Spectroscopic and Computational Investigations of Small Molecule Activation by [$MoFe_3S_4$] Clusters: Ligand Controlled Reactivity

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Biological activations of small molecules, such as dihydrogen, dinitrogen, carbon oxides are catalyzed by intricate iron-sulfur metalloproteins. The understanding of the chemical functions of these iron-sulfur clusters embedded into a protein matrix has been a challenging task for both experimentalists and theoreticians. Investigations of biomimetic compounds can provide the basic chemical background for the *in vivo* functions and hence, aid the deconvolution of complex chemical processes that can take place in protein environments. [$MoFe_3S_4$] clusters are such biomimetic compounds that can be considered as structural and functional analogues of the FeMo-cofactor of nitrogenase. These clusters structurally mimic the Mo-subcube of FeMo-co and can reduce single and double N, N bonds, but fail to activate dinitrogen. Detailed description of the potential energy surface of hydrazine, diazine and ethylene activation by [$MoFe_3S_4$] clusters can reveal important mechanistic insights about the potential role of the Mo-site in the biological nitrogen fixation.

Sulfur, chlorine and phosphorous K-edge and molybdenum L-edge X-ray absorption spectroscopic measurements have been carried out for a selected series of [$MoFe_3S_4$] clusters with various observed activities in N,N bond reductions. Due to the different effective nuclear charges of the molybdenum and iron ions (i.e. different oxidation states), the Mo-S and Fe-S bonds contribute to two separate, well-resolved pre-edge features in the sulfur XAS spectra. The intensities of these pre-edge features vary as a function of the ligands around the molybdenum. The chloride XAS also shows ligand environment dependence of the overall electronic structure of the clusters. The pre-edge features of the Mo L-edge spectra experimentally define the electrophilicity of the Mo-site and shows correlation with the observed chemical reactivity. By using the phosphorous K-edge data in addition to the other ligand and metal edges, the total experimental wave function (%P, %Mo, %S, %Cl) is determined, which is used to spectroscopically calibrate the basis sets and employed density functionals for systematic potential energy surface studies of substrate coordination, concomitant protonation and reduction, and product release.