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Synthesis and Characterizations of Chromium-Aluminium Mixed Oxides Catalysts to Produce FAME

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ABSTRACT

Biodiesel or fatty acid methyl ester (FAME) is a clean-burning renewable fuel that is alternative to petroleum fuel. In this study, chromium–aluminium (Cr-Al) mixed oxides were synthesized, characterized and used as catalyst in the transesterification of cooking palm oil (CPO) to produce FAME. The reactions were conducted in a batch reactor at temperature of 160 °C for 3 h. The effects of catalyst synthesis conditions, which are metal ratio and calcination temperature were studied. The metal ratio Cr:Al of 1:1, 2:1, 0:1 and 1:0 and calcination time between 400 °C and 600 °C contributed effects on the FAME density obtained from the reaction. The catalyst characteristics in terms of surface area, pore size, pore volume and thermal stability and surface functional groups were also affected by the various metal ratio and calcination temperature. The results showed that Cr:Al prepared at 1:1 metal ratio and calcined at 500 °C exhibit FAME density of 860 kg/m^3, which is within the value range of biodiesel fuel density. The catalyst has surface area of 105.00 m^2/g, pore size of 32.81 Å and pore volume of 0.086 cm^3/g sufficient to promote efficient heterogenous catalytic activity and has good thermal stability. Thus, Cr-Al mixed oxides has potential as heterogeneous catalyst to produce FAME from the transesterification of CPO.

Keywords: *cooking palm oil; biodiesel; transesterification;, heterogenous catalyst.*

1. INTRODUCTION

Biodiesel is a renewable, biodegradable, environmentally friendly alternative fuel that is capable to fulfill energy demands without sacrifice to engine's operational performance [1]. Because of the pollution caused by the petroleum fuel emission, researchers have come with an alternative to petroleum-based diesel. Hence, biodiesel is a solution to the issue of fossil fuel depletion and environmental degradation. It offers environmentally favorable emission profiles as it reduces carbon dioxide emissions by almost 70% compared to petroleum-based diesel and is free from sulfur and polycyclic aromatic hydrocarbons [2].

Biodiesel is technically known as fatty acid methyl ester (FAME). The common method being used to produce FAME is transesterification of plant oils such as palm oil with alcohol and aided by catalyst. Although homogeneous catalysts are still widely used, the major disadvantage is that homogenous catalysts cannot be separated from the reaction mixture easily, hence not suitable for continuous flow reactors. Heterogeneous catalyst was used instead of homogeneous catalyst due to its easy separation and recovery from the process [3]. Heterogeneous catalysis

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advantages include minimal reactor corrosion, reduction of aqueous waste production and prevents costly neutralization and separation steps. There are different catalysts used in the industry in order to produce FAME such as metal oxides, sulphate metal oxides and also nonmetal catalysts [4-5].

Previous study found that chromium-tungsten mixed oxides catalyst showed good performance with highest value of 86 % FAME [1]. Additionally, chromium-titanium mixed oxides catalyst was effective in esterification of palm fatty acid distillate (PFAD) to produce FAME [6]. Several Cr based catalysts were also reported to show good potentials in the FAME production due to their desirable properties such as acidity, porosity and surface area favorable for heterogeneous reaction [7-9]. In this work, the Cr-Al mixed oxides catalysts were synthesized via sol-gel method at various metal ratio and calcination temperature. The effects of synthesis conditions of Cr-Al mixed oxides were investigated based on the FAME density obtained via transesterification of CPO. In addition, the catalyst surface area and pore characteristics, thermal stability and functional groups 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 aluminium nitrate nonahydrate were purchased from Sigma Aldrich Malaysia Sdn. Bhd. Purified air, nitrogen and helium were purchased from Linde Malaysia Sdn Bhd. All the chemicals used were analytical reagent grade.

2.2 Catalyst Preparation

The catalyst of Cr-Al mixed oxides were prepared by sol-gel method [10] with the Cr:Al ratio of 1:0, 0:1, 1:1and 2:1. In a typical catalyst synthesis, chromium (III) nitrate nonahydrate and aluminium nitrate nonahydrate were weighed at 10.43 g and 5.77 g respectively and mixed with 10 ml of deionized water in separate beakers. After that, both solutions were transferred into a 250 ml beaker where 40 ml ethanol and 1ml of nitric acid were added. Then, the solution was vigorously stirred and heated at 40 °C for 4 hours [4]. The sample was left overnight to allow for aging process until gel was formed. Next, the sample was dried in an oven at 110 °C for 12 hours. After that, the sample was calcined in air using a muffle furnace at 500 °C for 2 hours. The same method was repeated for all remaining metal ratios. For the study on effects of calcination temperature, the temperature was varied at 400 °C, 500 °C and 600 °C.

2.3 Transesterification of CPO and Analysis of FAME

The transesterification of CPO is carried out in a 100 ml laboratory scale reactor from Amar Equipment Pvt. Ltd. The methanol, CPO and the prepared catalyst were placed into the reactor. For a typical condition, the CPO added is 31 ml with 19 ml methanol and 0.56 g of catalyst. The reaction was carried out at a temperature of 160 °C set by a heater with a programmable PID temperature controller and self-pressurized at 10-15 bar. The stirrer speed was set at maximum of 500 rpm in order to sufficiently keep the system uniform in temperature and suspension and to ensure the reaction is free from mass transfer limitations. At the end of the reaction of 3 hours, the heater and stirrer were turned off and the reactor was immediately

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cooled to room temperature by quenching in cold water bath. The catalyst was separated from the product mixture by centrifugation at 3000 rpm for 15 min. The products were collected and left to settle for 12 hours to separate into two phases which are FAME (top layer) and glycerol (bottom layer). The FAME density of the sample obtained was analyzed by Micromeritics pycnometer model AccuPyc II 1340 [7].

2.4 Catalyst Characterization

The Brunauer-Emmet-Teller (BET) surface area, pore volume and pore size of the prepared catalysts were obtained by nitrogen adsorption and desorption at 77 K on an ASAP 2020 Micromeritics instrument. The BET surface area was calculated from the linear part of the adsorption branches in the relative pressure range of 0.05–0.25 bar. 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. Fourier transform infrared (FTIR) was used to determine the active surface functional groups using a Nicolet, Thermo Scientific instrument at 4000–400 cm^{-1} spectra range.

3. RESULTS AND DISCUSSION

3.1 Synthesis of the Cr-Al Mixed Oxides Catalysts

The catalysts with the formula of $Cr_xAl_yO_2$ were comprised in different Cr:Al ratio by weight, where $0 \leq x \leq 2$; $0 \leq y \leq 2$. Table 1 listed the metal oxides accordingly based on the catalyst formula.

Table 1: The catalysts prepared by using various Cr:Al ratio by weight.

Sample			Catalyst Formula	Amount of each metal in 1.5g sample (g)		Cr:Al metal ratio
	x	y	$Cr_xAl_yO_2$	Cr	Al	
1	1	0	CrO_2	1.5	0	1:0
2	1	1	$CrAlO_2$	0.75	0.75	1:1
3	2	1	Cr_2AlO_2	1	0.5	2:1
4	0	1	AlO_2	0	1.5	0:1

3.2 Effects of Metal Ratio

Figure 1 shows the FAME density obtained from the transesterification of CPO with the catalysts prepared at various Cr:Al metal ratio. The results indicate that catalysts CrO_2, $CrAlO_2$, Cr_2AlO_2 and AlO_2 obtained FAME density in the range between 820 kg/m^3 and 922 kg/m^3. The FAME density is highest at 922 kg/m^3 for catalyst AlO_2, which was prepared at Cr:Al metal ratio of 0:1. However, the FAME density is lowest for CrO_2 that contains Cr:Al ratio of 1:0. The catalyst $CrAlO_2$ which contains 1:1 metal ratio of Cr:Al obtained the FAME density of 860 kg/m^3 which is closest to the standard palm oil biodiesel density of 864 kg/m^3 [11]. In addition, the mixed oxides Cr_2AlO_2 also obtained FAME density close to standard palm oil biodiesel density. However, both the single metal oxides of CrO_2 and AlO_2 obtained FAME density that is not within the standard palm oil biodiesel density, thus indicate the catalyst reduced activity. The synergistic effect of the mixed oxides Cr-Al catalysts may contribute to the improved FAME density obtained from the reaction. FAME density is important to determine the quality of fuel mainly in airless combustion systems because it influences the atomization efficiency

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of the fuel. High fuel density may result in increased emissions of particulate matter and undesirable NOx and SOx pollutant gaseous [12].

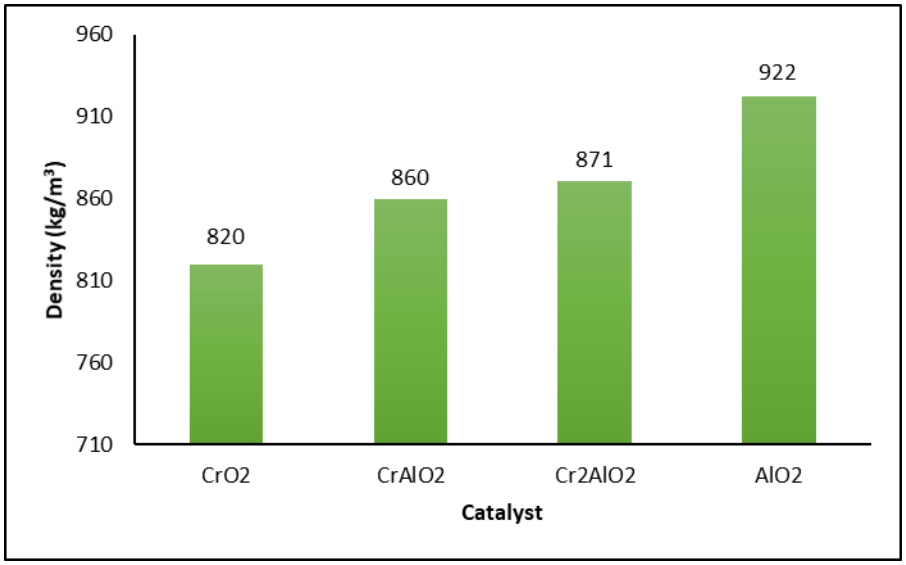

Figure 1: FAME density for different metal ratio of Cr-Al catalysts.

3.3 Characterizations of Catalysts with Different Metal Ratio

Table 2 shows the surface area, total pore volume and average pore size of the three selected catalysts prepared at Cr:Al metal ratio of 1:1, 2:1 and 0:1. The results indicate that the surface area increases as the chromium content in the mixed oxides increases, where $CrAlO_2$ has 105.0041 m^2/g and Cr_2AlO_2 has 140.4407 m^2/g. The findings may be due to the alteration of crystal structure and reduction of aluminium oxides sintering by chromium [13].

Table 2: BET surface area, average pore size and pore volume for various synthesized catalysts.

Catalyst	Surface Area (m^2/g)	Pore Size (Å)	Pore Volume (cm^3/g)
$CrAlO_2$	105.0041	32.8057	0.0861
Cr_2AlO_2	140.4407	41.8349	0.1469
AlO_2	196.1210	43.8229	0.2149

The catalyst Cr_2AlO_2 obtained FAME density of 871 kg/m^3, which is also close to the standard palm oil biodiesel density of 864 kg/m^3. The surface area of catalyst is essential in enhancing the catalytic activity of heterogeneous system. Thus, both catalysts $CrAlO_2$ and Cr_2AlO_2 possess sufficient surface area suitable for transesterification of CPO to produce FAME. The surface area of single metal oxides AlO_2 is also high at 196.1210 m^2/g, however, as shown in Figure 1, the catalytic activity is lower than the mixed oxides Cr-Al. The findings could be that other factors have effect on the catalytic performance instead of the surface area as the sole factor [14].

The results in Table 2 also indicate that as surface area increases, the pore volume and pore size also increase. The catalyst with a smaller pore size would limit diffusion of reactants and products. The pore size is an important requirement for efficient diffusion of reactants into the active sites in the reaction to produce FAME in order to accommodate the reactant molecules

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to adsorb onto the catalysts surface [10]. Average pore size for the catalysts is in the range of 32.8057 - 43.8229 Å, which can be classified as mesoporous since the pore diameters are within 20 - 500 Å.

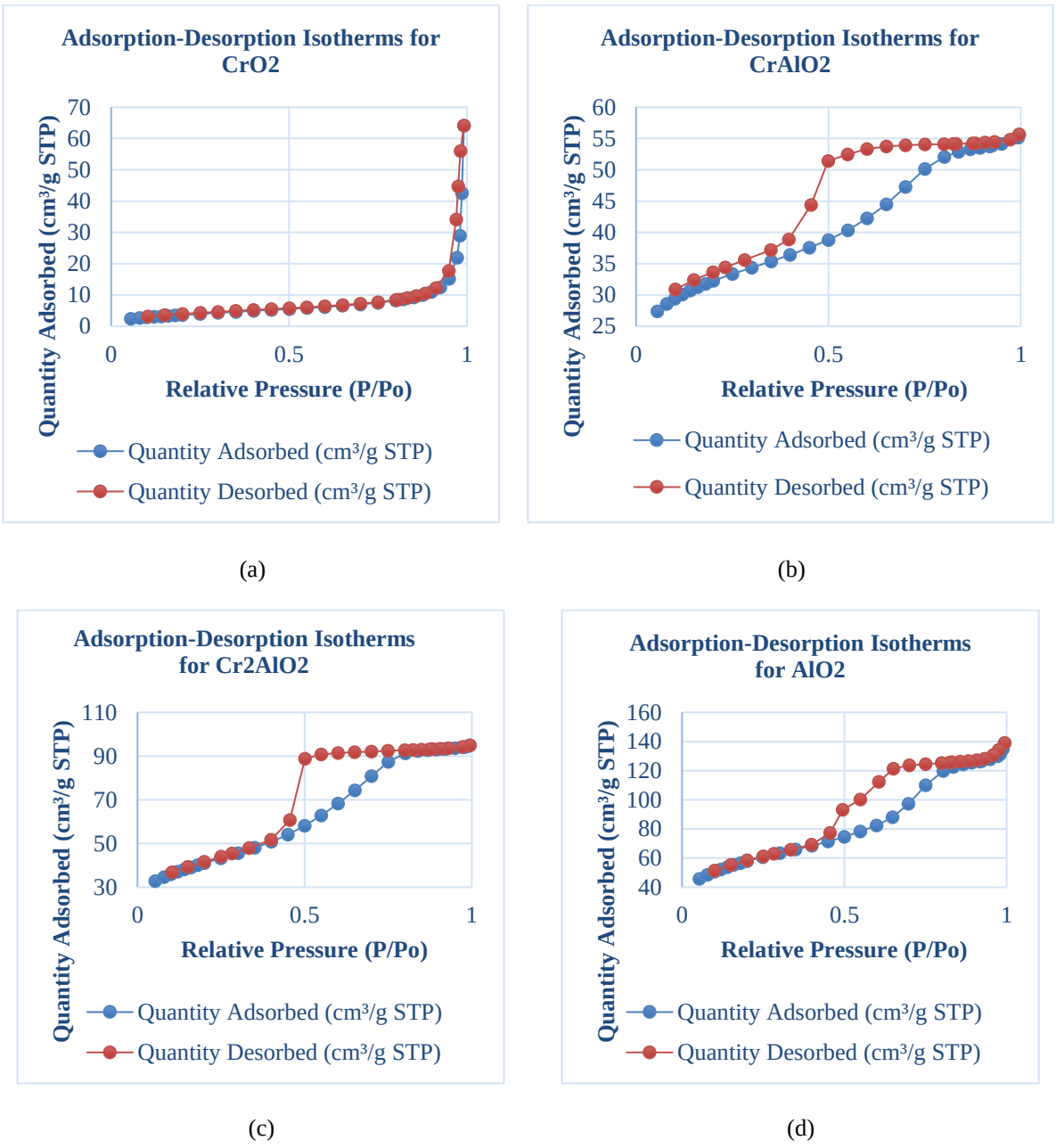

Figure 2: Nitrogen Adsorption-Desorption Isotherms of the Synthesized Catalysts (a) CrO_2, (b) $CrAlO_2$, (c) Cr_2AlO_2 and (d) AlO_2.

Figure 2 shows the nitrogen adsorption-desorption isotherms of CrO_2, $CrAlO_2$, Cr_2AlO_2 and AlO_2. The pattern for graph (a) is similar to type III isotherm that means there are weak adsorptive-adsorbent interactions which explains the formation of multilayer. Type IV isotherms can be observed for graph (b), (c) and (d) which is associated with capillary condensation taking place in mesoporous, and the limiting uptake over a range of high P/P_0

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[15]. It can be seen that (b) has a type H2 (B) hysteresis loop that can be associated with pore blocking. For (c), it appears to have a type H2 (A) hysteresis loop. The loop has a very steep desorption branch that may signal pore-blocking or percolation in a narrow range of pore necks. Graph (c) on the other hand, has a type H5 hysteresis loop that is less familiar as the form difference can be associated with certain pore structures containing both open and partially blocked mesopores. The adsorption-desorption process is reversible, and the hysteresis loop observed is due to the adsorbate molecules getting condensed in the small capillary pores of the adsorbent [16].

Figure 3 shows the TGA profiles of $CrAlO_2$, Cr_2AlO_2 and AlO_2 that are calcined at 500 °C for 2 hours. The TGA profiles of $CrAlO_2$, Cr_2AlO_2 and AlO_2 indicate weight loss of 6%, 8% and 7% respectively when the temperature increased from 30 °C to 110 °C due to moisture evaporation on catalyst surface. The findings could indicate that metal oxides catalysts have hygroscopic nature [17]. The subsequent weight loss between 110 – 300 °C could be due to the desorption of the interlayer physisorbed water molecules and the decomposition of nitrate compounds contained in the precursor substances [18]. Subsequently, the weight loss showed no significant changes from 300 °C onwards for both $CrAlO_2$ and Cr_2AlO_2 that indicates the formation of thermally stable mixed metal oxides. The finding shows that calcination temperature at 500 °C contributed towards the formation of a thermally stable catalyst. The weight changes above 300 °C is slightly more for the single metal oxides AlO_2, which indicate less thermally stable catalyst and could contribute its reduced activity in producing FAME.

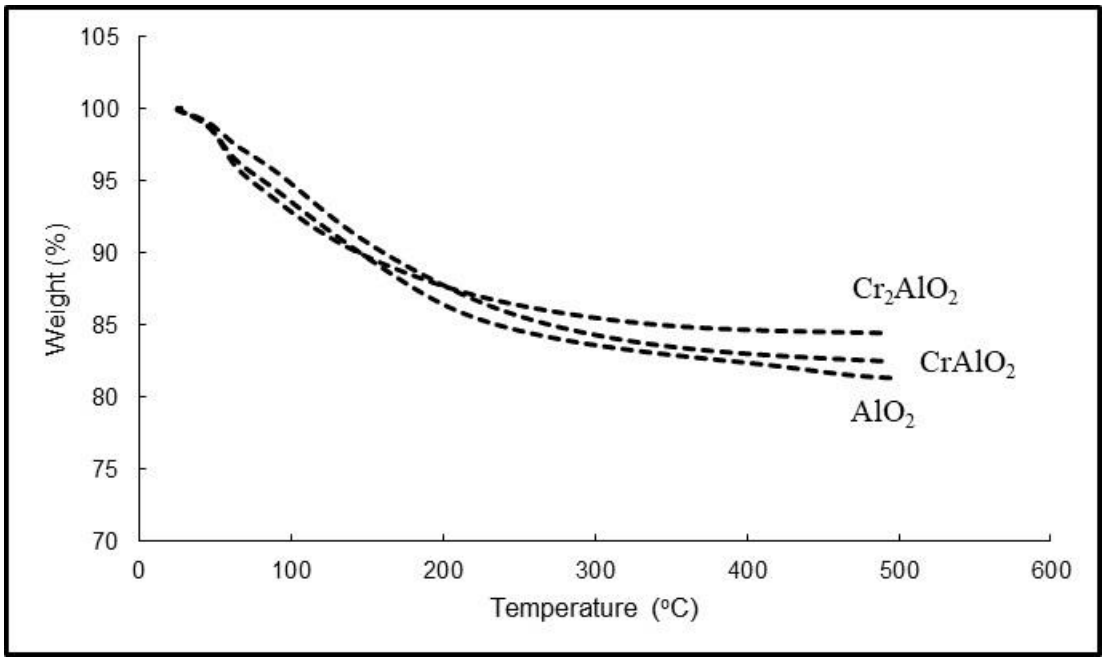

Figure 3: Thermal gravimetric analysis of catalysts at different metal ratio.

3.4 Characterization of Catalysts with Different Calcination Temperature

The calcination temperature has significant impact on the performance of the catalysts. As the calcination temperature increased so did the structural defects, while the content of oxygen-containing functional groups of catalysts decreased. These gave rise to an increase of oxygen vacancy of the elements [19]. Adequate calcination temperature induced the homogeneous

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dispersion of metal oxides with many active sites. The suitable calcination temperature allows complete evaporation and decomposition of solvent and precursor substances, thus leaving only the desired elements to form the metal oxides [6]. The catalyst $CrAlO_2$ that contained Cr:Al ratio of 1:1, which obtained the FAME density closest to the standard palm oil biodiesel density was selected for further investigation on the effect of calcination temperature at 400 °C, 500 °C and 600 °C during catalyst synthesis.

Figure 4 shows the spectrums characteristic bands of inorganic compounds that have sharper and more bands associated with the C-H and C-C bond stretching and bending vibrations as opposed to organic compound [13]. The bands characteristic of metal oxides includes the M-O bending or stretching vibrations that appear in the fingerprint region of 400-1100 cm^{-1}, where M represents the metal compound and O is oxygen. The small bands which appeared at approximately 1600 cm^{-1} are associated with the M-O-H bending vibrations of the surface hydrated layer. The observation showed there were presence of traces amount of water vapor that were physisorbed on the surface of the metal oxides [20]. The small bands in the wavenumber region of 3600-3800 cm^{-1} corresponded to the O-H stretching vibrations, which includes the hydrogen bonding in water molecules [21]. The findings suggest that variation in the calcination temperature affects the peak intensities possible due to the differences in the net dipole moment of the mixed-metal oxides during vibration, resulting in the less intense peak for catalyst calcined at 400 °C compared to catalysts calcined at 500 °C and 600 °C. Other than that, the spectrums showed no significant difference between the different calcination temperature.

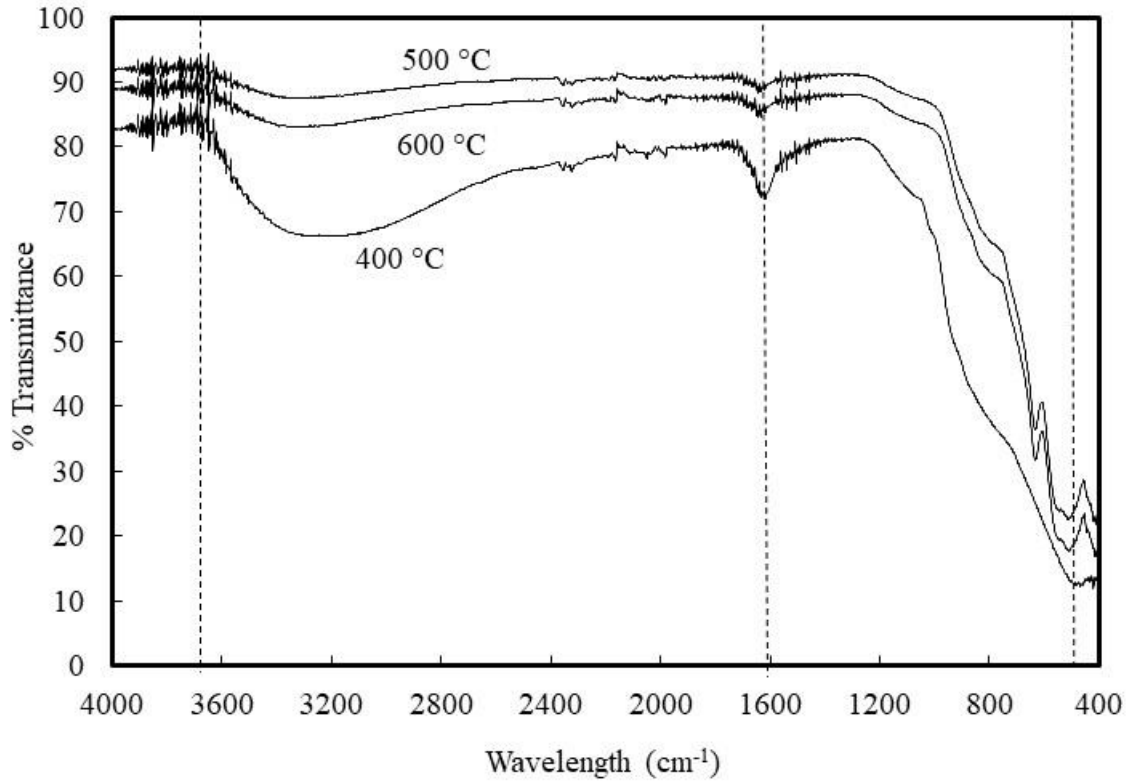

Figure 4: FTIR Spectra for catalysts at different calcinations temperature.

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4. CONCLUSION

The study on Cr-Al mixed oxides catalysts in the production of FAME from CPO found that $CrAlO_2$ which was prepared at Cr:Al metal ratio of 1:1 and calcined at 500 °C obtained the FAME density of 860 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 adequate surface area and porosity characteristics that are effective for heterogenous catalysis reaction. In addition, the catalyst has good thermal stability based on TGA analysis as well as surface functional group that are characteristics of inorganic compounds. The results indicate that Cr-Al catalyst has potential application in FAME production from CPO.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interest regarding the publication of this paper.

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