

Supporting Information for

Diamine-Appended Metal-Organic Framework: Enhanced Formaldehyde-Vapor Adsorption Capacity, Superior Recyclability and Water Resistibility

Zhong Wang^{a,b}, Wenzhong Wang^{*,a}, Dong Jiang^{a,b}, Ling Zhang^a and Yali Zheng^{a,b}

^a *State Key Laboratory of High Performance Ceramics and Superfine Microstructure,
Shanghai Institute of Ceramics, Chinese Academy of Sciences, 1295 Dingxi Road,
Shanghai 200050, People's Republic of China*

^b *University of Chinese Academy of Science, Beijing 100049, People's Republic of
China*

* Corresponding author, Fax: +86-21-5241-3122, Email: wzwang@mail.sic.ac.cn

Experimental

Synthesis

Synthesis of MIL-53. The synthesis was carried out by means of a solvothermal treatment using aluminum chloride hexahydrate ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, 0.51g), terephthalic acid (0.52g) and *N,N*-dimethylformamide (DMF, 30mL). The dissolved reactants were placed in a 50 mL Teflon-lined autoclave and heated at 130°C for 72 h in an oven. The resulting white powder was collected and activated by a two-stage solvent extraction method with refluxed in boiling DMF and methanol overnight. The activated product was dried and stored at 120°C under vacuum.

Synthesis of MIL-101. MIL-101 was hydrothermally synthesized according to the previous report with certain modification.¹ Briefly, $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.4g) and H_2bdc (0.166g) were added to 30 mL water, the resulting suspension was ultrasonic for 30 min then heated at 180°C for 8 h in a Teflon-lined autoclave. After cooling to room temperature, the green product was collected and activated as mentioned above.

Amine-functionalization of MIL-101. Activated MIL-101 (0.2g) was suspended in anhydrous toluene (20 mL). To this suspension, an appropriate amount of ethylenediamine (ED) [0.1, 0.2, 0.247 and 0.27 mL, corresponding to 7.5 ($0.1 \times 0.9/60/0.2 \times 1000 = 7.5$), 15, 18.5 and 20 mmol ED per gram of MIL-101] were added and the mixture was refluxed under magnetic stirring overnight.² The product was recovered by centrifugation and washed with methanol, and then dried and stored at 80°C under vacuum. The content of amine group was examined *via* thermal gravimetry analyses.

Characterization

Power X-ray diffraction (XRD) patterns of the samples were measured with a Rigaku D/MAX 2250V diffractometer using monochromatized $\text{Cu K}\alpha$ ($\lambda = 0.15418$ nm) ray radiation source, operated at 40 kV tube voltage and 100 mA tube current. The scanning rate was 0.5°/min in the range of $2\theta = 5\text{--}35^\circ$ for MIL-53 and $5\text{--}20^\circ$ for

MIL-101. The morphologies and microstructures of the obtained MOFs were characterized by transmission electron microscopy (TEM, JEOL JEM-2100F, accelerating voltage 200 kV). Surface area measurements were performed at 77K using a Micromeritics Tristar 3000 Brunauer-Emmett-Teller (BET) analyzer. The samples were degassed under vacuum at a temperature of 100°C overnight. Thermal stability and the content of amine group were studied using a thermogravimetric (TG) analysis recored on an NETZSCH STA 449C. TG-DTA data were recorded under an air flow of 100 mL/min at a heating rate of 10 K/min from room temperature up to 800°C. Nitrogen elementary analyses were performed on a CHN elemental analyzer (Elementar Vario MICRO CUBE). Infrared (IR) spectra were recorded on KBr/MOF pellets (1 wt% MOF) in a Burker Tensor 27 spectrometer. After accumulation of 64 scans, the spectra were collected with a resolution of 4 cm⁻¹.

Adsorption measurements

HCHO adsorption tests were performed in a home-made organic glass box with a volume of 60 L at ambient temperature. A 5 W electric fan was placed in the bottom of box during the adsorption process to promote the air circulation. The HCHO vapor was produced by injected aqueous solution of formaldehyde (Formalin) into the box by a microsyringe, and the initial concentration of HCHO can be adjusted by changing the amount of injected solution (volatilization of 30 uL Formalin leads to 150 ppm HCHO in the box). It is worth noting that it usual takes 4 hours for the completely volatilized of HCHO solution and stabilized the HCHO concentration. HCHO concentration in the reactor was analyzed by phenol spectrophotometric method (ensured the accuracy through the adsorption test of active carbon). Briefly, 10 mL gas sample containing trace HCHO was absorbed by 15 mL phenol reagent solution (1×10⁻⁴ wt %) for 5 min. Then, 1.2 mL (1 wt %) ammonium ferric sulfate solution was added as the coloring reagent. After being shaken and waiting for 15 min in the dark, HCHO concentration was determined by measuring light absorbance at 630 nm with a spectrophotometer (Hitachi U-3010 UV-vis spectrophotometer).³ The adsorption capacity can be calculated through the HCHO concentration difference

between the blank test and adsorption test. In the regenerate experiments, the used MOFs were degassed at 80°C under vacuum for 4 h before the next cycle of HCHO adsorption. For the water resistant experiments, another 50 uL water was injected into the test box and volatilized to determine the competitive adsorption between formaldehyde and water vapor.

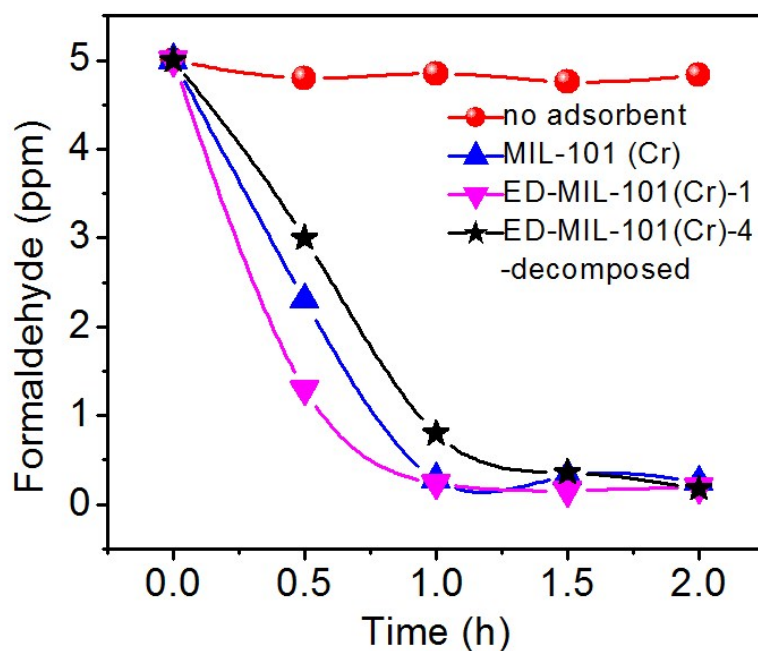


Figure S1. 5 ppm formaldehyde adsorption tests.

HCHO (ppm) \ Time (h)	No adsorbent	MIL-101(Cr)	ED-MIL-101(Cr)-1	ED-MIL-101(Cr)-4 decomopose
0.0	5	5	5	5
0.5	4.81	2.32	1.33	3.12
1.0	4.85	0.28	0.24	0.83
1.5	4.76	0.32	0.16	0.36
2.0	4.83	0.25	0.20	0.18

In order to reveal the importance of open-metal sites, we synthesized MIL-53(Al), which does not possess coordinatively unsaturated metal centers, treated it with ED, and testing their HCHO adsorption capacities. It is found that ED could not effectively graft in MIL-53, and the physisorption of amine in MIL-53 could disrupt its packing structures, leading to the turbostratic disorder (Fig. S3-S6).⁴ Consequently, the HCHO adsorption capacities were gradually decreased along with amine-treating processes (Fig. S7). These results demonstrated the essential role of open-metal sites played in efficient amine-grafting and subsequently, adsorption properties improvement.

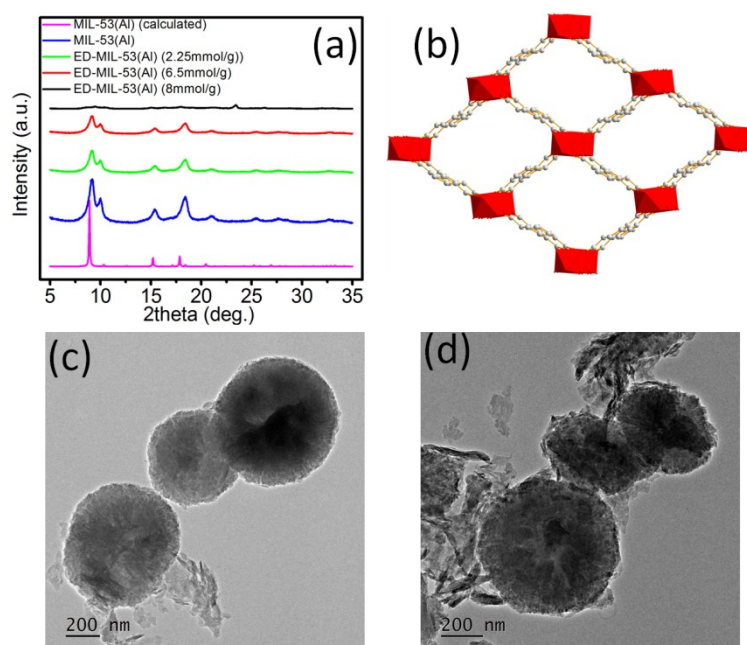


Figure S2. (a) XRD patterns of as-synthesized and ED-treated MIL-53; (b) Framework structures of MIL-53; (c)-(d) TEM images of as-synthesized and ED-treated MIL-53 (6.5mmol/g)

The pattern of the synthesized MIL-53 matches well with its calculated pattern, confirming the successful synthesis of this material. The ED-treated MIL-53 samples showed a gradually decreasing of peak intensity, which is indicated to the increasing disorder in interlayer packing, because of the adsorption of amine in one-dimensional

rhombic channels of MIL-53 (Figure S 2b) disrupted its packing structure between layers.⁴

From Figure S 2c, it can be seen that MIL-53 possesses typical sphere structure with a diameter about 600nm. After treated with ED, the sphere surface tends to be rough and some fragments stem from the destruction of framework can be clearly seen (Figure S 2d). These results show good accordance with the consequences of XRD analysis.

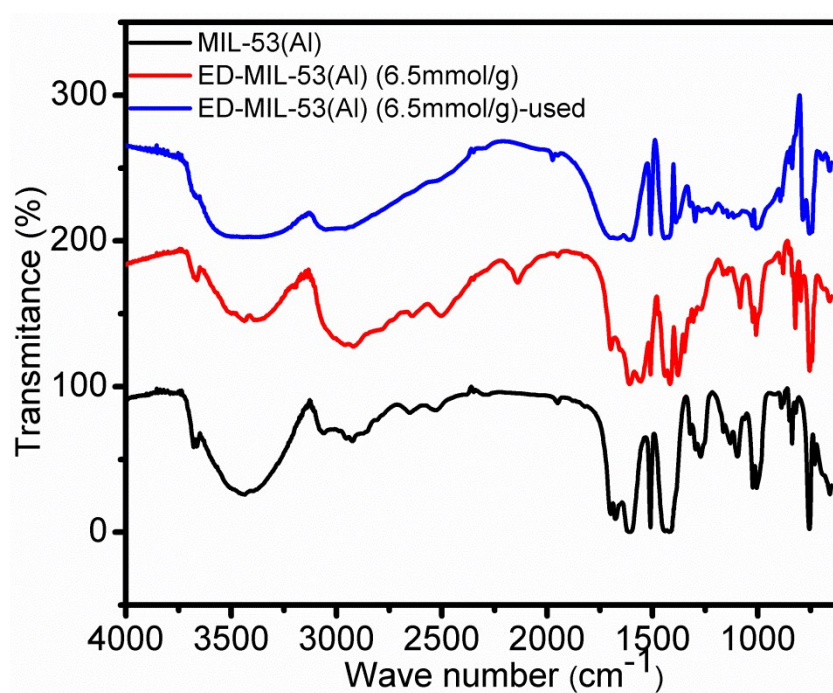


Figure S3. FTIR spectra of MIL-53 and ED-treated MIL-53

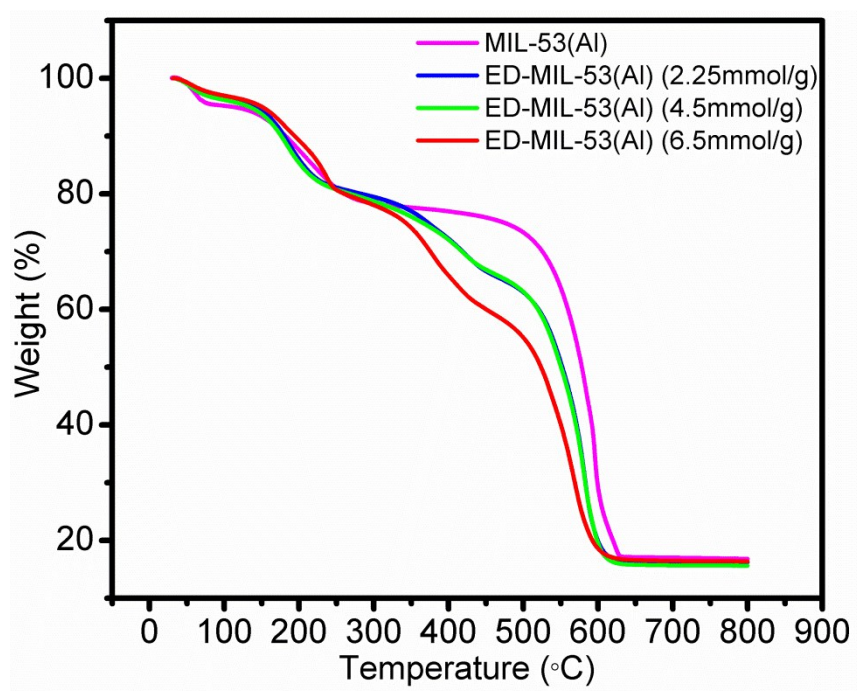


Figure S4. TGA profile of MIL-53 and ED-treated MIL-53

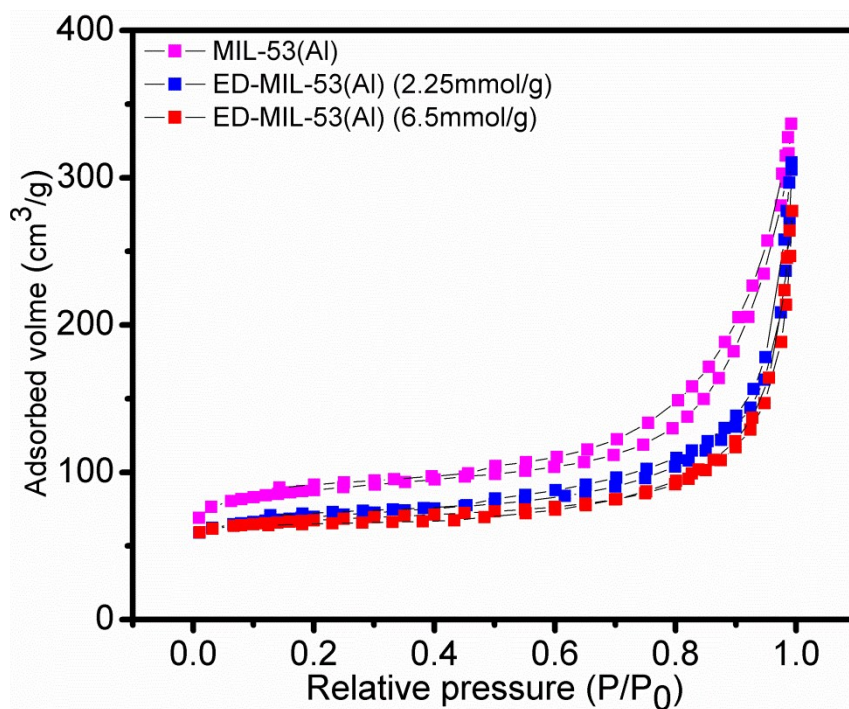


Figure S5. N₂ sorption-desorption isotherms of MIL-53 and ED-treated MIL-53

	BET surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)
MIL-53	747	0.435
ED-MIL-53 (2.25 mmol/g)	568	0.364
ED-MIL-53 (6.5 mmol/g)	524	0.343

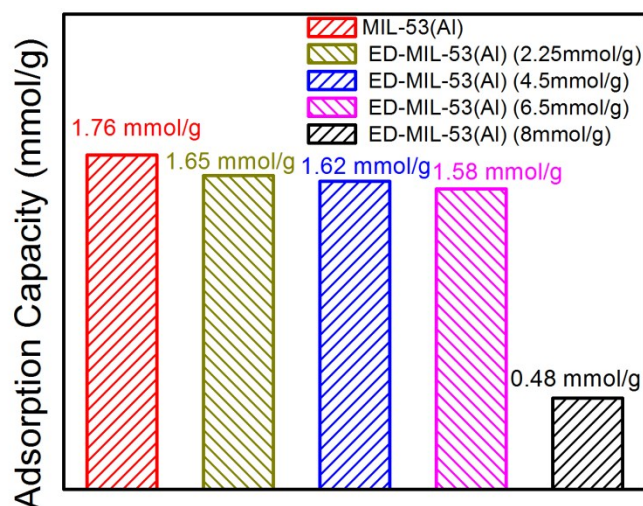


Figure S6. Formaldehyde adsorption capacity of the as-synthesized and ED-treated MIL-53

The HCHO adsorption capacity for MIL-53 is 1.76 mmol/g, the ED-treated samples shown a gradually decrease from 1.65 to 1.58 mmol/g and finally to 0.48 mmol/g for the damaged framework. The decrease of adsorption capacity can be ascribed to the increase of turbostratic disorder as confirmed by XRD and the decrease of BET surface area and pore volume as shown in Figure S5.

References

1. D. Jiang, A. D. Burrows and K. J. Edler, *CrystEngComm*, 2011, **13**, 6916.
2. Y. K. Hwang, D. Y. Hong, J. S. Chang, S. H. Jhung, Y. K. Seo, J. Kim, A. Vimont, M. Daturi, C. Serre and G. Ferey, *Angewandte Chemie*, 2008, **47**, 4144-4148.
3. Z. Wang, W. Wang, L. Zhang and D. Jiang, *Catalysis Science & Technology*, 2016. DOI: 10.1039/c5cy01709b
4. C. J. Doonan, D. J. Tranchemontagne, T. G. Glover, J. R. Hunt and O. M. Yaghi, *Nature Chemistry*, 2010, **2**, 235-238.