Record ammonia production achieved with inexpensive cobalt catalyst at low temperatures

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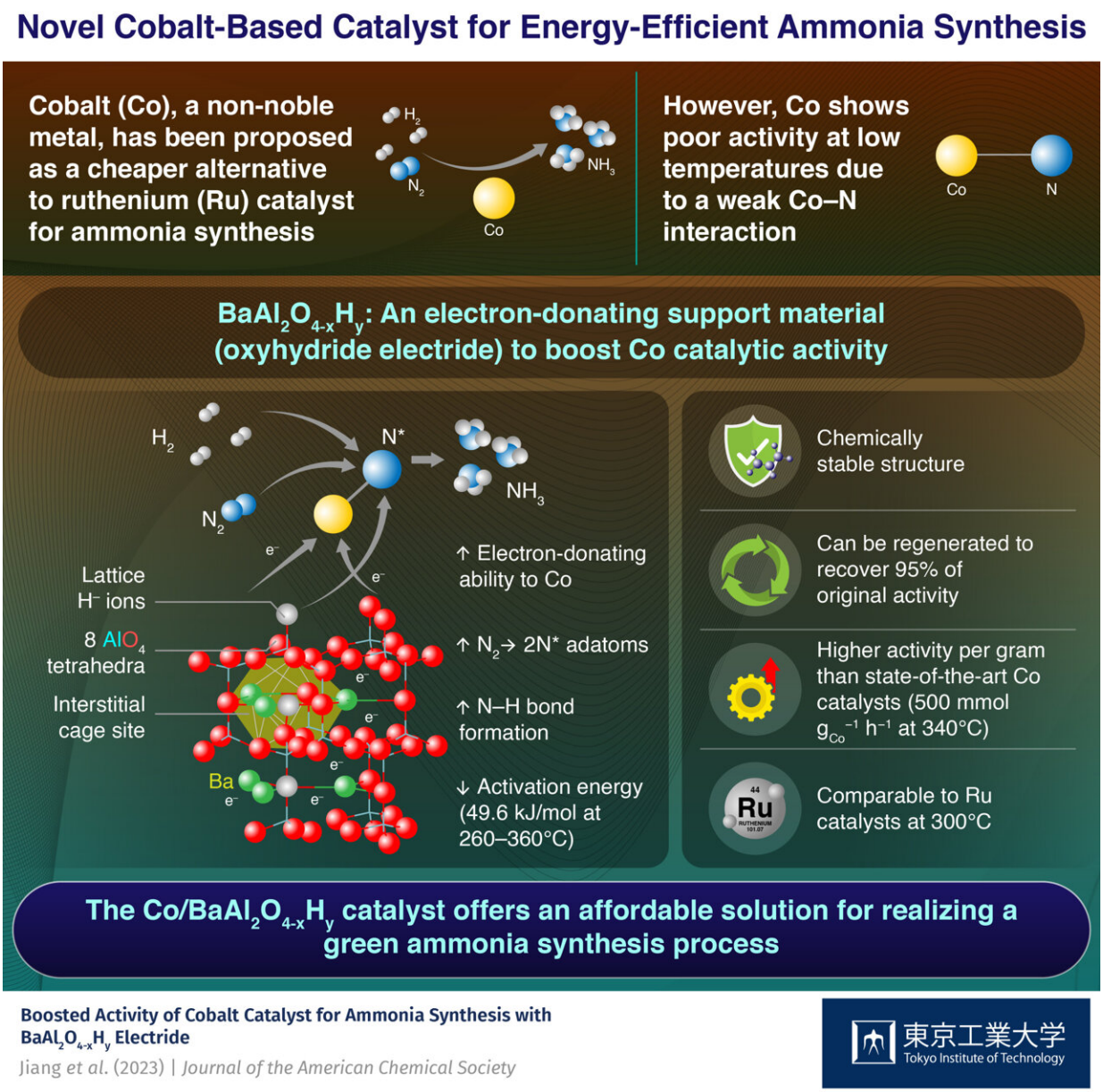

Credit: Tokyo Tech

Ammonia (NH_3) is one of the most widely produced chemicals in the world, with production at more than 187 million tons in 2020. About 85% of it is used to produce nitrogenous fertilizers, while the rest is used for refining petroleum, manufacturing a wide range of other chemicals, and creating synthetic fibers such as nylon. However, all this comes at a high energy cost.

Currently, most of the ammonia is produced using the conventional Haber-Bosch process, which requires combining nitrogen and hydrogen at high temperatures (400–450°C) and pressures (200 atmospheres). As a result, scientists are actively seeking catalysts that can reduce the energy requirements for ammonia production and make synthesis more sustainable.

Ruthenium (Ru), a noble metal, has been the primary candidate in this regard owing to its exceptional ability to absorb nitrogen at low temperatures. However, its high cost has prevented its widespread adoption in large-scale ammonia synthesis. While cobalt (Co) has been considered as a more cost-effective alternative, achieving the same catalytic activity as Ru at low temperatures has been difficult.

To enhance the catalytic activity of Co, a team of researchers including Professor Masaaki Kitano at Tokyo Institute of Technology (Tokyo Tech), Japan developed, in a recent study, a support material for Co nanoparticles. The material, a barium-containing oxyhydride electride called $BaAl_2O_{4-x}H_y$, increases the catalytic activity of Co to a level comparable to that of Ru catalysts at low temperatures, and protects the

H^- ions and electrons from the effects of air and moisture. The breakthrough was published in the *Journal of the American Chemical Society*.

"We attempted to develop a barium-containing oxyhydride electride, $Ba_2A_{l2}O_{4-x}H_y$ to obtain a highly effective and chemically durable catalyst and unlock a new approach to designing novel inorganic electride materials and triggering their application in other fields," explains Prof. Kitano.

How did the team achieve this feat? Put simply, $BaAl_2O_{4-x}H_y$ has a unique structure that promotes the dissociation of nitrogen over Co. The material exhibits a stuffed tridymite structure where AlO_4 tetrahedra are linked to form a three-dimensional (3D) network structure, creating cage-like void spaces between the barium ions. These interstitial sites are like pockets for holding negative charges, enabling the material to donate electrons to Co and facilitate the breakdown of nitrogen molecules into nitrogen adatoms.

To improve the electron-donating ability of the material, the researchers introduced electrons to the interstitial sites by replacing the O^{2-} lattice ions with H^- ions (O^{2-} (framework)+ ½ H_2 = H^- (framework) + 1/2 O_2 + e^- (cage)). The introduction of H^- ions not only improved the electron-donating ability of the $BaAl_2O_4$ but also facilitated the desired reduction of nitrogen to ammonia.

By promoting both the cleavage of N_2 and its subsequent reduction to ammonia, the $Co/Ba_2Al_2O_{4-x}H_y$ catalyst could produce more than 500 mmol of ammonia per gram of cobalt per hour, a record value for Co-based catalysts. Moreover, compared to conventional Co catalysts, which typically have activation energies for ammonia synthesis exceeding 100 kJ/mole, the proposed catalyst demonstrated an activation energy of just 48.9 kJ/mole.

Further, the stuffed tridymite structure was durable and reusable, with the AlO_4-based tetrahedra framework shielding the lattice H- ions and electrons from oxidation. Finally, after exposing the $Co/BaAl_2O_{4-x}H_y$ to air, the researchers could recover up to 95% of its original activity by simply heating it in hydrogen.

With its good chemical stability, enhanced catalytic activity, and high reusability, the $Co/BaAl_2O_{4-x}H_y$ catalyst shows great promise for synthesizing ammonia at low temperatures. "This novel inorganic electride offers a new approach to developing highly effective and stable Ru-free catalysts for green ammonia synthesis," concludes Prof. Kitano.

More information: Yihao Jiang et al, Boosted Activity of Cobalt Catalysts for Ammonia Synthesis with BaAl2O4–xHy Electrides, *Journal of the American Chemical Society* (2023). DOI: 10.1021/jacs.3c01074

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