



Catalytic conversion of guaiacol to alcohols for bio-oil upgrading

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ARTICLE INFO

Article history:

Received 13 February 2015

Revised 17 April 2015

Accepted 30 June 2015

Available online 10 August 2015

Keywords:

Hydrogenation

Hydrodeoxygenation

Guaiacol

Bio-oil upgrading

Biofuel

ABSTRACT

Guaiacol was chosen to represent O-containing chemicals with lower effective hydrogen carbon ratio (H/C_{eff} factor) in bio-oil, and the hydrodeoxygenation of guaiacol was investigated over non-precious and non-sulfided catalysts. Effects of metal composition, reaction temperature, and hydrogen pressure on conversion and selectivity were investigated systematically. Among various compositions of catalysts, NiCo/CNT exhibited best performance of guaiacol conversion with higher selectivity towards desired alcohols with higher H/C_{eff} factor. The reaction pathways of guaiacol in aqueous were proposed based on the product analyzed. Results show that metal composition and temperature have great effects on the conversion of guaiacol and the yields of desired products.

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1. Introduction

Recently the utilization of biomass to produce liquid fuels and chemicals has attracted increasing attention for the decrease of petroleum reserves. Many processes have been developed for the transformation of biomass to liquid fuels (so called bio-oil) [1]. The application of bio-oil was CO_2 neutral, and could not lead to the emission of SO_x for the negligible content of sulfur in bio-oil [1]. However, the obtained bio-oil cannot be directly used as a transport fuel due to the presence of different kinds of oxygen-containing compounds such as organic acids, aldehydes, ketones, phenols, etc. [2–4]. Efforts are needed to develop the upgrading processes to remove oxygen content including hydrodeoxygenation [4–8], esterification [9], etc., among which, hydrodeoxygenation (HDO) has become an attractive and effective method for the improvement of bio-oil quality.

It was widely reported that it is reasonable to choose model compounds, instead of real bio-oil for initial screening of catalysts [4,8,10–12]. HDO of model compounds mixture was also carried out over sulfided CoMo/ γ - Al_2O_3 and NiMo/ γ - Al_2O_3 catalysts [5,11,12], among which, guaiacol was an excellent model compound for bio-oil which contains hydroxyl and methoxy groups [13,14] with very low effective hydrogen carbon ratio ($H/C_{eff} = 0.57$). Hydrogenation of guaiacol catalyzed by transition-metal-based catalysts [5,15–17] or noble metal catalysts [18,19] was carried out with phenols and saturated deoxygenated hydrocarbons as products, respectively. However, those transition metal sulfide catalysts deactivated gradually during the

reaction for the loss of sulfur and the oxidation of active sulfide phase. The high cost of noble metal based catalysts would make them unprofitable for the large-scale hydroprocessing of bio-oil. In addition, these reactions always required high temperatures and pressures, which would also lead to the increase of cost. Thus, it was imperative to develop possible alternatives for the sulfide catalysts and noble metal catalysts for the upgrading of bio-oil and increase of H/C_{eff} factor at relatively lower temperature and hydrogen pressure.

Carbon nanotube (CNT) was a suitable support [8,20–22] compared with Al_2O_3 support and ZSM-5, owing to its intrinsic properties such as chemical inertness, and thermal stability [23,24]. In this study, CNT supported catalysts were prepared and successfully introduced to the conversion of guaiacol, and the final product turned to be mainly cyclohexanol with higher H/C_{eff} factor. And the upgrading of bio-oil was investigated over (10 + 10) wt% NiCo/CNT catalyst. The properties of raw bio-oil are improved to a certain extent after the upgrading process.

2. Experimental

2.1. Chemicals and catalyst preparation

All of the reagents except CNT were of analytic purity grade, and were purchased from local Sinopharm Chemical Reagent. CNT was purchased from Chengdu Organic Chemicals Co., Ltd. (purity >97%), which was synthesized from natural gas by catalytic cracking method. The raw bio-oil was obtained by vacuum pyrolysis of pine sawdust.

CNT supported bimetallic catalysts ($(x_1 + x_2)$ wt% NiCo/CNT, x_i represents the Ni or Co loading amount) were prepared in accordance with our previous studies [8,22].

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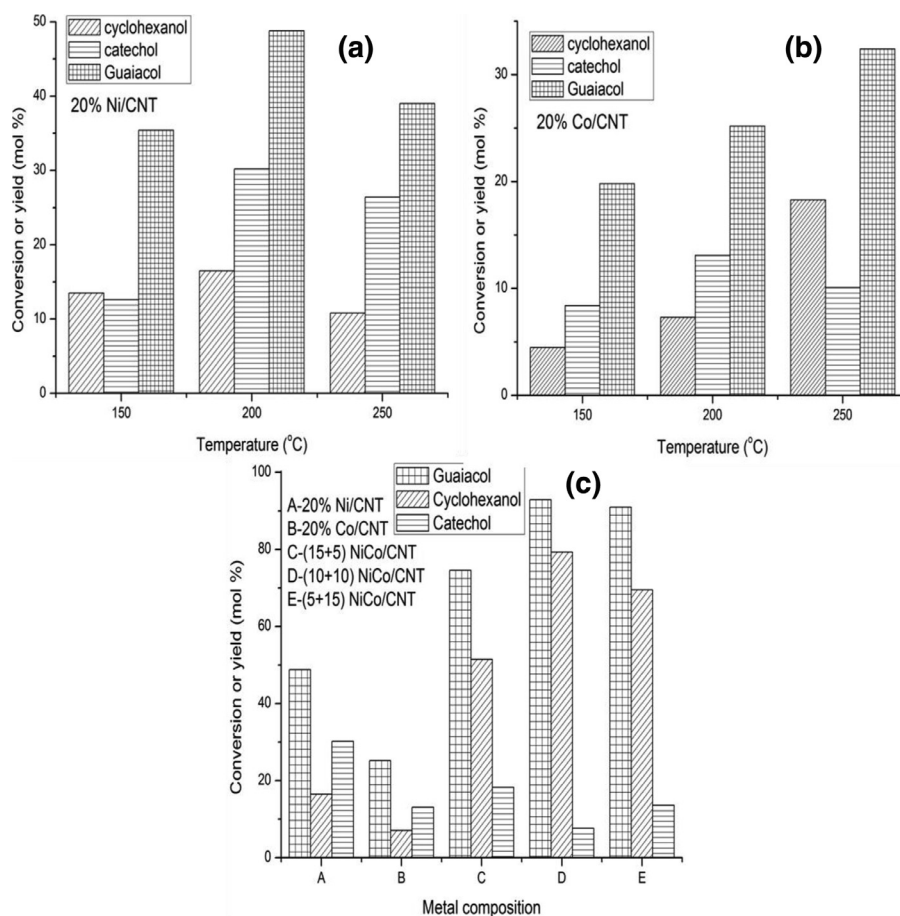


Fig. 1. Effect of the metal composition of CNTs supported catalysts.

2.2. Catalyst characterization

The catalysts were characterized by X-ray diffraction (XRD) on a Rigaku D/max-A instrument. The X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB-250. The spectrometer microstructure of the catalyst was examined with transmission electron microscopy (TEM) (Tecnai G2 20). The NH_3 -TPD and H_2 -TPR studies were carried out in a quartz tube reactor with a thermal conductivity detector.

2.3. Activity test and analytical methods

All the aqueous-phase catalytic hydrodeoxygenation of guaiacol was carried out in a 100 mL stainless autoclave equipped with an electromagnetic driven stirrer. For each run, 47 mL of water, 3 mL of guaiacol and 2 wt% of catalyst were added to areactor vessel, then the hydrogenation reaction was carried out in a temperature range of 100–250 °C to evaluate the effect of reaction temperature, for a reaction time of 2–8 h to evaluate the effect of reaction time. In addition, initial hydrogen pressure was also taken into consideration. After displacing air, the hydrogen pressure was raised to a certain value. Then the reactor was heated to the desired temperature and the stirring speed fixed to 600 rpm to eliminate the diffusion effects [8,22]. Finally, the reactor was quickly cooled down, and the reaction products were separated from the catalysts by centrifugation. The aqueous phase was analyzed by gas chromatography (Ouhua GC 9160) equipped with a SE-54 capillary column (30 m×0.32 mm×0.5 μm). The product yield and selectivity are calculated and defined as fol-

lows:

$$X_{GUA} = \frac{n_{GUA}^0 - n_{GUA}}{n_{GUA}^0} \times 100\%, \quad Y_i = \frac{n_i}{n_{GUA}^0} \times 100\%,$$

$$S_i = \frac{Y_i}{X_{GUA}} \times 100\%$$

where n_{GUA}^0 and n_{GUA} depict the amounts of guaiacol before and after reaction, respectively, in mol; and n_i is the amount of reaction product, in mol. The carbon balance accounting for the HDO reactions was approximately 95%. All the experiments were carried out two times and the results agreed within 5%.

The effective hydrogen carbon ratio ($\text{H}/\text{C}_{\text{eff}}$ factor) [25] is calculated and defined as follows:

$$\text{H}/\text{C}_{\text{eff}} = \frac{H - 2O}{C}$$

where H , O and C are the moles in the O-contained compounds.

3. Results and discussion

3.1. Hydrodeoxygenation of guaiacol

3.1.1. Effect of metal composition

As presented in Fig. 1, the hydrodeoxygenation of guaiacol was carried over both monometallic catalysts and bimetallic catalysts. The conversion of guaiacol over monometallic catalysts was much lower as compared with that of bimetallic catalysts. The highest conversion rate over 20% Ni/CNT was up to 48.8% when the reaction was carried out at 200 °C; and the highest conversion rate over 20% Co/CNT was

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