Supporting Information

High volumetric uptake of ammonia using Cu-MOF-74/Cu-CPO-27

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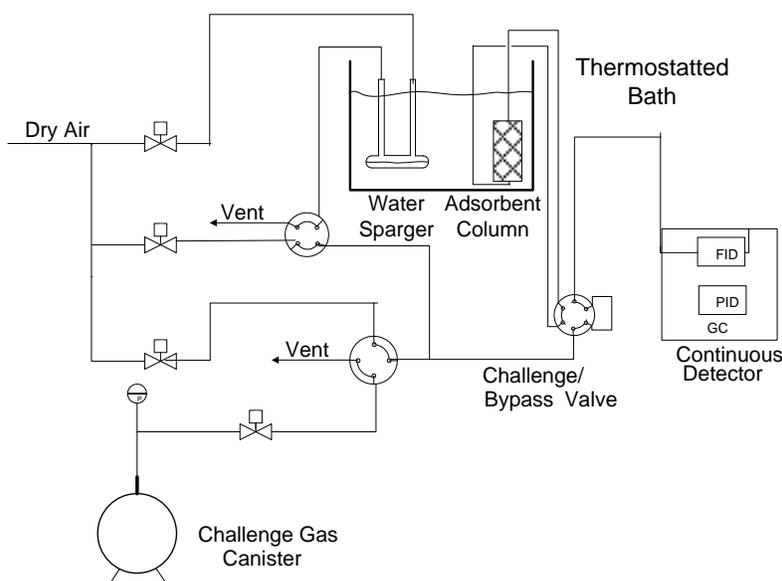
Experimental

Figure S1. Schematic of the apparatus used for ammonia breakthrough measurements
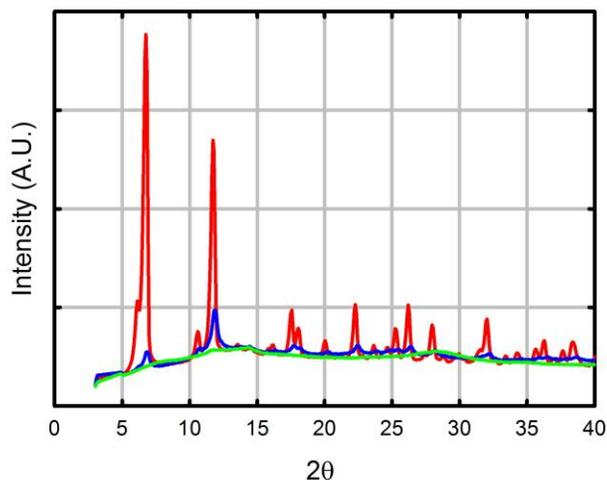
Powder X-ray Diffraction

Figure S2: Powder X-ray diffractograms of Cu-MOF-74/Cu-CPO-27 before ammonia uptake (red) after ammonia uptake at 0 % relative humidity (blue) and after ammonia uptake at 40 % relative humidity (green)

Computational Calculations

We calculated the binding energies of ammonia with M-MOF-74/M-CPO-27 (Figure S3) analogues containing different metals; M= Cu, Ni, Mg, Zn and Co. We performed DFT calculations using a representative cluster of M-MOF-74/M-CPO-27 described in our previous publication.[1] The initial atomic coordinates for the clusters were obtained from experimental crystal structures except for Cu-MOF-74/Cu-CPO-27 were the Co-MOF-74/Co-CPO-27 coordinates were used. In this cluster, the dangling bonds were terminated by –H, -CH_3 and Li. All peripheral atoms in the cluster were fixed during the geometry optimizations, whereas all other atoms and the ammonia molecule were allowed to relax. The geometry optimizations and energy calculations were performed at the M06 level of theory and the basis set of 6-31+G(d). The basis set superposition errors were corrected using the counterpoise method for all calculated binding energies. The binding energy (BE) is defined as:

$$BE_{ammonia} = E_{M\text{-}CPO\text{-}27+ammonia} - E_{M\text{-}CPO\text{-}27} - E_{ammonia}$$
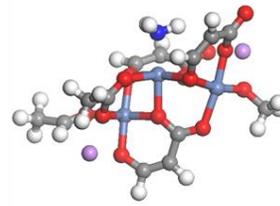
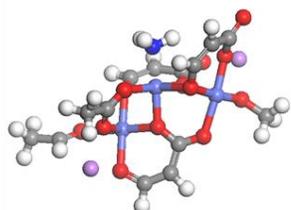where E is the electronic energy after optimization.
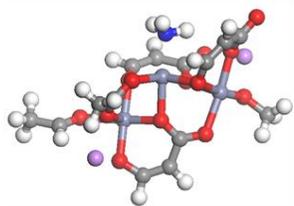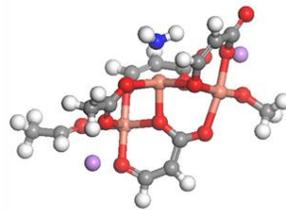
Zn BE: -120 kJ/mol
d = 2.09 Å
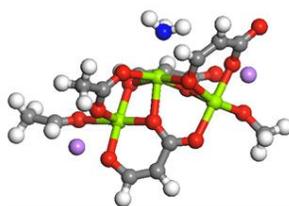
Mg BE: -116 kJ/mol
d = 2.19 Å

Ni BE: -112 kJ/mol
d = 2.04 Å

Co BE : -102 kJ/mol
d = 1.95 Å

Cu BE: -76 kJ/mol
d = 1.98 Å

Figure S3: The most stable position of an ammonia molecule binding with different metals in M-MOF-74/M-CPO-27. The numbers below each configuration represent the ammonia binding energy (BE) with the metal clusters. Red, blue, gray, white, purple spheres represent oxygen, nitrogen, carbon, hydrogen and lithium atoms, respectively.

References

1. D. Yu, A. O. Yazaydin, J. R. Lane, P. D. C. Dietzel and R. Q. Snurr, Chem. Sci., 2013, 4, 3544-3556.