



Co-Production of 1,2-propandiol and Ethyl Lactate from the Conversion of Glycerol co-fed with Bio-Ethanol over Reduced $\text{Cu}_{0.3}\text{Mg}_{1.7}\text{Al}$ LDH-derived Oxide Catalyst without External Hydrogen

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Usually, the hydrogenolysis of glycerol into 1,2-propandiol requires H_2 supply in the acetol hydrogenation step to 1,2-propandiol. However, *in-situ* hydrogen can be generated from glycerol dehydrogenation and glycerol reforming using metal catalysts. Moreover, ethanol can be co-fed as a hydrogen donor for this reaction and produce ethyl lactate via esterification with lactic acid which is by-product from glycerol conversion. In this study, the promotion effect of Cu partially-substituted $\text{Mg}_{1.7}\text{Al}$ mixed oxide was investigated on the conversion of glycerol co-fed with bio-ethanol in a PARR-reactor at 180 °C for 4 h without hydrogen feeding. Then, the products were analyzed using GC-MS/TOF. The catalysts were characterized using BET, XRD, XPS, XRF, and TPDR. As a result of the Mg_2AlO based catalyst, the glycerol can be converted to 1,2-propandiol, acetone, and acetaldehyde without ethyl lactate production at this condition. The reduced $\text{Cu}_{0.3}\text{Mg}_{1.7}\text{Al}$ LDH-derived catalyst significantly enhanced the selectivity of 1,2-propandiol and ethyl lactate to 47.3 and 22.8 %. 1,2-Propandiol and ethyl lactate as specialty chemicals were found to be co-produced from co-feeding glycerol and bio-ethanol using the reduced $\text{Cu}_{0.3}\text{Mg}_{1.7}\text{Al}$ LDH-derived catalyst.

1. Introduction

The biodiesel production generates a large amount of glycerol as a by-product that is inexpensive with a small market. Therefore, the conversion of glycerol into useful bio-based chemicals is an attractive alternative resource for glycerol utilization and value addition of glycerol. 1,2-Propanediol (1,2-PDO), widely used in chemicals, food, and pharmaceutical industries, is one of the products from the alternatives that utilize glycerol and increase the value of glycerol via hydrogenolysis (Delgado et al., 2013; Yun et al., 2014). Usually, the hydrogenolysis of glycerol requires H_2 supply in the acetol hydrogenation step to form 1,2-propandiol. Therefore, the *in-situ* simultaneous generation of hydrogen from glycerol reforming using a hydrogen-donating solvent, such as ethanol, can overcome these problems (Xia et al., 2013; Yun et al., 2014). Moreover, ethanol can, in parallel, produce ethyl lactate as a specialty chemical via the esterification with lactic acid that is also a by-product from glycerol conversion. Ethyl lactate is an important chemical widely used in the food, pharmaceutical, and chemical industries as well.

Based on the reaction mechanism, the acid-base properties of catalysts play a critical role in glycerol hydrogenolysis. The acid sites catalyze the dehydration of glycerol to acetol (Chiu et al., 2006), whereas basic sites catalyze the dehydrogenation of glycerol to glyceraldehyde that is subsequently dehydrated into pyruvaldehyde (Delgado et al., 2013). The Mg-Al mixed oxide catalysts derived from layered double hydroxides (LDHs) are therefore promising catalysts for the reactions because they possess specific acid-base properties and significantly-high surface area with mesoporosity (Kuljiraseth et al., 2019). In previous work, Cu metal catalysts have shown their superior performance in terms of the 1,2-PDO selectivity of the glycerol hydrogenolysis reaction due to the ability to catalyze the cleavage of C-O and C-C bonds in the presence of H_2 (Yun et al., 2014). Cu has been employed to enhance the activity, selectivity, and hydrogen utilization in various

Cu-based bimetallic catalysts, such as Cu-ZnO (Gao et al., 2016), Cu-Al₂O₃ (Cai et al., 2016), Cu-MgO (Balaraju et al., 2012), Cu-Ni-Al₂O₃ (Yun et al., 2014), and Cu-Mg-AlO (Xia et al., 2013). As for previous work, the Cu_{0.4}/Mg_{6.28}Al_{1.32}O_{8.26} (Cu:Mg:Al = 0.30: 4.76: 1) catalyst performed efficiently in the selective conversion of glycerol to 1,2-PDO, using ethanol as the hydrogen donor under N₂ at 200 °C; however, ethyl lactate has not found co-produced (Xia et al., 2013). Since some reactions such as esterification require the bi-functional acid-base sites of a catalyst (Kuljiraseth et al., 2019), the different Mg/Al ratios of MgAl-LDO can provide acid-base pairs with different quantities and strength, which can drive the conversion of a feed as efficiently as possible. In this work, a low Mg/Al ratio of 2 was expected to promote the high activity of glycerol conversion in the case due to its high acid and base density. Moreover, Cu was reported to be an active catalyst for producing H₂ from glycerol reforming (Yun et al., 2014) and ethanol dehydrogenation (Sato et al., 2012).

Therefore, the Mg₂AlO partially substituted by Cu was used as a catalyst. The objective of this study was to investigate the promotion effect of Cu by a partial substitution in the Mg₂Al derived-LDHs, and examine the potentials of the catalyst in the conversion of glycerol co-fed with bio-ethanol, targeting to the co-production of 1,2-PDO and ethyl lactate, in a PARR-reactor at 180 °C for 4 hours without hydrogen feeding.

2. Experimental

2.1 Catalyst preparation

The Cu_{0.3}Mg_{1.7}Al-LDH catalyst, whose atomic ratio of (Mg+Cu)/Al was 2, was prepared by co-precipitation. An aqueous solution of Mg(NO₃)₂·6H₂O (0.2975 mol), Cu(NO₃)₂·3H₂O (0.0525), and Al(NO₃)₃·9H₂O (0.175 mol) were mixed to make a homogeneous solution. Then, the aqueous solution was added into a Na₂CO₃ (0.35 mol) solution, and pH was controlled at about 10 using NaOH solution. The sample was next aged at room temperature for 16 h, filtered and washed several times by deionized water until pH 7, and dried in an air oven at 65 °C overnight. The Cu_{0.3}Mg_{1.7}Al-LDH was calcined at 500 °C in air, and reduced in 10%H₂ (H₂/He) at 500 °C for 2 h. The reduced catalyst was named as reduced Cu_{0.3}Mg_{1.7}AlO. For comparison purpose, Mg₂Al-LDH was also prepared, according to the above procedure, in order to investigate the effect of partial substitution of Cu. Before also used as a catalyst, the Mg₂Al-LDH was calcined at 500 °C in air, named calcined Mg₂AlO.

2.2 Catalyst characterization

The X-Ray diffraction (XRD) patterns of samples were obtained using a Bruker X-Ray diffractometer system (D8 Advance) with a CuK α radiation (1.5405 Å). The measurement conditions were in the range of $2\theta = 5^\circ$ to 70° and the scan speed of $0.02^\circ (2\theta)/ 0.6$ s. The Brunauer-Emmett-Teller (BET) technique was used to determine the specific surface area, pore diameter, and total pore volume of catalysts, using the surface area analyzer (Quantachrome, Autosorb-1MP). Before the measurements, the samples were degassed under vacuum at 250 °C for 16 h. The elemental concentrations of catalysts were determined using X-ray fluorescence (XRF), Model S8 Tiger. The Temperature Programmed Desorption/Reduction/Oxidation analyzer (TPDRO), BELCAT II, was employed to determine the acidity and basicity from the temperature desorption of NH₃ and CO₂, of the calcined catalysts. A sample was pretreated in He (50 cc/min) at 450 °C for 60 min. Pre-adsorption of 10 % NH₃/He or 99.995 % CO₂ at 100 °C for 30 min was performed prior to the analysis. Next, the temperature was increased to 650 °C at 10 °C/min, and later held for 30 min with He (30 cc/min). The reducibility of the calcined catalysts was determined using the temperature programmed reduction (TPR) technique with a heating rate of 10 °C/min to 800 °C under 5 % H₂/N₂. X-Ray Photoelectron Spectroscopy (XPS) was performed using the AXIS ULTRA^{DLD} to determine the oxidation state of the samples. The system was equipped with a monochromatic Al X-ray source and a hemisphere analyzer. All peaks were calibrated from referring to the C1s spectrum located at 284.8 eV.

2.3 Catalytic activity testing

The catalytic activity of glycerol hydrogenolysis was tested in a batch-type PARR reactor. The composition of the reaction mixture was 36.02 g of glycerol and 9 g of bio-ethanol and a fixed loading of 1 g of catalyst. The catalytic activity was carried out with the stirring rate of 300 rpm at 180°C for 4 h under auto-pressure. After the reaction, the catalyst was removed from the reaction mixture using a centrifuge, and the liquid product was analyzed using a Pegasas LECO GC-TOF/MS. The column was an Rxi-PAH (60 m x 0.25 mmID and 0.10 μ m film thicknesses). Initially, the column temperature was 40 °C, kept for 1 min, then increased temperature step-by-step by 5.5 °C/min to 55 °C, 1.5 °C/min to 90 °C, 4.0 °C/min to 168 °C, and 5.0 °C/min to 210 °C.

3. Results and discussion

3.1 Catalyst characterization

The elemental composition and d-spacing of the LDHs were examined using XRF and XRD, respectively. In Figure 1A(a-b), the XRD patterns show the characteristic peaks of a hydrotalcite (PDF No. 00-014-0191) in both Mg_2Al -LDH and $Cu_{0.3}Mg_{1.7}Al$ -LDH, indicating that all the LDH samples were successfully synthesized. Based on the chemical composition and d-spacing shown in Table 1, the mol % Al of $Cu_{0.3}Mg_{1.7}Al$ -LDH is similar with that of Mg_2Al -LDH, but the % mol of Mg is lower. It indicates that Cu substitutes in the position of Mg in the LDH sheets, which slightly enlarges the d-spacing of LDH from 7.63 to 7.78 Å.

After calcination at 500 °C, the peaks of metal oxide (PDF No.00-001-1235) and spinels ($MgAl_2O_4$; PDF No.01-075-4038 and $CuAl_2O_4$; PDF No.01-073-1958) appear in both calcined Mg_2AlO and calcined $CuMgAlO$, confirming the transformation to mixed metal oxide phases, as shown in Figure 1A(c-d). From the Al 2p XPS spectra (Figure 2a), only a single peak of Al^{3+} atoms appears. Al^{3+} is present in the octahedral position (74.3 eV) (Rao et al., 2005), and its peak shifts slightly to lower binding energy upon the partial substitution of Cu. Likewise, the Mg 2p XPS spectra that indicate the shifts of the Mg 2p peak to lower binding energy. It can be noted that the partial substitution of Cu has been made successful because the interaction with Mg and Al can be observed from the shifts of XPS peaks. Additionally, the spectrum of Cu2p of calcined $Cu_{0.3}Mg_{1.7}AlO$ (Figure 2(c)) presents the peak of Cu^{2+} (934.4 eV) (Jiang et al., 2013), confirming that Cu can partially substitute in the Mg^{2+} position.

Table 1: Chemical composition and physical properties of LDHs

Sample	Mol %Mg ^a	Mol %Al ^a	d-spacing ^b
Mg_2Al -LDH	29.7	14.6	7.63
$Cu_{0.3}Mg_{1.7}Al$ -LDH	24.5	14.0	7.78

^a determined using XRF, ^b determined using XRD

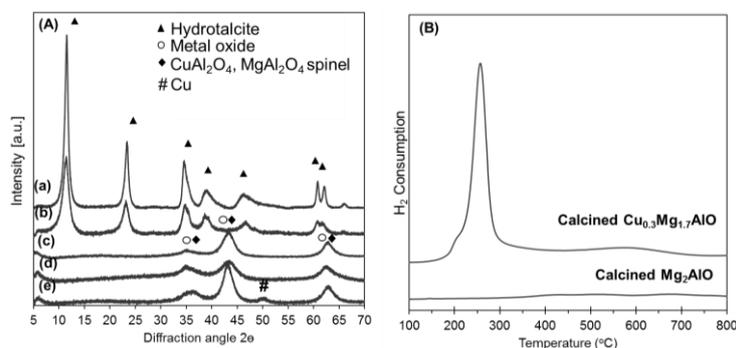


Figure 1: (A) XRD patterns of (a) Mg_2Al -LDH, (b) $Cu_{0.3}Mg_{1.7}Al$ -LDH, (c) calcined Mg_2AlO , (d) calcined $Cu_{0.3}Mg_{1.7}AlO$, and (e) reduced $Cu_{0.3}Mg_{1.7}AlO$, and (B) TPR of calcined LDHs

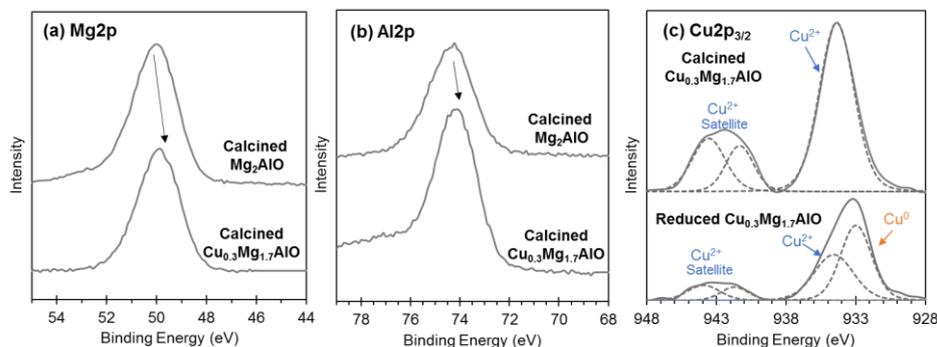


Figure 2: XPS spectra of (a) Mg 2p, (b) Al 2p, and (c) $Cu_{2p_{3/2}}$ of catalysts

The H₂-TPR profiles of calcined Mg₂AlO and Cu_{0.3}Mg_{1.7}AlO are shown in Figure 1B. It can be seen that there are mainly two H₂-TPR peaks; namely, the reduction peak of CuO species at a lower temperature (200–300 °C), and the reduction peak of CuAl₂O₄ at a higher temperature (500–700 °C) (Luo et al., 2005). After the reduction at 500 °C for 2 h, a Cu metallic peak ($2\theta = 43.5^\circ$, PDF No.00-001-1241) is observed in the XRD pattern of reduced Cu_{0.3}Mg_{1.7}AlO (Figure 1A(e)). Moreover, the Cu 2p XPS spectrum of reduced Cu_{0.3}Mg_{1.7}AlO (Figure 2c) shows a new peak at 932.7 eV, attributed to Cu⁰ (Jiang et al., 2013), while the peak of Cu²⁺ also appears (934.6 eV), confirming that the Cu in the catalyst was partially reduced at this condition.

Table 2 presents the surface area, pore volume, and pore diameter of catalysts. Both calcined Mg₂AlO and reduced Cu_{0.3}Mg_{1.7}AlO catalysts are thus mesoporous materials because their pore diameters are in the range of 133.4 - 152.5 Å. The partial substitution with Cu increases the surface area of 211.3 m²/g with the higher pore volume of 0.8056 Å, as compared with those of calcined Mg₂AlO. In addition, the total acidity and basicity are also shown in Table 2. The calcined Mg₂AlO catalyst presents both basic (0.575 mmol/g) and acidic (0.355 mmol/g) properties. Upon the partial substitution, Cu suppresses the density of basic sites because the Cu partially substitutes in the Mg²⁺ position that is the basic site. So, the partial substitution of Cu reduces the total basicity of the catalyst to 0.431 mmol/g, and consequently enhances the total acid density to 0.425 mmol/g.

Table 2: Chemical and physical properties of catalysts

Catalyst	Surface Area (m ² /g) ^a	Pore Volume (cm ³ /g) ^a	Pore Diameter (Å) ^a	Acid Density (mmol/g) ^b	Base Density (mmol/g) ^c
Calcined Mg ₂ AlO	165.2	0.5507	133.4	0.355	0.575
Reduced Cu _{0.3} Mg _{1.7} AlO	211.3	0.8056	152.5	0.425	0.431

^a determined using BET, ^b determined using TPD-NH₃, ^c determined using TPD-CO₂

3.2 Catalytic activity

The calcined Mg₂AlO and reduced Cu_{0.3}Mg_{1.7}AlO catalysts were tested for their activity on the glycerol co-fed with bio-ethanol. The conversion of glycerol, ethanol, and selectivity of products after a reaction time of 4 h without H₂ feed, are shown in Figure 3. The results show that the Mg₂AlO catalyst can produce 20.2 % 1,2-PDO at a low glycerol conversion (18.9 %) without ethyl lactate production. The conversion of glycerol catalyzed by the acid-base of catalysts is summarized in Figure 4. The acid function of a catalyst catalyzes the dehydration of glycerol to acetol (Chiu et al., 2006), whereas the basic site catalyzes the dehydrogenation of glycerol to glyceraldehyde (Delgado et al., 2013). In this work, the Mg₂AlO catalyst promotes ethanol dehydrogenation to acetaldehyde (19.6 % selectivity) with 23.3 % ethanol conversion (Figure 3a), as indicated in Scheme 1b. The hydrogen generated from ethanol dehydrogenation is simultaneously supplied to the hydrogenation of acetol to form 1,2-PDO.

With the partial substitution with Cu, the reduced Cu_{0.3}Mg_{1.7}AlO catalyst can enhance significantly the glycerol conversion to 49.8 % (Figure 3a), and increase the 1,2-PDO and ethyl lactate selectivity to 28.8 % and 14 % (Figure 3(b2)), respectively. As shown in Figure 4a, the *in-situ* hydrogen formation is possible either from glycerol reforming or from dehydrogenation of glycerol to glyceraldehyde. The hydrogen also can be produced from the ethanol dehydrogenation pathway (Figure 4b), which can be considered from production of ethyl acetate (4.4 %) as a product. Ethanol is co-fed not only as a hydrogen donor for this reaction, but also to simultaneously produce ethyl lactate via esterification with lactic acid that is a by-product from glycerol conversion, which can be assured by the existence of lactic acid in the final product. It is observed in this work that lactic acid is produced from oxidation of 1,2-PDO on the Cu metal site. Therefore, the Cu catalyst plays important roles in the reaction pathways; namely, (1) promotes the hydrogen production via glycerol reforming, glycerol dehydrogenation, and ethanol dehydrogenation pathways, which is then supplied to the hydrogenation of acetol to form 1,2-PDO, (2) drives the oxidation of 1,2-PDO to lactic acid, and then (3) promotes the esterification of lactic acid with ethanol to ethyl lactate. The nature of substituting metal appears to be more influential to the product selectivity than the acid-base properties. In summary, the reduced Cu_{0.3}Mg_{1.7}AlO catalyst gives an apparently-higher yield of 1,2-PDO (15.0 %) and ethyl lactate (6.8 %), as shown in Figure 5. It is noted that the product from reduced Cu_{0.3}Mg_{1.7}AlO consists of complex mixtures of oxygenates, which may be difficult to separate them to every single individual compound. As a result, one should be aware that the separation process may be not economical. However, it is possible that we can separate them by their groups such as alcohol, ester, and so on, using distillation and solvent extraction (Xiu & Zeng, 2008), and then used them in some applications such as bio-additive.

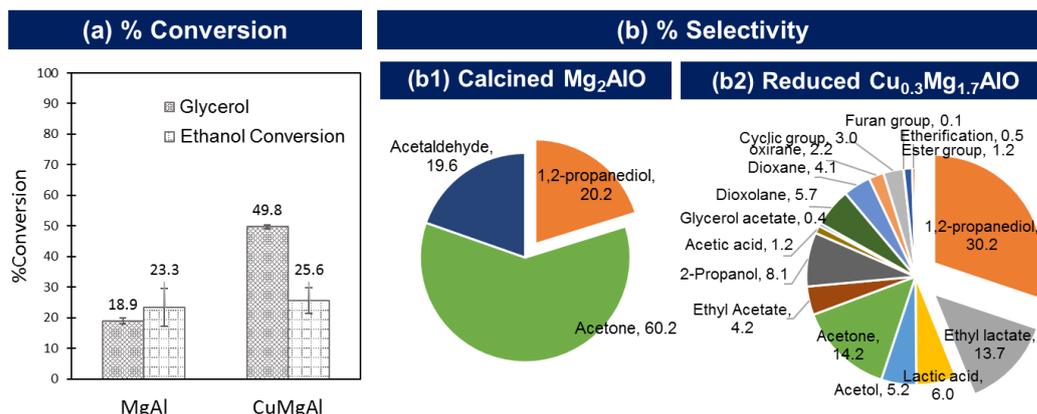


Figure 3: (a) Conversion of glycerol and ethanol, and (b) selectivity of products of the catalysts

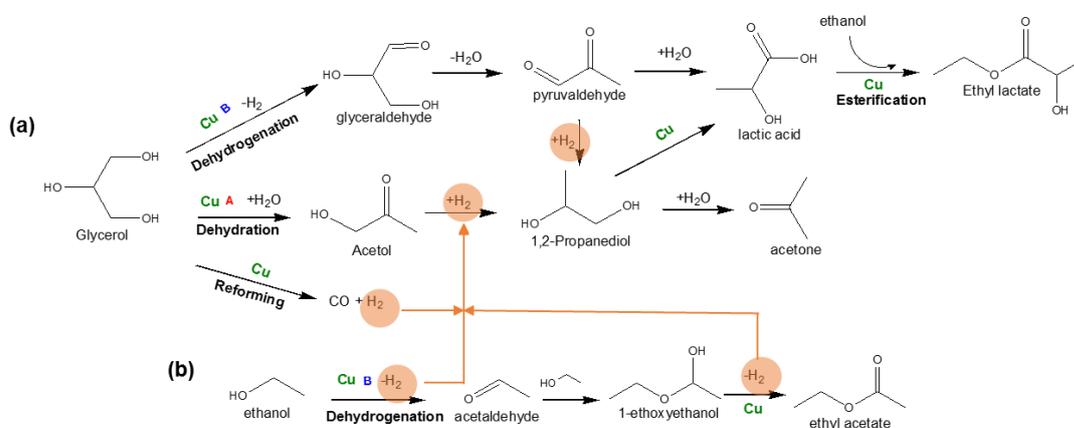


Figure 4: Proposed reaction pathways of reduced Cu_{0.3}Mg_{1.7}AlO catalyst: (a) glycerol hydrogenolysis, and (b) ethanol dehydration, where A = Acid site (Chiu et al., 2006), B = Base site (Delgado et al., 2013), and Cu = Copper metal sites proposed in this work

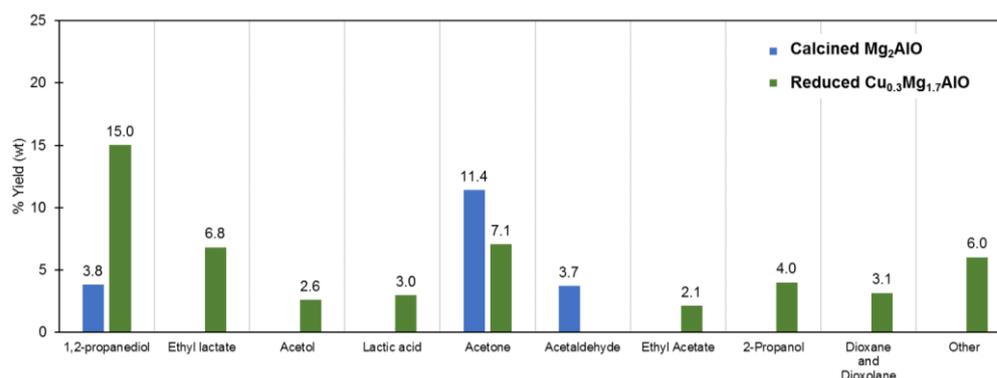


Figure 5: Yield of products

4. Conclusions

Mg₂Al-LDH and Cu_{0.3}Mg_{1.7}Al-LDH have been successfully synthesized in this work. They were next calcined and then reduced at 500 °C, and later found possessing both acidic-basic and metal sites. Subsequently, they were studied for their activity on the conversion of glycerol with bio-ethanol. It was found that the conversion of

glycerol was highly enhanced by the partial substitution of Cu in Mg_{1.7}Al-LDH. Based on the selectivity, the Cu-substituted catalyst promoted the glycerol hydrogenolysis pathway, producing 15.0 % yield of 1,2-PDO, together with the esterification of lactic acid with bio-ethanol that resulted in 6.8 % yield of ethyl lactate. The Cu catalyst played important roles in the *in-situ* hydrogen formation, oxidation of 1,2-PDO, and esterification to ethyl lactate. In addition, it should be noted that, due to their complexation, it may be difficult to separate the mixture of oxygenate products, generated using reduced the Cu_{0.3}Mg_{1.7}AlO catalyst, to individual compounds; therefore, the separation may cause the entire process uneconomical. Generally, the investment of a conventional petrochemical plant has a break-even point around 20-30 years, whereas a bio-based petrochemical plant may possibly take more than 50 years. Nevertheless, bio-based productions are environmentally and socially sustainable for the global economy and society in the future.

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References

- Balaraju M., Jagadeeswaraiah K., Prasad P.S., Lingaiah N., 2012, Catalytic hydrogenolysis of biodiesel derived glycerol to 1, 2-propanediol over Cu–MgO catalysts, *Catalysis Science & Technology*, 2, 1967-1976.
- Cai F., Zhu W., Xiao G., 2016, Promoting effect of zirconium oxide on Cu–Al₂O₃ catalyst for the hydrogenolysis of glycerol to 1, 2-propanediol, *Catalysis Science & Technology*, 6, 4889-4900.
- Chiu C.W., Dasari M.A., Suppes G.J., Sutterlin W.R., 2006, Dehydration of glycerol to acetol via catalytic reactive distillation, *AIChE Journal*, 52, 3543-3548.
- Delgado S.N., Yap D., Vivier L., Especel C., 2013, Influence of the nature of the support on the catalytic properties of Pt-based catalysts for hydrogenolysis of glycerol, *Journal of Molecular Catalysis A: Chemical*, 367, 89-98.
- Gao Q., Xu B., Tong Q., Fan Y., 2016, Selective hydrogenolysis of raw glycerol to 1, 2-propanediol over Cu–ZnO catalysts in fixed-bed reactor, *Bioscience, Biotechnology, and Biochemistry*, 80, 215-220.
- Jiang P., Prendergast D., Borondics F., Porsgaard S., Giovanetti L., Pach E., Newberg J., Bluhm H., Besenbacher F., Salmeron M., 2013, Experimental and theoretical investigation of the electronic structure of Cu₂O and CuO thin films on Cu (110) using x-ray photoelectron and absorption spectroscopy, *The Journal of Chemical Physics*, 138, 024704.
- Kuljiraseth J., Wangriya A., Malones J., Klysubun W., Jitkarnka S., 2019, Synthesis and characterization of AMO LDH-derived mixed oxides with various Mg/Al ratios as acid–basic catalysts for esterification of benzoic acid with 2-ethylhexanol, *Applied Catalysis B: Environmental*, 243, 415-427.
- Luo M.-F., Fang P., He M., Xie Y.-L., 2005, In situ XRD, Raman, and TPR studies of CuO/Al₂O₃ catalysts for CO oxidation, *Journal of Molecular Catalysis A: Chemical*, 239, 243-248.
- Rao M.M., Reddy B.R., Jayalakshmi M., Jaya V.S., Sridhar B., 2005, Hydrothermal synthesis of Mg–Al hydrotalcites by urea hydrolysis, *Materials Research Bulletin*, 40, 347-359.
- Sato A.G., Volanti D.P., de Freitas I.C., Longo E., Bueno J.M.C., 2012, Site-selective ethanol conversion over supported copper catalysts, *Catalysis Communications*, 26, 122-126.
- Xia S., Zheng L., Wang L., Chen P., Hou Z., 2013, Hydrogen-free synthesis of 1, 2-propanediol from glycerol over Cu–Mg–Al catalysts, *RSC Advances*, 3, 16569-16576.
- Xiu Z.-L., Zeng A.-P., 2008, Present state and perspective of downstream processing of biologically produced 1, 3-propanediol and 2, 3-butanediol, *Applied Microbiology and Biotechnology*, 78, 917-926.
- Yun Y.S., Park D.S., Yi J., 2014, Effect of nickel on catalytic behaviour of bimetallic Cu–Ni catalyst supported on mesoporous alumina for the hydrogenolysis of glycerol to 1, 2-propanediol, *Catalysis Science & Technology*, 4, 3191-3202.