Optimal Conditions for Butanol Production from Ethanol over MgAlO Catalyst Derived from Mg-Al Layer Double Hydroxides

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Abstract: The MgAlO catalyst was obtained from thermal decomposition of the MgAl-LDH catalyst having Mg/Al molar ratio of 5. The catalytic Guerbet reaction of ethanol was investigated to determine the effect of WHSV and nitrogen flow rate on butanol production and product distribution. It was performed in a fixed-bed microreactor under continuous flow of vaporized ethanol mixed with N₂. The MgAlO catalyst had high total basic sites and high total acid sites that were crucial for ethanol Guerbet reaction. The MgAlO catalyst showed the highest butanol selectivity at 300°C under WHSV = 3.10 h⁻¹ and nitrogen flow rate = 3,600 mL/h, and the highest butanol yield at 400°C under WHSV = 3.10 h⁻¹ and nitrogen flow rate = 900 mL/h. It can be summarized that in order to enhance the butanol yield, the low WHSV is preferred to increase the contact time of ethanol and catalyst under moderate temperature.

Key words: ethanol, butanol, mixed oxide catalyst, layered double hydroxides catalyst, Guerbet reactions

1 Introduction
Butanol is an essential chemical utilized as a solvent in various applications. Industrially, it has been also employed as a raw material to produce high potential substances such as acrylate esters, glycol ethers, butyl acetate, butylamines and amino resins. Currently, butanol is highly captivating in being used as a biofuel to replace the use of ethanol¹⁻³. There are many advantages of butanol as the additive in gasoline over ethanol including its higher energy density and its properties are more similar to gasoline⁴. In addition, it has low vapor pressure and less corrosive, which is suitable for transportation in infra-structure of industry as in pipelines, tank, pumps, etc. and probably safe to manipulate. Moreover, butanol can be added into gasoline in high concentration up to in pure form, while the ethanol can be added only up to 85%⁵. Besides the well-known biological process to produce butanol, butanol can be alternatively produced from ethanol using proper catalysts⁶. The catalytic reaction mechanism to convert ethanol into butanol can be achieved by a multistep reaction known as the Guerbet reaction⁷. The Guerbet reaction has four-step reaction, which involves the dehydrogenation, aldol condensation, dehydration and hydrogenation, respectively⁸.

There are many types of catalyst used to convert ethanol into butanol via Guerbet reaction. For instance, the catalysts used included hydroxyapatites (HAP)⁹⁻¹², zeolite¹³, metal oxides¹⁴,¹⁵, supported metal¹⁶,¹⁷ and activated carbon catalysts¹⁸,¹⁹. The Guerbet reaction essentially requires both acid and basic sites on catalysts in which hydroxyapatites and metal oxides contain both acid sites. Furthermore, the structure of catalyst can alter the acid and basic site on catalysts, which can affect the catalytic properties during the conversion of ethanol to butanol. It was reported that the Mg-Al layered double hydroxides (MgAl-LDH) having double layer structure of Mg and Al metal cation, while structure between layer has anion, have played important roles in various reactions due to the bifunctional cation and anion in their structure. The MgAl-LDH can be used as a precursor to obtain MgAl mixed oxide catalysts by calcination of MgAl-LDH. Moreover, the difference in catalyst structure apparently affects properties of catalysts.

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The MgAl-mixed oxide catalyst was obtained from a chemical preparation in which it had better acidic-basic properties than physical preparation. The MgO and Al2O3 physical mixture showed strong and medium basic and also acid sites. The basic structure of MgAl-LDH is layered magnesium cation and carbonate anions and some magnesium atoms are substituted with aluminium atoms. The special properties of MgAl-mixed oxide from MgAl-LDH structure are a memory effect in which the structure can revert to LDH structure by moisture after calcination. The molar ratio of Mg and Al in mixed oxide catalysts likely plays a key role on both basic and acidic site density. There were various molar ratios of Mg per Al in range of 0 to 4. It revealed that the Mg per Al molar ratio of 4 exhibited the highest butanol selectivity. Therefore, it is expected that the high Mg/Al molar ratio can result in high selectivity of butanol production from ethanol. This research aims to investigate the MgAlO catalysts having Mg/Al molar ratio of 5 used to convert ethanol to butanol via Guerbet reaction. It was thought that the catalyst with high molar ratio of Mg per Al would increase the butanol selectivity. In addition, this catalyst has the ability to operate in the reaction without reducing step. Therefore, the distinctive point of this catalyst is to facilitate the production process and save energy. However, butanol production can undergo at high temperature (>400°C) for Guerbet reaction. Thus, many researches were developed to decrease the operating reaction temperature using more active catalysts. As also known, the Guerbet reaction is multistep reaction, which requires long contact time between reactant and catalyst. In this case, the reduction of reactant flow rate is expected to prolong the contact time leading to increased butanol yield.

Recently, only few studies have focused on the conversion of ethanol to butanol using suitable catalysts. Therefore, in this research, the production of butanol from ethanol over Mg-Al mixed oxide (MgAlO) catalyst obtained from LDH precursors was investigated. The research aims to determine the suitable reaction condition to produce butanol from ethanol over MgAlO catalyst in order to improve the selectivity and yield of butanol. It would study the effect of ethanol flow rate and nitrogen flow rate that are suitable for butanol production and less energy consumption. The catalyst was characterized by X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) to confirm the catalyst structure. Other characterization techniques including nitrogen physisorption and temperature-programmed desorption (TPD) of CO2 and NH3 were also conducted. The reaction test was performed in a fixed bed microreactor under different nitrogen flow rate (carrier gas). The study was found that low ethanol flow rate and nitrogen flow rate had high butanol yield. Furthermore, the butanol production process was using low gas consumption leading to reducing the production substrate and costs as well.

2 Experimental

2.1 Materials

Mg-Al mixed oxide catalyst was obtained from calcination of MgAl-LDH. First, MgAl-LDH was prepared by coprecipitation method with a Mg/Al molar ratio of 5:1. In the first step, [Mg(NO3)2·6H2O] and [Al(NO3)3·9H2O] was dissolved in DI water to obtain 1.5 mole per liter of nitrate solution. Then, nitrate solution was slowly added to a continuous stirred solution, which contained NaOH and Na2CO3 in molar ratio of 3:2 and had concentration in 2 mole per liter. The pH of the solution mixture was adjusted to 10 by adding NaOH solution, and it was maintained at 65°C for 18 h. The solution mixture was formed to hydrotalcite structure. After that, the hydrotalcite solution was washed with DI water, separated with centrifuge and dried in oven at 110°C overnight to obtain MgAl-LDH. Finally, MgAl-LDH was calcined at 450°C for 6 h to obtain the MgAl mixed oxide catalyst and denoted as MgAlO.

2.2 Catalyst preparation

Mg-Al mixed oxide catalyst was obtained from calcination of MgAl-LDH. First, MgAl-LDH was prepared by coprecipitation method with a Mg/Al molar ratio of 5:1. In the first step, [Mg(NO3)2·6H2O] and [Al(NO3)3·9H2O] was dissolved in DI water to obtain 1.5 mole per liter of nitrate solution. Then, nitrate solution was slowly added to a continuous stirred solution, which contained NaOH and Na2CO3 in molar ratio of 3:2 and had concentration in 2 mole per liter. The pH of the solution mixture was adjusted to 10 by adding NaOH solution, and it was maintained at 65°C for 18 h. The solution mixture was formed to hydrotalcite structure. After that, the hydrotalcite solution was washed with DI water, separated with centrifuge and dried in oven at 110°C overnight to obtain MgAl-LDH. Finally, MgAl-LDH was calcined at 450°C for 6 h to obtain the MgAl mixed oxide catalyst and denoted as MgAlO.

2.3 Catalyst characterization

2.3.1 X-ray diffraction (XRD)

The XRD was used to verify the catalyst structure. The XRD was carried out in 20 range of 10 to 80 degree with scan speed of 0.5 sec/step using X-ray diffractometer (SIEMENS D500).

2.3.2 N2 physisorption

The surface area, pore volume and pore size catalyst were investigated by N2 physisorption method. The catalyst was dried at temperature of 150°C before tested to remove moisture.

2.3.3 Temperature-programed desorption (TPD)

The basicity properties of catalyst were measured by CO2 temperature programmed desorption using a Micromeritics Chemisorb 2750 automated system. The catalyst was preheated at 450°C under He for 1 h to remove water and impurity. Then, pure CO2 was continuously fed for 1 h at 30°C until saturation in order to adsorb CO2 on catalyst surface. After that, the flow of pure CO2 was stopped and the physisorbed CO2 was removed by flowing He. Finally, temperature-programmed desorption was started from 30°C to 800°C at heating rate of 10°C/min. The acidity properties of catalyst were measured by NH3 temperature-programed desorption using a Micromeritics.
Chemisorb 2750 automated system. This NH\textsubscript{3}-TPD was carried out in the similar way as mentioned for CO\textsubscript{2}-TPD. The catalyst was preheated at 450°C under He for 1 h to remove water and impurity. Then, NH\textsubscript{3} gas was fed for 1 h at 30°C until saturation in order to completely adsorb NH\textsubscript{3} on catalyst surface. After that, the flow of pure NH\textsubscript{3} was stopped and the physisorbed NH\textsubscript{3} was removed by flowing He. The temperature-programmed desorption was started from 30°C to 800°C at heating rate of 10°C/min.

2.3.4 Thermogravimetric analysis (TGA)

The thermal decomposition of catalyst was investigated by thermogravimetric analysis under the temperature range of ambient temperature to 1000°C at heating rate of 10°C/min in air with an STD analyzer model Q600 from TA instrument.

2.4 Catalytic reaction

The reaction test was performed in a fixed-bed microreactor under continuous flow of vaporized ethanol mixed with N\textsubscript{2}. In the first step, Mg-Al mixed oxide was packed in the reactor. Then, this catalyst was preheated at 200°C for 1 h in pure N\textsubscript{2} and cooled down to the reaction temperature prior to the test. The reaction was carried out at temperature from 150°C to 400°C under atmospheric pressure with various weight hourly space velocity (WHSV). The effluent was collected and analyzed by gas chromatography with flame ionization detector (GC-FID) using DB-5 capillary column. To clarify the reaction test system, the diagram of ethanol reaction system is constructed and shown in Scheme 1.

The weight hourly space velocity (WHSV), ethanol conversion, product selectivity and product yield were calculated based on the following equations; (1), (2), (3), and (4), respectively;

\textbf{Weight hourly space velocity;}

\begin{equation}
\text{WHSV} = \frac{\text{Ethanol flow rate (cm}^3\text{h}^{-1}) \times \text{Density of Ethanol (g cm}^{-3}\text{)}}{\text{Weight of catalyst (g)}} \quad (\text{h}^{-1})
\end{equation}

\textbf{Ethanol conversion;}

\begin{equation}
X(\%) = \frac{n_{\text{ethanol} (in)} - n_{\text{ethanol} (out)}}{n_{\text{ethanol} (in)}} \times 100
\end{equation}

\textbf{Product selectivity;}

\begin{equation}
S_i(\%) = \frac{n_i}{\sum n_i} \times 100
\end{equation}

\textbf{Product yield;}

\begin{equation}
Y_i(\%) = \frac{X_{\text{ethanol}} \times S_i}{100}
\end{equation}

Where \(n_i\) is mole of product and \(\sum n_i\) is total moles of products based on carbon balance.

3 Results and Discussion

3.1 Catalyst Characterization

The XRD patterns of MgAlO and MgAl-LDH precursor are displayed in Fig. 1. The XRD pattern of MgAl-LDH precursor showed poorly crystallized hydrotalcite-type structure\textsuperscript{25, 26}, while XRD pattern of MgAlO showed periclase MgO phase\textsuperscript{22}. The findings indicate that these catalysts were confirmed the hydrotalcite and oxide structure for MgAl-LDH and MgAlO, respectively. Figure 2 shows the adsorption-desorption isotherms for MgAl-LDH and MgAlO catalysts. For both catalysts, their isotherms exhibited the hysteresis loop at high relative pressure (P/P\textsubscript{0}>0.7) indicating that both catalysts have the mesoporous structure of type IV (IUPAC)\textsuperscript{27, 28}. The BET surface area, pore volume and pore size of catalyst are listed in Table 1. The BET surface area of MgAlO (calcined) catalyst (189.7 m\textsuperscript{2}/g) was much higher than that of MgAl-LDH (94.1 m\textsuperscript{2}/g). This is because after calcination, the structure of catalyst was

\begin{center}
\textbf{Scheme 1} The diagram of ethanol reaction system\textsuperscript{22}.
\end{center}
transformed from LDH to mixed oxide structure and released anion molecules leading to increased BET surface area and pore volume.

The acid and basic sites of catalyst were measured from NH$_3$-TPD and CO$_2$-TPD, respectively and the results are shown in Table 2. The NH$_3$-TPD and CO$_2$-TPD were conducted in temperature range of 30°C to 850°C. The catalyst had weak acid and basic sites, which desorbed ammonia and carbon dioxide, respectively at low temperature (< 250°C). The moderate acid and basic sites exhibited the desorption peaks between 250-400°C, and the strong acid and basic sites had desorption peaks over 400°C$^{29,30}$. It was found that the catalyst had high total basic and acid sites because the amount of Mg$^{2+}$ in MgAlO structure generating basicity property, and Al$^{3+}$ in this catalyst generated acidity property$^{21}$. It is suggested that the catalyst is bi-functional catalyst having both acid and basic sites that are crucial for Guerbet reaction of ethanol to butanol.

3.2 Catalytic Reaction

3.2.1 Effect of WHSV on catalytic conversion

The MgAlO catalyst was tested for Guerbet reaction of ethanol to butanol. The reaction was carried out at reaction temperature from 150°C to 400°C under atmospheric pressure with various weight hourly space velocity (WHSV) at constant nitrogen flow rate of 3,600 mL/h. Thus, the flow rates of ethanol were varied. The ethanol conversions of MgAlO catalyst under various WHSV are shown in Fig. 3. As expected, the ethanol conversion essentially increased with increased temperature and decreased ethanol flow rate (decreased WHSV). At 250°C, only acetaldehyde was produced, while butanol was initially formed at 300°C.

Figure 4 shows the butanol yield over MgAlO catalyst with various WHSV. For all WHSV, butanol was started to form at 300°C. Then, the butanol yield increased with increasing reaction temperature. The increased reaction temperature enhanced ethanol conversion resulting in increased butanol yield. The highest yield of butanol was observed at 400°C (WHSV of 3.10 h$^{-1}$) having the butanol yield of 3.60%. However, the highest selectivity of butanol (19.69%) was observed at 300°C at WHSV of 3.10 h$^{-1}$. It was found that at temperature higher than 300°C, it resulted in decreased selectivity of butanol. Thus, at 400°C, the butanol yield increased because of increased ethanol conversion, whereas

Table 1 BET surface area, pore volume and pore size of catalyst.

| Catalyst   | BET surface area (m$^2$/g) | Average pore volume (cm$^3$/g) | Average pore size (nm) |
|------------|---------------------------|-------------------------------|------------------------|
| MgAl-LDH   | 94.1                      | 0.50                          | 14.3                   |
| MgAlO      | 189.7                     | 0.79                          | 13.4                   |

Table 2 The amount of each element of catalyst, number of basic sites from CO$_2$-TPD and number of acid sites from NH$_3$-TPD.

| Catalyst | Mg/Al ratio | Amount of element (mg/L)* | CO$_2$ desorbed (µmol/g) | NH$_3$ desorbed (µmol/g) |
|----------|-------------|---------------------------|--------------------------|--------------------------|
|          |             | Mg | Al | W  | M  | S  | Total | W  | M  | S  | Total |
| MgAlO    | 5           | 2.721 | 0.611 | 117 | 16 | 89 | 223 | 191 | 594 | 882 | 1667 |

W is weak acid and basic sites, M is medium acid and basic sites, and S is strong acid and basic sites.

*Amount of element determined by ICP technique.
butanol selectivity decreased.

The selectivity of products with various WHSV at different reaction temperatures is shown in Fig. 5. This graph presents the comparison of product formation in the percentage of selectivity, which illustrates the overview of more or less of products. At the low temperature (i.e., T = 250°C), only acetaldehyde was produced. When reaction temperature was increased up to 300°C, it can observe the formation of various products including acetaldehyde, ethylene, diethyl ether and butanol. However, when the reaction temperature was higher than 300°C, other C₄ products were formed. At high reaction temperature, the dehydration of ethanol is more dominant leading to the formation of ethylene and diethyl ether. For the highest WHSV (at 11.38 h⁻¹), the selectivity of butanol was found to increase with increasing the reaction temperature and the highest butanol selectivity of 18.15% at 400°C. This result indicated that at high WHSV of ethanol, it had too short contact time to obtain butanol at low temperature. On the other hand, increased temperature can facilitate the conversion of ethanol to butanol up on high WHSV. Because the ethanol reaction to produce butanol is a multi-steps reaction involving the dehydrogenation of ethanol, aldol condensation, dehydration and hydrogenation, respectively, thus, low WHSV of ethanol feed is preferred to enhance the contact between the reactant and catalyst in order to complete the reaction at moderate temperature. The byproducts were occurred because the ethanol reaction was converted to butanol by multi-step reaction, which produced many other byproducts such as acetaldehyde that was formed with binding of acetaldehyde molecule by aldol condensation, crotonaldehyde that was obtained from dehydration of acetaldehyde, and butanal that was formed by hydrogenation of crotonaldehyde.

As seen in Table 3, the highest selectivity of butanol at 300°C was observed. However, due to higher ethanol conversion at 400°C, it led to the highest butanol yield at this temperature as mentioned earlier. In fact, the first product of ethanol dehydrogenation is to produce acetaldehyde, and then this reaction produces acetaldehyde and butanol at low temperature. When temperature is higher, side reactions can occur to obtain, especially ethylene. Besides, diethyl ether and other C₄ products were also observed at high temperature. At 400°C, yields of product was higher than those at 300°C due to increased ethanol conversion. However, due to the variety of products formed, it led to decreased butanol selectivity. In addition, at 300°C, the formation of other byproducts seemed less and higher selectivity of butanol can be obtained. At this stage, the enhancement of ethanol conversion should be considered to increase the butanol yield. Furthermore, the acid-base properties of the catalyst also affect the product formation. The aldol condensation step of acetaldehyde molecules reacts at the strong base sites, and the dehydration step likely reacts at the moderate acid sites, which are part of ethanol reaction to butanol. This catalyst displayed high strong base sites, high moderate acid sites and high strong acid sites (Table 2). However, the strong acid sites caused ethanol dehydration to diethyl ether and ethylene as by-
products, especially at high temperature.

3.2.2 Effect of N\textsubscript{2} flow rate on catalytic conversion

The ethanol conversion of MgAlO catalyst with various nitrogen flow rates at constant WHSV of 3.1 h\textsuperscript{-1} is shown in Fig. 6. The ethanol conversion increased with increased temperature and decreased nitrogen flow rate as expected. At 150°C, only acetaldehyde was produced, while butanol was initially formed at 250°C. Fig. 7 shows butanol yield over MgAlO catalyst with various nitrogen flow rate at constant WHSV of 3.1 h\textsuperscript{-1}. It indicated the highest yield of butanol (3.94%) at 900 mL/h of nitrogen flow rate at 400°C. At high reaction temperature (400°C), butanol yield increased with decreasing the nitrogen flow rate. At high reaction temperature, it was found that byproducts including ethylene, diethyl ether, and other C4 products were formed.

3.2.3 Stability of catalysts

The stability test of the MgAlO catalyst was performed at 400°C with nitrogen flow rate of 3,600 mL/h and WHSV of 3.1 h\textsuperscript{-1} for 10 h. The ethanol conversion and butanol yield are shown in Fig. 8, which slightly decrease over time on stream of 10 h. The initial yield at ethanol conversion of ca. 21% (Fig. 9) for ethylene, acetaldehyde, butanol, and diethyl ether was 10.48, 6.71, 2.40, and 0.94%, respectively. After reaction test for 10 h, the product yield was only slightly changed. This result indicated that the catalyst exhibited good stability under this specified reaction condi-

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|c|c|}
\hline
WHSV (h\textsuperscript{-1}) & Reaction temperature (°C) & EtOH conversion (%) & Selectivity (%) & Yield of butanol (%) & S.D. of butanol yield \\
\hline
\hline
3.1 & 300 & 2.87 & 8.45 & 71.86 & 0 & 19.69 & 0 & 0.57 & 0.19 \\
& 400 & 29.82 & 17.92 & 53.46 & 2.23 & 12.05 & 14.33 & 3.60 & 0.12 \\
\hline
6.23 & 300 & 3.55 & 8.81 & 73.53 & 0 & 17.66 & 0 & 0.63 & 0.06 \\
& 400 & 31.9 & 20.18 & 54.64 & 2.91 & 9.34 & 12.94 & 2.98 & 0.06 \\
\hline
9.36 & 300 & 0.76 & 23.54 & 50.88 & 9.27 & 16.30 & 0 & 0.12 & 0.02 \\
& 400 & 25.52 & 52.84 & 32.18 & 5.72 & 9.11 & 1.53 & 2.32 & 0.09 \\
\hline
11.38 & 300 & 0.77 & 7.94 & 80.20 & 4.15 & 7.0 & 0 & 0.07 & 0.01 \\
& 400 & 10.35 & 20.04 & 42.72 & 9.50 & 18.15 & 9.59 & 1.88 & 0.07 \\
\hline
\end{tabular}
\caption{A comparison of the selectivity of products with various WHSV and N\textsubscript{2} flow rate = 3,600 mL/h.}
\end{table}
The thermogravimetric analysis (TGA) was performed up to 1000°C under air atmosphere in order to determine the carbon deposition on the spent catalyst as shown in Figs. 10 and 11. Figures 10 and 11 show the results of present weight loss for spent catalysts with different WHSV and nitrogen flow rate, respectively. All spent catalysts from reaction test had first region of weight loss at 200°C referred to the removal of moisture. The second region at 200 to 400°C was the weight loss of dihydroxylation and decarbonation of hydrotalcite structure. The final region was in temperature range of 400 to 1000°C, which was used to measure the carbon deposition on the spent catalyst at decoking process period. The results suggested that only small amount of carbon deposition was found on the spent catalyst. For the reaction test under different nitrogen flow rate, the low nitrogen flow rate led to low carbon deposition. Furthermore, it exhibited the highest ethanol conversion with the lowest nitrogen flow rate (Fig. 6). Thus, nitrogen flow rate of 900 mL/h and WHSV of 3.1 h⁻¹ was the most suitable condition in this study.

4 Conclusions

The MgAlO catalyst exhibited the highest yield of butanol (3.94%) at 900 mL/h of nitrogen flow rate and WHSV of 3.10 h⁻¹ at 400°C. Although butanol yield was found to be the highest at 400°C, the side reactions apparently occurred leading to the formation of ethylene, diethyl ether and other C4 products. Therefore, nitrogen flow rate of 900 mL/h and WHSV of 3.1 h⁻¹ were the most suitable condition for ethanol Guerbet reaction to produce butanol on this catalyst at 400°C.

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Conflict of Interest

The authors declare there are no conflicts of interest.

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