

Synthesis of Catalyst Cobalt Impregnated on Activated Natural Zeolite, Co/ANZ

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Abstract

Research has been done on the synthesis of catalyst Co/Activated Natural Zeolite. The variables studied were the mass ratio of Cobalt to Zeolite and temperature of reduction during catalyst activation. The catalyst produced were analysed in their acidity and surface area. Acidity was presented in the form of ammonia and pyridine adsorption on the catalyst surface. The results showed the increasing Cobalt to Zeolite mass ratio will increase acidity of the catalyst produced. Reduction temperature during catalyst activation also gave same effect as Cobalt to Zeolite mass ratio did. Best ratio within the range of this study was Cobalt to Zeolite mass ratio of 6:20, which was found at reduction temperature of 400 C. This ratio gave catalyst acidity correspond to ammonia adsorption of 6.4615 mmol/g, and to pyridine adsorption of 2.6047 mmol/g catalyst. The best reduction temperature was 450 C at ratio of 6:20. The acidity of this catalyst was of 7.5202 mmol/g as in ammonia adsorption, and was of 3.662 mmol/g as in pyridine adsorption. Catalyst surface area of the best ratio was 32.63 m²/g, whilst catalyst surface area of the best reduction temperature was 38.95 m²/g. **Keywords:** Surfactant, methyl ester sulfonate, reaction time, ketapang seed oil

Keywords: catalyst, cobalt, activated natural Zeolite

Abstrak (Indonesian)

Telah diteliti pembuatan katalis Co/Zeolit Alam Aktif. Variabel yang diteliti adalah rasio massa Kobalt terhadap Zeolit dan suhu reduksi pada aktivasi katalis. Analisa hasil dilakukan terhadap karakter katalis yang meliputi keasaman dan luas muka katalis. Keasaman dinyatakan dalam adsorpsi terhadap amonia dan piridin pada permukaan katalis. Hasil penelitian menunjukkan bahwa kenaikan rasio massa Kobalt terhadap Zeolit menaikkan keasaman katalis hasil. Suhu reduksi selama aktivasi katalis juga memberikan hasil yang sama. Rasio terbaik pada range percobaan ini adalah 6:20, yang diperoleh pada suhu reduksi 400 C. Rasio ini memberikan keasaman katalis 6,4615 mmol/g pada adsorpsi dengan amonia dan 2.6047 mmol/g pada adsorpsi dengan piridin. Suhu reduksi terbaik pada range percobaan ini adalah 450 C yang diperoleh pada rasio 6:20. Keasaman katalis ini adalah 7.5202 mmol/g pada adsorpsi dengan amonia dan 3.6662 mmol/g pada adsorpsi dengan piridin. Luas muka katalis dengan rasio terbaik adalah 32.63 m²/g, dan luas muka katalis dengan suhu reduksi terbaik adalah 38.95 m²/g.

Keywords: katalis, kobalt, zeolit alam aktif

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INTRODUCTION

Biodiesel is vegetable oil having characteristics resemble of solar, with energy

content (37 MJ/kg) lower than of solar (42 MJ/kg). This is due to biodiesel has longer carbon chain (16-18 carbon atoms) than solar (14-17 carbon atoms).

Cracking toward vegetable oil (biodiesel) may result in substances with shorter carbon chain with higher energy content, namely biogasoline (5-10 carbon atoms), biokerosine (10-14 carbon atoms), and biosolar.

Many process of cracking were done simultaneously with hydrogenation, called hydrocracking. Hydrocracking process needs two components of catalyst, which are metal component as hydrogenation catalyst and acid component as cracking catalyst (Benito, 2000). For this purpose, the catalyst often used is the combination of transition metal and active Zeolite. Fanani (2006) has been successful in cracking of coal tar using catalyst of Ni/Co impregnated to natural Zeolite, to produce fractions of gasoline, kerosine and solar.

Among transition metals usually employed as hydrogenation process were Pt, Pd, Mo, Co, and Cr. Platinum, Pt, and palladium, Pd, are generally behave as good hydrogenation catalysts, but they are very expensive. Cobalt, Co, has empty orbital d as chromium has, yet Rakhmat, A., et al (2007) reported that Cobalt impregnated to active natural Zeolite has the ability to crack coal tar better than Chromium impregnated to active natural Zeolite. Based on those facts, this research was conducted to synthesize catalyst of Cobalt impregnated to active natural Zeolite, denoted as Co/ANZ, which will be used for hydrocracking of vegetable oil. The main goal of this work is to synthesize catalyst of Co/ANZ, with particular aim is to study the effect of mass ratio of cobalt to active natural Zeolite and the reduction temperature during catalyst activation to the characteristics of the catalyst produced. The products were analysed in their characteristics of acidity and surface area. The acidity was determined in term of ammonium and pyridine adsorption on the catalyst surface.

MATERIALS AND METHODS

The materials used in this research were: active Zeolite of 100 mesh size, demineralised water, HF 1%, HCl 1M, NaOH 2M, NH_4NO_3 1M, $(\text{NH}_4)_6\text{Co}_7\text{O}_{24}$, filter paper Whatman No.41, bottled hydrogen gas, bottled oxygen gas, metanol 99%, NaOH, phenolphthalein indicator, isopropyl alcohol.

Equipments used are: analytical scale, standard glass equipments (measuring flask, beaker glass, micro pipette, filter, vial bottle, etc), pH meter, oven,

crucible, desiccator, hotplate, magnetic stirrer, thermometer, reactor, furnace, thermocouple, flowmeter, gas valve, voltage regulator, stopwatch, porosimeter.

Preparation of H-Zeolite

Natural zeolite of 100 mesh was soaked in HF 1% for 60 minutes, followed by washing the Zeolite with demin water and filtering it until the pH of the filtrate become neutral. After that, the Zeolite was dried in oven at 130 °C for 3 hours. Dry Zeolite was soaked in HCl 1M for 24 hours, filtered, washed with demineralised water until the filtrate was neutral. After this, the Zeolite was dried in oven for 3 hours at 130 °C. Zeolite was then saturated with NaOH 2M for 24 hours, filtered and washed until the pH of the filtrate becomes neutral. This Zeolite is called as Na-Zeolite. This Na-Zeolite was soaked in NH_4NO_3 1M for 24 hours, filtered, washed and dried at 550 °C for 5 hours. This is called as H-Zeolite.

Catalyst impregnation

H-Zeolite was soaked with stirring in solution of $(\text{NH}_4)_6\text{Co}_7\text{O}_{24}$ for 24 hours. For the first 4 hours, ammonia was added drop by drop. After that, the Zeolite which contained cobalt was dried at 130 °C for 3 hours until it turned into paste. This was calcined at 550 °C for 5 hours. This procedure of catalyst impregnation was done out with variation of mass ratio of cobalt to Zeolite.

Catalyst oxydation

The product from cobalt impregnation to Zeolite (20 gram) was put in the reactor equipped with glasswool in its bottom. The reactor was placed inside furnace. Oxygen was flown into the furnace and the voltage regulator connected with the furnace was set at 160 V to keep the temperature at desired value. Time for oxydation started to be calculated after the temperature reach 350 °C. Furnace temperature was kept at 350 °C \pm 5 °C for 2 hours by adjusting the voltage regulator.

Catalyst reduction

The result from catalyst oxydation was hydrogenated with hydrogen gas at desired temperature for 2 hours. The product from this hydrogenation is called as Co/ANZ catalyst.

Product analysis

The characteristics of the catalyst were tested for their acidity and surface area. Acidity test covered the

adsorption of ammonia and pyridine on the catalyst surface area.

Acidity test

Acidity test was conducted with adsorption of NH_3 gas as follow: catalyst was heated in the oven for 24 hours at 110°C and then cooled inside desiccator. Amount of 1 gram of catalyst was put in a crucible inside desiccator together with ammonia of 5 ml in another crucible. Desiccator was vacuumed and left for 24 hours. The crucible with catalyst was taken out from desiccator, and weighted. Acidity was calculated from the amount of ammonia adsorbed by the catalyst using the formula:

$$\text{Amount of ammonia adsorbed} = (w_{\text{NH}_3} \cdot 1000) / (w_{\text{catalyst}} \cdot \text{MW}_{\text{NH}_3}) \dots\dots\dots(1)$$

with: w_{NH_3} = weight of NH_3 adsorbed, w_{catalyst} = weight of catalyst, MW_{NH_3} = molecular weight of NH_3 .

Determination of surface area

The surface area was calculated using equation:

$$\text{Surface area} = (\text{amount of nitrogen adsorbed}) \times (\text{catalyst cross sectional area}) \dots\dots\dots(2)$$

The porosity of the catalyst was determined using porosimeter NOVA 1000.

RESULT AND DISCUSSION

The effect of mass ratio of cobalt to active natural Zeolite to the acidity of the catalyst

Acidity is the amount of milimol acid per unit of catalyst weight or surface area. Acidity test was conducted in order to know the amount of acid situs in the catalyst, without considering how strong the acid situs was. The amount of acid situs with ammonia as adsorbate show the amount of total acid situs with assumption the size of ammonia molecule is small enough, made it possible to get into catalyst pores. The amount of acid situs with pyridine as adsorbate will give the amount of surface acid situs with assumption that the size of pyridine molecule was big that makes it enable only to adsorb at the outer area of the catalyst. The results of determination of the amount of acid situs at each sample ratio is presented in Figure 1. It was obvious from Figure 1 that acidity increased with the increase of mass ratio of Co to ANZ, both for adsorbate ammonia and pyridine. These suggest that cobalt is dispersed well, both on the outer surface and inside pores of activated natural Zeolite. This is because

cobalt has empty d orbital or partly filled with electrons, thus enabling it to accept electron pairs from ammonia and pyridine as the base adsorbates.

Best ratio within the range of this study was Co to ANZ mass ratio of 6:20, which was found at reduction temperature of 400°C . This ratio gives catalyst acidity correspond to ammonia adsorption of 6.4615 mmol/g, and to pyridine adsorption of 2.6047 mmol/g catalyst.

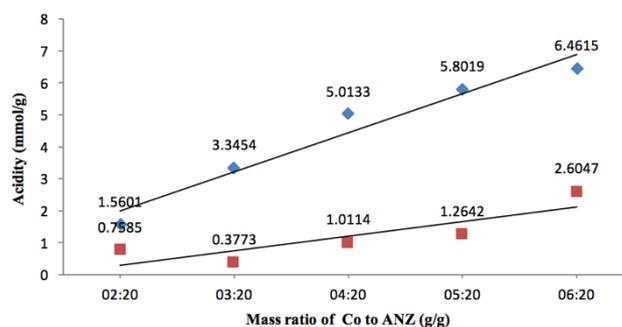


Figure 1. The effect of Co to ANZ ratio to the acidity of catalyst (reduction temperature of 400°C , flow rate H_2 gas of 1 ml/sec, 2 gram catalyst). Upper data were the results with adsorbate ammonia, and lower data were the results with adsorbate pyridine.

The effect of reduction temperature to the acidity of the catalyst.

Catalyst with best ratio from previous results, that is 6:20, was used to study the effect of reduction temperature. Data of acidity of the catalyst for each variation of reduction temperatures are presented in Figure 2. It is obvious from Figure 2 that increasing reduction temperature, increases acidity of the sample catalysts. These were because at high reduction temperatures cobalt oxide was loss from the catalyst. Consequently cobalt attached with ANZ in Co/ANZ catalyst, which was initially connected with oxygen as cobalt oxide, turns to cobalt metal, making it more reactive in adsorbing ammonia and pyridine. Best reduction temperature was 450°C at ratio of 6:20. The acidity of this catalyst was of 7.5202 mmol/g as in ammonia adsorption, and was of 3.662 mmol/g as in pyridine adsorption.

Effect of mass ratio of Co to ANZ to surface area of the catalyst

Results of the determination of each mass ratio of Co to ANZ were given in Figure 3. It is obvious from this figure that the surface area of the catalyst increases with the increase in ratio of Co to ANZ.

These might be due to the attachment of Co at the surface of ANZ causes the monolayer at ANZ surface opened. This opening causes the specific surface area of the catalyst increases. Best result for this variable is mass ratio Co to ANZ of 6:20, which gives surface area of 32.63 m²/g catalyst.

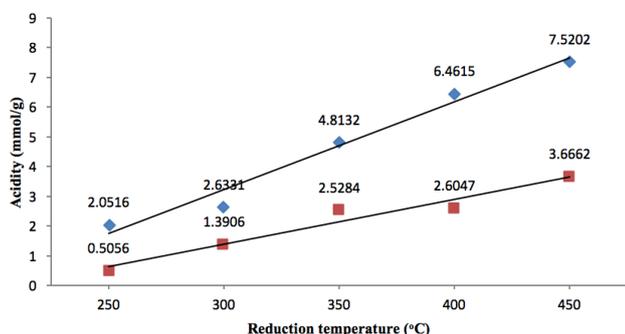


Figure 2. Effect of reduction temperature on the acidity of the catalyst (ratio Co to ANZ of 6:20, flow rate of H₂ gas 1 ml/sec, 2 gram catalyst). Upper data were with ammonia as adsorbate, lower data were with pyridine as adsorbate.

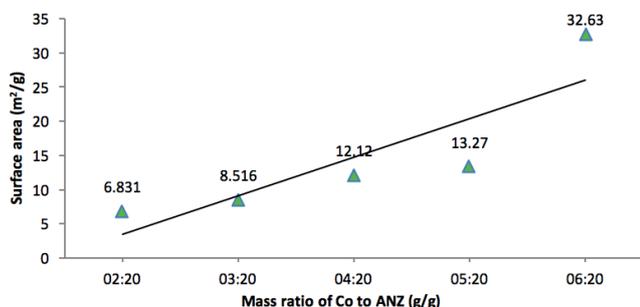


Figure 3. Effect of mass ratio of Co to ANZ to surface area of the catalyst (reduction temperature of 400 °C, 2 gram catalyst)

Effect of reduction temperature to the surface area of the catalyst

Catalyst with mass ratio Co to ANZ of 6:20 were used to study the effect of reduction temperature on the surface area of the catalyst. The data of surface area at each reduction temperature were presented in Figure 4. It can be seen from Figure 4, that the surface area of the catalyst increases with the increase of reduction temperature. These are maybe due to high reduction temperature helps in the opening of the new pores in the catalyst body. Also, the increase in reduction temperature will cause Co loss from its bond to ANZ. This may cause the formation of crevices at the catalyst, after the leave of cobalt oxyde. This, in turn causing the increase in the surface area of the catalyst.

Best result for this variable is temperature of 450 °C, which gives surface area of 38.95m²/g.

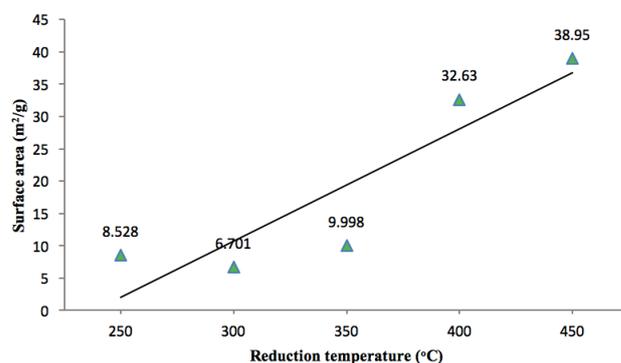


Figure 4. Effect of reduction temperature on the surface area of the catalyst (mass ratio of Co to ANZ of 6:20, 2 gram catalyst)

CONCLUSION

1. The mass ratio of Co to ANZ increases both the acidity and the surface area of the catalyst. Best value in the range of this study was Co to ANZ mass ratio of 6:20, which was found at reduction temperature of 400 °C. This ratio gave catalyst acidity correspond to ammonia adsorption of 6.4615 mmol/g, and to pyridine adsorption of 2.6047 mmol/g catalyst. The surface area at this best ratio is 32.63 m²/g.
2. Reduction temperature increases both acidity and surface area of the catalyst. Best reduction temperature is 450 o C, which was found at best mass ratio of Co to ANZ of 6:20. This best temperature gives acidity of 7.3502 mmol/g catalyst with adsorbate ammonia, and 3.6662 mmol/g catalyst with adsorbate pyridine. The surface area for this best reduction temperature is 38.95 m²/g catalyst.
3. Practical conclusion from this study is that acidity and surface area of the catalyst can be increased by increasing the ratio of Co to ANZ and increasing the reduction temperature.

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