Influence of Partially-Substituted Zr into Mg$_{4.78}$Al Layered Double Oxide on Glycerol Conversion to Valuable Specialty Bio-Based Chemicals

Tuangrat Leungcharoenwattana[a,b], Sirirat Jitkarnka[b,*]

[a]The petroleum and petrochemical college, Chulalongkorn University, Phayathai Rd. 254, 10330 Bangkok, Thailand;
[b]Center of Excellence on Petrochemical and Materials Technology, Chulalongkorn University Research Building, Soi Chulalongkorn 12, Phayathai Rd., Bangkok 10330, Thailand
sirirat.j@chula.ac.th

Glycerol is a by-product from bio-diesel production. It is used to be a feedstock for producing useful chemicals such as acrolein, lactic acid, ethanol, and 1,2 propanediol via various reactions such as oxidation, hydrogenolysis, acetalization, etherification, and transesterification. For this work, a Mg4.78Al-layered double oxide was used as a catalyst for glycerol conversion to 1,2 propanediol as a desired product. Moreover, the effect of zirconium on glycerol conversion was also investigated using the Zr partially-substituted layered double oxide catalyst (Zr0.38Mg4.54AlO). The catalysts were synthesized by using co-precipitation method. After calcination, the characterization was carried out using XRD, XRF, BET, NH$_3$-TPD and CO$_2$-TPD techniques. In addition, the products were analyzed by using a GC-TOF/MS. The reaction was performed in PARR reactor at 180 °C for 4 h. Using the Mg4.78AlO catalyst, ethanol, diglycerol, 1,2 propanediol, and acetone were observed as products at this condition. Using the Zr0.38Mg4.54AlO catalyst, the zirconium was found to improve the glycerol conversion, and the selectivity of acetaldehyde was increased to 68.6 %.

1. Introduction

In transportation, biofuels, derived from vegetable oil, soybean oil, animal fat through transesterification with methanol in the presence of an alkali or acid homogeneous catalyst, are mostly used as biodiesel (Quispe et al., 2013). During the reaction, glycerol is formed as a by-product with a low commercial value. Although 1,000 kg biodiesel production produces only 100 g glycerol (Thanasilp et al., 2016), high biodiesel demand leads to the increase of biodiesel production and then the accumulation of glycerol. Thus, the use of glycerol as feedstock for the production of valuable chemicals is an interesting topic. Among the various ways for glycerol conversion, the glycerol hydrogenolysis has been emerged as an attractive reaction because it can produce useful chemicals such as 1,2 propanediol, 1,3 propanediol, ethanol, and acetaldehyde (Sun et al., 2016). Generally, the glycerol hydrogenolysis involves the C-O bond cleavage or the dehydration of glycerol to form intermediate compounds such as acetol and 3-hydroxypropionaldehyde over an acid site, and then converted to various products such as 1,2 propanediol and 1,3 propanediol via hydrogenation in the need of H$_2$ (Nanda et al., 2017). Moreover, glycerol can be dehydrogenated over a basic site to provide H$_2$, which can be directly supplied to the hydrogenation step (Nakagawa et al., 2011). Therefore, the appropriate acid-base properties of the catalysts are required to produce specialty bio-based chemicals from glycerol conversion.

Layered double hydroxide (LDH), known as a hydrotalcite-like compound (HTlc), is an anionic clay whose general structure is $[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+}[X^{n-1}_{x/m} \cdot nH_2O]$ (Cavani et al., 1991). When calcined, it is converted to a layered double oxide (LDO) with high specific surface area, pore size, and pore volume (Yang et al., 2002). Additionally, the acid-base properties can also be adjusted by incorporation of a third ion that can be either M^{2+}, M^{3+} or M^{4+} (Dębek et al., 2017). It has been reported that a Zr partially-substituted layered double oxide is an effective catalyst for various reactions of glycerol conversion. For instances, ZrMgAl was used as a catalyst in the transesterification reaction of glycerol and dimethyl carbonate to glycerol carbonate. The experiment was set up at 75 °C, 90 min, and with the varied ratio of Mg:Al:Zr at 1:1:1, 2:1:1, and 3:1:1. It was found that the

Mg:Al:Zr ratio of 3:1:1 possessed some strong basic sites that were responsible for high transesterification activity. As a result, the Mg:Al:Zr ratio of 3:1:1 at a temperature calcination of 650 °C provided the highest glycerol carbonate selectivity of 91 % (Malyaadri et al., 2011). Moreover, Wang et al. (2018) studied the glycerol carbonate production from glycerol and urea with the varying $Zr^{4+}:(Al^{3+} + Zr^{4+})$ ratio from 0 to 0.7. It was revealed that the effective catalyst consisted of the balanced number of acid and basic sites, which provided a great amount of glycerol carbonate, and the MgAlZr with $Zr^{4+}:(Al^{3+} + Zr^{4+})$ ratio of 0.3 gave the best glycerol carbonate selectivity of 90.8 % and glycerol carbonate yield of 87.8 %. Moreover, Zr-mixed oxides in the forms of Ni-La-X mixed oxide (X: can be Ce and/or Zr) have found to be potential catalysts for H_2 production from the steam reforming of glycerol. The result showed that the low thermal conductivity of Zr reduced the thermal diffusion of different metal atoms in the catalyst, and then caused sintering that led to deceleration. Moreover, Zr also helped to increase the oxygen mobility in the Ce structure, and enhanced the vacancy formation, which was related to the stabilization of active phase of catalyst. As a result, the NiCeLaZr catalyst provided the highest H_2 yield of 63.7 % (Veiga et al., 2019). In addition, ZrO_2-grafted SBA-15 was used as a catalyst in the glycerol dehydration to acrolein, resulting that acrolein selectivity was decreased whereas acetol selectivity doubled. It can be explained that the introduction of ZrO_2 over SBA-15 increased the Lewis acid sites, which leads to the formation of acetol by the C-O cleavage of the terminal OH-group of glycerol (Katryniok et al., 2010). Therefore, the acid-base properties on the Zr-containing catalyst were beneficial parameters for the multi-step reactions of glycerol to specially bio-based chemicals.

In summary, the Zr-substituted layered double oxides were effective towards various reactions; namely, transesterification, steam reforming and dehydrogenation. However, the use of ZrMgAl in the glycerol hydrogenolysis reaction has been not extensively investigated. In this work, the glycerol conversion using Zr as a promoter partially substituted into a MgAl-layered double oxide was therefore investigated on the attempt to produce valuable chemicals from the hydrogenolysis of glycerol. It was expected that the presence of acidity and basicity of Zr, which is resulted from the partial substitution into the layered structure of a LDH, is essential for the glycerol hydrogenolysis reaction; that are, the new acid site evolved from Zr substitution can improve the dehydration step whereas the new basic sites, also created from the Zr substitution and from original Mg^{2+} in the structure, can improve the formation of in-situ H_2 that is necessary for the hydrogenation step. Furthermore, the parent MgAl-layered double oxide was also tested as a catalyst in order to investigate the effect of Zr on the performance of catalyst.

2. Methodology

2.1 Catalyst preparation

The $Mg_{4.78}Al$-LDH and $Zr_{0.38}Mg_{4.54}Al$-LDH was done using co-precipitation method. An aqueous solution, containing a mixture of $Mg(NO_3)_2 \cdot 6H_2O$, and $Al(NO_3)_3 \cdot 9H_2O$, with or without $ZrO(NO_3)_2 \cdot xH_2O$, and Na_2CO_3 dissolved in 700 mL deionized water at a constant pH ($\approx$10), were first prepared. After that, the mixture was stirred at room temperature for 10 h. The precipitate was filtered and washed with deionized water until pH 7. Next, the obtained solid was dried in an oven at 65 °C for 12 h. Finally, the $Mg_{4.78}Al$-LDO and $Zr_{0.38}Mg_{4.54}Al$-LDO catalysts were obtained from calcination of the precipitates at 500 °C for 5 h.

2.2 Catalyst characterization

The physicochemical properties of $Mg_{4.78}Al$-LDO and $Zr_{0.38}Mg_{4.54}Al$-LDO catalysts were characterized by various methods. X-ray diffraction (XRD) was used to identify the crystallinity of catalysts on a Rikagu SmartLab X-Ray Diffractometer. XRD patterns were recorded in the 5 – 70 ° (2θ) range using a scan speed of 5 ° (2θ)/min. Mole ratio of catalysts were analyzed by X-Ray fluorescence spectrometer (XRF) with measurement method of Best Detection-Vac8mm. The Brunauer-Emmett-Teller (BET) technique, Surface Area Analyzer (Quantachrome, Autosorb-1MP) with Multipoint nitrogen adsorption and desorption isotherm plots used to determined specific surface area, total pore volume, and pore size of catalysts. The acidity and basicity of the calcined catalysts were found via temperature programmed desorption of ammonia (NH_3-TPD) and carbon dioxide (CO_2-TPD) using the Temperature Programmed Desorption/Reduction/Oxidation Analyzer (TPDRO), TPDRO Analyzer, BELCAT II. The sample was pre-treated in 10.03 % NH_3/He or 99.995 CO_2 at 100 °C for 30 min. After that the temperature was heated from 100 to 650 °C at a heating rate of 10 °C/min and maintained for 30 min with He (30 cc/min), and the results were calculated from the peak area under the TPD profiles.

2.3 Catalytic reaction

The catalytic activity of glycerol hydrogenolysis was carried out in a 250 mL of Series 4576 HP/HT reactor (Parr company). Glycerol solution with 1 g of catalysts were introduced into the reactor, and the reactor was then purged with N_2 gas for 30 min. Next the reaction was performed at 180 °C for 4 h under constant stirring speed at 300 rpm. After that the reactor was cooled to room temperature. The liquid phase products were centrifuged

to separate the solid catalyst and analyzed by using a 1D Gas Chromatography-equipped with a Mass Spectrometry of Time-of-Flight Type (a LECO Pegasus GC × GC-TOFMS). The glycerol conversion, product selectivity, and yields were calculated using Eqs. (1)-(3), respectively.

$$Conversion\ (\%) = \frac{moles\ of\ glycerol\ consumed}{moles\ of\ glycerol\ initially\ charged} \times 100 \tag{1}$$

$$Selectivity\ (\%) = \frac{moles\ of\ specific\ product}{moles\ of\ detected\ product} \times 100 \tag{2}$$

$$Yield\ (\%) = \frac{glycerol\ conversion\ (\%) \times Selectivity\ of\ a\ product\ (\%)}{100} \tag{3}$$

3. Results and discussion

3.1 Catalyst characterization

The XRD patterns of as-prepared $Mg_{4.78}AlO$ and $Zr_{0.38}Mg_{4.54}AlO$ catalysts (Figure 1) show the characteristic diffraction peaks of hydrotalcite phase, which are located at 11.19°, 22.69°, 34.41°, 38.49°, 45.6°, 60.34°, and 61.55° with the sharp and intense reflections of (003), (006), (009), (015), (018), (110), and (113) planes. They indicated the successful synthesis of catalysts. The XRD patterns of catalysts calcined at 500 °C are also shown in Figure 1. Obviously, the characteristic pattern assigned to the hydrotalcite phases disappears, indicating that the layered structure was collapsed. The calcined $Mg_{4.78}AlO$ and $Zr_{0.38}Mg_{4.54}AlO$ catalysts exhibit three diffraction peaks at 35.6°, 43.2°, and 62.5°, which can be defined to the periclase MgO-like structure. Moreover, the calcined $Mg_{4.78}AlO$ catalyst also shows the diffraction peaks of $MgAl_2O_4$ spinel at 18.94°, 31.27°, 36.86°, 44.86°, 48.85°, 48.50°, 55.78°, 59.42°, and 65.30° whereas the major peaks of the tetragonal phase of zirconia at 30.3°, 50.4°, and 60.2° cannot be detected in the calcined $Zr_{0.38}Mg_{4.54}AlO$ catalyst, possibly because it is dispersed very well or forms as amorphous phase. The compositions of the synthesized layered double oxides are also shown in Table 1. The Mg/Al mole ratio of MgAlO-catalyst is 4.78 whereas the ratio of Mg/Al in the Zr/Mg/Al mole ratio is lower because of the insertion of Zr in the LDH sheets. Moreover, the ZrO_2 content in the $Zr_{0.38}Mg_{4.54}AlO$ catalyst is 20.4 wt%. The presence of Zr is also associated with the decrease of surface area, pore volume, and pore diameter of the $Zr_{0.38}Mg_{4.54}AlO$ catalyst (see Table 1). Both acidic and basic sites of catalysts are summarized in Table 2. The strength can be determined from the desorption temperature at which peaks appear. The peaks at a low temperature (150-200 °C), a medium temperature (200-260 °C), and a high temperature (260-350 °C) represent weak Bronsted basic sites (OH⁻ groups on the surface), medium strength Lewis basic site (Mg^{2+}-O^{2-} pairs), and strong Lewis basic sites (O^{2-}), respectively (Kuljiraseth et al., 2019). Moreover, the previous report has proven that the MgxAlO catalysts possess two identified types of acid.
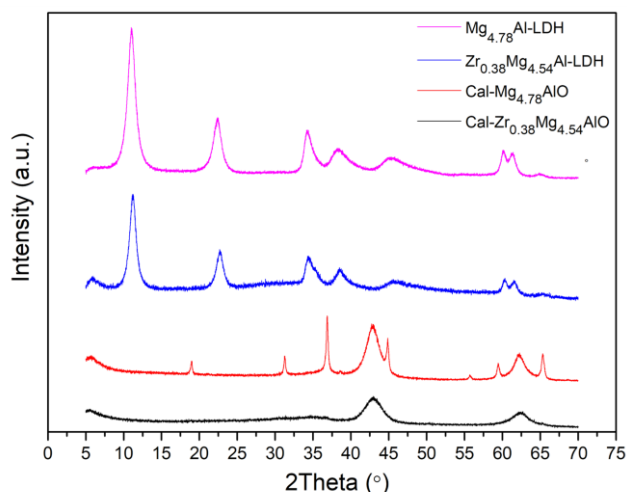

Figure 1: XRD patterns of catalytic samples before and after calcination

The weak acid site (150 -200 °C) was assigned to the surface OH group, and the strong acid site (200-350 °C) was assigned to Lewis acid site from Al^{3+}- O^{2-} pairs (Kuljiraseth et al., 2019). Therefore, the $Mg_{4.78}AlO$ and $Zr_{0.38}Mg_{4.54}AlO$ catalysts contain only weak and strong acid sites, as shown in Table 2. As a result, the partial substitution of Zr into the Mg-Al LDH enhances the total acidity and basicity. When Zr is substituted in the position of Mg^{2+} in the LDH layers, new Zr-O-Mg and Zr-O-Al bonds are formed. Since the electronegativity of Zr is higher than that of Mg, but lower than that of Al (Mg < Zr < Al = 1.31 < 1.33< 1.61), the new Zr-O-Mg bond

therefore creates a new weaker Lewis acid site (Zr^{2+}-O^{2-} pairs) than that from Al^{3+}-O^{2-} pairs whereas the new Zr-O-Al bond creates a new Lewis basic site (Zr^{2+}-O^{2-} pairs). Therefore, the OH group and low-coordination oxygen atoms in the vicinity of Zr are associated with the increase in weak and strong basic sites from 0.298 to 0.905 and 0.325 to 1.051 mmol/g.

Table 1: Physical properties of calcined catalysts

Catalyst	Relative mole ratio [a]	Content of ZrO_2 (wt%) [a]	Surface area (m^2/g) [b]	Pore Volume (cm^3/g) [b]	Pore Diameter (Å) [b]
$Mg_{4.78}AlO$	4.78/1.00	-	158.4	0.3757	94.85
$Zr_{0.38}Mg_{4.54}AlO$	0.38/4.54/1.00	20.4	107.3	0.1246	46.44

[a] determined using XRF, [b] determined using BET

Table 2: Acid-base properties of calcined catalysts

Catalyst	Density of acid sites (mmol/g)[a]			Density of basic sites (mmol/g)[b]			
	Weak [c]	Strong [d,e]	Total acidity	Weak [c]	Medium [d]	Strong [e]	Total basicity
$Mg_{4.78}AlO$	0.107	0.088	0.195	0.298	0.071	0.325	0.694
$Zr_{0.38}Mg_{4.54}AlO$	0.278	0.529	0.807	0.905	0.184	1.051	2.140

[a] Determined using NH_3-TPD, [b] Determined using CO_2-TPD, [c] Low temperature peak, [d] Medium temperature peak
[e] High temperature peak

3.2 Catalytic activity

The $Zr_{0.38}Mg_{4.54}AlO$ catalyst was tested on the glycerol hydrogenolysis at a reaction temperature of 180 °C for 4 time-on-stream as compared with the $Mg_{4.78}AlO$ catalyst in order to investigate the influence of Zr partially-substituted layered double oxide. The results of activity tests are summarized in Figures 2 and 3. The conversion of glycerol on the $Mg_{4.78}AlO$ catalyst is 14.3 % as shown in Figure 2a. Interestingly, ethanol is produced as the major product with 86.7 % selectivity as shown in Figure 3a. Additionally, the other products such as diglycerol, 1,2 propanediol, and acetone are also formed with the selectivity of 9.66 %, 2.14 %, and 1.47 % (Figure 3a). It is noticed that the 1,2 propanediol selectivity is low possibly because it can be further converted to ethanol, which can be explained using the possible reaction pathways (Figure 4). According to the pathways, glycerol can be dehydrogenated to glyceraldehyde on the basic sites, whereas the acid sites catalyze the dehydration of glycerol to acetol that is further hydrogenated to 1,2 propanediol. After that, 1,2 propanediol can be dehydrated to acetone by the acid sites, and it is also converted to ethanol via the hydrogenation reaction. Moreover, ethanol can be dehydrogenated to acetaldehyde, which is governed by basic sites. In addition, diglycerol can be formed by polymerization of glycerol on basic sites. Thus, mostly in this case, the $Mg_{4.78}AlO$ catalyst promotes the hydrogenation of 1,2 propanediol to ethanol as the main reaction pathway. All the product yields are shown in Figure 2b. It is found that the $Mg_{4.78}AlO$ catalyst gives 12.4 % ethanol, 1.38 % diglycerol, 0.31 % 1,2 propanediol, and 0.21 % acetone yield.

The $Zr_{0.38}Mg_{4.54}AlO$ catalyst enhances the glycerol conversion from 14.3 % to 36.8 %. Acetaldehyde is produced as the major product with 68.6 % selectivity as shown in Figure 3b. In addition, the other products such as ethanol, 1,2 propanediol, and acetone are also formed with the selectivity of 22.4 %, 7.21 %, and 1.86 %, respectively (Figure 3b). The introduction of zirconium ions increases the surface concentration of acid and basic sites, which are confirmed by results of NH_3-TPD and CO_2-TPD. The increasing acid density improves the dehydration of glycerol to acetol. The high basic density enhances the glycerol dehydrogenation that produces in-situ H_2 to boost up the hydrogenation of acetol to 1,2 propanediol, which can be confirmed by 1,2 propanediol yield that increases from 0.31 % to 2.65 %. Moreover, It can be seen that, $Zr_{0.38}Mg_{4.54}AlO$ provides acetaldehyde yield of 25.2 %; meanwhile, ethanol yield decreases from 12.4 % to 8.22 %. It can be explained that the further conversion of 1,2 propanediol to ethanol takes place, leading to further dehydrogenation of ethanol to acetaldehyde as shown in the possible reaction pathways (Figure 4). The reaction pathways for $Mg_{4.78}AlO$ and $Zr_{0.38}Mg_{4.54}AlO$ catalysts are hence similar, but the $Zr_{0.38}Mg_{4.54}AlO$ catalyst can further dehydrogenate ethanol to acetaldehyde. Thus, Zr partially substituted in the catalyst plays crucial roles on (a) the glycerol hydrogenolysis, (b) the in-situ H_2 generation via glycerol dehydrogenation, (c) the hydrogenation of 1,2 propanediol to ethanol, and (d) the dehydrogenation of ethanol to acetaldehyde.
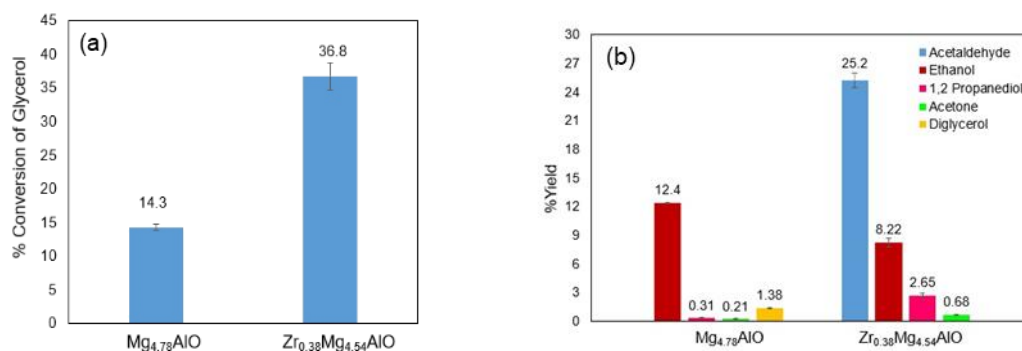
Figure 2: (a) Glycerol conversion, and (b) Yield of products obtained from using $Mg_{4.78}AlO$ and $Zr_{0.38}Mg_{4.54}AlO$ catalysts
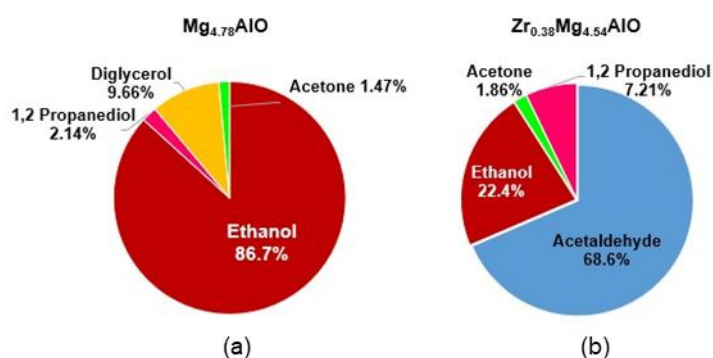

Figure 3: Selectivity of glycerol conversion products using (a) $Mg_{4.78}AlO$, and (b) $Zr_{0.38}Mg_{4.54}AlO$ catalysts
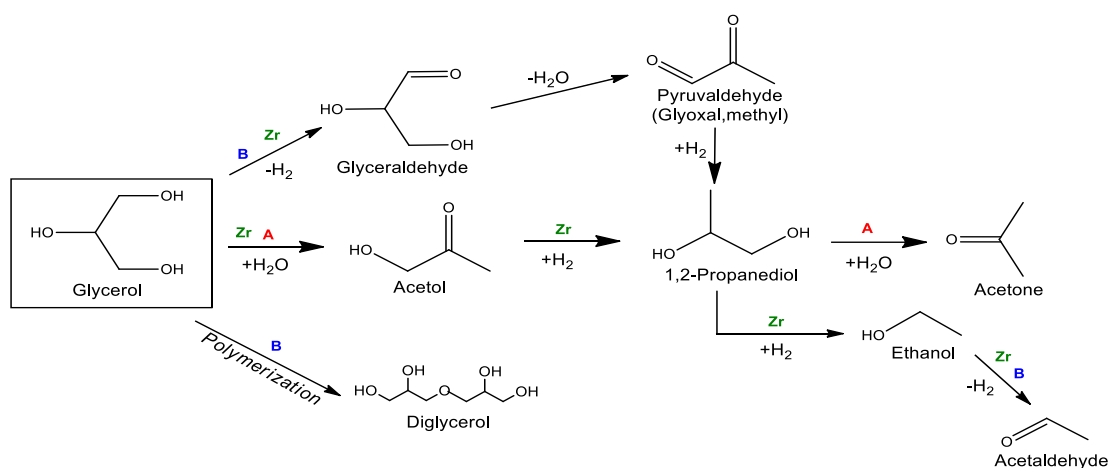

Figure 4: Proposed reaction pathways of glycerol conversion using $Mg_{4.78}AlO$ and $Zr_{0.38}Mg_{4.54}AlO$ catalysts, where A = Acid, B = Base, and Zr = Zirconia

4. Conclusions

The partial substitution of Zr into the MgAl-LDH markedly changed the physical and the chemical properties of the layered double oxide catalyst. Although the substitution led to the decreases of surface area, pore volume, and pore diameter, the catalyst possessed the markedly-greater density of basic sites. Consequently, the glycerol conversion increased, with the formation of ethanol, 1,2 propanediol, acetone, as the products. Acetaldehyde was produced via the further dehydrogenation of ethanol, So the Zr promoter played crucial roles

on glycerol hydrogenolysis, glycerol dehydrogenation, 1,2 propanediol hydrogenation, and ethanol dehydrogenation in the proposed pathways.

Acknowledgments

References

Cavani F., Trifiro F., Vaccari F., 1991, Hydrotalcite-type anionic clays: Preparation, properties and applications, Catalysis Today, 11(2), 173-301.

Dębek R., Motak M., Grzybek T., Galvez M., Da Costa P., 2017, A short review on the catalytic activity of hydrotalcite-derived materials for dry reforming of methane, Catalysts, 7(1), 32, DOI: 10.3390/catal7010032.

Katryniok B., Paul S., Capron M., Lancelot C., Bellière-Baca V., Rey P., Dumeignil F., 2010, A long-life catalyst for glycerol dehydration to acrolein, Green chemistry, 12(11), 1922-1925.

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.

Malyaadri M., Jagadeeswaraiah K., Prasad P.S., Lingaiah N., 2011, Synthesis of glycerol carbonate by transesterification of glycerol with dimethyl carbonate over Mg/Al/Zr catalysts, Applied catalysis A: General, 401(1-2), 153-157.

Nakagawa Y., Tomishige K., 2011, Heterogeneous catalysis of the glycerol hydrogenolysis, Catalysis Science & Technology, 1(2), 179-190.

Nanda M., Yuan Z., Shui H., Xu C., 2017, Selective Hydrogenolysis of Glycerol and Crude Glycerol (a By-Product or Waste Stream from the Biodiesel Industry) to 1, 2-Propanediol over B_2O_3 Promoted Cu/Al_2O_3 Catalysts, Catalysts, 7(7), 196, DOI: 10.3390/catal7070196.

Quispe C.A., Coronado C.J., Carvalho Jr J.A., 2013, Glycerol: production, consumption, prices, characterization and new trends in combustion, Renewable and Sustainable Energy Reviews, 27, 475-493.

Sun D., Yamada Y., Sato S., Ueda W., 2016, Glycerol hydrogenolysis into useful C3 chemicals, Applied Catalysis B: Environmental, 193, 75-92.

Thanasilp S., Schwank J.W., Meeyoo V., Pengpanich S., Hunsom M., 2016, Liquid Phase Oxydehydration of Glycerol to Acrylic Acid over Supported Silicotungstic Acid Catalyst: Influence of Reaction Parameters, Science, Engineering and Health Studies (Silapakorn Univ. of Science and Technology), 10(2), 9-21.

Veiga S., Romero M., Faccio R., Segobia D., Duarte H., Apesteguía C., Bussi J., 2019., Hydrogen-rich gas production by steam and oxidative steam reforming of crude glycerol over Ni-La-Me mixed oxide catalysts (Me= Ce and/or Zr), Catalysis Today, DOI: 10.1016/j.cattod.2019.02.008.

Yang W., Kim Y., Liu P.K., Sahimi M., Tsotsis T.T., 2002, A study by in situ techniques of the thermal evolution of the structure of a Mg–Al–CO3 layered double hydroxide, Chemical Engineering Science, 57(15), 2945-2953.