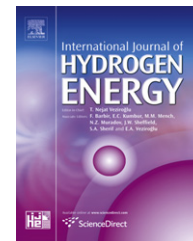


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Nanoporous Ni-based catalysts for hydrogen generation from hydrolysis of ammonia borane

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ABSTRACT

We report nanoporous Ni, Ni–Fe, and Ni–Pt as catalysts for hydrogen generation from hydrolytic dehydrogenation of ammonia borane (NH_3BH_3 , AB). The Ni and Ni–Fe nanoparticles with diameters of 20–25 nm were synthesized by a colloidal method in starch-containing aqueous solution. They exhibited considerable in situ catalytic performance but severely lost activity after separating from the reaction solution. Nanoporous $\text{Ni}_{1-x}\text{Pt}_x$ ($x = 0.01, 0.08$ and 0.19) with particle size below 5 nm was prepared from the isolated Ni nanoparticles through a replacement reaction. After centrifugation, drying, washing, and annealing, the obtained nanoporous Ni–Pt could attain remarkable activity, high hydrogen generation rate and efficiency, and low activation energy.

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1. Introduction

Hydrogen is considered to be one of the best alternative energy carriers to satisfy the increasing demand for a sustainable and clean energy supply [1]. Developing reliable, efficient methods for hydrogen generation and storage is the key prerequisite toward the future hydrogen economy [2]. Recently, the ammonia borane (NH_3BH_3 , AB) complex compound has been proposed as a promising hydrogen storage material due to its high hydrogen content (19.6 wt%) and nontoxicity [3,4]. The facile release of hydrogen from AB hydrolysis makes it an attractive medium for on-board hydrogen storage and generation that are demanded in hydrogen-utilization devices such as minitype H_2 – O_2 fuel cells. As AB is considerably stable in aqueous solution under ambient condition, catalysts are required to accelerate the sluggish hydrolysis reaction. Noble metals such as Pt and Pt-based alloys have been demonstrated

to show high catalytic activities [5,6]. However, the high cost and scarcity of noble metals limit their practical application. It is of great interest to develop well-performing catalysts that are composed of cheap elements or contain amount of precious metals as low as possible.

Studies on non-precious catalysts for borohydride hydrolysis have mainly focused on Co-based materials [7–9]. Compared to Co, Ni is cheaper and more environmentally benign. In addition, locating in the same VIII group of Pt, Ni can form alloys or solid-solution with a variety of transition metals such as Au, Ag, Co, Sn, Cu, etc [10]. It has been demonstrated that Ni nanoparticles and Ni alloys are catalytically active toward the AB hydrolysis [10–13]. The catalytic characteristics of Ni-based catalysts depend on their composition, size, shape, porosity, and preparation method. Our group has shown that the activity of submicrometer-sized Ni hollow spheres is negligible while the similar-sized PtNi

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spheres containing a small amount of Pt exhibit significantly improved activity [14]. Recently, dispersive sub-10 nm Ni nanoparticles protected by capping agents were identified as highly active catalysts [15,16]. It should be noted that the high catalytic activity is generally achieved on in situ synthesized nanoparticles. Post-synthesis treatments such as removing dispersing agent or heating would induce particle agglomeration and thus performance deterioration. Substituting Ni with a low amount of noble metals may simultaneously enhance the activity and durability of Ni-based catalysts.

In this study, we report the facile synthesis and application of nanoporous Ni, Ni–Fe, and Ni–Pt catalysts for the hydrolysis of AB. At first, Ni and Ni–Fe nanoparticles were prepared by chemical reduction in starch-containing aqueous solution at room temperature. The in situ synthesized Ni and Ni–Fe nanoparticles exhibited considerable catalytic performance toward hydrogen generation from AB hydrolysis. However, the activity was significantly decreased after separating the catalysts from the parent solution. Then, nanoporous Ni–Pt catalysts were prepared from the isolated Ni particles through a replacement route. The synthesized low-Pt-loading Ni–Pt nanoparticles, which were subjected to post treatments including centrifugation and drying, showed remarkable activity and durability. The results indicate the potential application of Ni-based nanoparticles as efficient, low-cost, and stable catalysts for hydrolytic dehydrogenation of AB.

2. Experimental

2.1. Catalysts preparation

The Ni nanoparticles were prepared by a colloidal synthesis route similar to that described by Xu and coworkers [16]. All reagents were of analytical grade and used without further purification. Starch powders (200.0 mg) were first dissolved in distilled water (20 mL) by heating at 95 °C for 15 min. Typical procedures for the preparation of Ni nanoparticles are as follows. A 14.0 mg NaBH₄ (Alfa Aesar) was added to a 50 mL three-necked round-bottom flask, of which two necks were connected to a constant pressure funnel and a water-filled gas burette while the remaining neck was plugged with a stopper. Under vigorous stirring, a 10 mL starch solution containing 62.2 mg NiCl₂·6H₂O was dripped into the flask using the funnel. The volume of generated hydrogen was determined through the inverted water-filled gas burette. When no gas was evolved in the flask, the reaction was completed and the obtained suspension was centrifuged, washed with anhydrous alcohol, and finally vacuum-dried at 60 °C overnight. To enhance crystallinity, the sample was annealed at 500 °C in Ar atmosphere for 2.5 h. The preparation of Ni_{1-x}Fe_x (x = 0, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8 and 1) nanoparticles followed similar procedures except that a starch solution containing the desired amount of NiCl₂·6H₂O and FeSO₄·7H₂O was used to afford the target composition.

The Ni_{1-x}Pt_x (x = 0.01, 0.08, and 0.19) porous nanoparticles were prepared from the isolated Ni particles through a replacement route [17]. A desired amount of H₂PtCl₆ was dissolved in isopropanol solution, which was slowly dripped to the dried Ni nanoparticles at room temperature. After

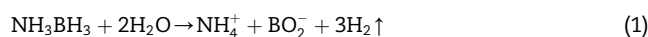
ultrasonication for 30 min, the formed suspension was centrifuged, washed with anhydrous alcohol, and vacuum-dried at 60 °C for 12 h. Finally, the obtained samples were heated at 500 °C in Ar atmosphere for 2.5 h.

2.2. Catalysts characterization

The prepared catalysts were characterized by powder X-ray diffraction (XRD, Rigaku D/max 2500 X-ray generator, Cu K α radiation, λ = 1.5406 Å), scanning electron microscopy (SEM, FEI Nano SEM-430 and JEOL 7500F), transmission electron microscope (TEM, Philips Tecnai F20), and X-ray photoelectron spectroscopy (XPS, Versa Probe PHI 5000). The composition of obtained samples was analyzed by atomic adsorption spectrometry (AAS, Hitachi 180-80 spectrophotometer). The specific surface area and pore size distribution were determined by Brunauer-Emmett-Teller (BET) nitrogen adsorption–desorption measurement (BELSORP-Mini) at 77 K.

2.3. Hydrogen generation test

The hydrogen generation experiments were carried out using the water displacement method [18]. A weighted catalyst (15 mg in situ prepared Ni, 17 mg in situ prepared Ni_{1-x}Fe_x, and 5 mg ex situ prepared Ni_{1-x}Pt_x) was placed in a three-neck round-bottom flask, to which an aqueous AB solution (0.4 wt %, 10 mL) was added. For in situ prepared catalysts, the catalyst loading was calculated on the basis of the amount of metal precursors. The evolved H₂ volume was monitored by an inverted, water-filled gas burette in a water-filled vessel and the volume of water vapor contained in the collected gas was neglected. For all tests, the three-neck round-bottom flask was immersed in a water bath to maintain the desired constant temperature (25, 30, 35 or 40 °C). The reaction of AB hydrolysis can be described by the following equation [19]:



3. Results and discussion

3.1. Catalysts characterization

3.1.1. In situ prepared Ni and Ni–Fe nanoparticles

Fig. 1 shows the XRD patterns of the in situ prepared and annealed Ni and Ni_{0.5}Fe_{0.5} nanoparticles. The absence of distinguishable diffraction peaks (Fig. 1(a)) implies the amorphous state of the synthesized sample. After heat treatment at 500 °C for 2.5 h in argon atmosphere, the in situ prepared Ni powders display well defined XRD pattern (Fig. 1(b)), in which the characteristic peaks can be readily indexed to the face-centered cubic Ni (fcc Ni, JCPDS No. 70-1849). Similarly, the amorphous Ni_{0.5}Fe_{0.5} sample (Fig. 1(c)) is transformed to a crystalline phase (Fig. 1(d)) after heating. The annealed Ni_{0.5}Fe_{0.5} sample exhibits similar diffractive profile to that of metallic nickel, suggesting that the introduction of Fe does not alter the Ni-type fcc structure and that Fe and Ni can be distributed homogeneously to form the Ni–Fe alloy [13]. However, the relatively less intensive and broader peaks

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