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Catalytic hydrogen oxidation: dawn of a new Iron Age**

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The production of hydrogen (H_2) from water is a robust method of storing renewable energy (solar, wind…) in chemical form. This energy can then be released on demand as electrical power through H_2 oxidation in fuel-cells. Currently however, only noble metals meet technological specifications for fuel-cell applications. Inspiration for alternative catalysts based on Earth-abundant elements can be drawn from Nature, namely the hydrogenase enzymes, which only utilise nickel and/or iron, whilst rivalling platinum as catalysts for reversible H_2 evolution/oxidation.[1]

In particular, detailed biochemical, structural and mechanistic information has been accumulated on NiFe hydrogenases (Figure 1). Their heterobimetallic active site contains a nickel ion ligated by four deprotonated (thiolate form) cystein residues, two of which bridge to an iron ion. One CO and two CN^- ligands are also bound to the Fe^{II} center. Although several mimics of this active site were reported after the structure had been determined,[2] construction of models with structural relevance, that also replicate enzymatic activity, has long been a challenge for chemists (Figure 2). Indeed, up to 2009 none of these structural mimics were shown to be catalytically active, and only the use of organometallic ruthenium moieties as surrogates for the $\{Fe^{II}(CN)_2(CO)\}$ fragment allowed for the preparation of active catalysts first for H_2 evolution[3] and later for its oxidation.[4] In both cases, the active intermediate contains a hydride ligand (H^-) in a bridging mode, between the two metal centers,[3c, 3f, 4a] and is thus relevant to the Ni-C state of NiFe hydrogenases (Figure 1).[5]

The next milestone was the design of nickel and iron-based functional models. Three such systems (Figure 2) were reported, albeit with catalytic activity restricted to H_2 evolution,[6] once again with bridging hydride species as the active intermediate. Recent work from Ogo and co-workers has described a novel nickel-iron mimic (Figure 3) able to mediate both hydrogen evolution and oxidation, thus reproducing for the first time at a binuclear core, the bidirectional activity of the [NiFe]-hydrogenases.[7]

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The novelty of this mimic, likely responsible for its functionality, is the use of three triethylphosphite ($P(OEt)_3$) ligands to modulate the electronic properties of the iron center, so as to promote coordination of H_2 as a first step towards its activation. Heterolytic splitting of H_2 is promoted in the presence of methanolate, a strong base that captures a proton while a hydride ligand remains coordinated to the iron center. From this hydride species, oxidation *via* methylviologen (MV^{2+}) and release of a proton regenerates the starting compound. The net reaction is the two-electron oxidation of molecular hydrogen, which is the process mediated by both hydrogenase and the anode of a H_2 fuel-cell. This new nickel-iron compound achieves only a single turn-over with a 12% yield, although a better yield (45%) could be measured when using a stronger oxidant such as the ferrocenium ion. The system also operates far from the thermodynamic equilibrium, as evidenced by the requirement of a strong base to activate H_2, while the natural process operates in water at neutral pH. Similarly, a strong acid is required to produce H_2 from the hydride species, and so whilst this system shows promise as a catalyst for hydrogen evolution, the necessity of large overpotentials, as noted for other Ni-Fe mimics,[6a, 6c, 6d] remains an issue. Nonetheless, this novel nickel-iron compound mediates both hydrogen oxidation and evolution, behaviour so far restricted to a single series of mononuclear nickel catalysts.[8]

In line with this result is the recent report from Bullock and co-workers, that a mononuclear iron diphosphine complex can act as an electrocatalyst for H_2 oxidation (Figure 4).[9] Here again, the electronic properties of the iron center have been tuned, thanks to a functionalised cyclopentadienyl ($C_6F_5Cp^-$) ligand. Although similar systems reported by Bullock were shown to bind H_2, they were only able to mediate H/D exchange from a mixture of H_2 and D_2.[10] Modification of the Cp^- ligand with an electron withdrawing group, renders bound H_2 suitably acidic to facilitate H_2 oxidation. As with previous nickel complexes designed by D. L. DuBois,[8] an amine function has been incorporated in the diphosphine ligand, to act as a proton transfer relay and allow for fast deprotonation of the coordinated H_2 molecule, with formation of a terminal hydride complex. This system catalyses electro-assisted H_2 oxidation (1 atm. and 22°C) from C_6H_5F solutions of N-methylpyrrolidine with a turnover frequency of 0.66-2.0 s^{-1} and overpotential requirement estimated to 160-200 mV. Coordinating species must however be excluded from the media for catalysis to occur which precludes any direct utilisation in water.

These two systems have several common properties: (i) they contain electron-rich, low spin d^6 centers, coordinated by soft bidentate ligands, a nickel bisthiolate moiety in one case and a diphosphine in the other; (ii) they interact with H_2 - in the case of Ogo's system however, it has not been definitively demonstrated that Fe is the primary binding site, whilst H_2 binding to Ni^{II} centers is now documented;[11] (iii) they stabilize an Fe-bound terminal hydride ligand; (iv) they can split molecular H_2 into electrons and protons.

Despite the structural similarity of Ogo's system with the active site of [NiFe] hydrogenase, direct comparison of catalytic mechanisms should be avoided. Other characterised[4a, 6a, 6b] or computed[3c, 3f, 6c, 12] dinuclear hydride derivatives, based on a $\{Ni^{II}(\mu\text{-}SR)_2M\}$ core with M a low-spin d^6 metal center, feature a bridging structure in contrast to the terminally bound hydride in question. One such Ni-Ru bridging hydride from Ogo[4a] is active for H_2 oxidation, making it difficult to form a clear association between a terminal binding mode and H_2 activation. Even if these two terminally Fe-bound hydrides are associated with H_2 activation, it is not in accordance with the observation of a bridging hydride in the Ni-C state of the enzyme,[5] that being said, the production of a bridging hydride derivative that does replicate the Ni^{III}/Fe^{II} electronic structure of the Ni-C state, remains elusive. The Ni^{II}/Fe^{II} center of Ogo's hydride derivative may correspond to the Ni-R (Figure 1) state of the enzyme, however no definitive data exists as to the nature of the additional ligand (H_2, H^-…) nor to its binding mode to the $\{Ni^{II}(\mu\text{-}SR)_2Fe^{II}\}$ core.

Very few systems based on first-row transition systems are known to catalyse hydrogen oxidation under technologically relevant conditions.[8, 13] These recent results from Ogo[7] and Bullock,[9] clearly indicate that chemists are making continued progress towards better understanding how Nature exploits abundant metals to achieve complex reactions, whilst channelling this knowledge into the design of original catalytic systems, which are now close to readiness for technological applications.

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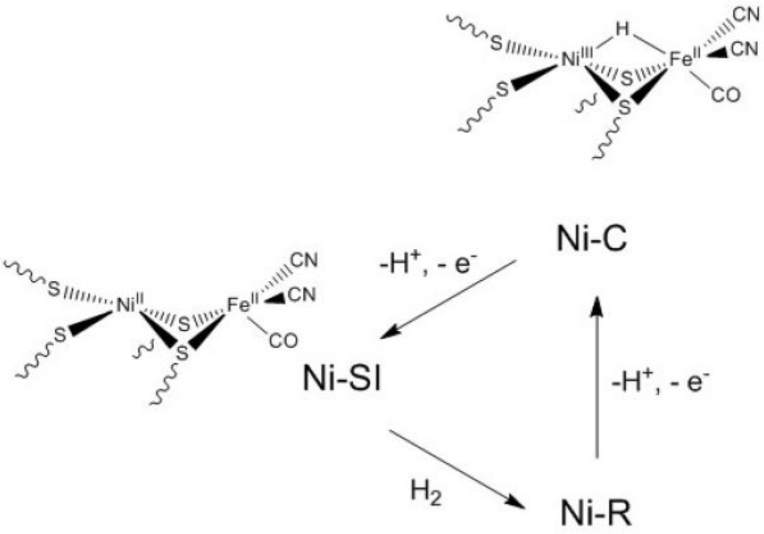

Figure 1.

Mechanism for catalytic H_2 oxidation mediated by [NiFe] hydrogenase.

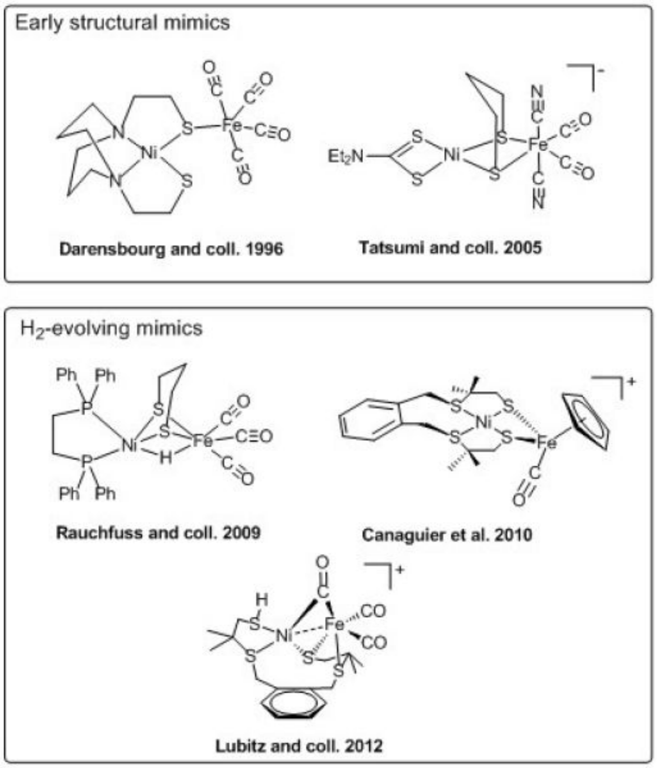

Figure 2.

Selected structural models (top) and representation of the H_2-evolving functional models (bottom) of the active site of [NiFe] hydrogenase (references lie in the text).

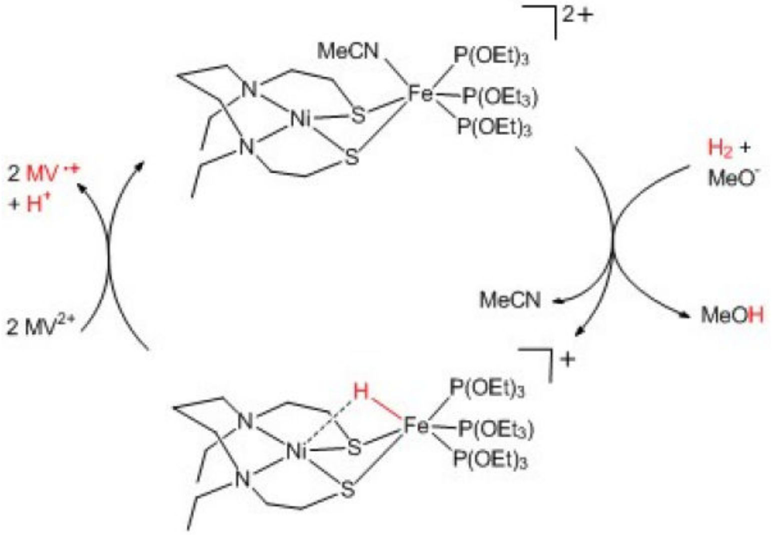

Figure 3.

Structure and reactivity of the novel Ni-Fe mimic from Ogo's group.

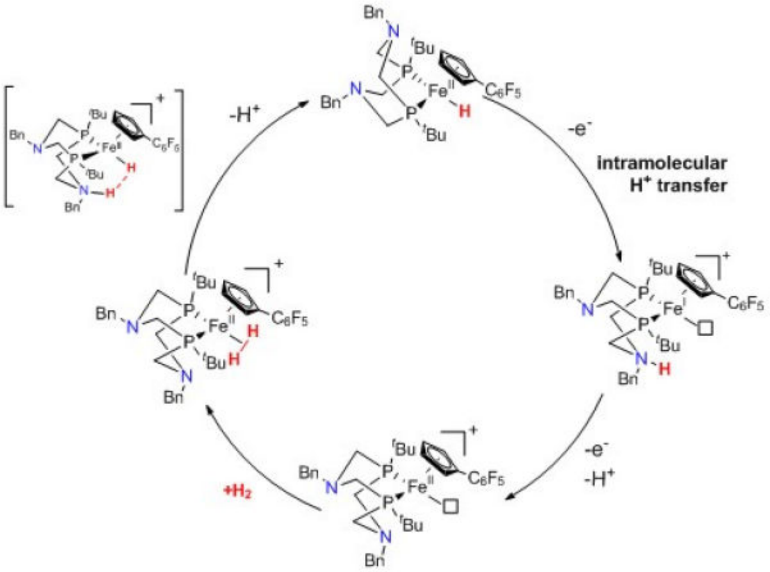

Figure 4.

Catalytic mechanism for H_2 oxidation mediated by the mononuclear iron diphosphine from Bullock and co-workers.