# Vapor-Phase Cyclohexene Epoxidation by Single-Ion Fe(III) Sites in Metal–Organic Frameworks

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Cite This: Inorg.	Chem. 2021, 60, 2457–2463	 Read Online		
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**ABSTRACT:** Heterogeneous catalysts supported on metal-organic frameworks (MOFs), which possess uniform porosity and crystallinity, have attracted significant interest for recent years due to the ease of active-site characterization via X-ray diffraction and the subsequent relation of the active site structure to the catalytic activity. We report the syntheses, structures, and oxidation catalytic activities of single-ion iron catalysts incorporated into the zirconium MOF NU-1000. Single-ion iron catalysts with different counteranions were anchored onto the Zr node through postsynthetic solvothermal deposition. Crystallographic characterization of the resulting MOFs (NU-1000-Fe-Cl and NU-1000-Fe-NO<sub>3</sub>) revealed that, while both frameworks have similar Fe coordination, the distance



between Fe and the  $Zr_6$  node differs significantly between the two. The product rate profiles of the two catalysts for vapor-phase cyclohexene epoxidation demonstrate different initial rates and product formations, likely originating from the different Fe–O distances.

# INTRODUCTION

As a new class of crystalline porous materials, porous coordination polymers (PCPs) or metal-organic frameworks (MOFs)<sup>1,2</sup> have been extensively investigated for a wide range of applications such as gas storage,<sup>3,4</sup> purification,<sup>5,6</sup> proton conduction,<sup>7,8</sup> sensing,<sup>9,10</sup> drug delivery,<sup>11,12</sup> and heterogeneous catalysis.<sup>13,14</sup> MOFs have a crystalline porous network structure composed of metal ions/clusters bridged by organic ligands. Through judicious choices of structural components, the structural and physical properties of MOFs can be finetuned.<sup>15,16</sup> Due to these advantages, MOFs have emerged as prominent candidates for catalytic supports.<sup>17</sup> Typically, the characterization of deposited species upon conventional catalyst supports, such as metal oxides, tends to be challenging due to the nonuniform surface and pore structures of the support. In contrast, the crystalline nature of MOFs enables visualization of the catalytically active species within the framework, which leads to a detailed characterization of active catalytic sites and provides insight into structure-activity relationships.<sup>18</sup> From this perspective, several groups have been investigating newly installed catalytic species in MOFs, which can be introduced using postsynthetic modification methods such as solvothermal deposition in MOFs (SIM) and atomic-layer deposition in MOFs (AIM).<sup>19</sup>

Separately, alkene oxidation catalysts have been of significant importance for decades, due to their potential applications in direct conversion of low-cost feedstocks, such as products obtained from the steam cracking of natural gas and naphtha, to valuable oxygenated products.<sup>24–26</sup> Among several candidate catalysts, iron catalysts have attracted particular interest owing to their low cost, high availability, and low

environmental toxicity. As with many heterogeneous catalysts, the investigation of a structure–activity relationship in most iron catalysts is challenging.<sup>27</sup> One possible solution is to generate single-site iron catalysts, which can lead to an atomically precise understanding of the catalyst design. Consequently, we have focused on synthesizing single-ion iron catalysts supported on MOFs.

In this study, we incorporated single-ion-based iron catalysts incorporated in the highly crystalline and porous MOF NU-**1000**  $([Zr_6(\mu_3-O)_4(\mu_3-OH)_4(OH)_4(H_2O)_4(TBAPy)_2]_{\infty}$ (TBAPy = 1,3,6,8-(*p*-benzoate)pyrene), which has Zr<sub>6</sub>-type oxide cluster nodes and high porosity (Figure 1).<sup>21,28</sup> Because NU-1000 contains spatially oriented -OH groups pointing into its mesopores and c pores, various catalytic species have been installed on NU-1000 to investigate their catalytic performance.<sup>17,22,29-31</sup> Herein, we deposited iron species inside this MOF using SIM with two different iron precursors,  $Fe(NO_3)_3$  and  $FeCl_2$ , and thoroughly characterized the species using a combination of analytical and spectroscopic techniques. In the resulting MOFs (denoted as NU-1000-Fe-NO<sub>3</sub> and NU-1000-Fe-Cl hereafter), single-ion iron(III) species were observed on the Zr<sub>6</sub> node with different Fe-O distances. Their catalytic properties were investigated through

Received: November 12, 2020 Published: January 26, 2021





**Figure 1.** Crystal structures of nonfunctionalized **NU-1000.** (a) View of the *ab* plane. Mesopores with a channel size of  $\sim 31$  Å and so-called "triangle pores" with a channel size of 10 Å are shown. (b) View along the *c* axis. Pores with a channel size of 10 Å are shown, which are the so-called "*c*-pores". (c) Structures of the inorganic nodes and the organic linkers.

alkene oxidation reactions with hydrogen peroxide. We found that they initially exhibit different catalytic behavior, which could be associated with the difference in the Lewis acidity of the Fe catalytic sites, but ultimately achieve the same level of catalytic activity. Our study of the structure—property relationship of isostructural MOF-based catalysts opens the door for the rational design of MOF-based catalysts through structural fine tuning.

#### **EXPERIMENTAL METHODS**

**Chemicals.** Reagents and solvents were purchased from Fisher Scientific Co., Ltd., and Sigma-Aldrich Chemical Co., Ltd., and used without further purification.

**Preparation of NU-1000.** NU-1000 was prepared by the published procedures using diethylformamide as the solvent.<sup>28</sup> A 60 mg portion of as-synthesized NU-1000 was then suspended in 20 mL of N,N-dimethylformamide (DMF) and 0.5 mL of 12 M HCl and heated at 120 °C for at least 12 h to remove acids and the synthetic modulators on the node.

**Syntheses of Catalysts.** For the synthesis of NU-1000-Fe-NO<sub>3</sub>, 60 mg of NU-1000 was immersed in 20 mL of a 0.05 M Fe(NO<sub>3</sub>)<sub>3</sub> solution in methanol for 2 days at room temperature and then washed three times with 20 mL of fresh methanol. A dark yellow powder was obtained. For the synthesis of NU-1000-Fe-Cl, 60 mg of NU-1000 was immersed in 20 mL of a 0.03 M FeCl<sub>2</sub> solution in DMF for 2 days at room temperature and then washed three times with fresh acetone. An orange powder was obtained.

Inductively Coupled Plasma–Optical Emission Spectroscopy (ICP-OES). ICP-OES spectra were recorded using a iCAP 7600 ICP-OES analyzer calibrated with standard solutions. Samples (ca. 1 mg) were digested in nitric acid (70%, 0.75 mL) and hydrogen peroxide (35% in  $H_2O$ , 0.25 mL) at 150 °C for 5 min in a microwave reactor.

**Diffuse Reflectance Ultraviolet–Visible Spectroscopy (UV– vis).** Diffuse reflectance UV–vis spectra were collected using a Shimadzu UV-3600 instrument with a Harrick Praying Mantis diffuse reflectance accessory. CaF<sub>2</sub> powder was used as a reflector for baseline measurements, and samples were diluted in CaF<sub>2</sub> powder for the measurements. The obtained reflectance spectra were converted to absorption spectra according to the Kubelka–Munk function  $F(R_{\infty})$ .

**Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS).** DRIFT spectra were recorded from a sample diluted in KBr powder on a Nicolet 6700 instrument equipped with KBr optics and a Praying Mantis diffuse reflectance accessory.

**Sorption Study.** N<sub>2</sub> sorption isotherms were collected on a Micromeritics Tristar II 3020 instrument at 77 K. Prior to the measurement, the sample was activated on a SmartVacPrep port by heating at 120 °C under vacuum for at least 12 h. Pore-size distributions were calculated from these isotherms using a DFT method, based on a molecular statistical approach.

**X-ray Photoelectron Spectroscopy (XPS).** XPS measurements were carried out with a Thermo Scientific ESCALAB 250 Xi instrument (Al K $\alpha$  radiation, 1486.6 eV) operated at 14.6 kV and 11.5 mA. An electron flood gun was utilized prior to the scans. Samples were ground and spread on conductive carbon adhesive tape attached to sample holders. The carbon 1s binding energy of graphite in the carbon tape (284.6 eV) was used to calibrate binding energies. Curve-fitting analyses were performed with XPS PEAK4.1 software by using a combination of Gaussian and Lorentzian line shapes.

**Single-Crystal X-ray Crystallography (SCXRD).** X-ray crystal diffraction data were carried out using a Bruker Kappa APEX II CCD detector equipped with a Mo K $\alpha$  ( $\lambda = 0.71073$  Å) I $\mu$ S microfocus source with MX optics. The single crystals were mounted on MicroMesh (MiTeGen) with Paratone oil. The structure was solved by intrinsic phasing methods (SHELXT-2014/S)<sup>32</sup> and refined by full-matrix least-squares refinement on  $F^2$  (SHELXL-2017/1)<sup>33</sup> using the Yadokari-XG software package.<sup>34</sup> Refinement results are summarized in Table S1. Crystallographic data in CIF format have been deposited with the Cambridge Crystallographic Data Centre (CCDC) under deposition numbers CCDC 2036844 and 2036845. The data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.).

Catalysis. Reaction tests were performed at 120 °C in a 1/1 ratio of reactant (cyclohexene) and oxidant  $(H_2O_2)$ , with both reactants in the vapor phase. A detailed description of the reactor was reported in prior work from our team.<sup>35</sup> Catalysts (10 mg) were diluted in 200 mg of quartz sand, and the catalyst beds were supported on quartz wool in a quartz tube reactor. Cyclohexene (Sigma-Aldrich,  $\geq$ 99.0%) was introduced by flowing He (5 mL/min, 99.999%, Airgas) through a quartz bubbler at 25  $^\circ\text{C},$  giving a saturated vapor pressure of 11.9 kPa. He (20 mL/min) was added to set the cyclohexene partial pressure at 3 kPa. Four molar H<sub>2</sub>O<sub>2</sub> in acetonitrile solution, previously dried over magnesium sulfate,<sup>36</sup> was loaded in a plastic syringe and injected directly into the reactor with a rate of 0.2 mL/h, corresponding to 3 kPa of H<sub>2</sub>O<sub>2</sub> partial pressure. The H<sub>2</sub>O<sub>2</sub> solution only contacted polypropylene and perfluorinated materials to minimize decomposition. C<sub>6</sub> products (cyclohexene oxide, trans-1,2cyclohexanediol, 2-cyclohexen-1-ol) and the reactant were detected and separated using a gas chromatograph (GC) (Agilent 7890) with an HP-INNOWAX (50 m length, 0.2 mm diameter, 0.4  $\mu$ m film) column, and signal intensities were calibrated using authentic standards. Concentrations of cis-1,2-cyclohexanediol and 2-cyclohexen-1-one, if present, were below the detection limit of 0.001 mol %

The product yield was calculated as per eq 1 and then was used to obtain the conversion rate.

$$product yield = \frac{mol_{product}}{mol_{reactant} + \sum mol_{product}}$$
(1)

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#### RESULTS AND DISCUSSION

Syntheses and Characterization. We synthesized NU-1000-Fe-NO<sub>3</sub> and NU-1000-Fe-Cl using solution-phase postsynthetic metalation. NU-1000 was exposed to a solutions of either  $Fe(NO_3)_3$  or  $FeCl_2$  in dimethylformamide at room temperature. Clear color changes from the characteristic yellow of NU-1000 to yellow-orange (NU-1000-Fe-NO<sub>3</sub>) or to orange (NU-1000-Fe-Cl)) were observed after treatment (Figure 2a), visually indicating the successful incorporation



Figure 2. (a) Photographic images of pristine NU-1000 (left), NU-1000-Fe-NO<sub>3</sub> (middle), and NU-1000-Fe-Cl (right). (b) PXRD patterns (after activation) of NU-1000 (black), NU-1000-Fe-NO<sub>3</sub> (blue), and NU-1000-Fe-Cl (red).

of iron species inside the MOFs. The PXRD patterns of both frameworks showed that the underlying **NU-1000** framework remained crystalline after SIM (Figure 2b). Consistent with the color changes, the diffuse reflectance UV spectra showed ligand to metal charge-transfer (LMCT) peaks centered at around 3.0 and 4.0 eV (Figure S1). ICP-OES measurements indicated Fe loadings of  $0.5 \pm 0.1$  and  $2.2 \pm 0.2$  per Zr<sub>6</sub> node

of NU-1000-Fe-NO<sub>3</sub> and NU-1000-Fe-Cl, respectively. In the DRIFT spectra (Figure S2), red shifts and decreases in intensity of the peaks associated with terminal and bridging -OH stretches on the  $Zr_6$  node at 3670 cm<sup>-1</sup> were observed for both NU-1000-Fe-NO<sub>3</sub> and NU-1000-Fe-Cl. These features suggest chemisorption of the iron species onto the node in both cases. In addition, for NU-1000-Fe-NO<sub>3</sub>, a relatively strong peak at 1270 cm<sup>-1</sup> was observed, which was attributed to the stretching vibration mode of nitrate anions, suggesting that one or more nitrate ions remain coordinated to Fe after SIM. To verify the porosity of NU-1000-Fe-NO<sub>3</sub> and NU-1000-Fe-Cl. N<sub>2</sub> sorption isotherm measurements were conducted (Figure 3). Decreases in Brunauer-Emmett-Teller (BET) area from 2120  $m^2/g$  (bare NU-1000) to 1480  $m^2/g$ for NU-1000-Fe-NO<sub>3</sub> and 1300 m<sup>2</sup>/g for NU-1000-Fe-Cl were observed. In addition, density functional theory (DFT) calculated average pore size distributions showed only small decreases in the mesopore and *c*-pore volumes, implying that the framework porosity remained intact. XPS measurements were completed to determine the oxidation states of the incorporated iron species in the MOFs (Figure S3). The Fe 2p core-level spectra of NU-1000-Fe-NO3 and NU-1000-Fe-Cl showed single-component peaks with binding energies of 712.2 eV ( $2p_{3/2}$ ; satellite at ~719 eV) and 725.3 eV ( $2p_{1/2}$ ; satellite at ~733 eV) for NU-1000-Fe-NO<sub>3</sub>; for NU-1000-Fe-Cl, these peaks were present at 711.8 eV ( $2p_{3/2}$ ; satellite at ~719 eV) and 724.9 eV ( $2p_{3/2}$ ; satellite at ~733 eV). These observed binding energies are similar to those of reported Fe(III) compounds,<sup>37</sup> and so the oxidation state of Fe in both frameworks was assigned as III. The result indicated that the Fe(II) precursor of NU-1000-Fe-Cl was oxidized to Fe(III) when it was incorporated on the nodes of MOFs, probably due to air exposure.

To obtain further structural insights into the incorporated iron species in the MOFs, single-crystal X-ray diffraction analyses on NU-1000-Fe-NO<sub>3</sub> and NU-1000-Fe-Cl were conducted (Figure 4, Figures S4–S6, and Table S1). Following the refinement of the underlying NU-1000 framework, the residual electron densities were calculated to identify and refine the Fe locations and occupancies. We used ShleXLe<sup>38</sup> and PLATON<sup>39</sup> software to visualize the electron densities that are assignable to Fe species (Figure 4 and Figure S5). Interestingly, the structures of the deposited iron ions were found to be different between NU-1000-Fe-NO<sub>3</sub> and NU-



Figure 3. (a)  $N_2$  adsorption (filled symbols) and desorption isotherms (open symbols) of NU-1000 (black squares), NU-1000-Fe-NO<sub>3</sub> (blue diamond), and NU-1000-Fe-Cl (red circles) (b) DFT-calculated pore size distributions of NU-1000 (black squares), NU-1000-Fe-NO<sub>3</sub> (blue diamonds), and NU-1000-Fe-Cl (red circles).



**Figure 4.**  $F_o - F_c$  contoured Fourier maps around the Zr<sub>6</sub> node of **NU-1000-Fe-NO**<sub>3</sub> calculated before assigning iron species. Shown are (a) slicing planes, (b) the contoured map in the (1–10) plane, and residual densities observed (c). The contoured map in the plane shifted 1.2 Å from the (1–10) plane; the residual electron densities due to iron species are visualized, (d) Contoured map in the (110) plane. (e) Contoured map in the (001) plane. The contours are from -1.80 to 0.90 e Å<sup>-3</sup> in steps of 0.10 eÅ<sup>-3</sup> for (b), from -0.80 to 1.80 e Å<sup>-3</sup> in steps of 0.10 e Å<sup>-3</sup> for (c), from -1.00 to 1.40 e Å<sup>-3</sup> in steps of 0.20 e Å<sup>-3</sup> for (d), fand rom -1.50 to 2.50 e Å<sup>-3</sup> in steps of 0.10 e Å<sup>-3</sup> for (e). PLATON software was used for the calculations.



Figure 5. Crystal structures of NU-1000-Fe-NO<sub>3</sub> and NU-1000-Fe-Cl (100 K): (a) node structure of NU-1000-Fe-NO<sub>3</sub>; (b) 3D structure of NU-1000-Fe-NO<sub>3</sub> viewed on the *ab* plane; (c) node structure of NU-1000-Fe-Cl; (d) 3D structure of NU-1000-Fe-Cl viewed along the *c* axis. Hydrogen atoms and nitrate and chloride anions are omitted for clarity.

**1000-Fe-Cl** (Figure 5a,b). For NU-1000-Fe-NO<sub>3</sub>, two crystallographically nonequivalent Fe sites were observed. The first site, denoted Fe1, resides in the *c*-pore and is coordinated to the  $Zr_6$  node through both terminal and bridging oxygens (O5 and O3, respectively). The second site,

denoted Fe2, is found in the hexagonal mesopore and exhibits very similar binding to the node through O6 (terminal) and O4 (bridging). The crystallographically estimated loadings of the Fe sites were 0.32 (Fe1) and 0.40 (Fe2) per  $Zr_6$  node, where the total crystallographically determined iron content

 $(0.72 \text{ Fe/Zr}_6)$  is in good agreement with that obtained from an ICP-OES analysis (0.5  $\pm$  0.1 Fe/Zr<sub>6</sub>). The observed Fe-O distances between Fe and the Zr node are 2.02 Å (Fe1-O5), 2.77 Å (Fe1-O3), 2.43 Å (Fe2-O6), and 2.60 Å (Fe2-O4). These distances point toward strong interactions between the Fe sites and Zr node for NU-1000-Fe-NO<sub>3</sub>.<sup>40-42</sup> The location of any nitrate anions could not be determined due to their disordered nature and low site occupancies. In the case of NU-1000-Fe-Cl, single-ion Fe species were observed at positions that were more than 3.0 Å away from the oxygen sites of Zr nodes (Figure 5c,d). There are two crystallographically independent Fe sites (Fe1 and Fe2); their occupancies were estimated to be 0.10 (Fe1, c-pore), 0.15 (Fe2, mesopore), which correspond to 0.80 and 1.20 irons per  $Zr_6$  node. The total crystallographically determined Fe content (2.0 Fe/Zr<sub>6</sub>) is in good agreement with that obtained from an ICP-OES analysis  $(2.2 \pm 0.2 \text{ Fe/Zr}_6)$ . The observed Fe-O distances between Fe and the Zr node are 3.13 Å (Fe1-O5), 3.57 Å (Fe1-O1), 3.50 Å (Fe1-O3), 3.08 Å (Fe2-O6), 3.54 Å (Fe2-O2), and 3.41 Å (Fe2-O4). Thus, relatively weak interactions between Fe sites and the Zr node are implied for NU-1000-Fe-Cl.

**Catalysis.** Vapor-phase cyclohexene epoxidation with vaporized  $H_2O_2$ —recently developed by our team<sup>35</sup>—was used to compare the reactivity and selectivity for the two catalysts. Simplified reaction pathways are given in Scheme 1,

Scheme 1. Proposed Mechanism of Cyclohexene Oxidation



presenting two proposed  $H_2O_2$  activation mechanisms. In short, heterolytic activation of  $H_2O_2$  yields cyclohexene epoxide, which in turn hydrolyzes rapidly to *trans*-cyclohexanediol, while homolytic activation of the oxidant produces the radical oxidation products cyclohexenone and cyclohexenol. Mechanistic details have previously been reported thoroughly.  ${}^{36,43,44}$  Cyclohexenone is often formed in an approximately 1/1 ratio with cyclohexenol, but in this study, we only observed cyclohexenol. Cyclohexenone may have been present but was at levels below the GC detection limits.

Product rate profiles of the two catalysts present different behaviors initially but then show both catalysts eventually reaching steady-state rates (Figure 6 and Figure S7). Interestingly, neither catalyst fully oxidizes the reactant to  $CO_2$ , unlike the case in our previous study, which may be due to low conversion by both catalysts.<sup>35</sup> Additionally, the radical pathway reaction that eventually yields CO<sub>2</sub> may be slower than decomposition of  $H_2O_2$  to  $H_2O$  over these catalysts. More importantly, NU-1000-Fe-NO<sub>3</sub> initially yields direct products at much higher rates than NU-1000-Fe-Cl, but these rates rapidly decrease to a steady state by  $\sim$ 3 h time on stream. This change in rate and selectivity suggests restructuring of the active site. Since isolation of the Fe sites from one another can be speculated, as seen in the ICP results (2.5 and 0.6 per  $Zr_6$ node for NU-1000-FeCl and NU-1000-Fe-NO<sub>3</sub>, respectively), we speculate that the difference in initial rates is related to the difference in Fe-O distances. The Fe sites present in NU-1000-Fe-NO<sub>3</sub>, as evidenced by their stronger interactions with electrogenative oxygen, may be stronger Lewis acid sites than the Fe sites in NU-1000-Fe-Cl.

# CONCLUSION

Two single-ion iron catalysts with different counteranions were synthesized by postsynthetic metalation of NU-1000 using  $Fe(NO_3)_3$  or FeCl<sub>2</sub>. The resulting MOFs, NU-1000-Fe-NO<sub>3</sub> and NU-1000-Fe-Cl, retained the structural characteristics of bare NU-1000 and exhibited isolated Fe(III) single-ion sites after deposition. SCXRD studies revealed that both frameworks had two crystallographically nonequivalent Fe sites coordinating to the bridging and terminal oxygens of the  $Zr_6$  node, with the Fe–O distances of NU-1000-Fe-Cl being much longer than those of NU-1000-Fe-NO<sub>3</sub>. Vapor-phase cyclohexene epoxidation by NU-1000-Fe-NO<sub>3</sub> yields direct products initially, whereas NU-1000-Fe-Cl exclusively yields a mixture of direct products and byproducts; as time passes, NU-1000-Fe-NO<sub>3</sub> achieves a steady state similar to that of NU-1000-Fe-Cl. This behavior is attributed to the initial



Figure 6. Time on stream  $C_6$  product rate profiles of cyclohexene epoxidation with  $H_2O_2$  at 120 °C, with cyclohexene 3 kPa and  $H_2O_2$  3 kPa over (a) NU-1000-Fe-Cl and (b) NU-1000-Fe-NO<sub>3</sub>.

# ASSOCIATED CONTENT

#### **Supporting Information**

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The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c03364.

Synthesis and characterization data, including DRIFTS, UV, and XPS spectra, and crystallographic data and details of the refinement for NU-1000-Fe-NO<sub>3</sub> and NU-1000-Fe-Cl (PDF)

#### Accession Codes

site catalysts.

CCDC 2036844–2036845 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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#### Author Contributions

"K.O and S.A. contributed equally to this work.

#### Notes

The authors declare the following competing financial interest(s): O.K.F has financial interest in the start-up company NuMat Technologies, which is seeking to commercialize metal-organic frameworks.

# ACKNOWLEDGMENTS

The authors gratefully acknowledge the Northwestern University Institute for Catalysis in Energy Processes

(ICEP), funded by the DOE, Office of Basic Energy Sciences (award number DE-FG02-03ER15457), for the synthesis of the catalysts. K.O. acknowledges Early-Career Scientists (JP19K15584) from the Japan Society of the Promotion of Science for financial support. S.A. acknowledges financial support from the Inorganometallic Catalyst Design Center, an EFRC funded by the DOE, Office of Basic Energy Sciences (DE-SC0012702), for the catalysis part. This work made use of the IMSERC X-ray facility at Northwestern University, which has received support from the Soft and Hybrid Nanotechnology Experimental (SHyNE) Resource (NSF ECCS-1542205), the State of Illinois, and the International Institute for Nanotechnology (IIN). Also, this work made use of the Keck-II facility of Northwestern University's NUANCE Center, which has received support from the Soft and Hybrid Nanotechnology Experimental (SHyNE) Resource (NSF ECCS-1542205), the MRSEC program (NSF DMR-1720139) at the Materials Research Center, the International Institute for Nanotechnology (IIN), the Keck Foundation, and the State of Illinois, through the IIN. MOFkey:<sup>45</sup> Zr.HVCDAMXLLUJLQZ.MOFkey-v1.csq (NU-1000).

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