Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supplementary Information

One-pot Synthesis of Bimetallic Metal-Organic Frameworks (MOFs) as Acid-Base Bifunctional Catalysts for Tandem Reaction

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1. ICP-AES Results

Table S1. ICP-AES (Inductively Coupled Plasma Atomic Emission Spectrometry)

Samples	Al %	Fe %
MIL-101(Al/Fe)-NH_2*(20:1)*	10.60±0.51	0.15±0.01
MIL-101(Al/Fe)-NH_2*(15:1)*	10.57±0.54	0.17±0.01
MIL-101(Al/Fe)-NH_2*(10:1)*	9.77±0.48	0.25±0.02
MIL-101(Al/Fe)-NH_2*(5:1)*	9.41±0.37	0.38±0.02

2. Figures

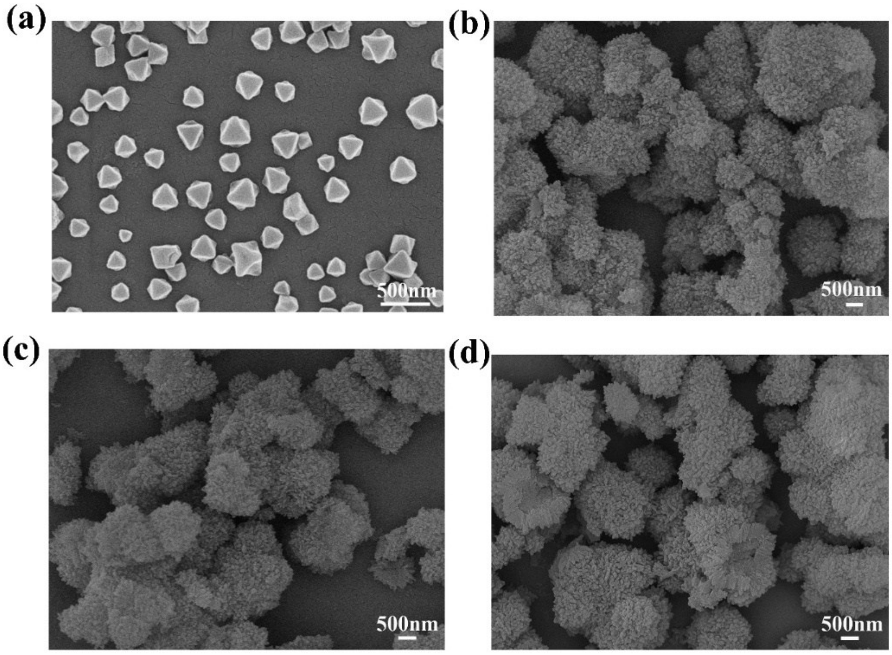

Fig. S1. The SEM image of MIL-101(Fe)-NH_2 MIL-101(Al/Fe)-NH_2*(20:1)* MIL-101(Al/Fe)-NH_2*(10:1)* and MIL-101(Al/Fe)-NH_2*(5:1)*.

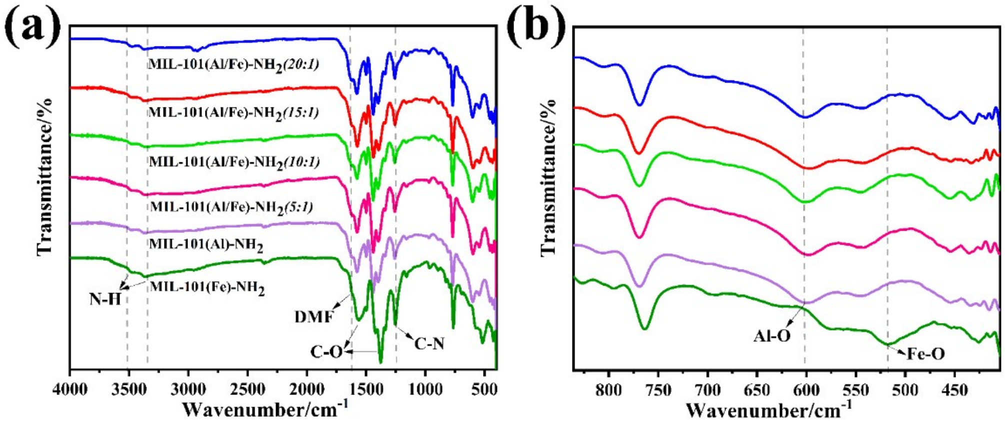

Fig. S2. (a) The ATR-FTIR spectra of the catalysts; (b) The magnified FTIR spectra of the catalysts.

The FT-IR spectra analyses were also performed to characterize the samples MIL-101(Al/Fe)-NH_2 (*X*), MIL-101(Al)-NH_2 and MIL-101(Fe)-NH_2. As shown in Figure S2, the band at 3498.5 cm^{-1} and 3370.5 cm^{-1} referred to the primary amines (-NH_2) on the organic linker.[1] The strong peaks at 1577 cm^{-1} and 1373 cm^{-1} occurring for all samples were attributed to the carboxylate linker, whereas bonds at 1644, 1441 and 1256 cm^{-1} corresponded to the carboxyl groups of free aromatic carboxylic acid, the C=C stretching of benzenoid rings, and C-N vibration, respectively. The peak at 765cm^{-1} was attributed to the out-of-plane bending vibration of C-H in the benzene ring.[2] All of the results were similar to those observed in MIL-101(Al)-NH_2 and MIL-101(Fe)-NH_2 samples. Nevertheless, the magnified IR spectra are shown in Figure S2b, the peaks below 1000 cm^{-1} are correspond to Al-O and Fe-O bonds vibration. Unfortunately, there were no Fe-O bonds in the bimetallic infrared spectra due to the extremely small amount of iron.

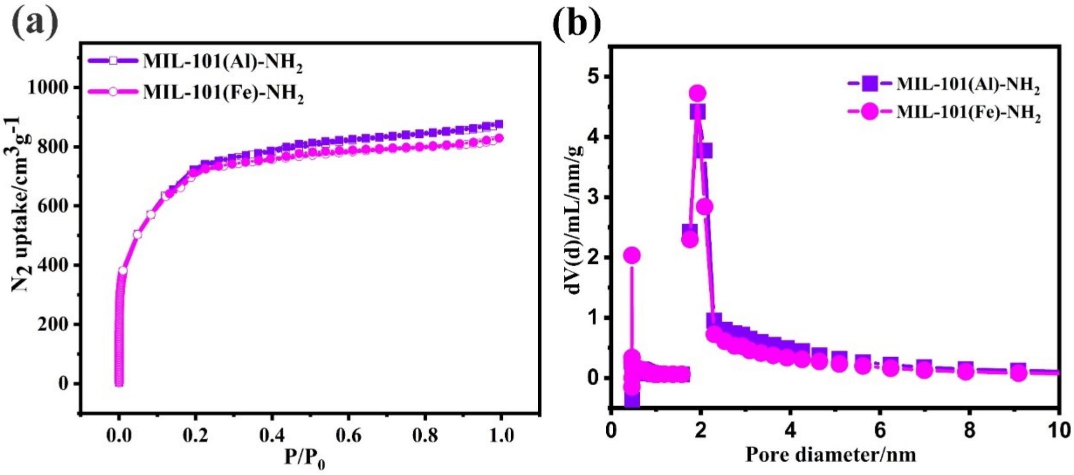

Fig. S3. (a) The N_2 adsorption-desorption isotherms; (b) The pore size distribution of MIL-101(Al)-NH_2 and MIL-101(Fe)-NH_2, respectively.

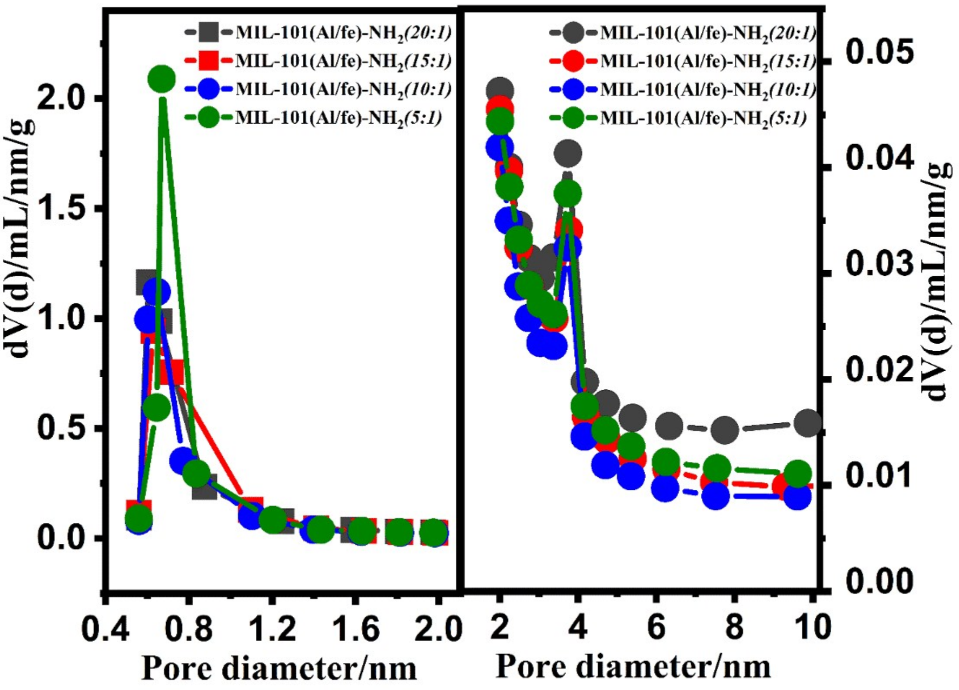

Fig. S4. The pore size distribution of MIL-101(Al/Fe)-NH_2*(20:1)*, MIL-101(Al/Fe)-NH_2*(15:1)*, MIL-101(Al/Fe)-NH_2*(10:1)* and MIL-101(Al/Fe)-NH_2*(5:1)*, respectively.

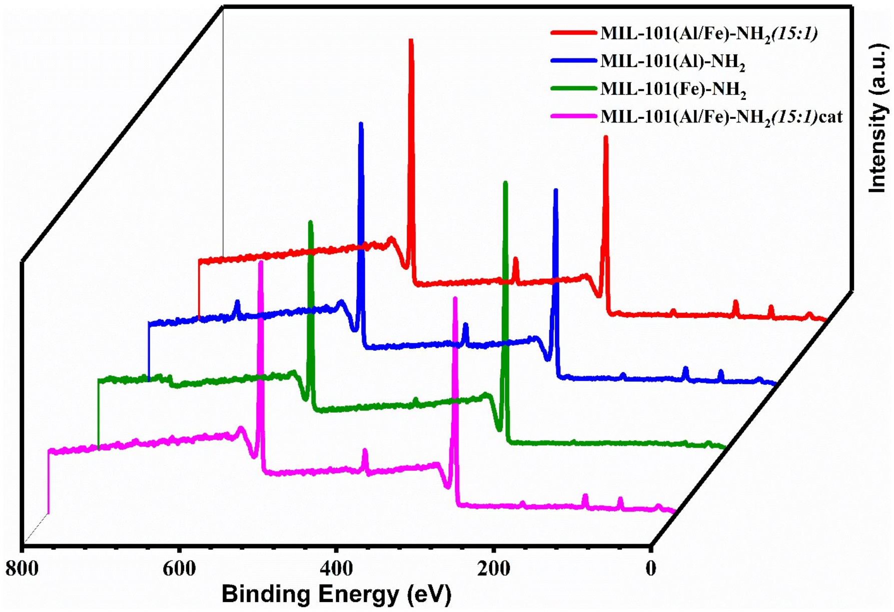

Fig. S5. The XPS spectra of the samples.

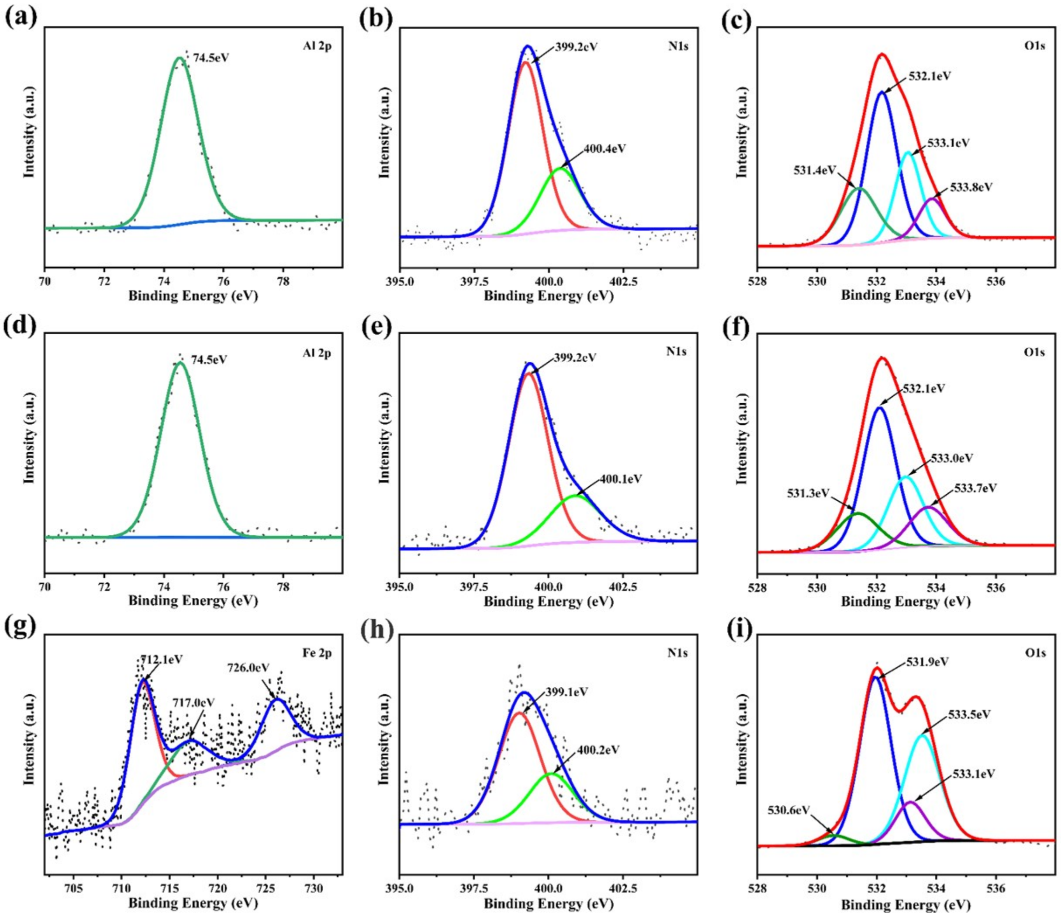

Fig. S6. High resolution of the XPS spectra of the catalysts. (a)-(c) MIL-101(Al/Fe)-NH_2 *(15:1)*; (d)-(f) MIL-101(Al)-NH_2; (g)-(i) MIL-101(Fe)-NH_2.

The surface chemistry of the as-synthesized samples was also analyzed by XPS, and the diagrams were shown in Figure S5 and Figure S6. The high resolution XPS spectra of Al 2p, Fe 2p, N 1s and O 1s spectrums of the MIL-101(Al/Fe)-NH_2 (*15:1*), MIL-101(Al)-NH_2 and MIL-101(Fe)-NH_2 shows in the Fig. S6. As shown in Fig. S6a and S6d the peak at the binding energy of 74.5 eV was ascribed to Al^{3+} *2p*.[3] The Fe *2p* XPS (Fig. S6g) electrons and binding energies of Fe^{3+} $2p_{3/2}$ and Fe^{3+} $2p_{1/2}$ peaks were located at 712.1 and 726.0 eV, respectively. Additionally, the peak at 717.0 eV was assigned to the satellite peak of Fe $2p_{3/2}$.[4-6] The N *1s* of the MIL-101(Al/Fe)-NH_2 (*15:1*), MIL-101(Al)-NH_2 and MIL-101(Fe)-NH_2 have the same peaks were shown in Fig. S6b, S6e and S6h, the N1s were fitted into two peaks at 399.2 eV and 400.4 eV, which corresponded to C-N and N-H of the amine group on the organic linkers, respectively.[7] Concurrently, the O *1s* XPS spectrum were fitted out four peaks with binding energies of 531.4 (Al-O), 532.1 (C=O), 533.1(C-O) and 533.8 eV(O-H) for the samples MIL-101(Al/Fe)-NH_2 (*15:1*) and MIL-101(Al)-NH_2. Whereas MIL-101(Al)-NH_2 has a unique Fe-O bond at 530.6 eV which was shown in Fig. S6i. In the XPS spectrum of sample MIL-101(Al/Fe)-NH_2 (*15:1*), there is still no trace of iron due to its very little amount in the structure.

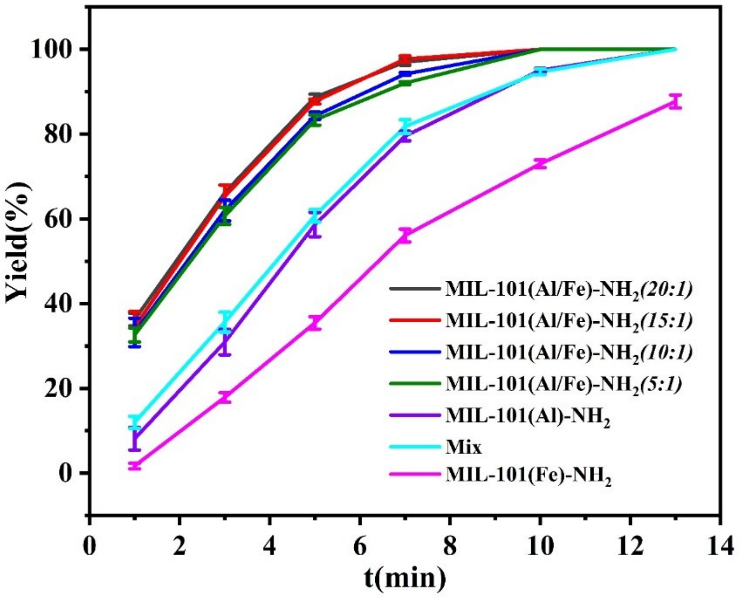

Fig. S7. The cascade reaction at 110°C.

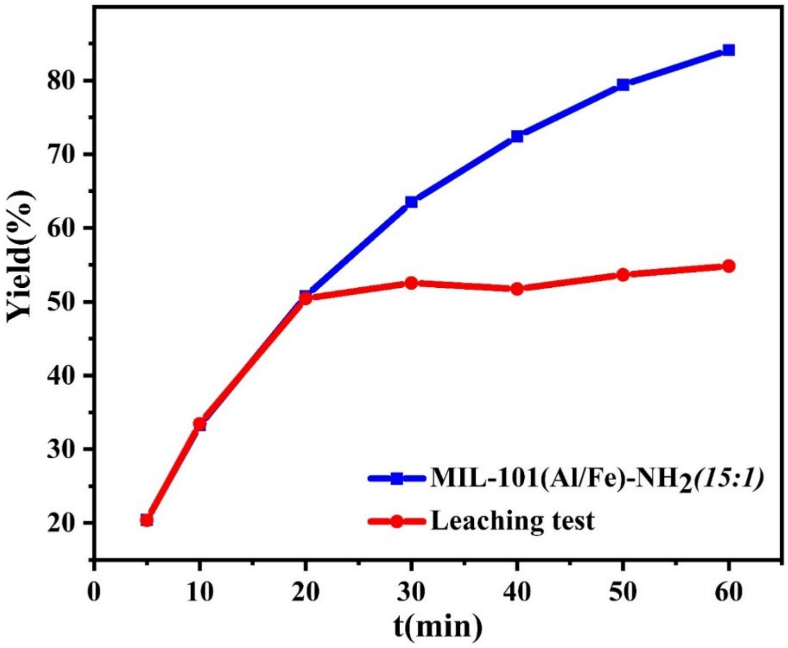

Fig. S8. The leaching test of the catalyst of MIL-101(Al/Fe)-NH_2*(15:1)*.

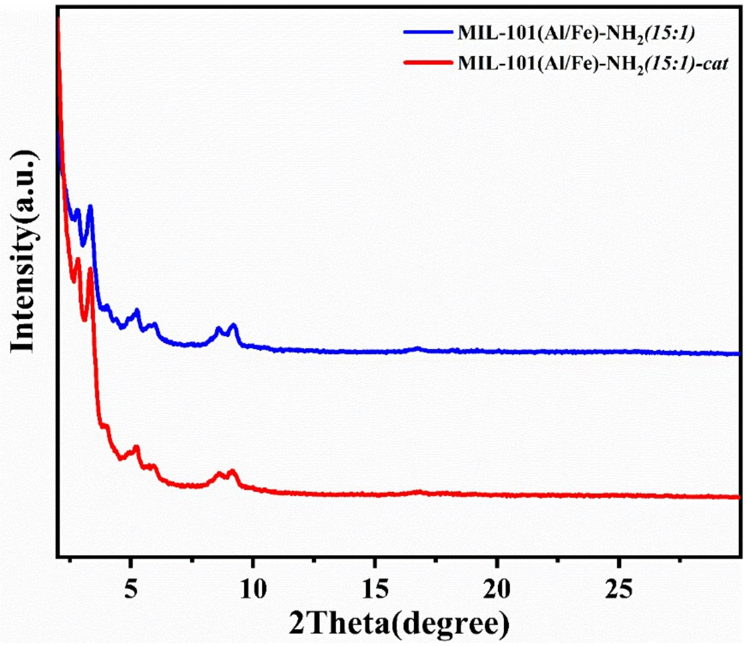

Fig. S9. The XRD of the MIL-101(Al/Fe)-NH_2 (*15:1*) and after catalyzed five cycles.

References:

1. X. Li, A. K. Tjiptoputro, J. Ding, J. M. Xue and Y. Zhu, *Catalysis Today*, 2017, **279**, 77-83.
2. T. Araya, M. Jia, J. Yang, P. Zhao, K. Cai, W. Ma and Y. Huang, *Applied Catalysis B: Environmental*, 2017, **203**, 768-777.
3. N. M. Figueiredo, N. J. M. Carvalho and A. Cavaleiro, *Applied Surface Science*, 2011, **257**, 5793-5798.
4. M.-W. Zhang, K.-Y. A. Lin, C.-F. Huang and S. Tong, *Separation and Purification Technology*, 2019, **227**.
5. L. Chi, Q. Xu, X. Liang, J. Wang and X. Su, *Small*, 2016, **12**, 1351-1358.
6. M. C. Biesinger, B. P. Payne, A. P. Grosvenor, L. W. M. Lau, A. R. Gerson and R. S. C. Smart, *Applied Surface Science*, 2011, **257**, 2717-2730.
7. J. Xu, J. Gao, Y. Qi, C. Wang and L. Wang, *ChemCatChem*, 2018, **10**, 3327-3335.