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Progress in Ammonia Synthesis Catalysts

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Abstract

Synthetic ammonia is widely used in the production processes of industrial nitric acid, ammonium salts, fertilizers, etc., playing an indirect role in promoting the development of the national economy. At the same time, as one of the basic raw materials for industrial construction and chemical development, the demand for ammonia in various related industries has also increased by tons. However, as an important participant in industrial development and the national economy, traditional synthetic ammonia often has huge energy consumption and low profitability. Therefore, research and development of synthetic ammonia catalysts have continuously emerged. This article elaborates on the research and development of synthetic ammonia catalysts, combining the latest content on the research and development of synthetic ammonia, looks forward to the trends in synthetic ammonia research and development, and provides a certain summary, in order to have a comprehensive understanding of the development and operation methods of synthetic ammonia catalysts.

Keywords

Ammonia; Synthetic Ammonia; Catalyst.

1. Research Progress on Electrocatalysts for Nitrate Reduction to Ammonia

Among the many alternatives, the method of using N_2 as the nitrogen source and H_2O as the hydrogen source for electrocatalytic ammonia synthesis (NRR) has attracted the attention of researchers. However, the high bond dissociation energy of the nitrogen-nitrogen bond (941 kJ/mol), the low solubility of N_2 in H_2O, and the high HOMO–LUMO energy gap (10.82 eV) lead to adverse situations such as intensified hydrogen evolution side reactions at higher current densities and low Faradaic efficiency of NH_3. Nitrate (NO_3^-) is widely present in the aqueous phase, and the N=O bond (204 kJ/mol) has a lower dissociation energy compared to the nitrogen-nitrogen bond (941 kJ/mol). At the same time, compared with the gas–liquid–solid reaction system of the NRR reaction, the solid–liquid reaction in electrocatalytic nitrate reduction for ammonia synthesis (NITRR) overcomes the unfavorable effects of mass transfer and has a lower reaction barrier. Therefore, selecting NO_3^- as the nitrogen source for the ammonia synthesis reaction has a theoretical basis[1].

Reducing NO_3^- to synthesize ammonia still faces challenges. From the perspective of reaction thermodynamics, compared with the overpotential of 0.88 V vs. RHE required for NH_3 formation, various by-products are generated at similar overpotentials, including N_2 (1.25 V vs. RHE), N_2O (1.12 V), NO (0.96 V), and NH_2OH (0.73 V). At the same time, as the overpotential increases, the hydrogen evolution reaction (0 V vs. RHE) gradually intensifies, thereby suppressing NH_3 production. From the perspective of reaction kinetics, because NO_3^- reduction to synthesize ammonia involves multi-electron and multi-proton transfer processes, it is kinetically more difficult compared to NO_3^- reduction to N_2, which involves only a five-electron transfer. Therefore, developing electrocatalysts with high ammonia selectivity and Faradaic efficiency becomes particularly critical[2].

Catalysts are generally composed of catalytically active sites and supports. Among them, the catalytically active sites are the main factors responsible for the catalytic effect, while the support needs to provide a good coordination environment for the active sites to maximize their catalytic efficiency. Excluding external factors such as the support, different active sites have different intrinsic activities for NO_3^- reduction to ammonia [3]. Therefore, developing active sites with high intrinsic activity is one of the keys to improving ammonia synthesis performance. As precious metals and transition metals are excellent catalytic active sites and their catalytic activity exhibits significant size effects, preparing and investigating catalytic active sites at different scales has become a current research hotspot. According to size from large to small, these are nanoparticles (>5 nm), nanoclusters (1–5 nm), and single-atom catalysts (SACs). Since SACs have 100% atom utilization [4], the density of active sites at the same mass is maximized, and they can efficiently anchor and activate reactants (NO_3^-), improving ammonia synthesis performance while reducing the amount of metal used. Wu et al. used FeCl3, phenylenediamine, and porous SiO_2 as precursors for N_2-containing metal-organic frameworks, and further stabilized single-atom Fe through a secondary pyrolysis combined with acid-base etching to form a loose and porous Fe–N–C structure. Studies found that compared with the N–C organic framework used as a matrix and Fe nanoparticles (FeNP/NC), Fe SACs exhibited the best ammonia synthesis yield and Faradaic efficiency. At the same time, using the same method (changing the type of metal precursor) to synthesize Co SACs and Ni SACs, their NH_3 production rates were significantly lower than Fe SACs, following the trend Fe SACs > Co SACs > Ni SACs. Density functional theory (DFT) calculations indicate that the overpotential required for the thermodynamically spontaneous reaction from NO_3 to NH_3 over Fe SACs is -0.3 V vs. RHE, significantly lower than Co's -0.42 V and Ni's -0.39 V, and the rate-determining step is the NO to NOH process [5]. This suggests that the Fe–N_4 active center formed by single-atom Fe has higher catalytic activity than FeNP/NC, Co–N_4, or Ni–N_4. Similarly, ammonia synthesis performance can be improved by tuning the properties of nanoclusters. Li et al. prepared and studied core-shell structured Ru strain nanocluster catalysts and applied them to the NITRR reaction. Results show that due to the strong Ru–O bond coordination between the core and shell, the NH_3 selectivity reached 100% at a current density of 120 mA cm^{-2}, and the system could operate stably for 100 hours.For single-component nanoparticle active sites, the catalytic activity often varies depending on the exposed crystal faces of different metals. Therefore, the activity of the catalyst can be tuned by adjusting the exposure and the exposure ratio of different metal crystal faces. Cu is one of the important non-precious metal ammonia synthesis catalysts. To reveal the relationship between different Cu exposed crystal faces and activity, Hu et al. used DFT calculations to investigate the NITRR performance of catalysts with fully exposed Cu (111), Cu (100), and Cu (110) crystal faces across different pH ranges along the reaction pathway $*NO_3 \rightarrow *NO_2 \rightarrow *NO \rightarrow *NOH \rightarrow *NH_2OH \rightarrow *NH_3$. Since the pH value significantly affects the catalytic deoxygenation and hydrogenation processes during the NITRR reaction, with the rate-controlling steps and overpotentials showing significant pH-dependence, it is necessary to discuss the relationship between Cu crystal face exposure and activity separately for different pH ranges. Across the entire pH range, Cu (100) and Cu (111) crystal faces are more likely to undergo the ammonia synthesis reaction compared to the Cu (110) crystal face. In neutral and alkaline environments, Cu (111) shows the best ammonia synthesis performance compared to Cu (100), while Cu (100) is more effective in strongly acidic environments. This is attributed to the stereochemically oriented Cu-Cu pairs, which enable strong *NOH adsorption and weak $*NH_3$ adsorption on both Cu (111) and Cu (100) crystal faces, thereby enhancing the reaction performance.

2. Research Progress on Catalysts for Nitrogen Reduction to Ammonia under Ambient Temperature and Pressure

This article mainly introduces the catalytic reaction mechanism of NRR under normal temperature and pressure conditions, as well as the latest research progress of electrocatalysts and photocatalysts.

2.1. Catalytic Reaction Mechanism of NRR

Designing and preparing highly active and stable electrocatalysts and photocatalysts requires a deep understanding of the NRR process on heterogeneous catalysts. On heterogeneous catalysts, nitrogen reduction to synthesize NH_3 mainly proceeds via two mechanisms: associative and dissociative. In the associative mechanism, N_2 molecules first bind to the catalyst surface, and hydrogenation occurs while the two nitrogen atoms in the N_2 molecule are still bonded, with NH_3 only being released when the N—N bond finally breaks. Hydrogenation in the associative mechanism can occur via two possible pathways: the distal pathway and the alternating pathway. In the distal pathway, hydrogenation may preferentially occur on the nitrogen farthest from the catalyst surface, leading to the release of one NH_3 molecule and leaving a metal-nitrogen (M—N) unit, which then continues hydrogenation to form another NH_3 molecule. In the alternating pathway, the two nitrogen atoms on the catalyst surface undergo single hydrogenation reactions alternately until one of the N atoms is converted into NH_3 and the N—N bond is broken, after which the second NH_3 molecule is released along with the first. In the dissociative mechanism, the N≡N bond breaks before hydrogenation occurs, with the N atoms adsorbing separately on the catalyst surface and then hydrogenating independently to form NH_3.

2.2. NRR Electrocatalysts

2.2.1. Precious Metal Electrocatalysts

Precious metals are widely used as electrocatalysts in various reactions. In recent years, many researchers have used precious metals as catalysts for the electrochemical nitrogen reduction reaction (NRR) to synthesize NH_3 for ammonia production. Theoretical and experimental studies have shown that gold (Au) exhibits better performance as an electrocatalyst for electrochemical NRR. Wang et al. reported a flower-like Au microstructure, and this 'gold flower' structure provides abundant electrocatalytic active sites for NRR. When used as an NRR catalyst, compared with the reversible hydrogen electrode, the gold flower achieved a higher NH_3 yield [25.57 μg/(h·mg)] and a Faradaic efficiency of 6.05% at an applied potential of -0.2 V under ambient temperature and pressure [6]. The icosahedral Au is a typical precious metal covered by {730} crystal planes. Because the surfaces of multiple facets of icosahedral Au consist of various types of high-index sites, it shows particularly excellent performance for N_2 adsorption and reduction. Bao et al. prepared icosahedral Au nanorods using a seed-growth method and applied them in a three-electrode setup in alkaline electrolyte. They unexpectedly found that this catalyst exhibits a high NH_3 yield [1.648 $\mu g/(h\cdot cm^2)$] and a low activation energy (13.704 kJ/mol) under ambient conditions, and they also observed the production of N_2H_4 during NRR [7].

2.2.2. Transition Metal Electrocatalysts

Compared with precious metals, the cost of transition metals is relatively low, and some of them are very abundant in the Earth. In recent years, researchers have studied transition metal nitrides such as V, Zr, Nb, Cr, Mo combined with transition metals like Ni and Fe as NRR electrocatalysts under ambient temperature and pressure. Abghoui[8] et al. reported the development of a novel efficient transition metal nitride catalyst, which can electrochemically reduce molecular N to NH_3 in aqueous media under ambient temperature and pressure, with a very low applied bias. Based on comprehensive density functional theory, they selected four of the most promising catalysts from a series of transition metal nitrides (VN, ZrN, NbN, CrN). Compared with pure metal catalysts, these four transition metal nitrides are more inclined to reduce N_2. Xie[9] et al. developed an efficient and stable VN nanosheet array as an NRR electrocatalyst for electrochemical NH_3 synthesis under acidic conditions. In 0.1 mol/L HCl, this catalyst exhibited a Faradaic efficiency and NH_3 generation rate of 2.25% and 8.40×10^$^{-11}$ mol/(cm^2·s) at -0.50 V, respectively. This catalyst outperforms most reported water-based NRR electrocatalysts and can even be comparable to high-temperature NRR electrocatalysts. Zhang et al. also used a MoN nanosheet array on carbon cloth as a high-performance NRR electrocatalyst to electrochemically synthesize NH_3, showing high catalytic activity and good selectivity under ambient temperature and pressure. At -0.3 V versus the reversible hydrogen electrode, this catalyst had an NH_3 yield of 3.01×10^$^{-10}$ mol/(cm^2·s) and a Faradaic efficiency of 1.15%, comparable to most reported water-based NRR electrocatalysts. Kim et al. reported the use of porous nickel foam (average pore size 5 μm) for NRR at ambient temperature in a mixed solution of 2-propanol and water. At a catalytic current of 0.5 mA/cm^2, the catalyst exhibited a current efficiency and NH_3 generation rate of 0.89% and 1.54×10^$^{-11}$ mol/(cm^2·s), respectively. Kim et al. also reported NRR studies on 1 mm diameter, 3 cm long nickel wires in 0.1 mol/L LiCl with ethylenediamine. Electrolysis at a cell voltage of 1.8 V for 1 hour resulted in a Faradaic efficiency of 17.2% and an NH_3 yield of 7.73×10^$^{-7}$ mol.Suryanto et al. reported that surface-enhanced α-Fe nanorods grown on carbon fiber paper were used as NRR cathodes in non-protonic fluorinated solvent ionic liquid mixtures. Through reasonable design of the electrode and electrolyte system, high NRR current efficiency (32%) and NH_3 yield [2.35×10^$^{-11}$ mol/(cm^2·s)] were achieved under ambient temperature and pressure.

2.2.3. Non-metal Electrocatalysts

Non-metallic carbon-nitrogen materials have attracted increasing attention in the field of catalysis in recent years due to their excellent properties such as high thermal stability, chemical stability, and unique energy band structures. Liu et al. reported that N-doped porous carbon was used as an electrocatalyst for the electrochemical reduction of N_2 to synthesize ammonia under ambient temperature and pressure. At -0.9 V, compared with electrocatalysts reported in the literature, N-doped porous carbon exhibited higher activity for NH_3 synthesis, with an NH_3 production rate of 1.40 mmol/(g·h) and improved current efficiency. Studies found that high contents of pyridinic and pyrrolic nitrogen in the catalyst promote ammonia synthesis. Hu Hongwei [10]et al. prepared graphitic carbon nitride (g-C_3N_4) by calcining dicyandiamide, and then reduced H_2PtCl_6 with ethylene glycol to synthesize Pt nanoparticles, depositing the Pt nanoparticles on g-C_3N_4 to prepare a Pt/g-C_3N_4 catalyst. When Pt/g-C_3N_4 was used as a cathode catalyst, NH_3 could be electrochemically synthesized under ambient temperature and pressure, with an NH_3 production rate of 7.68×10^{-11} mol/(cm^2·s) at an applied voltage of 1.2 V.

3. Conclusion and Outlook

Ammonia is one of the most important chemical raw materials and energy carriers, and the demand for ammonia in future society will continue to increase. Sustainable ammonia synthesis is not only one of the most attractive research topics but also one of the most challenging ones. Currently, industrial ammonia synthesis still uses the classic Haber-Bosch process, but it has disadvantages such as high energy consumption, complex processes, and greenhouse gas emissions. The rising energy costs and ammonia demand have prompted research and development of more efficient technologies, in which catalysts play a key role. This paper reviews the recently developed novel and efficient catalysts in the field of thermal catalytic ammonia synthesis. Although designing effective ammonia synthesis catalysts still poses significant challenges, continuous developments in the related fields will provide more opportunities for the development of new ammonia synthesis catalysts in the future. We believe that with the continuous advancement of research technologies and methods, sustainable ammonia production under mild conditions can ultimately be achieved.

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