

Supporting Information

Spectroscopic and Reactive Characterization of Mixed-Metal Fe-Cr Trimer Nodes in Metal-Organic Framework MIL-100

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S1. Experimental Procedures

S1.1. MIL-100(Fe) and MIL-100(Cr) Synthesis

MIL-100(Fe) and MIL-100(Cr) were synthesized and thoroughly characterized in previous work,^{1,2} following synthesis protocols adapted, respectively, from Zhang *et al.*³ and Mao *et al.*⁴ Characterization results for both materials are presented in this work as a comparison to bimetallic (Fe and Cr) materials analyzed herein.

S1.2. Mixed Fe-Cr MIL-100 Synthesis

Mixed metal MIL-100 samples of various Fe and Cr content were synthesized by adapting a low temperature, ambient pressure synthesis route previously reported for the synthesis of MIL-100(Fe) by Zhang *et al.*³ Fe(NO₃)₃·9H₂O (Alfa Aesar, > 98%) and Cr(NO₃)₃·9H₂O (Thermo Scientific Chemicals, ≥ 98.5%) were combined in various molar ratios - 0.75Fe:0.25Cr, 0.50Fe:0.50Cr, 0.25Fe:0.75Cr - at a total mass of 16.16 g and mixed with 7.56 g of trimesic acid (Alfa Aesar, 98%) and 24 mL deionized water (18.3 MΩ) in a 250 mL round-bottom flask. The synthesis mixture was mixed at 600 rpm for 14 hours at 368 K in an oil bath. Next, the produced material was washed alternately with deionized water and ethanol (Decon Laboratories Inc., 200 Proof) in 160 mL quantities at 343 K for a total of three washes with each respective solvent. The solid sample was separated from fresh ethanol by centrifugation (4000 rpm, 3 minutes) and allowed to dry overnight at 348 K to remove excess solvent. Lastly, the samples were dried at 423 K in a vacuum oven (MTI Corporation, P < 3 x 10⁻³ bar) for 10 hours. The mixed-metal series of MIL-100 samples are denoted using the following nomenclature: MIL-100(XFe,YCr), where X and Y are the percentage of Fe and Cr, respectively, per total metal, used for the synthesis of the material, not the final composition of the synthesized MOFs.

SI.3. Materials Characterization

N₂ physisorption experiments were conducted with a Micromeritics 3Flex Surface Characterization system. Prior to analysis, 0.05 g of sample was treated at 423 K for 15 hours under vacuum ($P \sim 10^{-4}$ bar) using a Micromeritics VacPrep degassing unit. Powder X-ray diffraction (XRD) data were collected with an Empyrean Malvern Panalytical diffractometer with a Cu K α X-ray source ($\lambda = 1.54$ Å). Materials were prepared for analysis in glass sample holders (Rigaku, 0.2 mm indentation) with approximately 0.02 g of sample. Diffraction patterns were collected at a step size of 0.013° and scan rate of 23.8 s per step in the range of 2.5 – 20°. Inductively coupled plasma – optical emission spectrometry (ICP-OES) measurements (Agilent 725; Department of Earth and Atmospheric Sciences at the University of Houston). X-ray photoelectron spectroscopy (XPS) measurements were completed with a Physical Electronics PHI 5800 ESCA system equipped with an Al K α X-ray source (1486.6 eV) in the Department of Chemistry at the University of Houston. Calibration of the XPS data was completed by shifting the C 1s binding energy to 284.6 eV.

SI.4. In-Situ Infrared Spectroscopy Experiments

Fourier-transmission infrared (FT-IR) spectroscopy measurements were conducted on a Nicolet iS50 FT-IR Spectrometer (Thermo Scientific) using a Harrick Dewar Transmission/Reflection Accessory stainless steel in-situ analysis cell. Spectra were collected averaging 64 scans at 4 cm⁻¹ resolution in the range of 720-4000 cm⁻¹ using a deuterated triglycine sulfate (DTGS) detector. The temperature of the samples was monitored using a built-in K-type thermocouple placed near the sample holder and was regulated by a temperature controller (Harrick, 110V). Analysis of the infrared spectra of as-synthesized MIL-100 samples was conducted at 298 K under N₂ flow

(Matheson, Ultra High Purity, 100 mL min⁻¹) after purging for a minimum of 6 hours and using the spectra of the empty cell under the same conditions as a background reference for all spectra.

For in-situ characterization of NO adsorption, samples were first thermally activated at 523 K under a 50 mL min⁻¹ N₂ flow for 15 hours. Next, samples were cooled to 473 K and allowed to dwell at the adsorption temperature for 1 hour. Spectra of the sample at 473 K were used as a background reference prior to adsorption measurements. NO (Matheson, Research Grade) was introduced at 0.003 kPa at 473 K and minimum of 0.5 h was allowed for complete saturation to occur at this condition. Samples were then cooled under NO flow to 313 K and spectra measured under this condition.

SI.5. Steady State CO Oxidation with N₂O

Catalytic experiments for the oxidation of CO with N₂O were conducted using a reactor system described previously for kinetic measurements.⁵ Briefly, approximately 0.2 g of sample (180 – 425 μm particles) were loaded and supported by quartz wool (CE Elantech) within a stainless steel tube and mounted vertically within a single-zone furnace (1060 W/115 V, Applied Test System Series 3210). The temperature of the sample was determined by a K-type thermocouple placed at the top of the catalyst bed. Thermal pretreatment of the samples was conducted at 523 K for 12 hours under He (Matheson, Ultra High Purity) flow (50 mL min⁻¹). Reaction feeds of N₂O (Matheson, Research Purity) and CO (Matheson, Ultra High Purity) in He carrier were fed to the catalyst bed at 473 K for reaction at constant total flow rates of 65 mL min⁻¹.

SI.6. Stoichiometric N₂O Reaction Measurements

The stoichiometric reaction of N₂O over the activated catalyst samples was conducted at 473 K using 64 kPa N₂O in Helium with Ar as an internal standard at a total flow rate of 65 mL min⁻¹. At the start of the measurements (t = 0 minutes), the reactant mixture was introduced to the catalyst

bed and the transient N_2 formation profile was monitored using an online mass spectrometer (MKS Cirrus 2) located at the outlet of the reactor. The cumulative quantity of N_2 formed ($\text{mol g}_{\text{catalyst}}^{-1}$) was used as a representation of the total available active site density in this material, assuming one mole of N_2 is formed per mole active center.

S1.7. NO Breakthrough Adsorption Measurements

NO breakthrough adsorption measurements were conducted using the reactor system described in Section 2.5. Thermally activated samples were exposed to 0.003 kPa NO (1000 ppm NO/ N_2 gas mixture, Research Grade) in He (Matheson, Ultra High Purity) at 473 K and the quantity of NO adsorbed was measured by a mass spectrometer through comparison of the breakthrough curve for NO with respect to Ar (internal standard).

S2. Supplementary Results and Discussion

S2.1. XRD and N_2 Physisorption Results

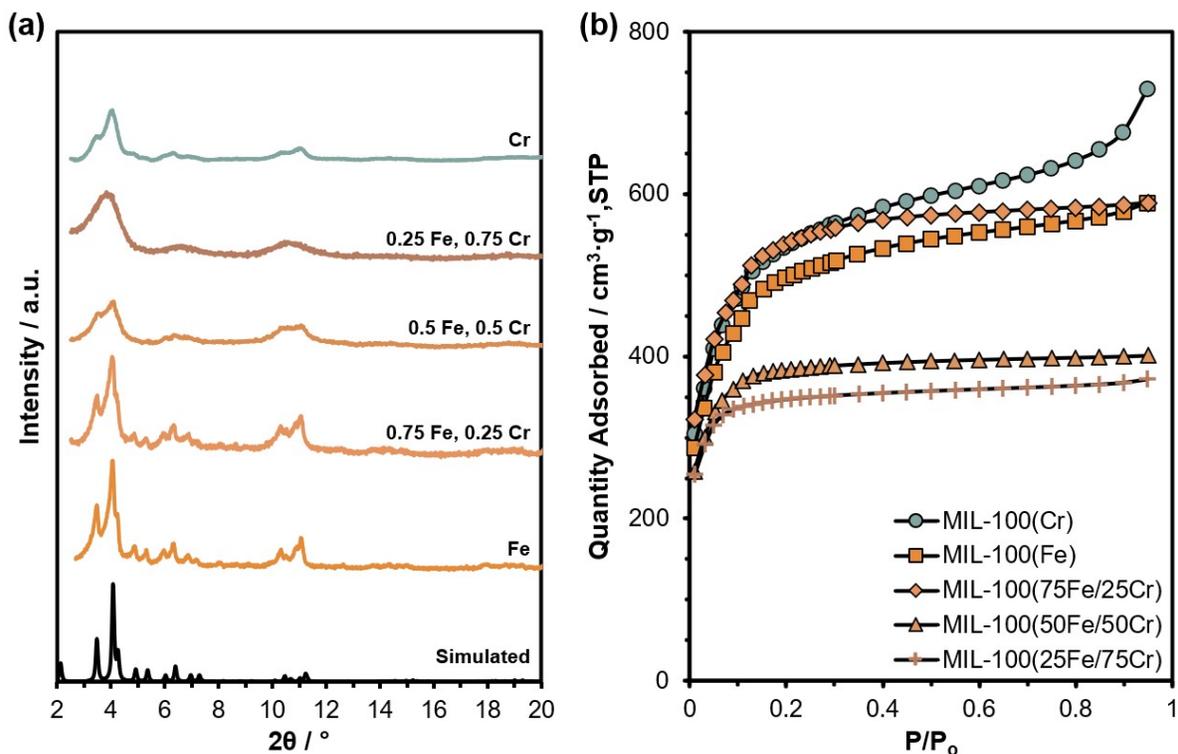


Figure S1. (a) N_2 physisorption isotherms (77 K) and (b) powder X-ray diffraction patterns for MIL-100 samples synthesized with various molar ratios of Fe and Cr.

S2.2. Target/Measured Fe-Cr Compositions in MIL-100(Fe,Cr)

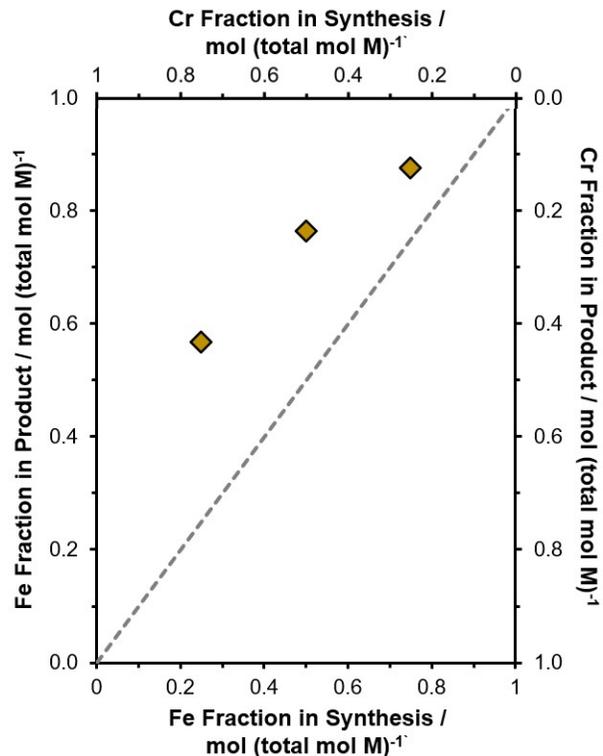


Figure S2. Comparison of the iron and chromium fractions (mol (total mol M)⁻¹) used in the synthesis of mixed-metal MIL-100(Fe/Cr) samples and that in the final material, as estimated by ICP-OES.

S2.3. XPS Peak Fitting for MIL-100(Fe) and MIL-100(Cr)

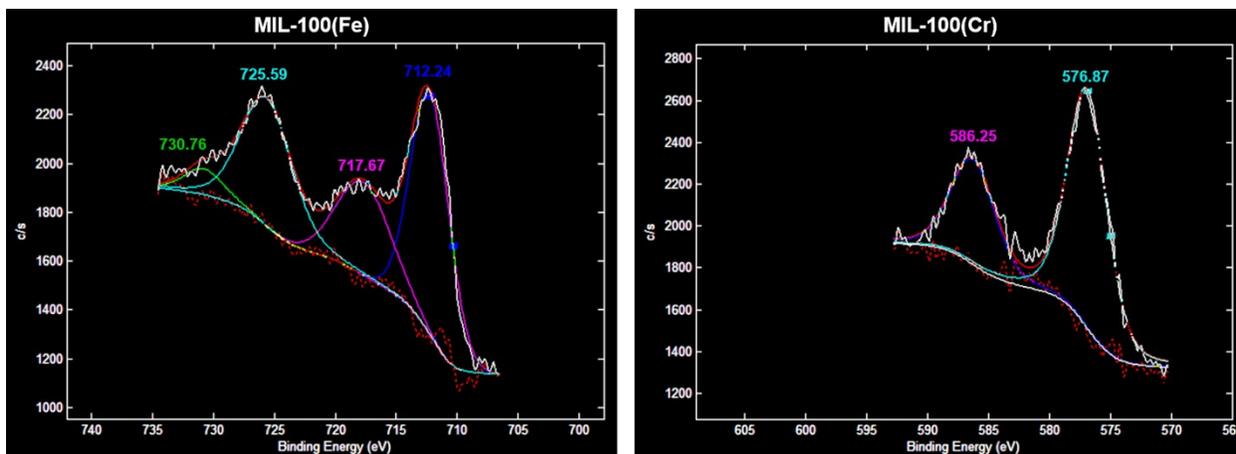


Figure S3. Fe2p and Cr2p spectral lines in the XPS spectra of MIL-100(Fe) and MIL-100(Cr), respectively.

S2.4. Schematic of M_3O Vibrational Modes

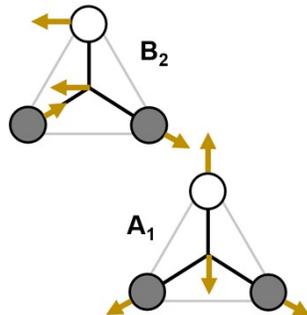


Figure S4. A_1 and B_2 asymmetric vibrational modes of the M_3O units in MIL-100.

S3. References

- 1 J. N. Hall and P. Bollini, *Chem. Eur. J.*, 2020, **26**, 16639–16643.
- 2 J. N. Hall and P. Bollini, *AIChE J.*, 2021, **67**, e17496.
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- 4 Y. Mao, H. Qi, G. Ye, L. Han, W. Zhou, W. Xu and Y. Sun, *Microporous Mesoporous Mater.*, 2019, **274**, 70–75.
- 5 J. N. Hall, A. J. Kropf, M. Delferro and P. Bollini, (*under review*).