Electronic Supplementary Information

# Bi-functional $NH_2$-MIL-101(Fe) for One-Pot Tandem Photo-oxidation/Knoevenagel Condensation between Aromatic Alcohols and Active Methylene Compounds

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**Fig. S1** XRD patterns of (a) calculated MIL-101(Fe); (b) as-synthesized $NH_2$-MIL-101(Fe).

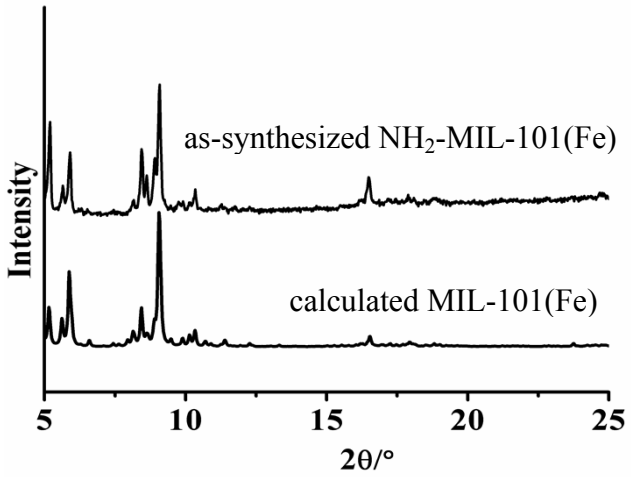

**Fig. S2** IR spectrum of fresh $NH_2$-MIL-101(Fe).

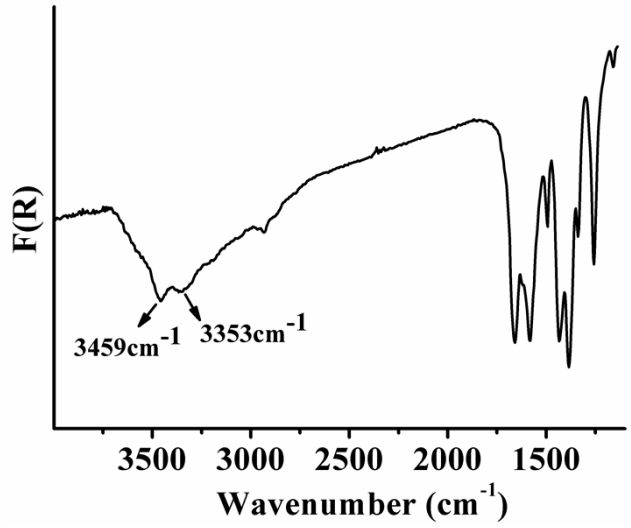

**Fig. S3** $N_2$ adsorption/desorption isotherms of fresh $NH_2$-MIL-101(Fe).

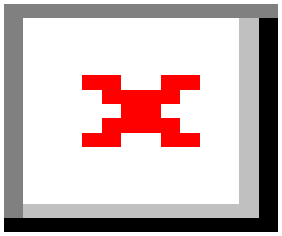

**Fig. S4** UV-vis spectrum of $NH_2$-MIL-101(Fe).

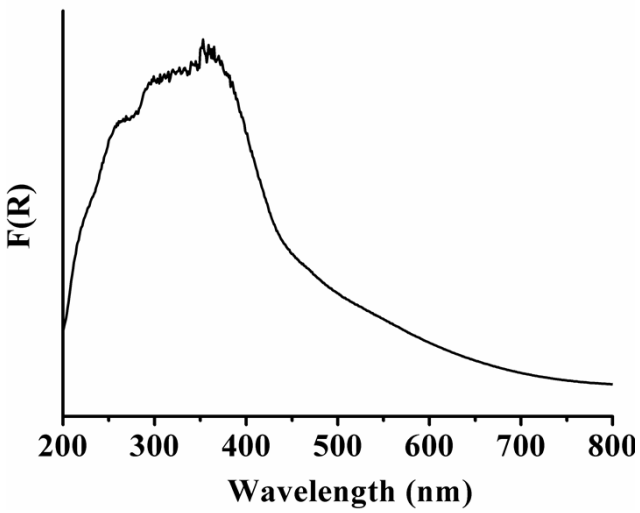

**Fig. S5** The XRD patterns of fresh and used $NH_2$-MIL-101(Fe).

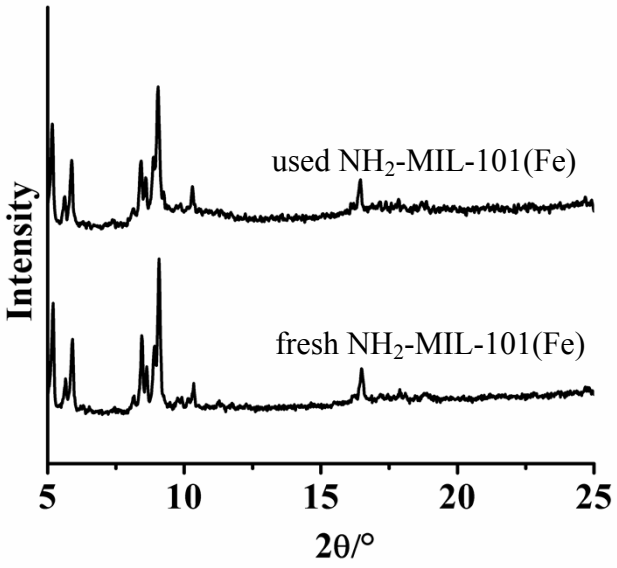

**Fig. S6** The IR spectra of fresh and used $NH_2$-MIL-101(Fe).

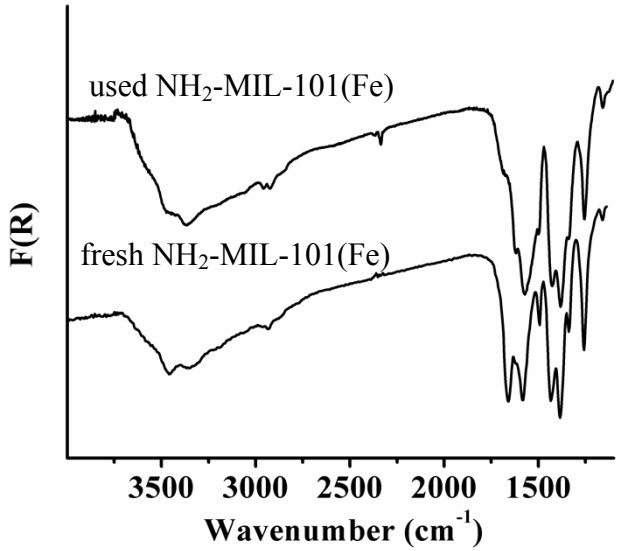

**Fig. S7** The BET of fresh and used $NH_2$-MIL-101(Fe).

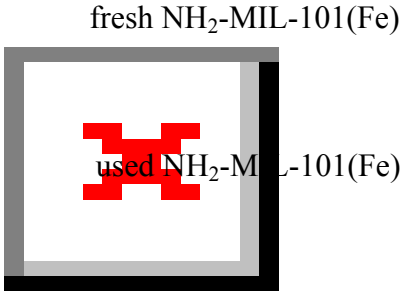

**Fig. S8**

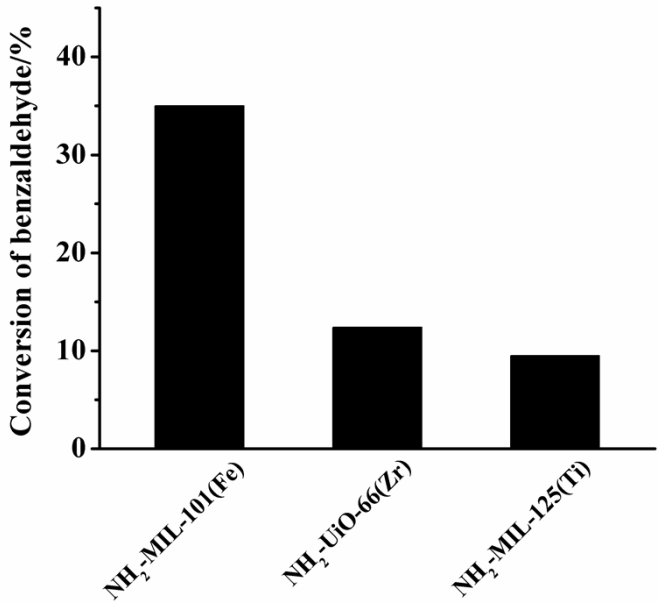
Conversion of benzaldehyde/%
0
10
20
30
40
NH2-MIL-101(Fe)
NH2-UiO-66(Zr)
NH2-MIL-125(Ti)

**Table S1** Influence of the solvent on the photocatalytic oxidation of benzyl alcohol to form benzyl aldehyde.

| entry | catalyst | solvent | conv. of alcohol (%) | selectivity (%) |
|---|---|---|---|---|
| 1 | $NH_2$-MIL-101(Fe) | benzotrifluoride | 27 | 93 |
| 2 | $NH_2$-MIL-101(Fe) | toluene | 15 | 95 |
| 3 | $NH_2$-MIL-101(Fe) | acetonitrile | 21 | 92 |
| 4 | $NH_2$-MIL-101(Fe) | B/A (10:1) | 39 | 95 |
| 5[a] | $NH_2$-MIL-101(Fe) | B/A (10:1) | 0 | 0 |
| 6[b] | No catalyst | B/A (10:1) | 0 | 0 |

Reaction conditions: benzyl alcohol (0.1mmol), solvent (3mL), catalyst (20mg), $O_2$ (1atm), light irradiation ($\lambda \geq 420$nm), 40h. [a] Without visible light irradiation. [b] No catalyst.

**Table S2** Photocatalytic oxidation of benzyl alcohol to form benzyl aldehyde over various catalysts.

| entry | catalyst | substrate | conv. of alcohol (%) | selectivity (%) |
|---|---|---|---|---|
| 1 | $NH_2$-MIL-101(Fe) | benzyl alcohol | 39 | 95 |
| 2 | $NH_2$-UiO-66(Zr) | benzyl alcohol | 28 | 91 |
| 3 | $NH_2$-MIL-125(Ti) | benzyl alcohol | 37 | 90 |

Reaction conditions: benzyl alcohol (0.1mmol), B/A (10:1, 3mL), catalyst (20mg), $O_2$ (1atm), light irradiation ($\lambda \geq 420$nm), 40h.