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Short communication

Hydrolytic hydro-conversion of cellulose to ethylene glycol over bimetallic CNTs-supported NiWB amorphous alloy catalyst

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ABSTRACT

NiWB/CNTs catalysts were prepared by ultrasonic impregnation chemical reduction method and showed high activity in the hydrolytic hydro-conversion of cellulose to ethylene glycol. The conversion of cellulose could be high to 100% with an ethylene glycol selectivity of 57.7%. The catalysts were characterized by XRD, TEM, NH_3-TPD and XPS. The hydrolytic hydro-conversion activity of the catalyst was related to it's highly dispersion of NiWB, appropriate particle size and the synergistic effect between strong acid sites in CNTs and NiW alloying structure.

1. Introduction

Cellulose is the most abundant source of biomass, and holds impressive potential as an alternative to fossil fuels for sustainable production of fuels and chemicals [1–4]. Various processes have been employed to convert cellulose biomass into fuels and chemicals [5–8]. One-pot conversion of cellulose with solid catalysts via hydrolytic hydrogenation is a green process for the sustainable production of polyols. Fukuoka et al. reported firstly that cellulose can be directly converted into hexitols over Pt/Al_2O_3 catalyst and the yield of hexitols was around 30% [9]. Recently, carbon has been advocated as a leading material for chemical biomass transformation process due to its large specific surface area, high porosity, excellent electron conductivity, and relative chemical inertness [10]. Luo et al. used a carbon supported Ru catalyst for the hydrogenolysis of cellulose and obtained a 39.3% yield of hexitols [11]. Deng et al. investigated the use of Ru supported on carbon nanotubes (CNTs) for cellulose conversion, and a 40% yield of hexitols could be achieved [12]. Van de Vyver et al. presented a study wherein Ni supported on carbon nanofibers (CNFs) was used. Under the applied reaction conditions, a 76% yield in hexitols with 69% sorbitol selectivity at 93% conversion of cellulose was obtained [13]. Interestingly, Zhang and co-workers developed a series of tungstenic catalysts including Ni-W_2C/AC, WC/MC and Ni-W/SBA-15, which can effectively catalyze the conversion of cellulose into polyols and the yield of ethylene glycol (EG) was as high as 61–75 wt.% [14–16]. Others recently reported the use of metallic tungsten and tungsten oxide based dual-functional catalysts for the cellulose conversion to EG [17–19]. All these findings opened the way for other combinations of hydrogenation catalysts and tungsten-based catalysts for the production of bulk valuable EG from biomass [20–22].

Amorphous catalyst possesses some interesting and intrinsic properties such as a microstructure of long-range disorder and short-range order [23–26], leading to its excellent activity in the catalytic hydrogenation reactions [27–31]. However, to our knowledge, it has not been examined for the conversion of cellulose. In the present work, a series of NiWB/CNTs amorphous catalysts were prepared by chemical reduction method, and were used in the conversion of cellulose into polyols.

2. Experimental

2.1. Catalyst preparation

CNTs were pretreated in concentrated HNO_3 (33 wt.%) at 80 °C under refluxing conditions to remove amorphous carbon. The purified CNTs were impregnated by a 0.1 mol/L NaOH solution of $Ni(NO_3)_26H_2O$ and ammonium metatungstate and were sonicated for 0.5 h. After being kept at room temperature for 12 h, the mixture was reduced by adding dropwise 0.5 mol/L $NaBH_4$ with the solution of 0.1 mol/L NaOH. The resulting catalyst was washed thoroughly with distilled water and anhydrous ethanol. The as-prepared sample was denoted as x % NiWB (y)/CNTs where x represented the theoretical weight percentage of Ni

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and W in catalyst: x = (Ni + W)/(Ni + W + CNTs) × 100, and y represented the mole ratio of Ni and W.

2.2. Catalyst characterization

XRD measurements were recorded using a Siemens D500 powder diffractometer with Al Kα radiation (40 kV, 30 mA). The surface morphology was characterized by TEM (JEOL JEM2011). The XPS spectra were recorded using Perkin Elmer PHI 5000C instrument. NH_3-TPD was performed by using a Micromeritics Autochem 2920IIinstrument.

2.3. Catalytic experiments

0.5 g microcrystalline cellulose (crystallinity 85%, Alfa Aesar), 0.15 g NiWB/CNTs and 15 mL deionized water were put into a 50 mL stainless steel autoclave and heated to the reactor to the preset temperature and then hydrogen was filled into the reactor with preset pressure. After reaction, the products were analyzed by a HPLC system (Shimadzu LC-20AB) equipped with RI detector and an USPpak MN-431 column.

3. Results and discussion

3.1. Catalyst characterization

Fig. 1 shows the TEM image for the 30% NiWB(1:1)/CNTs catalyst. From the TEM image, we can see that NiWB particles appear to be well distributed over the CNTs surface, and a rather broad distribution of the NiWB particle sizes centered around 15 nm. The SAED picture (inset in Fig. 1) revealed that the fresh NiWB nanoparticles displayed diffraction circle characteristic of amorphous structure [23]. TEM images of other NiWB/CNTs catalysts show that NiWB particles on 20% NiWB(1:1)/CNTs, 25% NiWB(1:1)/CNTs and 35% NiWB(1:1)/CNTs centered around 45 nm, 30 nm and 32 nm respectively (Figure S1 in SI). The relatively large particles could be attributed to particle agglomeration.

XRD patterns are shown in Fig. 2. Only one broad peak around 2θ = 45° appeared in Fig. 2 (a), indicating that the fresh NiWB sample pretreated at room temperature had a typical amorphous structure [32,33]. After the sample was treated at 473 K, the broad peak was not observed, and intensive peaks at 2θ = 45°, 52° appeared in the XRD pattern, attributing to Ni(111) and Ni(200), respectively, indicating that Ni metal particle formed. There are three diffraction peaks at around 26.5°,

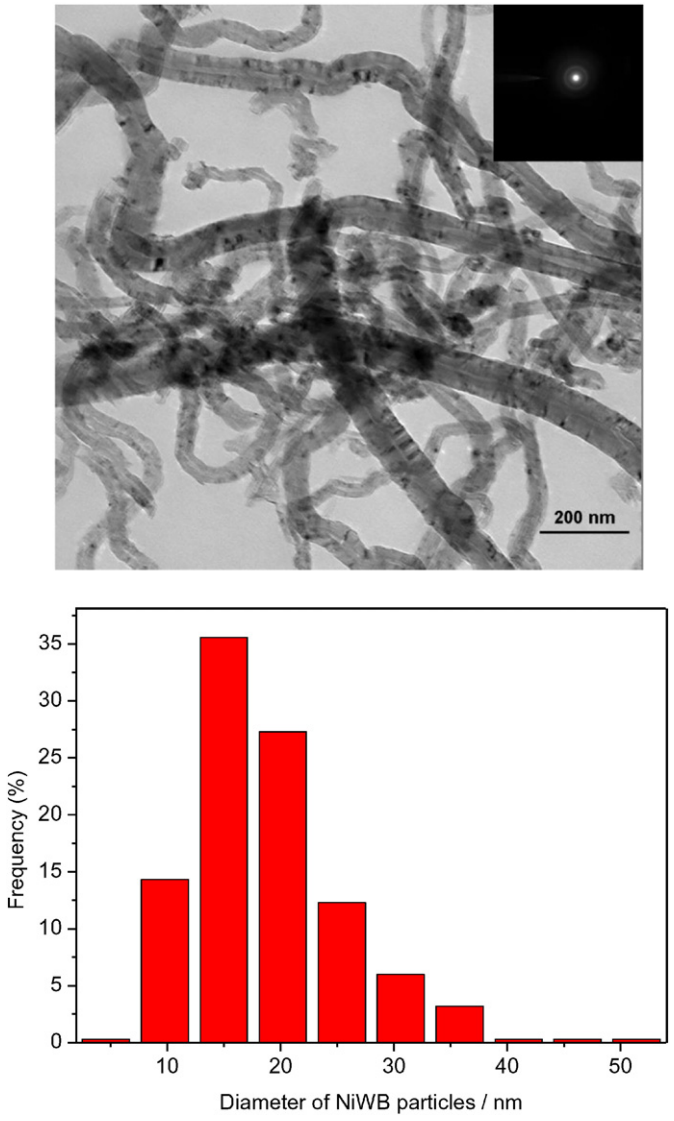

Fig. 1. TEM image and the corresponding histogram of the NiWB particle size distribution of the 30% NiWB(1:1)/CNTs catalyst.

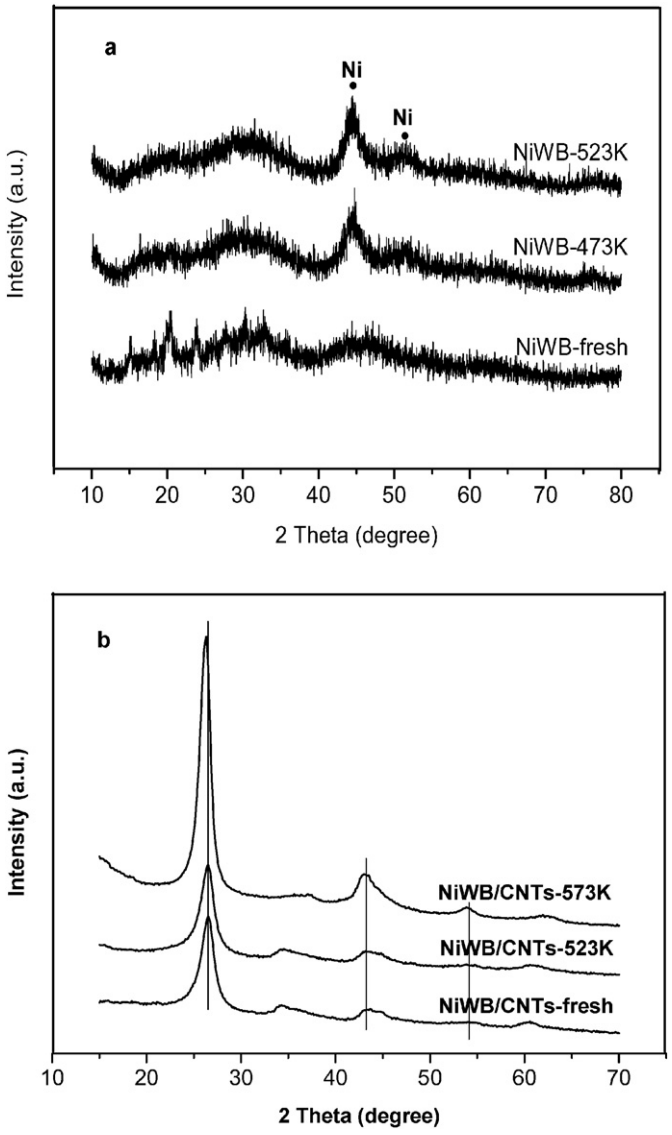

Fig. 2. XRD patterns of (a) NiWB amorphous catalysts and (b) 30% NiWB(1:1)/CNTs catalysts.