

Supplementary information

Direct observation of dimethyl sulfide trapped by MOF proving efficient removal of sulfur impurities

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General Procedures and Experimental section

General Procedures

The powder X-ray diffraction patterns (PXRD) measurements were carried out on a Rigaku MiniFlex600 40 kV, 15 mA for Cu K α ($\lambda = 1.5406 \text{ \AA}$) with a scan rate of 10 degree/min at room temperature.

Simulated powder patterns from single-crystal X-ray diffraction data were generated using Mercury 1.4.1 software.

N₂ adsorption measurements at 77 K were performed with BELSORP-mini (MicrotracBEL corp.). A sample was heated at 120 °C under vacuum for 6 h prior to the measurements.

The inductively coupled plasma-atomic emission spectrometry (ICP-AES) measurements were performed on an iCAP 7400 Duo (Thermo Fisher Scientific) to quantitate the silver contents in Ag–Y zeolite. A sample was heated and decomposed by adding nitric acid and hydrofluoric acid. After cooling, it was diluted with water and analyzed.

Experimental section

Chemicals

Synthesis of HKUST-1

Cu(NO₃)₂·3H₂O was purchased from Kanto Chemical Co., Inc., 1,3,5-benzenetricarboxylic acid (H₃btc) was from Tokyo Chemical Industry, acetic acid was from FUJIFILM Wako Pure Chemical Corp., ethanol (EtOH) and *N,N*-dimethylformamide (DMF) were from Nacalai Tesque.

Synthesis of Cu-JAST-1

Cu(HCOO)₂·4H₂O and toluene were purchased from FUJIFILM Wako Pure Chemical Corp., 1,4-benzenedicarboxylic acid (H₂bdc) and 1,4-diazabicyclo[2.2.2]octane (dabco) were from Tokyo Chemical Industry, methanol (MeOH) was from Nacalai Tesque and formic acid was from Kanto Chemical Co., Inc..

Preparation of Ag–Y zeolite

Na–Y zeolite (HSZ-320NAA) was purchased from Tosoh Corp., and 0.1 mol/L silver nitrate solution was from FUJIFILM Wako Pure Chemical Corp..

Experimental

Synthesis of HKUST-1^{S1}

An H₂O (24 mL) solution of Cu(NO₃)₂·3H₂O (2.79 g, 11.50 mmol) was mixed with a DMF (12 mL) solution of 1,3,5-benzenetricarboxylic acid (H₃btc, 1.68 g, 8.00 mmol) in a 50 mL Teflon-lined

stainless steel vessel. The vessel was sealed and heated in a convection oven for 3 days at 85 °C. After cooling to room temperature, the solids were separated by filtration and washed with MeOH four times (yield: 96%). The sample was heated at 120 °C under dynamic vacuum for 6 h to yield a degassed sample. The crystal structure was determined by SXRD (Fig. S1†).

A single crystal of HKUST-1 was prepared according to the previously reported procedure.^{S2} Cu(NO₃)₂·3H₂O (0.49 g, 2.03 mmol) and H₃btc (0.24 g, 1.14 mmol) were dissolved in a 9 mL solvent mixture of H₂O:DMF:EtOH = 1:1:1 (v/v/v) with acetic acid as a modulator (12 mL) in a glass container, which was tightly capped with a Teflon vial and heated at 55 °C for 3 days. After cooling to room temperature, the resulting blue crystals were collected and soaked in EtOH for 3 days. The crystals were heated at 120 °C under vacuum for 12 h to produce a degassed sample (yield: 78%).

Synthesis of Cu-JAST-1^{S3}

A MeOH solution (400 mL) of Cu(HCOO)₂·4H₂O (0.90 g, 3.99 mmol) and 8 mL of formic acid were mixed with a MeOH solution (400 mL) of 1,4-benzenedicarboxylic acid (H₂bdc, 0.66 g, 3.97 mmol) in a 1000 mL glass container; the mixture was stirred at room temperature for 2 days. The precipitate was collected and put into a 100 mL Teflon-lined stainless steel vessel with a 1,4-diazabicyclo[2.2.2]octane (dabco, 0.54 g, 4.81 mmol) solution [20 mL, Toluene: MeOH = 1:1 (v/v)]. The vessel was sealed and heated in a convection oven at 120 °C for 15 h. After cooling to room temperature, the solids were filtered and washed with Toluene and MeOH (yield: 67%). The sample was heated at 120 °C under vacuum for 6 h to yield a degassed sample. The crystal structure was determined by SXRD (Fig. S2†).

Preparation of Ag–Y zeolite^{S4}

Na–Y zeolite (2.6 g) with a SiO₂/Al₂O₃ molar ratio of 5.5 was added to a 0.1 mol/L solution of silver nitrate (100 mL) and stirred at room temperature for 24 h. Then, the precipitate was centrifuged and washed with H₂O. The sample was dried under vacuum at 80 °C for 12 h and then calcined in air at 400 °C for 2 h. An ICP analysis revealed that the silver content in Ag–Y zeolite was 20.6 wt%, which was reasonable based on the cation exchange capacity of Na–Y zeolite (4.0 mmol/g) and the amount of preparation.^{S4}

Structure

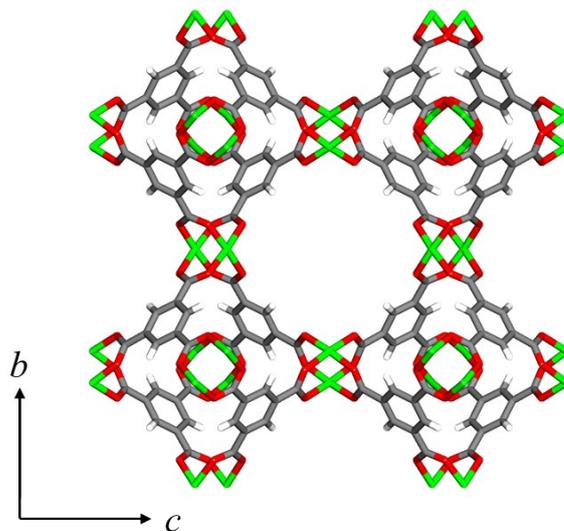


Fig. S1. Crystal structure of HKUST-1 (Cu, green; O, red; C, gray; H, white). Viewing along plane (100).

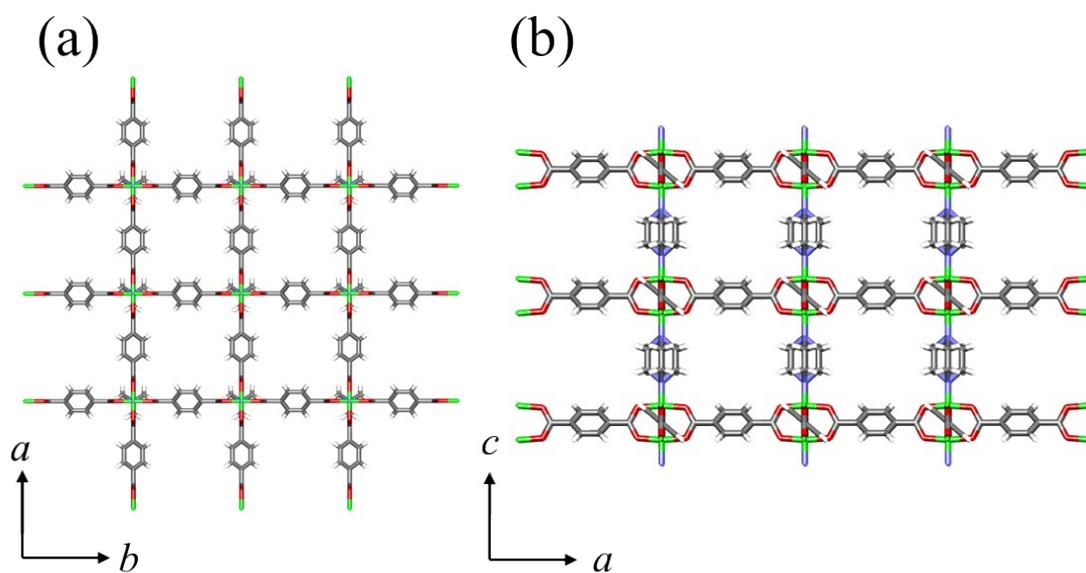


Fig. S2. Crystal structure of Cu-JAST-1 (Cu, green; O, red; N, purple; C, gray; H, white). Viewing along (a) plane (001) and (b) plane (010).

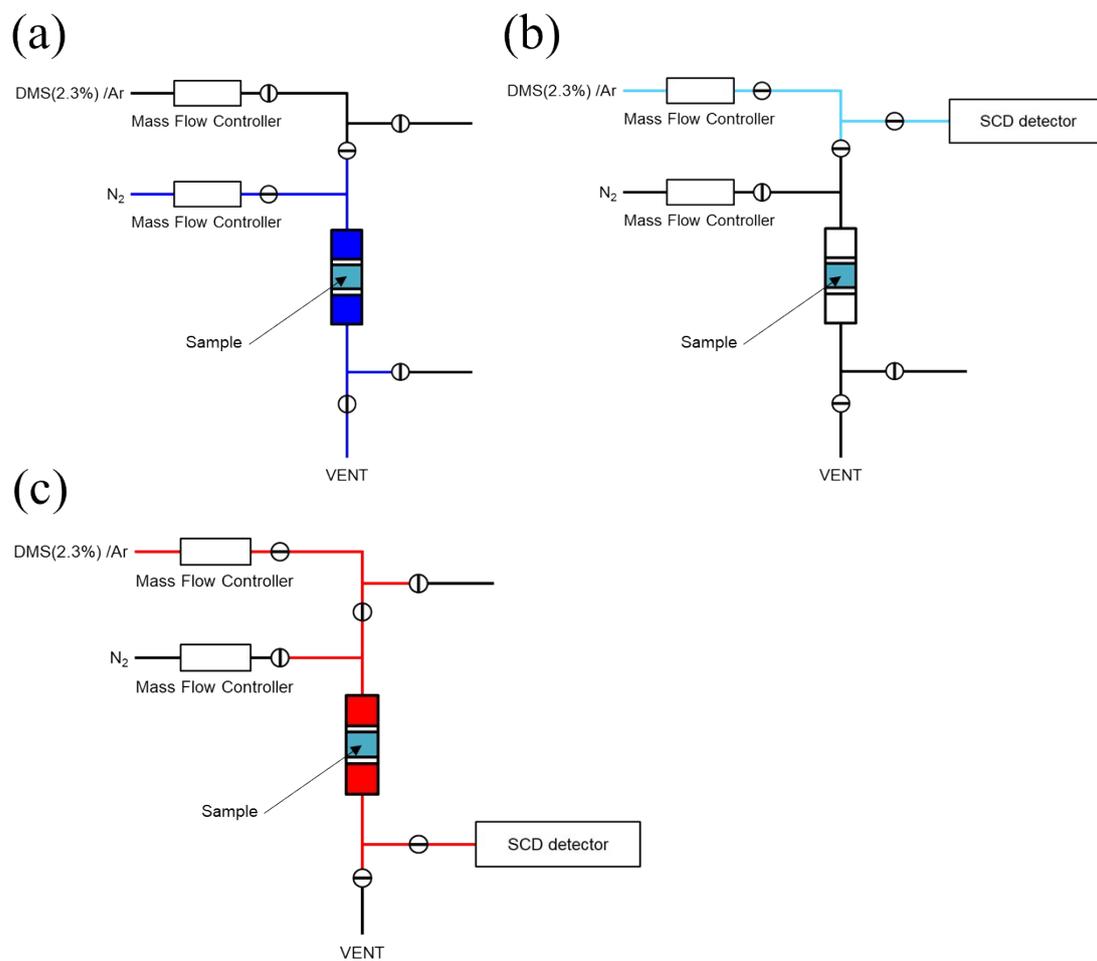


Fig. S3. Experimental procedure of DMS breakthrough measurements; (a) No. 1, (b) No. 2 and (c) No. 3.

- (a) No. 1. Heating the sample to obtain a degassed sample in the cell at 393 K for 12 h under N₂ flow.
- (b) No. 2. DMS (2.3 vol. %)/Ar gas flowing and measuring inlet sulfur concentration (C_0).
- (c) No. 3. Setting the sample at 303 K, measuring outlet sulfur concentration at each measurement time and calculating the relative concentration (C/C_0).

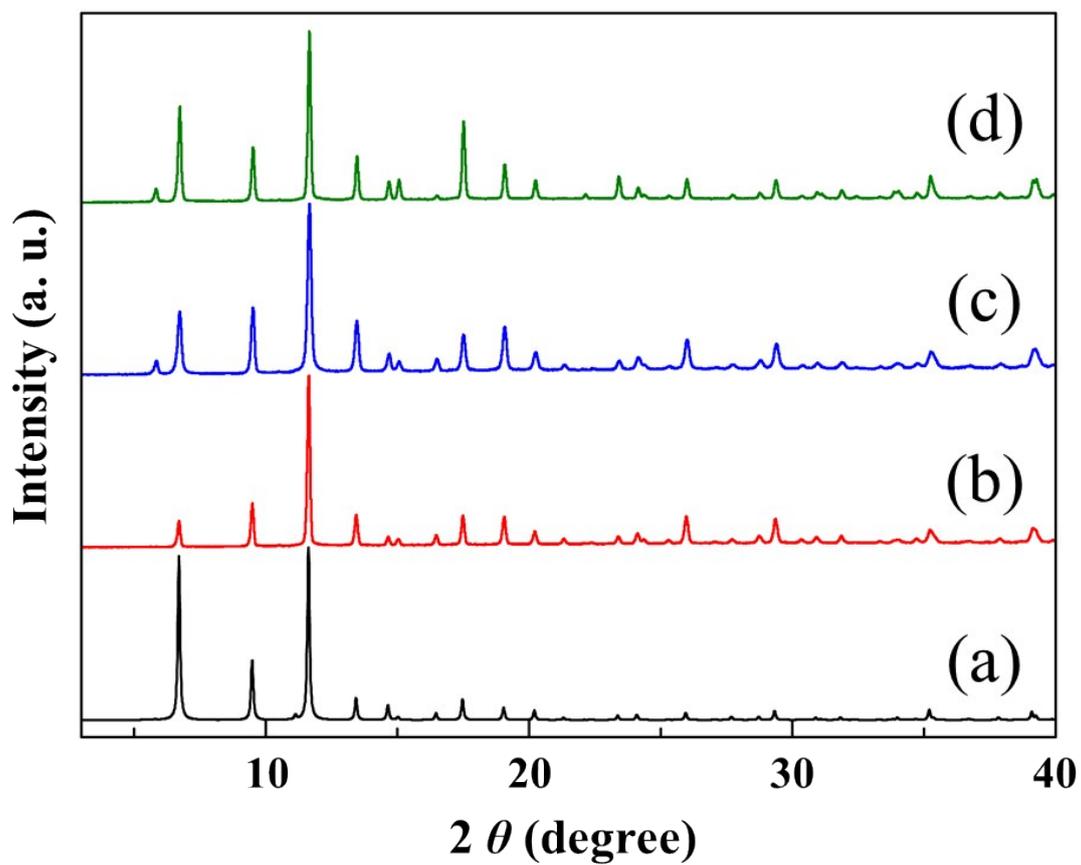


Fig. S4. PXRD patterns of (a) simulated HKUST-1, (b) as-synthesized HKUST-1, (c) degassed HKUST-1 and (d) DMS-adsorbed HKUST-1 after DMS breakthrough measurement.

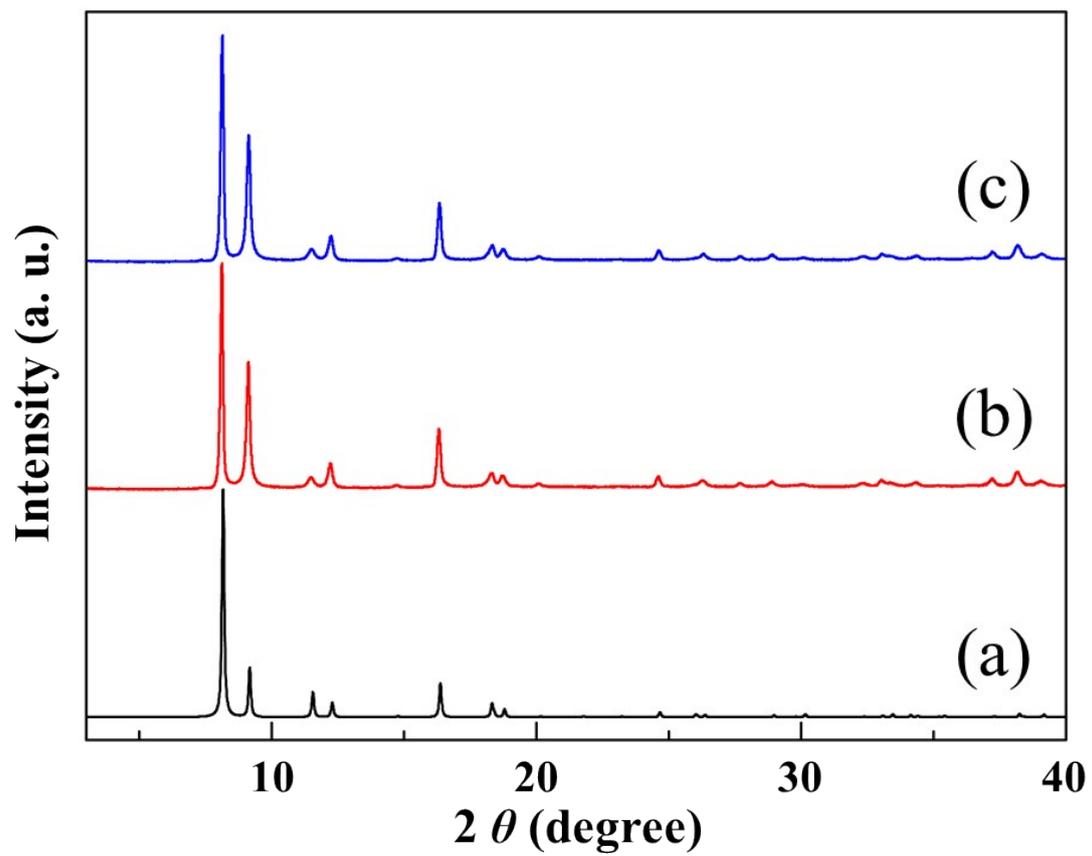


Fig. S5. PXRd patterns of (a) simulated Cu-JAST-1, (b) as-synthesized Cu-JAST-1 and (c) degassed Cu-JAST-1.

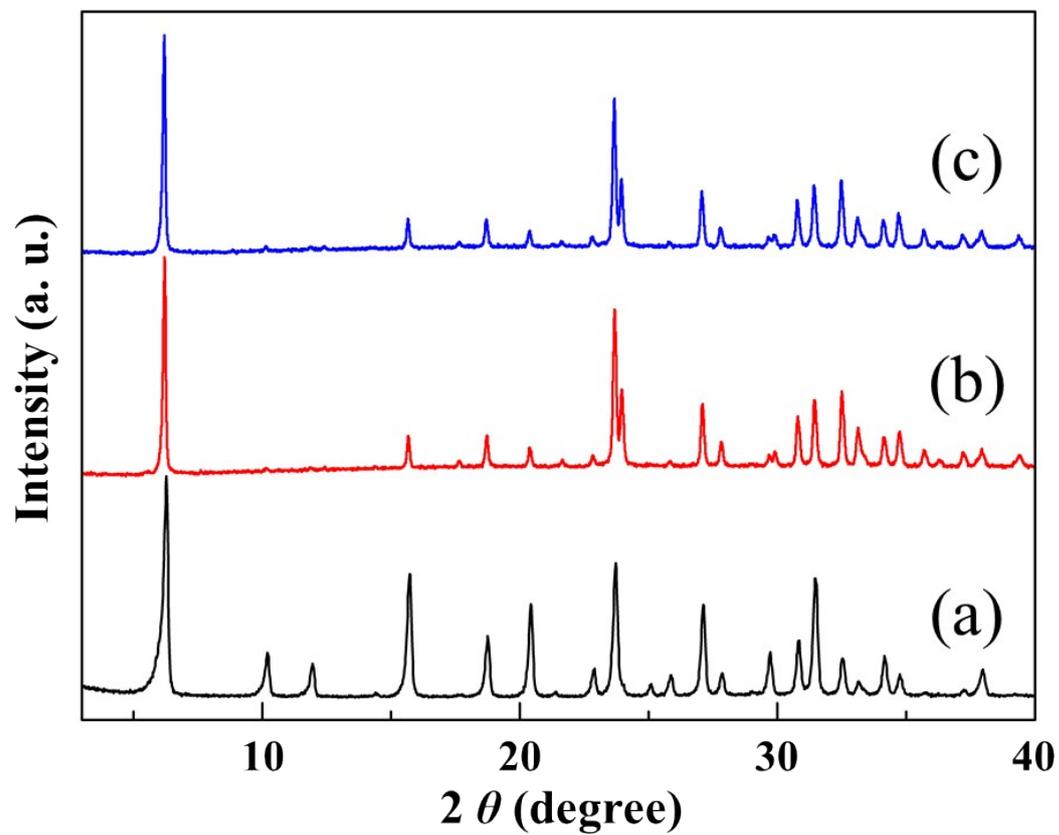


Fig. S6. PXRD patterns of (a) Na-Y zeolite, (b) as-synthesized Ag-Y zeolite and (c) degassed Ag-Y zeolite.

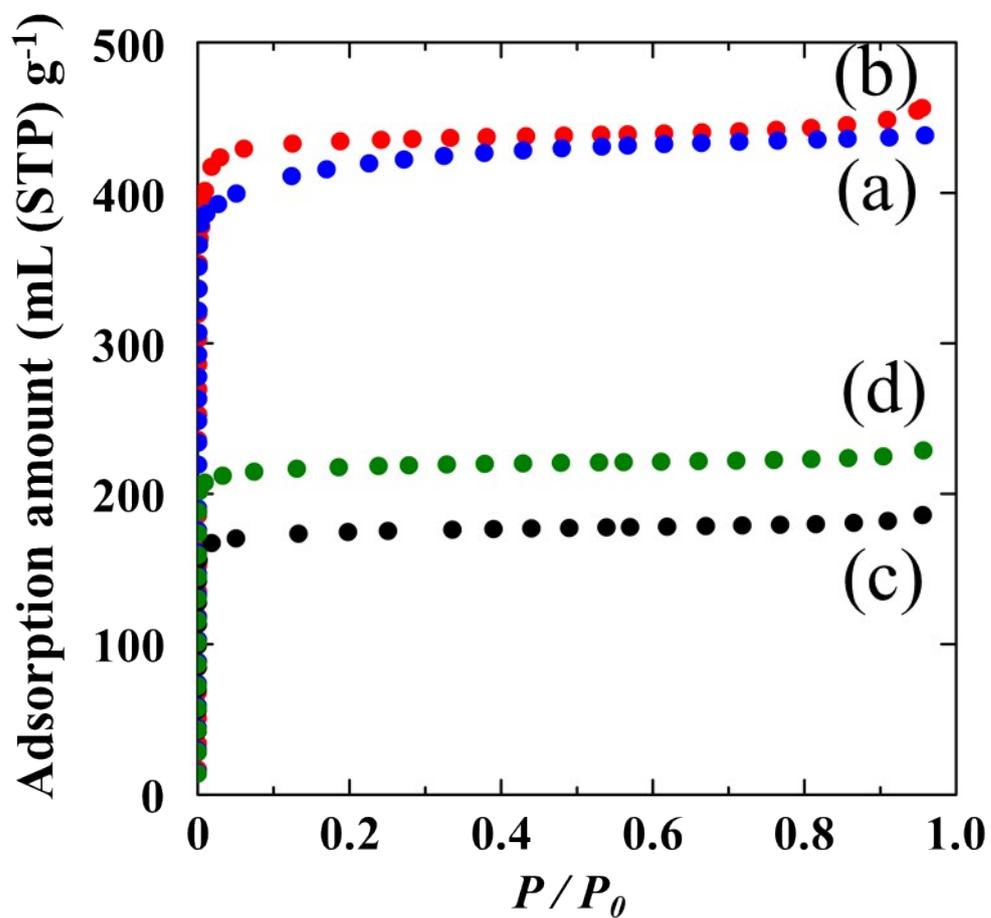


Fig. S7. Adsorption isotherms of N₂ for (a) HKUST-1, (b) Cu-JAST-1, (c) Ag-Y zeolite and (d) Na-Y zeolite at 77 K.

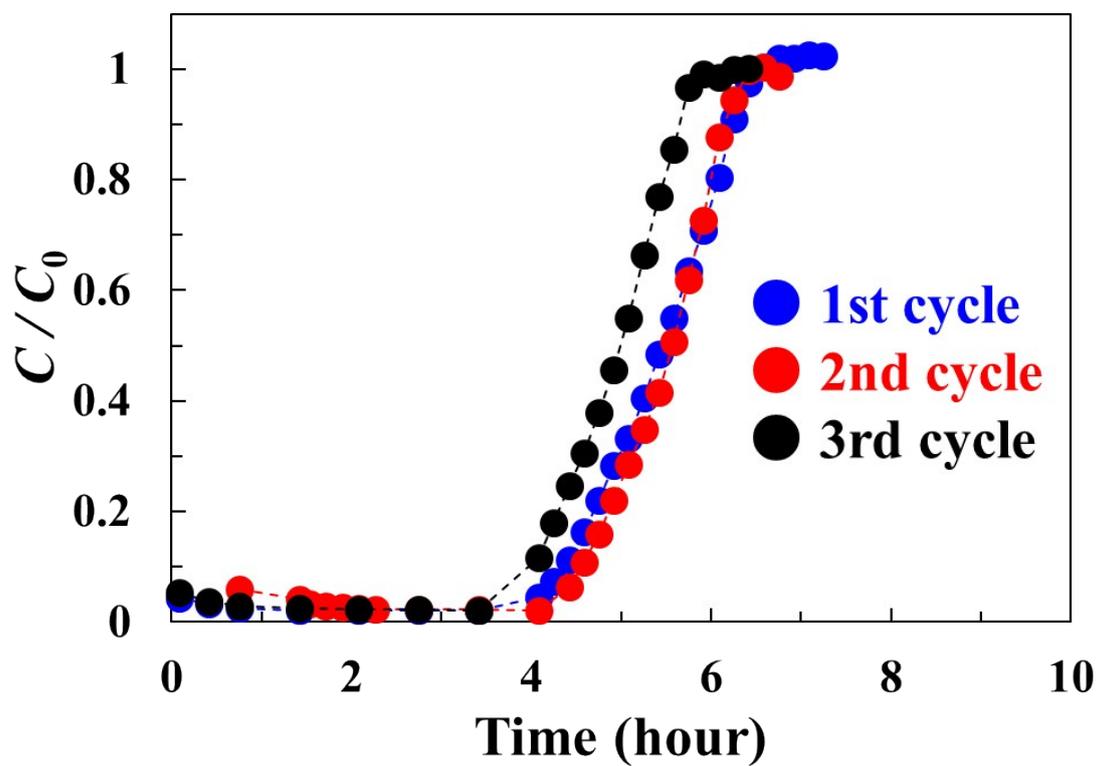


Fig. S8. Breakthrough curves of sulfur concentration with the flowed mixture gas of CH_4 (49.7 vol.%), Ar (49.3 vol.%) and DMS (1.0 vol.%) at each DMS adsorption cycle on HKUST-1.

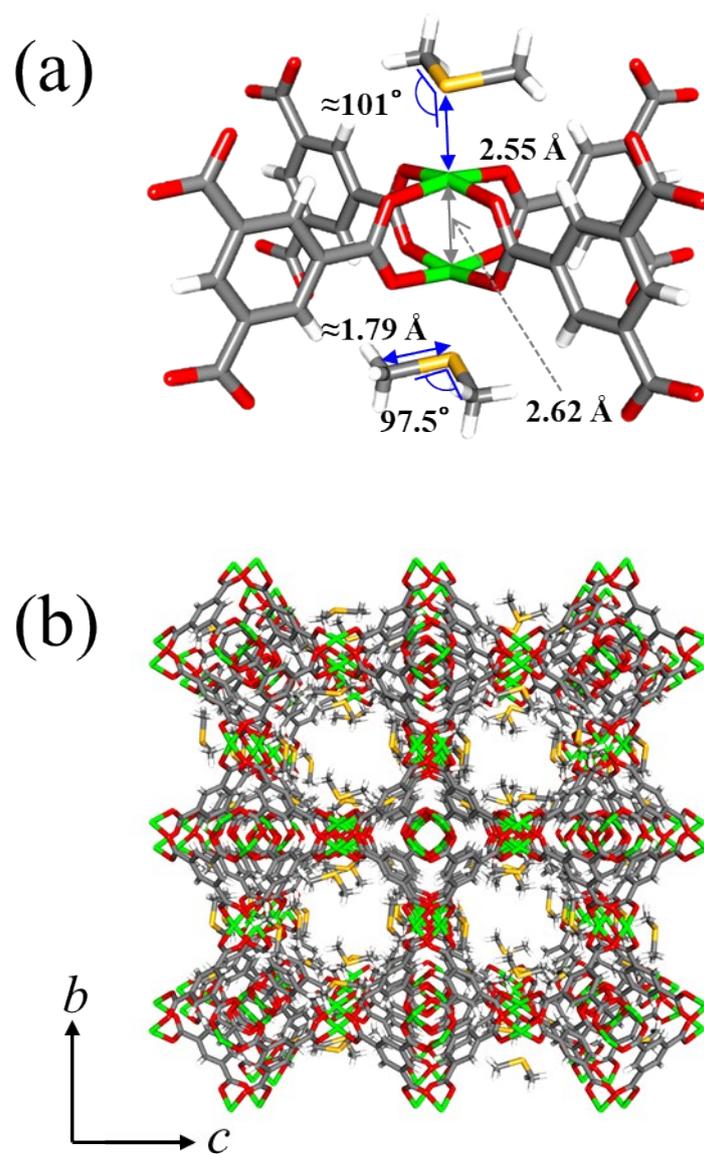


Fig. S9. Crystal structures of DMS-adsorbed HKUST-1. (a) Local paddle wheel structure with adsorbed DMS. (b) View of packing structure with DMS along the a axis. Atoms are colored as follows: Cu, green; O, red; C, gray; H, white; S, yellow.

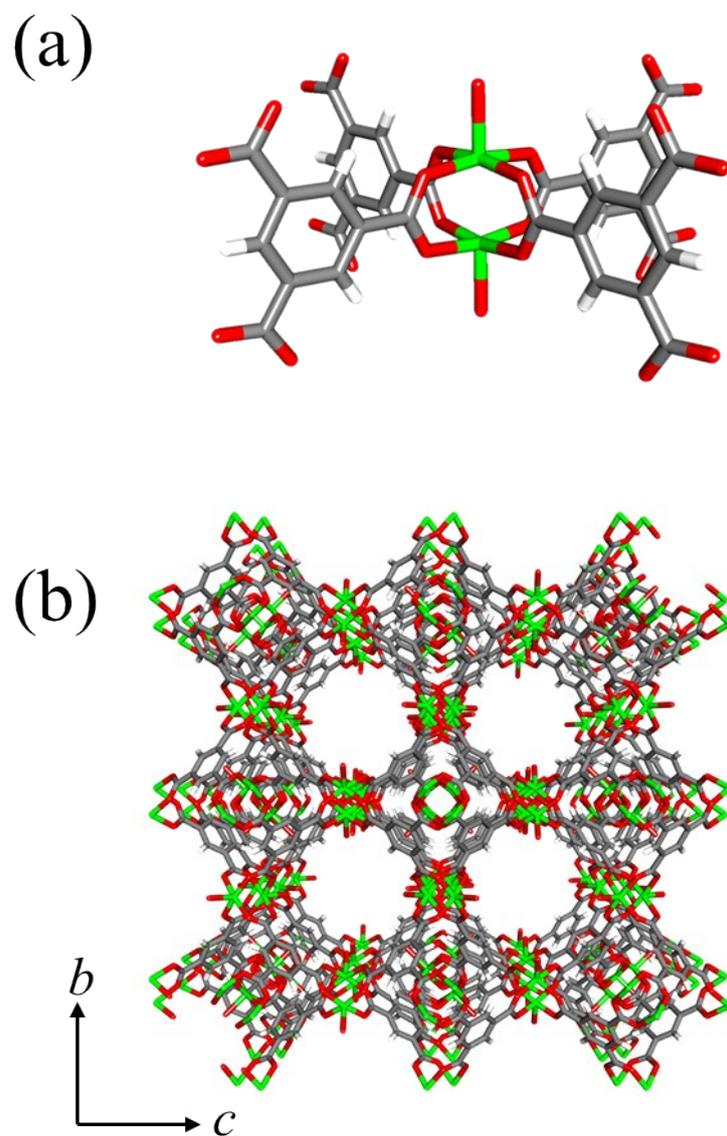


Fig. S10. Crystal structures of as-synthesized HKUST-1. (a) Local paddle wheel structure. (b) View of packing structure along the *a* axis. Atoms are colored as follows: Cu, green; O, red; C, gray; H, white.

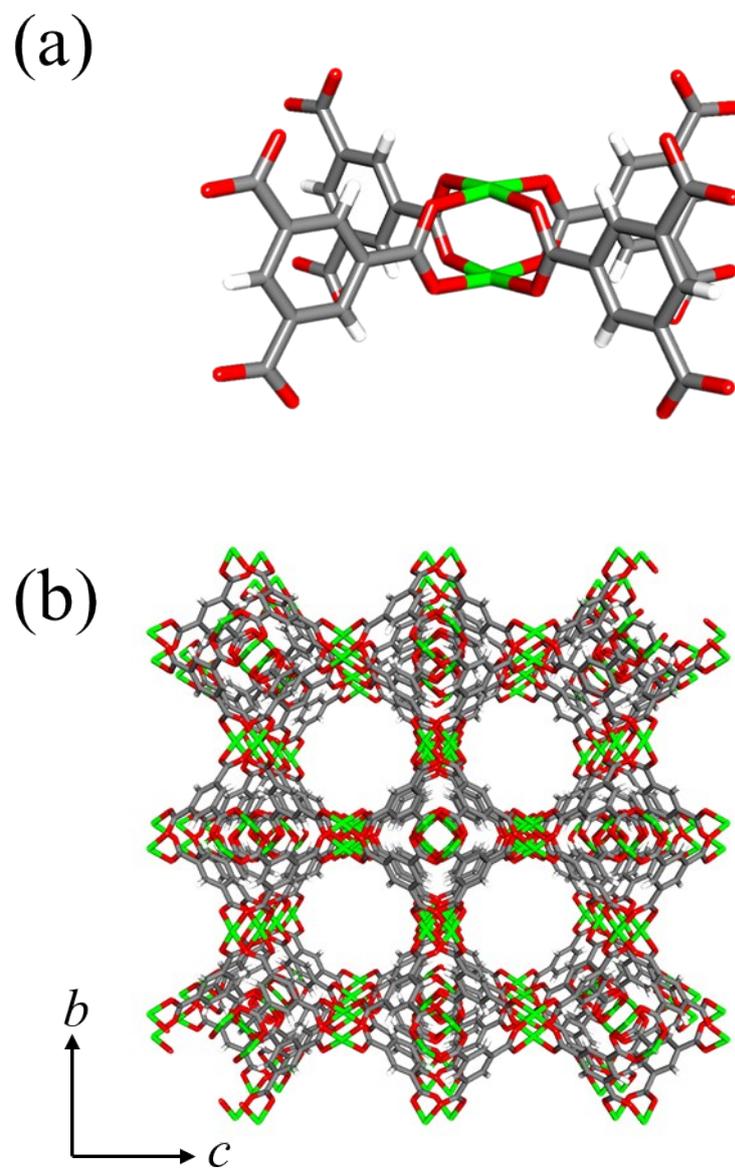


Fig. S11. Crystal structures of degassed HKUST-1. (a) Local paddle wheel structure. (b) View of packing structure along the *a* axis. Atoms are colored as follows: Cu, green; O, red; C, gray; H, white.

(a) Cu-Cu distance: 2.62 Å (b) Cu-Cu distance: 2.49 Å (c) Cu-Cu distance: 2.62 Å

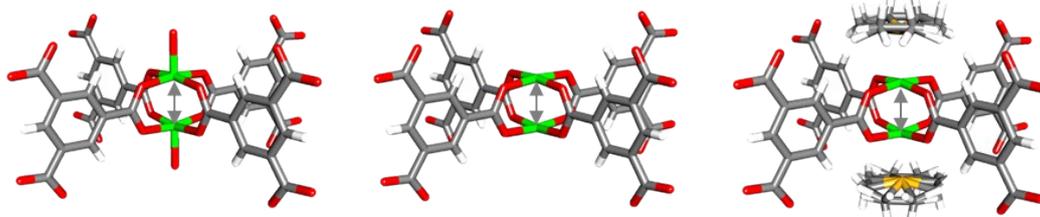


Fig. S12. Cu-Cu distance in the crystal structure of (a) as-synthesized HKUST-1, (b) degassed HKUST-1 and (c) DMS-adsorbed HKUST-1.

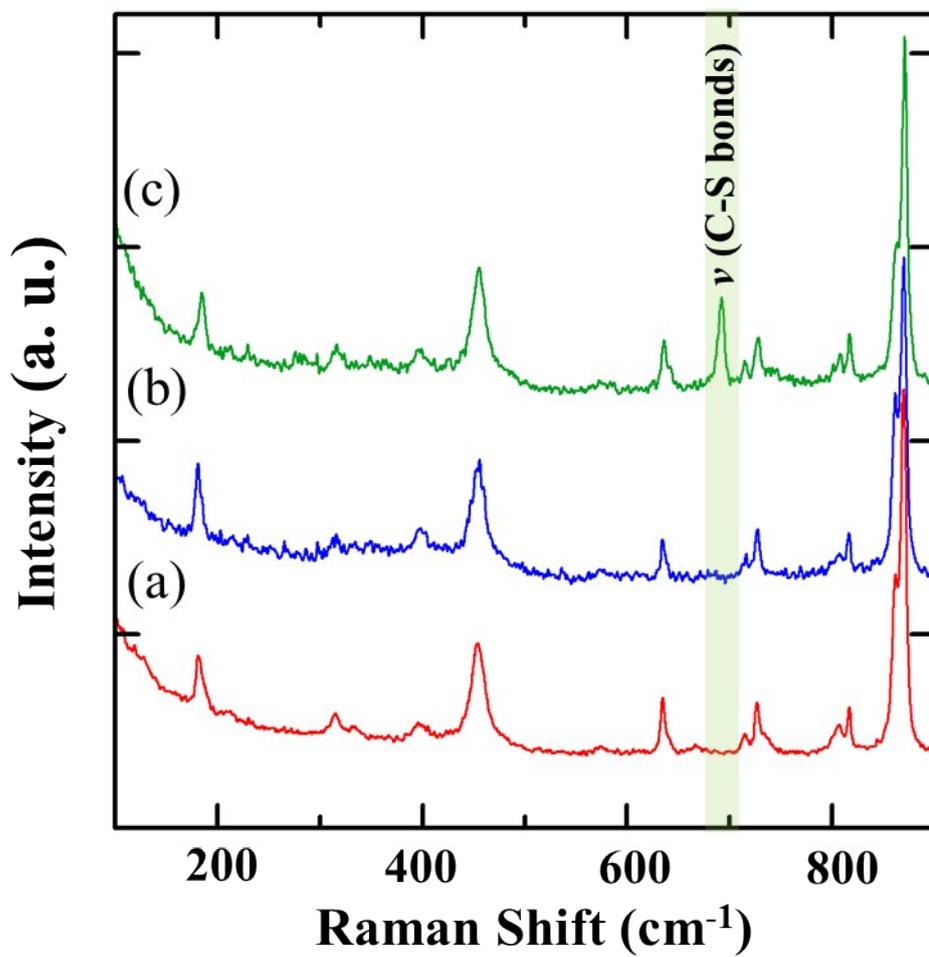


Fig. S13. Raman spectra of Cu-JAST-1 with DMS (2.3 vol. %)/Ar at room temperature: (a) as-synthesized, (b) degassed and (c) flowing DMS (2.3 vol.%) balanced by Ar.

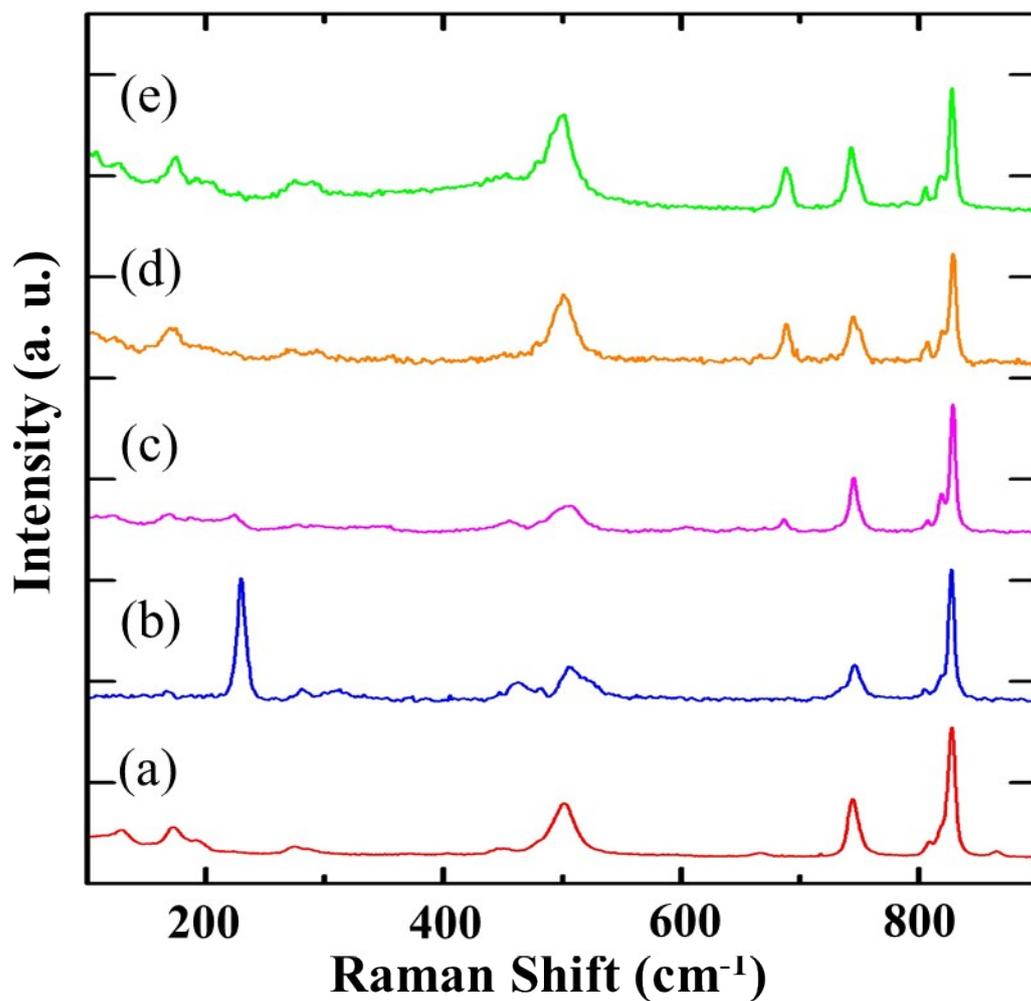


Fig. S14. Raman spectra of HKUST-1 with the flowed mixture gas of CH₄ (56.1 vol.%), Ar (42.5 vol.%), DMS (1.0 vol.%) and H₂O (0.4 vol.%): (a) as-synthesized, (b) degassed, (c) flowing for 15 min, (d) flowing for 30 min and (e) flowing DMS (2.3 vol.%) balanced by Ar.

Table S1. Crystallographic parameters of (a) as-synthesized HKUST-1, (b) degassed HKUST-1 and (c) DMS-adsorbed HKUST-1.

	(a)	(b)	(c)
Formula	C ₆ H ₂ CuO ₅	C ₆ H ₂ CuO ₄	C _{376.85} H _{362.54} Cu ₄₈ O ₁₉₂ S _{44.42}
Crystal system	Cubic	Cubic	Cubic
Space group	<i>Fm-3m</i>	<i>Fm-3m</i>	<i>Fm-3m</i>
<i>a</i> (Å)	26.3518(6)	26.2622(2)	26.3100(5)
<i>b</i> (Å)	26.3518(6)	26.2622(2)	26.3100(5)
<i>c</i> (Å)	26.3518(6)	26.2622(2)	26.3100(5)
α (°)	90	90	90
β (°)	90	90	90
γ (°)	90	90	90
<i>V</i> (Å ³)	18299.1	18113.1	18212.2
<i>Z</i>	48	48	1
Temperature (K)	203	203	203
<i>R</i> 1	0.0284	0.0175	0.0320
w <i>R</i> 2	0.0948	0.0538	0.1203
GOF on F2	1.079	1.106	1.298

References

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