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Research paper

Synthesis and Characterization of Alkali Free Mg-Al Layered Double Hydroxide for Transesterification of Waste Cooking Oil to Biodiesel: Effect of Mg/Al Ratio

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Abstract

The depletion of fossil fuels and the concerned toward environmental sustainability have created a considerable to alternate development of sources of energy as substitute for traditional fossil fuels. The biodiesel production has been reported to be an ideal solution as alternative diesel fuel due to its environmental benefits. Thus, the transesterification of waste cooking oil with methanol in the presence of Mg-Al layered double hydroxide (LDHs) as a heterogeneous catalyst was studied to produce the biodiesel. In this work, Mg-Al-LDH was fabricated via alkali free co-precipitation method with final Mg/Al ratio of 4:1, 3:1 and 2:1. The product of co-precipitation was undergone aging process for 24 h. Then it was placed in oven at 100 ^{0} C overnight and finally was calcined at 450 ^{0} C for 5 h. The correlation of crystallinity, morphology and particle size of Mg-Al-LDH before and after calcined were examined and compared. X-ray diffraction analyse (XRD) was used to study the textural and structural characteristics of the samples. Particle size, morphology and particle properties were characterize by Brunauer, Emmett and Teller (BET) and Scanning electron spectroscopy (SEM). The bonding and structural of Mg-Al-LDH was studied by Fourier transform infrared spectroscopy (FTIR). Energy dispersive X-ray spectroscopy (EDX) was used for the elemental analysis of the samples. The catalytic activity was evaluated by the transesterification reaction under the following reaction condition: temperature (60 ^{0} C-65 ^{0} C), time (24 h) and methanol to oil ratio (15:1) .The greatest yield was 85.2% and obtained with combination of 4:1 Mg/Al ratio followed by 3:1 and 2:1 ratio.

Keywords: *Alkali free, Biodiesel, Characterization, Esterification, Layered double hydroxide, Transesterification*

1. Introduction

Energy is the most fundamental requirement for human existence and activities. The need for energy is increasing continuously due to increase industrialization activity and also population growth. Nowadays, researchers are concerned on global warming and focus toward energy sustainability. Petroleum has been serving the world to meet its energy consumption. But, due to the depletion of fossil fuels and global warming issues biodiesel research has received significant attention in the past few decades. As it is renewable energy, it can be the most suitable alternative fuel to substitute petroleum.

Biodiesel is entirely produced from vegetable oils and animal fats. As it is environmentally benign and does not contain sulfur, metal and aromatic hydrocarbons. Thus, it can reduce the carcinogenicity of particulate emissions and other harmful matter [1].

Biodiesel can be produced via different techniques such as microemulsion, pyrolysis, direct/oil blends and transesterification [2]. However, transesterification is declare as the most notable ways for producing higher quality of biodiesel [3]. Briefly, transesterification is the reaction of oil to its corresponding fatty ester with low molecular weight alcohols such as methanol in the presence of catalyst [4]. Transesterification reaction is catalyzed by either homogeneous catalyst (potassium hydroxide, sulfuric acid, sodium hydroxide, etc.) and heterogeneous catalyst (layered double hydroxide, organic polymer, alkaline earth metal compound, etc.) [5].

In this experiment, heterogeneous Mg-Al layered double hydroxide have been used as a catalyst to accelerate the transesterification process. The structure of LDHs containing both divalent M^{2+} and trivalent M^{3+} cations attached to six OH^{-} hydroxyl groups [6]. In LDHs the layered materials consisting of positively charged layers with charge balancing anions between the layers. The latter can be replace by other species through an anion exchange process. In addition, the LDHs composition and their textural properties can be controlled [7]. As a result, researchers have been able to produce catalyst precursors by introducing various transition and noble metals into the sheet of the LDHs structure [8]. The accurate formula of hydrotalcite is [$Mg_6Al_{12}(OH)_{16}CO_3.4H_2O$]. This catalyst can be synthesized by using several of techniques such as co-precipitation, sol-gel method, electrochemical deposition and etc [9]. The selection of method depends on the cations forming the hydroxide layer, intercalated anions and also final material.

In biodiesel production, the selection of feedstock is very important to lower biodiesel production cost. The oil feeds containing high free fatty acids (FFA) from non-edible oils (waste oil) are much cheaper than edible oil and can also avoid the sensitive “food versus fuel” debate [10]. However, WCO contains a lot of FFA that must be removed or reduced before transesterification as it can decrease the final yield of biodiesel [11]. WCO transesterification catalyzed by alkali only become possible when the acid value of oil is less than 1 mg KOH/g oil [1].

In this work, the direct esterification of WCO in the presence of hydrochloric acid as a catalyst was done to reduce the FFA value. Then, the esterified oil was subjected to transesterification process with Mg-Al-LDH as a catalyst to determine the final yield of biodiesel**.**

2. Materials and Method

2.1. Materials

Waste cooking oils were collected randomly from the restaurants at Seksyen 7, Shah Alam Selangor whose average acid values are 2.87 mgKOH/g oil, Mg(ll) nitrate hexahydrate (R&M), Aluminium nitrate nonahydrate (R&M), Ammonium carbonate (Sigma), Ammonium hydroxide solution 30% (Sigma), Methanol 95% (purchased from ChemAR), Hydrochloric acid 37% (R&M).

2.2. Experimental procedure

In this study, a two-step catalyzed processes were performed for the biodiesel production from waste cooking oil. The first step is esterification was to reduce the FFA contents followed by the second alkali transesterification step. Since FFA in WCO will decrease process efficiency and can cause saponification so the concentration of FFA should be reduced (<1% FFA) through esterification process.

2.2.1. Preparation of layered double hydroxide via co-precipitation method

An alkali free co-precipitation method was used to synthesize LDHs with three different molar ratio which were 4:1, 3:1 and 2:1 Mg/Al ratio. The synthesis was prepared by mixing an aqueos solution of metallic cations (solution A) with a highly basic carbonate solution (solution B) simultaneously drop by drop under vigorous stirring at pH 8.5 [13]. Ammonium hydroxide solution was added drop by drop in order to maintain the pH. Solution A was prepared by mixing Mg(ll) nitrate hexahydrate, 1M with Aluminium nitrate nonahydrate, 1M according to different Mg/Al ratio to make up 100 mL solution. Solution B was 2M ammonium carbonate in 100 mL distilled water. The product of co-precipitation was brought to reflux for 24 h for aging process at 65 ^oC. Then, the solution was filtered and washed with distilled water until pH of the filtrate was 7. Next, the precursor was placed in oven at 100 ^oC for 24 h. Finally, the precursor was calcined at 450 ^oC for 5 h.

2.2.2. Characterization of catalyst precursor

The characterization of the catalyst structure was obtained by powder X-ray diffraction (XRD) model PANalytical X'pert Pro. Measurements were made with a diffraction angle 2Ɵ from 8 to 85^0 at a speed of 1.2 ^{0} min^{-1}. Fourier transform infrared spectroscopy (FTIR) model PerkinElmer Spectrum One was run to observe the bonding type in Mg-Al-LDHs. The sample was mixed with KBr and compressed into a thin transparent pellet then was scan from 0 to 4500 cm^{-1}. Scanning electron micrographs were obtained using a TM3030PLUS scanning electron microscope equipped with a XFlash MIN SVE EDS system.

2.2.3. Esterification process

Esterification is a pretreatment process where the FFA will react with acid catalyst (HCl) and form new ester so that the FFA content will decline. The esterification was performed in 500 mL two-neck round bottom flask. One neck was equipped with a thermometer to measure the temperature. A water cooled condenser was connected to another neck on the top of round bottom flask to reduce evaporative loss of methanol. The round bottom flask was placed in a paraffin oil and heated on a hot plate. In this experiment, 6:1 methanol to oil ratio was applied with 1% catalyst. Methanol and HCl were mixed before the reaction and oil were heated to 60-65 ^oC. After the temperature was reached, the mixture of methanol and HCl were added and let the reaction to complete for two hours. The mixture of methanol and oil are immiscible so the reaction was stirred to ensure efficient mixing. After two hours, the solution was transferred into separating funnel and the bottom layer of oil was discard. The esterified oil was washed three times with hot water before proceed with transesterifcation and acid value determination**.**

2.2.4. Transesterification procedure

The esterified oil was subjected to transesterification process to obtain the methyl ester. Methanol to oil ratio used for this process was 15:1 with 5% base catalyst. The procedures involved were the same as esterification process except for the reaction time. Transesterification using Mg-Al-LDH took 24 h to be completed in order to obtain high yield.

3. Results and discussion

3.1. Characterization of LDHs

3.1.1. X-ray Diffraction (XRD)

The layered structure of LDHs were confirmed via XRD patterns as in Figure 3.1 and Figure 3.2. The sharp and distinct peaks appeared in XRD diffraction pattern give an indication of the highly crystalline nature in the synthesis of LDHs-precursor [14]. There were slightly shifts in major peaks to the higher 2θ by lowering molar ratio of Mg/Al obviously for (003). All patterns reveal peaks close to 2θ = 10^o, 23^o, 35^o and 60^o, corresponding to the (003), (006), (009), and (110, 113 for the split peaks at 60^0) reflections of MgAl-LDH. These confirmed the LDH was successfully synthesized.
After calcination (Fig 3.2) decomposition of LDHs resulted in the formation of mixed Mg-Al oxide phases (MgO and AlO). As a result, typical LDH peaks and characteristic diffraction at 43^0 and 63^0 corresponding to the mixed Mg-Al oxides were clearly observed. This can be explained by the destruction of the LDHs brucite layer and production of mixed oxide during calcination at 450^0. The same diffraction pattern is shown in the work of Lin et. al [13], [14], [15].

3.1.2. Fourier Transform Infrared Spectroscopy

The FTIR spectra of samples LDHs before calcination are shown in Figure 3.3. All bands displayed rather similar features. The strong and broad bands in the range of 3445-3447 cm^{-1} are assigned to the stretch Al_2O_3 H groups. The absorption bands below 1000 cm^{-1} are associated with metal oxides (MgO, AlO) stretching modes in the brucite-like layer. Wavenumber near 1363-1384 cm^{-1} exist due to the CO_3^{2-} vibration [13] [14].
All calcined spectra shown less intensity compared to uncalcined spectra. After calcination, there were a peak appeared at 1600 cm^{-1} for all spectra which indicate the vibration of O-H bending vibration of the interlayer water molecule [13] [14] [15]. This peak maybe appeared due to improper storage of LDHs. LDHs is very sensitive to moisture, thus it must be keep properly to avoid absorption of moisture.

3.1.3. Scanning Electron Microscope- EDS System

Reported results reveal that the preparation route has a significant influence on the morphology of the LDHs giving rise to solids consisting of compact agglomerates of non-porous grains, solids with presence of platelets or hexagonal in form [6]. Before calcination (Figure 3.5), LDHs had a big compact agglomerate structure. The possible reason is that the compact structure was formed by agglomeration with numerous fine nanoparticles [18]. After calcination (Figure 3.6) at 450 ^{0} C, the compact agglomerate structure was destroyed due to the removal of hydroxyl groups in the metal hydroxide layers and from the decomposition of CO_3^{2-} existed in the interlayer space as charge-balancing anion [6] [18].
The composition of the observed particles on the surface material was determined by EDS. The result of elemental analysis of prepared LDHs at Mg/Al=4 before and after calcined were shown in Figure 3.7 and 3.8 respectively. It is clearly observed that, carbon element was existed before the calcination process but disappeared after the LDH was calcined. This is because of the degradation of carbonate compound at temperature 450 ^{0} C and above. Calcination process is needed to remove carbonate compound as it can be poison to the catalyst and cause catalytic activity to be reduced.

3.1.3. Brunauer, Emmett and Teller (BET)

Based on table 3.1, the surface area increase after decomposition at 450 ^{0} C that lead to the formation of mostly amorphous oxides (MgO and AlO). This improvement of the textural properties has been related to formation of channels and a more open porous network due to water vapour and carbonate removal during decomposition [6]. In addition, the preparation method has strongly effected the textural properties of LDHs. Reyero et al. [6] found that the specific surface areas of LDHs (Mg/Al=3) synthesized by coprecipitation ranged between 84 and 17 m^2/g after calcination. However, the specific surface areas increased up to 274-122 m^2/g for the samples prepared by a sol-gel method.

Table 3.1: BET surface area of LDH before and after calcined

Sample	**BET surface area, m^2/g**	
	Before calcined	**After calcined**
Mg/Al=2	42.7664	127.2550
Mg/Al=3	43.3691	87.7626
Mg/Al=4	34.5487	93.5296

3.2 Percent yield of biodiesel

The initial FFA content in WCO was found to be 2.87 mg KOH/g. After esterification process it reduced to 0.87 mg KOH/g. The esterified oil was used in transesterification process at 15:1 methanol:oil ratio, 5% catalyst loading and 24 h reaction time. Mg:Al 4:1 was observed to have highest % of biodiesel followed by 3:1 and 4:1. Although only 82% conversion of the feedstock to esters was achieved, Sharma et. al [17] found that the catalyst was easily separable. Sharma et. al [17] stated that basic site was found to be the influencing factor for the transesterification reaction. Thus, catalyst sample must be further investigated via Thermal Programme Desorption (TPD) to confirm the basicity of the catalyst.

4. Conclusion

It was confirmed that Mg-Al-LDHs were successfully prepared using alkali free co-precipitation method. The chemical properties of prepared LDHs was affected by Mg/Al ratio showed by diffraction pattern, FTIR analysis and BET. This study also shows the different of LDHs characteristics before and after the calcination process. Mg-Al LDHs synthesized in this work showed satisfactory catalytic for biodiesel production by the reaction of waste cooking oil with methanol. This results reinforce the possibility of obtaining biodiesel from transesterification of waste cooking oil using Mg-Al LDHs as a catalyst. The obtained results showed the greatest conversion obtained when the Mg/Al ratio is 4:1 with 82% yield followed by 3:1 and 2:1.

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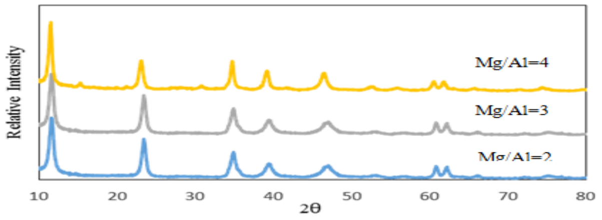

Fig. 3.1: XRD pattern of LDH before calcined with different molar ratio

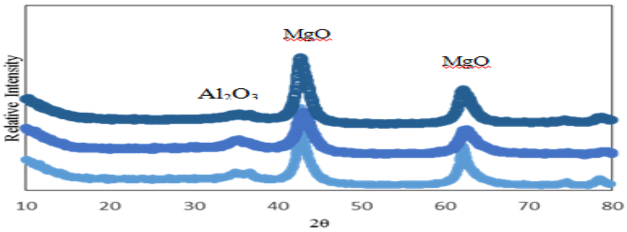

Fig. 3.2: XRD pattern of LDH after calcined with different molar

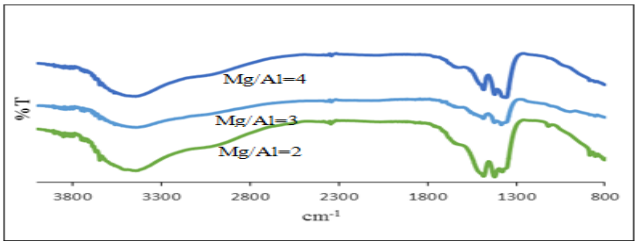

Fig. 3.3: FTIR spectra of LDH before calcined with different molar ratio

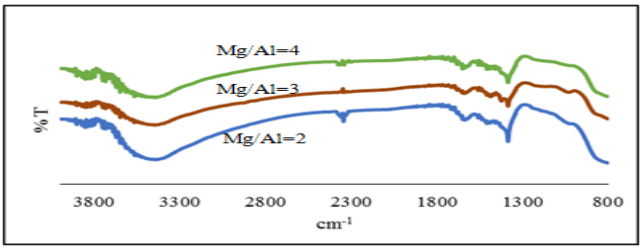

Fig. 3.4: FTIR spectra of LDH after calcined with different molar ratio

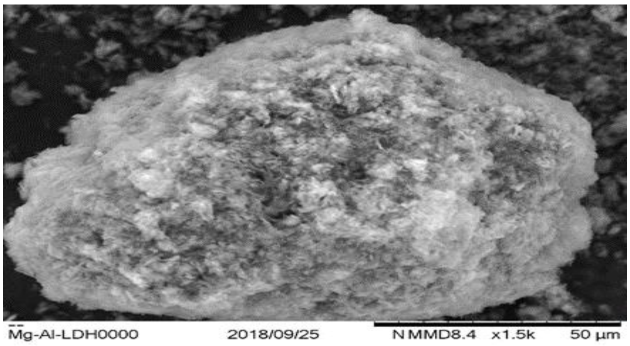

Fig. 3.5: SEM photo of LDH with Mg/Al=4 before calcined

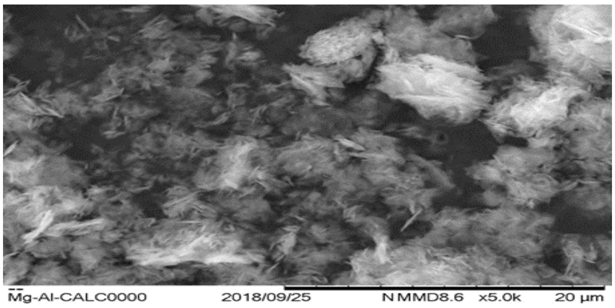

Fig. 3.6: SEM photo of LDH with Mg/Al=4 after calcined

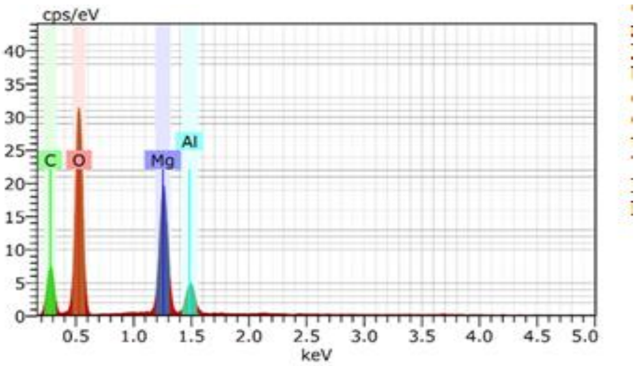

Fig. 3.7: EDS result of LDH with Mg/Al=4 before calcined

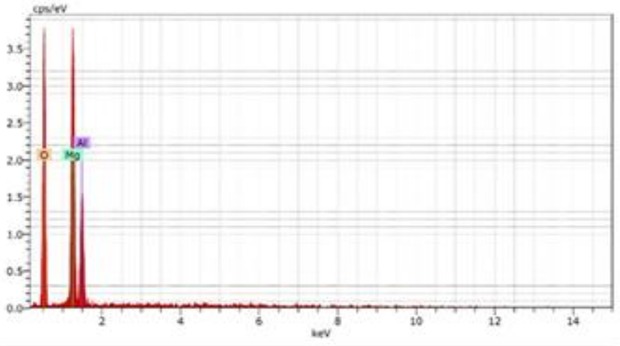

Fig. 3.8: EDS result of LDH with Mg/Al=4 after calcined

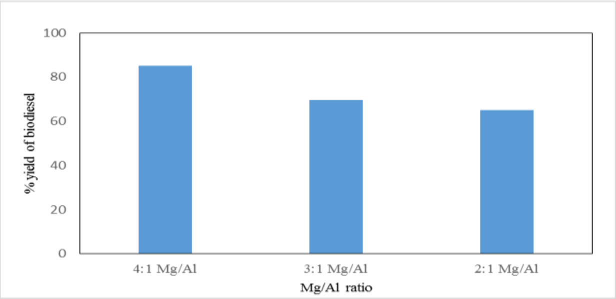

Figure 3.9: % yield of biodiesel with different calcined Mg/Al ratio