



Activated carbon supported molybdenum and tungsten carbides for hydrotreatment of fatty acids into green diesel



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ABSTRACT

The activated carbon supported Mo₂C and W₂C were synthesized successfully for hydrotreatment of fatty acids to produce diesel-like hydrocarbons. The carburization temperature, carburization gas as well as metal loading amount were studied. High carburization temperature was feasible for W₂C/AC, but not for Mo₂C/AC because it resulted in agglomeration of molybdenum compound and destruction of catalyst. Under hydrotreatment condition (360 °C, H₂ 3.0 MPa, 3.0 h) the conversion achieved 96.01% over Mo₂C/AC prepared at 700 °C and 54.88% over W₂C/AC prepared at 900 °C respectively. During carburization both flowing nitrogen and hydrogen were proper for formation of W₂C/AC, while only flowing hydrogen was appropriate for Mo₂C/AC. The hydrotreatment parameters (reaction temperature and reaction time) were also investigated. The high reaction temperature and long reaction time facilitated the conversion of fatty acids, meanwhile the high reaction temperature simultaneously improved the cracking degree of products.

1. Introduction

The abuse of limited fossil fuel has led to the serious environmental issues and energy shortage, as a result, other eco-friendly and sustainable energy, such as solar, wind, hydro, nuclear energy and bio-energy are explored. Among these substitutes the bio-energy is the only one that could be used as transportation fuel [1]. The lipids comprised mainly of triglycerides and fatty acids pose an especially promising application for bio-fuel production.

The pyrolysis, transesterification and hydrotreatment are generally applied for liquid fuel production from lipids [2]. The pyrolysis of lipids produces gasoline-range hydrocarbons (\leq C10), but the yield of target products is rather low due to the creation of excessive gas. The fatty acid methyl ester (FAME), namely the first generation bio-diesel, derived from transesterification of lipids, is used to be substitute for petroleum diesel [3]. Unfortunately, the disadvantages of FAME including high oxygen content, high viscosity, high cloud point temperature, and poor oxidation stability restrict its further development [4,5]. The lipids are converted into diesel-range alkanes (C15–C18) via hydrotreatment, which is commonly referred to as the second generation bio-diesel or green diesel. The green diesel could completely

replace petroleum diesel because both share identical composition and energy densities [6].

In general, the triglycerides and fatty acids can be converted into green diesel by three reaction pathways: decarboxylation (DCO), decarbonylation (DCO), and hydrodeoxygenation (HDO) [7]. The oxygen of lipids is removed by decarboxylation in the form of CO₂, and the decarbonylation is in the form of CO and H₂O, while the hydrodeoxygenation pathway removes oxygen only in the form of H₂O. The proposed pathway of hydrotreatment reaction of fatty acids is shown in Fig. 1. The unsaturated fatty acids are firstly converted into saturated fatty acids through hydrogenation. The saturated fatty acids are further converted either into either C17 or C15 alkanes directly by decarboxylation (step 7), or into corresponding aldehydes (step 2). The conversion of aldehydes has two possible reactions: decarbonylation to form C17 or C15 alkanes (step 8) or transformation to its enol form (step 3). The next step requires enol to be hydrogenated into saturated alcohols followed by dehydration to produce alkenes (step 5) that are eventually hydrogenated into alkanes (step 6) [8,9]. The C15–C18 alkanes could be further cracked into light hydrocarbons (step 11 and 12). In addition, the unsaturated fatty acids could be converted directly into alkenes as shown in step 9 [7].

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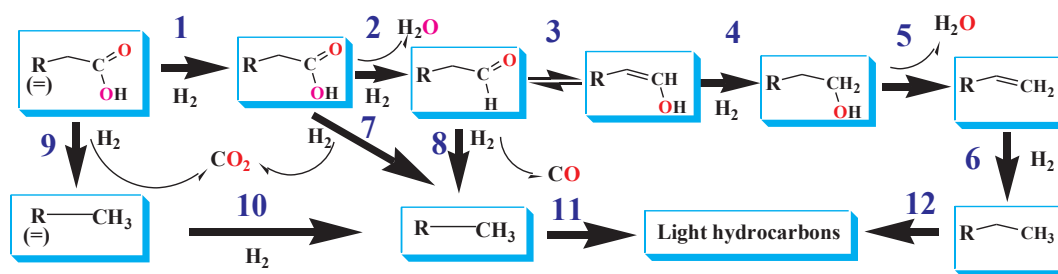


Fig. 1. Proposed scheme of hydrotreatment of fatty acids. R: C16 or C14.

Traditionally, two kinds of catalysts are applied in lipids hydro-treatment: sulfided molybdenum [10,11] and noble metal (Pt and Pd) [12]. However, the sulfurizing reagents employed for sulfided molybdenum pose a great threat to the environment [13]. The sulfur leaching, in addition, results in activity decline and contamination of products [8]. For expensive noble metal the scarcity restricts its large-scale application.

Recently the transition metal carbides, especially molybdenum carbide (Mo_2C) and tungsten carbide (W_2C), have gained increasing interest in hydrogen-involved reactions since the catalytic performance of low-cost transition metal carbides resembles Pt-group metal (Pd, Pt, Ru, Rh, and Os) [14]. Carburization in the stream of mixture of hydrocarbons and hydrogen is the most commonly used method to prepare metal carbides unsupported and supported on metal oxide [15]. Nevertheless, the catalysts prepared by this method are easily contaminated by polymeric carbon derived from the pyrolysis of carbonaceous gases since the char blocking the pores and covering the active sites is difficult to remove [16]. Strikingly, carbon material as support is endowed with many advantages, including excellent resistance to acid and base media, low cost and high thermal stability [17]. In addition, its high surface area and adsorption capacity greatly promote the dispersion of active sites and provide more contact with reactant that accelerate the reaction. Moreover, metal carbides supported on the carbon support could be synthesized in either hydrogen stream or nitrogen stream, instead of mixture of hydrocarbons and hydrogen [18]. The precious researches manifested that carbon supported Mo_2C exhibited excellent performance, even better than noble metal, nickel and sulfided molybdenum in hydrodeoxygenation of vegetable oils [19–21]. The Mo_2C and W_2C catalysts are commonly promising metal carbides, however the studies on their preparation and comparison in hydro-treatment of vegetable oil are deficient.

Therefore, in this work the Mo_2C and W_2C supported on activated carbon in H_2 or N_2 flow were synthesized and the catalytic activity of the prepared catalysts in hydrotreatment of fatty acids was compared as well. The research on the carburization temperature and loading amount of catalysts using XRD, XPS, N_2 adsorption/desorption, and TEM explained the catalytic activity in hydrotreatment of fatty acids. Moreover, the influence of hydrotreatment parameters (reaction temperature and reaction time) were studied.

2. Experimental

2.1. Materials

Ammonium molybdate tetrahydrate, ammonium metatungstate, tetramethylammonium hydroxide and activated carbon (AC) were purchased from Aladdin. The BET surface area and average pore size of the AC were $647.10 \text{ m}^2/\text{g}$ and 2.50 nm , respectively. The *n*-hexane, fatty acids, trichloromethane, and methanol were provided by Sinopharm Chemical Reagent Co., Ltd. The unsaturated fatty acids were composed of 11% palmitic acid and 89% oleic acid.

2.2. Catalyst preparation

Activated carbon supported molybdenum carbide ($\text{Mo}_2\text{C}/\text{AC}$) and tungsten carbide ($\text{W}_2\text{C}/\text{AC}$) were prepared by carbothermal hydrogen reduction method with some changes [20]. The method included four steps. First the 60 g AC was pretreated with 450 mL boiling nitric acid solution ($6 \text{ mol}\cdot\text{L}^{-1}$) for 3 h. After that the mixture was cooled to ambient temperature, filtered, washed several times, and dried at 80°C in vacuum overnight. Secondly, the solid was impregnated by ammonium molybdate solution or ammonium metatungstate solution at 40°C with the assistance of ultrasonic for 1.0 h. Then the obtained sample was dried at 80°C in a vacuum 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 $5^\circ\text{C}\cdot\text{min}^{-1}$, followed by final carburization temperature at $1^\circ\text{C}\cdot\text{min}^{-1}$, and holding for 2 h. Finally, the catalyst was passivated in a flow of $1\% \text{O}_2/\text{N}_2$ at ambient temperature for 2 h. $\text{N-Mo}_2\text{C}/\text{AC}$ (700°C) and $\text{N-W}_2\text{C}/\text{AC}$ (900°C) with 20% loading amount were also synthesized that the methods were similar to $\text{Mo}_2\text{C}/\text{AC}$ and $\text{W}_2\text{C}/\text{AC}$ respectively, and the difference was carburization in a flow of N_2 . For $\text{Mo}_2\text{C}/\text{AC}$ and $\text{W}_2\text{C}/\text{AC}$ the carburization temperature (600°C , 700°C , 800°C , and 900°C) and loading amount (10 wt%, 15 wt%, 20 wt%, 25 wt%, and 30 wt%) were studied. The corresponding catalysts were designated as $\text{Mo}_2\text{C}/\text{AC-T-W}$ and $\text{W}_2\text{C}/\text{AC-T-W}$ ($T = 600, 700, 800, \text{ and } 900$; $W = 10\%, 15\%, 20\%, 25\%, \text{ and } 30\%$).

2.3. Catalyst characterization

The X-ray diffraction (XRD) spectra were recorded on D8 Focus diffractometer at a rate of $10.0^\circ \text{ min}^{-1}$ in the range $2\theta = 10.0^\circ\text{--}90.0^\circ$ using $\text{Cu K}\alpha_1$ radiation at 40 kV. X-ray photoelectron spectroscopy (XPS) analysis was performed on ThermoFisher ESCALAB250Xi. The textural parameters of catalysts were analyzed by N_2 adsorption/desorption isotherm with Micrometric ASAP 2020 at -196°C . Prior to measurement the catalyst was degassed under a vacuum at 200°C for 10 h. The BET surface area and pore size distribution were calculated from the linear portion of BET plot and BJH model respectively. The transmission electron microscope (TEM) images were obtained using FEI Tecnai G2 operated at 200 kV.

2.4. Hydrotreatment test of fatty acids

The hydrotreatment of fatty acids was conducted in a 250 mL batch reactor. The typical method was as the follows. First of all, 1.0 g catalyst, 10.0 g fatty acids and 50.0 g *n*-hexane were introduced into the batch reactor. And then the reactor was purged for three times by H_2 , and pressured to 3.0 MPa. Afterwards, the liquid in reactor was heated electrically to the final reaction temperature and held for 3 h. Finally, when the reactor cooled down to the ambient temperature, the liquid products were collected. During the hydrotreatment reaction, the liquid was stirred mechanically with 500 rpm. The hydrotreatment parameters including reaction temperature (340°C , 350°C , 360°C , and 370°C) and reaction time (1 h, 2 h, 3 h, and 4 h) were investigated.

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