



Catalytic conversion of guaiacol in ethanol for bio-oil upgrading to stable oxygenated organics



Wen Chen^a, Zhongyang Luo^a, Chunjiang Yu^{a,*}, Yi Yang^a, Guoxiang Li^a, Jixiang Zhang^{a,b}

^a State Key Laboratory of Clean Energy Utilization, Zhejiang University, Hangzhou 310027, PR China

^b State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Beijing 102249, PR China

ARTICLE INFO

Article history:

Received 1 January 2014

Received in revised form 22 May 2014

Accepted 23 May 2014

Available online 11 June 2014

Keywords:

Guaiacol

Catalysts

Ethanol

Stable oxygenated organics

Mass and energy efficiency

ABSTRACT

In this paper, guaiacol was used as a model compound of bio-oil and its catalytic conversion was carried out in ethanol. The effect of supports (SBA-15, ZrO₂/SBA-15 and SO₄²⁻/ZrO₂/SBA-15) was studied on Pt–Ni based catalysts whereas the effect of active metals was investigated over C-supported Ru, Pt and Pd catalysts. Among the tested catalysts, Ru/C showed the best performance of total guaiacol conversion with high selectivity towards the desired products, cyclohexanol and 2-methoxycyclohexanol (MCH). The reaction pathways of guaiacol in ethanol were clarified based on the product analysis. With the catalysis of Ru/C, the effects of reaction temperature, initial hydrogen pressure, and other typical compounds from bio-oil were investigated. Temperatures had negligible effect on both the conversion of guaiacol and the yields of desired products in the range of 140–260 °C. Guaiacol conversion decreased significantly at initial hydrogen pressures lower than 4.0 MPa. The presence of furfural, acetone, and acetic acid decreased the conversion of guaiacol dramatically while the addition of water had a smaller impact. Further work revealed that the mass and energy efficiency of converting guaiacol into MCH are 100% and 97%, respectively.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Diminishing fossil fuel reserves, increasing demands for fuels especially liquid fuels and environmental concerns call for clean and sustainable fuel substitutes. Biomass has received widespread attention as the only renewable resource that can be converted to liquid fuels [1]. Since the first-generation biofuels have the potential to pose a threat to the world food supply, a lot of efforts have been paid to lignocellulosic biomass. Three major pathways including syngas production by gasification, bio-oil production by pyrolysis or liquefaction, and aqueous sugar by hydrolysis have been proposed to convert lignocellulosic biomass into liquid fuels [2]. Pyrolysis of biomass is a thermal decomposition process in the absence of oxygen to obtain char, gas, and liquid product called bio-oil [3]. High yield of bio-oil could be achieved by fast pyrolysis. However, bio-oil presents some undesirable properties such as low heating value, low pH value, high viscosity, and instability. It is widely accepted that bio-oil from fast pyrolysis of biomass cannot be considered as a realistic candidate for large scale liquid transport fuel substitution unless it is upgraded [4].

Hydrodeoxygenation and catalytic cracking are considered as two catalytic methods to upgrade bio-oil. Unfortunately, these two upgrading

methods are far from industrialization for low liquid yield and severe catalyst deactivation [5,6]. In fact, stable and combustible oxygenated organics such as alcohols (ethanol, n-butanol) and esters (bio-diesel) can be used as petroleum substitutes or gasoline additives. Recently, researchers have proposed to upgrade bio-oil in supercritical fluids (mainly methanol and ethanol) to convert unstable organics such as aldehydes, acids and phenols to stable and combustible oxygenated organics. As shown in the work by Peng et al. [7,8], the properties of bio-oil were improved significantly by upgrading bio-oil in supercritical ethanol. Tang et al. [9] carried out hydrocracking of pyrolytic lignin in supercritical ethanol over Ru-based meso-porous catalysts (Ru/ZrO₂/SBA-15 and Ru/SO₄²⁻/ZrO₂/SBA-15). Most of the pyrolytic lignin was converted to phenols, guaiacols and anisoles, etc. Zhang et al. [10] concluded that SO₄²⁻/ZrO₂/SBA-15-supported catalysts gave better performance than HZSM-5 supported catalysts in supercritical upgrading of bio-oil. Dang et al. [11] investigated the effect of reaction conditions on supercritical upgrading with the catalysis of Pt/SO₄²⁻/ZrO₂/SBA-15. However, in supercritical upgrading of bio-oil, acids and aldehydes can be completely converted while phenols are difficult to be converted and the reaction pathways of phenols in this upgrading process are still unclear.

Lignin derived compounds (phenols, guaiacols, and syringols) make up about 30 wt.% of bio-oils [12,13]. Guaiacyl unit is a primary structure in lignin [14]. A large number of guaiacyl compounds, including guaiacol, vanillin and eugenol can be detected in bio-oil. Lignin derived phenols such as guaiacol and substituted guaiacols tend to repolymerize forming heavy hydrocarbons and coke during upgrading process [15,20,

* Corresponding author at: State Key Laboratory of Clean Energy Utilization, Zhejiang University, Zheda Road 38, Hangzhou 310027. Tel.: +86 57187952801; fax: +86 57187951616.

E-mail address: chunjiang@cmee.zju.edu.cn (C. Yu).

30]. Therefore, the catalytic conversions of guaiacol have been extensively studied. Numerous catalysts including traditional CoMo and NiMo catalysts and noble metal catalysts (Rh, Ru, Pd) were employed. Over CoMo and NiMo catalysts, guaiacol experienced demethylation, demethoxylation, and deoxygenation, followed by benzene ring saturation [16–18]. Compared with traditional Co–Mo and Ni–Mo catalysts, noble metal catalysts exhibited higher catalytic activity [16]. Besides, the reaction pathways of guaiacol over noble metal catalysts (Ru, Pd, and Rh) were different from those over traditional catalysts. Guaiacol went through benzene ring saturation followed by demethoxylation and dehydroxylation over noble metal catalysts [16,19,20]. However, the reaction pathways of guaiacol over Pt-based catalysts were similar to those over CoMo or NiMo catalysts [38,39].

Most of the studies were carried out in aqueous phase or in nonpolar solvent (n-decane or n-hexadecane) while the papers about the conversion of guaiacol in ethanol were limited. To elucidate the reaction pathways of phenols in upgrading of bio-oil in supercritical monoalcohols (ethanol or methanol), guaiacol was employed as the model compound and ethanol was used as the reaction solvent. In our previous study [21], bimetallic Pt–Ni catalyst exhibited higher catalytic activity than monometallic catalyst (Pt, Pd, and Ru) for the conversion of furfural in supercritical ethanol. In this paper, Pt–Ni based catalysts (Pt–Ni/SBA-15, Pt–Ni/ZrO₂/SBA-15, and Pt–Ni/SO₄²⁻/ZrO₂/SBA-15) were employed to study the effect of supports. SBA-15 based supports were selected as they were widely used in supercritical upgrading of bio-oil as illustrated previously. The catalytic activities of different noble metal catalysts were investigated by Ru/C, Pd/C, and Pt/C as they have been widely used for model compound and real bio-oil hydrogenation [22,23,26,31,34–37]. Subsequently, the effects of reaction conditions and other typical compounds (aldehydes, ketones, acids, and water) were investigated. The calculation of mass and energy efficiency of the reactions of guaiacol to the desired products was conducted as our further work.

2. Experimental and method

2.1. Materials

SBA-15, zirconium nitrate pentahydrate (Zr(NO₃)₄·5H₂O), cetyltrimethylammonium bromide (CTAB), sulfuric acid, chloroplatinic acid (H₂PtCl₆·6H₂O), and Ni(NO₃)₂·6H₂O were purchased to prepare the Pt–Ni based catalysts. Self-made Pt–Ni based catalysts together with commercially available 5 wt.% Ru/C, 5 wt.% Pd/C, and 5 wt.% Pt/C were used in this study. Guaiacol (99.0%), acetic acid (99.5%), furfural (99%), and acetone (99.5%) were employed as the reactants and ethanol was used as the solvent. Cyclohexanol (99.0%) and 2-methoxycyclohexanol (MCH) (98%) were used as external standards. All chemicals were commercially available (Appendices Table A1) and used as received without further treatment.

2.2. Catalyst preparation and characterization

ZrO₂/SBA-15 and SO₄²⁻/ZrO₂/SBA-15 were prepared via a two-step wetness impregnation method according to Li [24]. 2 wt.% Pt–10 wt.% Ni/SBA-15 (designated as PNS), 2 wt.% Pt–10 wt.% Ni/ZrO₂/SBA-15 (designated as PNZ), and 2 wt.% Pt–10 wt.% Ni/SO₄²⁻/ZrO₂/SBA-15 (designated as PNSZr) were prepared by the incipient wetness co-impregnation method. The detailed description of the preparation methods was supplied in Appendices.

The characterization of Pt–Ni based catalysts was conducted prior to activation. X-ray diffraction (XRD) analysis was conducted on an X'Pert PRO X-ray diffractometer using CuKα radiation over 2θ ranges from 10° to 70° (Appendices Fig. A1). N₂ adsorption–desorption isotherms were measured by a Micromeritics ASAP 2020 system. All samples were pretreated in vacuum at 200 °C for 2 h. The specific surface area was calculated according to the Brunauer–Emmett–Teller (BET) equation. The

total pore volume was determined from the adsorption and desorption branches of the nitrogen isotherms at P/P₀ = 0.97.

Temperature-programmed desorption of ammonia (NH₃-TPD) was conducted to characterize the acidity of Pt–Ni based catalysts. In a typical run, 0.1 g of sample was pretreated at 500 °C in a flow of He (40 mL/min) for 1 h followed by the adsorption of NH₃ (10% in He, 30 mL/min) at 60 °C for 1 h. Then, the sample was treated in a flow of He (50 mL/min) at 100 °C for 90 min to remove the physically adsorbed NH₃, after which the sample was heated to 700 °C at a ramp of 10 °C/min under He flow (40 mL/min). The desorbed NH₃ was detected by a Mass Spectrometry (QIC20) system. The mass number of 17 was used to track NH₃ desorption.

2.3. Experimental procedure and product analysis

All the reactions were conducted in a 100 mL stainless steel batch autoclave equipped with an electrical heating jacket and a mechanical overhead agitator. The Pt–Ni based catalysts were activated in flowing H₂ at 400 °C for 3 h prior to reactions. In a typical run, 1.0 g of guaiacol was dissolved in 20 mL of ethanol as feedstock. The feedstock and 0.5 g of catalyst were added into the autoclave. After the leakage test, the autoclave was flushed five times with N₂ and H₂ respectively to exclude the air inside, followed by filling the reactor with H₂ to build up an initial pressure (2.0 MPa–5.0 MPa). The reactor was heated to the reaction temperature (140–260 °C) in 1 h, and the isothermal reaction proceeded for 3 h with stirring at 700 rpm. After the reactor was cooled to room temperature, the liquid products and the spent catalyst were recovered and separated, while the gas products were discharged without further analysis.

The liquid products were qualitatively analyzed by Gas chromatography–Mass Spectrometry (GC–MS, Thermo Fisher) with a DB-wax column (30 m × 0.25 mm × 0.25 μm). The injector temperature was 260 °C in split mode and the carrier gas was nitrogen. The GC–MS operating conditions were as follows: the oven temperature was 40 °C for 3 min, heated to 180 °C at 4.0 °C/min, then to 260 °C at 10 °C/min and held at 260 °C for 10 min. Compounds were identified by means of the National Institute of Standards and Technology (NIST) library. The peak area normalization method was applied to get the relative content of each compound (Appendices). The conversion of guaiacol and the yields of cyclohexanol and MCH were determined by GC–FID (Agilent 7890) with an HP-5 column (30 m × 0.25 mm × 0.25 μm) according to the external standard method. The GC–FID was equipped with an autosample injection instrument, which guaranteed that the amount of sample injected was 1 μL for all samples. Every sample was tested three times and the deviation was within 5%. Guaiacol conversion (X_{GUA}), product yields (Y), and product selectivities (S) were calculated according to Eqs (1)–(33).

$$X_{\text{GUA}} = \frac{n_{\text{initial GUA}} - n_{\text{residual GUA}}}{n_{\text{initial GUA}}} \quad (1)$$

$$Y(i) = \frac{n(i)}{n_{\text{initial GUA}}} \quad (2)$$

$$S(i) = \frac{Y(i)}{X_{\text{GUA}}} \quad (3)$$

where $n_{\text{initial GUA}}$, $n_{\text{residual GUA}}$, and $n(i)$ represent the mole number of initial guaiacol, guaiacol remained after reaction, and reaction products, respectively.

2.4. Mass and energy efficiency calculation

Various methods to upgrade bio-oil have been proposed, however, none of them have been commercialized. Low mass and energy

Download English Version:

<https://daneshyari.com/en/article/209741>

Download Persian Version:

<https://daneshyari.com/article/209741>

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