

Tuning Reactivity and Lewis Acidity in Molecule-Based Porous Metal Oxides for Alkane Dehydrogenation
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Catalytic oxidative dehydrogenation (ODH) is an attractive alternative to current dehydrogenation routes because it does not present these thermodynamic limitations. To gain fundamental insight into factors affecting ODH, careful control of synthetic conditions and precise assessment of species at the molecular level will be crucial. We aim to use the assembly of discrete polyoxometalate (POM) clusters into porous inorganic frameworks. These materials present a unique opportunity to build solid state materials with precisely defined of metal atom placement and environment. This route will allow explicit control over material properties such as redox potential and Lewis acidity, allowing us to evaluate fundamental questions and about structure-reactivity relationships. The development of effective ODH catalysts will be greatly strengthened by blending of principles from both inorganic coordination chemistry and solid-state materials.

Results from Year 1

Our lab developed the synthesis of a framework comprised of the Preyssler cluster ($[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$, denoted $\{\text{P}_5\text{W}_{30}\}$) assembled with $\text{Co}(\text{H}_2\text{O})_4^{2+}$ -bridging units (Figure 1).¹ Briefly, these frameworks are synthesized by addition of metal salt and $\text{K}_{14}\text{NaP}_5\text{W}_{30}\text{O}_{110}$ to an aqueous LiCl solution with $\text{pH} < 1$ at 90°C and reaction with stirring for ≥ 4 h. Single-crystals are obtained by vapor diffusion of methanol (MeOH) into the cooled solution. Single-crystal X-ray diffraction (XRD) reveals an orthorhombic *Imma* unit cell ($a = 52.037(1)$ Å, $b = 21.5548(5)$ Å and $c = 26.1839(1)$ Å) containing $\{\text{P}_5\text{W}_{30}\}$ linked with $\text{Co}(\text{H}_2\text{O})_4^{2+}$ bridging units. Each $\{\text{P}_5\text{W}_{30}\}$ is bridged to four neighboring clusters in the *ab* plane and to two other clusters along the *c* direction.

Importantly, the rich redox activity of $\{\text{P}_5\text{W}_{30}\}$ can be preserved in the assembled structures. In order to access this redox activity under relatively mild conditions that preserve framework integrity, we use photochemical reduction to post-synthetically introduce excess electrons. Briefly, UV illumination in the presence of an appropriate sacrificial reductant (MeOH) leads to multielectron accumulation in the cluster. These electrons, when kept anaerobic, are stable indefinitely, and may be titrated with a mild oxidant. Importantly, our frameworks can reversibly store up to 10 electrons per cluster unit without any change to the crystal structure. The corresponding electron density, on the order of 10^{21} cm^{-3} , is comparable to that observed in other highly doped metal oxides, including WO_{3-x} . These added electrons induced a 1000-fold enhancement in the conductivity. These results illustrate the delocalized nature of the added electrons and demonstrate the potential viability of these molecule-based semiconductors for electronic applications and motivate further exploration of these and similar materials. Additionally, the ability to post-synthetically add electrons provides a convenient avenue for evaluating the properties of the extended solids as well as for probing the coupling between clusters and the metal bridging unit.

We have since expanded the synthesis of $\{\text{P}_5\text{W}_{30}\}$ -based materials to include bridging units of Mn, Fe, Ni, Cu, Zn, Ag, Cd, Hg, W, Eu, Sn and Pb. Single crystal and powder (Figure 2a) X-ray diffraction data show that all of the frameworks bridged with first-row transition metals crystallize with the same structure, while the larger metals yield three-dimensionally bridged frameworks with different connectivity. As these first-row bridging units all yield similar structures, mixed-metal frameworks can easily be obtained. For example, scanning tunneling electron microscope energy dispersive X-ray spectroscopy (STEM-EDS) mapping on crystals synthesized with mixtures of Mn and Ni show that the metals are homogeneously dispersed on the size-scale of the measurement (Figure 2b). Similar mixtures

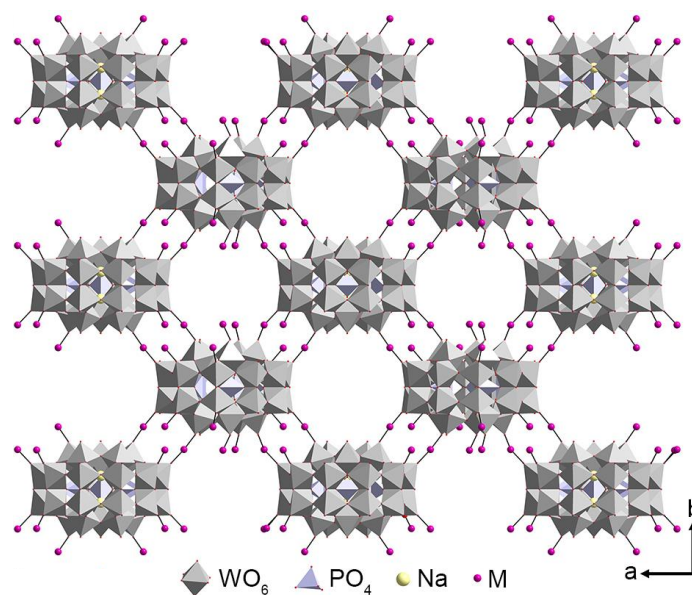


Figure 1. (a) Crystal structure of $\text{Co}(\text{H}_2\text{O})_4^{2+}$ -bridged $\{\text{P}_5\text{W}_{30}\}$ framework extending in the *ab* lattice plane. Disordered water and charge-compensating cations omitted for clarity.

can be obtained for a variety of binary and higher combinations of the first-row transition metals, providing access to widely tunable metal oxide compositions. The $\{P_5W_{30}\}$ cluster building block may also be doped with Mo (yielding $\{P_5MoW_{29}\}$) or the central cavity may be exchanged for a variety of cations (including Bi and many lanthanides) prior to assembly, providing additional handles for tunability. Initial investigations into composition–function relationships focused on conductivity as a preliminary probe of the effect of metal bridging unit. With the exception of Fe, frameworks bridged with first-row transition metals show little dependence of the conductivity on metal bridging unit. This trend is similar to that often observed in MOFs, in which mixed $Fe^{2+/3+}$ introduce mid-gap states that provide a means for conduction. These results motivate further exploration into purposefully modulating the oxidation state of the metal bridging unit. Nevertheless, all metal-bridged frameworks exhibit conductivity at least an order of magnitude higher than unlinked $\{P_5W_{30}\}$ clusters, suggesting that the metal bridging units can facilitate coupling between the clusters and facilitate charge transport. These results have been incorporated into a manuscript that has been submitted for publication.

Preliminary experiments show that we can access at least partially oxidized bridging units in both the Mn and Fe frameworks without compromising the crystal structure. Following synthesis, the crystals were finely powdered and washed with methanol. The powders were then soaked in a methanol solution of ceric ammonium nitrate or *meta*-chloroperoxybenzoic acid. Oxidation was evidenced by a change in color. In the case of Mn-bridged frameworks, the as-synthesized powders are pale yellow due to the lack of spin-allowed $d-d$ transitions in high-spin Mn^{2+} . Oxidation of the frameworks leads to a darkening, presumably due to the introduction of Mn^{3+} bridging units with spin-allowed $d-d$ absorption. Synthesis using Mn(III) acetate yields similarly colored powders, although single crystals were not obtained. Similarly, as-synthesized Fe-bridged frameworks are dark brown in color, which may suggest the presence of small amounts of Fe^{3+} , allowing intervalence charge transfer absorption between Fe^{2+} and Fe^{3+} centers. This color is lost upon oxidation, again due to the lack of spin-allowed $d-d$ transitions in the high-spin $d^5 Fe^{3+}$.

Summary and Impact

The development of next-generation ODH catalysts will require precise understanding and manipulation of the molecular nature in porous solid-state materials. POM-based frameworks present an ideal platform to investigate fundamental structure–reactivity relationships that can elucidate the important fundamental chemical factors governing ODH catalyst performance. The research performed in Year 1 has demonstrated the promise of using molecular metal oxide clusters as building blocks for widely tunable metal oxide materials with well-defined atom placement. This tunability will provide a platform for gaining insight into the microscopic factors affecting active sites in these materials and aid in the rational design of improved catalysts for ODH. The understanding gained through this paradigm will ultimately be used to develop guidelines for accessing designer materials that can be tailored to a range of desired applications.

The funding provided under this grant has enabled the PI to develop new routes to molecule-based metal oxide materials. These materials will provide a platform for studying emerging photophysical and electronic properties of complex metal oxide materials, which are a significant and integral component of the PI's research program and will provide a springboard for additional funding. This funding has also enabled three graduate students to work on the development and study of these materials with a reduced TA load. Their research on these materials has formed the cornerstones of their Ph.D. theses.

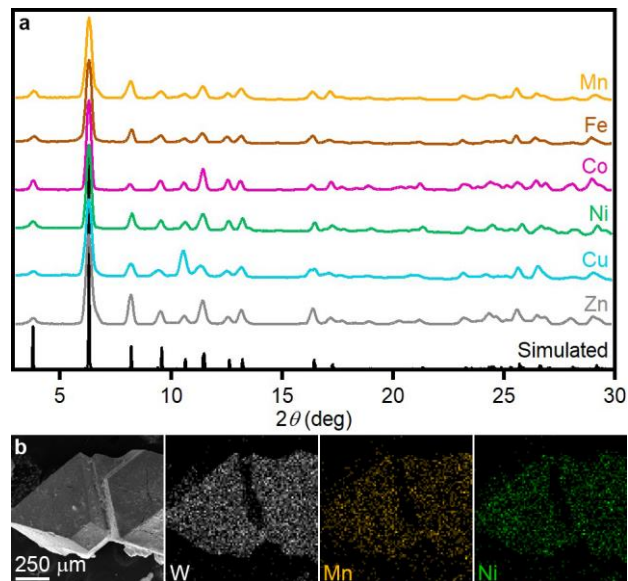


Figure 2. (a) Powder X-ray diffraction patterns for (top to bottom) Mn, Fe, Co, Ni, Cu and Zn bridging units compared to the simulated pattern for the *Imma* assembly. (b) STEM-EDS mapping of a framework bridged with both Mn and Ni.