

Chemistry

Special Topic: Chemistry Boosts Carbon Neutrality

Challenges and prospects in artificial nitrogen cycle for energy decarbonization

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Fossil fuels still dominate global energy structure in our modern society, and have led to massive CO₂ emissions. Recently, ammonia has been regarded as a clean energy carrier toward diminishing or even eliminating the CO₂ emissions and has received significant attention. The ammonia can be synthesized from atmospheric dinitrogen and green hydrogen from water electrolysis by renewable energies, and converted back into dinitrogen and water for energy release, as shown in Figure 1. Benefited from the matured ammonia manufacture and transportation throughout the world for over one century, the already existing high-capacity infrastructure helps efficient storage and redistribution of ammonia with lowest economic cost. However, although considerable progress has been made in this artificial nitrogen cycle, there are still many challenges in developing highly-efficient routes and catalysts. Herein, we evaluate the current catalytic routes of ammonia synthesis (including thermocatalytic synthesis, electrocatalytic synthesis and photocatalytic synthesis) and ammonia utilization (involving ammonia decomposition, direct ammonia fuel cells and ammonia combustion). We also discuss the key issue in each process, and anticipate that our viewpoints and opinions could facilitate the developments of artificial nitrogen cycle and energy decarbonization.

Thermocatalytic synthesis. Ammonia synthesis ($\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$) via traditional Haber-Bosch (H-B) process requires harsh reaction conditions (400–500°C, 10–30 MPa) [2,3]. The H₂ production, from fossil energy, further raises energy consumption and carbon emission. By contrast, water electrolysis, via renewable energies, is a green approach to H₂ production. Ammonia synthesis from renewable H₂ and N₂ will significantly enhance the storage of renewable energies, while compatibility between water electrolysis and ammonia synthesis is the key issue. The output H₂ conditions from water electrolysis is below 400°C and 5 MPa, while commercial catalysts of ammonia synthesis cannot realize a desired efficiency at the conditions. Therefore, it is highly desirable to develop efficient catalysts for NH₃ synthesis under mild reaction conditions. Besides, the integrated system, involving renewable energy application, H₂ production and ammonia synthesis, is extremely complicated, which requires rational design, overall optimization, and

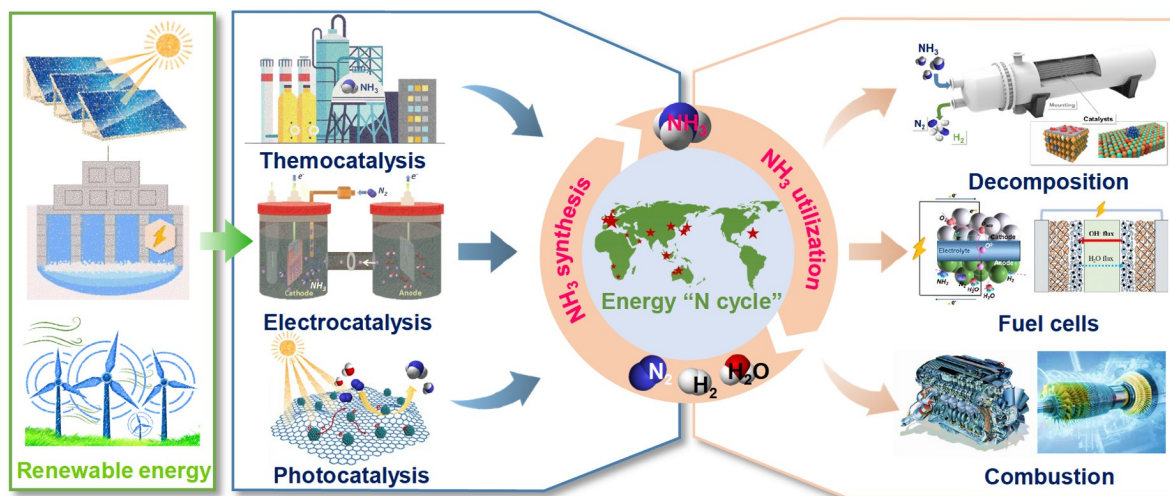


Figure 1 Schematic for ammonia synthesis and utilization via artificial nitrogen cycle for energy decarbonization. The map element in the figure was modified with permission from Ref. [1]. Copyright 2022 American Chemical Society.

dynamic management for the whole integrated process.

Electrocatalytic synthesis. Electrocatalytic synthesis of ammonia ($\text{N}_2 + 3\text{H}_2\text{O} \rightarrow 2\text{NH}_3 + 3/2\text{O}_2$) can be directly driven by electric power from renewable energy. Notably, N_2 reduction pathway in electrolysis is an associative route that enables ammonia synthesis under mild conditions, which is different from common dissociative route in thermocatalysis. The reported NH_3 synthesis rates are generally in the range of 10^{-13} – 10^{-9} mol cm^{-2} s^{-1} , and far away from the feasible target of 10^{-7} mol cm^{-2} s^{-1} in industry [4]. The main challenges of electrocatalytic synthesis of ammonia are low ammonia productivity and low Faraday efficiency, due to poor dissolution and diffusion of N_2 , weak N_2 activation, and competitive hydrogen evolution reaction [5,6]. To overcome these obstacles, the rational design of multi-active sites and the optimization of the interface of catalyst/electrolyte and electrode/catalyst are promising ways to improve electrocatalytic synthesis of ammonia.

Photocatalytic synthesis. The photocatalytic process for ammonia synthesis is driven by solar energy for activation of N_2 and H_2O . In the photocatalytic process, charge carriers are generated after light absorption. The electron-hole pairs are formed on photoactive sites, and ammonia is produced via combination of the photoactivated N_2 and protons. The technical bottlenecks, in photocatalytic synthesis of ammonia, are low utilization efficiency of solar energy and low productivity of ammonia. It is important to increase efficiency of the separation and migration of photo-induced electrons and the N_2 activation. The ideal photocatalysts are supposed to be compatible with proper band gap, highly efficient separation of electrons and holes, superior activation ability of H_2O and N_2 . Creation of vacancy sites, heteroatom doping and composite construction may be effective strategies to improve photocatalytic performance for ammonia synthesis.

Ammonia decomposition. Ammonia can be decomposed into hydrogen for further utilization, in support of “hydrogen economy” [7]. The ammonia decomposition and synthesis are strongly correlated according to the principle of microscopic reversibility. However, they are not necessarily the same cases because of varied N-binding energies with catalysts under different reaction conditions. Commercially, the ammonia decomposition is carried out by Ni-based catalysts under high temperatures ($>800^\circ\text{C}$), resulting in high energy

consumption and poor safety. Despite numerous efforts, the most challenge is still the precise design of low-temperature catalysts [1]. The guidance for improving catalysts is as follows: (1) precise control of particle size/shape of active metals (e.g., Ru and Ni) to maximize the number of active sites; (2) incorporating second metal for enhanced synergistic catalysis via structure stabilization and electronic effects; (3) introducing electronic and structural promoters/supports for activity promotion. Given that the obtained hydrogen from ammonia can be utilized in hydrogen refueling station, proton exchange membrane or solid oxide fuel cells (SOFCs), integrating ammonia decomposition with these systems to choose/design rational catalysts with matched operating temperatures might be the potential chance in the research area.

Direct ammonia fuel cells. Ammonia can be directly fed into fuel cells to generate power with superior ammonia-to-electricity conversions [8]. The NH_3 -SOFC is a feasible fuel cell operating at high temperatures (500–1000°C). Nevertheless, the performances of NH_3 -SOFCs were lower than hydrogen-fed SOFCs. The exploration of suitable anode catalysts that can catalyze both thermal NH_3 decomposition and NH_3/H_2 electro-oxidation is the main challenge. The anode degradation and deactivation (coarsening and poisoning of Ni species) are major concerns as well. To tackle these issues, two potential strategies were proposed: (1) *in-situ* construction of multifunctional region at anode, which can separate thermal cracking of NH_3 and electro-oxidation of H_2 on different catalyst layers with complementary interoperations; (2) functionalize and stabilize the anode catalysts at three phase boundaries to achieve superior thermal-electro catalysis. Recently, low-temperature direct ammonia alkaline exchange membrane fuel cells (NH_3 -AEMFCs) have attracted much attention due to their fast start-up and mobile superiority [9]. Nevertheless, the development of NH_3 -AEMFCs is at an earlier stage because of the more complex and sluggish NH_3 oxidation, which requires the further development of low Pt-based and non-noble catalysts.

Ammonia combustion. Ammonia combustion can directly generate heat and power in gas furnaces, turbines and engines [10]. The most advantage is that it can be carried out on existing power-generation infrastructure with simple modification of equipment. The large-scale application is limited by the narrow flammability, low laminar burning velocity and activity in direct ignition and flame stability. Notably, the ammonia combustion would result in the formation of harmful NO_x . Motivated by tackling these challenges, directional control strategies for combustion and tail-gas treatment are critical for improving the ammonia utilization and controlling NO_x emissions: (1) blending ammonia with hydrogen for combustion with production of harmless dinitrogen and water; (2) integrating ammonia combustion and selective catalytic reduction to achieve net-zero NO_x emission; (3) direct catalytic combustion of ammonia by using rational catalysts.

Energy decarbonization is vital to diminishing CO_2 emissions. To promote artificial nitrogen cycle for energy decarbonization, we focus on the catalytic processes of ammonia synthesis and ammonia utilization. Although the thermocatalytic, electrocatalytic and photocatalytic synthesis of ammonia can store renewable energies, the low compatibility of catalytic systems or the low ammonia yield rate significantly hinders the efficient storage of renewable energies. The decomposition, fuel cells and combustion of ammonia provide multiple methods to release the renewable energies, yet exploration of the low-temperature catalysts and reduction of side reactions are still challenging. This perspective proposes that the catalytic systems, routes and catalysts of artificial nitrogen cycle should be rationally designed for energy decarbonization. We would like to emphasize that artificial nitrogen cycle will offer a sustainable approach to realize complete decarbonization of energy system.

Data availability

The original data are available from corresponding authors upon reasonable request.

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Author contributions

L.J. and S.L. conceived this article; H.F. and Y.Z. wrote the original draft and prepared the figure; X.P., Y.L., and X.W. edited and revised the manuscript.

Conflict of interest

The authors declare no conflict of interest.

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