

Amorphous cobalt–boron/nickel foam as an effective catalyst for hydrogen generation from alkaline sodium borohydride solution

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Abstract

Low cost and catalytically effective transition metal catalysts are of interest for the development of on-board hydrogen generation systems for fuel-cell vehicles. In the present study a modified electroless plating method was developed for the preparation of amorphous Co–B catalyst supported on Ni foam. Compared to the conventional electroless plating method, the newly developed method is more effective and produces Co–B catalyst with much higher catalytic activity. The catalytic activity of the supported Co–B catalyst was found to be highly dependent on the plating times and calcination conditions. Through optimization of these preparation conditions we were able to prepare a catalyst capable of a hydrogen generation rate of $11 \text{ l (min g)}^{-1}$ (catalyst) in a 20 wt.% NaBH_4 + 10 wt.% NaOH solution. Preliminary phase analyses and microstructure characterization were performed to understand the effects of preparation conditions on the catalytic activity of the Co–B catalyst. © 2007 Elsevier B.V. All rights reserved.

Keywords: Hydrogen generation; Electroless plating; Co–B catalyst; NaBH_4 ; Ni foam

1. Introduction

Onboard hydrogen storage has been generally recognized as a key technical challenge in commercialization of hydrogen-powered vehicles [1]. Extensive research efforts over the last 20 years is yet to find a viable hydrogen storage system that can reversibly store more than 6 wt.% hydrogen at practical operating temperatures. Recently, the hydrolysis of chemical hydrides has gained renewed interest as an irreversible solution for onboard hydrogen storage. Among the chemical hydrides, sodium borohydride (NaBH_4) has received the most extensive attention owing to its combined advantages of high hydrogen capacity, good storability in alkaline solution, easy control of hydrogen generation rate, moderate operation temperature, and the environmentally benign hydrolysis product [2].

The use of a catalyst plays a key role in controlling hydrogen generation (HG) from the NaBH_4 solution. A number of substances have been identified to be effective for accelerating the hydrolysis reaction of NaBH_4 , including Ru, Pd, Pt,

Pt–Pd, Pt–Ru alloys [3–8], Ni and Co borides [9–11], Raney Ni and Co [10], and fluorinated Mg-based alloys [12]. While the noble metal catalysts show excellent catalytic activity, their use in practical applications is restricted by their high material cost. On the other hand, the cheaper transition metal (TM) catalysts generally exhibit only moderate catalytic activity. However, recent advances in catalyst preparation technologies have led to significant improvements in the catalytic activity of TM catalysts, even to a level comparable to that of noble metal catalysts [13,14].

Furthermore, it was found that the hydrolysis performance of the systems using TM catalysts could be improved by increasing the NaOH concentration in the reactor [11,15,16]. This is in great contrast to the case of the systems using noble metal catalyst, in which addition of the alkaline stabilizer always results in a degraded hydrolysis performance [3,17]. As a high NaOH concentration is required for storing NaBH_4 safely, the improved durability of the TM catalysts in NaOH solution clearly offers an advantage over noble metal catalysts in practical applications.

As a representative TM catalyst, Co–B catalyst is of particular interest for on-demand hydrogen generation due to its good catalytic activity and low cost. Utilization of catalyst preparation

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techniques such as dipping–coating [18], pulsed laser deposition [14], and electroplating [19] have produced Co–B catalysts with HG rates of 1–101 (min g)^{−1} (catalyst). Moreover, it is expected that greater HG rates can be achieved with advanced catalyst preparation techniques.

Electroless plating technology has been widely used in the preparation of functional coating on numerous substrate materials [20,21]. Its application in preparation of hydrolysis catalyst, however, is greatly limited because conventional electroless plating process always produces a dense coating that results in a low solution/catalyst contact area. In our efforts to address this problem, a modified electroless plating technology was developed. The key features of our modified electroless plating method are the utilization of high concentration of reducing agent (NaBH₄) and main salt (CoCl₂), and the elimination of the stabilizer. As a result of these modified plating conditions, the prepared Co–B catalyst supported on Ni foam possess much higher surface area and significantly better catalytic performance than those prepared by conventional electroless plating methods.

2. Experimental

2.1. Preparation and calcination of Co–B catalyst supported on Ni foam

The catalytic performance of the Co–B catalyst supported on Ni foam (referred as Co–B/Ni foam catalyst hereinafter) prepared using the modified electroless plating method was evaluated against two other types of catalysts in this study; a Co–B/Ni catalyst prepared by a conventional electroless plating method and a noble Ru–B catalyst prepared by using dipping–coating method. All the chemical reagents are of an analytical grade and were used as received.

Using the conventional electroless plating method, the Co–B/Ni catalyst was prepared in a coating bath with the following composition: 30 g l^{−1} of CoCl₂·6H₂O, 1.5 g l^{−1} of NaBH₄, 15 ml l^{−1} of ethylene diamine (H₂NCH₂CH₂NH₂), 40 g l^{−1} of sodium tartarate (KNaC₄H₄O₄·4H₂O), 20 g l^{−1} of NaOH, 1.2 mg l^{−1} of PbCl₂, and pH 14. The reaction temperature was 45 °C and plating time was 1 h. The Ru–B catalyst was prepared by using dipping–coating method. The preparation conditions were as follows: solution A contained 10 g l^{−1} of RuCl₃·6H₂O and 20 ml l^{−1} of 10 wt.% HCl, and solution B contained 10 g l^{−1} of NaBH₄ and 10 g l^{−1} of NaOH. The dipping–coating process was operated at 25 °C and repeated 10 times to obtain a Ru–B loading of approximately 10 mg cm^{−2}.

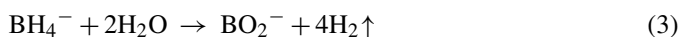
The modified electroless plating method for the preparation of Co–B/Ni foam catalyst used two solutions of the following compositions: solution A contained 50 g l^{−1} of CoCl₂·6H₂O, 80 g l^{−1} of NH₄Cl, 45 ml l^{−1} of NH₃·H₂O (25 wt.%) and the reductive solution B contained 40 g l^{−1} of NaBH₄ and 10 g l^{−1} of NaOH.

Ni foam was selected as the catalyst support material for its porous structure, low density, and its high thermal and chemical stability under the hydrolysis conditions. The Ni foam (INCO ATM Co. Ltd., 1.80 mm in thickness) has an open pore structure with an area density of about 575 g m^{−2}, and an average pore

size of 0.20–0.50 mm. Before use the Ni foam was cleaned by sonicating in ethanol for 10 min, followed by immersing in a 10 wt.% HCl solution for 1 min.

The pretreated Ni foam was immersed in solution A for 20 s at 25 °C and then, an equal volume of solution B was poured into solution A. The mixture was kept undisturbed until bubble generation ceased (which generally took several minutes). This process was repeated several times to obtain a desired Co–B loading. The Ni foam pieces were weighed before and after the electroless plating to determine the loading of Co–B catalyst on the Ni foam.

The chemical reactions involved in the electroless plating can be described as Eqs. (1)–(3) [22]:



Thus-prepared Co–B/Ni foam catalyst was calcined at temperatures ranging from 100 °C to 500 °C for 2 h under a high-purity Ar (purity 99.999%) atmosphere. The applied heating rate was 2 °C min^{−1}.

2.2. Characterization of catalyst materials

The Co–B/Ni foam catalysts were characterized by powder X-ray diffraction (XRD, Rigaku D/max-2500, Cu Kα radiation) and scanning electron microscope (SEM, LEO Supra 35) equipped with an energy dispersive X-ray (EDX) analysis unit (Oxford). The composition of the catalyst was analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES, Iris Intrepid).

2.3. Catalyst performance testing

The amount of hydrogen generated and the HG rate (as a measure of the catalytic activity) was measured using a classic water-displacement method. Typically, about 25 ml solution containing 20 wt.% NaBH₄ and 10 wt.% NaOH was thermostated in a sealed flask fitted with an outlet for the collection of evolved H₂ gas. One piece of the supported catalyst, with a typical size of 1 cm × 2 cm, was dropped into the solution to initiate H₂ generation. The H₂ amount was measured by monitoring the water displaced from a graduated cylinder (with a volume of 5.2 l) as the reaction proceeded. Because the volume of the generated hydrogen in a typical measurement (around 12 l at STP) was larger than the volume of the graduated cylinder, only the initial reaction of the HG process was recorded.

3. Results and discussion

The SEM images in Fig. 1 shows that the modification of catalyst preparation conditions results in a significant morphology change of the catalyst coating on Ni foam, from a relatively smooth surface to a coarse and porous structure. This can be attributed to the enhanced nucleation and deposition rate of

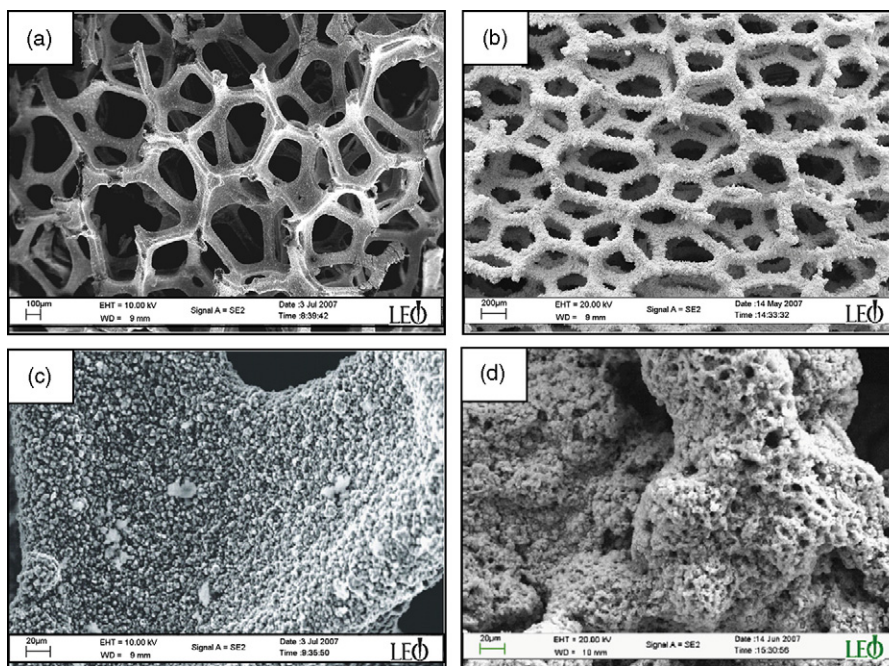


Fig. 1. SEM morphology of the Co–B catalysts supported on Ni foam that were prepared by conventional (a) and (c), and modified (b) and (d) electroless plating method, respectively.

Co–B, as well as the relatively poor coordination capability of ammonia, in the modified plating process.

Associated with the favorable morphology change, the catalytic performance of the Co–B catalyst was markedly improved. As seen from the HG curves in Fig. 2, the Co–B/Ni foam catalyst prepared by the present method (after the first plating time) exhibits a HG rate of $370 \text{ ml min}^{-1} \text{ cm}^{-2}$ (Ni foam), over six times higher than that of the Co–B/Ni foam catalyst prepared by conventional electroless plating method. The observed enhancement on catalytic effectiveness may be largely attributed to the significantly increased surface area of the Co–B catalyst,

as seen from the comparison between Fig. 1(c) and (d). Additionally, as seen in Fig. 2, the Co–B/Ni foam catalyst prepared by modified electroless plating method compares favorably with the Ru–B catalyst. This further evidences the high effectiveness of the modified electroless plating method. It should be noted that the Ru–B catalyst was prepared by using dipping–coating, rather than the electroless plating method, because RuCl_3 reacts with NH_4Cl and/or $\text{NH}_3 \cdot \text{H}_2\text{O}$ to generate insoluble ammonium salt.

According to the ICP–AES analysis results, the Co–B/Ni foam catalysts have a Co/B molar ratio close to 1.8. In the subsequent studies, the preparation and calcination conditions of the Co–B/Ni foam catalyst were optimized to pursue further improved catalyst activity.

3.1. Optimization of catalyst preparation and calcination conditions

The plating process was repeated to obtain an optimal supporting amount of Co–B catalyst on the Ni foam. Fig. 3 presents the effects of the times of plating on the catalyst loading and the HG rate of the hydrolysis system. It was found that the amount of Co–B supported on Ni foam increases nearly linearly with increasing the plating times, with an average loading rate of about 16 mg cm^{-2} per plating time. While for the HG rate a different trend was observed. The HG rate initially increases steeply with increasing the plating times, but after the third plating time the improvement in HG rate stabilizes. This suggests that surface of the Ni foam support has been almost completely coated by the Co–B catalyst after three plating repetitions. In subsequent experiments we repeated the plating process four times to ensure a full coverage of the Ni foam surface.

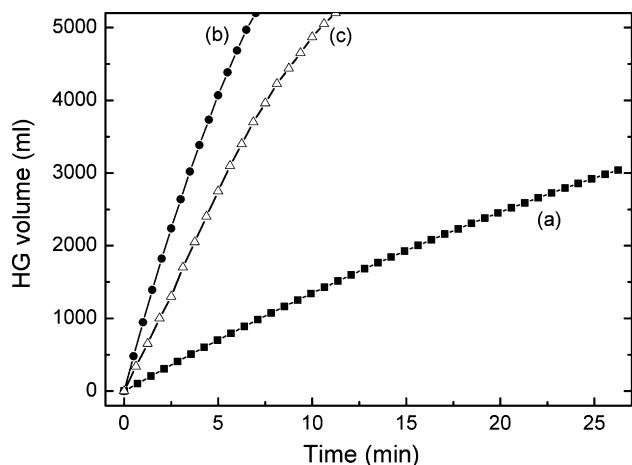


Fig. 2. Comparison of the catalytic effectiveness of (a) Co–B/Ni foam catalyst prepared by conventional electroless plating method, (b) Co–B/Ni foam catalyst prepared by modified electroless plating method, and (c) Ru–B/Ni foam catalyst prepared by dipping–plating method. The measurements were performed in a 20 wt.% NaBH_4 + 10 wt.% NaOH solution at 30°C . The size of Ni foam support is $1 \text{ cm} \times 2 \text{ cm}$.

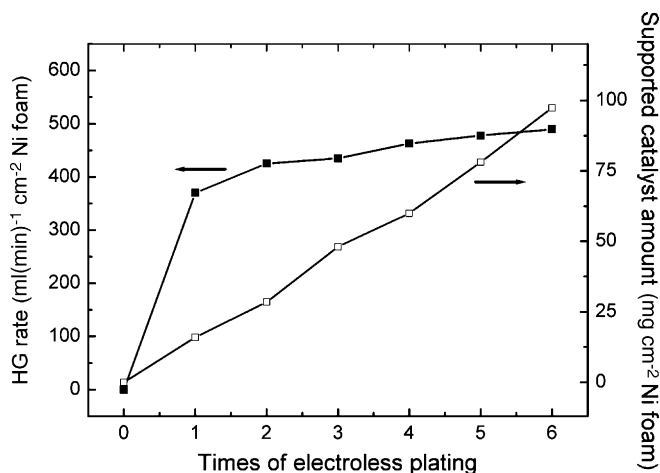


Fig. 3. Effects of the times of plating on the catalyst loading and the HG rate of the hydrolysis system.

A calcination step is required during the catalyst preparation to enhance the adhesion of the Co–B on the Ni surface. To evaluate the effect of the calcination step, the catalysts were calcined at varied temperatures and then treated in an ultrasonic water bath at a frequency of 40 kHz. Ultrasonic treatment times of 1–3 h were used. As seen in Fig. 4, the weight loss of the supported catalyst upon ultrasonic treatment increases with prolonging the treatment time, and decreases with increasing the calcination temperature, indicative of an increasingly strong catalyst/support adhesion.

On the other hand, it was found that calcination treatment also exerts considerable influence on the catalytic activity of the catalyst. Fig. 5 shows the HG rate of the hydrolysis system using the catalyst calcined at different temperatures. The HG rate initially increases with elevating the calcination temperature of the catalyst, and reaches the maximum $11 \text{ l (min g)}^{-1}$ (catalyst) (corresponding to $663 \text{ ml min}^{-1} \text{ cm}^{-2}$ (Ni foam)) at a calcination temperature of 300°C . However, calcination at temperatures above 300°C results in a reduced HG rate. We therefore selected

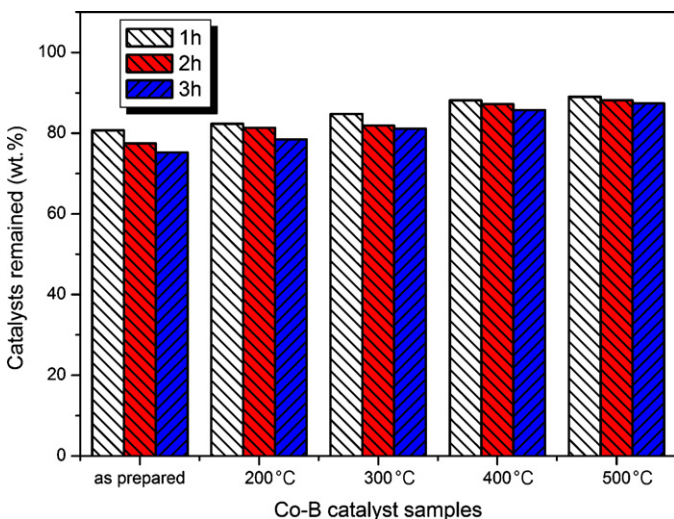


Fig. 4. Weight loss arising upon ultrasonic treatment of the Co–B catalysts calcined at varied temperatures.

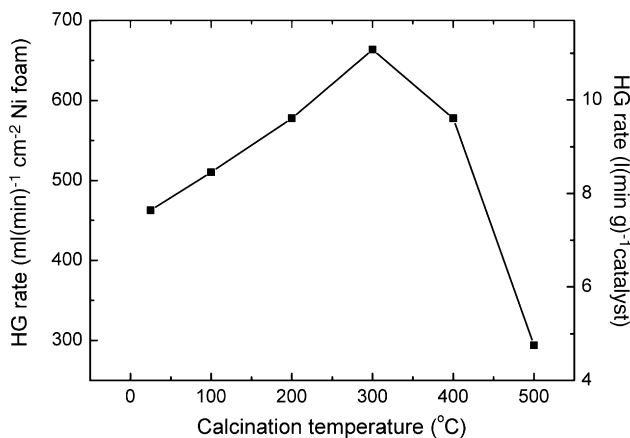


Fig. 5. Effect of calcination temperature on the HG rate of the hydrolysis system.

a calcination temperature of 300°C in the subsequent experiments to achieve a favorable catalytic activity and moderate catalyst/support adhesion.

In our effort to further understand the effect of calcination temperature on the catalytic activity, preliminary phase analyses and microstructure characterization were performed on a series of the calcined catalysts. Fig. 6 presents the SEM images of the as-prepared catalyst and those after being calcined at varied temperatures. As seen from the surface morphology in the SEM images, sample sintering became detectable at a calcination temperature of 300°C , and became more severe with calcination above 300°C . Additionally, as seen in Fig. 7, some crystal-like flakes with an average size of several tens of micrometer were observed in the catalyst samples calcined at over 300°C . According to the EDX results, the crystal-like material is cobalt oxide(s) that may originate from oxygen contamination of the catalyst during synthesis, storage and/or calcination processes. However, the cobalt oxide was not detected in the powder XRD analyses, indicating it is present in only low concentrations.

The XRD patterns of the as-prepared catalyst and catalysts after calcination are seen in Fig. 8. The wide and diffuse peak centered around $2\theta = 45^\circ$ clearly indicates an amorphous structure of the as-prepared Co–B catalyst. After calcination of the catalyst at 300°C for 2 h, nanocrystalline Co was observed to precipitate from the amorphous matrix, with an average grain size of around 15 nm, as estimated by using Scherrer equation. Calcination at 500°C increased the average grain size of Co to approximately 30 nm. Additionally, nanocrystalline Co_2B and Co_3B were detected after calcination at temperatures higher than 400°C . These results suggest that the nanocrystalline Co generated at mild calcination temperatures may be favorable for catalytic activity. The observed enhancement of catalytic activity should be understood as combined effects of the generated active species and catalyst sintering. However, such understanding fails to account for the improved catalytic activity of Co–B/Ni foam catalyst arising upon calcination below 200°C . In this regard, further investigation on the surface state of the as-prepared catalyst is still required.

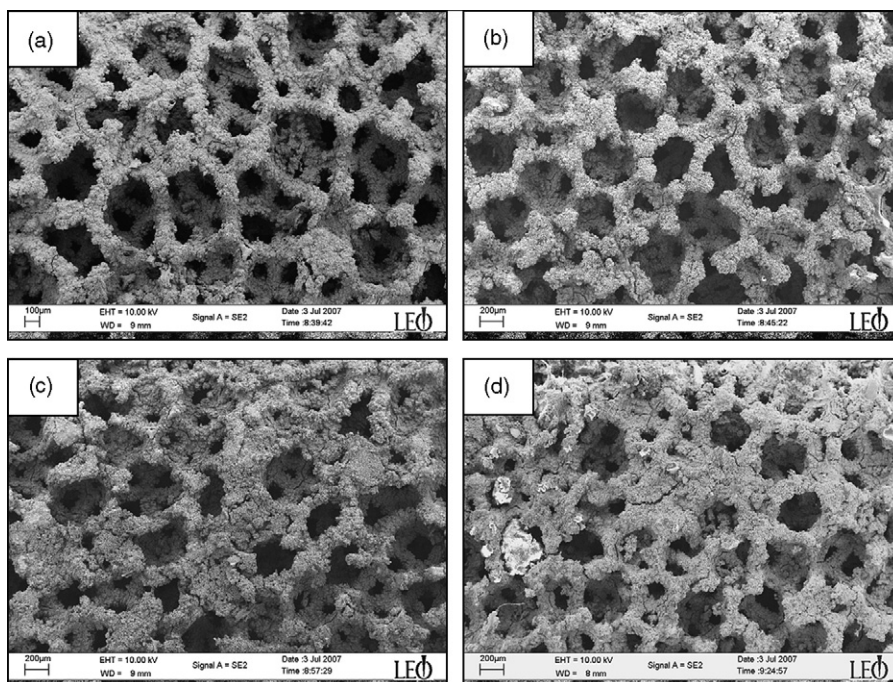


Fig. 6. SEM morphology of the as-prepared catalyst (a) and those after being calcined at 200 °C (b), 300 °C (c) and 500 °C (d), respectively.

3.2. Catalytic activity of the Co–B/Ni foam catalyst for hydrogen generation from alkaline NaBH_4 solution

The NaBH_4 hydrolysis kinetics was further investigated by conducting HG measurements at varied temperatures using the optimized Co–B/Ni foam catalyst. Fig. 9 presents the HG kinetic curves of the 20 wt.% NaBH_4 + 10 wt.% NaOH solution employing the Co–B/Ni foam catalyst at a solution temperature ranging from 25 °C to 45 °C. To minimize the effect of temperature changes due to the exothermic hydrolysis reaction, we checked and carefully controlled the solution temperature by adding ice-water blend. Additionally, the quantity of the catalyst used was reduced from a typical size of 1 cm × 2 cm to 0.5 cm × 0.5 cm. These additional measures allowed the solution temperature to be controlled to within ± 2 °C during the reaction. As expected,

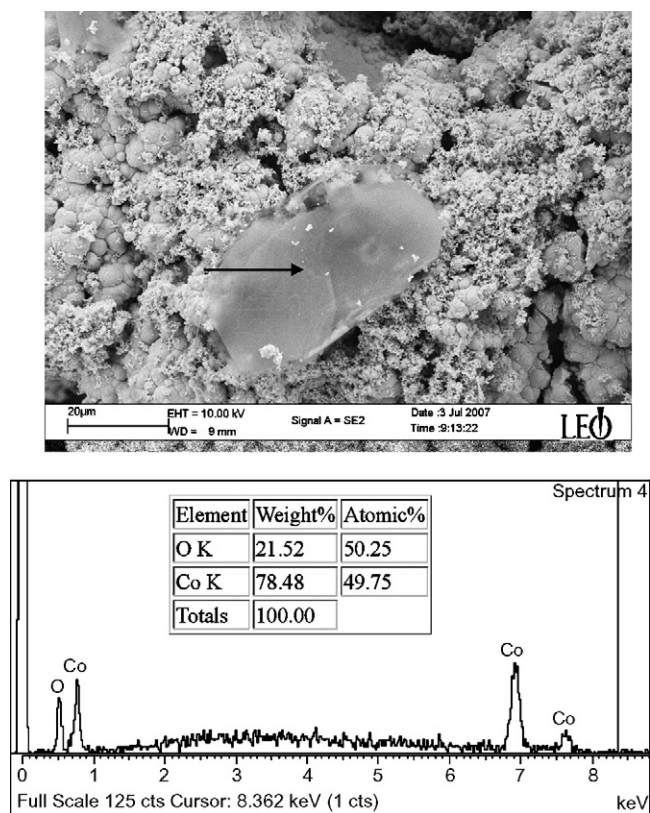


Fig. 7. SEM morphology of the Co–B/Ni foam catalyst calcined at 300 °C and the representative EDX result. The arrow indicates the center of the region of EDX analysis.

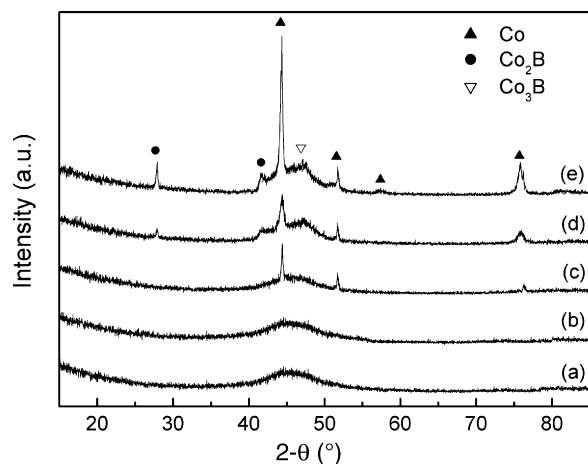


Fig. 8. XRD patterns of the as-prepared catalyst (a), as well as those after being calcined at 200 °C (b), 300 °C (c), 400 °C (d) and 500 °C (e), respectively.

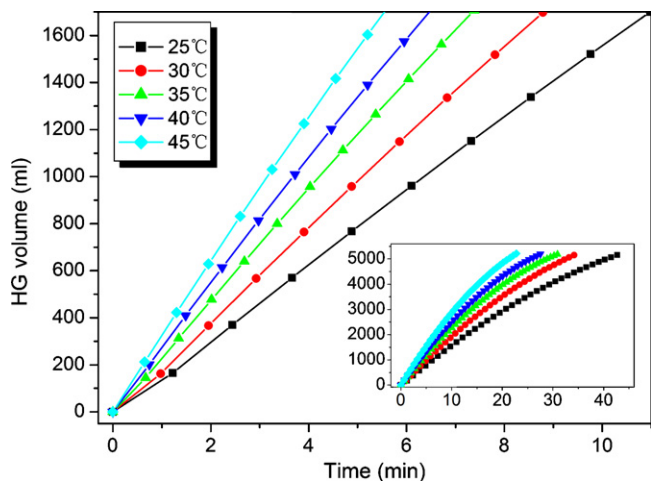


Fig. 9. HG kinetics curves of the 20 wt.% NaBH₄ + 10 wt.% NaOH solution employing the Co–B/Ni foam catalyst (0.5 cm × 0.5 cm) at different solution temperatures.

elevated solution temperature leads to an increased HG rate. In all cases, the amount of hydrogen generated increases linearly with increasing reaction time at the initial stage of hydrolysis reaction. However, as shown in the insert in Fig. 9, the HG curve gradually deviates from the linear relationship as the hydrolysis reaction proceeds. Presumably, it reflects an intrinsic reaction kinetics behavior, which is to say that the catalytic hydrolysis of NaBH₄ cannot be simply generalized as zero-order reaction [6]. Alternatively, the gradual decline in HG rate over time may be caused by accumulation of the hydrolysis product (NaBO₂) at the catalyst surface that block the fuel solution from contact with catalyst. To firmly establish this mechanism further investigations are required.

In the present study, the initial HG rates at varied solution temperature were used to determine the activation energy. As seen in Fig. 10, by plotting $\ln k$ (ml (min g)⁻¹) versus $1/T$, the activation energy was calculated to be 33 kJ mol⁻¹. This value compares favorably with the published results for Co–B/Ni foam catalyst prepared by dipping–coating method (45 kJ mol⁻¹)

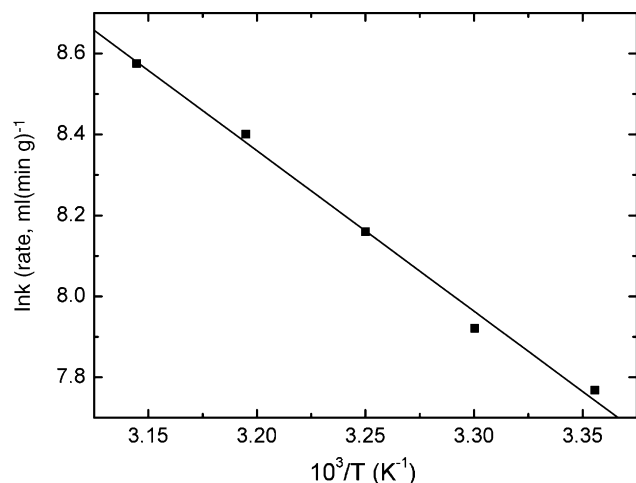


Fig. 10. Arrhenius plot for the determination of the activation energy employing a 20 wt.% NaBH₄ + 10 wt.% NaOH solution.

[18], Co–B powder catalyst (65 kJ mol⁻¹) [15], Raney Ni (63 kJ mol⁻¹) [17], Raney Co–Ni (52.5 kJ mol⁻¹) [10], and Ru catalyst (47 kJ mol⁻¹) [3]. The reduced activation energy is a further evidence of the improved activity of the Co–B/Ni foam catalyst prepared by modified electroless plating method.

4. Conclusions

A modified electroless plating method was developed for the preparation of an amorphous Co–B/Ni foam catalyst for the hydrolysis of alkaline NaBH₄ solution. Compared to the conventional electroless plating method, the newly developed method is more effective and produces Co–B catalyst with much higher catalytic activity, which is associated with a significantly increased surface area. Preliminary studies have determined the optimal preparation and calcination conditions of the Co–B/Ni foam catalyst. Employing thus-prepared catalyst in 20 wt.% NaBH₄ + 10 wt.% NaOH solution has produced a hydrogen generation rate of 11 l (min g)⁻¹ (catalyst). This high performance and low-cost Co–B/Ni foam catalyst shows promise for on-demand hydrogen generation applications.

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