



## Short Communication

## Preparation of Ni(Co)–W–B amorphous catalysts for cyclopentanone hydrodeoxygenation

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## ABSTRACT

Ni–Co–W–B, Ni–W–B and Co–W–B catalysts were prepared by chemical reduction method and showed high activity in the HDO of cyclopentanone. Co–W–B had higher thermal stability than Ni–Co–W–B and Ni–W–B catalyst. The conversion of cyclopentanone could be high to 96.6% with a cyclopentanol selectivity of 0.4% and a deoxygenation rate of 95.4%. The HDO activity of the catalyst was related to its thermal stability, surface area, hydrogen supplying ability and Brønsted acid sites.

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## 1. Introduction

Since the oil crisis in the mid 1970s, much attention has been focused on the conversion of wood biomass to liquid fuels [1]. Bio-oil, derived from wood biomass, has been considered as the most potential alternative energy because of the significantly less poisonous gas emission and zero net emission of CO<sub>2</sub> in the bio-oil combustion [2,3]. Unfortunately, the bio-oil contains many kinds of oxy-organics, including furans, phenols, ketones, aldehydes, etc. [4]. These oxy-organics lead to the high oxygen content in the bio-oil, which is responsible for some disadvantages such as poor stability, high viscosity, non-volatility, low heating value, immiscibility with fossil fuels and corrosiveness and tendency to polymerization during storage and transportation [5]. To be used as the engine fuel, the bio-oil needs to be upgraded and its oxygen content reduced. Many upgrading processes have been reported in the bio-oil upgrading, but only the hydrodeoxygenation (HDO) was deemed to be the most direct and effective way for selectively removing oxygen [3].

As reviewed in the papers [3,5], the current catalysts used in the HDO of bio-oil were mainly concentrated on conventional supported cobalt or nickel doped molybdenum or tungsten sulphide catalysts and supported noble metal catalysts. Noble metal catalyst exhibits high catalytic activity in the HDO reactions, but the high cost is its worst weakness. Sulfided catalyst is easily deactivated via the oxidation of the active catalyst phase during the HDO of bio-oil because of the high oxygen content and the low sulfur content in the bio-oil.

Some reports had shown that adding proper amount of sulfiding agent such H<sub>2</sub>S or CS<sub>2</sub> could maintain the catalytic activity or decrease the deactivation rate [6–8], but it would lead to sulfur contamination of the upgraded bio-oil. Therefore, there is a need to prepare a new kind of catalyst with cheap cost and high activity for the HDO process.

Amorphous catalyst has some interesting and intrinsic properties such as a microstructure of long-range disorder and short-range order, and high concentration of coordinative unsaturated sites, leading to its excellent activity and selectivity in the catalytic reactions [9–12]. For example, Chen et al. had prepared a series of Ni–Co–W–B amorphous catalysts with different W contents under the nitrogen protection and found they had very high activity in the hydrogenation of p-chloronitrobenzene [13]. Great efforts had been paid to the HDO of bio-oil on crystallized catalysts using the oxygen-containing model compounds [14–23], but the studies of the HDO of bio-oil on amorphous catalysts were still very few except for our studies [24,25], not to mention the HDO of ketones on amorphous catalyst. Cyclopentanone is one of the typical ketone compounds in bio-oil. Moreover, the final HDO product cyclopentane is supposed to be a good alternative for freon. Therefore, in this study, Ni(Co)–W–B amorphous catalysts were prepared with chemical reduction method and were applied in the HDO of cyclopentanone.

## 2. Experimental

## 2.1. Catalyst preparation

Ni–Co–W–B amorphous catalysts were prepared by the following steps. Sodium tungstate (2.94 g), nickel nitrate and cobalt nitrate

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were dissolved in 100 mL aqueous solution. This mixture solution was placed in a 250 mL three-necked flask. An 80 sodium borohydride aqueous solution (1 mol/L) was added dropwise to the three-necked flask with vigorous agitation at 273 K. Then, the black precipitate was produced. The black precipitate was washed with ultra-pure water several times until the pH=7 to remove the soluble boron species and Na<sup>+</sup> ions, followed by washing with absolute ethanol several times to remove the residual water and water-soluble impurities. Finally, the resulting product was dried under vacuum at 323 K for 8 h. Ni–W–B and Co–W–B catalysts were also prepared as described earlier. The Ni/Co, (Ni + Co)/W, Ni/W or Co/W molar ratio in each case was 1:1. In order to compare the thermal stability of fresh catalysts, the mixture of 0.5 g fresh catalyst and 50 mL dodecane was placed into the autoclave and then heat-treated at 548 K for 10 h under the condition of 4.0 MPa hydrogen pressure. This heated sample was donated as Ni–Co–Mo–B–C, Ni–W–B–C or Co–W–B–C.

## 2.2. Catalyst characterization

Specific surface area was measured by a Quantachrome's NOVA-2100e Surface Area instrument by physisorption of nitrogen at 77 K. X-ray diffraction (XRD) test was carried on a D/max2550 18 kW Rotating anode X-ray Diffractometer with Cu K $\alpha$  ( $\lambda = 1.5418 \text{ \AA}$ ) radiation (40 kV, 300 mA). The  $2\theta$  was scanned over the range of 10–80° at a rate of 10°/min to identify the amorphous structure. Bulk compositions were identified by Inductively Coupled Plasma analysis

(ICP) on a Varian VISTAMPX. The surface composition and surface electronic state were analyzed by X-ray Photoelectron Spectroscopy (XPS) using Kratos Axis Ultra DLD instrument at 160 eV pass energy. Al K $\alpha$  radiation was used to excite photoelectrons. C<sub>1s</sub> = 284.6 eV was used as a reference to correct the binding energy value of each element.

## 2.3. Catalyst activity measurement

The catalyst activity tests were carried out in a 300-mL sealed autoclave. The fresh catalyst (0.05 g), cyclopentanone (10.5 g) and dodecane (89.5 g) were placed into the autoclave. Air in the autoclave was evacuated by pressurization–depressurization cycles with nitrogen and subsequently with hydrogen. The mixture was heated at 10 K/min to desired temperature, then pressurized with hydrogen to 4.0 MPa, stabilized the stirring speed at 700 rpm. During the reaction, liquid samples were withdrawn from the reactor and identified by Agilent 6890/5973 N GC–MS. The amounts of cyclopentanone and products were analyzed by Agilent 7890 gas chromatography using a flame ionization detector (FID) with a 30 m AT-5 capillary column. The conversion, selectivity and deoxygenation rate for each experiment were calculated as follows:

$$\text{Conversion (\%)} = \left(1 - \frac{\text{moles of residual cyclopentanone}}{\text{moles of initial cyclopentanone}}\right) \times 100 \%$$

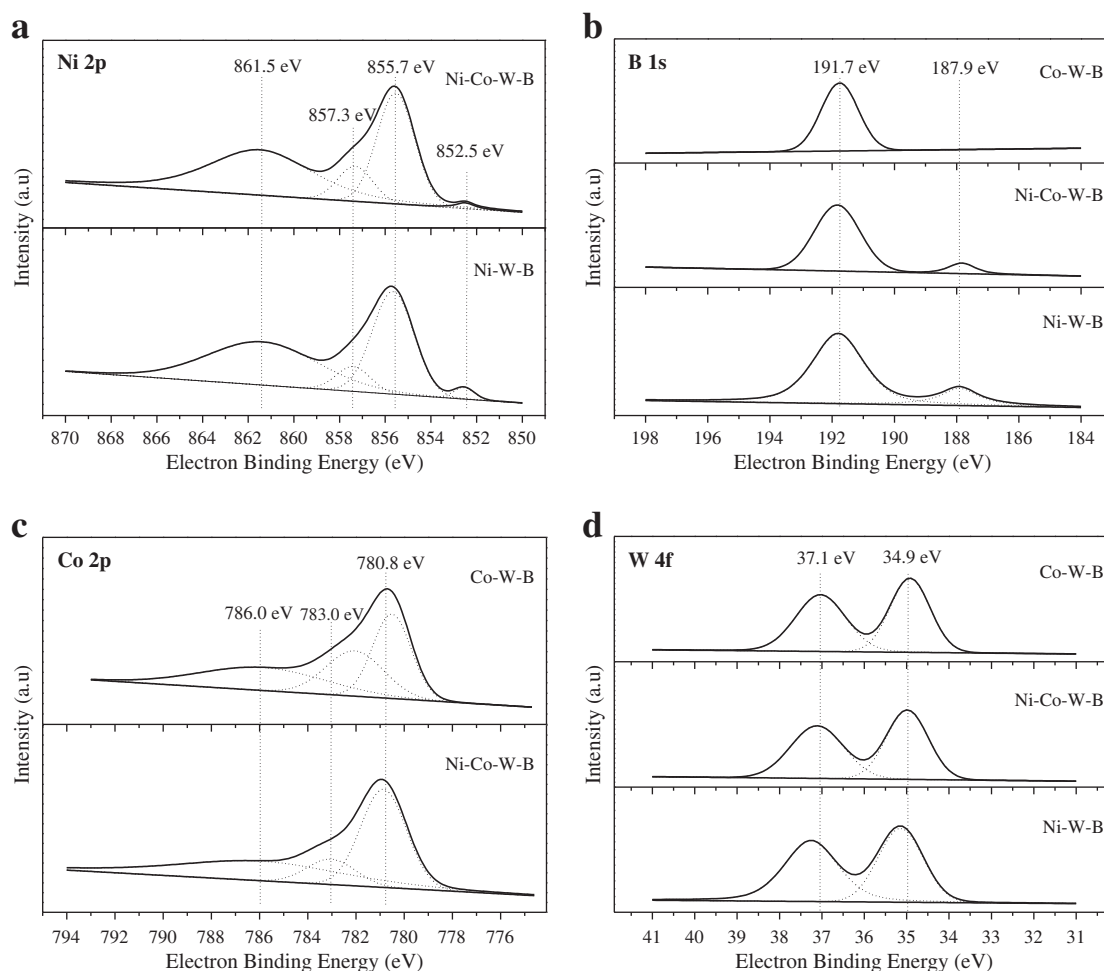


Fig. 1. XPS spectra of (a) Ni 2p, (b) Co 2p, (c) B 1s and (d) W 4f levels of Ni(Co)–W–B amorphous catalysts.

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