

# A Molecular View of Heterogeneous Solid-State Catalysts: The Case of Molybdenum Sulfide

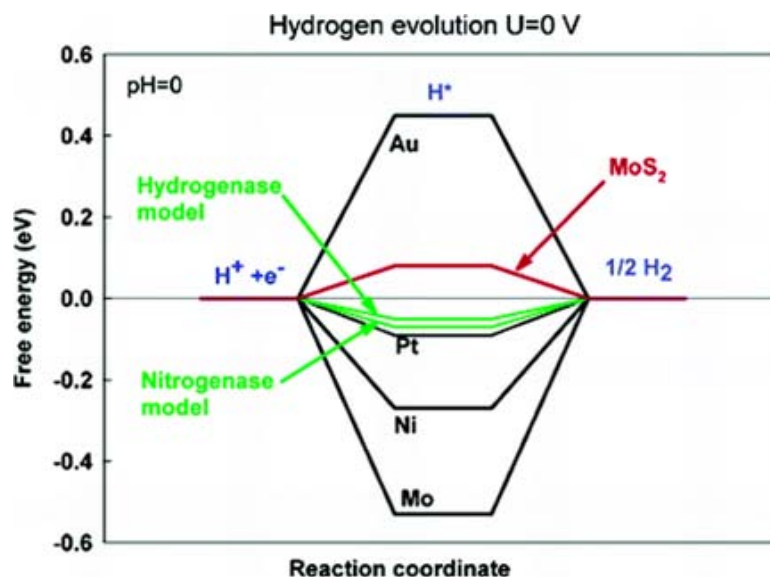
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Literature seminar

January 24, 2013

Heterogeneous catalysts are pivotal in industrial scale chemical synthesis, being responsible for the production of commodity chemicals such as sulfuric acid, nitric acid, ammonia and hydrogen.<sup>1</sup> The catalytic processes that occur at the surface of these materials in a number of systems are known to be the result of “active sites”.<sup>2,3</sup> Active sites, first formulated by Taylor in 1923 as under coordinated atoms<sup>4</sup>, are local regions structural and electronic properties that are distinct from the surface at large.<sup>5</sup> Today we know these active sites can be caused by a variety of effects including step edges,<sup>2</sup> imbedded atoms,<sup>6</sup> and crystal edges.<sup>7</sup> While this exact description of the active site has permitted a much clearer understanding of heterogenous catalysis; practically it has had minimal impact.

The ability to understand the nature of a catalyst’s active site and reproduce it either through site-selective synthetic methods or molecular mimics would mark a major advancement in this field. Such knowledge would allow one to make marked improvements in activity and selectivity while minimizing inactive material. An area where this approach is currently being applied is in the field of hydrogen evolution with molybdenum sulfide. Hydrogen is the center of a great deal of research as an energy storage medium though the generation of H<sub>2</sub> typically uses noble metal catalysts.<sup>8</sup> While noble metals have high activities their cost makes widespread use prohibitive, fueling the search for alternative catalysts. Thus a molecular view of the active site and its mechanism would enable rational engineering to maximize efficiency.

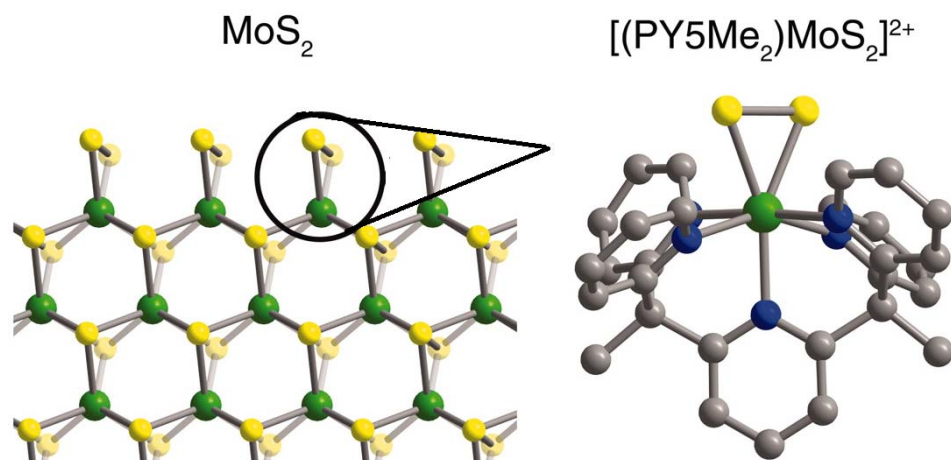


**Figure 1** Free energy diagram of bound hydrogen to known and potential catalysts.<sup>9</sup>

The interest in MoS<sub>2</sub> as an electrocatalyst for the evolution of hydrogen began in 2006 when Hinneman et. al. investigated the thermodynamics of hydrogen absorption (Figure 1).<sup>9</sup> The work calculated thermochemical information for the binding of hydrogen to systems with known catalytic activity (or lack of) and compared to unknown systems. Using their determined metric of Gibbs free energy of absorption the group screened for potential catalysts. Ultimately MoS<sub>2</sub> was predicted to be able

to catalytically produce hydrogen and was verified with electrochemical experiments.

The initial investigation of MoS<sub>2</sub> as hydrogen evolution catalyst spurred interest in utilizing this material. Since then work has gone to experimentally show edges sites to be responsible for catalytic hydrogen evolution.<sup>7</sup> Characterization of these edges to identify their structure would define the possible active site or active site precatalyst. Similarly, non-model systems with similar hydrogen evolution properties were shown by HAADF-STEM to be similarly terminated.<sup>10,11</sup>



**Figure 2** The MoS<sub>2</sub> edge site has been mimicked in a molecular catalyst.<sup>12</sup>

A molecular mimic of the active site of the MoS<sub>2</sub> sulfur dimer edge site (Figure 2) provides more insight into the catalytic mechanism. This mimic compound contained a Mo center with a persulfide ligand very similar to as synthesized model catalysts. As with the parent material this mimic shows promising catalytic properties. pH dependent electrochemical studies of this model catalyst showed an activation step consistent with the observed crystal termination. This as of yet unidentified molecular species may provide critical insight into the MoS<sub>2</sub> catalytically active species mechanism.

The study of heterogeneous catalysts with an emphasis of active site identification creates a bridge between molecular and solid state catalysis. The link of these fields will provide abounding opportunities for rational design. By considering the active site as a unique molecule, precise tuning of the active site becomes a foreseeable reality.

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