

THE CHARACTERIZATION OF Co/SiO₂ CATALYST FOR FISCHER TROPSCH SYNTHESIS

Bambang Suwondo Rahardjo

Technology Center for Energy Resources Development
 Deputy for Information, Energy and Material of Technology
 Agency for the Assessment and Application of Technology (BPP Teknologi)
 BPPT II Building 22ndFl, Jl. M.H. Thamrin No. 8 Jakarta 10340
 Email: bamsr52@yahoo.co.id

ABSTRACT

A variety of catalysts can be used for the Fischer–Tropsch process, but the most common are the transition metals cobalt, iron, and ruthenium. Nickel can also be used, but tends to favor methane formation. FT catalysts are sensitive to the presence of sulfur compounds in the syngas and can be poisoned by them. The sensitivity of the catalyst to sulfur is higher for Co-based catalysts than for their iron counterparts, which contributes to higher catalyst replacement costs for Co. For this reason, Co catalysts are preferred for FT synthesis with natural gas derived syngas, where the syngas has a higher H₂:CO ratio and is relatively lower in sulfur content. Available samples of Co/SiO₂ catalyst made of Cobalt-based 9.22%Co and Cobalt-based 31.08%Co₃O₄ from Co(NO₃)₂·6H₂O (Cobalt Nitrate) with 90.78%SiO₂ (nature zeolith) and 68.92%SiO₂ (Nacalai zeolith) respectively as buffer material. Preparing the Co//SiO₂ catalyst carried out at the Coal Liquefaction Laboratory – PUSPIPTEK – Serpong, while the characterization of catalyst using X-Ray Diffraction (XRD) and Berneur Emmet Teller (BET) conducted in the BATAN Materials Testing Laboratory. The characterization of catalyst using XRD spectrum performed with a diffraction angle range of 20°~80° and based on peak points (analyzed) taken on an intensity large enough. Cobalt (Co) dispersed / impregnated into the SiO₂ (buffer), where %crystallinity catalyst Co/SiO₂~Nacalai = 68.88, while the catalyst Co/SiO₂ ~ Zeolith = 29.96. Catalyst treatment consisting of leaching, ion-exchange, and calcination to get more pure zeolith with higher %crystallinity. Co metal is good enough impregnated on the surface of SiO₂ as catalyst support. A catalyst is identified there are 2 compounds, namely: weight fraction of 90.78% SiO₂ (Quartz) with a hexagonal crystal structure and the weight fraction of 9:22% Cobalt (Co) with a cubic crystal structure. B catalyst has a 15:25% crystallinity, it is caused by the still contain impurities, where identified only 100% weight fraction of SiO₂ with hexagonal crystal structure. C catalyst expected to form Co₃O₄ but the reality is not, it is because the air is used as the heating medium does not flow in the calcination reactor, giving rise to saturation of air that can not oxidize Co at temperature settings. D catalyst is identified there are 2 compounds, namely: weight fraction of 31.08% Co₃O₄ and weight fraction of 68.92%SiO₂ with a hexagonal crystal structure

Keywords : Co/SiO₂ catalyst, Fischer Tropch Synthesis

1. INTRODUCTION

A variety of catalysts can be used for Fischer-Tropsch synthesis, but the most common are transition metals of iron, cobalt, nickel and ruthenium. FT catalyst development has largely been focused on the preference for high molecular weight linear alkanes and diesel fuels production.

Iron (Fe) is relatively low cost and has a higher water-gas-shift activity, and is therefore more suitable for a lower hydrogen/carbon monoxide ratio (H₂/CO) syngas such as those derived from coal gasification. Fe catalyst will tend to form some

chemical compounds such as iron oxides and iron carbides during the reaction. Ferrous metals (Iron / Fe) suitable for syngas with a low hydrogen content (H₂/CO <1) prepared as lower quality raw materials to promote WGS (water gas shift). Fe is more economical than the Cobalt but susceptible to catalyst poisons such as sulfur (S).

Cobalt (Co) is more active and sensitive to the presence of sulfur compounds (S) which are toxic, and generally preferred over ruthenium (Ru) because of the prohibitively high cost of Ru. Co catalysts usually prepared for the raw materials derived from natural gas with a high content of H₂ so much higher

H₂/CO ratio so it does not require WGS [2]. Metal Co as catalyst Fischer-Tropsch Synthesis process generally dispersed in the buffer material with a large surface area (alumina, silica, titan, etc.) on loading 10 ~ 30 g per 100 g of buffer.[6]. In comparison to Fe, Co has much less water-gas-shift activity, and is much more costly

Nickel (Ni) tends to promote methane formation, as in a methanation process; thus generally it is not desirable. Ni catalyst make hydrogenation of CO produced the most of CH₄ at high temperature operating conditions that led to the formation of volatile carbonyls, thus making the metal is not attractive to the Fischer-Tropsch Synthesis.

Ru catalyst capable of synthesizing a molecular weight of paraffin over 200,000 at high pressure. From an economic perspective, the use of Ru catalyst is not very effective because it is much more expensive than the Cobalt.

Selection of a catalyst based on the ability to accelerate the reaction between some reaction (selectivity), has high activity and efficiency, ease of regenerated, i.e. the process of restoring the activity and selectivity of catalysts as they are, and have chemical stability, thermal and mechanical that will determine the age of the catalyst.

2. PROPERTIES

Cobalt is a ferromagnetic metal with symbol Co, atomic number 27, and specific gravity of 8.9. It is found naturally only in chemically combined form. The free element, produced by reductive smelting, is

a hard, lustrous, silver-gray metal. Cobalt has a relative permeability two thirds that of iron [1].

Cobalt is a weakly reducing metal that is protected from oxidation by a passivating oxide film. It is attacked by halogens and sulfur. Heating in oxygen produces Co₃O₄ which loses oxygen at 900°C to give the monoxide CoO [4].

The metal reacts with F₂ at 520 K to give CoF₃, with Cl₂, Br₂ and I₂, the corresponding binary halides were formed. It has no reaction with H₂ and N₂ even when heated, but it does react with boron, carbon, phosphorus, arsenic and sulphur [5].

At ordinary temperatures, it reacts slowly with mineral acids, and very slowly with moist, but not dry, air. Co catalyst at high pressure will give effect to the high amount of carbon.

Co catalysts. does not require WGS, where a test feed syngas with a high H₂ content so much higher H₂/CO ratio. SiO₂ as a buffer is more dominant compared to TiO₂ and Al₂O₃ (SiO₂> TiO₂> Al₂O₃).

3. RESEARCH

Preparing the Co//SiO₂ catalyst carried out at the Coal Liquefaction Laboratory – PUSPIPTK – Serpong, while the characterization of catalyst using X-Ray Diffraction (XRD) and Berneur Emmet Teller (BET) conducted in the BATAN Materials Testing Laboratory.

Table 1. The catalysts used for Fischer–Tropsch Synthesis by product

	H ₂ /CO	Catalysts	Temp. (°C)	Pressure (bar)	Products		
Syngas	1,0~1,4	Cu–Zn	200~420	51,7~261,99	Ethanol		
		Cu–Co			Alcohol blending		
	2,3	Cu–ZnO	<250	51,7~261,99	MeOH } DME } Gasoline Wax } Diesel Wax }	Zeolith catalyst } Hydro-cracking }	Gasoline Gasoline Diesel
	2	Fe	340	23,44			
	2	Co–K	240	25,51			

3.1. Materials

Figure 1 shows the raw materials used for making Co/SiO₂ catalyst, among others:

- Cobalt nitrat [Co(NO₃)₂.6H₂O].

- Silica sand and alumina as support.
- Cooling media (dry ice)
- Deionized water
- Indicator universal



Figure 1. The raw materials used for making Co/SiO₂ catalyst

3.2. Equipments

Figure 2 shows the equipments used for making Co/SiO₂ catalyst, among others:

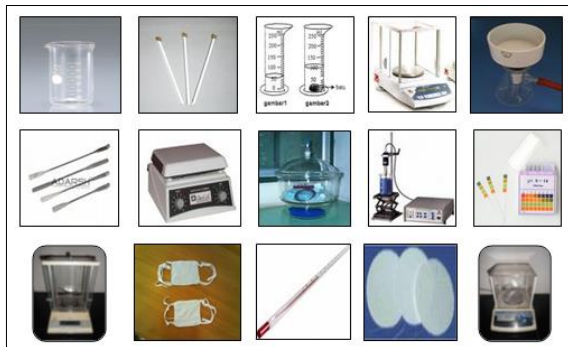


Figure 2. The equipment used for making Co/SiO₂ catalyst

- Furnace for catalytic reduction process
- Vacuum drying oven for catalyst drying process.
- Magnetic stirrer, hot plate stirrer.
- Desiccator
- Analytic scale
- Beaker glass (100 m & 250 m), spatula.
- Sample bottle, crucible
- Buchner funnel, glass funnel, thermometer

3.3. Methodology

3.3.1. Catalyst Preparation

Catalyst preparation mechanism as shown in Figure 3, which consists of :

- Impregnation to deposit metallic Co from Co(NO₃)₂·6H₂O (Co-Nitrat) in SiO₂ as buffer by drying in a vacuum dryer at (100~110°C, 12 hr) agar H₂O dan HNO₃ teruapkan.

- Calcination to remove H₂O content is still trapped in the pores of the SiO₂ crystal by heating at a temperature of 200~400°C (still below the melting point) for 2 hours but in the furnace to expand and stabilize heat surface of catalyst.
- Reduction for obtain metal Co in an active condition with a way transports gas H₂ as an the reducing in inside plug flow reactor which made of stainless steel (ID = 2") at a temperature 400oC during 6 hours.
- The characterization performed after calcination and reduction using a spectrum X-Ray Diffraction (XRD) to determine %crystallinity and the successful impregnation of metal Co on SiO₂ as catalyst support by looking at the effect of nature and the origin crystal structure treatment of the metal changes Co₃O₄ to CoO or Co.
- Reactivity test carried out after Co/SiO₂ catalysts were prepared and characterized using specific content of Co and reacted with mixed-gas in the autoclave 1L to investigate the performance of catalytic reaction that is measured in the amount of conversion and yield [conversion mixed-gas (H₂/CO) be compound HC].

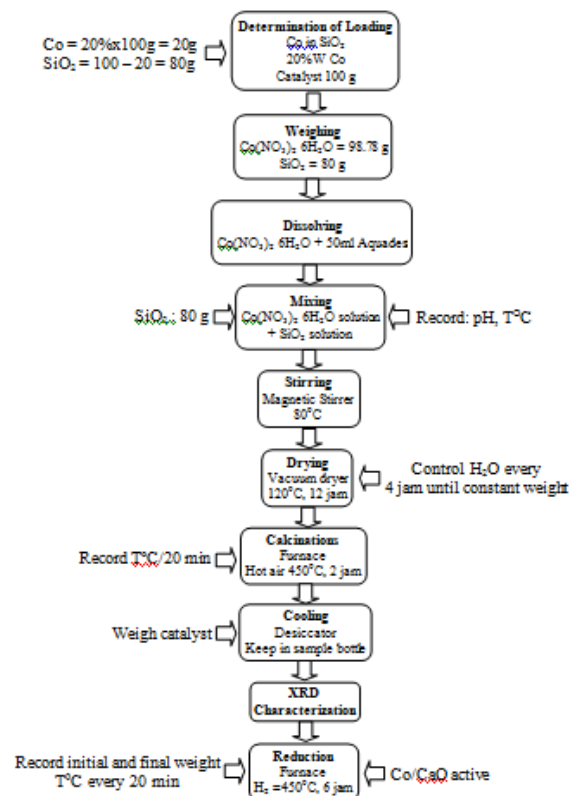


Figure 3. Co/SiO₂ catalyst preparation mechanism

4. RESULT AND DISCUSSION

Available samples of Co/SiO₂ catalyst made of Cobalt-based 9.22%Co and Cobalt-based 31.08%Co₃O₄ from Co(NO₃)₂.6H₂O (Cobalt Nitrate) with 90.78%SiO₂ (nature zeolith) and 68.92%SiO₂ (Nacalai zeolith) respectively as buffer material. The catalysts made through preparation mechanism mentioned above by treatment as follows:

- A. Catalyst : Nature zeolith, calcination (300°C, 2 hours), reduction (300°C, 1 hour)
- B. Catalyst : Nature zeolith without treatment
- C. Catalyst : Nacalai zeolith, calcination (300°C, 2 hours), reduction (300°C, 1 hour)
- D. Catalyst : Nacalai zeolith, calcination (200~400°C, 2 hours), reduction (400°C, 6 hours)

4.1. Results

Co/SiO₂ catalyst after calcination and reduction processing analyzed using spectrum X-Ray Diffraction (XRD) with a standard "AMCSD 96-901-2601" to determine %crystallinity and the success of impregnation metal Co on SiO₂ as a buffer catalyst against influence of the treatment the nature and origin crystal structure on changes metals Co₃O₄ become CoO or Co. The characterization of catalyst using XRD spectrum performed with a diffraction angle range of 20°~80° and based on peak points (analyzed) taken on an intensity large enough.

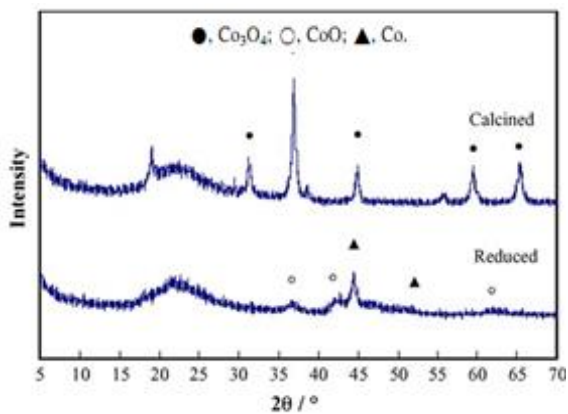


Figure 4. Profile of XRD "AMCSD 96-901-2601", 20%w CoSiO₂ catalyst [7]

Besides catalysts after calcination and reduction were also analyzed using Berneur Emmet Teller (BET) to determine the area of a solid particle including pore diameter. Both types of the catalyst characterization analyzes carried out in the BATAN Materials Testing Laboratory.

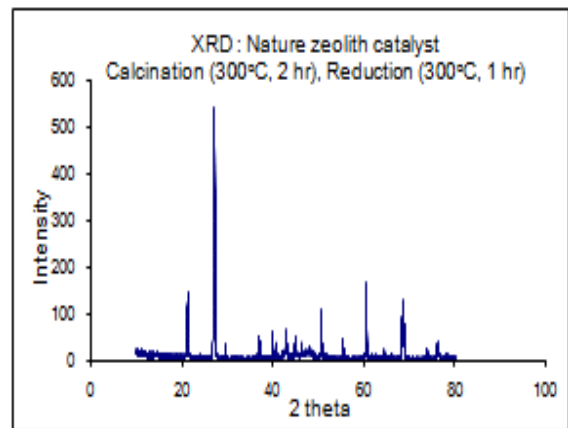


Figure 5. Profile of XRD "AMCSD 96-901-2601", nature zeolith catalyst, calcination (300oC, 2 hr), reduction (300oC,1 hr)

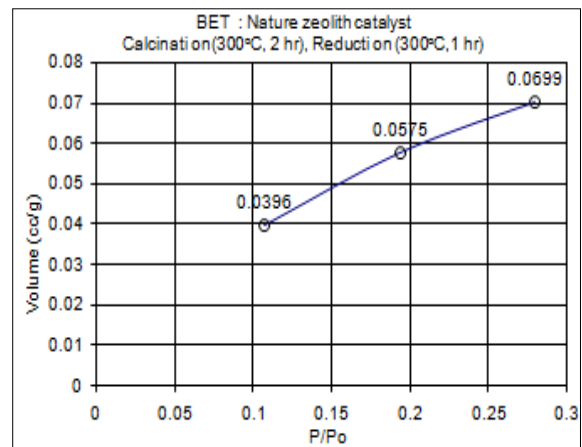


Figure 6. Profile of BET nature zeolith catalyst, calcination (300oC, 2 hr), reduction (300oC, 1 hr)

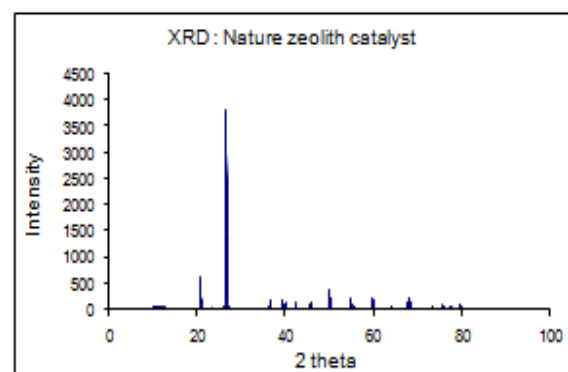


Figure 7. Profile of XRD "AMCSD 96-901-2601" nature zeolith catalyst

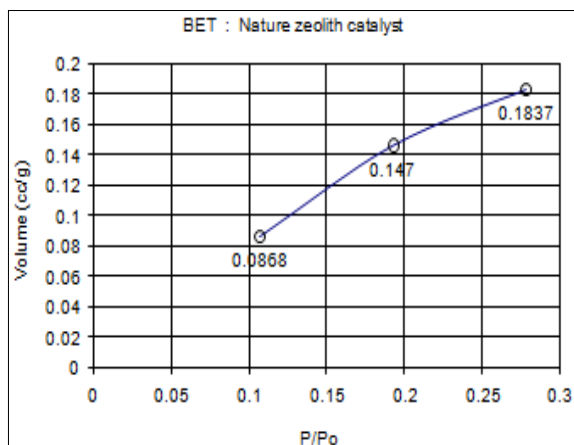


Figure 8. Profile of BET nature zeolith catalyst

Figure 10. Profile of BET Nacalai zeolith catalyst, calcination (200~400°C, 2 hr)

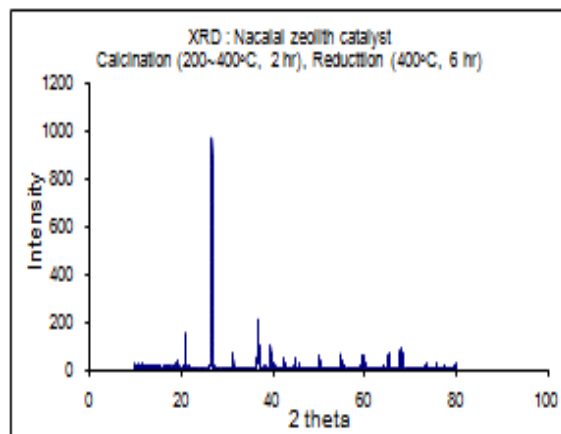


Figure 11. Profile of XRD “AMCSD 96–901–2601” Nacalai zeolith catalyst, calcination (200~400°C, 2 hr), reduction (400°C, 6 hr)

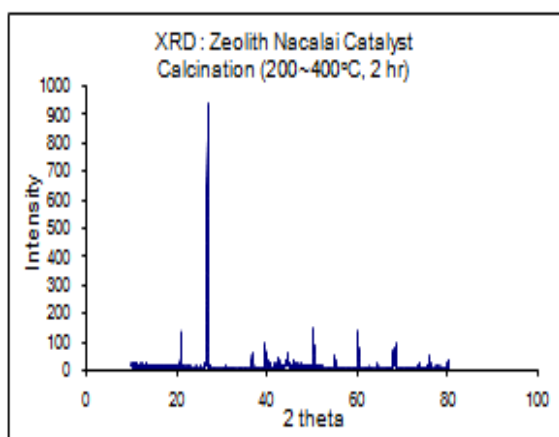


Figure 9. Profile of XRD “AMCSD 96–901–2601”, Nacalai zeolith catalyst, calcination (200~400°C, 2 hr)

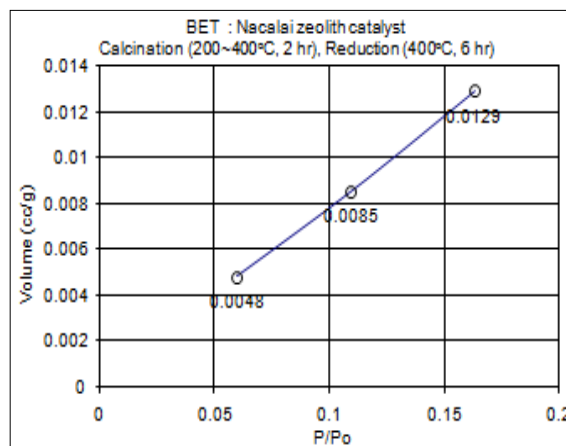
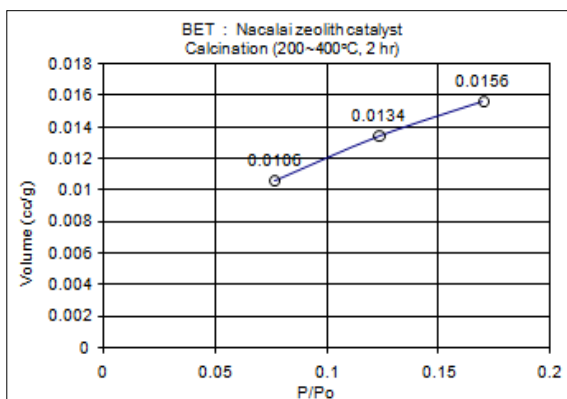


Figure 12. Profile of BET Nacalai zeolith catalyst, calcination (200~400°C, 2 hr), reduction (400°C, 6 hr)



4.2. Discussion

Figure 13 indicates that the Co-based catalyst (Co/SiO₂ ~ 20% Co) is more likely to reduce pressure over the range of reaction time 2 hours, so it needs the addition syngas pressure to stabilize pressure so as not to disrupt the process continuity of Fischer-Tropsch Synthesis.

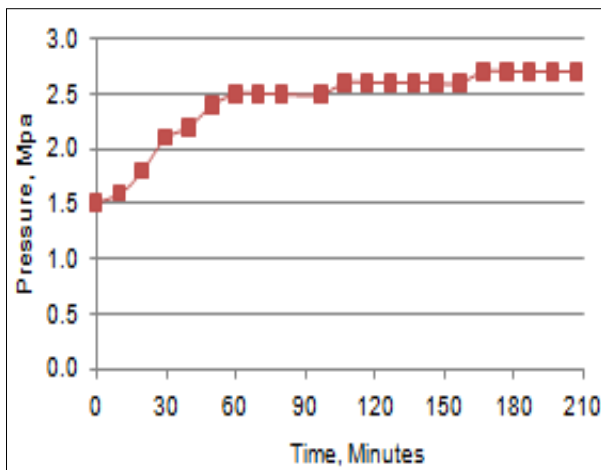


Figure 13. The effect of time on the operating pressure *Autoclave 1L*

Figure 14 shows the SiO₂ peak point (extra-pure) is at an angle 2θ : 11.73; 20.9; 26.88; 35.94; 36.80; 39.73; 40.5; 42.73; 44.89; 45.9; 50.32; 55.06; 55.56; 57.4; 60.16; 64.27; 66.05; 67.95; 68.52; 73.67; 75.84; 77.88; 78.12, whereas the peak point of CoSiO₂-20% (made in) estimated to be at an angle 2θ : 19.2; 30.15; 31.4; 36.96; 38.64; 55.80; 59.44; 65.3; 68.23; 78.54.

Arising cusp indicate that Cobalt (Co) dispersed / impregnated into the SiO₂ (buffer), where %crystallinity catalyst Co/SiO₂~Nacalai = 68.88, while the catalyst Co/SiO₂ ~ Zeolith = 29.96.

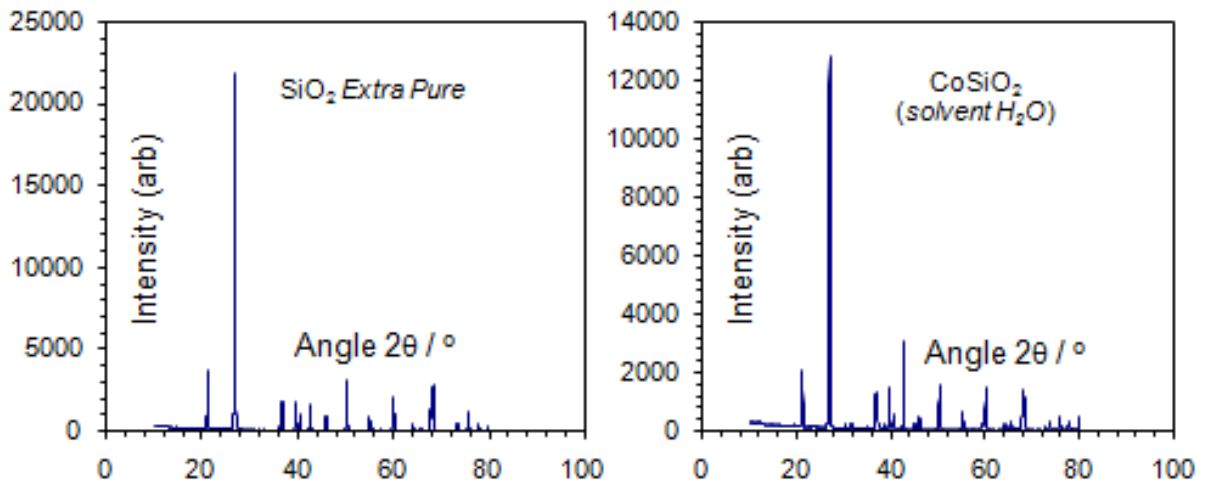


Figure 14. XRD profile of catalyst Co/SiO₂ (solvent H₂O)

Table 2. The XRD analysis result of Co/SiO₂ catalyst

Peak No.	Angle diffraction 2 theta	d-spacing				Peak Intensity (Height)					
		SiO ₂ Nacalai	Catalyst A	Catalyst B	Catalyst C	Catalyst D	SiO ₂ Nacalai	Catalyst A	Catalyst B	Catalyst C	Catalyst D
1	21.1887	4.1932	4.18171	4.27218	4.23223	4.23843	3250.1	118.86	585.89	123.57	131.02
	21.2475										
	20.7926										
	20.9910										
	20.9600										
2	23.4247	3.79776		3.79449			42.39		14.73		
	23.4451										
3	26.8812	3.31675	3.27908	3.35659	3.32591	3.33343	21074.59	489.17	3882.36	924.53	953.24
	27.1960										
	26.5563										
	26.8058										
	26.7442										
4	36.8019	2.44226	2.42703	2.46888	2.4488	2.45257	1611.16	42.47	173.4	50.16	54.05
	37.0412										
	36.3912										
	36.7002										
	36.6418										
5	39.7324	2.26863	2.25699	2.28997	2.27394	2.27712	1663.77	46.92	155.72	49.93	93.04
	39.9460										
	39.3468										
	39.6357										
	39.5780										
6	40.5973	2.22227	2.21035	2.2467	2.22846	2.2336	882.49	26.78	82.34	16.52	21.41
	40.8261										
	40.1369										
	40.4797										
	40.3824										
7	42.7302	2.11616	2.10731	2.13414	2.16299	2.12448	1384.27	50.35	91.65	11.95	34.19
	42.9186										
	42.3528										
	41.7612										
	42.5548										

Peak No.	Angle diffraction 2 theta	d-spacing				Peak Intensity (Height)					
		SiO ₂ Nacalai	Catalyst A	Catalyst B	Catalyst C	Catalyst D	SiO ₂ Nacalai	Catalyst A	Catalyst B	Catalyst C	Catalyst D
8	45.9846	1.97369					789.55				
	46.3049		1.96078					23.86			
	45.6705			1.98653					93.24		
	45.9618				1.97461					17.9	
	45.8427					1.97947					26.79
9	50.3201	1.81334					2324.33				
	50.6299		1.80867					79.52			
	49.9885			1.82459					337.3		
	50.2562				1.81549					124.77	
	50.1796					1.81808					51.83
10	55.0639	1.66782					735.41				
	55.3211		1.66067					35.22			
	55.1942			1.66502					57.77		
	54.9571				1.6708					37.76	
	54.9657					1.67056					63.5
11	57.4823	1.60327					44.79	-			
	57.1157			1.61268					7.5		
12	60.1628	1.53809					1819.95				
	60.3834		1.53173					160.04			
	59.7885			1.54554					209.42		
	60.1156				1.53919					66.99	
	59.9863					1.54219					53.04
13	64.2770	1.44922					358.83				
	64.4379		1.44479					12.32			
	63.8648			1.45637					28.88		
	64.1608				1.45156					9.09	
	64.0862					1.45307					9.21
14	67.9541	1.37948					1340.17				
	68.1911		1.37412					76.53			
	68.0967			1.3758					149.07		
	67.8193				1.38189					55.7	
	68.2848					1.3736					73.63
15	73.6758	1.28585					410.08				
	73.8674		1.28193					20.46			
	73.3140			1.29023					25.16		
	73.5323				1.28801					21.64	
	73.5073					1.28838					9.83

Peak No.	Angle diffraction 2 theta	d-spacing					Peak Intensity (Height)				
		SiO ₂ Nacalai	Catalyst A	Catalyst B	Catalyst C	Catalyst D	SiO ₂ Nacalai	Catalyst A	Catalyst B	Catalyst C	Catalyst D
16	75.8404	1.25341	1.25066	1.25815	1.2563	1.256	1162.43	26.33	59.98	32.17	26.89
	76.0365										
	75.5041										
	75.7086										
	75.6563										
17	76.0715	1.25328		1.25773		1.25555	2.73		24.8		16.24
	75.7549										
	75.9092										
18	77.8828	1.22557	1.22293	1.2306	1.22695		447.93	4.87	21.61	3.44	
	78.0827										
	77.5048										
	77.7782										
						Σ =	39344.97	1213.7	6000.82	1546.12	1617.91
				% crystallinity of Nacalai zeolith				3.0847653	15.25181	3.929651	4.112114
				% crystallinity of nature zeolith				20.225569			

Catalyst A : Nature zeolith, calcination (300°C, 2 hr), reduction (300°C,1 hr)

Catalyst B : Nature zeolith

Catalyst C : Nacalai zeolith, calcination (300°C, 2 hr), reduction (300°C,1 hr)

Catalyst D : Nacalai zeolith, calcination (200~400°C, 2 hr), reduction (400°C, 6 hr)

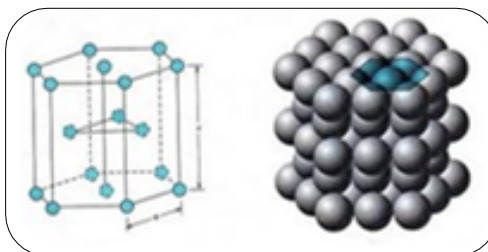


Figure 15. The crystal structure of hexagonal closed packed (HCP)



Figure 16. The crystal structure of faced centered cubic (FCC) dan body centered cubic (BCC)

Table 3. Identification of XRD “AMCSD 96–901–2601” for Co/SiO₂

Type of Catalyst	Preparation Process	X –Ray Diffraction Spectrum Analysis
		%Crystallinity, %wt Mass Fraction, Crystal Structure
A. Catalyst (Nature zeolith)	<ul style="list-style-type: none"> • Impregnation (80~110°C, 12 hr) • Calcination (300°C, 2 hr) • Reduction (300°C, 1 hr) 	<ul style="list-style-type: none"> • 20.225% crystallinity, an increase 4.97% compared to B catalyst • 90.78%wt of SiO₂ (<i>Quartz</i>) [3] with hexagonal crytall structure • 9.22%wt of Co [8] with cubic crytall structure
B. Catalyst (Nature zeolith)	Without <i>treatment</i>	<ul style="list-style-type: none"> • 15.25% crystallinity, still contains impurities • 100% of SiO₂ (<i>Quartz</i>) [3] with <i>hexagonal</i> crytall structure
C. Catalyst (Nacalai)	<ul style="list-style-type: none"> • Impregnation (80~110°C, 12 hr) • Calcination (200~400°C, 2 hr) 	<ul style="list-style-type: none"> • 3.929 %Crystallinity • 14.25%wt of Co [8] with cubic crytall structure • 85.75% SiO₂ (<i>Quartz</i>) [3] with hexagonal crytall structure
D. Catalyst (Nacalai)	<ul style="list-style-type: none"> • Impregnation (80~110°C, 12 hr) • Calcination (200~400°C, 2 hr) • Reduction (400°C, 6 hr) 	<ul style="list-style-type: none"> • 31.08%wt of Co₃O₄ with cubic crytall structure • 68.92%wt of SiO₂ (<i>Quartz</i>) [3] with cubic crytall structure

A. nature zeolith catalyst after processing impregnation (80~110°C, 12 hr), calcination (300°C, 2 hours), and reduction (300°C, 1 hour) has 20.225% crystallinity, there is a 4.97% increase in crystallinity so as to provide a higher purity than the nature zeolith catalyst alone. Based on the XRD profiles "AMCSD 96-901-

2601" [9] A catalyst is identified there are 2 compounds, namely: weight fraction of 90.78% SiO₂ (*Quartz*) with a hexagonal crystal structure (Figure 15) and the weight fraction of 9:22% Cobalt (Co) with a cubic crystal structure (Figure 16) as shown Table 3 and Figure 17.

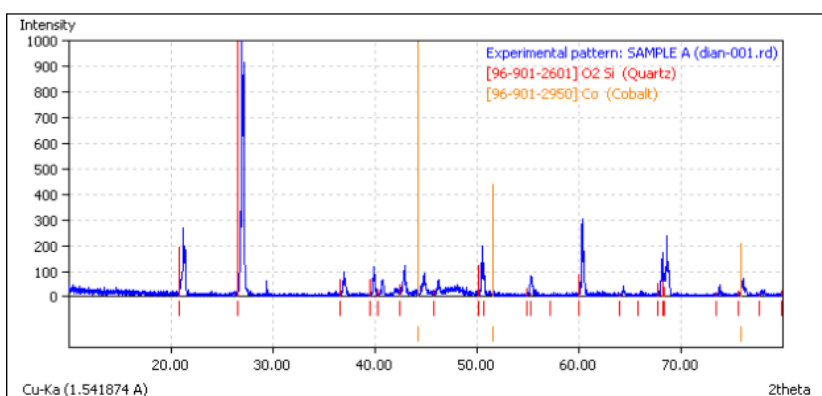


Figure 17. Identify of X–Ray Diffraction (XRD) profile catalyst A

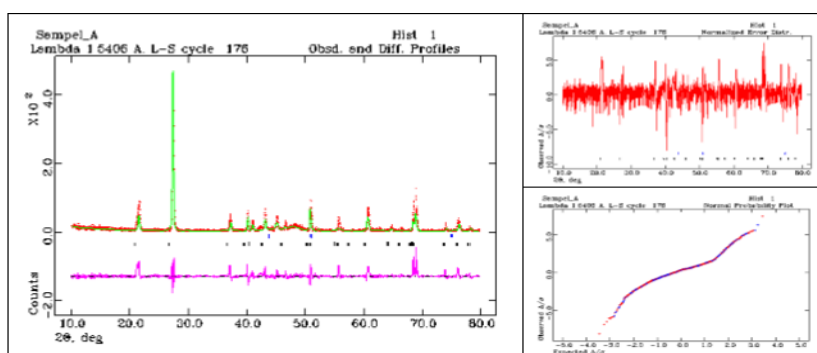


Figure 18. Refinement of X–Ray Diffraction (XRD) profile catalyst A

B. nature zeolith catalysts that do not undergo a process of impregnation, calcination, and reduction has a 15:25% crystallinity, it is caused by the still contain impurities, so that the necessary treatment i.e.:

- Wash to remove water-soluble impurities
- Ion-exchange using acid compounds to exchange cations that exist in the original zeolith-cations in order to obtain a more pure zeolith.

- Calcination to vaporize H_2O or other compounds that are still trapped in the zeolith pores after experiencing the process of leaching and ion exchange, hoping to increase the surface area and pore structure as well as providing thermal stability.

Based on the XRD profiles “AMCSD 96–901–2601” [9] B catalyst is identified only 100% weight fraction of SiO_2 with hexagonal crystal structure (Figure 15) as shown in Table 3.

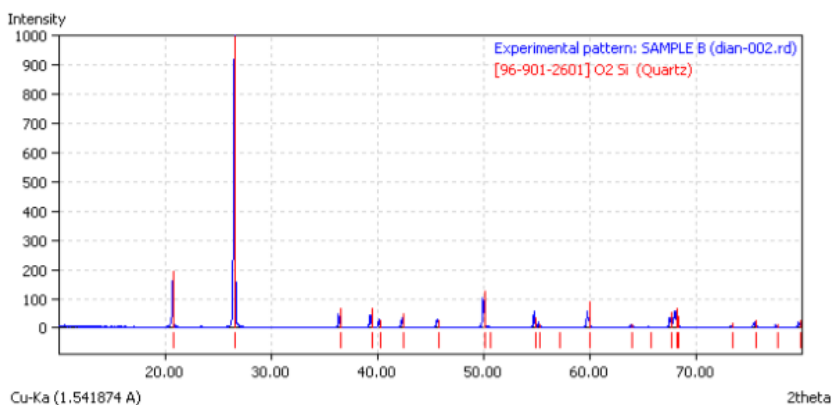


Figure 19. Identify of X-Ray Diffraction (XRD) profile catalyst B

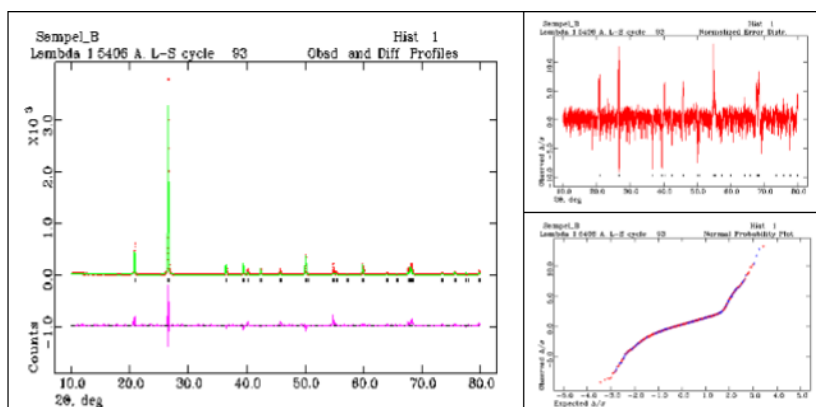


Figure 20. Refinement of X-Ray Diffraction (XRD) profile catalyst B

C. Nacalai zeolith catalysts that undergo a process of impregnation, calcination (300°C, 2 hours), and reduction (300°C, 1 hour) are expected to form Co_3O_4 but the reality is not, it is because the air is used as the heating medium does not flow in the calcination reactor, giving rise to saturation of air that can not oxidize Co at temperature settings. Based on the XRD profiles “AMCSD 96–901–2601” [9] C catalyst identified as having 3.929% crystallinity is still very far when

compared with A, but the formation of two compounds, namely: weight fraction 14:25wt% Co with cubic crystal structure (Figure 16) and weight fraction 85.75% SiO_2 with hexagonal crystal structure (Figure 15), which means that the Co metal is good enough impregnated on the surface of SiO_2 as catalyst support [8], as shown in Tabel 3.

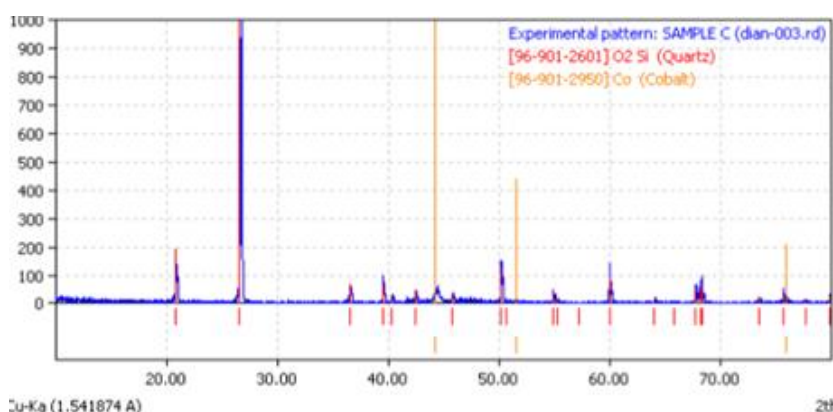


Figure 21. Identify of X-Ray Diffraction (XRD) profile catalyst C

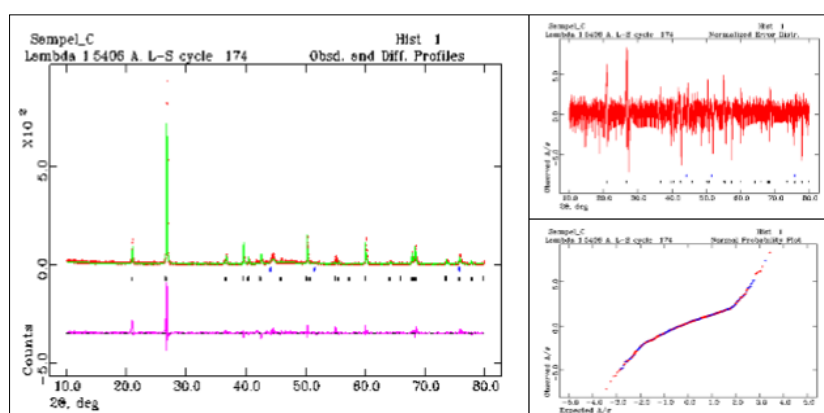
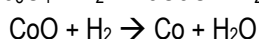
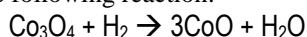


Figure 22. Refinement of X-Ray Diffraction (XRD) profile catalyst C

D. Nacalai zeolith catalysts are undergoing impregnation, calcination (200 ~ 400°C, 2 hours), and reduction processes (400°C, 6 hours) are expected to form metallic Co or CoO active through the following reaction:



In fact the desired target has not been achieved yet still better than C catalyst, this is because H₂ (technical) which is used as a reductor can not be reduced maximally, in addition to the plug-flow

reactor design that does not allow the reduction process takes place continuously during 6 hours with a flow rate of H₂ is large enough to be able to contact the entire surface of the catalyst and react with H₂. Based on the XRD profiles "AMCSD 96-901-2601" [9] D catalyst is identified there are 2 compounds, namely: weight fraction of 31.08% Co₃O₄ and weight fraction of 68.92% SiO₂ with a hexagonal crystal structure as shown in Tabel 3.

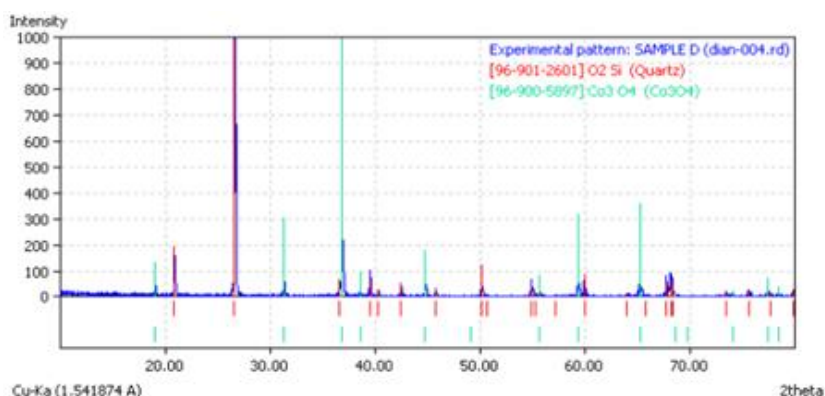


Figure 23. Identify of X-Ray Diffraction (XRD) profile catalyst D

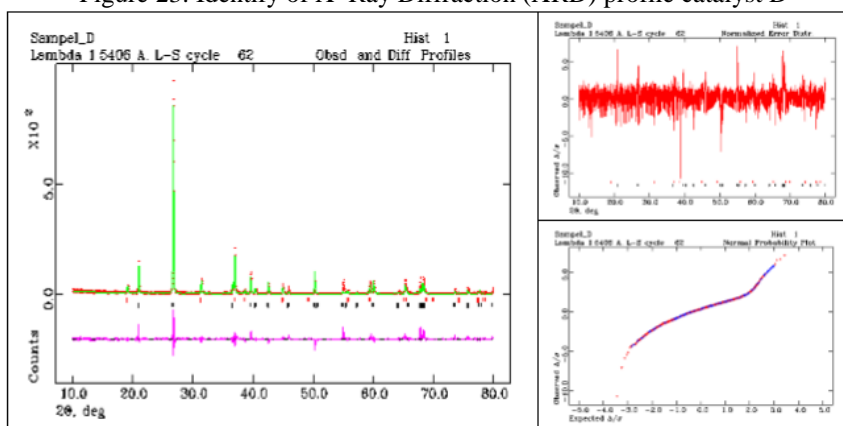
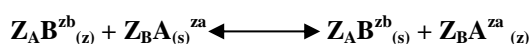


Figure 24. Refinement of X-Ray Diffraction (XRD) profile catalyst D

According to BET analysis that B catalyst is the nature zeolith with the smallest area of 7.2991 m²/gram, it occurs due to nature zeolith material still contained impurities, and other compounds such as phosphorus, K, Ca, Ti, Fe and S, as well as others that cover the zeolith pores thus reducing the area available [8]. Several stages of treatment and activation needs to be done to the nature zeolith to give a much better performance, namely:

- Washing, performed as early stage treatment is to dissolve impurities in the zeolith that can be dissolved by water.
- Ion exchange, in which the cations are located in the pore system of the zeolite will be exchanged with other cations derived from the solution that will achieve an equilibrium as the following equation:



A and B : cations are exchanged
 Z_a and Z_b : load of each cation
 Z and S : zeolith and solution

Cation exchange will take place completely when the solution concentration used is quite large and the temperature is high enough.

- Calcination, is an advanced heat treatment after drying is carried out in a furnace at a relatively high temperature in order to evaporate the water that is trapped in the zeolite crystal pores so as to increase its surface area. It also can occur alumina-silica rearrangement of unstable forms becomes a stable form by producing a better crystal structure and is more resistant to high temperatures.

Leaching, impregnation and calcination treatment applied to the nature zeolith can be seen the effect on surface area A catalyst is the extent to 22.0413 m²/gram or comparable in increments of 201.97% (almost 3 times the original area). While C catalyst is

a catalyst Co/SiO₂ with SiO₂ Nacalai buffer who has undergone calcination treatment for 2 hours at temperature of 200~400°C has a large enough surface area that is 42.1811 m²/gram. The addition of an area of 19.67 for the similar type of catalyst after a reduction in the temperature of 400°C for 6 hours can be found on D catalyst, reaching 50.4794 m²/gram. Reduction is carried out by flowing reducing gas H₂ enable catalyst in order to oxygen contained in the waste catalyst as shown in Tabel 4.

Tabel 4. Analysis BET : Surface area of catalyst

Parameter	Catalyst A	Catalyst B	Catalyst C	Catalyst D
Slope	0.17590	0.56610	0.11190	0.08710
Konstante C	0.02162	0.03029	-0.00106	-0.00084
Koefisien correlation, r	0.99486	0.99072	0.93416	0.99862
Vol. gas monolayer, V _m	5.06320	1.67670	9.68970	11.59590
Area, S	2.95130	0.91020	22.00160	34.93680
Surface area, m ² /g	22.04130	7.29910	42.18110	50.47940

The use of SiO₂ Nacalai as buffer catalyst is excellent in terms of surface area, because it has undergone a variety of treatments, which have a higher purity than the nature zeolith [9].

5. CONCLUSIONS

Based on the X-Ray Diffraction (XRD) spectrum analysis with standard "AMCSD 96-901-2601" that catalyst treatment consisting of leaching, ion-exchange, and calcination is able to provide higher purity and higher %crystallinity of nature zeolith catalyst.

Based on BET analysis that the nature zeolith as a buffer of Co/SiO₂ catalyst has the smallest area, because nature zeolith material still contained impurities, and other compounds that cover the zeolith pores thus reducing the area available.

Co metal is good enough impregnated on the surface of SiO₂ as catalyst support. Not formed CoO, because H₂ (technically) as a reductor can not be reduced maximally, so it could be using gas H₂ (pure)

The use of SiO₂ Nacalai as buffer catalyst is excellent in terms of surface area, because it has undergone a variety of treatments, which have a higher purity than the nature zeolith.

Design plug-flow reactor does not allow the reduction process continuously for 6 hours at a flow rate of H₂ is large enough, so that the entire surface of the catalyst cannot be in contact and react with H₂.

6. RECOMMENDATION

- Wet impregnation to the Cobalt metal with Degussa SiO₂ buffer using Cobalt concentration variation (<10%).
- Reacting a solution of Co (NO₃)₂·6H₂O with NH₄OH and SiO₂ buffer Degussa.
- The calcination process is done by jetting compressed air (compressor) which already passed the silica gel to absorb H₂O (air).
- Characterization of catalysts using the Weiss extraction method to determine magnetic properties to measure the paramagnetic properties after a reduction 650°C and measured grain size distribution.
- Using adsorpsi volumetric H₂ gas to measure the catalyst ability to adsorb gas H₂ and predict metal particles grain size.

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