



Short communication

Effect of loading method on selective hydrogenation of chloronitrobenzenes over amorphous Ni–B/CNTs catalysts

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ABSTRACT

Carbon nanotubes (CNTs)-supported amorphous Ni–B catalysts were prepared by selectively depositing Ni–B particles inside or outside the CNTs (Ni–B-in/CNTs or Ni–B-out/CNTs). Hydrogenation of chloronitrobenzenes was carried out to test how the Ni–B particle-loading method over the CNTs affected the catalytic performance. Compared with the Ni–B-out/CNTs, the Ni–B-in/CNTs, because of the nanospace limitation inside the CNTs, restricted the size and aggregative behavior of the Ni–B particles better, and formed an amorphous Ni–B alloy with high thermal stability. The Ni–B-in/CNTs exhibited a much higher catalytic activity for hydrogenation of chloronitrobenzenes than the Ni–B-out/CNTs.

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1. Introduction

Metal-metalloid amorphous alloys have been widely used in catalytic reactions due to their short-range ordering structure [1–4]. However, poor thermal stability and/or low surface area have limited their application in industrial catalysis. Supported amorphous alloy catalysts have proven to be promising candidates for industrial applications owing to the great improvement in thermal stability and active surface area as a result of the high dispersion of the amorphous alloy particles on the support.

After their discovery by Iijima, carbon nanotubes (CNTs) have attracted a great deal of interest due to their extraordinary physical and chemical properties [5]. Amongst their many potential applications, their use as catalysts or catalyst supports is of particular interest as CNTs display superior catalytic performance compared to traditional catalysts in reactions involving hydrogenation [6,7], selective dehydrogenation [8], catalytic oxidation [9], or Fischer–Tropsch synthesis [10]. Improved catalytic performance has been reported when CNTs were used as supports to disperse metal catalysts on the outside surface of the channels [11]. Alternatively, it was also found that nanoparticles encapsulated in CNTs exhibit better catalytic performance compared with those located outside the CNTs for some reactions due to the confinement effect of the CNTs [12]. Therefore, the loading method for the active component on the CNTs is one of the most important factors.

On the basis of research by Tessonier et al. [13], two CNTs supported amorphous Ni–B catalysts were prepared with Ni–B particles confined inside the channels of the CNTs (Ni–B-in/CNTs) or loaded on the CNTs outer surface (Ni–B-out/CNTs). Hydrogenation of chloronitrobenzenes (CNBs) was chosen as a probe reaction to investigate how the loading method of Ni–B particles over CNTs affects the catalytic performance.

2. Experimental

2.1. Catalyst preparation

Raw CNTs were refluxed in concentrated HNO₃ for 6 h, then filtered and washed with distilled water, and dried at 373 K for 12 h. The Ni–B-in/CNTs precursor was synthesized as follows: 1.0 g of CNTs was impregnated with 3.5 ml of NiCl₂ ethanol solution (0.54 M NiCl₂·6H₂O). Then, 2.6 ml H₂O was added. The impregnated sample was oven dried at 303 K for 12 h, and was denoted NiCl₂-in/CNTs. The theoretical loading of Ni on the CNTs was 10 wt.%. For the Ni–B-out/CNTs precursor, 1.0 g of CNTs was impregnated with 5.2 ml of ethanol. Then, 3.5 ml of NiCl₂ aqueous solution (0.54 M NiCl₂·6H₂O) was added. The sample was dried and denoted NiCl₂-out/CNTs. The above-prepared precursors (NiCl₂-in/CNTs and NiCl₂-out/CNTs) were reduced by adding 2 M KBH₄ solution containing 0.20 M NaOH (Ni²⁺:BH₄⁻ in a molar ratio of 1:3) dropwise with vigorous stirring in an ice-water bath until no gas was released. The resulting samples (Ni–B-in/CNTs and Ni–B-out/CNTs) were then thoroughly washed with distilled water and ethanol and were kept in ethanol until use. In addition, Ni-in/CNTs was prepared from NiCl₂-in/CNTs by H₂ reduction at 673 K for 4 h.

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2.2. Catalyst characterization

The morphologies of the catalysts were characterized by a transmission electron microscope (TEM, JEOL JEM-4000EX). The Ni loading and Ni–B composition were analyzed using an inductively coupled plasma spectrometer (ICPS-7510, Shimadzu). The active surface area (S_{act}) was determined by H_2 chemisorption using a dynamic pulse method [14]. The X-ray diffraction (XRD) patterns of the catalysts were recorded with a Rigaku D/max-2200 X-ray diffractometer with $\text{Cu K}\alpha$ radiation. Differential scanning calorimetry (DSC) measurements were conducted on a Netzsch 200 F3 analyzer under N_2 atmosphere at a rate of 10 K/min. Temperature programmed desorption of hydrogen (H_2 -TPD) was carried out in a CHEMBET 3000 (Quantachrome) instrument at a rate of 10 K/min. X-ray photoelectron spectroscopy (XPS) analyses were performed using Thermofisher Scientific K-Alpha X-ray photoelectron spectrometer with a monochromatized $\text{Al K}\alpha$ X-ray source.

2.3. Catalytic hydrogenation of CNBs

Selective hydrogenation of CNBs was carried out in a 100 ml stainless autoclave at 417 K and 2.0 MPa. Typically, the autoclave was charged with 0.05 g of catalyst and 20 ml of 0.1 mol/l CNBs ethanol solution. Then, the autoclave was sealed and purged more than six times with hydrogen to exclude air. The reaction lasted for 1 h. Products were analyzed using a gas chromatograph (GC, Shimadzu GC-14C, FID, SE-30 capillary column), and were identified by gas chromatography/mass spectrometry (GC/MS, Agilent 5890).

3. Results and discussion

The location and size of Ni–B particles were characterized by TEM analysis. The TEM image of Ni–B-in/CNTs shows that most of the Ni–B particles are evenly distributed within the CNT nanochannels (Fig. 1(a)). The TEM image of the Ni–B-out/CNTs clearly shows that the Ni–B particles are dispersed on the outer surfaces of the CNTs (Fig. 1(b)). Moreover, the Ni–B particles in the Ni–B-in/CNTs are uniformly sized (about 8 nm), while those in the Ni–B-out/CNTs are non-uniformly sized and range from 12 to 26 nm.

The physicochemical properties of the Ni–B-in/CNTs, Ni–B-out/CNTs and Ni-in/CNTs are listed in Table 1. Significant Ni component loss occurred in the Ni–B-out/CNTs, but not in the Ni–B-in/CNTs and Ni-in/CNTs. The Ni component loss is attributed mainly to the reaction between Ni^{2+} and BH_4^- , and it was inhibited by intratubal loading compared with extratubal loading.

Fig. 2 presents the XRD patterns of the CNTs, Ni–B-in/CNTs, and Ni–B-out/CNTs. The three peaks at 26.1° , 43.1° , and 53.5° observed in the three profiles can be indexed as the (002), (100), and (004) diffractions of hexagonal graphite [15], respectively, indicating the graphitization structure of the CNTs is not destroyed during the acid treatment. The characteristic diffraction peak of amorphous Ni–B alloy is reportedly a dispersion peak near $2\theta = 45^\circ$. For the Ni–B-in/CNTs and Ni–B-out/

Table 1

Physicochemical properties of Ni–B-in/CNTs, Ni–B-out/CNTs and Ni-in/CNTs.

Catalyst	Ni loading (wt.%)	Composition (atomic ratio)	S_{BET} (m^2/g)	V_{pore} (cm^3/g)	d_{pore} (nm)	S_{act} ($\text{m}^2/\text{g Ni}$)
Ni–B-in/CNTs	9.2	Ni58.6B41.4	80.64	0.360	17.45	17.83
Ni–B-out/CNTs	8.6	Ni61.7B38.3	77.15	0.329	16.64	15.46
Ni-in/CNTs	10.1	–	89.53	0.384	15.21	21.32

CNTs, except for the CNTs diffraction peaks, no other crystalline peak was observed, which indicates that the Ni–B exists as an amorphous phase [16].

The thermal stabilities of Ni–B-in/CNTs and Ni–B-out/CNTs were compared by DSC. Both catalysts exhibit two exothermic peaks, which correspond to phase transitions at around 704 and 741 K for Ni–B-in/CNTs and 692 and 735 K for Ni–B-out/CNTs (Fig. 3(a)). Li et al. reported that when the heat treatment temperature rose to 573 K, the amorphous Ni–B alloy started to transform to metallic Ni, crystal Ni_2B , Ni_3B alloy, and when increased further to 683 K, the substances decomposed to metallic Ni and free B [17]. Therefore, the thermal stability of the supported amorphous Ni–B alloys was improved greatly. The crystallization temperatures of Ni–B-in/CNTs were about 10 K higher than those of Ni–B-out/CNTs. The higher thermal stability of Ni–B-in/CNTs may be attributed to the confinement effect of CNTs on the amorphous Ni–B alloy.

Fig. 3(b) shows the H_2 -TPD profiles of the Ni–B-in/CNTs and Ni–B-out/CNTs. The Ni–B-in/CNTs has a significantly lower H_2 desorption temperature versus the Ni–B-out/CNTs (669 K vs. 697 K) and a larger H_2 desorption peak area. H_2 is a reactant in hydrogenation, and when the desorption temperature is far higher than the hydrogenation temperature (413 K), the lower desorption temperature is more favorable for CNBs hydrogenation [18]. Moreover, the desorbed quantity of H_2 increases under the same Ni loading amount, indicating the active centers in Ni–B-in/CNTs are more scattered and abundant.

The interaction between Ni and B was characterized by XPS (Fig. 4). For the two catalysts, both Ni and B were present in two states. However, Ni and B, which were at different states in the two catalysts, did not show a significant difference in binding energy (BE). In Ni $2p_{3/2}$ (Fig. 4(a)), the peaks around 852.5 and 855.7 eV are assigned to metallic Ni and oxidized Ni, respectively. In B 1s (Fig. 4(b)), the peaks around 188.4 and 192.3 eV are assigned to elemental B and oxidized B, respectively. In comparison with the standard BE of pure Ni (853.1 eV) and pure B (187.1 eV), the BEs of elemental Ni and B shifted by -0.6 and $+1.3$ eV, respectively, indicating some electrons transferred from B to Ni in the amorphous Ni–B alloy to form electron-rich Ni and electron-deficient B [19]. The degree of BE shift for metallic Ni is less than that of metallic B, which could be attributed to the relatively larger atomic weight of the Ni atom versus the B atom [20]. On the basis of the peak areas for reduced Ni and oxidized Ni (the peak area of Ni^0 to Ni^{2+} was denoted “R”), a comparison of the two catalysts shows that the Ni–B-in/CNTs ($R = 0.51$) contain more reduced Ni than the Ni–B-out/CNTs ($R = 0.38$).

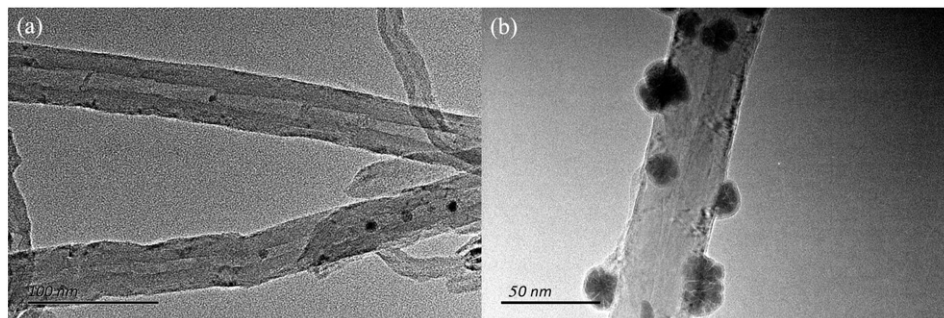


Fig. 1. TEM images of Ni–B-in/CNTs and Ni–B-out/CNTs.

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