

## THE CHARACTERIZATION OF Co/SiO<sub>2</sub> CATALYST FOR FISCHER TROPSCH SYNTHESIS

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### 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 H<sub>2</sub>:CO ratio and is relatively lower in sulfur content. Available samples of Co/SiO<sub>2</sub> catalyst made of Cobalt-based 9.22%Co and Cobalt-based 31.08%Co<sub>3</sub>O<sub>4</sub> from Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Cobalt Nitrate) with 90.78%SiO<sub>2</sub> (nature zeolith) and 68.92%SiO<sub>2</sub> (Nacalai zeolith) respectively as buffer material. Preparing the Co//SiO<sub>2</sub> 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 SiO<sub>2</sub> (buffer), where %crystallinity catalyst Co/SiO<sub>2</sub>–Nacalai = 68.88, while the catalyst Co/SiO<sub>2</sub> ~ 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 SiO<sub>2</sub> as catalyst support. A catalyst is identified there are 2 compounds, namely: weight fraction of 90.78% SiO<sub>2</sub> (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 SiO<sub>2</sub> with hexagonal crystal structure. C catalyst expected to form Co<sub>3</sub>O<sub>4</sub> 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% Co<sub>3</sub>O<sub>4</sub> and weight fraction of 68.92%SiO<sub>2</sub> with a hexagonal crystal structure

**Keywords :** Co/SiO<sub>2</sub> 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 (H<sub>2</sub>/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 (H<sub>2</sub>/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 H<sub>2</sub> so much higher

H<sub>2</sub>/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 CH<sub>4</sub> 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 Co<sub>3</sub>O<sub>4</sub> which loses oxygen at 900°C to give the monoxide CoO [4].

The metal reacts with F<sub>2</sub> at 520 K to give CoF<sub>3</sub>, with Cl<sub>2</sub>, Br<sub>2</sub> and I<sub>2</sub>, the corresponding binary halides were formed. It has no reaction with H<sub>2</sub> and N<sub>2</sub> 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 H<sub>2</sub> content so much higher H<sub>2</sub>/CO ratio. SiO<sub>2</sub> as a buffer is more dominant compared to TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> (SiO<sub>2</sub>> TiO<sub>2</sub>> Al<sub>2</sub>O<sub>3</sub>).

## 3. RESEARCH

Preparing the Co//SiO<sub>2</sub> 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 <sub>2</sub> /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	Zeolith } catalyst } Gasoline
	2	Fe	340	23,44	Gasoline } Wax }	Hydro- } cracking } Gasoline
	2	Co–K	240	25,51	Diesel } Wax }	

### 3.1. Materials

Figure 1 shows the raw materials used for making Co/SiO<sub>2</sub> catalyst, among others:

- Cobalt nitrat [Co(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O].

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



Figure 1. The raw materials used for making Co/SiO<sub>2</sub> catalyst

### 3.2. Equipments

Figure 2 shows the equipments used for making Co/SiO<sub>2</sub> catalyst, among others:

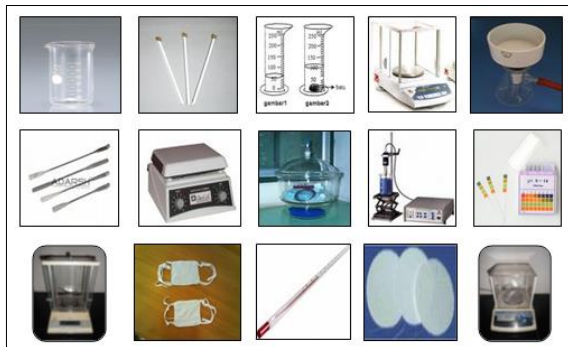


Figure 2. The equipment used for making Co/SiO<sub>2</sub> catalyst

- 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(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O (Co-Nitrat) in SiO<sub>2</sub> as buffer by drying in a vacuum dryer at (100~110°C, 12 hr) agar H<sub>2</sub>O dan HNO<sub>3</sub> teruapkan.

- Calcination to remove H<sub>2</sub>O content is still trapped in the pores of the SiO<sub>2</sub> 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 H<sub>2</sub> 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 SiO<sub>2</sub> as catalyst support by looking at the effect of nature and the origin crystal structure treatment of the metal changes Co<sub>3</sub>O<sub>4</sub> to CoO or Co.
- Reactivity test carried out after Co/SiO<sub>2</sub> 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 (H<sub>2</sub>/CO) be compound HC].

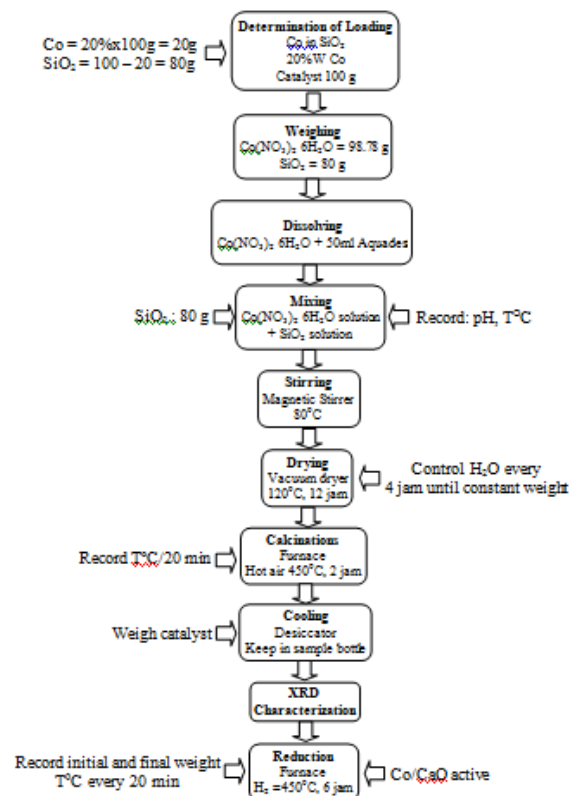


Figure 3. Co/SiO<sub>2</sub> catalyst preparation mechanism

#### 4. RESULT AND DISCUSSION

Available samples of Co/SiO<sub>2</sub> catalyst made of Cobalt-based 9.22%Co and Cobalt-based 31.08%Co<sub>3</sub>O<sub>4</sub> from Co(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O (Cobalt Nitrate) with 90.78%SiO<sub>2</sub> (nature zeolith) and 68.92%SiO<sub>2</sub> (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/SiO<sub>2</sub> 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 SiO<sub>2</sub> as a buffer catalyst against influence of the treatment the nature and origin crystal structure on changes metals Co<sub>3</sub>O<sub>4</sub> 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.

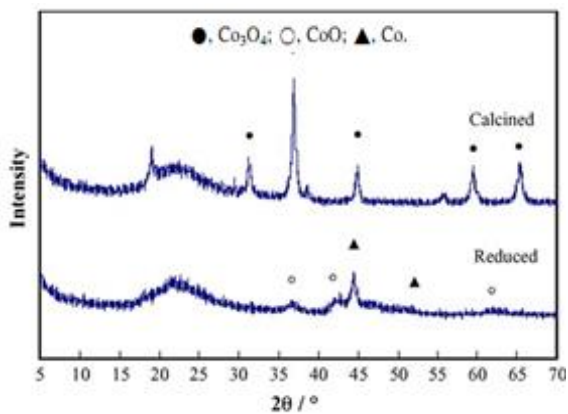


Figure 4. Profile of XRD "AMCSD 96-901-2601", 20%w CoSiO<sub>2</sub> catalyst [7]

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.

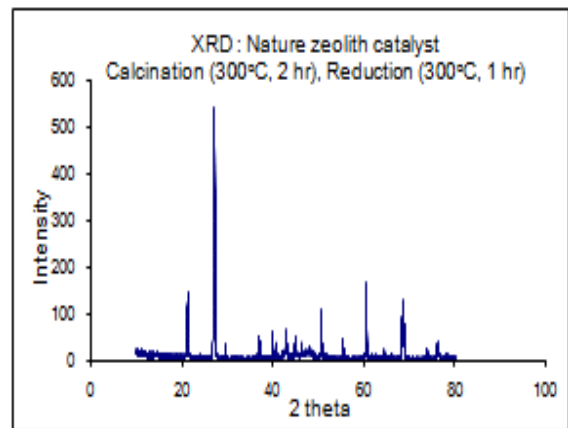


Figure 5. Profile of XRD "AMCSD 96-901-2601", nature zeolith catalyst, calcination (300oC, 2 hr), reduction (300oC,1 hr)

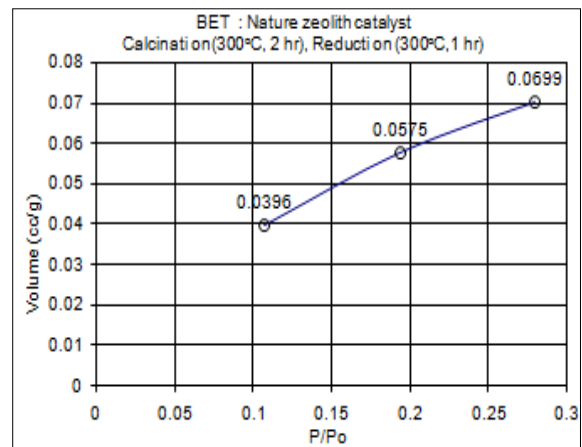


Figure 6. Profile of BET nature zeolith catalyst, calcination (300oC, 2 hr), reduction (300oC, 1 hr)

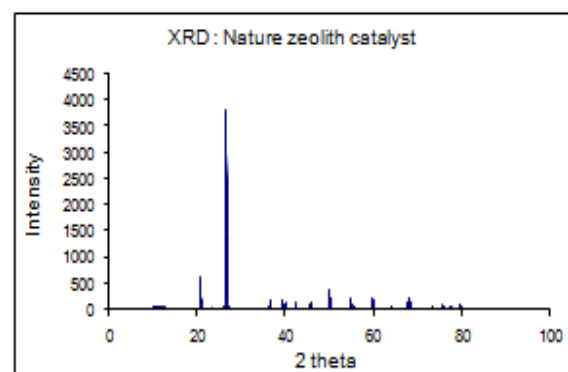


Figure 7. Profile of XRD "AMCSD 96-901-2601" nature zeolith catalyst

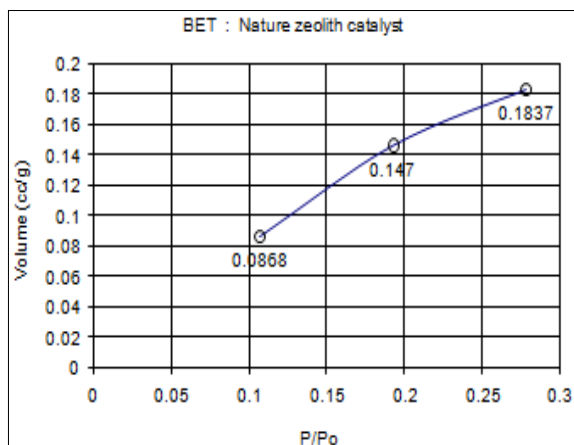


Figure 8. Profile of BET nature zeolith catalyst

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

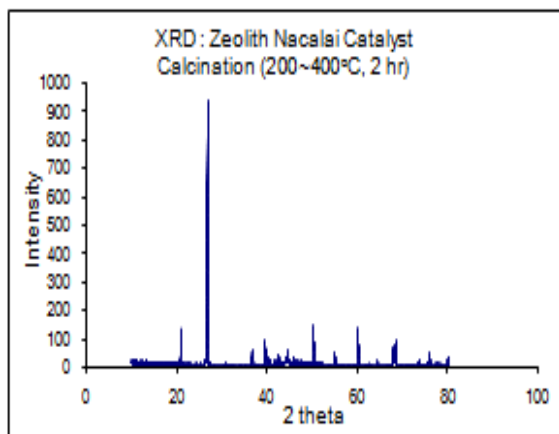
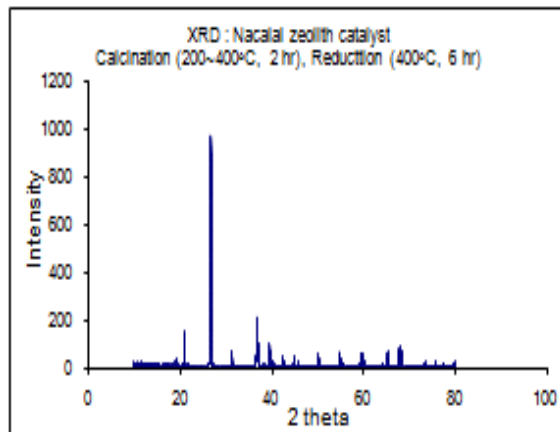


Figure 9. Profile of XRD “AMCSD 96–901–2601”, Nacalai zeolith catalyst, calcination (200~400°C, 2 hr)

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

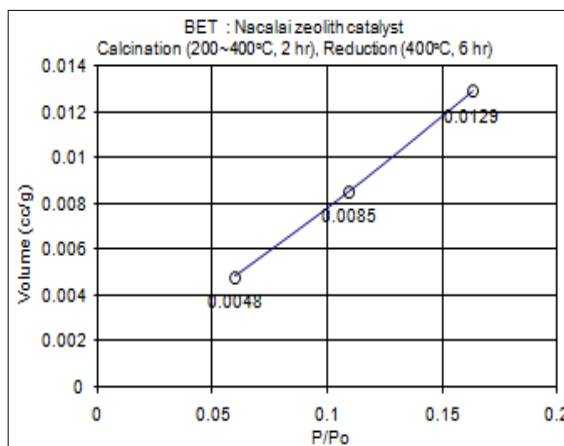
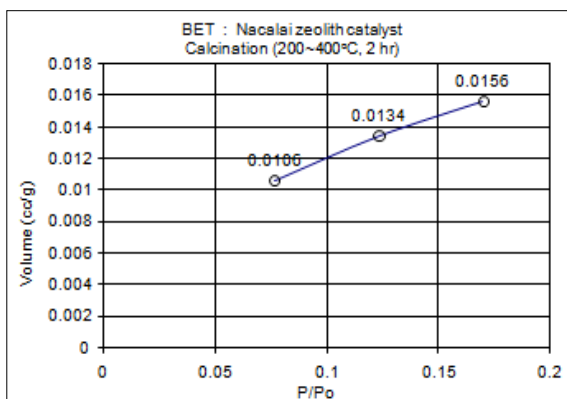


Figure 12. Profile of BET Nacalai zeolith catalyst, calcination (200~400°C, 2 hr), reduction (400°C, 6 hr)

## 4.2. Discussion

Figure 13 indicates that the Co-based catalyst (Co/SiO<sub>2</sub> ~ 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.

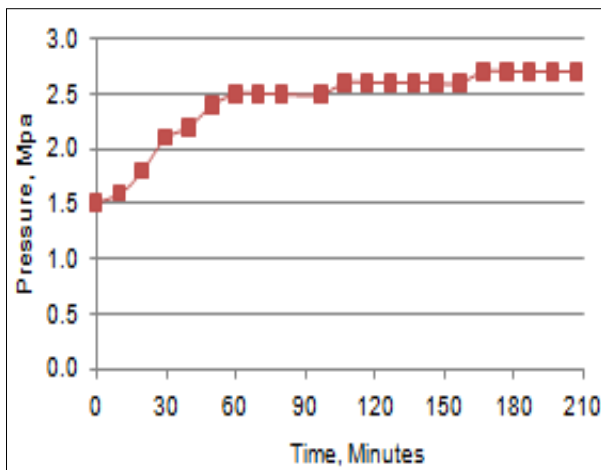


Figure 13. The effect of time on the operating pressure *Autoclave 1L*

Figure 14 shows the SiO<sub>2</sub> 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 CoSiO<sub>2</sub>-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 SiO<sub>2</sub> (buffer), where %crystallinity catalyst Co/SiO<sub>2</sub>~Nacalai = 68.88, while the catalyst Co/SiO<sub>2</sub> ~ Zeolith = 29.96.

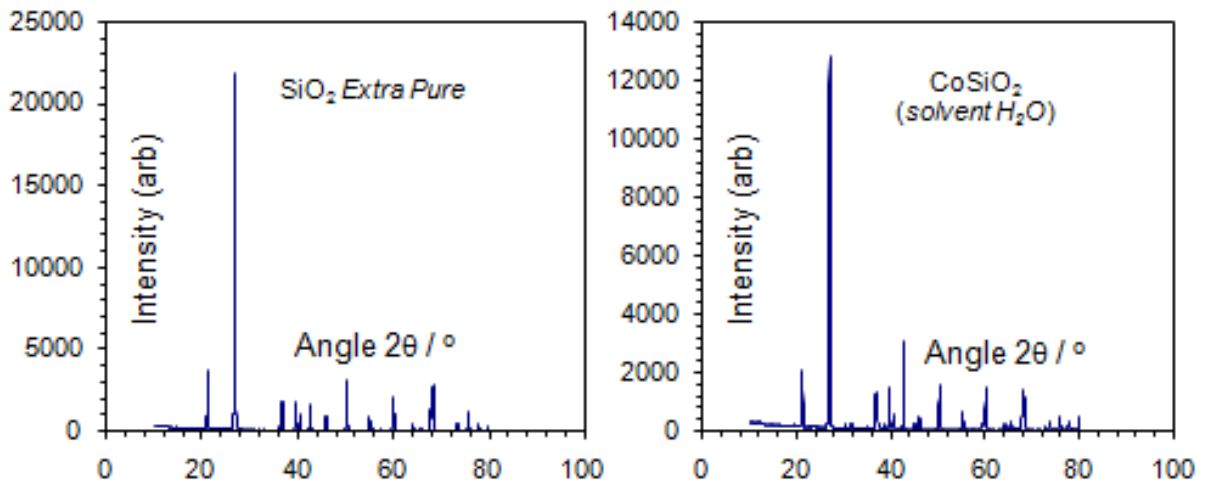


Figure 14. XRD profile of catalyst Co/SiO<sub>2</sub> (solvent H<sub>2</sub>O)



Table 2. The XRD analysis result of Co/SiO<sub>2</sub> catalyst

Peak No.	Angle diffraction 2 theta	d-spacing				Peak Intensity (Height)					
		SiO <sub>2</sub> Nacalai	Catalyst A	Catalyst B	Catalyst C	Catalyst D	SiO <sub>2</sub> 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 <sub>2</sub> Nacalai	Catalyst A	Catalyst B	Catalyst C	Catalyst D	SiO <sub>2</sub> 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





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"> <li>• Impregnation (80~110°C, 12 hr)</li> <li>• Calcination (300°C, 2 hr)</li> <li>• Reduction (300°C, 1 hr)</li> </ul>	<ul style="list-style-type: none"> <li>• 20.225% crystallinity, an increase 4.97% compared to B catalyst</li> <li>• 90.78%wt of SiO<sub>2</sub> (<i>Quartz</i>) [3] with hexagonal crytall structure</li> <li>• 9.22%wt of Co [8] with cubic crytall structure</li> </ul>
B. Catalyst (Nature zeolith)	Without <i>treatment</i>	<ul style="list-style-type: none"> <li>• 15.25% crystallinity, still contains impurities</li> <li>• 100% of SiO<sub>2</sub> (<i>Quartz</i>) [3] with <i>hexagonal</i> crytall structure</li> </ul>
C. Catalyst (Nacalai)	<ul style="list-style-type: none"> <li>• Impregnation (80~110°C, 12 hr)</li> <li>• Calcination (200~400°C, 2 hr)</li> </ul>	<ul style="list-style-type: none"> <li>• 3.929 %Crystallinity</li> <li>• 14.25%wt of Co [8] with cubic crytall structure</li> <li>• 85.75% SiO<sub>2</sub> (<i>Quartz</i>) [3] with hexagonal crytall structure</li> </ul>
D. Catalyst (Nacalai)	<ul style="list-style-type: none"> <li>• Impregnation (80~110°C, 12 hr)</li> <li>• Calcination (200~400°C, 2 hr)</li> <li>• Reduction (400°C, 6 hr)</li> </ul>	<ul style="list-style-type: none"> <li>• 31.08%wt of Co<sub>3</sub>O<sub>4</sub> with cubic crytall structure</li> <li>• 68.92%wt of SiO<sub>2</sub> (<i>Quartz</i>) [3] with cubic crytall structure</li> </ul>

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% SiO<sub>2</sub> (*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.

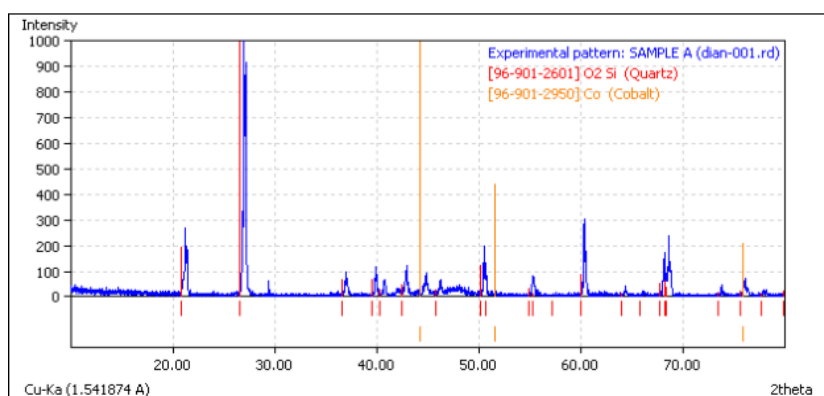


Figure 17. Identify of X–Ray Diffraction (XRD) profile catalyst A

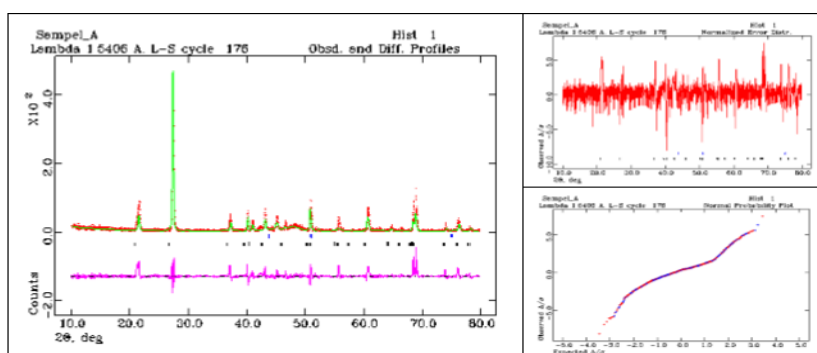


Figure 18. Refinement of X–Ray Diffraction (XRD) profile catalyst A

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.

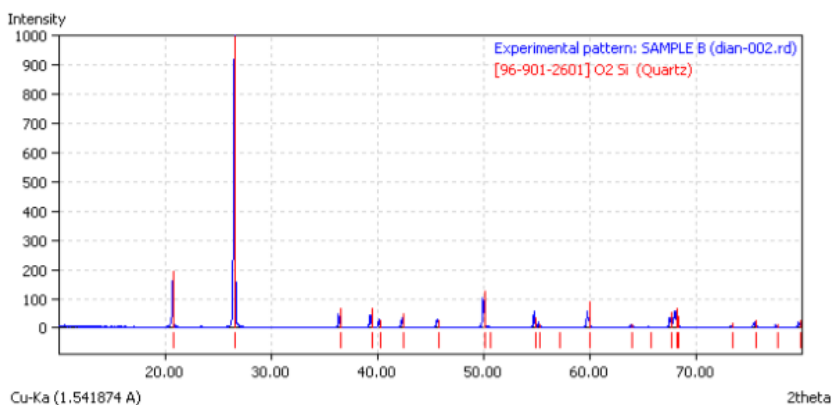


Figure 19. Identify of X-Ray Diffraction (XRD) profile catalyst B

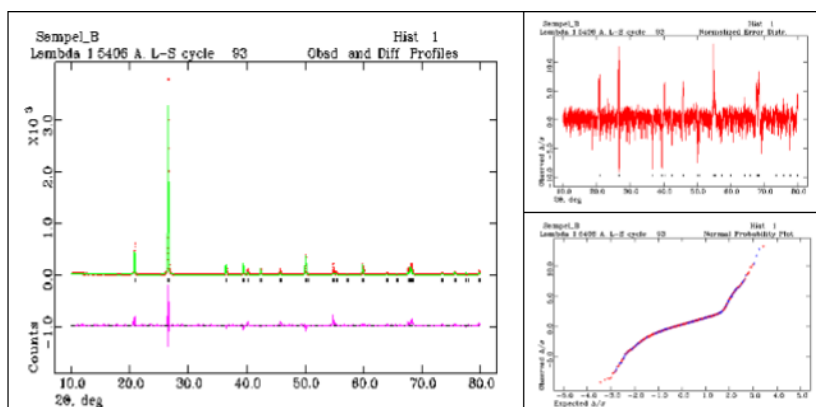


Figure 20. Refinement of X-Ray Diffraction (XRD) profile catalyst B

C. Nacalai zeolith catalysts that undergo a process of impregnation, calcination ( $300^{\circ}C$ , 2 hours), and reduction ( $300^{\circ}C$ , 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.

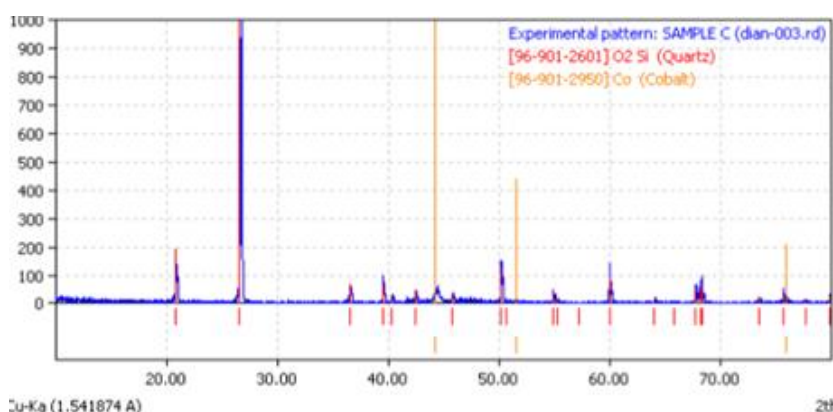


Figure 21. Identify of X-Ray Diffraction (XRD) profile catalyst C

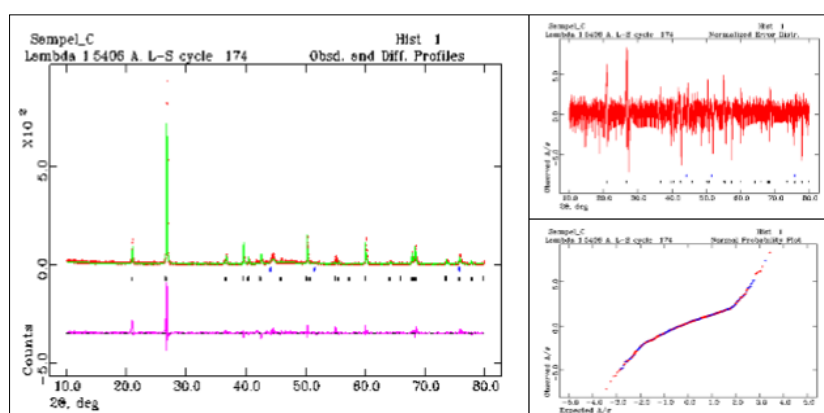
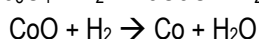
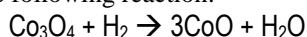


Figure 22. Refinement of X-Ray Diffraction (XRD) profile catalyst C

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 H<sub>2</sub> (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 H<sub>2</sub> is large enough to be able to contact the entire surface of the catalyst and react with H<sub>2</sub>. Based on the XRD profiles "AMCSD 96-901-2601" [9] D catalyst is identified there are 2 compounds, namely: weight fraction of 31.08% Co<sub>3</sub>O<sub>4</sub> and weight fraction of 68.92% SiO<sub>2</sub> with a hexagonal crystal structure as shown in Tabel 3.

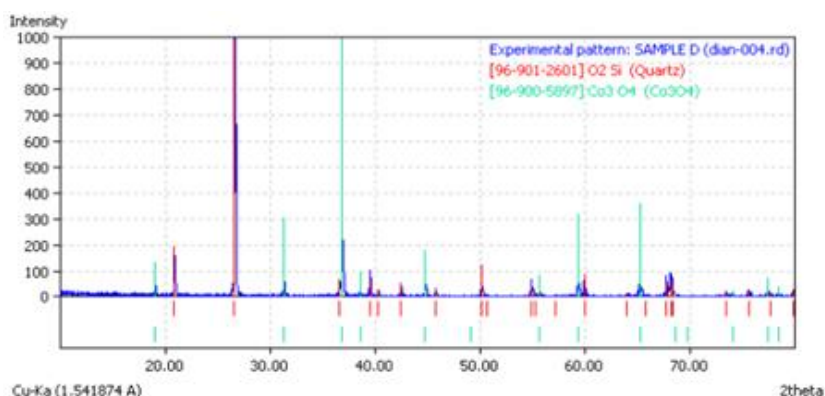


Figure 23. Identify of X-Ray Diffraction (XRD) profile catalyst D

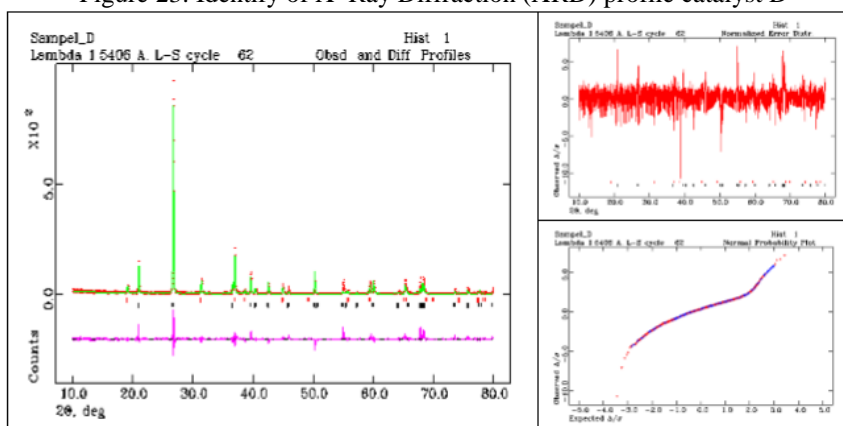
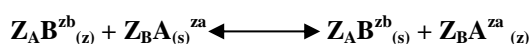


Figure 24. Refinement of X-Ray Diffraction (XRD) profile catalyst D

According to BET analysis that B catalyst is the nature zeolith with the smallest area of 7.2991 m<sup>2</sup>/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  
 Za and Zb : 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 m<sup>2</sup>/gram or comparable in increments of 201.97% (almost 3 times the original area). While C catalyst is

a catalyst Co/SiO<sub>2</sub> with SiO<sub>2</sub> 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 m<sup>2</sup>/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 m<sup>2</sup>/gram. Reduction is carried out by flowing reducing gas H<sub>2</sub> 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, Vm	5.06320	1.67670	9.68970	11.59590
Area, S	2.95130	0.91020	22.00160	34.93680
Surface area, m <sup>2</sup> /g	22.04130	7.29910	42.18110	50.47940

The use of SiO<sub>2</sub> 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/SiO<sub>2</sub> 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 SiO<sub>2</sub> as catalyst support. Not formed CoO, because H<sub>2</sub> (technically) as a reductor can not be reduced maximally, so it could be using gas H<sub>2</sub> (pure)

The use of SiO<sub>2</sub> 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 H<sub>2</sub> is large enough, so that the entire surface of the catalyst cannot be in contact and react with H<sub>2</sub>.

## 6. RECOMMENDATION

- Wet impregnation to the Cobalt metal with Degussa SiO<sub>2</sub> buffer using Cobalt concentration variation (<10%).
- Reacting a solution of Co (NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O with NH<sub>4</sub>OH and SiO<sub>2</sub> buffer Degussa.
- The calcination process is done by jetting compressed air (compressor) which already passed the silica gel to absorb H<sub>2</sub>O (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 H<sub>2</sub> gas to measure the catalyst ability to adsorb gas H<sub>2</sub> and predict metal particles grain size.

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