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Hydrogenases

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During the 14th International Conference on Biological Inorganic Chemistry (ICBIC) in Nagoya, Japan, in July 2009, we agreed with Dr. Preeti Vashi, Deputy Editor of this Journal, on a plan to assemble a cluster issue of *EurJIC* on hydrogenases and active site model complexes. Since the limitations of fossil energy sources and the global impact of oxidation products have become obvious, scientists and politicians have promoted the search for alternative energy sources. Besides the common renewable energy sources (exploitation of wind, sun, geothermal, and wave energy), there is a tremendous increase in interest in the production of hydrogen on a large scale, because it is a clean fuel, especially in highly efficient fuel cells. Dihydrogen has a high energy density and produces a clean combustion product, namely water. It is currently produced by several approaches, for example, steam methane reforming, electrolysis of water, coal gasification, and biomass processing techniques; all of these require considerable energy to produce one mole of dihydrogen. Hence, hydrogen utilization processes must be highly efficient to overcome the energy cost in its production in order for a macroscopic hydrogen economy to be feasible.

Hydrogen – a clean fuel

The electrolysis of water is accompanied by a high overpotential and therefore is a prime example of an unsustainable energy requirement for standard industrial applications. This should be reason enough for studying how H_2 is produced and consumed in nature. Microorganisms have been using H_2 as a primary fuel source for billions of years and consume an enormous amount of H_2 in different forms as energy source and transporter. The hydrogenase enzymes regulate the generation and depletion of H_2 either to avoid a surplus of reduction potential or to provide an energy source. Moreover, hydrogenases demonstrate highly efficient catalysis of the one-electron reduction of a proton. Impressively, the hydrogenases utilize base metals, iron and nickel, in their catalytically active sites, rivaling the expensive and resource-limited platinum that is the electrocatalyst of choice in fuel cells.

Hydrogenases – efficient catalysts

In the past 15 years, information from protein crystallography of the three types of hydrogenase enzymes was merged with spectroscopic data to confirm active site structures, inspiring synthetic chemists to produce small molecule synthetic analogues as potential molecular electrocatalysts for H_2 oxidation/H^+ reduction, which are currently discussed in literature. The hydrogenases are differentiated according to the shape of their active site, occurrence, localization, and function: (1) The cluster-free hydrogenase methylene-tetrahydromethanopterin (HMD) is found to possess a cofactor with a low-spin Fe^{II} atom. (2) The [FeNi]-hydrogenase exhibits a [FeNiS2] active site and catalyzes the oxidation of dihydrogen. A subgroup of [FeNi]-hydrogenase provides a [FeNiSe] center, whereby one cysteine is replaced by a selenocysteine. (3) The third type of hydrogenase, the [FeFe]-hydrogenase, is biased toward H_2 production. The remarkable structures of the active sites of both the [NiFe]- and [FeFe]-hydrogenases that exhibit seemingly "abiological" ligands as carbon monoxide and cyanide

Active site models

led to an enormous reinvestigation and development of aspects of the organometallic chemistry of iron carbonyl and cyanide complexes. An equally remarkable synergy has developed between chemists, microbiologists, structural biologists, spectroscopists, electrochemists, computational chemists, etc., many of whom have contributed to this issue.

This cluster issue of the *European Journal of Inorganic Chemistry* brings together twenty-six articles featuring the multidisciplinary nature of this timely topic. We are grateful for the wonderful response and contributions from the hydrogenase community. These contributions provide further understanding on how hydrogenases are synthesized in nature and how active site synthetic analogues are made at the chemist's bench, on the mechanisms of their performance at a molecular level, and on how this knowledge might be used to develop more effective electrocatalysts for the production and use of the most fundamental molecule on the planet, H_2.

Multidisciplinary investigations