A Synthetic Nickel Electrocatalyst with a Turnover Frequency Above 100,000 s⁻¹ for H₂ Production

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Reduction of acids to molecular hydrogen as a means of storing energy is catalyzed by platinum, but its low abundance and high cost are problematic. Precisely controlled delivery of protons is critical in hydrogenase enzymes in nature that catalyze hydrogen (H₂) production using earth-abundant metals (iron and nickel). Here, we report that a synthetic nickel complex, \( \text{[Ni(phen)₂(NH₃)₂]BF₄} \), produces H₂ at 2°C in dry acetonitrile and 106,000 s⁻¹ in the presence of 1.2 M of water, at a potential of −1.13 V vs. the ferrocenium/ferrocene couple. The mechanistic implications of these remarkably fast catalysts point to a key role of pendant amine function as proton relays.

Electrocatalysts that efficiently convert the energy from electricity into chemical bonds in fuels (such as hydrogen), or the reverse, converting chemical energy to electrical energy, will play a vital role in future energy storage and energy delivery systems. Hydrogenase enzymes (1, 2) efficiently catalyze both the production and the oxidation of hydrogen using earth-abundant metals (nickel and iron). Detailed information about catalytic reactions of enzymes has been obtained from protein film voltammetry (3), but enzymes are difficult to obtain in sufficient amounts to adapt for commercial applications, and their stability is often limited outside of their native environment (4). Platinum is an excellent catalyst for hydrogen oxidation and production, but the scarcity and high cost of precious metals pose serious limitations to widespread use. These considerations have led to efforts to design molecular catalysts that employ earth-abundant metals. Synthetic complexes of nickel (5–8), cobalt (9–12), iron (13–15), or molybdenum (16, 17) have been developed recently as electrocatalysts for the production of hydrogen.

In nature, [FeFe] hydrogenase enzymes catalyze the formation of H₂ from water, with reported rate constants as high as 9000 s⁻¹ at 30°C (18). Crystallographic and spectroscopic studies have led to the proposal of the structure of the active site of the [FeFe] hydrogenase enzyme shown in structure 1 of Fig. 1 (1). The amine base positioned near the iron center has been proposed to function as a proton relay that facilitates the formation of H₂ from water with a turnover frequency of 100,000 s⁻¹ for H₂ production.
and they provide functional models for the proton relay functions of the hydrogenase enzymes. For example, a series of [Ni(PPh2NPh)2]2+ catalysts with structure 2 have been studied. Under optimized conditions, [Ni(PPh2NPh)2]2+ with bromophenyl substituents on the amine ligand, catalyzed the formation of H2 with turnover frequencies as high as 1040 s−1 and an overpotential of ~290 mV (7).

Mechanistic (5, 7) and theoretical (24) studies of the [Ni(PPh2NPh)2]2+ catalysts suggest that the transition state for H2 production has structure 3 shown in Fig. 1, in which the formation of the H-H bond occurs in a heterolytic manner, with the pendant amine acting as a proton donor and the nickel functioning as a hydride donor. The formation of transition state 3 involves the reduction of the starting complex 2 by two electrons and the addition of two protons. Previous nuclear magnetic resonance spectroscopic studies on reduction and protonation of closely related analogs of 2 show that intermediates formed before transition state 3 are isomeric Ni(0) complexes in which an amine in each ligand is protonated. The double protonation reaction of Ni(PPh2NPh)2 (where Bn is benzyl) forms structure 4 as the kinetic product (Fig. 2) (25). The kinetic product isomerizes to form an equilibrium mixture of structures 4, 5, and 6 by an intramolecular process that involves deprotonation by a base in solution and reprotonation at an endo position. This process is assisted by water. Only isomer 6 can readily convert to transition state 3 by a simple intramolecular proton transfer from nitrogen to nickel, and therefore only isomer 6 is active in the catalytic cycle. These studies led us to propose that only a fraction of the doubly protonated Ni(0) intermediates formed during hydrogen production are in the catalytically active form, isomer 6, and that significantly higher catalytic rates might be achieved if the stabilized exo protonated structures could be avoided. We also proposed that the observed enhancement of turnover frequencies by water is a result of its role in converting the exo protonated states to the catalytically active form, isomer 6 (7).

Here, we report the synthesis of [Ni(PPh2NPh)2](BF4)2, 7, which was isolated as orange crystals in 75% yield from the reaction shown in Scheme 1 (26). The new complex contains two seven-membered cyclic diphosphine ligands, PPh2NPh (where PPh2NPh = 1,3,6-triphenyl-1-aza-3,6-diphosphacycloheptane). Because this ligand has just one pendant amine, it precludes the possibility of forming nonproductive pinched isomers analogous to 4 and 5 upon reduction and protonation of 7. Although the reduced form of 7 can be protonated either endo or exo with respect to Ni, stabilization by a second N⋯H⋯H interaction in an exo-exo form (e.g., as in 4) is not possible. The molecular structure of 7 determined by x-ray diffraction (Fig. 3) is a distorted square planar complex with all four Ni-P bond distances nearly equal at 2.21 to 2.22 Å.

Complexation of both phosphorus atoms in each PPh2NPh ligand in 7 forms one five-membered chelate ring and a six-membered ring that incorporates the pendant amine. In contrast, both of the eight-membered cyclic ligands in 2 form two six-membered chelate rings upon binding to the metal. As a result, the P-Ni-P bond angle (79.83°) for each of the two diphosphine ligands in 7 is smaller than the 82° to 84° typically observed for the P-Ni-P bonds in derivatives of 2 (5, 7). This smaller bite angle leads to a decrease in the steric interactions between the phenyl substituents on adjacent phosphorus atoms of the two ligands in 7. As a result, 7 is much more planar than the corresponding derivatives of 2. For [Ni(PPh2NPh)2(HMe2)]2+, the dihedral angle between the two planes defined by the Ni atom and the two phosphorus atoms of each diphosphine ligand is 24.16° (7), whereas for 7, it is 0.0°. Thus, the replacement of two eight-membered cyclic ligands with two seven-membered cyclic ligands in these nickel complexes has significant structural consequences.

The cyclic voltammogram of an acetoniitride solution of [Ni(PPh2NPh)2]2+ shows one reversible reduction wave assigned to overlapping Ni(II)/Ni(0) couples at -1.13 V versus the ferrocenium/ferrocene couple (simulated as two one-electron waves at -1.09 and -1.16 V). (See Supporting Online Material for a cyclic voltammogram of 7, fig. S3, and a detailed analysis.) Figure 4 shows successive cyclic voltammograms of 7 recorded in acetonitrile with increasing concentrations of protonated dimethylformamide ([(DMF)H]OTf, pKa = 6.1 in acetonitrile) (27). A catalytic wave for the reduction of protons is observed with a half-wave potential of -1.13 V in the presence of 0.20 M acid, corresponding to an overpotential of ~625 mV determined using the method of Evans (28). The catalytic production of H2 was confirmed by a gas chromatographic analysis of the gas produced during a controlled potential electrolysis experiment (~1.4 V, current efficiency 99 ± 5% for H2 production, 11 turnovers with no observable decomposition). At high acid concentrations relative to the catalyst, Eq. 1 can be used to calculate pseudo first-order rate constants, kobs, for H2 evolution.

$$i_\text{cat} / i_p = \frac{2}{0.446} \sqrt{\frac{RT\epsilon_{\text{obs}}}{F\nu}}$$  \hspace{1cm} (1)

In this equation, i_\text{cat} is the catalytic current, i_p is the peak current measured in the absence of acid, 2 is the number of electrons involved in the catalytic reaction, kobs is the observed first-order rate constant, R is the universal gas constant, T is the temperature in Kelvin, F is Faraday’s constant, \nu is the scan rate, and 0.446 is a constant determined by numerical solution of the diffusion equations (29). The value of kobs increases linearly with acid concentration (fig. S9), indicating a first-order dependence of the catalytic rate on acid concentration. At the highest acid concentration studied (0.43 M), a value of i_\text{cat}/i_p = 38 was measured, corresponding to a turnover frequency of 33,000 s\(^{-1}\) at 22°C. At 0.43 M [(DMF)H]OTf, cyclic voltammetry and ultraviolet-visible absorption spectra indicated that less than 5% decomposition of the catalyst occurred over the 0.5 hours required for the catalytic studies. However, higher acid concentrations could not be used to determine reliable turnover frequencies because of catalyst decomposition under more strongly acidic conditions. The catalyst is stable in the presence of

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**Fig. 1.** Proposed structure of the [FeFe] hydrogenase active site (1) based on crystallographic data (1); synthetic Ni complex (2) that catalyzes H2 formation, with pendant amines that function as proton relays (7); proposed transition state (24) (3) for production of hydrogen catalyzed by 2.

**Fig. 2.** Doubly protonated Ni(0) intermediates (isomers 4, 5, and 6) involved in the production of H2 catalyzed by 2. For clarity, organic substituents on the N and P are not shown.

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H₂O, and the addition of H₂O (1.2 M) to the mixture results in a further enhancement of the catalytic current beyond the maximum i_cat achieved with acid alone, resulting in a value of i_cat/i_p = 74, corresponding to a turnover frequency of 106,000 s⁻¹. Simulations of the voltamograms obtained under catalytic conditions are in agreement with the experimentally measured i_cat/i_p = 74 (fig. S10 and table S3). The additional rate enhancement in the presence of water is attributed to the ability of water to enhance the rate of conversion of exo to endo isomers.

The turnover frequencies measured for 7 substantially exceed the highest turnover frequency reported for the formation of H₂ catalyzed by the [FeFe] hydrogenase enzyme, 9000 s⁻¹ at 30°C (18). This comparison, however, must be tempered by the recognition that the overpotential of the natural hydrogenase is thought to be less than 100 mV, significantly lower than the overpotential for 7. The exceptionally high turnover frequency observed for 7 is about two orders of magnitude larger than that observed for 2 under comparable conditions (590 s⁻¹ with an overpotential of 300 mV, increasing to 720 s⁻¹ when water is added) (7). Most important, our results clearly indicate that properly designed pendant amine bases in the second coordination sphere that function as proton relays are capable of promoting extremely fast H-H bond formation and proton transfer from solution to the metal center.

The observed first-order dependence on acid is consistent with a one- or two-electron reduction of 7, followed by rate-determining protonation of the reduced complex. In contrast, 2 exhibits catalytic rates that are second-order in acid at concentrations below ~0.1 M and independent of acid above ~0.2 M concentrations (7). Although the overall catalytic mechanisms for 2 and 7 are likely quite similar, changing the rate-determining step has significant effects on the observed catalytic rates. For derivatives of 2, the overall catalytic rate is predominantly controlled by two factors, the formation of endo-endo isomers such as 6 and H₂ elimination via transition state 3. For 7, the endo-protonation of a reduced intermediate is the rate-determining event. This implies that the rate of H₂ elimination via transition state 3 must be faster for 7 than for 2. This is likely the result of a more hydridic Ni-H bond for 7, which has been shown to correlate with more negative Ni(II/I) reduction potentials in these [Ni(diphosphine)₂]²⁺ complexes (30). The more negative Ni(II/I) potential for 7 (–1.13 V) compared with that of 2 (–0.84 V) is expected on the basis of their structural differences (greater planarity of 7), and this modification contributes to the significantly larger overpotential for H₂ production observed for 7.

In conclusion, the observation of an extremely high turnover frequency for 7 clearly demonstrates that its positioned proton relays support high rates for all of the individual catalytic steps, that is, inter- and intramolecular proton transfer, electron transfer (or proton-coupled electron transfer steps), and heterolytic formation of H₂. These results highlight the substantial promise that designed molecular catalysts hold for the electrocatalytic production of hydrogen. The high sensitivity of catalytic rates to the incorporation and arrangement of pendant amine bases in the ligand suggests a potentially broader role that proton relays may play in other important multi-proton, multi-electron catalytic reactions, such as the reduction of oxygen and oxidation of water.
The Persistently Variable “Background” Stratospheric Aerosol Layer and Global Climate Change

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Recent measurements demonstrate that the “background” stratospheric aerosol layer is persistently variable rather than constant, even in the absence of major volcanic eruptions. Several independent data sets show that stratospheric aerosols have increased in abundance since 2000. Near-global satellite aerosol data imply a negative radiative forcing due to stratospheric aerosol changes over this period of about -0.1 watt per square meter, reducing the recent global warming that would otherwise have occurred. Observations from earlier periods are limited but suggest an additional negative radiative forcing of about -0.1 watt per square meter from 1960 to 1990. Climate model projections neglecting these changes would continue to overestimate the radiative forcing and global warming in coming decades if these aerosols remain present at current values or increase.

Understanding climate changes on time scales of years, decades, centuries, or more requires determining the effects of all external drivers of radiative forcing of Earth’s climate, including anthropogenic greenhouse gases and aerosols, natural aerosols, and solar forcing, as well as natural internal variability. Much debate has focused on whether the rate of global warming of the past decade or so is consistent with global climate model estimates (1), requiring careful examination of all radiative forcing terms. Most of the global warming of the past half-century has been driven by continuing increases in anthropogenic greenhouse gases (2), but natural aerosols from particular “colossal” volcanic eruptions [see the index of volcanic activity definitions in (3)] have significantly cooled the global climate at times, including, for example, the “year without a summer” experienced after the eruption of the Tambora volcano in 1815 and notable cooling after the Pinatubo eruption in 1991 (4, 5). As used here, “colossal” or “major” refers to specific volcanic eruptions that have been generally recognized not only as extremely large but also as having injected a great deal of gaseous sulfur directly into the tropical stratosphere. Tropical eruptions are thought to be especially important for climate change because the injected material can be transported into the stratosphere of both hemispheres and affect the entire globe for many months.

The cooling effect of volcanic eruptions mainly arises not from the injected ash but from SO2 injected by plumes that are able to reach beyond the tropical tropopause into the stratosphere, whereupon the SO2 oxidizes and temporarily increases the burden of stratospheric particles. Stratospheric aerosols are composed largely of dilute sulfuric acid droplets that effectively reflect some incoming solar energy back to space. The radiative cooling due to increases in these particles is linked to the associated optical depth increases. Observations show that the volcanic particles from the colossal eruptions of El Chichón and Pinatubo in 1982 and 1991, respectively, decayed from the stratosphere with e-folding times (the time interval in which an exponentially decaying quantity decreases by a factor of e) of about a year (5).

Early measurements of the stratospheric aerosol layer around 1960 by Junge et al. (6) were carried out at a time when no colossal eruptions had occurred in many years. These data are subject to large instrumental uncertainty, but suggested an apparent “background” stratospheric aerosol layer, with aerosol burdens too small to measurably influence the global climate system. Crutzen (7) proposed that the dominant source of the background stratospheric aerosol layer was carbonyl sulfide (OCS), because other sulfur sources were thought to be too reactive or too soluble in rainwater to reach the stratosphere in significant amounts. But observations of the amount of background stratospheric aerosol since at least the 1970s using improved instrumentation reveal abundances that are far too large to be due mainly to OCS (8). Some studies have suggested that an important source of the background stratospheric aerosol layer may be anthropogenic sulfur (SO2 from coal burning, biomass burning, etc.) that can be transported...