The enzyme nitrogenase and its catalysis: Biological ammonia synthesis and hydrogen production

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The enzyme nitrogenase catalyzes one of the most important reactions in biology, the conversion of nitrogen to ammonia. Industrially, ammonia synthesis is accomplished by the Haber-Bosch process, which needs high temperatures and pressures, about 400°C and 100atm. Since the biological ammonia synthesis can take place at ambient temperatures and pressures, an understanding of the biological process might contribute to the development of better ammonia synthesis catalysts that function under milder conditions. The active site of nitrogenase is the FeMo cofactor (FeMoco), a unique iron-sulfur cluster with the stoichiometry $MoFe_7S_9N$. In this talk, a detailed investigation of the structure and reactivity of the nitrogenase FeMoco is presented.

In a recent crystal structure (Einsle et al., Science 297, 1696 (2002)) it was found that the cavity of the FeMoco, which was hitherto thought to be empty, contains a small atom as a central ligand. The crystal study could show that the central ligand is nitrogen, oxygen or carbon. We have performed calculations on the FeMoco structures with the three different ligands and find that the FeMoco with a central nitrogen ligand is most consistent with experimental results. An important question is whether the central ligand is located inside the FeMoco at all times, or if it is possible to insert or remove it. We have studied possible insertion pathways and find that they have too high energy barriers to be accessible at ambient conditions. Furthermore, we have studied a possible pathway for N_2 reduction, which involves binding of N_2 on one of the triangularly coordinated Fe atoms. We find this pathway to be energetically accessible and consistent with much of the experimental information.

Nitrogenase catalyzes also the hydrogen evolution reaction. Currently there is an interest in hydrogen evolution catalysts, as molecular hydrogen is considered as a future fuel. The most common industrial catalyst for this reaction is Pt, but nature uses the enzymes hydrogenase and nitrogenase which do not contain noble metals. We have studied the details of the hydrogen evolution reactions of metals and enzymes and have used this knowledge to design new inorganic catalysts for this reaction.