Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A. This journal is © The Royal Society of Chemistry 2022

Supporting Information

A robust ethane-selective hypercrosslinked porous organic adsorbent with

high ethane capacity

Hyein Park,^a Minjung Kang,^a Dong Won Kang,^a and Chang Seop Hong^{*a}

^aDepartment of Chemistry, Korea University, Seoul 02841, Republic of Korea.

E-mail: cshong@korea.ac.kr

Experimental Section

Materials.

Most of the chemicals and solvents used in this experiment were purchased from commercial companies (Sigma Aldrich and TCI). All solvents were reagent grade (\geq 99.0%) and were used without further purification.

Synthesis of HCP_TPB

Under N_2 atmosphere, anhydrous AlCl₃ (4.9 g, 36.8 mmol) was added to a solution of 1,3,5-triphenylbenzene (1.53 g, 5 mmol) in DCM (60 mL) and the mixture was stirred at reflux for 24 h. The resulting suspension was collected by filtration and washed with ethanol and water. Then the polymer was stirred for 6 h in acetone, methanol, ethanol, chloroform, THF. The brown powder was then collected by filtration and dried at 120 °C under vacuum for 12 h.

Synthesis of HCP_TMPB

Under N₂ atmosphere, anhydrous AlCl₃ (4.9 g, 36.8 mmol) was added to a solution of 1,3,5-tris(2methylphenyl)benzene (1.74 g, 5 mmol) in DCM (60 mL) and the mixture was stirred at reflux for 24 h. The resulting suspension was collected by filtration and washed with ethanol and water. The polymer was stirred for 6 h in acetone, methanol, ethanol, chloroform, THF, then stirred under reflux for 6 h in toluene. The brown powder was then collected by filtration and dried at 120 °C under vacuum for 12 h.

Synthesis of HCP_BCMBP

Under N_2 atmosphere, anhydrous FeCl₃ (810 mg, 5 mmol) was added to a solution of 4,4'bis(chloromethyl)-1,1'-biphenyl (1.25 g, 5 mmol) in DCE (32.5 mL) and the mixture was stirred at reflux for 12 h. The resulting suspension was collected by filtration and washed with ethanol and water. The polymer was stirred for 6 h in acetone, methanol, ethanol, chloroform, THF, then stirred under reflux for 6 h in toluene. The brown powder was then collected by filtration and dried at 120 °C under vacuum for 12 h.

Synthesis of HCP_p-DCX

Under N₂ atmosphere, anhydrous FeCl₃ (810 mg, 5 mmol) was added to a solution of α, α' -dichloro-*p*-xylene (875 mg, 5 mmol) in DCE (32.5 mL) and the mixture was stirred at reflux for 12 h. The resulting suspension was collected by filtration and washed with ethanol and water. The polymer was stirred for 6 h in acetone, methanol, ethanol, chloroform, THF. The brown powder was then collected by filtration and dried at 120 °C under vacuum for 12 h.

Synthesis of HCP_m-DCX

Under N₂ atmosphere, anhydrous FeCl₃ (810 mg, 5 mmol) was added to a solution of α, α' -Dichloro-*m*-xylene (875 mg, 5 mmol) in DCE (32.5 mL) and the mixture was stirred at reflux for 12 h. The resulting suspension was collected by filtration and washed with ethanol and water. The polymer was stirred for 6 h in acetone, methanol, ethanol, chloroform, THF. The brown powder was then collected by filtration and dried at 120 °C under vacuum for 12 h.

Synthesis of HCP_o-DCX

Under N₂ atmosphere, anhydrous FeCl₃ (810 mg, 5 mmol) was added to a solution of α, α' -Dichloro-*o*-xylene (875 mg, 5 mmol) in DCE (32.5 mL) and the mixture was stirred at reflux for 12 h. The resulting suspension was collected by filtration and washed with ethanol and water. The polymer was stirred for 6 h in acetone, methanol, ethanol, chloroform, THF. The brown powder was then collected by filtration and dried at 120 °C under vacuum for 12 h.

Synthesis of HCP_CMBA

Under N_2 atmosphere, anhydrous FeCl₃ (810 mg, 5 mmol) was added to a solution of 4-(Chloromethyl)benzyl alcohol (783 mg, 5 mmol) in DCE (32.5 mL) and the mixture was stirred at reflux for 12 h. The resulting suspension was collected by filtration and washed with ethanol and water. The polymer was stirred for 6 h in acetone, methanol, ethanol, chloroform, THF. The brown powder was then collected by filtration and dried at 120 °C under vacuum for 12 h.

Synthesis of HCP_TPB_mg

Under N_2 atmosphere, anhydrous AlCl₃ (0.98 g, 7.36 mmol) was added to a solution of 1,3,5-triphenylbenzene (306 mg, 1 mmol) in DCM (15 mL) and the mixture was stirred at reflux for 24 h. The resulting suspension was collected by filtration and washed with ethanol and water. Then the polymer was stirred for 6 h in acetone, methanol, ethanol, chloroform, THF. The brown powder was then collected by filtration and dried at 120 °C under vacuum for 12 h.

Synthesis of HCP_TMPB_mg

Under N_2 atmosphere, anhydrous AlCl₃ (0.98 g, 7.36 mmol) was added to a solution of 1,3,5-tris(2methylphenyl)benzene (348 mg, 1 mmol) in DCM (15 mL) and the mixture was stirred at reflux for 24 h. The resulting suspension was collected by filtration and washed with ethanol and water. The polymer was stirred for 6 h in acetone, methanol, ethanol, chloroform, THF, then stirred under reflux for 6 h in toluene. The brown powder was then collected by filtration and dried at 120 °C under vacuum for 12 h.

Physical measurements

Infrared (IR) spectra were obtained using a Nicolet iS10 FTIR spectrometer. Powder X-ray diffraction (PXRD) patterns were obtained using Cu K α radiation ($\lambda = 1.5406$ Å) on a Rigaku Ultima III diffractometer with a scan speed of 2° min⁻¹ and a step size of 0.01°. Scanning electron microscopy (SEM) images were acquired using a JSM-7001F scanning electron microscope. Thermogravimetric analysis (TGA) was carried out in N₂ (99.999%) atmosphere in the temperature range 30-900 °C (heating rate = 2 °C min⁻¹) using a TA instrument Discovery TGA. X-ray photoelectron spectroscopy (XPS) was measured using ULVAC-PHI X-TOOL at Semiconductor & Display Green Manufacturing Research Center (GMRC) at Korea University. ¹³C solid-state NMR were measured using 400 MHz AVANCE II+ Bruker solid-state NMR at KBSI Seoul Western Center. Contact angle was measured by Phoenix-MT(T).

Gas sorption measurements

Before sorption analysis, the samples were activated at 120 °C under vacuum for 12 h. All gases used in measurements were highly pure (99.999%). N_2 isotherms were performed using a Micrometrics 3flex instrument. Gas sorptions with C_2H_6 and C_2H_4 were performed using a Micrometrics ASAP 2020 instrument up to 1200 mbar of gas pressure. Gas adsorption measurements of N_2 at 77 K for stability test were carried out using a BEL Belsorp mini II instrument. Filled and open symbols indicate adsorption and desorption, respectively. The water vapor isotherms were recorded by an ASAP 2020 instrument at 298 K.

Computational methods

Grand canonical Monte Carlo (GCMC) simulations were performed for the binding energy calculation by the Sorption module of Material Studio (Accelrys. Materials Studio Getting Started, release 2019).¹

Breakthrough measurements

The breakthrough curves of mixed gas C_2H_6/C_2H_4 (1:1 and 1:15, v/v) for HCPs were performed by a BELCAT-II linked with BELMASS mass spectrometer. A fixed-bed column filled with HCPs was prepared and the total gas flow rate was fixed to total 5 sccm for 1:1, and 10 sccm for 1:15. The flow rates of binary mixture C_2H_6/C_2H_4 were controlled at 3 sccm for 1:1, 8 sccm for 1:15, respectively, balanced with He gas. Before breakthrough measurements, all samples were activated at 120 °C for 12 h. All outgas was continuously monitored by the mass spectrometer. In the case of the cyclic test, the samples were regenerated at 120 °C for 2 h before each cycle.

Calculations of IAST selectivity

Gas adsorption isotherms and gas selectivities for C_2H_6 and C_2H_4 at 298 K were calculated based on the ideal adsorbed solution theory (IAST) proposed by Myers and Prausnitz.² In order to predict the sorption performances of HCPs for the separation of binary mixed gases, the single-component adsorption isotherms were first fit to a Dual Site Langmuir-Frendlich model (DSLF), as below:

$$n(P) = \frac{q_1(k_1 P)^{n_1}}{1 + (k_1 P)^{n_1}} + \frac{q_2(k_2 P)^{n_2}}{1 + (k_2 P)^{n_2}}$$
(Eq. S1)

Where n(P) is the amount of adsorbed gas, P is the equilibrium pressure and $q_1, q_2, k_1, k_2, n_1, and n_2$ are constants.

The adsorption selectivity, $S_{i,j}$ is defined as:

$$S_{i,j} = \frac{x_i/x_j}{y_i/y_j} \tag{Eq. S2}$$

Where x_i and x_j are the gas uptake capacity at the adsorbed equilibrium of components i and j respectively. The gas molar fractions the i and j components are represented by y_i and y_j , respectively.

Isosteric heat of adsorption calculations.

The coverage-dependent adsorption enthalpy profiles were calculated from the sorption data measured at 273, 298, 323 K by Virial fitting method and Clausius-Claperyron equation. A Virial-type expression was used (Eq. S3), which is composed of parameters a_i and b_i , which are independent of temperature. In Eq. S3, p is the pressure in atm, N is the adsorbed amount in mmol g^{-1} , T is the temperature in Kelvin, a_i and b_i are the Virial coefficients, and m and n represent the number of coefficients required to adequately describe the isotherms.

$$\ln p = \ln N + \frac{1}{T} \sum_{i=0}^{l} a_{i} n^{i} + \sum_{j=0}^{m} b_{j} n^{j}$$
 (Eq. S3)

To calculate Q_{st} , the fitting parameters from the Eq. S3 were used for the Eq. S4.

$$Q_{st} = -R \left[\frac{\partial \ln \ln p}{\partial \left(\frac{1}{T} \right)} \right]_n = -R \sum_{i=0}^l a_i n^i$$
 (Eq. S4)



Scheme S1. (a) Synthesis route of HCP_TPB and HCP_TMPB. (b) Synthesis route of HCP_p-DCX, HCP_m-DCX, HCP_o-DCX, HCP_CMBA, and HCP_BCMBP



Fig S1. FT-IR spectra of (a) HCP_BCMBP, (b) HCP_p-DCX, (c) HCP_m-DCX, (d) HCP_o-DCX, (e) HCP_CMBA.



Fig S2. PXRD patterns of HCPs.



Fig S3. TGA analysis of HCPs.



Fig S4. FT-IR spectra of (a) **HCP_TPB** and (b) **HCP_TMPB** after thermal treatment at 200, 400, and 600 °C for 30 min.



Fig S5. SEM images of (a) **HCP_TPB**, (b) **HCP_TMPB**, (c) **HCP_BCMBP**, (d) **HCP_p-DCX**, (e) **HCP_m-DCX**, (f) **HCP_o-DCX**, and (g) **HCP_CMBA**.





Fig S6. Survey scans of XPS data for (a) **HCP_TPB**, (b) **HCP_TMPB**, (c) **HCP_BCMBP**, (d) **HCP_p-DCX**, (e) **HCP_m-DCX**, (f) **HCP_o-DCX**, and (g) **HCP_CMBA**.





Fig S7. N₂ isotherms at 77 K and pore size distributions (inset) of (a) **HCP_TPB**, (b) **HCP_TMPB**, (c) **HCP_BCMBP**, (d) **HCP_p-DCX**, (e) **HCP_m-DCX**, (f) **HCP_o-DCX**, and (g) **HCP_CMBA**. The x-axis of inset indicates the pore width (Å) and y-axis of inset shows the differential pore volume (cm³ g⁻¹ Å⁻¹).

	$S_{BET}^{a} / m^2 g^{-1}$	$V_{total}{}^{b}$ / cm ³ g ⁻¹	V_{micro}^{c} / $cm^3 g^{-1}$	
НСР_ТРВ	2780	1.342	1.145	
HCP_TMPB	1010	0.453	0.391	
HCP_BCMBP	1810	0.969	0.376	
HCP_p-DCX	1250	0.576	0.402	
HCP_m-DCX	1170	0.526	0.379	
HCP_o-DCX	1000	0.451	0.385	
HCP_CMBA	940	0.428	0.257	

Table S1. Textural porosities of HCP materials.

 ${}^{a}S_{BET}$ is the BET surface area calculated from N₂ isotherms using the BET equation. ${}^{b}V_{total}$ is the total pore volume determined by N₂ adsorption isotherms at P/P₀=0.95. ${}^{c}V_{micro}$ is the micropore volume derived using t-plot method based on the Halsey thickness equation.³





Fig S8. C₂H₆ and C₂H₄ sorption isotherms at 298 K of (a) HCP_TPB, (b) HCP_TMPB, (c) HCP_BCMBP, (d) HCP_*p*-DCX, (e) HCP_*m*-DCX, (f) HCP_*o*-DCX, and (g) HCP_CMBA.



Fig S9. C_2H_6 and C_2H_4 sorption isotherms at 273 K, 323 K of (a) HCP TPB and (b) HCP TMPB.



Fig S10. Comparison of experimental isotherms to the ones obtained from Virial modelling carried out using (a) C_2H_6 and (b) C_2H_4 sorption isotherms of **HCP_TPB** collected at 273, 298, 323 K.



Fig S11. Comparison of experimental isotherms to the ones obtained from Virial modelling carried out using (a) C_2H_6 and (b) C_2H_4 sorption isotherms of **HCP TMPB** collected at 273, 298, 323 K.



Fig S12. Adsorption heats of C_2H_6 and C_2H_4 for (a) HCP_TPB and (b) HCP_TMPB.



Fig S13. C₂H₆ and C₂H₄ sorption isotherms at 298 K of (a) **HCP_TPB**_mg, (b) **HCP_TMPB**_mg. (c) IAST selectivity of **HCP_TPB**_mg and **HCP_TMPB**_mg at 298 K for 1:1 C₂H₆/C₂H₄ (v/v) mixture.

	C ₂ H ₆	C ₂ H ₄
R ²	0.99994	0.9999
a ₀	-3509.4363	-3446.2389
a ₁	143.36409	291.08735
a ₂	7.60073	-50.68759
a ₃	-2.93112	3.91581
b ₀	15.66147	15.9231
b ₁	-0.07573	-0.63556
b ₂	-0.07363	0.13742
b ₃	0.01344	-0.01123

Table S2. Summary of the fitted Virial parameters for HCP_TPB.

Table S3. Summary of the fitted Virial parameters for HCP_TMPB.

	C ₂ H ₆	C ₂ H ₄
R ²	0.99985	0.99896
a ₀	-3832.60732	-3744.22275
a ₁	473.19661	935.96493
a ₂	-138.53548	-201.1712
a ₃	22.08117	-105.67339
b ₀	17.02508	17.3108
b ₁	-0.69324	-2.37754
b ₂	0.41837	0.56366
b ₃	-0.06583	0.41528



Fig S14. Adsorption site distribution of (a), (c) C_2H_4 and (b), (d) C_2H_6 for TPB and TMPB, respectively, observed by GCMC simulations.



Fig S15. Calculated interaction energy of monomers with C_2H_6 and C_2H_4 .



ratios of (a) 1:1 and (b) 1:15 at 298 K and 1 bar.



Fig S17. Experimental breakthrough curves of HCP_TMPB for a C2H6/C2H4 mixture in volumetric ratios of (a) 1:1 and (b) 1:15 at 298 K and 1 bar.



Fig S18. Water vapor adsorption isotherm of HCP_TPB at 298 K.



Fig S19. Experimental breakthrough curves of HCP_TPB for wet C_2H_6/C_2H_4 (1:1, v/v) mixture at 298 K and 1 bar under 60 % RH.



Fig S20. IR spectra of (a) **HCP_TPB** and (b) **HCP_TMPB** after breakthrough tests at 298 K and 1 bar.



Fig S21. IR spectra of (a) **HCP_TPB** and (b) **HCP_TMPB** after water, pH 1 HCl, and pH 14 NaOH solution exposures for 24 h.

НСР_ТРВ	HCP_TPB_water	НСР_ТМРВ	HCP_TMPB_water
127.63°	125.86°	127.09°	126.76°

Fig S22. Contact angles of HCP_TPB, HCP_TPB_water, HCP_TMPB, and HCP_TMPB_water.



Fig S23. N₂ isotherms of (a) **HCP_TPB** and (b) **HCP_TMPB** after water, pH 1 HCl, and pH 14 NaOH solution exposure for 24 h.

C ₂ H ₆ -selective materials	S _{BET} / m ² g ⁻¹	C_2H_6 uptake / cm ³ g ⁻¹	C_2H_4 uptake / cm ³ g ⁻¹	IAST selectivity (1:1, v/v)	Q _{st, ethane} / kJ mol ⁻¹	Q _{st, ethylene} / kJ mol ⁻¹	Ref.
HCP_TPB	2780	120.2	100.5	1.48	29.1	28.4	This work
ZJU-HOF-1	1465	109		2.25	31.5	22.8	4
CPOC-301	1962	87ª		1.3ª	32.4	24.2	5
HCP_BCMBP	1810	80.8	66.2	1.50	-	-	This work
HCP_p-DCX	1250	75.6	67.4	1.49	-	-	This work
HCP_m-DCX	1170	72.3	64.6	1.53	-	-	This work
HOF-BTB	955	69.2 ^b	55.7 ^b	-	25.4	22.6	6
HOF-76a	1121	66.08°		2.05°	~22.8		7
HCP_o-DCX	1000	63.1	57.5	1.50	-	-	This work
HCP_CMBA	940	59.1	52.9	1.42	-	-	This work
HCP-1.5	1103	55.55		1.3	-	-	8
COF-1	819	55	43	1.92	22.5	22.2	9
HCP_TMPB	1010	51.7	43.1	1.68	31.5	30.4	This work
ZJU-HOF-10 (sc)	1169	49°		1.9°	~25.4	~21.4	10

Table S4. The BET surface area, adsorption capacity, C_2H_6/C_2H_4 selectivity, and Q_{st} of representative C_2H_6 -selective metal-free materials at 298 K and 1 bar.

*a: measured at 293 K; b: measured at 295 K; c: measured at 296 K

References

- 1. Sorption Module Accelrys Inc. San Diego, 2011.
- 2. A. L. Myers and J. M. Prausnitz, *AIChE J*, 1965, **11**, 121-127.
- 3. Y. Luo, B. Li, W. Wang, K. Wu and B. Tan, *Adv. Mater.*, 2012, 24, 5703-5707.
- 4. X. Zhang, J.-X. Wang, L. Li, J. Pei, R. Krishna, H. Wu, W. Zhou, G. Qian, B. Chen and B. Li, *Angew. Chem. Int. Ed.*, 2021, **60**, 10304-10310.
- 5. K. Su, W. Wang, S. Du, C. Ji and D. Yuan, *Nat. Commun.*, 2021, **12**, 3703.
- 6. T.-U. Yoon, S. B. Baek, D. Kim, E.-J. Kim, W.-G. Lee, B. K. Singh, M. S. Lah, Y.-S. Bae and K. S. Kim, *Chem. Commun.*, 2018, **54**, 9360-9363.
- X. Zhang, L. Li, J.-X. Wang, H.-M. Wen, R. Krishna, H. Wu, W. Zhou, Z.-N. Chen, B. Li, G. Qian and B. Chen, *J. Am. Chem. Soc.*, 2020, 142, 633-640.
- 8. X. Luo, J. Shi, H. Zhao, C. Ma, D. Hu, H. Zhang, Q. Shen, N. Sun and W. Wei, *J. Solid State Chem.*, 2019, **271**, 199-205.
- 9. C. He, Y. Wang, Y. Chen, X. Wang, J. Yang, L. Li and J. Li, *ACS Appl. Mater. Interfaces*, 2020, **12**, 52819-52825.
- 10. J.-X. Wang, X.-W. Gu, Y.-X. Lin, B. Li and G. Qian, *ACS Materials Lett.*, 2021, **3**, 497-503.