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Hydrogen generation by hydrolysis of alkaline sodium borohydride using a cobalt-zinc-boron/ graphene nanocomposite treated with sodium hydroxide



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ABSTRACT

A Co–Zn–B/graphene nanocomposite was prepared by in situ reduction of cobalt and zinc salts on the surface of graphene (GP), and its catalytic performance in hydrogen generation (HG) by hydrolysis of NaBH₄ was investigated. This composite exhibited excellent catalytic properties and great promise for real-world applications in HG and hydrogen storage. Characterization using X-ray diffraction, scanning electron microscopy, and Brunauer –Emmett–Teller (BET) adsorption analysis showed Co–Zn–B nanoparticles attached to the GP surface. The catalytic activity was further improved by treating the nanocomposite with NaOH to remove zinc from the composite matrix and increase the active surface area. The BET measurements showed the specific area of the treated material increasing from 86.4 to 120.2 m²/g. The effects of temperature, NaBH₄ concentration, and NaOH concentration on HG were investigated. The measured HG rate was 2180 mL/(min·g) at 30 °C in a 5 wt.% NaOH + 3 wt.% NaBH₄ solution, much higher than rates obtained for unsupported Co–Zn –B catalysts. The stability of the fabricated composite catalyst was also explored.

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Introduction

Hydrogen has emerged as a promising energy source in recent years because of its high efficiency and near-zero greenhousegas emissions from its production. Extensive efforts have been made over the last 20 years to find a viable hydrogen-storage system for use at practical operating temperatures. Recently, chemical hydrides have gained much interest as irreversible

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sources for on-demand hydrogen storage [1-3]. Among the chemical hydrides, sodium borohydride (NaBH₄) is considered the most promising hydrogen source because of its high hydrogen capacity (10.8 wt.%), inflammability, stability in alkaline solutions, easily controllable hydrogen generation (HG) rate, moderate operation temperature, and nontoxic hydrolysis byproducts [4,5].

The generation of hydrogen from the reaction of NaBH₄ with water follows the hydrolysis reaction (1), in which half of the produced hydrogen originates from water and heat is generated ($\Delta H = -300$ kJ/mol):

$$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2 \uparrow + heat$$
 (1)

This hydrolysis reaction only occurs when an alkaline NaBH₄ solution is in contact with certain catalysts such as Ru, Pt, Pd, Ni, Co, Ni–B, Co–B, Co–P–B, and Co–W–B, all of which have been investigated and reported in the literature [6–14]. The prevalent limitation of these catalysts is their deterioration, which occurs owing to processes such as agglomeration of catalyst particles, surface oxidation of catalysts, and dissolution of the catalyst component in the alkaline NaBH₄ solution [15]. The search for catalysts with superior activity and durability remains the current focus of research in this field.

Amorphous Co–B has been widely investigated as a catalyst for the hydrolysis of NaBH₄ because of its high catalytic performance. Furthermore, a Co–B-based catalyst can be effortlessly synthesized by simple chemical processes in which the transition metal ions in cobalt salts are reduced to the elemental state by most common reducing agents [16]. However, its shortcomings, such as potential agglomeration (owing to the exothermicity of the reaction) and difficulty in separating fine powders from the fuel solution, may restrict its practical application in HG reactors. It is anticipated that particle agglomeration in the Co–B composite, which lowers the effective surface area of the catalyst powder and thus limits its catalytic activity, can be alleviated by depositing Co–B on a supporting material with a high specific surface area [17].

Supporting materials such as carbon nanotubes and metal oxides not only buttress the active metals, but also provide large active surface areas and improve dispersion of the active phases. Furthermore, the catalyst support allows diffusion of reactants through its pores to the active phase, therefore improving dissipation of the reaction heat, retarding sintering of the active phase, and increasing its resistance against catalyst poisoning [3,18-20]. Two-dimensional (2D) graphene has been extensively studied in recent years because of its superior chemical stability, large surface-tovolume ratio, and high conductivity. It has also been widely investigated as a nanocarrier for catalyst loading. After being oxidized in an acid solution, graphene sheets become strongly hydrophilic, which is favorable for modification in solution [21]. However, the hydrolysis of borohydride using graphene as a nanocarrier has yet to be thoroughly investigated or understood.

It has been demonstrated that the effective surface area of transition metals (such as Ni) can also be increased by alloying the metal with an active metal like Al or Zn, followed by dissolution of the secondary component with a concentrated alkali solution [22]. In this study, in order to improve the catalytic activity of the Co–B catalyst for hydrolysis of NaBH₄ in an alkali solution, a Zn-incorporated Co–B catalyst supported on GP was first prepared via chemical reduction. The graphene support was enlisted to yield highly dispersed catalyst particles for better utilization of the active sites. The possible enhancement of the catalytic activity of the Co–Zn–B/GP nanocomposite by activating them with a NaOH solution was also investigated.

Experimental

Materials

Sodium borohydride (NaBH₄), cobalt sulfate heptahydrate (CoSO₄·7H₂O), and zinc sulfate heptahydrate (ZnSO₄·7H₂O) were purchased from Aldrich Chemical Co., USA. Graphene was obtained from Chengdu Organic Chemical Industries Ltd., China. All chemicals were purchased and used without further purification. All experiments were performed using deionized water.

Synthesis of Co-Zn-B/GP and Co-B/GP catalysts

The Co-Zn-B/GP nanocomposite catalyst was prepared through in situ reduction of CoSO₄·7H₂O and ZnSO₄·7H₂O by NaBH₄, and the Co–Zn–B particles were attached to the surface of GP. In a typical procedure, 5 g of $CoSO_4 \cdot 7H_2O$ and 1 g of $ZnSO_4 \cdot 7H_2O$ were first dissolved in 100 mL of deionized water, followed by the addition of 0.1 g of GP, and the mixture was sonicated for 1 h. The suspension was stirred vigorously in a 0 °C ice bath while 20 mL of a 10 wt.% NaBH₄ solution was added dropwise. A strong dark color was observed immediately after the addition of NaBH₄. The suspension was stirred for another 30 min before 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 $^\circ\text{C}$ for 24 h. The nanocomposite catalysts Co-B and Co-Zn-B were synthesized under similar conditions to ensure consistent comparison metrics.

For the treatment of the Co–Zn–B/GP nanocomposite, the sample was re-suspended in 10 mL of a 30 wt.% NaOH solution using sonication. After 30 min, the particles were filtered out and thoroughly washed with deionized water. Finally, the sample was dried in air and ground into powder.

Characterization of the catalyst

Scanning electron microscopy (SEM) and energy-dispersive Xray analysis (S4800, Hitachi, Japan) were used to characterize the morphology of the Co–Zn–B/GP nanocomposite. The applied accelerating voltage was 10 kV. The crystalline phases were characterized by X-ray diffraction (XRD) on a diffractometer (1820, Philips, The Netherlands) with Cu K_α radiation ($\lambda = 1.5418$ Å). The specific surface areas (SSAs) of the catalyst samples were measured by N₂ adsorption at –196 °C using the Brunauer–Emmett–Teller (BET) method and an adsorption Download English Version:

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