Supporting Information

Immobilization of Ag(I) into a Metal-Organic Framework with $–SO_3H$ Sites for Highly Selective Olefin/Paraffin Separations at Room Temperature

Ganggang Chang[†], Minhui Huang[†], Ye Su[†], Huabin Xing[†], Baogen Su[†], Zhiguo Zhang[†], Qiwei Yang[†], Yiwen Yang[†], Qilong Ren[†], Zongbi Bao*[†], Banglin Chen*[‡]

**Corresponding authors*

[†]Key Laboratory of Biomass Chemical Engineering of the Ministry of Education,
College of Chemical and Biological Engineering,
Zhejiang University, Hangzhou 310027, P. R. China
Email: baozb@zju.edu.cn

‡Department of Chemistry, University of Texas at San Antonio, One UTSA Circle,
San Antonio, USA
E-mail: banglin.chen@utsa.edu

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1.1. Materials

Monosodium 2-sulfoterephthalate ($C_8H_5NaO_7S$, 98%) and Chromium(III) nitrate nonahydrate ($CrNO_3\ 9H_2O$, 99.95%) were purchased from TCI Co. (Japan), and Aladdin Co.(China), respectively. $AgBF_4$ (99.8%) were obtained from Alfa Aesar Co. All other chemicals (AR grade) were commercially available and used without further purification.

1.2. Preparation of the adsorbents

Synthesis of MIL-101-SO$_3$H. MIL-101-SO$_3$H was synthesized and purified following the reported method.[1] 5.4 g Monosodium 2-sulfoterephthalic acid (20.15 mmol), 4 g $CrNO_3\ 9H_2O$ (10 mmol), and 520 μL aqueous HF solution (37 wt%) were dissolved in 60 mL ultrapure water, then transferred to a Teflon-lined stainless steel autoclave. This highly acidic solution was heated at 190 °C for 24 h. After that, the autoclave was slowly cooled down to ambient temperature. The produced dark green solid was filtered and washed with deionized water and then with methanol for three times. Afterward, the solid was dried under high vacuum pressure at 110 °C for 12 h and stored in a desiccator.

Synthesis of MIL-101-SO$_3$Ag. 0.8 g $AgBF_4$ was dissolved in 20 mL CH_3CN/H_2O (1:1) solution, then 250 mg MIL-101-SO$_3$H was added. The mixture was under continuous vigorous stirring at room temperature for 24 h, and then the solid was collected by filtration followed by washing thoroughly with water. The exchange process was repeated two times, then the resultant was dried at 110 ^oC overnight for further use. The whole process was performed carefully under dark environment.

1.3. Characterization of the adsorbents

The phase of the samples was determined with a Powder X-ray diffraction (XRD) diffractometer (Panalytical Corp., Netherlands), which was operated at 40 kV for CuKa (λ= 0.1543 nm) radiation from 3^o to 50^o (2θ angle range) with a scan step size of 0.01°. X-ray Photoelectron Spectroscopy (XPS) measurements to confirm the presence of Ag(I) were performed on a combined VG ESCALAB MARK II instrument at a base pressure of 7.1×10^{-10} mbar which was operated at Mg $K\alpha$: 1253.6 eV, CAE: 50 eV and Step: 0.2 eV, 0.5 eV. Scanning electron microscope (SEM) was performed on a SIRION-100 instrument which was performed on a sample powder previously dried and sputter-coated with a thin layer of gold. Besides, energy-dispersive X-ray spectroscopy (EDX) analyses were also performed to confirm the presence and the distribution of Ag(I). Adsorption isotherms of N_2 on these adsorbents were obtained at 77 K with ASAP 2020 Micromeritics instrument. Prior to the nitrogen adsorption experiments, adsorbents were evacuated overnight at 120 °C to remove the water molecules.

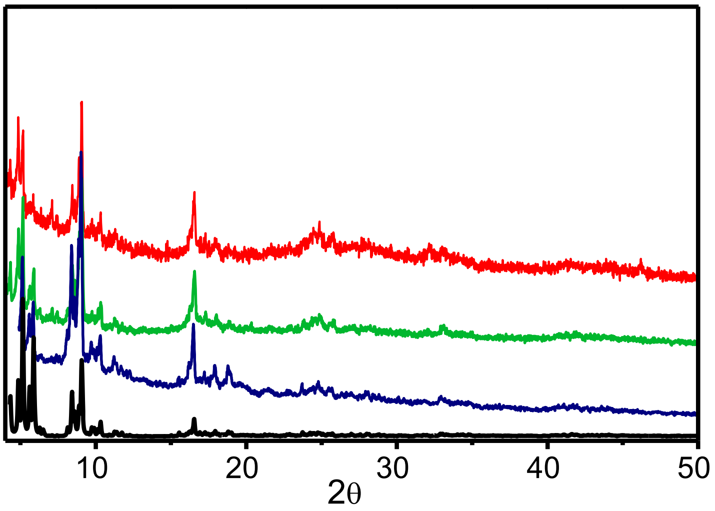
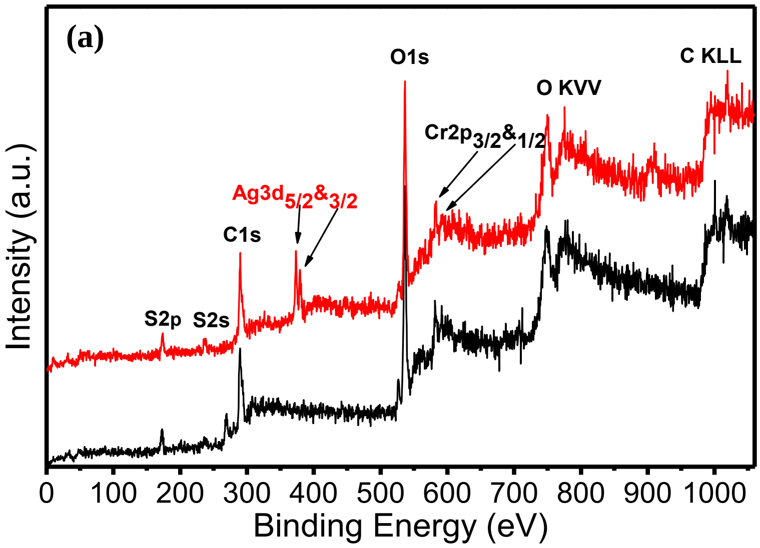


Figure S1. Experimental X-ray diffraction patterns for MIL-101-SO_3Ag (red), MIL-101-SO_3H (olive), and MIL-101(blue) compared with the simulated for MIL-101 (black).



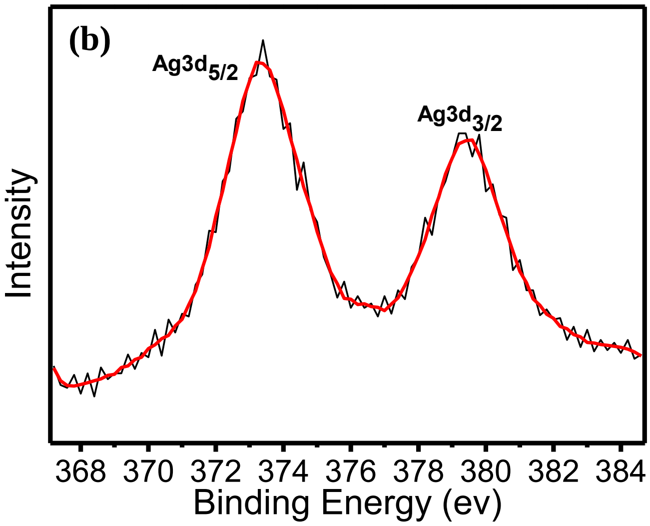


Figure S2. (a) XPS of MIL-101-SO_3H (black) and MIL-101-SO_3Ag (red); (b) the enlarged XPS for Ag(I) sites of MIL-101-SO_3Ag.

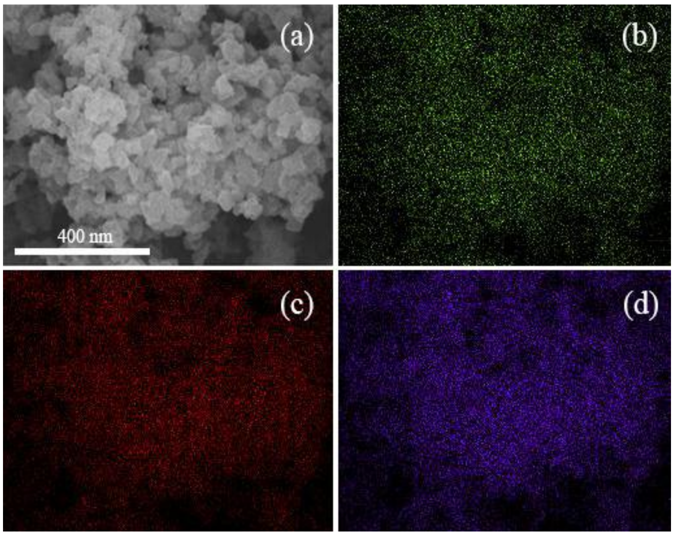
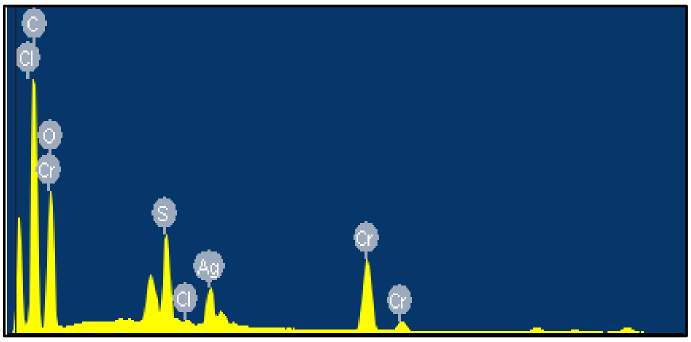


Figure S3. (a) SEM image and element maps for (b) Ag, (c) S, and (d) Cr of MIL-101-SO_3Ag.



Element	Weight %	Atom %
C K	51.77	64.82
O K	32.63	30.67
S K	3.39	1.59
Cl K	0.16	0.07
Cr K	7.79	2.25
Ag L	4.26	0.59
Total	100.00	

Figure S4. Element Analysis for MIL-101-SO_3Ag by EDX.

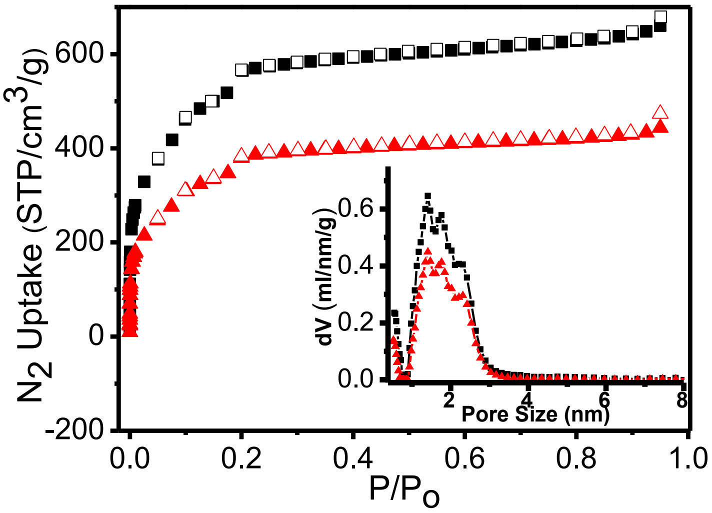


Figure S5. N_2 adsorption (solid)-desorption (open) isotherms and pore size distribution curves for (Cr)-MIL-101-SO_3H (black) and (Cr)-MIL-101-SO_3Ag (red).

1.4. Gas adsorption

Gas adsorption measurements were performed volumetrically in a Micromeritics ASAP 2050 adsorption apparatus. The adsorption isotherms were obtained at temperatures from 293 K to 313 K and gas pressures from 0 to 1 bar. About 150 mg sample was used for the gas adsorption studies. The initial outgassing process was carried out under a vacuum at 120 °C for 12 h. The free space of the system was determined by using the helium gas. The degas procedure was repeated on the same sample between measurements for 12 h. Ultrahigh purity grade helium (99.999%), ethane (99.99%), ethylene (99.99%), propane (99.98%), and propylene (99.98%) were purchased from Jingong Co., Ltd. (China).

The adsorption isotherms for ethylene, ethane, propane, and propylene, were fitted with the dual-Langmuir-Freundlich isotherm model.

$$q = q_{A,sat}\frac{b_A p^{v_A}}{1+b_A p^{V_A}} + q_{B,sat}\frac{b_B p^{v_B}}{1+b_B p^{V_B}} \qquad (1)$$

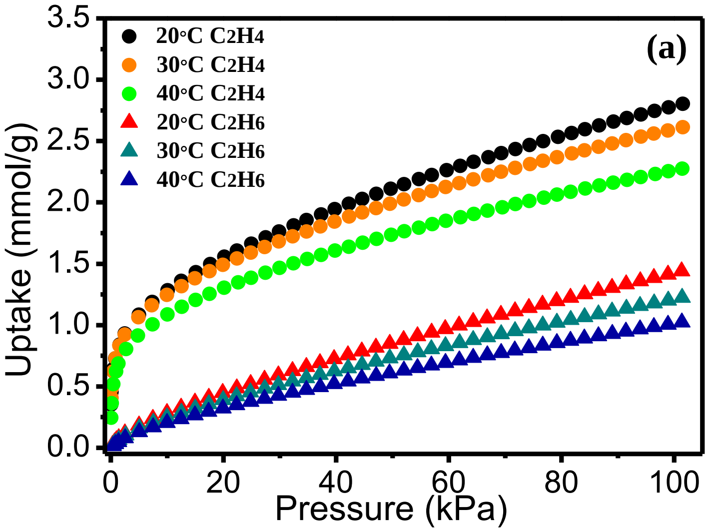
Isosteric heats of adsorption were estimated based upon Clausius-Clapeyron equation by differentiation of the dual-Langmuir-Freundlich fits of the isotherms at two different temperatures (303 K and 313 K) to compare the binding enthalpies of these gases under various loadings.

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

To predict mixed gas behavior from experimentally measured single-component isotherms, adsorption selectivities of olefin/paraffin mixtures (C_2H_4/C_2H_6 and C_3H_6/C_3H_8) were calculated using ideal adsorbed solution theory (IAST) with the fitted isotherms of the experimental isotherm data for relevant gas mixtures.

$$S_{ij} = \frac{x_i / x_j}{y_i / y_j} \tag{3}$$

where x_i and x_j are the equilibrated adsorption capacity of component i and j respectively, and y_i and y_j are the molar fractions of component i and j in gas phased respectively.



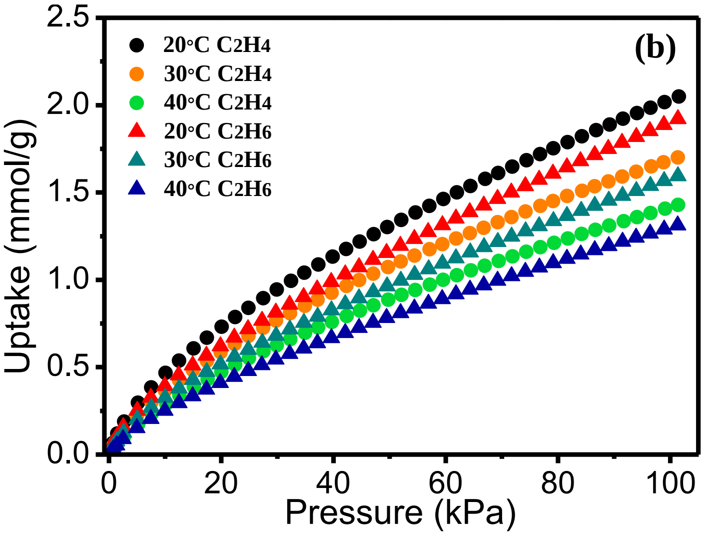


Figure S6. Adsorption isotherms of ethane and ethylene on (a) MIL-101-SO_3Ag and (b) MIL-101-SO_3H at 1 bar and at temperature of 20 °C, 30 °C and 40 °C.

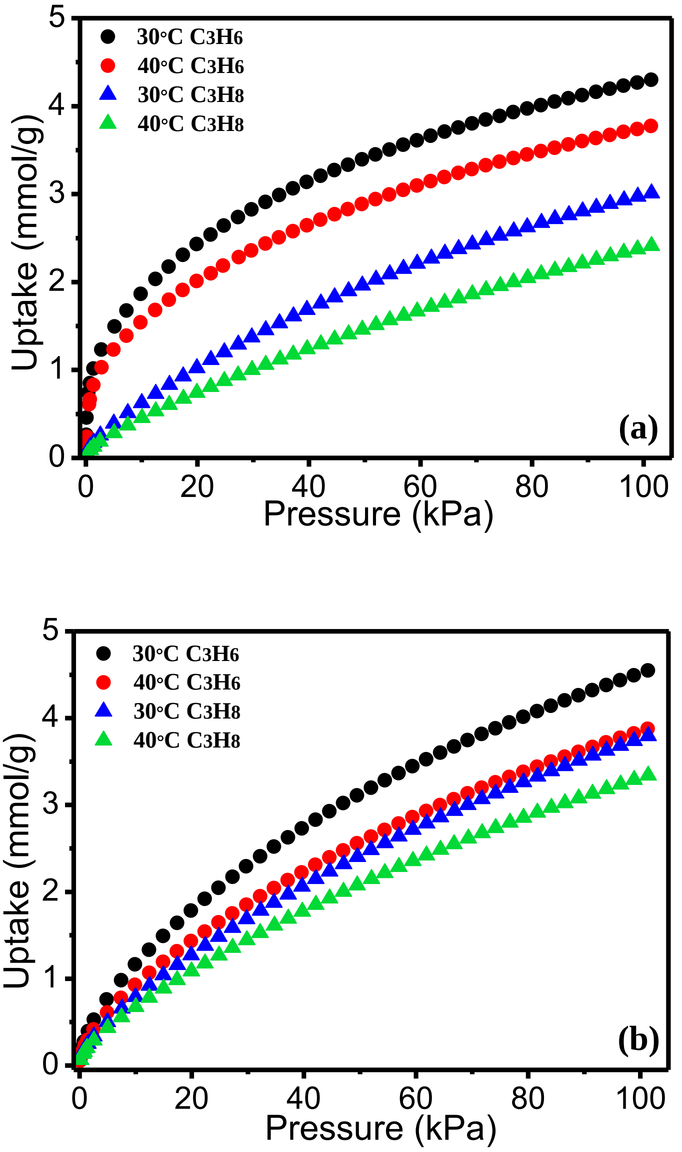


Figure S7. Adsorption isotherms of propane and propylene on (a) MIL-101-SO_3Ag and (b) MIL-101-SO_3H at 1 bar and at temperature of 30 °C and 40 °C.

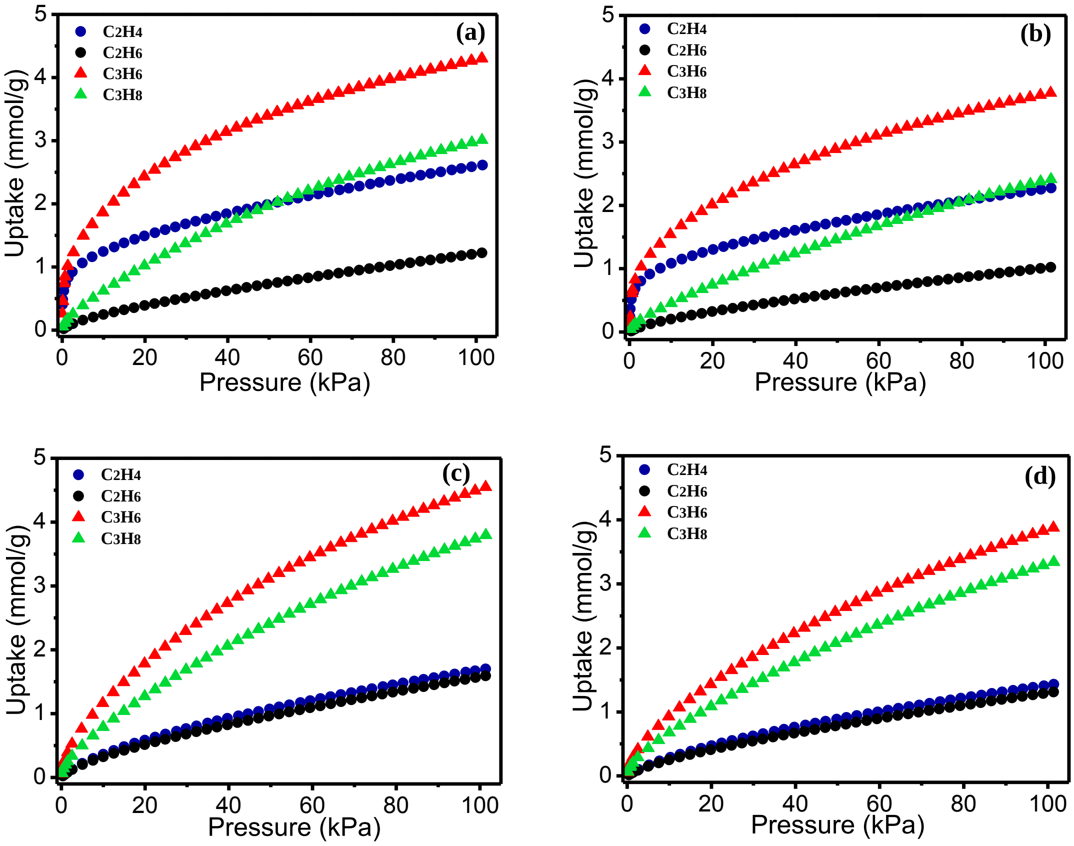


Figure S8. Comparision of single-component sorption isotherms for light hydrocarbons on MIL-101- SO_3Ag (a: 30 °C, b: 40 °C) and MIL-101-SO_3H (c: 30 °C, d: 40 °C).

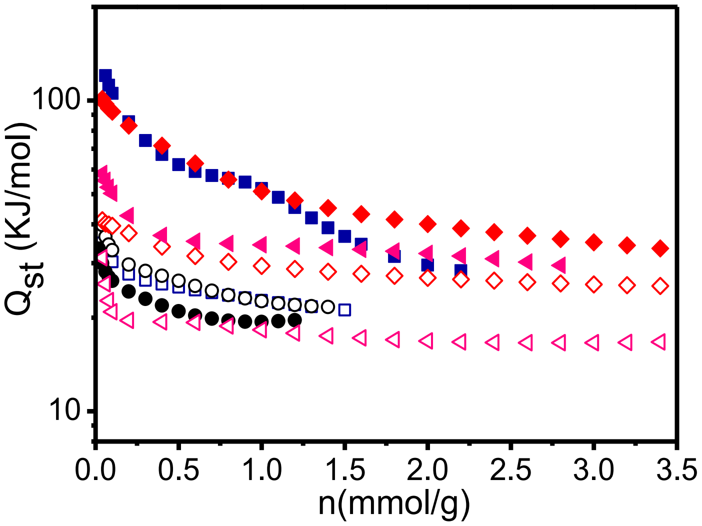


Figure S9. Isosteric heats of adsorption as a function of loading for ethylene (square), ethane (circle), propene (diamond) and propane (lefttriangle) on (Cr)-MIL-101-SO_3H (open) and (Cr)-MIL-101-SO_3Ag (solid).

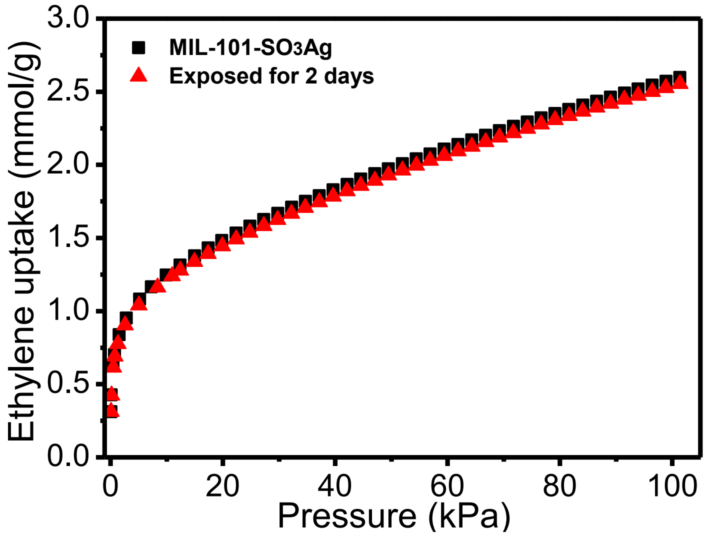


Figure S10. Ethylene adsorption isotherms after exposed in humidity (95%) for 2 days.

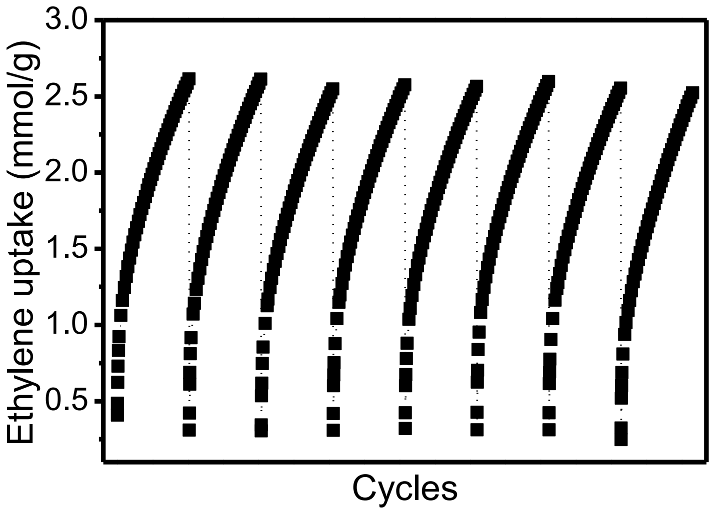


Figure S11. Recyclability of (Cr)-MIL-101-SO_3Ag for ethylene adsorption after 8 cycles. (To investigate the recyclability of (Cr)-MIL-101-SO_3Ag, successive adsorption and desorption experiments were carried out at 303 K without moisture exposure.)

Table S1. Comparison of equilibrium adsorption amount of C_2H_4/C_2H_6 and IAST selectivities of various adsorbents at ~303 K and 100 kPa.

Adsorbents	*q* (mmol/g)		IAST Selectivity (equimolar)	Ref.
	C_2H_4	C_2H_6		
zeolite 5A	2.45	1.72	4.5	2
NaX	4.2	3.5	8	3
Na-ETS-10	1.7	1.3	15	4
HMS	0.6	0.4	2	5
PCN-16	7.14	7.05	2.8	3b
NOTT-102	5.80	5.80	3	3b
UTSA-30a	2.01	2.01	—	6
UTSA-33a	2.58	2.58	—	7
UTSA-35a	2.05	2.41	—	8
HOF-4a	0.49	0.16	14	9
ZIF-7	1.75	1.75	—	10
ZIF-8	1.5	2.5	—	11
HKUST-1	7.20	6.03	3.6	3b
Mg-MOF-74	7.2	6.7	5.6	3b
Co-MOF-74	6.78	6.47	6.4	3b
Fe-MOF-74	6.02	5.0	11	3b,12
PAF-1-SO_3Ag	4.1	2.59	27	13
(Cr)-MIL-101	2.22	1.84	1.8	14
Cu^+@MIL-101	2.46	1.22	6.5	14
(Cr)-MIL-101-SO_3H	1.70	1.6	1.2	This work
(Cr)-MIL-101-SO_3Ag	2.61	1.22	16	This work

Table S2. Comparison of equilibrium adsorption amount of C_3H_6/C_3H_8 and IAST selectivities of various adsorbents at ~303 K and 1kPa.

Adsorbents	*q* (mmol/g)		IAST Selectivity (equimolar)	Ref.
	C_3H_6	C_3H_8		
NaX	2.51	2.01	6.8	3b,12
ITQ-12	1.3	0.80	15	12,15
HKUST-1	7.9	6.2	-	16
[a]Fe-MIL-100	1.3	0.6	7	12,17
Mg-MOF-74	7.1	8.0	7.2	3b,12
Co-MOF-74	7.2	5.2	15	18
Fe-MOF-74	6.66	5.67	13.8	12
Mn-MOF-74	6.1	4.4	18	18
(Cr)-MIL-101-SO_3H	4.54	3.80	1.83	This work
(Cr)-MIL-101-SO_3Ag	4.32	3.00	32	This work

a: The pure component experimental data are available only up to pressures of 7 kPa.

Table S3. Dual-site Langmuir-Freundlich parameters for pure hydrocarbons (C_2, C_3) isotherms in MIL-101-SO_3Ag at 293 K, 303 K, and 313 K.

MIL-101-SO_3Ag		Site A			Site B		
		$q_{i,\mathrm{A,sat}}$ mol/kg	$b_{i,\mathrm{A}}$ $k\mathrm{Pa}^{-Vi}$	$V_{i,\mathrm{A}}$ dimensionless	$q_{i,\mathrm{B,sat}}$ mol/kg	$b_{i,\mathrm{B}}$ $k\mathrm{Pa}^{-Vi}$	$V_{i,\mathrm{B}}$ dimensionless
C_2H_4	293K	7.79	4.79×10^{-3}	0.8635	1.34	1.1822	0.4243
	303K	8.71	4.24×10^{-3}	0.8319	1.29	1.2598	0.4404
	313K	6.65	4.69×10^{-3}	0.8479	1.07	1.2947	0.5261
C_2H_6	293K	3.77	3.55×10^{-4}	1.4107	1.34	0.0476	0.6820
	303K	6.98	1.19×10^{-3}	1.0580	0.34	0.1378	0.7813
	313K	4.84	1.31×10^{-3}	1.0810	0.28	0.1249	0.8307
C_3H_6	303k	7.62	3.73×10^{-2}	0.6848	0.72	9.5729	1.1152
	313k	7.76	2.42×10^{-2}	0.7154	0.69	4.7599	1.3537
C_3H_8	303k	5.31	5.11×10^{-3}	1.1294	0.53	0.2942	0.5757
	313k	4.86	1.78×10^{-3}	1.2217	1.63	0.0617	0.5857

Table S4. Dual-site Langmuir-Freundlich parameters for pure hydrocarbons (C_2, C_3) isotherms in MIL-101-SO_3H at 293 K, 303 K, and 313 K.

MIL-101-SO_3H		Site A			Site B		
		$q_{i,\mathrm{A,sat}}$ mol/kg	$b_{i,\mathrm{A}}$ $k\mathrm{Pa}^{-Vi}$	$V_{i,\mathrm{A}}$ dimensionless	$q_{i,\mathrm{B,sat}}$ mol/kg	$b_{i,\mathrm{B}}$ $k\mathrm{Pa}^{-Vi}$	$V_{i,\mathrm{B}}$ dimensionless
C_2H_4	293K	3.11	2.92×10^{-4}	1.5354	1.92	0.0469	0.7911
	303K	3.48	4.97×10^{-4}	1.3802	1.32	0.0470	0.8348
	313K	5.44	9.41×10^{-4}	1.1454	0.77	0.0516	0.8732
C_2H_6	293K	4.80	5.19×10^{-4}	1.3725	1.19	0.0679	0.7627
	303K	4.10	5.15×10^{-4}	1.3638	0.96	0.0634	0.8059
	313K	5.54	1.14×10^{-3}	1.1276	0.43	0.0849	0.8809
C_3H_6	303k	9.22	9.99×10^{-3}	0.9410	0.56	0.6687	0.6827
	313k	8.33	5.98×10^{-3}	1.0115	0.69	0.3886	0.6816
C_3H_8	303k	8.23	3.95×10^{-3}	1.0773	1.27	0.1489	0.5217
	313k	8.82	4.27×10^{-3}	1.0304	0.47	0.4071	0.5969

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