Supporting Information

Enabling Access to Reduced Open-Metal Sites in MOF Materials through Choice of Anion Identity: The Case of MIL-100(Cr)

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Table of Contents

S1. Experimental Methods

S1.1. Synthesis of MIL-100(Cr)

MIL-100(Cr) was synthesized by adapting a reported procedure.[1] $CrCl_3 \cdot 6H_2O$ (9 g, Sigma Aldrich, ≥ 98.0%) and trimesic acid (3.55 g, Alfa Aesar, 98%) were ground with a mortar and pestle for approximately 30 minutes at room temperature. The mixture was then heated at 493 K for 15 h in a 45 mL PTFE-lined stainless steel autoclave (Parr Instruments) under rotation. The resulting product was washed with 500 mL of deionized water (18.3 MΩ) and 500 mL of ethanol at 343 and 338 K, respectively, for 3 h in a 500 mL Erlenmeyer flask (Wilmad-LabGlass) fitted with a reflux condenser (Glassco, 200 mm). The product was collected with fresh ethanol and dried at 343 K overnight. Further solvent removal was completed in a vacuum oven (MTI Corporation, $P < 3 \times 10^{-3}$ bar) maintained at 423 K for 12 h. Several repetitions were combined to produce a large enough quantity of material to be used for all of the analyses in this work.

S1.2. Material Characterization

Powder X-ray diffraction (XRD) patterns were generated using an Empyrean Malvern Panalytical diffractometer with a Cu Kα X-ray source (λ = 1.54 Å). 0.02 g of sample was loaded on a glass sample holder (Rigaku, 0.2 mm indentation) for pattern collection (2.5 – 20 °, step size of 0.013 °, 23.8 s per step). Nitrogen physisorption (77 K) isotherms were collected on a Micromeritics 3Flex Surface Characterization Analyzer. For a typical analysis, 0.05 g of sample was evacuated ($P \approx 1 \times 10^{-4}$ bar) at 423 K for 15 h on a Micromeritics VacPrep degassing system. Thermogravimetric analysis (TGA) were conducted with approximately 20 mg of sample under a flow of 40 mL min^{-1} of air (Matheson, zero-grade) at a heating rate of 1 K min^{-1} using a Tarsus TG 209 F3 instrument.

S1.3. Characterization Results

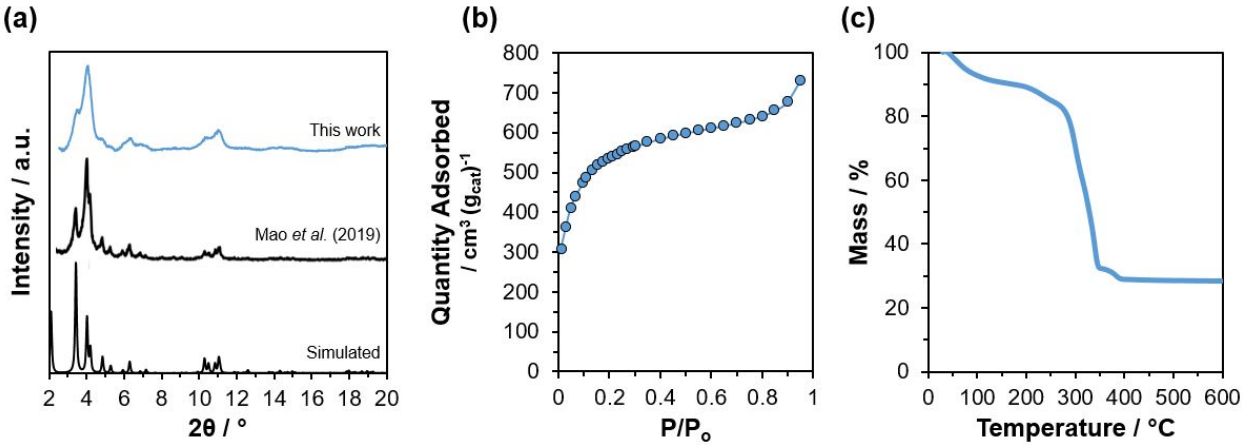

Figure S1: (a) X-ray diffraction pattern of MIL-100(Cr) compared to the literature[1] and simulated diffraction patterns. Mao *et al.* x-ray diffraction pattern reprinted from Ref. 1, Copyright (2019), with permission from Elsevier. (b) N_2 physisorption (77 K) isotherm with a corresponding BET surface area of approximately 2050 $m^2 \cdot g_{cat}^{-1}$, consistent with the previously reported value.[1] (c) TGA profile for MIL-100(Cr).

S2. Supplementary Results & Discussion

S2.1. Literature Comparison

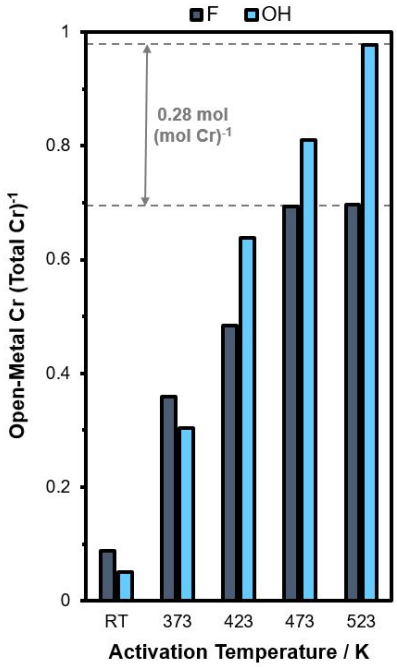

Figure S2: Comparison of the open-metal site densities measured for MIL-100(Cr) in this report (anion = OH^-) and reported by Vimont *et al.* for MIL-100(Cr) synthesized with HF (anion = F^-).[2] Samples were outgassed at the indicated temperature (RT = 303 K in this study) prior to open-metal site quantification.

S2.2. Infrared Spectroscopy

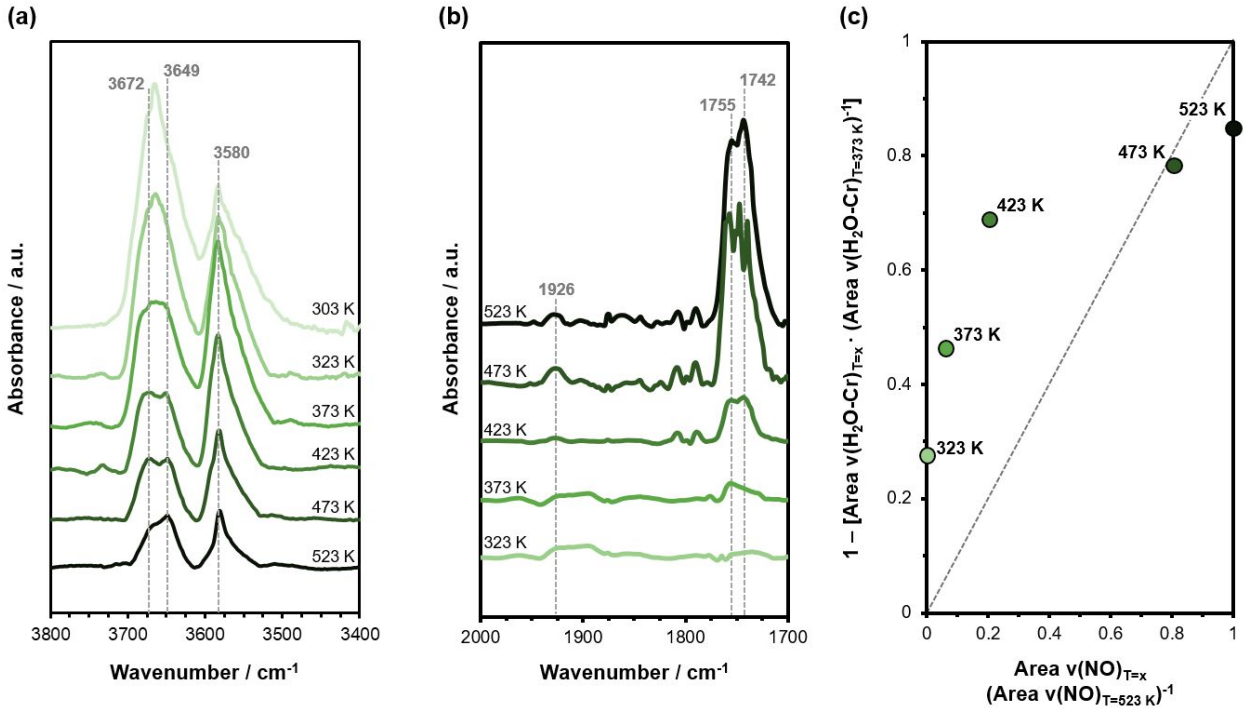

Figure S3: (a) IR spectra of MIL-100(Cr) following activation at the indicated temperature (303 – 523 K) for 2 hours in vacuum (8 – 11 x 10^{-5} bar), featuring the ν(OH) bands corresponding to coordinated water and hydroxides. (b) IR spectra of MIL-100(Cr) following activation at the same conditions and then exposed to 10% NO in N_2 (50 ml min^{-1}, 303 K). (c) Comparison of the fractional reduction in coordinated water (3672, 3649 cm^{-1} bands) to the relative increase in the area of the NO-Cr^{2+} species.

S2.3. CO Adsorption

S2.3.1. Adsorption Model Fitting

The dual-site Langmuir adsorption model was fit to the experimental adsorption isotherms using the following equation:

$$q = q_{A,sat}\frac{b_A P}{1 + b_A P} + q_{B,sat}\frac{b_B P}{1 + b_B P}$$

where,

	P	pressure / bar
	q	quantity adsorbed / mol (mol Cr)$^{-1}$
	$q_{i,sat}$	saturation capacity of site i
	b_i	affinity parameter for site i

Table S1: Summary of Fitting the Dual-Site Langmuir Adsorption Model to the Experimental Adsorption Isotherms for Samples Activated at the Indicated Temperature.

Temperature	$q_{A,sat}$	$q_{B,sat}$	b_A	b_B	R^2
250	0.332	0.275	800	1.462	0.93
200	0.265	0.277	800	1.462	0.98
150	0.035	0.220	800	1.462	0.63
100	0.005	0.120	800	1.462	0.97
50	0	0.069	800	1.462	0.99
30	0	0.044	800	1.462	0.97

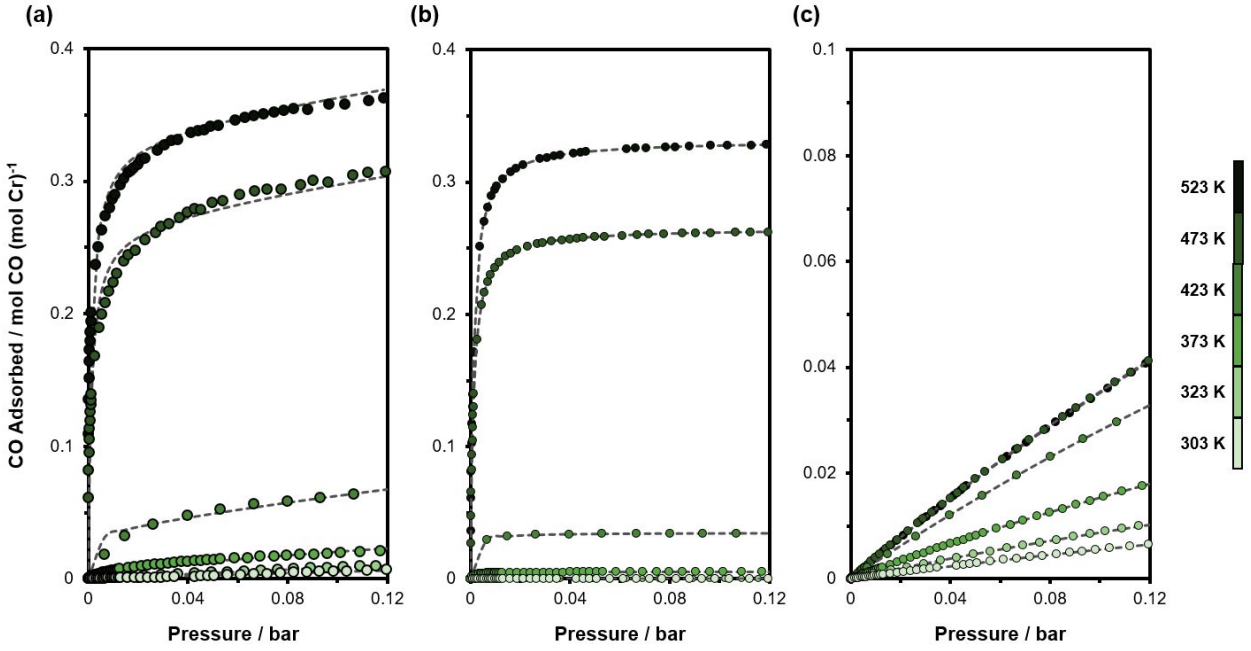

Figure S4: (a) Dual-site Langmuir adsorption model (dashed line) compared to the experimental data (●). (b) Adsorption model including only the parameters associated with site A. (c) Adsorption model including only the parameters associated with site B.

S2.3.2. Cr^{2+} Site Densities

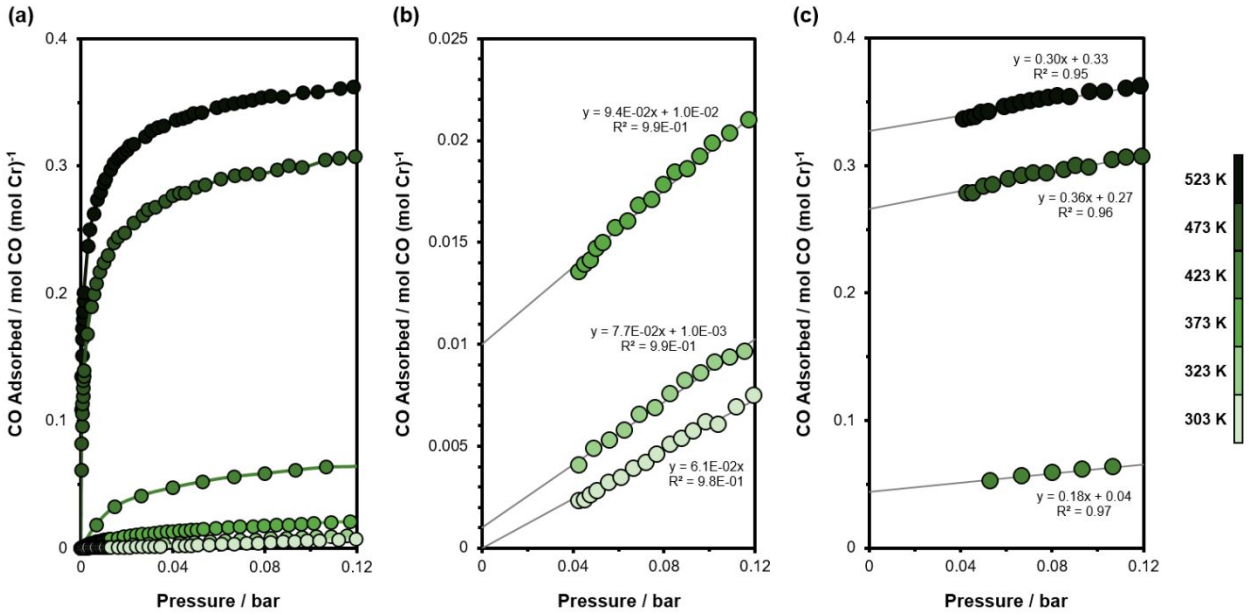

Figure S5: (a) CO adsorption isotherms (303 K) following activation at elevated temperature (303 – 523 K) for 6 hours under vacuum (P < 6.7 x 10^{-5} bar). (b) Estimation of the Cr^{2+} site density based on y-intercept of the fitted line for activation temperatures of 303 – 373 K. (c) Estimation of the Cr^{2+} site density based on y-intercept of the fitted line for activation temperatures of 423 – 523 K.

S2.3.3. Comparison to Total Site Density

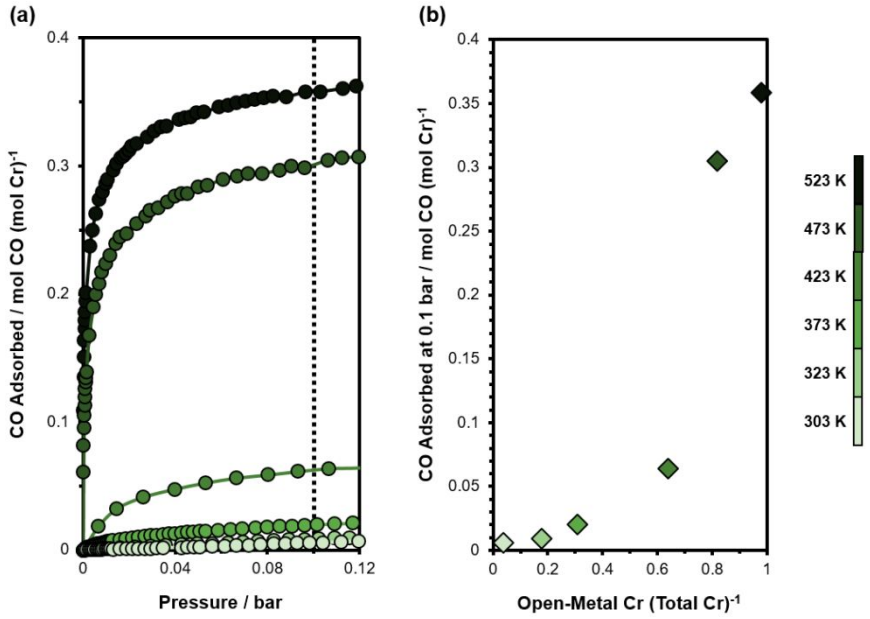

Figure S6: (a) CO adsorption isotherms (303 K) following activation at elevated temperature (303 – 523 K) for 6 hours under vacuum (P < 6.7 x 10^{-5} bar). (b) Comparison of the total open-metal site density determined via irreversible water adsorption to the amount of CO adsorbed at 0.1 bar.

S3. References

(1) Mao, Y.; Qi, H.; Ye, G.; Han, L.; Zhou, W.; Xu, W.; Sun, Y. Green and Time-Saving Synthesis of MIL-100(Cr) and Its Catalytic Performance. *Microporous Mesoporous Mater.* **2019**, *274*, 70–75.

(2) Vimont, A.; Goupil, J.-M.; Lavalley, J.-C.; Daturi, M.; Surblé, S.; Serre, C.; Millange, F.; Fé, G.; Audebrand, N. Investigation of Acid Sites in a Zeotypic Giant Pores Chromium(III) Carboxylate. *J. Am. Chem. Soc.* **2006**, *128*, 3218–3227.