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Comparative Review and Future Outlook for Ammonia Production from Conventional to Emerging Technologies

Shien Yan

Sedbergh School Fuzhou, Fuzhou, China
shien22@qq.com

Abstract. Ammonia, a crucial chemical in global industrial production, plays an indispensable role in agricultural fertilizers as well as in emerging energy areas. The conventional Haber-Bosch method converts nitrogen and hydrogen into ammonia under high temperatures and high pressures, but it depends heavily on fossil fuels together with high operational conditions which results in large amounts of energy being consumed and serious carbon emissions. To overcome this issue, alternative production methods are required. This study explored the use of zeolite to advance the production method of ammonia. Zeolite is a molecular sieve and is widely used in various applications: as a catalyst in the chemical industry owing to its pore size, as a soil conditioner in agriculture, and as a water softener through ion exchange. However, these properties do not make it incompatible with modern sustainable development requirements. (Or: This versatility makes it compatible with modern sustainable development requirements.)

Keywords: ammonia applications, thermodynamic - kinetic interplay, zeolite - mediated NH_3 enhancement

1. Introduction

Ammonia synthesis is a crucial industrial process that converts nitrogen into essential compounds, supporting global agriculture, industrial production, and emerging energy applications [1]. However, the Haber-Bosch process, which is currently the main method for large-scale ammonia synthesis, has two aspects: on the one hand, it is crucial in providing food for billions of people worldwide. On the other hand, it is highly energy-intensive, using up roughly 1% - 2% of the world's total energy and being responsible for almost 1.5% of global carbon emissions. As demands for reducing pollution, ensuring food security, and developing clean energy become increasingly urgent, re-evaluating the traditional methods of ammonia synthesis has become essential [2].

This re-evaluation extends beyond mere operational, encompassing the combination of chemical tenets, engineering systems, and environmental sustainability. Conventional ammonia synthesis depends on high pressure, high temperature, and specific catalysts to propel the reaction between nitrogen and hydrogen [3]. However, its drawbacks in economic and ecological terms remain glaring, including over-reliance on fossil fuels and a low energy utilization rate. To align ammonia synthesis, this critical process, with evolving global challenges, it is necessary to clarify its production mechanism from molecular-level interactions to large - scale industrial operations [4, 5].

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This study utilized the systematic review method to sort out the core literature on the optimization of traditional Haber-Bosch process and emerging synthetic routes over past 20 years. It demonstrates a multi-dimensional analysis framework covering technical principles. By comparing the maturity and bottlenecks of different technological approaches, this study explores the future directions and challenges of the ammonia synthesis process as it moves towards decentralization and low-carbon development.

2. Applications of ammonia

2.1 Fertilizer production for agricultural protection

The production of ammonia has far-reaching global consequences, especially in on food security and environmental protection [6]. Regarding food security, as the world's population grows, enhancing the efficiency and sustainability of ammonia production is imperative. Ammonia-based fertilizers play a vital role in boosting crop yields by providing crops with the necessary and easily absorbable nitrogen that promotes their growth and development. This makes it crucial to optimize production procedures to ensure adequate food supplies for the expanding population [7].

2.2 A key tool for environmental protection

In environmental protection, especially in industrial denitrification, power plants use urea hydrolysis to generate ammonia as a denitrification-reducing agent. However, challenges persist: urea solidification during low-load operation remains an unresolved issue [8]. Overall, ammonia production, with its dual role in feeding the global population and protecting the planet, demands continuous innovation and problem-solving in its production methods to better align with the global development framework [1].

Given the critical importance of ammonia in global food systems and environmental protection, the methods by which it is produced must come under intense scrutiny.

3. The mechanism of the Haber-Bosch process

3.1 Feedstock gaspreparation and purification

In the initial phase of industrial ammonia production, two main feed gases are prepared: nitrogen (N_2) from air, and hydrogen (H_2) typically produced via steam methane reforming of natural gas or through water electrolysis. Atmospheric nitrogen is purified using air separation methods such as cryogenic distillation or pressure swing adsorption, which efficiently remove oxygen, carbon dioxide, and other trace gases. Hydrogen feedstock also undergoes rigorous purification to eliminate "catalyst poisons" such as sulfur compounds and carbon monoxide. If these substances are not removed, they will reduce catalyst activity in subsequent steps [9-11].

3.2 Ammonia synthesis reaction and catalysis

The purified gases are precisely measured at a stoichiometric volume proportion of 1:3 (nitrogen to hydrogen) and then introduced into a synthesis reactor. The operation conditions of this reactor were extremely severe with the pressure surpassing 200 atmospheres and the temperature is maintained between 400°C and 500°C. Inside the reactor, the feed gases made contact with a solid catalyst composed mainly of iron (Fe) as the principal element along with aluminum oxide (Al_2O_3),

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potassium oxide (K_2O), and calcium oxide (CaO) added as promoters. This multi-functional catalyst facilitates the dissociative adsorption of the highly stable nitrogen-nitrogen triple bond (N≡N), creating conditions for the stepwise hydrogenation of nitrogen atoms. The reaction mechanism involves the formation of several surface intermediates: chemisorbed nitrogen atoms first convert to imide (NH) and amide (NH_2) species, ultimately forming gaseous ammonia (NH_3) [12, 13].

3.3 Product separation and gas recycling

Due to the constraints set by thermodynamic equilibrium, the conversion efficiency of the feed gases during one passage through the reactor was rather low. The effluent gas is rapidly cooled to condense ammonia into a liquid, which is then separated and collected. Unreacted nitrogen and hydrogen are recycled to the synthesis process via a compression system, maximizing overall raw material utilization. This continuous working pattern, which combines high-pressure reaction, condensation, separation, and gas recycling, acts as the basic engineering structure for the large-scale catalytic transformation of elemental gases into anhydrous ammonia [14, 15].

4. Potential alternative materials for ammonia synthesis

While the Haber-Bosch process is a triumph of chemical engineering, its severe operating conditions and high carbon footprint present significant sustainability challenges. Scientists have found alternative materials and pathways that enable ammonia synthesis under milder conditions. Among these, zeolites have emerged as a promising choose due to their unique structural properties.

4.1 Structural characteristics and fundamental advantages

Zeolites are a class of aluminosilicate minerals that occur in a crystalline form with regular microporous structures. The framework of zeolites gains a net negative charge when Al^{3+} substitutes for Si^{4+}, and this charge is balanced by exchangeable cations (e.g., Na^+, K^+, Ca^{2+}) within the pores. The connection between these cations and the zeolite framework is relatively weak, and possess exchangeability [16]. The most decisive feature is their uniform system of channels and cavities, with sizes between 0.3 and 1.0 nanometers, which endows them with an ultra-high specific surface area (300-1000 m^2/g) [16]. The ultra-high porosity from this regular pore system endows zeolites with extremely high specific surface areas, usually ranging from 300 to 1000 square meters per gram, far exceeding that of most traditional porous materials.

Meanwhile, the pore size of zeolites is fixed and uniform, enabling precise sieving based on the size and shape of molecules. Only molecules smaller than the pore size of the zeolite can enter the pores and be adsorbed, while larger molecules are excluded. This property is widely applied in the separation and purification of mixtures. For instance, during the purification process of natural gas, carbon dioxide and water vapor are removed and in the refining process of petroleum, straight-chain hydrocarbons and branched-chain hydrocarbons are separated out, thereby improving the quality of the product [17].

Zeolites' unique structures combine excellent catalytic activity and stability, which making them widely Used in industry. Acidic sites in the crystal structure and the pore environment form efficient catalytic centers, which stabilize reaction intermediates and enable shape-selective catalysis. Additionally, zeolites exhibit thermal stability (600–800°C), resistance to chemical corrosion (except to strong acids and strong bases), regenerability through simple methods, a long service life, and favourable economic performance [18].

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4.2 Catalytic mechanisms in ammonia synthesis

Zeolites' large specific surface area and microporous structures enable selective adsorption of nitrogen (N_2) and hydrogen (H_2) molecules, increasing the probability of collisions between molecules, which promoting the reaction. Nitrogen activation is the slowest step in ammonia synthesis due to the high bond energy of the N≡N triple bond, and zeolites can interact with nitrogen molecules, particularly those modified with metal cations [19].

Zeolites weaken the N≡N bond and promote activation, making nitrogen more reactive with hydrogen, as cations in the zeolite framework can coordinate with N_2. The porous structure of zeolite act as a nanoscale reaction chamber. after adsorption and activation of nitrogen molecules, the activated nitrogen molecules and hydrogen molecules are limited within the pores, where ammonia is generated through surface reactions.The size and shape selectivity of zeolite pores influence the reaction pathway, inhibiting side reactions and enhancing the selectivity of ammonia production [20].

4.3 Current research status and future prospects

Researchers are exploring zeolites as potential alternatives; zeolites are a kind of mineral with very minute, uniform pores and a large internal surface area and scientists are investigating how these substances could promote the generation of ammonia gas (NH_3), whether via the reaction of nitrogen (N_2) and hydrogen (H_2) gases or by decomposing nitrogen-rich waste compounds. The microchannels and active sites in zeolites may enhance reaction efficiency under milder conditions (lower pressure and temperature) compared to the traditional process. Although their use remains mostly at the research stage, zeolites offer a promising prospect for manufacturing this vital compound in a more energy-efficient manner in the future [21, 22].

5. Discussion

5.1 Challenges

Zeolites have transcended their traditional role as gas purification adsorbents in the field of ammonia synthesis research. They are mainly utilized by taking advantage of the special microporous structure of zeolites and their adjustable acidity to enhance the energy-intensive Haber process. Additionally, by loading metals such as ruthenium and cobalt onto zeolite catalysts, researchers have developed systems that enable the activation of nitrogen and hydrogen at lower temperatures and pressures. In electrochemical and photocatalytic processes, zeolites serve as catalyst carriers or selective membranes to enhance efficiency [23].

Despite promising prospects, this field faces multiple challenges. For example, the catalytic activity and rate of ammonia production of zeolite are far below the requirements of industrial standards. Hydrothermal stability is insufficient, as the zeolite framework may degrade under hydrothermal reaction conditions. In addition, the unclear understanding of the reaction mechanism and active sites within the confined space hinders the design of rational catalysts. Precise control and large-scale production of metal active sites are also challenging, and the integration with industrial systems and cost-benefit assessment require further improvement [24].

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5.2 Future directions

Future development requires the adoption of a multidisciplinary approach to make breakthroughs. Advanced synthesis methods are required to produce layered zeolites to reduce diffusion and precisely control active sites. In-situ characterization, theoretical calculations, and AI should be combined to clarify the reaction mechanism and establish the relationship between zeolite structure and performance. Based on this, reactors should be optimized to achieve deep compatibility between zeolites and the green ammonia production process. Moreover, improving material lifespan assessment and regeneration methods, and integrating the optimized zeolite into novel reactors for pilot-scale green ammonia production, are key to advancing large-scale industrial application of zeolites and making the ammonia industry greener and more efficient [25].

6. Conclusion

This study reviews the operational principles and application shortcomings of the traditional Haber-Bosch process and analyzes the dual use of ammonia in both global agricultural production and environmental protection fields, as well as the application prospects of using zeolite materials as alternative catalysts for sustainable ammonia production. The analysis indicates that ammonia is a core component that cannot be easily replaced in global food security and industrial denitrification. However, the traditional Haber-Bosch process is highly dependent on fossil energy and has strict reaction conditions, resulting in significant energy and environmental burdens. On the other hand, the unique microporous structure, high surface area, and exchangeable cations of zeolites provide a highly promising platform for achieving industrial ammonia synthesis under mild conditions.

The current research results related to this topic have confirmed that zeolite catalysts can enhance the activation of nitrogen gas by restricting the regional effect, thereby improving the reaction selectivity of the zeolite. However, this technology still faces many challenges that need to be overcome, such as catalytic activation performance below industrial standards, insufficient hydrothermal stability, an unclear reaction mechanism in the confined space, and difficulties in large-scale production.

Although this study integrated and summarized the existing relevant literature, there are still some limitations in the research. This analysis mainly relied on secondary literature and qualitative comparison, rather than experimental data. Moreover, the zeolite catalyst and the traditional iron-based catalyst were not systematically compared under unified experimental conditions, so it is difficult to accurately assess the actual market competitiveness. Additionally, this article does not include an economic feasibility analysis or a life cycle environmental assessment, both of which are essential for determining the feasibility of ammonia synthesis technology using zeolite catalysts.

Future research can make use of advanced methods such as multi-level porous zeolites through multi-disciplinary collaboration to reduce diffusion limitations.At the same time, verification should be accelerated to evaluate the stability and regeneration capacity of the catalyst under actual operating conditions. Integrating catalytic research with technical and economic analysis as well as environmental assessment is crucial for promoting the industrialization of zeolite-based catalysts and supporting the development of a sustainable ammonia economy.

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