Chemical and electrocatalytic ammonia oxidation by ferrocene

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Abstract

Recognizing the potential of ammonia to serve as a carbon-free fuel, we describe an electrocatalytic system for the oxidation of ammonia based on ferrocene (Cp_2Fe), an inexpensive, robust catalyst utilizing Earth-abundant iron. Ferrocenium (Cp_2Fe^+), the 1-electron oxidized form of ferrocene, cleanly oxidizes ammonia to generate nitrogen gas (N_2) and protons captured by excess ammonia as NH_4^+ with electrons reducing ferrocenium to ferrocene. This process occurs under electrocatalytic conditions to generate N_2 with sustained current. Simple modification of ferrocene through sulfonation allows for solubility in liquid ammonia to enable electrocatalysis in highly concentrated, energy dense solutions of ammonia. Kinetic and computational analysis provides mechanistic insight into the oxidation of ammonia by ferrocenium.

Ammonia (NH₃) represents a promising carbon-free fuel.¹⁻³ Produced on a scale of over 175 M tons / y primarily for fertilizer applications,⁴ liquified ammonia (25 °C, 10 bar) is energy-dense at 13.5 GJ/m³ compared to high pressure hydrogen (700 bar) that only has a density of 5.3 GJ/m³.⁵ Due to its extensive use in agriculture, a global transportation network exists for ammonia delivery that includes sea shipping routes and terrestrial pipelines. Coupled with electrochemical ammonia production from renewable resources,^{6,7} efficient extraction of energy from ammonia enables a carbon-free fuel cycle.⁸

While ammonia possesses essentially the same fuel value on a hydrogen atom basis as hydrogen gas, strong N-H bonds (BDE = 108.2 kcal/mol) must be broken en route to the robust triple bond of N₂ (226 kcal/mol).⁹ Thus, catalysts are required to efficiently employ ammonia in fuel applications. Conversion of ammonia to its constituent elements highlights ammonia as a hydrogen storage vector (Fig. 1A).⁵ Transition metals as well as alkali metals promote ammonia decomposition at 400 - 600 °C¹⁰ while catalyzed electrolysis occurs at lower temperatures but with high overpotentials,¹¹⁻¹³ each approach generating hydrogen for potential use in a fuel cell. On the other hand, conversion of ammonia to nitrogen gas, protons, and electrons (Fig. 1A) enables the direct use of ammonia in a fuel cell. While a number of heterogeneous anodes have been developed for ammonia oxidation at high temperatures, advances are still required to increase the rate and lower the overpotential.^{8, 10, 14, 15}

Figure 1 | Ammonia oxidation reactions. (A) Thermodynamics of ammonia as an energy carrier. (B) Model ammonia oxidation reactions explored with precious metal molecular catalysts based on Ru.^{16, 17}

Coordination complexes enable opportunities to outline mechanistic pathways that can lead to innovations in electrocatalyst design.^{18, 19} Transition metal complexes stoichiometrically convert ammonia to nitrogen in the presence of appropriate oxidants^{20, 21} or under electrochemical forcing,²² while a molybdenum complex releases hydrogen from bound ammonia under mild conditions.²³ Coupling these steps, a molecular complex based on the precious metal ruthenium catalyzes the electrolysis of NH₃ to N₂ and H₂ (Fig. 1A).²⁴ Other model reactions catalyzed by molecular ruthenium complexes include the H-atom abstraction of ammonia by the 2,4,6-tri-*t*-butylphenoxyl radical ^tBu₃ArO•¹⁶ as well as oxidation of ammonium (NH₄⁺) in the presence of a specialized base or under electrochemical cycling (Fig. 1B).¹⁷

Sustainability concerns strongly motivate the development of inexpensive catalysts based on Earth-abundant metals, especially ones that can function in energy-dense liquid ammonia. In this light, we considered the ferrocenium / ferrocene (Fc^+ / Fc) redox couple for the catalytic oxidation of ammonia (Fig. 2A). This simple organometallic system serves as an electrocatalyst for the oxidation of 1°, 2°, and 3° amines such as propylamine, diethylamine, and trimethylamine.²⁵ Ferrocene is exceptionally thermally and electrochemically stable,²⁶ recommended by IUPAC as a reference for non-aqueous solvents.^{27, 28} Moreover, ferrocene is a commodity chemical available at a cost of dollars / kg whose derivatives are ubiquitous across varied fields of chemistry.²⁶

Results

Chemical Ammonia Oxidation by Ferrocenium. Ferrocenium (Fc^+), the one electron oxidized form of ferrocene, cleanly converts ammonia (NH_3) to dinitrogen (N_2) (Figure 2A). Addition of excess ammonia gas to a solution of ferrocenium hexafluorophosphate (FcPF_6) in acetonitrile (MeCN) at room temperature results in rapid conversion of Fc^+ to Fc with concomitant formation of N_2 and NH_4^+ . Recognizing that the oxidation of NH_3 to N_2 is an overall 6 e⁻ reaction that consumes 6 equiv. Fc^+ , analysis of the headspace by GC-TCD reveals 95% yield of N_2 whereas ¹H NMR analysis indicates the formation of Fc in 90-100% yield. Protons derived from the oxidation of ammonia are captured by excess ammonia and appear in quantitative yield as NH_4^+ , isolated as $[\text{NH}_4]\text{PF}_6 \cdot \frac{1}{3} \text{NH}_3$ under our workup conditions.

Figure 2 | Ammonia oxidation by ferrocenium. (A) Stoichiometric oxidation of ammonia. (B - D) Kinetic plots ammonia oxidation at 25 °C. (B) Pseudo first-order kinetics following loss of $[\text{Fc}^+]$. Plots of k_{obs} (s^{-1}) vs. $[\text{NH}_3]$ (M) in NH_3 oxidation by Fc^+ (C) without and (D) with added electrolyte. Free energies of activation ($\Delta G^\ddagger$) in kcal/mol at 298 K.

Kinetic Analysis of Ammonia Oxidation by Ferrocenium. Kinetic analysis provides further insight into the chemical reactivity between Fc^+ and NH_3 . Under conditions of excess ammonia (0.07 - 0.41 M) in acetonitrile at 25 °C, loss of Fc^+ (initially 2.4 mM) is clearly first-order from which a series of k_{obs} values associated with individual NH_3 concentrations is obtained (Fig. 2B). To deduce the order in $[\text{NH}_3]$, a plot of $\log k_{\text{obs}}$ vs. $\log [\text{NH}_3]$ was prepared which gave a slope of 2.55 (Fig. S6B), suggesting that the rate exhibits a combined second and third order dependence on $[\text{NH}_3]$. This results in the experimentally determined rate law: $\text{rate} = (k_2[\text{NH}_3]^2 + k_3[\text{NH}_3]^3)[\text{Fc}^+]$ with $k_2 = 5.4 \text{ M}^{-2}\text{s}^{-1}$ and $k_3 = 8.6 \text{ M}^{-3}\text{s}^{-1}$ at 25 °C (Fig. 2C). Eyring analysis over the temperature range -20 to 20 °C estimates the free energy of activation $\Delta G^\ddagger = 16.7(8) \text{ kcal/mol}$ with $\Delta H^\ddagger = 8.0(5) \text{ kcal/mol}$ and $\Delta S^\ddagger = -29.5(2.1) \text{ cal/mol}$.

Ammonia oxidation by ferrocenium is quite sensitive to ion-pairing effects. While we find that 0.10 M $[\text{Bu}_4\text{N}]\text{PF}_6$ enhances the solubility of NH_3 in MeCN, it also results in a significant decrease in rate. Employing an identical initial concentration of Fc^+ (2.4 mM), the pseudo first-order rate constant (k_{obs}) for ammonia oxidation is 0.59 s^{-1} at $[\text{NH}_3] = 0.41 \text{ M}$ without electrolyte but drops to 0.0016 s^{-1} in the presence of 0.10 M $[\text{Bu}_4\text{N}]\text{PF}_6$ at this ammonia concentration. The reaction still exhibits a combined second and third order dependence on $[\text{NH}_3]$ over the concentration range 0.30 - 4.0 M ($k_2 = 4.7 \times 10^{-4} \text{ M}^{-2}\text{s}^{-1}$; $k_3 = 9.6 \times 10^{-3} \text{ M}^{-3}\text{s}^{-1}$), but with a higher barrier $\Delta G^\ddagger = 19.5(6) \text{ kcal/mol}$ (Fig. 2D).

Computational Analysis of Ammonia Oxidation by Ferrocenium. Recognizing that the Fc^+/Fc couple can serve as a redox mediator capable of oxidizing substrates in an outer-sphere manner,^{29,30} 1-electron oxidation thermodynamics for ammonia³¹ were evaluated by *ab initio* and DFT methods to compare these energies against the experimentally determined ionization energy of Fc to Fc^+ in MeCN (+114.8 kcal/mol).³² MP2/aug-cc-pVTZ/gas//MP2/aug-cc-pVTZ/SMD-MeCN calculations reveal a substantial lowering of the ionization energy of discrete NH_3 molecules from +234.9 kcal/mol in the gas phase (exp: 232.2(5) kcal/mol)³³ to 155.2 kcal/mol in a MeCN solvent continuum (Fig 3A). Since this ionization is chemically inaccessible from the Fc^+/Fc couple, instead we considered ionization of the weakly H-bonded ammonia dimer ($\text{NH}_3 \cdots \text{NH}_3$). Though ammonia dimerization is endergonic by 6.0 kcal/mol in MeCN, ionization of $\text{NH}_3 \cdots \text{NH}_3$ to $[\text{H}_2\text{N} \cdots \text{HNH}_3]^+$ is more favorable at +138.2 kcal/mol, yielding a total free energy of +144.2 kcal/mol. Conversion of $[\text{H}_2\text{N} \cdots \text{HNH}_3]^+$, an amidyl-ammonium complex loosely held by H-bonding³⁴, to hydrazine (N_2H_4) and ammonium (NH_4^+) is significantly downhill ($\Delta G = -32.7 \text{ kcal/mol}$). Nonetheless, the 1-electron ionization of 2 equiv. NH_3 proceeding via $[\text{H}_2\text{N} \cdots \text{HNH}_3]^+$ is still 29.4 kcal/mol uphill from the Fc^+/Fc couple. DFT methods previously examined for ammonia clusters (M06-2X, B3LYP-D3)^{34,35} similarly predict ionization energies for the ammonia dimer in MeCN over 25 kcal/mol above the experimentally determined Fc^+/Fc couple (Fig 3B, Table S6). All of these thermodynamic values for ammonia oxidation are considerably higher than the experimentally measured free energy of activation of 16.7(8) kcal/mol for ammonia oxidation by Fc^+ .

Figure 3 | Computational analysis of ammonia oxidation by Fc^+ . (A) Ionization of ammonia and ammonia dimer with free energies from the MP2/aug-cc-pVTZ/gas//MP2/aug-cc-pVTZ/SMD-MeCN level of theory. (B) Thermodynamics of outer-sphere ammonia oxidation by *ab initio* and DFT methods compared with the experimental ionization energy of Fc in MeCN.³² (C) Inner-sphere oxidation of NH_3 by Fc^+ at the B3LYP-GD3BJ/6-311++G(d,p)/SMD-acetonitrile level of theory. All free energies in kcal/mol at 298 K.

As the combination of experimental and computational data weigh against an outer-sphere electron transfer mechanism, an inner-sphere mechanism was considered that involves coordination of NH_3 to Fc^+ to give $[\text{Fc-NH}_3]^+$ (Fig. 3C). Indeed, ferrocenium functions as a Lewis acid catalyst in a number of organic transformations.³⁰ We employed DFT at the B3LYP+GD3BJ/6-311++G(d,p)/SMD-MeCN level of theory that predicts the Fc/Fc^+ couple at 116.9 kcal/mol in MeCN (exp: 114.8 kcal/mol).³² Coordination of ammonia to give $[\text{Fc-NH}_3]^+$ is only slightly endergonic ($\Delta G = +1.9$ kcal/mol) with a minimal barrier ($\Delta G^\ddagger = 4.5$ kcal/mol) despite the slippage of one Cp ring from η^5 to η^2 . The interaction of NH_3 with Fc^+ ($\text{Fe-NH}_3 = 2.03$ Å) enhances the N-H acidity of the ammine ligand enabling formation of the H-bonded intermediates $[\text{Fc-NH}_3 \cdots \text{NH}_3]^+$ and $[\text{Fc-NH}_3 \cdots \text{NH}_3 \cdots \text{NH}_3]^+$ at +5.8 and +13.1 kcal/mol from Fc^+ , respectively. These species may precede deprotonation of the $[\text{Fc-NH}_3]^+$ moiety to give the neutral iron amide $[\text{Fc-NH}_2]$ ($\text{Fe-NH}_2 = 1.81$ Å) and either NH_4^+ or $[\text{NH}_4 \cdots \text{NH}_3]^+$ with thermodynamic barriers $\Delta G = 19.7$ or 17.7 kcal/mol from Fc^+ , respectively. Relaxed potential energy scans involving deprotonation to $[\text{Fc-NH}_2]$ from $[\text{Fc-NH}_3 \cdots \text{NH}_3]^+$ and $[\text{Fc-NH}_3 \cdots \text{NH}_3 \cdots \text{NH}_3]^+$ did not reveal barriers above these thermodynamic values. These competing deprotonation pathways to form the high energy Fc-NH_2 intermediate are consistent with the experimentally observed rate law that exhibits a mixed second- and third-order dependence on the ammonia concentration. Finally, bimolecular coupling of Fc-NH_2 to give hydrazine and ferrocene is exergonic by 21.5 kcal/mol (per Fc).

While these mechanistic considerations predict hydrazine as a product of the 1-electron oxidation of ammonia, we do not experimentally detect hydrazine. Addition of 20 equiv. hydrazine to Fc^+ in MeCN at RT ($[\text{Fc}^+]_0 = 3.1 \text{ mM}$, $t_{1/2} \ll 1\text{s}$) instantly reduces Fc^+ and gives N_2 in 93% experimental yield (eq 1). Thus, hydrazine would not be observed in the slower reaction of Fc^+ with ammonia. These findings are consistent with the use of the 1,1'-dicarboxylic acid derivative of ferrocene as an electrocatalyst for the oxidation of hydrazine in aqueous solution.³⁶

Electrocatalytic Ammonia Oxidation by Ferrocene. Cyclic voltammetry of 1.0 mM Fc in 3.6 M NH_3 / MeCN using a 0.07 cm^2 glassy carbon (GC) electrode in the presence of 0.1 M $[\text{Bu}_4\text{N}]\text{PF}_6$ showed large, irreversible oxidative waves at different scan rates that correspond to electrocatalytic ammonia oxidation (Fig. 4A). Thus, catalyzed ammonia oxidation in MeCN occurs at a potential approximately 420 mV lower than in the absence of ferrocene (Fig. S14A).³¹ Controlled potential electrolysis (CPE) for 13 h using a 10 cm^2 reticulated vitreous carbon (RVC) electrode in a 10% ammonia: MeCN (v:v) solution (ca. 4.6 M) at -10°C with 1.0 mM Fc produced N_2 with a Faradaic yield of 44% (Fig. 4B). Analysis of the recovered Fc catalyst on a separate, polished GC electrode revealed only a 10% loss of electrochemical activity when compared against a fresh Fc / electrolyte solution.

Figure 4 | Electrocatalytic ammonia oxidation by ferrocenes. (A) Cyclic voltammetry of Fc in 3.6 M NH_3 / MeCN with 0.1 M $[\text{Bu}_4\text{N}]\text{PF}_6$. (B) Controlled potential electrolysis of ammonia catalyzed by ferrocene. (C) Double potential step chronoamperometry of Fc in 6 M NH_3 . (D) CV of sulfonated ferrocene in 80% NH_3 / MeCN with 0.1 M KPF_6 at -40°C .

Beyond experimental limitations in N₂ collection, we considered the possibility of a lowered Faradaic yield due to electrode modification under electrocatalytic conditions. Chronoamperometry at +0.05 V vs. Fc⁺/Fc using a 0.07 cm² GC electrode with 1 mM Fc in 4 M NH₃ / MeCN demonstrates a stable catalytic current during the first 2 min followed by a substantial decrease in current after 10 min (86%). Under the identical conditions, a similarly-sized edge plane pyrolytic graphite (EPPG) working electrode³⁷ provides a longer-lasting current stable for 5 min, but also gradually decays after 10 min (49%) (Fig. S15).

Thus, an EPPG electrode was utilized in double potential step chronoamperometry experiments to calculate the rate constant in the electrocatalytic reaction between Fc⁺ (1.0 mM) and NH₃ (6 M) in the presence of 0.1 M [Bu₄N]PF₆ in MeCN at RT. Using an oxidative step interval (50 s) that results in a stable current at 0.05 V vs. Fc⁺/Fc, a rate constant $k_{\text{obs}} = 0.86 \text{ s}^{-1}$ was calculated from the slope of i_c/i_p vs. $t^{-1/2}$ (Figs. 4C and S17). This value is comparable to that expected in the chemical reaction of Fc⁺ with 6 M NH₃ in the presence of 0.1 M [Bu₄N]PF₆ (Fig. 2D; extrapolated $k_{\text{obs}} = 2.1 \text{ s}^{-1}$).

The thermodynamics of the N₂ / NH₃ redox couple have recently been considered in MeCN.³⁸ When excess NH₃ is used to capture protons generated in the oxidation of NH₃, the potential has been assigned as -0.94 V vs. Fc⁺/Fc (eq. 2).³⁸ Thus, ferrocene exhibits an overpotential $\eta \approx 940 \text{ mV}$ for ammonia oxidation under these conditions. To lower the overpotential, we have preliminarily explored somewhat more electron-rich ferrocenes with lower Fc^{+/0}/Fc⁰ redox potentials such as 1,1'-Me₂Fc ($E_{1/2} = -0.130 \text{ V}$; $\eta \approx 810 \text{ mV}$) and 1,1'-Me₂FcSO₃K ($E_{1/2} = -0.120 \text{ V}$; $\eta \approx 820 \text{ mV}$). While these substituted ferrocenes function as electrocatalysts, they also result in lower rates for ammonia oxidation in 6 M NH₃ / MeCN ($k_{\text{obs}} = 0.20$ and 0.11 s^{-1} , respectively) (Figs. S18 - S19). The electron-rich, yet sterically congested ($\eta^5\text{-C}_5\text{Me}_5$)₂Fe ($E_{1/2} = -0.590 \text{ V vs. Fc}^+/\text{Fc}$) does not show electrocatalytic oxidation of ammonia under these conditions.

Importantly, the sulfonated ferrocene 1,1'-Me₂FcSO₃K is soluble in liquid ammonia at -40 °C. CV experiments in a 80 : 20 (v:v) mixture of NH₃ and MeCN at -40 °C with KPF₆ as electrolyte reveal electrocatalysis (Fig. 4D) and CPE for 8 h at -40 °C produces N₂ with a Faradaic yield of 35%. Although the recovered catalyst exhibits a significant loss in electrochemical activity (Fig. S24), these results nonetheless establish the viability of molecular electrocatalysts to generate N₂ and current from highly concentrated ammonia solutions.

Discussion and Conclusion

Ferrocenium efficiently oxidizes ammonia to nitrogen along with protons and electrons captured as ammonium and ferrocene, respectively, resulting in a robust electrocatalytic system. Based on Earth-abundant iron, this system offers significant promise in terms of sustainability and cost as compared to systems that employ precious metals for the extraction of electrical energy from ammonia as part of a carbon-free fuel cycle.

Mechanistic studies indicate that the reaction between Fc^+ and NH_3 is first-order in $[\text{Fc}^+]$ with competing second- and third-order pathways in $[\text{NH}_3]$ supported by computational studies that outline deprotonation of a Fc^+ -bound NH_3 by one or two equiv. NH_3 to give a highly reactive Fc-NH_2 species. This iron-amide is quite susceptible to N-N coupling to form hydrazine which experimentally undergoes oxidation to N_2 by Fc^+ faster than ammonia. Electrochemical cycling of reduced Fc with oxidized Fc^+ enables the electrocatalytic oxidation of ammonia that produces sustained current at carbon-based electrodes. These studies also identify the importance of the electrode materials, highlighting the improved performance of EPPG over GC electrodes in electrocatalysis.

Building upon these insights, the hundreds of ferrocene derivatives known²⁶ underscore the promise of this framework for the development of ammonia oxidation electrocatalysts with decreased overpotentials and improved rates. For instance, simple synthetic modification enables access to ferrocene derivatives such as 1,1'- $\text{Me}_2\text{FcSO}_3\text{K}$ that function as electrocatalysts in energy-dense, highly concentrated ammonia solutions. The ability to graft ferrocenes onto GC electrodes³⁹ may allow extension of the homogeneous advances reported herein to solid-state electrodes that function as heterogeneous electrocatalysts. Furthermore, these advances may enable new approaches for the environmental remediation of ammonia, a key nitrogen pollutant in wastewater.¹⁴

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Additional information

The authors declare no competing financial interests. Correspondence and requests for materials should be addressed to T.H.W.

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