Achieving highly efficient ammonia synthesis by altering the rate-determining step

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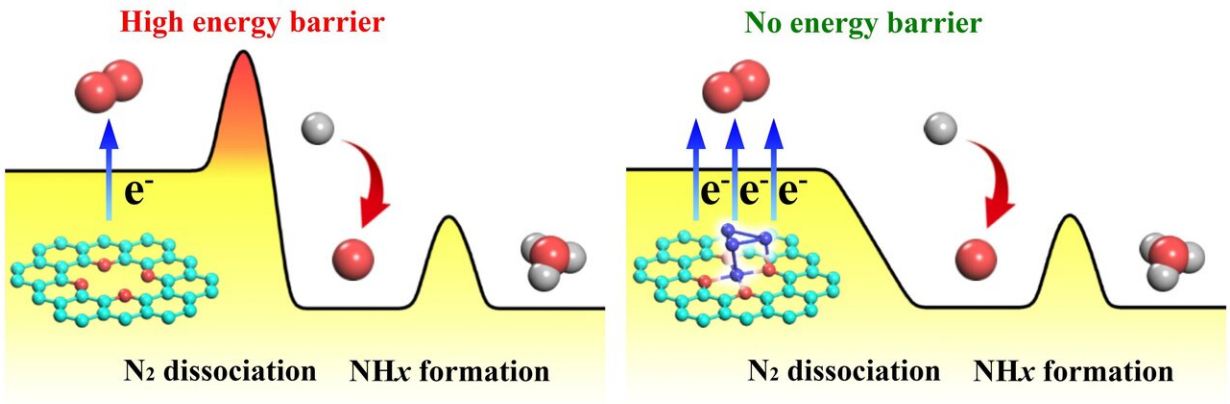

Schematic illustration of altering the rate-determining step of nitrogen reduction reaction by introducing cobalt single-cluster in the catalyst. The cyan, red, purple, and gray spheres represent C, N, Co, and H atoms, respectively. Credit: ©Science China Press

The electrochemical conversion of nitrogen to ammonia is the most promising alternative of the traditional Haber-Bosch process to achieve nitrogen fixation under ambient conditions. In this strategy, activation of high-energy triple bonds of nitrogen is the most significant bottleneck, and is commonly considered as the rate-determining step of ammonia synthesis. Scientists based in China have successfully altered the rate-determining step of electrochemical nitrogen reduction, and outlined guidance for future design of catalysts.

Ammonia is a generic precursor for the manufacture of fertilizer and most nitrogen-containing organic chemicals. To date, industrial ammonia production is predominantly conducted by the Haber-Bosch process, in which nitrogen is fixed using the chemical reductant hydrogen. However, despite more than 100 years of development, this process still requires harsh conditions, including high temperatures (673-873 K) and pressures (20-40 MPa), accounting for 1.5% of worldwide energy consumption. In this context, it a sustainable and less energy-intensive technology to produce ammonia is essential.

An alternative method to achieve N2 fixation under ambient conditions is the electrocatalytic N2 reduction reaction (NRR) using protons from water as the hydrogen source and powered by renewable electricity sources. However, in practice, it is still difficult to achieve desirable NRR performance, which causes great energy loss. The key challenge lies in the activation of the inert nitrogen-nitrogen triple bond, which is generally considered as the rate-determining step. In this context, highly active catalysts that could alter the rate-determining step of electrochemical ammonia synthesis represent an ideal candidate for ammonia synthesis.

In a new research article published in the Beijing-based *National Science Review*, scientists at the Soochow University in Suzhou, China, present the latest advances in overcoming the bottleneck of ambient ammonia synthesis. Co-authors Sisi Liu, Mengfan Wang, Haoqing Ji, Xiaowei Shen, Chenglin Yan and Tao Qian have successfully altered the rate-determining step of ambient ammonia synthesis by deliberate introduction of cobalt single clusters as the electron-donating promoter in nitrogen-doped carbon, and achieved an outstanding ammonia yield rate of 76.2 μg h-1 mg-1, with superior Faradaic efficiency of 52.9%. With this strategy, the superior performance would greatly reduce the energy loss of the system and cut down the fundamental cost, thus contributing to future practical applications.

These scientists likewise outline the potential development directions of future electrocatalysts for sustainable NRR systems. "When chemically adsorbed on the Co cluster, N2 is spontaneously activated and experiences a significant weakening of the nitrogen-nitrogen triple bond due to the strong electron back-donation from the metal to the N2 antibonding orbitals, and the N2 dissociation becomes an exothermic process over the cobalt single cluster," says Prof. Tao Qian. "Thus, the rate-determining step has been successfully shifted from the usual N2 activation to the subsequent hydrogenation with only a small energy barrier of 0.85 eV."

More information: Sisi Liu et al, Altering the rate-determining step over cobalt single clusters leading to highly efficient ammonia synthesis, *National Science Review* (2020). DOI: 10.1093/nsr/nwaa136

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