Phosphine Gas Adsorption in a Series of Metal-Organic Frameworks

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Supporting Table

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Section S-1: General Procedure

All reagents and solvents unless otherwise stated were obtained from commercial sources (Alfa Aesar and Sigma Aldrich) and were used without further purification. The 1.5 mm glass capillary tubes used to load Powder X-ray diffraction (PXRD) samples were purchased from Hampton Research. All experiments, including MOF synthesis, nitrogen isotherms, and phosphine isotherms, were performed at NuMat Technologies. PXRD measurements were performed at Northwestern University.

Section S-2: Synthesis of MOFs

Synthesis of MOF-5

Zinc nitrate hexahydrate (4.50 g, 15 mmol) and 1,4-benzenedicarboxylic acid (0.830 g, 5 mmol) were dissolved in 500 mL of 49:1 (v/v) solution of N,N-dimethylformamide (DMF) and H$_2$O. The solution was evenly distributed between forty 30 mL vials. The vials were placed in an oven at 85 °C for 12 h. The sample was cooled down to room temperature and the supernatant solution
was decanted. The clear cubic crystals were washed with DMF and solvent exchanged with dichloromethane three times each over a 72 h period. The samples were activated at 150 °C to yield MOF-5 (Zn₄O(C₈H₄O₄)₃).

**Synthesis of MOF-74**

**Cu-MOF-74**

2,5-dihydroxyterephthalic acid (2.20 g, 11.2 mmol) and copper nitrate (II) trihydrate (5.9 g, 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 h. 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 using Soxhlet extraction in methanol for 12 hours. The sample was activated at 150 °C under vacuum (10⁻² torr) to yield Cu-MOF-74 (Cu₂(C₈H₂O₆)).

**Co-MOF-74**

2,5-dihydroxyterephthalic acid (1.45 g, 7.30 mmol) and cobalt nitrate (II) hexahydrate (7.13 g, 24.5 mmol) were dissolved in 600 mL of 1:1:1 (v/v/v) solution of DMF, EtOH, and H₂O in a 1L screw cap bottle. The suspension was sonicated until a homogenous solution was achieved and placed in an oven at 100 °C for 18 h. The sample was cooled down to room temperature and the supernatant solution was decanted. Then, the crystals were washed with DMF and solvent exchanged using Soxhlet extraction in methanol for 12 hours. The sample was activated at 250 °C under vacuum (10⁻² torr) to yield Co-MOF-74 (Co₂(C₈H₂O₆)).

**Mn-MOF-74**

2,5-dihydroxyterephthalic acid (2.0 g, 10.1 mmol) and manganese chloride (II) tetrahydrate (6.59 g, 33.3 mmol) were dissolved in 900 mL of 15:1:1 (v/v/v) solution of DMF, EtOH and H₂O in a 1L screw cap bottle. The suspension was sonicated until a homogenous solution was achieved and placed in an oven at 135 °C for 18 h. The sample was cooled down to room temperature and the supernatant solution was decanted. Then, the crystals were washed with DMF and solvent exchanged using Soxhlet extraction in methanol for 12 hours. The sample was activated at 150 °C under vacuum (10⁻² torr) to yield Mn-MOF-74 (Mn₂(C₈H₂O₆)).
using Soxhlet extraction in methanol for 12 hours. The sample was activated at 150 °C under vacuum (10⁻² torr) to yield Mn-MOF-74 (Mn₂(C₈H₂O₆)).

**Mg-MOF-74**

2,5-dihydroxyterephthalic acid (2.0g, 10.1 mmol) and magnesium nitrate (II) hexahydrate (8.55g, 33.3 mmol) were dissolved in 900mL of 15:1:1 (v/v/v) solution of DMF, EtOH and H₂O in a 1L screw cap bottle. The suspension was sonicated until a homogenous solution was achieved and placed in an oven at 125 °C for 18 hrs. The sample was cooled down to room temperature and the supernatant solution was decanted. Then, the crystals were washed with DMF and solvent exchanged using Soxhlet extraction in methanol for 12 hours. The sample was activated at 150 °C under vacuum (10⁻² torr) to yield Mg-MOF-74 (Mg₂(C₈H₂O₆)).

**Section S-3: Powder X-ray Diffraction**

PXRD experiments were conducted at the Jerome B. Cohen X-ray Diffraction Facility located at Northwestern University using the 18 kW Rigaku ATX-G Thin-film Diffraction Workstation. The samples were analyzed over a two theta range of 2 to 30 degrees and with a scan rate of 8 degrees/min.
Figure S1. PXRD of MOF-5 (Blue, experimental; Red, simulated)
Figure S2. PXRD of Cu-MOF-74 (Blue, experimental; Red, simulated)
Figure S3. PXRD of Co-MOF-74 (Blue, experimental; Red, simulated)
Figure S4. PXRD of Mg-MOF-74 (Blue, experimental; Red, simulated)
Section S-4: Nitrogen Isotherms

All N₂ gas adsorption and desorption measurements, unless stated otherwise, were performed on the Micromeritics Tristar II 3020 system (Micromeritics, Norcross, GA) at 77 K. Between 75-200 mg of samples were employed in each measurement. The specific surface areas for N₂ were calculated using the Brunauer-Emmet-Teller (BET) model in the range of 0.005 < P/P₀ < 0.05.

Figure S5. PXRD of Mn-MOF-74 (Blue, experimental; Red, simulated)
Figure S6. Nitrogen isotherm of Activated Carbon (Closed, adsorption; Open, desorption)

Figure S7. Nitrogen isotherm of MOF-5 (Closed, adsorption; Open, desorption)
**Figure S8.** Nitrogen isotherm of Cu-MOF-74 (Closed, adsorption; Open, desorption)

**Figure S9.** Nitrogen isotherm of Co-MOF-74 (Closed, adsorption; Open, desorption)
Figure S10. Nitrogen isotherm of Mg-MOF-74 (Closed, adsorption; Open, desorption)

Figure S11. Nitrogen isotherm of Mn-MOF-74 (Closed, adsorption; Open, desorption)
Figure S12. Nitrogen isotherm of MOF-5 after phosphine desorption (Closed, adsorption; Open, desorption)

Figure S13. Nitrogen isotherm of Co-MOF-5 after phosphine desorption (Closed, adsorption; Open, desorption)
**Figure S14.** Nitrogen isotherm of Mn-MOF-5 after phosphine desorption (Closed, adsorption; Open, desorption)

**Table S1.** BET Surface Area of MOF-5, M-MOF-74 (M=Cu, Co, Mg, Mn) after i) activation, ii) first phosphine isotherm and room temperature activation under $10^{-2}$ vacuum, iii) second phosphine isotherm and 150 °C activation under $10^{-2}$ vacuum

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**Section S-6. Phosphine Isotherm**

All Phosphine adsorption and desorption measurements were performed at 22 °C on a Micromeritics 3Flex Surface Characterization Analyzer (Micromeritics, Norcross, GA). The first run was activated as reported in the procedure (Section S-2). The second run was reactivated at 22 °C. The third run was reactivated at 150 °C.
**Figure S15.** Phosphine isotherm of Activated Carbon (Closed, adsorption; Open, desorption)

**Figure S16.** Phosphine isotherm of MOF-5 (Closed, adsorption; Open, desorption)
Figure S17. Phosphine isotherm of Cu-MOF-74 (Closed, adsorption; Open, desorption). Insert shows isotherm at pressures up to 0.1 P/P₀.

Figure S18. Phosphine isotherm of Co-MOF-74 (Closed, adsorption; Open, desorption). Insert shows isotherm at pressures up to 0.1 P/P₀.
**Figure S19.** Phosphine isotherm of Mg-MOF-74 (Closed, adsorption; Open, desorption). Insert shows isotherm at pressures up to 0.1 P/P₀.

**Figure S20.** Phosphine isotherm of Mn-MOF-74 (Closed, adsorption; Open, desorption). Insert shows isotherm at pressures up to 0.1 P/P₀.
**Figure S21.** Second run of Phosphine isotherm of MOF-5 (reactivated at room temperature) (Closed, adsorption; Open, desorption)

**Figure S22.** Second run of Phosphine isotherm of Co-MOF-74 (reactivated at room temperature) (Closed, adsorption; Open, desorption)
Figure S23. Third run of Phosphine isotherm of Co-MOF-74 (reactivated at 150 °C) (Closed, adsorption; Open, desorption)

Figure S24. Second run of Phosphine isotherm of Mn-MOF-74 (reactivated at room temperature) (Closed, adsorption; Open, desorption)