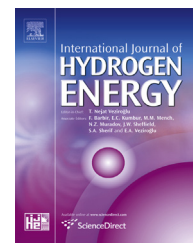




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Cobalt–boron/nickel–boron nanocomposite with improved catalytic performance for the hydrolysis of ammonia borane

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ARTICLE INFO

Article history:

Received 25 May 2015

Received in revised form

4 August 2015

Accepted 9 August 2015

Available online 2 September 2015

Keywords:

Hydrogen generation

Ammonia borane

Ni–B/Co–B

Hydrolysis

Nanocomposite catalyst

ABSTRACT

A cobalt–boron/nickel–boron (Co–B/Ni–B) nanocomposite was synthesized in a two-step process by in situ reduction of nickel and cobalt salts. Characterization of the nanocomposite using X-ray diffraction, scanning electron microscopy, and Brunauer–Emmett–Teller adsorption analysis showed that the Co–B nanoparticles were well dispersed on the Ni–B surface. Enlisted as a catalyst in the hydrolysis of ammonia borane (AB) for hydrogen generation (HG), the nanocomposite exhibited better catalytic activity than Co–B and Ni–B at room temperature; the HG rate was 1368.2 mL min^{−1} g^{−1} at 25 °C in a 1.5 wt.% AB solution, with a low activation energy of 33.5 kJ mol^{−1}. The effect of the complexing agent (sodium citrate) on the nanocomposite's catalytic activity was also investigated. In addition, recycling tests showed that Co–B/Ni–B was still highly active and preserved 84% of its initial catalytic activity after 11 recover-and-reuse cycles.

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Introduction

In recent years, clean energy has received much attention as greenhouse gas emissions have been proved to contribute to climate change. The urgent need to stem global warming has driven the increased demand for exploration of new energy sources and technology. Hydrogen appears to be one of the

most promising and cleanest energy sources because of its high combustion efficiency and zero emission [1–3]. However, efficient and safe production of hydrogen remains a critical challenge that has hindered practical implementation. Boron hydrides have the most potential to solve these issues and help realize a hydrogen economy in the near future [4–6]. Among these hydrides, ammonia borane (AB, H₃NBH₃ or

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<http://dx.doi.org/10.1016/j.ijhydene.2015.08.017>

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BNH_6 , also called boron–nitrogen hydride) with high gravimetric density (19.6 wt.%) has been regarded as an attractive candidate for production of pure hydrogen by room-temperature hydrolysis. However, a favorable catalyst is required to accelerate this hydrolysis reaction in a controllable manner for practical applications [4,7]. Among the available catalysts, noble metals such as Pt and Pt-based alloys show unsurpassable catalytic activity, but their high cost and low abundance limit practical applications. Therefore, it is of great interest to develop alternative high-performance and low-cost catalysts [8–11].

Nanoscale catalysts based on transition metals, such as Co or Ni, are generally used to accelerate the hydrolysis reaction of AB because of their exceptional catalytic activity and low cost, and especially because of their large surface area, tunable size- and shape-dependent properties, and high concentration of undercoordinated active surface sites and magnetic property. The HG rate can be simply controlled under an externally applied magnetic field [12]. Moreover, rather than using a single transition metal alone as a catalyst, it is better to form an alloy with another element to create a synergistic effect to enhance the catalytic activity. Among the transition-metal-based binary alloys, metal borides show excellent catalytic activity mainly owing to their unique properties with high concentration of unsaturated sites and amorphous structure with short-range order and long-range disorder [4]. However, the stability, surface oxidation, and agglomeration of these catalyst particles limit their application in hydrogen-generation reactors [8].

Much effort has been made to develop techniques to enhance the catalytic activity and stability of catalyst materials, such as varying the preparation parameters [13], using organic templates [14], doping with transition metals [15–17], or supporting the catalyst on high-surface-area materials [18–20]. For instance, Sahiner and co-workers enlisted hydrogels as templates to prepare nanocatalysts for the hydrolysis of AB and NaBH_4 [21–23]. However, the activity of the catalysts needs to be improved because the catalysts are embedded in the gels. Although significant progress has been made, the proper form of a catalyst must still be selected in order to implement hydrogen production on an industrial scale. The preparation process is highly influenced by the catalytic activity [24,25], which can vary widely even among catalysts with the same composition. In this study, a novel amorphous Co–B/Ni–B nanocomposite was prepared by in situ reduction in a two-step process. The resultant catalyst exhibited superior catalytic performance toward the hydrolysis of AB.

Experimental

Materials

Ammonia borane (AB, 97%), sodium borohydride (NaBH_4 , $\geq 99\%$), cobalt sulfate heptahydrate ($\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, $\geq 99\%$), sodium citrate (SC, $\geq 99\%$), and nickel sulfate hexahydrate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\geq 99\%$) were purchased from Aldrich Chemical Co., USA. All chemicals were used without further purification. All experiments were performed using deionized water.

Synthesis of the Co–B/Ni–B catalyst

The Co–B/Ni–B nanocomposite was prepared as follows. Typically, 0.5 g of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and 0.15 g (6 mmol) of SC were dissolved in 80 mL of deionized water to form a clear solution. The solution was sonicated in a water bath while 20 mL of a 10 wt.% NaBH_4 solution was added dropwise. A strong dark color was observed immediately after the addition of NaBH_4 . The suspension was sonicated for another 30 min, after which 1.5 g of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ was dissolved in 20 mL of deionized water and mixed with the suspension. Another 20 mL of a 10 wt.% NaBH_4 solution was added dropwise. A schematic diagram of the process is shown in Fig. 1. The suspension was kept sonicating for 30 min. Finally, the solid was removed by filtration and washed thoroughly with water and ethanol. The sample was then left to dry in a vacuum oven at 60 °C for 24 h. For comparison, the catalysts Ni–B, Co–B, and Co–Ni–B were synthesized by chemical reduction under similar conditions.

Characterization of the catalyst

Scanning electron microscopy (SEM) and energy-dispersive X-ray (EDX) analysis (S-4800, Hitachi, Japan) were used to characterize the morphology of the Co–B/Ni–B nanocomposite at an accelerating voltage of 10 kV. Powder X-ray diffraction (XRD) measurements were performed using a diffractometer (1820, Philips, The Netherlands) with Cu K_α radiation ($\lambda = 1.5418 \text{ \AA}$). X-ray photoelectron spectroscopy (XPS) were obtained using a SCIENTA ESCA250 instrument equipped with a monochromatic $\text{Al K}\alpha$ (1486.6 eV) X-ray source and a hemispherical analyzer. The specific surface areas of the catalysts were measured by N_2 adsorption at $-196 \text{ }^\circ\text{C}$ using the Brunauer–Emmett–Teller (BET) method (Autosorb iQ2, Quantachrome Instruments, USA). The samples were degassed at 150 °C until the vacuum pressure was below 10^{-4} Pa . An average value was obtained by taking three measurements for

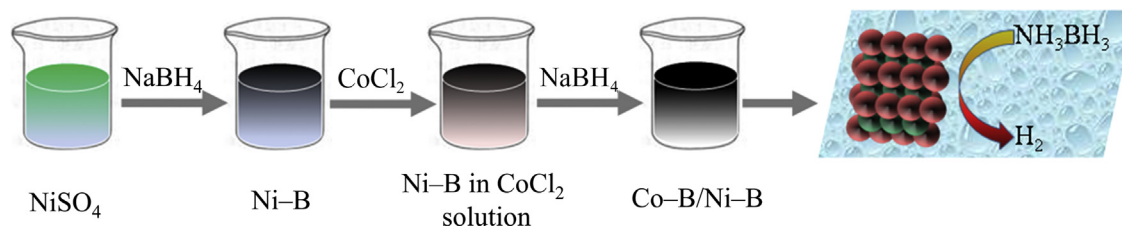


Fig. 1 – Schematic diagram of the preparation of the Co–B/Ni–B nanocomposite.

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