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

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ABSTRACT

A highly active cobalt-iron-phosphorus catalyst was fabricated to generate hydrogen from the hydrolysis of NH_3BH_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 mA/cm^2, the particle sizes of the Co–Fe–P catalysts increased from 1 to 15 μm. 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 mA/cm^2 for 5 min, which had a particle size of 2 μm, exhibited the best hydrogen generation rate of 2858 ml min^{-1}g^{-1}-*catalyst* in 1 *wt%* NH_3BH_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 ml *min*$^{-1}$*g*$^{-1}$-*catalyst* in the 1 *wt%* NH_3BH_3 solution. The activation energy for the hydrolysis of NH_3BH_3 by the Co–Fe–P catalyst was calculated and found to be approximately 25 ± 3 kJ/mol, which is comparable to those of noble metal-based catalysts. Furthermore, with an increase in the concentration of NH_3BH_3 from 0.5 *wt%* to 3 *wt%*, the hydrogen generation rate of the Co–Fe–P catalyst increased gradually from 1900 ml min^{-1}g^{-1}-*catalyst* to 8105 ml min^{-1}g^{-1}-*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 NH_3BH_3, $NaBH_4$, $LiBH_4$, MgH_2, Mg–Ca hydride, and Zr_3Fe hydride have drawn much attention as hydrogen storage materials because they can storage hydrogen safely and generate hydrogen conveniently from hydrolysis using catalysts [5–22]. Ammonia borane (NH_3BH_3) has the highest theoretical hydrogen storage capacity (19.6 *wt%* H_2) and can produce hydrogen by pyrolysis or hydrolysis in neutral water. The hydrolysis of NH_3BH_3 is expressed by Eq. (1) [23], generating hydrogen (8.96 *wt%* H_2) through the use of catalysts [24–40].

$$NH_3BH_3 + 2H_2O \rightarrow NH_4^+ + BO_2^- + 3H_2 \quad (1)$$

Since the rate of hydrolysis of NH_3BH_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 NH_3BH_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 NH_3BH_3. Even though powder type Co–B catalysts have fast hydrogen generation [61,62], it is difficult to use catalysts repeatedly in the NH_3BH_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

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