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## Catalytic hydroliquefaction of rice straw for bio-oil production using Ni/CeO<sub>2</sub> catalysts

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### ABSTRACT

A series of Ni/CeO<sub>2</sub> catalysts were synthesized via a simple one-pot hydrothermal method and characterized by XRD, SEM, TEM, EDX, EDX mapping, Raman, H<sub>2</sub>-TPR, BET, XPS, TGA and ICP-MS. Their catalytic performances were systematically evaluated in hydroliquefaction of rice straw. The impact of reaction temperature, reaction time, H<sub>2</sub> pressure and Ni/Ce molar ratios on product yields and distribution was also investigated. The conversion (89.08%) of rice straw and bio-oil yield (66.7%) obtained over Ni/CeO<sub>2</sub> catalyst with a Ni/Ce molar ratio of 2/10 are superior to those over no catalyst (conversion of 73.65%, bio-oil yield of 47.96%) and pure CeO<sub>2</sub> catalyst (conversion of 77.79%, bio-oil yield of 56.67%) under the optimum condition (290 °C, 1.0 h, and 2.0 MPa H<sub>2</sub> pressure). GC-MS results show that the main components of bio-oil are phenols, which are high-value-added, important and useful chemicals in transportation and chemical industries. It is worth noting that the highly dispersed Ni nanoparticles and their stronger interaction between Ni and CeO<sub>2</sub> with more oxygen vacancies facilitate high conversion of rice straw and bio-oil yield. In addition, a possible catalytic mechanism of Ni/CeO<sub>2</sub> catalyst for hydrogenation of rice straw is accordingly proposed. This work thus offers an effective approach to improve the conversion of rice straw and bio-oil yield over Ni/CeO<sub>2</sub> catalysts.

### 1. Introduction

Nowadays, biomass is considered as one of the most promising substitutes for fossil fuels to mitigate energy crisis due to its renewable, low-cost, carbon neutral and high productivity characteristics [1–3]. Rice straw is one of the most abundant biomass produced annually about 200 billion kilograms in China, but its unreasonable utilization such as direct combustion and discarded anywhere leads to serious environment pollution [4–6]. Therefore, it is meaningful to find strategies to fully utilize the cheap and renewable rice straw for producing biofuels or other valuable chemicals.

It has been reported that lignocellulosic biomass including rice straw can be processed by pyrolysis [7], gasification [8,9], and liquefaction [4,10–14], for the production of biofuels (e.g. bio-oil), gas fuels (e.g. H<sub>2</sub>), and other high value added chemicals. At present, pyrolysis and liquefaction are main thermochemical methods to degrade lignocellulosic biomass into biofuels [15]. Compared with pyrolysis, hydrothermal liquefaction (HTL) has attracted wide research interests due to the fact that it is cost-effective with relatively mild conditions to produce bio-oil with a higher heating value [16].

Among different liquefaction processes, catalytic hydrogenation,

which is conducted using hydrogen donor solvent e.g. methanol [17,18], ethanol [19], H<sub>2</sub>O [20], i-propanol [21], glycerol [22], oxygenates [23], hydrocarbon hydrogen donors [24], and other organic solvents [25] under H<sub>2</sub> atmosphere in the presence of catalysts, has been extensively investigated for decades. Previous studies indicated that catalytic HTL using co-solvent can significantly enhance the biomass conversion and bio-oil yield, which is more efficient than either water or pure alcohol [26–28]. Xu et al. [29] reported that a much higher bio-oil yield of 65 wt% and conversion of 95 wt% were obtained from woody biomass liquefaction in water-ethanol co-solvent. Li and Yuan [27] investigated the bio-oil production from liquefaction of rice straw in the presence of ethanol-water and 2-propanol-water mixture. The results showed that the maximum yield of bio-oil can reach 39.7 wt% with the 2-propanol: water volume rate of 5:5 at 300 °C. In addition, Cao et al. [22] reported that the bio-oil yield increased remarkably when glycerol-water was used as a co-solvent during hydrothermal liquefaction of rice straw. As a result, 50.31 wt% of bio-oil and 26.65 wt% of solid residue were produced. Although HTL in water-alcohol co-solvent system can be considered as an effective and alternative method to improve biomass conversion and bio-oil yield, bio-oil yield obtained from HTL of biomass are still unsatisfactory to date. Therefore, catalysts

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should be used in HTL of biomass in co-solvent system for higher bio-oil yield.

So far, many homogenous catalysts such as acid, alkali, alkali salts have been involved in catalytic HTL of biomass, leading to additional separation steps with high cost and energy consumption for catalyst recovery. Zhu et al. [30] reported that the maximum bio-crude yield of 34.85 wt% was obtained using  $K_2CO_3$  as catalyst at 300 °C via hydrothermal liquefaction of barley straw. Instead, heterogeneous catalysts including zeolites [19,31,32], transition metal sulfides [33–35], transition metal carbides [35–37], metal oxides [35,38,39], and supported metals [40–44] are considered as promising options. Younas and co-workers [45] used NiO catalyst in the HTL of rice straw, they found that in presence of nanocatalyst, the yields of LO and HO were maximized up to 13.2% and 17.2% at 300 °C, respectively. Shi and co-workers [46] investigated HTL of rice husk using metallic oxide catalysts ( $La_2O_3$  and  $Dy_2O_3$ ). The results showed that the bio-crude yields were obviously increased and the highest bio-crude yield of 32.5 wt% was obtained with  $La_2O_3$  catalyst at 300 °C for 10 min and a water/rice husk mass ratio of 5. Murnieks et al. [47] studied the hydrotreating of wheat straw at 300 °C for 4 h using 66% Ni/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> and obtained the hydroliquefied bio-oil yield of 11.5% in ethanol. Previously, studies on catalytic materials for hydrodeoxygenation (HDO) were mainly focused on sulfided Co-Mo, Ni-Mo catalysts due to their high HDO activity. Unfortunately, they were prone to deactivate and easily contaminated by products because of the addition of sulfiding agent. Besides, reductive noble metals (e.g., Ru, Rh, Pd, Pt) loaded on various oxide supports (e.g., SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Carbon, ZrO<sub>2</sub>, CeO<sub>2</sub>, TiO<sub>2</sub>), have also been employed in HTL in the past few years. Nevertheless, even with excellent performance in laboratory work, high cost and low availability are fatal weaknesses in engineering scale-up. Consequently, there are great interest in development of non-sulfided, non-noble metal catalysts to obtain a feasible and cost-effective process.

As a well-known functional rare earth material, ceria has wide applications in catalysis [48]. It is well recognized that ceria (CeO<sub>2</sub>) displays a high ability to store and release oxygen associated with rich oxygen vacancies, which is conducive to the activation of C–O bonds in organic oxygenates [49]. Recently, Yim and co-workers [50] investigate the effect of metal oxide catalysts on HTL Malaysian oil palm biomass to bio-oil under supercritical condition and found that CeO<sub>2</sub> generated the highest relative yield of bio-oil due to lower redox potential between Ce<sup>3+</sup> and Ce<sup>4+</sup> compared to other metal oxides. However, supercritical condition desires a higher temperature and pressure, resulting in a strict requirement on reaction equipments. Therefore, catalytic HTL on lignocellulosic biomass using modified CeO<sub>2</sub> catalysts to gain better catalytic performances under mild condition is more promising.

In this paper, non-noble transition metal Ni was chosen as an active component and loaded on CeO<sub>2</sub> nanorods to investigate their catalytic performances towards hydrogenation of rice straw. GC–MS and FTIR were used to analyze the component of bio-oil. The results show that Ni/CeO<sub>2</sub> catalysts effectively improve the conversion of rice straw and bio-oil yield. This work thus offers a report on the synthesis of non-noble transition metal Ni modified CeO<sub>2</sub> nanorods via one-pot hydrothermal method and the application of the resulting catalysts for hydrogenation of rice straw for relatively high conversion and bio-oil yield.

## 2. Experimental

### 2.1. Materials

Cerium (III) nitrate hexahydrate (Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, 99.0%), nickel nitrate (Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 99.0%), sodium hydroxide (NaOH, 99.0%), and ethanol (99.0%) were all purchased from Shanghai Chemical Reagent Company in analytical grade and used as received without further purification. Deionized water was used throughout the

**Table 1**  
Properties of rice straw.

Properties	Value
Elemental analysis (wt%)	
Carbon	39.47 ± 0.04
Hydrogen	5.53 ± 0.12
Oxygen <sup>a</sup>	54.43 ± 0.06
Nitrogen	0.51 ± 0.03
HHV (MJ/kg)	11.52 ± 0.12
Proximate analysis (wt%)	
Volatile matters	68.17 ± 0.01
Fixed carbon	22.53 ± 0.04
Ash	9.3 ± 0.0
Component analysis (wt%)	
Lignin	41.4 ± 0.1
Cellulose	24.2 ± 0.3
Hemicellulose	25.1 ± 0.1
Ash	9.3 ± 0.0
BET area <sup>b</sup> (m <sup>2</sup> /g)	2.86
PSD <sup>c</sup> (mm)	0.25–1.0

<sup>a</sup> Calculated by the difference.

<sup>b</sup> BET area obtained from  $p/p_0 = 0.20$ .

<sup>c</sup> PSD means particle size distribution.

experiment process. Rice straw, collected from an agricultural processing factory in China, was crushed and filtered through a 60-mesh sieve and dried in vacuum at 80 °C for 24 h. The particle size of rice straw was ranging between 0.25 and 1.0 mm. The properties of the rice straw are given in Table 1. Cellulose, hemicellulose and lignin content in the rice straw were determined by the NREL Chemical Analysis and Testing Standard Procedures: NREL LAP, TP-510-42618. Ash content was determined by burning sample at 550 °C for 6 h in a muffle furnace. The proximate analysis was carried out by the thermal gravimetric analysis (TGA) (TGA Shimadzu) from the ambient temperature to 900 °C at a heating rate of 10 °C/min under a nitrogen flow of 100 mL/min. The elemental analysis was performed by Elemental analyzer Vario EL III model.

### 2.2. Catalyst preparation and characterization

#### 2.2.1. Synthesis of CeO<sub>2</sub> nanorods

CeO<sub>2</sub> nanorods were successfully prepared via a simple hydrothermal method as reported previously [36]. Typically, 1.74 g Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O and 19.2 g NaOH were dissolved in 40 mL of deionized water, respectively. The two solutions were mixed together and kept stirring for 30 min. Then the mixture was transferred to a stainless steel autoclave with PTFE lining (100 mL) and the autoclave was sealed tightly. The autoclave was transferred into a temperature-controlled electric oven and hydrothermally treated at 100 °C for 24 h. After cooling to room temperature naturally, the fresh precipitates were separated by centrifugation, thoroughly washed with deionized water and ethanol for several times and dried in vacuum at 60 °C overnight. Finally, the resulting powders were calcined at 500 °C for 4 h in air with a heating rate of 4 °C/min.

#### 2.2.2. Synthesis of Ni modified CeO<sub>2</sub> nanorods

A series of Ni modified CeO<sub>2</sub> nanorods were prepared via one-pot hydrothermal method and H<sub>2</sub> reduction process. Ce<sup>3+</sup> concentration was fixed at 0.05 mol/L during the whole process. Typically, for the synthesis of Ni/CeO<sub>2</sub> catalysts with a Ni/Ce molar ratio of 1/10, 2/10 and 3/10, procedures were the same as mentioned above, except the adding of a nickel precursor (0.23 g, 0.47 g and 0.70 g Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) together with Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O. Finally, the calcined materials in the form of NiO/CeO<sub>2</sub> were put into a quartz tube and reduced in a flow of H<sub>2</sub> (15 mL/min) at 450 °C for 3 h to gain the final product Ni/CeO<sub>2</sub> with the Ni/Ce molar ratios of 1/10, 2/10 and 3/10.

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