Catalytic Activity of Reduced Cu-Mg-Al Layered Double Oxide on Transformation of 1-Butanol into Butyl Butyrate

Sirinan Pattane[a], Sirirat Jitkarnka[a,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

Butyl butyrate can be synthesised from 1-butanol through two steps; that are, 1-butanol dehydrogenation to butanal over basic sites and metal sites, and then the butanal Tishchenko reaction-type self-esterification of butanal, forming butyl butyrate over an acid site and a basic site. The 1-butanol conversion to butyl butyrate requires a catalyst that has the combination of an acid site, a basic site and a metal site. In this work, the activity of reduced $Cu_{0.3}Mg_{1.7}AlO$ towards the production of butyl butyrate was studied in a PARR reactor at 300 °C for 4 h. The liquid samples were analysed using a Pegasus LECO GC-TOF/MS. The gas samples were analysed using a gas chromatograph equipped with a flame ionized detector (GC-FID). The catalysts were characterised using powder-XRD, BET, TPD-CO_2, TPD-NH_3 and XRF techniques. The results indicated that the non-catalytic case gave 28.6 % 1-butanol conversion, and butyl butyrate was not found. In contrast, the reduced $Cu_{0.3}Mg_{1.7}AlO$ gave 29.6 % 1-butanol conversion. The relative yield of butyl butyrate over the reduced $Cu_{0.3}Mg_{1.7}AlO$ was enhanced to 74.0 % because the metallic Cu and basic sites promoted the dehydrogenation of 1-butanol, acid and basic sites promoted the Tishchenko reaction-type self-esterification of butanal to butyl butyrate.

1. Introduction

Butyl butyrate has a specific fruity smell similar to pineapple, as it is widely used as flavour-giving compounds in food, cosmetic, and pharmaceutical industries (Ndaba et al., 2015). It is also used as a solvent in the plastic, texture and fiber industries and biofuel sector (Xin et al., 2019). It is produced from several methods such as extraction, acetone-butanol-ethanol fermentation, and fischer esterification process. The interesting method is the production of butyl butyrate from 1-butanol as a bio-based raw material. 1-butanol is normally produced through the fermentation of renewable biomass such as sugar, starch, and lignocellulose (Ndaba et al., 2015). It can be used as a reactant to produce several chemicals such as butyl butyrate, 2-butene, butyl acrylate, and methacrylate (Ndaba et al., 2015). Several researchers have studied 1-butanol dehydrogenation and dehydration using vanadium aluminium oxynitrides, MgO, CaO, $SiO_2Al_2O_3$ (Florea et al., 2011), Rh/ZrO_2 (Harju et al., 2016), and Cu/ZrO_2 and Cu/ZrO_2-CeO_2 (Requies et al., 2012). Florea et al. (2011) studied 1-butanol dehydrogenation and dehydration over vanadium aluminium oxynitrides, MgO, CaO and $SiO_2Al_2O_3$. The dehydrogenation of 1-butanol to butanal occurred on the basic catalysts (MgO or CaO) and the dehydration reaction was driven on acid catalysts ($SiO_2Al_2O_3$). They used vanadium aluminium oxynitrides that have both acid and basic sites, which can promote both 1-butanol dehydrogenation to butanal and dehydration to 1-butene. Harju et al. (2016) studied conversion of 1-butanol over Rh/ZrO_2 catalyst. They reported that the 1-butanol can convert to butanal via dehydrogenation over the Rh and ZrO_2 basic catalysts while the 1-butanol dehydration was driven on ZrO_2 acid catalysts. The small amount of butyl butyrate was found in butanal conversion via Tischenko reaction. Requies et al. (2012) studied Cu catalysts supported on ZrO_2 and ZrO_2 modified with CeO_2 for the production of butanal from 1-butanol, and they found that the copper loading had a strong influence on increasing the butanal yield. Tsuji et al. (1994) studied the conversion of butanal over solid base catalysts such as MgO, CaO and alkali-modified alumina catalysts and alkali ion-exchanged zeolite, and they found that two main pathways were promoted, including butanal aldol condensation to 2-ethyl-3-hydroxyhexanal over basic

sites and the Tishchenko reaction-type self-esterification of butanal to butyl butyrate over acidic and basic sites. The acid and basic properties of catalysts play a critical role on butanal conversion to butyl butyrate via Tishchenko reaction-type self-esterification. However, the previously employed catalysts were reported to give a low 1-butanol conversion and a low butyl butyrate yield.

In summary, the production of butyl butyrate from 1-butanol is driven through two steps of consecutive reactions. The first step is 1-butanol dehydrogenation to butanal, and then the Tishchenko reaction-type esterification of butanal to butyl butyrate as presented in Figure 1. Based on the reaction step of 1-butanol conversion to butyl butyrate, all acid, basic and metal sites play the critical role. Layered Double Hydroxides (LDHs) that have both acid and basic sites can play important roles on the conversion of 1-butanol to butyl butyrate. When an LDH is calcined, a layered double oxide (LDO) is formed. The calcination does not only increases acid and base sites (Díez et al., 2003), but also improves the surface area as well (Dixit et al., 2013). In our previous work, Kuljiraseth et al. (2019) studied the different Mg/Al ratios of LDH-derived Mg_xAlO catalysts for the esterification of benzoic acid with 2-ethylhexanol. They found that the Mg_2AlO catalyst (Mg : Al = 2 : 1) had the highest acidity and basicity, and gave the highest yield of 2-ethylhexyl benzoate. The selectivity of products was found to depend on the phase compositions, elemental composition, and acid-base pairs sites (Mg^{2+}-$O^{2-}$and Al^{3+}-O^{2-}pairs). Cu–Mg–Al mixed metal oxide, derived from the hydrotalcite precursor, was easily synthesised, and presented a good metal dispersion (Mazarío et al., 2020). Based on the literature review, not so many catalysts had been widely investigated on 1-butanol conversion to butyl butyrate. Most of them still presented a low 1-butanol conversion and butyl butyrate yield. Consequently, the attempt to enhance 1-butanol conversion and butyl butyrate yield over a catalyst is challenging. Since a reduced $Cu_{0.3}Mg_{1.7}AlO$ catalyst possesses a combination of acid, basic, and metal sites that play important roles on the conversion of 1-butanol to butyl butyrate, the catalytic activity of reduced $Cu_{0.3}Mg_{1.7}AlO$ on the conversion of 1-butanol into butyl butyrate was investigated in this research work. The purpose of this work was to enhance the 1-butanol conversion and butyl butyrate yield. The metallic Cu and base sites were expected to promote the dehydrogenation of 1-butanol to butanal, and then the acid and basic sites promote the Tishchenko reaction-type self-esterification of butanal to butyl butyrate. The catalyst samples were characterised using powder XRD, BET, $TPD-CO_2$, $TPD-NH_3$ and XFR techniques were carried out in PARR reactor at 300 °C for 4 h.
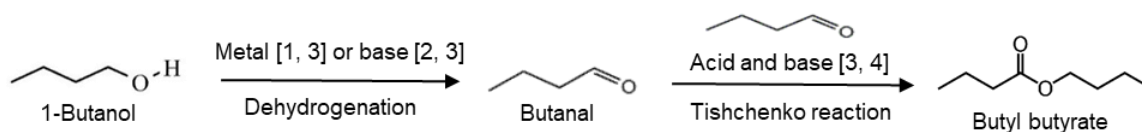

Figure 1: Reaction pathway of 1-butanol conversion to butyl butyrate. [1] = Requies et al., (2012); [2] = Florea et al., (2011); [3] = Harju et al., 2016); [4] = Tsuji et al., (1994)

2. Experimental

2.1 Synthesis of reduced $Cu_{0.3}Mg_{1.7}AlO$

The reduced $Cu_{0.3}Mg_{1.7}AlO$ catalyst was prepared using a co-precipitation method according to the following steps. First, Solution A was prepared by dissolving 0.2975 mol magnesium nitrate hexahydrate ($Mg(NO_3)_2 \cdot 6H_2O$), 0.0525 mol copper nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$), and 0.175 mol aluminum nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$) into 700 mL of deionized water in a beaker. Solution B was prepared by dissolving 0.35 mol sodium carbonate in 700 mL of deionized water in a three-neck round bottom flask. Next, Solution A was added drop-wise to Solution B, at a rate of 140 mL/min under vigorous stirring as a speed of 1,000 rpm. At the same time, the 4 M sodium hydroxide was added to the mixture little by little. The pH was kept constant at 10. After stirring for 16 h, the obtained slurry was filtered, and the solid product was washed with deionized water to pH at 7, and then dried in air oven at 65 C for overnight. The obtained $Cu_{0.3}Mg_{1.7}Al$-LDH was calcined at 500 °C for 5 h in air to form $Cu_{0.3}Mg_{1.7}Al$-LDO, followed by reduction at 500 °C under 5 % H_2/N_2 (30 mL/min) to obtain the reduced $Cu_{0.3}Mg_{1.7}AlO$ catalyst.

2.2 Catalyst characterisation

XRD was used to analyse the crystal structure and the chemical composition of a sample. The Powder X-ray diffraction (XRD) patterns were recorded using a X-Ray diffractometer (Rigaku SmartLab). The X-Ray Diffractograms were recorded with scan 0.02° (2θ) steps over the 5-70° (2θ) angular range with 0.6 s counting time per step. The chemical composition and the concentration of elements in a sample were determined by X-Ray Fluorescence (WDXRF) using a Bruker S8 Tiger spectrometer. The Brunauer-Emmett Teller method, Surface Area Analyser (Quantachrome, Autosorb-1MP) was used to calculate specific surface area, total pore

volume, and pore diameter of a sample. Prior to nitrogen adsorption, the sample was initially outgassed under vacuum at 250 °C for 18 h. Temperature-programmed reduction was used to determine the acidity and basicity of the catalyst using the temperature-programmed desorption/ oxidation analyser (TPDRO) (BELCAT II).

2.3 Catalytic testing

The catalytic conversion of 1-butanol was carried out in a PARR reactor (Model 4576 High Temperature/High Pressure Reactor) equipped with a stirrer and an automatic temperature controller (Model 4843). Frist, a 40 ml of pure 99.5 % 1-butanol and 1 g of a catalyst were added into the reactor. Prior to the reaction, the reactor was sealed and flushed out with 99.99 % N_2 gas at room temperature for 30 min to eliminate air in the PARR reactor. The reaction was typically conducted under the following conditions: 300 °C, 300 rpm stirring rate and 4 h reaction time. After reaction, the liquid sample was centrifuged to separate the catalyst, and then analysed using a 1D-Model Pegasas LECO GC-TOF/MS equipped with the Rxi-PAH (60 m × 0.25 mmID and 0.01 ⌈m film thicknesses) column. The gas sample was collected in a gas sampling chamber, and then analysed using a gas chromatography (Agilent Technologies 6890 Network GC system) using an HP-PLOT S Al_2O_3 column (50m × 0.53 mm ID and 15 μm film thicknesses) equipped with and a flame ionized detector (GC-FID).

3. Result and discussion

3.1 Characterisation

The XRD patterns of the $Cu_{0.3}Mg_{1.7}Al$-LDH, calcined $Cu_{0.3}Mg_{1.7}AlO$, and reduced $Cu_{0.3}Mg_{1.7}AlO$ are presented in Figure 2. The pattern of $Cu_{0.3}Mg_{1.7}Al$-LDH exhibits the typical peaks of hydrotalcite-like structure (Kuljiraseth et al., 2019). The sharp peak at 2θ = 11.64 °, 23.50 ° and 34.86 ° together with the other broad and less intense peaks at 2θ = 39.30 °, 47.04 °, 60.80 ° are attributed to the diffraction by (003), (006), (009), (015), (018), (110), and (113). After calcination at 500 °C, for the calcined $Cu_{0.3}Mg_{1.7}AlO$, the typical diffraction peaks of hydrotalcite-like structure disappear, and the MgO phase occurs at 2θ of 35.24, 43.64, and 62.54 ° (Cheng et al., 2018). The $CuAl_2O_4$ and $MgAl_2O_4$ spinels cannot be found because they have characteristic peaks overlapping with the broad peak of MgO. The reduced $Cu_{0.3}Mg_{1.7}AlO$ exhibits the typical peaks similar to the XRD pattern of calcined $Cu_{0.3}Mg_{1.7}AlO$ showing the diffraction peaks at 51.04 ° that was defined to the presence of Cu (Salavati-Niasari et al., 2008) as shown in Figure 2c. Table 1 lists the molar concentration, specific surface area, total pore volume and pore diameter of reduced $Cu_{0.3}Mg_{1.7}AlO$ catalyst. The concentration of Cu, Mg and Al are 10.7, 23.1 and 14.5 wt %. The Cu/Al/Mg mole ratio is 0.31 / 1.77 / 1, which is almost the same as the expected mole ratio. The specific surface area and total pore volume are 167.3 m^2g^{-1} and 0.9363 cm^3g^{-1}. Pore diameter of 158.5 Å indicating a mesoporous material. The total acidity is 0.505 mmol/g and the total basicity is 0.625 mmol/g as shown in Table 2. The reduced $Cu_{0.3}Mg_{1.7}AlO$ catalyst was successfully synthesised and composed of acid, base and metal sites.
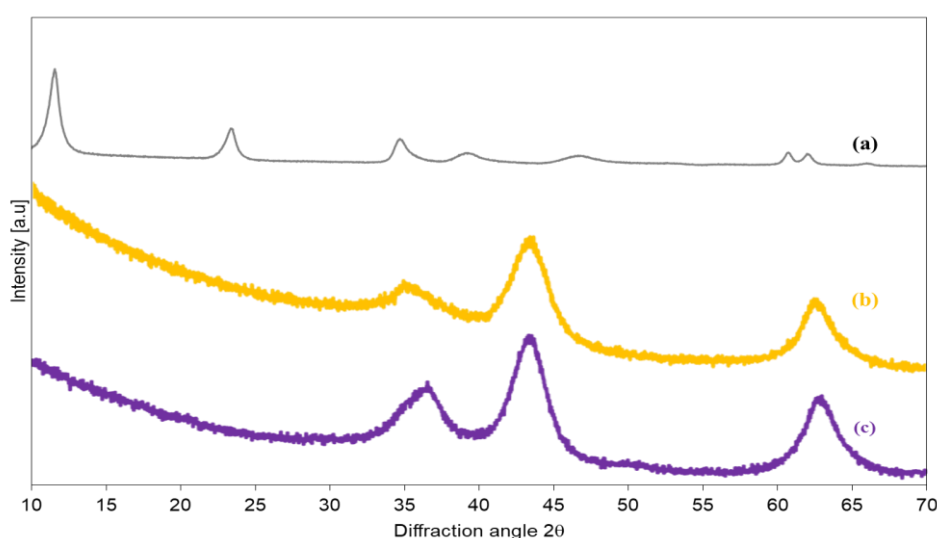

Figure 2: XRD patterns of (a) $Cu_{0.3}Mg_{1.7}Al$-LDH, (b) calcined $Cu_{0.3}Mg_{1.7}AlO$, and (c) reduced $Cu_{0.3}Mg_{1.7}AlO$ samples

Table 1: Physical properties of the reduced $Cu_{0.3}Mg_{1.7}AlO$ catalyst

Catalyst	Concentration (wt %)[a]			Mole ratio of Cu/ Mg/ Al[a]	Specific Surface Area (m^2g^{-1})[b]	Total Pore Volume (cm^3g^{-1})[b]	Pore Diameter (Å)[c]
	Cu	Mg	Al				
reduced $Cu_{0.3}Mg_{1.7}AlO$	10.73 ± 0.13	23.1 ± 0.00	14.50 ± 0.22	0.31 / 1.77 / 1	167.3	0.9363	158.5

[a] Determined using XRF method, [b] Determined using BET method, [c] Determined using BJH method

Table 2: Total acidity and basicity of the reduced $Cu_{0.3}Mg_{1.7}AlO$ catalyst

Catalyst	Total Acidity (mmol/g)[a]	Total Basicity (mmol/g)[b]
Reduced $Cu_{0.3}Mg_{1.7}AlO$	0.505	0.625

[a] Determined using TPD-NH_3, [b] Determined using TPD-CO_2

3.2 Catalytic activity

The 1-butanol conversion to butyl butyrate was studied at 300 °C at 4 h. The 1-butanol conversion of the non-catalytic case and on the reduced $Cu_{0.3}Mg_{1.7}AlO$ catalyst are 28.5 and 29.6 %, observing that both cases are not significantly different, indicating that at 300 ºC, 1-butanol was in a vapor phase that can be thermally converted, and its products can directly make a contact with the catalyst. However, the catalyst did not convert more 1-butanol, but it can convert the products from thermally-converted 1-butanol, as indicated by the differences in selectivity as follows. Without using the catalyst, 1-butanol is converted to various products via thermal conversion, giving acetone (60.2 %) as a major product. The other products such as mixed C4, butanal, 2-propanol, and ethanol are also formed with the relative yield of 3.1 %, 15.0 %, 6.0, and 0.8 %, as shown in the Figure 4a. It can be explained that 1-butanol can be converted to acetone in 3 steps. Firstly, 1-butanol radicals primarily undergo □-scission to form ethanol (Sarathy et al., 2012), and then ethanol is dehydrogenated to acetaldehyde (Zhang et al., 2006), followed by the acetaldehyde condensation to acetone (Dagaut et al., 2009). Acetone can be further converted to 2-propanol via hydrogenation reaction.

The reduced $Cu_{0.3}Mg_{1.7}AlO$ catalyst significantly produces butyl butyrate with 74.0 % yield (Figure 4b). The other products such as mixed C4, acetone, butanal, and ethanol are also formed with the relative yield of 2.5 %, 0.1 %, 0.2 %, and 0.1 %, which can be explained using the possible reaction pathways (Figure 1). 1-Butanol can be converted to butyl butyrate in two steps. The First step is 1-butanol dehydrogenation to butanal, which can be performed over basic sites (Harju et al., 2016) and metal sites (Requies et al., 2012), and then to butyl butyrate via the Tishchenko reaction-type self-esterification of butanal over acid sites (Harju et al., 2016) and basic sites (Tsuji et al., 1994).
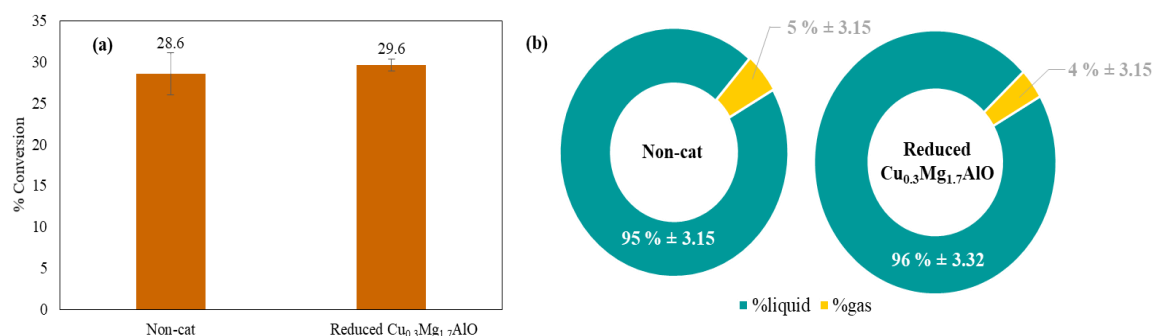

Figure 3: (a) % conversion of pure 1-butanol, and (b) % yield of liquid and gaseous products with and without using reduced $Cu_{0.3}Mg_{1.7}AlO$ catalys

In order to elucidate the selectivity of the catalyst, the products can be classified into three groups: dehydrogenation, dehydration and β-scission products based on the pathways. The dehydrogenation of 1-butanol leads to various products, including butyl butyrate, butanal, butanoic acid, 2-ethylhexanal, alcohol group, ketone group, ester group and C_5^+ hydrocarbon. The dehydration of 1-butanol gives various products, including n-butylether, Mixed C4 and C_1-C_3 hydrocarbon. The 1-butanol β-scission produces various products, including acetone, ethanol and 2-propanol. Without using the catalyst, 1-butanol is converted to various products via thermal conversion, giving acetone (60.2 %) as the major product. The products are produced via β-scission

pathway (67.7 %) the most. The other pathways such as dehydrogenation and dehydration pathways are as selectivity as 29.2 % and 3.1 %, as shown in Figure 5a. When the reduced $Cu_{0.3}Mg_{1.7}AlO$ catalyst was used, the 1-butanol is converted to butyl butyrate (74.0 %) as a major product from the dehydrogenation pathway as shown in Figure 1. It can be explained that the $Cu_{0.3}Mg_{1.7}AlO$ catalyst mainly drives the dehydrogenation pathway of 1-butanol (96.3 %). The other pathways as shown in Figure 5b are driven only 3.5 % (dehydrogenation) and 0.2 % (β-scission).
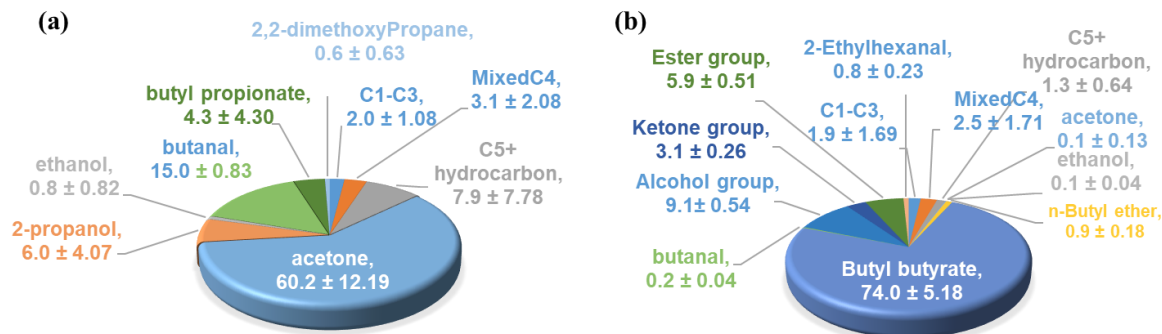

Figure 4: Relative yield of products, defined based on chemical structure, from conversion of 1-butanol using (a) non-cat and (b) reduced $Cu_{0.3}Mg_{1.7}AlO$ catalyst
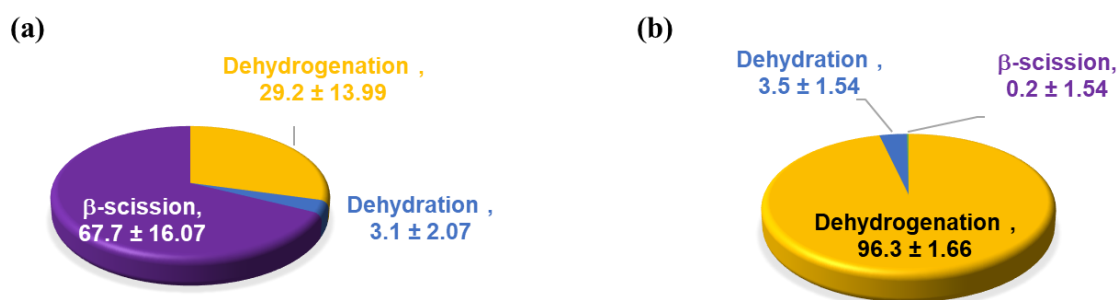

Figure 5: Relative yield of products, defined based on pathway, from conversion of 1-butanol using (a) non-cat and (b) reduced $Cu_{0.3}Mg_{1.7}AlO$ catalyst

4. Conclusions

Without using the catalyst, 1-butanol can be converted at 300 ºC to various products via thermal conversion such as acetone, butanal, mixed C4 and ethanol. The relative yield of acetone was 60.2 % as a major product. Butyl butyrate was not found in this case. The products were produced via β-scission pathway (67.7 %) the most. The reduced $Cu_{0.3}Mg_{1.7}AlO$ gave 1-butanol conversion of 29.6 % and the relative yield of butyl butyrate of 74.0 % as a major product via the dehydrogenation pathway. It can be explained that the catalyst mainly drives the dehydrogenation pathway of 1-butanol (96.3 %), which is markedly greater than the β-scission and dehydration pathways. It can be explained that the metallic Cu and basic sites promoted the dehydrogenation of 1-butanol and the acid sites and basic sites promoted the Tishchenko reaction-type self-esterification of butanal to butyl butyrate. The acid, basic and metal properties of catalyst played the critical role on 1-butanol conversion to butyl butyrate. Although the catalyst gave the high relative yield of butyl butyrate, the limitation of this work is on the still low 1-butanol conversion. Future work could firstly be the study on the effect of reaction variables, such as time and temperature that possibly increase the conversion of 1-butanol and the selectivity of butyl butyrate.

Acknowledgement

References

Cheng F., Guo H., Cui J., Hou B., Xi H., Jia L., Li D., 2018, Coupling of methanol and ethanol over CuMgAlOx catalysts: the roles of copper species and alkalinity, Reaction Kinetics, Mechanisms and Catalysis, 126, 119-136.

Dagaut P., Sarathy S.M., Thomson M.J., 2009, A chemical kinetic study of n-butanol oxidation at elevated pressure in a jet stirred reactor, Proceedings of the Combustion Institute, 32, 229-237.

Díez V.K., Apesteguía C.R., Di Cosimo J.I., 2003, Effect of the chemical composition on the catalytic performance of MgyAlOx catalysts for alcohol elimination reactions, Journal of Catalysis, 215, 220-233.

Dixit M., Mishra M., Joshi P.A., Shah D.O., 2013, Physico-chemical and catalytic properties of Mg–Al hydrotalcite and Mg–Al mixed oxide supported copper catalysts, Journal of Industrial and Engineering Chemistry, 19, 458-468.

Florea M., Delsarte S., Keulen E., Grange P., 2011, 1-butanol dehydration and dehydrogenation over vanadium aluminium oxynitride catalysts, Revue Roumaine de Chimie, 56, 151-159.

Harju H., Lehtonen J., Lefferts L., 2016, Steam reforming of n -butanol over Rh/ZrO2 catalyst: role of 1-butene and butyraldehyde, Applied Catalysis B: Environmental, 182, 33-46.

Kuljiraseth J., Wangriya A., Malones J.M.C., 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.

Mazarío J., Concepción P., Ventura M., Domine M.E., 2020, Continuous catalytic process for the selective dehydration of glycerol over Cu-based mixed oxide, Journal of Catalysis, 385, 160-175.

Ndaba B., Chiyanzu I., Marx S., 2015, n-Butanol derived from biochemical and chemical routes: A review, Biotechnol Rep (Amst), 8, 1-9.

Requies J., Güemez M.B., Maireles P., Iriondo A., Barrio V.L., Cambra J.F., Arias P.L., 2012, Zirconia supported Cu systems as catalysts for n-butanol conversion to butyraldehyde, Applied Catalysis A: General, 423-424, 185-191.

Salavati-Niasari M., Davar F., Mir N., 2008, Synthesis and characterization of metallic copper nanoparticles via thermal decomposition, Polyhedron, 27, 3514-3518.

Sarathy S.M., Vranckx S., Yasunaga K., Mehl M., Oßwald P., Metcalfe W.K., Westbrook C.K., Pitz W.J., Kohse-Höinghaus K., Fernandes R.X., Curran H.J., 2012, A comprehensive chemical kinetic combustion model for the four butanol isomers, Combustion and Flame, 159, 2028-2055.

Tsuji H., Yagi F., Hattori H., Kita H., 1994, Self-condensation of n-butyraldehyde over solid base catalysts, Journal of Catalysis, 148, 759-770.

Xin F., Zhang W., Jiang M., 2019, Bioprocessing Butanol into More Valuable Butyl Butyrate, Trends Biotechnol, 37, 923-926.

Zhang B., Tang X., Li Y., Cai W., Xu Y., Shen W., 2006, Steam reforming of bio-ethanol for the production of hydrogen over ceria-supported Co, Ir and Ni catalysts, Catalysis Communications, 7, 367-372.