

CATALYTIC FORMATION OF AMMONIA FROM DINITROGEN

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INTRODUCTION

Ammonia is an important feedstock molecule for a wide range of industrial processes, with an estimated 183 million metric tons produced annually. Roughly 70% of all ammonia produced globally is used for the synthesis of fertilizers, that are needed to feed the ever-growing global population.¹ Currently, the industrial standard for ammonia production is the Haber-Bosch process that utilizes dihydrogen to reduce dinitrogen at high temperature and pressure over a heterogeneous iron catalyst. Although extremely robust, the Haber-Bosch process is damaging to the environment, being the source of roughly 2% of global energy consumption and 3% of global carbon dioxide emissions.¹ Therefore, the need for a highly efficient, environmentally friendly catalytic ammonia synthesis is of the utmost importance.

Nitrogenase Enzyme

Nature developed a way to reduce dinitrogen at ambient temperature and pressure utilizing a tetrameric iron-molybdenum cofactor (FeMo-co).² Although the structure of the molybdenum containing subunit has been determined, the exact mechanism of nitrogen reduction by the nitrogenase enzyme is still not known. Nonetheless, a theoretical model proposed by Chatt (**Figure 1**) highlights the most likely cycle that serves as the basis for most abiotic systems.²

MOLYBDENUM BASED SYSTEMS

The first abiotic reduction of dinitrogen to ammonia at ambient temperature and pressure was published by Schrock in 2003.⁴ Using a molybdenum (III) complex bearing tetradentate triamidoamine ligand, he was able to produce eight equivalents of ammonia per catalyst in four turnovers. A key strategy employed by Schrock to achieve catalysis is to maintain an excess of the catalyst relative to the proton source and reducing

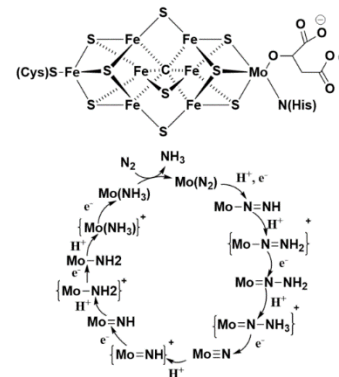


Figure 1. Structure of FeMo-co (top) and proposed Chatt cycle for biotic nitrogen reduction (bottom).

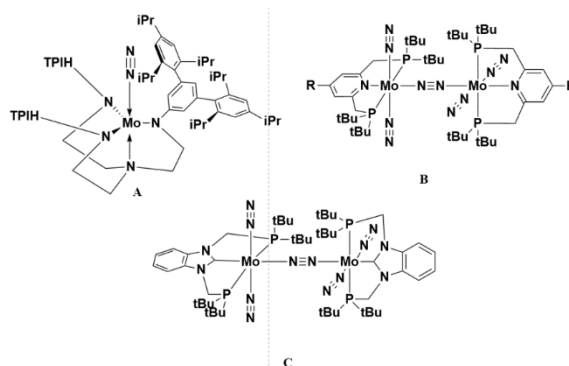


Figure 2. Successfully employed molybdenum catalysts by Schrock (A) and Nishibayashi (B, C). R = H, Ph, TMS, Me, OMe

agent, which is achieved by using a weakly soluble proton source and slow addition of the reducing agent by a syringe pump.⁴ Using a similar system to Schrock but with a Mo(0) complex bearing a strongly σ -donating tridentate pincer ligand (**Figure 2**), Nishibayashi can achieve catalytic ammonia formation.⁵ Optimizing the electronics of the ligand backbone leads to yields of up to 230 equivalents of ammonia per catalyst.^{6,7,8,9}

OTHER METALS

Although only molybdenum-based complexes show reduction of dinitrogen to ammonia and ambient temperature and pressure, other metals have been successful in reducing dinitrogen at ambient pressures and cryogenic temperatures (-78 °C). Peters *et. al.* showed in 2013 that an iron(-I) complex bearing a trigonal tris(phosphino)borane ligand could successfully reduce dinitrogen to ammonia, producing 88 equivalents of ammonia per catalyst.⁸ The use of cryogenic temperatures is necessary to inhibit the formation of dihydrogen gas as an unwanted side product. Spectroscopic observation of diazene and hydrazine complexes not found in the analogous molybdenum systems highlight the possibility that iron may reduce dinitrogen through a different catalytic cycle.⁸ Changing the donor atom on the ligand backbone from boron to silicon promotes catalytic dinitrogen reduction in ruthenium and osmium systems, with the latter producing up to 120 equivalents of ammonia per catalyst.⁹ Similar pincer ligands to those used by Nishibayashi have also been applied to iron, rhenium, cobalt, and chromium systems to catalytically reduce dinitrogen to ammonia; however, only the iron system produces comparable yields (252 equiv. per catalyst) to the molybdenum systems.¹⁰

EFFECTS OF PROTON AND ELECTRON SOURCES

The most common proton sources employed are 2,6-lutidinium salts bearing an anion that would weakly coordinate to the metal center, *e.g.* triflate or tetrakis(3,5-bis(trifluoromethyl)phenyl)borate. This proton source is often coupled with a strong inorganic reducing agent, such as cobaltocene, decamethylchromocene, and potassium graphite.^{3,4,8} Although the lutidinium/cobaltocene pair is still the best performing across most metals, Nishibayashi recently showed that samarium diiodide can work with alcohols or water to reduce dinitrogen in the molybdenum based systems.¹¹ Recent work by Chirik is focused on quantifying the thermodynamic driving forces behind specific proton/electron pairs for ammonia production from dinitrogen and applying it in a predictive fashion for catalytic systems.¹²

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