

Inorganic Electride as a Catalyst for Ammonia Synthesis

Associate Professor Masaaki Kitano



Catalytic ammonia synthesis is vital for production of fertilizer, which is needed to produce food for the world's expanding population. The rate-determining step of ammonia synthesis is cleavage of the $N\equiv N$ bond, because the bond energy is extremely large. In the reaction, a N_2 molecule adsorbs on surface of transition metal catalyst such as Fe and Ru by donating electrons from its bonding orbitals and accepting electrons to the antibonding π orbitals (back-donation). This back-donation produces weakening $N\equiv N$ bond resulting in enhancement of efficiency of cleavage of N_2 . Electron donation from appropriate promoters is therefore a key to enhancing the efficiency of NH_3 synthesis using Fe or Ru-catalysts. One significant difference between the kinetics of ammonia synthesis over Ru and Fe is the dependence of the rate on H_2 pressure. Typically, Ru catalysts are strongly inhibited by hydrogen under high pressure conditions. A supported Ru catalyst that is less inhibited by hydrogen is therefore highly desirable.

In our study, we have focused on a stable electride; $[Ca_{24}Al_{28}O_{64}]^{4+}(e^-)_4$ (abbreviated as "C12A7:e⁻") (Fig.

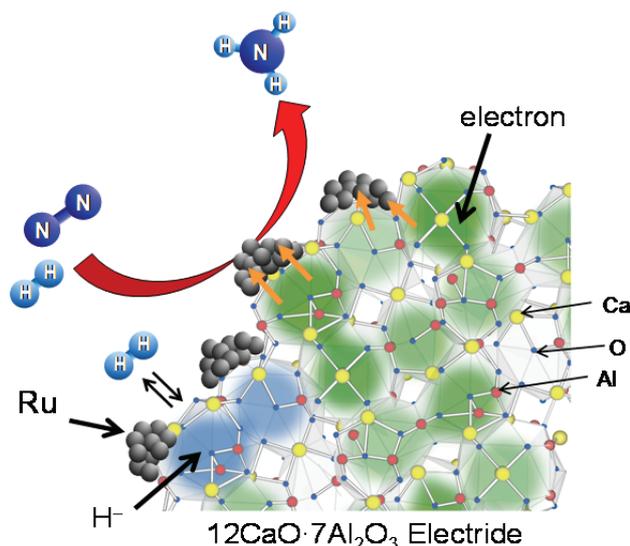


Fig. 1 Schematic illustration of ammonia synthesis over Ru/C12A7:e⁻.

1) as an efficient promoter with high electron donating efficiency for a Ru catalyst [1]. C12A7:e⁻ is the first

stable solid material of electrides in which electrons serve as anions and has a low work function (2.4 eV) comparable to those of alkali metals, with chemical and thermal stability. The encaged electrons can also be replaced by H^- ions by thermal treatment in H_2 atmosphere. The electrons encaged in C12A7:e⁻ would be effectively donated to metal Ru (work function 4.7 eV) due to its low intrinsic work function. In addition, the hydrogen absorption capability of C12A7:e⁻ may prevent the poisoning of Ru surface by hydrogen adatoms.

Ru/C12A7:e⁻ exhibits much higher catalytic activity than conventional Ru catalysts reported so far. In addition, the activation energy of Ru/C12A7:e⁻ is almost half that of the conventional catalysts (Fig. 2). Kinetic

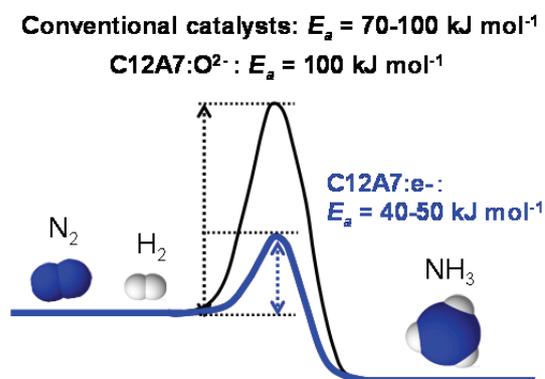


Fig. 2 Energy diagram for ammonia synthesis.

analysis with infrared spectroscopy reveals that C12A7:e⁻ markedly enhances N_2 dissociation on Ru by back donation of electrons and that the poisoning of ruthenium surfaces by hydrogen adatoms can be effectively suppressed because of its ability to reversibly store hydrogen.

[1] M. Kitano, T. Yokoyama, M. Hara, H. Hosono, et al *Nat. Chem.* **4** (2012) 934.