Thermal Cycling of a MOF-Based NO Disproportionation Catalyst
Ashley M. Wright, Chenyue Sun, and Mircea Dinca*  

**ABSTRACT:** The metal–organic framework CuI-MFU-4l reacts with NO, initially forming a copper(I)-nitrosyl at low pressure, and subsequently generates NO disproportionation products CuII−NO2 and N2O. The thermal stability of MFU-4l allows NOx to be released from the framework at temperatures greater than 200 °C. This treatment regenerates the original CuI-MFU-4l, which can engage in subsequent cycles of NO disproportionation.

**NOx**, the Latin for “hurt” or “injury,” is the etymological root of noxious, a word that might as well be derived from NOx, the common name for the noxious oxides of nitrogen. A class of pollutants emitted by combustion engines, NOx have a lasting negative impact on the environment and human health.1,2 Despite significant advances in mitigating automobile emissions through technologies such as the three-way catalytic converter, transportation still contributes nearly half of all NOx emissions.3 Consequently, new NOx abatement systems are needed, particularly as stricter automobile emission regulations come into effect.4,5 Even though current new technologies like selective catalytic reduction (SCR) and NOx adsorber catalysts are effective in reducing tailpipe NOx emissions, SCR catalysts must operate at temperatures exceeding 200 °C to achieve the optimal reduction of 97% NOx.6 However, catalyst beds, especially in diesel and lean-burn engines, do not reach this optimal temperature for several minutes after an engine cold-start, which leads to an initial NOx emissions spike.7 This initial spike is sufficient to cause NOx abatement systems to begin NOx adsorption, and a second NOx emissions spike must be addressed independently of the NOx emissions during steady-state engine operation. A potential solution to this challenge is the development of a method that stores NOx at low temperature (i.e., <200 °C), while the main catalyst bed reaches its optimal operating temperature, and then releases NOx back into the catalyst system at temperatures higher than 200 °C.7–9

One method to capture NOx at least partially, is to enable NO disproportionation at a metal site by allowing three NO molecules to react and generate N2O and a bound metal-nitrite:

\[ 3\text{NO} + M^{\bullet} \rightarrow M^{\bullet+1} - \text{NO}_2 + \text{N}_2\text{O} \]

This process corresponds to a two-third reduction of the overall NOx emissions at low temperatures. Although thermodynamically favorable (ΔG° = −24.6 kcal/mol), NO disproportionation is kinetically sluggish and generally requires a catalyst or high pressures to proceed.10,11 Potential catalysts include transition metal complexes such as species containing Mn,12,13 Fe,14–16 Co,17,18 Ni,19 and Cu.20–27 Metal–organic frameworks (MOFs) are porous crystalline materials and can contain metal sites that display reactivity toward small molecules like NO. Here, we show that Zn2Cu2Cl4(BTDD)3 (CuII-MFU-4l) and CuI-MFU-4l (M = Cu, Zn) (Figure 2) feature tetrahedral N3Cl sites, adsorbs the lowest amount, 0.51 mmol NO/g at 750 Torr. The low NO uptake is likely due to a weak physisorption interaction with the framework, the saturated coordination environment around Zn18,19,26,27 makes NO to approach much closer and enable a stronger interaction with CuII than with ZnII, although still weak enough to allow reversible NO desorption without hysteresis (Figure 1).

**Figure 1.** Reminiscent of the NO disproportionation complexes TpCuII (Tp = tris(pyrazol-1-yl)hydroborate),28–30 a MOF featuring CuI sites in site-isolated coordination environments performs NO disproportionation at low NO concentration. Critically, the thermal stability of MFU-4l allows for the starting CuI material to be regenerated through thermal release of NOx from the resulting CuII-nitrite at high temperature. These results demonstrate a potentially attractive scheme for cold-start NO capture.

Armed with the knowledge of previous reports of NO binding in the MFU-4l family27,33,34 and of NO disproportionation at molecular Tp metal complexes, we initiated our study by investigating how the material properties such as cation identity and oxidation state influence the NO sorption profile in M-MFU-4l (M = Cu, Zn) (Figure 2). The parent Zn-MFU-4l, featuring tetrahedral N3Zn–Cl sites, adsorbs the lowest amount, 0.51 mmol NO/g at 750 Torr. The low NO uptake is likely due to a weak physisorption interaction with the framework, the saturated coordination environment around Zn preventing a stronger metal–NO interaction.

Zn2CuII2Cl4(BTDD)3 (CuII-MFU-4l), accessible by exchanging two ZnII atoms in original MFU-4l with CuII (Figure 1),31 adsors 1.43 mmol NO/g at 750 Torr, significantly more NO than MFU-4l. This is not surprising: CuII is much less accommodating of a tetrahedral coordination environment, and the N3Cu–Cl geometry is likely sufficiently distorted to allow NO to approach much closer and enable a stronger interaction with CuII than with ZnII, although still weak enough to enable reversible NO desorption without hysteresis (Figure 1).
Variable temperature NO isotherms fitted to the dual-site Langmuir model revealed a coverage-dependent isosteric enthalpy of adsorption ($\Delta H_{\text{ads}}$) curve that starts at $-37$ kJ/mol at zero-coverage and remains flat up to $\sim 0.5$ mmol/g, whereupon it gradually decreases to $-19$ kJ/mol over the 0.5−1.5 mmol/g range (Figures S11 and S12). The relatively low zero-coverage enthalpy of adsorption indicates a weak CuII−NO interaction, as also observed in molecular CuII nitrosyl species.37,38

The formation of a weak CuII-nitrosyl species was confirmed by vibrational spectroscopy. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) of CuII-MFU-4 exposed to increasing concentrations of NO in Ar (ranging from 0.5−5% v/v) indicates the growth of a band at 1846 cm$^{-1}$, only slightly red-shifted relative to free NO at 1875 cm$^{-1}$ (Figure S14). For comparison, HKUST-1, a MOF featuring dicopper(II) paddlewheel units capable of weakly binding NO, features a CuII−NO species with $\nu_{\text{NO}} = 1887$ cm$^{-1}$.39 Likewise, structurally characterized molecular complexes, [CuII(NO)-(MeNO$_2$)$_5$][PF$_6$]$_2$ and [TBA][CuII(NO)Cl$_3$], exhibit NO stretches at 1930 and 1834 cm$^{-1}$, respectively.37,38,40 Notably, the band at 1846 cm$^{-1}$ does not change upon continued...
exposure of CuI-MFU-4l to NO, but disappears upon purging the sample with Ar (Figure S15), confirming that NO binding to CuI-MFU-4l is indeed weak and reversible, consistent with the adsorption and desorption data.

Formal reduction of CuI to Cu0 with concomitant loss of chloride31 causes a significant improvement in the low-pressure NO uptake, with CuI-MFU-4l adsorbing 1.24 mmol/g below 1.4 Torr. This uptake is 3 orders of magnitude greater than that of CuII-MFU-4l (0.008 mmol/g) and original MFU-4l (0.002 mmol/g) at the same pressure (Figure 2). The NO isotherm for CuI-MFU-4l rapidly plateaus above ~1.5 Torr (1.2 mmol/g, Figure S10), reaches 1.84 mmol NO/g at 760 Torr at 298 K, and is notably hysteretic upon desorption. A 1:1 ratio of NO-Cu0 (1.70 mmol NO/g) is reached at 525 Torr. We assign the steep, hysteretic uptake of NO here to a strong binding interaction between Cu0 and NO, in line with previous observations of strong binding of small molecules such as ethylene, propylene, and carbon monoxide at the open CuI sites in CuI-MFU-4l.31,33,41

To gain deeper insight into the nature of the NO binding to CuI-MFU-4l, we once again used DRIFTS. Flowing a relatively dilute stream of NO (10–10,000 ppm in Ar) over a powder sample of CuI-MFU-4l results in the appearance of a new band at 1726 cm−1, which shifts to 1692 cm−1 when 15NO is used (Δ = 34 cm−1; expected shift from Hooke’s law = 33 cm−1) (Figure 3a). We assign this band to a copper(I) nitrosyl species based on comparable IR bands in molecular copper(I)-nitrosyl complexes with similar coordination environments, such as Tp3Cu(NO) (1712 cm−1) and Tp2Cu(NO) (1720 cm−1).21,42 In the context of cold-start NOx emissions, it is particularly noteworthy that NO binds to CuI-MFU-4l at concentrations as low as 10 ppm in Ar (Figure S19).

Remarkably, exposure to more concentrated NO streams (1% in Ar) causes loss of the band at 1726 cm−1 and formation of several new spectral features over a span of approximately 30 min (Figure 3b). Because many of these new spectral features overlap with bands pertaining to the MOF itself, we identified those relevant to the NO transformations by monitoring the reaction using both natural-abundance NO, and isotopically labeled 15NO (Figure S17). Comparison of the di thermodynamic analysis of the headspace using real time gas analysis mass spectrometry revealed generation of N2O (Figure S28). Additionally, analysis of the reaction product, CuI-MFU-4l-(NOx), by electron paramagnetic resonance (EPR) revealed a signal consistent with a CuIII species (Figure S20). Overall, these results support a CuI-MFU-4l mediated NO disproportionation reaction.

CuI-MFU-4l-(NOx) presents modest further uptake of NO (Figure 4a, red diamonds) of only 0.002 mmol/g at 1.5 Torr and 0.40 mmol/g at 750 Torr, significantly lower than CuII-MFU-4l-(Cl) and CuI-MFU-4l, but comparable to MFU-4l. We attribute the lower NO uptake in CuI-MFU-4l-(NOx) to the bidentate O2O′-nitrito binding mode, which blocks the coordination sites at CuI0.

Given the thermal stability of the Cu-MFU-4l materials, we hypothesized the CuII−nitrito bond could be homolyzed at high temperature, releasing an equivalent of NO2 and regenerating CuI-MFU-4l (Scheme 1). Heating CuI-MFU-4l-(NOx) at 240 °C under dynamic vacuum for 16 h results in a color change from green to beige, a discoloration characteristic of transitioning from CuI to Cu0, which would indeed imply thermal release of one NO2 equivalent and closure of a catalytic NO disproportionation cycle. NO sorption analysis of the beige solid revealed isomerotherm characteristics that are comparable to those of pristine CuI-MFU-4l, albeit with somewhat reduced low and high pressure capacities of 0.83 mmol/g and 1.41 mmol/g at 1.5 and 750 Torr, respectively, (Figure 4a).

Further insight into the nature of thermal regeneration of CuI-MFU-4l came from thermogravimetric analysis of CuI-MFU-4l-(NOx), which revealed two partial mass loss events of ~2.4 and ~8.9 wt% at 150 and 220 °C, respectively, prior to framework degradation at temperatures greater than 300 °C (Figure S21). Evolved gas analysis via mass spectrometry (TGA-MS) revealed that, surprisingly, the major NOx species released from CuI-MFU-4l-(NOx) is NO (m/z = 30) at 220 °C, further supported by release of 15NO (m/z = 31) from CuI-MFU-4l-(15NOx) Indeed, we do not observe a m/z = 46 associated with NO2. Evidently, the mechanism of regenerating
Cu-I-MFU-4 from Cu-II-MFU-4-(NO2) is not simple homolysis of the Cu–NO3 bond and may require more extensive future studies. We hypothesize that thermal release of the NO2 equivalent instead occurs through evolution of NO through thermal decomposition of nitrite. Under our reaction conditions, at least one of the pathways in which this reactive species is reduced back to Cu(I) is through oxidative decomposition of the framework. In agreement with this hypothesis, TGA-MS reveals a peak with m/z 44, which after 15N isotopic labeling of the nitrite and 2-position of the hypothesis, TGA-MS reveals a peak with m/z 44, which after 15N isotopic labeling of the nitrite and 2-position of the framework allows for release of NOx and catalyze NO disproportionation. The high thermal stability of the material recovered after thermal treatment of Cu-II-MFU-4-(NO2) at 250°C under a flow of N2.

The above results demonstrate that well-defined Cu(I) sites in Cu-I-MFU-4 react with low concentrations of NO (10 ppm) and catalyze NO disproportionation. The high thermal stability of the framework allows for release of NOx from the framework and regeneration of the starting material. The capture and regeneration of the starting material. The capture and no further loss in subsequent cycles. Future efforts will focus preparing a catalytic system with added reductants to prevent oxidative degradation of the framework.

**ASSOCIATED CONTENT**

*Supporting Information* The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.0c12134.

**AUTHOR INFORMATION**

**Corresponding Author**

Mircea Dinca — Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States; orcid.org/0000-0002-1262-1264; Email: mdinca@mit.edu

**Authors**

Ashley M. Wright — Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States; orcid.org/0000-0002-9475-2638

Chenyue Sun — Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States

Complete contact information is available at: https://pubs.acs.org/10.1021/jacs.0c12134

**Author Contributions**

All authors have given approval to the final version of the manuscript.

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work was funded by the Ford Motor Company. We thank Luming Yang for assistance in collecting EPR spectra.

**REFERENCES**


(15) Brozek, C. K.; Miller, J. T.; Stoian, S. A.; Dincă, M. NO Disproportionation at a Mononuclear Site-Isolated Fe+2 Center in Fe2+–MOF-5. J. Am. Chem. Soc. 2015, 137 (23), 7495–7501.


(25) Alternative reduction pathways of NO include reduction of NO to N2O and H2O in the presence of protons and an electron source. This is how NO reductase reduces NO, the hyponitrite intermediate is intercepted by a proton transfer. See refs 26 and 27.


