Metal–Organic Framework Supported Cobalt Catalysts for the Oxidative Dehydrogenation of Propane at Low Temperature

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ABSTRACT: Zr-based metal–organic frameworks (MOFs) have been shown to be excellent catalyst supports in heterogeneous catalysis due to their exceptional stability. Additionally, their crystalline nature affords the opportunity for molecular level characterization of both the support and the catalytically active site, facilitating mechanistic investigations of the catalytic process. We describe herein the installation of Co(II) ions to the Zr₆ nodes of the mesoporous MOF, NU-1000, via two distinct routes, namely, solvothermal deposition in a MOF (SIM) and atomic layer deposition in a MOF (AIM), denoted as Co-SIM+NU-1000 and Co-AIM+NU-1000, respectively. The location of the deposited Co species in the two materials is determined via difference envelope density (DED) analysis. Upon activation in a flow of O₂ at 230 °C, both materials catalyze the oxidative dehydrogenation (ODH) of propane to propene under mild conditions. Catalytic activity as well as propene selectivity of these two catalysts, however, is different under the same experimental conditions due to differences in the Co species generated in these two materials upon activation as observed by in situ X-ray absorption spectroscopy. A potential reaction mechanism for the propane ODH process catalyzed by Co-SIM+NU-1000 is proposed, yielding a low activation energy barrier which is in accord with the observed catalytic activity at low temperature.

INTRODUCTION

Selective dehydrogenation of light alkanes (e.g., ethane and propane) to produce the corresponding olefins (ethene and propene) is an industrially important process, because it provides the basic building blocks of various chemicals such as polymers and oxygenates. The development of new dehydrogenation catalysts, however, is a great challenge due to unavoidable side reactions such as thermal cracking and coke formation that occur under the harsh reaction conditions (temperature >500 °C) required by this thermodynamically unfavorable process. The oxidative dehydrogenation (ODH) of alkanes, in which an oxidant such as O₂ is included in the reaction stream, leads to a distinct decrease of the overall enthalpy change, e.g., ΔH°₂₉₈ for the ODH of propane is −28.3 kcal mol⁻¹, in contrast to +29.7 kcal mol⁻¹ for propane dehydrogenation. Therefore, the ODH of alkanes can occur at lower reaction temperatures, in turn minimizing coke deposits and thereby potentially increasing the lifetimes of the catalysts. To achieve good overall efficiency, however, the overoxidation of the alkanes and/or the desired alkene products to CO/CO₂ needs to be minimal. Of the reported catalysts for propane ODH, VOₓ, CrOₓ, or MoOₓ on metal oxide supports such as silica, zirconia, and alumina are probably the most investigated. The activity and the selectivity toward propene formation for these catalysts have been found to be highly dependent not only on the identity of the support, but also on the methods of preparation of the catalysts.

As compared to these aforementioned traditional metal oxide supports, metal–organic frameworks (MOFs) a now enormous family of porous materials, are more amenable to structural tuning due to the wide variety of combinations of...
metal nodes and organic linkers, the building blocks of MOFs. Their structural diversity has underscored their potential for applications in gas storage, fuel production, chemical sensing, and catalysis. More recently, efforts have been directed at exploring their use as catalyst supports in heterogeneous catalysis, such as selective alkene dimerization/oligomerization reactions and high temperature catalysis of gas-phase reactions. Although they are typically less stable than industrially used solid supports such as zeolites, a number of Zr- and Hf-based MOFs stand out due to their extraordinary stability as well as high porosity.

Notably, the active sites in a MOF-supported catalyst are readily characterized due to the high structural uniformity and crystallinity of the MOF supports—factors that can facilitate mechanistic studies as well as aid in the construction of structure−activity relationships among members of the same family of catalysts.
We selected NU-1000, a MOF composed of Zr6(μ3-O)(μ2-O)4(H2O)4(OH)4 nodes and tetratopic 1,3,6,8-tetrakis(p-benzoate)pyrene (TBAPy4+) linkers, as our catalytic platform \(^{27}\) (Figure 1) due to its previously observed behavior as a near-ideal support for Ir- and Ni-based gas-phase catalysts. \(^{28,29}\) Notably, the lengthy pyrene ligands can effectively prevent the anchored Ni active sites on the Zr6 nodes from sintering during the hydrogenation catalysis, achieving long-term stability. In our current work, we targeted cobalt as the deposited metal ions on NU-1000 since nanosized spinel Co3O4 have been shown to catalyze the propane ODH process under gentle reaction conditions. \(^{30}\) Two deposition techniques were used to anchor Co(II) ions to NU-1000: solvothermal deposition in a MOF (SIM), \(^{31,32}\) and atomic layer deposition in a MOF anchor Co(II) ions to NU-1000: solvothermal deposition in a MOF (AIM). \(^{33,34}\) We demonstrate that both materials, namely, Co-SIM+NU-1000 and Co-AIM+NU-1000, are active for propane ODH catalysis at temperatures as low as 200 °C, in contrast to the commonly used 300 °C required for supported VOx catalysts. \(^{2}\) Additionally, their catalytic behaviors are demonstrated to be different under the same experimental conditions, which can be attributed to differing distributions of the Co sites in these two materials during catalysis.

## RESULTS AND DISCUSSION

The syntheses and characterization of Co-SIM+NU-1000 and Co-AIM+NU-1000 are detailed in Figures S1–S6. The catalytic activity of both materials for the ODH of propane was preliminarily tested under steady-state conditions (weight hourly space velocity, WHSV = 0.126 h\(^{-1}\)) while the reaction temperature was varied from 150 to 250 °C, from which 230 °C was determined to be the upper limit where the crystallinity and porosity of the samples are retained after catalysis. These findings align with those from temperature-programmed oxidation (TPO) experiments where the onset for the oxidation of Co(II) is observed below 230 °C (Figure S7). Thereafter, all catalyst samples were subjected to an activation process, namely, heating at 230 °C with a flow of propane and O\(_2\) (propane:O\(_2\)_2(mol) = 3:5) until the propane conversion reached a steady state. By varying the propane molar space time \((W/F)\), in which \(W\) is the amount of catalyst used and \(F\) is the flow rate of propane, propane:O\(_2\)_2(mol) = 6:5, the turnover frequency (TOF, on a per cobalt basis) was determined to be 1.02 ± 0.09 and 0.54 ± 0.12 h\(^{-1}\) for Co-AIM+NU-1000 and Co-SIM+NU-1000 at 230 °C, respectively (Figure 2a; for catalysis at 200 °C, see Figure S8). In addition to the desired propene production, CO\(_2\) was observed as the only side product for both catalysts after 20 min time on stream (TOS). Both catalysts are also highly functionally stable; e.g., after ~24 h TOS, propane conversion slightly decreased from 8.7% to 8.3% for Co-AIM+NU-1000 as the ODH catalyst, and from 3.8% to 3.7% for Co-SIM+NU-1000 (Figure 2b). For comparison, we also prepared, activated, and evaluated, under identical conditions, highly dispersed cobalt on zirconia powder (Co-ZrO\(_2\); 10 wt % cobalt, BET surface area ~225 m\(^2\) g\(^{-1}\)). (See Supporting Information text and Figure S9 for details of Co-ZrO\(_2\) synthesis and characterization.) The TOF for the same catalytic process was determined to be only 0.15 h\(^{-1}\) on a per cobalt atom basis at 230 °C (Figure S10), highlighting the advantages of using a MOF as the catalyst support.

The relationship between propane conversion and propene selectivity was investigated for both catalysts at various temperatures, during which the propane conversion was varied by adjusting the molar space time \((W/F)\) of propane at each temperature. The obtained results for Co-SIM+NU-1000 and Co-AIM+NU-1000 are plotted in Figures 2d and 2e (see Figure S11 for delplots), respectively, and are used to illustrate the selectivity of different catalytic pathways involving the propane ODH process (Figure 2c).\(^{35}\) As depicted, at each temperature the selectivity toward propene formation increases as the propane conversion decreases, ultimately reaching 100% at 180 °C (or lower) under our experimental conditions. This is an indication that the primary product from the catalytic process is propene \((k_2 \sim 0)\) and the observed CO\(_2\) formation is predominantly from the combustion of the in situ generated propene. For each catalyst, at any given propane conversion the propene selectivity increases as the reaction temperature decreases, implying that the apparent activation energy, \(E_a\), for propene ODH is lower than that of propene combustion. Additionally, propene selectivity, under the same conversions and conditions, is higher for Co-AIM+NU-1000 (Figure 2e) than Co-SIM+NU-1000 (Figure 2d).

To gain further information on how temperature affects propene selectivity during the ODH catalysis by the two MOF-supported catalysts, Arrhenius plots for both the propane ODH...
and propene combustion processes were constructed (Figure 2f) and phenomenological activation energies were determined therefrom. For the propane ODH process, the experimental conditions for both catalysts were further optimized where propane conversion is in the differential region and the selectivity toward propene formation is 100%. As can be seen, the propene formation rate is higher than that of propene combustion for both materials at all investigated temperatures (200−230 °C, by extrapolation from T > 220 °C), and this difference becomes more distinct at lower temperature. This is in accord with the observed higher propene selectivity when lowering the reaction temperature (vide supra). The higher rate for propene formation, in combination with the lower rate for propene combustion reaction catalyzed by Co-AIM+NU-1000 as compared to Co-SIM+NU-1000, indicates at the simplest level the basis for the superior catalytic performance by the Co catalyst prepared via AIM. Nevertheless, temperature affects the rate of these two processes for both catalysts in a similar fashion—a more profound effect on propene combustion than propane ODH. These different experimental observations (Figure 2d−f) imply that there may be some structural difference between the two catalysts.

By using a few low-order, intense, and nonoverlapping reflections from the powder X-ray pattern, a surface (surface envelope) dividing the regions with high and low electron densities can be produced. Differential analysis of this surface electron envelope between a postsynthetically modified MOF and the parent material can yield the coarse maps of the electron density associated with the deposited metal ions, according a reliable way of determining their location.36,37 In our current study, difference envelope densities (DEDs) of the as-synthesized samples were collected to elucidate the distribution of the anchored cobalt atoms in the two materials (Figure 3). The electron density from the cobalt-containing species in both materials primarily localizes in the ∼8 Å windows along the c axis, although additional electron density is evident at hydroxyl groups pointing into the hexagonal pores in Co-SIM+NU-1000 (only) (Figure 3b,d).

We used in situ X-ray absorption spectroscopy to probe the valence and structural information on the deposited Co ions in these two materials. The pre-edge feature at 7709.2 eV (1s → 3d) in the X-ray absorption near edge structure (XANES, Figure S12) spectra indicates that the deposited Co ions in both as-synthesized materials remain in the +2 oxidation state, the same as the used Co precursors. The edge energy of all the MOF-supported samples is shifted slightly to lower energy as compared to the Co(II) standards, which is not uncommon for Co samples depending on their coordination environment.38 Upon activation in O2 at 230 °C for 4 h, there is a slight increase in the intensity of the pre-edge peak together with a decrease in the white-line intensity at ∼7724 eV, indicating the formation of Co(III) species.38 The appearance of Co(III) after activation was further confirmed by X-ray photoelectron spectroscopy (XPS) data obtained from the postcatalysis samples and the TPO profile of the two catalysts (vide supra). The Fourier-transformed extended X-ray absorption fine structure (EXAFS) spectra of both as-synthesized samples (Figures S13−S17, Table S2) are dominated by a single peak at ∼1.5 Å (phase-uncorrected distance) associated with Co−O distances within the first coordination sphere (Figure 4). Fitting this peak indicates that the average Co−O bond distance is ∼2.0 Å. Following activation in O2 at 230 °C for 4 h, however,
different (and differing) EXAFS features were observed for the samples. For both activated Co-SIM and Co-AIM+NU-1000, fitting the first coordination sphere of the Co center suggests that its average coordination number decreases by ca. 1 (0.8 for Co-SIM, 0.7 for Co-AIM) and the Co−O bond distance decreases to ∼1.96 Å, which may be well explained by the appearance of tetrahedral Co centers via a loss of one H2O ligand. Additionally, two new peaks at ∼2.4 and ∼3.1 Å are clearly evident in the spectrum of the activated Co-AIM+NU-1000 (Figure 4b,c) and they match well with the region in the EXAFS spectrum of a spinel Co3O4. Given the evident cobalt mixed valency, the EXAFS analysis, and the known ODH activity of the spinel Co3O4, the catalytic cluster might well possess a spinel-like structure (Figure 4d, the SIM form less so).

We have studied the mechanism of the propane ODH process catalyzed by activated Co-SIM+NU-1000 using density functional theory (DFT) calculations. Due to the weak contribution from well-defined Co−Co scattering signals in the EXAFS spectrum of activated Co-SIM+NU-1000 (Figure 4a), we have used a cluster model containing one Co atom (Figure 5), although polymeric sites may also be competent for this reaction.

All calculations were carried out at the DFT level using the M06-L local density functional. More details about the methodology and computational models are reported in the Supporting Information. All reported energies are gas phase enthalpies at the experimental temperature of 230 °C (503.15 K) in kcal mol⁻¹.

Upon activation, the structural change of the Co sites in Co-SIM+NU-1000 entails the loss of one ligand as evidenced by EXAFS analysis. At high temperature, further release of water is expected, forming the active species A-1 (Figure 6a). (Thus, hydroxo ligands provide the protons and O₂ provides an oxygen atom, thereby leaving the cobalt coordination number unchanged.) The most stable spin state of A-1 is the quartet (S = 3/2) state, corresponding to a Co(III) center (Figure S21), which is in agreement with the appearance of Co(III) species upon activation (Figure S12). We therefore select A-1-(S=3/2) as the starting point of the propane ODH catalytic cycle (Figure 6b). Charges and spin densities for all intermediates in the cycle are reported in Table S4.

The cycle (Figure 6b) begins with propane interacting with A-1 to form adduct A-2. Subsequently, one oxygen atom abstracts a secondary hydrogen atom from propane via A-TS2-3. Analogous structures in the sextet spin state were found higher in energy (see values in parentheses, Figure 6b). The resulting isopropyl radical in A-3 can then bond to the Co center, forming the more stable intermediate A-4. From here, A-4 can undergo (i) C−H bond abstraction to produce propene and A-5 or (ii) isopropyl migration to form the rebound intermediate A-6, which may also form via direct rebound from A-3, although we have not modeled that process.
The enthalpy reaction coordinate for propane ODH catalyzed by A-1 is shown in Figure 7. The activation enthalpies of the first and second C–H bond abstractions are 12.6 and 15.8 kcal mol\(^{-1}\) for A-TS2-3 and A-TS4-5, respectively. The second C–H bond abstraction to produce propene via A-TS4-5 is 7.3 kcal mol\(^{-1}\) more favorable than the isopropyl migration via A-TS4-6 to form the rebound intermediate A-6. This hypothesis about kinetic control is in line with experimental results since the selectivity toward propene decreases when increasing the reaction temperature due to the competing transition states. Estimated transmission coefficients \(\kappa(T)\)\(^{42}\) for A-TS2-3 and A-TS4-5 indicate that tunneling appears to be not very significant at such high temperatures,\(^\text{43}\) although it will further enhance the rate of hydrogen atom abstraction compared to isopropyl migration.

This computational study demonstrates the potential of mononuclear Co-decorated MOF sites to promote the oxidative dehydrogenation of propane. Of course, polynuclear sites may also be competent for this reaction, and computational modeling studies of activated Co-AIM containing spinel-like \(\text{Co}_3\text{O}_4\) structures, among others, are in progress.

**CONCLUSION**

We presented herein two approaches of anchoring Co(II) ions to the crystallographically well-defined and uniform hexazirconium(IV)-containing nodes of a mesoporous MOF, NU-1000: solution-phase SIM and vapor-phase AIM. The resulting materials, Co-SIM+NU-1000 and Co-AIM+NU-1000, are found to be active for catalytic oxidative dehydrogenation of propane to propene at reaction temperatures as low as \(\sim 200\) °C. Of particular note, different catalytic activity as well as selectivity toward propene formation is observed under the same experimental conditions for these two materials. The behavioral differences are consistent with the presence of different active-site structures for the otherwise closely related catalysts. In particular, upon activation in \(\text{O}_2\), a new Co···Co interaction appears for Co-AIM+NU-1000, which is absent in Co-SIM+NU-1000. Computational modeling of the propane ODH catalysis by Co-SIM+NU-1000 yields a reasonable catalytic cycle that matches well with the experimental observations. The generality of both synthetic routes, effective in tuning activity and selectivity of the targeted catalysis, in combination with the highly modular nature of MOFs, suggests a seemingly infinite number of new catalytic species. Aided by computational modeling, the mechanistic investigation provides an excellent opportunity for building structure–activity relationships among this new family of MOF-supported catalysts, thereby facilitating the design of improved catalysts. These investigations are currently in progress in our laboratories.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscentsci.6b00290.

Synthetic procedure, characterization, and calculations (PDF)

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**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work was supported by the Inorganometallic Catalyst Design Center, an EFRC funded by the DOE, Office of Basic Energy Sciences (DE-SC0012702). A.W.P. and M.R.D. were supported by the Department of Defense (DoD) through the National Defense Science and Engineering Fellowship (NDSEG) program. A.E.P.-P. acknowledges a Beatriu de Pinós fellowship (BP-DGR 2014) from the Ministry of Economy and Knowledge from the Catalan Government. This work made use of the J.B. Cohen X-ray Diﬀraction Facility supported by the MRSEC program of the National Science Foundation (DMR-1121262) at the Materials Research Center at Northwestern University. This work made use of the EPIC and Keck-II facilities of the NUANCE Center at Northwestern University, which has received support from the Soft and Hybrid Nanotechnology Experimental (ShyNE) Resource (NSF NNCI-1542205); the MRSEC program (NSF DMR-1121262) at the Materials Research Center; the International Institute for Nanotechnology (IIN); the Keck Foundation; and the State of Illinois, through the IIN. Use of the Advanced Photon Source is supported by the U.S. Department of Energy, Office of Science, and Office of Basic Energy Sciences, under Contract DE-AC02-06CH11357. Materials Research Collaborative Access Team (MRCAT, Sector10-ID-B) operations are supported by the Department of Energy and the MRCAT member institutions. The authors acknowledge the Minnesota Supercomputing Institute (MSI) at the University of Minnesota for providing computational resources.
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(43) We have estimated the transmission coefficient $\kappa(T)$ that relates semiclassical and observed rate constants by using the Skodje−Truhlar truncated parabola method (see ref42). At 230 °C (503.15 K) the $\kappa$ values for the reactions via A-TS2-3 and A-TS4-5 are 1.4 and 3.8, respectively; at 190 °C (463.15 K) similar values of $\kappa$ are found, 1.5 and 5.5, respectively.