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Nanostructured cobalt-phosphorous catalysts for hydrogen generation from hydrolysis of sodium borohydride solution

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ABSTRACT

Nanostructured Co–P/Cu sheet catalysts were successfully synthesized by electroless plating method. The effects of the deposition temperature on microstructures of Co–P catalysts and their catalytic properties for hydrogen generation from NaBH₄ solution were systematically investigated. By tuning the deposition temperature, the morphology of the surface of the Co–P catalysts changed significantly, such as nanoplatelets, nanospheres, pores and nanoclews. When the deposition temperature was 50 °C, the as-prepared Co–P catalysts with novel hierarchical architectures exhibited enhanced catalytic performance during the hydrolysis of NaBH₄. The hydrogen release rate of 2275.1 mL min⁻¹ g⁻¹ was achieved. This enhanced activity might be due to the novel hierarchical architectures, small size of Co phase precipitated from the amorphous Co–P phase, or the high surface roughness, which provided many defects (such as angle, step, or edge etc.) and formed more active sites on the catalyst surface. Meanwhile, the lower apparent activation energy of 27.9 kJ mol⁻¹ was calculated. Furthermore, the Co–P catalyst retained about 67% catalytic activity of its first activity after 5 cycles, which illustrated that the hydrogen release rate decreased gradually. The reason might be due to the reduction of in the amount of P and Co on the catalytic surface analyzed by XPS.

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1. Introduction

Because of the increasing fossil fuels consumption and the deterioration of ecological environment, there is an urgent demand to search for an alternative energy. Hydrogen is a good energy carrier owing to its chemical energy easily converted to electric energy, its high energy content, zero pollutant emissions, and so on [1,2]. However, the widespread application of hydrogen is hampered by the lack of cheap, safe and efficient hydrogen storage methods. Traditional methods of hydrogen storage are not suitable for practical application because of the standard of providing reversible storage for hydrogen density > 5 wt.% at mild conditions. In the past few years, complex hydrides (such as NaBH₄, NH₃BH₃, LiAlH₄ and LiBH₄) have been demonstrated to be promising

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hydrogen sources due to their high hydrogen storage density [3,4]. Among them, sodium borohydride (NaBH₄) is recognized as an ideal candidate for hydrogen storage and generation due to its multi-advantages, including high theoretical hydrogen content of 10.8 wt.%, low-lost and non-toxic nature [5,6]. Furthermore, the high-purity hydrogen can be released through hydrolysis of NaBH₄ in the presence of certain catalysts [7–12]. Therefore, it is necessary to investigate the effects of various catalysts on the hydrogen generation performance from hydrolysis of NaBH₄.

It is well known that noble metals catalysts like Pt/C [13], Pt/ LiCoO₂ [14] and Ru [15–17] have been utilized to enhance the hydrogen production rate for NaBH₄ hydrolysis. However, such catalysts are very expensive and seem to be not viable for the broad application. In recent years, some low-cost transition metals and alloys, including Ni [9], Co [7,18], Fe–Co [19], Ni–B [20–22], Co–B [23–27], Fe–B [28], Zn–Ni [29] and Co–P [30–32] have been reported and showed promising catalytic activities. Among them, because of their high catalytic efficiency and much lower cost compared with noble metal catalysts, nanostructured Co–P catalysts have been paid great attention. However, nanoparticles in a





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powdery form are difficult to separated and easily aggregated owing to their high surface energy, which may decrease their catalytic performance. In contrast, nanoparticles in thin film form can avoid above-mentioned problems and easily recover [27,32], which make it more attentive in the hydrolysis of NaBH₄. For instance, Cho and Kwon [32] have reported that Co–P catalysts electrodeposited on Cu sheet exhibit high catalytic activity. Later, Eom et al. [33] have prepared Co–P/Cu sheet catalyst by electroless deposition method and systematically researched the effects of the deposition conditions (such as deposition time, temperature, and pH value) on the catalytic activity for NaBH₄ hydrolysis. Besides, Zhang et al. [34] have investigated the effect of the reactant concentration on the catalytic properties of the Co–P/Cu sheet catalyst. Nevertheless, the effects of the deposition temperature on microstructures of Co–P/ Cu sheet catalysts and their catalytic properties for hydrogen generation from NaBH₄ solution have not been systematically investigated in the previous research reports. In addition, it is well known that the catalytic activity is sensitively dependent on their morphology and architectures. Compared to the traditional nanocatalysts (such as Co, Co-Mn-B, Co-Ni-P/Pd-TiO2 and so on), those anisotropic nanocatalysts can provide much higher catalytic activity due to the existence of more edges, corners and faces [35-37].

In this study, nanostructured Co–P catalysts with different morphologies were successfully synthesized on the Cu sheet for NaBH₄ hydrolysis by electroless plating method at different deposition temperature. The influences of the deposition temperature on microstructures of Co–P catalysts and their catalytic activity were systematically studied. Compared with those conventional Co–P films, our prepared Co–P catalysts display novel nanoarchitectures, including nanoplatelets, nanospheres, pores and nanoclews. It should be pointed out that the Co–P nanomaterials used as catalysts for NaBH₄ hydrolysis with these morphologies have not been reported before. More particularly, the as-prepared Co–P catalyst with novel hierarchical architectures exhibit enhanced catalytic ability for the hydrolysis of NaBH₄.

2. Experimental section

2.1. Catalysts preparation

In order to investigate the effects of the deposition temperature on microstructures of Co–P catalysts and their catalytic properties for hydrogen generation from NaBH₄ solution, nanostructured Co–P catalysts were deposited on Cu sheet at different temperature by electroless plating method.

A smooth sheet of Cu with an exposed surface area of 16 cm² was used as the substrate material. The sheet was sensitized in the SnCl₂/HCl system for 3 min, activated in the PdCl₂/HCl system for 2 min and washed with distilled water before undergoing electroless deposition. The coating bath composition was 0.1 mol L⁻¹ CoCl₂·6H₂O, 0.6 mol L⁻¹ NH₂CH₂COOH, and 0.8 mol L⁻¹ NaH₂. PO₂·H₂O. The pH value of the coating bath was adjusted to 12.5 with sodium hydroxide (NaOH). The deposition temperature was adjusted and maintained to 35, 45, 50 and 60 °C by means of a thermostat, respectively. Finally, electroless plating was performed for 2 min.

2.2. Characterization

The synthesized Co–Pt catalysts were characterized by power X-ray diffraction (XRD, Rigaku-Dmax 2500). The morphologies and compositions of the catalysts were analyzed by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) on Hitachi S-4800. Inductively coupled plasma-optical emission spectroscopy (ICP-OES, ICP-9000, Thermo Jarrell-ASH Corp.) analysis was carried out to determine the actual amount of Co of the catalysts. Surface topography was investigated by atomic force microscopy (AFM, Bruker Dimension icon). The electron bonding structures of Co and P on the surface of the Co–P catalysts were determined by X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra DLD multi-technique).

2.3. Measurement of hydrogen generation kinetics

Hydrolysis experiments were performed in 10 mL 1 wt.% NaOH + 5 wt.% NaBH₄ solution at 30 °C. The volume of the generated hydrogen gas was measured by the water displacement method [38]. The hydrogen generation rate (mL min⁻¹ g⁻¹) was calculated on the basis of the mass of Co–P catalyst, excluding the weight of Cu sheet. To determine the activation energy, the hydrogen generation reaction was carried out at 25, 30, 35 and 40 °C. To evaluate the reusability of the as-prepared catalyst, we repeated the hydrolysis reaction 5 times with the same catalyst.

3. Results and discussion

3.1. Catalysts characterization

Fig. 1 shows the XRD patterns of Co-P catalysts deposited on Cu sheet from the Co-P bath at different deposition temperature are shown in. It is shown that the two peaks at $2\theta = 43.3$ and 50.5° can be indexed as cubic Cu substrate (Joint Committee on Powder Diffraction Standards (JCPDS) No. 65–9026) at various deposition temperature of 35–60 °C. Fig. 1(a) shows that when the deposition temperature is 35 °C, except for the peaks of Cu substrate, there is one broad peak at $2\theta = 44.8^{\circ}$, corresponding to the amorphous nature of the Co-P compound. When the deposition temperature increases to 45 $^{\circ}$ C, the (100), (002) and (101) planes of the hexagonal close packed (hcp) Co phase exist for the Co-P catalysts at $2\theta = 41.9$, 44.8 and 47.6°, respectively. Further increasing deposition temperature to 50 $^{\circ}$ C, the peak intensity ascribed to the (002) plane of Co phase increases obviously. Meanwhile, compared with the Fig. 1(a), (b) and (c), the peak intensity of amorphous Co-P compound is almost unchanged. Continue to increase the deposition temperature to 60 °C (see Fig. 1(d)), however, the peak intensity attributed to the (100) plane of Co phase significantly increases, and the other diffraction peaks (such as the (002) and (101) planes) of Co phase are obviously weaken, even disappear. In

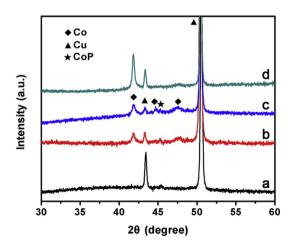


Fig. 1. XRD patterns of Co–P catalysts deposited on Cu sheet from the Co–P bath at different deposition temperature: (a) 35, (b) 45, (c) 50 and (d) 60 $^{\circ}$ C.

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