Characteristics of chromium based mixed oxide catalyst in biodiesel production

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Abstract. Renewable energy from biodiesel or fatty acid methyl ester (FAME) has become important in recent decades as one of the promising alternative for petroleum-derived fuel. In this study, chromium based mixed oxide catalysts which are Cr/Ca oxide and Cr/Zn oxide were synthesized via precipitation method and used in the transesterification of cooking palm oil to produce FAME. The reactions were conducted in a batch reactor at temperature of 60 °C, methanol:oil molar ratio of 6:1 and catalyst loading of 1wt%. The characterization through N2 adsorption-desorption showed BET surface area, pore volume and pore size of Cr/Ca oxide are 3.6915 m²/g, 0.00684 cm³/g and 93.919 Å, respectively while for Cr/Zn oxide are 3.9897 m²/g, 0.00630 cm³/g and 80.113 Å, respectively. Both catalysts showed similar type isotherm which are type IV and hysteresis loop H3. The catalyst Cr/Ca oxide is found to be more active in the transesterification whereby FAME content of 27.8% was achieved compared to 7.4% by utilizing Cr/Zn oxide. The results showed that Cr/Ca oxide catalyst and Cr/Zn oxide have potential as heterogeneous catalyst to produce FAME from palm oil.

1. Introduction

The Malaysian government is now moving towards energy security via green approach in 11th Malaysia Plan Green Technology Master Plan (GTMP) by 2020. The aim is to minimize the emission of carbon up to 40% in terms of emission intensity of Gross Domestic Production (GDP). In order to achieve this target, Malaysia’s dependency on fossil fuel as the main energy sources needs to be reduced and switching into renewable energy. Thus, production of biodiesel plays an important part as an alternative for fossil fuels due to its sustainability and eco-friendly characteristic compared to diesel. Currently, transesterification process is commonly used to produce biodiesel. Since the demand of biodiesel is increased, thus the researchers keep continuously search for the better solution to increase the production of biodiesel. Since the transesterification is a slow process, therefore the reaction is always assisted with catalyst. The conventional method on producing biodiesel is through transesterification with homogeneous catalyst. Nevertheless, there are some drawbacks on this process such as the discharge of alkaline waste water, soap formation and complexity in the synthesis process. In recent years, the development of heterogeneous catalyst become focal area since its benefit to reduce production cost and waste by eliminating separation steps and washing on excess homogeneous catalyst in the process [1]. The heterogeneous catalyst also facing drawback and one of the main problems is deactivation with time due to poisoning, coking, sintering and leaching. Calcium Oxide (CaO) and Zinc Oxide (ZnO) catalyst show very popular among alkali earth metal and transition metal catalyst, respectively due to CaO poses relatively high basic strength while ZnO poses acidic properties [2]. Previous researchers have reported on various solid based catalyst includes single metal CaO based and ZnO based catalyst in
transesterification reaction. However, the chromium based catalyst is rarely found in transesterification reaction of biodiesel. Several works reported the used of chromium catalyst in the reaction could enhanced the catalytic performance under specific conditions such as in hydrogenation of glycerol [3] and propane [4]. By considering a good potential of chromium based catalyst in other processes and good performance of CaO and ZnO catalysts in transesterification process, the incorporation of chromium in CaO and ZnO could overcome the drawbacks of these single metal oxide. In recent work on the enhancement of biodiesel yield using mixed metal oxide (ZnO-CaO) catalyst has showed their ability to produce 73% with 10wt% of catalyst in the process [5]. The used of chromium based catalyst also has great potential to improve the esterification of biodiesel production as revealed in works by [6], [7], [8]. Thus in this work, the aims are to synthesize new chromium based mixed metal oxide catalyst with CaO and ZnO as well as to investigate the potential of developed mixed oxides catalyst in the transesterification of palm oil to produce FAME. The catalysts which are chromium-calcium oxide (Cr/Ca oxide) and chromium-zinc oxide (Cr/Zn oxide) were prepared via co-precipitation method. The percentage of FAME content were analysed using GC-MS and their textural properties characterization were investigated via nitrogen adsorption-desorption analyser.

2. Materials and Methods

2.1. Materials and Chemicals

The chemical used for mixed oxide catalysts preparation were zinc nitrate, calcium nitrate both at 98% purity from Sigma-Aldrich, potassium dichromate and sodium hydroxide. While for transesterification reaction, the commercial palm cooking oil was used and methanol purchased from Qrec. For GC-MS analysis, five FAME standards were used includes methyl myristate, methyl palmitate, methyl oleate, methyl stearate, and methyl linoleate, all purchased from Fluka. To dissolve the FAME sample, hexane was used as solvent.

2.2. Catalyst preparation and characterization

The Cr/Ca oxide and Cr/Zn oxide catalysts which both contain of 1:1 metal ratio by mol were synthesized by precipitation method. The procedures to synthesize the catalysts are as followed: Firstly, 100 mL of 1 M sodium hydroxide (NaOH) solution with 100mL of 1 M potassium dichromate (K2Cr2O7) solution were mixed in a beaker and stirred at 100 rpm for 10 minutes for reaction to produce sodium chromate (Na2CrO4) and potassium chromate (K2CrO4). For precipitation reaction, 1M calcium nitrate (Ca(NO3)2) solution and 1M zinc nitrate (Zn(NO3)2) solution were prepared. Then, 100 mL of each solution were mixed separately in different beaker with 10 0mL of Chromate solution, respectively. Both mixtures were stirred at 100 rpm for 1 hour at room temperature. Each solution was left for 20 minutes to allow the precipitate from each reaction to settle down. Then the precipitate was filtered by using vacuum filter. Then, the filtered precipitate was dried by using oven at temperature 70°C for 12 hours. Finally, the dried precipitates which contain Cr/Ca and Cr/Zn metal respectively were calcined at 600°C for 3 hours in furnace to remove remaining impurities in the sample. The metal elements then form a strong bond with oxygen to generate Cr/Ca oxide and Cr/Zn oxide. The sample from Cr/Ca oxide and Cr/Zn oxide catalysts were used for further characterization using Nitrogen adsorption-desorption analysis at temperature 77K to determine the isotherms, pore size distribution and textural properties such as surface area, pore volume and pore size. The surface area and pore volume of the catalyst were calculated using Brunauer-Emmett- Teller (BET) technique while pore size distribution and average pore width were determined by the Barret-Joyner-Haleda (BJH) method. The BJH method is common method use to describe the adsorption-capillary condensation process that takes place in mesopores [9].

2.3. Transesterification and analysis of FAME

The transesterification reaction was carried out in batch process using commercial cooking palm oil and methanol (MeOH) at 6:1 methanol to oil molar ratio in the presence of 1 wt% catalyst. Firstly, 100 g of MeOH was mixed with 1 g of Cr/Ca oxide catalyst in a beaker and stirred vigorously. Then, 100 g of oil was added into the beaker contained MeOH and Cr/Ca oxide catalyst and heated at 60°C for 1 hour.
The mixed solution was continuously stirred at 300 rpm to ensure the catalyst, triglycerides and MeOH were well mixed during the reaction. After that, the final mixtures were transferred into separation funnel to cool down for 20 minutes until a layer of glycerol and a layer of FAME-excess reactants mixtures were observed. Finally, the desired product of FAME was separated from the undesired product of glycerol and analyzed using GC-MS (Perkin Elmer Clarus 600). The FAME obtained was calculated using the EN14103 application note (the recommended standard for obtaining total FAME content in biodiesel). From the analysis, the % of FAME content which based on five main components i.e methyl myristate, methyl linoleate, methyl oleate, methyl stearate and methyl palmitate were obtained. All these procedures were repeated using Cr/Zn oxide catalysts. Then the results of FAME content (%) from both catalysts were compared.

3. Results and Discussion

3.1. Catalytic performance of different metal oxide

The chromium mixed oxide catalysts (Cr/Ca oxide and Cr/Zn oxide) were used in the transesterification of palm oil with methanol at constant reaction conditions (6:1 MeOH:oil molar ratio, temperature 60°C, 300 rpm stirrer speed and 1wt% catalyst). Figure 1 shows the FAME content (%) in the product sample after reaction completed. The observed trend indicates the different type of the mixed oxide gives different catalyst performances. Cr/Ca oxide shows 27.8% of FAME content which is higher about 20.4% than Cr/Zn oxide. The textural properties of catalysts may contribute to the difference in the catalytic performance. According to [8], the surface area, pore size and pore volume are very important parameter to investigate in order to understand the reaction mechanism because catalyst surface provides the active sites where heterogeneous catalytic reaction occurs. To understand further on the difference catalytic performance between Cr/Ca oxide and Cr/Zn oxide, the characterization on the textural properties was conducted using N₂ adsorption-desorption analysis.

![Figure 1. FAME content of Cr/Zn oxide and Cr/Ca oxide (reaction conditions: 6:1 methanol:oil molar ratio; 1 wt.% catalyst dosage; 3 h)](image)

Lee et.al [10] has shown interest on synthesized mixed metal oxide catalyst for biodiesel production from jatropha oil. Various mixed metal oxide (CaO-MgO, CaO-ZnO, CaO-La₂O₃ and MgO-ZnO) have been synthesized using co-precipitation method and their catalytic performance were compared with single metal oxide catalyst. In this work, it was found that, most of the mixed metal oxide produce higher yield than single metal oxide and observed better when the metal oxide is mixed with CaO. This finding is aligned with the finding from chromium based mixed metal oxide where the Cr/Ca oxide shows higher FAME content than Cr/Zn oxide. According to [9], the behavior of ZnO oxide as Lewis acid metal oxide
is more suitable to the oil which contains higher free fatty acid (FAA). While the CaO poses alkaline characteristic, shows better in transesterification process.

3.2. Effects of mixed metal oxide on textural properties

The catalyst surface contains active sites where heterogeneous catalytic reaction occurs. Thus, textural properties of Cr/Ca oxide and Cr/Zn oxide such as surface area, pore volume and average pore size were identified using N\textsubscript{2} adsorption-desorption analyzer. Table 1 shows the comparison of surface area, pore volume and pore size for both catalysts.

|       | Surface Area (m\textsuperscript{2}/g) | Average Pore Volume (cm\textsuperscript{3}/g) | Average Pore Size (Å) |
|-------|--------------------------------------|-----------------------------------------------|-----------------------|
| Cr/Ca oxide | 3.6915                               | 0.00684                                      | 93.919                |
| Cr/Zn oxide | 3.9897                               | 0.00630                                      | 80.113                |

It is observed that the Cr/Zn oxide poses higher surface area than Cr/Ca oxide which is 3.9897 m\textsuperscript{2}/g and 3.6915 m\textsuperscript{2}/g, respectively. However, Cr/Ca oxide indicates higher pore volume (0.00684 cm\textsuperscript{3}/g) than Cr/Zn oxide (0.006304 cm\textsuperscript{3}/g). The analysis denotes that mixed metal oxides have lower surface area and pore volume. In terms of pore size, Cr/Ca oxide shows higher than Cr/Zn oxide, which is 93.919Å and 80.113Å, respectively. Since the average pore size of both catalyst is larger than 60Å, the triglycerides can diffuse and contact with the active sites in the catalyst pore since the typical diameter of triglyceride is less than 60Å [5]. Based on these comparisons, it can be concluded the Cr/Ca oxide poses larger pore size despite has comparable surface area and pore volume with Cr/Zn oxide. Thus reactant molecules easily penetrate into the interior of the Cr/Ca oxide catalyst and most of the active sites will be utilized to promote reaction [11]. The pore size also indicates both catalysts are classified as mesopores based on IUPAC classification which the size is ranging between 20Å - 500Å. Hence these catalysts are in starting range of mesopores material.

3.3. Nitrogen adsorption-desorption isotherms

In the characterization of porous solids, the adsorption process is usually observed through isotherms. Isotherms indicate the amount of the adsorbate on the adsorbent as function of its partial pressure at constant temperature [12]. Figure 2 and figure 3 show the isotherms for Cr/Ca oxide and Cr/Zn oxide, respectively. According to IUPAC classification, the isotherms of Cr/Ca oxide and Cr/Zn oxide catalysts are fitted to typical type IV adsorption which indicates mesoporous solid since it is characterized by hysteresis loop H3 shape.

The figures show the adsorption of the N\textsubscript{2} gas by filling the gas on the surface includes the pores surface until adsorption reach saturation. The quantity of adsorbent (N\textsubscript{2} gas) fairly increased with pressure within lower pressure region and then it undergoes monolayer-multilayer adsorption [13]. The isotherm shows flat shape at middle region that corresponds to the monolayer adsorbate formation and observed sharp shape when the relative pressure near to 1 which indicates multilayer formation on the surface of the adsorbent. The condensation in mesopore dominates when pressure approaches near saturation pressure [13]. Hysteresis takes place during desorption activities. This happen because of the adsorbate is desorped from the surface but evaporation from mesopores occurs at a pressure lower than capillary condensation. The hysteresis loop H3 shape indicates the solid consist of aggregates and forming slit shape pores [9]. The reversible adsorption-desorption activities shows this process is only involved physisorption. Wan et.al [6] have worked on synthesis of mixed metal oxide which mixed chromium (Cr) with tungsten (W). Based on the observation of the N\textsubscript{2} adsorption desorption isotherms
for Cr:W mixed metal oxide, it shows typical type IV adsorption which similar to the finding in this work.

![Figure 2. Adsorption-desorption isotherms of Cr/Ca oxide](image1)

3.4. Pore size distribution (PSD)

PSD curve of Cr/Ca oxide and Cr/Zn oxide estimated by BJH method are shown in figure 4. The pore diameter of Cr/Ca oxide is ranging between 17Å to 3000Å as well as Cr/Zn oxide. Both catalysts show maximum pore volume at diameter 17.8Å and 17.3Å for Cr/Ca oxide and Cr/Zn oxide, respectively which close to mesopores (20Å). The PSD for Cr/Ca oxide and Cr/Zn oxide both show wide range of pore size ranging from 17.8Å to 2784.8Å and 17.3Å to 2076.8Å, respectively. Some of the previous
researchers had investigated the characteristic of mixed metal oxide in various conditions as shown in Table 2. The pore size in PSD indicates most of the mixed metal oxide appears at mesopores region. The pore size is very dependence on the process parameter such as preparation method, the metal ratio and calcination temperature.

Figure 4. Pore size distribution of Cr/Ca oxide and Cr/Zn oxide

Table 2. Pore size distribution of various mixed metal oxide.

| Catalyst          | Preparation method | Metal ratio       | Calcination temperature, (time) | Pore size (Å) | Author |
|-------------------|-------------------|------------------|-------------------------------|---------------|--------|
| Ca/Z-O            | Templating route  | Ca:Z (0.3:1)     | 700°C (6 hrs)                 | 35 Å          | [14]   |
| Zn/Ca-O           | Impregnation      | Zn:Ca (1:4)      | 600°C (6 hrs)                 | <20Å          | [15]   |
| Cr/Al-O           | Precipitation     | Cr:Al (1:1)      | 500°C (12 hrs)                | Range 290-700 Å | [16]   |
| Cr/Ca/γ-Al₂O₃     | Wet impregnation  | Cr: Ca/γ-Al₂O₃ (10:90) | 700°C (5hrs)               | <300Å         | [17]   |

4. Conclusion
In this present study, the Cr based mixed oxide catalysts (Cr/Ca oxide and Cr/Zn oxide) has been synthesized and its catalytic performance during transesterification of cooking palm oil was investigated and compared. It is observed that the Cr/Ca oxide catalyst poses better performance than Cr/Zn oxide catalyst in term of production of biodiesel. This finding was supported by the characterization using N₂ adsorption-desorption analysis. Based on the textural properties, the Cr/Ca oxide catalyst shows larger pore volume and pore size than Cr/Zn oxide which contributed to the higher performance obtained by Cr/Ca oxide catalyst. The N₂ adsorption-desorption isotherms shows typical type IV with hysteresis H3 and PSD shows the pores is placed in mesoporous region.
Acknowledgments

The authors acknowledge the financial supports provided by Universiti Teknologi MARA Cawangan Pulau Pinang and Institute of Quality and Knowledge Advancement (InQKA) Universiti Teknologi MARA.

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