Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

Efficient Separation of C_2 Hydrocarbons in a Permanently Porous Hydrogen-Bonded Organic Framework

Tae-Ung Yoon,[†a] Seung Bin Baek,[*†b] Dongwook Kim,[c] Eun-Jung Kim,[a] Wang-Geun Lee,[b] Bhupendra Kumar Singh,[b] Myoung Soo Lah,[c] Youn-Sang Bae[*a] and Kwang S. Kim[*b]

*Corresponding authors: sepbirth@gmail.com (S. B. Baek), mowbae@yonsei.ac.kr (Y.-S. Bae) and kimks@unist.ac.kr (K. S. Kim)

1. General considerations

H_3BTB was purchased from Tokyo Chemical Industry Co. Methanol and DMF were purchased from Samchun Chemical Co. H_3BTB-DMF crystals were prepared by thoroughly dissolving excess H_3BTB in minimal DMF in a hot oven, then cooling it down in a refrigerator. The resulting crystals were collected and dried in air, and then soaked into methanol. Standing the methanol solution in an oven at 50 °C produced HOF-BTB crystals suitable for X-ray diffraction analysis. TGA measurements were carried out at a rate of 5 °C/min over the temperature of 25-700 °C under an air atmosphere using a thermogravimeter (Pyris 1 TGA Lab System, Perkin Elmer). Powder X-ray diffraction patterns were recorded by a Rigaku MiniFlex diffractometer operated at 30 kV and 15 mA with a scan rate of 2.0 deg/min.

2. Gas adsorption experiments

All gas adsorption measurements were performed using a BELSORP-Mini II low-pressure gas adsorption measuring system (BEL Japan, Inc) equipped with a temperature control unit. At least 50 mg of the crystals were pretreated at 120 °C under vacuum for 15 hours before gas adsorption measurements. Adsorption isotherms were measured at 273 K and 295 K up to 1 bar. The BET surface area was calculated from a N_2 adsorption isotherm measured at 77 K. The extra high-purity quality (>99.999 %) of gases was used for all adsorption measurements. All the adsorption data were manipulated using BEL-Master software provided by BEL Japan Inc.

3. Fitting of isotherms and ideal adsorbed solution theory calculations[1-3]

The parameters for ideal adsorbed solution theory (IAST) selectivity calculations were obtained by fitting the experimentally measured pure single-component isotherms using the single-site Langmuir-Freundlich model, purely on the basis of giving the best fit with highest adjusted R^2-values. The single-site Langmuir-Freundlich equation looks as follows:

$$q = \frac{q_{sat} \times b \times p^{1/n}}{1 + b \times p^{1/n}} \qquad (1)$$

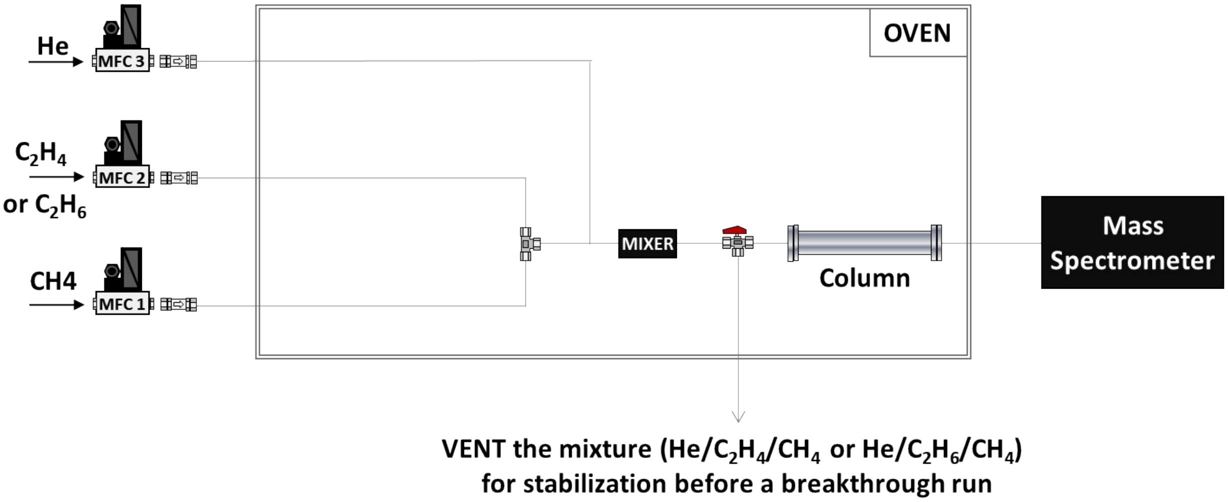
where, n represents the deviation from an ideal homogeneous surface. The parameters q_{sat}, b and n can be determined by fitting the experimental adsorption isotherms (q versus p). They are then used to calculate IAST selectivity. The adsorption selectivity (S_{ads}) for binary gas mixtures of components *1* and *2* is defined as:

$$S_{ads} = \frac{q_1/q_2}{p_1/p_2} \qquad (2)$$

Where q_i is the molar loading of the species *i* and p_i is the partial pressure of species *i*. The integrals were computed at the website http://integrals.wolfram.com and the adsorbed phase composition that minimized the difference between the integrals of the two spreading pressures was found at the website http://www.wolframalpha.com. Selectivities were then calculated according to the equation 2.

4. Breakthrough experiments

The breakthrough experiments for evaluating the potential of HOF-BTB for mixture gas separations were performed in a custom-built fixed bed equipment. Three mass flow controllers (0~100 ml/min) (Bronkhorst, Germany) were used to regulate the gas flow rates. Two of them were used for making combinations of C_2H_6/CH_4 or C_2H_4/CH_4 streams and the last one was used for He stream. First, this He stream was used for the in-situ regeneration of the adsorbent packed in the column, which is placed in a ventilated thermostatted oven for measurements at a constant temperature. Secondly, the He flow was mixed with hydrocarbon mixture (C_2H_6/CH_4 or C_2H_4/CH_4) to adjust the total hydrocarbon pressure. The effluent gas composition from the column was measured online by a mass spectrometer (Extrel Max300-LG, USA). The detailed description of breakthrough experimental setup and procedures can also be found elsewhere.[4,5] The as-synthesized powder sample was pelletized into binderless pellets with a size of 500~1000 μm using a carver press (Carver, Inc., USA). The obtained pellets were initially activated at 393 K for 15 h under vacuum and then packed into a stainless steel column (15 cm × 0.44 cm). The remainder of the column was filled with glass beads with a diameter of 750 μm. Before the breakthrough experiments, the column was degassed by a He flow of 40 ml/min at 393 K for 2 h to remove all the impurities adsorbed during the packing procedure. All the experiments were carried out at 298 K and 1 bar. Before each measurement, a He flow of 40 ml/min at 298 K was introduced into the column for at least 10 min. Simultaneously, a feed mixture for a breakthrough run was prepared as follows: a 20 ml/min of He flow was combined with a 20 ml/min of equimolar hydrocarbon mixture (C_2H_6/CH_4 or C_2H_4/CH_4) and then mixed well with each other by flowing through a gas mixer. It should be noted that the obtained mixture can be considered as equimolar hydrocarbon mixture (C_2H_6/CH_4 or C_2H_4/CH_4) at 0.5 bar. At t = 0, the He flow for in-situ regeneration was stopped and a flow of the feed mixture was introduced into the packed column.



Scheme S1. A schematic diagram of the dynamic breakthrough experimental setup

Table S1. Comparison of C_2H_4 and C_2H_6 uptakes in various organic frameworks.

Materials	SA_{BET} (m^2/g)	C_2H_4 (mmol/g)		C_2H_6 (mmol/g)		Qst (kJ/mol)		Ref
		273 K	295 K	273 K	295 K	C_2H_4	C_2H_6	
MCOF-1	874	-	1.61	-	1.97	19	41	6
ZnP-CTF-400	1411	-	-	4.25	3.12	-	30-25	7
ZnP-CTF-500	1848	-	-	5.58	4.02	-	-	7
ZnP-CTF-600	1331	-	-	3.34	2.41	-	-	7
MesoPOF-1	1027	-	-	2.54	-	-	-	8
DBA-3D-COF-1	5083	2.52	1.70	3.24	2.09	15.9	16.8	9
Ni-DBA-3D-COF	4763	2.36	1.83	3.02	2.16	9.7	11.6	9
N-COF	692	-	-	-	3.09	-	35.7	10
P-COF	435	-	-	-	2.64	-	-	10
T-COF	1149	-	-	-	5.31	-	-	10
HOF-BTB	955	3.80	2.48	4.25	3.09	22.6	25.4	This work

Table S2. IAST-calculated selectivities for the 50:50 binary gas mixtures at 273 K.

Gas mixtures	Selectivity		
	0.25 bar	0.5 bar	1 bar
$C_2H_2 : CH_4$	9.5	10.9	12.5
$C_2H_4 : CH_4$	9.3	10.2	10.9
$C_2H_6 : CH_4$	15.3	17.0	17.7

Table S3. IAST-calculated selectivities for the 50:50 binary gas mixtures at 295 K.

Gas mixtures	Selectivity		
	0.25 bar	0.5 bar	1 bar
$C_2H_2 : CH_4$	7.8	8.5	9.3
$C_2H_4 : CH_4$	7.9	8.4	9.0
$C_2H_6 : CH_4$	10.8	12.3	13.7

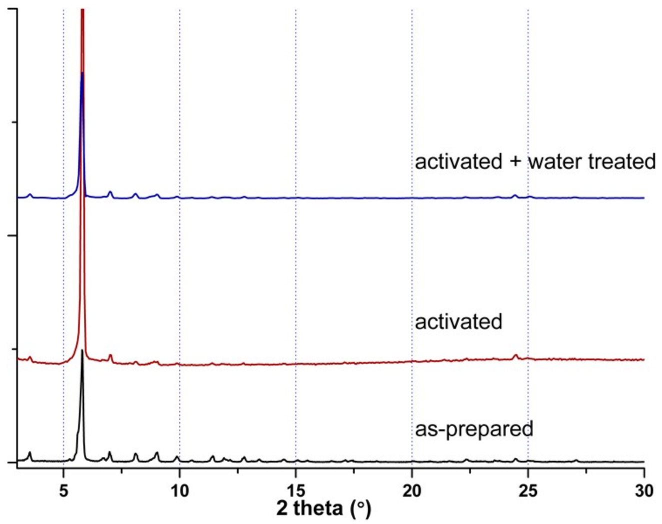


Fig. S1 Comparison of powder X-ray diffraction patterns of HOF-BTB crystals. PXRD pattern of water-treated HOF-BTB is identical to those of both as-prepared and activated HOF-BTB crystals, meaning that the HOF-BTB crystals are stable in water. The crystals were immersed in water for 20 days immediately after having activation done at 120 °C.

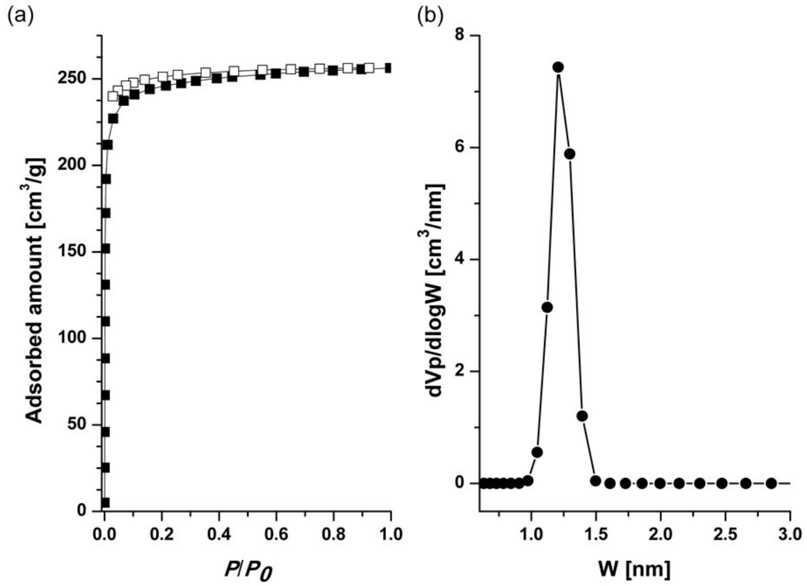
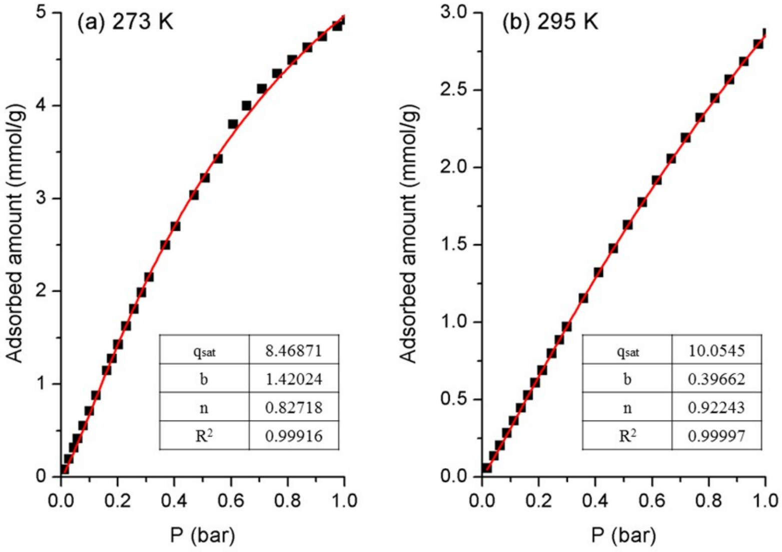


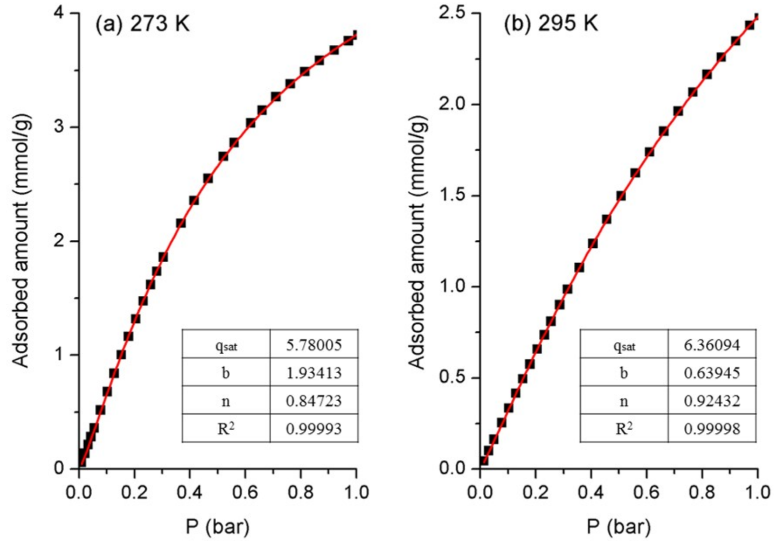
Fig. S2 (a) N_2 adsorption isotherm of HOF-BTB at 77 K and (b) micropore size distribution calculated using NLDFT method.



q_{sat}	8.46871
b	1.42024
n	0.82718
R^2	0.99916

q_{sat}	10.0545
b	0.39662
n	0.92243
R^2	0.99997

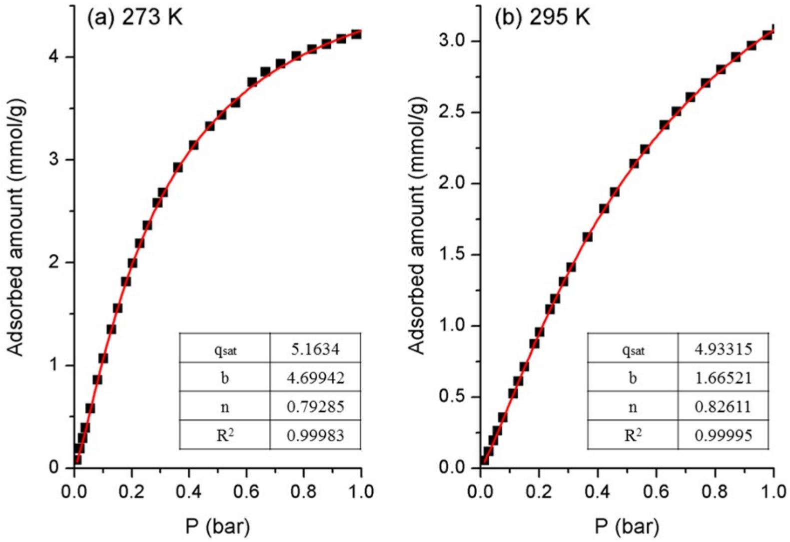
Fig. S3 Single-site Langmuir-Freundlich fits of C_2H_2 adsorption isotherms (Left: 273 K, Right: 295 K). The fitting results are presented in the inset tables.



q_{sat}	5.78005
b	1.93413
n	0.84723
R^2	0.99993

q_{sat}	6.36094
b	0.63945
n	0.92432
R^2	0.99998

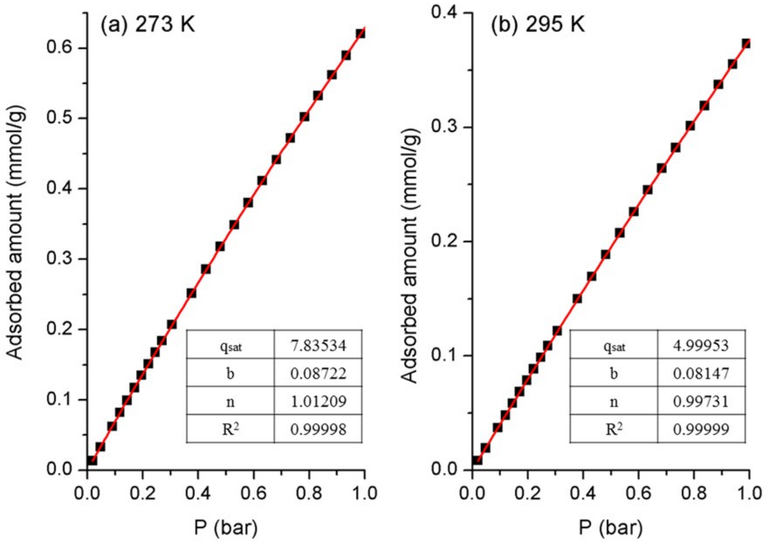
Fig. S4 Single-site Langmuir-Freundlich fits of C_2H_4 adsorption isotherms (Left: 273 K, Right: 295 K). The fitting results are presented in the inset tables.



q_{sat}	5.1634
b	4.69942
n	0.79285
R^2	0.99983

q_{sat}	4.93315
b	1.66521
n	0.82611
R^2	0.99995

Fig. S5 Single-site Langmuir-Freundlich fits of C_2H_6 adsorption isotherms (Left: 273 K, Right: 295 K). The fitting results are presented in the inset tables.



q_{sat}	7.83534
b	0.08722
n	1.01209
R^2	0.99998

q_{sat}	4.99953
b	0.08147
n	0.99731
R^2	0.99999

Fig. S6 Single-site Langmuir-Freundlich fits of CH_4 adsorption isotherms (Left: 273 K, Right: 295 K). The fitting results are presented in the inset tables.

References

1. J. M. Simmons, H. Wu, W. Zhou and T. Yildirim, *Energy Environ. Sci.,* 2011, **4**, 2177-2185.
2. J.A. Mason, K. Sumida, Z. R. Herm, R Krishna and J. R. Long, *Energy Environ. Sci.,* 2011, **4**, 3030-3040.
3. Z. R. Herm, J. A. Swisher, B. Smit, R. Krishna and J. R. Long, *J. Am. Chem. Soc.,* 2011,**133**, 5664-5667.
4. S.-J. Lee, K.C. Kim, T.-U. Yoon, M.-B. Kim and Y.-S. Bae, *Microporous and Mesoporous Materials*, 2016, **236**, 284-291.
5. S.-J. Lee, T.-U. Yoon, A.-R. Kim, S.-Y. Kim, K.-H. Cho, Y. K. Hwang, J.-W. Yeon and Y.-S. Bae, *Journal of Hazardous Materials*, 2016, **320**, 513.
6. H. Ma, H. Ren, S. Meng, Z. Yan, H. Zhao, F. Sun and G. Zhu, *Chem. Commun.*, 2013, **49**, 9773.
7. H. Ma, H. Ren, S. Meng, F. Sun and G. Zhu, *Sci. Rep.*, 2013, **3**, 2611.
8. A. P. Katsoulidis and M. G. Kanatzidis, *Chem. Mater.*, 2012, **24**, 471.
9. L. A. Baldwin, J. W. Crowe, D. A. Pyles and P. L. McGrier, *J. Am. Chem. Soc.*, 2016, **138**, 15134.
10. J. Dong, Y. Wang, G. Liu, Y. Cheng and D. Zhao, *CrystEngComm*, 2017, **19**, 4899.