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Hydrotreatment of bio-oil over Ni-based catalyst

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HIGHLIGHTS

- ▶ Ni/HZSM-5 catalyst possesses the catalytic activity for cracking and hydrogenation.
- ▶ Cracking reaction and hydrogenation reaction take place simultaneity during the hydrotreating process.
- ▶ Reaction temperature has great effect on product selectivity for benzene and cyclohexane.
- ▶ The pH value of bio-oil increased from 2.27 to 4.07 after upgrading.

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ABSTRACT

Inexpensive non-sulfided Ni-based catalysts were evaluated for hydrotreatments using phenol as model compound. HZSM-5, a zeolite with different ratio of Si/Al and γ-Al_2O_3 were impregnated with $Ni(NO_3)_2{\cdot}6H_2O$ and calcined at 450 °C. Conversion rates and product distribution for treatment of phenol at 160–240 °C in the presence of catalysts with nickel loads of 6, 10, 14 and 17 wt.% were determined. Phenol conversion was highest (91.8%) at 240 °C in the presence of HZSM-5(Si/Al = 38) loaded with 10% Ni. When hydrotreatment was carried out with bio-oil obtained from pyrolysis of pine sawdust under the optimal conditions determined for phenol, the pH of bio-oil increased from 2.27 to 4.07, and the hydrogen content increased from 6.28 to 7.01 wt.%. The decrease in acidity is desirable for the use of upgraded bio-oil.

1. Introduction

Biomass is a promising alternative energy source owing to its renewability and zero emission (Zhang et al., 2005). Fast pyrolysis is the leading method for conversion of biomass to liquid products, known as bio-oils; however, these oils cannot be directly used as transportation fuels due to their high oxygen and water content (Fisk et al., 2009; Peng et al., 2009). The oxygenated compounds in bio-oil cause high viscosity, poor thermal and chemical stability, corrosion and immiscibility with hydrocarbon fuels (Gong et al., 2011; Scholze et al., 2001; Vitolo et al., 2001;Yang et al., 2009).Consequently, upgrading is needed to reduce the oxygen content.

Hydrodeoxygenation (HDO) is considered the most effective method for bio-oil upgrading (Ardiyanti et al., 2011; Gandarias et al., 2008; Yang et al., 2009; Zhao et al., 2009) and hydrodesulfurization (HDS) catalysts such as sulfided Co–Mo and Ni–Mo supported on γ-Al_2O_3 have been employed (Bunch et al., 2007; Gandarias et al., 2008; Senol et al., 2007). However, such HDS catalysts are not desirable for bio-oil hydrotreating because HDS catalysts require the addition of sulfur-containing compounds, such as H_2S or thiophene, in the reaction zone to keep the catalysts active, which increase the contamination risk of bio-oil (Bui et al., 2011) and because water in bio-oil can react with alumina (Laurent and Delmon, 1994; Zakzeski et al., 2010). For example, alumina is known to be metastable under hydrothermal conditions and can partially transform into boehmite under processing conditions. In addition, pyrolysis oil has been upgraded by high pressure thermal treatment (Mercader et al., 2010a), followed by co-processing in standard refinery units (Mercader et al., 2010b). Catalysts based on Pd and Pt have also been studied due to their high selectivity towards alkanes (Bejblová et al., 2005; Díaz et al., 2007; Fisk et al., 2009; Zhao et al., 2009; Oasmaa et al., 2010), but the treatments were carried out at over 350 °C, facilitating production of polymer and coke-like products and causing catalyst deactivation (Adjaye and Bakhshi, 1995; Vitolo et al., 2001; Yang et al., 2009). Furthermore, since HDO of bioliquids is expected to be a large-scale process, employment of noble metal-based catalysts could

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