Short communication

Confined preparation of ultrafine NiB amorphous alloys for hydrogenation

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ABSTRACT

How to control the size distribution and morphology of amorphous alloy is of vital importance in improving their catalytic performance. In this work, uniform and ultrafine NiB amorphous alloy catalysts were prepared by using a hydrogelator, 2,4-(3,4-dichlorobenzylidene)-D-sorbitol, as growth controller as well as PEG800 and tannin for co-additives, which exhibit excellent performance toward the selective hydrogenation of cinnamic acid into hydrocinnamic acid. TEM images indicated the addition of PEG800 and tannin affected the self-assembly of gelator from large aggregates into small assemblies and then affected the morphology of NiB catalysts, leading to enhancement of catalytic activity and stability.

1. Introduction

In the past decades, amorphous alloys have received a growing interest in a number of fields including catalysis. Owing to their unique long-range disordered and short-range ordered structure, amorphous alloys provide a novel alternative to prepare efficient catalysts in hydrogenation reactions [1–5]. Unfortunately, small nanoparticles (NPs) prepared by chemical reduction are typically unstable and tend to aggregate, resulting in catalysts with broad size distribution and irregular shape. To overcome these drawbacks, the use of templates [6], ultrasound [7], modifiers [8] and polymers [9] during preparation or construction of supporting catalyst have been previously investigated [10]. However, the existing methods need precise control of conditions during catalyst preparation. Therefore, developing a simple approach to obtain ultrafine amorphous alloy catalyst is highly desirable.

Recently, the possibility of using low molecular organic geltors (LMOGs) has been proposed as a means to control the morphology of metallic nanoparticles [11]. For example, it has been reported that the Ag or Au metal NPs could be formed *in situ* on the gel nanofibers formed by an acyl hydrazide modified 1,3:2,4-dibenzylidenesorbitol gelator [12]. Ballabh has reported that silver nano-particles stabilized by a melamine-based two component gelator could be stable for several months at room temperature [13]. However, there are few reports on the preparation of amorphous alloy catalysts with controllable particle size by using supramolecular assembly with a low molecular weight gelator.

In the present work, we have explored the possibility of using a hydrogelator, 2,4-(3,4-dichlorobenzylidene)-D-sorbitol (Fig. S1), as a new additive in the preparation of uniform ultrafine NiB amorphous

alloy NPs. Our early work on NiB preparation has found that PEG800 is effective in inhibiting the agglomeration of the active Ni particles in NiB amorphous alloy catalysts and then increase the activity of catalysts [9,14]. Moreover, tannin was also found to be an excellent stabilizer for metal particles owing to the abundant phenolic hydroxyl group in its molecular [15]. Therefore, PEG800 and tannin are also used as co-additive during the synthesis process. The activity of these catalysts has been examined in the selective hydrogenation of cinnamic acid into hydrocinnamic acid, which is an important chemical intermediate for the preparation of food additives.

2. Experimental section

2.1. Materials

All chemicals were analytical or technical grades and used without further purification. $NiCl_2 \cdot 6H_2O$, *tert*-butanol, cinnamic acid, Tannin (TA, MW 1701.23) and PEG800 (MW 770~860) were obtained from Tianjin Guangfu Chemical Reagent Factory. KBH_4 was obtained from Aladdin. NaOH was purchased from Tianjin Beichen Chemical Reagent Factory.

2.2. Preparation of NiB amorphous alloy catalysts

All the NiB amorphous alloys were prepared though chemical reduction uses KBH_4 as reducing agent. The molecular ratio of KBH_4 to nickel was 5:1 to ensure complete reduction. Upon the addition of DCBS, PEG800 and tannin during preparation, a transparent solution was firstly prepared by dissolving a certain amount of additive in

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distilled water and used as solvent for metal salts and reducing agent. For example, when NiB-DCBS-PEG800-TA was prepared, the solvent was firstly prepared with the concentration of DCBS, PEG800 and Tannin was 1 mg/mL, 4 mg/mL and 2 mg/mL, respectively. Then $NiCl_2·6H_2O$ (1.18 g, 5.0 mmol) was dissolved in the pre-prepared solvent and treated with ultrasound for 10 min to ensure good mixing. Subsequently, 25 mL pre-prepared solvent containing KBH_4 (aq) (25 mmol) and NaOH (0.20 M) was added dropwise to the $NiCl_2$ solution with vigorous stirring in an ice bath to reduce Ni^{2+}. In the step of reduction, the NiB particles were formed under the confinement and stabilize effect of the additives, so the particle size could be controlled and the agglomeration could be avoid. The solid obtained after reduction was filtered and washed thoroughly with H_2O until pH = 7 and then transferred into 250 mL absolute ethanol to extract the additives by refluxing for 12 h and stored in absolute ethanol. The other catalysts were prepared by the similar process except using different solvent for metal salts and reducing agents. For example, DCBS (1 mg/mL) aqueous solution for NiB-DCBS, DCBS (1 mg/mL)-PEG800 (4 mg/mL) mixed solution for NiB-DCBS-PEG800, and distilled water for NiB. The catalysts so obtained were denoted as NiB-DCBS, NiB-DCBS-PEG800 and NiB.

2.3. Activity test

Cinnamic acid hydrogenation was conducted in a 100 mL stainless steel autoclave equipped with electric heating and mechanical stirrer under following conditions: 1.5 g cinnamic acid, 0.03 g catalyst (pre-conceived molar ratio of substrate: metal is 20: 1), 30 mL solvent, initial H_2 pressure 2.5 MPa, reaction temperature 363 K, and reaction time 2 h. The reaction mixtures were analyzed by gas chromatography using a 30 m HP-5 capillary column. The used catalysts were separated by suction filtration, washed and kept under ethanol for recycling.

2.4. Characterization

The BET surface areas of the catalysts were measured using a Micromeritics Tristar II 3020 apparatus. X-ray diffraction (XRD) patterns were acquired with a Bruker D8 diffactometer using a CuKα radiation source. Fourier transform infrared spectra (FT-IR) were recorded on a Bruker VERTEX 70 Fourier transform spectrophotometer using KBr pellets. The amounts of Ni in the catalysts was identified by inductively coupled plasma (ICP) on an Agilent 7500a spectrometer. H_2-chemisorption and temperature-programmed desorption of hydrogen (H_2-TPD) were carried out on a TP-5000 instrument supplied by Xianquan Co. Ltd. Transmission electron microscopy (TEM) was performed on a FEI Tecnai G2 F20 S-TWIN microscope. Metal particle size distributions have been determined from the measurement of ca. 100 particles found in arbitrarily chosen area of the images.

3. Results and discussion

The X-ray diffraction (XRD) patterns showed a broad peak at $2θ = 45°$ for each freshly prepared catalyst, no diffraction peaks corresponding to the crystalline of Ni_2B were detected in all samples [16], indicating the typical amorphous structure of the prepared catalysts (Fig. 1), which means that the addition of DCBS, PEG800 and tannin had not changed the amorphous structure of the NiB catalyst [17,18]. In contrast, no peak related to Ni was observed in these catalysts, further indicating the amorphous nature of the Ni. Moreover, the FTIR spectra of NiB-DCBS-PEG800-TA revealed that the no adsorption peaks attributed to the vibration of C−H bond were observed in the range of 2800–3000 cm^{-1}, suggesting that all the additives have been completely removed after the treatment with ethanol (Fig. S2).

The impact of DCBS, PEG800 and tannin addition on the morphology of the catalyst was evaluated by Transmission Electron Microscopy (TEM). It should be noted that, NiB particles exhibited
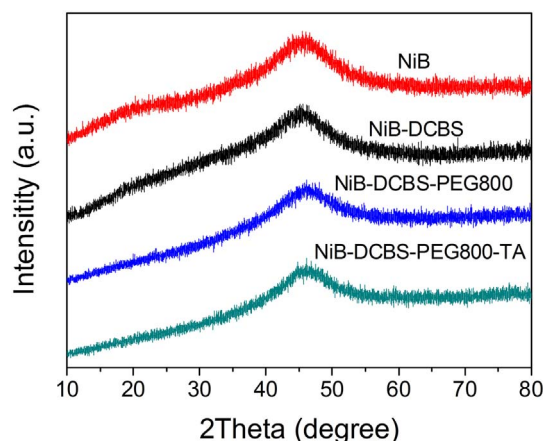

Fig. 1. XRD patterns of the amorphous alloy catalysts.

obvious agglomeration and presents a cotton-like structure (Fig. 2a). With the addition of DCBS, nanochains with average diameter of ~41 nm of NiB were observed (Fig. 2b). These superstructures seem to be strongly affected by the presence of DCBS. However, a significant decrease in the particle size was observed by adding PEG800 (4 mg/mL). The particle size of NiB-DCBS-PEG800 decreased to ~32 nm and agglomeration was also inhibited upon addition of PEG800 with DCBS (Fig. 2c and Fig. S3d). This effect is even greater with the addition of tannin (2 mg/mL) into the preparation system, for which nearly monodispersed NiB nanoparticles with a mean diameter of ~4 nm are obtained (Fig. 2d and Fig. S3f). In addition, narrower size distributions were achieved, which may result in a larger surface area and more active sites than the standard NiB catalyst.

Here, it is worth emphasizing that a synergistic effect of DCBS, PEG800 and tannin occurred during the preparation of NiB catalysts. In aqueous medium, DCBS can aggregate into fiber-like structures of a few hundreds of nanometers [19], which could be also detected in the NiB-DCBS sample before removing the DCBS (Fig. S4a). However, the sparse and loose network formed by DCBS was not efficient enough to act as a "cage" to control the formation of NiB nanoparticles. In the presence of PEG800, the DCBS aggregates tend to be smaller and adsorbed on the surface of NiB particles, which can effectively limit the growth of NiB particles and avoid the agglomeration (Fig. S4b). In the situation of further addition of tannin, the aggregates of DCBS were dissociated into small assemblies, which were hard to be distinguished in the hybrid materials. Herbois demonstrated that small assemblies could interact more strongly with the Ru centers and controlled the particle size more efficiently than large aggregates [20]. Similarly in the present work, the presence of high amounts of disaggregated DCBS would be more efficient in controlling the growth of NiB NPs, an almost monodispersed NiB catalyst with a narrow particle distribution was obtained.

In the preliminary study, the optimal concentration of DCBS in the pre-prepared solvent was confirmed to be 1 mg/mL, addition of greater DCBS resulted gel formation in the solvent, which hindered Ni^{2+} reduction during preparation. For comparison, NiB NPs were also prepared with PEG800 (4 mg/mL) or tannin (2 mg/mL) as additive, but the results showed that neither additive improved the NiB activity significantly (Table S1). Table 1 summarizes some structural parameters and the catalytic performances of different catalysts in cinnamic acid hydrogenation. As shown in Table 1, it was found that the surface areas of these NiB catalysts gradually increased with successive addition of DCBS, PEG800 and tannin into the preparation system. NiB-DCBS-PEG800-TA has the largest surface area (82.9 m^2/g) among the catalysts studied. With respect to H_2-chemisorption, the successive addition of DCBS, PEG800 and tannin during preparation also led to increase value of NiB catalysts, the maximum extent of H_2-chemisorption was also obtained for the NiB-DCBS-PEG800-TA catalyst (0.7 cm^3/g).