Catalytic Oxidation of H_2 by Means of
a Water-Stable [NiFe]hydrogenase Model Complex

Takeshi Yatabe

Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Fukuoka, Japan

International Institute for Carbon-Neutral Energy Research, Kyushu University, Fukuoka, Japan

[NiFe]hydrogenases catalyze the transfer of electrons from H_2 to a redox partner.[1] This activation of H_2 for the release of electrons has tremendous potential applications from energy generation to industrial synthesis. Therefore, hydrogenases are currently the focus of much research across many disciplines. Previously, we have reported the first NiFe model complex that activates H_2 to form a hydride complex and proceeds electron transfer, H_2 evolution, and hydride transfer reactions (Figure 1b).[2] The NiFe model complex, however, performs the single turnover for these reactions because this complex is unstable in water and needs a strong organic base to activate H_2. Here, we report a water-stable NiFe model complex $[[Ni^{II}(Z)Fe^{II}(Cl)(CO)(L)](Cl)]$ {[**1**](Cl), Z = *N,N'*-diethyl-3,7-diazanonane-1,9-dithiolato, L = 1,2-bis(diphenylphosphino)ethane} that catalyzes H_2 oxidation in water at pH 6 under H_2 (0.8 MPa) with turnover number as 86 without any organic base.[3] We have also isolated and characterized three hydride intermediates in our proposed catalytic reactions.
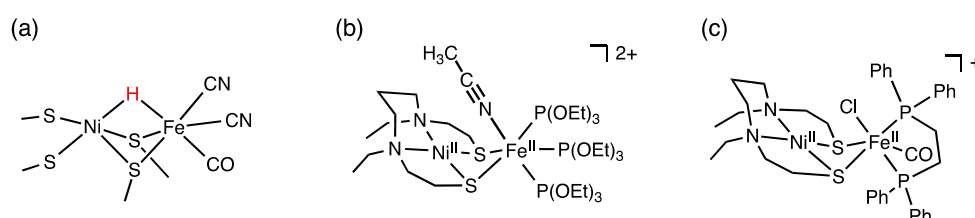

Figure 1 (a) The active site structure of [NiFe]hydrogenase, (b) the previously reported NiFe complex, and (c) a water-stable NiFe complex **1** (This work).

References
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[3] S. Ogo, T. Kishima, T. Yatabe, K. Miyazawa, R. Yamasaki, T. Matsumoto, T. Ando, M. Kikkawa, M. Isegawa, K.-S. Yoon, S. Hayami, *Sci. Adv.* **2020**, *6*, eaaz8181.