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DISSERTATION ABSTRACT

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学 位 論 文 題 名

Title of dissertation submitted for the degree

Hydrogen desorption properties of $\text{NH}_3\text{BH}_3\text{-MH}_n$ mixtures: How to control by-product gases

($\text{NH}_3\text{BH}_3\text{-MH}_n$ 複合物質の水素放出特性: 副生成ガス放出の抑制方法)

Hydrogen storage is a big challenge for a future hydrogen energy society. Currently, the compressed hydrogen gas tanks are utilized for fuel cell vehicles. For future applications, more compact and lightweight storage of hydrogen is demanded. Therefore, novel hydrogen storage materials should be explored.

Chapter 1 shows the introduction. Ammonia borane (NH_3BH_3 , AB) is a promising hydrogen storage material because of its high hydrogen capacities. Nevertheless, its poor recyclability, sluggish kinetics and by-product gas emissions (ammonia (NH_3), diborane (B_2H_6) and borazine ($\text{B}_3\text{H}_6\text{N}_3$)) are disadvantages for its applications. To overcome these disadvantages, ammonia borane - metal hydride (AB-MH_n) mixtures, such as AB-LiH and AB-MgH_2 , have been extensively studied. However, systematic investigation on these mixtures has not been explored. In this study, various kinds of AB-MH_n ($\text{M} = \text{K, Na, Li, Ca, Mg, Al}$) mixtures were synthesized. The objectives of the thesis are following three parts; (1) Exploring important factors to reduce H_2 desorption temperature and amounts of by-product gas emissions from the systematic investigation on H_2 desorption properties, (2) Synthesizing advanced AB-MH_n mixtures based on the factors and investigating their H_2 desorption properties, (3) Investigating H_2 desorption processes of the advanced mixtures. In the following chapters, those issues were targeted on the basis of a series of experiments.

In chapter 2, the crystalline phases and H_2 desorption properties of AB-MH_n ($\text{M} = \text{K, Na, Li, Ca, Mg, Al}$) mixtures were investigated. The results revealed that the Pauling electronegativity of metal, χ_p , is an important factor to predict the crystalline phases, H_2 desorption temperatures and amounts of by-product gas emissions. The correlation between H_2 desorption temperatures and χ_p was observed. Coulombic attraction between $\text{H}^{\delta-}$ of MH_n and $\text{H}^{\delta+}$ of AB would result in the temperature decrease. The amount of NH_3 has a tendency to be low when χ_p becomes high value. On the other hand, the amount of B_2H_6 has a tendency to be low when χ_p becomes low value. The key issues for NH_3 and B_2H_6 suppressions are NH_3 absorption properties of MH_n and the formation of stable $\text{M}(\text{BH}_4)_n$ phase,

respectively.

In chapter 3, AB- $MAIH_4$ ($M = Na, Li$) mixtures were synthesized based on the factor proposed in chapter 2. The mixtures were synthesized by hand-mixing and ball-milling methods. Hand-mixing was performed in an Ar purified glovebox. In case of hand-mixing, the violent exothermic H_2 desorption reaction occurred. By-product gases were not suppressed. Ball-milling under Ar atmosphere also showed a similar reaction as hand-mixing. On the other hand, ball-milling under H_2 atmosphere can generate a novel hydrogen storage material of $NaAl(NH_2BH_3)_4$ in AB- $NaAlH_4$ system. The synthesized $NaAl(NH_2BH_3)_4$ desorbed about 8.3 mass% H_2 with a small amount of by-product gas emissions. AB- $MAIH_4$ mixture with a molar ratio of 1 : 1 showed no by-product gas emissions. Thus, $MAIH_4$ is effective to decrease the by-product gas emissions from AB.

Chapter 4 shows general discussions and conclusions. The strategy for synthesizing advanced AB- MH_n mixtures was proposed. AB- AlH_3 mixture should be considered as base material because it showed the highest hydrogen amount among the investigated mixtures. By combining alkali metal hydride and $FeCl_2$ ($CuCl_2$) with the mixture, it would be possible to synthesize the material with high hydrogen amounts, low desorption temperature and no by-product gas emissions.