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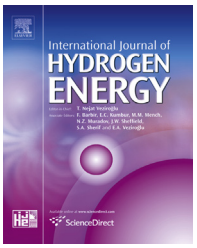

Fast hydrogen generation from $NaBH_4$ hydrolysis catalyzed by nanostructured Co–Ni–B catalysts

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ABSTRACT

Nanostructured Co–Ni–B catalysts were prepared on the Cu sheet by electroless plating for catalytic hydrogen evolution from alkaline $NaBH_4$ solution. Depositional pH values were adjusted to enhance catalytic activity. The result revealed that the increase of pH value from 9.5 to 10.0 leaded to obvious improvement in catalytic activity because of the formation of a furrow-like Co–Ni–B catalyst. The novel architecture provided high surface roughness and lots of active sites on the catalyst surface. The fastest hydrogen evolution rate for $NaBH_4$ hydrolysis was 14778.1 mL min^{-1} g_{cat}^{-1} and the activation energy was calculated to be 42.8 kJ mol^{-1}. More importantly, the hydrogen generation rate maintained about 87.9% of its initial value after 5 cycles. It can be concluded that the catalytic performance and stability of the furrow-like Co–Ni–B catalyst was favorably comparable to those of recently reported catalysts.

Introduction

Because of the growing energy crisis and environmental pollution, hydrogen is considered to be a much promising energy carrier due to its high calorific value and environmental benignity. However, the practical application in large scale of hydrogen is severely limited by the lack of the convenient, highly efficient hydrogen generation approaches. Nowadays, as an important member of hydrogen storage materials, sodium borohydride ($NaBH_4$) has attracted extensive research interest due to high theoretical hydrogen capacity (10.8 wt. %), low price and high stability in alkaline solution [1–3]. The production of hydrogen by means of hydrolysis of $NaBH_4$ has proven to be a potential

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approach at room temperature. Although ruthenium, platinum and other noble metals or their alloys have shown excellent catalytic activity to accelerate the hydrogen generation rate for $NaBH_4$ hydrolysis process, high cost and low abundance have hindered their wide applications. Therefore, it is urgent to exploit a highly efficient and inexpensive catalyst material.

Recently, non noble metal catalysts have been extensively concerned and gradually developed towards the hydrolysis of $NaBH_4$, including Fe [4], Co [5–8], Ni [9], Cu [9], Fe–B [10], Co–B [11,12], Ni–B [13], Cu–B [11], Co–P [14], Ni–P [15], Co–Ni–B [16,17], Co–Ni–P–B [18], Co–Ni–P [19] and so on. Traditionally, impregnation-chemical reduction method is a common preparation method for non noble metal catalysts in powder form. However, powder catalysts are easy to aggregate and difficult to be recovered from the reaction system, which limits the reuse in multi-cycle applications. Hence, from a practical point of view, it is necessary to prepare above-mentioned catalysts in a thin film form.

Electroless plating has been widely used as a convenient method to prepare supported metal based thin films. This technique can easily deposit nanostructured films on various substrates with good bonding strength, high average roughness and small particle size distribution. For the past few years, Co–P [20], Ni–P [15], Ni–B [21], Co–B [22], Co–P [23] and Co–Ni–P [24] thin films have been successfully prepared on the Cu sheet, Cu foam or Ni foam by this method. By optimizing the deposition conditions (such as temperature, time, concentration and pH value), the microstructure of the films can be changed and the catalytic activity for $NaBH_4$ hydrolysis can be improved. Among them, Co–and Ni–based catalysts have demonstrated to be the inexpensive materials with high catalytic activity. Especially, the catalytic activity can be remarkable improved by introducing boron to transition metals (Co and Ni). Moreover, the active sites of metal Co and Ni in metal borides (Ni–B and Co–B) can be protected against oxidation. Li et al. [17] have reported that the mixed boride (Co–Ni–B) shows excellent activity for the hydrogenation of CH_3CN. Recently, Ingersoll et al. [25] indicate that Co–Ni–B catalyst can be also used for the hydrolysis of $NaBH_4$. Fernandes et al. [26] have revealed that Co–Ni–B catalyst can exhibit much superior catalytic activity as compared with Co–B powder for the hydrolysis of $NaBH_4$. They have pointed out that the synergetic effect of the Co and Ni atoms is beneficial to lower the activation energy of the hydrolysis reaction. But the preparation of Co–Ni–B catalyst has not been reported by electroless plating in the form of supported thin films for $NaBH_4$ hydrolysis before, except for chemical reduction method.

In this paper, Cu sheet supported nanostructured Co–Ni–B catalysts in the form of thin film were prepared by electroless plating for $NaBH_4$ hydrolysis. The catalytic activity was proved to be correlated to depositional pH values. When pH value was 10.0, the as-prepared Co–Ni–B catalyst with a furrow-like nanostructure presented the fastest hydrogen evolution rate of 14778.1 mL min^{-1} g_{cat}^{-1} and low activation energy of 42.8 kJ mol^{-1} for the hydrolysis reaction of $NaBH_4$. Stability was also investigated and about 87.9% of its initial activity was maintained after 5 cycles.

Experimental

Catalyst preparation

In order to study the influence of the depositional pH values on the microstructure and catalytic activity, nanostructured Co–Ni–B catalysts were prepared at different pH values. Cu sheet (0.5 mm thick, 99.95%), Cobalt chloride hexahydrate ($CoCl_2 \cdot 6H_2O$, AR), glycine (NH_2CH_2COOH, AR), nickel chloride hexahydrate ($NiCl_2 \cdot 6H_2O$, AR), sodium hydroxide (NaOH, AR) and ethanol absolute (CH_3CH_2OH, AR) were purchased from Sinopharm Chemical Reagent Co., Ltd. and. Sodium borohydride ($NaBH_4$, 95%) were purchased from Sigma Aldrich. All of the reagents are not further purified. The detailed plating parameters of reagents and conditions have been listed in Table 1. Before deposition, commercial Cu sheet chosen as the substrate was cut into 4 × 4 cm^2 pieces and then pretreated, including acid pickling, alkaline cleaning, sensitizing and activating process. Subsequently, the pretreated Cu sheet was dried, weighted and then transferred to the electroless plating bath for 3 min to deposit Co–Ni–B catalyst. Finally, the as-deposited Co–Ni–B/Cu sheet sample was removed from the plating bath, washed, dried and weighted. The weight of the Co–Ni–B catalyst was determined according to the following equation:

$$m_{Co-Ni-B\ catalyst} = m_{Co-Ni-B/Cu\ sheet} - m_{Cu\ sheet} \quad (1)$$

where $m_{Co-Ni-B\ catalyst}$, $m_{Co-Ni-B\ catalyst}$ and $m_{Cu\ sheet}$ represent the weight of Co–Ni–B catalyst, Co–Ni–B/Cu sheet sample and bare Cu sheet before depositing, respectively.

Catalyst characterization

Powder X–ray diffraction (XRD) patterns of the as-prepared Co–Ni–B catalysts were obtained with a Rigaku–Dmax 2500 X–ray diffractometer using Cu Kα radiation (λ = 1.54178 Å). The surface morphologies were characterized by the Scanning electron microscopy (SEM) on Hitachi S–4800. Surface topographies in three dimensions were studied by atomic force microscopy (AFM) using Bruker Dimension Icon.

Hydrogen generation testing

The hydrogen generation catalyzed by the Co–Ni–B catalyst in an alkaline solution (5 wt% $NaBH_4$ + 1 wt% NaOH)

Table 1 – Detailed plating parameters of reagents and conditions for preparing the Co–Ni–B catalysts.

Reagents and conditions	Plating parameters
$CoCl_2 \cdot 6H_2O$	0.1 mol L^{-1}
$NiCl_2 \cdot 6H_2O$	0.1 mol L^{-1}
NH_2CH_2COOH	0.6 mol L^{-1}
$NaBH_4$	0.08 mol L^{-1}
Deposition temperature	25 °C
Deposition pH	9.5, 10.0, 10.5 and 11.0
Deposition time	3 min

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