Modeling Mo/W formate dehydrogenase catalytic intermediates

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The utilization of fossil fuel increases the global demand for CO_2 sequestration due to the potential impacts of this greenhouse gas toward global climate change and ocean water acidification. Molybdenum and tungsten formate dehydrogenase (Fdh) enzymes catalyze the reversible conversion of formate to carbon dioxide ($HCOO^- \rightleftharpoons CO_2 + 2e^- + H^+$). Understanding the mechanism of Mo- and W-Fdh enzymes is expected to contribute to a better understanding how to design new chemical catalysts. An additional impetus for these studies focuses on the use of formate as a storable form of energy in chemical bonds. We now know that these enzymes possess an ancillary ligand selenocysteine ligand (Se_{cys}) that contributes to lowering the activation energy of the reactions these enzymes catalyze. However, it is unknown how this ancillary ligand contributes to catalysis. Thus, it is critical to understand the basic electronic and geometric structure features of Fdh enzymes if we are to fully understand their catalytic mechanism. Presence of Fe-S clusters makes more difficult to get detailed electronic structures. Although a combination of EXAFS and EPR data have been collected for these enzymes, our understanding electronic structure contributions to reactivity have been hampered by the inability to optical spectroscopies to probe these active sites. This arises from the presence of other strongly absorbing chromophores that mask the electronic transitions associated with the catalytic Mo and W centers in the enzymes. To address this issue, we have synthesized the first *des*-oxo synthetic analogs of Fdh enzyme active sites and have studied these models using a combination of EPR, electronic absorption, and XAS spectroscopies. Here, we will present our most recent results on the synthesis, spectroscopy, and electronic structure of novel 6-coordinate EPR active analogs for Fdh enzymes that indicate a potential role for the Se_{cys} ligand in catalysis.