Recyclable and Reusable Catalyst of Chitosan-Modified MgAl-Layered Double Hydroxide for Biodiesel Production

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ABSTRACT

Study of chitosan modification to MgAl-LDH to increase surface basicity for improving biodiesel production from palm oil has been performed. Modification was conducted by chitosan gel impregnation onto prepared MgAl-LDH. Furthermore, the physicochemical character of material was evaluated by X-ray diffraction (XRD), scanning electron microscope, transmission electron microscope, gas sorption analysis, and determination of solid basicity. The XRD, specific surface area, pore distribution, and TEM analyses confirmed the reduced specific surface area due to the exfoliated LDH conformation. However, the increased surface basicity aroused from the modification leads to improved catalytic activity and yield. The maximum biodiesel yield of 92.8 % was achieved by the methanol to oil ratio of 10:1 at 90 °C for 2 h. The prominent reusability until the 5th cycle of usage without significant activity change is a potency for advocating the suitability of the low-cost catalysis technology for commercial biodiesel production.

Keywords: biodiesel, chitosan, heterogeneous catalyst, MgAl-LDH.

INTRODUCTION

Biodiesel is notified as the potential renewable energy sources for substitute and replacing the fossil fuels. Some advantageous such as low greenhouse gas emissions and ease in production make it applicable as a promising solution to energy security and environmental concerns. In addition, some progressions and adaptations have been challenged for optimizing some aspects for production costs, ecological benefits, non-edible feedstock and fuel performance (Chuah et al., 2021; Manikandan et al., 2022; Nath, 2024). Within these aspects, optimizations have been attempted to look for efficient catalytic processes with better reusability and lifetime performance of catalyst. The conventional method utilizes NaOH or some mineral acids catalysts for the process which lead to the consumable chemical and corrosive reaction. To cover these problems, heterogeneous catalysts including the use of some porous solids having surface basicity or acidity were the developed. Several benefits of heterogeneous catalyst usage are simply in product separation, reducing saponification reaction, and minimizing the number of operations. In the perspective of low-cost and more economical material, some natural minerals such as clay, zeolite, biochar, and silica-based catalysts were developed.

Layered double hydroxides (LDH) materials including Mg-Al LDH or generally called as hydrotalcites (HT) have shown promising potential as catalysts for biodiesel production through transesterification of some vegetable oils. LDH exhibits basicity and high surface area, making them effective for biodiesel production with moderate fatty acid methyl ester (FAME) yield (Prabu et al., 2019). Moreover, the reusability is an important

issue. Some strategies for improving the activity of HT have been proposed by attaching some metal or metal oxide, KF-treatment, and combination with other solids. In other side, chitosan is a polymer having capability to provide basicity and adsorptive properties to support reactant interaction during transesterification mechanism in biodiesel production. Chitosan has been proven to enhance surface basicity of some solids for catalysis applications (Dhakshinamoorthy et al., 2021; Wang et al., 2021). Amine functional group and polymeric structure of chitosan have been proven to be active in biodiesel production. Based on this potential, in this work chitosan was combined with LDH to enhance the surface reaction of biodiesel production with a hypothetical approach of its provided hydrophobic site. Study was conducted by investigating the chemical structure of the chitosan-modified MgAl-LDH composite (furthermore called as Chit/LDH) by using such instrumental analysis consisting of XRD, fourier-transform infra-red (FTIR) spectroscopy, gas sorption analysis (GSA), scanning electron microscopy, and surface basicity. The activity of composite was examined in biodiesel production from palm oil.

MATERIALS AND METHOD

Materials

Chemical reagents used in this research were $Al(NO_3)_3 \cdot 9H_2O$ (Merck; Purity: 97%), $Mg(NO_3)_2 \cdot 6H_2O$ (Merck; Purity: 99–104%), Sodium hydroxide (NaOH) (Merck; Purity: ≥ 98%), potassium hydroxide (KOH) (Merck; Purity: ≥ 98%), methanol (Merck; purity > 99%), butylamine (Aldrich; purity > 95%), H_3PO_4 (Merck, purity > 97%), acetic acid (Merck, purity > 90%) and palm oil was purchased from traditional market in Yogyakarta city, Indonesia.

Method

MgAl-LDH (1:3) was prepared by the coprecipitation-hydrothermal method. About 100 mL of an aqueous solution of $Mg(NO_3)_2 \cdot 6H_2O$ (0.25 M) and $Al(NO_3)_3 \cdot 9H_2O$ (0.75 M) were mixed along with stirring, then NaOH was added to the mixture for adjusting the pH to 10. The mixture was transferred into a-Teflon-lined autoclave at 150 °C overnight, and then the slurry obtained from the process was washed with distilled water

and methanol. Finally, the solid was oven-dried at 70 °C for 12–14 h. The sample was encoded as LDH. Chitosan/LDH sample was prepared by mixing LDH with solution composed from 0.5 g chitosan in 1% of acetic acid, by stirring for 6 h. The solution was then precipitated by the addition of NaOH. Figure 1 represents the procedure of materials synthesis.

Physico-chemical characterization

The character of LDH and Chit/LDH was evaluated by analyses using XRD (Rigaku, Tokyo), scanning electron microscope-energy dispersive X-ray (Phenom-X, Singapore), Fourier transform infrared (FT-IR) spectroscopy (PerkinElmer 2000, Waltham, MA, USA) and gas sorption analysis on NOVA 1200e (Quantachrome). Solid basicity was determined by back titration method using KOH as a standard solution. About 0.5 g of solid sample was mixed with acetic acid in excess amount followed by stirring overnight. The filtrate obtained by the mixing was then titrated using KOH, and the basicity was calculated as mg KOH/g).

Activity test of materials

Catalytic activity of prepared catalysts was examined in biodiesel production from pam oil. For each run, a mixture of methanol and palm oil was placed in a round-bottom flask with certain amount of Chit/LDH catalyst, followed by heating at reflux condition (temperature = 90 °C). To investigate the influence of some factors affecting the biodiesel production, the effects of catalyst dosage and reaction time to biodiesel yield under
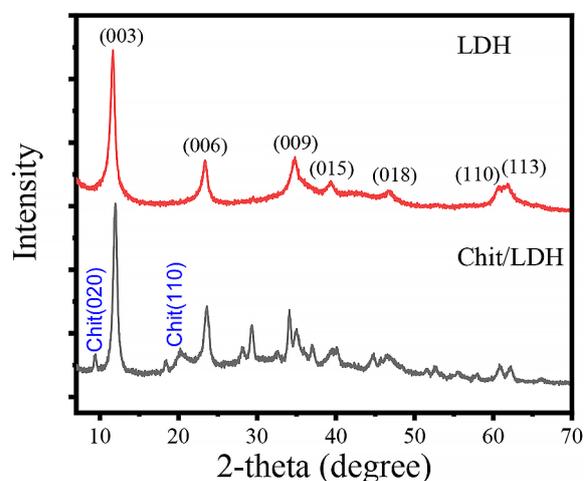

Figure 1. XRD pattern of LDH and Chit/LDH

the condition of methanol to oil molar ratio (MTO) of 10:1 were examined. The yield was calculated based on gas chromatography-mass spectrometry (GCMS) analysis on Shimadzu instrument to the product of reaction after separation from glycerol as byproduct and filtration from catalyst particle. The analytical conditions were the fixed phase of HP-5MS 5% (phenyl methyl siloxane) capillary column (30 × 250 um i.d., 0.25 um film thickness), a spilt injector and FID detector. Helium with an average velocity of 37 cm/sec at 200 °C was employed as a carrier gas. The yield (%) was calculated based on following Equation 1:

$$Yield\ (\%) = \frac{mass\ of\ extracted\ biodiesel\ (g)}{mass\ of\ TBO\ (g)} \times 100\ \%\ (1)$$

The composition of methyl ester in the biodiesel was based on the peak area of identified component refer to MS peaks compared to the peak area of standard methyl esters.

RESULTS AND DISCUSSION

The XRD analysis result (Figure 1) provides main reflection peaks of LDH at 11.6° 23.3°, 34.7°, 39.0°, 46.8°, 60.8° and 62.1° that are correspond to (003), (006), (009), (015), (018), (110), and (113), respectively. The pattern is associated with the JCPDS No: 890460 (Cao et al., 2019). No peak associated with crystalline $Mg(OH)_2$ or $Al(OH)_3$ phases were detected, also no residual sodium-based salts phase presented from the analysis, suggesting the high crystallinity and purity of the LDH sample. In addition, the cell parameter a and c demonstrated the distance of 0.15 nm and 0.23 nm, respectively which represents a Mg/Al ratio of 3. The determined parameters are similar with previous investigation on crystallite structure of Mg-Al hydrotalcite with this ratio.

After modification with chitosan, Chit/LDH, the basal spacing (003) and other peaks (006), (009), (015), were shifted into wider angle, that

are positioned at 11.9°, 23.6°, 34.9°, and 39.3°, respectively. In addition, there are two peaks positioned at 10.9° and 20.1° that are attributed to (020) and (110) planes of chitosan structure, respectively (El-Naggar et al., 2023; S. Silva et al., 2016). Detail of the parameters is provided in Table 1. The shifts of peaks associated with LDH are assigned to the decreased distance of the layers which possibly caused by the change network of hydrogen bonds between the OH groups of the LDH surface and OH groups of the chitosan through the hydration water and determines the nearer distance among the layers (Bugatti et al., 2011). The shifts may also indicate the exfoliation of LDH which tend to reflect heterogeneous formation of polymer/layers structure similar found by the combination of polymer and clay structure (Kakuta et al., 2021). Figure 2 represents the schematic representation of the exfoliated-LDH structure.

The attached chitosan onto LDH structure is confirmed by FTIR analysis as determined by compared spectra in Figure 3.

The LDH shows broad band at around 3300 cm^{-1} corresponding to the presence of OH from its chemical structure which is associated with the absorption band at around 1370 cm^{-1}. Some peaks at the range of 400–700 cm^{-1} are indication of the Mg-O and Al-O from Mg-Al double layered. By
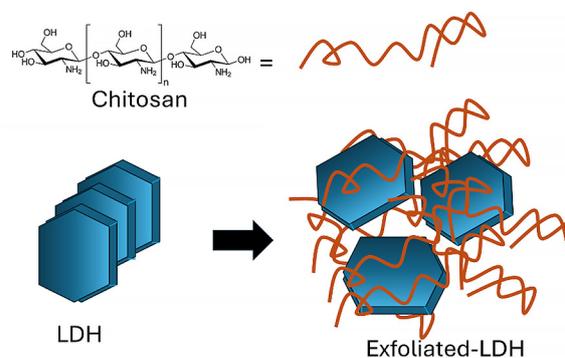

Figure 2. Schematic representation of exfoliated-LDH (Mao et al., 2017)

Table 1. Some lattice parameters from XRD measurement

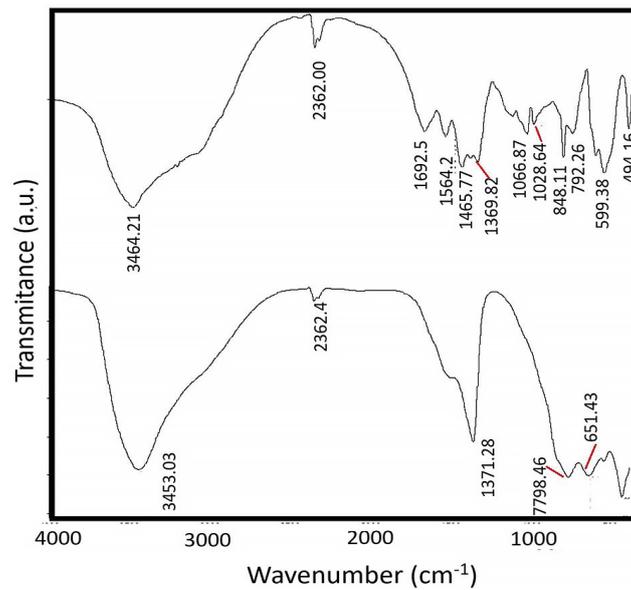| Parameter	LDH	Chit/LDH
$d_{(003)}$ (Å)	7.59	7.39
$d_{(006)}$ (Å)	3.80	3.77
$d_{(009)}$ (Å)	2.58	2.62
Lattice parameter a (Å)	2.90	2.90
Lattice parameter c (Å)	22.77	22.17
Crystallite size (nm)	13.19	14.70
Mg/Al	3.0	3.0

Figure 3. FTIR spectra of LDH and Chit/LDH

the modification into Chit/LDH exhibits the absorption band at around the wavenumber of 3500–3300 cm^{-1} designated as stretching and symmetrical vibration of amine (-NH) groups symmetrical which shows absorption bands at wave numbers 3400 and 3500 cm^{-1}. In addition, the primary amine (-NH) bending vibration groups can also be observed at wavenumbers around 1640–1560 cm^{-1}. The existence of C-O bonds is found within the wavenumbers of 1300–1000 cm^{-1} (Khitous et al., 2016; Zheng et al., 2019).

The influence of chitosan attachment is also reflected by the change of surface profile consist of specific surface area, pore size distribution, pore radius, and surface basicity. Adsorption-desorption isotherm and pore size distribution of the materials are depicted in Figure 4, and the results of calculation are tabulated in Table 2. Reduced

adsorption/desorption feature leads to the decreased specific surface area and pore volume of LDH is in line with the reduced basal spacing d$_{003}$ from XRD measurement. As can be seen from Figure 4b, there is an evolution of the pore size distribution whereas there is a reduced volume of the pore size ranged at 0–40 Å. The range is a characteristic of LDH structure implying the multiple layers related to interlayer anion. Similar phenomenon were reported by the chitosan exfoliated-bentonite (Eskandari et al., 2017) and polymer-modified/grafted LDH (Ghanbari and Ghafuri, 2022; Johnston et al., 2021).

This chitosan modification effect to LDH of reducing specific surface area is reflected by SEM image (Figure 5). Generally, all the samples are composed of smaller particles and aggregates with a typical plate-like structure with the size of
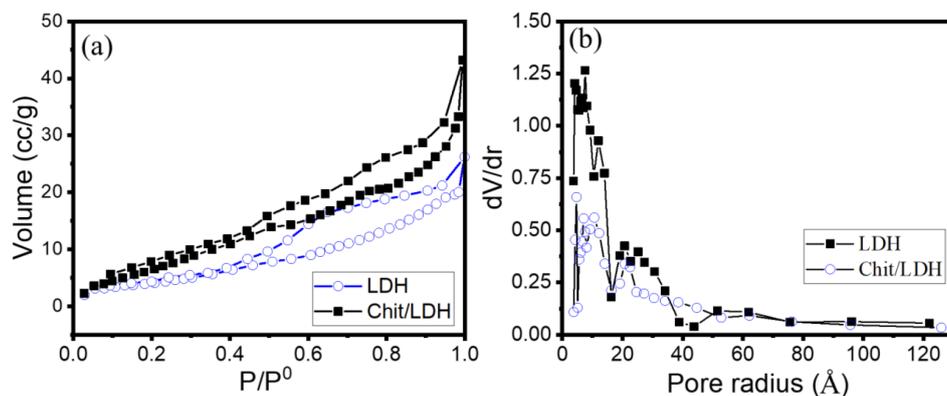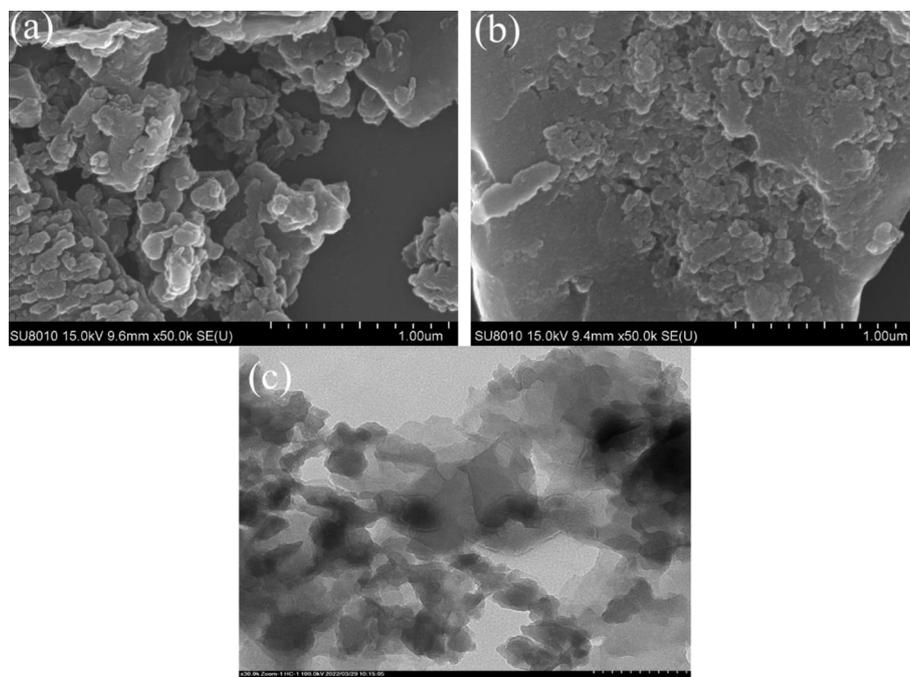

Figure 4. a) Adsorption/desorption isotherm, b) Pore size distribution of LDH and Chit/LDH

Table 2. Surface parameters and surface basicity of materials

Parameter	LDH	Chit/LDH
Specific surface area (m²/g)	64.00	49.39
Pore volume (cc/g)	1.92×10^{-2}	2.77×10^{-2}
Pore radius (Å)	1.82	2.62
Surface basicity (mg KOH/g)	772.90	889.98

Figure 5. (a–b) SEM image of LDH and Chit/LDH, respectively, c) TEM image of Chit/LDH

the particle ranging at several hundred nanometres. In more detail, the LDH looks to be rougher compared to Chit/LDH which is in line with the surface area and porosity data. This is in line with the TEM image (Figure 5c) expressed the irregular positioned plate which strengthened the exfoliation conformation.

The influenced surface by attached chitosan structure leads to the improved surface basicity which was measured by back titration using phosphoric acid method. This implies that availability of amine functional groups coming from the attached chitosan provide more basic sites to bind with acid, then it is theoretically reflecting the capability of catalyst surface for conducting more intensive surface reaction.

Activity test

The initial examination of the comparison between Chit/LDH and LDH catalytic activity for converting palm oil into biodiesel is presented by

kinetics plot of reaction at MTO of 10:1 in Figure 6, and details on compositions of biodiesel is listed in Table 3. It is seen that the appreciable enhancement on yield is expressed by Chit/LDH at all varied times, and specifically it reaches stable after 2 h of reaction.

As can be seen from the kinetic plot in Figure 6a, the data confirms that the increasing yield is from the beginning of the reaction which is reflected by the higher yield over Chit/LDH. Moreover, where LDH gives a maximum yield of 80.2% for 3 h of reaction while Chit/LDH produces 92.8% yield at the same time. Theoretically, the activity of solid catalyst is determined by the enhanced factors of the specific surface area and the surface basicity. The higher specific area represents the higher surface interaction among reactant and catalyst surface to conduct surface reaction. Similarly, the more available basicity will facilitate the formation of active agent of methoxide for producing intermediate. Referred to the possible interaction in catalysis by ammine and hydroxide as basic
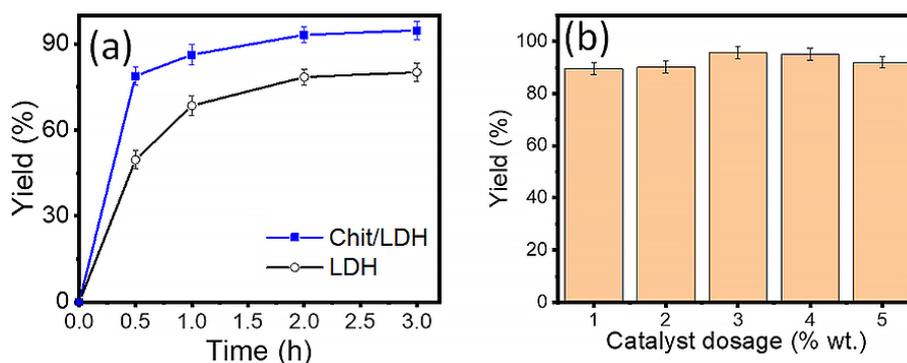
Figure 6. a) Kinetics of biodiesel production over materials (reaction condition: temperature = 90 °C, MTO = 8:1, catalyst amount = 5% w/v), b) Effect of catalyst dosage on yield (reaction condition: temperature = 90 °C, MTO = 8:1)

Table 3. Comparison on catalytic activity of LDH-based material for biodiesel production

LDH/ oil	Yield (%)	Remark	Reference
K_2CO_3/MgAl-LDH/vegetable oil	99.48	Increased basicity remarkable enhanced biodiesel yield	(Yang et al., 2024)
MgAl-LDH/Sunflower oil	55	The yield achieved at 120°C with methanol to sunflower oil ratio of 12:1	(Brito et al., 2009)
Ba-modified MgAl-LDH/ Sunflower oil	90	The yield of more than 90% was obtained at 10% MgAl catalyst and lower reaction temperature (from 75 to 55 °C) for 8h	(Zanjani et al., 2020)
K-modified MgAl-LDH/Rapeseed oil	99	The yield of 99% at 6.25 wt% catalysts, for methanol/rapeseed oil molar ratio of 12:1, and reaction at 60°C for 1 h.	(Zhang et al., 2019)
KF-CaAl-LDH/Palm oil	97.98	Maximum yield is achieved at 3 h for 1 h reaction.	(Gao et al., 2010)
MgAl-LDH/Palm oil waste	95.75	The optimum condition of transesterification was at 1.5% catalyst weight	(Agustina et al., 2022)
MgAl-LDH/Jatropha oil	95	The optimal experimental conditions for achieving maximum yield were rection temperature of 70 °C, catalyst loading of 3 % wt., MTO (Jatropha oil) of 12 to 1.	(Praveen et al., 2023)
MgAl-LDH/Palm oil	86-97	Yields are ranging 86 to 97% with MTO of 12:1	(Praveen et al., 2023)
CaAl-LDH/Euphorbiaceae curcas oil (ECO).	99	The highest conversion was achieved at 60°C with molar ratio of methanol/oil of 15:1, reaction time 3 h, and catalyst amount 3 wt%.	(Eskandari et al., 2017)
Chitosan/LDH	92.80	The highest conversion was achieved at 92.08 with MTO of 8:1 for 2h, at temperature of 90°C	This work

catalysts from previous research works, Figure 7 depicts the possible catalytic mechanism of reaction (Farzaneh et al., 2018; Rahman et al., 2019).

Even though there is decreased surface area by chitosan modification, the provided amine functional group as basic site dominantly supports to active surface reaction rather than the specific surface area of the solid. Similar phenomenon was observed from the active surface of amine functionalized mesoporous silicas for the transesterification of tributyrin with methanol (Elimbinzi et al., 2018). From the obtained values, it can be said that the yield from the use of LDH is comparable to a previous similar works. Depending on the kind of oil,

MTO and reaction condition, biodiesel yield using several oils were at the range of 90–95% for around 2–5 h (Jaimasith and Phiyanalinmat, 2007). Mg-Al LDH produced 95 % yield from jatropha oil by 3 h of reaction on MTO of 12:1 (Praveen et al., 2024). MTO is also a crucial factor affecting the yield. Referring to previous study on the effect of MTO for canola oil conversion to biodiesel, the MTO of 8:1 produced about 90% yield at 3h by Mg-Co-Al LDH. Considering the higher basicity of Mg-Co-Al LDH, yield from this work is in line with the possible mechanism that occurred (Li et al., 2009). Furthermore, the effect of Chit/LDH catalyst dosage on yield is reflected by the plot in Figure 6b. The
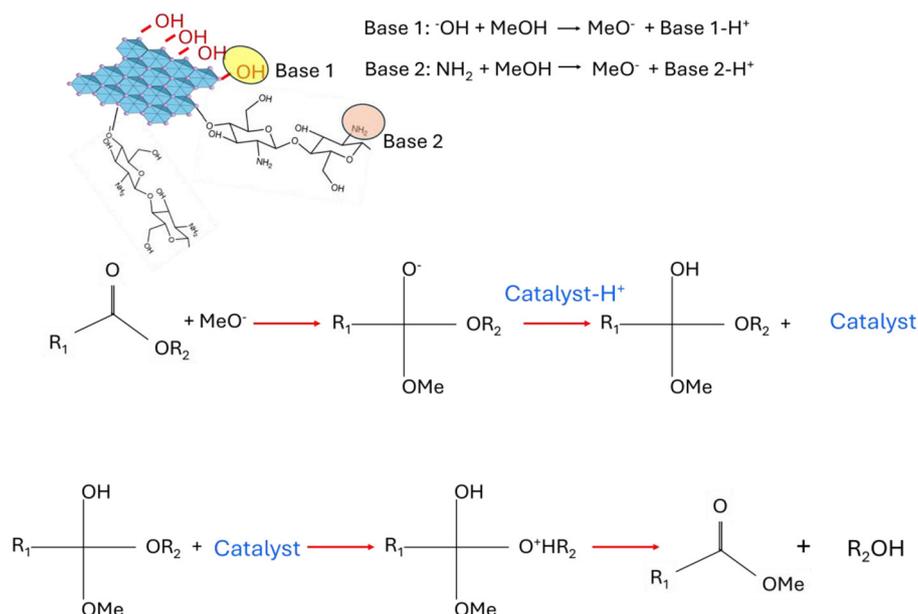
Figure 7. Possible mechanisms of biodiesel conversion over Chit/LDH

positive impact on the surface sites availability is reflected by the increased yield along the increased the catalyst dosage ranging at 1–3 % wt. However, the additional amount of catalyst until 5%wt. gives the reduced yield. The possibility for this is related to the adsorption capability of the catalyst towards the yield. Similar phenomenon was observed from the use of carbon, magnetic solid-base catalyst such as $K/ZrO_2/\gamma\text{-}Fe_2O_3$ catalysts (Bharti et al., 2021; Sulaiman and Ruslan, 2017).

In more detail, the major components are methyl oleate, methyl palmitate and methyl stearate as presented by the GCMS analysis results presented in Figure 8. Depending on kind of oil, specific surface area and solid basicity that respect to the synthesis method, these results are comparable among the catalytic activities of LDH-based nanocomposites from similar works as listed in Table 3. Yield and conversion of biodiesel depends on some factors influencing the kinetics and thermodynamic of reaction consist of catalyst dose, temperature, reaction time, and MTO. From Table 3, it is seen that generally the LDH-based nanocomposite gave yield ranging at 86–99.9 %. With the relatively low MTO (10:1) and reaction duration of 2 h, the yield of 92.8% is valued to be significant result. This is conclusively obtained that this study expressed the versatility of chitosan-modified LDH for catalysing biodiesel production.

Reusability and recyclability of catalyst are the important character in applied scale. Not only the increased yield compared to LDH, Chit/LDH presents the insignificant reduced yield at recycled form until 5th cycle (Figure 9a). Detail investigation of catalyst stability is confirmed by the insignificant change of structure identified by XRD analysis (Figure 9b). The reduced activity is
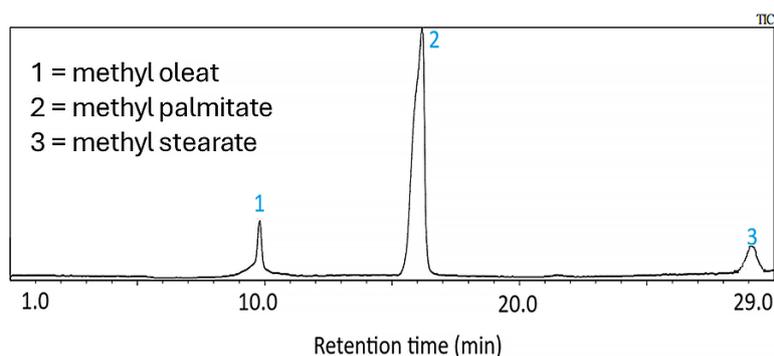

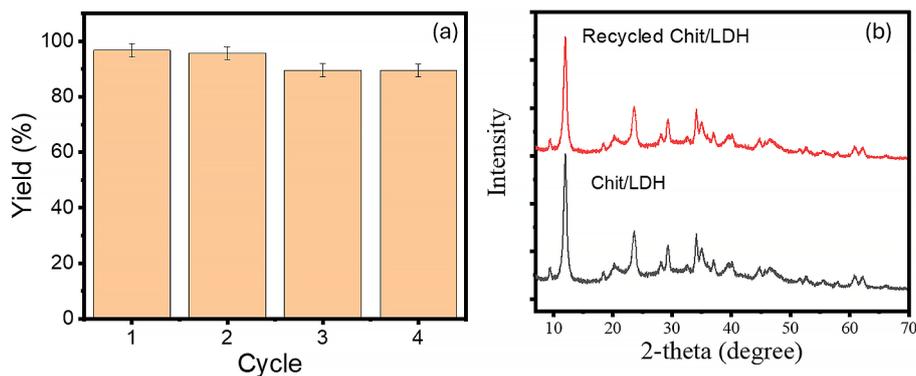**Figure 8.** Chromatogram of produced biodiesel

Figure 9. a) The yield of biodiesel using Chit/LDH at 1st until 5th cylcle, b) XRD pattern of fresh and recycled Chit/LDH (reaction condition: temperature = 90 °C, MTO = 8:1, catalyst amount= 5% w/v)

mainly affected by the reduced basicity caused by chitosan inactivation or surface basicity leaching, which the same phenomenon with was occurred in the use of CTA-MCM-41 catalyst for transesterification (Silva et al., 2024). This is also confirmed by the determination of basicity revealed that after 5th cycle usage, the solid basicity of Chit/LDH is 820 mgKOH/g. Based on these data, Chit/LDH is a promising avenue for developing efficient and cost-effective catalysts for biodiesel synthesis as shown by the reusability test.

CONCLUSIONS

Modification to MgAl-layered double hydroxide was developed for the application as a catalyst in biodiesel production from palm oil. The physico-chemical analysis of material demonstrated the increased surface basicity, which is responsible to improved biodiesel production, meanwhile from XRD, gas sorption analyzer, SEM and TEM analyses expressed the exfoliated structure. These properties are attributed to the enhanced catalyst stability as shown by reusability with insignificant reduced yield. Furthermore, the data suggest that the material is potential to be advanced studies and developed for upscaling. Further studies utilizing other plant oils mainly second or third-generation of biodiesel sources will be interesting.

Acknowledgements

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