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Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr

Review

Thermal and photocatalytic production of hydrogen with earth-abundant metal complexes

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ARTICLE INFO

Article history:

Received 19 May 2017

Received in revised form 9 July 2017

Accepted 21 July 2017

Available online xxxxx

Keywords:

Hydrogenase mimic

Earth abundant metal complex

Hydrogen production

Electrocatalyst

Photocatalyst

ABSTRACT

Structural and functional models of [Fe], [FeFe] and [NiFe] hydrogenases using earth abundant metals (Fe and Ni) have been developed for electrocatalytic and photocatalytic hydrogen evolution reaction (HER) in relation to the structure and functions of the hydrogenases. In the X-ray crystal structure of the μ -hydride complex of [NiFe] hydrogenase from *Desulfovibrio vulgaris* Miyazaki F, the hydride ion is located on the Ni center rather than the Fe center. Thus, mononuclear Ni-hydride complexes act as the most efficient HER catalyst among various metal (Fe, Mn, Cu and Co) hydrides, enabling the reversible interconversion between H₂ and H⁺. A number of X-ray crystal structures of metal-hydride complexes, which are regarded as intermediates for HER, have been clarified. The X-ray crystal structures of polyhydrido copper clusters provide valuable insight into the HER functions of rhombus-shaped Cu nanoparticles (NPs). The detailed catalytic mechanisms of HER via cobalt-hydride complexes are discussed in both thermal and photocatalytic HERs, providing rational design principles for development of more efficient, selective and robust earth-abundant metal catalysts for thermal and photocatalytic HER to replace precious and high cost Pt catalysts.

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1. Introduction

Developments of clean, renewable alternatives to fossil fuels have become ever more important as the world concerns more and more on rapid depletion of fossil fuels, the resulting global warming, climate change and environmental damage by consumption of fossil fuels [1–6]. Among them, molecular hydrogen (H₂) is

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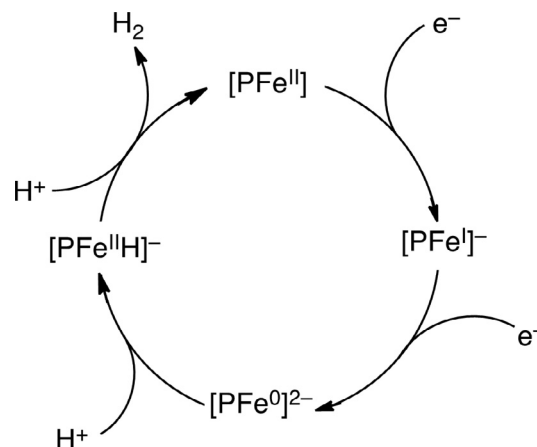
one of the most attractive alternatives for the sustainable energy system, since H₂ can be produced via water splitting using solar energy [7–23]. H₂ production via electrochemical water splitting is a promising approach for storing solar energy, because a photovoltaic (PV)-electrolysis system has achieved an average solar-to-hydrogen (STH) efficiency of 30% over a 48 h period of continuous operation [24]. In industry, steam methane reforming and coal gasification make more than 95% of the whole H₂ production, while only 4% of H₂ is produced by water electrolysis, because the cost of H₂ production by electrolysis is still much higher than that produced by fossil fuels [14]. Platinum-based materials are currently used as the hydrogen evolution catalysts for electrolysis of water [17]. Low abundance and high cost of platinum have limited its application to produce hydrogen resource more economically. In contrast, nature uses hydrogenases, which catalyze the conversion of protons and electrons into molecular H₂ ($2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2$) using the earth abundant metals (i.e., Ni and/or Fe) in their active site under ambient pressure and temperature [25]. H₂ was one of the earliest energy sources available on Earth when life evolved without dioxygen [26]. Hydrogenases are classified according to the metal ion composition of their active sites in [Fe], [FeFe], and [NiFe] hydrogenases [27–31]. Inspired by efficient catalysis of hydrogenases in nature, developing efficient non-noble metal catalysts, composed of earth-abundant elements such as Fe, Ni, Cu and Co, has recently attracted much attention to produce cost competitive H₂ [32–37]. On the other hand, inspired by photosynthesis, photocatalytic production of H₂ has extensively been studied [38–51]. However, the thermal and photocatalytic production has yet to be discussed together by focusing on earth-abundant metal-based catalysts.

This review focuses on recent developments in noble metal-free catalysts for both the thermal and photocatalytic hydrogen evolution reaction (HER). The thermal and photocatalytic mechanisms of iron complexes as structural and functional models of [Fe], [FeFe] and [NiFe] hydrogenases are discussed in relation with the enzymatic mechanisms. Catalysis of other earth abundant metal complexes such as Ni, Cu, Co and Mn complexes is also discussed and their catalytic reactivity is compared between thermal and photocatalytic production of hydrogen in terms of turnover number (TON), turnover frequency (TOF), overpotentials and quantum efficiencies. The overpotential is defined as difference between the applied potential and the standard potential of a proton source (HA: $E^\circ(\text{HA}/\text{H}_2)$) [52]. The lower the overpotential and the higher the TOF of HER, the catalytic HER activity of metal complexes is defined higher. The characterization and detection of active metal hydride species during the thermal and photocatalytic hydrogen evolution reactions are also discussed. In some cases, homogeneous metal complexes are converted to heterogeneous metal nanoparticles which become more active catalysts depending on the catalytic reaction conditions of hydrogen evolution.

2. Hydrogenase mimics

2.1. [Fe] hydrogenase mimics

The most attractive candidate for the catalytic metal center of HER is Fe, which is the most earth-abundant transition metal. The [Fe] hydrogenase contains a mononuclear iron center and no iron–sulfur cluster [29,53,54]. A unique active site structure has led to a series of synthetic studies of the [Fe] hydrogenase, which can activate H₂ [55–59]. Saveant and coworkers reported that an Fe porphyrin complex, [(TPP)Fe(Cl)] (TPP = tetraphenylporphyrin), catalyzes the electrocatalytic reduction of protons to H₂ at an applied potential of the Fe^{I/0} couple (−1.63 V vs. SCE) in *N,N*-dimethylformamide (DMF) in the presence of protonated triethy-



Scheme 1. Mechanism of electrocatalytic reduction of protons to produce H₂ with an iron porphyrin ([PFe^{II}]) [60].

lamine ($\text{Et}_3\text{NH}^+\text{Cl}^-$) with 100% Faradaic efficiency [60]. The catalytic mechanism is shown in Scheme 1, where the Fe(II)-hydride complex ([PFe^{II}H][−]) is a key intermediate, which reacts with H⁺ to produce H₂, accompanied by regeneration of [PFe^{II}] [60]. However, the standard potential of the catalyst couple (−1.63 V vs. SCE = −1.39 V vs. aqueous NHE) is far beyond biological potentials [60].

The hangman iron porphyrins with hanging groups of differing proton-donating abilities (Fig. 1) were synthesized and their electrocatalytic hydrogen-evolving activity was evaluated by Graham and Nocera [61]. Cyclic voltammograms (CVs) of hangman iron porphyrins in MeCN display a catalytic wave that grows from the Fe^{II/I} reduction wave [−1.4 ~ −1.5 V vs. ferrocenium/ferrocene ($\text{Fc}^+/\text{Fc} = 0.37$ V vs. SCE)] upon addition of HBF₄ to solution [61]. The comparison of the rate constant of H₂ evolution revealed that the hangman iron porphyrin (R = SO₃[−]: $\log(k/\text{M}^{-1}\text{s}^{-1}) = 6.12$ in the presence of 20 mM HBF₄) is by far the highest performing catalyst, outperforming the non-hangman porphyrin (R = H: $\log(k/\text{M}^{-1}\text{s}^{-1}) = 3.66$) [61]. Iron porphyrin complexes with second-sphere distal triazole residues also show a hydrogen evolution reaction (HER) catalyzed by the Fe(I) state rather than the Fe(0) state in both organic and aqueous media, whereas an analogous iron porphyrin complex without the distal residues catalyzes the HER in the formal Fe(0) state [62].

Winkler and coworkers reported that a Fe^{II} complex containing a fluorinated ligand 1,2-bis(fluorophenyl)ethane-1,2-dione diimine, [(dAr^F₂HBF₄)Fe(py)₂] (see Fig. 2 for the crystal structure)

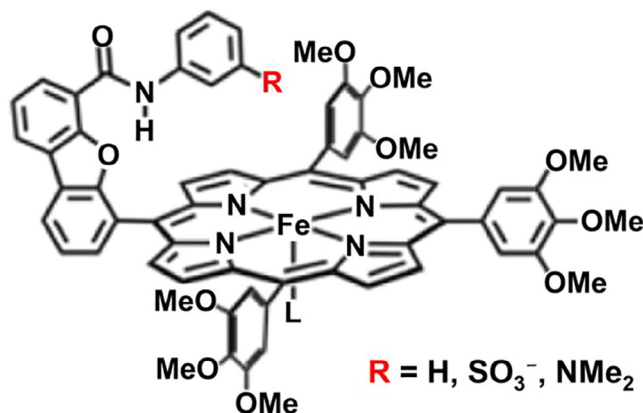


Fig. 1. Hangman iron porphyrins. Reprinted with permission from Ref. [61]. Copyright 2014, American Chemical Society.

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