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Flexible Self-Supported Metal-Organic Frameworks Mats with Exception High Porosity for Enhanced Separation and Catalysis

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Preparation of fibrous metal oxide mats

Al_2O_3

According to our previously reported method,[1] 6.03 mL of HCOOH (Sinopharm Chemical Reagent Company, 88%), 6.86 mL of CH_3COOH (Sinopharm Chemical Reagent Company, 99.7%), and 1.08 g of aluminum powder (Sinopharm Chemical Reagent Company, 98%) were added in 17.28 mL of DI water and the mixture was magnetically stirred at 60~80 °C and further refluxed for 12 h until the aluminum powder completely dissolved. A colorless transparent sol was obtained after filtration. Then 0.1 g of PEO (Sinopharm Chemical Reagent Company, 98%) was added to improve the spinnability. For electrospinning, the as-prepared sol was added to a 20.0 mL plastic syringe with a metallic needle (inner diameter ~0.8 mm) at a speed of 2.0 mL h^{-1}. The distance between the collector and the needle was adjusted at 18.0 cm, and the applied voltage was fixed at 18 kV. The humidity was controlled below 10% during the electrospinning process. The electrospun gel fibers were dried at 80 °C and then calcined in the air firstly at 600 °C for 2 h with a ramping rate of 1 °C min^{-1}, and then at 700, 800, or 900 °C for 2 h with a ramping rate of 5 °C min^{-1}.

CuO

1.9052 g of $Cu(CH_3COO)_2$ (Shanghai Macklin Biochemical Co., Ltd., 99.5%) was dissolved in 10 mL deionized water. Then, 5 mL 10 wt% of PVA (Aladdin Reagent Company, alcoholysis: 87.0~89.0%) was added and the mixture was continuously stirred at room temperature for 3 h. For electrospinning, the as-prepared solution was added to a 10.0 mL plastic syringe with a metallic needle (inner diameter ~0.8 mm) at a speed of 1.0 mL h^{-1}. The distance between the needle and the collector was set to be 15.0 cm, and the applied voltage was fixed at 16 kV. The humidity was controlled below 10% during the electrospinning process. The electrospun gel fibers were dried at 80 °C and then calcined in the air at 400 °C for 2 h with a ramping rate of 1 °C min^{-1}.

Co_3O_4

Following a literature method,[2] 3 g of $Co(CH_3COO)_2 \cdot 4H_2O$ (Sinopharm Chemical Reagent Company, 99%) was dissolved in 7.5 mL DMF. Then 1 g of PVP was added and the mixture was continuously stirred at room temperature for 6 h. For electrospinning, the as-prepared solution was added to a 20.0 mL plastic syringe with a metallic needle (inner diameter ~0.8 mm) at a speed of 1.0 mL h^{-1}. The distance between the needle and the collector was set to be 15.0 cm, and the applied voltage was fixed at 20 kV. The humidity was controlled below 10% during the electrospinning process. The electrospun gel fibers were dried at 80 °C and then calcined in the air at 400 °C for 2 h with a ramping rate of 1 °C min^{-1}.

ZnO

Following a literature method,[3] 2 g of PVP was dissolved in 5 mL DMF (Sinopharm Chemical Reagent Company, 99.5%). To this solution, 5 g of $Zn(CH_3COO)_2 \cdot 2H_2O$ (Sinopharm Chemical Reagent Company, 99.5%) was added under vigorous magnetic stirring at room temperature. For electrospinning, the as-prepared solution was added to a 20.0 mL plastic syringe with a metallic needle (inner diameter ~0.8 mm) at a speed of 1.5 mL h^{-1}. The distance between the needle and the collector was set to be 10.0 cm, and the applied voltage was fixed at 15 kV. The humidity was controlled below 10% during the electrospinning process. The electrospun gel fibers were dried at 80 °C and then calcined in the air at 500 °C for 5 h with a ramping rate of 1 °C min^{-1}.

ZrO_2

0.3g of PVP was dissolved in 5 mL of ethanol (Sinopharm Chemical Reagent Company, 98%). To this solution, 10 g of $Zr(CH_3COO)_4$ (Sinopharm Chemical Reagent Company, Zr~15.0-16.0% in ethanol) was added under vigorous magnetic stirring at room temperature. For electrospinning, the as-prepared sol was added to a 20.0 mL plastic syringe with a metallic needle (inner diameter ~0.8 mm) at a speed of 2.0 mL h^{-1}. The distance between the needle and the collector was 25.0 cm and the applied voltage was 20 kV. The humidity was controlled below 10% during the electrospinning process. The electrospun gel fibers were dried at 50 °C for 12 h and then calcined in the air at 600 °C for 2 h with a ramping rate of 1 °C min^{-1}.

Fe_2O_3

5 g of $Fe(NO_3)_3 \cdot 9H_2O$ (Sinopharm Chemical Reagent Company, 99%) was added slowly into a ethanol (5.0 mL) and deionized water (5.0 mL) solution containing 4.5 g of PVP under vigorous magnetic stirring at room temperature. For electrospinning, the as-prepared solution was added to a 20.0 mL plastic syringe with a metallic needle (inner diameter ~0.8 mm) at a speed of 1.8 mL h^{-1}. The distance between the needle and the collector was set to be 10.0 cm, and the applied voltage was fixed at 16 kV. The humidity was controlled below 10% during the electrospinning process. The electrospun gel fibers were dried at 80 °C and then calcined in the air at 500 °C for 4 h with a ramping rate of 3 °C min^{-1}.

Preparation of MOF powders

MIL-53(Al)

1.3 g of $Al(NO_3)_3 \cdot 9H_2O$ (Sinopharm Chemical Reagent Company, 99.5%) and 0.288 g of H_2BDC were dissolved in 4.9 mL of deionized water. Then this solution was transferred to a 10 mL Teflon-lined steel autoclave and heated at 110 °C for 72 h. After the reaction, the powder was collected by centrifugation and washed with copious water for three times before dried overnight at 80 °C under vacuum.

MIL-53(Al)-NH_2

3.1 g of Al $(NO_3)_3 \cdot 9H_2O$ and 5 g of NH_2-H_2BDC were dissolved in 22.8 mL of deionized water. Then this solution was transferred to a 50 mL Teflon-lined autoclave and heated at 110 °C for 72 h. After the reaction, the powder was collected by centrifugation and washed with acetone for three times before dried overnight at 80 °C under vacuum.

HKUST-1

0.3 g of $Cu(NO_3)_2 \cdot 3H_2O$ (Sigma-Aldrich, 99%) and 0.5367 g of H_3BTC were dissolved in 15 mL ethanol and water (V/V=1:1) and stirred continuously for 15 min. Then the mixture were transferred to a 50 mL Teflon-lined autoclave and heated at 110 °C for 8 h. The precipitate was collected by centrifugation and washed with hot ethanol and water before dried under vacuum at 80 °C overnight.

ZIF-8

0.136 g of $Zn(OAc)_2 \cdot 2H_2O$ (Sinopharm Chemical Reagent Company, 99.5%) and 0.1 g of 2-MeIM were dissolved in 10 mL DMF under magnetic stirring for 10 min. Then the mixture was transferred to a 20 mL Teflon-lined autoclave and heated at 100 °C for 5 h. The precipitate was collected by centrifugation and washed with ethanol before dried under vacuum at 80 °C overnight.

ZIF-67

0.459 g of $Co(OAc)_2 \cdot 4H_2O$ (Sinopharm Chemical Reagent Company, 99.5%) and 1.187 g of 2-MeIM were dissolved in 15 ml methanol under magnetic stirring. Then the mixture was transferred to a 20 mL Teflon-lined autoclave and heated at 110 °C for 24 h. The precipitate was collected by centrifugation and washed with ethanol before dried under vacuum at 80 °C overnight.

UiO-66

0.177 g of $ZrCl_4$ (Sigma-Aldrich, 99%) and 0.474 g of H_2BDC were added to a 50 mL Teflon-lined stainless-steel autoclave that contains 10 mL deionized water and 1 mL acetic acid. Then the autoclave was sealed and heated in the oven at 140 °C for 24 h. After the reaction the product was collected and washed thoroughly with DMF for three times and dried under vacuum at 150 °C.

MIL-88B(Fe)

1.0 g of $Fe(NO_3)_2 \cdot 3H_2O$ (Sinopharm Chemical Reagent Company, 99%) and 0.948 g of H_2BDC were dissolved in 10 mL DMF and water (V/V = 100:1) together with 0.3 mL acetic acid under magnetic stirring. Then the mixture was transferred to a 20 mL Teflon-lined autoclave and heated at 100 °C for 48 h. The precipitate was collected by centrifugation and washed with DMF and ethanol for five times before dried under vacuum at 80 °C overnight.

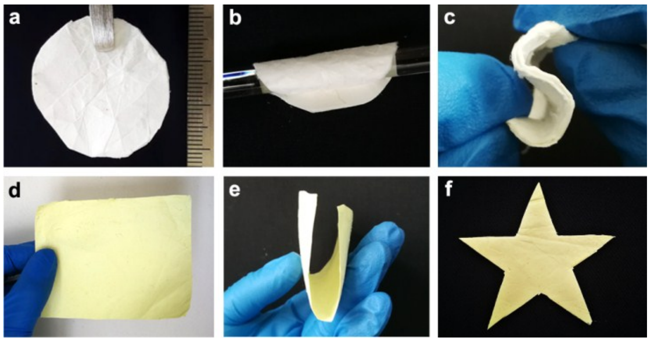

Fig. S1 Photographs of the FS-MIL-53(Al) (a-c) and MIL-53(Al)-NH_2 FMs (d-e).

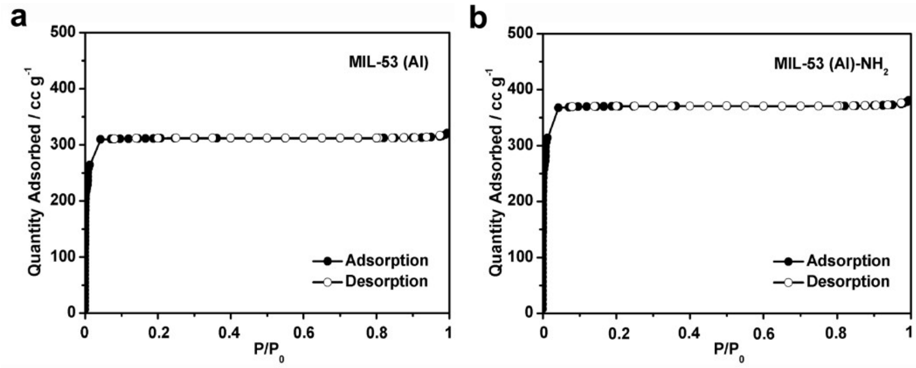

Fig. S2 N_2 adsorption-desorption isotherms of the MIL-53(Al) (a) and MIL-53(Al)-NH_2 powders (b).

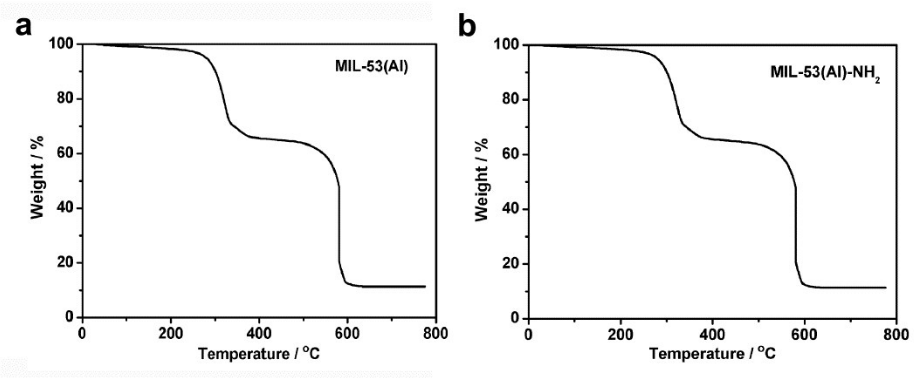

Fig. S3 TGA curves of MIL-53(Al) (a) and MIL-53(Al)-NH$_2$ powders (b).

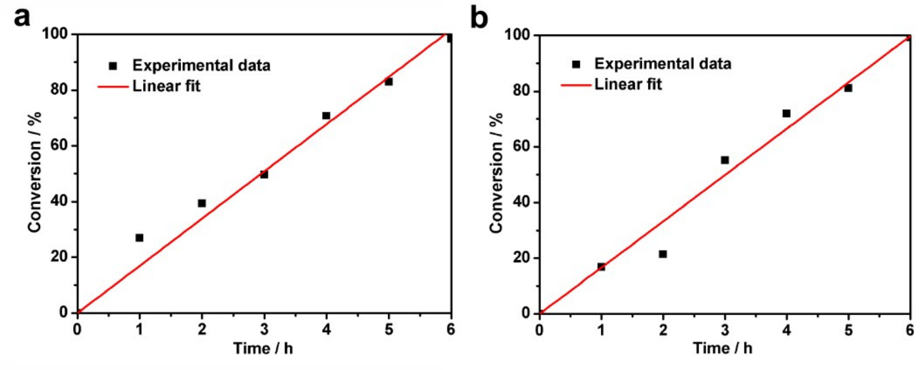

Fig. S4 Plots of the conversion yield versus reaction time for FS-MIL-53(Al) (a) and MIL-53(Al)-NH$_2$ FMs (b).

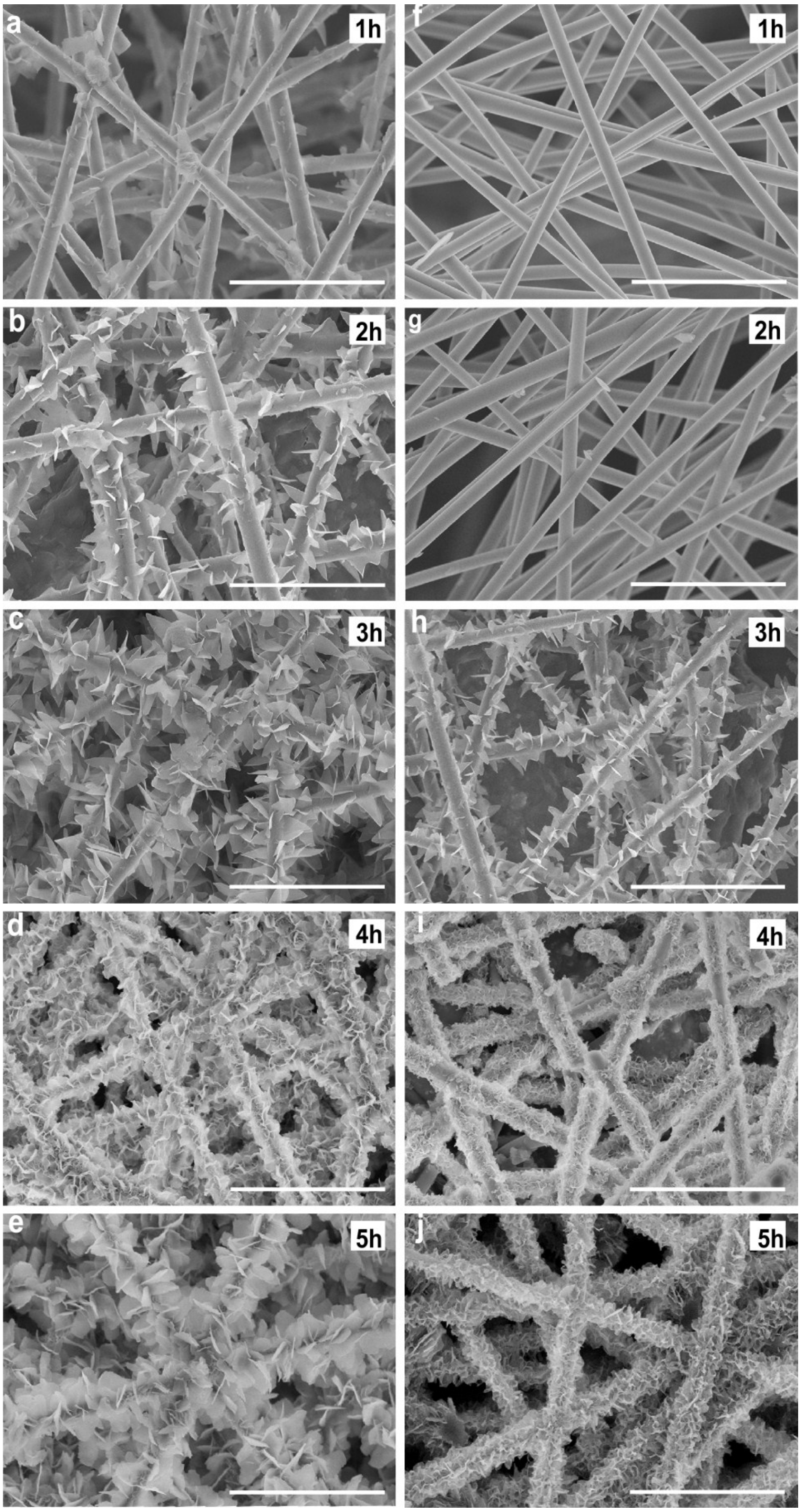

Fig. S5 SEM images of mid-term products of the conversion reactions of Al_2O_3 FMs with H_2BDC (a-e) and $H_2BDC-NH_2$ (f-j). Scale bars represent 5 μm.

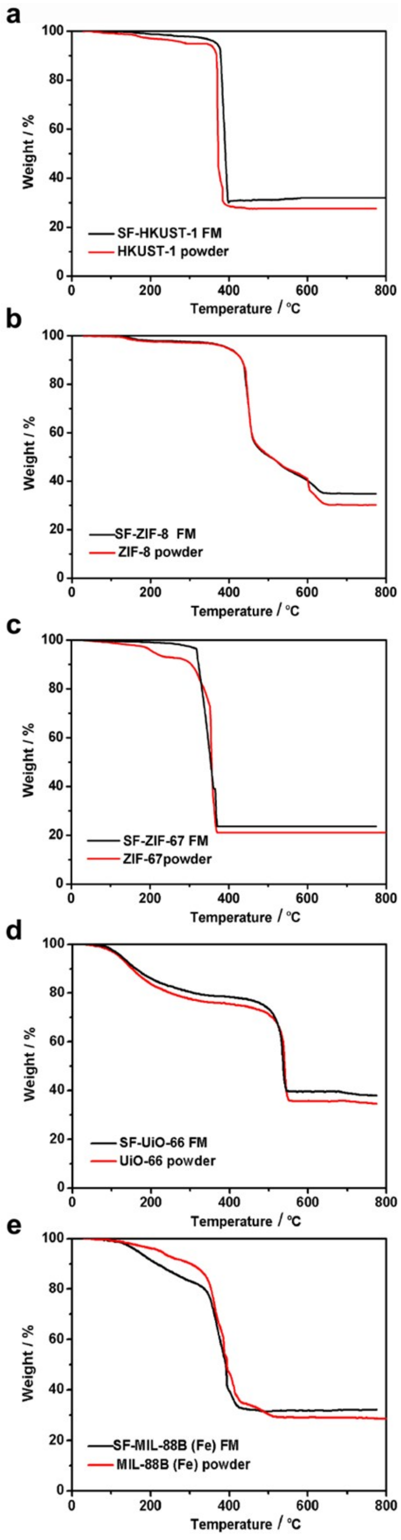

Fig. S6 TGA curves of the FS-MOFs FMs and MOF powders: (a) HKUST-1, (b) ZIF-8, (c) ZIF-67, (d) UiO-66, and (e) MIL-88B (Fe).

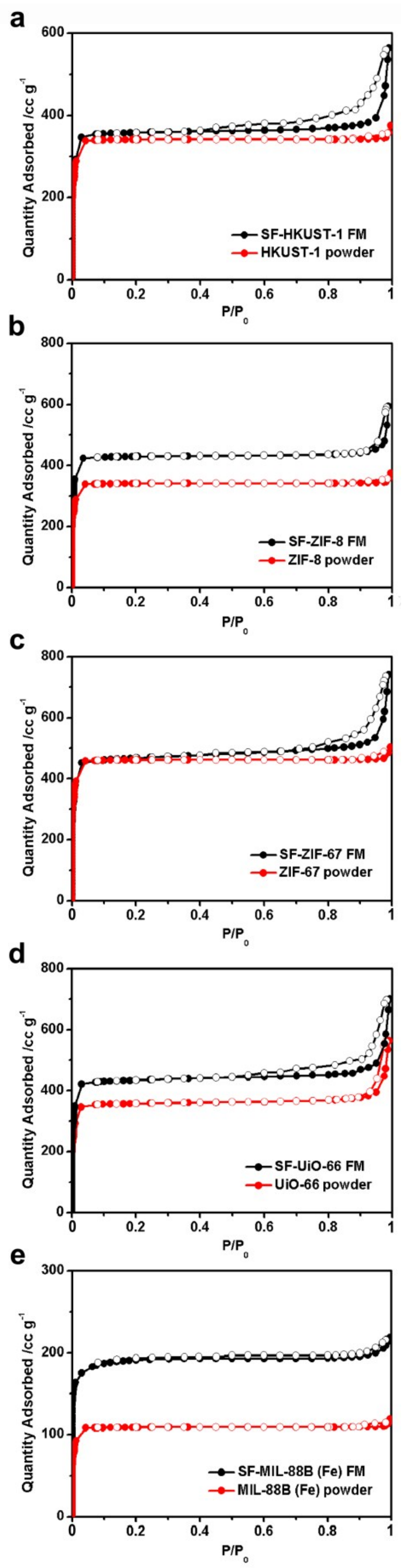

Fig. S7 N_2 sorption-desorption isotherms of the FS-MOFs FMs and MOF powders: (a) HKUST-1, (b) ZIF-8, (c) ZIF-67, (d) UiO-66, and (e) MIL-88B(Fe).

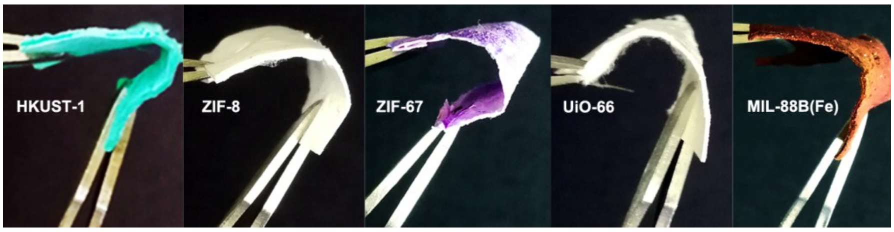

Fig. S8 Photographs of various FS-MOF FMs showing they can be readily manipulated.

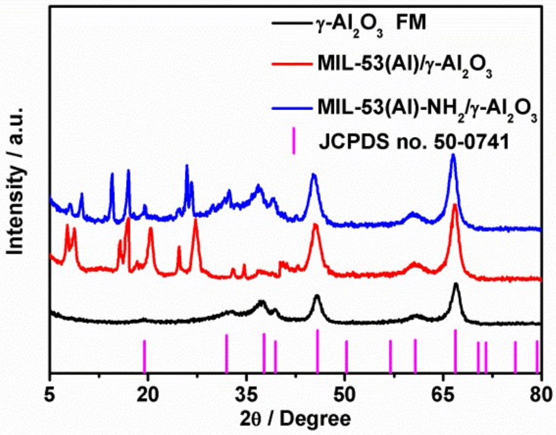

Fig. S9 XRD patterns of γ-Al_2O_3 FMs before and after the conversion reactions with H_2BDC and H_2BDC-NH_2.

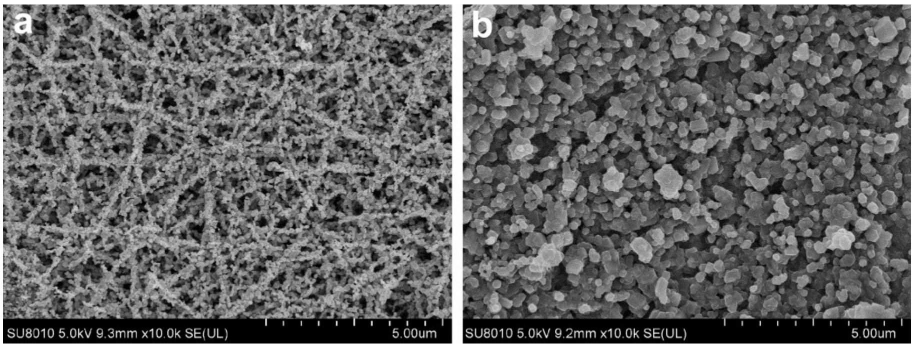

Fig. S10 SEM images of the products of the reaction between ZnO FMs and 2-MeIM in water (a) and methanol (b).

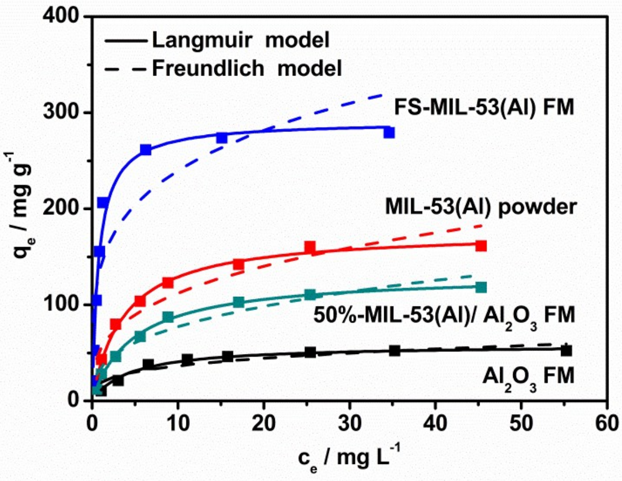

Fig. S11 Adsorption isotherms of DMP on the FS-MIL-53(Al) FM, MIL-53(Al) powder, 50% MIL-53(Al)/Al_2O_3 FM and Al_2O_3 FM.

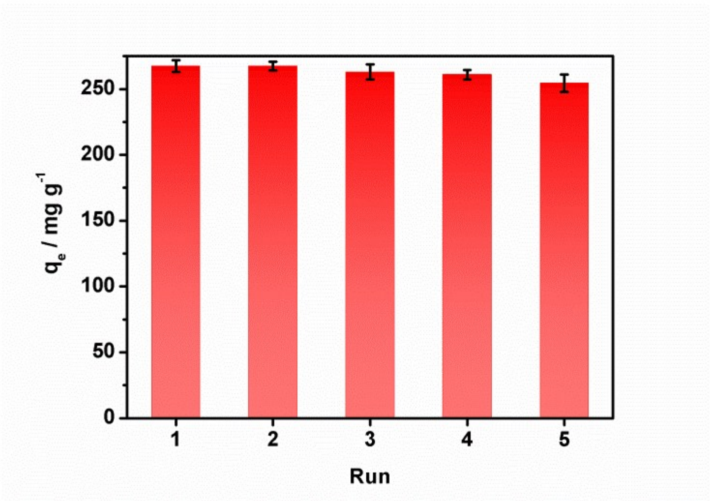

Fig. S12 DMP adsorption capacity on the FS-MIL-53(Al) FM at different adsorption runs.

Fig. S13 Photographs showing the FS-MIL-53(Al) FM applied as the filter in a filtration device for the separation of methylene blue from water. Inset shows the FS-MOF FM before and after filtration.

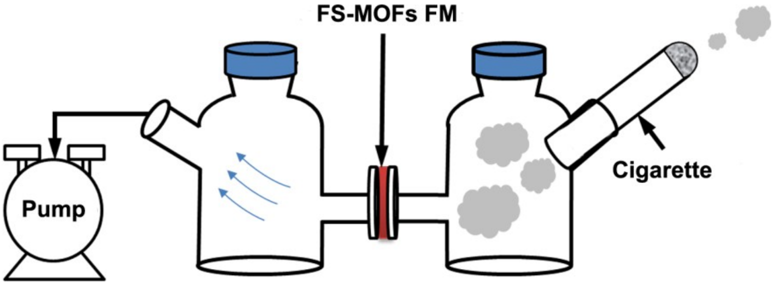

Fig. S14 Illustration of the ‘smoking’ device with SF-MOFs FM as the filter.

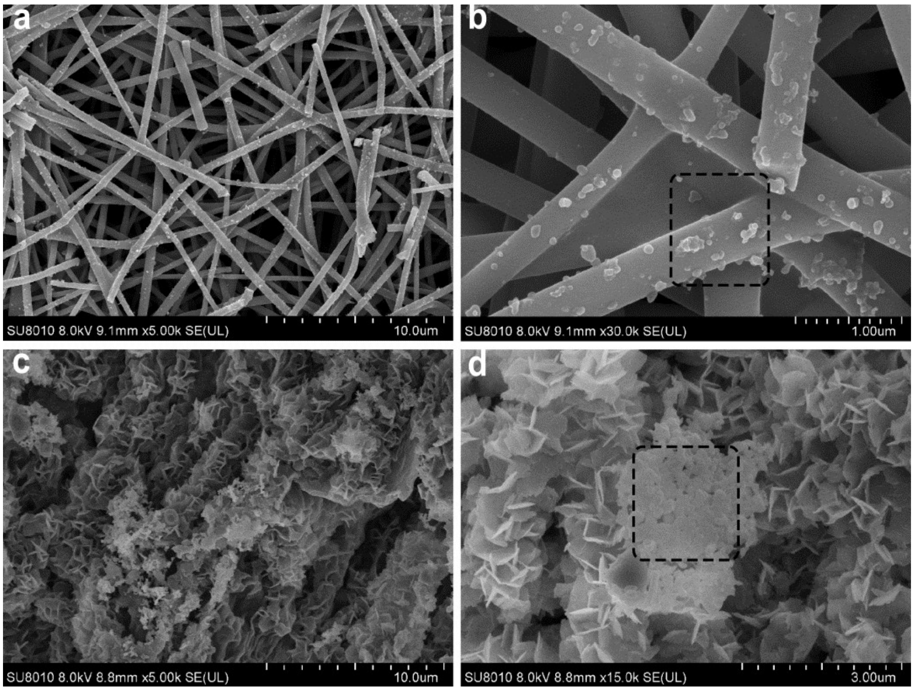

Fig. S15 Low- and high-magnification SEM images of Al_2O_3 FM (a, b) and FS-MIL-53(Al) FM (c, d) after smoke filtration. Dashed squares indicate the PM particles.

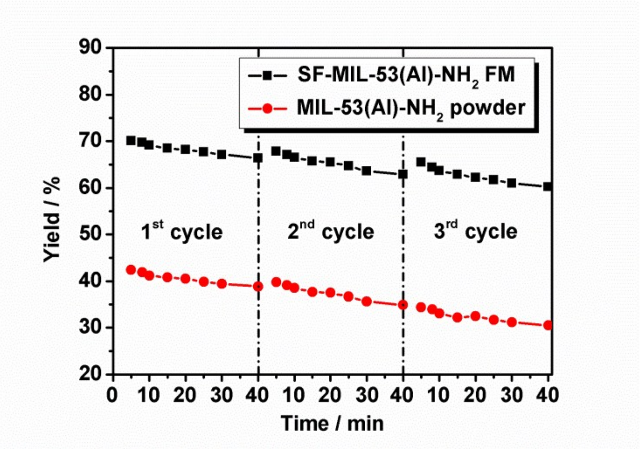

Fig. S16 Time-dependent yield of Knoevenagel condensation at different cycles catalyzed by the FS-MIL-53(Al)-NH$_2$ FM and MIL-53(Al)-NH$_2$ powder in a plug-flow reactor at 50 °C.

Table S1 Pore-texture properties of MIL-53(Al) and MIL-53(Al)-NH_2 samples.

	BET SA (m^2 g^{-1})	**V_{micro} (cm^3 g^{-1})**	**V_{total} (cm^3 g^{-1})**	**Ref.**
FS-MIL-53(Al) FM	1500	0.57	1.1	This work
MIL-53(Al) powder	1035	0.49	0.50	This work
	1140,[4] 1064[5]	0.51[5]	0.54[5]	[4, 5]
FS-MIL-53(Al)-NH_2 FM	1419	0.51	1.1	This work
MIL-53(Al)-NH_2 powder	1082	0.52	0.55	This work
	950	0.23	1.03	[6]

Table S2 Conversion yield for various FS-MOFs FMs.

Metal oxide FMs	CuO	ZnO	Co_3O_4	ZrO_2	Fe_2O_3
FS-MOFs FMs	HKUST-1	ZIF-8	ZIF -67	UiO-66	MIL-88B (Fe)
Conversion yield (%)[a]	95	95	96	95	95

[a] The conversion yield was calculated by: Y (%) = W_{FM}/W_P (W_{FM}: the total weight loss of FS-MOF FM, W_P: the weight loss of MOF powder). For example, $Y_{HKUST-1}$ (%)=0.68/0.72×100 %=95%.

Table S3 Pore-texture properties of HKUST-1, ZIF-8, ZIF-67, UiO-66 and MIL-88B(Fe) samples.

	BET SA (m^2 g^{-1})	**V_{micro} (cm^3 g^{-1})**	**V_{total} (cm^3 g^{-1})**	**Ref.**
FS-HKUST-1 FM	1300	0.47	0.66	This work
HKUST-1 powder	1109	0.40	0.41	This work
	692,[7] 1143[8]	–	0.33,[7] 0.65[8]	[7, 8]
FS-ZIF-8 FM	1574	0.62	0.82	This work
ZIF-8 powder	1398	0.57	0.62	This work
	1072,[9] 1370[10]	0.53,[9] 0.51[10]	–	[9, 10]
FS-ZIF-67 FM	1701	0.66	0.91	This work
ZIF-67 powder	1486	0.58	0.61	This work

	1319	0.61	–	[11]
FS-UiO-66 FM	1512	0.52	0.77	This work
UiO-66 powder	1134	0.48	0.49	This work
	1380	0.53	0.58	[12]
FS-MIL-88B(Fe) FM	729	0.29	0.51	This work
MIL-88B(Fe) powder	249.8	0.21	0.24	This work
	209.83	–	0.42	[13]

Table S4 Adsorption isotherm model parameters for DMP adsorption on the Al_2O_3 FM, MIL-53(Al) powder, and FS-MIL-53(Al) FM.

	Langmuir model[a]			**Freundlich model**[a]		
	q_m (mg g^{-1})	**K_L (L mg^{-1})**	**R^2**	**n**	**K_F (mg(1-1/n) L(1/n)/g)**	**R^2**
Al_2O_3 FM	31.6156	1.7190	0.9814	0.3905	31.8434	0.9568
MIL-53(Al) powder	176.7085	1.1341	0.9923	0.2556	84.1614	0.8913
50%-MIL-53(Al)/ Al_2O_3 FM	126.5823	1.0739	0.9969	0.3088	65.7597	0.9502
FS-MIL-53(Al) FM	267.5247	1.3317	0.9907	0.2335	139.9132	0.7789

[a] The Langmuir and Freundlich model were described by Equation 1 and 2 respectively, and used to fit the adsorption isotherms,

$$\frac{1}{q_e} = \frac{1}{K_L q_m C_e} + \frac{1}{q_m} \quad (1)$$

$$\lg q_e = \frac{1}{n} \lg C_e + \lg K_F \quad (2)$$

where q_e is the amount of adsorbate adsorbed per unit weight of the adsorbent at equilibrium (mg g^{-1}), q_m is the maximum adsorption capacity (mg g^{-1}), c_e is the equilibrium concentration of adsorbate in the solution (mg L^{-1}), K_L is the Langmuir constant, K_F (mg(1-1/n) L(1/n)/g) is the Freundlich constant that relates to the adsorption capacity, and n is the constant that signifies adsorption intensity.

Table S5 Adsorption kinetics model parameters for DMP adsorption on the Al_2O_3 FM, MIL-53(Al) powder, and FS-MIL-53(Al) FM.

	Pseudo-first-order[a]		**Pseudo-second-order**[a]		
	k_1 (min^{-1})	**R^2**	**q_e (mg g^{-1})**	**k_2 (g mg^{-1} min^{-1})**	**R^2**
Al_2O_3 FM	0.0180	0.9892	48.3092	0.3172	0.9980
MIL-53(Al) powder	0.0255	0.9705	188.9776	0.5447	0.9902
50%-MIL-53(Al)/ Al_2O_3 FM	0.0168	0.9859	149.2537	0.4753	0.9980
FS-MIL-53(Al) FM	0.0260	0.9769	279.3296	1.3480	0.9959

[a] The pseudo-first-order and pseudo-second-order models were represented by Equation 3 and 4, respectively, and used to fit the adsorption kinetics:

$$\ln\left(q_e - q_t\right) = \ln q_e - k_1 t \qquad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (4)$$

where q_e is the equilibrium adsorption capacity (mg g^{-1}), q_t is the adsorption capacity at contact time t (mg g^{-1}), k_1 is the pseudo-first-order rate constant (min^{-1}), and k_2 is the pseudo-second-order rate constant (g mg^{-1} min^{-1}).

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