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Synthesis of Alumina Supported Calcium Based-Chromium Oxides Catalyst Using Modified Method for Transesterification of Refined Cooking Oil

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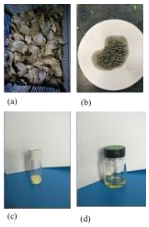
GRAPHICAL ABSTRACT



(a) Sapodilla leaves,
(b) Uncalcined $Ca/Cr(10:90)/Al_2O_3$,
(c) Calcined $Ca/Cr(10:90)/Al_2O_3$,
(d) Triglycerides conversion

ABSTRACT

Environmental concerns in fossil fuel depletion enhanced the search for an alternative fuel from renewable resources. Biodiesel is commonly produced by transesterification of vegetable oil in the presence of homogeneous catalyst. However, this catalyst was required many steps of purification such as use large amount of water which can cause saponification in biodiesel. This research mainly focused on the use of heterogeneous base catalysts that are easily separated in biodiesel production. Therefore, calcium-chromium oxides supported on alumina was prepared via modified and unmodified wetness impregnation methods for the transesterification reaction of refined cooking oil. For modified method, the extraction solution of sapodilla leaves was incorporated in the catalyst solution. All synthesized catalysts were then calcined at temperatures of 600-800 °C and the conversion were monitored by gas chromatography-flame ionization detector (GC-FID). From the result, $Ca/Cr(10:90)/Al_2O_3$ catalyst calcined at 700°C with 1 g dosage of sapodilla leaves was exhibited the highest conversion of triglycerides. Around 95% conversion was achieved at mild reaction conditions of 65 ºC reaction temperature, 6 wt.% catalyst loading, 1:18 oil to methanol ratio and 3 hours reaction time. The physicochemical analysis of this catalyst was accomplished using several characterization techniques. The catalyst showed polycrystalline structure with sparsely populated nanosheet with unhomogeneous shapes and sizes. It also posseses high surface area of 399.33 m^2g^{-1} with small particle sizes in the range of 10-60 nm and less metal leaching. The observed results are much better than unmodified catalyst preparation.

Keywords: Sapodilla leaves, transesterification, calcium-chromium oxides, biodiesel, triglyceride

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1. INTRODUCTION

The increasing energy demands nowdays intensified the search for an alternative fuel from renewable resources. It is due to the depletion of non-renewable fossil fuel and unstable of crude oil price. The biodiesel is an alternative fuel that has been used to replaced the conventional fossil fuels. It has gained much attention among researcher due to biodegradable and renewable fuel which can be obtain from waste cooking oil, vegetable oil and animal fats that containing triacylglycerols (TAGs). Triacylglycerols are esters which typically contain three fatty acids linked together by one glycerol molecule that comprise the fatty acid composition. Different feedstock would have different composition in their fatty acid due to different physical and chemical properties.

Biodiesel has many advantages such as more favourable combustion emission profile that can give low emissions of carbon monoxide and unburned hydrocarbons. Combustion of biodiesel produces carbon dioxide that can be recycled by photosynthesis then, minimized the greenhouse effects [1] . Biodiesel are safer to transport or handle compared to petroleum diesel due to relatively high flash point at 150 ºC which makes it less volatile and inflammable. It is also biodegradable and non-toxic which is able to replace diesel fuel in several applications such as in boilers and internal combustion engines without major modifications [2].

Transesterification process of oil is shown in Figure 1. The reaction between the triglyceride and methanol producing fatty acid methyl ester and the side product of glycerol several type of alcohols such as methanol, ethanol, propanol, and butanol which can be used for this reaction. However, the most frequently used is methanol as it gives high reaction rate, cheap and has shortest chain compared to other commercial alcohol. In addition, there are two types of catalysts used in transesterification of biodiesel which are homogeneous (acid or base) and heterogeneous (acid, base and enzymatic) catalysts. Thus, the heterogeneous catalyst has been chosen for the transesterification reaction due to its high selectivity, recyclable and easily to be separated after the reaction in this research.

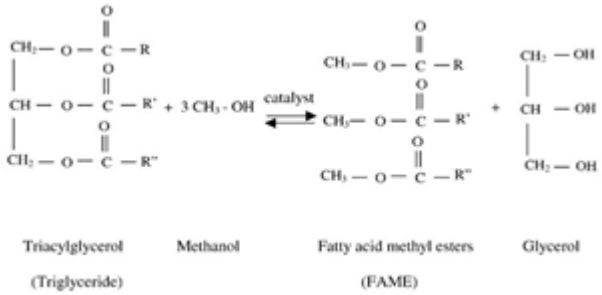

Figure 1. Transesterification reaction of triglyceride with methanol

2. EXPERIMENTAL

The experiment was divided into four main stages. The first stage was synthesized the alumina supported calcium based with chromium catalyst using modified and unmodified wetness impregnation methods. The second stage was optimized the preparation catalyst based on several calcination temperatures and concentration of sapodilla leaves which act as a binder in catalyst to avoid leaching between reactant and catalyst. The third stage was measured the performances of the catalytic activity and test the leaching properties over prepared catalyst. Then, the final stage was the characterization of prepared catalyst using various spectroscopic techniques.

3. RESULTS AND DISCUSSION

3.1. X-ray Diffraction (XRD)

Figure 2 displays the XRD diffractograms over modified Ca/Cr(10:90)/Al_2O_3 catalysts with different calcination temperatures and dosages of sapodilla leaves. The peak assignments of each species found in XRD diffractograms are based on Figure 2. It illustrated Ca/Cr(10:90)/Al_2O_3 catalysts displayed polycrystalline state dominated by Al_2O_3. The broad diffraction peaks over Ca/Cr(10:90)/Al_2O_3 catalyst at different calcination temperatures and dosages of sapodilla leaves indicated cubic of Al_2O_3 at 2θ of 67.20º (*I*100), 45.85º (*I*100), 37.70º (*I*80), 39.41º (*I*50) and cubic of CaO species with 2θ of 37.29º (*I*100) and 67.20º (*I*16). Meanwhile, the overlapping peak observed due to the effect of low crystallinity behaviour of this catalyst that could not change to separate the peak.

Furthermore, the tetragonal of CrO_2 species were detected at 2θ of 37.29º (*I*60) and 45.85º (*I*10), tetragonal of CaC species were observed at 2θ of 32.62º (*I*100), 43.45º (*I*52), 27.12º (*I*48), and 26.83 (*I*46), hexagonal Cr_2C species was indicated in diffraction peak at 2θ of 45.45º (*I*100), 67.20º (*I*60), and 37.29º (*I*20). Therefore, the presence of CaC and Cr_2C species in the modified catalyst confirmed that carbon from sapodilla leaves were acts as binder to hold the Ca and Cr from being leach out during the transesterification reaction. These peaks were not observed from the diffractogram of unmodified catalyst in Figure 2b.

As shown in Figure 2, the variations in calcination temperatures and dosage of sapodilla leaves unable to detect any differences in XRD diffractograms as all the phases over Ca/Cr(10:90)/Al_2O_3 catalysts showed low degree of crystallinity and broad peaks. Therefore, the physical structure on the surface of Ca/Cr(10:90)/Al_2O_3 catalysts that varies with different sapodilla leaves dosage and calcination temperatures was then be confirmed by FESEM-EDX.

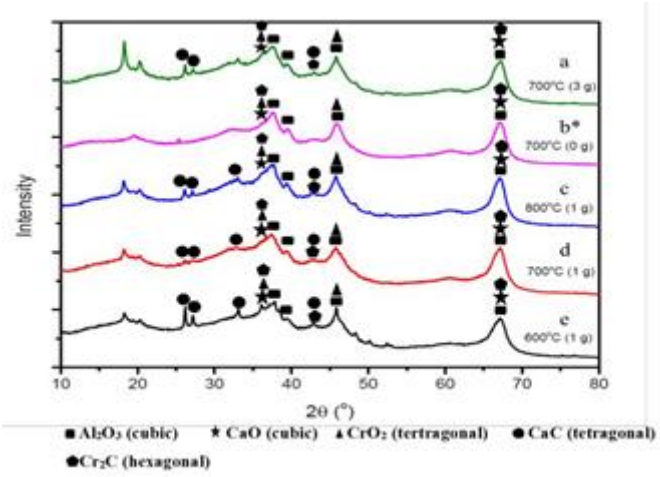

Figure 2. XRD diffractograms for Ca/Cr(10:90)/Al_2O_3 catalysts calcined at temperatures of 600, 700, 800 °C for 5 hours with dosage of sapodilla leaves 0 g, 1 g, and 3 g.

3.2. Nitrogen Adsorption (NA)

The textural properties of BET surface area, average pore diameter and total pore volume of the prepared Ca/Cr(10:90)/Al_2O_3 catalysts are shown in Table 1. In general, the calcination temperature and dosage of sapodilla leaves would influence the textural properties of the catalyst. Obviously, the increasing of the calcination temperatures catalysts had caused a decreasing of BET surface area. It clearly showed that Ca/Cr(10:90)/Al_2O_3 catalyst calcined at 600 ºC gave the highest BET surface area of 570.06 m^2/g. Upon calcined the catalyst at 700 ºC with 1 g and 3 g of sapodilla dosages, surface area showed slightly lower to 402.00 m^2/g and 399.33 m^2/g. However, the BET surface area reduced drastically to 281.39 m^2/g when the catalyst was calcined at 800 ºC due to the sintering of the pore structure at higher calcination temperature. Thus, it would reduce the surface area due to increasing of particles size of the catalyst.

From the result, it can be seen that the addition of sapodilla leaves in the catalyst preparation caused the surface area increase from 104.33 m^2/g (unmodified-0 g) to 402.00 m^2/g (modified-1 g). It can be due to the presence of CaC and Cr_2C that were detected from XRD analysis as the new species in modified catalyst which can be considered as the active phases that would help in the increasing of surface area.

Table 1. Textural properties of catalyst Ca/Cr(10:90)/Al_2O_3 calcined at temperatures of 600, 700 and 800 ºC for 5 hours with different dosages of sapodilla leaves dosages.

Calcination temperature (°C)	BET surface area (m^2/g)	Average pore diameter (nm)	Total pore volume (cm^3/g)
600(1 g)	570.06	21.68	0.41
700(0 g)	164.32	10.66	0.41
700(1 g)	402.00	18.19	0.43
700(3 g)	399.32	18.24	0.42
800(1 g)	281.39	22.36	0.39

3.3. Field emission scanning electron microscopy-energy dispersive X-ray (FESEM-EDX)

The surface morphologies of Ca/Cr(10:90)/Al_2O_3 catalysts at different calcination temperatures and dosages of sapodilla leaves were examined using FESEM and presented in Figure 3. Overall, it could be seen that the catalysts have rough surface morphology consisting of aggregation and agglomeration of smaller and bigger particles sizes. The surface morphology of unmodified catalyst calcined at 700 ºC (Figure 3a) showed the formation of agglomerated particle with densely packed on the surface of the catalyst. By incorporated with 1 g sapodilla leaves dosage on the catalyst, the structure changed to with nanosheet sparsely populated with unhomogeneously shapes and sizes. Interestingly, it is also seen that some of nanosheets were arranged in flower like morphology with an average diameter of 18.19 nm. The small particles of the catalyst help to improve the catalytic activity which able to give 95.22% of triglyceride conversion from 84.40%

(unmodified catalyst). However, the large agglomerated particle mixed with nanosheets was observed after increasing the dosage of sapodilla leaves to 3 g as shown in Figure 3 (e). Thus, this is in good correlation with the decreasing of triglyceride conversion to 81.60%.

The surface morphology to compact nanoshape was observed in which the particle become larger and densely packed (Figure 3f) after calcined the catalyst at 800 ºC. This is in good correlation with nitrogen adsorption which mentioned the decreasing surface area to 281.39 m^2/g from 402.00 m^2/g of the modified Ca/Cr(10:90)/Al_2O_3. The small particles were merged together giving large agglomerates after calcined at high temperatures [3].

The elemental composition of Ca/Cr(10:90)/Al_2O_3 catalysts at different calcination temperatures and dosages of sapodilla leaves expressed in weight percentage were tabulated in Table 2. In general, EDX confirmed the presences of Ca, Cr, Al, O and C. Since alumina was used as the support for all the catalysts, it was then showed major composition which around 39-47 wt.%. Meanwhile, the elemental composition of O was determined around 38-47 wt.% due to the oxide of the all elements on the catalyst surface. The composition of Ca (3.4-4.0 wt.%) was higher than Cr (0.70-3.35 wt.%) over modified catalysts. As expected, the C element was also detected on the modified catalyst surface, hence confirmed the presence of CaC and Cr_2C as observed in XRD analysis.

Table 2. Elemental composition by EDX analysis of Ca/Cr(10:90)/Al_2O_3 catalyst with different calcination temperature and dosages of sapodilla leaves.

Calcination temperature (ºC)	**Composition (wt.%)**				
	Ca	**Cr**	**Al**	**O**	**C**
600(1 g)	3.40	1.70	44.30	38.20	12.30
700(0 g)	1.20	3.35	47.20	47.20	-
700(1 g)	3.30	1.30	42.00	42.40	11.00
700(3 g)	3.60	0.70	40.40	44.20	11.20
800(1 g)	4.00	1.70	39.30	43.70	11.30

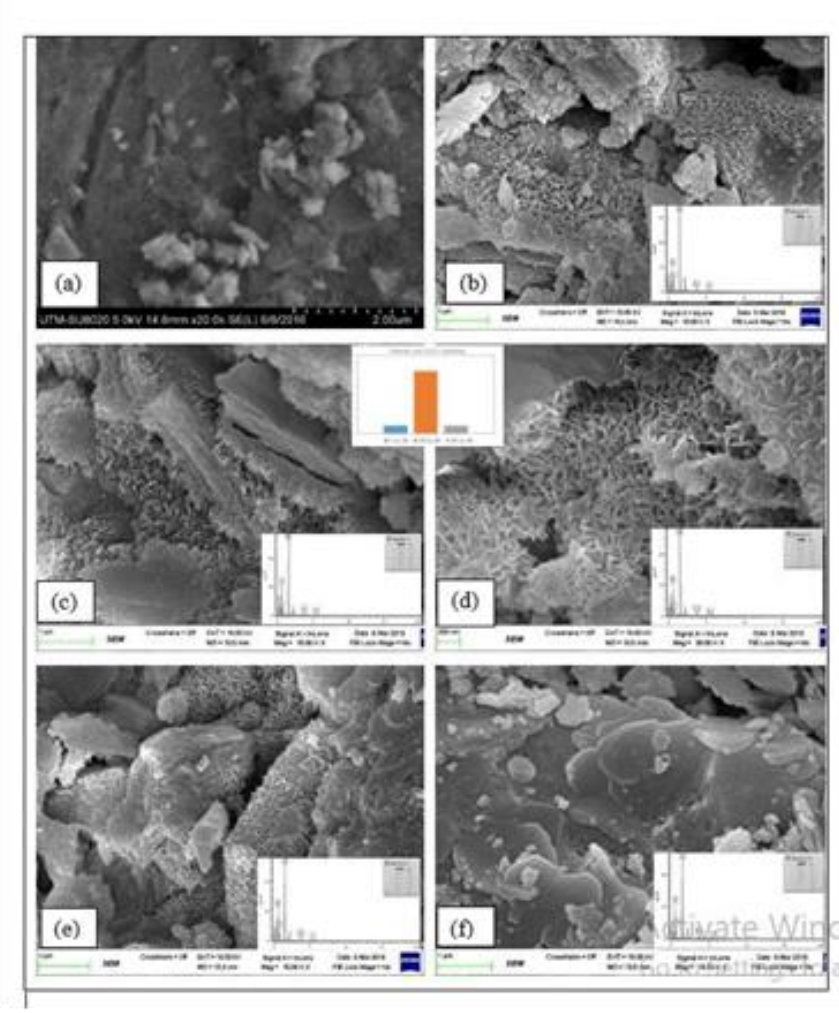

Figure 3. FESEM micrographs for Ca/Cr(10:90)/Al2O3 catalysts with different dosages of sapodilla leaves and calcination temperatures. The unmodified Cr/Ca(10:90)/Al2O3 catalyst calcined at (a) 700ºC (20 kV) and modified Ca/Cr(10:90)/Al2O3 with 1 g of sapodilla leaves calcined at (b) 600ºC (15 kV), (c) 700ºC (15kV), (d) 700ºC (30kV), (f) 800ºC (15 kV), while (e) with 3 g of sapodilla leaves calcined at 700ºC (15 kV).

3.4 Thermogravimetric analysis (TGA)

The TGA analysis was carried out to study the weight loss of uncalcined modified and unmodified Ca/Cr(10:90)/Al_2O_3 catalyst as well as dried sapodilla leaves. Results of the thermal decomposition profile of the catalyst and sapodilla leaves were shown in Figure 4. Overall, this catalyst was decomposed by three steps of weight loss process in the temperature range between 60 ºC to 700 ºC.

Based on Figure 4a for unmodified Ca/Cr(10:90)/Al_2O_3 catalyst, the first step occurred at temperature range from 60 ºC to 150 ºC with a weight loss of 3.78% represented the removal of physically adsorbed water on the catalyst surface. The second step of major weight loss about 9.11% were corresponded to the decomposition of hydroxyl and basic nitrate precursor that occurred at temperature range between 150 ºC to 450 ºC. The decomposition at these temperature regions was capable of producing water and nitrogen dioxide simultaneously. The third step from 450 ºC to 700 ºC with a weight loss of 5.91% was attributed to the decomposition of amorphous hydroxycarbonates, $M_2CO_3(OH)_2$ which occurred at high temperature before metal oxide was produced. Therefore, the total weight loss over Ca/Cr(10:90)/Al_2O_3 catalyst was 18.80%. Based on Figure 6.15, it can be inferred that the decomposition occurred faster at temperature between 60 ºC to 450 ºC and further slowly decomposed until it reached the maximum temperature of 700 ºC.

For modified Ca/Cr(10:90)/Al_2O_3 catalyst, the first step occurred at temperature range from 60 ºC to 150 ºC with a weight loss of 5.54% represented the removal of physically adsorbed water on the catalyst surface. The second step of weight loss about 8.71% were correlated to the decomposition of basic nitrate precursor that occurred at temperature range between 150 ºC to 380 ºC. Besides that, the decomposition at these temperature regions was capable of producing H_2O and

NO_2 simultaneously. The third step from 380 ºC to 600 ºC with a weight loss of 7.39% due to the decomposition of amorphous hydroxyl carbonates, $M_2CO_3(OH)_2$ which occurred at high temperature before metal oxide was produced. The decomposition was further slowly decomposed when it reached until maximum temperature of 700 ºC thus, the sample weight remained constant after 700 ºC. Overall, the total weight loss of modified Ca/Cr(10:90)/Al_2O_3 catalyst was 21.64%.

In addition, the weight loss of sapodilla leaves is shown in Figure 4b. The first step occurred at temperature range from 60 ºC to 150 ºC with a weight loss 2.88% due to water loss when the temperature rise. The second step was around 150 ºC to 480 ºC with weight loss 63.03 due to desorption of bio-organic in leaves sample [4]. The third step of weight loss occurred at temperatures from 480 ºC to 950 ºC which gave 18.19% due to removal of carbonate which were decomposed into CO_2.

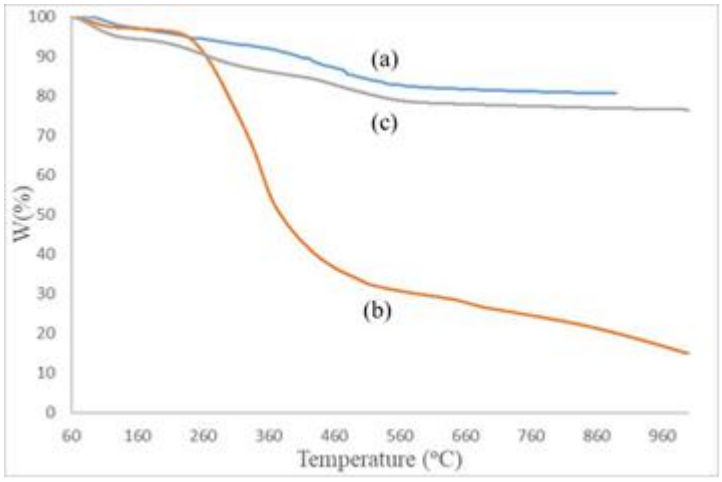

Figure 4. TGA analysis of (a) unmodified and (c) modified Ca/Cr(10:90)/Al2O3 catalysts and (b) dried sapodilla leaves.

3.5 Fourier-transform infrared spectrum (FTIR)

FTIR spectrum was used to identify the functional groups presence in dried sapodilla leaves, modified and unmodified Ca/Cr(10:90)/Al_2O_3 catalysts. As illustrated in Figure 4.7(a), the spectrum of the FTIR spectra of dried sapodilla leaves showedA broad band at 3448 cm-1 which attributed to the stretching vibration of O-H group, IR bands at 2920 cm-1 and 2852 cm-1 represented C–H asymmetric stretching vibration in alkane, The C=O stretching vibration may have appeared at 1636 cm-1 and C–O vibration at 1050 cm-1. The presence of these bands indicating that the dried sapodilla leaves has the flavonoid compound in it. The FTIR spectra of modified catalyst was displayed the similar peaks as sapodilla leaves which proved that the compound might present on the catalyst surface.

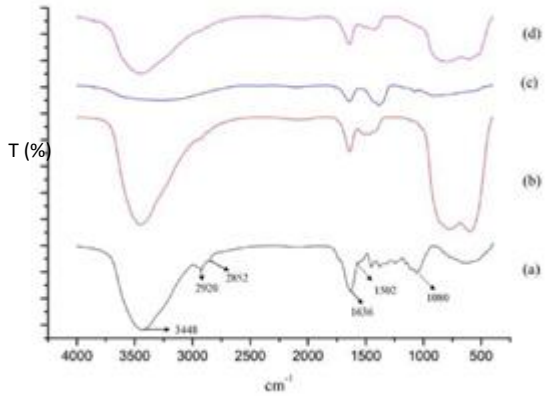

Figure 5. The IR spectrum of (a) sapodilla leaves, (b) unmodified Ca/Cr(10:90)/Al_2O_3 catalyst, (c) uncalcined and (d) calcined of modified Ca/Cr(10:90)/Al_2O_3 catalysts.

4. CONCLUSION

This research was successfully synthesized Ca/Cr(10:90)/Al_2O_3 catalysts via unmodified and modified impregnation method for the transesterification process refined cooking oil for biodiesel production. For modified method, the catalysts prepared were incorporated with different dosages of sapodilla leaves. Both methods were calcined at various temperatures of 600, 700 and 800 ^oC for 5 hours. Catalytic activity of prepared catalysts monitored by GC-FID to determine the percentage conversion of refined cooking oil was successfully carried out. Optimum conditions over potential catalyst was achieved with 1 g of sapodilla leaves dosages and calcined at 700 ^oC for Ca/Cr(10:90)/Al_2O_3 catalyst, which gave the highest conversion of refined cooking oil of 95.22 % with fixed reaction conditions of 65 ^oC, 1:18 wt.% oil to methanol ratio, 6 wt.% catalyst loading and 3 hours of reaction time only 84.40% of conversion obtained for unmodified catalyst with the same conditions. XRD results for potential modified catalyst showed that the catalyst had a polycrystalline structure, while FESEM analysis displayed a morphology of nanosheets with unhomogeneous shapes and sizes in which the fine sized particles in the range of 10-60 nm. NA analysis showed the surface area of 402 m^2/g with average diameter of 18.19 nm and 0.43 cm^3/g of pore volume .TGA analysis proved that 700 ^oC was the optimum calcination temperature. The observed results are much better than unmodified catalyst.

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