

Communication

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Single-Atom Based Vanadium Oxide Catalysts supported on Metal– Organic Frameworks: Selective Alcohol Oxidation and Structure– Activity Relationship

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Supporting Information Placeholder

ABSTRACT: We report the syntheses, structures, and oxidation catalytic activities of a single-atom-based vanadium oxide incorporated in two highly crystalline MOFs, Hf-MOF-808 and Zr-NU-1000. These vanadium catalysts were introduced by a postsynthetic metalation, and the resulting materials (Hf-MOF-808-V and Zr-NU-1000-V) were thoroughly characterized through a combination of analytic and spectroscopic techniques including single-crystal X-ray crystallography. Their catalytic properties were investigated using the oxidation of 4-methoxybenzyl alcohol under an oxygen atmosphere as a model reaction. Crystallographic and variable-temperature spectroscopic studies revealed that the incorporated vanadium in Hf-MOF-808-V changes position with heat, which led to improved catalytic activity.

Owing to their high catalytic performance in various redoxmediated reactions and availability,¹⁻⁶ vanadium oxide catalysts have found extensive applications in chemical and environmental industries, including the mass production of sulfuric acid and phthalic anhydride and the remediation of environmental pollution.^{2,5–7} Most vanadium catalysts used industrially are deposited on the surface of a porous solid support, such as silica, alumina, titania, zirconia, and zeolites, primarily to increase the surface area and stability, essential to creating a superior catalyst.⁴ These catalyst supports were initially assumed to be inert in terms of reactivity.⁴ However, subsequent studies revealed that the performance of these and many other supported catalysts are often highly dependent on the identity of the support. These observations, termed 'support effects', typically thought to derive from supportinduced, catalytically relevant changes in the geometric and/or electronic structures of the active species.⁸⁻¹¹ However, the origin and detailed mechanism of such effects often are unclear, primarily due to the difficulty in determining the "true" active-species structure under operando conditions. To better understand "support effects" and move toward the goal of "catalyst formation by design", comprehending structure-activity relationships in heterogeneous catalysis is essential.^{12–18} Unfortunately, conventional catalyst supports, such as high-area metal oxides, lack uniform surfaces and pore structures, making unambiguous structural



characterization of deposited species somewhat difficult. Furthermore, multiple forms of active sites may be present.

Figure 1. Structures of pristine (a) Hf-MOF-808 and (b) Zr-NU-1000 with the corresponding structures of their inorganic nodes organic Hf-MOF-808 $([Hf_6(\mu_3-O)_4(\mu_3$ and linkers. OH)₄(OH)₆(H₂O)₆(BTC)₂]_∞; H₃BTC = benzene-1,3,5tricarboxylylic acid and Zr-NU-1000 $([Zr_6(\mu_3-O)_4(\mu_3 OH_4(OH_4(H_2O)_4(TBAPy)_2]_{\infty}$; $H_4TBAPy = 1,3,6,8-(p-benzoic$ acid)pyrene).

As an alternative to conventional catalyst supports, metalorganic frameworks (MOFs) – infinite coordination networks composed of metal ions or clusters connected by organic linkers and possessing well-defined structures^{19–24} – have emerged as prominent candidates. MOFs offer uniform porosity and a high degree of freedom for structural tuning.^{25,26} Furthermore, unambiguous structural determination of the installed catalytic species through crystallographic techniques is viable due to the periodicity of MOF structures. These advantages can lead to an atomically precise understanding the compositions of catalyst active sites, and their attachment to supports, thereby elucidating structure–activity relationships. From this perspective, our group as well as others have investigated 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).^{27–38}

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Here we report the syntheses, structures, and catalytic properties of single-metal-atom vanadium species incorporated in two highly crystalline MOFs, Hf-MOF-808³⁹⁻⁴¹ and Zr-NU-1000.² Both feature M_6 -type oxide cluster nodes (M = Hf or Zr) and high porosity (Figure 1). The vanadium species were deposited in the two MOFs using the SIM method (creating V-SIM MOFs: Hf-MOF-808-V and Zr-NU-1000-V), and the resulting MOFs were characterized using a combination of analytical and spectroscopic techniques including N2 sorption isotherms, infrared (IR), Raman, diffuse reflectance UV, X-ray photoelectron (XPS) spectroscopies, as well as single-crystal X-ray diffraction (SCXRD) analyses. In these MOFs, the single-vanadium(V)-atom species were anchored on the metal oxide nodes with different binding motifs, specifically chelating in Hf-MOF-808-V and both bridging and monodentate binding in Zr-NU-1000-V. Their catalytic properties were investigated via alcohol oxidation reaction using oxygen as the oxidant. Heat treatment was found to alter the locations of a fraction of the vanadium ions in Hf-MOF-808-V, resulting in significantly higher catalytic activity and an overall simplification of siting.



Figure 2. Powder X-ray diffraction patterns (PXRD; rt) and N₂ isotherms (77 K). PXRD for (a) Hf-MOF-808 (black), Hf-MOF-808-V (red), and Hf-MOF-808-after catalysis (rose) and (b) Zr-NU-1000 (black), Zr-NU-1000-V (blue), and Zr-NU-1000-after catalysis (light blue). N₂ adsorption (filled symbol) and desorption isotherms (open symbol) of (c) Hf-MOF-808 (black circle), Hf-MOF-808-V (red square), and Hf-MOF-808-after catalysis (rose triangle) (b) Zr-NU-1000 (black circle), Zr-NU-1000-V (blue square), and Zr-NU-1000-after catalysis (light blue triangle). V_{ads} = adsorbed amount.

Hf-MOF-808-V and Zr-NU-1000-V were obtained via solution-phase metalation, SIM, of pre-existing Hf-MOF-808 and Zr-NU-1000. (See Supporting Information for detailed procedures and characterization, Figures 2, S1-S7.). Briefly, vanadyl acetylacetonate $(V(O)(acac)_2)$, was dissolved in a methanol solution containing each MOF. Striking color changes (from white to yellow for Hf-MOF-808-V and from yellow to dark yellow for Zr-NU-1000-V) were observed during the SIM process, indicating the successful incorporation of vanadium species. Consistent with the color changes, ligand-to-metal charge-transfer (LMCT) peaks centered at around 4.0 eV appeared in the diffuse reflectance UV spectra (Figure S3). Inductively coupled plasma optical emission spectroscopy (ICP-OES) measurements indicated vanadium loadings of 1.1 ± 0.2 and 1.0 ± 0.2 per node for Hf-MOF-808-V and Zr-NU-1000-V, respectively. To verify the porosity of Hf-MOF-808-V and Zr-NU-1000-V, N2 sorption isotherm measurements at 77 K were conducted (Figures 1c-d, and S4). The Brunauer-Emmett-Teller (surface) areas only decrease from 1620 to 1400 m^2/cm^3 for Hf-MOF-808-V and from 1030 to 680 m^2/cm^3 for Zr-NU-1000-V, indicating that porosity is retained during V-SIM. In addition, density function theory (DFT) calculated average pore size distribution showed only small decreases in their pore sizes, from 18 to 15 Å for Hf-MOF-808-V and from 30 to 27 Å for the mesopore of Zr-NU-1000-V, suggesting partial occupation of these pores by the vanadium species but overall retention of the pore structures.

In the diffuse reflectance infrared Fourier transform spectra (DRIFTS; Figure S5), a sharp peak at ~3650 cm⁻¹ and a broad peak at around 900 cm⁻¹ emerged for both Hf-MOF-808-V and Zr-NU-1000-V, which were attributed to the V–O–H stretching mode and the vibration modes involving the V–O–M (M = Hf or Zr) bond, respectively.^{1,42,43} In addition, a decrease in intensity of the peak associated with terminal and bridging–OH stretches on the node at 3670 cm⁻¹ was observed. These features suggest chemisorption of vanadium oxide species on the node for both Hf-MOF-808-V and Zr-NU-1000-V; this conclusion was corroborated by Raman spectroscopy measurements (Figure S6).

To determine the oxidation states of the incorporated vanadium species, X-ray photoelectron spectroscopy (XPS) measurements were performed (Figure S7). The V 2*p* core-level spectra of Hf-MOF-808-V (Figure S7a) and Zr-NU-1000-V (Figure S7b) fit well with single-component binding energies of 517.0 (2*p*_{3/2}) and 524.3 (2*p*_{1/2}) eV for MOF-808-V, and 517.6 (2*p*_{3/2}) and 524.6 eV (2*p*_{1/2}) for NU-1000-V, respectively, which are similar to the energies of other reported V(V) compounds.⁴⁴ These data indicated that the V(IV) precursor was oxidized to V(V) when incorporated on the nodes of MOFs.

To obtain further structural insight about the incorporated vanadium species, SCXRD analyses were conducted (Figures S8-11, and Table S1). The structures of vanadium species were found to be quite different in Hf-MOF-808-V (Figure 3) versus Zr-NU-1000-V (Figures S10-11). In Hf-MOF-808-V, three types of crystallographically non-equivalent single-atom vanadium sites were observed, binding to the Hf₆-node in chelating mode (V1, V2, and V3 in Figures 3b-e, S8). This positional disorder of vanadium sites might be explained by the partial hydration of vanadium sites; V1 and V3 would be assigned as the hydrated vanadium. The crystallographically estimated loadings were 0.48 (V1), 0.54 (V2), and 0.48(V3) vanadium per Hf₆-node, aligning well with the loadings determined by ICP-OES (see Supporting Information for detailed discussion). For Zr-NU-1000-V, multiple single-atom vanadium species were observed on the bridging position (V1) and the monodentate positions (V2, V3) of the Zr_{6} node (Figures S11d-f). In addition to vanadium, acac ligands crystallographically were also observed coordinated on the MOF node of Zr-NU-1000-V (Figure S11c). Their crystallographically

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estimated loadings were 0.56 (V1), 0.40 (V2), and 0.12(V3) vanadium per Zr_6 -node, consistent with the loadings observed by ICP-OES, *i.e.*, a single atom per node, but each occupying one of three possible sites.

Given the structural information, the V-SIM MOFs were examined as catalysts for a model reaction, the oxidation of 4methoxybenzyl alcohol (1) by O_2 in toluene as solvent at $105^{\circ}C$ (Figure 4a).⁴⁵ The reactions were performed with suspensions of the V-SIM MOFs (7.5 mol% of V to the substrate 1) (Figure 4, S12; see Supporting Information for details). As shown in the reaction time profiles monitored by GC-FID, the V-SIM MOFs catalyzed the oxidation (Figure 4b for Hf-MOF-808-V and S12a for Zr-NU-1000-V), while the bare MOFs displayed negligible activity. Additionally, high selectivity (>99%) was confirmed by GC-MS towards the formation of 4-methoxybenzaldehyde (2) was observed without any generation of the over-oxidized product, 4methoxybenzoic acid. At 4h reaction time, their turnover numbers (TONs) are estimated to be 11.3 (Hf-MOF-808-V) and 8.2 (Zr-NU-1000-V). Turnover frequencies (TOFs) at low conversion (<12% Fig. 4b) were essentially identical:1.9 \pm 0.1 h⁻¹ for Hf-MOF-808-V and 2.1 ± 0.1 h⁻¹ for Zr-NU-1000-V. Interestingly, with Hf-MOF-808-V as catalyst the rate of reaction increased over the first hour, with the TOF averaging $3.8 \pm 0.1 \text{ h}^{-1}$ between the 1st and 2nd hours. (See Figures 4b and S12a.)



Figure 3. Crystal structures of Hf-MOF-808-V collected at 100 K. (a) 3D structure (b) the magnified figure of the node where V1 (blue), V2 (red-orange), and V3(green) sites are represented in different colours. (c–e) the crystal structures of the node and structure representations for clarity. In (c)–(e), the side views of the MOF node are shown, where V1, V2, V3 sites are extracted.

To elucidate the origin of the increase in TOF, we determined the single-crystal X-ray structure of Hf-MOF-808-V after heating the material overnight at 105 °C (Figure S13, Table S2). As seen in F_{o} - F_{c} electron density maps after the heat treatment (Figure S13b), the residual densities corresponding to V2 intensify, while those for V1 and V3 became negligible. Thus, the catalytic material evolves from one featuring multiple single-V-atom sites, to one characterized by a single site.

Variable-temperature IR and Raman measurements clearly indicated reversible changes in structure of the anchored vanadium species, ascribable to dehydration and rehydration (Figures S14-17. see Supporting Information for details). The combined results indicated that a dehydrated form of V2 of Hf-MOF-808-V is the active site for catalytic oxidation of the alcohol by Hf-MOF-808-V. Consistent with this picture, catalyst heating under vacuum, followed by transfer to the reaction solution under conditions that preclude re-hydration of Hf-MOF-808-V, boosted the initial TOF to 6.1 ± 0.1 h⁻¹ (open red circles in Figure 4b; TONs are 12.4 at 4h reaction time). For Zr-NU-1000-V, no clear dependence of TOF on heating time was observed, suggesting that either the catalytic performances of bridging (V1) and monodentate (V2 and V3) vanadium sites are similar, or that this catalyst, in contrast to Hf-MOF-808-V, does not evolve with time. In addition, XPS spectra after heating and vacuum, the V2 $p_{3/2}$ peak of Zr-NU-1000 did not show any shift, while that of Hf-MOF-808-V showed a slight shift of 0.2 eV toward higher binding energy (Figure S18).



Figure 4. (a) Catalytic reaction scheme of 1 to form 2 (b) Reaction time profiles for the catalytic oxidation of 1 to 2. Inset is the structure of the putative active site of the Hf-MOF-808-V catalyst.

The substrate scope was further expanded (Table S3, entries 3– 8). In all cases, Hf-MOF-808-V showed higher catalytic activities than Zr-NU-1000-V with the selectivity towards the aldehyde product. The origins of this distinct difference in catalytic activities between Hf-MOF-808-V and Zr-NU-1000-V could be ascribed to their difference in the binding motif of the vanadium oxide spiecies on the node ("chelating" on Hf-MOF-808 and "bridging and monodantate" on Zr-NU-1000).^{2, 46}

To assess the catalysts' stability, recollected Hf-MOF-808-V and Zr-NU-1000-V were washed several times with fresh toluene to remove residual substrates and products, and the oxidation reaction was performed with the recycled material. No significant decreases in product conversion or aldehyde selectivity were observed (Figure S19). Importantly, ICP-OES measurements of the reaction mixture filtrates revealed no detectable vanadium, implying that no catalyst leaching. Additionally, ICP-OES assessments of vanadium loadings of Hf-MOF-808-V and Zr-NU-1000-V following use as catalysts matched those the pristine compounds. Additionally, hot filtration tests showed no leaching which further support the heterogeneous nature of the catalysts (Figure. S20). Furthermore, multiple post-catalysis characterization studies indicated the structure and composition of Hf-MOF-808-V and Zr-NU-1000-V were retained during and after catalysis (Figures S21–22).

In summary, the structures of the incorporated vanadium oxide species were elucidated through spectroscopic techniques and SCXRD studies, which showed that they coordinate differently to the nodes of Hf-MOF-808-V versus those of Zr-NU-1000-V. SCXRD and variable-temperature spectroscopic studies of Hf-MOF-808-V revealed that the as-prepared material, while featuring only a single vanadium atom per node, employs three distinct vanadium binding sites. Remarkably, heating consolidates the siting such that the vanadium ions occupy essentially only a single site. The activity of the single-site version of the catalyst is three times that of the multi-site version. The thermal and temporal evolution of the Hf₆-supported, single-atom catalyst from multi-site to single-site form, is manifested in kinetic measurements as striking, and otherwise puzzling, increases in TOF values with time. We anticipate that the observed, remarkable persistence of crystallinity of the MOF supports over the course of catalyst installation and subsequent thermal treatment - even for crystals large enough to support SCXRD will yield additional insights into the design and methodology for creating more effective MOF-supported, single-metal-ion, and/or single-site, catalysts.

ASSOCIATED CONTENT

Supporting Information

The photographs of single crystals, crystallographic data, Diffusereflectance UV and IR, Raman, XPS spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interests.

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Figure 1. Structures of pristine (a) Hf-MOF-808 and (b) Zr-NU-1000 with the corresponding structures of their inorganic nodes and organic linkers. Hf-MOF-808 ($[Hf_6(\mu_3-O)_4(\mu_3-OH)_4(OH)_6(H_2O)_6(BTC)_2]\infty$; H3BTC = benzene-1,3,5-tricarboxylylic acid and Zr-NU-1000 ($[Zr_6(\mu_3-O)_4(\mu_3-OH)_4(OH)_4(H_2O)_4(TBAPy)_2]\infty$; H4TBAPy = 1,3,6,8-(p-benzoic-acid)pyrene).

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Figure 2. Powder X-ray diffraction patterns (PXRD; rt) and N₂ isotherms (77 K). PXRD for (a) Hf-MOF-808 (black), Hf-MOF-808-V (red), and Hf-MOF-808-after catalysis (rose) and (b) Zr-NU-1000 (black), Zr-NU-1000-V (blue), and Zr-NU-1000-after catalysis (light blue). N₂ adsorption (filled symbol) and desorp-tion isotherms (open symbol) of (c) Hf-MOF-808 (black circle), Hf-MOF-808-V (red square), and Hf-MOF-808-after catalysis (rose triangle) (b) Zr-NU-1000 (black circle), Zr-NU-1000-V (blue square), and Zr-NU-1000-after catalysis (light blue trian-gle). Vads = adsorbed amount.

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Figure 3. Crystal structures of Hf-MOF-808-V collected at 100 K. (a) 3D structure (b) the magnified figure of the node where V1 (blue), V2 (red-orange), and V3(green) sites are represented in different colours. (c-e) the crystal structures of the node and structure representations for clarity. In (c)–(e), the side views of the MOF node are shown, where V1, V2, V3 sites are extracted

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Figure 4. (a) Catalytic reaction scheme of **1** to form **2** (b) Reac-tion time profiles for the catalytic oxidation of **1** to **2**. Inset is the structure of the putative active site of the Hf-MOF-808-V catalyst.

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