Synthesis and Characterization of Cr-Co/γ-Alumina Catalyst for Ethanol Dehydration

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Abstract. Primary alcohol dehydration reaction catalysis by using γ-Al_2O_3 catalyst can produce ether compounds and alkenes. The combination chrome-cobalt and alumina catalyst could convert ethanol to diethyl ether in the ethanol dehydration process. The purpose of this study was to determine the performance of Cr-Co with the support of γ-Al_2O_3 catalyst for ethanol dehydration to diethyl ether. Cr-Co/γ-Al_2O_3 catalyst was prepared using incipient wetness impregnation.γ-Al_2O_3 catalyst was impregnated with chrome and cobalt metals at various metal loading 5 and 10% and impregnated ratio of Cr-Co (1:1; 1:2; and 2:1). The samples were calcined at 550°C for 3 hours in nitrogen and then reduced continuously by hydrogen at 600°C for 5 hours. Then catalyst was analyzed for characterization using BET, XRD, and SEM-EDX. Treatment of γ-Al_2O_3 in various ratio of chrome and cobalt impregnation decreased the total surface area. Increasing metal loading in Cr-Co impregnation on γ-Al_2O_3 decreased total surface area and increased average pore diameter. Impregnation process lowered the crystallinity but still maintained the material crystal structure. The reduced surface area of the catalyst does not mean the effectiveness of the catalyst is reduced, but the metal will actually increase the active site of the catalyst and will affect the rate of reaction in the catalyst.

INTRODUCTION

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 monolic 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).

The impregnation method is carried out by contacting a porous support with a solution consisting of one or more metal salts that have a certain concentration (Satterfield, 1991). The impregnation process begins with selecting the support / buffer to be used. In this case the support has the function of providing a wide surface area to make it easier to spread the active site, so that the contact surface is wider and more efficient. The buffer materials that are often used in the catalyst carrier are alumina (Al_2O_3), zeolite, and magnesia (Topsoe et al., 1996).

The purpose of impregnation is to fill the pores using a metal salt solution with a certain concentration. After impregnation, the next step is drying and heating at high temperature (calcination), so that the precursor decomposes into active species. Calcination in the impregnation method aims to increase the stability of the catalyst against temperature changes. In dry impregnation (incipient wetness impregnation) method, the amount of active precursor solution (impregnant) added is equal to the volume of the buffer. The advantage of this method is that it is accurate in controlling the active components to be combined in the catalyst, the disadvantage is that it is difficult to make a large% by weight of the active component.

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 (Srinivasan et al, 2019). This study investigated the performance of Cr-Co with the support of γ-Al_2O_3 catalyst for ethanol dehydration to diethyl ether. Cr-Co/γ-Al_2O_3 catalyst was prepared using incipient wetness impregnation.γ-Al_2O_3 catalyst was impregnated with chrome and cobalt metals at various metal loading and impregnated ratio of Cr-Co.

EXPERIMENTAL

Instrumentation

The impregnation equipment used in this study were beaker glass, spatula, and spray bottle. Beaker glass was used to put catalysts and spray bottles filled with a metal solution that has been diluted using distilled water. Then the metal solution is sprayed onto the catalyst.

The calcination equipment used in this study was a tubular furnace with the German Linn Elektro Therm brand. This tubular furnace has a length of 80 cm with a diameter of 10 cm. This tubular furnace is equipped with temperature control to regulate the calcination operating temperature. For the place to put the catalyst in the furnace used nacelle from quartz material. The nacelle used is ½ inch in diameter and 10 cm long. This calcination equipment is equipped with an air compressor to supply air and nitrogen gas to the calcination reactor and hydrogen gas which is used to reduce the metals contained in the synthesized catalyst. Erlenmeyer filled with water is used as a marker that the gas flow out through the calcination reactor. The range of calcination tools is presented in Fig. 1.

Catalyst Preparation

γ-Al_2O_3 as support was impregnated with metal salt solutions, $Cr(NO_3)_3.9H_2O$ and $Co(NO_3)_2.6H_2O$ 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-Al_2O_3 catalyst (Merck), then dissolve $Cr(NO_3)_3.9H_2O$ (Merck) according to the variable loading of the catalyst into distilled water. Next, do dry impregnation of $Cr(NO_3)_3.9H_2O$ solution by spraying the metal solution gradually into the γ-Al_2O_3 catalyst until the volume of the metal solution is equal to the volume of the γ-Al_2O_3 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 ºC for 12 hours. Do the same for the $Co(NO_3)_2.6H_2O$ (Merck) solution. The impregnated sample was dried for 12 hours in an

oven at 120 °C, then calcined using N_2 at 550 °C for 3 hours. Metal catalyst which is still in the form of oxide is reduced with H_2 gas at 600 °C for 5 hours in the furnace. After the reduction, the H_2 gas flow and the heater were turned off but the N_2 gas was still flowed until the catalyst reached room temperature. This catalyst was used on ethanol dehydration reaction at 100-200°C in continuous fixed bed reactor for 2 hours.
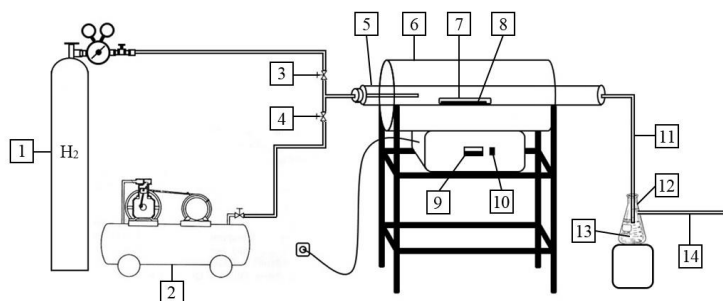

FIGURE 1. Tube Furnace Reactor (Linn Elektro Therm) for Calcination Process

1. H_2 gas cylinder
2. Compressor
3. H_2 gas valve
4. Air valve
5. Calcination reactor tube
6. Furnace
7. Nacelle
8. Catalyst
9. Furnace temperature control panel
10. Power button
11. Gas outlet tube calcination reactor
12. Erlenmeyer
13. Water
14. Gas outlet tube Erlenmeyer

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-Al_2O_3 buffer.

RESULT AND DISCUSSION

This study used a Merck γ-Al_2O_3 catalyst. The impregnation method was carried out using incipient wetness impregnation or dry impregnation method using distilled water. The catalyst was then impregnated using the active metal obtained by dissolving the precursor salt $Cr(NO_3)_3.9H_2O$ and $Co(NO_3)_2.6H_2O$ with a metal loading presentation of 5% and 10% and the ratio of Cr and Co metals is 1:1, 1:2, and 2:1. The impregnated catalyst was then dried in the oven for 12 hours at a temperature of 120 °C to remove the remaining moisture content and calcined using N_2 gas for 3 hours to decompose the nitrate salts that have been impregnated onto the γ-Al_2O_3 support surface to become oxide and NO_2 gas. The calcination temperature used was 550 °C, this is because at 200 °C the water molecules in the inter lamellar 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. Metal catalyst which is still in the form of oxide is reduced with hydrogen gas at 600 °C for 5 hours in the furnace. After the reduction, the H_2 gas flow and the heater are turned off, but the N_2 gas is still flowed until the catalyst reaches room temperature.

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-Al_2O_3 with active metals Cr and Co. A good Cr-Co catalyst is a catalyst that is evenly dispersed on the γ-Al_2O_3 surface. The better it is dispersed, the better the diethyl ether synthesis process will be.

XRD analysis is used to identify the crystalline material phase, crystallinity and to determine the crystal size of the synthesis results. Each crystal peak shown gives a specific pattern and the diffractogram peak is an indication of the presence of a particular compound. XRD analysis was used to determine the characters formed after the impregnation process using Cr-Co metal. The XRD analysis also reviewed whether the impregnation of Cr-Co metal into the γ-Al$_2$O$_3$ pore was successful or not. X-ray diffractometer is an instrument used to find out structural information and identify the material phase of the catalyst. From the XRD measurement results, the value of d (crystal field distance) and the angle of 2θ and the intensity were obtained by comparing them with standard data. The XRD γ-Al$_2$O$_3$ pattern used as a reference is the JCPDS document (Joint Committee on Powder Diffraction Standards) no. 50-0741. In this reference diffraction pattern, the standardized peaks of the diffractogram reading for γ- Al$_2$O$_3$ are at an angle of $2\theta = 37$ °; 45 °; 67 °.

(a)

(b)
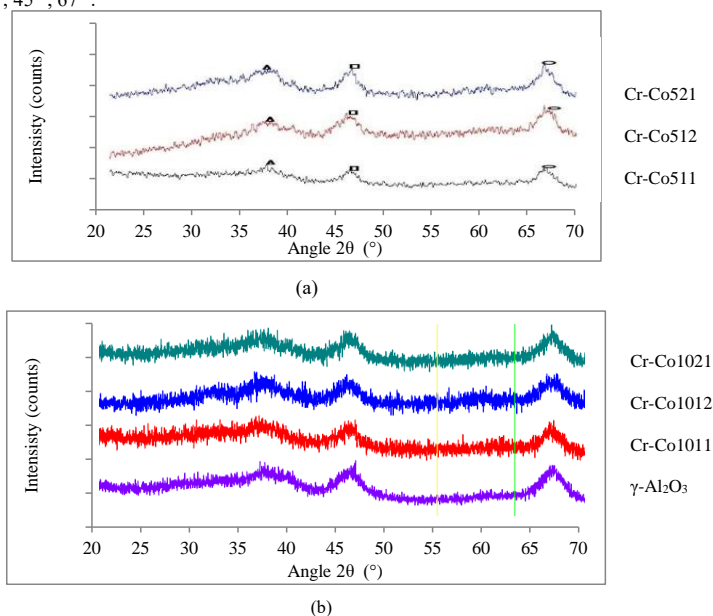
FIGURE 2. Diffractogram of Cr-Co/γ-Al$_2$O$_3$ Catalyst (a) 5% Metal Loading and (b) 10% Metal Loading

Fig. 2 shows that all catalysts have the same typical peak without any new peaks appearing. There were no typical peaks of Cr or Co metal in the form of oxide compounds (Cr$_2$O$_3$ with JCPDS 38-1479; CrO with JCPDS 30-1468; Co$_3$O$_4$ with JCPDS 42-1467; CoO with JCPDS 43-1004) and in elemental form (Cr with JCPDS 01-085-1336; Co with JCPDS 05-0727) on 5% and 10% metal loading Cr-Co diffractogram. γ-Al$_2$O$_3$ after impregnation process still has the same characteristic structure as γ-Al$_2$O$_3$ before impregnation process (Cr-Co/γ-Al$_2$O$_3$). Impregnation process lowered the crystallinity but still maintained the material crystal structure. Loading of Cr-Co metal did not change the structure of the Cr-Co/γ-Al$_2$O$_3$ catalyst and only a slight shift in intensity occurred at each diffraction peak. This shows that the metal is evenly distributed in γ-Al$_2$O$_3$ 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.

The Cr-Co/γ-Al$_2$O$_3$ catalyst was analysed again using BET analysis to determine the changes in surface area, pore volume, and mean pore diameter after impregnation with Cr and Co metals. The results of BET analysis of various samples after the impregnation process are presented in Table 1.

Table 1 shows that there was a decrease in the surface area of the Cr-Co/γ-Al$_2$O$_3$ catalyst after impregnation with Cr and Co metals. The surface area of γ-Al$_2$O$_3$ was obtained at 162.84 m^2/g while the addition of Cr and Co metals to γ-Al$_2$O$_3$ caused the surface area of the Cr-Co/γ-Al$_2$O$_3$ catalyst to decrease. Treatment of γ-Al$_2$O$_3$ in various ratio of chrome and cobalt impregnation decreased the total surface area. Increasing metal loading in Cr-Co impregnation on

γ-Al_2O_3 decreased total surface area and increased average pore diameter. The more metal added to γ-Al_2O_3, 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-Al_2O_3 surface and enter the γ-Al_2O_3 pore. In addition, a large pore diameter provides a better opportunity for the feed molecules to enter the pore.

TABLE 1. BET Analysis Results of Cr-Co/γ-Al_2O_3 Catalyst

Catalyst sample	Surface area (m^2/g)	Pore volume (cm^3/g)	Average pore diameter (nm)
γ-Al_2O_3	162.8400	0.3178	3.4276
Cr-Co511	156.0686	0.1941	4.9757
Cr-Co512	160.3335	0.2527	21.2743
Cr-Co521	162.4794	0.2982	19.6498
Cr-Co1011	91.9190	0.1214	3.5064
Cr-Co1012	124.2530	0.2134	4.6423
Cr-Co1021	133.4990	0.2288	3.9027

The visible phenomena are a decrease in pore volume and an increase in average pore diameter on the catalyst surface after impregnation with Cr and Co metal. This can be explained as follows, a decrease in surface area is accompanied by a decrease in pore volume and an increase in average pore diameter: Increasing the size of the catalyst particles will reduce the surface area of the catalyst then an increase in the mean pore diameter occurs due to the closure/blockage of metal particles at the pore mouth which has a small pore diameter. Then a decrease in pore volume occurs because metal particles have entered and filled the pore volume on the catalyst and this occurs sticking metal particles to the pore mouth.

The reduced surface area of the catalyst does not mean the effectiveness of the catalyst is reduced, but the metal will actually increase the active side of the catalyst and will affect the reaction rate in the catalyst (Fogler, 1999).

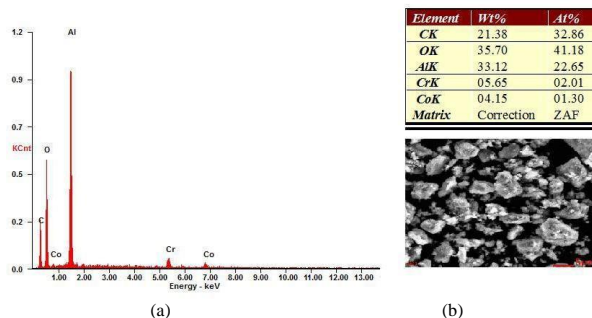| Element	Wt%	At%
CK	21.38	32.86
OK	35.70	41.18
AlK	33.12	22.65
CrK	05.65	02.01
CoK	04.15	01.30
Matrix	Correction	ZAF

(a)   (b)

FIGURE 3. (a) EDX Analysis Results and (b) SEM Analysis Result of Cr-Co1021 Catalyst

EDX analysis results aim to determine the metal content of Cr and Co contained in the Cr-Co/γ-Al_2O_3 catalyst. It can be seen the results of EDX analysis in Fig.3 for 10% metal loading metal ratio 2:1.Table 2 shows that the metals Cr and Co have been successfully impregnated into γ-Al_2O_3 and have entered the support pore. The metal content of Cr and Co contained in γ-Al_2O_3 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.

TABLE 2. EDX Analysis Result of Metal Content in Cr-Co/ γ-Al_2O_3 Catalyst

Metal loading	Cr-Co ratio	Catalyst sample	%metal (%weight) Cr	Co
5%	1:1	Cr-Co/γ-Al_2O_3 511	3.25	2.69
	1:2	Cr-Co/γ-Al_2O_3 512	2.68	6.10
	2:1	Cr-Co/γ-Al_2O_3 521	4.15	2.09
10%	1:1	Cr-Co/γ-Al_2O_3 1011	6.86	7.44
	1:2	Cr-Co/γ-Al_2O_3 1012	4.06	9.39
	2:1	Cr-Co/γ-Al_2O_3 1021	5.65	4.15

CONCLUSION

The chrome and cobalt impregnation decreased the total surface area from 162.84 m^2/g (on γ-Al_2O_3) to 91.919-162.4794 m^2/g (on Cr-Co/γ-Al_2O_3). The addition of metal with the dry impregnation method decreases the surface area caused by the blockage of alumina pores. The reduced surface area of the catalyst does not mean the effectiveness of the catalyst is reduced, but the metal will actually increase the active side of the catalyst and will affect the reaction rate in the catalyst. The visible phenomena are a decrease in pore volume and an increase in average pore diameter on the catalyst surface after impregnation with Cr and Co metal. Impregnation process lowered the crystallinity but still maintained the material crystal structure. Cr-Co/γ-Al_2O_3 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

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