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Electronic Supporting Information (ESI)

A novel mechanochemical method for reconstructing the moisture-degraded HKUST-1

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Experimental Section

1. Materials

Copper (II) acetate monohydrate ($Cu(OAc)_2 \cdot H_2O$, Tianjin, 98%), 1,3,5-benzenetricarboxylic acid (H_3BTC, Alfa,98%) and ethanol (EtOH, 99.7%, Fuyu) are obtained from suppliers and used without further purification.

2. Materials Synthesis

The fresh HKUST-1 material was prepared in a QM-3C ball mill via a fast room-temperature solvent-free mechanochemical synthesis. The precursor materials with a molar composition of 3 $Cu(OAc)_2 \cdot H_2O$: 2H_3BTC were ground at 40 Hz for 30 min. Then, the sample was washed with ethanol for several times and dried at 423 K under vacuum overnight.

The fresh HKUST-1 was stored naturally at room temperature. After more than one year, the porous network was completely collapsed. The degraded HKUST-1 was then reconstructed back into high-quality HKUST-1 by the solvent-assisted mechanochemical method and liquid immersion method. For liquid immersion reconstruction, the degraded HKUST-1 was added to ethanol (80 mL per gram degraded sample) and stirred at 298 K (samples L-1, L-2). Samples were periodically taken, isolated by centrifugation and dried at 423 K overnight. For mechanochemical reconstruction, the degraded HKUST-1 was ground with pure ethanol and ethanol/water (3/2, v/v) mixtures in QM-3C ball mill for the required time at 40 Hz (samples M-1, M-2, M-3, M-4, M-5). The products were dried at 423 K under vacuum overnight.

3. Characterization

Powder X-ray diffraction (PXRD) data were recorded on a Bruker D8 Advance X-ray diffractometer with Cu Kα emission at room temperature with a scan speed of 2^{o}/min and a step size of 0.02^{o} in 2θ. Scanning electron microscope (SEM) was performed on a Hitachi SU8010 instrument. Scanning was performed on a sample powder previously dried and sputter-coated with a thin layer of gold. The FTIR spectra were obtained on a Bruker Vector 33 spectrometer with KBr pellets in the 4000–400 cm^{-1} region. Thermogravimetric analysis (TGA) of samples was performed on a TA Q500 instrument heating from 303 to 873 K in nitrogen atmosphere at a rate of 10 K min^{-1}. N_2 adsorption/desorption isotherms of the samples at 77 K were measured to investigate the pore textural properties by using 3Flex Surface Characterization Analyzer (Micromeritics Instrument Corporation, USA) equipped with commercial software of calculation and analysis. The pore textural properties including BET surface area, pore size and pore volume can obtained by analyzing the N_2 adsorption/desorption isotherm. Pore size distribution calculation was provided by 3Flex Surface Characterization Analyzer equipped with the software based on Density Functional Theory (DFT).

4. Benzene vapor adsorption experiments

The vapor-phase adsorption of benzene was performed at 298 K on a volumetric adsorption apparatus, i.e., 3Flex Surface Characterization Analyzer (Micromeritics Instrument Corporation, USA). The vapor generation system included a stainless steel chamber with a hard seal, manual cutoff valve to be attached in place of the Psat tube, and a heating mantle to control the temperature of the chamber at an operator-specified temperature between ambient and 316 K. The constant adsorption temperature was achieved by putting sample cell into circulating water bath. The sample was weighed about 40 mg for each run. The initial outgassing process for each sample was carried out at 423 K under vacuum overnight.

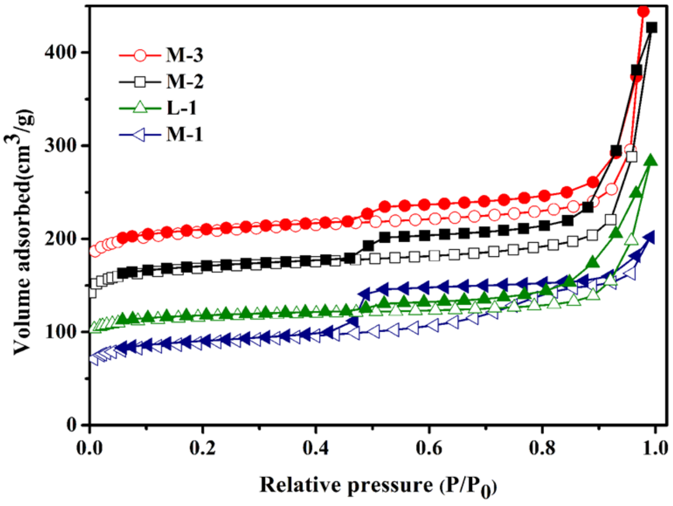

Fig. S1 At 77 K, isotherms of N_2 on the reconstructed samples after treatment for 15 min. (The open symbols refer to the adsorption isotherms, and the solid symbols represent the desorption isotherms.)

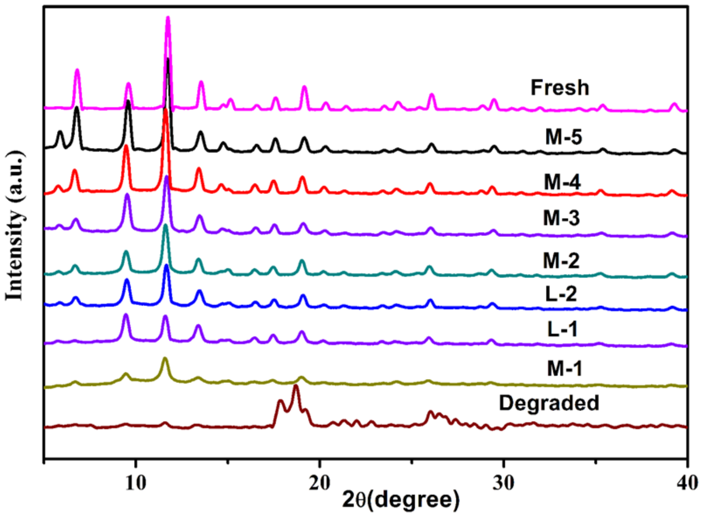

Fig. S2 XRD patterns of the fresh HKUST-1, degraded HKUST-1 and the reconstructed samples

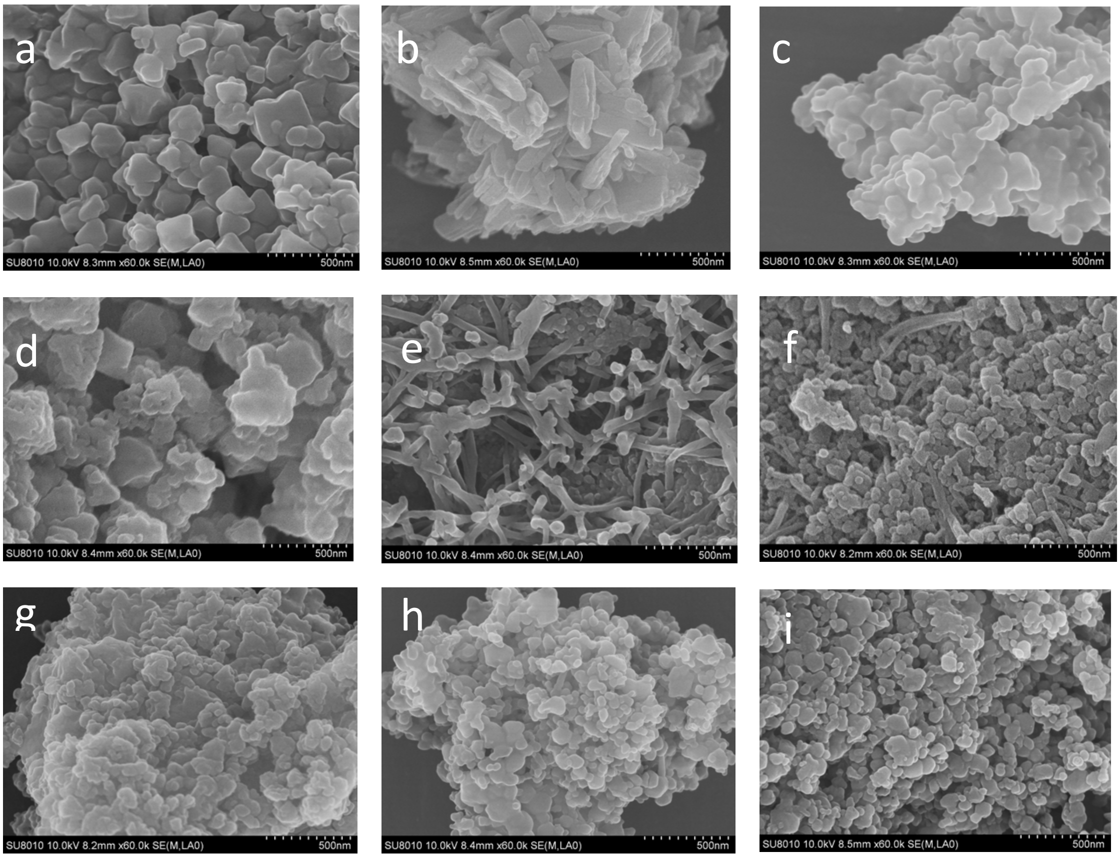

Fig.S3 SEM images of (a) the fresh HKUST-1, (b) the degraded HKUST-1, (c) L-1, (d) L-2, (e) M-1, (f) M-2, (g) M-3, (h) M-4 and (i) M-5.

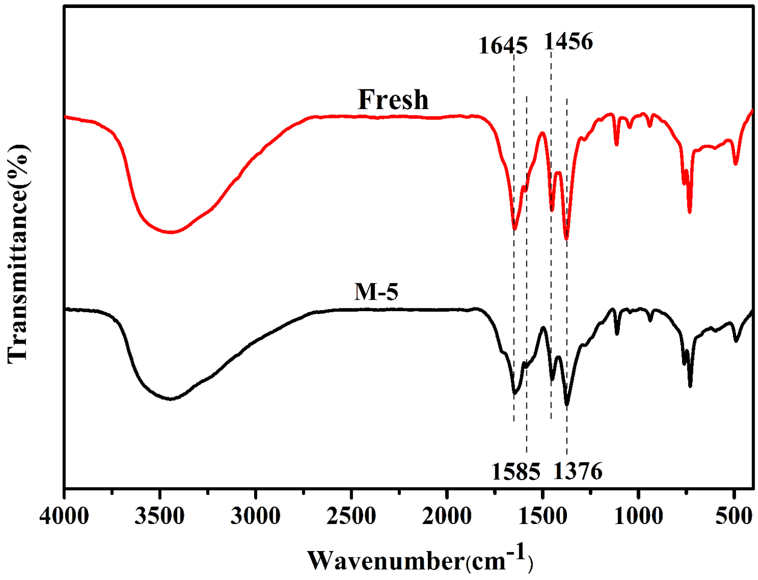

Fig. S4 FTIR spectra of the fresh HKUST-1 and the reconstructed sample M-5.

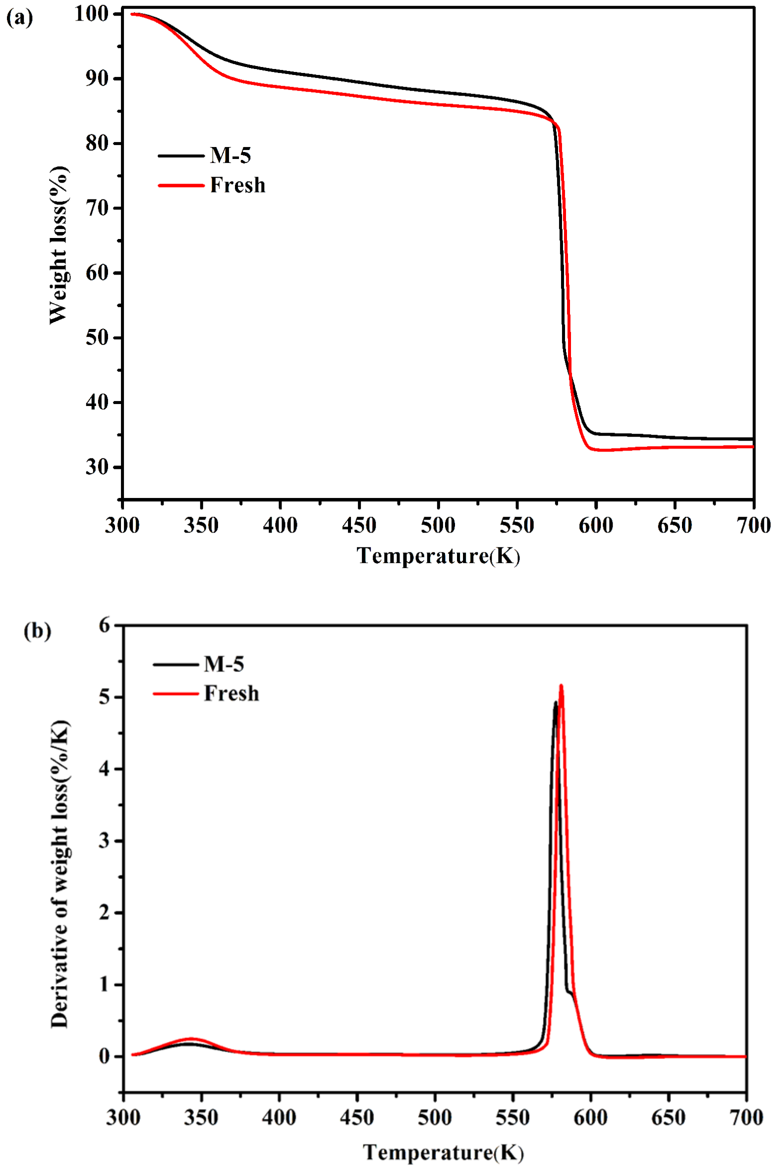

Fig. S5 TG(a)-DTG(b) curves of the fresh HKUST-1 and the reconstructed sample M-5.

Table S1 Adsorption capacities of benzene on the prepared materials and some other adsorbents reported from the literature.

Adsorbents	BET surface area (m^2 g^{-1})	Temperature (K)	Capacity (mmol g^{-1})		Ref
			2.5 mbar	100 mbar	
H-ZSM-5	550	303	1.0	2.2	[1]
MCM-48	900	294	0.5	5.2	[2]
Activated carbon BPL	923	295	3.8	4.9	[3]
Hydrophobic zeolite Y	692	295	3.2	3.5	[3]
MIL-101	3054	298	1.5	15.5	[4]
Fresh HKUST-1	1215.1	298	4.7	6.2	present work
L-2	585.6	298	1.8	3.5	present work
M-4	1081.4	298	3.8	5.6	present work
M-5	1150.4	298	4.3	5.7	present work

[1] S. H. Jhung, J.-H. Lee, J. W. Yoon, C. Serre, G. Férey, J.-S. Chang, *Adv. Mater.,* 2007, **19**, 121–124.

[2] M. Hartmann and C. Bischof, *J. Phys. Chem. B*, 1999, **103**, 6230-6235.

[3] X. Zhao, Q. Ma and G. Lu, *Energ. fuel.*, 1998, **12**, 1051-1054.

[4] Z. Zhao, S. Wang, Y. Yang, X. Li, J. Li, Z. Li, *Chem. Eng. J.*, 2015, **259**,79–89.