

# Tuning the Ethylene Gas Adsorption via Metal Node Modulation: Cu-MOF-74 for Ethylene Storage with High Deliverable Capacity

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## ■ Supporting Information

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## Materials

All chemicals for the M-MOF-74s synthesis were used as received. Cobalt nitrate hexahydrate, nickel nitrate hexahydrate, magnesium nitrate hexahydrate, zinc nitrate hexahydrate, 2,5-dihydroxyterephthalic acid(H<sub>4</sub>dobdc), acetone, N,N-dimethylformamide, were purchased from Sigma Aldrich Chemicals Company, Inc. (Milwaukee, WI). Copper nitrate trihydrate was purchased from Alfa Aesar Company, Inc. (Haverhill, MA).

Ethylene gas used for the adsorption/desorption measurements was Ultra High Purity Grade.

## Physical Measurements

Micromeritics Tristar II 3020 (Micromeritics, Norcross, GA) were employed in measuring all N<sub>2</sub> isotherms at 77 K (~100 mg of MOF per measurement). BET surface area calculations were performed using the data points  $P/P_0 = 0.005-0.05$ . All samples were activated prior to the measurement at 120 °C overnight under high vacuum with Masterprep (Quantachrome Instruments, Boyton Beach, FL).

Dynamic gas sorption was collected on a Hiden Isochema Intelligent gravimetric analyzer (IGA-200) equipped with water bath adjusted to 298 K. All ethylene isotherms were recorded using IGASwin software (v1.06) by monitoring the mass change at any given absolute pressure point. The gas flow rate was controlled to be at 100 cc/min.

Rigaku Smartlab (Tokyo, Japan) was used in collecting all powder X-ray diffraction patterns with a  $2\theta = 0.05^\circ$  scan rate over 3-40° range at 45 kV and 160 mA.

## Synthesis of M-MOF-74s

*Co-MOF-74*: The following synthesis is based on the previously reported procedure.<sup>1</sup> 2.377 g of cobalt nitrate hexahydrate (8.67 mmol) and 482 mg of H<sub>4</sub>dobdc (2.43 mmol) were added to a 1:1:1 (v/v/v) DMF-ethanol-water mixture (total volume of 200 mL) in a 500 mL screw cap jar. The mixture was sonicated until complete solvation of the precursors. The solution was capped tightly and was placed in a 100 °C oven for 24 hours. The sample was left at room temperature for cooling prior to decantation of the mother liquor, followed by addition of 200 mL of methanol four times over two days. The solvent was removed by pulling dynamic vacuum at 250 °C for 5 hours, resulting in dark red crystals.

*Ni-MOF-74*: The following procedure is a minor modification to the reported protocol.<sup>2</sup> 0.602 g of

nickel nitrate hexahydrate (2.04 mmol) and 120 mg of H<sub>4</sub>dobdc (0.60 mmol) were added to 15:1:1 (v/v/v) DMF-ethanol-water mixture (total volume of 50 mL) in a 100 mL screw cap jar. The mixture was sonicated until complete solvation of the precursors. The solution was capped tightly and was placed in a 100 °C oven for 24 hours. The mother liquor was decanted while hot and was washed with 30 mL of fresh DMF for three times and was subsequently replaced with 30 mL of methanol for three times. At the last wash, methanol was left overnight to assure complete solvent exchange. After filtration, the sample was placed in a vacuum oven at 80 °C oven overnight prior to activation at 250 °C for six hours.

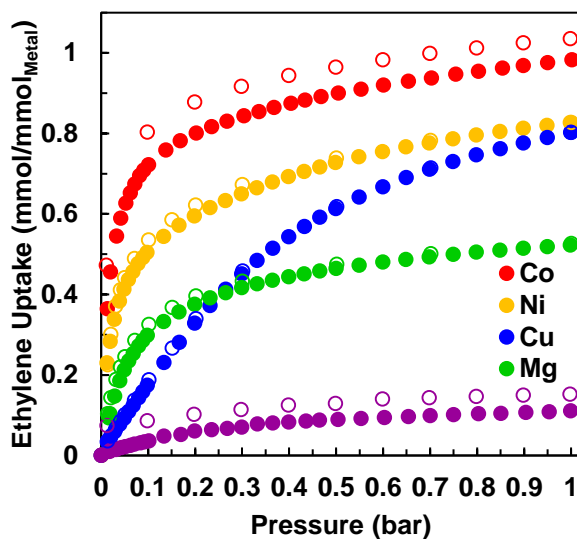
*Cu-MOF-74*: 2.20 g of 2,5-dihydroxyterephthalic acid (11.2 mmol) and 5.9 g of copper nitrate trihydrate (24.6 mmol) were dissolved in 250 mL of 20:1 (v/v) solution of N,N-dimethylformamide (DMF) and 2-propanol in a 1 L screw cap bottle. The suspension was sonicated for approximately 10 minutes until a homogenous solution was achieved and then placed in an oven at 80 °C for 18 hours. The sample was cooled down to room temperature and the supernatant solution was decanted. The reddish needle-shaped crystals were washed with DMF and solvent exchanged with methanol 4 times over a 48 h period. The sample was activated at 150 °C for overnight.

*Zn-MOF-74*: The following procedure is a minor modification to the reported protocol.<sup>3</sup> 1.021 g of zinc nitrate hexahydrate (3.43 mmol) and 250 mg of H<sub>4</sub>dobdc (1.30 mmol) were added to 50 mL of DMF and 3 mL of water in a 100 mL screw cap jar. The mixture was sonicated until complete solvation of the precursors. The solution was capped tightly and was placed in a 100 °C oven for 24 hours. The mother liquor was decanted after cooling to room temperature and washed with 30 mL of fresh DMF for three times and was subsequently replaced with 30 mL of methanol for three times. At the last wash, methanol was left overnight to assure complete solvent exchange. After filtration, the sample was placed in a vacuum oven at 80 °C oven overnight prior to activation at 250 °C for six hours.

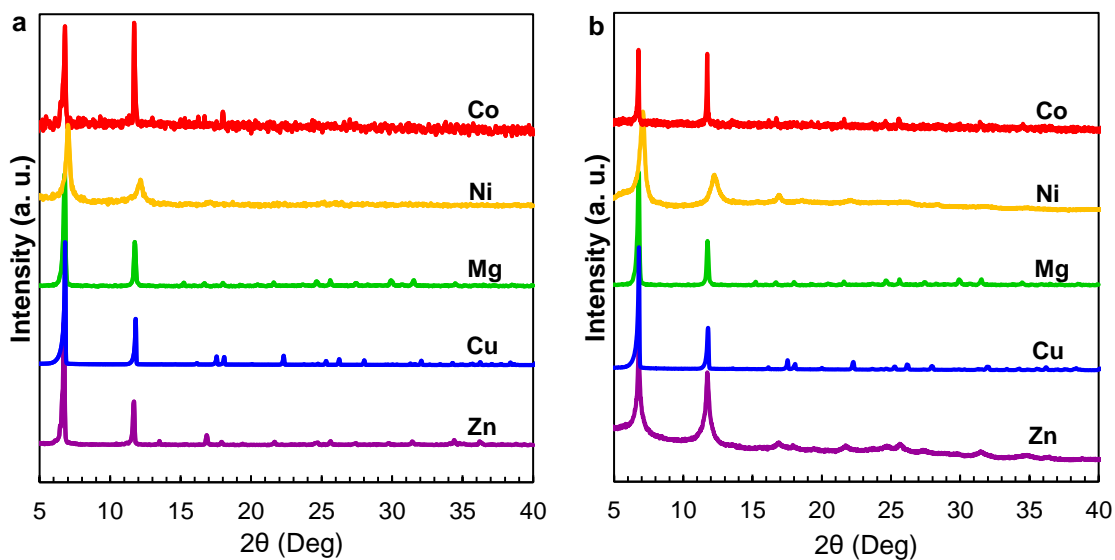
*Mg-MOF-74*: The following procedure is a minor modification to the reported protocol.<sup>1</sup> 0.476 g of magnesium nitrate hexahydrate (1.85 mmol) and 111 mg of H<sub>4</sub>dobdc (0.56 mmol) were added to 15:1:1 (v/v/v) DMF-ethanol-water mixture (total volume of 50 mL) in a 100 mL screw cap jar. The mixture was sonicated until complete solvation of the precursors. The solution was capped tightly

and was placed in a 125 °C oven for 24 hours. The mother liquor was decanted after cooling to room temperature and washed with 30 mL of fresh DMF once and was subsequently replaced with 30 mL of methanol for three times. At the last wash, methanol was left overnight to assure complete solvent exchange. After filtration, the sample was placed in a vacuum oven at 80 °C overnight prior to activation at 250 °C for six hours.

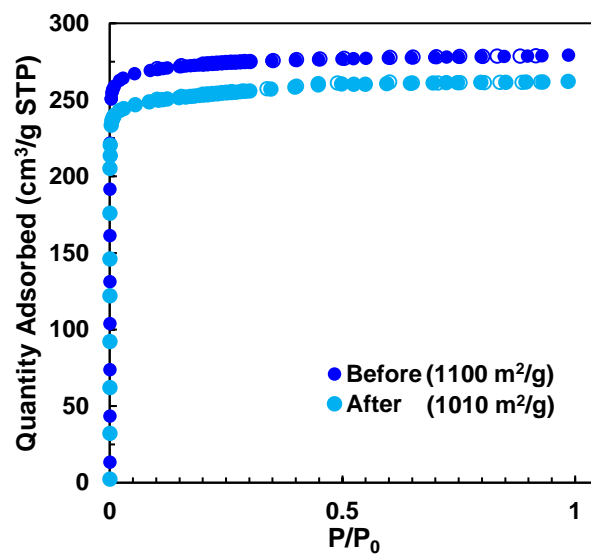
## Characterization



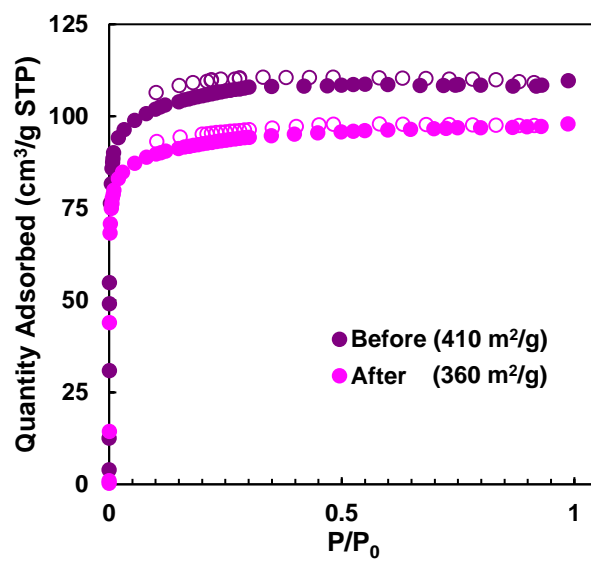
**Figure S1.** Ethylene isotherms of M-MOF-74 normalized with moles of metal sites. The filled and empty symbols represent adsorption and desorption, respectively.



**Figure S2.** PXRD patterns of M-MOF-74s a) before and b) after the ethylene uptakes.



**Figure S3.** N<sub>2</sub> isotherms and BET surface areas of Cu-MOF-74s before and after ethylene uptakes.



**Figure S4.** Typical N<sub>2</sub> isotherms and BET surface areas of Zn-MOF-74s before and after ethylene uptakes.

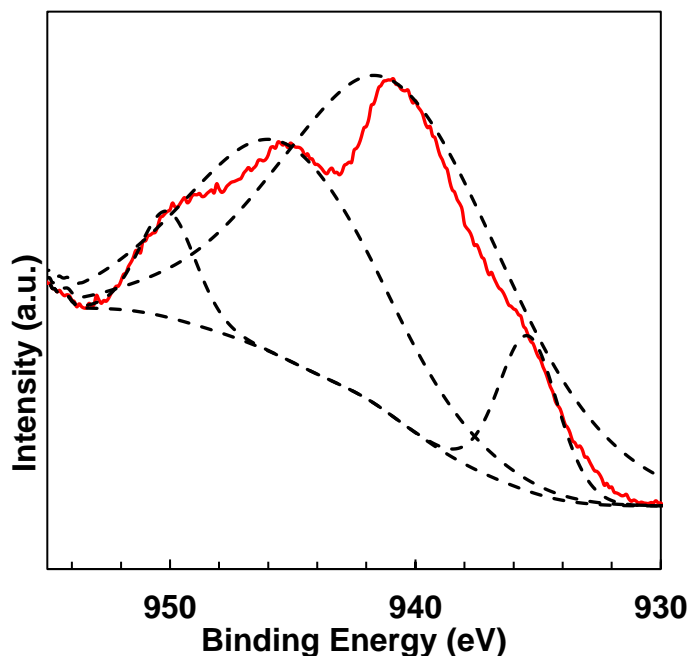


Figure S5. XPS spectrum of Cu-MOF-74 at Cu 2p region.

### Calculation of Isothermic Heats of Adsorption

The virial equation was used to calculate the isothermic heats of adsorption of ethylene on Co(Cu)-MOF-74 at 298 K, 308 K, and 318 K. The virial equation can be written as following:

$$\ln p = \ln n + \frac{1}{T} \sum_{i=0}^M a_i n^i + \sum_{i=0}^N b_i n^i$$

where  $n$  is the amount adsorbed (mmol/g),  $p$  is the adsorption pressure (Torr),  $T$  is the adsorption temperature (K),  $a_i$  and  $b_i$  are temperature independent empirical parameters, and  $M$  and  $N$  determine the number of terms required to adequately describe the isotherms.<sup>4,5</sup>

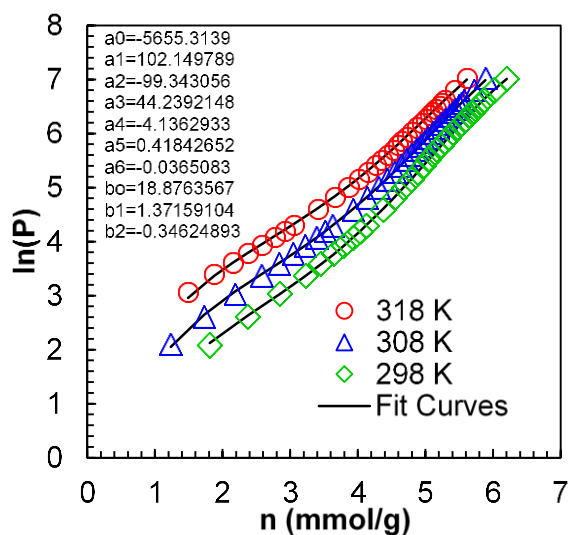
The isothermic heats of adsorption  $Q_{st}$  (kJ/mol) can be calculated by the resulting virial coefficients  $a_0$  through  $a_M$  with the following equation.

$$Q_{st} = -R \sum_{i=0}^M a_i n^i$$

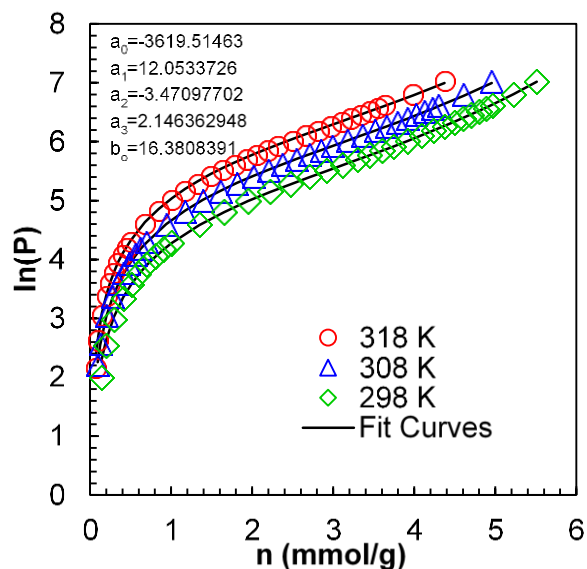
where  $R$  is the universal gas constant (8.314E-3 kJ/(mol • K)).

The isosteric heats of adsorption at zero-coverage (loading independent) is given by

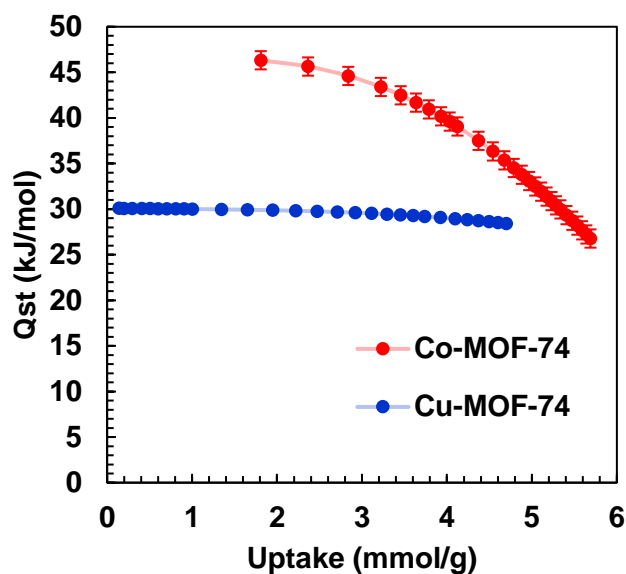
$$Q_{st} = -Ra_0$$



**Figure S6.** Experimental data (symbol) and corresponding fittings (solid line) of  $C_2H_4$  adsorption isotherms of Co-MOF-74 at 298 K, 308 K, and 318 K. Fit curves are obtained by the virial-type expansion.



**Figure S7.** Experimental data (symbol) and corresponding fittings (solid line) of  $C_2H_4$  adsorption isotherms of Cu-MOF-74 at 298 K, 308 K, and 318 K. Fit curves are obtained by the virial-type expansion.



**Figure S8.** Isosteric heats adsorption,  $Q_{st}$  of  $C_2H_4$  for Co-MOF-74 and Cu-MOF-74.  $Q_{st}$  values are calculated using experimental points only without any extrapolation. The lowest pressure achieved for Co-MOF-74 is about 8 Torr where the uptake is about 1.8 mmol/g.

#### References:

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