Supporting Information

Construction of a thiourea-based metal-organic framework with open Ag^+ sites for the separation of propene/propane mixture

Zhiduo Chang, [ab] Rui-Biao Lin, [b] Yingxiang Ye, [bc] Chunying Duan* [a] and Banglin Chen* [b]

[a] State Key Laboratory of Fine Chemicals, Zhang Dayu College of Chemistry, Dalian University of Technology, Dalian, 116024, P. R. China. E-mail:cyduan@dlut.edu.cn.

[b] Department of Chemistry, University of Texas at San Antonio, One UTSA Circle, San Antonio, Texas 78249-0698, United States. E-mail: banglin.chen@utsa.edu.

[c] Fujian Provincial Key Laboratory of Polymer Materials, College of Chemistry and Materials Science, Fujian Normal University, 32 Shangsan Road, Fuzhou 350007, PR China.

Table of contents

Materials and Physical Measurements

4-pyridinecarboxaldehyde, ethanol, acetic acid, thiosemicarbazide, pentafluoropropionic acid, silver(I) oxide, triethylamine, N, N-dimethylformamide (DMF), acetonitrile were purchased from Fisher Scientific. All chemistry were used without further purification unless otherwise mentioned. Compressed He, CO_2, C_3H_6, C_3H_8, N_2, and C_3H_6/C_3H_8 (50/50 *v*/*v*) gases were bought from Airgas.

Single-crystal X-ray diffraction analysis data were collected on a Bruker SMART APEX CCD diffractometer with graphite monochromated Mo-Kα (λ = 0.71073 Å) using the SMART and SAINT programs.[1] The structure was solved by direct methods and refined on F^2 by full-matrix least-squares methods with SHELXTL version 5.1.[2] Non-hydrogen atoms of the ligand backbones were refined anisotropically. Hydrogen atoms within the ligand backbones were fixed geometrically at calculated positions and allowed to ride on the parent non-hydrogen atoms. Several bond distances constraints were used to help the refinement on the solvents moiety. The CF_3 groups of anion $C_2F_5COO^-$ disorder in two positions. The detailed crystal data are given in table S1.

Powder X-ray diffraction (PXRD) was carried out with a BRUKER D8-Focus Bragg-Brentano X-ray Powder Diffractometer equipped with a Cu sealed tube (λ = 1.54178 Å) at 40 kV and 40 mA. Gas sorption isotherms were measured using a Micromeritics ASAP 2020 system at various temperatures. ThermoFisher water bath is used to keep the BET sample tube at a constant temperature of 273 or 298 K. Thermogravimetric analysis (TGA) was carried out using a Shimadzu TGA-50 analyzer. ^{19}F-NMR spectra were collected on Bruker 500 MHz Avance III HD. The samples for the ^{19}F-NMR test were prepared by dissolve MOF in the DMSO solution of thiourea. supercritical fluid extraction was carried out using TOUSIMIS SAMDRI-PVT-3D with supercritical carbon dioxide.

Synthesis of AGTU-3

Ligands 2-(4-pyridinylmethylene)hydrazine-carbothioamide (TU)[3] and silver salt AgC_2F_5COO[4] were synthesized according to the reported method.

AGTU-3 was synthesized by reacting ligands TU and silver salt through slowly diffusion. In a glass tube, 2 mL 30 mM AgC_2F_5COO solution in acetonitrile (with 5 ‰ *v*/*v* pentafluoropropionic acid) was allowed to diffused slowly in to a solution 2 mL 10 mM ligands TU in DMF at room temperature, and the interlayer solvent was 6 mL DMF/acetonitrile solution (v/v =1/5). After two weeks, pale-yellow prismatic crystals can be obtained after filtration (Yield: 80 %). These crystal samples were suitable for single-crystal X-ray structural analysis.

Synthesis of AGTU-3a

AGTU-3a was prepared from the obtained **AGTU-3** samples through dealing with weak base triethylamine. 1 g **AGTU-3** was added into a 40 mL mixed solution of triethylamine and ethanol (*v*/*v*=1/40, room temperature, and 12 h), followed by exchanging with 40 mL ethanol (room temperature, 6 exchange cycles of 6 hours), to removing the anions in **AGTU-3**. Then, the activated sample **AGTU-3a** was obtained through further desiccation process with supercritical fluid extraction (SFE). Elemental Analysis Calcd. (%):

C, 29.29; H,2.46; N, 19.52; S, 11.17. Found: C, 29.14; H, 2.65; N, 19.32; S, 10.98. These samples can be used in gas adsorption analysis and breakthrough experiments after degassing at room temperature.

Organic Moieties in AGTU-3a

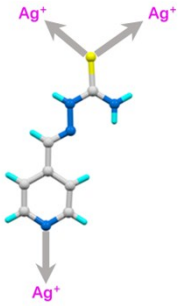


Figure S1 The schematic diagram shows the coordination configuration of organic moieties in **AGTU-3a**.

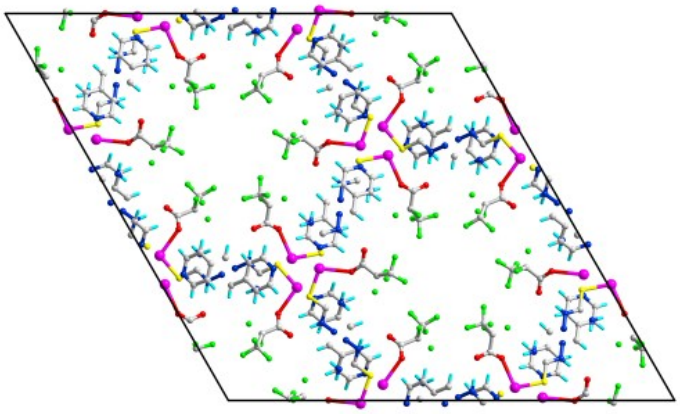


Figure S2. The single-crystal structure view of unit cell of **AGTU-3** along the c-axis (Ag: purple, C: grey, H: light blue, O: red, N: blue, S: yellow, F: green).

PXRD Spectra

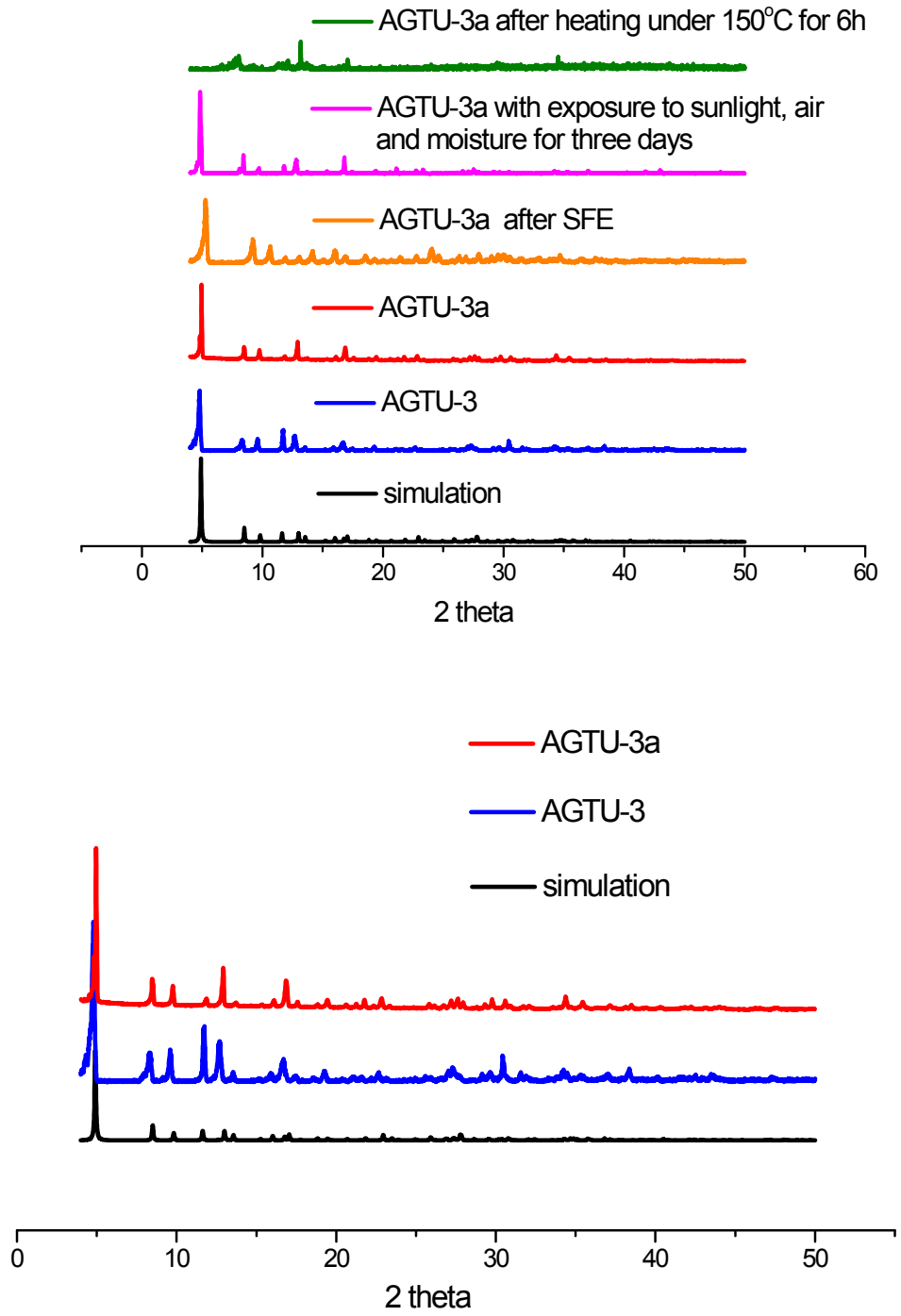


Figure S3. Top: PXRD patterns for **AGTU-3** and **AGTU-3a** under different conditions; bottom: enlarged PXRD patterns.

TGA Experiments

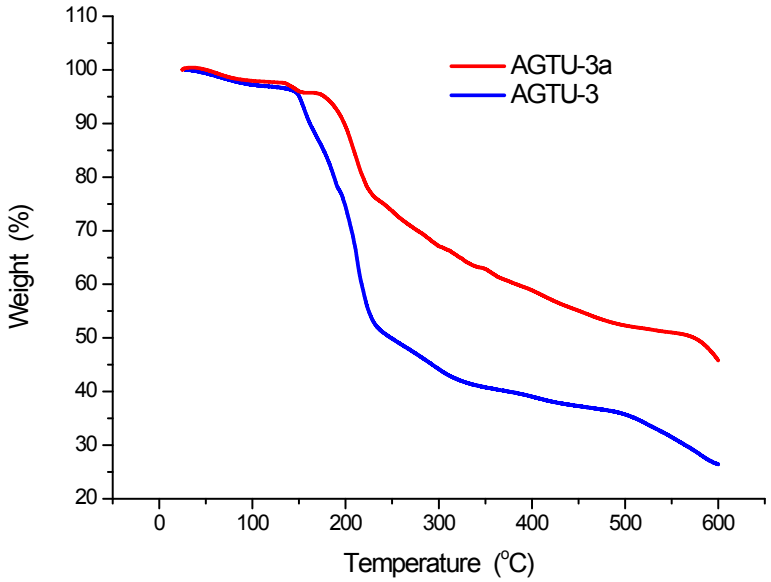


Figure S4. TGA analysis of **AGTU-3** and **AGTU-3a** performed under air atmosphere with a flow rate of 30 mL/min. The temperature was raised from room temperature to 600 °C at a heating rate of 5 °C/min.

Gas Adsorption Measurement

The sample was degassed at room temperature until the outgas rate was 5 μmHg/min prior to measurements. N_2, CO_2, C_3H_6, and C_3H_8 adsorption isotherms were collected on Micromeritics ASAP 2020 surface area analyzer for the guest-free sample.

Langmuir-Freundlich fitting of adsorption isotherm for IAST selectivity calculation

The experimental data of pure component isotherms at 298 K for C_3H_6, C_3H_8 were fitted with the single-site Langmuir-Freundlich model:

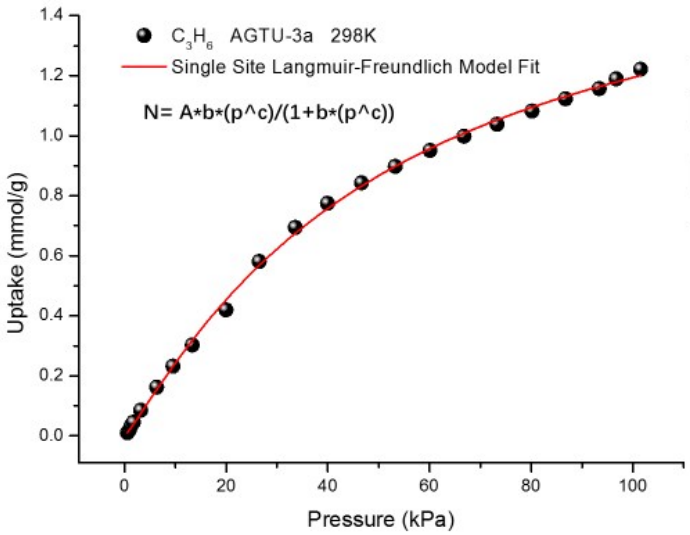
$$N = A\frac{bp^c}{1+bp^c} \qquad \text{(Equation 1)}$$

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, A (unit: mmol/g) is the saturation capacities, b (unit: 1/kPa) is the affinity coefficients, and c represents the deviation from an ideal homogeneous surface. Here, the single-component C_3H_6 and C_3H_8 adsorption isotherms have been fit to enable the application of IAST in simulating the performance of **AGTU-3a** under a mixed component gas. Adsorption isotherms and gas selectivity calculated by IAST for C_3H_6/C_3H_8 (*v*/*v*=50/50) at 298 K in **AGTU-3a**.

The selectivity of preferential adsorption of component 1 over component 2 in a mixture containing 1 and 2, can be formally defined as:

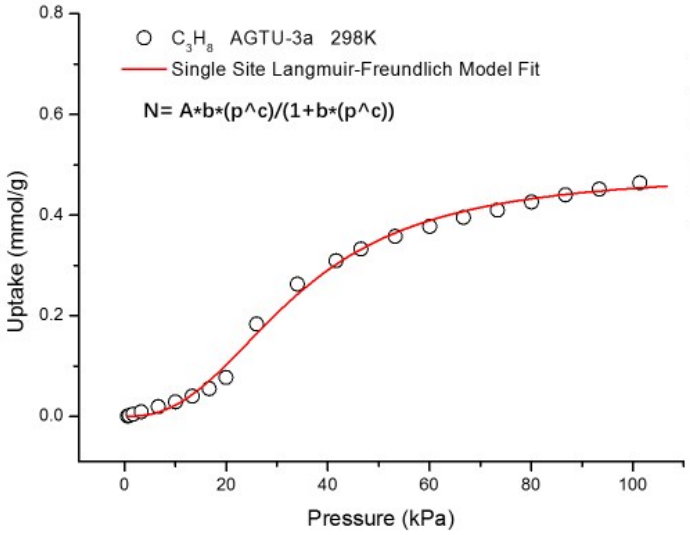
$$S_{ads} = \frac{q_1/q_2}{p_1/p_2} \qquad \text{(Equation 2)}$$

In the above equation, q_1 and q_2 are the absolute component loadings of the adsorbed phase in the mixture. These component loadings are also termed the uptake capacities. We calculate the values of q_1 and q_2 using the Ideal Adsorbed Solution Theory (IAST) of Myers and Prausnitz.[5]



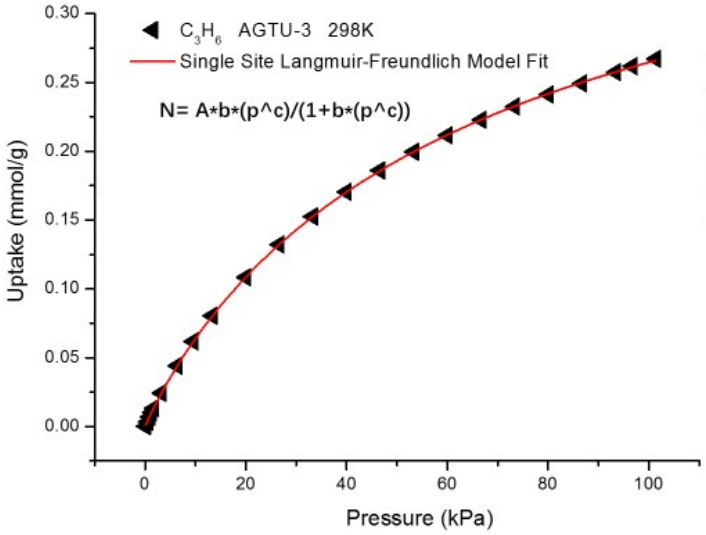
	Value
A	1.75744
b	0.01212
c	1.12098
Adj. R-Square	0.99901

Figure S5. Langmuir-Freundlich fitting of C_3H_6 adsorption data of **AGTU-3a** at 298K for IAST simulation. The resulting fitting parameters are listed in the left table.



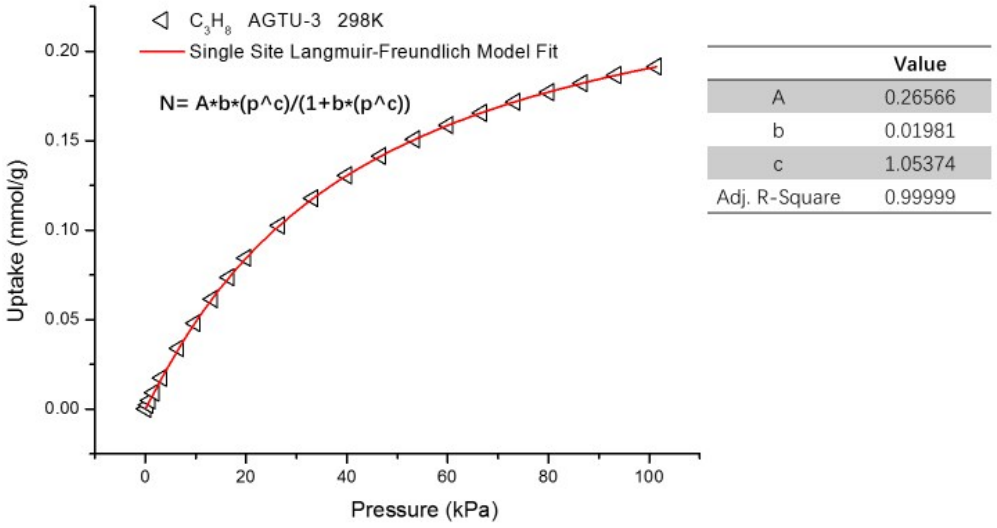
	Value
A	0.484
b	1.6032E-4
c	2.47909
Adj. R-Square	0.99573

Figure S6. Langmuir-Freundlich fitting of C_3H_8 adsorption data of **AGTU-3a** at 298K for IAST simulation. The resulting fitting parameters are listed in the left table.



	Value
A	0.44014
b	0.01908
c	0.94861
Adj. R-Square	0.99573

Figure S7. Langmuir-Freundlich fitting of C_3H_6 adsorption data of **AGTU-3** at 298K for IAST simulation. The resulting fitting parameters are listed in the left table.



	Value
A	0.26566
b	0.01981
c	1.05374
Adj. R-Square	0.99999

Figure S8. Langmuir-Freundlich fitting of C_3H_8 adsorption data of **AGTU-3** at 298K for IAST simulation. The resulting fitting parameters are listed in the left table.

Isosteric heat of adsorption

The pure component isotherms for C_3H_6 and C_3H_8 were measured at 298 K and 273 K. The isosteric heat of adsorption was calculated with Clausius-Clapeyron equation:

$$Q_{st} = RT^2\left(\frac{\partial \ln p}{\partial T}\right)_q \qquad \text{(Equation 3)}$$

by drawing ln*p vs.* loadings plots of pure component gas at 298 K and 273 K, respectively.

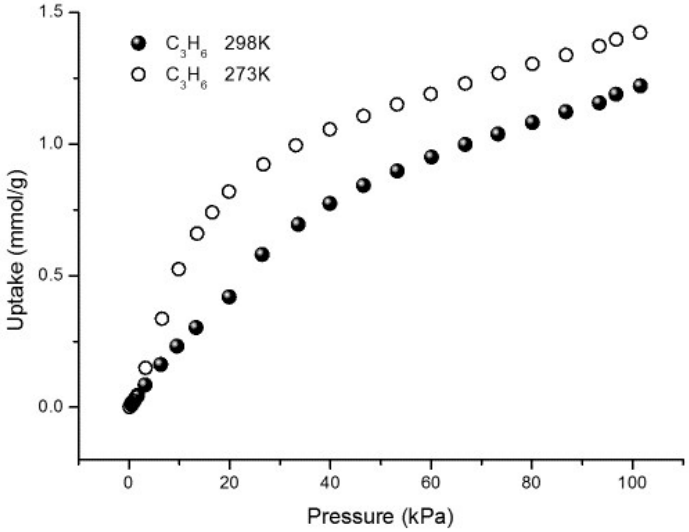


Figure S9. Adsorption isotherms of C_3H_6 at 298 K (solid circles) and 273 K (empty circles) in **AGTU-3a**.

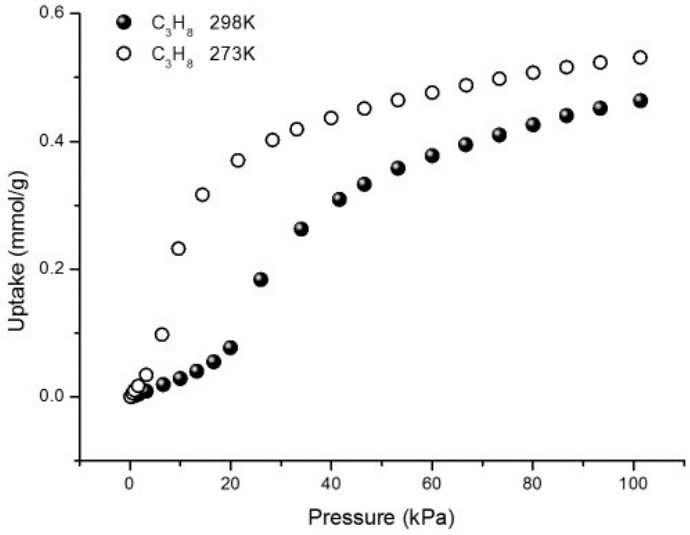
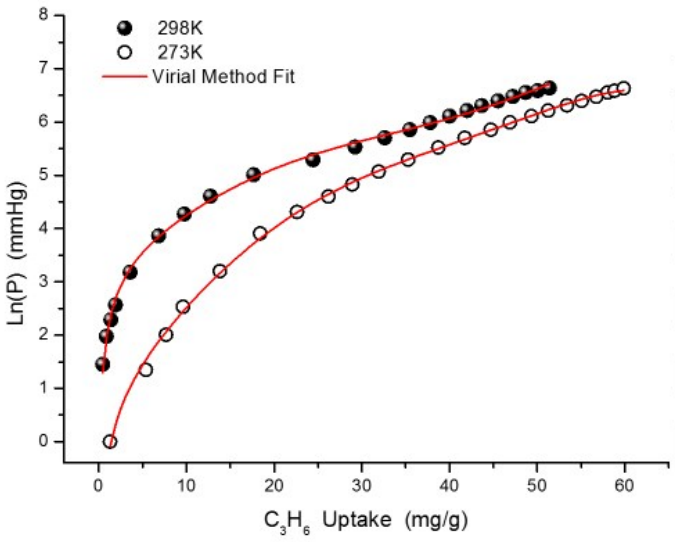
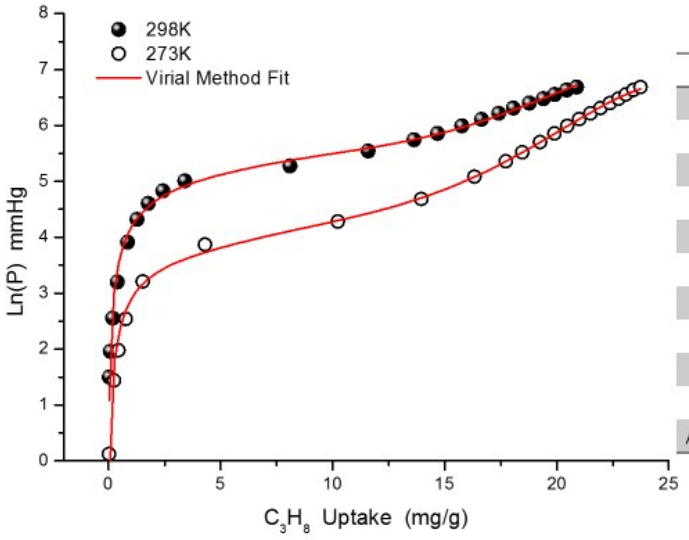


Figure S10. Adsorption isotherms of C_3H_8 at 298 K (solid circles) and 273 K (empty circles) in **AGTU-3a**.



	Value
a0	-8190.11522
a1	272.65257
a2	-0.8062
a3	-0.0983
a4	0.00169
a5	-1.02966E-5
b0	29.64316
b1	-0.99305
b2	0.01113
K	298
Adj. R-Square	0.99839

Figure S11. The virial fitting of the C_3H_6 adsorption isotherms of **AGTU-3a** at 298 K (solid circles) and 273 K (empty circles).



	Value
a0	-4079.33095
a1	-110.03006
a2	20.53146
a3	-1.33782
a4	0.06038
a5	-9.97546E-4
b0	18.17725
b1	0.0044
b2	-0.01739
K	298
Adj. R-Square	0.99161

Figure S12. The virial fitting of the C_3H_8 adsorption isotherms of **AGTU-3a** at 298 K (solid circles) and 273 K (empty circles).

Brunauer-Emmett-Teller (BET) and Langmuir surface areas

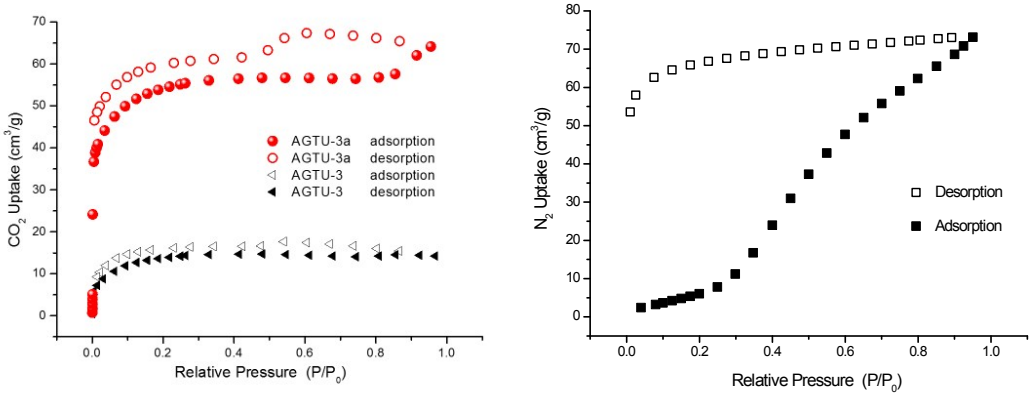


Figure S13. Adsorption isotherms of CO_2 at 196 K (left) and N_2 at 77K (right).

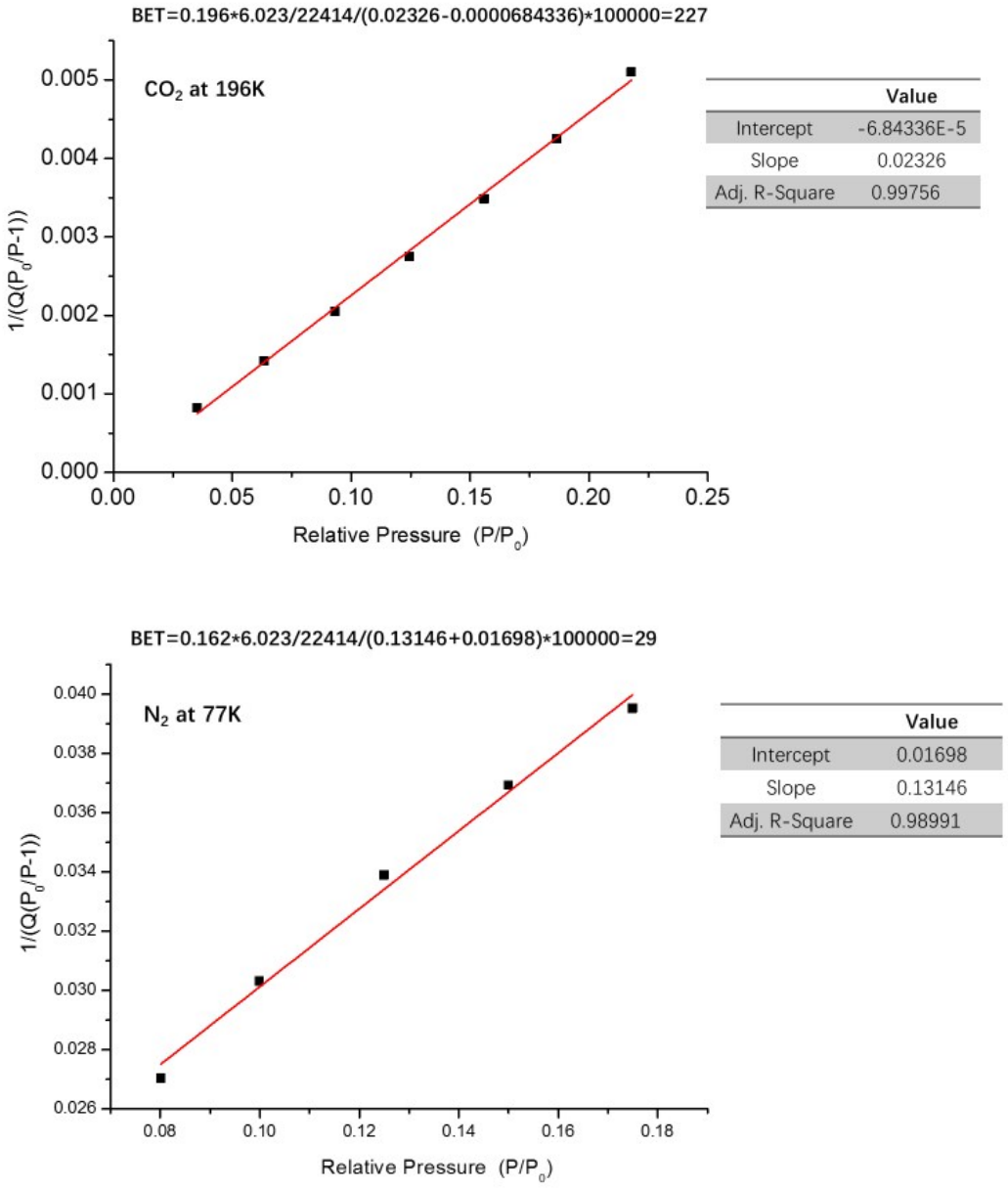


Figure S14. Calculation of BET surface area for **AGTU-3a**.

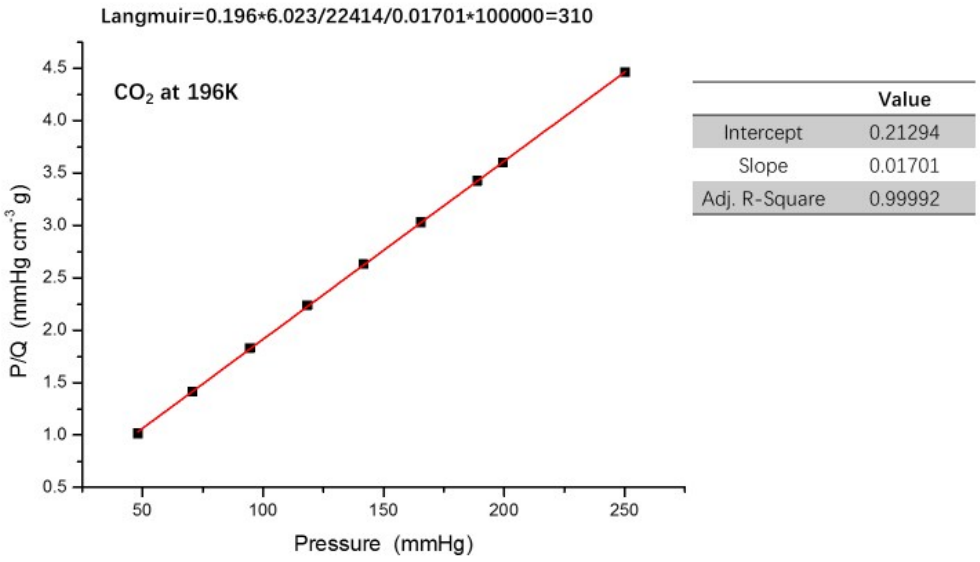


Figure S15. Calculation of Langmuir surface area for **AGTU-3a**.

Reversibility of propene adsorption

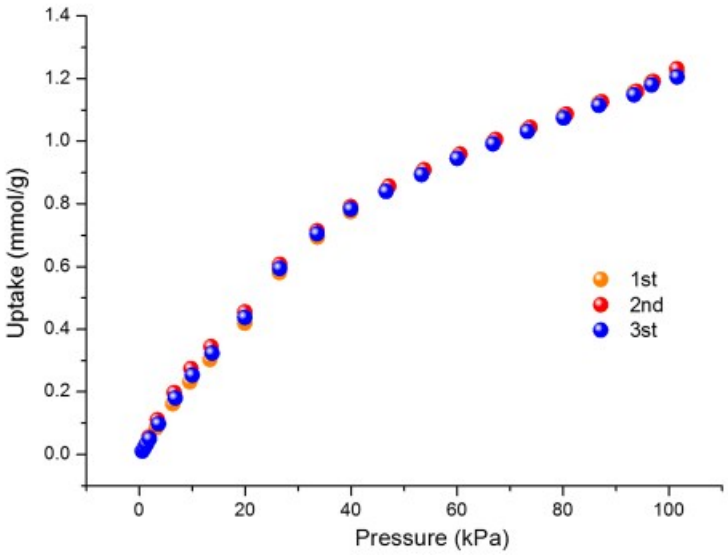


Figure S16. Three cycles of C_3H_6 adsorption isotherms for **AGTU-3a** at 298 K (degass under room temperature).

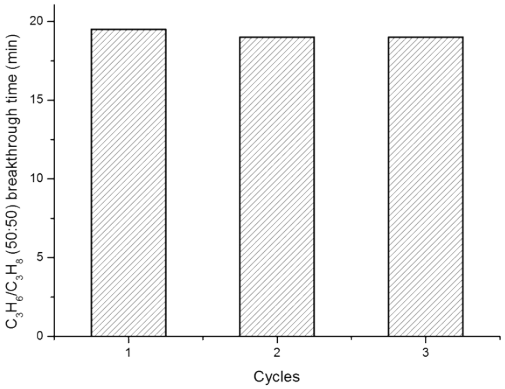


Figure S17. The recyclability of **AGTU-3a** in multiple runs of breakthrough experiments under the same condition.

Breakthrough Experiments

The experimental set-up consisted of two fixed-bed stainless steel column. One column was loaded with the adsorbent **AGTU-3a** (sample mass: 1.9 g), while the other was used as a blank control group to stabilize the gas flow. The flow rates of all gases mixtures were regulated by mass flow controllers, and the effluent gas stream from the column was detected by gas chromatography (SHIMADZU GC-2014) with a thermal conductivity detector (TCD, detection limit 0.1 ppm). Experimental condition: 298 K, 1 bar, gas flow: 1 mL/min. We performed regeneration conditions using a similar method described in our group's previous work. After every separation operation, the adsorption bed was regenerated by He flow (50 mL/min) for 2 h at 313 K.

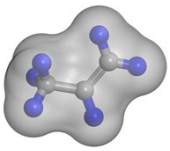
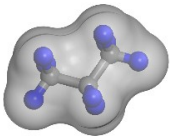
Supporting tables

Table S1 Crystal data and structure refinement for AGTU-3a.

Compound	**AGTU-3** · 0.848 DMF
Formula	$(C_{10}H_8AgF_5N_4O_2S)\cdot 0.848(C_3H_7NO)$
Formula weight	513.12 g/mol
Temperature	180(2) K
Crystal system	Trigonal
Space group	R-3
Unit cell dimensions	a = b = 35.9998(10) Å α = β = 90° c = 7.8373(4) Å γ = 120°
Volume	8796.2(7) Å^3
Z	18
Density	1.744 g/cm^3
Theta range for data collection	2.263 to 24.991°
Reflections collected	18182
Independent reflections	3436 [R(int) = 0.0296]
Completeness to theta = 24.991°	99.8 %
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.056
Final R indices [I>2sigma(I)]	R1 = 0.0791, wR2 = 0.2427
R indices (all data)	R1 = 0.0925, wR2 = 0.2572
CCDC	1945811

$R_1 = \sum|F_o - |F_c||/\sum|F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

Table S2 The selected physical and chemical properties of propene and propane.[6]

	propene	propane
Structure		
Boiling point (K)	225.46	231.02
Kinetic Diameter (Å)	4.678	5.1
Polarizability (10^{25} cm^3)	62.6	62.9-63.7
Dipole Moment (10^{18} esu cm)	0.366	0.084
Molar Volume (cm^3/mol)	184.6	200.0

Reference

1 (a) SMART, Data collection software (version 5.629) (Bruker AXS Inc., Madison, WI, 2003); (b) SAINT, Data reduction software (version 6.45) (Bruker AXS Inc., Madison, WI, 2003).

2 Sheldrick, G. M. SHELXTL97, Programfor crystal structure solution (University of Göttingen: Göttingen, Germany, 1997).

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5 A. L. Myers and J. M. Prausnitz, *AIChE Journal*, 1965, **11**, 121-127.

6 (a) Y. Ye, Z. Ma, R.-B. Lin, R. Krishna, W. Zhou, Q. Lin, Z. Zhang, S. Xiang and B. Chen, *J. Am. Chem. Soc.*, 2019, **141**, 4130-4136; (b) J.-R. Li, R. J. Kuppler and H.-C. Zhou, *Chem. Soc. Rev.*, 2009, **38**, 1477-1504.