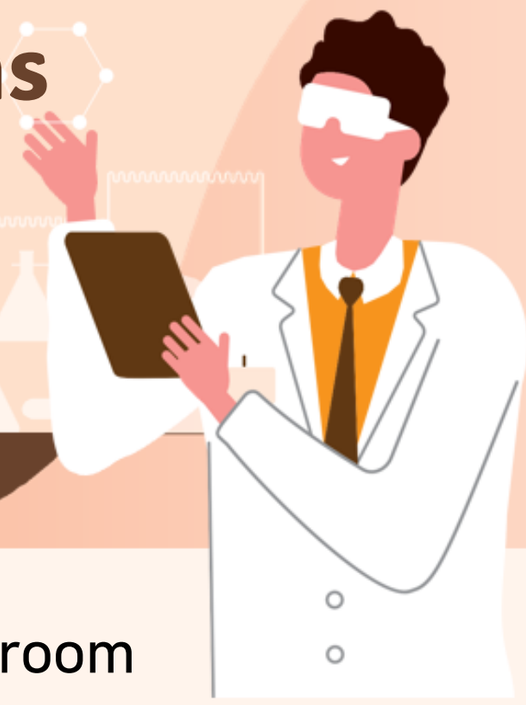
UNIST | SCHOOL OF ENERGY AND CHEMICAL ENGINEERING

# Separately Storing Electrons and Protons at Ru Particles and Base Promoters to Facilitate Ammonia Synthesis



• Time: 2025.10.28. (Tue) 16:00-17:15

• Place: 104-E206 Classroom

## Speaker


**Prof. Minkee Choi**

Dept. of Chemical and Biomolecular Engineering, KAIST


## Abstract


Ammonia ($NH_3$) is crucial for the production of fertilizers, pharmaceuticals, and explosives, and it has attracted great attention as a carbon-free fuel and hydrogen carrier. Recently, there has been a strong demand for catalysts that enable ammonia synthesis under mild conditions (<573 K, <2 MPa) to efficiently integrate with electrolytic $H_2$ production. The main challenge of $NH_3$ synthesis under such conditions lies in activating the stable N≡N bonds of $N_2$, which necessitates the development of more advanced catalysts. Ru catalysts combined with base promoters (e.g., Ba, Cs, La oxides) have shown promising $NH_3$ synthesis activities under mild conditions. However, even the most recent catalysts suffer from insufficient activities and significant $H_2$ poisoning. Furthermore, a comprehensive understanding of the promoting mechanism and the structure-property correlation of the catalysts is still lacking.

In this study, we carried out rigorous analysis of 24 catalysts (22 carbon-supported and 2 MgO-supported Ru catalysts) during $NH_3$ synthesis under mild conditions (573 K and 10 bar). An extremely wide range of $NH_3$ production rates (0.9–342.3 mmol $g_{Ru}^{-1}$ $h^{-1}$) was observed, depending on the types of supports and BaO promotion. This variation is striking, considering that all catalysts have similar Ru dispersions and loadings. Rigorous spectroscopic analyses indicated that H atoms generated by $H_2$ activation on Ru dissociate into $H^+/e^-$ pairs. Subsequently, $H^+$ migrates over the carbon surfaces to titrate remotely placed basic BaO, while $e^-$ accumulates in conductive Ru/carbon bodies (Fig. 1). Conversely, on the surface of the insulating MgO support, H splitting into $H^+/e^-$ occurs only at the intimate BaO–Ru interfaces. As the work function of the carbon support decreases relative to that of Ru (4.67 eV), $e^-$ is gradually localized in Ru particles in Ba-Ru/carbon catalysts, facilitating $N_2$ activation via π-backdonation and alleviating $H_2$ poisoning. Consequently, the work function of the carbon support turns out to be the most critical descriptor for the $NH_3$ production rates of the Ba-Ru/carbon catalysts. The best catalyst, synthesized using low-work-function N-doped multiwalled carbon nanotubes, exhibited 7.4 times higher activity than Ba-Ru/MgO, a benchmark catalyst. Our results demonstrate that Ru and BaO domains, connected by conductive low-work-function carbon supports, can store $e^-$ and $H^+$ separately under the reductive reaction conditions, leading to very high $NH_3$ synthesis activities. These catalysts can be considered 'chemical capacitors' because they store two differently charged species, electrons ($e^-$) and $H^+$ ions, through the chemical action of BaO (a strong base). The electronic promotion effects of BaO, well-recognized in the literature for a long time, appear not to stem from simple inductive effects, but rather from such charge capacitive effects. This study provides crucial atomistic insights into the role of base promoters and offers significant perspectives for designing advanced $NH_3$ synthesis catalysts.

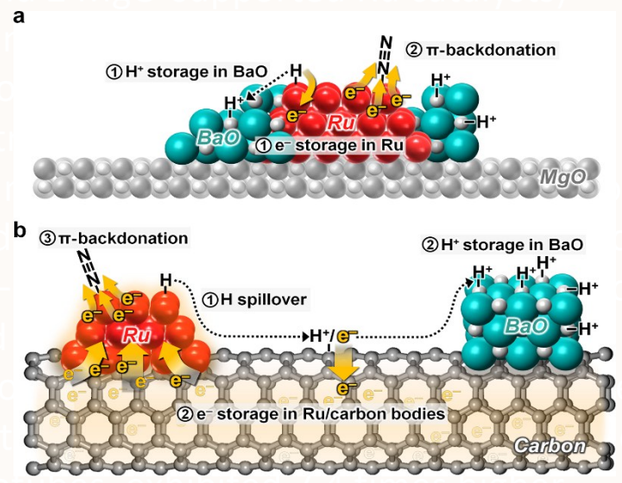




**Fig. 1.** Hydrogen-aided electron donation of BaO to Ru during $NH_3$ synthesis. a, BaO-promoted Ru catalysts on an insulating MgO support. Chemisorbed H atoms on Ru polarize into $H^+/e^-$ pairs at the BaO–Ru interfaces, where nonreducible BaO selectively captures $H^+$ while leaving $e^-$ in Ru. b, BaO-promoted Ru catalysts on a conductive carbon support. $H^+/e^-$ pairs can migrate over long-distances across the carbon surface. BaO can capture $H^+$ even without direct contact with Ru, while accumulating $e^-$ in the conductive Ru/carbon bodies