

Conversion of Bio-Ethanol to 1,3-Butadiene over Grafted ZrO₂/FeMgAl-Layered Double Oxide Catalyst

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Bio-ethanol is a liquid organic compound mainly produced from the fermentation of renewable sources such as sugar, starch, and lignocellulose. It can be used as a feedstock for the production of several bulk chemicals, including hydrocarbon and oxygenate compounds. 1,3-butadiene is one of the most important chemicals that can also be produced from the catalytic conversion of bio-ethanol. The conversion of bio-ethanol to 1,3-butadiene is a series of continuous reactions that require different active sites for each step. In this work, a FeMgAl-Layered double oxide (LDO) catalyst was selected as a catalyst for 1,3-butadiene production using bio-ethanol as a feedstock. The effect of ZrO₂, grafted on the FeMgAl-LDO catalyst, on 1,3-butadiene production is also investigated. The physical and chemical properties of catalysts were studied using various characterization techniques, including XRD, XRF, NH₃-TPD, CO₂-TPD, and BET. It was found that the 1,3-butadiene yield was enhanced (8.4 %) with using ZrO₂/FeMgAl-LDO as a catalyst. The total basicity of the catalyst was also increased (0.780 mmol/g) with the addition of the grafted-ZrO₂. The presence of grafted ZrO₂ on the catalyst helped promote the condensation reaction of acetaldehyde to crotonaldehyde and Meerwein-Ponndorf-Verley (MPV) reduction of crotonaldehyde to crotyl alcohol, which are the important steps for 1,3-butadiene production. It also promoted the side reaction that is ethanol dehydration to ethylene and other hydrocarbon gasses.

1. Introduction

Bio-ethanol is a liquid fuel mainly obtained through the fermentation of renewable feedstocks such as wheat, corn, and soybeans, etc (Yan et al., 2018). It can be directly used as an automobile fuel or a fuel additive due to its high octane rating that help increases engine efficiency and also results in cleaner emissions (Anderson et al., 2012). Bio-ethanol can also be used as a platform chemical for the production of several basic chemicals such as acetic acid, acetaldehyde, isobutene, and 1,3-butadiene (Ahn et al., 2020). Especially, the conversion of bio-ethanol to 1,3-butadiene, which becomes more interesting route because it is an important intermediate for the polymers production. The major uses of 1,3-butadiene is for the production of styrene-butadiene rubber (SBR), accounting for 54 % of 1,3-butadiene production (White, 2007). 1,3-Butadiene is commonly produced from three main processes, including steam cracking of paraffinic hydrocarbon, catalytic dehydrogenation of n-butane and n-butene and oxidative dehydrogenation of n-butene (White, 2007). 1,3-butadiene can be alternatively produced by the conversion of bio-ethanol. The conversion of bio-ethanol to 1,3-butadiene is a series of continuous reactions that can be divided into four main reactions, including (a) ethanol dehydrogenation to acetaldehyde, (b) condensation of acetaldehyde to crotonaldehyde, (c) reduction of crotonaldehyde to crotyl alcohol via the dehydration of 3-hydroxybutanal, and (d) dehydration of crotyl alcohol to 1,3-butadiene (Zhao et al., 2019). The other important side reaction is the dehydration of ethanol to hydrocarbons such as ethylene and aromatics.

Based on several articles, ZrO₂ catalysts provided a good activity on the acetaldehyde condensation reaction. Ordonsky et al. (2010) studied the role of acid and base sites on the condensation of acetaldehyde over MgO/SiO₂ and ZrO₂/SiO₂ catalysts. The reaction was performed in a continuous flow micro-reactor system at the temperature of 773 K. They found that the selectivity of crotonaldehyde, a product from acetaldehyde condensation, was high on both MgO/SiO₂ and ZrO₂/SiO₂ catalysts. To understand the nature of the active sites

of the catalysts, the CO₂ or pyridine was used as an acid or base molecular probe in order to poison the corresponding active sites. The result showed that the conversion of acetaldehyde decreased when pyridine was co-fed with acetaldehyde. It can be concluded that the Lewis acid site of ZrO₂ catalyst played an important role on the condensation of acetaldehyde to crotonaldehyde. Sushkevich et al. (2014) studied the effect of oxide catalysts (ZrO₂, Nb₂O₅, TiO₂, MgO, and Al₂O₃) on the synthesis of 1,3-butadiene from ethanol over Ag-promoted catalysts. The results revealed that the highest 1,3-butadiene selectivity was observed over the Ag/4 ZrO₂/SiO₂ catalyst. The effect of ZrO₂ content over the Ag-containing catalyst also investigated. It was found that the increase in the ZrO₂ content from 1 to 4 wt% resulted in the higher ethanol conversion and 1,3-butadiene selectivity, while the further increase in ZrO₂ content did not significantly change the performance of the catalyst. The effect of ZrO₂ content on the formation of 1,3-butadiene from the mixed bio-ethanol and acetaldehyde feed over ZrO₂/SiO₂ catalyst was also studied (Han et al., 2015). The results revealed that the formation of ethylene, a product from dehydration of ethanol, increased when the ZrO₂ content increased, resulted from the increasing of weak acid site as evidenced from NH₃-TPD analysis. They also found that a 2 % ZrO₂ content provided the highest 1,3-butadiene selectivity. Possibly, the 2 % ZrO₂ content balanced the dehydration and dehydrogenation reactions. ZrO₂ was also studied as an MPV reduction catalyst. Komanoya et al. (2015) investigated the role of acid and base sites on the MPV reduction of cyclohexanone to cyclohexanol using 2-propanol as a hydrogen donor over different catalysts, including Nb₂O₅, TiO₂, and ZrO₂. It was found that ZrO₂ gave the highest cyclohexanone conversion and cyclohexanol yield, despite ZrO₂ that had the lowest Lewis acid site. According to the kinetic studies, the Lewis acid site is responsible for the adsorption of cyclohexanone while the base site is responsible for the adsorption of 2-propanol and also plays an important role on the formation of six-membered ring intermediate. Since the ZrO₂ catalyst had the highest density of base site provided by the hydroxyl group on the surface, and such base site was very important for the formation of six-membered ring intermediates on the Lewis acid site of the catalyst. It can be concluded that the synergy between Lewis acid and base site of ZrO₂ catalyst leads to an efficient on MPV reduction of cyclohexanone to cyclohexanol.

Layered double hydroxides (LDHs) or hydrotalcite-like compounds are anionic clays materials with the general formula of [M²⁺_{1-x}M³⁺_x(OH)₂][(Aⁿ⁻)_{x/n}·mH₂O] where M²⁺ and M³⁺ are divalent and trivalent cations. Aⁿ⁻ is an inorganic or organic anion (Pazoki et al., 2020). LDHs have been widely applied in a catalyst field due to their high surface area, acid-base properties, and thermal stability (Mishra et al., 2018). The acid-base properties, related to the activity of the catalyst, strongly depend on the preparation method and chemical composition. Napatsorn et al. (2017) studied the effect of Mg/Al ratio of layered double hydroxide on the conversion of bio-ethanol to 1,3-butadiene. It was found that the Mg/Al ratio of 4 provided the highest bio-ethanol conversion and 1,3-butadiene yield. According to the results from TPD analysis, the Mg/Al ratio of 4 provided the optimum ratio of acid and base sites. So, it can be concluded that 1,3-butadiene yield strongly depended on the Mg/Al ratio. León et al. (2011a) investigated the effect of preparation method on the ethanol condensation over Mg-Al mixed oxide catalyst. They found that the acid-base of the catalyst was strongly affected by the preparation method. The result also indicated that ethylene and acetaldehyde were obtained as two primary products from the ethanol conversion through dehydration and dehydrogenation reactions. The effect of partial substitution of Al by Fe on the ethanol condensation over the Mg/Al mixed oxide catalysts was also investigated (León et al., 2011b). The reaction was carried out in the fixed bed reactor at the temperature range of 200 - 450 °C, atmospheric pressure, and WHSV = 0.215 h⁻¹. The results revealed that ethylene and acetaldehyde were obtained as two primary products over Mg/Al and Mg/Fe/Al mixed oxide catalysts. The results from NH₃-TPD and thermogravimetry suggested that the substitution of Al by Fe led to the decreasing the surface acidity of the catalyst while the density of the base site was not significantly changed. As a result, the selectivity of ethylene was suppressed when Fe was inserted into Mg/Al mixed oxide structure, indicating that Fe favored dehydrogenation reaction that produced acetaldehyde.

Based on the literature review, the catalytic conversion of bio-ethanol to 1,3-butadiene is a set of consecutive reactions that require different active sites for each step. First, ethanol was dehydrogenated to acetaldehyde over a base or metal site. Next, acetaldehyde generated from the previous step can undergo condensation to crotonaldehyde over also a base site. After that, the MPV reduction of crotonaldehyde takes place on both acid and base sites, forming crotyl alcohol that is then further converted to 1,3-butadiene via crotyl alcohol dehydration. To achieve high 1,3-butadiene yield, the Fe/Mg/Al-LDO catalyst, modified by chemically-grafted ZrO₂, was selected as a catalyst due to its amphoteric property of the grafted ZrO₂ that was expected to promote the acetaldehyde condensation to crotonaldehyde. Then, the MPV reduction of crotonaldehyde to crotyl alcohol can be driven further by the metallic Fe and acid-base pairs on Fe/Mg/Al-LDO. In this work, the Fe/Mg/Al-LDO catalyst was selected and tested for on its activity on bio-ethanol conversion to investigate the function of all catalysts components.

2. Methodology

2.1 Catalyst preparation

Preparation of g-FeMgAl-LDO catalyst

The FeMgAl-LDO catalyst was prepared using co-precipitation method. First, a mixed solution of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was added into a three-neck flask containing a 700 mL of 0.25 M sodium carbonate solution with constant stirring. The pH was controlled at 10 using 5 M of NaOH solution. After ageing for 16 h. the resulting solid was filtered and washed with deionized water until pH 7 was reached. Next, the precipitate FeMgAl-LDH was dried in an oven at 65 °C overnight, followed by calcination at 500 °C for 5 h to yield FeMgAl-LDO catalyst. After that, the calcined FeMgAl-LDO catalyst was mixed with 20 wt% Al_2O_3 binder, and then formed into a granular shape using a hydraulic press machine. The pelletized catalyst was ground and sieved to 0.8 mm diameter granules using a mesh no.20 stainless steel wire sieve. Next, the sieved catalyst was calcined at 500 °C for 5 h to obtain g-FeMgAl-LDO catalyst, where g stands for “granular”.

Preparation of grafted $\text{ZrO}_2/\text{g-FeMgAl-LDO}$ catalyst

The grafted $\text{ZrO}_2/\text{FeMgAl-LDO}$ was prepared by chemical grafting method. First, the 3 g of calcined FeMgAl-LDO catalyst was dispersed into 100 mL of anhydrous toluene at constant stirring, followed by the addition of 2.4 g of zirconia-sec-butoxide precursor. After ageing for 6 h, the unreacted Zr in the solution was removed by centrifugation, and the resulting slurry was maintained in deionized water for 6 h. After 6 h of ageing, the solid product was filtered and subsequently dried in an oven for 24 h, followed by calcination at 500 °C for 5 h to obtain gf- $\text{ZrO}_2/\text{g-FeMgAl-LDO}$ catalyst, where gf stands for “grafting”.

2.2 Catalyst characterization

The crystallinity of catalysts was investigated using Rikagu SmartLab X-Ray Diffractometer. The crystallinity of catalysts was investigated using Rikagu SmartLab X-Ray Diffractometer equipped with CuK alpha radiation (1.5405). The diffraction patterns were collected in the 2θ range of 5 ° - 70 ° using a scan speed of $0.02 \times (2\theta)/0.6$ second. X-Ray fluorescence spectrometer (XRF) was used to identify the elemental composition of the catalysts using the Best Detection-Vac8mm method. The temperature-programmed desorption of ammonia (NH_3 -TPD) and carbon dioxide (CO_2 -TPD) was applied to study the acid-base properties of the catalyst using the Temperature Program Desorption/Reduction/Oxidation analyzer (TPDRO), BELCAT II. The Brunauer-Emmett-Teller (BET) technique was employed to determine the specific surface area, total pore volume, and pore size of catalysts using Surface Area Analyzer (Quantachrome, Autosorb-1MP) with Multipoint nitrogen adsorption and desorption isotherm plots.

2.3 Catalyst characterization

The activity testing was carried out in a continuous U-tube fixed bed reactor under atmospheric pressure. 1 g of a catalyst was loaded into the reactor using quartz wool as a bed supporter. After that the ethanol was fed into the reactor at the rate of 3.2 mL/h. The liquid product was collected in the cooling condensing flask while the gas product was passed from the condensing flask to online gas chromatography (GC) equipped flame ionized detector with a Plot alumina column. The liquid product from the condensing flask was extracted by CS_2 , and then the obtained non-aqueous products were analyzed for their composition using a LECO Pegasas 1D-mode Gas Chromatograph equipped with a mass spectrometer of Time-of-flight Type (GC-TOFMS) using a capillary column, Rxi-PAH (60 m \times 0.25 mm and 0.10 μm film thicknesses).

3. Results and discussion

3.1 Catalyst characterization

The XRD patterns of the g-FeMgAl-LDO and gf- $\text{ZrO}_2/\text{g-FeMgAl-LDO}$ catalysts (Figure 1) provide the diffraction peaks of Al_2O_3 binder at $2\theta = 25.44^\circ, 35.02^\circ, 37.64^\circ, 43.22^\circ, 52.42^\circ, 57.36^\circ, 61.18^\circ, 66.38^\circ, \text{ and } 68.08^\circ$. The g-FeMgAl-LDO and gf- $\text{ZrO}_2/\text{g-FeMgAl-LDO}$ catalysts also show the diffraction peaks at $2\theta = 43.2^\circ, \text{ and } 62.7^\circ$, which correspond to the periclase MgO phases (León et al., 2011). The g-FeMgAl-LDO and gf- $\text{ZrO}_2/\text{g-FeMgAl-LDO}$ catalysts also show the diffraction peaks of MgAl_2O_4 spinel at $2\theta = 44.86^\circ, \text{ and } 65.30^\circ$ (León et al., 2011). It is noted that all the layered double oxides catalysts are successfully synthesized. After the deposition of ZrO_2 using chemical grafting method, no diffraction peak of ZrO_2 is observed over the gf- $\text{ZrO}_2/\text{g-FeMgAl-LDO}$ catalyst, indicating that ZrO_2 is formed as an amorphous phase or very well-dispersed on the surface of g-FeMgAl-LDO catalyst. The physical properties of the catalysts are stated in Table 1. The surface area, pore volume and pore diameter decrease with the addition of ZrO_2 from 70.21 to 33.29 m^3/g , 0.1406 to

0.0626 cm³/g and 36.16 to 35.71 Å. The elemental composition of the mixed oxide catalysts are also shown in Table 1. The ZrO₂ content on the grafted ZrO₂/FeMgAl-LDO catalyst is 6.6 wt%. The acid and base properties of the g-FeMgAl-LDO and gf-ZrO₂/g-FeMgAl-LDO catalysts are summarized in Table 2. After ZrO₂ was grafted, the total basicity of the catalyst significantly increases from 0.557 to 0.780 mmol/g while the total acidity is slightly enhanced.

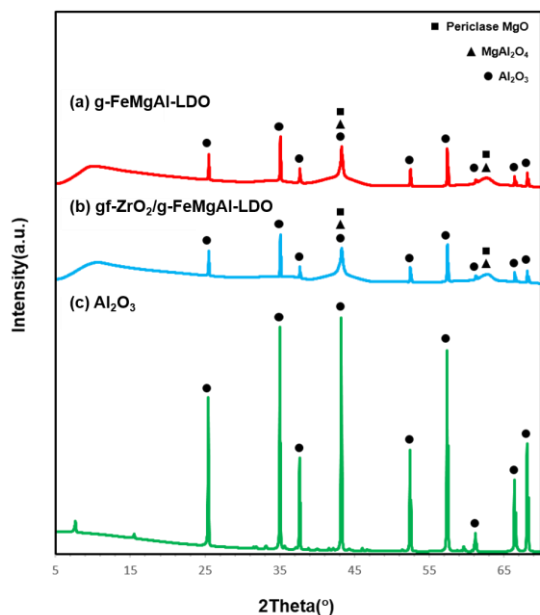


Figure 1: XRD patterns of the (a) g-FeMgAl-LDO, (b) gf-ZrO₂/g-FeMgAl-LDO, and (c) Al₂O₃ binder.

Table 1: Physical properties of the g-FeMgAl-LDO and gf-ZrO₂/g-FeMgAl-LDO catalysts

Catalyst	Fe/Mg/Al (mol) ^a	Zr content (wt%) ^a	Surface area (m ² /g) ^b	Pore volume (cm ³ /g) ^b	Pore diameter (Å) ^b
g-FeMgAl-LDO	0.26 / 3.57 / 1.00	-	70.21	0.1406	36.16
gf-ZrO ₂ /g-FeMgAl-LDO	0.26 / 3.15 / 1.00	6.60	33.29	0.0626	35.71

^a Determined by XRF method, ^b Determined by BET method

Table 2: Acid-base properties of the g-FeMgAl-LDO and gf-ZrO₂/g-FeMgAl-LDO catalysts

Catalyst	Total acidity (mmol/g) ^a	Total basicity (mmol/g) ^b
g-FeMgAl-LDO	0.322	0.557
gf-ZrO ₂ /g-FeMgAl-LDO	0.384	0.780

^aDetermined using TPD-NH₃, and ^b Determined using TPD-CO₂

3.2 Catalyst activity and discussion

The conversion of bio-ethanol and the product yields obtained at 400 °C with or without a catalyst are given in Table 3. The non-catalytic conversion of ethanol is 56.3 % while ethylene is obtained as a primary product with the yield of 12.7 %. Acetaldehyde, crotonaldehyde, and crotyl alcohol are also co-produced, whose %yield is presented in Figure 2. The conversion of ethanol over g-FeMgAl-LDO catalyst is 99.9 %. Ethylene is obtained as a major product with the yield of 17.9 % while 1,3-butadiene, the targeted product, is formed with the yield of 6.7 %. The other liquid products including acetaldehyde, crotonaldehyde, crotyl alcohol, butanal, 1-butanol and ethyl butyrate are also produced over the g-FeMgAl-LDO catalyst with 7.1 %, 2.3 %, 1.4 %, 1.2 % and 1.5 % yield. It is noted that FeMgAl-LDO catalyst enhances the conversion of bio-ethanol from 56.3 % to 99.9 % and also promotes both dehydration and dehydrogenation of ethanol, as confirmed by the increasing ethylene and acetaldehyde yields. According to the ethanol conversion pathways in Figure 3, ethylene can be formed via the ethanol dehydration over the acid site of the FeMgAl-LDO catalyst (León et al., 2011b) while the base site is responsible for the dehydrogenation of ethanol to acetaldehyde that then undergoes condensation to

crotonaldehyde over the acid site (León et al., 2011b). The acid and base sites of the FeMgAl-LDO catalyst also help promote the MPV reduction of the crotonaldehyde, forming crotyl alcohol that is then converted to 1,3-butadiene via the dehydration reaction over the acid site of FeMgAl-LDO catalyst.

In case of gf-ZrO₂/g-FeMgAl-LDO, the main product obtained from the ethanol conversion is ethylene with the yield of 27.4 %, higher than that obtained from its FeMgAl-LDO support. The liquid products; that are, acetaldehyde, crotonaldehyde, crotyl alcohol, butanal, 1-butanol, and ethyl butyrate are also produced over the gf-ZrO₂/g-FeMgAl-LDO catalyst. The %yield of each product are also presented in Figure 2. According to the CO₂-TPD results, the presence of ZrO₂ on the g-FeMgAl-LDO support leads to the increasing total basicity of the catalyst, which helps catalyze the MPV reduction of crotonaldehyde to crotyl alcohol as evidenced from the decreasing crotonaldehyde yield from 2.3 % to 1.3 %. When ZrO₂ is grafted on the g-FeMgAl-LDO catalyst, the yield of acetaldehyde, a product from ethanol dehydrogenation, decreases from 7.1 % to 5.0 % and 1,3-butadiene yield increases from 6.7 % to 8.4 %. It can be explained that ZrO₂ helps promote condensation of acetaldehyde to crotonaldehyde, which is governed by basic sites, and also enhances the MPV reduction of crotonaldehyde to crotyl alcohol over both acid and base sites of the catalyst as shown in the pathways (Figure 3). It can be concluded that the grafted ZrO₂ plays the important roles on ethanol dehydration to ethylene over the acid sites, acetaldehyde condensation to crotonaldehyde over the basic site, and promotes the MPV reduction of crotonaldehyde to crotyl alcohol over both acid and base sites of the catalysts.

Table 3: Ethanol conversion and %yield of ethylene and 1,3-butadiene

Catalyst	Conversion (%)	Gas Yield	Liquid Yield	Water yield	%Yield Ethylene	1,3-Butadiene
Non catalyst	56.3	33.7 ± 2.0	4.8 ± 0.8	17.8 ± 1.2	12.7 ± 0.6	0.0 ± 0.0
g-FeMgAl-LDO	99.9	47.4 ± 4.6	16.4 ± 1.4	36.0 ± 5.9	17.9 ± 3.7	6.7 ± 0.6
gf-ZrO ₂ /g-FeMgAl-LDO	99.9	52.4 ± 0.8	16.3 ± 1.6	31.3 ± 0.8	27.4 ± 0.1	8.4 ± 1.9

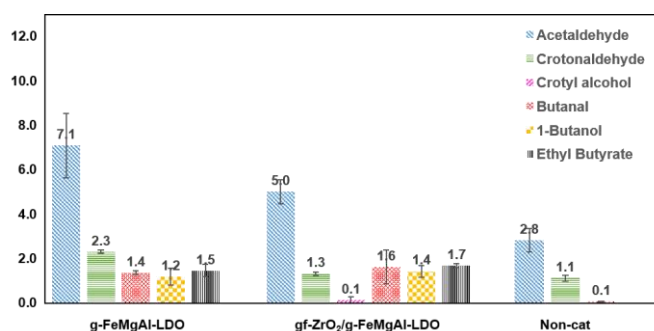


Figure 2: Yield of liquid products from ethanol conversion over g-FeMgAl-LDO and gf-ZrO₂/g-FeMgAl-LDO catalysts

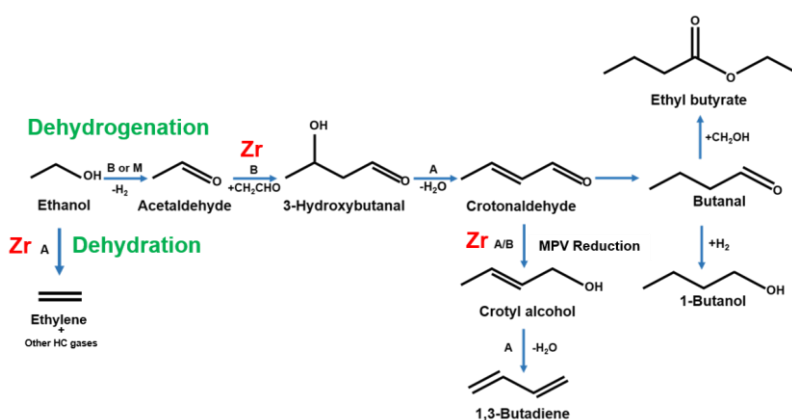


Figure 3: Proposed intervention of grafted ZrO₂ on two major ethanol conversion pathways; dehydrogenation and dehydration, where A = Acid, B = Base, M = Metal, and Zr = Zirconia

4. Conclusions

In conclusion, the presence of the grafted ZrO_2 on the FeMgAl-LDO catalyst resulted in a marked change the physical and chemical properties of the catalyst; namely, the decreases in the surface area (70.21 to 33.29 m^2/g), pore volume (0.1406 to 0.0626 cm^3/g), and pore diameter (36.16 to 35.71 Å). The total basicity of $\text{ZrO}_2/\text{FeMgAl-LDO}$ catalyst significantly increased (from 0.577 to 0.780 mmol/g). The presence of grafted ZrO_2 promoted ethanol dehydration to ethylene, acetaldehyde condensation to crotonaldehyde and MPV reduction of crotonaldehyde to crotyl alcohol, which the two latter reactions resulted in higher 1,3-butadiene yield. The bio-ethanol was considered as an effective bio-based raw material that can replace the petroleum-based feedstock for the production of highly-valuable 1,3-butadiene in one process. Despite the conversion of bio-ethanol is high, the 1,3-butadiene yield obtained over the grafted $\text{ZrO}_2/\text{FeMgAl-LDO}$ catalyst is still low. In the future work, the catalyst improvement, in terms of catalyst design, such as using a hybrid catalyst will be adopted in order to improve 1,3-butadiene yield.

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