Production of Diethyl Ether Over Cr-Co/γ-Al₂O₃ Catalyst

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Abstract. Diethyl ether (DEE) is an important chemical in practical application. This substances actually very interesting to be object of study because its can be substitute the fuel oil such gasoline from the fossil. Its mean that DEE is one of alternative sources of energy. In this study the production of DEE was based on ethanol dehydration over a granule Cr-Co/γ-Al₂O₃ catalyst. The reaction was conducted in a fixed bed reactor at range temperature of 100 to 200°C and atmospheric pressure. Un nitrogen gas is fed in reactor to push the ethanol vapor. Sampling the product of reaction is taken after the condition is steady state. The catalyst was analyzed by the BET and XRD method and the result indicated that the prepared catalyst has surface area of 162,840 m²/g with pore diameter of 0,3178 cc/g. The ethanol conversion under the variable condition attains of 93.122% of and DEE yield is 0.34%.

1. INTRODUCTION
Ethanol is one of the organic chemicals can be used a solvent for diethyl ether production. Diethyl ether can be produced using a heterogeneous catalyst [1]. Diethyl ether (DEE) is one of the most important chemicals in industrial application. Diethyl ether was commonly used to dissolve oils, gums, resins, microselulose, parfumes, alkynid, and butadiene. Other than that application DEE is also used as anesthetic [2]. In the field of renewable energy DEE can also be utilized mixture or substitute fuel, mixed with gasoline to overcome the shortage of fuel [3]. The mixed of DEE with gasoline more compatible than ethanol- gasoline because the different of their boiling point and also has the advantage of being a renewable energy source because very low carbon monoxide emissions [4].
DEE can be utilized to increase the octane number in the use of gasoline fuel. DEE compound began to utilize as octane level on the material diesel or biodiesel because has a high cetane number. The use of heterogeneous catalyst is very developed in the industrial chemicals. The most important factor in a heterogeneous catalyst is a acidity, surface area, porosity, mechanical properties, and stability. One of the developments in this field catalyst sectors is the preparation of nano-catalyst to improve their performance to accelerate the reaction. Nano-catalyst is a catalyst which has size of 1-100 nm. Dimension reduction of catalyst into nano-sized catalyst would increase the catalyst surface area and consequently increase the activity of catalysts in certain reactions. DEE is compound colors with distinctive aroma small and very low boiling point. Diethyl ether generally is made though the dehydration process of ethanol (Barbet process) using sulfuric acid catalyst (homogeneous catalyst).
This process has weaknesses of difficulty of catalyst separation after the reaction. To avoid this difficulty homogeneous catalysts are replaced by heterogeneous catalysts. The heterogeneous catalyst generally used for dehydration of ethanol to DEE is \( \text{Al}_2\text{O}_3 \) with promotor Cr-Co. \( \gamma\text{-Al}_2\text{O}_3 \) has been known for having a large surface area with acidic and alkaline active sides. Butt et al., (1962), and De boer et al., (1967), have studied reaction kinetics of dehydration of ethanol to DEE. The results shown that reaction is similar than mechanism theory formed Langmuir Hinshelwood reaction mechanics simultaneously. An excessive effort is very necessary to produce diethyl ether as an better energy resources. This research used granulated Cr-Co/ \( \gamma\text{-Al}_2\text{O}_3 \) catalyst prepared by impregnation method. Then, to test the activity of prepared Cr-Co/ \( \gamma\text{-Al}_2\text{O}_3 \) nano-catalyst. Ethanol dehydration reaction was carried out in a fixed bed reactor.

2. EXPERIMENTAL

2.1 Materials

The chemicals were used in this experiment are: \( \text{Al(NO}_3)_3\cdot9\text{H}_2\text{O}, \text{NH}_4\text{OH}, \text{HCl} \) and 99% ethanol. This study was used the \( \text{Al}_2\text{O}_3 \) catalyst purchased at the Merck company, Aluminium nitrate nonahydrate (Merck), \( \text{Cr(NO}_3)_3\cdot9\text{H}_2\text{O}, \text{Co(NO}_3)_2\cdot6\text{H}_2\text{O}, \) molecular sieve, nitrogen gas (PT. Aneka Gas Industry) were also employed.

The starting materials, fructose (D-(+)-type, Sigma-Aldrich, 99%), silver nitrate (\( \text{AgNO}_3 \), AR, QRëC\textsuperscript{TM}), titanium tetraisopropoxide (TTIP, Sigma-Aldrich, 97%) and absolute ethanol (\( \text{EtOH}, \text{HmbG} \textsuperscript{®} \text{Chemicals} \)) were used as the precursor for carbon microspheres, silver, and TiO\(_2\) microspheres, respectively.

2.2 Preparation of catalyst

The first \( \text{Al}_2\text{O}_3 \) was synthesized using the precipitation method. Alumina nitrate monohydrate was prepared with different concentration different (0.2, 0.3, 0.4, 0.5, and 1 M) was dissolved in a solution of HCl (0.5 M). the precipitate was carried out by adding ammonium nitrate into the solution. The precipitate formed was stirred with variation of time between (3.4.5 and 6 hours) at 60, 70, 80, 90, 100°C. Furthermore, the precipitate was filtered and washed by using distilled water and ethanol and then dried at 75°C for 24 hours. The solid precipitate calcined for 6 hours at 600°C with air flow to produce catalyst \( \gamma\text{-Al}_2\text{O}_3 \). \( \gamma\text{-Al}_2\text{O}_3 \) in synthesis using XRD and BET. Size of crystal calculated by using Scherrer formula based on the data of XRD analysis. Scherrer formula used is:

\[
D = \frac{\kappa \lambda}{\beta \cos \theta}
\]  

(1)

Where D is the diameter of the crystal, \( \kappa \) is the shape factor with a value of 0.9-1.4 (generally used \( \sim \) 0.9), \( \lambda \) is the wavelength of X-ray (0.15406 nm), \( \theta \) is the Bragg angle (radians), and \( \beta \) is the FWHM (Full Width Half maximum) of the highest peak (radians).

2.3 Preparation of Cr-Co/\( \gamma\text{-Al}_2\text{O}_3 \) Catalyst

\( \gamma\text{-Al}_2\text{O}_3 \) as a support was impregnated with \( \text{Cr(NO}_3)_3\cdot9\text{H}_2\text{O} \) and \( \text{Co(NO}_3)_2\cdot6\text{H}_2\text{O} \) metal salt solution using the Dry Impregnation method with loading 10%. Phase stage as follows: The impregnation \( \text{Cr(NO}_3)_3\cdot9\text{H}_2\text{O} \) on \( \gamma\text{-Al}_2\text{O}_3 \) is done by spraying metal solution to \( \gamma\text{-Al}_2\text{O}_3 \). In stirring using magnetic stirrer at temperature 80 °C for 3 hours. After which the catalyst is dried at temperature of 110 °C for 12 hours. \( \text{Co(NO}_3)_2\cdot9\text{H}_2\text{O} \) is impregnated in same manner. and then dry catalyst was calcined with \( \text{N}_2 \) at 550 °C for 3 hour and followed by a reaction reduction with \( \text{H}_2 \) at a temperature of 600 °C for 6 hour and characterized.
2.4 The production process of diethyl ether (DEE)
The catalytic production of diethyl ether was conducted in fixed bed reactor using 3 g of catalyst. This temperature operation was of 100 – 200 °C, and in atmospheric pressure in the reactor. The ethanol and liquid products were analyzed using gas chromatography with a FID detector and using helium with a flow rate of 27.4 mL/min, temperature operation of 125-250 °C. Arrangement of equipment used for the production process DEE is shown in Figure 1 below.

![Diethyl Ether Production Equipment](image)

Figure 1. Diethyl Ether Production Equipment

3. RESULTS AND DISCUSSION
3.1 Surface area and pore volume analysis of catalyst by BET
The specific surface area, average pore diameter, and pore volumes of the γ-Al₂O₃ and Cr-Co/γ-Al₂O₃ catalyst shown in Table 1. The specific surface area for the γ-Al₂O₃ catalyst is 162.84 m²/g. After impregnation of Cr and Co on to the γ-Al₂O₃ catalyst reduced the surface area, is 133.499 m²/g. the results indicated that the impregnation of Cr and Co particle blocked of the γ-Al₂O₃ catalyst [5].

| Catalyst         | Specific Surface Area (m²/g) | Average Pore Diameter (nm) | Pore volume (cm³/g) |
|------------------|------------------------------|----------------------------|---------------------|
| γ-Al₂O₃          | 162.840                      | 0.3178                     | 3.4276              |
| Cr-Co/γ-Al₂O₃    | 133.499                      | 0.2288                     | 3.9027              |

3.2 The production process of diethyl ether (DEE)
3.2.1 GC-MS analysis
Figure 2 show the chromatogram results of the DEE production process at a gas rate of 600 mL/min. At temperature of 150 °C the ethanol component was detected at retention time of 3.985 minute, while DEE detected at retention time of 5.367 minutes. From chromatogram, diethyl ether compounds was detected.
Figure 2. Chromatogram of liquid product in DEE production process using catalyst Cr-Co/ γ-Al$_2$O$_3$ of reaction temperature

Figure 2 shows that at nitrogen rate 200 mL/min, the conversion of ethanol more significant value compared with 400 mL/min nitrogen gas rate. The largest conversion produced at rate of 200 mL/min is 93.12% at temperature of 100°C. For the conversion of 400 mL/min nitrogen gas rate 93.03% at 100 °C and at conversion rate of 600 mL/min nitrogen gas was 84.40% at temperature of 100 °C. This indicate that the greater the rate of carrier gas caused then the smaller the contact time between ethanol with surface area of the catalyst [6]. Increased temperatures can increase the conversion of ethanol according to the Arrhenius equation. In this equation, the increase of temperature will increase the reaction rate constants that will increase the rate of reaction [7].

Figure 3. Ethanol conversion vs reaction temperature of dehydration (°C).

Figure 3 shows that the nitrogen gas rate of 600 mL/min produce diethyl ether greater compared which rate of nitrogen gas 200 mL/min and 400 mL/min. The higher yield of DEE in this experiment attained 0.3 % with N$_2$ gas rate 600 mL/min at temperature of 200 °C. As shown in Figure 4, the Increasing reaction temperature can increase the yield of DEE. Using of catalyst generally produce dehydration reaction conversion high. This is happened because it has been know that the catalyst has greater surface area. Greater surface area will increase the conversion of ethanol because it can increase the opportunity for the conversion process.
Figure 4 show that the nitrogen gas rate of 600 mL/min produce diethyl ether greater compared which rate of nitrogen gas 200 mL/min and 400 mL/min. The higher yield of DEE in this experiment attain 0.3 % with N$_2$ gas rate 600 mL/min at temperature of 200 °C. As shown in Figure 5, the Increasing reaction temperature can increase the yield of DEE. due to more minimum (more negative) value of the Gibbs energy change (ΔGreaction) make the reaction more easy to be occurred [8].

4. CONCLUSION

Based on this research, it may be concluded that diethyl ether can be produced by using. The ethanol dehydration with γ-Al$_2$O$_3$ as a catalyst and Cr-Co as metal. The catalyst prepared in the granular state has surface area from 162.84 m$^2$/g to 133.499 m$^2$/g, and the catalyst pore volume from 3.4276 cm$^3$/g to 3.9027 cm$^3$/g. The higher conversion of ethanol attain 92,12% and yield 0.3 % of DEE yield was biggest conversion reaction has been 93.12% from temperature of 100$^0$ C. The biggest DEE yield was resulted at temperature of 200 $^0$C.

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