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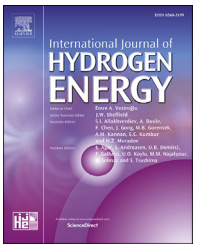

Highly stable and controllable CoB/Ni-foam catalysts for hydrogen generation from alkaline $NaBH_4$ solution

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ABSTRACT

In this work, a series of shaped CoB/Ni-foam catalysts were directly synthesized by using a convenient and simple electroless plating method. Despite the low loading amount of CoB, the catalysts showed high catalytic performance in the hydrolysis of $NaBH_4$ solution, and the maximum hydrogen generation rate reached 1930 mL min^{-1} (g CoB)$^{-1}$ in 1 wt % $NaBH_4$ + 5 wt % NaOH solution at 293 K. The catalysts demonstrated distinct stability, and the hydrogen generation rate was almost unchanged after 6 cycles. Furthermore, the catalysts could be easily recovered from the reaction system by a magnet. These characteristics make CoB/Ni-foam a high performance and cost effective catalyst for practical applications of hydrogen generation.

Introduction

In recent years, there have been increasing demands for new energy sources owing to the heavy dependence on fossil fuels and environmental problems [1,2]. Hydrogen is the most promising energy carrier to replace fossil fuels due to its cleanness, high caloric value and broad source. However, hydrogen storage and delivery is a major scientific and technological challenge for practical applications [3]. Storing hydrogen in steel cylinders suffers from a low mass capacity and a dangerous high-pressure process [4]. Newly developed methods such as adsorbing hydrogen in carbon materials [5–7] and storing in metal hydrides [8,9] suffer from high costs and unfavorable hydrogen releasing conditions. Compared to these approaches, storing hydrogen in borohydrides such as $NaBH_4$ is a promising method. The hydrogen capacity of $NaBH_4$ is as high as 10.8 wt %, and $NaBH_4$ is facile to transport

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due to its good stability. Hydrogen can be released by hydrolyzing $NaBH_4$ conveniently [10]:

$$NaBH_4(s)+2H_2O(l)\rightarrow NaBO_2(aq)+4H_2(g)\ \ \Delta H^{\Theta}=-216.7\,kJ\,mol^{-1}$$

NaOH is commonly used as a stabilizer to suppress the self-hydrolysis of $NaBH_4$. To obtain hydrogen from the stabilized $NaBH_4$ aqueous solution effectively, catalysts are required to accelerate the hydrolysis reaction [11]. Because of the strong basicity of the fuel solution, the quick hydrogen release and the strong exothermic nature of the reaction, the stability of the catalyst must be high. In addition, from the view of practical application, the cost effectiveness and the recovery of catalysts as well as the controlled released of hydrogen are important.

Many kinds of catalysts have been developed to catalyze the $NaBH_4$ hydrolysis reaction in basic solution. Although noble metal catalysts have shown high catalytic activities, their scarcity and high cost have severely limited their applications [12–14]. Many efforts have been made to search for alternative non-noble metal/oxide-based catalysts. Among the reported catalysts, Ni and Co-based metals, alloys and borides nanoparticles have received a great deal of attention because of their low costs and relatively high catalytic activities [15–21].

There are many disadvantages in directly using nanoparticles as catalysts for hydrolyzing $NaBH_4$. Nanoparticles aggregate severely during the reaction due to their high surface energy. Therefore, the catalytic activity of the nanoparticles diminishes gradually and the reusability is poor. Loading the nanoparticles onto a proper support (such as TiO_2 and Al_2O_3) can separate the nanoparticles and restrict their agglomeration. J. Zhao et al. dispersed CoB nanoparticles onto carbon black, giving a hydrogen generation rate of 2073 mL min^{-1} g_{cat}^{-1} in 0.75 wt % $NaBH_4$ + 8 wt % NaOH solution at 298 K [22]. Y. C. Lu et al. investigated the supporting effects for CoB catalysts for catalyzing borohydride hydrolysis reaction. The results revealed that the supported CoB catalysts had superior activity over the unsupported CoB nanoparticles [23]. Although the catalytic performance of supported CoB shows improvement to some extent, the weak interaction between the CoB nanoparticles and the support is still adverse to its stability [10].

Electroless plating method has been widely used for preparing supported catalysts. Z. J. Wu et al. synthesized TiO_2 supported nickel nanoparticles by using the electroless plating method and applied these to catalyze the hydrogenation of *p*-nitrophenol to *p*-aminophenol. The Ni/TiO_2 catalyst showed good activity, high selectivity and perfect stability [24]. M. Rakap et al. used the electroless plating method to prepare a Co–Ni–P/Pd–TiO_2 catalyst and obtained a maximum hydrogen generation rate of 460 mL min^{-1} g_{cat}^{-1} in 1.13 wt % $NaBH_4$ + 10 wt % NaOH solution at 298 K [25]. X. W. Zhang deposited CoP catalyst on copper sheet by using the electroless plating method and the catalyst showed a hydrogen generation rate of 1846 mL min^{-1} g_{cat}^{-1} in 5 wt % $NaBH_4$ + 1 wt % NaOH solution at 298 K [26]. Since the composition and structure of the plating layer can be easily controlled by adjusting the plating conditions such as concentration, temperature, and pH, the catalytic properties of the catalysts can be tuned conveniently [27–29]. Furthermore, the plating layer has a strong interaction with the substrate, which endows the catalyst with good stability, and the agglomeration of active species is suppressed effectively [30].

Ni-foam is a commonly used substrate for fabricating catalysts [31,32]. In particular, it is a suitable substrate for the hydrolysis of $NaBH_4$ due to its following merits: Ni-foam has a porous structure, which is conducive to the diffusion of the reactants and products. The high heat transfer coefficient contributes to the transfer of the reaction heat. Furthermore, the magnetic properties of Ni-foam guarantee the recovery of the catalyst and the controlled release of hydrogen.

In this work, a series of CoB/Ni-foam catalysts were directly synthesized and shaped by using a simple and convenient electroless plating method. Their catalytic properties in hydrolyzing $NaBH_4$ solution were evaluated. The catalysts showed good catalytic activity and distinct stabilities. The catalysts were cost-effective and could be easily recovered. Furthermore, the catalysts were controllable for releasing hydrogen according to the requirement. The reasons for the high performance of the CoB/Ni-foam catalysts were also elucidated.

Experimental

Sensitization of Ni-foam substrate

Ni-foam substrates were cut into flakes (2 cm × 2 cm) and rinsed with absolute ethanol under ultrasonication for 15 min. Then, the flakes were immersed into HCl aqueous solution (1 mol L^{-1}) under ultrasonication for an additional 15 min to remove the surface oxide. The flakes were rinsed with deionized water several times. A 0.4 wt % $AgNO_3$ solution was used as the sensitizing solution. The Ni-foam flakes were soaked into the sensitizing solution and the solution was kept in the dark at 298 K for 24 h. Then, the sensitized Ni-foam flakes were washed thoroughly with deionized water several times and dried in vacuum at 323 K for 12 h. Finally, each dried Ni-foam flake was marked and weighed carefully.

Electroless plating of CoB on Ni-foam substrate

CoB was supported on the sensitized Ni-foam substrate by the electroless plating method. The typical procedure was as follows: Each Ni-foam flake was immersed into 5.33 mL of plating solution (3.78 mmol L^{-1} $Co(Ac)_2{\cdot}4H_2O$, 21.7 mmol L^{-1} $C_4H_6O_6$, 0.52 mmol L^{-1} $Na_2B_4O_7{\cdot}10H_2O$ and 37.4 mmol L^{-1} NH_4Cl. The pH of the solution was adjusted to 12–13 by adding 1.0 mol L^{-1} NaOH solution), and 4.67 mL of 0.237 mol L^{-1} $NaBH_4$ reduction solution (mixed with 1.0 mol L^{-1} NaOH as the stabilizer) was added slowly. The temperature of the plating solution was elevated to 318 K. The reaction was proceeded until no bubbles emerged from the solution. The Ni-foam flake became black, which indicated that CoB had been successfully deposited onto it. Then, the CoB/Ni-foam flake was rinsed with deionized water 3 times under ultrasonication to get rid of the loosely attached CoB particles. The electroless plating was repeated several times, and the obtained CoB/Ni-foam catalysts were denoted as 1EP, 3EP, 5EP, 7EP, 9EP and 11EP (the

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