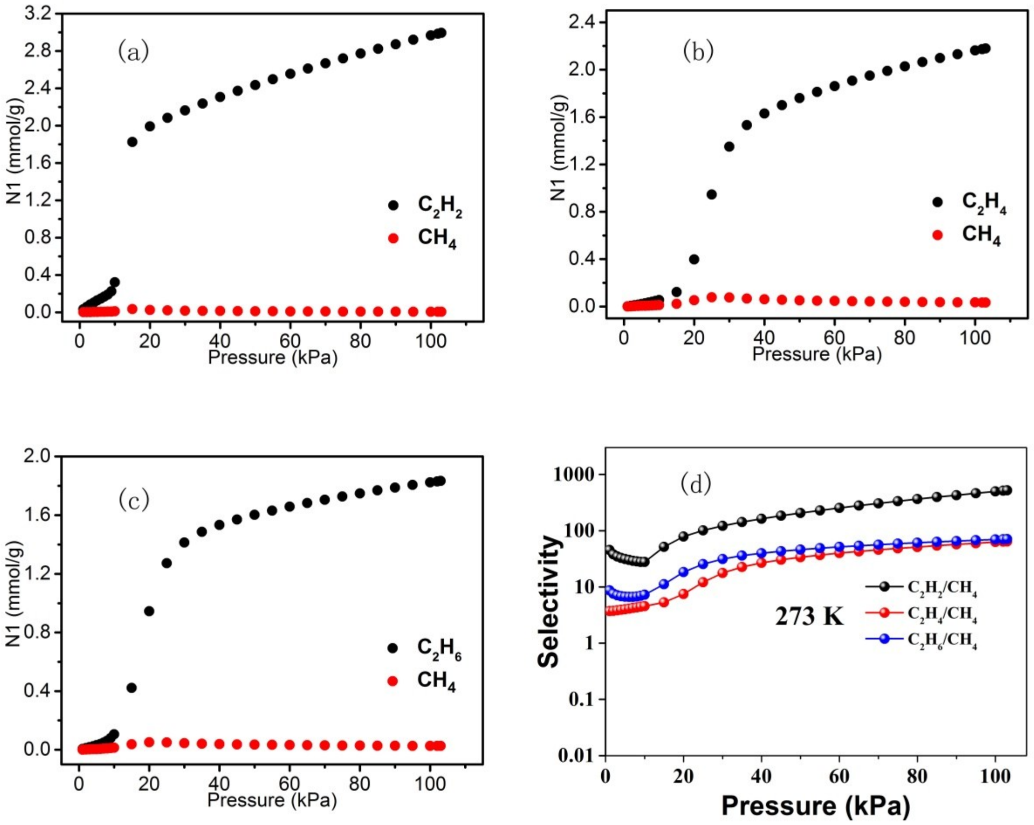

Fig. S5. Mixture adsorption isotherms (a–c) and selectivities (d) of **1a** for various equimolar binary hydrocarbon mixtures at 273 K predicted by IAST.

GCMC simulations.

All the GCMC simulations in the MS modeling 5.0 package.[1] It should be noted that this MOF showed certain flexibility and its framework showed slightly distortion after different gas loading. Considering the sorption behaviors of C2 hydrocarbons in guest-free **1** are almost the same as that of C_3H_8 (similar gate opening) reported in literature,[2] as well as their similar hydrocarbon moiety, the open crystal structure of C_3H_8-loaded sample was chosen for related simulations without further geometry optimization. The framework and the individual hydrocarbon molecules were considered to be rigid during the simulation. Partial charges for atoms of guest-free **1** were derived from QEq method and QEq_neutral1.0 parameter. The simulations were carried out at 298 K, adopting the Fixed Loading task, Metropolis method in Sorption module and the universal force field (UFF). The partial charges on the atoms of C_2H_2 (C: −0.112e, H: 0.112e, where e = 1.6022×10^{-19} C is the elementary charge), C_2H_4 (C: −0.271e, H: 0.136e) and C_2H_6 (C: −0.452e, H: 0.151e) were also derived from QEq method. The interaction energy between hydrocarbon molecules and framework were computed through the Coulomb and Lennard-Jones 6-12 (LJ) potentials. The cutoff radius was chosen as 15.5 Å for the LJ potential and the long-range electrostatic interactions were handled using the Ewald & Group summation method. The loading steps and the equilibration steps were 1×10^5, the production steps were 1×10^6.

Measurement of breakthrough experiment

The breakthrough experiment was carried out in dynamic gas breakthrough set-up. A stainless steel column with inner dimensions of 4 × 150 mm was used for sample packing. Microcrystalline sample (1.9387 g) with particle size of 200–300 mm obtained via sieving was then packed into the column. The column was placed in a temperature controlled environment (maintained at 298 K). The mixed gas flow and pressure were controlled by using a pressure controller valve and a mass flow controller (Fig. S6). Outlet effluent from the column was continuously monitored using gas chromatography (GC-2014, SHIMADZU) with a thermal conductivity detector (TCD). The column packed with sample was firstly purged with He flow (100 mL min^{-1}) for 6 hours at room temperature 298 K. The mixed gas flow rate during breakthrough process is 20 mL min^{-1} using 50/50 (v/v) C_2H_6/CH_4. After the breakthrough experiment, the sample was regenerated under vacuum.

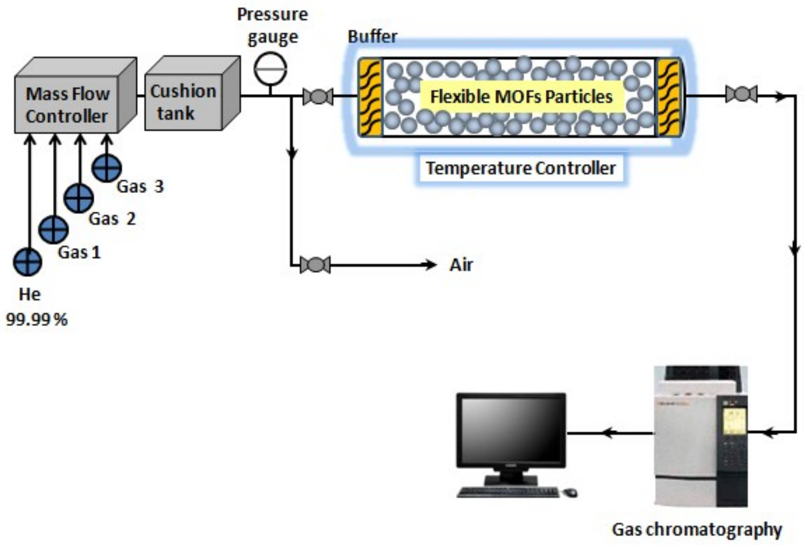

Fig. S6. Schematic illustration of the apparatus for the breakthrough experiments.

Table S1. Crystal data and structure refinements for **1**

	1
Empirical formula	$C_{13}H_{12}N_2O_5Mn$
Formula weight	331.19
Color and Habit	colorless plate
Crystal Size (mm)	0.10×0.20×0.30
Crystal system	Monoclinic
Space group	*P*21/*c*
a (Å)	10.0292(3)
b (Å)	13.5724(3)
c (Å)	10.3629(4)
α (°)	90
β (°)	104.700(3)
γ (°)	90
V (Å^3)	1364.43(8)
Z	4
D_{calcd} (g·cm^{-3})	1.612
μ (mm^{-1})	0.991
F (000)	676
θ (°)	2.1 to 26.0
Goodness-of-fit on F^2	1.07
Reflections measured	8858
Independent reflections (R_{int})	2678 (0.030)
Observed reflection [$I > 2\sigma(I)$]	2455
Final R_1, wR_2 indices (obs.)	0.0599, 0.1374
R_1, wR_2 indices (all)	0.0640, 0.1389

Table S2. Equation parameters for the DSLF isotherm model.

Adsorbates	N_1^{max}(mmol/g)	b_1(kPa^{-1})	$1/n_1$	N_2^{max}(mmol/g)	b_2(kPa^{-1})	$1/n_2$
CH_4 (273 K)	0.03348	0.01256	1.53755	1.16312	2.74978E-4	1.39958
C_2H_2 (273 K)	6.67199	0.00885	0.85309	1.64953	1.30647E-13	16.38823
C_2H_4 (273 K)	1.56073	0.00325	1.47316	1.42596	3.36123E-12	10.51166
C_2H_6 (273 K)	1.19391	0.00909	1.12655	1.35103	5.15904E-7	6.51883
CH_4 (298 K)	0.03275	0.00365	1.72473	0.59709	8.52959E-5	1.6022
C_2H_2 (298 K)	1.59176	0.00923	1.13032	1.67774	1.75033E-13	10.28926
C_2H_4 (298 K)	1.83739	2.77556E-13	8.49842	0.47323	9.92296E-11	5.35072
C_2H_6 (298 K)	0.97881	4.72733E-4	1.94773	1.17473	6.48351E-14	9.8715

Note: Dual-site Langmuir-Freundlich (DSLF) model is listed as below:

$$N = N_1^{\max} \times \frac{b_1 p^{1/n1}}{1+b_1 p^{1/n1}} + N_2^{\max} \times \frac{b_2 p^{1/n2}}{1+b_2 p^{1/n2}}$$

where *p* (unit: kPa) is the pressure of the bulk gas at equilibrium with the adsorbed phase, N (unit: mmol/g) is the adsorbed amount per mass of adsorbent, N_1^{max} and N_2^{max} (unit: mmol/g) are the saturation capacities of sites 1 and 2, b_1 and b_2 (unit: 1/kPa) is the affinity coefficient of sites 1 and 2, and n_1 and n_2 represent the deviations from an ideal homogeneous surface.

Reference

1. *Accelrys*, Materials Studio Getting Started, release 5.0, Accelrys Software, Inc., San Diego, CA, 2009.
2. D. Banerjee, H. Wang, A. M. Plonka, T. J. Emge, J. B. Parise and J. Li, *Chem. Eur. J.*, 2016, 22, 11816.