Anchoring bond in Ru/Ca$_2$NH catalyst keeping high NH$_3$ synthesis activity

Hitoshi Abe (IMSS KEK, SOKENDAI, JST-ACCEL), Yasuhiro Niwa (IMSS KEK), Masaaki Kitano (Tokyo Tech.), Yasinori Inoue (Tokyo Tech.), Masato Sasase (Tokyo Tech.), Takuya Nakao (Tokyo Tech.), Tomofumi Tada (Tokyo Tech.), Toshiharu Yokoyama (Tokyo Tech., JST-ACCEL), Michikazu Hara (Tokyo Tech., JST-ACCEL), and Hideo Hosono (Tokyo Tech., JST-ACCEL)
hitoshi.abe@kek.jp

Industrial ammonia (NH$_3$) synthesis is crucial for our lives since NH$_3$ is used to manufacture fertilizers. The most widely used industrial process known as Haber-Bosh process is usually operated under high temperatures (673-773 K) and pressures (10-30 MPa).

Developments of new catalysts are demanded to produce NH$_3$ under mild conditions. A Ru catalyst supported by an inorganic electride [Ca$_{24}$Al$_{28}$O$_{64}$]$_{4+}$ (e$^-$) was reported showing high activity for NH$_3$ synthesis[1]. The high activity was understood being realized by the electron donation from the electride to Ru particles in order to dissociate the triple bond of N$_2$. A Ru/Ca$_2$NH catalyst, showing higher activity, has been developed[2] by using Ca$_2$N:e$^-$ as a support, which is a two dimensional electride. Another catalyst of less activity, Ru/CaNH, was also prepared for comparison. Ru K-edge XAFS experiments were carried out in order to investigate local structures of these catalysts at BL AR-NW10A, Photon Factory, KEK.

Ru K-edge XANES spectra of the Ru(0.1wt%)/Ca$_2$NH and Ru(0.1wt%)/CaNH catalysts were analysed, and they showed both of them were in metallic states. EXAFS analyses revealed a definite difference between the two. Ru-Ru interactions in their FT of EXAFS oscillations resulting from Ru nanoparticles were observed for the both catalysts. In addition, another distinct peak, which was assigned to a Ru-N bond, was recognized only in the FT of EXAFS of Ru(0.1wt%)/Ca$_2$NH[3]. Such a bond, however, wasn’t observed for the Ru/CaNH catalyst. The Ru-N bond was formed between Ru atoms of Ru nanoparticles and N atoms in the Ca$_2$NH support. This Ru-N bond works as an anchor to fix Ru nanoparticles on the support. The anchoring effect of the Ru-N bond plays a key role to keep the high NH$_3$ synthesis activity. The anchoring bond was also observed in another highly active catalyst, Ru/Ca(NH$_2$)$_2$[4].

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References