Nickel Complexes with Non-innocent Ligands as Highly Active Electrocatalysts for Hydrogen Evolution



Zhixin Chen,[†] Tao Wang,[†] Tingting Sun, Zhiyong Chen, Tian Sheng, Yu-Hao Hong, Zi-Ang Nan, Jun Zhu,* Zhi-You Zhou,* Haiping Xia,* Shi-Gang Sun

ABSTRACT Rational design of a molecular catalyst for a hydrogen evolution reaction (HER) with both high rates and low overpotential remains a challenge. Here we report a series of Ni-based catalysts incorporating non-innocent ligands and aimed at reduction of the overpotential by reserving electrons in the ligand, which could decouple the correlation between metal center reduction and metal hydride formation. The third-order rate constant of our catalysts can be increased by 2 orders of magnitude without increased of overpotential by altering the substituents in the imide since the electronic effect of substituents can change the kinetics of metal hydride formation dramatically. Furthermore, constructing a proton shuttle in the ligand further improves the activity. The catalyst with both these features can catalyze HER at a turnover frequency of 2572 s⁻¹ with low concentrations of acid and an extremely high third-order rate constant of 2.7×10^6 M⁻² s⁻¹ at a low overpotential.

KEYWORDS hydrogen evolution, molecular electrocatalysis, non-innocent ligand

Introduction

Producing hydrogen by electrolysis of water is an environmentally-friendly and sustainable method because it requires only water and electricity.¹ Hydrogen is a promising candidate as a clean fuel. The oxidation of hydrogen through fuel cells can regenerate energy without CO_2 emission and within the limit of the Carnot cycle. Hydrogen produced by steam reforming contains CO and causes poisoning of Pt catalysts. In contrast, hydrogen produced by an electrocatalytic hydrogen evolution reaction (HER) is very clean, and can be used in fuel cells directly. As a side benefit, intermittent electricity from solar cells and wind turbines can be utilized effectively in such a process.

For molecular catalysts,² the overpotential and the reaction rate of HER are related to metal center reduction and metal hydride formation but in general, these two element procedures are deleteriously coupled. On the one hand, the modification of the catalysts with electron-withdrawing substituents would reduce the electron density on the metal center, lowering the overpotential and making it easily reducible. On the other hand, the low electron density on the metal center hinders its protonation, which lowers the rate of metal hydride formation, or lowering the reaction rate of HER.^{2f-g} Consequently, rational design of a molecular catalyst for HER with both low overpotential and a high reaction rate remains a challenge.^{3,4}

Hydrogenases are highly active catalysts for hydrogen evolution.⁵ Previous work showed that an amine base positioned near the metal center can function as a proton shuttle which can speed up the proton transfer and facilitate the formation of the H-H bond.² Furthermore, [4Fe-4S] clusters in prokaryotic [FeFe] hydrogenase have multiple redox centers, allowing storage of electrons, which helps to stabilize electron-rich low valence metal centers,⁶ suggesting that a building block for electron storage may play a vital role in the catalytic redox process of the enzyme. Non-innocent ligand is a ligand in a metal complex where the oxidation state is not clear.^{7a} Metal complexes with non-innocent ligands can operate as an electron reservoir and usually exhibit high catalytic activity and controllability in catalytic reactions.^{3d-i,7} We assume non-innocent ligands such as diiminopyridine may be able to store electrons for redox reactions like [4Fe-4S] clusters in

Z. X. Chen,⁺ T. Wang,⁺ T. T. Sun, Z. Y. Chen, Dr. T. Sheng, Y. H. Hong, Z. A. Nan, Prof. Dr. J. Zhu, Prof. Dr. Z. Y. Zhou, Prof. Dr. H. P. Xia, Prof. Dr. S. G. Sun, Collaborative Innovation Center of Chemistry for Energy Materials, State Key Laboratory for Physical Chemistry of Solid Surfaces, College of Chemistry and Chemical Engineering Xiamen University, Xiamen, 361005 (China) natural enzymes, and this can stabilize the intermediate containing a low valence metal center in order to reduce the overpotential for reduction reaction (Scheme 1).

Scheme 1 Similarities between hydrogenase and Ni complex with non-innocent diiminopyridine ligands.



Herein, we demonstrate that the design of Ni complexes with suitable non-innocent diiminopyridine ligands can lead to efficient catalysts for HER. In particular, we found that replacing the π -acceptor aryl substituent of a ligand with a σ -donor cyclohexyl group would tune the basicity of a one electron reduced metal center and enhance the kinetics of metal hydride formation without increasing the overpotential, indicating that the substituent of the non-innocent ligand could significantly affect the performance of a catalyst. Decoupling the correlation between metal center reduction and the kinetics of metal hydride

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formation is a new approach.

Results and Discussion

The catalysts **1**, **2** and **3** were synthesized via the one-pot reaction of NiCl₂ with a slight excess of 2,6-diacetylpyridine and excess of an amine in THF at 85 °C in a sealed tube. The product precipitated in the reaction was purified by recryst- allization from CH_2Cl_2/Et_2O . The solid-state structures of **1**, **2** and **3** verified by single-crystal X-ray diffraction as well as high-resolution ESI(+)-MS and elemental analysis are shown in Figure 1.

Scheme 2 Synthesis of complexes 1, 2, and 3.





The HER catalytic activity was tested in CH₂Cl₂ solution with Bu₄NBF₄ as supporting electrolyte, trifluoromethanesulfonic acid (TfOH) as proton source, and a glassy carbon disk ($\phi = 3 \text{ mm}$) as the working electrode. Figure 2a shows linear sweep voltammograms of complex **1**, **2**, and **3** catalyzing HER in 10 mM TfOH. The comparison of kinetic parameters among **1**, **2**, and **3** is shown in Figure 2b and Table 1 and Figure S8-S9. In order to quantitatively evaluate the HER performance of this catalyst, we made a linear plot of i_{cat}/i_p vs acid concentrations, as shown in Figure 2b. The i_{cat} is the catalytic current of HER, and i_p is the peak current of a one-electron reduction wave before the catalytic wave (Figure S10).^{3b,3p} The i_{cat}/i_p represents the catalytic turnover number of each molecular catalyst molecule making contact with the electrode surface. The linear plot indicates a second order catalytic rate dependent on acid according to Equation 1.

$$\left(\frac{i_{\text{cat}}}{i_{\text{p}}} = \frac{n}{0.4463} \sqrt{\frac{RT}{F}} \sqrt{\frac{k[\text{H}^+]^2}{v}} = 0.72 \sqrt{\frac{k[\text{H}^+]^2}{v}}$$
(1)

In Equation 1, n is the number of electrons transferred in the catalytic process (n = 2 for HER); v is potential scan rate; R is the universal gas constant; T is the temperature, and F is Faraday's constant.



Figure 2 (a) Comparison of HER behaviors of **1**, **2**, and **3** (0.15 mM in CH_2Cl_2) with 10 mM TfOH (b) Linear plot of i_{cat}/i_p versus acid concentrations with 0.15 mM of **1** (blue), **2** (green) and **3** (red). Complexes **2** and **3** decompose when the acid concentration is beyond 15 mM.

Table 1 Half wave potential, i_{cat}/i_p and third-order rate constant for **1**, **2** and **3** catalysing HER. Experimental conditions: 0.2 M Bu₄NBF₄; scan rate: 100 mV s⁻¹.

	Onset potential / V vs. Cp₂Fe ^{+/0} (10 mM TfOH)	(i _c /i _p) _{max}	<i>k</i> / M ⁻² s ⁻¹
1	-0.70	123	2.7×10^{6}
2	-0.76	36	1.5×10^{6}
3	-1.01	7	3.7×10^{4}

In this work, we prefer using a third-order rate constant and overpotential to assess the activity of catalysts, since TOF is relative to the concentration of protons. The moderate HER catalytic activity of complex 3 is consistent with previous reports.^{3e} Surprisingly, we found that the catalytic activity is increased significantly when the aryl substituent in 3 is replaced by a cyclohexyl group, as in 2: the third-order rate constant is increased by 2 orders of magnitude, and the HER onset potential is decreased from -1.01 to -0.76 V. On the other hand, the increase in the activity from 2 to 1 is relatively lower than from 3 to 2, and consequently, our discussion begins with the catalysts 2 and 3. Through theoretical calculations, we found metal hydride formation of 3 occurs only after two-electron reduction whereas in 2, it occurs just after one-electron reduction, indicating the significant change achieved in the kinetics of metal hydride formation by altering the imide substituents. Possible catalytic

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cycles are presented in Scheme 3. The only difference between these two complexes are the substituents on the nitrogen atom in the imine groups (the cyclohexyl group in 2, and the phenyl group in 3), and we carried out the density function theory (DFT) calculations (for details, see the SI) on these two catalysts to reveal the origin of the substituent effect. The calculated one electron reduced potentials of 2 and 3 are -0.54 and -0.63 V, respectively, in good agreement with experimental values (-0.68 and -0.76 V), supporting the reliability of our calculations. Furthermore, there is no major difference in the one electron reduced potentials between 2 and 3, so we consider the characters of the geometries after the catalysts accept one electron and lose a chlorine ligand, namely, 2' and 3'.

Scheme 3 Possible electrocatalytic hydrogen evolution cycles of catalysts
2 and 3. Protonation occurs on 2 after a one electron reduction while the protonation of 3 occurs only after a two electron reduction.



Figure 3 Orbital contribution, HSOMO energy (eV) and spin density of 2', 3' in the doublet state and 3' in triplet state.

The much lower overpotential of 2 compared to 3 for HER suggests that complex 3' does not react with H^+ in CH_2Cl_2 but 2' does, leading to the formation of a complex in which the H atom is bonded to the Ni center. So we first compared the geometries of 2' and 3'. The highest singly occupied molecular orbital (HSOMO) and spin densities of the optimized geometries for complexes 2' and 3' in the doublet state are shown in Figure 3. First, the

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HSOMO energy in CH₂Cl₂ of 3' is lower than that of 2' by 0.12 eV, suggesting that it is more difficult for the proton to attack 3' than 2'. This is understandable because as a π -acceptor, the phenyl group is able to lower the molecular orbitals whereas the cyclohexyl group is a σ -donor only. Second, in the HSOMO of 2', the metal contribution is 44% but becomes 40% in that of 3, which could be another factor for the lower reactivity of 3' because an electron-rich metal center should have higher reactivity towards protons. Third, the lower spin density a metal center has, the lower reactivity it has towards protons. The spin densities on the metal center in complexes 2' and 3' are 0.892 and 0.859, respectively, in the doublet state (Figure 3), indicating that the Ni atom in 2' is more favorable for the proton attack than the Ni atom in 3'. Furthermore, the spin density on the phenyl group in 3' is higher than that on the cyclohexyl group in 2' by 0.106, which could again be attributed to the π -acceptor character of the phenyl ring. Thus the interplay among HSOMO energy, orbital contribution and spin density results in a lower reactivity of catalyst 2' than that of 3'. Consequently, the protonation did not occur on 3 after the one electron reduction. The inverse kinetic isotope effect of 3 is $k_{\rm H}/k_{\rm D}$ =0.52, which is different from that of 2 (Table S5), indicated a proton-coupled electron transfer (PCET) process during the hydrogen evolution reaction.⁴

Our approach to construct a proton shuttle in the ligand was adopted to improve the activity of catalysts. Figure 4 shows the cyclic voltammograms of complex 1 for electrochemically catalyzing hydrogen evolution with various concentrations of TfOH. The onset potential of the catalytic peak is at about -0.67 V (vs. $Cp_2Fe^+/0$, or -0.04 V vs. NHE) with 31.1 mM TfOH. Without the complex 1, the background current on the glassy carbon electrode is very low (<0.2 mA cm⁻² at -1.5 V), confirming the catalytic function of the complex (Figure S11). A second feature is that prior to the main peak, there is a weak reduction peak at a potential from -0.69 to -0.52 V, which shifts positively as the acid concentration increases (Figure 4, inset). This result indicates a combination of protonation and electron transfer processes during the hydrogen evolution reaction, which was also supported by KIE (Table S5).⁴ To evaluate the Faradaic efficiency of HER, constant potential electrolysis at -1.1 V was performed for 4 h to generate H₂ gas in the head space of electrolytic cell. The concentration of H₂ was analyzed by gas chromatography, and the Faradaic efficiency for H_2 was determined to be >99% (Table S6).



Figure 4 Cyclic voltammograms of 1 (0.15 mM) in CH_2Cl_2 with varying concentrations of TfOH.

The half wave potential of 2 is about 0.2 V higher than that observed for 1, indicating that the pendant bases into the second coordination sphere promote the HER. As described previously by

Dubois et al.^{2a}, pendant bases in ligand can couple the electron and proton transfer, and avoid the large energy barrier of Ni(III)-H for the hydrogen oxidation reaction. In our case, the proton relay may also promote the proton coupled electron transfer process, and provide a new pathway for hydrogen evolution reaction without a high energy intermediate Ni(0)-H being involved, thus lowering the overpotential significantly. Besides, the pendant base in the ligand can be protonated preferentially to form a quaternary ammonium cation in acidic conditions, which helps to prevent the complex decomposition, because the cation will hinder further protonation of the diiminopyridine ligand. The complex 1 can be stable in 50 mM TfOH but as a control, the complex 2 and 3 without a pendant base decompose when the acid concentration is in excess of 15 mM.

The i_{cat}/i_p of complex 1 is as high as 123 when the acid concentration is 31.1 mM. Through the slope of the linear plot, a third-order rate constant was calculated to be 2.7×10^6 M⁻² s⁻¹, indicating a remarkable turnover frequency of 2572 s⁻¹ in 31.1 mM TOH. This third-order rate constant is 10-100 times larger than that of Ni complexes with non-redox active cyclic diphosphine, but also with pendant amines in the second coordination sphere reported previously by DuBois (Table S4).2 Electron paramagnetic resonance (EPR) of complex 1 after one-electron reduction by 1 eq of 1.0 M Li(BEt₃H) shows the existence of the ligand radical (Ni²⁺ \rightarrow Ni⁺) after one-electron reduction (Figure S12), which supports our assumption that is presented in Scheme 1.

Conclusions

We have designed a Ni complex with high electrocatalytic activity for hydrogen evolution by incorporation of a non-innocent diiminopyridine ligand with a pendant base in the second coordination sphere for nickel. We further showed that the electronic structure of a non-innocent ligand plays a critical role in regulation of the activity of molecular catalysts. The electronic withdrawing/donating effect of substituents could alter the kinetics of metal hydride formation without making any obvious change in the potential for molecular reduction, and this finally leads to a large difference in catalytic activity. Thus, a practical approach was found to eliminate the deleterious coupling between metal center reduction and metal hydride formation. Our findings are critical to a further understanding of the properties of non-innocent ligands and the hydrogen evolution reaction, which opens an avenue to the design of new catalysts with non-innocent ligands for redox reactions.

Supporting Information

The supporting information for this article is available on the WWW under https://doi.org/10.1002/cjoc.2018xxxxx.

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Regulation of metal center reduction and metal hydride formation for ${\sf HER}$ - lower overpotentials and faster reaction rates.