



# Cobalt-iron-phosphorus catalysts for efficient hydrogen generation from hydrolysis of ammonia borane solution

SeKwon Oh <sup>b,\*</sup>, DongHoon Song <sup>a</sup>, HyoWon Kim <sup>a</sup>, DongRak Sohn <sup>a</sup>, KyungSik Hong <sup>a</sup>, MinHyung Lee <sup>b</sup>, SeongHo Son <sup>b</sup>, EunAe Cho <sup>a,\*\*</sup>, HyukSang Kwon <sup>a,\*\*\*</sup>

<sup>a</sup> Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, Daejeon, 305-701, Republic of Korea

<sup>b</sup> Surface R&D Group, Korea Institute of Industrial Technology, Incheon, 21999, Republic of Korea

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## ABSTRACT

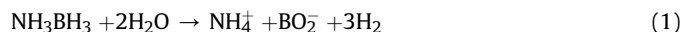
A highly active cobalt-iron-phosphorus catalyst was fabricated to generate hydrogen from the hydrolysis of  $\text{NH}_3\text{BH}_3$  by facile one-step electrodeposition method. The performance of the catalyst was optimized by electrodeposition condition via controlling microstructure and composition. As the applied cathodic current density was increased from 10 to 400  $\text{mA}/\text{cm}^2$ , the particle sizes of the Co–Fe–P catalysts increased from 1 to 15  $\mu\text{m}$ . With the increase in a deposition time, the particles of the Co–Fe–P catalyst became densely agglomerated. The Co–Fe–P catalyst deposited at 50  $\text{mA}/\text{cm}^2$  for 5 min, which had a particle size of 2  $\mu\text{m}$ , exhibited the best hydrogen generation rate of 2858  $\text{ml min}^{-1}\text{g}^{-1}\text{-catalyst}$  in 1 wt%  $\text{NH}_3\text{BH}_3$  solution at 30 °C. With an increase in the solution temperature from 10 to 60 °C, the hydrogen generation rate increased exponentially from 1543 to 8915  $\text{ml min}^{-1}\text{g}^{-1}\text{-catalyst}$  in the 1 wt%  $\text{NH}_3\text{BH}_3$  solution. The activation energy for the hydrolysis of  $\text{NH}_3\text{BH}_3$  by the Co–Fe–P catalyst was calculated and found to be approximately  $25 \pm 3$  kJ/mol, which is comparable to those of noble metal-based catalysts. Furthermore, with an increase in the concentration of  $\text{NH}_3\text{BH}_3$  from 0.5 wt% to 3 wt%, the hydrogen generation rate of the Co–Fe–P catalyst increased gradually from 1900  $\text{ml min}^{-1}\text{g}^{-1}\text{-catalyst}$  to 8105  $\text{ml min}^{-1}\text{g}^{-1}\text{-catalyst}$  at 30 °C.

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## 1. Introduction

Hydrogen energy has received great attention as a future energy source because it is clean and abundant and has high power density [1–4]. For utilization of hydrogen energy, developments of safe and convenient hydrogen storage systems are important. Recently, chemical hydrides such as  $\text{NH}_3\text{BH}_3$ ,  $\text{NaBH}_4$ ,  $\text{LiBH}_4$ ,  $\text{MgH}_2$ , Mg–Ca hydride, and  $\text{Zr}_3\text{Fe}$  hydride have drawn much attention as hydrogen storage materials because they can store hydrogen safely and generate hydrogen conveniently from hydrolysis using catalysts [5–22]. Ammonia borane ( $\text{NH}_3\text{BH}_3$ ) has the highest theoretical hydrogen storage capacity (19.6 wt%  $\text{H}_2$ ) and can produce hydrogen by pyrolysis or hydrolysis in neutral water. The hydrolysis of  $\text{NH}_3\text{BH}_3$  is expressed by Eq. (1) [23], generating

hydrogen (8.96 wt%  $\text{H}_2$ ) through the use of catalysts [24–40].



Since the rate of hydrolysis of  $\text{NH}_3\text{BH}_3$  is dependent on the catalyst performance, it is crucial for fast hydrogen generation to develop outstanding catalysts [41–43]. Precious-metal based catalysts such as Ru and Pt have been used to enhance the hydrolysis rate of  $\text{NH}_3\text{BH}_3$  [44–50]. However, these precious metals are too expensive for commercialization. In consideration of cost, research on Co and Ni based catalysts has been reported [51–60]. Among other catalysts, Co–B and Co–P exhibit fast hydrogen generation rate via hydrolysis of  $\text{NH}_3\text{BH}_3$ . Even though powder type Co–B catalysts have fast hydrogen generation [61,62], it is difficult to use catalysts repeatedly in the  $\text{NH}_3\text{BH}_3$  solution. In contrast, film or foam type Co–P catalysts can be reused many times and have good durability, as confirmed by previous results [51–55]. Recent reports have found that the addition of transition metals such as Fe, Ni, and Cr to Co-based catalysts can contribute to the catalyst activity [63–66]. Among the various transition metals, Fe has drawn

\* Corresponding author.

\*\* Corresponding author.

\*\*\* Corresponding author.

E-mail addresses: [sk0514@kitech.re.kr](mailto:sk0514@kitech.re.kr) (S. Oh), [eacho@kaist.ac.kr](mailto:eacho@kaist.ac.kr) (E. Cho), [hskwon@kaist.ac.kr](mailto:hskwon@kaist.ac.kr) (H. Kwon).