POSSIBILITY OF USING A NEWLY-SYNTHESIZED LDH-BASED OXIDE CATALYST FOR GLYCEROL CONVERSION TO VALUABLE CHEMICALS

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ABSTRACT

Mg2Al-layered double hydroxide (LDH) was first prepared by the co-precipitation method. After calcination, a layered double oxides (LDO) was formed. The Mg2Al-LDO was characterized by BET, XRF, XRD, NH_3-TPD, and CO_2-TPD. The catalytic activity was tested on liquid phase glycerol conversion at 275 °C for 2 h, and the liquid product was next analyzed using GC-TOF/MS. From BET method, the surface area increased from 83.2 m^2 g^{-1} to 310.7 m^2 g^{-1} after calcination. The catalytic activity results showed that 68% conversion was achieved for Mg2Al-LDO while the non-catalytic reaction gave only 45% conversion. In addition, Mg2Al-LDO was found to effectively transform glycerol to valuable products, like 1,3-dioxolane and 1,2-propandiol, 56% and 22% selectivity, respectively, whereas the non-catalytic case effectively transformed glycerol to 89% selectivity of diglycerol.

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INTRODUCTION

Known as one of the major problems to the commercialization of biodiesel, the market of its co-product, glycerol, has become saturated, causing a reduction in prices and consequently affecting the biodiesel economy. One route for increasing value of glycerol is transforming glycerol into more economically valuable end-products, which fit applications in many industrial fields, including chemicals, fuels, plastics, or even medical materials. The catalytic conversion of glycerol into valuable chemicals are mainly performed through different processes such as hydrogenolysis, tranesterification, dehydration, and so on (Luo *et al*., 2016). 1,2-propanediol (1,2-PDO) is produced through hydrogenolysis between glycerol and hydrogen in the presence of acid and metal catalysts. Generally, acid sites catalyze the dehydration of glycerol into acetol that is then hydrogenated into 1,2-PDO over transition metal catalysts, such as Pt, Ru, and Cu. The glycerol conversion and 1,2-PDO selectivity obtained were 50% and 85%, respectively (Lee and Moon, 2011). Glycerol reacts with the biomass-derived furfural through acid-catalyzed condensation reaction, producing a mixture of 1,3-dioxolanes and 1,3-dioxanes used as a powerful aprotic solvent in formulations, an essential ingredient in biopolymers industry and niche pharmaceutical intermediates (San Kong *et al*., 2016). Another catalyzed pathway is by a base catalyst through glyceroldehyde and 2-hydroxy-2-propenal as the intermediates that give rise to into 1,2-PDO.

Layered double hydroxides (LDHs) are anionic clay materials. The structure of hydrotalcite is related to that of brucite, $Mg(OH)_2$, in which some of the Mg^{2+} cations in the layer

structure are replaced by Al^{3+}. Carbonate anion is intercalated between the layers to maintain electroneutrality. The original LDHs (dried below 150 °C) are denoted as LDHs, and the calcined one are denoted as layered double oxides (LDOs) (Braterman *et al*., 2004; Cavani *et al*., 1991). Hamerski and Corazza (2014) studied the MgAl-CO_3 LDH-catalyzed esterification of lauric acid with glycerol at various conditions. It was observed that the catalyst presented a good catalytic activity, and gave mono, di and trilaurine as the products. LDHs or LDOs catalysts consist of both acid and basic sites that are the important parameters affecting the activity. Acid–Base properties mainly depend on the composition, amount, strength and density of sites. Possible effective catalysts for glycerol conversion reactions are LDH-based oxide catalysts with pronounced acid and base properties. In this work, a newly-synthesized LDH was prepared using a special treatment in a post treatment step, which can increase the specific surface area and pore volume of the LDH. The aims of this work was to investigate possibility of using the novel LDH-based LDO as a catalyst for the conversion of glycerol and the selectivity of possible products.

EXPERIMENTAL

A. Catalyst Preparation
A MgAl-LDH sample with a molar ratio of Mg/Al = 2 was synthesized using co-precipitation method as follows. $Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ were dissolved in deionized water (called Solution A). Na_2CO_3 was separately dissolved in deionized water (called Solution B). After that, Solution A was added into Solution B with continuous stirring together with maintaining the pH at 10 ± 0.05 using a NaOH solution. Then, the precipitate was aged at room temperature for 16 h. Subsequently, the precipitate was separated using a buchner funnel and washed with deionized water until neutral. The precipitate was next treated with a special treatment, and then, it was filtered, dried (Mg2Al-LDH) and calcined (Mg2Al-LDO).

B. Catalyst Characterization
Elemental analyses for Mg and Al contents were determined by XRF method using PANalytical analysis instrument with AXIOS&SUPERQ version 4.0 systems. The textural properties were determined from N_2 adsorption-desorption isotherms using a surface area analyzer (Quantachrome, Autosorp-1MP). Before the measurement, the samples were degassed in a vacuum at 150 °C (for LDH) and 250 °C (for LDO). X-ray Powder Diffraction (XRD) was used to identify the phase of a crystalline material and confirm the structure of layered double hydroxide by matching the pattern of references, which was carried on a Rigaku/Smarthlab Guidance (2θ = 5–70°, steps: 0.02°) using Cu tube for generating CuKα radiation (λ = 1.5406 Å). The acid-basic properties of the catalysts were investigated by using TPD of NH_3 and CO_2, respectively. A catalyst was pretreated in a He flow at 450 ˚C, and then cooled down. The temperature was ramped at a heating rate of 10 °C/min to 950 °C to desorb the chemically-absorbed NH_3 or CO_2.

C. *Catalytic Testing*
The catalyst was tested for its activity on liquid-phase glycerol conversion performed in a triple neck round bottom flask equipped with a condenser system. 50 ml glycerol and 0.30

g catalyst were added into the reaction flask, and then the mixture was stirred and heated at 275 °C for 2 h. After completion of reaction, the catalyst was separated, and the liquid products were analyzed by One-Dimension Gas Chromatograph (Agilent Technologies 7890) with Flight Mass Spectrometer (LECO, Pagasuss® 4D TOF/MS) equipped with the 1st GC colume was a non-polar : polar (50:50) Rtx-PAH (60 m x 0.25 mm ID x 0.10 μm) in a temperature-programming mode (heating rate of 15 °C /min) with heating from 40 to 310 °C. The rate of the carrier gas (helium) was 1.2 L/h. The evaporator temperature was 300 °C. The detector temperature was 300 °C.

RESULTS AND DISCUSSION

A. Catalyst Characterization

Table 1 shows the characteristics of Mg2Al samples. According to chemical analysis data, the actual Mg/Al ratio in the studied sample is close to the expected one. The surface area of dried samples (Mg2Al-LDH) is 83.2 m^2/g, and it increases to 310.7 m^2/g after calcination (Table 1). Furthermore, the type of hysteresis was studied and displayed in Figure 1, and the adsorption–desorption isotherms indicate the characteristics of a mesoporous material (Type II of the IUPAC classification).

Table 1 Characteristics of the Mg2Al samples

| Samples	Mg : Al molar ratio		Surface Area (m^2/g)	Pore Diameter (Å)	Pore Volume (cm^3/g)
	Expected[1]	Actual[2]			
Mg2Al-LDH	2.0 : 1	2.3 : 1	83.20	430.0	0.8945
Mg2Al-LDO	-	-	310.7	164.0	1.274

[1]In precursor mixture
[2]XRF
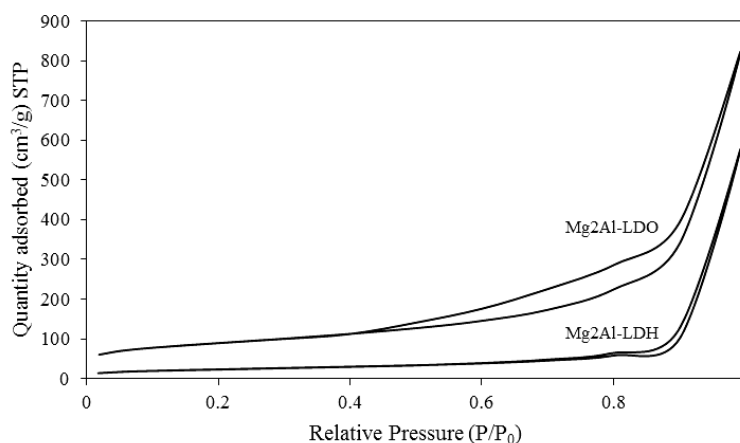
**Figure 1** Nitrogen adsorption–desorption isotherms of Mg2Al samples.

The XRD patterns of the Mg2Al samples are shown in Figure 2. The peaks observed at 2θ of 11.57, 23.26, 34.65, 39.09, 46.33, 60.86, and 62.19° in the XRD pattern of Mg2Al-LDH indicate the characteristic formation of layered double hydroxides of the hydrotalcite-like

structure, while that of the calcined sample (Mg2Al-LDO) shows the structure of mixed oxides. The (003) reflection indicates the layered structure of the hydroxides, and the d-spacing (d_{003}) indicates the size of interlayer. The d_{003} values of Mg2Al-LDH catalyst is approximately 7.6 Å, which is approximately equal to the interlayer anion CO_3^{2-}. In contrast, the calcined samples have no (003) peak, implying that the layered structure has collapsed and the interlayer disappears.
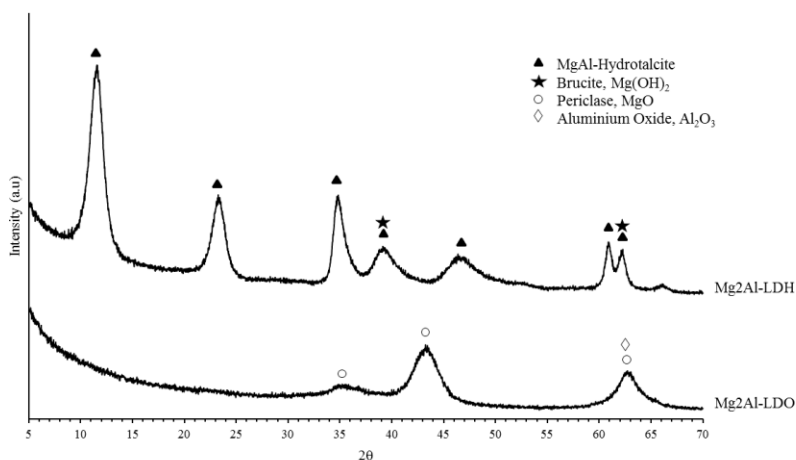
Figure 2 XRD patterns of Mg2Al samples.

The acid-base properties were investigated using the temperature-programmed desorption of ammonia (NH_3-TPD) and carbon dioxide (CO_2-TPD), respectively, over the calcined sample. The TPD profiles are shown in Figure 3. The NH_3-TPD profile displays one peak, whereas the CO_2-TPD profile displays one board peak at a low temperature (125 °C) and a small one at a higher temperature (238 °C). The total acidity and basicity are summarized in Tables 2 and 3, respectively. The acid density is 0.561 mmol/g, and the basic density is 0.449 mmol/g. As a result, Mg2Al-LDO has higher acidity than basicity.
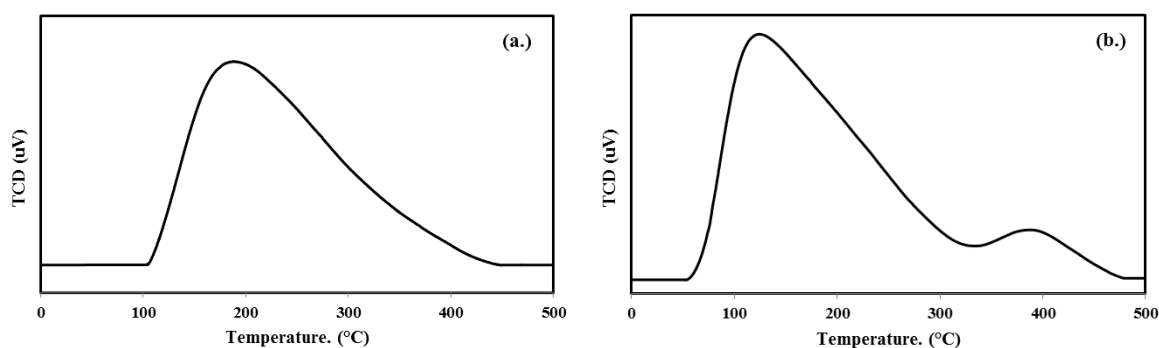
Figure 3 Temperature-programmed desorption profiles of Mg2Al-LDO: (a) NH_3-TPD, and (b) CO_2-TPD.

Table 2 Total acidity and NH_3 desorption temperature

Sample	Acid site #1		Total acidity (mmol/g)
	°C	mmol/g	
Mg2Al-LDO	186.0	0.561	0.561

Table 3 Total basicity and CO_2 desorption temperatures

| Samples	Basic site #1		Basic site #2		Total basicity (mmol/g)
	°C	mmol/g	°C	mmol/g	
Mg2Al-LDO	125.0	0.115	238.0	0.334	0.449

B. *Catalytic Testing*

The products obtained from the catalytic activity testing on glycerol conversion are shown in Figure 4. This figure exhibits the percentage of conversion and selectivity of products obtained from the reaction without a catalyst and with the Mg2Al-LDO catalyst. The results show that the catalytic reaction can increase the percentage of conversion from 45% to 70% as shown in Figure 4 (a). This result indicates that the layered double oxide catalyst can promote glycerol conversion. The results indicate that the conversion reaction without a catalyst can produce around 90% diglycerol whereas the catalytic reaction can instead increase the production of other chemicals. Namely, Mg2Al-LDO catalyst do not produce diglycerol as a product, but enhances 1,3-dioxolane and 1,2-propandiol formation (Figure 4 (b)). These results can be explained using the values of acidity and basicity in Tables 2 and 3, which indicate that Mg2Al-LDO provides higher acidity than basicity, leading to the promotion of pathways governed by an acid catalyst, which is diglycerol via glycerol condensation reaction. Likewise, 1,2-PDO is produced though glycerol hydrogenation reaction between glycerol and hydrogen in the presence of acid catalyst. Generally, acid sites catalyze the dehydration of glycerol into acetol that is then hydrogenated into 1,2-PDO. Subsequently, 1,2-PDO is dehydrated to allyl alcohol using an acid catalyst. Another catalyzed pathway is by a base catalyst through glyceroldehyde and 2-hydroxy-2-propenal as the intermediates that give rise to into 1,2-propanediol. The dehydration of glycerol results in two main products; that are, acrolein and acetol. Acetol is an intermediate of 1,2-PDO formation. Acrolein is selective in the presence of a Bronsted acid-containing catalyst while acetol is produced in the presence of a Lewis acid-containing catalyst. From this result, it can be concluded that Mg2Al-LDO may have Lewis acid sites much more than Bronsted acid sites.

(a)

%CONVERSION
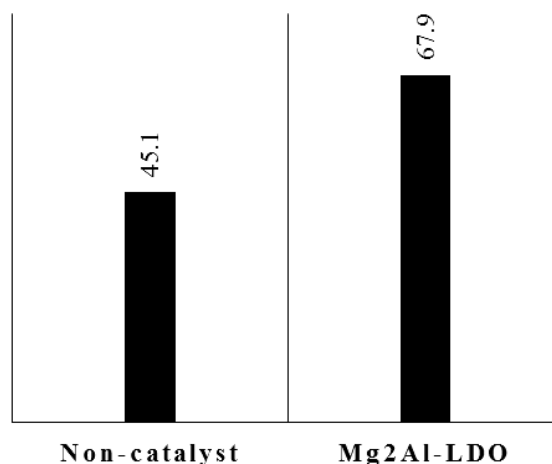
(b)
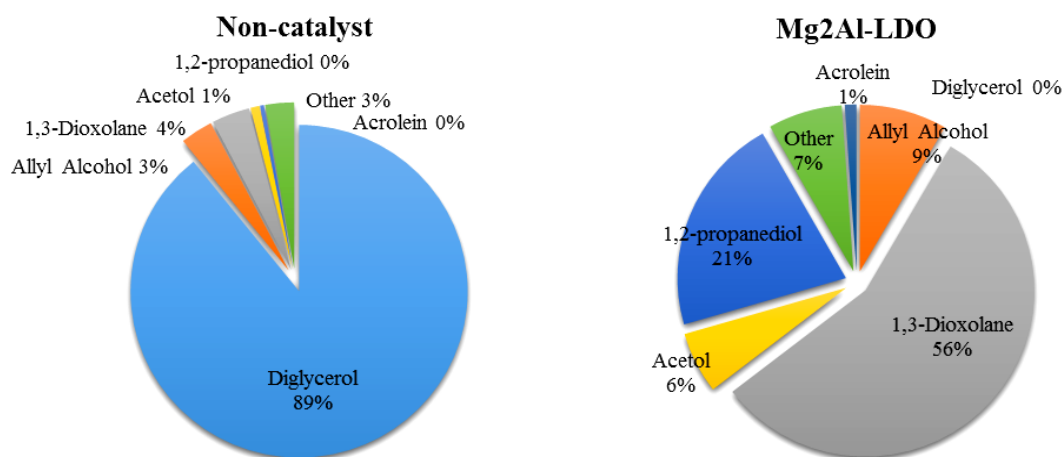
Figure 4 Conversion of glycerol (a) and selectivity of products (b): from non-catalytic case (left) and Mg2Al-LDO catalyst (right).

CONCLUSIONS

The study on the catalytic performance of Mg2Al-LDO in the liquid phase glycerol conversion showed that the catalyst presented a good catalytic activity. It can improve the glycerol conversion and enhance the production of 1,3-dioxolane and 1,2-propandiol. Furthermore, the results obtained in this work using Mg2Al-LDO as a catalyst suggested that this material would be an interesting catalyst and a potential application to obtain many products, like 1,3-dioxolane, allyl alcohol, and 1,2-propandiol via glycerol conversion.

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