

# Novel Alternative Production of Bio-Based Chemicals Via One Pot Glycerol and Bio-Ethanol Conversion Using Impregnated 1 %Pd/Mg<sub>2</sub>Al-LDO Derived Catalysts

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Recently, the trend of bio-based and sustainable societies has led to an increasing production of biodiesel, resulting in a huge amount of glycerol as a waste product from the biodiesel production process. The production of specialty bio-based chemicals from glycerol has been considered as a new opportunity to utilize inexpensive chemicals to valuable chemicals. This study investigated the alternative production of specialty chemicals from glycerol and bio-ethanol co-feed. The purpose of adding bio-ethanol as a hydrogen donor was to enhance the glycerol conversion to valuable products. 1 %Pd impregnated- and parent Mg<sub>2</sub>Al-layered double oxide catalysts derived from the layer double hydroxide (LDH) were selected as the catalysts. The reaction was performed in a PARR reactor at 180 °C for 4 hours, and the effects of Pd and ethanol addition were observed. The catalysts were characterized by using BET, XRD, TPR, and XPS. The acid-base properties were studied by NH<sub>3</sub>-TPD and CO<sub>2</sub>-TPD. The results from pure glycerol feed showed that 53 %, 17 %, 12 %, and 9 % selectivity of propylene glycol, diglycerol, acetol and ethanol, respectively were achieved. Instead, when glycerol and ethanol were used as the mixed feed, 1,2-PDO, acetaldehyde, ethyl lactate and ethyl acetate were observed as the products.

## 1. Introduction

Biodiesel, a renewable fuel, used as a replacement for diesel, has been considered as an alternative fuel and applied in several countries. The major sources of raw material for making biodiesel are triglyceride molecules of vegetable oils and waste animal fats through esterification process that generates glycerol as a by-product. The rapidly rising production of bio-diesel has led an excess of crude glycerol. In order to solve the problem, crude glycerol is burnt in some biodiesel plant for energy; however, the heat value obtained from burning crude glycerol is very low. Some plant owners build a refinery unit to upgrade crude glycerol to technical grade glycerol. Nevertheless, the price of technical has been decreased (Quispe et al., 2013). Several researchers studying on the alternative uses of the crude glycerol found a variety of products that can be produced from crude glycerol conversion such as 1,2-propanediol, 1,3-propanediol, glycerol carbonate, ethylene glycol, acrolein and lactic acid (Clark et al., 2015). Among these products, the catalytic synthesis of 1,2-propanediol from glycerol is more attractive than the others because of lower price and less toxicity than the conventional petroleum-based propylene oxide synthesis (Talebian-Kiakalaieh et al., 2014). 1,2-Propanediol, or 1,2-PDO, can be produced from glycerol via the reaction called glycerol hydrogenolysis, where a C-O single bond is broken down in the presence of hydrogen. To synthesize 1,2-PDO, the C-O bond must break at the 1<sup>st</sup> position, followed by hydrogenation. Generally, the mechanism of glycerol hydrogenolysis was proposed in different pathways, depending on acidic or basic environment of supports such as ZnO and Al<sub>2</sub>O<sub>3</sub> (Chaminand et al., 2004), activated carbon (Maris et al., 2007), and MgO (Guo et al., 2011). It was suggested that a bi-functional acid/base catalyst was expected to show the good performance in this reaction. Layered double hydroxides (LDHs) consist of positively-charged metal hydroxide layers and negatively-charged anions with water in the inter-layer. The

general composition is  $[M^{2+}_{1-x}M^{3+x}(OH)_2]^{x+} (A^{n-})_{x/n} \cdot yH_2O$ , where  $M^{2+}$  is divalent cations such as  $Mg^{2+}$ ,  $Ca^{2+}$  or  $Zn^{2+}$  and  $M^{3+}$  is trivalent cation such as  $Al^{3+}$ ,  $Cr^{3+}$  or  $Fe^{3+}$  (Grigoriev., 2015). The excess positive charges are balanced by incorporation of anion ( $A^{n-}$ ) in the interlayer. The advantages of LDHs as a catalyst over glycerol hydrogenolysis reaction are summarized as follows: (i) The high adsorption capacity, (ii) The basicity and acidity that can be applied in multifunctional reactions, and (iii) uniform dispersion of cations in the layers, resulting in a high degree of dispersion (Bravo-Suárez., 2015). The acid-base properties of LDHs are related to structure and composition. The functional  $OH^-$  represents a Bronsted-basic site and  $O^{2-}-M^{2+}$  site is related to the Lewis basicity, whereas the Lewis acidity is contributed from the  $M^{3+}-O^{2-}$  site. In order to increase the concentration of acid and basic sites, calcination was performed to remove water/anion and break down the LDHs structure, forming a derived mixed metal oxide (MMO) called layered-double oxide (Yang et al., 2014). The calcination temperature not only break down the LDHs structure but also increases the accessibility of  $OH^-$  species and strong Lewis basic and mild Lewis acid sites (Constantino., 1995). In addition, the ratio between  $M^{2+}$  and  $M^{3+}$  can affect the density and strength of acid-basic sites. Kuljiraseth et al. (2019) conducted the experiments using AMO LDH-derived  $Mg_xAlO$  catalysts with the different ratios of Mg/Al. The structure of  $Mg_xAlO$  catalysts were proven by using XANES, EXAFS, and XPS. They found that both acidic and basic sites, varying with the Mg/Al ratio, can change the acid-base properties of the materials, which was contributed from acid-base pairs (both  $Mg^{2+}-O^{2-}$  and  $Al^{3+}-O^{2-}$ ). Moreover, the correlation between acid-base properties of  $Mg_xAlO$  mixed oxides, derived from the AMO-layered double hydroxides, affected the catalytic activity of benzoic acid esterification (Kuljiraseth., 2019). Yuan et al. (2009) studied the influence of the support nature by using  $MgO$ ,  $Al_2O_3$  and layered double hydroxides (LDHs) with Pt-based catalysts, and found that the bi-functional supports of an LDH had a significant influence on the conversion and selectivity of 1,2-PDO (Yuan et al., 2009). Various noble metal catalysts (Pd, Pt, Ag etc.), as well as non-noble ones (Ni, Co, Cu etc.), have been studied and found working well in the glycerol hydrogenolysis reaction. Among these metals, palladium has not been widely investigated over an LDH support. This work investigated the novel alternative production of specialty chemicals from a glycerol and bio-ethanol co-feed over 1 %Pd impregnated- and parent  $Mg_2Al$ -layered double oxide catalysts derived from the layered double hydroxide (LDH). The catalytic conversion was carried out in an absence of external  $H_2$ . The purpose of adding bio-ethanol as a hydrogen donor was to enhance the glycerol conversion to valuable products. The reaction was performed in a PARR reactor at 180 °C for 4 hours, and the effects of Pd and ethanol addition were determined. The catalysts were characterized by using BET, XRD, TPR, and XPS. The acid-base properties were studied by  $NH_3$ -TPD and  $CO_2$ -TPD.

## 2. Experimental

### 2.1. Synthesis of $Mg_2Al$ -layered double hydroxide

$Mg_2Al$ -LDH as the catalyst precursor was synthesized by co-precipitation method. The synthetic procedure was accomplished as follows. A solution mixture of  $Mg(NO_3)_2 \cdot 6H_2O$  (0.2125 mol),  $Al(NO_3)_3 \cdot 9H_2O$  (0.125 mol),  $Cu(NO_3)_2$  (0.0375 mol) and  $NaCO_3$  (0.125 mol) dissolved in 700 ml deionized water was prepared in a 3-necks round bottom flask. The mixed solution was vigorously stirred at room temperature for 10 h. The resulting precipitate ( $Mg_2Al$ -LDH) was filtered, washed with deionized water until pH 7, and then dried in an oven at 65 °C for 12 h. To achieve the calcined  $Mg_2AlO$  catalyst,  $Mg_2Al$ -LDH was calcined at 500 °C. After calcination, the solid was ground and sieved through a mesh for 325  $\mu m$ .

### 2.2. Synthesis of 1%Pd impregnated- $Mg_2Al$ catalyst

Calcined 1 %Pd/ $Mg_2AlO$  were synthesized by impregnation method. The aqueous solution containing 0.067 gram of palladium chloride in 20 ml of DI water was used as the metal precursor, and then 3.96-gram of calcined  $Mg_2AlO$  as the support was added into the solution. The solution was next stirred for 2 h. The solid was filtered, washed with deionized water, dried in an oven at 65 °C for 12 h, and then calcined at 500 °C for 5 h. After calcination, the catalysts were freshly reduced in 10 %  $H_2/Ar$  at 500 °C for 2 h in an autoclave reactor.

### 2.3. Characterization

The surface area of samples was determined by using the Brunauer-Emmett-Teller (BET) technique, and Surface Area Analyzer (Quantachrome, Autosorb-1MP). The X-Ray patterns of samples were determined by X-Ray diffractometer (Rigaku SmartLab), collecting data from 5-50° at 5°/min. Temperature-programmed reduction (TPR) measurements were made using a Micromeritics TPDRO analyser (BELCATII) to determine the reduction temperature of palladium. X-ray photoelectron spectroscopy (XPS) data were recorded using an AXIS ULTRADLD XPS machine to determine the oxidation state of elements in samples.

## 2.4. Catalyst Activity Testing

Hydrogenolysis reaction was performed in a Parr reactor at stirring speed at 300 rpm. The different feeds; that are, pure glycerol, 20 % ethanol in glycerol, and pure ethanol were used in this work. Before running the reaction, N<sub>2</sub> gas (99.99 %) was purged for 30 min. Next, the reaction was run under inert atmosphere at 180 °C for 4 h using each feed. The liquid sample was centrifuged to separate the catalyst from the mixture, and then analyzed by using a Pegasus LECO GC-TOF-MS, equipped with a capillary column, Rxi-PAH (60 m × 0.25mmID and 0.10 μm film thicknesses). The conversion and selectivity of glycerol were calculated according to the following equations:

$$\text{Conversion (\%)} = \frac{\text{moles of reacted feed}}{\text{moles of feed}} \times 100 \quad (1)$$

$$\text{Selectivity (\%)} = \frac{\text{moles of defined product}(i)}{\text{moles of reacted glycerol}} \times 100 \quad (2)$$

## 3. Results

### 3.1 Characterization

The X-ray diffraction (XRD) patterns of Mg<sub>2</sub>Al-LDH materials (Figure 1A) with the located peaks around 10°, 23°, 35°, indexing to (003), (006), and (009) reflections, confirm the successful preparation of layered double hydroxide structure. All characteristic peaks well define the highly-crystalline structure of LDH materials. Calcination performed at 500°C resulted in the disappearance of LDH characteristic peaks due to the collapsing layers, leading to the formation of an amorphous mixed oxide structure called a layered double oxide (LDO). The typical peaks of Pd cubic structure at 40.1° and 46.7° cannot be observed, which may coincide with the LDH characteristic peaks. The TPR profile of 1 %Pd/Mg<sub>2</sub>AlO (Figure 3B) exhibits a reduction peak of palladium at 173 °C. Moreover, the binding energy of calcined Pd 3d 5/2, centering at 336.8 eV, shifts to 335.08 eV, confirming the existence of Pd (0) (Figure 3C). The physical and chemical properties of catalysts are given in Table 1. The BET surface area of reduced Mg<sub>2</sub>AlO and reduced 1 %Pd/Mg<sub>2</sub>AlO is in the range of 100-600 m<sup>2</sup>g<sup>-1</sup>. The surface area and total acid density increase with adding palladium onto the surface.

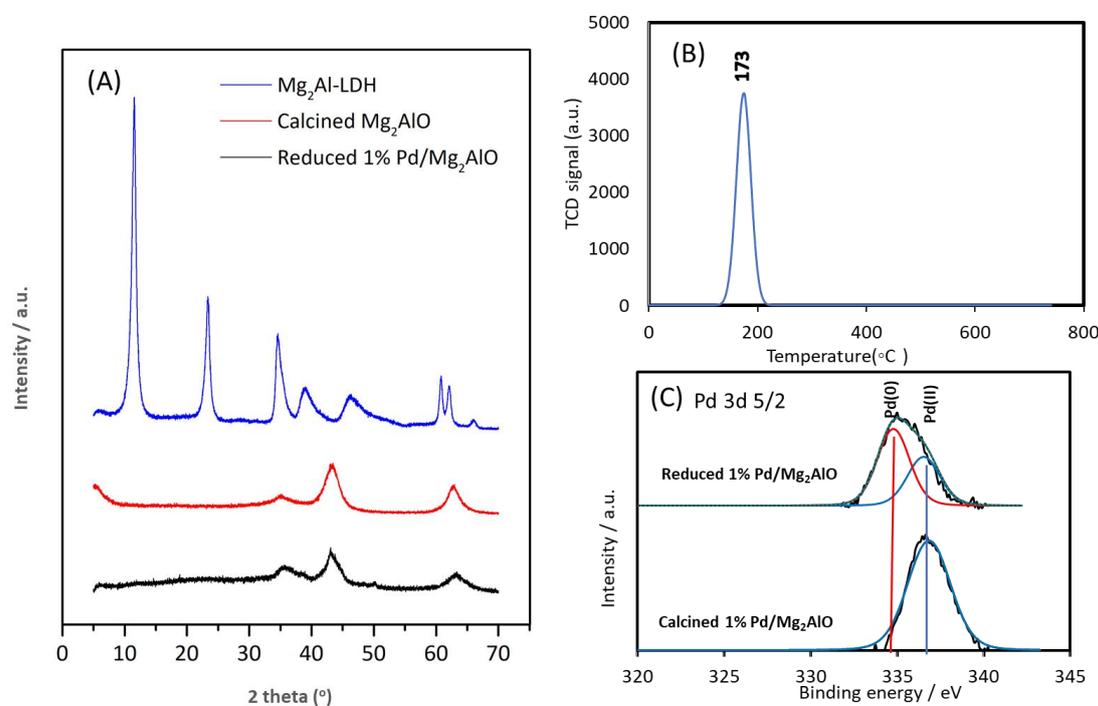


Figure 1: (A) XRD patterns of Mg<sub>2</sub>Al-LDH, calcined Mg<sub>2</sub>AlO, and Reduced 1 %Pd/Mg<sub>2</sub>AlO, (B) TPR of calcined 1 %Pd/Mg<sub>2</sub>AlO, and (C) XPD of calcined 1 %Pd/Mg<sub>2</sub>AlO and Reduced 1 %Pd/Mg<sub>2</sub>AlO

Table 1: Physical properties of calcined Mg<sub>2</sub>AlO and reduced 1 %Pd/Mg<sub>2</sub>AlO catalysts

Catalyst	Surface Area (m <sup>2</sup> /g) <sup>a</sup>	Pore Volume (cm <sup>3</sup> /g) <sup>a</sup>	Pore Diameter (Å) <sup>a</sup>	Total Basicity (mmol/g) <sup>b</sup>	Total Acid (mmol/g) <sup>c</sup>
Calcined Mg <sub>2</sub> AlO	165.2	0.5507	133.4	0.575	0.355
Reduced 1 % Pd/Mg <sub>2</sub> AlO	566.8	1.471	103.8	0.413	0.419

<sup>a</sup> Determined using BET method, <sup>b</sup> Determined using TPD-CO<sub>2</sub>, and <sup>c</sup> Determined using TPD-NH<sub>3</sub>

### 3.2 Hydrogenolysis of glycerol over Pd/Mg<sub>2</sub>Al.

The different feeds; that are, pure glycerol, 20 % ethanol in glycerol, and pure ethanol were used in this work. Figures 2, 3, and 4 illustrate the activity of calcined Mg<sub>2</sub>AlO and reduced 1 %Pd/Mg<sub>2</sub>AlO catalyst on the hydrogenolysis of glycerol at 180 °C, 4-hour reaction time in absence of H<sub>2</sub> feed. First, the effect of feed was investigated. As a result, the experiment using the calcined Mg<sub>2</sub>AlO catalyst and pure glycerol feed results in the glycerol conversion and selectivity of 1,2-PDO of 10.4 % and 27.1 %, respectively. Ethanol, 1,2-PDO, and acetone were identified as major products with 36.6 %, 27.1 %, and 23.0 % selectivity, respectively. A small amount of dioxane, dioxolane, 3-butyn-1-ol, and allyl alcohol was also detected as minor products (<10 %). The reaction was also run with pure ethanol feed in order to determine the products from ethanol conversion. It was found that the main products were acetaldehyde, ethane, 1,1-diethoxy-, and acetone. When the mixed feed (20 % ethanol in glycerol) was used, the glycerol conversion increased from 10.4 % to 18.9 %, and only 3 major products were observed; that are, acetone (60.2 %), 1,2-PDO (20.2 %), and acetaldehyde (19.6 %). The high selectivity of acetone (60.2 %) was obtained from both glycerol and ethanol feeds, followed by 20.2 % 1,2-PDO and 19.6 % acetaldehyde.

To determine the effect of palladium, the reduced 1 %Pd/Mg<sub>2</sub>AlO catalyst was also evaluated at the same reaction conditions. The results were compared with those obtained from the calcined Mg<sub>2</sub>AlO catalyst. It was found that the conversion in both pure feed glycerol and ethanol significantly increases from 10.4 % to 21.5 % and 17.1 % to 32.9 %, respectively. However, the conversion in case of the mixed feed slightly increases because of the competitive reactions between two pathways; that are, glycerol hydrogenolysis route (Figure 5A) and ethanol dehydrogenation route (Figure 5B). In case of pure glycerol, 1,2-PDO is found as a main product, followed by diglycerol, acetol, and ethanol. The selectivity of 1,2-PDO increases from 27.1 % to 53 %. The presence of acetol (12 % selectivity) indicates the lack of H<sub>2</sub> supply in this system. Moreover, palladium also drives ethanol dehydrogenation to ethyl acetate, then generating more *in-situ* H<sub>2</sub> supplied to the system (Figure 5B). With the *in-situ* production of H<sub>2</sub>, it was expected to see the increasing 1,2-PDO selectivity in the mixed feed system. However, the selectivity of 1,2-PDO in the mixed feed case significantly drops because 1,2-PDO further reacts with ethanol, forming a new product, ethyl lactate (46 % selectivity). Ethyl lactate can be therefore produced from 1,2-PDO via the pathway shown in Figure 5A. In addition, acetol was not found in the case of mixed feed system because the ethanol dehydrogenation generates *in-situ* H<sub>2</sub> that helps acetol to be hydrogenated to 1,2-PDO.

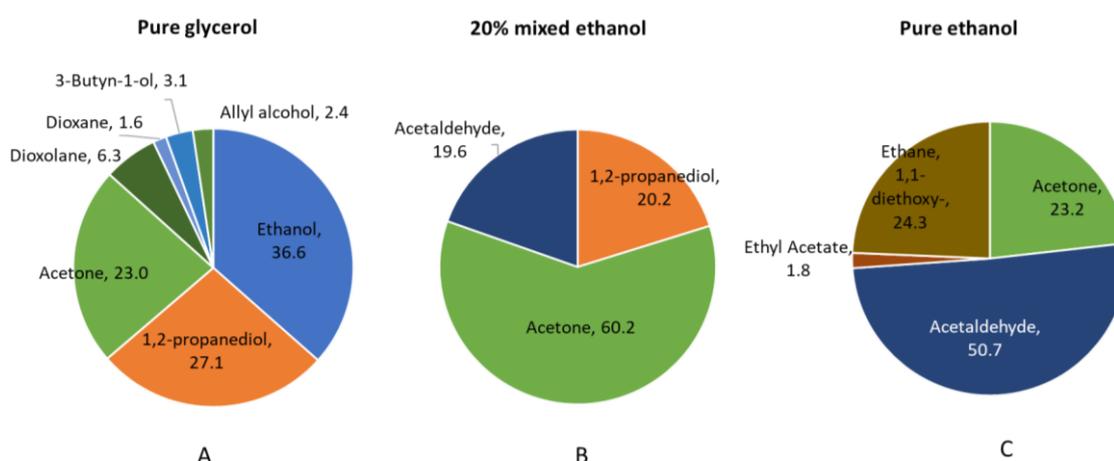


Figure 2: Selectivity of hydrogenolysis products from various feeds: (A) pure glycerol, (B) 20 % mixed ethanol in glycerol, and (C) pure ethanol using calcined Mg<sub>2</sub>AlO catalyst at 180 °C for 4 h in the absence of external H<sub>2</sub>

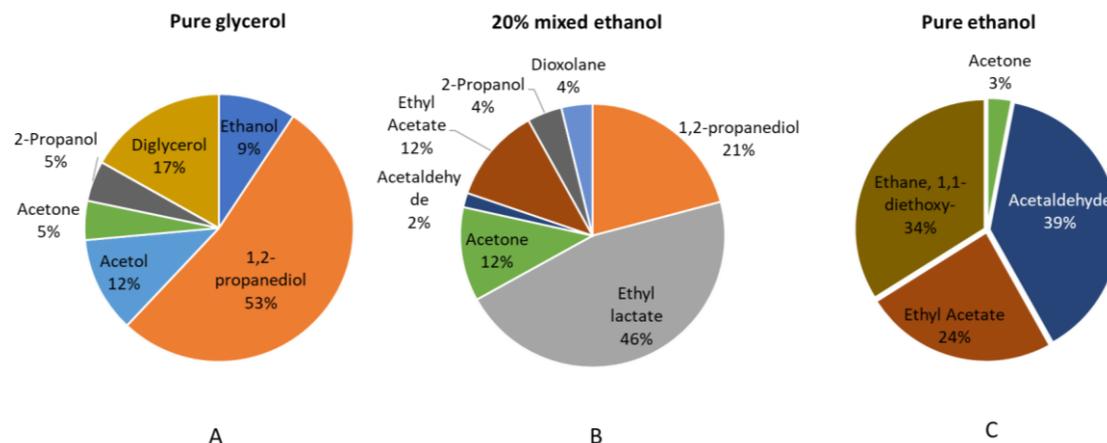


Figure 3: Selectivity of hydrogenolysis products from various feeds: (A) pure glycerol, (B) 20 % mixed ethanol in glycerol, and (C) pure ethanol using reduced 1%Pd/Mg<sub>2</sub>AlO catalyst at 180 °C for 4 h in the absence of external H<sub>2</sub>

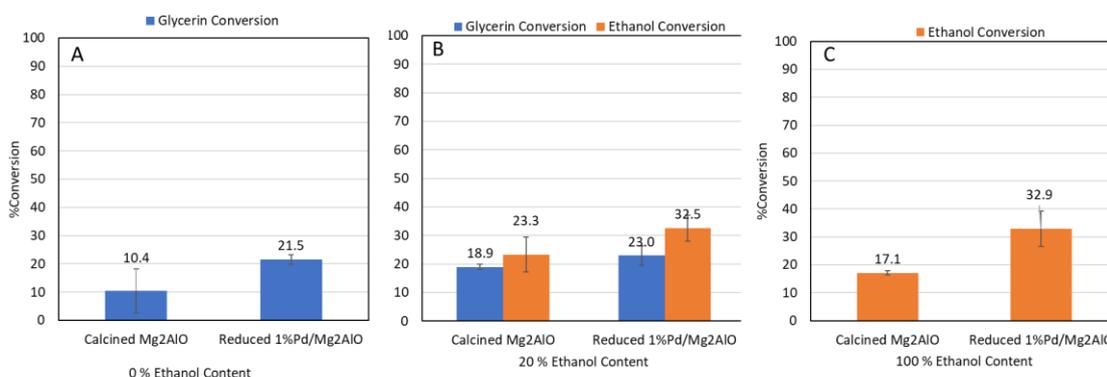


Figure 4: Conversion of hydrogenolysis products from various feeds: (A) pure glycerol, (B) 20 % mixed ethanol in glycerol, and (C) pure ethanol using calcined Mg<sub>2</sub>AlO and reduced 1 %Pd/Mg<sub>2</sub>AlO catalyst at 180 °C for 4 h in the absence of external H<sub>2</sub>

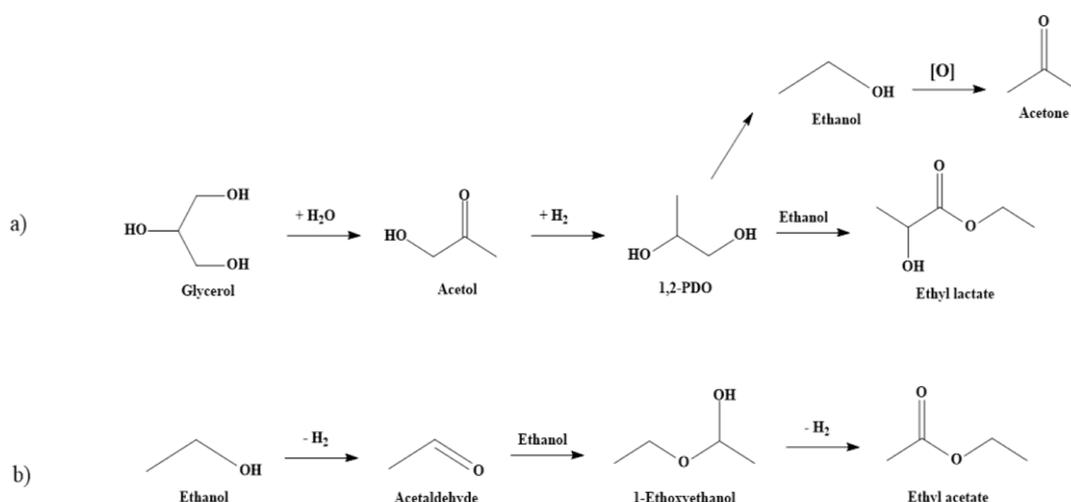


Figure 5: (a) Proposed pathway of glycerol hydrogenolysis that forms 1,2-PDO, ethyl lactate, ethanol and acetone, and (b) ethanol dehydrogenation, forming ethyl acetate and H<sub>2</sub>

#### 4. Conclusions

In summary, Mg<sub>2</sub>Al-LDH was synthesized using co-precipitation. After calcined, it was impregnated with 1 %Pd, followed by calcination and reduction, forming the reduced 1 %Pd Mg<sub>2</sub>AlO catalyst. The catalyst was further tested for its activity on glycerol hydrogenolysis under absent H<sub>2</sub> condition using various feeds. The results demonstrated that the addition of Pd promoted both direct conversion of glycerol to 1,2-PDO, and the dehydrogenation of ethanol to ethyl acetate. H<sub>2</sub> can be *in-situ* generated through ethanol dehydrogenation, which enhanced the catalytic activity, resulting in the conversion of acetol to 1,2-PDO in the case of mixed feed system. Furthermore, 1,2-PDO further reacted with ethanol, forming ethyl lactate as a new product.

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