Effect of Synthesis Conditions of Cr-Ti Mixed Oxides on FAME and Catalyst Characteristics

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Abstract. Biodiesel or fatty acid methyl ester (FAME) is one of the best alternative renewable energy source and environmental friendly fuel to replace diesel. Cr-Ti mixed oxides catalysts were synthesized via sol-gel method for the transesterification of cooking palm oil (CPO) to produce FAME. The reactions were conducted in a batch reactor. The effects of calcination time and ethanol solvent volume were studied. The calcination time of the Cr-Ti mixed oxides between 1 h to 5 h and ethanol volume between 20 mL to 60 mL shows effect on the FAME density obtained in the reaction. It was also observed that calcination time affects the catalyst surface area, pore diameter and pore volume. The results shows that the Cr-Ti catalyst prepared at 2 h calcination time with 50 mL ethanol volume has the highest surface area, pore volume and pore diameter among the prepared catalysts and obtained FAME density of 841.5 kg/m³. The FAME density is within the value range of the biodiesel fuel property. Thus, Cr-Ti mixed oxides catalyst shows good potential as heterogenesous catalyst for transesterification of CPO to produce FAME.

1. Introduction
The world's population continuous growth and rapid urbanization will result in a substantial increase in energy demand over the coming years. The use of non-renewable energy such as fossil fuel is considered unsustainable due to depleting resources as well as accumulation of greenhouse gases detrimental to the environment. Biodiesel or fatty acid methyl ester (FAME) is one of the best alternative fuels which have environmentally benign nature and its fuel properties and energy content are similar to those of petroleum diesel [1].

FAME is mainly produced from reaction of plant oil with methanol via transesterification with the aid of catalyst. The use of homogeneous catalyst such as NaOH contributes to costly manufacturing process and environmental hazards due to complex separation and purification steps. Heterogeneous catalyst could overcome the homogeneous catalyst limitation as it offers catalyst reusability, simpler product separation and purification, reduce waste generation and environment friendly [2].

Several of reported works utilized heterogeneous catalyst based on metal oxides to produce FAME such as TiO₂-MgO and Cr₂O₃ [3][4]. In our previous work, Cr based mixed oxides catalyst have shown good potentials in the FAME production [5]. In this work, the Cr-Ti mixed oxides catalysts were synthesized via sol-gel method and prepared at various calcination time and different solvent.
volume. The effects of synthesis conditions of Cr-Ti mixed oxides was tested by the analysing the FAME density produced via trans esterification of CPO. In addition, the catalyst porosity characteristics were also analysed.

2. Methodology

2.1. Materials and Chemicals
The chemicals that were used in the catalyst preparation are chromium (III) nitrate nonahydrate with 99 wt% purity (Merck), titanium (IV) butoxide with 97 wt% purity (Merck), nitric acid with 65 wt% purity (Qrec), ethanol with 99.8 wt% purity (Qrec) and methanol with 99 wt% purity (Qrec). CPO was purchased from local supermarket in Penang, Malaysia.

2.2. Catalyst preparation
Cr-Ti mixed oxides catalysts were prepared with various calcination time of 1 h, 2 h, 3 h, 4 h and 5 h via sol-gel method. In a typical catalyst preparation, chromium (III) nitrate nonahydrate and titanium (IV) butoxide ratio by mass of 1:2 were weighed and mixed with 10 mL of deionized water in separate beaker. For 40 mL ethanol solvent volume, the ethanol was mixed with 1 mL of nitric acid and 10 mL titanium (IV) butoxide solution prepared into a 250 mL beaker and continuously stirred. Then, 10 mL chromium (III) nitrate nonahydrate solutions prepared was slowly added into the same beaker and the solution was allowed to stir on the magnetic stirrer hot plate at 400 rpm and 55 °C for 4 h. For aging process, the sample was then left for 24 h until gel is formed. The sample was then dried in an oven for 24 h at 130 °C. For 1 h calcination time, it was calcined in air using a muffle furnace at 500 °C. The steps were repeated for all remaining calcination time. For the study on the effect of solvent volume, the volumes of ethanol used were varied at 20 mL, 30 mL, 40 mL, 50 mL and 60 mL.

2.3. Transesterification of CPO and FAME Analysis
The transesterification of CPO was carried out using the prepared catalyst. For a typical conditions, the reactants mixture consists of 15:1 methanol to oil molar ratio was filled into a 250 mL beaker with catalyst loading of 2.5 wt.% of oil. The system and its content was continuously stirred at maximum of 500 rpm with an overhead stirrer throughout the reaction to keep the system in uniform suspension and maintain at 55 °C temperature. The reaction time was set for 3 h. At the end of the reaction, the hot plate and overhead stirrer were switched off and the system were left to cool down at room temperature. Finally, the catalysts were separated from the product mixture via centrifugation at 3000 rpm for 15 min and left to settle for 12 h to separate into 2 phases. FAME was observed at the top layer while glycerol at the bottom layer. The FAME density of the sample obtained was analyzed by Micromeritics pycnometer model AccuPyc II 1340.

2.4. Catalyst Characterization
ASAP 2020 Micromeritics instrument was used to determine the Brunauer-Emmett-Teller (BET) surface area, pore volume and pore size distribution properties of the Cr-Ti mixed oxides catalysts.

3. Results and Discussions

3.1. Effect of calcination time
Calcination is essential in the preparation of heterogeneous catalyst, and it can influence the structural and catalytic activities [6]. Figure 1 shows the FAME density obtained from the trans esterification reaction of CPO with Cr-Ti mixed oxides catalysts prepared at various calcination times. The FAME density is constant at 910.2 kg/m³ for catalyst calcined at 1 h, 3 h and 4 h. However, when the catalyst was calcined for 5 h, FAME density increased to 911.2 kg/m³. The catalyst calcined at 2 h obtained the FAME density of 905.9 kg/m³ which is close to standard palm oil biodiesel density [7]. The FAME density obtained is similar to the reaction using palm fatty acid distillate (PFAD) via Cr-Ti catalyst [2].
3.2. Effect of solvent volume

Figure 2 shows the graph of FAME density for the effect of solvent volume in the preparation of Cr-Ti mixed oxides. FAME density increased from 840.7 kg/m$^3$ to 1098.2 kg/m$^3$ when the ethanol volume was increased from 20 mL to 30 mL. However, for 40 mL to 60 mL ethanol solvent used, the FAME density decreased from 905.9 kg/m$^3$ to 839.4 kg/m$^3$. It was observed that the mixture of the chromium (III) nitrate nonahydrate and titanium (IV) butoxide has formed a gel when 20 mL and 30 mL ethanol volume were used. This condition might occur due to low amount of solvent used during the preparation of the catalyst. Also, there was only a slight reduction of FAME density between 50 mL and 60 mL ethanol solvent used. This could be due to sufficient volume of solvent required was reached between 50 mL and 60 mL of ethanol used. The catalyst prepared with 50 mL solvent volume obtained the FAME density of 841.5 kg/m$^3$ which is close to standard palm oil biodiesel density [7].
3.3. Catalyst Characterization

Table 1 shows the surface area, total pore volume and average pore size of the three selected catalysts prepared at various calcination time and ethanol solvent volume. The result indicates that catalyst prepared with 50 mL ethanol solvent and calcined for 2 h produced the closest FAME density comparable to the standard of palm oil biodiesel density [7] with highest surface area, total pore volume and average pore size among the catalysts. Average pore size for the catalysts was in the range of 104 – 121.9 Å, which can be classified as mesoporous since the pore diameter are within 20 – 500 Å. The pore size is a vital requirement for an ideal solid catalyst in the reaction to produce FAME since a typical triglyceride molecule has a diameter of approximately 58 Å [8]. Thus, it is sufficient to accommodate the reactant molecules to adsorb on the active sites of the catalysts.

| Catalyst no. | Reactivation temperature (°C) | 1 | 2 | 3 |
|--------------|--------------------------------|---|---|---|
| Calcination time (h) | Ethanol volume (mL) | Surface area (m²/g) | Pore volume (cm³/g) | Pore size (Å) | FAME density (kg/m³) |
| 5 | 40 | 70.8903 | 0.184597 | 104.1594 | 911.2 |
| 2 | 40 | 82.7358 | 0.219711 | 106.2229 | 905.9 |
| 2 | 50 | 93.1493 | 0.284051 | 121.9765 | 841.5 |

It is observed that the pore diameter of the catalyst increased correspondingly with the volume of ethanol solvent used. However, as the calcination time increase, the pore size of the catalyst decreases that could be due to sintering effect at high calcination temperature [9]. Surface area of a catalyst also plays an important role in enhancing the catalytic activity of heterogeneous system. The catalyst calcined for 5 h had the lowest surface area and pore volume of 70.89 m²/g and 0.1846 cm³/g, respectively and obtained FAME density of 911.2 kg/m³. The FAME density obtained is not within the standard palm oil biodiesel density, thus indicate the catalyst reduced activity. The catalyst prepared with 50 mL ethanol solvent and calcined for 2 h shows the highest surface area and pore volume among the selected catalysts at 93.15 m²/g and 0.284051 cm³/g, respectively and obtained the FAME density closest to the standard palm oil biodiesel density [7].

4. Conclusions

This study on Cr-Ti mixed oxides catalysts in production of FAME from CPO has shown that the catalyst prepared with 50 mL solvent volume and calcined at 2 h obtained the FAME density of 841.5 kg/m³. The value is closest to the standard palm oil biodiesel density of 864 kg/m³, which indicates good catalytic activity. The catalyst also has the highest surface area, pore volume and pore diameter among the selected catalysts. The results indicate that Cr-Ti catalyst has promising application in FAME production from CPO.

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