Effects of Metal Ratio and Aging Time of Cr-Ti Mixed Oxides on Catalyst Characteristics and FAME Density

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Abstract. Fatty acid methyl ester (FAME) or biodiesel is alternative source for diesel fuel due to its renewability and environmentally friendly nature. In this study, mixed oxides catalysts of Cr-Ti were synthesized by using sol-gel method and used in transesterification of cooking palm oil (CPO) in a batch process to produce FAME. The effects of metal ratio and aging time were studied. The metal ratio Cr:Ti of 1:1, 1:2, 2:1, 0:1 and 1:0 and aging time between 1 day and 5 days contributed effects on the FAME density obtained from the reaction. The catalyst characteristics in term of surface area, pore size, pore volume and thermal stability were also affected by the various metal ratio and aging time during catalyst synthesis. The results show that Cr-Ti catalyst prepared at 2:1 metal ratio and 5 days aging time exhibit FAME density of 854 kg/m^3, which is within the value range of biodiesel fuel property. The catalyst has surface area of 45.88 m^2/g, pore size of 190.52 Å and pore volume of 0.1984 cm^3/g sufficient to promote efficient heterogenous catalytic activity and has good thermal stability. Thus, Cr-Ti mixed oxides have potential as heterogeneous catalyst to produce FAME from the transesterification of CPO.

1. Introduction
To meet the rising energy demand and reducing petroleum reserves, fuels such as biodiesel and bioethanol are in the forefront of alternative energy sources. Accordingly, the viable alternative fuel for compression ignition engines is biodiesel or technically known as fatty acid methyl ester (FAME) [1]. The physical and chemical properties of FAME are similar to the petroleum diesel and its benefits are low emissions of hazardous pollutants such as SO_2 and NO_2 emissions. At present, the most common way to produce FAME is by transesterification of plant oils with alcohols. Although the transesterification rate is high by using homogenous catalyst, the large amount of water is required during washing and purification steps resulting in wastewater pollution. On the other hand, the use of a heterogeneous catalyst for FAME production has many advantages such as environmentally friendly with less wastewater produced, non-corrosive to reactor and easily separated from reaction mixture [2].

Previous study showed that chromium-titanium mixed oxides catalyst possesses good potential in esterification of palm fatty acid distillate (PFAD) [3]. Additionally, CrWO_4 is another type of heterogeneous catalyst that showed good performance with highest value of 86% FAME [4]. Titanium dioxide nanoparticles are among most widely studied, which reported above 90% FAME yield. The catalysts exhibit properties such as high acidity, high surface area, thermal stability, low toxicity and high reusability [5]. Chromium-aluminum mixed oxides were effective in FAME production from microalgae [6]. Some independent properties of these Cr based catalyst and Ti based catalyst have been reported that shows desirable properties such as its acidity, porosity and surface area. In our
previous work, Cr based mixed oxides catalyst have shown good potentials in the FAME production [7]. In this work, the Cr-Ti mixed oxides catalysts were synthesized via sol-gel method and prepared at various metal ratio and aging time. The effects of synthesis conditions of Cr-Ti mixed oxides were evaluated based on the FAME density obtained via transesterification of CPO. In addition, the catalyst porosity characteristics and thermal stability were also studied.

2. Methodology

2.1. Materials and chemicals
Cooking Palm Oil (CPO) was purchased from Vesawit Malaysia. Methanol (99% purity), nitric acid (65% purity) and ethanol (99.8% purity) were purchased from Qrec (Asia) Sdn Bhd. Chromium (III) nitrate nonahydrate and titanium (IV) butoxide was purchased from Sigma Aldrich Malaysia Sdn. Bhd. Nitrogen, helium and purified air were purchased from Linde Malaysia Sdn Bhd. All the chemicals used were analytical reagent grade.

2.2. Catalyst preparation
Cr-Ti mixed oxides catalysts were prepared with various Cr:Ti metal ratio of 1:0, 0:1, 1:1, 1:2 and 2:1 via sol-gel method. In a typical catalyst preparation, chromium (III) nitrate nonahydrate and titanium (IV) butoxide ratio by mass of 1:1 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 1 day until gel is formed. The sample was dried in an oven for 24 h at 130 °C and then calcined in air using a muffle furnace at 500 °C for 2 h. The steps were repeated for all remaining metal ratio. For the study on the effect of aging time, the duration was varied at 1 day, 2 days, 3 days, 4 days and 5 days.

2.3. Transesterification of CPO and FAME analysis
The transesterification of CPO was carried out using the prepared catalyst. For a typical condition, 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 were 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 4 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. The sample was separated from the product mixture via centrifugation at 3000 rpm for 15 minutes. It was left to settle for 12 hours to separate into 2 phases, which are FAME layer at the top and glycerol layer at the bottom. The FAME density of the sample obtained was analyzed by Micromeritics pycnometer model AccuPyc II 1340 [8].

2.4. Characterization of catalysts
The ASAP 2020 Micromeritics instrument was used to determine the Brunauer-Emmet-Teller (BET) surface area, pore volume and pore size of the prepared catalysts. The SDT Q600 Thermal Gravimetric Analysis (TGA) instrument was used to measure the weight changes in the catalysts as a function of temperature in a controlled atmosphere in order to determine their thermal stability.
3. Results and Discussions

3.1. Effects of metal ratio

Figure 1 shows the FAME density obtained from the transesterification of CPO with Cr-Ti mixed oxides catalysts prepared at various Cr:Ti metal ratio. The FAME density is almost constant at 914 kg/m$^3$ and 915 kg/m$^3$ for catalyst prepared at Cr:Ti metal ratio of 1:0 and 1:1, respectively. However, the FAME density are lower for Cr:Ti metal ratio of 2:1, 1:2 and 0:1. The catalyst prepared at Cr:Ti metal ratio of 2:1 obtained the FAME density of 906 kg/m$^3$ which is closest to the standard palm oil biodiesel density [9].

![Figure 1](image1.png)

**Figure 1.** FAME density for different metal ratio of Cr:Ti mixed oxides

3.2. Effects of aging time

The sol-gel method involves dissolving the precursors in a solvent such as ethanol. The precursors are then activated by the addition of nitric acid. The polarized solvent then becomes attracted to the activated precursors, thus binds the different precursors to form a network. The aging process allows the network to grow over time that increases the viscosity of the solution. Figure 2 shows FAME density decreased gradually from 906 kg/m$^3$ to 854 kg/m$^3$ when the aging time was increased from 1 day to 5 days. The mixture of the precursors (chromium (III) nitrate and titanium (IV) butoxide) need sufficient aging time to form a stable network during the sol gel process. The catalyst prepared at aging time of 5 days obtained the FAME density of 854 kg/m$^3$ which is closest to the standard palm oil biodiesel density of 864 kg/m$^3$ [9]. The FAME density obtained is similar to the reaction using palm fatty acid distillate (PFAD) via Cr-Ti catalyst. FAME density is an important property of biodiesel because it influences the efficiency of atomization of the fuel [10].
3.3. **Catalysts characterization**

Table 1 shows the surface area, total pore volume and average pore size of the four selected catalysts prepared at various Cr:Ti metal ratio and aging time. The result indicates that catalyst prepared with Cr:Ti metal ratio of 2:1 and aging time of 5 days obtained the closest FAME density comparable to the standard of palm oil biodiesel density [9] and it has the highest pore size of 190.52 Å among the prepared catalysts. The pore size is important requirement for efficient diffusion of reactants into the active sites in the reaction to produce FAME since a typical triglyceride molecule has a diameter of approximately 58 Å. Thus, it is sufficient to accommodate the reactant molecules to adsorb on the active sites of the catalysts [11]. Average pore size for the catalysts were in the range of 113.82 - 190.52 Å, which can be classified as mesoporous since the pore diameter are within 20 - 500 Å. The catalyst surface area is essential in enhancing the catalytic activity of heterogeneous system. The catalyst with Cr:Ti metal ratio of 1:1 and aging time of 1 day has the lowest surface area of 40.52 m²/g and obtained FAME density of 915 kg/m³. The FAME density obtained is not within the standard palm oil biodiesel density, thus indicate the catalyst reduced activity. The catalyst with Cr:Ti metal ratio of 2:1 and aging time of 5 days has higher surface area of 45.88 m²/g and pore volume of 0.1984 cm³/g, obtained the FAME density closest to the standard palm oil biodiesel density [9].

**Table 1.** FAME density, surface area, pore volume and average pore size of prepared catalysts

| Cr:Ti metal ratio | Cr-Ti aging time | Surface Area (m²/g) | Pore Size (Å) | Pore Volume (cm³/g) | FAME Density (kg/m³) |
|------------------|-----------------|---------------------|---------------|---------------------|---------------------|
| 1:1              | 1 day           | 40.5217             | 183.2648      | 0.185655            | 915                 |
| 2:1              | 1 day           | 57.4459             | 113.8178      | 0.163459            | 906                 |
| 2:1              | 2 days          | 44.1458             | 179.7671      | 0.218510            | 884                 |
| 2:1              | 5 days          | 45.8767             | 190.5195      | 0.198399            | 854                 |
Figure 3 shows the nitrogen adsorption-desorption isotherm of Cr:Ti metal ratio of 2:1 with aging time of 5 days. The isotherm is found to be consistence with the type IV, which is typically for mesoporous materials that is a finite multi-layer formation corresponding to complete filling of the capillaries. The hysteresis loop that appeared in the isotherms is due to the capillary condensation and evaporation that occur at different pressure. Many inorganic oxide compounds show characterization of H2 loops in which the pore structures are complex and made up of interconnected pore networks of different sizes and shapes [3].

![Figure 3. Nitrogen adsorption-desorption isotherm of Cr:Ti metal ratio of 2:1 (5 days aging time)](image)

Figure 4 shows the thermal gravimetric analysis (TGA) comparisons for 2:1 metal ratio Cr:Ti with aging time of 1 day and 5 days. Both TGA profiles observe distinct percent weight loss from 25 – 100 °C attributed to the evaporation of moisture from the catalyst surface. Further weight loss due to desorption of the interlayer physisorbed water molecules and decomposition of nitrate compounds [12]. The weight loss appears to be less significant beyond 500 °C indicating a stable mixed oxides compound.

![Figure 4. TGA profiles of 2:1 metal ratio Cr:Ti with aging time (a) 5 days (b) 1 day](image)
4. Conclusion
This study on Cr-Ti mixed oxides catalysts in production of FAME from CPO has shown that the catalyst prepared with Cr:Ti metal ratio of 2:1 and aging time of 5 days obtained the FAME density of 854 kg/m$^3$. The value is closest to the standard palm oil biodiesel density of 864 kg/m$^3$, which indicates good catalytic activity. The catalyst also has the high surface area, pore volume and average pore size, sufficient of effective heterogenous catalysis reaction. The TGA profile also indicates the catalyst has good thermal stability. The results indicate that Cr-Ti catalyst has potential application in FAME production from CPO.

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