Anchoring bond in Ru/Ca_2NH catalyst keeping high NH_3 synthesis activity

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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_2NH catalyst, showing higher activity, has been developed[2] by using $Ca_2N{:}e^-$ 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_2NH 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_2NH[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_2NH 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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