Characterization of Cr/SiO$_2$ / Al$_2$O$_3$ Catalyst from Rice Husk using Impregnation Method

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ABSTRACT

Rice husk is one of biomass which has very high silica content (18-22%). It can be used as one of support material in the form of SiO$_2$ / Al$_2$O$_3$ which if it is varied with metals, it will produce a catalyst. In this research, a Cr / SiO$_2$ / Al$_2$O$_3$ catalyst was made by using wetness impregnation and dry impregnation methods to obtain the best amount of Cr metal. According to FTIR test results on SiO$_2$ / Al$_2$O$_3$ material, it formed Si-OH bond (3250.2 cm^{-1}), Al-OH (1620 cm^{-1}), Si-O-Si (1410.6 cm^{-1}), O-Al -O (767.8 cm^{-1}). The results of SEM-EDX and Brunauer Emmet Teller (BET) test on variations in the concentration of 0.5 M precursor solution; 1 M; 1.5 M showed that A3 variant had the highest Cr content of 19.79% with a surface area of 68.939 m^2 / gr, a pore volume of 0.06675 cc / gr and a pore radius of 19.36 Å. Based on isothermal desorption adsorption curve with nitrogen gas the A3 catalyst variant was classified into type IV with mesoporous structure based on International Union of Pure and Applied Chemistry (IUPAC).

1. INTRODUCTION

Rice husk is one of biomass which has very high silica content. Rice husk has a silica content of 18-22% higher than other types of biomass. The silica content contained in this rice husk has potential to be used as a raw material for making catalysts. Silica found in rice husks is very easy to obtain and has low cost. It can be obtained by extracting silica in rice husks using alkaline solvents (NaOH, KOH).

Silica which has been extracted from rice husk can be used as a catalyst for cracking petroleum by adding metal elements as a support. One of them is chromium metal. Chromium is a type of metal which can be used as a catalyst for cracking petroleum. It cannot be found as exempted metal in nature. Chromium can be found in the form of compounds such as potassium dichromate (K$_2$Cr$_2$O$_7$). In this study, the researchers reviewed the characteristics of the catalyst produced from silica in rice husks with the addition of metal chromium (VI) contained in a solution of potassium dichromate as a catalyst for cracking petroleum.

Silica or silicon dioxide (SiO$_2$) is a chemical compound formed from silicon and oxygen atoms. Since oxygen is the most abundant element in the earth's crust, while silicon is the second most abundant element. Silica form is a form that is very commonly found in nature. Silica is widely found in plants as Diatoms and in animals as radiolarians. Silica which accumulates in living things, whether animals or plants, has an amorphous form. Meanwhile, silica which is not from living founded in rocks and dust [1].

Rice husk is one of potential source of silica as it contains organic and inorganic components. The main organic components in rice husks are 33-44% cellulose, 19-47% lignin, 17-26% hemicellulose, 3.03% protein, and 1.18% fat. Inorganic component contained in rice husk is ash with a content ranging from 13-30%. Thus, for husk containing high silica ranging from 87-97% [2,3].

Impregnation is a method of loading a metal or metal into a pore bearer. The catalyst is carried out by contacting the bearer or solid bearer with liquid containing metal components or

components that want to be deposited on surface bearer. This liquid is generally referred to as a precursor solution made by dissolving precursor salt.

Preparation of catalysts with this method usually involves several stages starting from the succession of impregnation, drying, until calcination. Impregnation can be done by wetness and dry impregnation methods. Wetness impregnation is an impregnation method using excess solvents. Excess solvents are removed by evaporation or by filtration. The quantity deposited depends on the ratio of the solid and Liquid. Depositions are slow, requiring several hours or days. Dry impregnation is generally done by distributing precursor salts through a spray dryer or it can also be done mechanically where the precursor solution is mixed with bearer with stirring in a solid phase [4].

2. EXPERIMENTAL

2.1. Research Stages

The research phase began with the preparation of rice husks to remove impurities, then proceed with the process of silica extraction. At this stage, silica gel was formed and then there was process of making silica-alumina SiO_2/Al_2O_3. After SiO_2/Al_2O_3 material was produce, Cr metal impregnation stage was continued. Impregnation was done by two methods, namely wetness and dry impregnation. Then, continued by the calcination process for 5 hours with a temperature of 500 ºC.

2.2. Research Matrix

The independent variables used in this study were variations in concentration of the precursor solution and kind of impregnation method used. The research matrix is obtained as shown in Table 1.

TABLE 1. Research Matrix

No	Impregnation method	Concentration of Precursor Solution (M)
A1		0.5
A2	Dry impregnation	1
A3		1.5
B1	Wetness impregnation	0.5
B2		1
B3		1.5

3. RESULTS AND DISCUSSION

3.1. Characterization of SiO_2 / Al_2O_3 Materials

Synthesis result of SiO_2 / Al_2O_3 produced through electrolysis process were characterized by using Fourier Transform Infra-Red Spectrophotometer (FTIR) analysis. The result shows in Figure 1. FTIR spectrum test results showed that the absorption peak at wave numbers 3250.2 cm^{-1} and 1640 cm^{-1} which came from OH group proved that there was formation of Si-OH and Al-OH in barrier material. Then, the absorption peak at wave numbers 1410.6 cm^{-1} and 767.8 cm^{-1} showed the presence of Si-O groups in the siloxane group (Si-O-Si) and also O-Al-O stretching vibrations [11]. Spectrum with strong absorption peak was found at wavelength of 991.8 cm^{-1} which was a stretching vibration of Si-O group on silanol (Si-OH) and Al-O on Al-OH [11]. Rahman et al. (2009) assumed that the absorption area for zeolite-Y was in area under 1200 cm^{-1} [3]. The zeolite frequency vibrations resulting from stretching and bending Al / Si-O units were observed in the range of 1300-300 cm^{-1}. It showed that the existence of functional group bonds which formed SiO_4 and AlO_4.
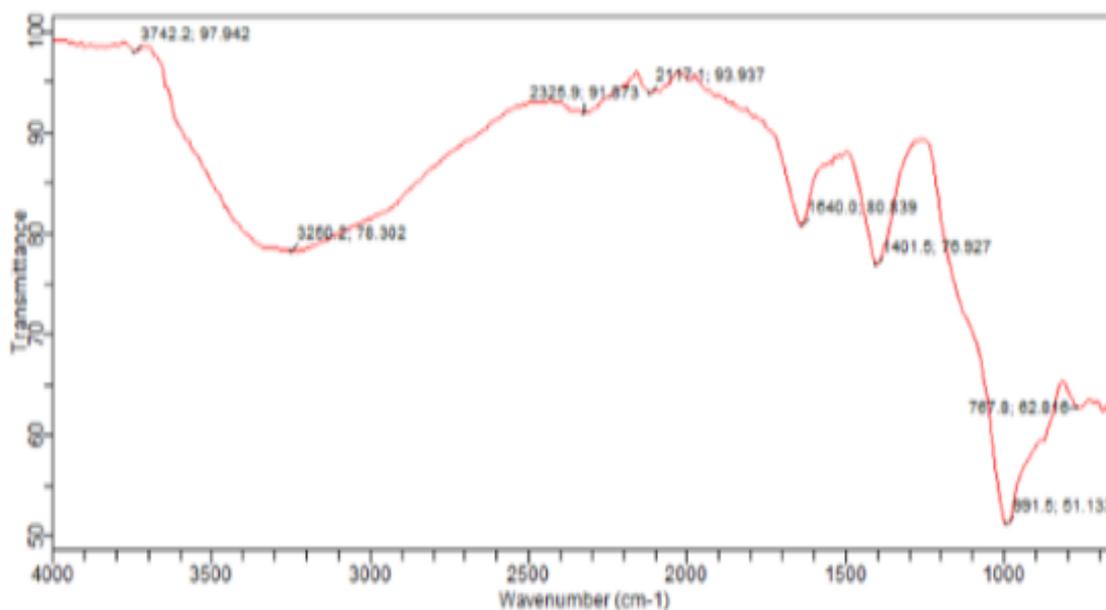
Figure 1. The Result of *Spektrofotometer Fourier Transform Infra-Red* (FTIR) with Zeolit Y (SiO_2/Al_2O_3) Sample

SiO_2/Al_2O_3 material samples were also characterized by using a Scanning Electron Microscope-Energy Dispersive X-ray (SEM-EDX) analysis to review atomic elements contained and their percentage weight levels can be seen in Table 2 below.

TABLE II. Data levels of the atomic elements contained in SiO_2 / Al_2O_3 material

Atomic Element	Atomic Level (%wt)
O	52.31
Si	28.84
Na	11.5
C	5.5
Al	1.85

Based on the data from Scanning Electron Microscope-Energy Dispersive X-ray (SEM-EDX) analysis shown in Table 2 showed high levels of oxygen atomic elements, this could be due to the ability of SiO_2/Al_2O_3 material to adopt highly reactive air. It was in line with the previous Fourier Transform Infra-Red Spectrophotometer (FTIR) analysis which showed a lot of absorption for the functional groups which bound to oxygen atom. The EDX showed that the percentage of silica content in SiO_2/Al_2O_3 material was 28.84%.

3.2. Scanning Electron Microscope-Energy Dispersive X-ray (SEM-EDX) Characterization

The impregnated $Cr/SiO_2/Al_2O_3$ catalyst was characterized by using Scanning Electron Microscope-Energy Dispersive X-ray (SEM-EDX) to see the levels and composition of atoms contained in catalyst material and morphology of catalyst material formed. Characterization was done on all variations of impregnation method and variations in addition of precursor solution concentrations. The percentage of Cr metal content produced in the process of dry and wetness impregnation with variations in the concentration of precursor solution can be seen in Figure 2.
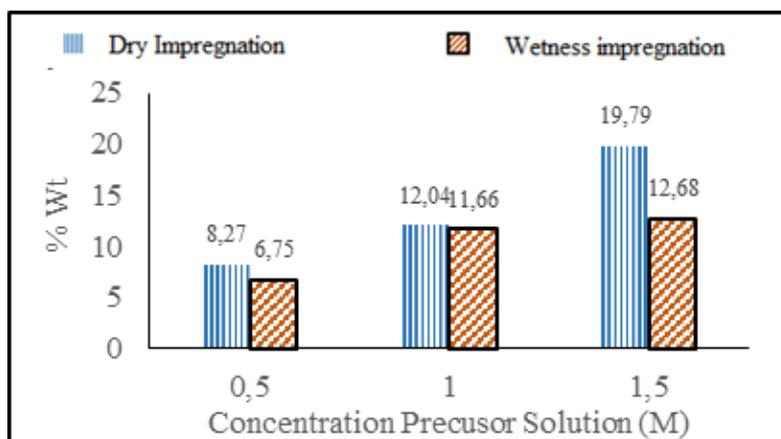
Figure 2. Effect of Precursor Solution Concentration on Cr Metal Levels on Variations in Catalyst Material Impregnation Method

Based on the results of Scanning Electron Microscope-Energy Dispersive X-ray (SEM-EDX) analysis shown in Figure 2. It can be seen that the type of dry impregnation method in the process of making catalyst material had higher Cr metal content which was borne compared to the type of wetness impregnation method in the same concentration value of precursor solution. It showed that the type of impregnation method used could also affect the levels of Cr metal which was embedded in SiO_2/Al_2O_3 material. Since wetness impregnation process used bigger volume of precursor solution than dry impregnation process so there was possibility for dissolved Cr metal in precursor could not be impregnated properly, only physically adopted which tended to cloister. The results of Scanning Electron Microscope-Energy Dispersive X-ray (SEM-EDX) analysis of samples A1 (0.5 M), A2 (1 M), and A3 (1.5 M) for dry impregnation method and sample B1 (0.5 M), B2 (0.5 M), and A3 (1.5 M) for wetness impregnation method shown in Figure 2 also showed data that the greater concentration of precursor solution used, the greater the Cr metal content could be the most bearable. The results showed that the highest Cr metal content was obtained through dry impregnation with concentration 1.5 M precursor solution of 19.79%. According to Nugrahaningtyas (2014), the higher the concentration of precursor solution could cause the substance which was collected on bearer surface [4]. Thus, diffusion displacement increased by the increasing concentration of precursor solution used. These results could show that the concentration of $K_2Cr_2O_7$ compound in a precursor solution was able to affect the amount of Cr metal which could be embraced in SiO_2/Al_2O_3 material.

3.3. Characterization of Brunauer Emmet Teller (BET)

The impregnated $Cr/SiO_2/Al_2O_3$ catalyst was characterized by using Brunauer Emmet Teller (BET) to review the surface area, pore volume, and pore distribution found in each variation of catalyst sample. Sample analysis conducted was the entire sample variation on type of impregnation method used to increase the concentration of precursor solution. The entire analysis data generated can be seen in Table 3.

TABLE III. The Data of Brunauer Emmet Teller (BET) Result

Catalyst Sample	Surface Area (m²/g)	Pore Volume (cc/g)	Pore Radius (Å)
A1	12.852	0.01714	26.67
A2	15.812	0.01703	21,54
A3	68.939	0.06675	19.36
B1	11.204	0.01274	24.53
B2	60.613	0.04167	13.75
B3	68.161	0.06817	20.00

The samples A1 and B1 had the lowest catalyst surface area of 12.852 m^2/g and 11.204 m^2/g. It was based on Scanning Electron Microscope-Energy Dispersive X-ray (SEM-EDX) analysis data which showed low levels of Cr metal borne on catalyst material produced. In the A3 and B3 samples the highest surface area was 68.939 and 68.161 m^2/g. This was also consistent with Scanning Electron Microscope-Energy Dispersive X-ray (SEM-EDX) analysis data showing high levels of Cr metal borne on catalyst material produced. Whereas A2 and B2 samples would follow linearly, which was larger than A1 and B1 samples, then smaller than A3 and B3 samples. The increased surface area of the catalyst showed that the quality of catalyst produced was getting better, because catalyst surface area would contain more active sites and more reactant compounds which were adsorbed on surface so that the occurring reaction process would be faster. In addition, one of the cracking catalyst requirements was having a surface area of between 10 and 1000 m^2/g [5]. Indeed, all catalyst samples produced in this study had been able to meet the requirements as cracking catalysts where the best sample was A3 sample by using a type of dry impregnation method in addition to the precursor solution concentration of 1.5 M which produced a surface area of 68.939 m^2/g.

Based on the analysis of Brunauer Emmet Teller (BET), the overall sample of the study results had pore size ranging from 2.7 to 5.3 nm or 27 to 53 Å. Based on other classifications of IUPAC, catalysts with mesoporous structures must have a pore size ranging from 2 to 50 nm or 20 to 500 Å. It proved that the overall catalyst sample from this study was mesoporous.
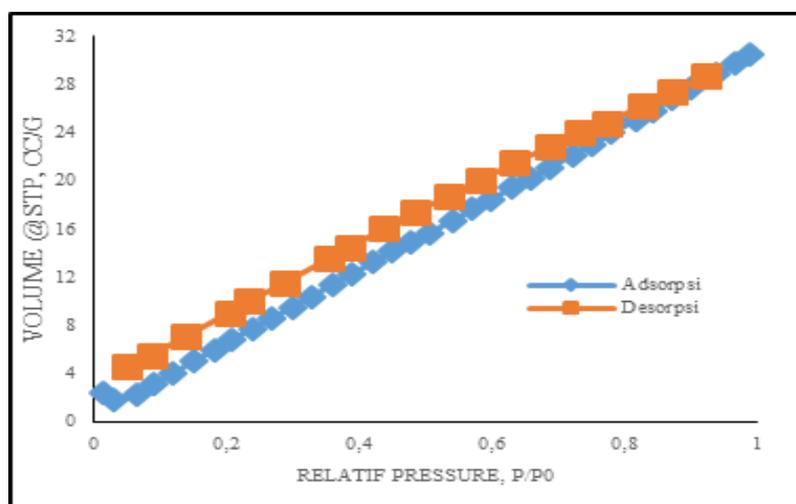

Figure 3. Isothermal Desorption Adsorption Nitrogen Gas

Based on Figure 3, it was known that the catalyst was classified into type IV isothermal adsorption graphs based on classification of the International Union of Pure and Applied Chemistry (IUPAC). It was indicated by the slight difference in adsorption and desorption line, desorption would release the adsorbent with an amount or volume greater than the amount of adsorbent adsorbed on the adsorption at the same relative pressure. This phenomenon was better known as hysteresis. In Figure 3, the phenomenon of hysteresis occurred when relative pressure was 0.2 to 0.9. The hysteresis phenomenon indicated that when the physical adsorption process took place on the catalyst, a multi-layer or multi-layer adsorption occurred [6]. The process of multi-layer adsorption would cause capillary condensation. Capillary condensation or pore condensation was a gas phenomenon condensed into a liquid-like phase in a pore material at pressure lower than the saturation pressure of all its fluids (Lowell, 2006). The phenomenon of hysteresis, multi-layer physical adsorption, and capillary condensation indicated that the catalyst produced in this study had a certain pore character, which was mesoporous. The catalytic cracking reaction would produce different product quality based on the character of catalyst used. One type that affects catalytic cracking is surface area and pore size. Basically, the greater the surface area of the catalyst, the greater the chance for cracking reaction. In addition, the pore size of the catalyst material, the greater the pore radius of the catalyst would provide more opportunity for bait molecule to enter the pore.

In this type of mesoporous-sized catalyst material was widely used in cracking reaction process. In a review of research from Dewi (2014), it showed the process of cracking used oil into fractions of short-chain petroleum such as gasoline, diesel and kerosene using Cr/Zeolite catalysts which had mesoporous-sized pores [7]. Mesoporous-sized catalysts generally had high selectivity [8]. It was used to crack reaction processes which had more than one product or processes that have side reaction. Pinto (1999) assumed that the length of a catalytic cracking product was influenced by the pore size of catalyst used [9]. The larger the portion size, the longer the hydrocarbon chain of the product produced. Thus, if a catalyst with a large pore size was used, it would increase the number of products with longer chains and decrease the number of products with lower chains. Shi (2005) said that a chemical industry process was done by conducting a cracking reaction of gas and petroleum, where mesoporous-sized medicated zeolites were used [10]. Gas and oil cracking reaction process using mesoporous catalysts would produce shorter hydrocarbon chain products compared to the use of micropores catalysts which only produced longer chain hydrocarbon products. The use of mesoporous catalysts had benefits in many types of medium chain hydrocarbon which could be converted. It proved that mesoporous-sized catalysts are more suitable for use in the process of cracking gas and petroleum. In addition, mesoporous catalysts could be used in cracking plastics, vegetable oils, cracking aromatic compounds, hydrogenation of ester compounds and other cracking reaction processes.

3.4. Morphology Characterization of Catalyst Material

Morphology characterization of Catalyst Material was conducted by using a Scanning Electron Microscope-Energy Dispersive X-ray (SEM-EDX) analysis. The results showed that there were morphological images of catalyst materials with a magnification of 1000x which aimed to review structure changes and pore size of catalyst material with research variation treatment used. The results of the morphological analysis of catalyst materials can be seen in Figure 4 and Figure 5 below.
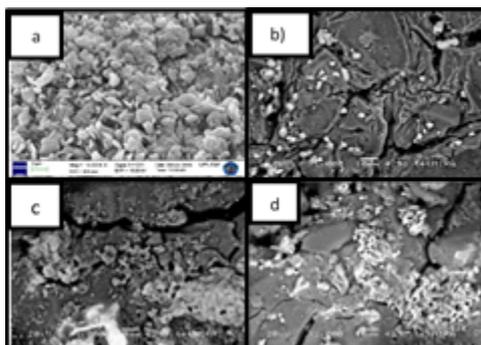

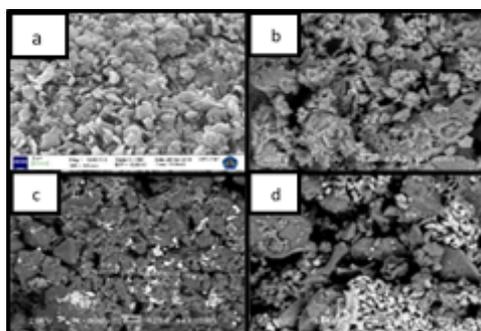Figure 4. Morphology of Catalyst Material with 1000x magnification, a) SiO_2/Al_2O_3, b) A1 Sample, c) A2 Sample, d) A3 Sample

Figure 5. Morphology of Catalyst Material with 1000x magnification, a) SiO_2/Al_2O_3, b) B1 Sample, c) B2 Sample, d) B3 Sample

4. CONCLUSION

The dry impregnation method produces higher levels of Cr metal contained in conjunction with the addition of concentrated solution precursor rather than using the wet impregnation method. SEM-EDX characterization results showed that the highest levels of Cr metal contained in the A3 sample with chromium content of 19.79%, BET analysis results showed that each addition of Cr metal precursor solution will increase the surface area and pore volume of the catalyst. The results of the isothermal desorption adsorption curve analysis of the A3 catalyst sample are mesoporous. SEM-EDX and BET results show that all $Cr/SiO_2/Al_2O_3$ catalyst samples have characterization in accordance with the characteristics of cracking catalyst.

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