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MgAl Mixed Oxide Derived Alkali-free Hydrotalcite for Transesterification of Waste Cooking Oil to Biodiesel

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The heterogeneous catalyst, MgAl hydrotalcite (MgAl HT) was synthesised via alkali-free method spanning from 4:1 to 2:1 ratio of Mg and Al respectively and underwent subsequent calcination process at 450°C for 3 h. The diffraction patterns of MgAl HT indicated the high crystalline structure was obtained. The increasing of the reflection intensity and the sharpness of diffraction lines were seen with the increasing of Mg:Al ratio. Calcination has removed the carbonates and hydroxyl layers, thus left only the mixed oxide of MgO and Al_2O_3 as proven by XRD, SEM, EDX and FTIR. This catalyst was used in the transesterification reaction with Waste Cooking Oil (WCO) as feedstock for the production of biodiesel. WCO underwent a pretreatment process to remove the impurities and moisture content. Acid-base titration was performed to determine the acid value and percentage of Free Fatty Acid (%FFA). The FFA content was 0.073% (less than 1%), hence transesterification reaction has been proceeded without before esterification process using methanol to oil ratio 30:1 for 24 h. Results show high percentage yield of biodiesel in 5 wt% 3:1 MgAl (87.23%) compared to 84.01% yield in 5 wt% 4:1 catalyst and only 79.23% yield with 5 wt% 2:1 catalyst.

Keywords: MgAl hydrotalcite; alkali-free; catalyst; transesterification; waste cooking oil

I. INTRODUCTION

The exhaustion of petroleum nowadays rising concern for the world to find an alternative way to overcome this problem. Bio-based fuel is one of the alternative fuel resources which is biodiesel. Biodiesel molecules consist of fatty acid methyl ester in its chemical structure. It has advantages such as biodegradable and renewable resources, thus making it as an alternative fuel to traditional petroleum diesel. Biodiesel can be produced from several natural and renewable sources such as vegetable oil like palm, rapeseed, soybean, coconut, sunflower, and canola oil etc. (A.Tajuddin *et al.*, 2018; Ullah *et al.*, 2015). Due to the cost of the raw materials are quite high; therefore, waste cooking oil (WCO) is a suitable raw material to reduce the high cost of biodiesel. This research is significant to increase the rate of diesel production based on price and availability. Also, biodiesel has many advantages compared to biodegradable petroleum diesel, renewable sources and low content of sulphur (Kumar *et al.*, 2018; Wilson and Lee, 2016; Aransiola *et al.*, 2014).

Biodiesel is synthesised commonly by transesterification reaction from renewable sources reacts with common alcohol (methanol) in the presence of catalysts. Mg-Al hydrotalcite is one of the catalysts that play a vital role in the transesterification process. The general formula for hydrotalcite is $[M^{2+}_{(1-x)}M^{3+}_{x}(OH)2]^{x+}(A_{x/n})^{n-}\cdot yH_2O$ (Ibrahim *et al.*, 2017). The hydrotalcite is also called as layered double hydroxides (LDH) due to its two-dimensional brucites like structure ($Mg(OH)_2$) with M^{2+} (divalent metal cations) and M^{3+} (trivalent metal cations). In the interlayer space, there is A^{n-} which acts as a counter anion to balance the residual positive charges of hydroxides layer comes from the isomorphous substitution of M^{2+} by M^{3+} (Reyero *et al.*, 2013). Hydrotalcites (HT) have two representative properties due to its unique properties which can capture and exchange organic and inorganic anions and memory

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*Corresponding author's e-mail: nazriza@uitm.edu.my effect (Mishra *et al.,* 2018; Takehira *et al.,* 2017; Lee *et al.*, 2016).

Mg/Al hydrotalcite is depicted as a raw material for high-temperature insulation porous ceramics for two reasons, the loss of weight during its thermal decomposition results in a large number of pores, and it induces aluminium-magnesium spinel ($MgAl_2O_4$) formation (Salomão *et al.*, 2011). Hydrotalcites is applied in various applications which are as ion exchangers, adsorbents, CO2 capture and carrier of bioactive molecules (Kikhtyanin et al., 2016). The most important part that we are going to investigate is its role as a catalyst, and catalyst support due to its high surface area, structural stability, and phase purity (Wiyantoko *et al.*, 2015). Also, by using the di- and trivalent salts, the preparation of hydrotalcite is simple and most importantly is its lower cost of production (Petrolini *et al.*, 2017).

Hydrotalcite is a type of heterogeneous catalyst, and it has many advantages over a homogenous catalyst which are catalyst reusability, high purity by-products, separation and purification more convenient, no neutralisation step required and catalyst recoverability (Jing *et al.*, 2019; Lam *et al.*, 2010). Furthermore, the heterogeneous catalyst should have high selectivity for the formation of the desired product and produces a high yield (Creasey *et al.*, 2014; Issariyakul and Dalai, 2014). In biodiesel production, when the homogenous catalyst is used, it needs multi-steps of production and purification because such catalyst cannot tolerate with free fatty acids (FFA) and moisture (Baroi and Dalai, 2013). Hence, it will lead to the high cost of refined feedstocks results in a high price of biodiesel compared to petrol diesel (Tajuddin *et al.,* 2016).

Most synthetic HTs/LDHs are prepared via coprecipitation method in basic conditions, which results in the entrainment of residual alkali (Creasey *et al.*, 2015; Creasey *et al.*, 2014). Also, due to its propensities to produce soap formation and mono- and di-glycerides during transesterification, it will cause separation and purification problem. To overcome this drawback, alkali-free LDHs has been introduced and applied in this study.

II. MATERIALS AND METHOD

A. Catalyst Synthesis

MgAl LDHs were prepared by alkali-free coprecipitation method (A.Tajuddin *et al.*, 2018). Solution A has been prepared by adding 19.20 g $Mg(NO_3)_2.9H_2O$ and 28.12 g of $Al(NO_3)_3.9H_2O$ in 100 cm^3 of distilled water in different volumetric flasks. The Mg:Al ratio is varied such that x+y = 0.15 mol and x:y= 2:1, 3:1 and 4:1. The buffer ammonium nitrate (NH_3NO_3) (0.2 mol) was prepared as solution B by dissolving 16 g of NH_3NO_3 in 100 cm^3 of distilled water. Solution B has been added dropwise into the solution A until the pH constant at 7.6-8.0 by detecting using a Jenway 3030 pH meter. The mixture was ageing at 65˚C while stirring vigorously for 24 h. The catalyst then has been filtered and calcined at 450 ˚C for 3 h.

B. Catalyst Characterisation

Fresh and calcined catalysts were characterised by X-ray Powder Diffraction using X'pert-Pro PANanalytical diffractometer with a Cu Kα X-ray radiation (λ= 1.54056) with 2θ range of 5˚- 80˚. The Scanning Electron Microscope (SEM) images (fitted with Energy Dispersive X-Ray Spectroscopy, EDX) were obtained on a JSM-6700F field emission (FE) microscope operating at 15kv. The samples were immobilised on a copper holder using conducting resin and were coated with prior platinum characterisation. The infrared spectra were obtained on Jasco FT-IR-460 spectrometer in range of 4500-900 cm^{-1} using KBR pellet technique.

C. Biodiesel Production

1. Pre-treatment of waste cooking oil (WCO)

The pre-treatment process was carried out to remove excess free fatty acid content in waste cooking oil. The activated carbon (0.5 g) was added to 100 ml of waste cooking oil. Then, the mixture was kept in a shaker flask at 150 rpm for 30 min under room temperature. After that, the oil was filtered before biodiesel production. To determine the free fatty acid (FFA) content, 1 g of oil was dissolved in 25 mL of ethanol, and 25 mL of diethyl ether with a few drops of phenolphthalein was added as an indicator. The titration process was stopped when the solution turned into light pink colour. The acid value (AV) was calculated using the equation:

$$AV\ (mg\ KOH/g) = \frac{56.1 \times C(KOH) \times V(KOH)}{\text{Mass of oil}}$$

where: 56.1 is the MW of the KOH
V(KOH) is the volume of KOH consume during titration
C(KOH) is the concentration of KOH

2. Transesterification process

The 25 g of waste cooking oil was poured in a three-necked round bottom flask equipped with a reflux condenser and cool-water chiller. The WCO was heated at 100˚C for 30 min to remove traces of water. A mixture of methanol to oil ratio used for this process was 30:1 with 5 wt% base catalyst were added, and the reaction was run at 65 ˚C at 24 h. The reaction mixture was transferred into the separating funnel. The biodiesel from the upper layer was collected, and the bottom layer of oil was discarded. The rotary evaporator was used to remove the glycerol leaving only biodiesel completely. The final product which is biodiesel was characterised by using Gas Chromatography (Agilent Technologies 6890N) equipped with Flame Ionization Detector (FID) and 30m x 250 µm HP5-MS capillary column. The injection port was furnished with split mode (40:1) with 250 °C injection port temperature. The column temperature was initially set at 100 °C and increased until 290 °C at 40 °C min^{-1}. The carrier gas (nitrogen) flow was 30 ml s$^{-1,}$ and the detector temperature was fitted at 250 °C.

III. RESULT AND DISCUSSION

A. Catalyst Characterisation

The successful synthesis of alkali-free MgAl HTs with molar ratios spanning 2.0-4.0 was performed by powder XRD, EDX, SEM and FTIR analyses. The phase composition of fresh and calcined MgAl HTs was first monitored by XRD. Definite crystalline phases were observed for fresh catalyst (Figure 1a), attributing to the reflections of 2θ=11.6 °, 23.4 °, 35.0 °, 39.6 °, 47.1 °, 61.1 °, and 61.8° which associated to MgAl HTs (Wang et al., 2016). The intensity of basal spacing d(003) is increased with the ratio shows the more crystalline structure is obtained at a higher Mg:Al composition. Decomposition occurred during the calcination process resulting in the formation of MgO periclase phases as can be seen in Figure 1b. The XRD diffraction patterns also confirmed the removal of HT layers as the basal spacing of d(003) and d(009) are collapsed (Ibrahim *et al.,* 2017). The same diffraction pattern is portrayed by (Bankauskaite and Baltakys, 2015). No reflections of the MgAlO and MgAlCO$_3$ were observed in the diffraction patterns except MgO similar as reported by (Chen *et al.*, 2016).

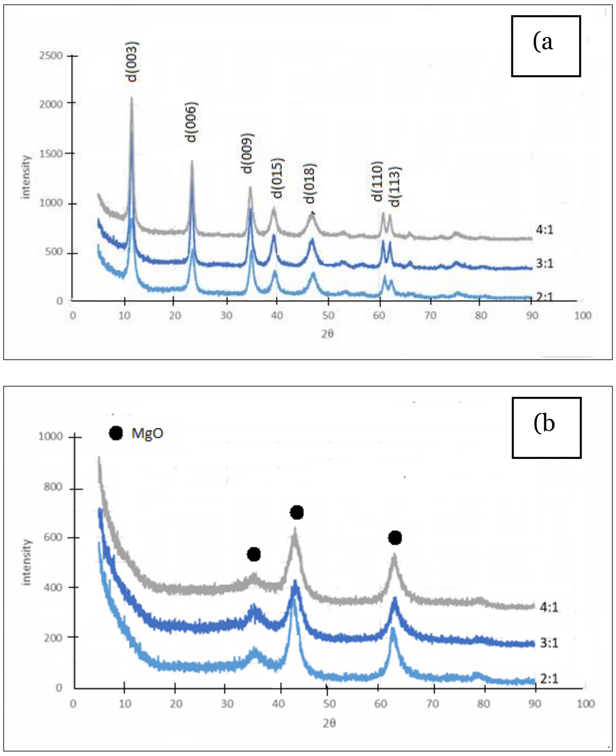

Figure 1. The XRD patterns of fresh (a) and calcined (b) MgAl HTs with ratio spanning from 2:1 to 4:1, respectively

The pure HTs were further characterised by EDX spectroscopy. Figure 2a, b and c of the EDX spectra confirmed the presence of Mg, Al and O in MgAl HTs catalyst and no other impurities were detected. Results on weight % and atomic % of each element are tabulated in Table 1. Data shows the incorporation of Mg:Al is associated with the synthesised ratio. As the ratio of Mg to Al is increased, the inclusion of Mg is observed in the HT framework as both weight and atom % are substantially increased.

Fig. 3a-c presents the SEM images of MgAl HTs at a different synthesised ratio. A layered crystalline structure with irregular edges is observed here (K. Kaul *et al.,* 2017). As the ratio of Mg to Al increased, the catalysts are homogenously grown without aggregation has been observed (Jing *et al.,* 2019), indicating proper incorporation of Mg^{2+} and Al^{3+} during coprecipitation process. This further demonstrated that crystallinity formation of HTs improved with the ratio as previously proven by XRD. In this study, the calcined HTs were subsequently characterised by FTIR to identify the functional group present. Table 2 shows the three main characteristic band and the wavelength number of Mg/Al hydrotalcite at a different ratio. The strong and broad absorption band at 3445.37 cm^{-1} is correlated to O-H stretching vibrations present in the interlayer of catalyst. The C-O vibration appeared around 1412 cm^{-1} affirmed the interaction of the metal with unidentate carbonate (Chen *et al.,* 2016; Li and Guo, 2015). The AlO deformation and Mg-O translation were found later in the region wavelength around 816-854 cm^{-1} (Fahami and Beall, 2016; Tittabut and Trakarnpruk, 2008).

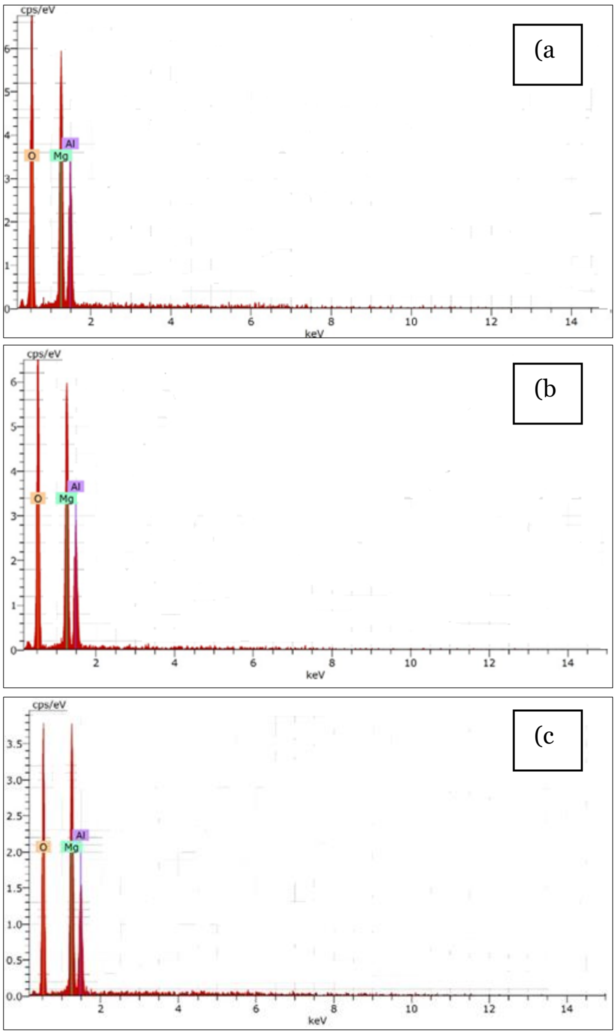

Figure 2. The EDX spectra of MgAl HTs catalyst on ratio 2:1(a), 3:1(b) and 4:1(c)

Table 1. Weight and atomic per cent of each element in MgAl HTs obtained by EDX spectroscopy

Mg/Al ratio	Element	Weight %	Atomic %
	Oxygen	57.89	68.55
2:1	Magnesium	24.31	18.95
	Aluminium	17.80	12.50
	Oxygen	57.55	68.19
3:1	Magnesium	25.67	20.02
	Aluminium	16.78	11.79
	Oxygen	54.99	65.84
4:1	Magnesium	28.28	22.29
	Aluminium	16.73	11.88

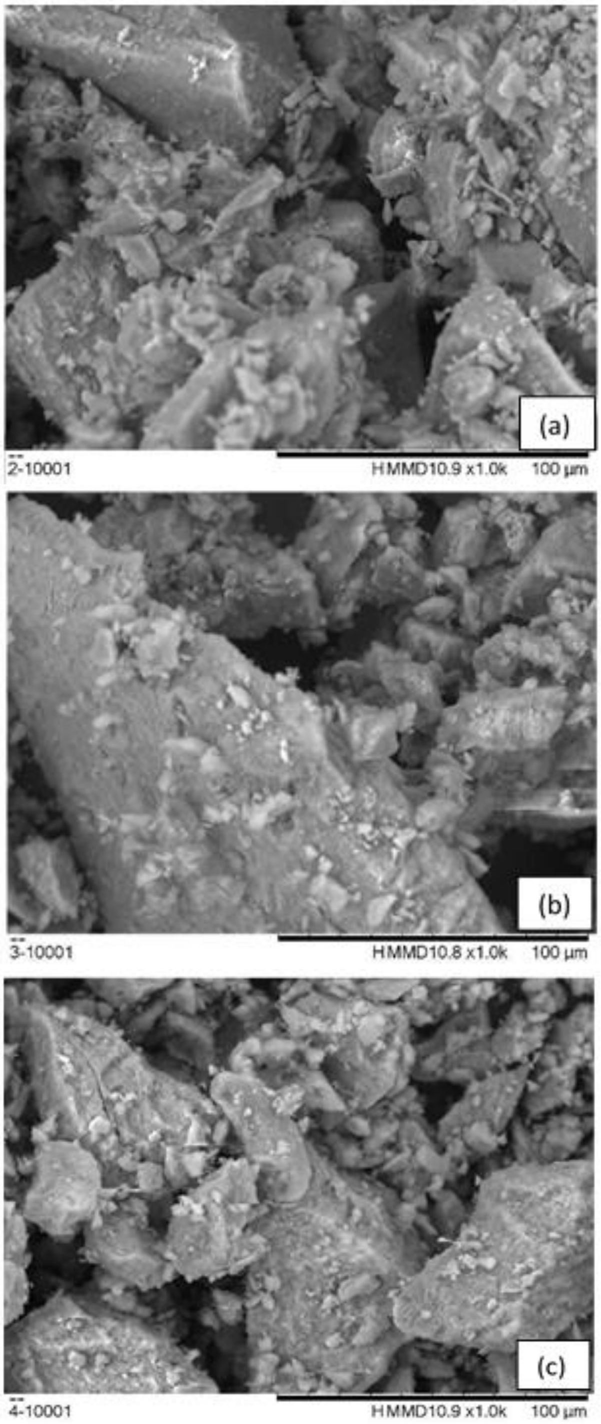

Figure 3. SEM images of MgAl HT at different ratio; 2:1 (a), 3:1(b) and 4:1 (c)

Table 2. Comparison of data infrared spectra at different Mg/Al hydrotalcite ratio

	Wavelength number		
Characteristic band	Mg/Al 2:1	Mg/Al 3:1	Mg/Al 2:1
O-H stretching Vibration	3469.23	3445.04	3445.37
C-O/C=O vibration	1412.47	1412.18	1412.08
Al-O/Mg-O vibration	816.25	851.95	854.41

B. Biodiesel Production

WCO was converted into biodiesel via transesterification process in the presence of MgO from calcined catalyst to produce methyl esters and glycerol as the by-product. Previously, WCO underwent a pre-treatment process by centrifuged and heated to remove any traces and moisture content (Javidialesaadi and Raeissi, 2013). Table 3 shows the acid value and FFA% before and after pre-treatment process. Results show the FFA value is less than 1% (0.0730%) indicated no esterification process requires before transesterification reaction.

Table 3. Acid value and percentage of free fatty acid in WCO before and after pre-treatment process

	Value	
Parameter	Titration of WCO before heating	Titration of WCO after heating
Acid value, mgKOH/g	0.90	0.73
Free fatty acid (FFA) content (%)	0.0898	0.0730

Gas Chromatography was used to analyse the fatty acid methyl ester (FAME) contents in biodiesel. To determine the presence of FAME in biodiesel, the retention time of the sample was compared with the retention time of standard FAME. Table 4 shows the retention time of individual FAME standard and biodiesel samples from the chromatogram. Results show the retention time for both standard and samples were slightly different due to several factors such as polarity of the FAME and volatility of the compound (Girish *et al.*, 2013).

Methyl laurate was eluted first due to it is less non-polar compared to methyl stearate, which is more non-polar and eluted at a longer time. Apart than that, methyl laurate is the most volatile compound and has the lowest boiling point, thus it eluted at a shorter time compared to other compounds (García *et al.*, 2012). The biodiesel was produced by the reaction of 30:1 methanol/oil with 5 wt% of MgAl hydrotalcite in the transesterification process. The yield of biodiesel for 2:1, 3:1 and 4:1 Mg:Al ratio were 79.23 %, 87.23 % and 84.01 % respectively. Figure 4 shows the GC chromatogram of the biodiesel at 3:1 ratio with the highest yield of 87.23 %.

Table 4. Average of retention time of individual FAME on standard and biodiesel samples from WCO at a concentration of 100 ppm

FAME	Retention time, min	
	Standard	Samples
Methyl laurate	1.941	1.948
Methyl myristate	2.711	2.715
Methyl palmitate	4.295	4.263
Methyl linoleate	6.823	6.815
Methyl stearate	7.431	7.382

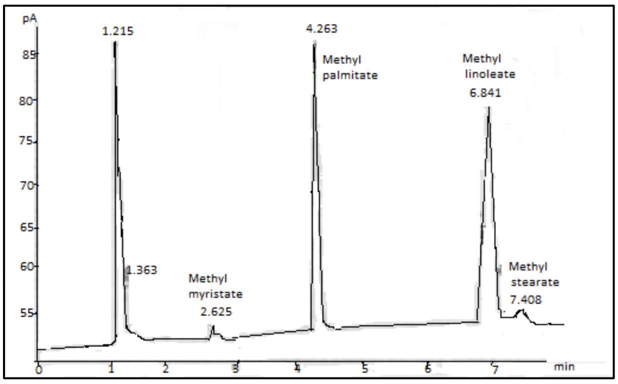

Figure 4 GC chromatogram of biodiesel from WCO with the 5 wt% catalyst loading of 3:1 ratio of Mg:Al and 30:1 methanol/oil ratio.

IV. CONCLUSION

MgAl HTs catalyst was successfully synthesised via the alkali-free method and further underwent a calcination process. The XRD confirmed the successful synthesised of pure and calcined HTs. HTs compound possesses only Mg, Al and O atom as proven by EDX. The pronounced characteristic bands observed by FTIR further affirmed the characteristic of HTs. The SEM shows irregular edges of HTs images, and the coprecipitation shown better growth on a higher Mg to Al ratio. The transesterification reaction was performed by added 5 wt% catalyst loading of 3:1 ratio of Mg:Al with 30:1 methanol/oil ratio has produced 87.23 % biodiesel yield.

V. ACKNOWLEDGEMENT

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