



Hydrodeoxygenation of pyrolysis oil for hydrocarbon production using nanospring based catalysts



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ABSTRACT

Nickel (Ni) and ruthenium (Ru) decorated nanosprings (Ni-NS and Ru-NS) were prepared for use as potential hydrodeoxygenation (HDO) catalysts. The nanocatalysts were characterized by BET surface area measurements, electron microscopy and X-ray diffraction (XRD) and showed the NSs had a helical and mesoporous structure. The Ni and Ru decorated NSs showed good metal dispersity at the NS surface. Catalytic HDO conversion of phenol (model bio-oil compound) using NS were compared to conventional alumina (Al₂O₃) and silica (SiO₂) gel catalyst supports. Ni–Al₂O₃ was easily deactivated in the presence of water while the Ni-NS catalysts performed very well irrespective of water being present. An increase in Ni loading (up to 50%) increased the Ni-NS activity while the high loading resulted in a detrimental effect on the activity of silica gel based catalysts. Ru based catalysts showed better activity and conversion on phenol HDO than Ni based catalysts, even in the presence of water. Ponderosa pine pyrolysis bio-oil was fractionated into water-soluble (WS) and water-insoluble (WI) fractions. The bio-oil WI fraction was first hydrocracked to lower its molar mass and then HDO treated with Ni-NS to successfully form cycloalkanes products. These NS based HDO catalysts show promise for upgrading pyrolysis bio-oils to biofuels.

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1. Introduction

Fast pyrolysis of lignocellulosic biomass is considered a feasible and efficient process to convert biomass into a crude bio-oil (pyrolysis oil). However, bio-oil from fast pyrolysis contains a large amount of oxygen, distributed in hundreds of oxygenated compounds [1]. These compounds lead to many negative properties, such as low heating value, high corrosiveness, high viscosity, and instability. In order to make drop-in transportation fuels from bio-oil, HDO (hydrodeoxygenation) is a necessary step to remove oxygen in the presence of hydrogen with a suitable catalyst. HDO of bio-oil has been extensively studied and well documented during the past decades [2]. The key for bio-oil HDO is the catalyst. Solid catalysts are preferred for this process because these heterogeneous catalysts can be easily separated from the substrate after reaction. As reported, noble metals such as ruthenium (Ru), platinum (Pt), and palladium (Pd) are active metals for use in HDO catalysts of bio-oil or its model compounds [3–5]. In contrast to

noble metals, nickel (Ni) based catalysts show great potential for industrial application due to its low cost and high activity toward hydrogenation (HYD) and hydrogenolysis of several chemical functional groups [6,7]. However, pure Ni has a relatively low surface area and poor stability. Therefore, Ni catalysts used in industry are usually supported on a carrier or support for achieving better metal dispersion and thus higher reaction activity [8]. For this reason, materials with large surface area are highly desirable as a good support. Alumina, silica, and SiO₂–Al₂O₃ as well as zeolites (such as HZSM-5) have been studied as Ni catalyst supports [9]. As a shape-selective zeolite, HZSM-5 has intermediate pore sizes and good thermal stability. Only small molecules are able to diffuse into the zeolite's micropores. Although this microporous material is very effective for aromatic hydrocarbon production, coke is easily formed on it in terms of bio-oil HDO. One important reason is that there are many high molar mass oligomers/polymers present in the bio-oil and thus easily block the micropores of HZSM-5. Thus, amorphous silica or alumina is preferred for HDO of bio-oil, but efforts need to be made to increase their surface area and selectivity.

Silica nanosprings (NS) with large surface-to-volume ratios are one of the most promising silica based catalyst supports. Amorphous NS can be consistently synthesized via chemical vapor deposition (CVD) developed by Wang et al. [10]. The formation of

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the amorphous silica NS is explained in terms of the contact angle anisotropy model [11]. It should be noted that silica NS are grown on a substrate, such as aluminum foil, stainless steel, glass and quartz. Luo et al. successfully synthesized SiO₂ NS on quartz frits which were decorated with cobalt (Co) by wetness impregnation method for Fischer–Tropsch synthesis of C₁–C₁₈ hydrocarbons from synthesis gas [12]. However, a catalyst in liquid phase HDO generally needs a high accessible surface area. Therefore, free standing NSs can be obtained by removing the NS mat through mechanical action and then decorated with the desired active catalytic metal [14].

Due to the complexity of bio-oil, phenol is used as a model compound to represent lignin derived components in pyrolysis bio-oil. Phenol and its derivatives are the least active compounds in HDO treatment, but the most studied with substrates of different catalysts [13–20]. Phenol HDO has been carried out in either stirred batch reactors or in fixed bed tubular reactors [21]. In some of these studies a phenol solution in different organic solvents (tetradecane, *n*-hexadecane, decalin, and propanol) was used to investigate the oxygen-removal capability of the catalyst [22]. Solvents, such as alkanes or alcohols, can act as effective hydrogen donors since they have excellent solubility in H₂ in a supercritical state [23]. However, this will increase the reaction process cost. A more challenging but cost effective way to carry out phenol HDO reaction is using water as the medium. Although the water–phenol mixture can better represent the bio-oil, some Ni based catalysts are easily deactivated in water due to partial Ni leaching from the catalyst into water [24]. Nevertheless, water has been already successfully employed as the solvent for phenol HDO with Ni catalysts [20,25]. However, water involved in the system may affect the catalytic behavior on phenol. Therefore, one of the aims of this study is to investigate how water influences the selectivity of product from phenol HDO catalyzed by Ni catalysts. Bio-oil HDO was subsequently carried out using the catalysts showing good performance on phenol HDO.

This research focused on the potential of Ni or Ru decorated silica NS as catalysts for the HDO of pyrolysis bio-oil HDO. The activities of the catalysts were tested using phenol as a model bio-oil compound. For comparison purposes, conventional silica and alumina gels with different particle size were also used as Ni catalyst supports. Other catalyst properties, including metal loading and catalyst deactivation, were also investigated in this research. The potential to HDO bio-oil over NS catalyst was also studied. The commercial catalyst was used beforehand to optimize the HDO process of bio-oil. The NS based catalyst was then introduced to validate its capability of HDO of bio-oil.

2. Materials and methods

2.1. Catalyst preparation

All the catalysts used in HDO of phenol were prepared by using the wetness impregnation method as described elsewhere [18]. NiCl₂·6H₂O and RuCl₃·6H₂O were used as Ni and Ru precursors, respectively. The catalyst supports were silica gel (40–63 μm (#1) and 210–500 μm (#2), Fisher Chemicals), alumina (γ-Al₂O₃, 74–177 μm, Fisher Chemicals) and silica NS. The NS were synthesizing on an aluminum foil substrate using flow furnace CVD technique [10]. After the NS mats were formed, they were easily peeled off from the foil to give free standing NS. The desired amounts of precursors were dissolved in water (100 mg mL⁻¹ for 20% Ni, 400 mg mL⁻¹ for 50% Ni, 15 mg mL⁻¹ for 5% Ru) in a flask (10 mL) and then the silica or alumina gel support (1 g) was introduced to the solution and the mixture was ultrasonicated for 4 h at room temperature. For NS (200 mg), the metal precursors were dissolved in ethanol (10 mL, 25 mg mL⁻¹ for 20% Ni, 100 mg mL⁻¹ for 50% Ni, 3 mg mL⁻¹ for 5% Ru, 14.3 mg mL⁻¹ for 20% Ru) due

to the NS hydrophobicity and again the mixture ultrasonicated. Note, ultrasonication is a critical step to disperse the freestanding NS. The solvent was then evaporated and dried overnight at 104 °C. The dried catalysts were ground and then calcined in air for 4 h (450 °C for Ni catalysts and 350 °C for Ru catalysts). The calcined catalyst materials were reduced in a tubular quartz reactor (10 mm Ø × 300 mm) by heating at 400 °C under a H₂ flow (60 mL min⁻¹) for 4 h. After cooling to room temperature, the reduced sample was quickly transferred to the reactor for HDO.

2.2. Catalyst characterization by BET, TEM, XRD and H₂-TPR

The specific surface area, pore volume, and average pore radius of the catalysts were determined by N₂ physisorption (Micromeritics TriStar II 3020). Before the analysis, samples were degassed at 300 °C for 1 h under vacuum. The specific surface area was obtained using the Brunauer–Emmett–Teller (BET) model.

The morphologies of the catalysts were characterized by transmission electron microscopy (TEM, Jeol JEM-2010 TEM, 200 kV). Sample specimens for TEM were prepared by dispersion of catalysts in ethanol (2 mg mL⁻¹) and the suspension dropped onto a copper grid. Several micrographs were recorded for each sample to determine the particle size distribution of the metals and their oxides.

The X-ray powder diffraction (XRD) pattern of the catalysts were obtained using a Siemens D5000 powder diffractometer with Cu/Kα radiation (λ = 1.54 Å). The diffractograms were recorded from 2θ = 2° to 80° with 0.01° step using a 1 s acquisition time per step. The average particle size of metal oxides were calculated according to Scherrer's equation ($d = K \lambda / \beta \cos \theta$), where *K* is the shape factor (*K* = 1), λ is the wavelength of X-ray, β is the line broadening at half the maximum intensity (FWHM) in radians, and θ is the Bragg angle.

The H₂-temperature programmed reduction (H₂-TPR) was performed to investigate the reducibility of the catalyst, as well as determine the optimum temperature to reduce the metal oxide completely. The H₂-TPR traces were recorded using a Micromeritics AutoChem II 2920 Chemisorption Analyzer equipped with a thermal conductivity detector (TCD). The sample (50 mg) was loaded in a U-shape quartz reactor and first purged in a flow of He (50 mL min⁻¹) at 250 °C for 1 h to remove water, cooled to 50 °C, then a 10% H₂ in Ar (50 mL min⁻¹) was purged and heated to 800 °C at 10 °C min⁻¹.

2.3. Catalyst activity measurement

In a typical test, phenol (5 g, 53 mmol), water (15 g), and a catalyst (0.05–0.20 g) were loaded into a stirred Parr Instruments reactor model 4561 (300 mL). For Ni catalysts, a series of experiments using phenol (5 g) HDO were performed without water. The amount of Ni catalyst applied was 0.20 g with a catalyst to feedstock (C/F) ratio of 1:25. For the Ru catalysts, the phenol (5 g) HDO experiments were performed in the presence of water (15 g). The amount of Ru catalyst used was 0.20 g, giving a C/F = 1:25. An additional series of phenol HDO experiments over Ru catalysts were performed under the same conditions as above, but using a decreased amount of catalyst (0.05 g), giving a C/F = 1:100. The phenol, water and catalysts were loaded into the reactor, which was flushed with H₂ five times to remove air. The reactor was then pressurized with H₂ (2.8 MPa) and heated (6 °C min⁻¹) to 300 °C with stirring (500 rpm). The start time was recorded when the required temperature was reached. After the completion of the reaction (6 or 12 h), the reactor was cooled to room temperature. The liquid products were separated into an organic and aqueous phases and were analyzed by GC–MS.

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