

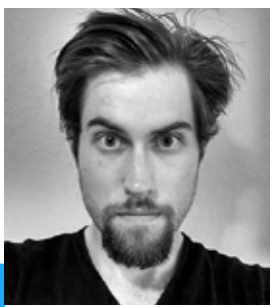


RESNICKINSTITUTE
science + energy + sustainability

RESEARCH HIGHLIGHTS

+ From Caltech's Resnick Fellows

Toward Sustainable Nitrogen Fixation: Elucidating the Mechanism of Nitrogen Reduction by Molecular Catalysts



Niklas Thompson

Dow-Resnick Graduate Research Fellow

Toward Sustainable Nitrogen Fixation: Elucidating the Mechanism of Nitrogen Reduction by Molecular Catalysts

Niklas Thompson

Global Significance

The maintenance of global health is intimately linked with technologies for the reduction—or “fixation”—of dinitrogen (N_2) to ammonia (NH_3) for the purpose of fertilizer production. However industrial fertilizer production depends on a nitrogen fixation process that requires enormous energy and natural gas inputs, and results in severe environmental pollution.

As rapid population growth in the developing world continues to drive up the demand for fixed nitrogen, it is critical that we develop sustainable technologies for the catalytic conversion of dinitrogen to ammonia. The prototype for such a process is found in nature, where photosynthesis is coupled to nitrogen fixation by nitrogenase enzymes.

If we can understand the molecular basis of biological nitrogen fixation, synthetic catalysts may be developed that couple artificial photosynthesis schemes to the reduction of dinitrogen.

The mechanism of nitrogenase is poorly understood, and it is only very recently that molecular catalysts for the reduction of dinitrogen to ammonia have been developed. We propose to advance the mechanistic understanding of nitrogen fixation by molecular catalysts by exploiting a unique spectroscopic technique applicable to the study of Fe-based systems. Such studies constitute an important first step in the rational design of a sustainable nitrogen fixation process.

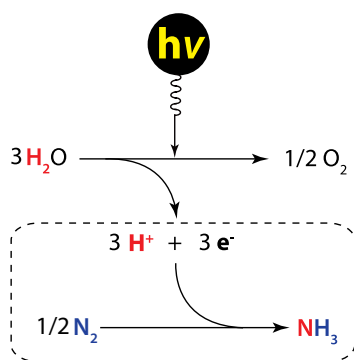
Toward Sustainable Nitrogen Fixation: Elucidating the Mechanism of Nitrogen Reduction by Molecular Catalysts

Niklas Thompson

Project Summary

To date only four synthetic systems capable of catalyzing the direct reduction of N_2 to NH_3 with protons and electrons are known. While prior systems have exploited Mo-based catalysts, the system recently described by the Peters lab is Fe-based. This Fe-based system is uniquely suited to spectroscopic study under turnover conditions via ^{57}Fe Mössbauer spectroscopy, a physical technique which enables in situ monitoring of the catalyst speciation during the reaction.

Utilizing this technique, we have gained unprecedented insights into the catalytic reaction. These insights include the characterization of a major catalyst resting state as a known Fe hydride species previously thought to be a catalyst deactivation product and the observation that the active precatalyst is regenerated from this hydride species once substrate is consumed. With this knowledge, we have been able to improve the maximum turnover number for NH_3 formation by nearly an order of magnitude.



Scheme for an artificial "Solar-to- NH_3 " system in which a solar-driven water splitting reaction provides proton and electron equivalents for the fixation of N_2 . The reaction shown within the dashed lines is the subject of our work

Potential Impact

With the demonstration of significantly improved turnover, we have validated earth-abundant Fe-based compounds as viable catalysts for the low-pressure and low-temperature reduction of N_2 to NH_3 . Moreover, this study demonstrates the utility of coupling in situ ^{57}Fe Mössbauer spectroscopy with the kinetic analysis of product formation as a powerful tool for the mechanistic study of Fe-catalyzed N_2 fixation, establishing a crucial methodology to aid the rational design of novel catalysts moving forward.

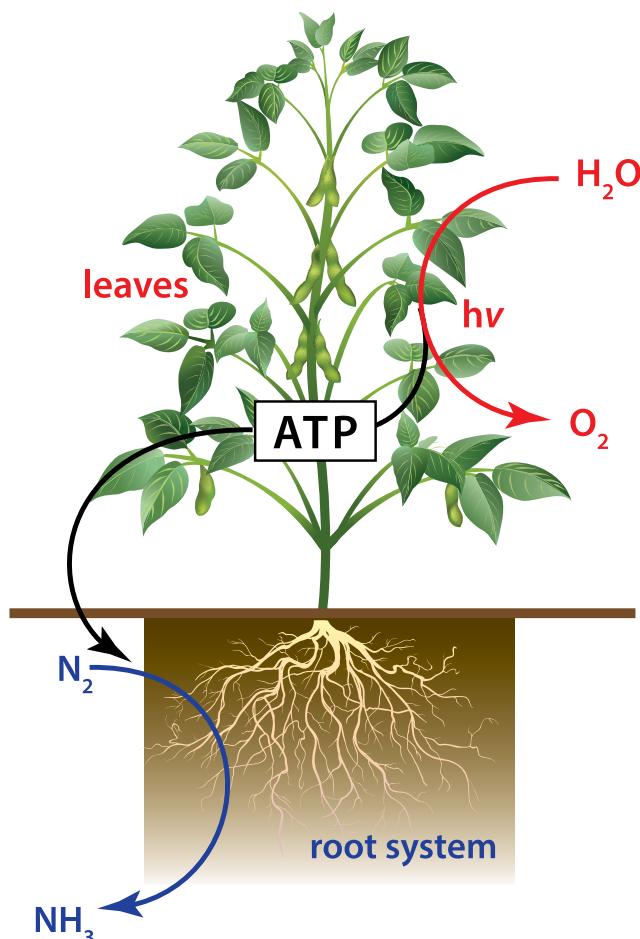


Illustration showing the coupling of photosynthesis and nitrogen fixation in nature. Energy (ATP) from the water-splitting reaction of photosynthesis drives the reduction of N_2 .

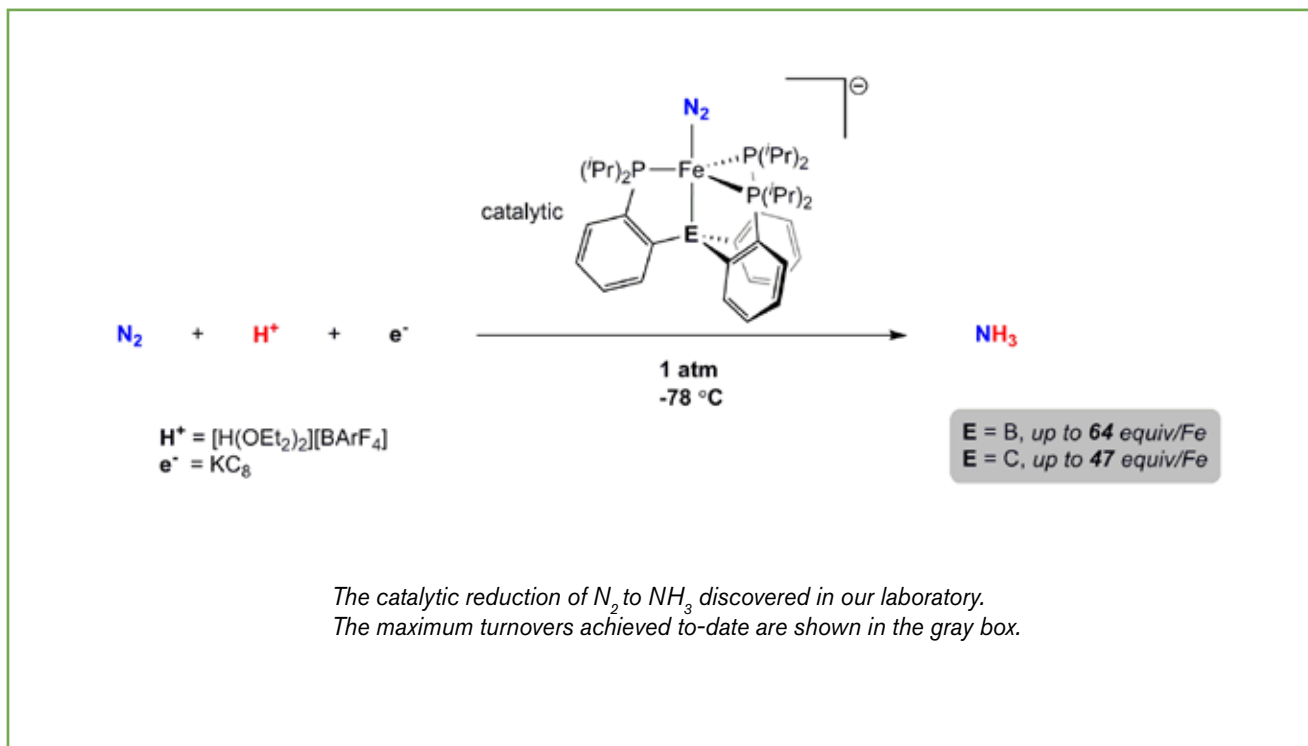
Toward Sustainable Nitrogen Fixation: Elucidating the Mechanism of Nitrogen Reduction by Molecular Catalysts

Niklas Thompson

The Science

By understanding the mechanism(s) by which molecular catalysts achieve the direct conversion of N_2 to NH_3 using protons and electrons, we can inform the design of improved second-generation catalysts for this fundamental process. We sought to exploit the combination of traditional chemical kinetics with ^{57}Fe Mössbauer spectroscopy to study a synthetic N_2 fixation catalyst in situ.

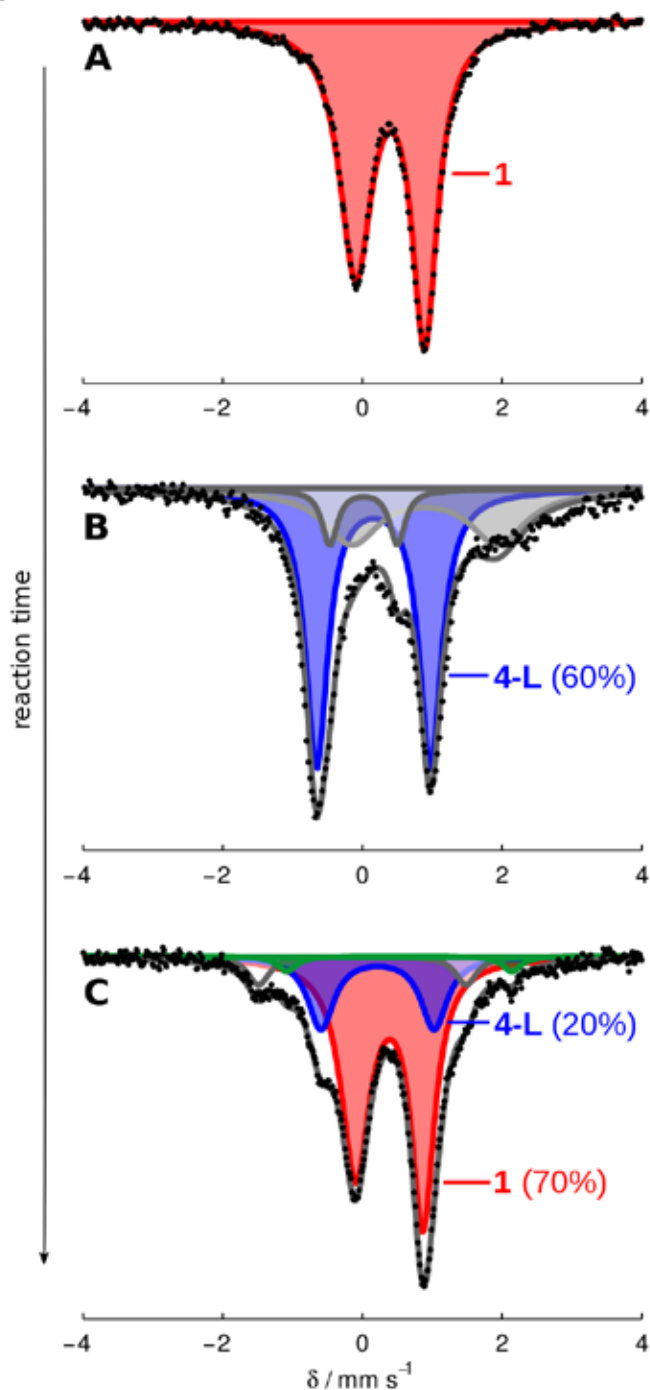
^{57}Fe Mössbauer spectroscopy has no selection rule for Fe-containing species, and is insensitive to non-Fe-containing material in a sample, and thus enables observation of the total Fe speciation under turnover conditions. By developing chemical quenching methods to study the dynamics of product formation it is then possible to correlate the species observed spectroscopically with N_2 fixing activity.



Toward Sustainable Nitrogen Fixation: Elucidating the Mechanism of Nitrogen Reduction by Molecular Catalysts

Niklas Thompson

The Science



Time resolved Mossbauer spectra of a catalytic reaction mixture, showing the conversion of precatalyst (red) into hydride resting state (blue) under active turnover, and regeneration of precatalyst (red) from hydride (blue) at longer times.

Toward Sustainable Nitrogen Fixation: Elucidating the Mechanism of Nitrogen Reduction by Molecular Catalysts

Niklas Thompson

Key Results

We have applied this methodology to one of the few known Fe-based catalysts for N_2 fixation, and have been able to directly observe the behavior of the catalyst during the time course of a reaction. This has allowed us to identify the major catalytic resting state as a known Fe-hydride compound, and to demonstrate that this hydride species can be reverted to the active precatalyst Fe compound under catalytically-relevant conditions. The most significant implication of this result is that, contrary to previous hypotheses, the catalyst is not irreversibly deactivated under turnover, thus enabling the observation of nearly an order of magnitude increase in overall turnover number under optimal conditions.

Future Steps

We believe that the strategy developed here has the possibility to complement the study of model complexes and reactions in establishing a fuller mechanistic understanding of N_2 -to- NH_3 conversion by these systems and may be applied to other Fe-based synthetic N_2 -to- NH_3 conversion catalysts as they are developed. In a more direct sense, the longevity of the catalyst studied here suggests that the system may be tuned for the electrochemical synthesis of NH_3 , replacing chemical reductants with an electrode as the source of reducing equivalents. Providing such a demonstration represents the next phase of our research and would constitute a significant and necessary step toward the goal of a sustainable N_2 -fixing technology.

