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Review

Hydrogen-activating models of hydrogenases

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ABSTRACT

Hydrogenases are biological catalysts for hydrogen evolution and activation. While many model complexes of hydrogenases can catalyze the hydrogen evolution reaction, few of them can react with hydrogen. Here we review the hydrogen-activating models of hydrogenases, in particular, [NiFe]- and [FeFe]-hydrogenases. The mechanism of these reactions is described.

1. Introduction

Hydrogenases are enzymes that catalyze the production and consumption of hydrogen [1–6]. Hydrogenases were discovered as early as 1930s, but their crystal structures have only been known in the last two decades [7–13]. Based on the structures of the active sites, hydrogenases are classified as [FeFe]-, [NiFe]- and [Fe]-hydrogenases [1,4–6].

The crystal structures of [FeFe]-hydrogenase were first determined in 1998 and 1999, and showed an active site made of a homodinuclear $Fe_2(CO)_3(CN)_2$ core bridged by a SCH_2XCH_2S (X = CH_2, NH or O) dithiolate ligand (Fig. 1, left) [7–9]. Since then, its structure and mechanism have been subjected to many studies [14–19]. In 2013, Berggren et al. introduced three synthetic complexes $[Fe_2(SCH_2XCH_2S)(CO)_4(CN)_2]_2$ into the apoprotein of [FeFe]-hydrogenase, and only the semi-synthetic enzyme with X = NH was active [20]. This result provided a strong confirmation that the bridging dithiolate ligand in the active site of [FeFe]-hydrogenase is an azadithiolate [20–22].

The crystal structures of [NiFe]-hydrogenases have been extensively studied [10–12,23–25]. The active site of the oxygen sensitive [NiFe]-hydrogenases consists of a heterodinuclear [('S')$_2$Ni(μ-'S')$_2$(μ-X)Fe(CO)(CN)$_2$] (S = Cysteine, X = O or OH) fragment (Fig. 1, middle). Recently, the crystal structure of a standard [NiFe] hydrogenase was determined at 0.89 Å resolution [26]. Both [FeFe]- and [NiFe]-hydrogenases catalyze the reversible conversion of H_2 into protons and electrons.

The [Fe]-hydrogenase is unique in both structure and activity. The active site of [Fe]- hydrogenase contains only one Fe center coordinated by one cysteine sulfur, two *cis*-oriented CO, and a bidentate guanylylpyridinol ligand (Fig. 1, right) [13]. [Fe]-hydrogenase does not catalyze the same hydrogen production

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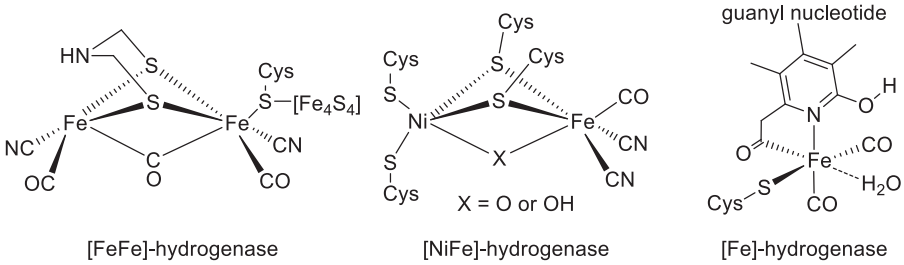
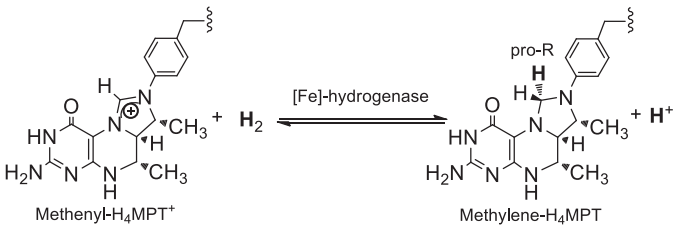
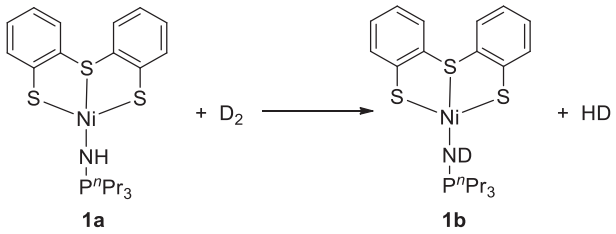


Fig. 1. The active sites of three types of hydrogenases [7–13].



Scheme 1. Reactions catalyzed by [Fe]-hydrogenase [13].



Scheme 2. Reaction of **1a** with D_2 [33].

and activation reactions as [FeFe] and [NiFe]-hydrogenases. Instead, it catalyzes the hydrogenation of methenyltetrahydromethanopterin (methenyl-H_4MPT^+) to form methylenetetrahydromethanopterin (methylene-H_4MPT) and proton, respectively (Scheme 1) [4–6,27,28].

Hydrogen is a clean energy carrier and an important chemical reagent. The impressive catalytic activity of hydrogenases has inspired a large body of biomimetic chemistry of hydrogenases [4,16]. While many models can catalyze the hydrogen evolution reaction, very few of them can mediate or catalyze the reverse reaction, the hydrogen activation. This article reviews the current state of biomimetic hydrogen activation. Although several reviews on hydrogenases and their models have been published [4–6,27–31], this topic has not been exclusively covered.

2. Reactions of [NiFe]-hydrogenase models with hydrogen

Since the determination of the crystal structure of [NiFe]-hydrogenase, many synthetic models of its active site have been synthesized [4–6,31,32]. However, only a few models can react with H_2.

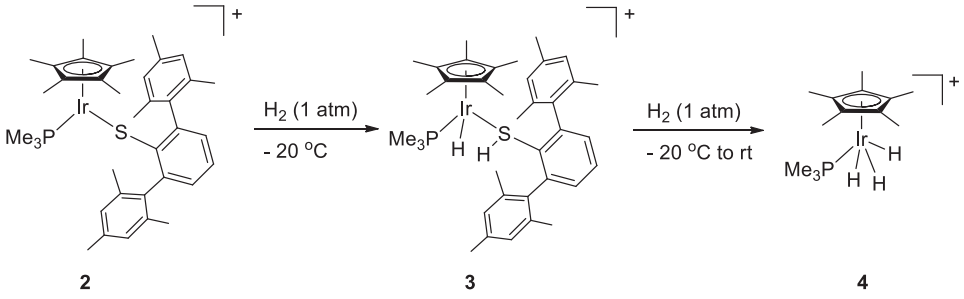
A Ni thiolate complex [Ni(NHP^nPr_3)('S_3')] (**1a**) ['S_3'$^{2-}$ = bis(2-sulfanylphenyl)sulfide (2-)] that modeled the nickel core of [NiFe]-hydrogenase reacted slowly with D_2 at high pressure, giving HD and [Ni(NHP^nPr_3)('S_3')] (**1b**) (Scheme 2). **1a** also catalyzed the H/D exchange reaction between D_2O and H_2, a characteristic reaction of [NiFe]-hydrogenase [33].

The complex [Cp*Ir(PMe_3)(SDmp)](BAr^F_4) (**2**) (Dmp = 2,6-dimesitylphenyl) [34] reacted with 1 atm of H_2 even at −20 °C, forming a thiol-hydride complex [Cp*Ir(PMe_3)(H)(HSDmp)](BAr^F_4) (**3**). When the temperature was increased to room temperature, complex **3** further reacted with H_2 to give complex [Cp*Ir(PMe_3)H_3](BAr^F_4) (**4**) with concomitant release of HSDmp (Scheme 3).

Several dinuclear Ru–Ge complexes could heterolytically activate H_2 [35–37]. For example, complex [(Dmp)(Dep)Ge(μ-S)(μ-O)Ru(PPh_3)] (**5**, Dep = 2,6-diethylphenyl) reacted slowly with H_2 (10 atm.) at 75 °C to afford two isomers, *anti*-**6** and *syn*-**6**, *via* Ru–O bond cleavage [35]. The proton was accepted by the μ-O ligand, while the H^- was accepted by the Ru ion. Protonation of **5** yielded complex [(Dmp)(Dep)Ge(μ-S)(μ-OH)Ru(PPh_3)](BAr^F_4) (**7**) which could split H_2 under 1 atm, giving [(Dmp)(Dep)Ge(μ-S)(μ-H)Ru(PPh_3)](BAr^F_4) (**8**) and H_2O (Scheme 4). The reaction of **7** with H_2 was reversible: complex **8** reacted with excess H_2O to give **7** and H_2 [36]. Very recently, Matsumoto and co-workers published the theoretical study on this activation of H_2 with the Ru–Ge complex [38].

Although the above-mentioned complexes exhibit some functions of hydrogenases, none of them contains a $^{10}M(\mu\text{-}S)_2{}^8M$ moiety (^{10}M = group 10 metals, ^8M = group 8 metals) that is the core of the active site of [NiFe]-hydrogenase.

The dinuclear Ni-Ru complex [(NiL)Ru(H_2O)(η^6-C_6Me_6)](NO_3)$_2$ (**9a**, L = *N*,*N*′-dimethyl-*N*,*N*′-bis(2-mercaptoethyl)-1,3-propanediamine) reacted with H_2 in water under ambient conditions, resulting in [(NiL)(H_2O)(μ-H)Ru(η^6-C_6Me_6)](NO_3) (**10a**) with a bridging hydride (Scheme 5) [39]. When deprotonated, **10a** was transformed into the neutral complex [(NiL)(OH)(μ-H)Ru(η^6-C_6Me_6)] (**11a**). **11a** catalyzed the hydrogenation of



Scheme 3. Reactions of **2** with H_2 [34].