

Chapter 12: Learning Objectives

- * Hydrogenases are used by anaerobic organisms both to reduce protons (using H^+ as a terminal oxidant) and to oxidize H_2 (gaining energy by reducing other species). Both iron-only and iron-nickel hydrogenases have two-metal active sites. The more recently discovered Hmd hydrogenase has a single-iron active site with a methanopterin cofactor. In each hydrogenase, there are CO and/or CN^- ligands on a low-spin iron atom.
- * The Wood-Ljungdahl and methanogenesis pathways move methyl groups to acetyl-coenzyme A and to CH_4 for energy production in anaerobes
- * The bifunctional carbon monoxide dehydrogenase/acetyl-coenzyme A synthase (CODH/ACS) has two interesting iron-nickel cofactors that do the biological analogues of the water-gas shift reaction and the Monsanto process, respectively. CO is transferred between active sites through a channel in the enzyme that prevents its loss.
- * Acetyl-coenzyme A provides a cautionary tale, showing that weakly-bound metals can be displaced during enzyme isolation and/or crystallization.
- * Methane and methionine are produced through cobalt and nickel macrocycle cofactors.
- * There are four nitrogenase enzymes, which perform the six-electron reduction of N_2 to NH_3 . Three of them have closely analogous active site clusters: the iron-molybdenum cofactor ("FeMoco") in Mo-dependent nitrogenase; the iron-vanadium cofactor ("FeVco") in V-dependent nitrogenase; the iron-iron cofactor ("FeFeco") in iron-only nitrogenase. The fourth nitrogenase is dependent on superoxide, and is not well-understood yet.
- * Mo-nitrogenase uses two very unusual iron-sulfur clusters, the "P cluster" and the FeMoco. The biosynthesis of the FeMoco involves a host of proteins working in concert. Especially important is the "Fe protein," which has a [4Fe-4S] cluster that uses ATP to drive 1-electron reductions during catalysis and during the synthesis of the FeMoco.
- * The mechanism of nitrogenase is understood through the "Lowe-Thorneley scheme" of 1-electron processes. The nature of these intermediates is slowly being unraveled through spectroscopic and kinetic studies, which benefit from the EPR activity of the FeMoco.
- * Dissimilatory (*i.e.*, used for energy, not for raw materials) reduction of nitrate uses NO_3^- reductase (Mo), NO_2^- reductases (heme or Cu), NO reductase (heme), and N_2O reductase (Cu) in different steps. Each enzyme involves an interesting metal-catalyzed transformation of a small molecule.
- * Molybdenum and tungsten enzymes are generally used for transfer of oxygen *atoms*, a 2-electron conversion. They commonly have a dithiolene ("molybdopterin") as a ligand, and often have O and S ligands with multiple bonds to the metal.