Anchoring bond of catalysis particles found in highly active NH₃ synthesis catalysts

Hitoshi Abe: KEK-IMSS, SOKENDAI, JST-ACCEL, Yasuhiro Niwa: KEK-IMSS,

Masaaki Kitano: Tokyo Tech, Yasunori 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,

Hideo Hosono: Tokyo Tech, JST-ACCEL

A Ru catalyst using inorganic electride $[Ca_{24}Al_{28}O_{64}]^{4+}(e^{-})$ as a support was reported showing high activity for NH₃ synthesis[1]. Ru/Ca(NH₂)₂ and Ru/Ca₂NH catalysts showing higher activity have been developed. XAFS experiments were carried out in order to investigate local structures of these catalysts. A Ru/CaNH catalyst was also analyzed to be compared. Ru-N bonds between Ru particles and N in supports have been found in the highly active Ru/Ca(NH₂)₂ and Ru/Ca₂NH catalysts. However, such a bond wasn't observed for the Ru/CaNH catalyst.

The particle size of the $Ru/Ca(NH_2)_2$ catalyst is very small as ~2 nm even for high loading of 10wt%, and aggregation was not observed after NH_3 synthesis reaction. The Ru-N bond between Ru particles

and N in the support works as an anchoring bond, and aggregation was prevented[2].

The Ru/Ca₂NH catalyst shows much higher activity than the Ru/CaNH catalyst, and it is interesting to compare local structures of these catalysts. XAFS analyses revealed that the Ru/Ca₂NH catalyst has a Ru-N bond between Ru particles and N in the support, while the Ru/CaNH catalyst does not have such as bond[3]. In the Ru/Ca₂NH, H exists as an anion (H⁻), while H exists as proton (H⁺) in the Ru/CaNH. This difference may be related whether a Ru-N bond is formed or not.

Thus, it is clarified that Ru particles are fixed to the supports by the Ru-N anchoring bonds for the highly



Fig. 1. Processed data of XAFS experiments showing local structures around Ru. The Ru-N bond was clearly found for the Ru/Ca₂NH.

active $Ru/Ca(NH_2)_2$ and Ru/Ca_2NH catalysts, and the particles will not aggregate. The anchoring effect of the Ru-N bonds plays a key role to keep the high NH_3 synthesis activities.

Bibliography

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