



Utilization of Potassium and Chromium Doped Calcium Oxide Catalysts for Effective Conversion of Refined Used Cooking Oil to Biodiesel

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Abstract

World fossil fuel resource shortages and rising environmental concerns have driven the exploration of alternative fuels for non-renewable fossil fuels. As a result, biodiesel identified as a promising alternative to the conventional fossil fuels, has been gaining a lot of attention these days. This research emphasized on the use of alumina supported calcium oxides-based catalyst while potassium and chromium as its dopant synthesized by wetness impregnation methods for the transesterification reaction of refined used cooking oil. Percentage of oil mass conversion were determined and screening for optimized calcination temperature and transesterification reaction time for the synthesized catalysts were performed. Biodiesel purity was monitored by GC-FID and biodiesel yield was identified. Optimum conditions were achieved with calcination temperature of 700°C for 5 hours and transesterification reaction time of 4 hours for K/Cr/Ca/ γ -Al₂O₃ catalyst. The percentage yield obtained was 11.05% from oil mass conversion of 85.60%. The physicochemical analysis of the optimum catalysts was accomplished by using several characterization techniques. XRD results revealed that K/Cr/Ca/ γ -Al₂O₃ catalyst had a polycrystalline structure while FESEM analysis displayed surface morphology with inhomogeneous shapes and sizes. NA analysis showed the surface area of 61.03 m²/g with average diameter of 13.00 nm and 0.29 cm³/g of pore volume for the catalyst. K/Cr/Ca/ γ -Al₂O₃ catalysts yielded low percentage of biodiesel, which could be due to triglycerides which were not fully converted to biodiesel and could still be in monoglycerides and diglycerides form during transesterification reaction.

Keywords: Biodiesel, transesterification, chromium, calcium, trimetallic

1. Introduction

It is undeniable that long-term survival of mankind mainly relies on energy. Majority of the world's energy needs are met by conventional fuels like gasoline, coal, and natural gas [1,2]. The transportation sector as well as our daily lives all involve significant fuel and gasoline consumption by private automobiles and public transports. As a result, the depletion of energy has emerged as one of the most crucial global challenges [3]. Research exploring alternatives to conventional fossil fuels are undertaken in an effort to address the problem of resource depletion while also ensuring environmental sustainability. One of the alternatives identified are biodiesel, which generally produced from biological resources and has a number of advantages over fossil fuels [2,4].

Feedstocks can be blended with alcohol in a transesterification reaction to produce biodiesel. Transesterification reaction are commonly aided by catalyst to speed up the reaction and improve the fuel's characteristics [4]. Therefore, the type of catalyst employed play crucial role for producing biodiesel from refined used cooking oil with best catalytic activity. Catalysts of several kinds can be used to produce biodiesel. In general, heterogeneous catalytic transesterification is effective since the reaction does not consume or dissolve the heterogeneous catalysts. As a result, the products are free of catalyst contaminants, which lowers ultimate separation costs [5,6]. Furthermore, heterogeneous catalysts can be easily recovered and reused multiple times with acceptable efficacy, making them more cost-effective than homogeneous catalyst [4,5]. Acid, base, bifunctional and biocatalyst heterogeneous catalysts are among the few types of heterogeneous catalysts that are used. Nowadays,

researchers are actively examining bimetallic or trimetallic heterogeneous base catalysts for transesterification reactions with best catalytic activity.

Compared to monometallic catalyst, bimetallic and trimetallic catalysts at which metal particles consisting of two or three distinct metal elements demonstrate the different activity of catalysts [7]. In previous studies, the catalytic activity of bimetallic catalyst is greater when compared to monometallic catalyst. Even under the presence of biomass-derived contaminants and under extreme reaction conditions, the incorporation of additional metals to monometallic catalysts will alter the surface properties to enhance the activity of the catalyst, change the selectivity of the target component, and increase the stability of catalyst [8]. Due to differences in their electronic structure, the composition of structure and oxidation state, bimetallic and trimetallic catalysts are more advantageous and desirable than monometallic catalysts [7]. With addition of dopant the catalytic activity and thermal stability of catalyst were found to increase [9]. This was due to the high dispersion of metal on the supported catalyst. Hence, in this study potassium and chromium oxides were doped to calcium oxide catalyst supported with alumina in order to form trimetallic catalyst which can be applied for transesterification reaction.

This research mainly focused on the synthesis of K/Cr/Ca/ γ -Al₂O₃ heterogeneous catalyst using wetness impregnation method which can be used for the biodiesel production from refined used cooking oil. In order to find the most optimum condition of catalyst for best catalytic activity, several parameters were considered and optimized such as calcination temperature and transesterification reaction time. Since calcination temperature will influence the basic properties of alkaline earth metal oxide, catalysts with several calcination temperatures were prepared and tested. The catalyst was later characterized using several techniques in order to identify the chemical and physical properties of the catalyst.

2. Methodology

2.1. Catalyst Preparation

Heterogeneous K/Cr/Ca/ γ -Al₂O₃ catalyst was prepared by wetness impregnation method using potassium dichromate and calcium nitrate tetrahydrate as the metal precursors with ratio of 10:90. 5.00 g of Ca(NO₃)₂·4H₂O and 0.2877 g of K₂Cr₂O₇ were dissolved separately in two separate beaker with a minimum amount of distilled water, 3 mL for K₂Cr₂O₇ and 2 mL for Ca(NO₃)₂·4H₂O. The solutions were then mixed and ultrasonicated for 30 minutes. The ultrasonic processor with 125 watt and 20 kHz was set at conditions of 70% amplitude, pulse on of 9 seconds and pulse off of 5 seconds. Then, 5.00 g of alumina bead, γ -Al₂O₃ was dipped into catalyst solution for one hour. Later, the alumina supported catalyst was transferred onto a filter paper and aged overnight in an oven at temperature 95°C. The catalyst was then calcined at temperature of 600°C using a ramp rate of 5°C/min for 5 hours to eliminate all metal precursor impurities.

2.2. Transesterification Reaction of Refined Used Cooking Oil

The catalytic activity of the prepared K/Cr/Ca/ γ -Al₂O₃ catalyst was measured through transesterification process of refined used cooking oil. 6 wt.% of catalyst loading with 1:18 of oil to methanol ratio were prepared and placed in biodiesel reactor. Transesterification process was performed by refluxing the reaction mixture for 3 hours at 65°C under constant magnetic stirring. The mixture then was distilled for 15 minutes to remove excess methanol. Next, the reaction mixture was centrifuged to separate the catalyst from the solution. Top layer of oil which is biodiesel was collected while the glycerol and catalyst at the bottom layer was discarded. The obtained biodiesel was later subjected to Gas Chromatography-Flame Ionization Detector (GC-FID) analysis. Percentage of oil mass conversion and biodiesel yield was calculated.

2.3. Optimization of K/Cr/Ca/ γ -Al₂O₃ catalyst

Two parameters were studied for the optimization of the synthesized catalysts which were effect of calcination temperature and transesterification reaction time. The synthesised K/Cr/Ca/ γ -Al₂O₃ catalyst were calcined at various temperatures ranging from 600°C to 800°C using a ramp rate of 5°C/min for 5 hours to identify the optimum calcination temperature for best catalytic activity. Identified catalyst with best calcination temperature was later subjected to parameter analysis of transesterification reaction

time ranging at 2 hours, 3 hours and 4 hours under reaction conditions of 6 wt.% of catalyst loading, 1:18 wt% mol ratio of oil to methanol at $65 \pm 5^\circ\text{C}$.

2.4. Characterization of $\text{K/Cr/Ca}/\gamma\text{-Al}_2\text{O}_3$ catalyst

The physicochemical characteristics of synthesized catalyst were investigated through characterization techniques such as X-ray diffraction spectroscopy (XRD), nitrogen sorption analysis (NA) and field emission scanning electron microscopy-energy dispersive X-ray (FESEM-EDX). XRD pattern was measured by using the Rigaku SmartLab X-ray Diffractometer equipped with $\text{Cu-K}\alpha$ radiation over 2θ values between 20° to 80° . The data was analyzed by using software, SmartLab Studio II. Scanning electron microscopy Hitachi SU8020 FESEM coupled with EDX analyzer was used in FESEM analysis in order to determine the morphology, particle size and shape of the catalyst while elemental composition was determined through Energy Dispersive X-ray analysis. Average pore size and surface area of catalyst were measured by nitrogen adsorption analysis using Micromeritics ASAP 2010. 0.2 of powder sample was degassed at 120°C and cooled at room temperature. Specific surface area was calculated by Brunauer–Emmett–Teller (BET).

3. Results and Discussion

3.1. Effect of Calcination Temperature

To obtain the desired catalytic activity, calcination was done to activate the catalysts. The modification of structure and texture on the catalyst surface and the generation of active phases occurred during calcination process which contributes to the catalyst activation [10]. Percentage of oil mass conversion of the prepared catalyst, $\text{K/Cr/Ca}/\gamma\text{-Al}_2\text{O}_3$ which were calcined at different calcination temperatures are as shown in Figure 1 below.

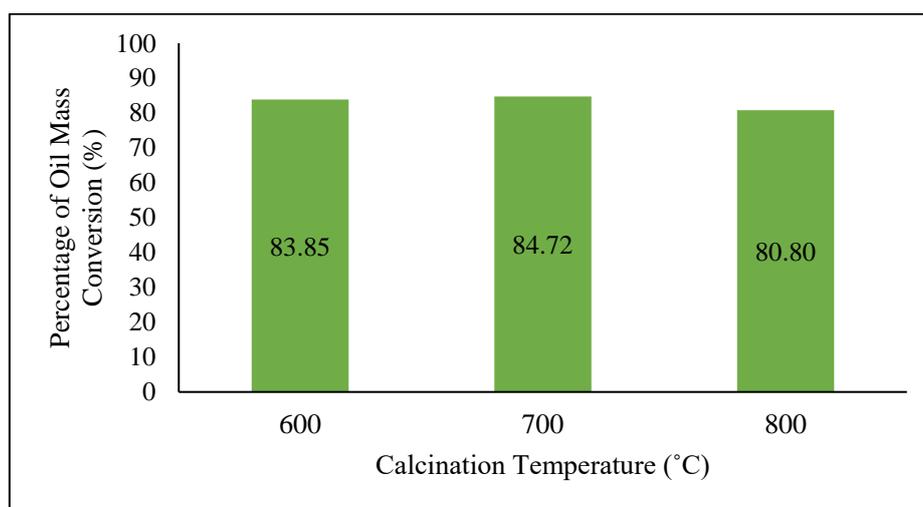


Figure 1. Percentage oil mass conversion using $\text{K/Cr/Ca}/\gamma\text{-Al}_2\text{O}_3$ catalyst calcined for 5 hours at different calcination temperatures.

From Figure 1, the trend showed that the catalytic activity for catalyst slightly increases with the increasing temperature from 600°C to 700°C and decreased with the increase in calcination temperature to 800°C . This was most likely caused by the texture of catalyst being altered through the sintering process [11]. The highest percentage conversion was observed at 84.72% for catalyst calcined at 700°C followed by 83.85% and 80.80% for catalyst calcined at 600°C and 800°C respectively. Increase in the oil mass conversion from 83.85% to 84.72% when increasing the calcination temperature from 600°C and 700°C due to the increasing surface area of catalyst which provide sufficient surface sites for the transesterification reaction [12]. Highest conversion at 700°C observed due to strong interaction between metal oxides and support. When the calcination temperature was increased to 800°C , the catalytic activity observed decreases. This was most likely due to catalyst particle agglomeration, which reduce catalyst surface area and could restrict catalyst active site production [11,13].

3.2. Effect of Transesterification Reaction Time

The effect of transesterification reaction time on biodiesel was carried out to identify the optimum transesterification reaction time for biodiesel production. The prepared catalyst of $K/Cr/Ca/\gamma-Al_2O_3$ which was calcined at optimum temperature of $700^\circ C$ were tested for the most optimum transesterification reaction time. The results are as shown in Figure 2 below.

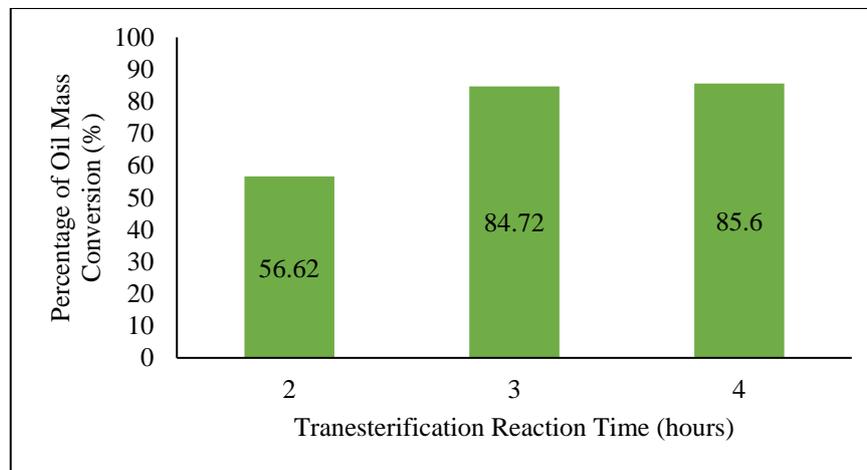


Figure 2. Percentage oil mass conversion of $K/Cr/Ca/\gamma-Al_2O_3$ catalyst at different transesterification reaction time.

The trends showed that the percentage of oil mass conversion for unmodified catalyst calcined at optimum calcination temperature of $700^\circ C$ increases with the increasing transesterification reaction time from 2 to 4 hours. The highest percentage conversion was observed at 85.60% for transesterification reaction time of 4 hours followed by 84.72% for catalyst calcined at 3 hours. Lowest mass conversion of 56.62% was obtained due to the incomplete transesterification reaction within a short time period of 2 hours. This was most likely due to the presence of the catalyst's heterogeneous mass transfer system [14]. Furthermore, the transesterification reaction did not reach equilibrium in a reasonable amount of time hence lower percentage of oil mass conversion obtained. As a result, it seems to be likely that mixing and dispersion between reactants are insufficient to produce a significant fatty acid methyl ester content.

Collisions become more frequent as the contact period between the reactants and the catalyst increases. As a result, a suitable reaction time is required to generate high fatty acid methyl ester content in the transesterification reaction. However, due to time constraint further research on reaction time greater than 4 hours could not be performed. It is expected that the percentage of oil mass conversion decrease when reaction time increased to 5 hours and more. This is because fatty acid methyl ester content formation was no longer favourable due to the reversible reaction between fatty acid methyl ester content and glycerol [12,15].

Based on the results obtained from the study of calcination temperature and transesterification reaction time over $K/Cr/Ca/\gamma-Al_2O_3$ catalyst, it can be concluded that calcination temperature of $700^\circ C$ was the optimum condition with 4 hours of transesterification reaction obtained maximum 85.60% of oil mass conversion. The biodiesel was later subjected to GC-FID analysis and low biodiesel yield from refined used cooking oil of 11.05% was obtained. This might could be due to the insufficient transesterification reaction time of 4 hours to fully convert monoglycerides and diglycerides to biodiesel.

3.3. Leaching

The leaching of active species over $K/Cr/Ca/\gamma-Al_2O_3$ catalyst calcined at $700^\circ C$ was measured using X-ray fluorescence (XRF) to identify the presence of K, Cr and Ca leached elements in biodiesel during transesterification process. The concentration of element contents is shown as in Figure 3.

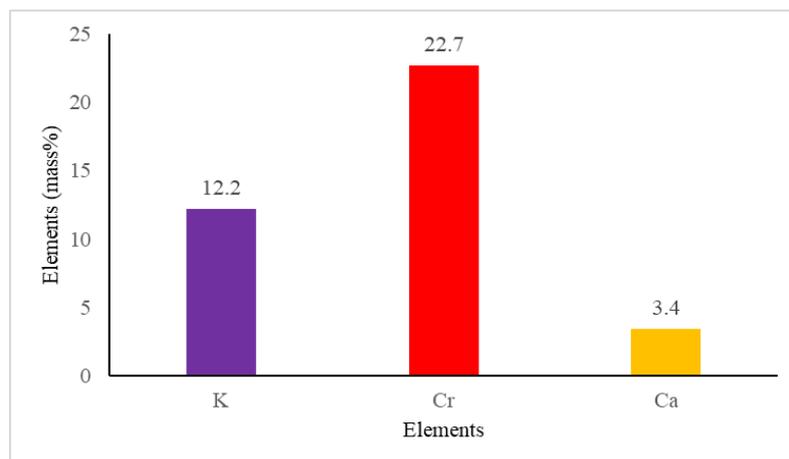


Figure 3. X-ray fluorescence data for element concentrations leached out in biodiesels of K/Cr/Ca/ γ - Al_2O_3 catalyst calcined at 700°C for 5 hours and with transesterification reaction time of 4 hours

It was detected around 22.7 mass% of Cr and 3.4 mass% of Ca element over K/Cr/Ca/ γ - Al_2O_3 catalyst leached out in biodiesel. Detection of K was observed at 12.2 mass%. The total metal leaching for K/Cr/Ca/ γ - Al_2O_3 catalyst preparation was 38.3 mass%.

3.4. Characterization of Catalyst

3.4.1 X-ray Diffraction

XRD diffractogram over K/Cr/Ca/ γ - Al_2O_3 catalyst calcined at 700°C presented as in Figure 4. Catalyst displayed polycrystalline state dominated by Al_2O_3 . The broad diffraction peaks show cubic of Al_2O_3 at 2θ of 37.68° , 46.17° and 67.28° , both correspond to hkl of (111), (200) and (220) according to d-I List of DB Card Number 1010461. Meanwhile, the catalyst shows cubic at CaO species of 2θ of 33.42° , 37.68° and 67.28° . The overlapping peak observed due to the effect of low crystallinity behaviour of the prepared catalyst that could not separate the peak. Furthermore, hexagonal of Cr_2O_3 species were detected at 2θ around 24.55° , 33.42° , 37.68° and 42.97° correspond to hkl (012), (104), (110) and (113) for the prepared catalyst (DB Card Number 2104122). Two peaks of orthorhombic of K_2O_2 species were detected at 2θ around 42.97° and 49.20° correspond to hkl (131) and (023) according to d-I List of DB Card Number 9008989.

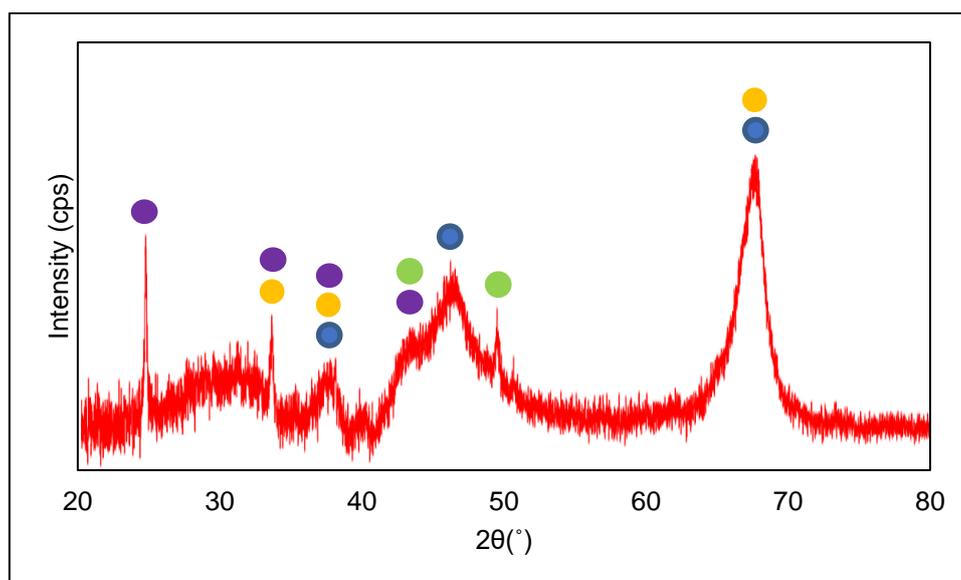


Figure 4. XRD diffractograms for K/Cr/Ca/ γ - Al_2O_3 catalyst calcined at 700°C for 5 hours [● Al_2O_3 , ● CaO, ● Cr_2O_3 , ● K_2O_2]

3.4.2 Nitrogen Adsorption Analysis

Various types, lengths, and diameters of triglycerides can enter the pores of the catalyst largely as a result of large pore volume and smaller pore size with high surface area, which gives sufficient surface site for the transesterification reaction. Thus, the textural properties of Brunauer–Emmett–Teller (BET) surface area, average pore diameter and total pore volume of the prepared K/Cr/Ca/ γ -Al₂O₃ catalyst calcined at 700°C for 5 hours were studied as shown in Table 1.

Table 1 Textural properties of K/Cr/Ca/ γ -Al₂O₃ catalyst calcined at 700°C for 5 hours

BET Surface Area (m ² /g)	Average pore diameter (nm)	Total pore volume (cm ³ /g)
61.03	13.00	0.29

The total pore volume of the catalysts was 0.29 cm³/g. Large pore volume of the catalysts enables access of a large amount of reactants to enter the catalyst, resulting in greater percentage of oil mass conversion obtained as in Figure 1 and Figure 2. The larger surface area and pore volume of K/Cr/Ca/ γ -Al₂O₃ catalyst calcined at 700°C provides a large number of accessible active sites. Thus, 85.60% of oil mass conversion was obtained. Furthermore, the average pore diameter obtained was 13.00 nm. This finding of higher pore diameter could be explained due to the decrease in the number of micropores.

3.4.3 Field Emission Scanning Electron Microscope Coupled with Energy Dispersive X-Ray

The surface morphologies of K/Cr/Ca/ γ -Al₂O₃ catalyst with optimum calcination temperature 700°C were investigated using FESEM and presented in Figure 5.

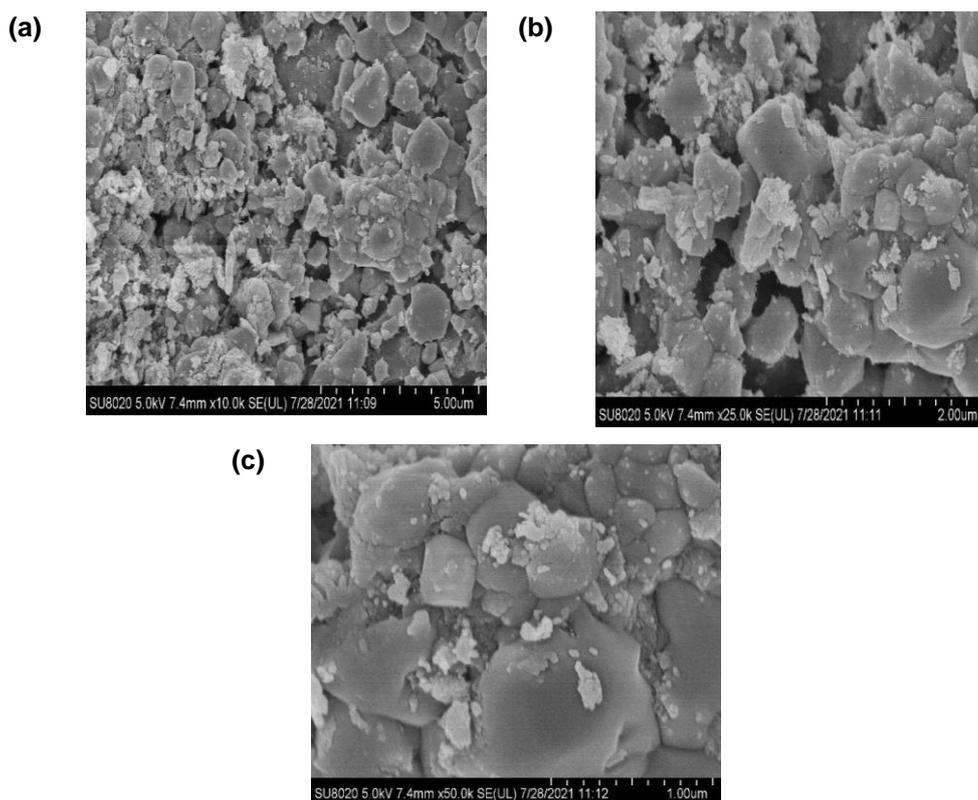


Figure 5. FESEM micrographs for K/Cr/Ca/ γ -Al₂O₃ catalysts calcined at 700°C with magnification of (a) 10.0k, (b) 25.0k, (c) 50.0k

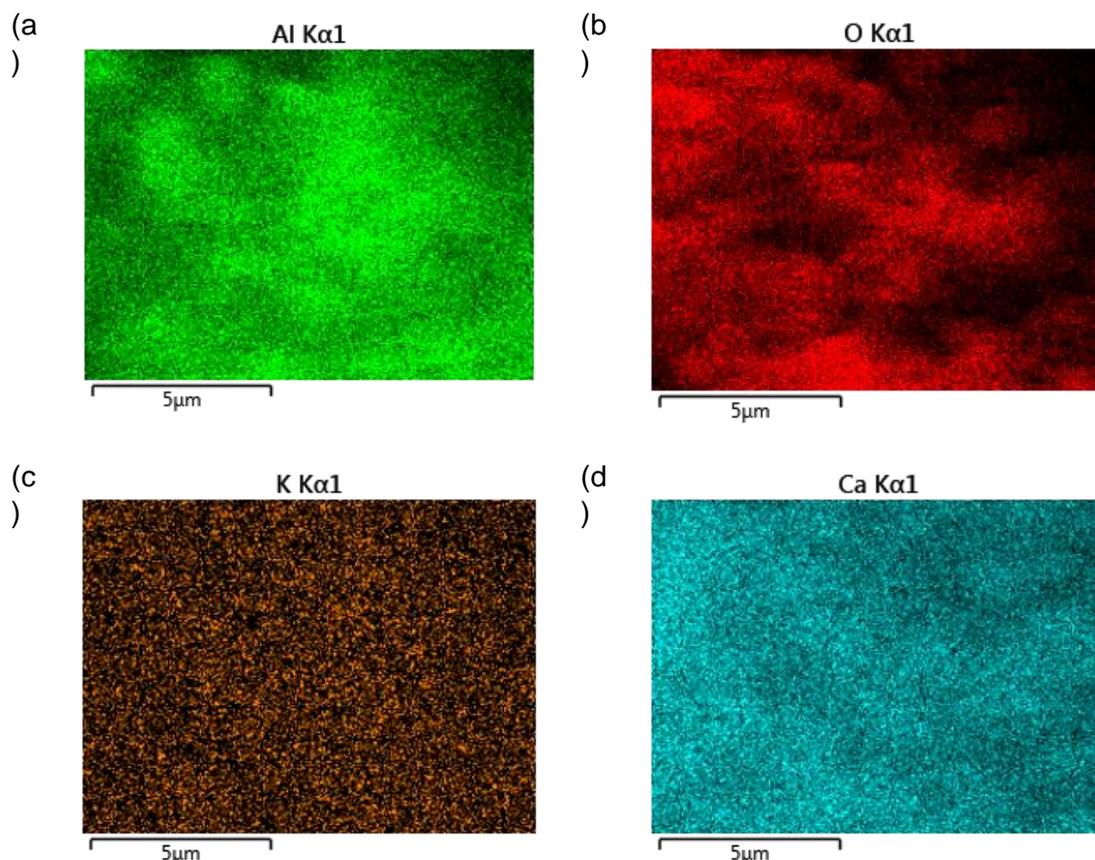
Generally, it can be seen that the catalysts have a rough surface morphology that incorporates aggregation and agglomeration of smaller and larger particle sizes. The surface morphology of the unmodified K/Cr/Ca/ γ -Al₂O₃ catalyst calcined at 700°C displayed the development of agglomerated particles densely packed on the surface of the catalyst (Figure 5c).

The elemental composition of the K/Cr/Ca/ γ -Al₂O₃ catalysts at calcination temperature of 700°C obtained by EDX analysis is summarized in Table 2.

Table 2. Elemental composition by EDX analysis K/Cr/Ca/ γ -Al₂O₃ catalyst calcined at temperature of 700°C for 5 hours

Elements	Composition (wt.%)
K	0.7
Cr	12.7
Ca	17.4
Al	21.1
O	48.2

As it can be clearly observed from Table 2 above, the O composition dominated the overall weight percentage around 48.2 wt.% due to the oxide from all elements on the catalyst surface. Al composition observed to be the second highest of overall weight percentage around 21.1 wt.% due to the alumina that was used as the support material. Figures 5 below illustrates the EDX mapping profile for K/Cr/Ca/ γ -Al₂O₃ catalyst calcined at 700°C. According to this mapping, it shows the inhomogeneous distribution of elements presence in K/Cr/Ca/ γ -Al₂O₃ catalyst. However, the elemental distribution indicates that the elements K and Ca had been highly dispersed on the surface of Al₂O₃ support.



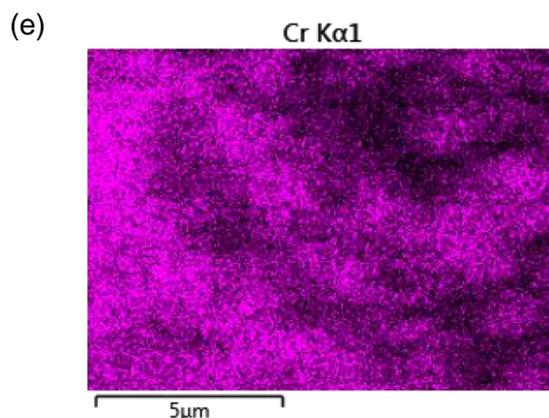


Figure 6. EDX mapping profile of K/Cr/Ca/ γ -Al₂O₃ catalyst calcined at 700°C for 5 hours [(a) Al, (b) O, (c) K, (d) Ca, (e) Cr]

Conclusion

In this study, K/Cr/Ca/ γ -Al₂O₃ heterogeneous catalysts were successfully synthesized and applied for transesterification of refined used cooking oil to biodiesel. Optimization of prepared catalyst according to the various calcination temperatures and transesterification reaction time resulted in 700°C as the optimum calcination temperature and transesterification reaction time of 4 hours with 85.60% of oil mass conversion. XRF data for element concentrations leached out in biodiesels revealed K/Cr/Ca/ γ -Al₂O₃ catalyst shows concentration of leached elements with total 38.3 mass%. XRD results showed that the K/Cr/Ca/ γ -Al₂O₃ catalyst had a polycrystalline structure. FESEM analysis displayed surface morphology of the catalyst with inhomogeneous shapes and sizes while BET analysis revealed large surface area and pore volume of the catalyst calcined at 700°C provides a large number of accessible active sites. Thus, 85.60% of oil mass conversion with 11.05% biodiesel yield was obtained.

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