INFLUENCE OF DUAL PREPARATORY TREATMENT PROCESS ON THE ACTIVITY OF HETEROGENEOUS CATALYSTS TOWARDS FAME SYNTHESIS

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Abstract

The activity of a heterogeneous catalystsynthesized by co-precipitation methods was investigated. Dual treatment was employed for catalyst synthesis and the obtained catalyst from both treatments was calcined at 460 °C for 4.5h. N_2*physisorption, X-ray diffraction, and scanning electron microscopy measurements were used to characterize the catalysts before transesterification of palm oil. The catalytic activity was evaluated based on yield performance under temperature, methanol/oil ratio, catalyst loading and time variables. The hot treated co-precipitated catalyst performed better than the cold treated with 73% and 57% FAME yield respectively. The morphology of the synthesized catalyst showed identical pattern, but the gradual release of* NH_3*,* NO_2 *gases and water vapor from the precipitate mixture during the hot synthesis was the attributes for the observed differences.The release of these gases also gives rise to a more dense synergetic mixed oxide. The compositions of elemental analysis revealedthat the hot-treated samples have better textural properties and hence high catalytic performance.*

Keywords*:* Dual treatment; Heterogeneouscatalyst; Co-precipitation; Transesterification; Morphology

Introduction

The synthesis of fatty acid methyl esters (FAME) has been widely studied over a range of homogeneous and heterogeneous catalysts (Ma *et al.*, 1999; Llorca *et al.*, 2004; Dias *et al.*, 2008; Benjapornkulaphong *et al.*, 2009). The more advantageous heterogeneous catalysts are solids of simple oxides, mixed oxides, metal salts, solid acids and bases, metals, and dispersed metals typically employed in FAME synthesis to overcome some of the limitations of homogeneous catalyst which include: free fatty acid in feedstock formed saponified products, water in raw materials interferes with the reaction, glycerol separation is usually difficult, and purification of methyl esters require repeated washing with water which when discharged make the environment unsafe (Ayato *et al.*, 2009; Hameed *et al.*, 2009; Sree *et al.*, 2009).Heterogeneous catalysts are used in a wide variety of chemical and environmental processes worldwide including the most recent energy sector to produce biodiesel. Various methods of preparation and treatments are employed in the synthesis of heterogeneous catalysts which contributes significantly in the determination of the structural properties and catalytic activities of the final catalyst. A challenging step in catalyst preparationis the establishment of optimum parameters for pH, calcination temperature, and time. The materials from various chemicals used in catalyst synthesis, as well as, the form and shape of thematerial determine to a large extent its performance in the process of application (Balikci *et al.*, (2008). The preparation processes of wide variety of catalysts and their activities have been investigated by several authors (Benjapornkulaphong *et al.*, 2009; D'Cruz *et al.*, 2007; Yan *et al.*, 2009; Teng *et al.*, 2010). In a particular case, Balikci *et al.*, (2008) investigated activity of Ag_2O/CO_3O_4 catalysts prepared by the sol-gel and the co-precipitation techniques on CO oxidation. Similarly, Cantrell *et al.*, (2005) studied the structure and reactivity correlations inMgAlhydrotalcite catalysts for biodiesel production. The formulation and preparation employed were found to have influenced the chemical and physical properties of the final catalyst. Activity is the primary indicator of catalyst effectiveness, which depends on the loading of the catalyst and active metal distribution (dispersion). The objective is to choose the catalyst preparation and pre-treatment condition such that a well dispersed catalyst structure will be achieved. A well-developed catalyst pore is required for contacts between the catalyst sites and the reaction medium (Aderemi & Hameed, 2009). Thus, this study is intended to highlight effects of dual preparatory treatment method on the synthesis of a heterogeneous catalyst and investigate the influence of various parameters as temperature, methanol/oil ratio, catalyst loading and time on the transesterification of refined palm oil (PO) with methanol to produce FAME.

Materials and Methods

Materials

Commercial edible grade palm oil was purchased fro:m the supermarket at NibongTebal, Malaysia. The acid value, moisture content and saponification values of the oil were 0.36 %,0.07 % and 143 mg KOH/g of oil, respectively. Analytical reagent grade 99.9% methanol (HPLC) purchased from Merck (Malaysia) was used for the transesterification reactions. Analytical grade of (pro analysi) KOH (≥ 85%), Mg $(NO_3)_2.6H_2O$ (≥ 99%), Zn $(NO_3)_2.6H_2O$ (≥ 98%) and KNO_3 (99%) used to synthesize the catalysts were purchased from Sigma-Aldrich Pty Ltd., Malaysia. Methyl heptadecanoate (99.5%) used as internal standard for gas chromatography (GC) analysis was purchased from Sigma-Aldrich (Malaysia) and n-hexane (96%) used as solvent for GC analysis was purchased from Merck (Malaysia). These reagents were used without further purification for catalyst synthesis and transesterification reaction.

Catalyst Preparation

Different synthesis routes were followed to obtain two groups of catalyst, each composed of five samples with difference in calcination temperature. The role of different treatment methods was investigated using sets of experiments in which the composition and the combination ratios were varied. The theoretical amount of KNO_3 was fixed at 50 wt. % whatever the preparation method used. All the solid catalysts (labeled A-J) were prepared by co-precipitation method at controlled pH of 10, determined by the indicator method. In a typical batch of 20 g sample preparation, 3.5 g Mg $(NO_3)_2.6H_2O$, 6.5 g Zn $(NO_3)_2$ $.6H_2O$ and 10 g KNO_3 were dissolved in 50 mL of distilled water to obtain a mixed nitrate solution. Aqueous solution containing 5.6 g of KOH in 50 mL was added drop wise to precipitate the metal hydroxides and the mixture was stirred vigorously for 6 h to allow itto homogenize. At the end of mixing, the precipitate obtained was filtered, dried overnight at 85 ^oC, and it was calcined at variedtemperatures for 4.5 h to obtain the synergetic mixed oxide catalyst. This procedure was repeated for the catalysts prepared by co-precipitation with hot treatment and the precipitate mixture was stirred continuously at 80 ^oC. The various preparationswere denoted as Cat. A-E for hot treatment and the cold treatment denoted as Cat F-J. The as-synthesized catalysts were employed immediately for transesterification of palm oil with methanol.

Catalyst Characterization

Formation of the mixed oxide catalysts was confirmed by XRD measurements. Powder X-ray diffraction patterns were recorded on a diffractometer (Phillips PW 1710), Cu Kα radiation were used to check the purity and to determine the unit cell parameters of developed oxides catalyst. The thermal stability experiment for the prepared catalyst samples were assessed by Thermogravimetric (TGA and DTA) analysis using SETARAM TGA-DTA 92-12 and to avoid oxidation effects, the sampling was carried out innitrogenatmosphere at a flow rate of 20 mL/min. The particle microstructure was studied on a Philips XL30S model ScanningElectron Microscopy (SEM). The elemental composition was analyzed by using energy dispersive X-ray detector (EDX) mounted on the microscope. Fourier transform infrared (FT-IR) was used to determine the active surface functional groups. The spectra were recorded in therange 4000-400 cm^{-1}. The surface areas, pore volume and pore size distribution of thesynthesized catalysts were measured by data from nitrogen adsorption/desorption at 77 K using a BET apparatus (Micromeritics, ASAP 2010) by Brunauer-Emmett-Teller (BET) method.

Catalyst Activity and Product Analysis

To determine the influence of the dual preparatory methods, the synthesized catalyst was employed in transesterification of PO with methanol. The reactions were carried out in a 300 mL batch pressure reactor under vigorous stirring. In a particular batch reaction, 96 mL of palm oil and 24 mL of methanol (methanol to vegetable oil molar ratio 6:1) were charged into the reactor using 1.404 wt. % catalyst based on weight of oil at temperature of 150 ^oC for 6 h. The reaction products were separated from the catalyst and glycerol by a centrifuge. The separation wasachieved due to high density of glycerol, the solid catalyst and the less viscous esters and excess methanol forming the top layers. The methanol was removed using an oven dryer. The product obtained was analyzed with gas chromatography with FID detector where the yield to methyl ester was determined.

Catalyst Stability Tests

In order to address the problem of leaching encountered during transesterification, the catalyst was examined for its reusability. In this study, the reusability tests aimed at establishing the extent of leaching were conducted at the conditions of the highest FAME yield based on the treatment method. The reactor and its contents were cool to room temperature after the first run and the catalyst was collected, washed thoroughly with methanol and dried in an oven at 100^oC for 48 h. It was weighed and reused for second, third and fourth runs. The consistence in treatment after each use was maintained throughout the experimental runs.

Results and Discussion

Catalyst Characterization and Activity Test

In other to establish the influence of catalyst treatment method during the preparation, samples of the synthesized catalyst were characterized and their textural properties were measured. Table 1 shows the results obtained with the dual preparation methods. It revealed that the hot co-precipitated catalyst samples have better textural properties such as specific surface area and pore volume than the cold precipitated catalyst sample.

Table 1: Elemental analysis and textural properties of the as-synthesized catalyst treated using hot and cold precipitation method

Catalyst sample	Preparation method, Co-precipitation	Calcination temperature, °C	Chemical Analysis, wt %				S_{BET}, m^2/g	Ave. pore dia., nm	Pore vol., mm^3/g
			O	Zn	Mg	K			
A: $K_2Mg_{0.7}Zn_{1.3}O_3$	Hot	400	26.42	38.52	4.22	30.84	4.94	13	31
B: $K_2Mg_{0.3}Zn_{1.7}O_3$	″	461	24.67	39.84	3.72	31.77	7.92	18	35
C: $K_2Mg_{0.9}Zn_{1.1}O_3$	″	550	25.56	35.54	4.63	34.27	6.11	12	22
D: $K_2Mg_{0.7}Zn_{1.3}O_3$	″	600	19.64	53.47	4.54	22.35	3.89	11	16
E: $K_2Mg_{0.2}Zn_{1.8}O_3$	″	700	20.45	65.36	5.04	9.15	5.41	14	19
F: $K_2Mg_{0.7}Zn_{1.3}O_3$	Cold	400	29.88	56.12	6.40	7.60	4.72	14	32
G: $K_2Mg_{0.3}Zn_{1.7}O_3$	″	461	25.65	53.64	4.85	15.86	5.06	13	12
H: $K_2Mg_{0.9}Zn_{1.1}O_3$	″	550	32.40	48.68	5.43	13.49	5.82	11	24
I: $K_2Mg_{0.7}Zn_{1.3}O_3$	″	600	29.50	55.72	6.70	8.08	4.21	12	17
J: $K_2Mg_{0.2}Zn_{1.8}O_3$	″	700	26.66	56.86	5.69	10.79	3.47	12	23

The results of the tested activity, during transesterification of PO with methanol to produce methyl esters using the synthesized catalyst are presented in Table 2. It represents the data of methyl ester content obtained after 360 min of reaction for the different catalysts (A-J). Triglyceride transesterification consists of a sequence of three reversible reactions, in which the triglyceride successively transformed into diglyceride, monoglyceride and finally glycerol and methyl esters. The yield of the primary products depends largely on the operating parameters which increased as the reaction conditions were varied. The effect of the catalyst treatment further showed that ester yield decreased when temperature, methanol/oil ratio, catalyst loading and reaction time increased. Similar observation to the catalyst investigated in this study was reported by Serio *et al.*, (2006) and Yee *et al.*, (2010). The FAME content of 73% and 57% were obtained for both hot and cold treatments respectively and these values slightly decreased with longer reaction time. Fig. 1 shows the plot of refined oil conversion to methyl ester using catalysts B and G which was run for longer reaction time.

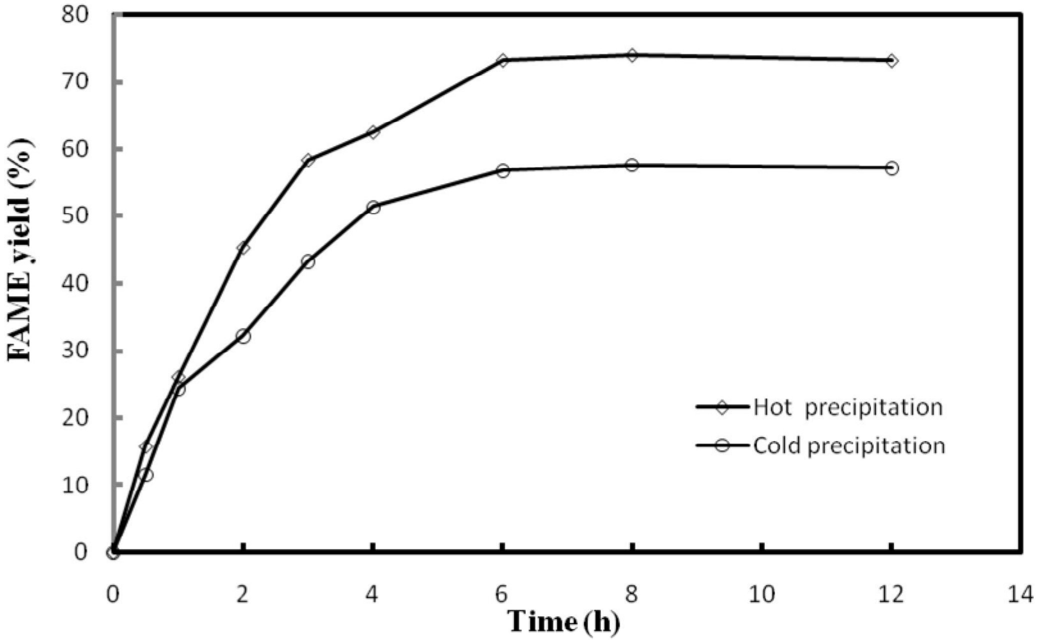

Figure 1: FAME yield (%) versus transesterification time (h) during test of activity with as synthesized catalyst $K_2Mg_{0.3}Zn_{1.7}O_3$ at different treatment methods: Hot and cold treatment with methanol/oil ratio 6:1, catalyst loading 1.404 wt %, reaction time 12 h and temperature 150 ^oC

The performance of other catalysts during transesterification is as presented in Table 2 for comparison.

Table 2: FAME yield from the dual treatment at different calcination temperature

Catalyst sample	Calcination Temperature, ^oC	%Fame yield	
		Hot method	Cold method
A&F	400	50	40
B&G	461	73	57
C&H	550	64	60
D&I	600	45	38
E&J	700	41	35

At the beginning of reaction, the yield increased because reactant contacted fresh catalyst and decreased as the time increased. It was attributed to the enhanced formation of diglyceride andmonoglyceride in the system during the reaction due to generation of RO^-on the active sites which is rapidly attracted to the polarized C=O bond of the triglyceride to obtain the partialglycerides. With reference to catalyst samples B and G in Table 1, the hot treatment method used played an important role in the formation of catalyst pore diameter, 18 nm compared to 13 nm of the cold treatment method. The lower values of average pore size and the surface area for the cold treated samples explained the reduced activity during the reaction. The formulation with $K_2Mg_{0.3}Zn_{1.7}O_3$ was chosen for further investigation from preliminary studies as it yielded the highest methyl ester content. In order to compare the effect of the two treatment methods, the conditions for Cat B that gives the highest value of

FAME was employed in further experiment. This research took into consideration various combinations of the metal components from the high and the low extremes. Elemental analysis was used to determine the composition of each element in the solid combination and the results is aspresented in Table 1. The structure of the synthesized catalyst was studied by XRD and is presented in Fig. 2. It consists mainly of hexagonal, cubic and orthorhombic structures of ZnO, MgO and K_2O, respectively. After heat treatment, the peaks corresponding to MgO and ZnOwere conspicuous in all the solids indicating the precipitation of these oxides out of solution. A broad peak from 2θ = 20 to 30º and 72 to 82º seemed to indicate that the cold samples contain other peaks which may be due to the combination of the unvapourised gases in the solids. Thethermal treatment of the catalyst during drying and calcination could have impact on thestructure because the calcination atmosphere will change the arrangement of the surface molecules to some degree and affects the final formation of solid synergetic mixed oxides.

The pore size of the hot treated samples were found to be in the range of 11-18 nmcompared to the 11-14 nm of the cold treated samples. The excess water used during the hot precipitation favours the porosity. Similarly, during calcination, the observed activity of the hot treated samples could also be due to the release of gases such as NO, H_2O, and O_2 which usuallyinduced strong inhibiting effects depending on the surface properties of the solids particularly the surface mobility of oxygen from $K_2Mg_{0.34}Zn_{1.66}O_3$. This observation is corroborated by the work of Dacquin *et al.* (2009). The treatment employed during the catalyst preparation indicates that the overall activity is closely related to the mobility of oxygen species during the process of release and re-combination from the nitrates and hydroxides in the aqueous phase and during heat treatment at 460 ^oC and this is believed to have influenced the activity of the synthesized catalysts.

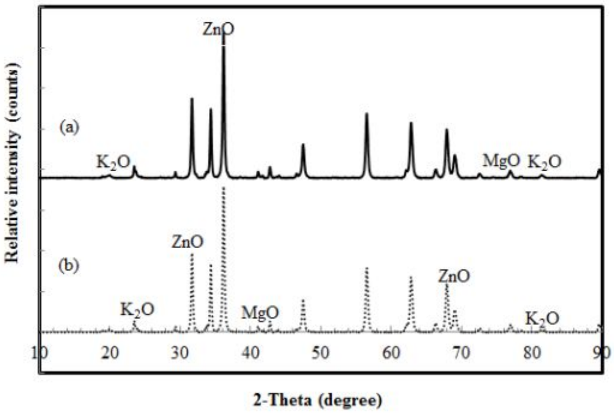

Figure 2: XRD pattern for the synthesized catalyst; (a) $K_2Mg_{0.3}Zn_{1.7}O_3$; (b) $K_2Mg_{1.7}Zn_{0.34}O_3$both calcined at 460 ^oC for 4.5 h.

In order to establish the influence of calcination temperature, the synthesized catalysts werecalcined at different temperatures. As presented in Fig. 3, the thermo-gravimetric analysis (TGA) shows the weight loss and derivative weight loss as a function of temperature. As can be seen from this figure, various stages of decomposition are distinguishable in different temperature zones.

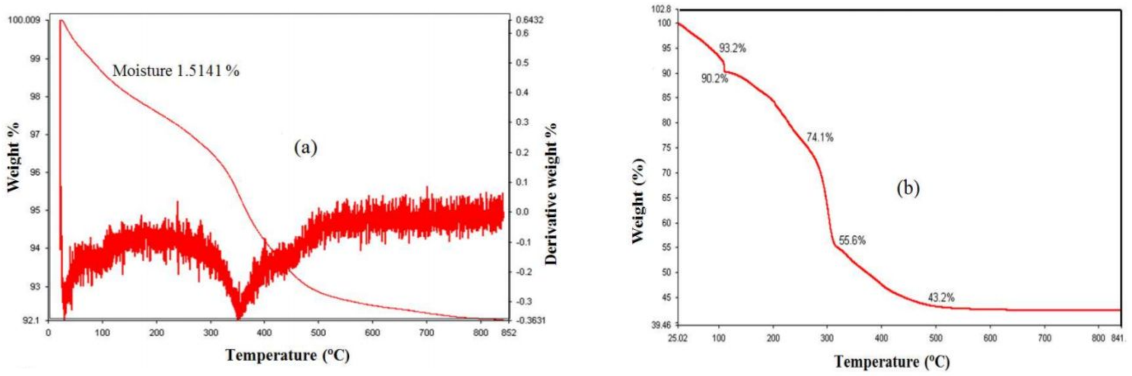

Figure 3: Representative TGA and DTA curves for the synthesized catalyst, $K_2Mg_{0.3}Zn_{1.7}O_3$

It was also revealed that the suitability of the calcination temperature at 460 °C in the case of Cats. B and G produced synergetic mixed oxides with higher yield of FAME during transesterification. The TGA further revealed that beyond this temperature, the components which make-up the individual oxides become less active as it was shown from the drop in conversion obtained for FAME during the test of activity. The derivative weight lossshowed losses of weight at 250 °C to be slightly less than 25 %, at 320 °C (< 45.0 %), and at temperature greater than 600°C with a loss of < 4.0 %. This result indicated that calcination above 600 °C decomposed the catalyst structure to inactive components. Thus, the XRD patterns of the catalyst calcined at 460 °C showed good selectivity towards FAME production.

The hot treated samples showed a very high catalytic activity for the transesterification of virgin palm oil with high yield at the operating conditions. On the contrary, a reduction in the activity of cold treated catalyst was observed. These results show a correlation with the gases removed during precipitation as a function of the active surface present on the catalyst. In fact the catalyst prepared with hot treatment shows the presence of more active sites as evidenced by the higher surface area and conversion of the oil to FAME. The lower conversion observed in the cold treated samples could be due to the filling of the fewer available pores with hydrocarbon liquid which blocks the active sites preventing further reaction.

Effect of reaction parameters on the activity of synthesized catalyst during transesterification of palm oil

The effect of parameters such as temperature, methanol/oil ratio, catalyst loading and time were investigated using refined palm oil. The obtained value of highest methyl ester content (73 %) at methanol/oil ratio of 6:1, reaction time of 6 h when catalyst loading was 1.404 wt % based on the weight of oil at a temperature of 150 °C was used for further experiment. The results confirmed the dependency of transesterification on each parameter such as temperature, methanol/oil molar ratio, catalyst loading and the reaction time. However, beyond an optimum value for each factor resulted in a decreased conversion to products (methyl esters). The observed results are presented in Figures 4 (a-d). The profiles of dependency of various parameters during transesterification of refined palm studied in this work is in agreement with the work of Aderemi and Hameed, (2009) where alum was employed as heterogeneous catalyst intransesterification of palm oil with methanol. This further justifies the effectiveness of the treatment method employed for the synthesized catalysts in this work for FAME production.

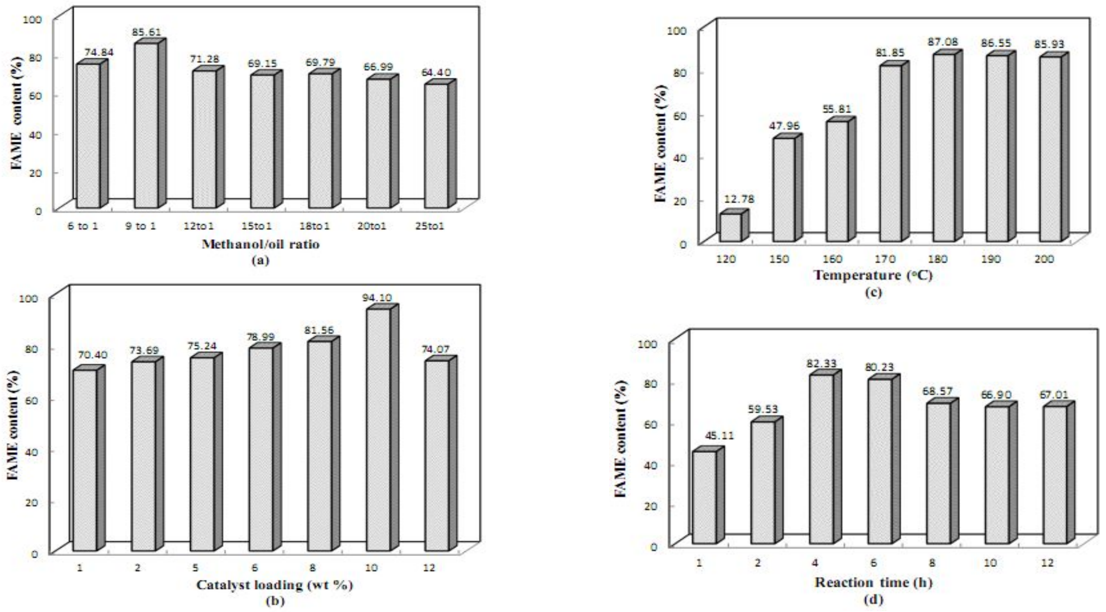

Figure 4: Dependency of FAME yields on various parameters:

(a) Methanol/oil ratio at catalyst loading of 4.19 wt %, temperature 186 ^{o}C, and reaction time 4 h;

(b) Catalyst loading at methanol/oil ratio 10:1, temperature 186 ^{o}C, and reaction time 4 h;

(c) Temperature at methanol/oil ratio 10:1, catalyst loading of 4.19 wt %, and reaction time 4 h; and

(d) Reaction time at methanol/oil ratio 10:1, catalyst loading of 4.19 wt %, and temperature 186 ^{o}C

Catalytic activity tests for reusability and stability of the synthesized catalyst

The stability of catalyst was tested in transesterification reactions in order to determine possible deactivation processes and its reusability. To achieve this, the study involving reusability and regeneration of the catalyst was carried out using refined palm oil at methanol/oil ratio of 6:1, reaction time of 6 h when catalyst loading was 1.404 wt. % based on the weight of oil at a temperature of 150 ^{o}C. The catalyst was collected, washed thoroughly with methanol and dried in an oven at 100 ^{o}C for 48 h. It was weighed and reused after the first cycle for second, third and fourth runs. The results obtained showed good activity for the catalyst during reusability studies with 76%, 70%, 63% and 55% in the first, second, third and fourth cycles,respectively. The leaching of active sites was in the range of 8-13% based on the total cycles of re-run experiment. Although, the value is quite high, the selectivity of the catalyst to esters at the operated conditions is valuable and it is hoped that the leaching problem will be addressed in future study.

Conclusion

The synthesized catalysts using the dual preparatory methods were tested in the transesterification reaction of refined palm oil with methanol to produce FAME. The hot treated co-precipitated catalyst performed better than the cold treated with 73% and 57% FAME yield, respectively under the same experimental conditions. Further investigation with hot treated co-precipitated catalyst showed a high yield of up to 94.1%. The textural properties of the synthesized hot precipitated catalysts revealed the high activity in transesterification. The reusability of the catalyst was stable up to four cycles with good separation from the product mixture.

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