



Hydroprocessing of waste cooking oil over a dispersed nano catalyst: Kinetics study and temperature effect



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ABSTRACT

The kinetics of hydrodeoxygenation of waste cooking oil (WCO) is investigated with unsupported CoMoS catalysts. A kinetic model is established and a comprehensive analysis of each reaction pathway is carried out. The results show that hydrodecarbonylation/decarboxylation (HDC) routes are the predominant reaction pathways in the elimination of oxygen, with the rate constant three times as high as that of hydrodeoxygenation (HDO). However, the HDC activity of the CoMoS catalyst deactivates due to gradual loss of sulfur from the catalyst. HDO process is insensitive to the sulfur deficiency. The kinetic modeling shows that direct hydrodecarbonylation of fatty acids dominates the HDC routes and, in the HDO route, fatty acids are transferred to aldehydes/alcohols and then to C₁₈ hydrocarbons, a final product, and the reduction of acids is the rate limiting step. The HDO route via alcohols is dominant over aldehydes due to a significantly higher reaction rate constant. The difference of C₁₈/C₁₇ ratio in unsupported and supported catalysts show that a support with Lewis acid sites may play an important role in the selectivity for the hydrodeoxygenation pathways and promoting the final product quality.

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1. Introduction

Waste cooking oil (WCO) is accepted as a second generation resource for biofuel production [1–3]. Its main component, triglycerides, can be easily converted to combustible biofuel. However, due to the high oxygen content in triglycerides, the final products containing oxygen e.g. FAME, lead to poor storage stability, lower blending degree with petroleum diesel, and even cause engine compatibility issues [4,5]. Therefore, production of oxygen-free biodiesel is necessary to overcome these drawbacks and hydrotreating is a promising technique [6,7].

In order to produce oxygen-free biodiesel, many efforts have been made to study the mechanism of deoxygenation process. Previous works summarized that the deoxygenation process of triglycerides primarily occurs through two parallel paths: hydrodeoxygenation (HDO) route and hydro decarbonylation/decarboxylation (HDC) route. A main difference between the two pathways is the carbon yield in the final products: hydro decarbonylation/decarboxylation route leads to hydrocarbons with one carbon number lower than the feed oxygenates due to formation of CO or CO₂, while hydrodeoxygenation product maintains the same carbon number [8–12]. Carboxylic acids, aldehydes, and alcohols

are identified as the major intermediates, and their generation and consumption rates determine the total deoxygenation capability and selectivity [5,13,14]. Therefore, the real-time concentrations (RTC) of these intermediates are of great importance when studying deoxygenation process kinetics. Presently, most mechanism studies are focused on the model oils, which generally contain only one or few components [5,13–16]. This may lead to misunderstanding of the actual deoxygenation process on real WCO feed as the RTC could be altered without considering the influence of the complex feedstock compositions [8].

Another factor that may influence the oxygen removal is the support material of catalysts. Currently, commercial supported catalysts are widely employed in hydrotreatment of vegetable oils. The hydrotreating performance may involve the contribution of support material, and the catalyst support, alumina, alone has catalytic activity in hydrotreating reactions due to the Lewis acid site [16]. Centeno et al. investigated the effects of different support materials on the reaction pathways and product distribution. The report showed that acidity of support materials can influence the formation of catalysts' active sites for hydrogenation and decarboxylation of diethylsebacate [17]. Use of unsupported catalysts is a good alternative to investigate the activity of the active phase without involvement of support materials. In addition, unsupported catalyst presents minimal mass transfer resistance so as to minimize secondary effects, such as adsorption, re-adsorption and diffusion. A recently published work reported that the hydrodeoxygenation reaction of guaiacol (2-methoxyphenol) over unsupported and

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Table 1
Comparison of hydrotreating results with and without catalyst at 375 °C.

Hydrotreating time	Blank (without catalyst)		With catalyst	
	1 h	8 h	1 h	8 h
Oxygen conversion (%)	2.94	9.62	41.72	98.31
Glycerides conversion (%)	8.93	35.16	90.90	99.87

supported MoS₂ and CoMoS catalysts [18]. Guaiacol was used to represent pyrolysis oil of ligno-cellulosic biomass. However, limited reports were on the application of unsupported catalysts in the hydrodeoxygenation of triglyceride-type bio-oil.

In this work, a comprehensive kinetics analysis was carried out to understand the deoxygenation process using waste cooking oil and unsupported CoMoS. Reaction mechanisms and catalyst deactivation were investigated using kinetic modeling based on a proposed reaction network. The calculated rate constants indicate dominant reactions and rate-limiting steps in a series of parallel and consecutive reactions. Other reactions including hydrocracking, polymerization, hydrogenation, and cyclization were also studied as well as the reaction temperature effect. The comprehensive analysis of deoxygenation process would provide valuable information on the mechanism study of vegetable oil type feedstock with unsupported catalysts.

2. Experimental

2.1. Catalyst synthesis

Unsupported catalyst CoMoS was synthesized using a hydrothermal method with MoO₃ (purchased from the STEM Scientific), Na₂S·9H₂O and Co(NO₃)₂·6H₂O (from the Fisher Scientific) as precursors. The precursors were dissolved in deionized water before introducing them into an autoclave reactor. The hydrothermal reaction lasted for 2 h at 320 °C. The detailed synthesis procedure is referred to Zhang et al. [19].

2.2. Hydrotreating process

A batch reactor (Autoclave Engineers Inc.) was used in this study, 0.6 g of unsupported CoMoS catalyst and 120 g of waste cooking oil (WCO) were added to the reactor, making the catalyst-to-oil ratio 1:200 by weight. The reactor was heated to pre-set temperatures (300–375 °C) and kept for 8 h under a stirring speed of 1000 rpm. The pressure was maintained at 1300 psi at the reaction temperatures. Liquid samples were taken at different time intervals during the reaction. The gaseous products were collected when the reaction was complete and the reactor was cooled down to room temperature. In this experiment, the internal and external mass transfer for the catalyst was assumed to be negligible, since nano-sized dispersed catalyst powders were applied [20]. For comparison purpose, a blank experiment (without catalyst) was carried out under the same hydrotreating condition at 375 °C. Table 1 shows low glycerides and oxygen conversions compared to the situation with catalyst. Therefore, the thermal effect was not considered in the kinetics studies.

2.3. Characterization

Transmission electron microscopy (TEM) was performed on an electron microscope (JEOL 2011 STEM, JEOL Ltd., Tokyo, Japan) operating at 200 keV. The catalyst powder was ultrasonically dispersed in ethanol and deposited on a carbon-coated copper grid, then vacuum-dried for 12 h before analysis. The length and layer numbers of CoMoS crystalline were determined using image

analysis software and the average was calculated based on at least 100 CoMoS measures from various particles. Selected area electron diffraction (SAD) pattern was used for the determination of catalyst crystal structure. The Co/(Co + Mo) ratio of the catalyst was estimated by energy dispersive X-ray emission (EDX) coupled with TEM.

The fatty acids of WCO were analyzed following the procedure described by Simaek et al. [21]. The oil sample was added to a flask containing methanolic NaOH solution and heated until all WCO was completely dissolved. By introducing BF₃-methanol and boiling for 2 min complete esterification occurred. Petroleum ether and saturated NaCl solutions were then added to extract and separate the organic components. The resultant fatty acid methyl esters appeared in the top petroleum ether layer and were analyzed using a gas chromatography–mass spectrometry (Shimadzu GCMS-QP5000) with a weak-polarity column (Agilent J&W HP-5).

The components in the oil products were identified by GC–MS (Shimadzu GCMS-QP5000) and quantified using gas chromatography (Varian 450) equipped with a hydrogen flame ionization detector. A non-polarity capillary column Agilent J&W VF-1ms was used to quantify hydrocarbons. The free fatty acids were analyzed using both gas chromatography (Shimadzu GC-17A) and titration (ZD-2A Automatic potentiometric titrator, Saegmoter Company, Shanghai, China) according to ASTM-D664. The content of intermediate alcohols and aldehydes was estimated by the peak area (MS%) and response factor to *n*-heptadecane of 1.3 and 1.4, respectively [22]. The unreacted triglycerides were derived from the oxygen content.

The original WCO and the upgraded products were analyzed using a Fourier transform infrared spectrometer (FTIR) (Nicolet 6700, Thermo Scientific, US). The spectra were collected for 32 scans at a resolution of 4 cm⁻¹ in the range of 400–4000 cm⁻¹. ¹H nuclear magnetic resonance (NMR) spectra were recorded with a high-field multinuclear Agilent UNITY INOVA NMR spectrometer (Varian Unity 400) under standard acquisition conditions. The operating frequencies were 300 MHz; *d*-chloroform was used as solvent.

The elemental analysis for WCO and upgraded products were conducted on CHNS-O 932 elemental analyzer (LECO Corporation, MI, US). The oxygen content was calculated from the balance. The minimum measurability is 10 ppm for carbon and 100 ppm for hydrogen on the basis of a normal sample load (i.e. 2 mg). The density of the liquid oil was measured using a portable density meter (DMA 35N, Anton Paar GmbH, Graz, Austria).

CO and CO₂ generated during hydrotreating were analyzed using a gas chromatography Varian 3400 equipped with a thermal conductivity detector. Hydrocarbons, C1–C6, were examined using a Shimadzu GC-17A equipped with a flame ionization detector.

3. Results and discussion

3.1. Unsupported catalysts

The TEM images shown in Fig. 1 illustrate a well dispersed (a) and layered crystalline structure (b) of unsupported nano-sized CoMoS catalyst. The average crystalline size was calculated by Eqs. (1) and (2), where *L*, *N* and *n* stand for slab length, number of layers in each crystal, and the total number of crystalline measured, respectively. The statistic results show that the catalysts have an average layer number of 3 and an average slab length of 7.8 nm. According to Rim and Edge theory, Co decorated at the edge of MoS₂ [23,24]. EDX results show the average Co/(Co + Mo) atomic ratio is 25%. The well-dispersed MoS₂ slabs provide abundant active sites for hydrodeoxygenation. The MoS₂ crystalline structure was also confirmed by electron diffraction spectra on the selected area

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