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Article / Book Information

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論 文 要 旨

THESIS SUMMARY

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要旨（英文 800 語程度）
Thesis Summary (approx.800 English Words)

Ammonia has garnered massive attention within the whole society, not only due to its diverse application as a source material but also because of the exceptional properties as a hydrogen carrier such as high hydrogen capacity and easy liquefaction. Although ruthenium (Ru) is widely acknowledged as the most active transition metal catalyst for ammonia synthesis, its commercial feasibility is diminished by the low natural abundance and thereby increasing price. Most importantly, in order to achieve the future of carbon-free society, artificial ammonia synthesis utilizing hydrogen gases generated by renewable energy requires to be operated under much milder conditions than the current Haber-Bosch process. This new process, known as the ″green ammonia synthesis process,″ poses a significant yet challenging research target: the development of a Ru-free, high-performance catalyst. However, the development of high-performance non-noble metal catalysts is very challenging because of the obstacle caused by the necessity of utilization of unstable support materials, like hydrides, nitride, imides, amides and so on.

Here, we propose our catalyst design concept for a desired Co catalyst: (a) The cations of the desired support material should consist of alkali metal or alkaline earth metal elements to utilize their well-known promotion effects on ammonia synthesis. (b) The support materials should contain active anions, such as anionic electrons, H^- ions or N^{3-} ions, to utilize their unique effects on catalysis. (c) The support materials should have robust resistance towards ambient atmosphere.

First, we focused on the stuffed tridymite material $BaAl_2O_4$. In its crystal, AlO_4 tetrahedra are connected with each other to form a three-dimensional (3D) network. Such a 3D network structure without non-bridging oxygens leads to robustness toward air and moisture. By solid state reaction of BaH_2/$Ba(NH_2)_2$, $BaCO_3$, Al_2O_3, we succeeded in introducing multiple types of anions into the $BaAl_2O_4$ to acquire the novel mixed-anion materials, $BaAl_2O_{4-x}A_y$ (A = N, H). As expected, it was demonstrated by this research that the stuffed tridymite structure can protect active anions from O_2 or moisture. The chemical formula of this oxyhydride was estimated to be $BaAl_2O_{3.66}H_{0.40}{:}e^-_{0.28}$, and that of oxynitride was determined to be $BaAl_2O_{3.713}N_{0.191}$.

This research proves that oxyhydrides and oxynitrides promote ammonia synthesis over Co via different mechanism using $BaAl_2O_{4-x}A_y$ as model materials. There was no anion substitution and valence state changes observed after ammonia synthesis over various $Co/BaAl_2O_{4-x}A_y$. $Co/BaAl2O_{4-x}H_y$ exhibited significantly higher efficiency than $Co/BaAl_2O_{4-x}N_y$, based on their activity and activation energy. Our results update the answer to catalyst design using mixed-anion materials that oxyhydrides are more effective than oxynitrides in the case of Co-based catalysts, i.e., low work function of supports should be the key for an efficient ammonia synthesis catalyst.

Although high catalytic performance has been achieved over $Co/BaAl_2O_{4-x}H_y$, this catalyst would be deactivated after exposure to air. $BaAl_2O_{4-x}H_y$ adsorbs CO_2 easily to form catalytically detrimental carbonate species, leading to the decrease in activity, because its surface contains alkaline earth metal oxide structure which can react with CO_2 easily. High temperature reduction (> 600° C) was required to remove the surface carbonate. To overcome the deactivation by CO_2 adsorption, an ionic material, $SrCN_2$, was chosen as support for Co catalysts. $SrCN_2$ has excellent air durability, resulting from its chemical inertness toward air components, thus, it does not require any high-temperature regeneration treatment after exposure to the air or CO_2 or even O_2. Under ammonia synthesis conditions, $SrCN_2$ was transferred from a stochiometric state to a surface electride by the formation of CN_2^{2-} vacancy trapping 2 electrons under ammonia synthesis atmosphere. As a result, electrons can be effectively donated from the support surface to Co particles, which enhances N_2 activation to further boost ammonia synthesis over Co. The optimized catalyst, $Co(10\ wt\%)/SrCN_2/Al_2O_3$, achieved high activity (4.43 mmol g^{-1} h^{-1}; at 300° C and 0.90 MPa) with low apparent activation energy (52.7 kJ mol^{-1}; 300-380° C; at 0.90 MPa).

This study distinguishes the roles of anionic electrons, H^- ions, and N^{3-} ions and reveals their promotion effects and mechanisms on Co catalysts. It is the first to clearly demonstrate that the effects of anionic electrons and H^- ions are significantly superior to those of N^{3-} ions. This research uncovers how the crystal structures and surface adsorption characteristics of the materials influence its stability, which is expected to provide important guidance for future catalyst design.

備考 ： 論文要旨は、和文 2000 字と英文 300 語を 1 部ずつ提出するか、もしくは英文 800 語を 1 部提出してください。

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