



Short communication

## Preparation of Ni–W–P–B amorphous catalyst for the hydrodeoxygenation of *p*-cresol



Weiyan Wang, Sijun Yang, Zhiqiang Qiao, Pengli Liu, Kui Wu, Yunquan Yang\*

School of Chemical Engineering, Xiangtan University, Xiangtan City, Hunan 411105, PR China

### ARTICLE INFO

#### Article history:

Received 2 August 2014

Received in revised form 18 November 2014

Accepted 20 November 2014

Available online 22 November 2014

#### Keywords:

Hydrodeoxygenation

Ni–W–P–B

Catalyst preparation

*p*-Cresol

Bio-oil

### ABSTRACT

Ni–W–P–B amorphous catalysts were prepared by a modified chemical reduction method. The formation of a complex between  $\text{Ni}^{2+}$  and  $\text{NH}_3 \cdot \text{H}_2\text{O}$  inhibited the reaction rate of  $\text{Ni}^{2+}$  with  $\text{BH}_4^-$ , leading to a high  $\text{Ni}^0$  content on the catalyst surface. The effects of Ni/W molar ratio on the catalytic activity in the hydrodeoxygenation (HDO) of *p*-cresol were studied. The deoxygenation degree reached to 100% with a toluene selectivity of 5.1% at 498 K. The HDO reaction temperature and aromatic yield decreased obviously. Some of toluene was produced from the dehydrogenation of 3-methylcyclohexene. Ni–W–P–B exhibited high HDO activity and dehydrogenation activity.

© 2014 Elsevier B.V. All rights reserved.

### 1. Introduction

The increase of energy consumption and emissions of greenhouse gases in the utilization of fossil fuels have aroused a wide research in the exploration of a sustainable and renewable replacement for petroleum based fuel [1–3]. Bio-oil, a liquid fraction derived from the pyrolysis of lignocellulosic materials, is considered as a significant candidate for fuel due to its  $\text{CO}_2$ -neutral and  $\text{SO}_x$ -free emission upon combustion [4]. However, this bio-oil contains high oxygen content, leading to some disadvantages such as low heating value, chemical instability and immiscibility with fossil fuels, which prevents its direct utilization as a transportation fuel. The main challenge for upgrading bio-oil to liquid hydrocarbons is to remove the oxygenated functionalities effectively. One of the most efficient technologies is catalytic hydrodeoxygenation (HDO).

Until now, many studies regarding HDO have been carried out by using model compounds [5–13]. Among these oxygenated functionalities in the bio-oil, phenolic hydroxyl oxygen is considered as the most difficult one to remove because the direct scission of this C–O bond requires the highest activation energy [4], leading to a high reaction temperature for achieving the high deoxygenation degree. For example, K. J. Smith et al. [14] had studied the HDO of phenols on  $\text{MoS}_2$  with different morphologies and found that the highest conversion of *p*-cresol was 75% after 7 h reaction at 623 K and 2.8 MPa of  $\text{H}_2$ . Adopting the synergistic effect between W and Mo and the promoter effect, Wang et al. [15] had studied the HDO of *p*-cresol on Ni–Mo–W–S and obtained a

conversion of 97.8% after 5 h reaction at 573 K and 3.0 MPa of  $\text{H}_2$ . Yang et al. [16] had reported that the conversion of phenol on CoMoP/MgO was 89.8% with a benzene selectivity of 64% at 723 K and 5 MPa of  $\text{H}_2$ . Our previous study [17] had found that *p*-cresol conversion on Ni–P catalyst was only 85.0% after 10 h reaction at 623 K and 4.0 MPa of  $\text{H}_2$ .

The HDO of phenols usually proceeds with two parallel routes: direct hydrogenolysis (DDO) yielding aromatics and hydrogenation–dehydration producing cycloalkanes (HYD). According to the quality standards for clean fuel and World Fuel Oil Regulation IV, benzene and aromatic contents in gasoline were strictly limited because of their harmfulness for human health. The latter one avoids the direct scission of C–O  $\sigma$ -bond in phenolic hydroxyl, which can decrease the HDO reaction temperature but require a high hydrogenation activity for the catalyst. We had reported that Ni–W–B amorphous catalyst exhibited high HDO activity and the activity depended on the numbers of metal  $\text{Ni}^0$  sites and Brønsted acid sites [18]. However,  $\text{Ni}^0/\text{Ni}$  on the surface of Ni–W–B catalyst was only 0.27 [18], suggesting that its HDO activity, especially for hydrogenation, could be further improved. Li et al. [19] had reported that adding P into Ni–B catalyst enhanced its hydrogenation activity. In fact,  $\text{Ni}^{2+}$  can react with  $\text{NH}_4^+$  to produce a complex, which might decrease the reaction rate of  $\text{Ni}^{2+}$  with  $\text{BH}_4^-$  after forming the complex and then promote the reduction of  $\text{Ni}^{2+}$  to  $\text{Ni}^0$ . Therefore, aiming to prepare a HDO catalyst with high activity, we used  $\text{Ni}(\text{NO}_3)_2$ ,  $\text{Na}_2\text{WO}_4$ ,  $\text{NH}_3 \cdot \text{H}_2\text{O}$ ,  $\text{NaH}_2\text{PO}_2$  and  $\text{NaBH}_4$  as raw materials to synthesize Ni–W–P–B amorphous catalysts and studied their activity by taking the HDO of *p*-cresol as a probe.

\* Corresponding author.

E-mail address: [yangyunquan@xtu.edu.cn](mailto:yangyunquan@xtu.edu.cn) (Y. Yang).

## 2. Experimental

### 2.1. Catalyst preparation

Ni–W–P–B amorphous catalysts were prepared by the following steps. NiSO<sub>4</sub>·6H<sub>2</sub>O (1.57 g) and NaH<sub>2</sub>PO<sub>2</sub> (1.0 g) were dissolved in 25 mL H<sub>2</sub>O solution, and then NH<sub>3</sub>·H<sub>2</sub>O (25 wt.%, 1.6 g) and Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O were added into the above solution following placed in a 250 mL three-necked flask. A 20 mL NaBH<sub>4</sub> (1.0 g) aqueous solution was added dropwise to the three-necked flask with vigorous agitation at 273 K. The resulting black precipitate was washed with water and ethanol. Finally, the sample was dried under vacuum at 323 K for 4 h and was donated as Ni–W–X, where X represented the Ni/W molar ratio in the initial solution.

### 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. The prepared samples were dehydrated at 460 K using vacuum degassing for 12 h before analysis. X-ray diffraction (XRD) test was carried on a D/max 2550 18 kW Rotating anode X-ray Diffractometer with Cu Kα (λ = 1.5418 Å) radiation (40 kV, 300 mA). The surface composition and surface electronic state were analyzed by X-ray Photoelectron Spectroscopy (XPS) using Kratos Axis Ultra DLD instrument.

### 2.3. Catalyst activity measurement

The catalyst activity tests were carried out in a 300-mL sealed autoclave. The fresh catalyst (0.2 g, particle size ≤ 75 μm), *p*-cresol (13.51 g) and dodecane (86.49 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 298 K, then pressurized with hydrogen to 4.0 MPa, and stabilized the stirring speed at 900 rpm. During the reaction, the pressure, stirrer speed, and temperature were kept constant. Liquid samples were withdrawn from the reactor and analyzed by Agilent 6890/5973N GC–MS. To separate the reaction products, the temperature in the GC oven was heated from 313 K to 358 K with the ramp of 20 K/min, held at 358 K for 4.0 min, then heated to 473 K at a rate of 20 K/min and kept at 473 K for 5.0 min. The carbon balance in the sample for each of experiment was better than 95 ± 3%. External and internal mass transfer limitations could be neglected because of the small catalyst particle size and high stirring speed. The amounts of *p*-cresol and products were analyzed by Agilent 7890 gas chromatography using a flame ionization detector (FID) with a 30 m AT-5 capillary column. The deoxygenation degree (DD) for each experiment was calculated as follows:

$$\text{Deoxygenation degree (DD, wt.\%)} = \left( 1 - \frac{\text{oxygen content in the final organic compounds}}{\text{total oxygen content in the initial material}} \right) \times 100\%.$$

## 3. Results and discussion

### 3.1. Characterization of Ni–W–P–B catalysts

Fig. 1 shows the XP spectra of Ni 2p, B 1s, P 2p and W 4f levels of Ni–W–P–B samples. Each of the spectra was deconvoluted, and the relative content of each state was calculated based on the corresponding peak area. It had reported that the standard binding energy of elemental Ni, B, P and W was 853.0, 187.0, 130.4 and 31.0 eV [19,20], respectively, revealing that all species in the prepared catalysts were present in both oxidized state and elemental state. Two strong peaks at 852.4 and 855.8 eV and one weak peak at 860.4 eV appeared in Fig. 1a, corresponding to metal Ni, NiO and Ni(OH)<sub>2</sub> [20,21], respectively. All B 1s

spectrums displayed two peaks at 187.8 and 192.1 eV. The former one was attributed to elemental B, while the latter one was attributed to B<sup>3+</sup> [20,21]. In the Fig. 1c, the peaks around 129.5 and 133.4 eV were assigned to elemental phosphorus with metal nickel and oxidized phosphorus, respectively. In comparison with the standard binding energies of pure Ni, B and P, a positive shift of the elemental B and a negative shift of the elemental Ni and P were observed in all the as-prepared samples. These observations implied that the elemental B donated partial electrons to the metal Ni and the phosphorus accepted electrons from the nickel metal, which was in good accordance with previous investigations [22,23]. The peaks around 31.4 eV and 33.4 eV in Fig. 1d were attributed to W<sup>0</sup>, while the peaks around 35.6 eV and 37.7 eV were attributed to WO<sub>3</sub> [20]. The appearance of W<sup>0</sup> suggested that some W<sup>6+</sup> was reduced to metal W.

The surface compositions of Ni–W-2, Ni–W-1, Ni–W-0.5 and Ni–W-0.33 samples are summarized and listed in Table 1. With the decrease of Ni/W mole ratio in the raw material, Ni/W mole ratio on the catalyst surface was decreased from 1:0.22 for Ni–W-2 to 1:4.36 for Ni–W-0.33. This resulted from the reaction of Ni<sup>2+</sup> with NH<sub>4</sub><sup>+</sup>. The amount of Ni<sup>2+</sup> in the reaction system decreased gradually, but the total of NH<sub>4</sub><sup>+</sup> kept constant. After forming the complex, the remained NH<sub>4</sub><sup>+</sup> was increased with the decrease of Ni<sup>2+</sup>, leading to the rise on pH value for the reaction solution. As a result, the reaction of Ni<sup>2+</sup> with BH<sub>4</sub><sup>−</sup> was inhibited and then decreased Ni/W mole ratio on the catalyst surface. On the other hand, the formation of complex hindered the precipitation reaction between Ni<sup>2+</sup> and OH<sup>−</sup> to produce Ni(OH)<sub>2</sub>, causing the increasing Ni<sup>0</sup> content and decreasing Ni(OH)<sub>2</sub> on the catalyst surface. Table 1 showed that Ni<sup>0</sup> content on the catalyst surface in this study was much higher than that in the previous study [18]. This suggested that adding NH<sub>3</sub>·H<sub>2</sub>O was beneficial to improve the Ni<sup>0</sup> content on the catalyst surface, but adding exceeding NH<sub>3</sub>·H<sub>2</sub>O lowered the total of Ni content.

As shown in Fig. 2, all the samples displayed only one broad peak centered at 2θ = 45°, presenting a typical amorphous structure [19–21]. The intensity of this peak (2θ = 45°) corresponded to amorphous degree [22]. Ni–W-2 exhibited a weaker peak than Ni–W-1, indicating the higher amorphous degree of Ni–W-2 and the lower amorphous degree of Ni–W-1. It had reported that tungsten oxides and phosphorus oxide could act as dispersant agents [20,24]. Hence, W<sup>6+</sup> and P<sup>n+</sup> species could prevent the particle agglomeration efficiently, resulting in the high amorphous degree. On the contrary, there existed a strong interaction between Ni<sup>0</sup> and B<sup>0</sup> and Ni<sup>0</sup> and P<sup>0</sup> in the prepared catalysts, leading to the promoted agglomeration of particles. The more the B<sup>0</sup> and P<sup>0</sup> contents on the catalyst surface are, the lower the amorphous degree. The surface area results also supported this inference. As shown in Table 1, the surface area decreased in the order of Ni–W-0.5 (28.0 m<sup>2</sup>/g) > Ni–W-2 (24.5 m<sup>2</sup>/g) > Ni–W-0.33 (22.4 m<sup>2</sup>/g) > Ni–W-1 (17.2 m<sup>2</sup>/g). In addition, the XPS results demonstrated that the prepared catalysts contained W<sup>0</sup>, W<sup>6+</sup>, P and P<sup>n+</sup>, but these species were not observed in Fig. 2, indicating that these species were in amorphous state and dispersed evenly in the catalyst.

### 3.2. Hydrodeoxygenation of *p*-cresol on Ni–W–P–B catalysts

The conversion and product selectivity versus reaction time in the HDO of *p*-cresol on Ni–W-1 at 498 K are shown in Fig. 3a. Methylcyclohexane, 3-methylcyclohexene, toluene, 4-methylcyclohexanol and 4-methylcyclohexanone were produced during *p*-cresol HDO reaction. After 1 h, the conversion reached to 99.6% with a selectivity of 51.1% 4-methylcyclohexanol. Then, the HDO reaction in this system was changed to the HDO of 4-methylcyclohexanol. The selectivity of methylcyclohexane increased to 92.6% while the selectivity of toluene increased to 5.1% for 5 h. Hence, it was concluded that the main reaction route was HYD, where 4-methylcyclohexanone and 4-methylcyclohexanol acted as intermediates. The toluene selectivity increased from 2.1% to 5.1% in the following 4 h. However, according to

Download English Version:

<https://daneshyari.com/en/article/49467>

Download Persian Version:

<https://daneshyari.com/article/49467>

[Daneshyari.com](https://daneshyari.com)