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Transesterification of used cooking oil (UCO) catalyzed by mesoporous calcium titanate: Kinetic and thermodynamic studies

Noor Yahida Yahya, Norzita Ngadi*, Syieluing Wong, Onn Hassan

Department of Chemical Engineering, Faculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor, Malaysia

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ABSTRACT

Due to the superior catalytic property of calcium oxide in biodiesel production via transesterification, it is necessary to modify such catalyst to retain the catalytic property while overcoming the disadvantages related to the catalyst application in the process. The present study focused on the kinetic and thermodynamic studies on the transesterification of used cooking oil (UCO) catalyzed by mesoporous calcium titanate (MCT). The experiments were performed at room temperature, 65 °C, and 100 °C. Among the various models being studied, the Pseudo First order is the best model to describe the reaction kinetic. Data analysis showed that the rate constants, k, varied in the range of 0.0233–0.058 s^{-1}, while the activation energy, E_a was determined to be 21.25 $kJ{\cdot}mol^{-1}$. The following parameters were also obtained: −24 $kJ{\cdot}mol^{-1}$ for enthalpy (ΔH), −0.16 $kJ{\cdot}mol^{-1}{\cdot}K^{-1}$ for entropy (ΔS) and 25.62–35.70 $kJ{\cdot}mol^{-1}$ for Gibb's free energy (ΔG). The results showed that the reaction was exothermic ($\Delta H < 0$), and that the biodiesel oxidation reaction is non-spontaneous and endergonic in nature ($\Delta G > 0$). This study demonstrates the potential of MCT catalyst in promoting the conversion UCO into biodiesel with high quality fuel properties.

1. Introduction

There is ongoing research in the development of heterogeneous catalysts for biodiesel production. Among the numerous heterogeneous basic catalysts, calcium oxide (CaO) seems to be the most promising candidate, as it is abundantly available, environmentally friendly, while possessing high catalytic activity [1–5]. However, the major challenge of CaO application in transesterification is the undesired reaction with the free fatty acid (FFA) and water content in the feedstock, especially used cooking oil (UCO) [6,7]. In addition, the low surface area, instability and the bulky structure also adversely affect the catalytic activity of CaO in transesterification to a significant extent. Therefore, a higher amount of catalyst and a longer reaction time are often required during the biodiesel production [1,8]. Besides that, CaO is unstable, thus leaching problem is often reported during the reaction [9]. Consequently, the catalytic property and lifespan of the catalyst, as well as the quality of biodiesel are affected [10]. Furthermore, the bulky structure of CaO restricts contact of the large triglyceride molecules of UCO with all the active basic sites of the catalyst, hence the catalytic property is not fully utilized.

Currently, research on the application of various catalyst supports for CaO has increased exponentially, with the hope to overcome the mentioned challenges [11,12]. Titanium is one of the catalyst supports being studied due to the high surface area, high structural strength, chemical durability, thermal stability and non-toxic properties associated with the element [13–16]. Furthermore, the surface of titanium is excellent in adsorption of the reactant molecules, followed by reaction and the subsequent dissociation of products, which is the important property for the catalyst [17]. It should be noted that CaO suffers the lack of porosity, which is important to minimize diffusion limitations of the reactant molecules during biodiesel production via transesterification. Among the different types of porosity, mesoporous structure has been extensively studied in recent years [18–20]. However, no study was carried out on the possible improvement of biodiesel production over the mesoporous CaO supported on titanium oxide (denoted as MCT) MCT as a heterogeneous basic catalyst. Therefore, our previous work [21] explored on biodiesel production from UCO. The study demonstrated a simple method to synthesize the heterogeneous basic catalyst. The catalyst properties were analyzed and discussed extensively, with correlation to the change of process performance under different conditions for a better understanding on the catalytic activity. Herein, this paper focuses on the kinetic and thermodynamic studies on the transesterification reaction over MCT catalyst. Additionally, the quality of the biodiesel produced was also examined using ASTM D6751 and EN 14214 standard methods. This study is expected to contribute to the knowledge pool on the use of heterogeneous basic catalyst to

* Corresponding author.
E-mail address: norzita@cheme.utm.my (N. Ngadi).

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improve the CaO catalytic reaction system for biodiesel production from UCO.

2. Materials and methods

2.1. Materials

UCO was obtained from a local restaurant in Johor, Malaysia. Titanium tetrabutoxide (97%) was purchased from Sigma-Aldrich. Calcium oxide (CaO) was acquired from Alfa Aesar. Ethanol (95%), glacial acetic acid and methanol were supplied by QRec. n-Heptane (99%) used in the product analysis was obtained from Merck. All chemicals were of analytical grade.

2.2. MCT catalyst preparation

The MCT catalyst was prepared by sol-gel hydrothermal method as described in the previous work [21]. Firstly, glacial acetic acid was mixed with ethanol with stirring. Then, titanium tetrabutoxide was added drop-wise to the solution, followed by vigorous stirring until a white gel was formed. After that, the gel was added to the calcium oxide solution. Subsequently, the mixture was transferred into a Teflon-lined stainless steel autoclave and heated at 150 °C for 24 h. Then, the material was dried in the oven for 12 h at 80 °C, followed by calcination at 550 °C for 3 h.

2.3. MCT catalyst characterization

X-ray photoelectron spectroscopy (XPS) analysis was performed on the prepared catalyst using a Shimadzu Axis Ultra DLD spectrometer, with aluminium X-ray source. The spectra of C 1s, Ca 2p, O 1s and Ti 2p were recorded and deconvoluted using the Casa XPS software. The morphology of the catalyst was investigated by transmission electron microscopy (TEM) (JEOL JEM-2100F, accelerating voltage of 120 kV). The sample was ultrasonically dispersed in acetone and deposited on an amorphous, porous carbon grid. Raman spectroscopy was performed using LabRAM HR Evolution microscope (HORIBA) with an argon ion laser as illumination source (514.5 nm) equipped with charge-coupled device (CCD) detector. The Raman equipment was coupled with a LECA microscope (50× magnification) with a collection optic used in back-scattering configuration. The laser power was kept in a range of 1.0–3.0 mW to prevent sample overheating. In order to investigate the Ca dispersion on the MCT surface, temperature-programmed reduction (H_2-TPR) was carried out using Micromeritics Chemisorb 2720 Pulse Chemisorption Analyzer. Prior to the H_2 chemisorption, 30 mg of the catalyst was reduced by pure H_2 gas (20 mL min^{-1}) at 900 °C for 1 h. The amount of H_2 uptake was determined by injecting 10% of H_2/Ar gases periodically into the reduced catalyst at 10 °C min^{-1}. The Ca dispersion and MCT surface area were calculated by assuming that one hydrogen atom reacts with one Ca atom.

2.4. Catalytic run

Typically, transesterification reaction was carried out in a two-neck round bottom flask (250 mL) equipped with a reflux condenser, a thermometer and a digital hot plate with a magnetic stirrer. The following conditions were used: 3:1 for the molar ratio of methanol to triglyceride, 0.2 wt% for the catalyst loading, and 1 h for the reaction time under vigorous stirring in a silicon oil bath. The reaction mixture was cooled upon reaction completion, prior to the separation of the used catalyst by filtration. After that, the mixture was allowed to settle by gravity, followed by separation of biodiesel and glycerol layers using a separating funnel. The percentage of biodiesel yield was calculated using Eq. (1), and the product composition was analyzed using gas chromatography coupled with mass spectroscopy (GC–MS) as explained in previous work [21].

$$\%\ Biodiesel\,yield = \frac{\text{Amount of biodiesel(g)}}{\text{Amount of UCO(g)}} \times 100\% \tag{1}$$

2.5. Kinetic and thermodynamic study

2.5.1. Determination of reaction order

Generally, the whole scheme of the transesterification reaction occurs via three successive steps, in which diglycerides (DG), monoglycerides (MG) and glycerol (GL) are formed as specified in Eqs. (2)–(4). Each intermediate step involves reaction between one mole of methanol and *n*-glyceride compound, producing one mole of methyl ester (ME). Upon the reaction completion, three molecules of ME and one molecule of glycerol are formed, thus the reaction can be summarized as Eq. (5), without considering the formation of monoglyceride and diglyceride.

$$\text{TG} + \text{MeOH} \leftrightarrow \text{DG} + \text{M} \tag{2}$$

$$\text{DG} + \text{MeOH} \leftrightarrow \text{MG} + \text{ME} \tag{3}$$

$$\text{MG} + \text{MeOH} \leftrightarrow \text{GL} + \text{ME} \tag{4}$$

$$\text{TG} + 3\text{MeOH} \leftrightarrow \text{GL} + 3\text{ME} \tag{5}$$

The reaction kinetic was investigated by performing the transesterification in six experimental setups, each with different time intervals (10, 20, 30, 40, 50 and 60 min). The experiment was carried out at three different temperatures (room temperature, 65 °C and 100 °C). The molar ratio of methanol to oil and catalyst loading were selected based on the result from previous work [21]. In this study, the rate of reaction was determined based on the rate of product yield, $\frac{dME}{dt}$. To obtain the kinetic parameters of transesterification reaction, the experiment data was fitted to linear forms of Zero, First, Pseudo first and Second Order models respectively. This was followed by determination of the reaction rate constants, (k) from the linear graphs for all the models, and the one with the highest correlation coefficient was used to determine the particular reaction order for the reaction.

Zero order:

$$\text{ME} = -\text{kt} + \text{c} \tag{6}$$

The linear graph can be obtained by plotting ME (yield of product) against time, t, and the rate constant, k, is represented by the slope of the graph.

First order:

$$2.303\log\frac{ME_t}{ME_o} = -kt \tag{7}$$

The linear graph can be obtained by plotting $\log\frac{\text{ME}_t}{\text{ME}_o}\left(\frac{\text{ME}_t}{\text{ME}_o}=\text{ME}\right)$ against time, t, and the rate constant, k, is represented by the slope of the graph.

Pseudo First order:

$$\ln(1-\text{x}) = -\text{kt} \tag{8}$$

The linear graph can be obtained by plotting ln (1 − x) (ln (1 − x) = $\left(\frac{\text{ME}_t}{\text{ME}_o}=\text{ME}\right)$) against time, t, and the rate constant, k, is represented by the slope of the graph.

Second order:

$$\frac{1}{ME} = kt + C \tag{9}$$

The linear graph can be obtained by plotting $\frac{1}{\text{ME}}$ against time, t, and the rate constant, k, is represented by the slope of the graph.

2.5.2. Determination of activation energy

The activation energy, E_a, of the reaction was calculated based on the reaction rate constants (k) by using Arrhenius equation (Eq. (10)). The linear form of the Arrhenius equation is expressed in Eq. (11). Based on the equation, the value of E_a can be determined based on the