Catalysis Communications 16 (2011) 86–89

Contents lists available at SciVerse ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short Communication

Preparation of Ni–B amorphous alloy catalyst from nickel hydrazine complex with ultrasonic assistance

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ARTICLE INFO

Article history:
Received 22 July 2011
Received in revised form 5 September 2011
Accepted 12 September 2011
Available online 17 September 2011

Keywords:
Ni–B amorphous alloy catalyst
Nickel hydrazine complex
Ultrasonic assistance
Hydrogenation
Glucose

ABSTRACT

Fine Ni–B amorphous alloy catalysts with uniform particles were prepared by means of chemical reduction of nickel hydrazine (N_2H_4) complex by BH_4^- in aqueous solution with ultrasonic assistance. During glucose hydrogenation, the as-prepared Ni–B catalyst exhibited much higher activity than the conventional Ni–B catalysts obtained via direct reduction of Ni^{2+} by BH_4^- and Raney Ni. The higher activity could be attributed to both higher dispersion of Ni active sites and electronic effect. The nickel hydrazine complex was found to retard and prevent an abrupt formation and agglomeration of Ni–B catalysts during the catalysts preparation. It was also found that the ultrasound plays a positive role.

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1. Introduction

Compared with the crystalline metals, the amorphous alloys present unique homogeneous structure and metastable nature [1–3]. Among these, Ni–B amorphous alloy attracts more and more attention in many fields, for example it is made into electrode, it is a corrosion-resistant material, and it is an especially excellent catalyst in many hydrogenation reactions [4–6].

The chemical reduction of the nickel metallic ions with borohydride (BH_4^-) is a conventional method of Ni–B amorphous alloy preparation. The reduction procedure is as following:

$$2BH_4^- + 3H_2O \rightarrow B + BO_2^- + OH^- + 6.5H_2 \tag{1}$$

$$NiCl_2 + BH_4^- + 2H_2O \rightarrow Ni + BO_2^- + 4H^+ + 2Cl^- + 2H_2 \tag{2}$$

It shows several advantages: such as simple process, lower cost (most of the byproducts could be easily used elsewhere) and greener procedure (almost no pollutant). However, the strongly exothermic chemical reaction causes high local temperature, which inevitably leads to particle aggregation. Thus, conventional Ni–B amorphous alloy usually displays low surface area and irregular particle shape, which negatively affects activity, selectivity, and even thermal stability [7–9].

To increase the active surface area and improve the thermal stability of Ni–B amorphous alloys, various kinds of preparation strategies had been tried during the past years. For instance, Ni–B was supported on several carriers to improve the dispersion with impregnation reduction method [10–12]. Metal-dopants, such as La, W, Cr, etc. had also been used during the Ni–B preparation to prevent the aggregation.[13]. In addition, ultrasonic had been introduced in the preparation of Ni–B amorphous alloy nanoparticles [14]. However, all these methods still cannot solve the problem fundamentally.

In fact, the key point to directly solve the problem should be effectively controlling the rate of exothermic reaction, and thus eventually avoiding particle aggregation. However, to our knowledge, it has not been studied in detail so far. The nickel complex precursors are often used to control reaction rate and particle size in the preparation of Ni nanoparticles. Park [15] reported smaller size and non-agglomerated Ni powders prepared from the reduction of nickel hydrazine complexes. Sabine [16] prepared small nickel particles of Ni/SiO_2 catalysts with nickel ethylenediamine complexes. The stabilization of nickel cation by hydrazine or ethylenediamine ligand retards and prevents an abrupt formation of Ni powders, thus produces more stable and fine uniform particles.

Based on this idea, in this paper, we report that the nickel complex ions in solution play a crucial role in controlling phase composition of the Ni–B amorphous alloy catalysts. The as-prepared catalysts are characterized by XRD, TEM, XPS etc. Finally, all catalysts were evaluated by the reaction of glucose hydrogenation.

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doi:10.1016/j.catcom.2011.09.008

Table 1
Physicochemical properties of obtained catalysts and Raney Ni.

Catalyst	BET surface $m^2\ g_{cat}^{-1}$	H_2-chemisorption $cm^3\ g_{cat}^{-1}$	Active centers 10^{22} Ni atoms g_{cat}^{-1}
Raney Ni	11.3	0.41	3.02
Ni–B	12.8	0.37	2.73
Ni–B-u	28.2	0.58	4.28
Ni–B-c	32.4	0.60	4.42

According to H_2-chemisorption, the active center of catalysts was calculated assuming H/Ni = 1.
Active centers $=\frac{\text{mol Ni}(2\times\text{mol } H_2)}{0.5\text{g catalyst}}\times 6.022\times10^{23}\text{mol}^{-1}$.

2. Experimental

2.1. Catalyst preparation

The $Ni(N_2H_4)_2^{2+}$ complexes were synthesized by mixing hydrazine monohydrate ($N_2H_4\cdot H_2O$) with aqueous $NiCl_2.6H_2O$ (molar ratio = 2:1) and the resulting mixtures were stirred at 293 K for about 2 h. Then, the products were filtered, washed with deionized water several times and dried in a vacuum dry oven at 303 K for 24 h. Then, the nickel hydrazine complexes were gradually added into the KBH_4 aqueous solution under gently stirring. The pH was kept stable at 12 by NaOH. The reduction of $Ni(N_2H_4)_2^{2+}$with BH_4^- was induced by a 20 kHz ultrasound at 273 K by ice water. The amount of KBH_4 used was three times (mol) that of Ni to ensure that all the nickel complexes were reduced. After complete reduction of $Ni(N_2H_4)_2^{2+}$ in the solution, the resultant black solid was washed thoroughly with deionized water, absolute alcohol (EtOH) subsequently, and finally stored in EtOH until the time of use. The as-prepared Ni–B amorphous alloy was denoted as Ni–B-c. For comparison, conventional Ni–B sample, hereinafter denoted as Ni–B, was prepared by direct reduction of Ni^{2+} with KBH_4 [13]. When ultrasound was applied during conventional Ni–B sample preparation, the catalyst was denoted as Ni–B-u. Raney Ni catalyst was prepared by alkali leaching of a commercial Ni–Al alloy. All chemicals used in this experiment were reagent grade and used without further purification.

2.2. Catalyst characterization

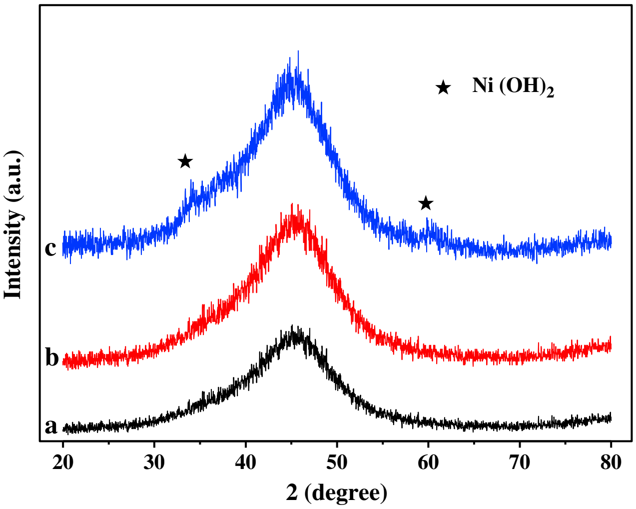

Fig. 2. XRD spectra of amorphous alloy catalysts. a: Ni–B, b: Ni–B-u, and c: Ni–B-c.

The crystal structures of the Ni–B alloys were identified by X-ray diffraction analysis (XRD,RIGAKU D/max-2500). The morphological images and particle size were obtained by transmission electron microscopy (TEM, H-7650, Hitachi). The X-ray photoelectron spectroscopy (XPS) measurements were recorded with a PHI-1600 ESCA using Mg X-ray source for excitation. H_2-chemisorption and H_2-TPD were performed using a TP-5000 instrument from Xianquan Ltd. The BET surface area was measured using a Quantachrome 2000 surface area analyzer. The crystallization process was followed by differential scanning calorimetry (DSC, Shimadzu TA50).

2.3. Catalyst activity test

The liquid-phase hydrogenation of glucose was performed in a 250 mL stainless steel autoclave equipped with electric heating and mechanical stirrer. The hydrogenation reactor contained 0.5 g catalyst and 150 mL 20% (w/w) glucose aqueous solution. The reaction system was heated to 393 K and pressured to 4.0 Mpa with H_2, stirred vigorously (500 rpm) to eliminate the diffusion effect. Each reaction lasted for 2 h,then the products were analyzed by the Fehling reagent titration in order to determine the glucose conversion.

3. Results and discussion

The results of BET areas and H_2-chemisorption of Ni–B, Ni–B-u and Ni–B-c samples were summarized in Table 1. From the BET analysis, with utrasonic assistance the BET area increased noticeably. The Ni–B-c sample had the largest surface area among the catalysts studied. With respect to H_2-chemisorption, the Ni–B-u sample showed higher values than the Ni–B sample. The maximum extent of H_2-chemisorption was also obtained for the Ni–B-c sample, which meant that the Ni–B-c sample had the largest number of active Ni centers.

A further investigation of morphology was made by TEM. The pictures (Fig. 1) revealed that the Ni–B sample displayed almost shapeless particles with severe agglomeration, which might result from the high local temperature caused by uncontrolled strongly exothermic

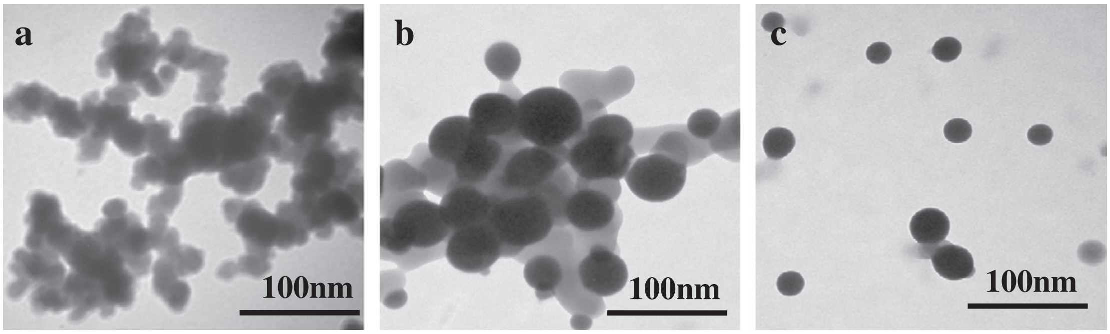

Fig. 1. TEM images of the amorphous alloy catalysts. a: Ni–B, b: Ni–B-u, and c: Ni–B-c.

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