Efficient removal of low concentration methyl mercaptan by HKUST-1 membrane constructed on porous alumina granules

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Experimental section

1. Materials

Cu(NO$_3$)$_2$·3H$_2$O (AR), ethanol (AR), methanol (AR) were purchased from Xilong Cop. N,N-dimethylformamide (DMF, AR) and commercial alumina granules were purchased from Sinopharm. 1,3,5,-benzenetricarb-oxylic acid (98%) was purchased from Aladdin. The water was made from Millipore Milli-Q water (15MΩ cm). The gaseous CH$_3$SH (50 ppm) was purchased from HuaYuan Gas Chemical industry. The alumina granules were degased at 200 ℃ in an oven over night before thermal seeding.

2. Preparation of materials

2.1 Preparation of HKUST-1 powders

HKUST-1 powders were synthesized according to the previously reported method. [1] Briefly, 1 g of 1,3,5,-benzenetricarb-oxylic acid was dissolved in 30 ml of a solvent mixture of DMF and ethanol (1 : 1, v/v). In another flask, 2.077 g of copper nitrate trihydrate was dissolved in 15 ml deionized water. The two solutions were mixed and stirred for 10 min. They were then transferred into Telflon-lined stainless steel autoclave and heated at 80 ℃ for 16 h. The reaction vessel was then cooled naturally to room temperature. The blue crystals were washed with methanol three times by centrifugation. Then the products were placed in methanol overnight and dried under vacuum at 80 ℃ overnight.

2.2 Preparation of HKUST-1@Al$_2$O$_3$

HKUST-1@Al$_2$O$_3$ granules were prepared according to the previously reported work with modifications. [2]

HKUST-1 seed crystals were synthesized by the following method. In a typical synthesis, 2.16 g of Cu(NO$_3$)$_2$·3H$_2$O was dissolved in 30 mL of water and 1.05 g of 1,3,5,-benzenetricarb-oxylic acid was dissolved in 30 mL of ethanol. Then the two solution were mixed and stirred for about 30 min. The precursor solution was then transferred into Telflon-lined stainless steel autoclave and heated at 120 ℃ for 6 h. The reaction vessel was then cooled naturally to room temperature. The resulting

solution containing HKUST-1 crystals was stored for seeding (labeled as solution A).

Prior to seeding, 20 g of the alumina granules in a beaker were heated in an oven at 200 ℃ for 15 min. While the granules were still inside the oven, the solution A containing HKUST-1 and un-reacted ligands and copper species was poured into the beaker until the granules were completely covered. To make sure the solvent evaporated completely, the granules were kept inside the oven for about 20 min. This seeding process was repeated three times to completely cover the granules with seed crystals. The seeded granules were then washed with ethanol and sonicated for 1 min to remove crystals loosely attached to the granules. The entire process (including three times of pouring of solution A, washing and sonication) was repeated three times until the granules were uniformly coated with strongly bound seed crystals.

To prepare the precursor solution for the growth of HKUST-1 seed crystals, 1.09 g of $Cu(NO_3)_2 \cdot 3H_2O$ was dissolved in 30 mL of water and 0.69 g of 1,3,5,-benzenetricarb-oxylic acid was dissolved in 30 mL of ethanol. Then the two solutions were mixed and stirred for about 30 min. Meanwhile, 10 g of seeded granules were placed in the bottom of Telflon-lined stainless steel autoclave, and the two solutions were transferred into the autoclave. After being heated at 120 ℃ for 6 h, the reaction vessel was then cooled naturally to room temperature. The granules were washed with ethanol and sonicated for 5 min to remove crystals loosely attached to the granules. Finally, the granules were dried under vacuum at 100 ℃ overnight.

3. Characterization of materials

Powder X-ray diffraction (XRD) patterns of the catalysts were measured on a Panalytical X'Pert PRO system using Cu-Kα radiation. Thermogravimetric analysis (TGA) was performance on a NETZSCH STA449F3 apparatus with a heating rate of 10 °C min^{-1} from 35 °C to 900 °C under air atmosphere. The N_2 adsorption-desorption isotherms of Al_2O_3 was measured on automatic surface analyzer (SSA-7300, China). The N_2 adsorption-desorption isotherms of HKUST-1@Al_2O_3 was measured on an automatic surface analyzer (AS-1-C TCD, Quantachorm Corp., USA). Before the measurement, the samples were outgassed at 100 °C for 10 h. The morphology of materials were characterized by field-emission scanning electron microscopy (SEM)

via an electron microscope (JEOL 2100F, operating at 15 kV).

4. Breakthrough testing

The adsorption experiments were carried out in an isothermal plug flow reactor under steady-state conditions at 25 ℃ by using a water bath. The adsorbents (40-60 mesh, 100 mg) for HKUST-1 powders and 1 g for HKUST-1@Al_2O_3 granules were placed in the U-shaped reactor respectively. The gas flow passing the reactor was 490 ml min^{-1} (CH_3SH: 20 ml min^{-1}, air: 470 ml min^{-1}). The inlet concentration of CH_3SH in the mixed gas was about 5 ppm. The value of "breakthrough" in this study was 4 % of the feed concentration which was about 0.2 ppm. The time at which the concentration of CH_3SH in the effluent surpassed the breakthrough concentration is designated as the "breakthrough time". The concentration of CH_3SH in the mixed gas was analyzed by a CH_3SH detector with detection line of 0.01 ppm (Yuan technology Co., Ltd, SKY 2000 series). When the breakthrough tests were conducted under humid condition, the air flow was used for bubbling water and mixed with CH_3SH gas flow. The relative humidity of gas flow was estimated to be 90 % (RH=90 %).
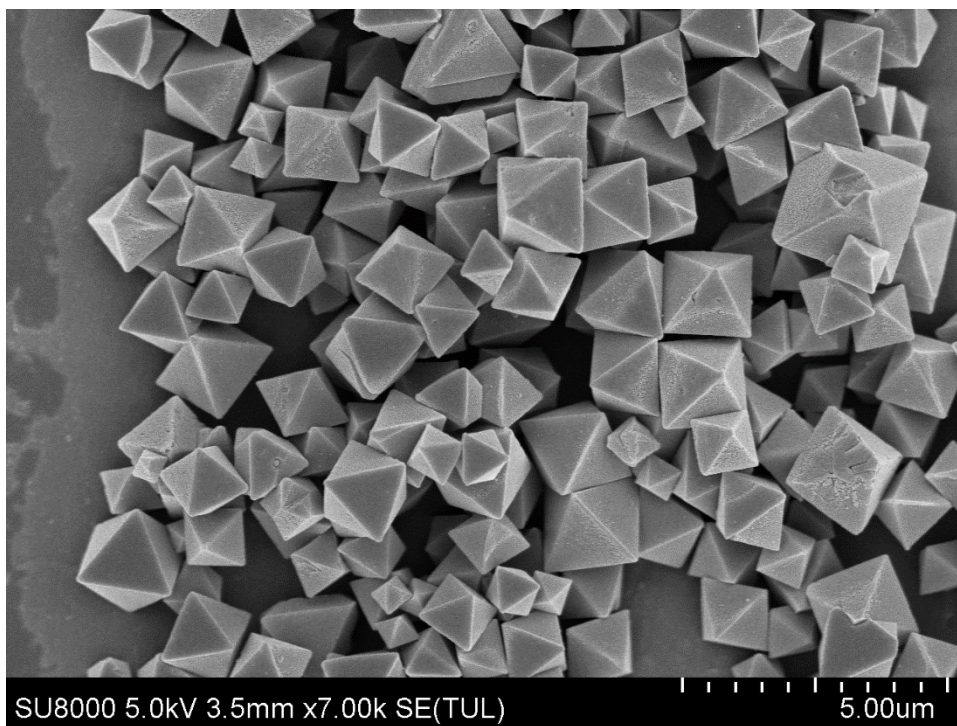
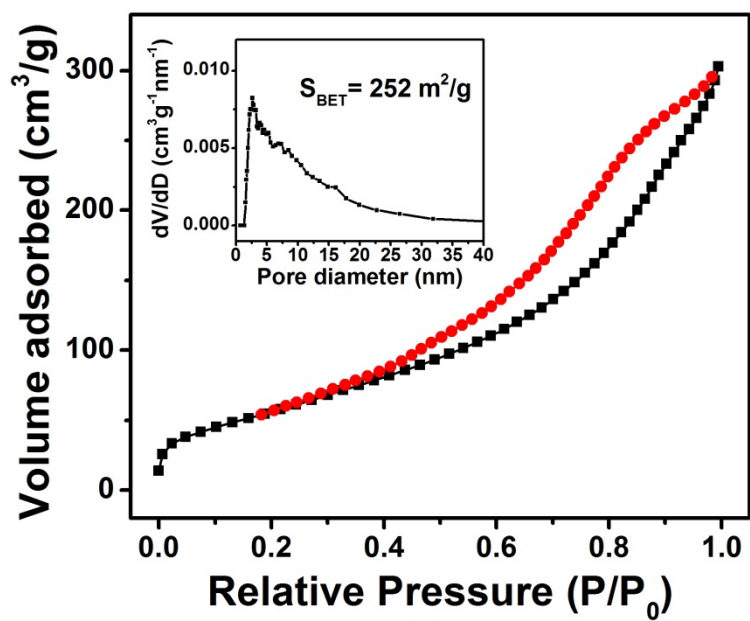Fig. S1. SEM image of synthesized HKUST-1 crystals.

Fig. S2. N_2 adsorption-desorption isotherm of bare Al_2O_3, the inset is the corresponding BJH pore size distribution.
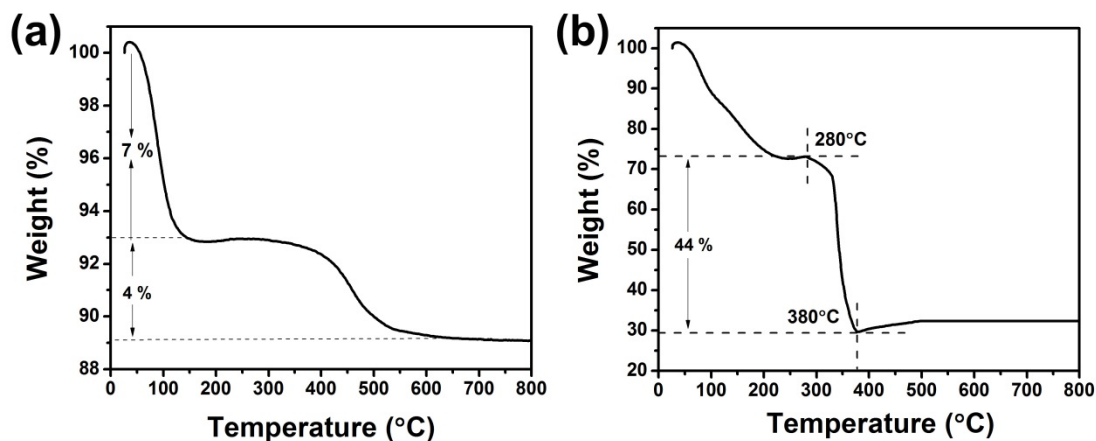
Fig. S3 TGA curve of (a) bare Al_2O_3 and (b) HKUST-1

A two-step thermal decomposition process was observed for bare alumina support that included the first weight loss of 7 % from 40 °C to 150 °C which is attributed to the loss of physically adsorbed H_2O molecules from alumina support. This indicates the hydroscopicity of porous alumina. The second weight loss of 4 % between 380 °C to 550 °C is ascribed to the loss of chemically adsorbed H_2O molecules from alumina support. [3]

A two-step thermal decomposition process was observed for HKUST-1 powders that included the first weight loss of 26 % from 40 °C to 280 °C which is ascribed to the loss of adsorbed water and solvent molecules from the surface and pores of HKUST-1 powders. The second weight loss of 44 % between 280 °C to 380 °C is attributed to the decomposition of organic ligands of HKUST-1. Therefore the relative weight loss of the HKUST-1 crystals at this stage is approximately 60 % corresponding to the theoretical weight loss caused by the burning of the organic ligands ($Cu_3(BTC)_2 \rightarrow$ CuO, the reactant of the reaction does not contain any water or ethanol).

Calculated relative weight loss = 0.44 / 0.74 = 0.6 (0.74 represent the weight of HKUST-1 without water or ethanol)

Therefore, the loading amount of HKUST-1 in HKUST-1@Al_2O_3 is estimated to be 7.5 wt%

Calculated loading amount = 4.5 % / 0.6 = 7.5 %

Calculation of CH₃SH capacity

Unit transformation ppm CH_3SH (labeled as C_1) to mg/m^3 CH_3SH (labeled as C_2)

$$C_2 = \frac{C_1 \times M}{22.4*(1+\frac{T}{273})} = \frac{5*48}{22.4*(1+25/273)} = 9.81 \ mg/m^3$$

T =temperature (℃)   M= relative molecular mass (CH_3SH=48)

1) 100 mg HKUST-1 under humid condition (t_1=780 min)

CH_3SH capacity (mg/g HKUST-1) = ($V \times C_2 \times t_1$) × 10 = 490 ml/min × 9.81 mg/m³ × 780 min × 10 = 37.7 mg

2) 100 mg HKUST-1 under dry condition (t_2=1545 min)

CH_3SH capacity (mg/g HKUST-1) = ($V \times C_2 \times t_2$) × 10 = 490 ml/min × 9.81 mg/m³ ×1545 min × 10 = 74.7 mg

3) 1g HKUST-1@Al₂O₃ (containing 75 mg of HKUST-1) under humid condition (t_3=1500 min)

CH_3SH capacity (mg/g HKUST-1) = ($V \times C_2 \times t_3$) × 1000/75 = 490 ml/min × 9.81 mg/m³ ×1500 min × 1000/75 = 96.7 mg

4) 1g HKUST-1@Al₂O₃ (containing 75 mg of HKUST-1) under dry condition (t_4=1682 min)

CH_3SH capacity (mg/g HKUST-1) = ($V \times C_2 \times t_4$) × 1000/75 = 490 ml/min × 9.81 mg/m³ ×1682 min × 1000/75 = 108.6 mg

t=breakthrough time (min)   V=gas velocity (ml/min)
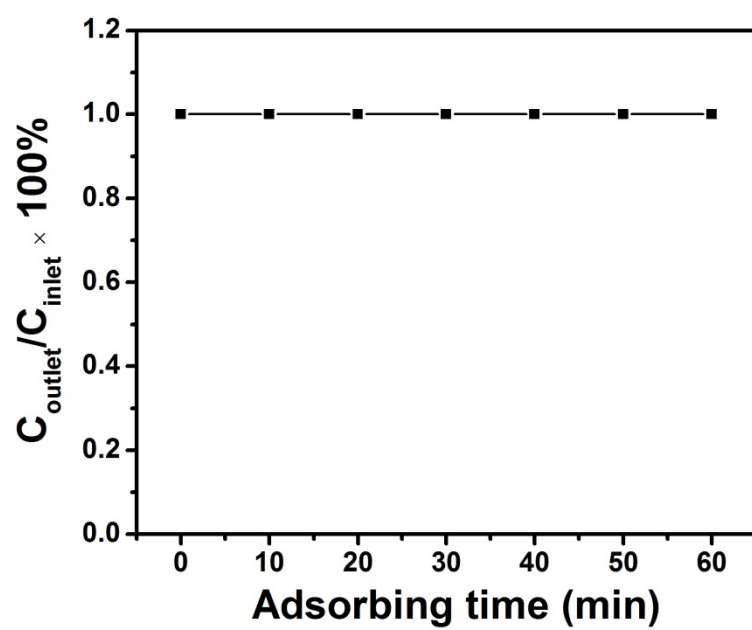
Fig. S4. CH$_3$SH breakthrough curve of bare alumina granules.
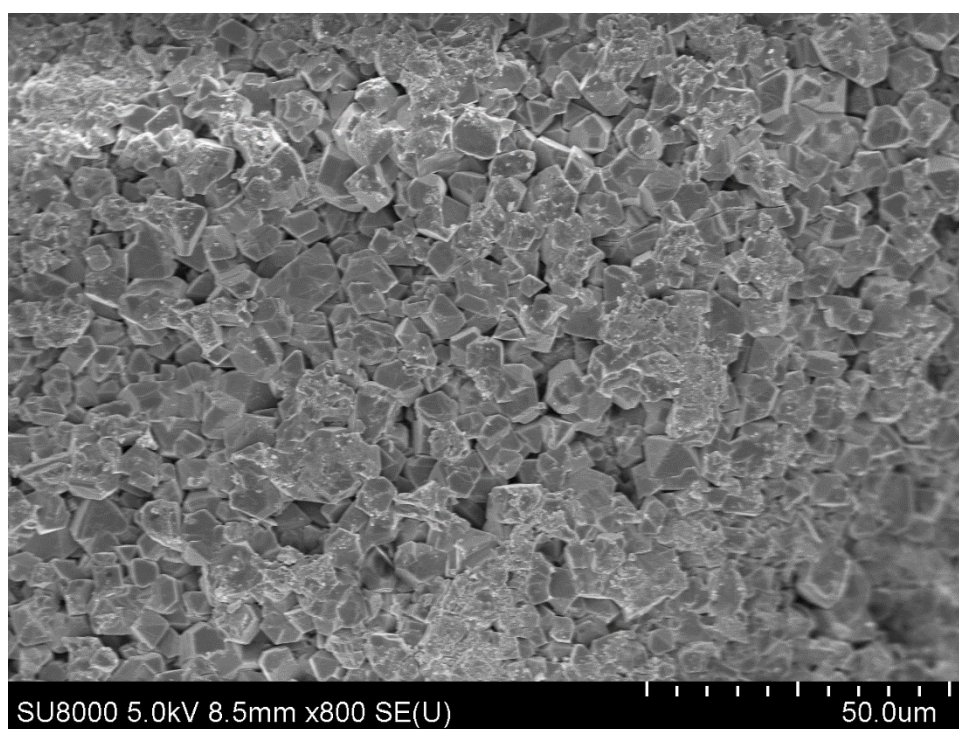

SU8000 5.0kV 8.5mm x800 SE(U)   50.0um

Fig. S5 Top view SEM image of HKUST-1@Al$_2$O$_3$ after CH$_3$SH adsorption process.

Table S1. Porosity data of synthesized HKUST-1@Al$_2$O$_3$

Paramater	value	unit
BET surface area	284	m^2/g
Langmuir surface area	296	m^2/g
t-plot external surface area	259	m^2/g
t-plot micro pore area	25	m^2/g
DR method micro pore area	311	m^2/g

Table S2. Summary of sulfur compound capacity of HKUST-1@Al$_2$O$_3$ and previously reported work.

Sample	Sulfur compound	Sulfur compound capacity (mg/g HKUST-1)	Ref.
HKUST-1@Al$_2$O$_3$	CH$_3$SH	108.6	our
HKUST-1	CH$_3$SH	74.7	our
HKUST-1	SO$_2$	32	[4]
HKUST-1 with GOPSN	H$_2$S	109	[5]
HKUST-1 with GOSA	H$_2$S	133	
HKUST-1	C$_2$H$_5$SH	18.3	[6]
	CH$_3$SCH$_3$	24.4	
HKUST-1	dibenzothiophene	45	[7]
Cu-BTC	t-butylmercaptan	300	[8]

Table S3. Assignment of XPS peaks of fresh and exhausted HKUST-1 materials

Species	Cu 2p$_{3/2}$	S 2p	
Fresh HKUST-1	935.1 eV Cu-O	—	
Exhausted HKUST-1		168.3 eV methyl thiolate	
	935.1 eV Cu-O	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

References

[1] J. L. C. Rowsell and O. M. Yaghi, J. Am. Chem. Soc., 2006, 128, 1304-1315.

[2] V. V. Guerrero, Y. Yoo, M. C. McCarthy and H. K. Jeong, J. Mater. Chem., 2010, 20, 3938-3943.

[3] T. Morimoto, M. Nagao and J. Imai, bulletin of chemical society of japan, 1971, 44, 1282-1288.

[4] D. Britt, D. Tranchemontagne and O M. Yaghi, PNAS, 2008, 105, 11623-11627.

[5] A. M. Ebrahim, J. Jagiello and T. J. Bandosz, J. Mater. Chem. A., 2015, 3, 8194-8204.

[6] Y. Li, L. J. Wang, H. L. Fan, J. Shangguan, H. Wang and J. Mi, Energy Fuels, 2015, 29, 298-304.

[7] G. B. Brieva, J. M. C. Martin, S. M. A. Zahrani and J. L. G. Fierro, Fuel, 2011, 90, 190-197.

[8] G. Chen, S. Tan, W. J. Koros and C. W. Jones, Energy Fuels, 2015, 29, 3312-3321.