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論文審査の要旨（2000字程度）

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. 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.

Here, we propose our catalyst design concept for a desired Co catalyst: (a) The cations of the desired support material should consist of alkaline earth metal elements to utilize their well-known promotion effects. (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, which enhances N_2 activation to further boost ammonia synthesis over Co (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.

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