Imparting magnetic functionality to iron-based MIL-101 via facile Fe₃O₄ nanoparticles encapsulation: an efficient and recoverable catalyst for aerobic oxidations Zhaokui Jin,^a Yi Luan,^a Mu Yang,^a Jia Tang, ^a Jingjing Wang,^a Hongyi Gao,^a Yunfeng Lu^b and Ge Wang*^a

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Supporting Information

1. Preparation of Fe₃O₄/Fe-88B

As control, Fe₃O₄/Fe-MIL-88B was synthesized by a similar method. A solution containing FeCl₃· $6H_2O$ (2.984 g, 5.52 mmol), H₂BDC (0.917 g, 11.04 mmol), 15 mL DMF, 12 mL Fe₃O₄ source solution was dispersed by ultrasonication, and then the suspension was transferred into a 50 mL Teflon liner steel autoclave and reacted at 170 °C for 24 h. After cooling to room temperature, a brick-red precipitate was obtained by centrifugation, washed with DMF two times each day for two days to activate the composite. The brick-red solid was washed with methanol in the same way to replace DMF. Finally, the solid was dried at 80 °C for 24 h.

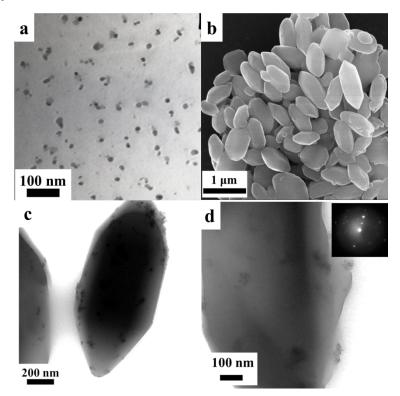


Fig. S1 (a) TEM image of PAA-modified Fe₃O₄ nanoparticles; (b) SEM image of F2;
(c) and (d) TEM images of F2. The insert in (d) is the corresponding selected area electron diffraction (SAED) SAED pattern.

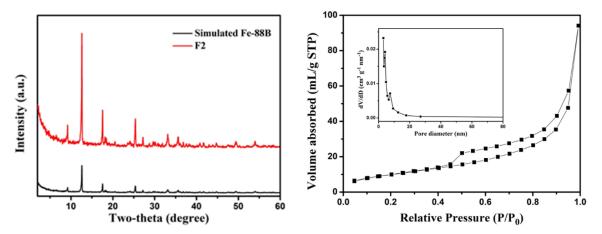


Fig. S2 (a) XRD patterns of the simulated from the crystallographic data of Fe-MIL-88B and F2; (b) Nitrogen adsorption–desorption isotherms of F2, and its corresponding pore size distribution curve.

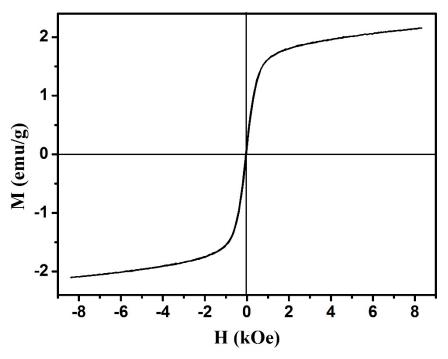


Fig. S3 VSM curves of F2 at room temperature.

2. Characterization of the recycled catalyst F1

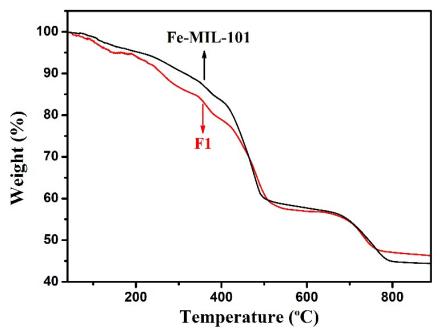


Fig. S4 TG curves of Fe-MIL-101 and as-prepared F1.

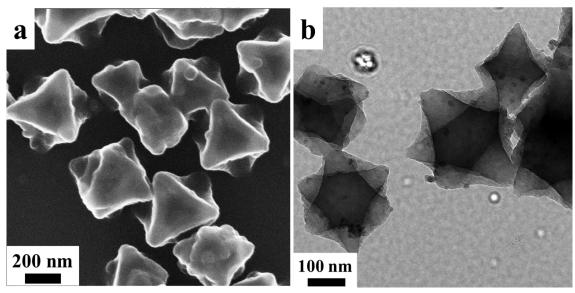


Fig. S5 SEM (a) and TEM (b) images of F1 after eight runs.

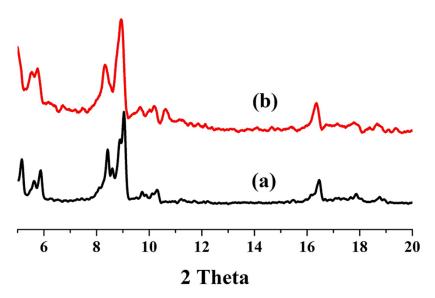


Fig. S6 XRD patterns of (a) F1 before reaction and (b) after eight runs.

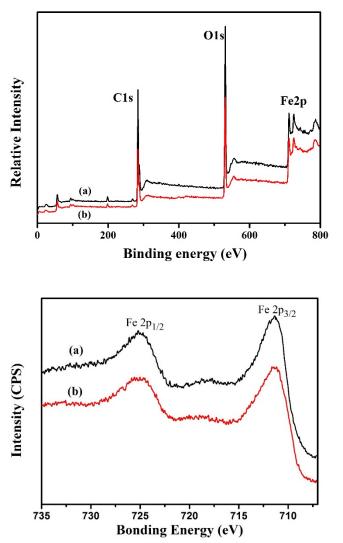


Fig. S7 XPS spectra (above) and the high resolution Fe2p spectra (below) of (a) **F1** before reaction and (b) after eight runs

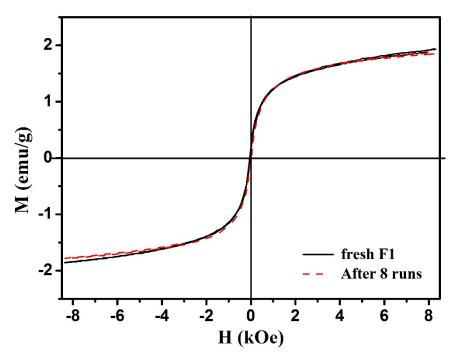


Fig. S8 VSM curves of F1 before reaction and after eight runs.

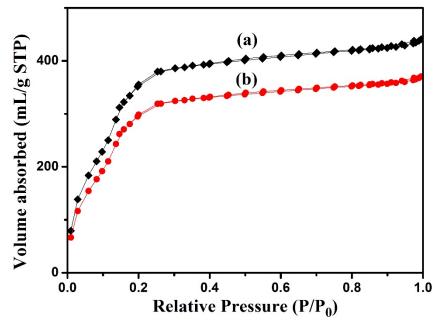


Fig. S9 Nitrogen adsorption isotherms of (a) F1 before reaction and (b) after eight runs.

3.	Catalytic	performance	evaluation
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Table S1. A comparison of catalytic activity of different catalysts in aerobic oxidation of Benzyl alcohol.

Entry	Catalyst	Mol%	Time/	Solvent	T/°C	Yiel	ТО	Ref.
			h			d	Ν	
1	Octahedral molecular sieves	50	4	PhCH ₃	110	85%	1.7	1
2	Cu ₂ Mn	10	6	CH ₂ Cl ₂	120	98%	9.8	2
3	CuFe ₂ O ₄	10	24	H ₂ O	100	95%	9.5	3

4	MCM-41-TEMPO/CuCl	5	48	DMF	25	35	7	4
5	CuCl/TEMPOIL/MS3A	5	5	[bmim][PF ₆]	80	98	13.6	5
6	FeMPA	1.67	20	CH ₃ CN	80	35%	21	6
7	Cu ₃ (BTC) ₂	25.5	22	CH ₃ CN	75	89%	3.5	7
8	Fe ₃ O ₄ /Fe-MIL-101	10	14	CH ₃ CN	75	99%	9.9	This work

1. Y. C. Son, V. D. Makwana, A. R. Howell, S. L. Suib, Angew. Chem. 2001, 113, 4410-4413.

G. Yang, J. Ma, W. Wang, J. Zhao, X. Lin, L. Zhou, X. Gao, *Catal. Lett.* 2006, 112, 83-87.

 X. Zhu, D. Yang, W. Wei, M. Jiang, L. Li, X. Zhu, J. You, H. Wang, *RSC Adv.* 2014, 4, 64930-64935.

4. D. Brunel, F. Fajula, J. B. Nagy, B. Deroide, M. J. Verhoef, L. Veum, J. A. Peters,H. van Bekkum, *Appl. Catal. A: Gen.* 2001, *213*, 73-82.

5. L. Liu, J. Ma, L. Ji, Y. Wei, J. Mol. Catal. A-chem. 2008, 291, 1-4.

6. P. Nagaraju, N. Pasha, P. S. S. Prasad, N. Lingaiah, Green Chem. 2007, 9, 1126-1129

7. A. Dhakshinamoorthy, M. Alvaro, H. Garcia, ACS Catal. 2011, 1, 48-53.