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Hydroprocessing of carinata oil for hydrocarbon biofuel over Mo-Zn/Al_2O_3

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ABSTRACT

Hydroprocessing of carinata oil over an Al_2O_3 supported Mo-Zn catalyst in a batch reactor at 350 °C with an initial H_2 pressure of 300 psi was carried out to produce hydrocarbon biofuel. A series of Mo-Zn/Al_2O_3 catalysts with different Zn/Mo molar ratios (0, 1, 2, 3, ∞) were prepared and characterized using XRD, FT-IR, BET and TEM. The effects on the physicochemical properties and yield of products from using no catalyst and Al_2O_3 based catalysts were discussed. The introduction of Mo and/or Zn did not change the crystalline structure of Al_2O_3. The combining of Mo and Zn on Al_2O_3 improved catalytic performance and was helpful to improve some of the physicochemical properties of hydrocarbon biofuel including hydrocarbon content, moisture content, density, total acid number and higher heating value (HHV). The catalyst which exhibited the best catalytic performance had a Zn/Mo molar ratio of 2:1. At the 2:1 ratio of Zn/Mo, the hydrocarbon biofuel produced displayed the highest hydrocarbon content (81.05%) and the lowest moisture content, and the highest sum content of CO and CO_2 in the gas produced. The introduction of Mo and Zn on Al_2O_3 was helpful for the hydroprocessing of carinata oil for hydrocarbon biofuel production.

1. Introduction

More than 80% of all petroleum extracted from the earth is processed as fuels including jet fuel, gasoline, diesel and other fuel oils. The depletion of finite oil reserves and increase in the greenhouse gas emissions is contributed to the excessive use of petroleum. Due to concerns of sustainability, environmental impact, increased global population and geopolitical stability, there is a growing political, social and economic interest for the development of alternative fuel sources. Biomass such as vegetable oilseed is usually used to produce carbon-neutral biofuel. Burning biofuel does not increase the CO_2 concentration in the atmosphere [1–4]. In recent years, concerns of resource competition between food and energy crops have been growing, which lead to a major interest in the development of biofuel production from a variety of non-food crops [5,6]. Brassica carinata is non-food crop which is an arid-resistant species [1]. It is commonly referred to as Ethiopian mustard or Abyssinian. Brassica carinata is highly drought and heat tolerant, and resistant to aphids, flea beetles and blackleg disease [7]. The positive agronomic attributes of the carinata oilseed make it compatible with fallow cropping and off-season cropping. The U.S. military has shown an interest in the carinata oilseed feedstocks and begun flight trials with carinata based jet fuel in 2012 [8]. Field tests of Brassica carinata commercial varieties have been successful across North Dakota, Montana, Mississippi and Florida in the United States [9].

There are several common methods to convert biomass to biofuel, such as fermentation, pyrolysis and upgrading, gasification, transesterification, catalytic cracking, and hydroprocessing [10]. Among these above methods, the thermochemical techniques used for vegetable oil conversion to biofuel include transesterification, catalytic cracking, and hydroprocessing. Due to the undesirable properties produced via transesterification such as low oxidative stability of biodiesel, and the low biofuel yield obtained from catalytic cracking of vegetable oil, hydroprocessing is an effective method to convert vegetable oil to biofuel even though the introduction of hydrogen contributes a portion of the processing cost [11]. Hydroprocessing is a widely used technology applied in petroleum refineries, whereas oxygen can be removed through three pathways. The first pathway, hydro-decarbonylation pro-

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duces CO and H_2O. The second pathway, hydro-decarboxylation produces CO_2; and the last pathway, hydro-dewatering produces H_2O [12,13]. Zarchin et al. [12] studied the hydroprocessing of soybean oil over nickel-phosphide supported catalyst and 47% of oxygen was removed as CO and CO_2 from triglycerides.

Catalyst plays a significant role in the hydroprocessing of vegetable oil and commercial hydrotreatment catalysts such as Co-Mo/Al_2O_3 have been studied to investigate the hydrodeoxygenation of oxygen containing compounds [13]. The catalysts of CoMo and NiMo supported on Al_2O_3 had a high surface area, stable chemical properties and good mechanical properties. The loading of an acidic oxide MoO_3 to the Al_2O_3 support could increase the acidity due to the molybdate anions preferentially reacting with the basic hydroxyl groups on the Al_2O_3 support [14]. MoO_x, an oxide form of a transition metal, exhibited variable valence and might possess the ability for the activation of oxy-groups in oxygenates [15]. Srifa et al. [16] studied the hydrodeoxygenation of palm oil over the Al_2O_3 supported monometallic catalysts (Ni, Co, Pt and Pd) in a trickle-bed reactor at 330 °C and H_2 pressure of 5 MPa to produce green diesel. The deoxygenation of palm oil was proposed by the initial hydrogenation of unsaturated triglycerides to saturated triglycerides. Then, fatty acids and propane were formed through the hydrogenolysis of saturated triglycerides. Finally, green diesel was obtained through the deoxygenation of free fatty acids on the metallic sites of the catalysts. Krar et al. [17] studied the hydrotreating of sunflower oil over Co-Mo/Al_2O_3 catalyst to produce biofuel. The hydroprocessing parameters were: temperature (300–380 °C) and total pressure (20–80 bar). It was demonstrated that the Co-Mo/Al_2O_3 catalyst was suitable for the conversion of sunflower oil to new generation biofuel. The yield of the high paraffin containing (> 99%) gas oil boiling range product was between 73.7% and 73.9%. $ZnCl_2$ is a moderate strength Lewis acid with an effective cost and is proved to modify the zeolite catalysts for converting vegetable oil to hydrocarbon biofuel [11,18,19]. Karnjanakom et al. [20] found that when Zn was loaded on Al_2O_3, the acidity of the catalyst was promoted. A high acidity plays an important role in the conversion of oxygenates to hydrocarbons. Also, the zinc species might promote the hydrogen transfer during the catalytic upgrading of bio-oil process. The Zn/Al_2O_3 catalyst exhibited a high catalytic activity and long-term stability for the conversion of oxygenates to hydrocarbons, which was related to its acidity and coke resistance properties. There have been a few studies related to the biofuel production over a variety of Al_2O_3 support catalysts, but the report about using Mo and Zn co-modified Al_2O_3 as a catalyst for the hydroprocessing of inedible vegetable oil is lacking.

The objective of this work is to study the hydroprocessing of inedible carinata oil to produce hydrocarbon biofuel in a batch reactor at a temperature of 350 °C. The effect of Mo-Zn/Al_2O_3 catalyst on the product yield and hydrocarbon biofuel properties such as total acid number (TAN) and moisture content was explored and discussed. The catalysts were characterized using a variety of techniques and the composition of the gas produced was analyzed. The possible main reactions for hydroprocessing of carinata oil to hydrocarbons over Mo-Zn/Al_2O_3 catalyst were proposed. In addition, the pressure of the batch reactor was recorded to investigate its initial, maximum and final pressure.

2. Experimental

2.1. Feedstock and catalyst preparation

Carinata (Brassica) oil was provided by Dr. Dwayne Beck from the Dakota Lakes Research Farm, South Dakota, USA. The carinata oil was directly used for hydroprocessing trials without any pretreatment. Aluminum oxide (powder, ≤ 10 μm average particle size, 99.5% trace metals basis) and ammonium molybdate tetrahydrate (99.98% trace metals basis) were purchased from Sigma-Aldrich Inc., Milwaukee, Wisconsin. Zinc chloride was purchased from Fisher Scientific. A series of Mo-Zn/Al_2O_3 catalysts with different Zn/Mo molar ratios (0, 1, 2, 3, ∞) were prepared using a wet impregnation method. For example, Mo-Zn(2)/Al_2O_3 was defined as the Mo-Zn/Al_2O_3 catalyst with the Zn/Mo molar ratio of 2. The aluminum oxide support was impregnated with an aqueous solution of a certain amount of ammonium molybdate tetrahydrate and zinc chloride. The Al_2O_3 support was doped with 4 wt.% Mo to form Mo-Zn(0)/Al_2O_3 (Mo/Al_2O_3) catalyst. Based on Mo/Al_2O_3, the catalysts of Mo-Zn(1)/Al_2O_3, Mo-Zn(2)/Al_2O_3 and Mo-Zn(3)/Al_2O_3 were synthesized through doping a suitable amount of Zn. For catalysts of Mo/Al_2O_3, Mo-Zn(1)/Al_2O_3, Mo-Zn(2)/Al_2O_3 and Mo-Zn(3)/Al_2O_3, the molar ratios of Mo to Al_2O_3 was the same, 0.05. The Al_2O_3 support was doped with 4 wt.% Zn to form Mo-Zn(∞)/Al_2O_3 (Zn/Al_2O_3) catalyst, whose molar ratio of Zn to Al_2O_3 was 0.07. The catalysts were dried at 106 °C for 4 h and then calcined at 550 °C for 4 h. The catalysts were ground into powders using a pestle for hydroprocessing use [18,21].

2.2. Catalyst characterization

The catalysts were characterized using X-ray Diffractometer (XRD), Fourier transform infrared spectroscopy (FT-IR), automated gas adsorption analyzer, and transmission electron microscope (TEM). The phase identification and crystalline structure of Mo-Zn/Al_2O_3 catalysts were determined using an automated multipurpose XRD (SmartLab, Rigaku Corporation) with Cu Kα radiation. The X-ray pattern was scanned from 10° to 90° (2θ) with a step of 0.02° and a scan speed of 2.00°/min, in a continuous mode and an absolute range. The tube voltage and tube current of the X-ray generator were 40 kV and 44 mA, respectively [11,22]. The detail on the procedure of FT-IR, automated gas adsorption analyzer and TEM could be found in our previous research [11,23].

2.3. Hydroprocessing

The hydroprocessing of carinata oil was carried out in a batch reactor (Parr, model 4843) with a heating rate of 5/min. The maximum pressure tolerance of the stainless steel autoclave is 3.44×10^7 Pa (5000 pounds per square inch (psi)). The stirring speed of the turbine paddle stirrer was set as about 1600 rpm. Hydrogen was used to remove the air throughout the reactor system for 5 min, and then it was filled to charge the reactor system until the pressure was 2.07×10^6 Pa (300 psi) at room temperature (25 °C). After that, the hydrogen cylinder was turned off and the autoclave was heated to 350 °C, which was then maintained for 5 h. In each test, 100 g of carinata oil was poured into the autoclave and then 10 g of catalyst was added (there was no catalyst added into the autoclave for no catalyst test). The catalyst-to-oil ratio was selected as 1:10 mainly due to the considerations that the catalyst could be deactivated during the oil hydroprocessing and a large amount of catalyst could increase the cost. Also, it was determined based on our previous research and literature review [24,25]. During each test, the maximum pressure of the reactor system was recorded. After the test, the autoclave was left overnight to cool down to room temperature; then, the final pressure of the reactor system was recorded. A Virgin PTFE (polytetrafluoroethylene) gasket was used to seal the autoclave. The cap screws and connections were tightened properly. The gas leaks in the autoclave after an overnight were very few or negligible. The gas remaining in the reactor system was collected using a gas sampling bag to determine its composition. The mixture of liquid and solid was filtered using a separation funnel to separate the liquid from the solid. The liquid was considered as hydrocarbon biofuel in this study; and the