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# Novel Ni–Co–B hollow nanospheres promote hydrogen generation from the hydrolysis of sodium borohydride

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## ABSTRACT

Ni–Co–B hollow nanospheres were synthesized by the galvanic replacement reaction using a Co–B amorphous alloy and a NiCl<sub>2</sub> solution as the template and additional reagent, respectively. The Ni–Co–B hollow nanospheres that were synthesized in 60 min (Ni–Co–B-60) showed the best catalytic activity at 303 K, with a hydrogen production rate of 6400 mL<sub>hydrogen</sub>min<sup>-1</sup>g<sub>catalyst</sub><sup>-1</sup> and activation energy of 33.1 kJ/mol for the NaBH<sub>4</sub> hydrolysis reaction. The high catalytic activity was attributed to the high surface area of the hollow structure and the electronic effect. The transfer of an electron from B to Co resulted in higher electron density at Co sites. It was also found that Ni was dispersed on the Co–B alloy surface as result of the galvanic replacement reaction. This, in turn, facilitated an efficient hydrolysis reaction to enhance the hydrogen production rate. The parameters that influenced the hydrolysis of NaBH<sub>4</sub> over Ni–Co–B hollow nanospheres (e.g., NaOH concentration, reaction temperature, and catalyst loading) were investigated. The reusability test results show that the catalyst is active, even after the fifth run. Thus, the Ni–Co–B hollow nanospheres are a practical material for the generation of hydrogen from chemical hydrides.

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## Introduction

Hydrogen is universally regarded as a clean energy source. It requires only oxygen for combustion, and water is the only product [1,2]. When hydrogen fuel is used in engines, it can reduce the amount of greenhouse gases, smog, and acid rain. In practical applications, however, the storage and transportation of hydrogen fuel remain major issues. Since the early 2000s, various strategies for hydrogen storage and transport have been investigated. One strategy is the

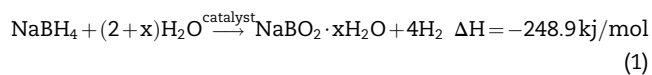
exploration of chemical hydrogen-storage materials, such as NaBH<sub>4</sub>, KBH<sub>4</sub> and NH<sub>3</sub>BH<sub>3</sub> [3–6]. These materials have large storage capacities for hydrogen and release pure hydrogen gas via hydrolysis reactions in the presence of catalysts at room temperature. Among various chemical hydrides, NaBH<sub>4</sub> is considered the most promising hydrogen storage material because it produces clean H<sub>2</sub> gas, at a very high rate at room temperature, and nontoxic hydrolysis byproducts. It produces 4 mol of H<sub>2</sub> in the presence of a catalyst, as shown in equation (1) [7–9], and half of the produced hydrogen originates from water.

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Numerous studies have focused on the development of an appropriate catalyst. Noble metal-based catalysts, using Ru and Pt, have been reported to promote high catalytic activity for the hydrolysis of  $\text{NaBH}_4$  [10–13]. However, they have many limitations in real applications due to their high cost and short lifetime.

Among the various non-noble metal catalysts, Co-based catalysts are the most attractive due to their good catalytic activities and low cost [14–22]. Chemical reduction methods are widely used for the synthesis of Co-based alloys. However, the exothermicity during the reduction of metal ions leads to the agglomeration of particles, which decreases the effective surface area and number of active sites on the material. Hence, supports, such as copper, clay, or graphene, are used to increase the surface area, improve nanoparticle dispersion on the surface, thus preventing agglomeration. Wei et al. demonstrated the formation of a furrow-like Co–Ni–B catalyst on a Cu sheet [23]. Saha et al. used a graphene-supported Co–Ni catalyst [24], and Tian et al. designed an attapulgite clay-supported Co–B catalyst for hydrogen generation [25]. However, metal leaching from the surface of the support cannot be avoided, and metal leaching is not suitable for large-scale production.

Another way to increase the catalytic activities is by including other metals, such as Ni, W or Zn [21,22,26,27]. Among them, Co- and Ni-based catalysts are inexpensive materials with high catalytic activity. Fernandes et al. and Wu et al. indicated that the presence of mixed Co–Ni catalysts with B atoms resulted in an enhanced catalytic effect with respect to Co–B powders [21,22]. Rahul et al. reported Ni as a co-catalyst in Ni–Co–B alloys [28]. However, Ni–Co–B alloys are still synthesized by a traditional chemical reduction of Ni and Co metal ions [21,29]. One strategy to improve the catalytic activity of these catalysts is to reduce the catalyst particle size, thereby increasing the surface area and number of active sites. However, smaller nanoparticles are more susceptible to agglomeration. Thus, the specific surface area is generally less than  $100 \text{ m}^2 \text{ g}_{\text{cat}}^{-1}$ . Another strategy is based on the synergetic effect. The optimal molar ratio of Ni:Co is beneficial to the hydrolysis reaction. The catalysts synthesized by chemical reduction method are limited inhomogeneous mixing Co and Ni not reaching atomic cluster level. Thus, the distribution and dispersion of Ni and Co in a Ni–Co–B alloy cannot be adjusted. Few studies have investigated the mechanism of the Ni–Co–B alloy synergetic effect in the hydrolysis of  $\text{NaBH}_4$ , but this mechanism needs further clarification.

Hollow structures could increase the surface area of catalysts. Versatile and simple hollow nanostructures can be prepared by the galvanic replacement reaction [30,31]. Currently, this technique has been used to prepare binary noble-metal catalysts [32,33] or catalysts that include combinations of transition and noble metals [34,35]. In this paper, hollow Co–Ni–B nanosphere catalysts for  $\text{NaBH}_4$  hydrolysis were first synthesized by the galvanic replacement reaction using a Co–B amorphous alloy and a  $\text{NiCl}_2$  solution as the

template and additional reagent, respectively. The method effectively increased the surface area of the catalysts, and it produced well-dispersed Ni atomic clusters, with optimal content, on the surface of the catalyst. The morphology, BET surface area, electronic interaction and catalytic performance of the products were investigated. The catalytic activity was correlated with the duration of replacement reactions. When the replacement time was 60 min, the as-prepared hollow nanosphere Co–Ni–B catalyst presented a higher surface area and superior catalytic activity towards hydrogen generation than other samples, which shows great potential for its use in  $\text{NaBH}_4$  hydrolysis. Additionally, the mechanism of the hydrolysis of  $\text{NaBH}_4$ , based on the synergetic effect of Ni–Co–B alloys, was proposed.

## Experimental

### Catalyst preparation

The Co–B sample was prepared by reducing 0.5 mol/L cobalt chloride [ $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ] (Aladdin Reagent Co., Shanghai, China) and 0.5 mol/L tartaric acid (Aladdin Reagent Co., Shanghai, China) mixed solution (10 mL each) with potassium borohydride ( $\text{KBH}_4$ ) (Chuandong Chemical Co., Ltd., Chongqing, China). The metal to  $\text{KBH}_4$  molar ratio was 1:4 to ensure the complete reduction of Co ions. The temperature of the flask was maintained at 273 K during the reaction to prevent a vigorous reaction. After completion of the reaction, the product was filtered and washed several times with deionized water and ethanol. For the synthesis of Ni–Co–B hollow nanospheres, the Co–B amorphous alloy was prepared using a similar synthesis procedure to the Co–B sample. The Co–B amorphous alloy was mixed with 10 mL of 0.5 mol/L nickel chloride [ $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ] (Aladdin Reagent Co., Shanghai, China) solution and sonicated for 30, 60 and 90 min; the samples were marked as Ni–Co–B-30, Ni–Co–B-60 and Ni–Co–B-90, respectively. Finally, the as-obtained Ni–Co–B samples were washed with deionized water and ethanol, dried in a vacuum oven, and weighed.

### Catalyst characterization

The morphology of Co–B and Ni–Co–B catalysts was characterized by transmission electron microscopy (TEM, JEOL, JEM-2100). The quantitative chemical composition of catalysts was measured by energy-dispersive X-ray spectroscopy (EDX, Genesis Spectrum, 200 kV). The structure of the catalysts was analyzed by X-ray diffraction (XRD, Rigaku, D/max 2500PC) with Cu  $K\alpha$  radiation ( $\gamma = 1.5418 \text{ \AA}$ ) in the  $2\theta$  range of 20–80. X-ray photoelectron spectroscopy (XPS, Perkin, PHI-1600 ESCA) measurements were recorded with a spectrophotometer using an Mg X-ray ( $h\nu = 1253.6 \text{ eV}$ ) source for excitation. The binding energy (BE) values were calibrated using C 1s = 284.6 eV as a reference. Hydrogen temperature-programmed desorption ( $\text{H}_2$ -TPD) measurements were performed on a TP-5076 instrument (Tianjin Xianquan Instrument Co. Ltd., China). The BET surface area was measured using a surface area analyzer (Quantachrome Instruments, Autosord-IQ).

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