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A Mini Review of Catalytic Reducing Nitrogen to Ammonia under Ambient Conditions

Jianjun Yang[1,2]*

[1]*Department of Chemical Engineering, School of Environmental Science and Engineering, China*

[2]*Key Laboratory of Subsurface Hydrology and Ecological Effects in Arid Region Chang'an University, China*

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***Corresponding author:** Jianjun Yang, Department of Chemical Engineering, School of Environmental Science and Engineering, China

Abstract

Ammonia(NH_3) has played an essential role in meeting the increasing demand for food and the worldwide need of nitrogenous fertilizer since 1913. Unfortunately, the traditional Haber-Bosch process for producing NH_3 from nitrogen(N_2) is a high energy-consumption process. Under ambient conditions catalytic reducing N_2 to NH_3 is an attractive and promising alternative approach which would emerge huge opportunity to directly provide nitrogenous fertilizers in agricultural fields as need in a distributed manner. In this review, some research findings showed alternative, available, sustainable NH_3 production processes from N_2 in the presence of electro-catalysts and photo-catalysts under ambient conditions.

Keywords: Catalyst; Nitrogen; Ammonia; Ambient condition

Introduction

As one of the most important chemicals to our planet, NH_3 has played an essential role in meeting the growing demand for food and the worldwide need of nitrogenous fertilizer since 1913 [1]. The total worldwide NH_3 production exceeded 140 million tons, and demand for NH_3 continues to grow in 2014 [2], and about 80% of the NH_3 product usually is used as nitrogenous fertilizer. Fritz Haber discovered that NH_3 could be directly synthesized by reacting atmospheric N_2 with hydrogen in the temperature range of 400-500°C and at pressures of 130-170bar [3], and Carl Bosch subsequently developed it on an industrial scale [4]. As the most important invention of the 20th century, the Haber-Bosch process, a thermo-chemical catalytic conversion technology, is a primary choice of industrial production of NH_3 for human beings until now. According to the Haber-Bosch process, NH_3 is produced from the reaction:

$$N_2 + 3H_2 \leftrightarrow NH_3$$

The Haber-Bosch process reacts the pure feed gases at high temperatures and pressures, requiring energy input of around 485 kJ mol-1of N_2 and almost 2% of global energy consumption [5]. The high dissociation energy of triply bonded N_2 molecule (911 kJ mol^{-1}) presents a significant activation energy barrier, however, the negative entropy (ΔH300= -46.35 kJ mol^{-1}) of the reaction dictates that N_2 could be converted to NH_3 at lower temperatures [6]. There are several advantages for NH_3 synthesis at low temperatures [7,8]. Firstly, the reaction of producing NH_3 from N_2 with dihydrogen is spontaneous. Secondly, the proton conductivity of low-temperature electrolytes has more excellent behaves than the other temperature ones. Thirdly, the reaction kinetics of NH_3 production processes is extremely slow when the operating temperatures are below 100°C. It is Kordali et. al. [9] who firstly reported that NH_3 was produced from N_2 and water using a Nafion electrolyte at low temperature in 2000. In additional, it would be a key joint to build foundational principles of designing new efficient catalysts for sustainable NH_3 synthesis production process. The new methods of catalyst design need us to understand the catalytic mechanisms by integrating theory and experiment of discovering the active, scalable, selective, long-lived efficient catalysts for sustainable NH_3 synthesis.

Therefore, how to activate the N≡N bond to produce NH_3 with less fossil energy consumption is great opportunity and challenges for chemists. Although researchers tried to develop the artificial catalysts to facilitate the reaction at more ambient conditions and there are many new approaches, the nowadays used industrial catalysts are extremely similar to the original one discovered by Mittasch [10] in 1910s. In this review, some research findings showed alternative, available, sustainable NH_3 production processes from N_2 in the presence of electro-catalysts, photo-catalysts and analogous catalysts of nitrogenases metalloclusters under ambient conditions.

Discussion

Recently, electro-catalysis depending on renewable electricity produced from renewable energy (such as wind or solar) has played an increasingly role in the NH_3 synthesis at ambient temperature(T<100°C) [2,7,8,11]. Some novel functional materials as catalysts used in typical N_2 reductions were explored by researchers [12].

Electro-Driven Catalytic Reducing N_2 to NH_3

Under ambient conditions, Liu et al. [13,14] developed $Sm1.5Sr0.5MO_4$(M=Ni, Co, Fe) and SmFe0.7Cu0.3-xNix-O3(x=0–0.3) as electro-catalysts for NH_3 synthesis with Nafion used as proton solid electrolyte. Such systems, while impressive in current efficiency, require careful control experiments due to low overall yields and observed ambient NH_3 absorption by polymer electrolyte membranes. Further, researchers have taken their efforts to develop ideal electro-catalysts for improving N_2 reduction rates and the NH_3 yield. Impressively, SmFe0.7Cu0.1Ni0.2O3 showed the record-high NH_3 production rate of 1.1×10^{-8} $mol{\cdot}s^{-1}{\cdot}cm^{-2}$ at 80°C. The NH_3 yield was up to 8.7×10^{-9} $mol{\cdot}s^{-1}{\cdot}cm^{-2}$ in the present of electro-catalyst SmBaCuMO5+i (M=Fe, Co,Ni) at 80°C and 2.5V [15]. However, there are still big spaces to improve the NH_3 yield which currently are not enough to the future industry application.

An alternative strategy would like to consider using metal nitrides as electro-catalyst cathodes for N_2 reduction except pure metals. Respectively at potentials of -0.76V and -0.51V, producing NH_3 from N_2 took place on the surface of Zr N and VN as electro-catalyst cathodes which were not covered by adsorbed H-atoms [16], the same to Nb N and CrN [17]. The theoretical analysis of Abghoui et al. [18-20] predicted stable operation and Faraday Efficiency(FE) higher than 75% for V, Cr, Nb and Zr mono-nitrides at applied bias between 0.5 and 0.76V. Unfortunately, there would not be such nitride materials which were tested experimentally like above mentioned for NH_3 synthesis [21]. Beside mono-nitrides, binary nitrides such as Co_3Mo_3N are amongst the most active electro-catalysts for NH_3 synthesis [22]. A thorough investigation of their electro-catalytic behaves should be performed in real NH_3 synthesis situations.

These reports show that there was a universal phenomenon that these electro-catalysts often contain big proportions of oxides on their surfaces, which is harmful to keep their normal conductivity and could significantly reduce their catalytic efficiency. Actually, an ideal electro-catalyst should have the capacities of high catalytic activity and excellent electronic conductivity at ambient conditions and could suppress the hydrogen evolution reaction. The electro-catalytic NH_3 synthesis is still under experiment stage, huge challenges are still faced the lack of the solid oxide electrolyte materials [23]. Future research should focus on theory-guided screening and discovery of new NH_3 catalysts, as well as developing novel methods for NH_3 synthesis at low temperatures and pressures. One important issue on the successful demonstration of NH_3 being from reducing N_2 and Overcoming N_2 and NH_3 contamination should be done with 15 N_2 dinitrogen, FTIR analysis and choice of system materials.

Photo-Driven Catalytic Reducing N_2 to NH_3

With the global population increasing, the photon-driven N_2 fixation technologies will become very critical to capture solar energy and produce nitrogenous fertilizers [24]. In the late 1970s, Schrauzer and Guth discovered that TiO_2 powders doped with Fe_2O_3 could catalyze the reduction of N_2 to NH_3 under ambient conditions [25,26]. Since then, TiO_2 became the workhorse photo-catalyst for subsequent studies, and CuCl, WO3 and FeOx as possible photo-catalysts for NH_3 synthesis have been investigated [27,28]. Maybe, surface oxygen defects of titanium metal caused by high temperatures could play an important role in the photo-driven catalytic reduction of N_2 to NH_3. Although there is not an insight regarding the atomic scale phenomena on photo-catalytic N_2 reduction, the TiO_2 crystal polymorph and its iron impurity concentration are identified to be the key factors to underlay photo-catalytic performance.

Co-catalysts, such as Co, Mo, Ni, Ru and Pt dopants, have been added to the titanium-based materials for increasing the NH_3 yield [24,29]. Transition metal dopants as electron sinks in titanium photo-catalysts could minimize the probability for carrier recombination to promote greater NH_3 yields. Dopants inducing defect states could assist in charge separation of photo-generated electrons and holes but are not a part of the active site for N_2 dissociation. Therefore, the conduction band position of photo-catalysts (Figure 1) should be more negative than the reduction potential of the N_2 hydrogenation, as well as the valance band should be more positive than the oxygen evolution potential [30].

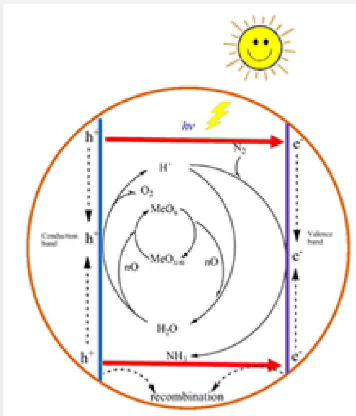

Figure 1: Schematic of photo-catalysts for reducing N_2 to NH_3 [30].

The partial current densities for photo-catalytic producing NH_3 are lower 3 to 5 orders of magnitude than the other electro-driven NH_3 production processes. To solve the problem, maybe the efficient photo-catalysts attached to electrodes would show us an amazing result of the higher NH_3 yields. In additional, like

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electrochemical NH_3 synthesis, photo-catalytic approaches must employ proper methods and controls.

Conclusion

Under ambient conditions, some seminal literatures have been reviewed on describing the electro-catalytic NH_3 synthesis from commonly available feedstock such as purified H_2 and N_2. The electro-catalytic NH_3 synthesis is still under experiment stage due to the lack of the suitable electrolyte materials as electro-catalysts with high catalytic activity, excellent electronic conductivity, and hydrogen evolution reaction. Transition metals which can achieve selective N_2 reduction maybe are good choice for further researches. Additionally, it is with the high-energy UV light that photo-catalytic NH_3 synthesis from N_2 could overcome the N≡N band energy barrier under ambient conditions. Currently, titanium oxide with transition metal dopants is a not bad choice in practice. Future studies should encourage investigating on how N_2 reduction happen on the photo-catalysts with the application of modern computational and experimental techniques from molecular level viewpoint.

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Conflict of Interest

The author has declared that any economic interest or any conflict of interest exists.

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