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Hydrotreatment of vegetable oil for green diesel over activated carbon supported molybdenum carbide catalyst

Fei Wang[a], Junming Xu[a,b,*], Jianchun Jiang[a,b,*], Peng Liu[a], Fanglin Li[a], Jun Ye[a], Minghao Zhou[a]

[a] *Institute of Chemical Industry of Forest Products, Chinese Academy of Forestry, National Engineering Lab. for Biomass Chemical Utilization, Key and Open Lab. of Forest Chemical Engineering, SFA, Key Lab. of Biomass Energy Sources and Materials, Nanjing 210042, China*
[b] *Jiangsu Qianglin Biomass Energy Co., Ltd., Liyang 213364, China*

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ABSTRACT

Catalysts were prepared and utilized in the hydrotreatment of vegetable oil and FAME to produce diesel-like hydrocarbons. Mo_2C/AC catalyst displayed the higher catalytic activity with 100.00% conversion and 21.01% cracking ratio, compared to MoO/Al_2O_3 (85.64%, 25.79%), MoS_2/Al_2O_3 (83.46%, 11.88%), Mo/Al_2O_3 (67.99%, 33.19%), NiP/Al_2O_3 (48.72%, 3.49%), Ni/Al_2O_3 (18.12%, 0.00%), and MoO/AC (56.05%, 18.55%). The reaction condition was also optimized, and the bio-diesel achieved 100.00% conversion, 9.67% cracking ratio and 0.73 HDO/DC ratio over Mo_2C/AC under the optimal condition. The conversion over Mo_2C/AC dropped from 100.00% to 87.08% and 71.06% with cycles. The results of XRD, XPS and N_2 adsorption–desorption demonstrated that the coke deposited on the surface of catalyst and the formation of MoO_2 and MoO_3 led to the deactivation. After regeneration, the catalyst recovered and achieved 99.36% conversion.

1. Introduction

The energy shortage and environmental pollution resulted from the abuse of fossil fuel, are becoming severe seriously. Fats and oils, which mainly consist of triglyceride, are considered as the most promising feedstock for bio-fuels since they have high carbon content. Compared to the pyrolysis, which conducts at 400–600 °C, hydrotreatment and transesterification of triglyceride are superior because of higher utilization ratio of carbon source. The first generation biodiesel (FAME) obtained from transesterification of triglyceride, was once used as the substitute for petroleum diesel [1]. However, the disadvantages of FAME, for instance, high oxygen content and poor cold-flow properties, limit its further development [2–4]. Through hydrotreatment the triglycerides were converted into diesel-like hydrocarbons, namely the second generation biodiesel and green diesel. As well as low oxygen content and high cold-flow properties, the green diesel processes high cetane number 85–99 even over fossil diesel (45–55) [4].

In the process of hydrotreatment of triglyceride, two fundamental steps take place. The first step is decomposition of triglyceride mainly by β-elimination to produce fatty acids. And the next step is deoxygenation of intermediate fatty acids to form diesel-like hydrocarbons by three major pathways: decarbonylation (DCO), decarboxylation (DCO), and hydrodeoxygenation (HDO) [5]. The catalysts and reaction parameters during hydrotreatment play an important role in the three pathways.

The two classes of catalysts commonly studied in hydrotreatment of triglyceride are noble metal catalyst (Pd or Pt) [6–9], and sulfided transition metal catalyst (Ni or Mo) [7,8,10,11]. Noble metal catalysts performs high catalytic activity but with expensive cost because of its scarcity. The sulfided transition metal catalysts are relatively cheap; however, the usage of sulfurizing reagent poses a great threat to the environment [10,11]. Moreover, the sulfur leaching also leads to the deactivation of catalysts and contamination of products [12]. Recently, transition metal carbides catalysts, especially molybdenum carbide (Mo_2C) were used in electrocatalytic hydrogen evolution and hydrodeoxygenation of biomass-derived oxygenation because of their noble metal behavior [13]. Lee et al. studied the hydrodeoxygenation of anisole over Mo_2C, and the result showed that Mo_2C exhibited remarkable selectivity for C—O cleavage and the benzene selectivity reached 90% [14]. The propanal, propanol and acetone were converted into propylene over Mo_2C in the study of Ren et al. [15]. Moreover, Han et al. [16,17] and Bitter et al. [12,18] also conducted the hydrodeoxygenation of triglyceride and fatty acids over Mo_2C to yield diesel-like hydrocarbons. It was proved that the high catalytic activity of Mo_2C was ascribed to interposition of carbon atom into lattice of molybdenum that broadens the distance between Mo atoms and enhances the d-band

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* Corresponding authors at: Institute of Chemical Industry of Forest Products, Chinese Academy of Forestry, National Engineering Lab. for Biomass Chemical Utilization, Key and Open Lab. of Forest Chemical Engineering, SFA, Key Lab. of Biomass Energy Sources and Materials, Nanjing 210042, China.
E-mail addresses: lang811023@163.com (J. Xu), bio-energy@163.com (J. Jiang).

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electron density at Fermi level of Mo [19].

However, the direct comparison of Mo_2C/AC and other catalysts for production of green diesel is impossible because the experiments are not conducted under the identical condition. What is more, rare researches reported the deactivation and regeneration of Mo_2C/AC during hydrotreatment. Therefore, in this study we compared the catalytic performance of Mo_2C/AC to MoO/Al_2O_3, MoS_2/Al_2O_3, Mo/Al_2O_3, NiP/Al_2O_3, Ni/Al_2O_3, and MoO/AC under the same condition. The reaction condition was also optimized. Moreover, the deactivation and regeneration of Mo_2C/AC was studied by XRD, XPS, and N_2 adsorption-desorption.

2. Experiment

2.1. Materials

Nickel nitrate hexahydrate, ammonium molybdate tetrahydrate, aluminum oxide, ammonium thiosulfate, and activated carbon were purchased from Aladdin. Ammonium hypophosphite and n-hexane were provided by Sinopharm Chemical Reagent Co., Ltd. The unsaturated fatty acid methyl ester (FAME) and vegetable oil, including soybean oil (SO) and rubber seed oil (RSO), were provided from Jiangsu Qianglin Biological Energy Co., Ltd. The FAME contained oleic acid methyl ester (85%) and methyl palmitate (15%). The compositions of vegetable oils were established by transesterification with methanol using potassium hydroxide as catalyst. The distribution of fatty acids of SO was following: oleic acid 71.5%, stearic acid 8.0%, and hexadecanoic acid 20.5%. The distribution of fatty acids of RSO was following: oleic acid 83%, stearic acid 7.5%, and hexadecanoic acid 9.5%.

2.2. Catalyst preparation

Mo_2C/AC with 15 wt% loading of Mo was prepared by carbothermal hydrogen reduction method with some changes[17,20]. The method was finished by four steps. First 60 g activated carbon was pretreated with 450 mL boiling nitric acid solution (6 mol L^{-1}) for 7 h. After that the mixture was cooled to ambient temperature, filtered, washed several times, and dried at 105 °C overnight. Secondly, the solid was impregnated by ammonium molybdate solution at 40 °C with the assistance of ultrasonic for 1.5 h. Then the water was removed by a rotary evaporator, and the obtained sample was dried at 105 °C overnight. Thirdly, the carburization was carried out in tube furnace in H_2 flow with the following temperature ramp: from ambient temperature to 450 °C at 5 °C min^{-1}, followed by 700 °C at 1 °C min^{-1}, and holding for 2 h. Finally, the catalyst was passivated in a flow of $1\%O_2/N_2$ at ambient temperature for 4 h. For comparison, MoO/AC was also synthesized while the method was similar to that of Mo_2C/AC. The difference was that carburization stage was carried out in a flow of N_2 at 700 °C for 2 h.

MoO/Al_2O_3 with the 15 wt% loading of Mo was prepared by incipient wetness [21]. The process began with the dry Al_2O_3 was impregnated using appropriate aqueous solution of ammonium molybdate tetrahydrate. Subsequently, the mixture was sonicated at 100 W at 40 °C for 1.5 h and dried at 105 °C overnight. Finally, the solid was calcined in air at 450 °C for 4 h.

The ammonium thiosulfate was used as sulfuration agent for preparation of MoS_2/Al_2O_3. At first MoO/Al_2O_3 was impregnated using aqueous solution of ammonium thiosulfate, and then dried at 105 °C overnight. At last the reduction of solid was conducted at 300 °C for 3 h in a H_2 flow.

The method to prepare NiP/Al_2O_3 with the 15 wt% Ni and 7.5 wt% P, was also incipient wetness, similar to the previous [22]. The nickel nitrate hexahydrate and ammonium hypophosphite were used as the sources of nickel and phosphorus respectively. Before the hydrotreatment experiment, the catalyst experienced reduction at 650 °C for 3 h in H_2 flow and passivation in 1% O_2/N_2 flow.

2.3. Catalyst characterization

The X-ray diffraction (XRD) spectra were recorded on D8 Focus diffractometer at a rate of 10.0° min^{-1} in the range $2\theta = 10.0°–90.0°$ using Cu $K_{\alpha 1}$ radiation at 40 kV. X-ray photoelectron spectroscope (XPS) analysis was performed on Thermofisher ESCALAB250Xi. Raman spectra were scanned on Thermofisher DXRxi with an excitation wavelength of 780 nm. The textural parameters of catalysts were analyzed by N_2 adsorption/desorption isotherm with Micrometric ASAP 2020 at 195.85 °C. Prior to measurement the catalyst was degassed under a vacuum at 200 °C for 10 h. The BET surface area and micropore volume were calculated from the linear portion of BET plot and t-plot method. The pore size distribution was determined by the BJH analysis from the desorption branch of the isotherms. The transmission electron microscope (TEM) images were obtained using FEI Tecnai G2 operated at 200 kV.

2.4. Typical hydrotreatment procedure

The hydrotreatment of FAME, SO, and RSO was performed in 250 mL autoclave batch reactor. The catalysts (2.0 g), feedstock (20.0 g), and n-hexane (60.0 g) as solvent were firstly added into reactor. And then the reactor was purged for three times by H_2, and pressured to 2.0 MPa. Subsequently, the batch reactor was heated electrically to 370 °C and held for 3 h. The mixture in reactor was stirred mechanically with 500 rmp during reaction.

Compounds of the liquid products were identified by Agilent 7890A/5975C. The 0.2 μL of liquid products were injected into the instrument. The capillary chromatographic column was a HP-5MS (30 m × 0.25 mm × 0.25 μm); the temperature of the injector was 260 °C, and the split ratio of the carrier gas was 1:50. The carrying gas used was high-purity helium. The oven temperature program proceeded as follows: first, the temperature was held at 150 °C for 2 min; then, the temperature was increased from 150 °C to 280 °C at 10 °C min^{-1}, and held at 280 °C for 10 min. For the MS condition, the ionization parameters were as follows: ionization methods, EI; ionization energy, 70 eV; scan per second over range electron (m/z), 30–500 amu; ion source temperature, 230 °C. The relative contents of compounds in liquid products were calculated based on the peak areas from GC.

Intermediate oxygenates in liquid were rarely detected, hence, the conversion of feedstock (Eq. (1)) was defined for the proportion of hydrocarbons (HC) in liquid products.

$$\text{Conversion} = C_{HC}/C_{TOL} \times 100\% \tag{1}$$

Where C_{HC} and C_{TOL} are the relative content of hydrocarbons and total compounds respectively.

HDO/DCO ratio of hydrodeoxygenation versus decarboxylation plus decarbonylation was calculated by the following Eq. (2):

$$\text{HDO/DCOratio} = (C16 + C18)/(C15 + C17) \times 100\% \tag{2}$$

Where C16, C18, C15 and C17 are the relative contents of hexadecane, octodecane, pentadecane, and heptadecane respectively.

The composition of FAME and transesterification products of SO and RSO mainly contained C16 and C18 fatty acid methyl ester. In liquid products, hydrocarbons with smaller carbon chains were also identified, which resulted from the cracking reaction. These hydrocarbons mainly were C9–C14. Cracking ratio was evaluated by the following Eq. (3):

$$\text{Cracking ratio} = (C_{HC}{-}C15{-}C16{-}C17{-}C18)/C_{TOL} \times 100\% \tag{3}$$

Where C_{HC}, C15, C16, C17, C18, and C_{TOL} are the relative contents of total hydrocarbons, pentadecane, hexadecane, heptadecane, octodecane, and total compounds respectively in liquid products.