Catalytic hydrothermal liquefaction of spirulina to bio-oil in the presence of formic acid over palladium-based catalysts

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ABSTRACT

This paper reports our investigation of the catalytic hydrothermal liquefaction (HTL) of microalgae spirulina to bio-oil. Palladium-based catalysts Pd/HZSM-5@meso-SiO$_2$ (Pd/HZSM-5@MS) and Pd/HZSM-5 were synthesized. X-ray diffraction analysis, scanning electron microscopy, and transmission electron microscopy were used to characterize the catalysts that were applied to the HTL of algae in the presence of formic acid. Elemental analysis and gas chromatography–mass spectrometry were used to analyze the resulting bio-oil. The characterizations indicated that the Pd/HZSM-5@MS-catalyzed HTL had a high bio-oil yield of 37.30% and a low coke yield of 8.56%, and that the obtained bio-oil contained no acids. Furthermore, this study suggests that Pd/HZSM-5 promoted hydrodenitrogenation of the bio-oil and that Pd/HZMS-5@MS promoted hydrodeoxygenation of the bio-oil. Catalyst recycling and the performance of the recycled catalyst were also investigated and discussed.

1. Introduction

Algae suffers from a relatively high heterogeneous atom content [1,2], especially when the direct pyrolysis process is used [3]. To overcome these shortcomings, hydrothermal liquefaction (HTL) has become an effective method to reduce the high energy consumption and heterogeneous atom content, as it could eliminate complicated drying processes [4]. The high temperature is conducive to algae decomposition, but the acidity of the water is not high enough to decompose the algae completely, so it is essential to add a catalyst [5–7].

To date, heterogeneous catalysts such as active carbon, zeolites, Pt/C [8], Pd/C [9], Ni/Al$_2$O$_3$ [10], Mo$_2$C [11], and Raney Ni [12] have been used. Duan and Savage [8] applied a two-step method and a Pt/C catalyst with H$_2$ for algae conversion. This process could produce high-quality high-yield bio-oil with a higher heating value (HHV) of 43.00 MJ·kg^{-1}. However, the two-step method used an energy-intensive process. Furthermore, H$_2$ addition was dangerous and required complicated operation procedures [13,14]. In many reports, HCOOH was chosen as the in situ hydrogen atom donor [15] because it can decompose completely to H$_2$ at approximately 300 °C [16]. Nevertheless, HCOOH can react with the formed product, resulting in a high O content [17]. Thus, ways of facilitating HCOOH decomposition to H$_2$ instead of the reaction with the formed product became a focus of research. Consequently, to simultaneously obtain high-quality bio-oil and reduce the energy consumed in the algae conversion reaction, the

development of a bifunctional catalyst that facilitates the hydrogenation and catalysis of HCOOH decomposition is desired.

As a cracking catalyst in the petrochemical industry, HZSM-5 zeolite reportedly affects bio-oil deoxygenation, but it has not exhibited the desired performance [18]. Loading palladium on HZSM-5 increased its hydrogenation ability [19], and the catalyst reduced the heterogeneous atom content and modified the bio-oil simultaneously. The nanopores in HZSM-5 do not allow the biomacromolecules from algae degradation products to freely enter and exit, thus limiting mass transport. Therefore, increasing the diameters of the nanopores in zeolite was advantageous for bio-oil modification. Covering the surface of HZSM-5 with meso-SiO$_2$ yielded the core–shell catalyst HZSM-5@meso-SiO$_2$ (HZSM-5@MS) with a certain shell thickness, and the layer of mesoporous silica covered the external Brønsted acid sites on HZSM-5 [20]. The existence of mesopores allows biomacromolecules to enter and affords connectivity between the nanopores of mesoporous silica and the subnanopores of the HZSM-5 zeolite, allowing the cracking product to freely enter and exit and thereby at least partially overcoming the mass-transport limitations. Further, mesoporous zeolites have the advantage of improving the dispersion of metal nanoparticles rather than their localization on the external surface, which occurs in their conventional microporous counterparts [21]. Consequently, this core–shell catalyst is expected to afford good bio-oil modification.

In this work, a new core–shell catalyst, Pd/HZSM-5@MS, was synthesized and applied in the HTL of algae by a conversion reaction in a

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Table 1
Characteristics of spirulina (data shown is the mean $\pm$ SD, n = 2).

Lipid (%)	Protein (%)	Carbohydrate (%)	C (%)	H (%)	N (%)	Ash (%)
7.60 $\pm$ 1.20	67.10 $\pm$ 8.00	15.30 $\pm$ 2.00	48.45 $\pm$ 0.31	7.13 $\pm$ 0.19	10.13 $\pm$ 0.20	6.88 $\pm$ 0.04

batch reactor with added HCOOH to produce H_2. To investigate the catalytic performance, a series of experiments were conducted with different related catalysts, and the effect of covering the catalyst with meso-SiO_2 was examined in detail. Commercial Pd/C was also employed in the reaction for comparison. Furthermore, the recycling of the Pd/HZSM-5@MS catalyst and its stability in the reaction were studied. After recycling, a high yield of Z-9-octadecenamide was obtained. As a lubricant in polymer machining, Z-9-octadecenamide is widely used in the chemical industry. A possible formation pathway for this compound was given, and it was proved that its content was related to the denitrogenation ability of the catalyst.

2. Materials and methods

2.1. Materials

Spirulina was purchased from Fuqing Xindaze Spirulina Co. The composition and results of the elemental analysis are listed in Table 1. Dichloromethane (DCM), formic acid (HCOOH, 98%), palladium nitrate [Pd(NO$_3$)$_2$], and Pd/C (palladium content of 5%) were purchased from Sinopharm Chemical Reagent Co. Ltd. Absolute ethanol, hydrochloric acid (37 wt% HCl), and anhydrous magnesium sulfate (MgSO$_4$) were purchased from Shanghai Chemical Reagent Co. Ltd. All the reagents were analytically pure (AR grade) and used directly without any purification.

3. Experimental procedure

3.1. Synthesis of catalysts

HZSM-5 (Si/Al ratio of 80) and HZSM-5@MS (tetraethyl orthosilicate/HZSM-5 ratio of 3) were synthesized according to the literature [20]. Pd(NO$_3$)$_2$ (0.6 g) in a water solution (15 mg·g^{-1}) and 0.3 g of HZSM-5 or HZSM-5@MS were added to a beaker with 10 mL of water. The mixture was stirred at room temperature for 24 h. Then, the solution was placed in an oven at 120 °C for 10 h. The dry powders were washed with water and filtered. After filtering, the catalyst was calcined in H_2 at 400 °C for 4 h.

3.2. Hydrothermal liquefaction

A 304-stainless steel reactor with a volume of 30 mL was purchased from the Yantai Muping Shuguang precision instrument factory. Algae (0.5 g), HCOOH, water, and 0.01 g of the catalyst were added to the reactor. Then, the reactor was placed in a salt bath consisting of sodium nitrite, sodium nitrate, and potassium nitrate in the mass ratio 40:7:53 [22]. The reaction was conducted at 380 °C for 2 h. After it was complete, the reactor was quenched by cool water for 40 min. DCM (150 mL) and 50 mL of absolute ethanol were used to wash the reactor so that all the products could be washed out. The mixture was filtered by a membrane with an aperture of 0.45 μm. After filtering, the solid was calcined at 650 °C for 6 h to calculate the coke yield, and the solution was dried by 2 g of MgSO$_4$. After another filtering by the membrane, the liquid was evaporated at 60 °C to remove the solvent, and the bio-oil product was obtained. Each experiment was repeated twice, and the average values of the oil and coke yields are reported. The experimental procedures are illustrated in Fig. 1, and the formulas for the oil and coke yields are given as

$$X_{\text{Oil yield}}\,(\text{wt\%}) = \left(\frac{\text{weight of bio}-\text{oil}}{\text{weight of algae power}} \right) * 100 \tag{1}$$

$$Y_{\text{Coke yield}}\,(\text{wt\%})$$
$$= \left(\frac{\text{weight of solid from filtering} - \text{weight of solid after calcination}}{\text{weight of algae power}} \right)$$
$$* 100. \tag{2}$$

3.3. Catalyst recycling

After calcination in a muffle furnace, the solid residue was placed in a 250 mL beaker. Then, 150 mL of 2 mol·L^{-1} HCl was added to the beaker and stirred for 12 h at room temperature. After filtering and drying, the solid was placed in a tube furnace and calcined at 400 °C for 4 h in a H_2 atmosphere to obtain the catalyst. Considering the catalyst loss during recycling, the experiment was performed six, five, four, three, and two times for one, two, three, four, and five catalyst reuses, respectively, and the average values of the oil and coke yields are reported. The elemental analysis and gas chromatography–mass spectrometry (GC–MS) methods are described below.

4. Characterization techniques

4.1. Analysis of the catalyst

X-ray diffraction (XRD) patterns of the catalysts were obtained using a Bruker D8 diffractometer with Cu Kα radiation from 2° to 50° 2θ values at a scan speed of 10°·min^{-1}. Scanning electron microscopy (SEM) was performed on a Philips XL 30 microscope operating at 30 kV. Transmission electron microscopy (TEM) was performed on a JEOL 2100F instrument operating at 30 kV. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) measurements were made on a Thermo Scientific iCAP 6300 instrument. X-ray photoelectron spectroscopy (XPS) was performed using a PHI-5500 spectrometer with Al Kα X-ray radiation as the X-ray source for excitation. N_2 adsorption-desorption isotherms were measured using a BELSORP mini II analyzer at liquid N_2 temperature. The surface area (S_{BET}) was calculated by the Brunauer–Emmett–Teller (BET) method, and the pore volume (V_p) was determined by nitrogen adsorption at a relative pressure of 0.98.

4.2. Elemental analysis

The elemental compositions (C, H, and N) of the spirulina and bio-oil were determined using a Vario EL III instrument. For each experiment, the oil obtained from two experiments in parallel was mixed to obtain the results. The HHV was estimated using the Dulong formula [23]:

$$\text{HHV}\,(\text{MJ·kg}^{-1}) = 0.338\text{C} + 1.423\text{H} - 0.154\text{O} - 0.145\text{N}, \tag{3}$$

$$\text{O} = 100 - \text{C} - \text{H} - \text{N} \tag{4}$$

where C, H, N, and O are the weight percentages of each atom in the bio-oil.

4.3. GC–MS analysis

GC–MS analysis was performed using an Agilent Technologies 7890A-5975C instrument equipped with an auto-sampler and auto-