

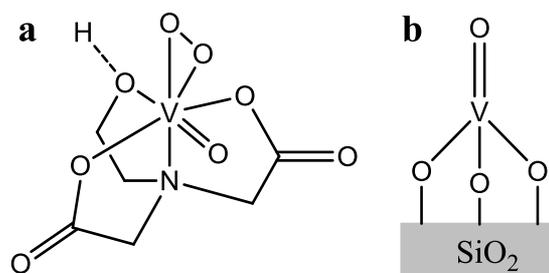
# Bridging the Gap between Heterogeneous and Enzyme Catalysis: *In Situ* Spectroscopic Study of Vanadium Haloperoxidase Enzyme Functional Mimics

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## Abstract

Vanadium haloperoxidases (VHPOs) are a class of redox enzymes characterized by their vanadate-dependent active site and are named for their ability to catalyze the aqueous two-electron oxidation of halide ions (Cl<sup>-</sup>, Br<sup>-</sup>, or I<sup>-</sup>) in the presence of hydrogen peroxide to produce hypohalous acids (HOCl, HOBr, or HOI).<sup>1</sup> Various research groups have designed different metal-organic compounds with the intention of mimicking the structure and function of the active peroxidated form of VHPOs.<sup>2-4</sup> The most studied mimic compound is K[VO(O<sub>2</sub>)(heida)], a vanadium peroxy-oxo compound chelated with N-(2-hydroxyethyl) iminodiacetic acid (heida), depicted in Figure 1a.<sup>2</sup>



**Figure 1.** a. Structure of K[VO(O<sub>2</sub>)(heida)] mimic of VHPO showing peroxy and oxo groups and b. structure of dehydrated supported vanadia species on silica possessing the trigonal pyramidal structure.

There are significant structural differences between the active site of supported vanadium oxide catalysts and the K[VO(O<sub>2</sub>)(heida)] complex. The vanadium peroxy-oxo structure present for K[VO(O<sub>2</sub>)(heida)] is not present for vanadia supported on inorganic oxides such as silica.<sup>5</sup> Dehydrated supported vanadia on silica at low coverage is present as the trigonal pyramidal structure shown in Figure 1b with the surface VO<sub>4</sub> species possessing one terminal V=O bond and three bridging V-O-Si bonds. Despite the differences in these vanadium oxide structures, both K[VO(O<sub>2</sub>)(heida)] and silica-supported VO<sub>4</sub> are capable of selectively oxidizing methanol to formaldehyde. The reaction mechanisms for both catalysts, however, would not be expected to be the same, given the different molecular structures of their vanadium oxide catalytic active sites and reaction environments (gas phase *vs.* aqueous phase).

In this study, we have demonstrated that there are significant structural and reactivity differences between the active site of supported vanadium oxide catalysts and the K[VO(O<sub>2</sub>)(heida)] complex. We have used *in-situ* Raman, UV-Vis, and ATR-IR spectroscopy during aqueous methanol oxidation to examine K[VO(O<sub>2</sub>)(heida)], bridging the gap between inorganic and protein based vanadate oxidation catalysts. The use of methanol as a molecular probe was used to provide important information on the active site and mechanism of oxidation by K[VO(O<sub>2</sub>)(heida)]. Density Functional Theory (DFT), isotope labeling, and kinetic experiments were also used to compliment experiments. This study elucidates the K[VO(O<sub>2</sub>)(heida)] catalytic active site, reaction intermediates, and the important role of the vanadium peroxy structure. These studies will be used as a benchmark for future studies of vanadium haloperoxidase (VHPO) enzymes.

## References

- (1) Butler, A. *Coord. Chem. Rev.* **1999**, 187, 17.
- (2) Colpas, G. J.; Hamstra, B. J.; Kampf, J. W.; Pecoraro, V. L. *J. Am. Chem. Soc.* **1996**, 118, 3469.
- (3) Butler, A.; Baldwin, A. H. in *Vanadium Bromoperoxidase and Functional Mimics*; **1997**; p 109.
- (4) de la Rosa, Roger I.; Clague, M. J.; Butler, A. *J. Am. Chem. Soc.* **1992**, 114, 760.
- (5) Molinari, J. E.; Wachs, I. E. *J. Am. Chem. Soc.* **2010**, 132, 12559.