

## POSSIBILITY OF USING A NEWLY-SYNTHESIZED LDH-BASED OXIDE CATALYST FOR GLYCEROL HYDROGENOLYSIS AND DEHYDROGENATION

*Nichaphat Jittangkoon<sup>a</sup>, Sirirat Jitkarnka<sup>a</sup>*

<sup>a</sup>The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, Thailand

Keywords: LDH-based oxide catalyst, Glycerol hydrogenolysis, Glycerol dehydrogenation

### ABSTRACT

Glycerol is a low-value byproduct from biodiesel production. Therefore, it is important to convert glycerol into highly valuable products. The hydrogenolysis of glycerol and glycerol dehydrogenation are possible ways of glycerol conversion into useful chemicals, and can proceed by using acid and base catalyst, respectively. Thus, Layered double oxide (LDO) catalyst, which can promote both acid and base-catalyzed reactions, may have potential as the catalyst for this work. The research objectives were to determine possibility of using a newly-synthesized LDH-based oxide catalyst for glycerol hydrogenolysis and dehydrogenation, and to study the effect of acid-base properties of Mg<sub>2</sub>Al-LDO in order to design an optimal catalyst. From the results of the reaction without a catalyst at various reaction time-on-stream, it was found that the glycerol conversion was 8.6% at 5 hours. Using Mg<sub>2</sub>Al-LDO, both glycerol conversion and selectivity of hydrogenolysis and dehydrogenation product increased to 58.0% and 39.5%, respectively, because of the high density of acid and basic sites of the catalyst, which governed both hydrogenolysis and dehydrogenation. Thus, the LDH-based oxide catalyst can possibly drive both glycerol hydrogenolysis and dehydrogenation simultaneously.

### INTRODUCTION

Crude glycerol is a main byproduct from biodiesel production via transesterification reaction of triglycerides in vegetable oils, animal fats, waste cooking oils, and algae oil with an alcohol. Its production rapidly increases due to the increasing use of biodiesel, which every 10 kg of biodiesel produced, approximately 1 kg of crude glycerol is generated. Because of its low value, the rapidly-accumulating quantity of crude glycerol affects to the biodiesel industry in terms of economic sustainability and environmental impacts of waste disposal. Therefore, it is important to convert crude glycerol into high value products in order to make the biodiesel industry sustainable. One way for value-added processing of crude glycerol is to purify crude glycerol by distillation, but it is costly. Another way is to convert crude glycerol into useful products via biological or chemical pathways, which are highly beneficial and could reduce the cost of biodiesel manufacturing (Anitha *et al.*, 2016; Daolai *et al.*, 2016).

The hydrogenolysis of glycerol and glycerol dehydrogenation are possible ways of glycerol conversion into valuable products (Pei *et al.*, 2016; Shoujie *et al.*, 2015), which can be used as a humectant, solvent, and preservative in food and tobacco products. Moreover, they can be used as a solvent in preparations of many pharmaceuticals, and as an additive in paints, coating, foods, cosmetics, and pharmaceuticals (Xiaolan *et al.*, 2016). Lu *et al.*, (2015) studied glycerol dehydrogenation using solid catalysts (CaO, MgO, and SrO) and different copper-containing catalysts. They found that a base catalyst plays an important role in the dehydrogenation of glycerol, and copper in the catalyst can promote dehydrogenation reaction. The data showed the catalytic activities of different base ingredients were

SrO>CaO>MgO, which related to their basic strength. However, SrO is more expensive than CaO, so CaO was considered to the best choice.

Layered double hydroxides (LDHs) are anionic clays, and also called hydrotalcite-like compounds (HTLcs) (Cavani *et al.*, 1991; Braterman *et al.*, 2004). The general formula of LDHs is  $[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+}(A^{n-})_{x/n} \cdot mH_2O$ , where  $M^{II}$  represents a divalent metal cation (e.g.  $Mg^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ , and  $Zn^{2+}$ ),  $M^{III}$  denotes a trivalent metal cation (e.g.  $Al^{3+}$ ,  $Fe^{3+}$ ,  $Co^{3+}$ , and  $Cr^{3+}$ ),  $A^{n-}$  is an anion (such as  $CO_3^{2-}$ ,  $SO_4^{2-}$ ,  $NO_3^{2-}$  and  $Cl^-$ ), and  $x$  is defined as the molar ratio of  $M^{3+}/(M^{2+}+M^{3+})$  (Taylor, 1973; Zhi *et al.*, 2011). LDH materials are used widely because there are many potential applications and can promote both acid and base-catalyzed reactions (Braterman *et al.*, 2004; Zhi *et al.*, 2011). Moreover, there are many advantages of LDH materials; for example, LDHs are inexpensive and environmentally friendly catalysts, and have high porosity, high surface area, and high thermal stability. Zhenle *et al.*, (2011) studied the hydrogenolysis of glycerol over dispersed copper on hydrotalcites with different Cu:Mg:Al molar ratios, which gave 80.0% glycerol conversion and 98.2% selectivity of hydrogenolysis products with the molar ratio of 0.4 : 5.6 : 2 (low Cu content) at 180 °C, 3.0 MPa  $H_2$ , and 20 h. They found that Cu promoted selectivity in hydrogenolysis of C-O bond rather than C-C hydrogenolysis, and limited the cleavage of C-C bond, resulting in a high yield of hydrogenolysis products. However, the sintering of active copper sites might occur at high Cu loading. From the literature reviews, the hydrogenolysis of glycerol and glycerol dehydrogenation could be catalyzed by using acid and base catalyst, respectively. Since an LDH-based layered double oxide (LDO) can promote both acid and base-catalyzed reactions (Braterman *et al.*, 2004; Zhi *et al.*, 2011), LDO thus has great potential as the catalyst for this work. Based on the technique previously developed by our collaborator, a novel LDH was synthesized using coprecipitation technique and special treatment, resulting in high surface area, pore volume, and pore diameter. The objectives of this work were therefore to determine the possibility of using this newly-synthesized LDH-based oxide catalyst for glycerol hydrogenolysis and dehydrogenation, and to design the optimal catalyst for glycerol hydrogenolysis and glycerol dehydrogenation by studying the effect of acid-base properties of  $Mg_2Al$ -LDO.

## EXPERIMENTAL

### A. Catalyst preparation

$Mg_2Al$ -LDH catalyst was synthesized by using co-precipitation method as follows. First, the aqueous solution of  $Mg(NO_3)_2 \cdot 6H_2O$  and  $Al(NO_3)_3 \cdot 9H_2O$  was mixed into a three-neck round-bottom flask that contains a sodium carbonate aqueous solution ( $Na_2CO_3$ ) with stirring using a magnetic stirrer. Second, the pH of the mixture was kept to be 10 by controlling the addition of sodium hydroxide aqueous solution. Third, the resulting product was aged at room temperature for 16 hours, washed with de-ionized water until pH equal to 7, then filtered, used special treatment, and dried in oven at 65°C for 8 hours. Finally,  $Mg_2Al$ -LDH was calcined at 500°C with a heating rate of 10°C/min for 5 hours to form  $Mg_2Al$ -LDO.

### B. Catalyst characterization

The catalyst was characterized by XRD, XRF, AS-1MP, TPD- $NH_3$ , and TPD- $CO_2$ . X-Ray Diffraction spectroscopy (XRD) was used to confirm hydrotalcite structure by using the Rigaku SmartLab X-Ray Diffractometer system equipment with anode Cu  $K\alpha$  source. X-Ray Fluorescence (XRF) was used to identify and determine the concentration of elements present in the catalyst. Surface Area Analyzer (Quantachrome, Autosorb-1MP), which is based on

the physical adsorption of nitrogen gas, was employed to determine the surface area, total pore volume, and pore diameter of catalyst by using the Brunauer-Emmett-Teller (BET) technique. The acid and base properties can be determined using Temperature-Programmed Desorption of ammonia (TPD-NH<sub>3</sub>) and carbon dioxide (TPD-CO<sub>2</sub>), respectively. The heating rate was 10°C/min until 950°C with 30mL/min helium flowing, and the holding time at the final temperature was 1 hour.

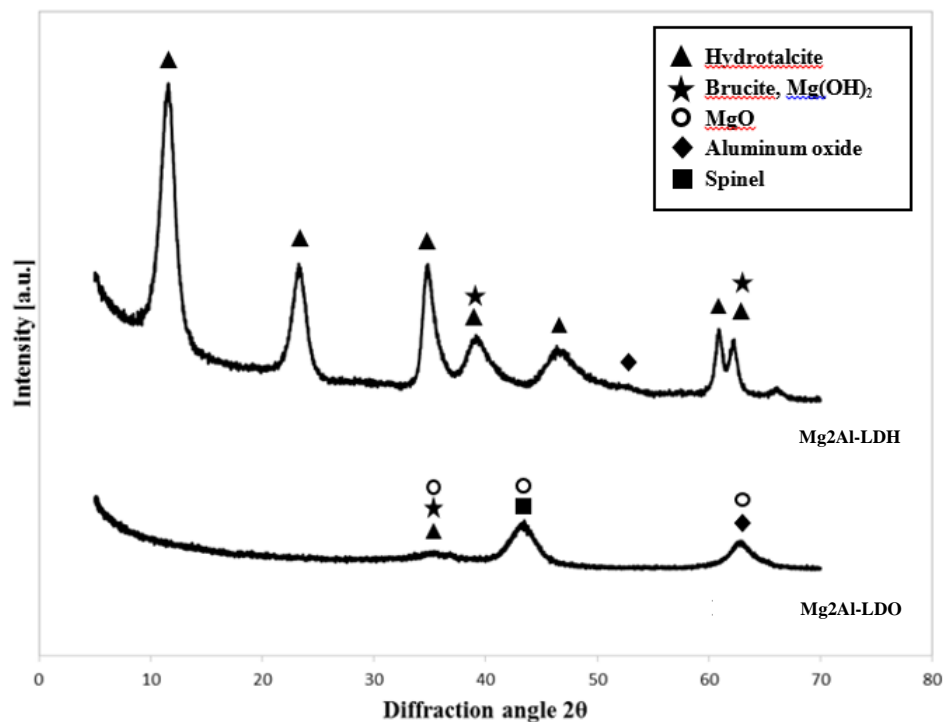
### *C. Catalyst reaction*

The reaction was carried out in a Parr reactor (250 mL) with the stirring rate of 500 rpm at 180°C under auto pressure. The reaction mixture contained 50 mL aqueous solution of glycerol and 1.0 g of catalyst, which were loaded into the reactor together since the beginning. The reaction time of all experiments was fixed at around 5 hours. The liquid products from the reactions were weighed and analyzed by using a one-dimensional Gas Chromatography-equipped with a Mass Spectrometry of Time of Flight type (1D GC-MS/TOF), Agilent© 7890-LECO, Pagasuss® 4D. The GC column was a non-polar: polar (50:50) Rtx-PAH (60m x 0.25mm ID x 0.10µm). The conditions for 1D GC-MS/TOF were set as follows: the initial temperature was 40°C, the heating rate was 15°C/min with split ratio of 200, and the final temperature was 310°C.

## **RESULTS AND DISCUSSION**

### *A. Catalyst Characterization*

The XRD results of the catalyst samples are shown in Figure 1. The XRD pattern of the newly-synthesized LDH (Mg<sub>2</sub>Al-LDH) shows the hydroxalite-like structure, which confirms the formation of layered double hydroxides while the XRD pattern of the calcined LDH (Mg<sub>2</sub>Al-LDO) shows the structure of mixed oxides. The d-spacing (d<sub>003</sub>) value of Mg<sub>2</sub>Al-LDH is 7.6 Å, which is the size of interlayer anion that is CO<sub>3</sub><sup>2-</sup>. On the other hand, there is no LDH characteristic peak that indicates the d-spacing value for Mg<sub>2</sub>Al-LDO, meaning that the brucite layers are collapsed when the catalyst is calcined, resulting in the interlayer disappearance.



**Figure 1** X-ray diffraction (XRD) patterns of the newly- synthesized LDH ( $Mg_2Al-LDH$ ), and the corresponding LDO ( $Mg_2Al-LDO$ ).

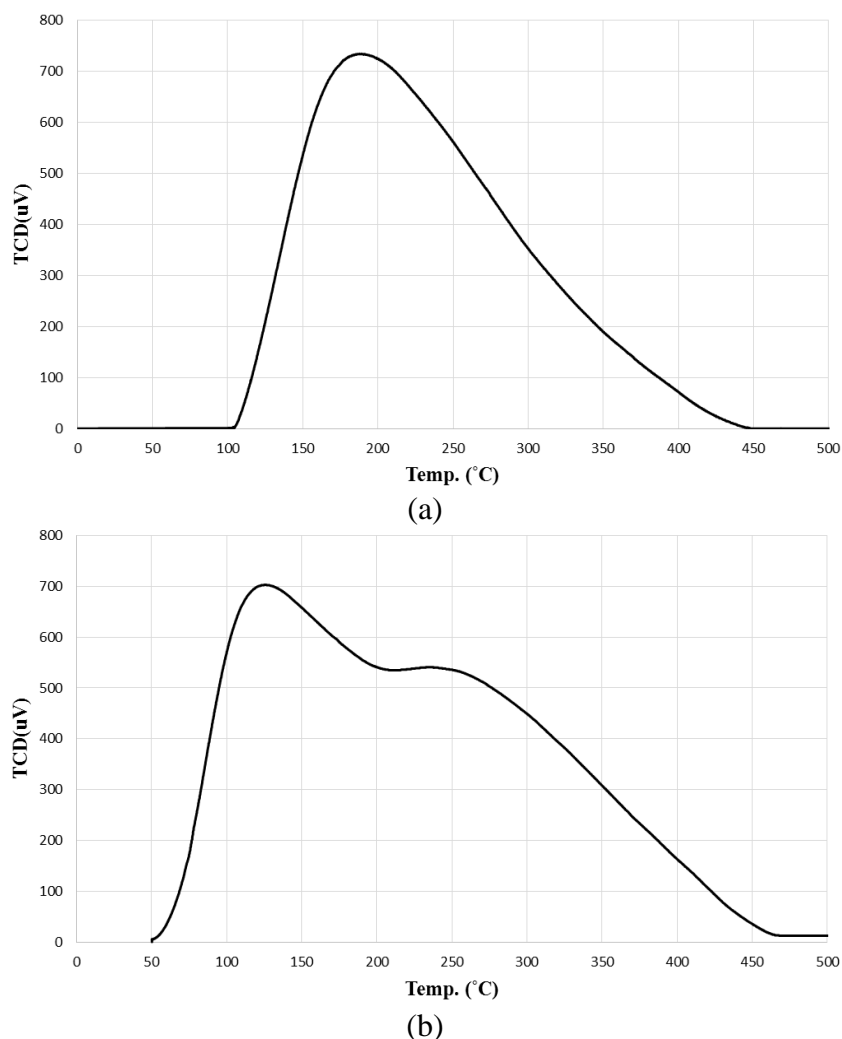
**Table 1** Physical properties of the catalyst samples

Sample	Mole ratio <sup>a</sup>		Surface area ( $m^2/g$ ) <sup>b</sup>	Pore volume ( $cm^3/g$ ) <sup>b</sup>	Pore diameter ( $\text{\AA}$ ) <sup>b</sup>
	Mg	Al			
$Mg_2Al-LDH$	2.35	1	83.20	0.8945	430.0
$Mg_2Al-LDO$	-	-	310.7	1.274	164.0

<sup>a</sup> determined by using XRF

<sup>b</sup> determined by using BET

The physical properties of catalyst samples are presented in Table 1. The weight percentages of elements in  $Mg_2Al-LDH$  are 12.2 for Mg, and 5.77 for Al, which are used to determine the mole ratio that is 2.35 : 1 (Mg:Al). The surface area, total pore volume, and pore diameter of catalysts are also shown in Table 1, which are  $83.20 m^2/g$ ,  $0.8945 cm^3/g$ , and  $430.0 \text{\AA}$  for  $Mg_2Al-LDH$  and  $310.7 m^2/g$ ,  $1.274 cm^3/g$ , and  $164.0 \text{\AA}$  for  $Mg_2Al-LDO$ . The pore diameters of catalysts are in the range of 200-500  $\text{\AA}$ , so the catalysts are mesoporous materials. Figure 2 shows the TPD- $NH_3$  and TPD- $CO_2$  profiles of  $Mg_2Al-LDO$ . The acid-base properties of the catalyst, which are the acid-basic strength, acid-basic site, and total acidity-basicity are presented in Table 2. The acid site is  $0.561 mmol/g$ , the basic site#1 is  $0.115 mmol/g$ , the basic site#2 is  $0.334 mmol/g$ , and the total basicity is  $0.449 mmol/g$ .



**Figure 2** Temperature-Programmed Desorption (TPD) profiles of  $Mg_2Al-LDO$ : (a) TPD- $NH_3$  and (b) TPD- $CO_2$ .

**Table 2** Acid-Basic sites and total acidity-basicity of catalyst from  $NH_3$ -TPD and  $CO_2$ -TPD results

Sample	Acid site <sup>c</sup>		Basic site#1 <sup>d</sup>		Basic site#2 <sup>d</sup>		Total basicity <sup>d</sup>
	°C	mmol/g	°C	mmol/g	°C	mmol/g	
$Mg_2Al-LDO$	186.0	0.561	125.0	0.115	238.0	0.334	0.449

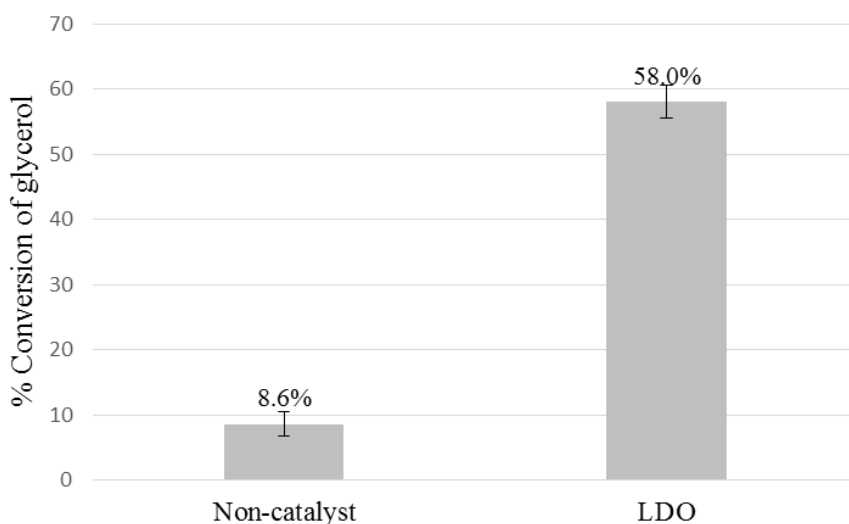
<sup>c</sup> determined by using TPD- $NH_3$

<sup>d</sup> determined by using TPD- $CO_2$

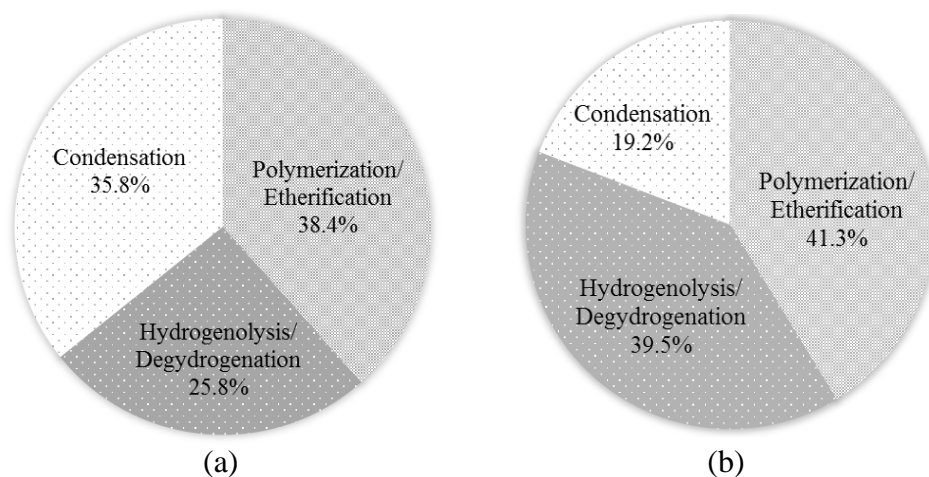
### B. Catalytic Activity

The catalytic activity of the LDO is compared with that of the non-catalytic run. Figure 3 shows the comparison of glycerol conversion between with and without catalyst. The conversion of glycerol increases from 8.6% to 58.0% with using the catalyst, indicating that the catalyst can catalyze glycerol conversion. The major products of non-catalytic reaction are polymerization/ etherification and condensation products existing in a high content of around 38.4%, and 35.8%, respectively, as shown in Figure 4(a). The selectivity of

hydrogenolysis and dehydrogenation products is quite low without a catalyst. Using  $Mg_2Al$ -LDO, the selectivity of hydrogenolysis and dehydrogenation products increases from 25.8% to 39.5% because  $Mg_2Al$ -LDO consists of both acid and basic sites as shown in Figure 2(a-b), which can promote both hydrogenolysis and dehydrogenation reactions, resulting in the higher selectivity of products. Moreover, the basic sites also govern polymerization/etherification reactions, so the selectivity of polymerization/etherification products also increases.



**Figure 3** Conversion of glycerol with and without the catalyst.



**Figure 4** Selectivity of products using (a) no catalyst, and (b)  $Mg_2Al$ -LDO.

## CONCLUSIONS

The possibility of using LDH-based oxide catalyst for glycerol hydrogenolysis and dehydrogenation was investigated, and also the effect of acid-base properties of the oxide catalyst was studied. The results showed that both glycerol conversion and selectivity of hydrogenolysis and dehydrogenation products were enhanced with using the catalyst. It was also found that the selectivity of hydrogenolysis and dehydrogenation products depended on



the acid-base properties of the catalyst. Both acid and basic sites can govern both reactions. Thus, the LDH-based oxide catalyst can possibly drive both glycerol hydrogenolysis and dehydrogenation simultaneously.

## ACKNOWLEDGEMENTS

This work was funded by Center of Excellence on Petrochemicals and Materials Technology. Furthermore, I would like to thank the Petroleum and Petrochemical College for the mutual support.

## REFERENCES

- Anitha, M., Kamarudin, S.K. and Kofli, N.T.** (2016) *Chemical Engineering Journal*. **295**, 119-130.
- Braterman, P.S., Xu, Z.P., Yarberr and F.** (2004). *Layered double hydroxides*. pp 373-474. Handbook of Layered Materials.
- Cavani, F., Trifirò, F. and Vaccari, A.** (1991) *Catalysis today*. **11**, 173-301.
- Daolai, S., Yasuhiro, Y., Satoshi, S. and Wataru, U.** (2016) *Applied catalysis B: Environmental*. **193**, 75-92.
- Lu, L. and Philip, Y.X.** (2015) *Fuel Processing Technology*. **137**, 55-65.
- Pei, S.K., Mohamed, K.A. and Wan, M.A.W.D.** (2016) *Renewable and Sustainable Energy Reviews*. **63**, 533–555.
- Shoujie, R. and Philip, Y.X.** (2015) *Fuel Processing Technology*. **140**, 148-155.
- Taylor, H.F.W.** (1973) *Mineralogical Magazine*. **39**, 377-389.
- Xiaolan, L., Xumeng, G., Shaoqing, C. and Yebo, L.** (2016) *Bioresource Technology*. **215**, 144-154.
- Zhenle, Y., Lina, W., Junhua, W., Shuixin, X., Ping, C., Zhaoyin, H. and Xiaoming, Z.** (2011) *Applied catalysis B: Environmental*. **101**, 431-440.
- Zhi, P.X., Jia, Z., Moses, O.A., Hong, Z. and Chunhui, Z.** (2011) *Applied Clay Science*. **53**, 139–150.