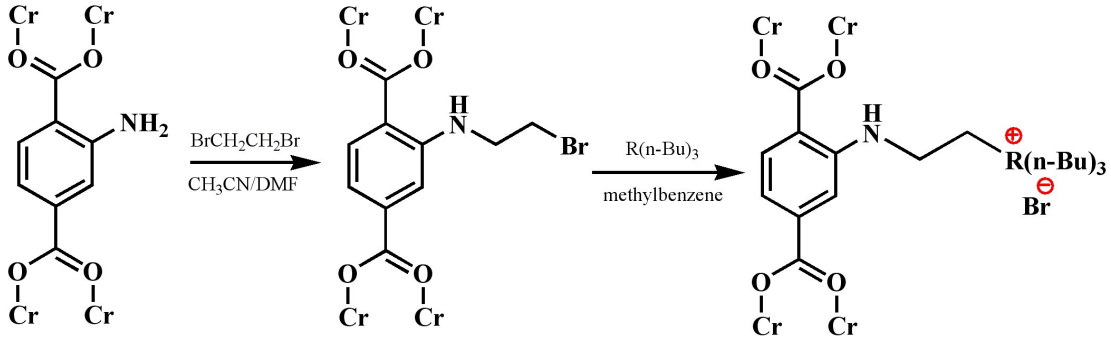
Supporting Information

Bifunctional MOF heterogeneous catalysts based on the synergy of dual functional sites for efficient conversion of CO_2 at mild and co-catalyst free conditions

Dingxuan Ma, Baiyan Li,* Kang Liu, Xianlong Zhang, Weijian Zou, Yongquan Yang, Guanghua Li, Zhan Shi,* and Shouhua Feng

1. Experimental Details



Scheme S1. The route to synthesize the catalyst MIL-101-N(n-Bu)$_3$Br and MIL-101-P(n-Bu)$_3$Br (R = N or P).

1.1 Synthesis of MIL-101-N(n-Pr)$_3$Br, MIL-101-N(n-amyl)$_3$Br, or MIL-101-N(n-hexyl)$_3$Br

100 mg MIL-101-Br was placed in a round bottomed three necked flask under a slow stream of Ar. 8 mL toluene was added and gently stirred. Then 0.3mmol of tri-n-propylamine, tri-n-amylamine or tri-n-hexylamine was added and the flask was heated to 110 ºC in an oil bath for seven days with continuous stirring under Ar. The product was recovered by filtration and washed with acetone, followed by methanol and ethyl ether. Then it was dried in air for several minutes. The resulting product was degassed at room temperature for 1 h, 50 ºC for 30 min, then 100 ºC for 1 h. The resulting solid was stored in a desiccator.

2. Characterization

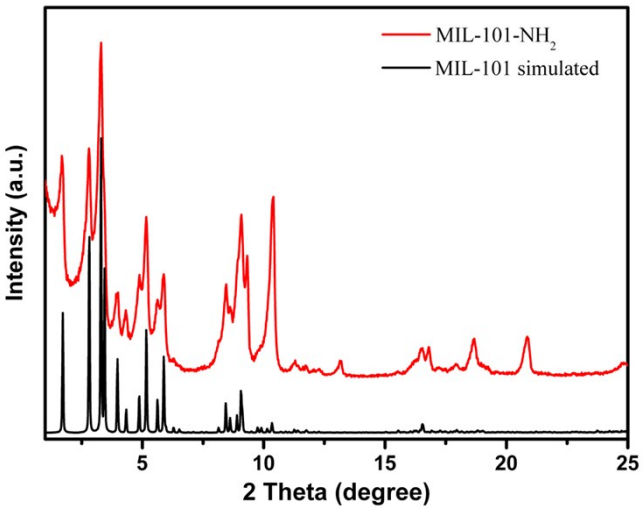


Figure S1. PXRD patterns of MIL-101-NH$_2$ and the simulated pattern for MIL-101 from ref. 1.

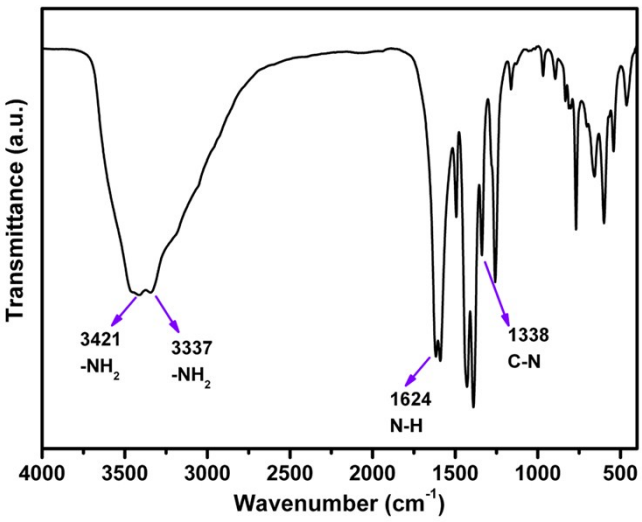


Figure S2. IR spectra of MIL-101-NH_2.[2]

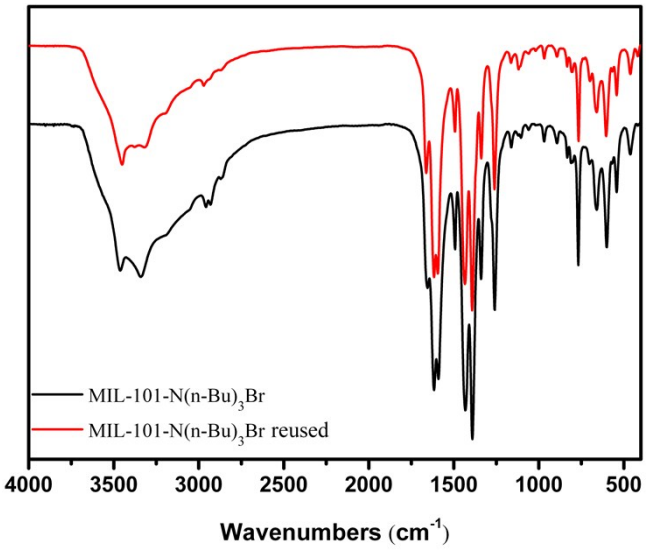


Figure S3. Comparison of IR spectra of the as-made sample MIL-101-N(n-Bu)$_3$Br and the MIL-101-N(n-Bu)$_3$Br after catalysis cycles.

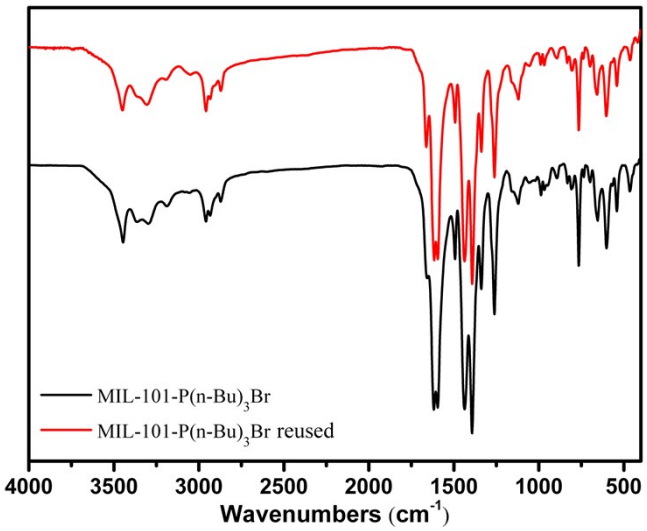


Figure S4. Comparison of IR spectra of the as-made sample MIL-101-P(n-Bu)$_3$Br and the MIL-101-P(n-Bu)$_3$Br after catalysis cycles.

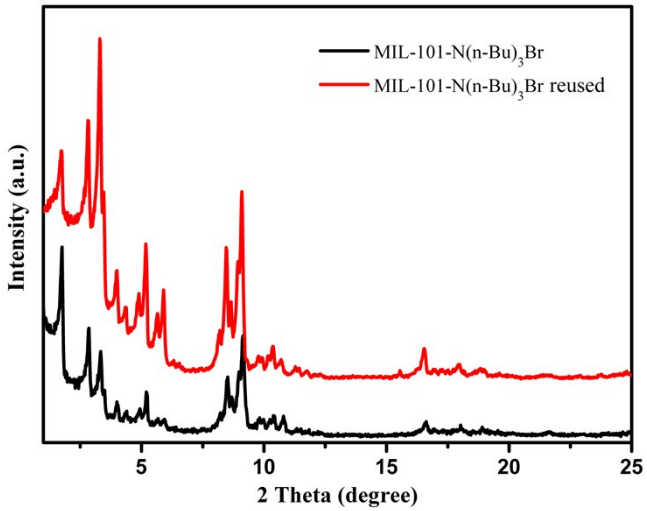


Figure S5. Comparison of PXRD patterns of the as-made sample MIL-101-N(n-Bu)$_3$Br and the MIL-101-N(n-Bu)$_3$Br after catalysis cycles.

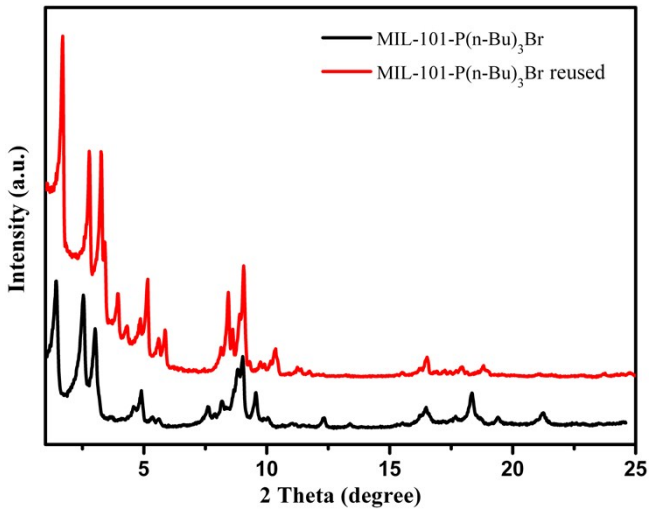


Figure S6. Comparison of PXRD patterns of the as-made sample MIL-101-P(n-Bu)$_3$Br and the MIL-101-P(n-Bu)$_3$Br after catalysis cycles.

Reference

[1] G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surblé and I. Margiolaki, *Science.,* 2005, **309**, 2040.

[2] Y. Lin, C. Kong and L. Chen, *RSC Advances.,* 2012, **2**, 6417.