



## Review

## Developing more sustainable processes for ammonia synthesis



Yoshiaki Tanabe, Yoshiaki Nishibayashi\*

Institute of Engineering Innovation, School of Engineering, The University of Tokyo, Yayoi, Bunkyo-ku, Tokyo 113-8656, Japan

## Contents

1. Introduction.....	2551
2. Stoichiometric formation of ammonia by reaction with Brønsted acid.....	2552
2.1. Chatt cycle: Protonation of molybdenum- and tungsten-dinitrogen complexes.....	2552
2.2. Protonation of other transition metal-dinitrogen complexes.....	2553
2.3. Non-metal activation of dinitrogen towards formation of ammonia.....	2554
3. Stoichiometric formation of ammonia by reaction with dihydrogen.....	2554
3.1. Activation of dinitrogen using dihydrogen complex.....	2554
3.2. Direct reaction of transition metal-dinitrogen complex with dihydrogen.....	2555
4. Catalytic formation of silylamine.....	2556
4.1. Molybdenum complexes.....	2556
4.2. Iron complexes.....	2557
5. Catalytic formation of ammonia.....	2559
5.1. Schrock cycle: Molybdenum complex with a tetradentate triamidoamine ligand.....	2559
5.2. Dimolybdenum complex with PNP-type pincer ligands.....	2559
6. Conclusion.....	2561
Acknowledgements.....	2561
References.....	2561

## ARTICLE INFO

## Article history:

Received 14 November 2012  
 Received in revised form 8 February 2013  
 Accepted 11 February 2013  
 Available online 1 March 2013

## Keywords:

Ammonia  
 Dinitrogen complex  
 Ferrocene  
 Ferrocenylphosphine  
 Hydrazine  
 Hydrogenation  
 Iron  
 Molybdenum  
 Nitrogen fixation  
 Pincer ligand  
 PNP  
 Silylamine

## ABSTRACT

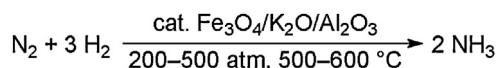
This paper describes a recent advance on the conversion of molecular dinitrogen into ammonia or ammonia equivalent, silylamine, by using transition metal-dinitrogen complexes. Two effective systems for the catalytic transformation of molecular dinitrogen under ambient reaction conditions have been achieved by the use of molybdenum and iron complexes as catalysts. The former system employs a molybdenum-dinitrogen complex bearing two ferrocenyl diphosphines or an iron complex such as iron carbonyl or substituted ferrocene as a catalyst to afford up to 226 equiv of silylamine based on the catalyst. The latter system employs a dinitrogen-bridged dimolybdenum complex bearing two PNP-type pincer ligands as a catalyst to afford up to 23 equiv of ammonia based on the catalyst. Both systems provide a new aspect in the development of novel nitrogen fixation under mild reaction conditions.

© 2013 Elsevier B.V. All rights reserved.

## 1. Introduction

The conversion of molecular dinitrogen into ammonia is one of the most important chemical processes both in the industrial and biological fields. The Haber-Bosch process is the main industrial route to ammonia from the reaction of dinitrogen and dihydrogen gasses (Fig. 1) [1,2]. This process now produces approximately 160

\* Corresponding author. Tel.: +81 3 5841 1175.  
 E-mail address: [ynishiba@sogo.t.u-tokyo.ac.jp](mailto:ynishiba@sogo.t.u-tokyo.ac.jp) (Y. Nishibayashi).



**Fig. 1.** First industrial Haber–Bosch process operated at the BASF's Oppau plant in 1913. Improved method using a ruthenium-based catalyst (Kellogg advanced ammonia process) is operated at much lower pressure and temperature (70–105 atm, 350–470 °C).

million metric tons of ammonia per year used for agricultural and industrial purposes, but requires drastic reaction conditions and consumes 1–2% of the world's annual primary energy supply. It also generates more than 300 million metric tons of fossil-derived carbon dioxide per year from ammonia production [3].

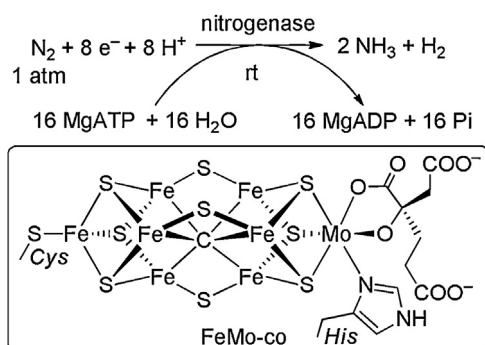
In contrast, bacterial nitrogenase enzymes perform biological nitrogen fixation mainly via an iron-molybdenum cofactor (FeMo-co) [4] under ambient temperature and pressure (Fig. 2) [5]. This highly endergonic reaction to produce ammonia from the reaction of dinitrogen, proton sources, and electron carriers, accompanied by the co-formation of at least an equimolar amount of dihydrogen (standard transformed Gibbs energy of the reaction in aqueous solution ( $\Delta_r G^\circ$ ) is +239.8 kJ/mol per dinitrogen at pH 7 and 0 ionic strength), is coupled to the hydrolysis of at least 16 equiv of ATP [6]. Although its precise reaction mechanism still remains unclear [5,7], biological nitrogen fixation can be a model for an alternative method to the Haber–Bosch process to produce ammonia under ambient conditions. It has thus been attracting much attention.

Since the discovery of the first transition metal–dinitrogen complex, a ruthenium–dinitrogen complex [8], the preparation of various transition metal–dinitrogen complexes (Fig. 3) [9–13] and the stoichiometric transformation of their coordinated dinitrogen into ammonia and hydrazine, has been thoroughly investigated towards the goal of achieving nitrogen fixation under ambient conditions [14,15]. Although dinitrogen coordinates to most transition metals to form “dinitrogen complexes” [16], only molybdenum–dinitrogen complexes have been shown, so far, to catalyze the conversion of dinitrogen into ammonia under ambient conditions [17,18]. A recent advance for the reduction of molecular dinitrogen into ammonia or silylamine is summarized in this review.

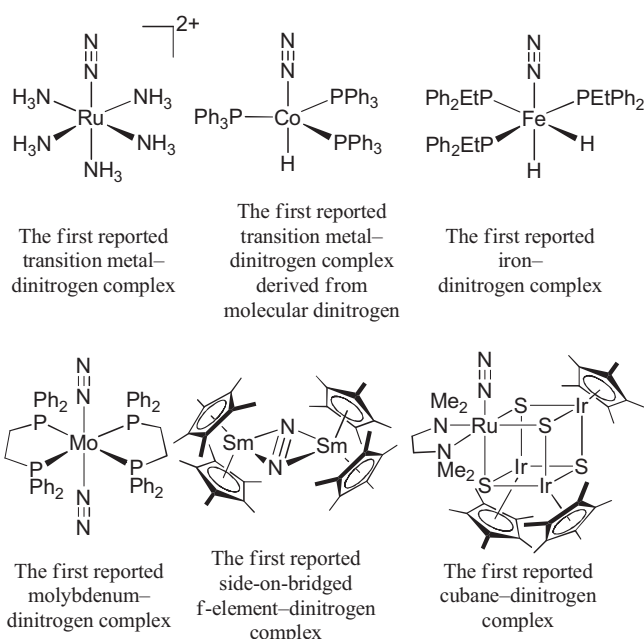
## 2. Stoichiometric formation of ammonia by reaction with Brønsted acid

### 2.1. Chatt cycle: Protonation of molybdenum- and tungsten–dinitrogen complexes

The formation of ammonia from the reaction of molybdenum and tungsten dinitrogen complexes has been reported by the groups of Chatt and Hidai (Fig. 4) [19,20]. In this reaction system, the coordinated dinitrogen can be transformed into ammonia under mild reaction conditions by treatment with inorganic acids such as



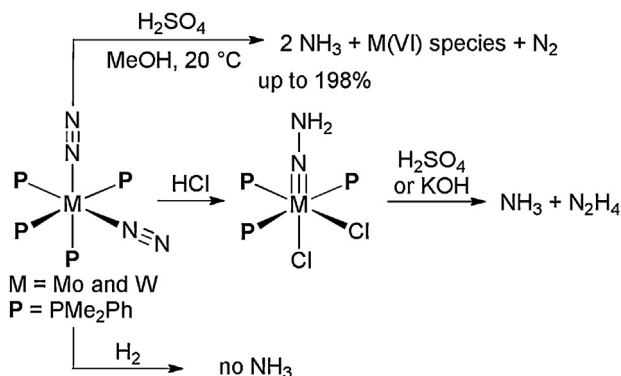
**Fig. 2.** Typical biological nitrogen fixation by nitrogenase and structure of FeMo-co.



**Fig. 3.** Selected examples of transition metal–dinitrogen complexes.

sulfuric acid. A detailed reaction mechanism for the protonation of the ligating molecular dinitrogen leading to ammonia has been proposed on the basis of reactivities of isolable diazenido (MN=NH), hydrazido (MN–NH<sub>2</sub>), and hydrazidium complexes (MN–NH<sub>3</sub>) as reactive intermediates. Here, all of the electrons required for the formation of ammonia are supplied from the zerovalent molybdenum and tungsten metals. In fact, high valent metal(VI) species may be formed together with a stoichiometric amount of ammonia (2 equiv of ammonia based on the metals) after the reaction. Hydrazine (H<sub>2</sub>N–NH<sub>2</sub>) is also obtained rather as a by-product in some cases, and seems to be obtained mainly from the intermediate hydrazido complex on quenching [21]. Moreover, no nitrogen–hydrogen bond formation was observed when reactions of transition metal–dinitrogen complexes with molecular dihydrogen were carried out (Fig. 4) [22]. This result indicates that the ligand exchange of the coordinated molecular dinitrogen with molecular dihydrogen easily occurred under the reaction conditions examined.

Isolation and identification of the diazenido, hydrazido, and hydrazidium complexes derived from dinitrogen complexes, as well as of nitrido (MN), imido (MNH), amido (MNH<sub>2</sub>), and ammine complexes (MNH<sub>3</sub>) led to the hypothetical catalytic formation of ammonia called the Chatt cycle (Fig. 5) [23]. The cycle operated



**Fig. 4.** Conversion of molybdenum- and tungsten–dinitrogen complexes to form ammonia.

Download English Version:

<https://daneshyari.com/en/article/1299568>

Download Persian Version:

<https://daneshyari.com/article/1299568>

[Daneshyari.com](https://daneshyari.com)