

Supporting information

Reactive adsorption of low concentration methyl mercaptan on Cu-based MOF with controllable size and shape

Xiang Ma,^{ab} Haidi Liu,^a Weiman Li,^{ab} Shengpan Peng,^{ab} and Yunfa Chen ^{*a}

^a State Key Laboratory of Multiphase Complex System, Institute of Process Engineering, Chinese Academy of Sciences, Beijing, 100190, China.

^b University of Chinese Academy of Sciences, No. 19A Yuquan Road, Beijing, 100049, China.

Corresponding author Email: yfchen@ipe.ac.cn Tel: 86-10-8254 4896

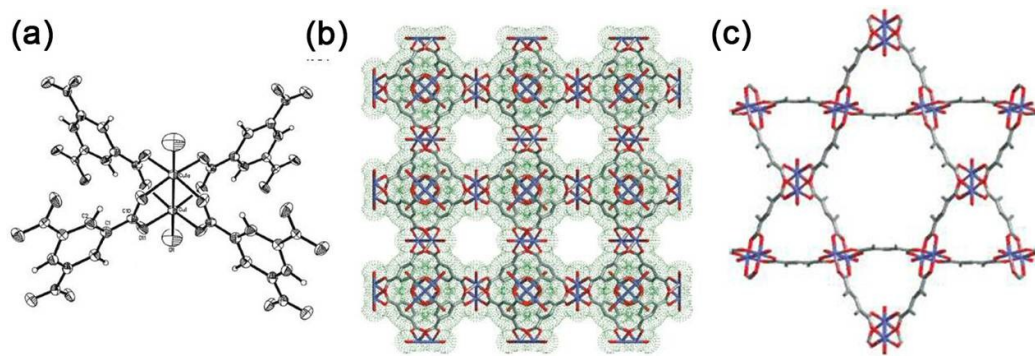


Figure S1. (a) Dicopper tetracarboxylate building block of HKUST-1. (b) HKUST-1 polymer framework viewed down the (1 0 0) direction. (c) HKUST-1 viewed along the cell body diagonal (1 1 1).

MOF-199 is a well-known Cu-based MOF material first reported by Chui et al. [1]. The structure of MOF-199 is as follows. The polymer forms face-centered-cubic crystals that contain an intersecting three-dimensional system of large square-shaped pore (9 Å by 9 Å). The pores themselves contain up to 10 additional water molecules per formula unit. A view down the (1 0 0) direction of the cubic cell of HKUST-1 reveals about 1 nm size channels with fourfold symmetry. A view through the cell body diagonal (1 1 1) reveals a honeycomb arrangement of large hexagonal-shaped windows, each composed of a ring of six metal dimers and six trimesate groups, which measure 18.6 Å between opposite vertices. The windows are cross sections of the “cavities” formed at the intersection of the three orthogonal sets of channels.

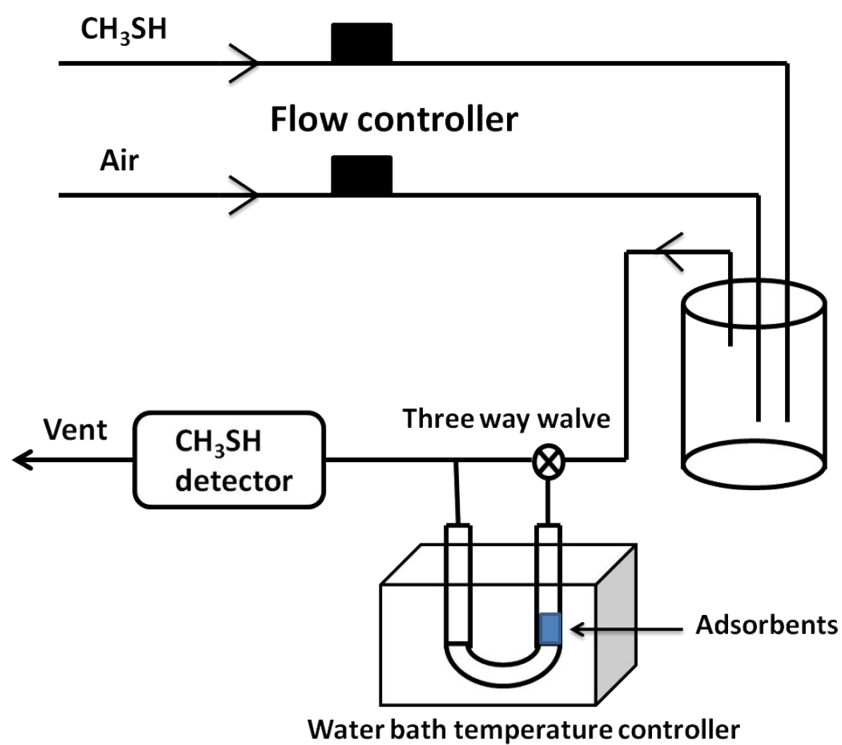


Figure S2. The adsorption system for gaseous CH_3SH .

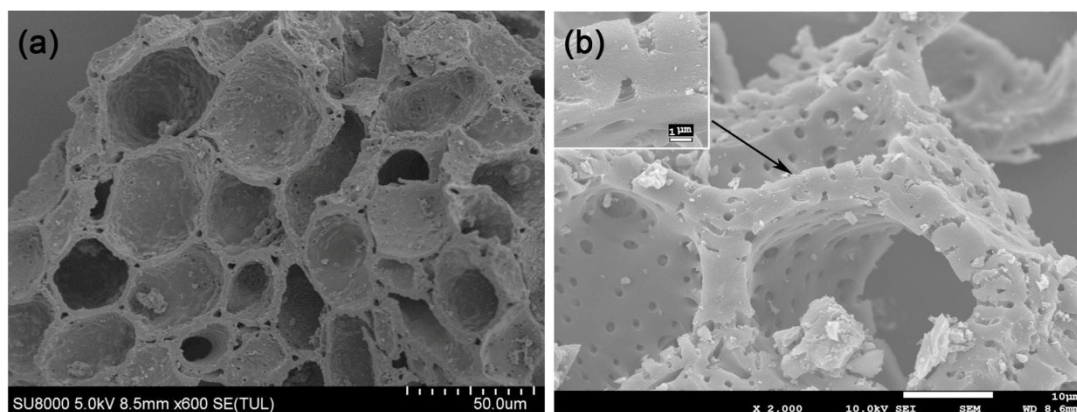


Figure S3. SEM image of (a) commercialized AC and (b) Cu-0.7.

Table S1. Comparison of BET surface area between MOF-199 in our work and previously reported work.

Ref.	Activation temperature (°C)	BET surface area (m ² /g)
our	70	903.9, 684.5, 580.7
our	150	960.4, 729.8, 631.1
[2]	170	1264
[3]	85	857, 1482
[4]	120	1040
[5]	120	909
[6]	150	940
[7]	170	1507

We also measured the BET surface area activating at 150 °C and BET surface area of L O, S O, and sphere like MOF-199 is 960 m²/g, 729 m²/g and 631 m²/g, respectively.

The BET surface area activated at 150 °C is little higher than that of 70 °C which proves that the activation temperature at 70 °C is enough to activate the synthesized MOF-199. The room temperature synthesis of MOF-199 has even lower BET surface area because of the partial inclusion of PVP [8], interconnected MOF networks [9], or the existence of nanocrystalline domains [10].

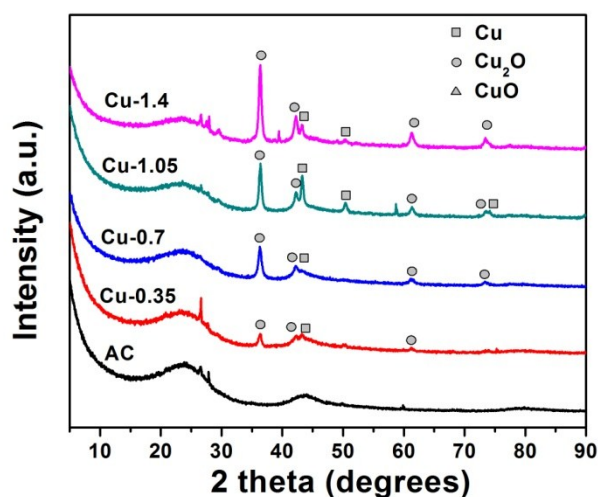


Figure S4. XRD patterns of AC and Cu loaded AC with different loading amount.

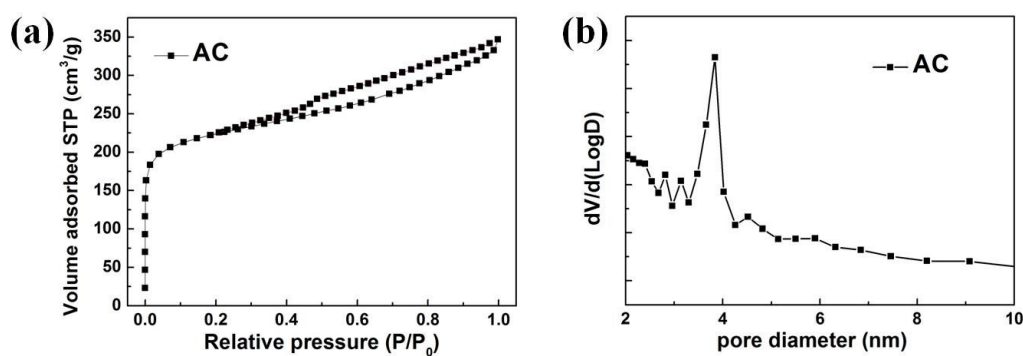


Figure S5. (a) N_2 adsorption-desorption and (b) pore size distributions of commercialized AC.

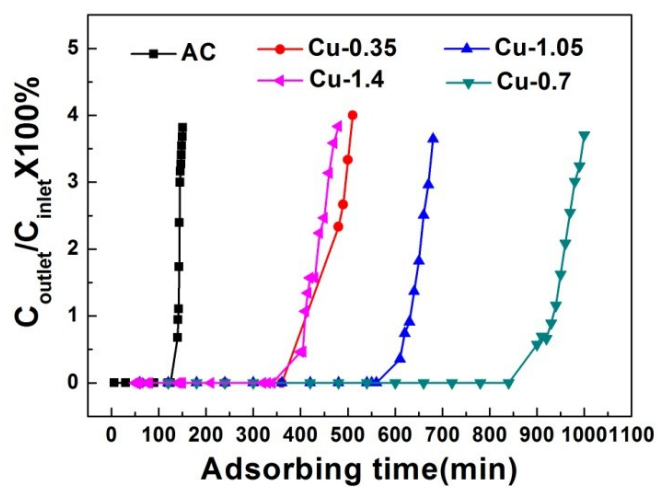


Figure S6. CH_3SH breakthrough curves for different loading amount of Cu on AC.

Preparation of Cu loaded AC. Certain amount of copper nitrate trihydrate was dissolved in ethanol and 10 g of AC was added in the solution with continuous stirring. After stirring for 8 h, the ethanol was removed by heating the solution. The modified AC was then dried at 80 °C for 5 h. Then the dry Cu loaded AC was placed in a tube furnace, heated to 300 °C with a ramping rate of 5 °C min⁻¹ and maintained for 4 h in nitrogen. At last, the temperature was decreased to 25 °C. The Cu loaded AC was labelled as Cu-x, and x represent the loading amount of Cu (mmol/g AC)

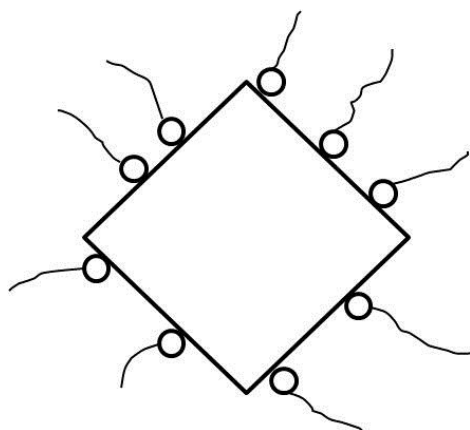


Figure S7. Illustration of the remaining PVP on the surface of S O MOF-199.

The remaining PVP attached on the surface of S O MOF-199 can reduce the surface energy of S O MOF-199 and alter the coordination equilibrium at the crystal surface during the growth process in the synthesis. However, the remaining PVP occupy the surface sites of S O MOF-199 resulting to steric hindrance. Therefore, The CH₃SH molecule is more difficult to get access to the open metal Cu in MOF-199 leading to bad performance in the breakthrough experiment.

Table S2. Summary of sulfur compound capacity of L O and previously reported work.

Sample	Sulfur compound	Sulfur compound capacity (mg/g adsorbent)	Ref.
HKUST-1	CH ₃ SH	74.7	Our
HKUST-1	SO ₂	32	[11]
HKUST-1 with GOPSN	H ₂ S	109	[12]
HKUST-1 with GOSA	H ₂ S	133	
HKUST-1	C ₂ H ₅ SH	18.3	[13]
	CH ₃ SCH ₃	24.4	
HKUST-1	dibenzothiophene	45	[14]
Cu-BTC	t-butylmercaptan	300	[15]

Table S3. Assignment of XPS peaks of fresh and exhausted L O MOF-199 materials

Species	Cu 2p _{3/2}	S 2p	
Fresh L O	935.1 eV Cu-O	—	
Exhausted L O	935.1 eV Cu-O	168.3 eV methyl thiolate	
		162.0 eV 2p _{3/2} sulfur anions	162.6 eV 2p _{1/2} sulfur anions
	933.2 eV CuS	163.4 eV 2p _{3/2} CuS	164.3 eV 2p _{1/2} CuS

Reference

- [1] S. S.-Y. Chui, S. M.-F. Lo, J. P. H. Charmant, A. G. Orpen and L. D. Williams, *Science*, 1999, 283, 1148-1150.
- [2] D. Britt, D. Tranchemontagne and O M. Yaghi, *PNAS*, 2008, 105, 11623-11627.
- [3] P. Chowdhury, C. Bikkina, D. Deister, F. Dreisbach and S. Gumma, *Microporous and Mesoporous Materials*, 2009, 117, 406-413.
- [4] A. M. Ebrahim, J. Jagiello and T. J. Bandoz, *J. Mater. Chem. A.*, 2015, 3, 8194-8204.

- [5] C. Petit, B. Levasseur, B. Mendoza and T. J. Bandoza, *Microporous and Mesoporous Materials*, 2012, 154, 107-112.
- [6] O. Fleker, A. Borentein, R. Lavi, L. Benisvy, S. Ruthstein and D. Aurbach, *Langmuir*, 2016, 32, 4935-4944.
- [7] L. C. Rowsell and O. M. Yaghi, *J. Am. Chem. Soc.*, 2006, 128, 1304-1315.
- [8] G. W. Zhan and H. C. Zeng, *Chem. Commun.*, 2016, 52, 8432-8435.
- [9] L. Qiu, T. Xu, Z. Li, W. Wang, Y. Wu, X. Jiang, X. Tian, and L. D. Zhang, *Angew. Chem. Ind. Ed.*, 2008, 47, 9487-9491
- [10] J. Cravillon, S. Münzer, S. J. Lohmeier, A. Feldhoff, K. Huber and M. Wiebcke, *Chem. Mater.*, 2009, 21, 1410-1412.
- [11] D. Britt, D. Tranchemontagne and O M. Yaghi, *PNAS*, 2008, 105, 11623-11627.
- [12] A. M. Ebrahim, J. Jagiello and T. J. Bandoz, *J. Mater. Chem. A.*, 2015, 3, 8194-8204.
- [13] Y. Li, L. J. Wang, H. L. Fan, J. Shangguan, H. Wang and J. Mi, *Energy Fuels*, 2015, 29, 298-304.
- [14] G. B. Brieva, J. M. C. Martin, S. M. A. Zahrani and J. L. G. Fierro, *Fuel*, 2011, 90, 190-197.
- [15] G. Chen, S. Tan, W. J. Koros and C. W. Jones, *Energy Fuels*, 2015, 29, 3312-3321.