

Catalytic Dehydration of Ethanol to Produce Diethyl Ether Using Cr-Co Supported γ -Alumina Catalyst: Effects of Nitrogen Stream and Metal Ratio

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Abstract

The depletion of fossil fuels and the environmental impacts generated by their use, so it is necessary to find alternative energy that is environmentally friendly. Diethyl ether is one of the additive alternative fuels that can replace fossil fuels. Diethyl ether is made through the dehydration process of ethanol compounds and use alumina catalysts. Cr-Co/ γ -Al₂O₃ catalyst with various metals loading was prepared using incipient wetness impregnation. The objective of this research was to study the effect of Cr-Co metal impregnated on γ -Al₂O₃ to catalyst activity and to find the optimum temperature and rate of nitrogen stream as carrier gas for the production process of diethyl ether from absolute ethanol. γ -Al₂O₃ catalyst was impregnated with Cr and Co metals at 10% loading by the ratio metals of Cr-Co (1:1; 1:2; and 2:1) and characterized by XRD, BET, and SEM- EDX. The activity test of Cr-Co/ γ -Al₂O₃ catalyst for the production process diethyl ether from dehydration ethanol was conducted in the fixed bed reactor with 125-200 °C operating temperature and 200-600 ml/min nitrogen stream, and then the reaction product will be analyzed with GC. The result showed that the largest ethanol conversion and largest yield of diethyl ether was produced by the 200 ml/min nitrogen stream. At temperature 200 °C and metal ratio impregnation 2:1 the highest ethanol conversion of 93.12% and highest DEE yield of 1.323% was achieved.

Keywords: Ethanol; Dehydration; Diethyl ether; γ -Al₂O₃

1. Introduction

Among fossil fuels, petroleum is the easiest fuel to use for transportation. Therefore, if petroleum reserves are used continuously without alternative fuels to replace fossil fuels, petroleum reserves will become increasingly depleted. To meet the need for renewable fuels as a substitute for fossil fuels, so it is necessary to find alternative energy that is environmentally friendly. Diethyl ether is an alternative fuel that can replace fossil fuels. Diethyl ether (DEE) is often used as a mixing agent to overcome the weakness of ethanol fuel. In addition, DEE can be used as an additive in diesel fuel which is proven to improve engine performance and reduce fuel consumption (Ibrahim, 2016).

Ethanol and some ethers have very high octane numbers, more than 100 (Varişlı, 2007). Ethanol with an octane number 113 and Reid's low vapour pressure is considered an excellent alternative to gasoline. Ethanol is considered as a promising biofuel, but the use of ethanol as a diesel fuel has begun to be abandoned due to several factors such as high evaporation rate and low ignition quality. Ethanol can be easily converted via dehydration reaction to diethyl ether which is considered as an alternative fuel source for diesel engines. Diethyl ether can be used as fuel for diesel engines because it has a high cetane number which can reach more than 125.

Diethyl ether compounds are generally made by the dehydration process of ethanol compounds with a sulfuric acid (homogeneous) catalyst known as the Barbet process. The disadvantage of this process is that the separation of the catalyst is still difficult and expensive and the catalyst is corrosive. Corrosive

catalysts require investment in equipment which is quite expensive (Fogler, 1987). Thus, a study is needed to overcome this weakness. One of the efforts to overcome this weakness is to develop heterogeneous catalysts.

One of the most important components in heterogeneous catalysts is the catalyst support. Support catalyst is a catalyst component that has a high surface area, porosity, mechanical properties, and good stability. Generally, the catalyst support is in the form of metal oxides with high melting points, clay (clay) or carbon (Richardson, 1989). Based on this function, catalyst manufacture is one of the various efforts made in catalyst engineering to maximize the effectiveness of the catalyst.

Alumina (Al_2O_3) is one of the most widely used ceramic materials as a catalyst, catalyst support, absorbent, and is also used as a resistant coating (Murjalili, Mohamad, and Chuah, 2011). In its application, alumina has been widely used for processes at high temperatures. This is because alumina has good strength and a low coefficient of thermal expansion. However, like other monolithic ceramics, alumina tends to have low ductility and low fracture strength (Khorrami et al, 2012). Alumina, especially γ -alumina, is widely used as a catalyst and catalyst support, because in addition to having a large surface area, it also has active sites that are acidic and alkaline. This active side results from the release of water molecules (Wibowo, Sunardi, and Yulia, 2007). The dehydration reaction of primary alcohol catalysis using γ - Al_2O_3 catalyst can produce ether and alkene compounds. Meanwhile, the secondary alcohol reaction with an acid catalyst will produce an alkene, while with a base catalyst it produces ketones through a dehydrogenation reaction (Shi and Davis, 1995).

Increasing the nature of the catalyst by adding a promoter far exceeds the effect that can be achieved by the promoter's action alone. The promoter itself does not necessarily have catalytic activity. Substances added to catalysts in small amounts in order to enhance properties such as activity, selectivity or stability are one means of promoters which can simultaneously express their utility.

Chromium metal serves to bring the catalyst conditions to an acidic atmosphere which encourages the selectivity of the reaction towards the formation of diethyl ether (Poole, 1967). Srinivasan has studied γ - Al_2O_3 catalyst support which is modified by dispersed cobalt dispersion through strong adsorption electrostatic (SEA) synthesis method. Measurement of the acidity and alkalinity of the catalyst by the TPD-FTIR-MS method of pyridine and adsorbed CO_2 , respectively, shows that the Co- Al_2O_3 catalyst has about half Lewis acidity (accessible to pyridine) and is moderately higher alkaline than the parent γ - Al_2O_3 . The Co- Al_2O_3 catalyst, under identical reaction conditions, can achieve the same ethanol conversion and ethylene selectivity at lower temperatures than the original γ - Al_2O_3 catalyst. In addition, the ME-PSD-DRIFTS results showed the participation of adsorbed ethanol and ethoxide species as well as terminal and hydroxyl bridges attached to the octahedral and tetrahedral aspects of Al in Al_2O_3 (100) and (110) as possible intermediate reactions in the conversion of ethanol to diethyl ether and ethylene (Srinivasan et al, 2019).

In this research, diethyl ether was made through ethanol dehydration reaction in a fixed bed reactor with γ - Al_2O_3 catalyst in which Cr and Co metals act as promoters. Cr-Co/ γ - Al_2O_3 catalyst with various metals loading was prepared using incipient wetness impregnation. The objective of this research was to study the effect of Cr-Co metal impregnated on γ - Al_2O_3 to catalyst activity and to find the optimum temperature and rate of nitrogen stream as carrier gas for the production process of diethyl ether from absolute ethanol.

2. Experimental

2.1. Catalyst Preparation

γ - Al_2O_3 as support was impregnated with metal salt solutions, $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ using the dry impregnation method. The dry impregnation method was carried out by catalyst with a 10% total metal loading. The stages of the dry impregnation process in this study generally follow the

procedures that have been carried out (Haber et al, 1995) and the research variables from (Kumar et al, 2016).

The first step was to weigh γ -Al₂O₃ catalyst, then dissolve Cr(NO₃)₃.9H₂O according to the variable loading of the catalyst into distilled water. Next, do dry impregnation of Cr(NO₃)₃.9H₂O solution by spraying the metal solution gradually into the γ -Al₂O₃ catalyst until the volume of the metal solution is equal to the volume of the γ -Al₂O₃ catalyst and kept the catalyst dry. The suspension is stirred slowly at room temperature, until the solution is used up. The catalyst is stored overnight in a desiccator. Then dried in an oven at a temperature of 120 °C for 12 hours. Do the same for the Co(NO₃)₂.6H₂O solution. The impregnated sample was dried for 12 hours in an oven at 120 °C, then calcined using N₂ at 550 °C for 3 hours. Metal catalyst which is still in the form of oxide is reduced with H₂ gas at 600 °C for 5 hours in the furnace. After the reduction, the H₂ gas flow and the heater were turned off but the N₂ gas was still flowed until the catalyst reached room temperature.

2.2. Catalyst characterization

The catalyst was characterized by XRD, BET, and SEM/EDX analysis methods. The catalyst samples that have been obtained were analysed by Brunauer Emmett Teller (BET) to determine the surface area and pore volume of the catalyst. X-Ray Diffraction (XRD) to see the crystallinity of the catalyst and to determine the elements contained in the catalyst. Scanning Electron Microscopy Energy Dispersive X-ray (SEM-EDX) to determine the morphology of the catalyst and metal distribution as well as to determine the metal content impregnated on the γ -Al₂O₃ buffer.

2.3. Catalytic ethanol dehydration

The feed (absolute ethanol) is filled into a vaporizer tank with a diameter of 5 inches and a height of 15 cm. The vaporizer tank is made of stainless steel. This vaporizer tank is equipped with a 1000 watt heating jacket and temperature control to adjust the vapor temperature. The vaporizer tank is connected to a nitrogen gas cylinder. Nitrogen gas is used as a booster gas for reactant vapor (ethanol absolute) to pass through the catalytic reactor. The catalytic reactor is a fixed bed reactor with 3 grams of Cr-Co/ γ -Al₂O₃ catalyst. This reactor is made of stainless steel with a diameter of ¼ inch and a length of 30 cm. The reactor consists of 3 parts with a length of 10 cm each, each part is connected by a screw system. The middle part is the place to put the catalyst. The catalyst is placed first covered with quartz wool insulation and then covered with quartz wool. This reactor is equipped with temperature control to adjust the reaction temperature. The reactor output vapour is passed through a Liebig and Graham condenser made of glass. In this condenser ice water is used as a cooling medium. The condensate was then collected in a container and analysed using Gas Chromatography (GC).

3. Results and Discussion

3.1. Catalyst characterization

The process of making a catalyst is influenced by many factors, including the chemical properties of the catalyst components and their precursors, the concentration of the components, the physical strength, the reaction conditions of the catalyst used and the ease of removing contaminants. In this study, the catalyst used for the ethanol dehydration process is solid acid γ -Al₂O₃ with active metals Cr and Co. A good Cr-Co catalyst is a catalyst that is evenly dispersed on the γ -Al₂O₃ surface. The better it is dispersed, the better the diethyl ether synthesis process will be.

The γ -Al₂O₃ catalyst used in this study was commercial γ -Al₂O₃ with an average pore volume of 0.3178 cc/gr. The γ -Al₂O₃ catalyst was impregnated using a precursor solution of Cr(NO₃)₃.9H₂O and Co(NO₃)₂.6H₂O with a metal ratio of 1:1, 1:2, and 2:1 using the dry impregnation method. The impregnated catalyst was then dried in the oven for 12 hours to remove the remaining moisture content and calcined using N₂ gas to decompose the nitrate salts that have been impregnated onto the γ -Al₂O₃ support surface to become oxide and NO₂ gas. The calcination temperature used was 550 °C, this is because at 200 °C the water molecules in the interlamellar space begin to release, and at 450 °C some

of the nitrate molecules begin to release, while at 650 °C the remaining hydroxide ions will decompose and cause pore holes (craters) so that the optimum temperature of calcination is used, namely 550 °C.

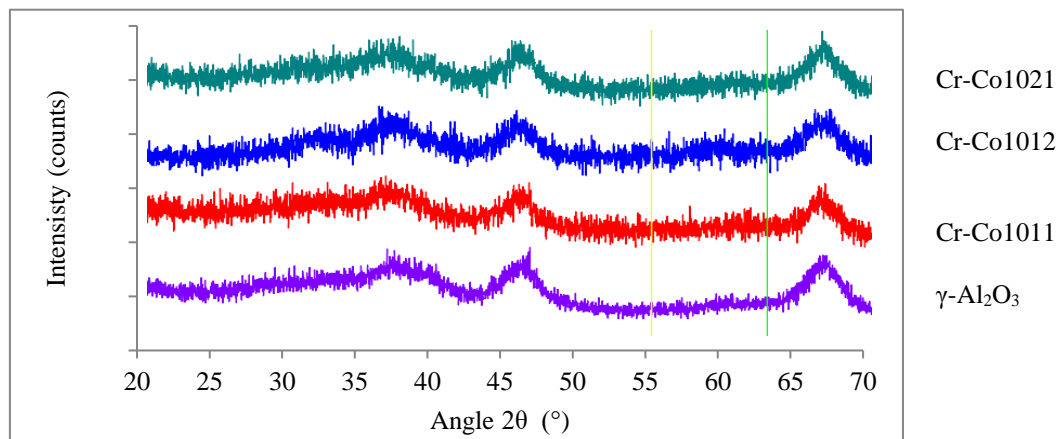


Figure 1 Diffractogram of Cr-Co/ γ -Al₂O₃ Catalyst 10% Metal Loading

The XRD spectra of the γ -Al₂O₃ catalyst and the Cr-Co/ γ -Al₂O₃ catalyst with 10% loading are shown in Figure 1. The typical γ -Al₂O₃ peaks appear at an angle of $2\theta = 36.80^\circ$, $2\theta = 45.49^\circ$ and $2\theta = 67.02^\circ$. Where the results obtained are in accordance with the peak γ -Al₂O₃ in JCPDS no. 50-0741 which has a peak of $2\theta = 37^\circ$, $2\theta = 45^\circ$, and $2\theta = 67^\circ$.

Loading of Cr-Co metal did not change the structure of the Cr-Co/ γ -Al₂O₃ catalyst and only a slight shift in intensity occurred at each diffraction peak. This shows that the metal is evenly distributed at γ -Al₂O₃ and the particle size is below the detection limit of the XRD technique (~ 5 nm). This result is in accordance with that reported by K Vishwakarma, 2007. According to Marsih et al., 2012 low intensity and wide diffraction peaks imply low crystallinity or small crystal size of the particles.

Table 1. BET Analysis Results of Cr-Co/ γ -Al₂O₃ Catalyst

Catalyst sample	Surface area (m ² /g)	Pore volume (cm ³ /g)	Average pore diameter (nm)
γ -Al ₂ O ₃	162.840	0.3178	3.4276
Cr-Co1011	91.919	0.1214	3.5064
Cr-Co1012	124.253	0.2134	4.6423
Cr-Co1021	133.499	0.2288	3.9027

Table 1 shows that there was a decrease in the surface area of the Cr-Co/ γ -Al₂O₃ catalyst after impregnation with Cr and Co metals. The surface area of γ -Al₂O₃ was obtained at 162.84 m²/g while the addition of Cr and Co metals to γ -Al₂O₃ caused the surface area of the Cr-Co/ γ -Al₂O₃ catalyst to decrease. The more metal added to γ -Al₂O₃, the effect on the decrease in surface area (Savitri et al, 2016). Judging from the pore structure, the addition of metal with the impregnation method decreases the surface area caused by the blockage of alumina pores (Vishwakarma, 2007) and indicates that metal particles have successfully spread on the γ -Al₂O₃ surface and enter the γ -Al₂O₃ pore (Sardar et al, 2011). In addition, a large pore diameter provides a better opportunity for the feed molecules to enter the pore (Eka et al., 2016).

Table 2. EDX Analysis Result of Metal Content in Cr-Co/ γ -Al₂O₃ Catalyst

Cr-Co Ratio	Catalyst sample	%metal (%weight)	
		Cr	Co
1:1	Cr-Co/ γ -Al ₂ O ₃ 1011	6.86	7.44
1:2	Cr-Co/ γ -Al ₂ O ₃ 1012	4.06	9.39
2:1	Cr-Co/ γ -Al ₂ O ₃ 1021	5.65	4.15

EDX analysis results aim to determine the metal content of Cr and Co contained in the Cr-Co/ γ -Al₂O₃ catalyst. Table 2 shows that the metals Cr and Co have been successfully impregnated into γ -Al₂O₃ and have entered the support pore. The metal content of Cr and Co contained in γ -Al₂O₃ has reached 10% by weight. However, the metal weight ratio is not in accordance with the desired ratio, this result can be due to the inequality of the impregnated precursor solution during the impregnation process of the catalyst so that the metal ratio at the time of the analysis result is not suitable.

3.2. Effect of Reaction Temperature and Nitrogen Stream

The independent variables used in this study and the parameters observed were the effect of operating temperature and inert gas flow rate (nitrogen stream) on the effectiveness of the reaction in producing DEE compounds which were interpreted by % conversion and % yield. The following is a graph of the relationship between ethanol conversion (%) vs reaction temperature with a catalyst mass of 3 grams with a Cr-Co metal ratio of 2: 1 and a loading percentage of 10% to the total catalyst in a fixed bed reactor with temperature variations from 100-200 °C and the flow rate variations of nitrogen gas were 200, 400, and 600 ml/minute.

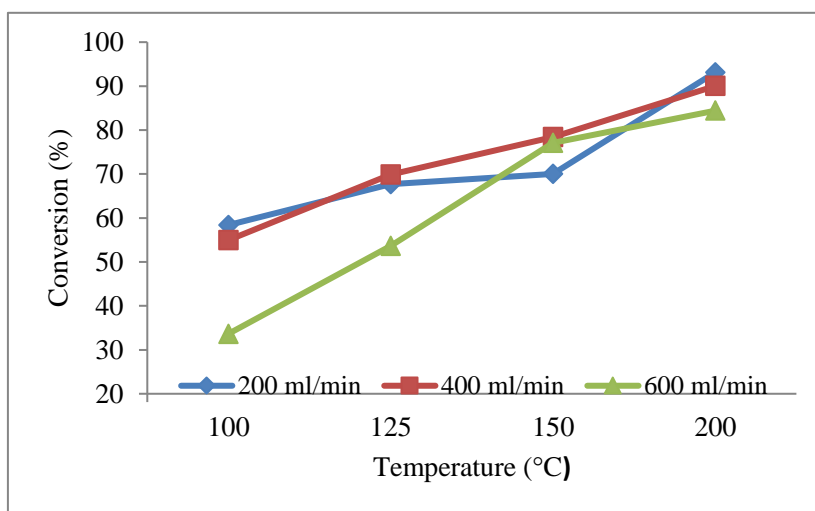


Figure 3. Effect of reaction temperature and nitrogen streams on ethanol conversions

Figure 3 shows that the nitrogen stream of 200 ml/min has a greater conversion value than the nitrogen stream of 400 ml/min and 600 ml/min. The largest conversion produced by a nitrogen stream of 200 ml/min was 93.12% at 200 °C, for the conversion of nitrogen stream of 400 ml/min which was 93.03% at 200 °C, and the conversion of nitrogen stream at 600 ml/min was 84.41 % at 200 °C. This shows that the greater the inert gas flow rate, the smaller the contact time between ethanol and the catalyst surface so that less ethanol reacts to form a product compound (Xu et al, 1989).

From Figure 3, it can be seen that the ethanol conversion increases with the increase in reaction temperature. The lowest conversion results were found at a reaction temperature of 100 °C and nitrogen stream of 600 ml/min with a conversion value of 33.64%. The highest conversion results were found at a reaction temperature of 200 °C and nitrogen stream of 200 ml/min with an ethanol conversion value of 93.12%.

In addition to the ethanol conversion, diethyl ether yield was also observed on various catalysts at various reaction temperatures. The yield value calculation is done to determine the degree of comparison between the desired and undesirable reactions (Fauziyah, 2009). In this study, the ethanol dehydration reaction that occurs can produce two types of products, namely diethyl ether and ethylene, and the desired product is diethyl ether. The basis used in the calculation of yield of diethyl ether is the flow rate, namely moles per unit time, where the yield can be calculated by comparing the amount of product desired per the amount of reactants used or consumed.

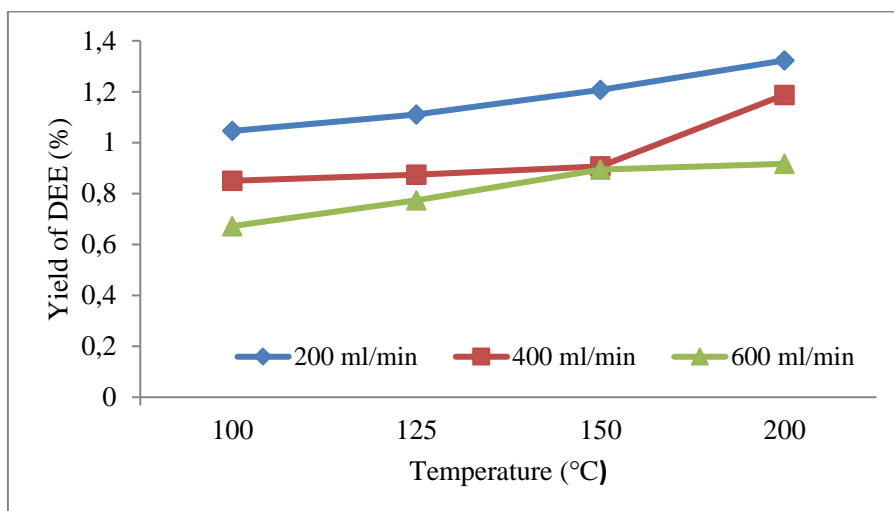


Figure 4. Effect of reaction temperature and nitrogen streams on diethyl ether yield

Figure 4 shows that the DEE yield was detected at 200, 400 and 600 ml/min nitrogen stream at various temperatures. At nitrogen stream of 200 ml/min, the yield value of diethyl ether is the largest when compared to nitrogen stream of 400 and 600 ml/min. This shows that the greater the inert gas flow rate, the smaller the contact time between ethanol and the catalyst surface so that less ethanol reacts to form a product compound (Xu et al, 1989). At 200 ml/min nitrogen stream, the highest yield of DEE was 1.323% at 200 °C.

3.3. Effect of Reaction Temperature and Metal Catalyst Loading

Below is a graph of the relationship between ethanol conversion (%) vs. reaction temperature with a catalyst mass of 3 grams with a 10% Cr-Co loading presentation to total catalyst at different metal loading in a fixed bed reactor using nitrogen stream 200 ml/minute.

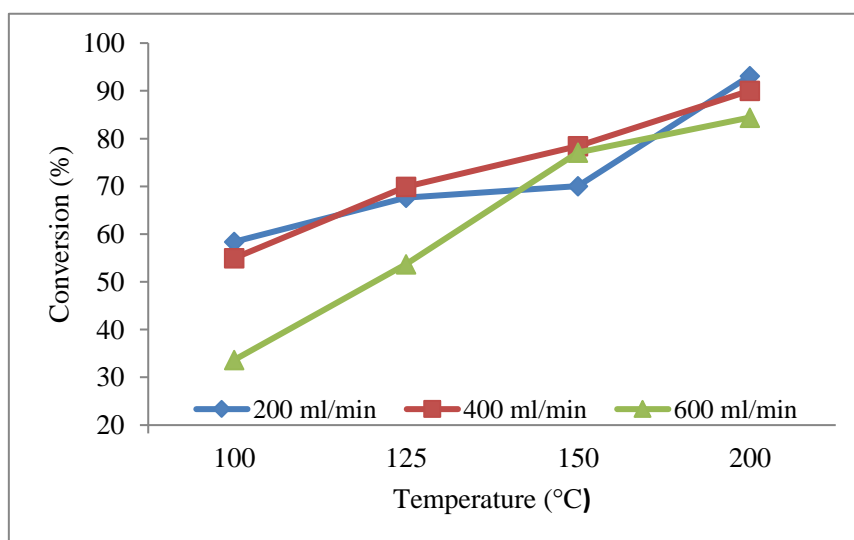


Figure 5. Effect of reaction temperature and metal ratio on ethanol conversions

Figure 5 shows that the ethanol conversion increases with increasing reaction temperature at the same metal loading. The lowest conversion yield occurs when the operating temperature is 100 °C with a conversion value of 50.54%, which is obtained when using a metal impregnation ratio of 1:1 ratio. In 1: 1 metal impregnation, the ethanol conversion was 57.78% at 125 °C, the conversion was 67.85% At 150 °C and the conversion was 81.92% at 200 °C. In 1:2 metal impregnation, 52.33% conversion was

obtained at 100 °C, then 61.39% conversion at 125 °C was obtained, 68.05% conversion was obtained at 150 °C, and 91.64% conversion was obtained at 200 °C. In 2:1 metal impregnation, 58.39% conversion was obtained at 100 °C, 67.66% conversion was obtained at 125 °C, 70.05% conversion was obtained at 150 °C, and 93.12% conversion was obtained at 200 °C. Increasing the temperature can increase the ethanol conversion according to the Arrhenius equation. In this equation, increasing the temperature will increase the reaction rate constant so that it will increase the reaction rate. This is in accordance with the results of research by Widayat et al. (2011) which showed that the higher the reaction temperature, the greater the resulting ethanol conversion.

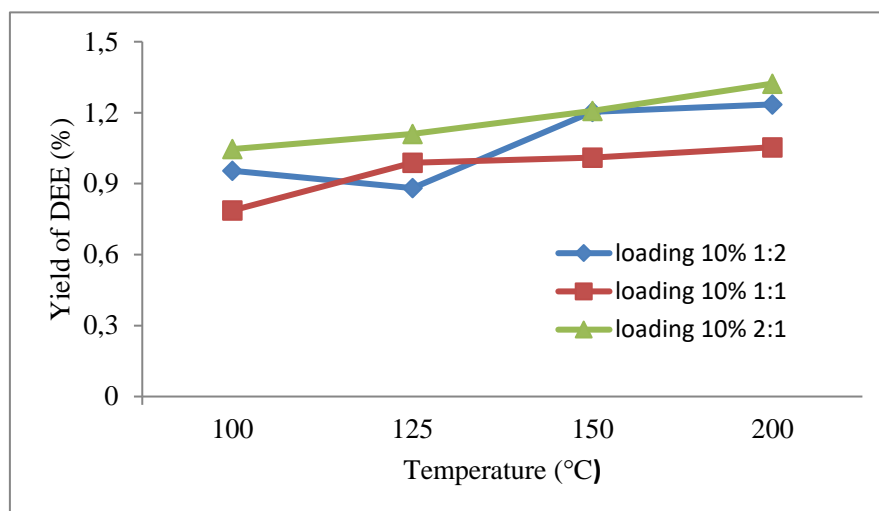


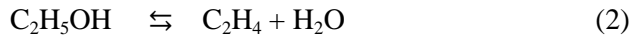
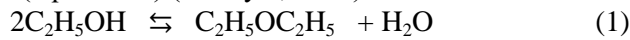
Figure 6. Effect of reaction temperature and metal ratio on diethyl ether yield

Figures 6 show that 2:1 catalyst impregnation produces higher yield values for diethyl ether compared to 1:1 and 1:2 catalyst impregnations. The amount of DEE yield occurs because 2:1 catalyst impregnation has a larger surface area than 1:1 and 1:2 catalyst impregnations. For 10% metal loading, the largest DEE yield produced at 1:1 catalyst impregnation is 1.054% at 200 °C, for 1:2 catalyst impregnation the yield is 1.235%, and 2:1 impregnation the DEE yield is 1.323% at 200 °C.

From Figures 6 it can be seen that the increase in yield of diethyl ether is linear with the increase in reaction temperature. The increase in DEE yield was due to the increase in ethanol conversion. In this study, the ethanol dehydration reaction was operated at temperatures between 100-200 °C. This is because the dehydration reaction of ethanol to DEE is an exothermic reaction, at temperatures higher than 200 °C ethanol will dehydrate to ethylene. So that at temperatures higher than 200 °C, the DEE yield will decrease while the ethylene yield will increase. In the research conducted (Kamsuwan and Jongsomjit, 2016) using an Al-based solid acid catalyst, the ethanol dehydration reaction will produce large amounts of diethyl ether at low temperatures but ethylene will form at higher temperatures. At 200 °C, all types of catalysts only form diethyl ether products but the ethanol conversion is very small, which is approximately 10%. Low DEE yields due to low conversion. To improve the DEE yield, a chemical promoter may be required. Chen et al, 2007 studied the addition of several promoters to improve catalytic dehydration. The chemical promoters used for this reaction include titania, niobia, molybdenum oxide, and silica.

It can be seen in Figures 6 that the DEE yield obtained is very small. This can occur due to several factors, the first factor is that when do sampling, the product has not condensed completely into a liquid, so that products that are still in the gas phase come out and evaporate in the air, DEE itself has a boiling point of 35 °C. The second factor is that the reaction that occurs in this catalytic test process is not a single reaction, where other reactions occur besides the reaction of the formation of diethyl ether from ethanol. Other chemical reactions that may occur in this ethanol catalytic process are the

dehydration reaction of ethanol to diethyl ether (equation 1) and the dehydration reaction of ethanol to ethylene (equation 2) (Widayat, 2012):



Ethylene compounds may occur in the gas phase, but in this study the gas product was not subjected to chromatographic analysis due to difficulty in sampling.

4. Conclusion

Cr-Co/ γ -Al₂O₃ catalyst with various metal ratio loading prepared using incipient wetness impregnation is considered to be the potential catalyst for the production of diethyl ether through ethanol dehydration reaction. The result showed that the largest ethanol conversion and largest yield of diethyl ether was produced by the 200 ml/min nitrogen stream. At temperature 200 °C and metal ratio impregnation 2:1 the highest ethanol conversion of 93.12% and highest DEE yield of 1.323% was achieved.

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