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Performance of Bimetallic Fe and Co Catalyst Supported on HZSM-5 for Fischer-Tropsch Synthesis

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Abstract. Fischer-Tropsch synthesis is a polymerization reaction which produces various products such as paraffin, olefins, alcohols, and aldehydes. The purpose of this study was to determine the performance of Fe and Co bimetallic catalysts with the support of HZSM-5 for Fischer-Tropsch synthesis. This study consists of two stages. The first stage was started by making a mesopore sized HZSM-5 catalyst through desilication, then impregnated with bimetallic Fe and Co which acted as a promoter. The impregnation method used was the incipient wetness impregnation. In the impregnation, process variations were made in the ratio of Fe to Co 1:9 and 2:8 metal loading was 10%. The Fe-Co catalyst / HZSM-5 was analyzed for characterization and activity tests. The characteristic tests were BET, XRD, FTIR, and EDX. The second stage was activity test of Fe-Co / HZSM-5 catalyst in the biofuel production process from syngas through Fischer-Tropsch reaction: The best performance catalyst was used for the biofuel production process. Fischer-Tropsch process was carried out in a fixed bed reactor, with an operating temperature of 200, 225, 250 °C carried out for 100 hours in one run, then analysis of product composition by GC-MS.

1. Introduction

To meet the needs of renewable fuels as a substitute for fossil fuels, efforts are needed to make new fuels. So that the solution offered as an alternative to reducing petroleum can be achieved is the use of biofuels. Biofuel is a fuel derived from organic material called non-fossil energy. Making biofuels can be done by catalytic cracking. The catalyst that is often used in the catalytic cracking process is zeolite. Zeolite is an alumino-silicate that occurs in nature with high cation exchange capacity, high adsorption and hydration-dehydration. Efforts continue to be made to maximize the work of zeolite which is used as a catalyst that is by activating and modifying zeolite with active metal carrying materials or commonly called impregnation. In addition to zeolite as a catalyst also used metal-based commercial catalysts. Metal catalysts (Fe and Co) are widely used in the Fischer-Tropsch reaction to produce long chain (wax) hydrocarbons.

In previous research using Fe/HZSM-5 catalyst showed that the addition of zeolite to the Fischer-Tropsch reaction reduced the formation of oxygenates thereby increasing the conversion of hydrocarbons, in addition zeolite also increased the selectivity of CO₂. The selectivity produced from Fe/HZSM-5 increases the production of gasoline (gasoline) fraction. The use of this catalyst also yields isoparaffins and water gas shift reactions [1]. While other research using Co/HZSM-5 catalysts with



mesoporous HZSM-5 zeolite has increased CO conversion. At the end of the process, more efficient catalysts reduce the production of C_{12+} . The Co/HZSM-5 mesoporous catalyst is more selective in the gasoline production range with selectivity of 60% [2]. The use of bimetal metal (Fe and Co) in previous research shows that bimetal metal is able to shift the product distribution to the selectivity of light hydrocarbons. The use of Co metal yields CH_4 selectivity higher than Fe metal. Thus, the addition of Fe reduces the production of CH_4 and olefin compounds. Bimetal catalyst is good for producing olefin compounds [3].

Fuel products that are identical to fossil fuels through the Fischer Tropsch reaction, can add to the diversification of the synthesis of new and renewable energy sources. Modification of bimetal-bifunction catalyst (Fe-Co/HZSM-5) can improve process efficiency through increasing the selectivity of biofuel formation and simplifying the process into one stage. The novelty of the research is the simplification of FT synthesis into one stage by combining the FT-cracking reaction using a bimetallic catalyst supported by mesoporous HZSM-5 (Fe-Co/HZSM-5). Previous research states that the use of zeolite-supported metal catalysts can produce biofuels directly, and the combination of Fe and Co metals produce biofuels with better conversion. This study tried to combine the two concepts to get a synergy effect. Each of these advantages will be combined in the new catalytic system in the form of a combination of Fe and Co metal catalysts with zeolite HZSM-5 support.

This catalyst system is expected to improve the process efficiency and selectivity of biofuels. Overall process efficiency is characterized by increased catalyst activity (increase in CO reactant conversion), increase in selectivity of C_5 - C_{11} hydrocarbons, decrease in selectivity to CO_2 , CH_4 and wax. In this study, catalyst was manufactured and then subsequently was applied for reaction Fischer-Tropsch.

2. Material and Methods

2.1. Materials

The commercial ZSM-5 zeolite powders with nominal Si/Al mole ratio of 40 was purchased from Zeolyst International, USA (CBV 8014). NaOH, 65 wt% HNO_3 solution, NH_4NO_3 , $Fe(NO_3)_3 \cdot 9H_2O$ and $Co(NO_3)_2 \cdot 6H_2O$ was provided by Merck. Mixture Gas (CO 15%, H_2 30% N_2 balance) was purchased by Samator.

2.2. Ultrasonic Atomization Spray Coating.

NH_4 -ZSM-5 was calcined at 550 °C for 5 h to obtain parent H-ZSM-5. Desilication of HZSM-5 powder was carried out in 1 M NaOH solution and stirred using a magnetic stirrer at 70 °C for 1 h in an oil bath above the heater. The residue was separated from the zeolite crystallite through continued dispersion in deionized water and filtered with vacuum filtration to neutral pH. If the pH is neutral, NH_4NO_3 0.1 M solution was added. The sample was dried at 120 °C for 12 h and calcination at 550 °C for 5 h. HZSM-5 mesopore fraction was treated using 1 M HNO_3 solution at 70 °C for 2 hours and stirred to form an amorphous phase. The sample is washed with deionized water to separate the desilication agent residue to neutral pH. Dry in an oven at 120 °C for 12 hours [4]. The Fe-Co/HZSM-5 catalyst was prepared via impregnation wetness impregnation with the procedure as reported by a previous studies [5,6]. The amount of HZSM-5 zeolite was impregnated with aqueous solution of iron (III) nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$) and cobalt (II) nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$) containing the required amount of iron and cobalt. In the first step, aqueous solution of iron (III) nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$) was introduced into HZSM-5 slowly and the catalyst was kept overnight in a desiccator and dried at 120 °C for 12 h in the oven. Then, the aqueous solution of cobalt (II) nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$) was introduced into Fe/HZSM-5 catalyst slowly and the catalyst was kept overnight in a desiccator and dried at 120 °C for 12 h in the oven. After being dried, the powder catalyst was calcined in 550 °C in the air for 3 h and reduced in flowing H_2 at 550 °C for 12 hours, as reported in the previous study [7]. The Fe-Co/HZSM-5 catalyst was obtained with different metal ratio of 1:9 and 2:8 for iron-cobalt.

2.3. Characterization

To determine the surface area and pore size catalyst mesoHZSM-5 and Fe-Co/HZSM-5 using Brunauer-Emmett-Teller (BET) and Barret-Joyner-Halenda (BJH) analyses series Quantachrome NovaWinVersion 11.03. Analyzed morphology and composition of metals in Fe-Co/HZSM-5 catalyst was using Energy-Dispersive X-ray (EDX) analysis. To determine the crystallinity of meso HZSM-5 and Fe-Co/HZSM-5 catalyst using X-Ray Diffraction (XRD), patterns were recorded in PANalytical X'Pert PRO performed at room temperature, using monochromatic Cu K α radiation source operating at 40 kV and 30 mA in the 2θ region between 5° and 70° with a step size 0.02.

2.4. Fischer-Tropsch Synthesis

Fe-Co/HZSM-5-meso catalyst according to the variable entered into the reactor fixed-bed. Nitrogen gas was then flowed for 15 minutes. The reactor was flowed syngas at a pressure of 20 bar for 100 h. Then heating was carried out at a temperature of 200-250 °C. The liquid hydrocarbon product formed will then be analyzed by GC-MS (Gas Chromatography - Mass Spectrometry) to determine the composition of the hydrocarbon formed. Whereas for gas products in the form of CO, H₂, N₂, CO₂, CH₄, C₂-C₄ will be analyzed using GC (Gas Chromatography).

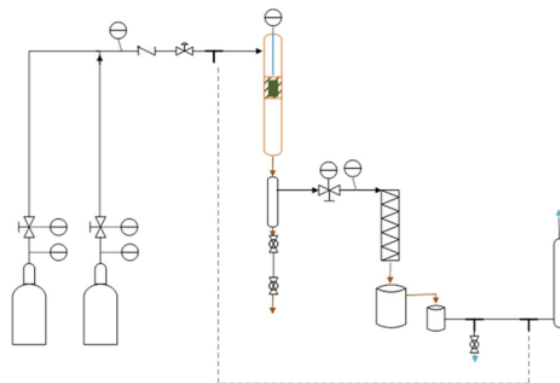


Figure 1. Fischer-Tropsch reaction equipment.

3. Result and Discussion

3.1 Catalyst characterization

To find out the surface area, pore volume and pore diameter of a catalyst, an SAA analysis was used on the BET equation (Brenauer Emmet Teller). Table 1 shows the SAA (Surface Area Analyzer) analysis data with the BET method of the HZSM-5 before treatment and after treatment, with desilication using alkaline treatment of NaOH concentration of 1 M. From these results it can be seen that the treatment of desilication method causes an increase in pore diameter of micropore size (2.104 nm) to mesoporous size (3.029 nm). As it is known that a catalyst can be said to be mesoporous if the pore diameter size is 2 nm to 50 nm. Unlike the size of micropore, which is less effective as a catalyst support because of the difficulty of metal salts to enter the pore. Therefore, a material synthesis method has begun to be developed so that the size of the micropore can be transformed into mesoporous, is the desilication method [8].

Besides that one of the disadvantages of micropore, is the limitation of diffusion especially for large molecules. Limited access and slow molecular transport, from limited active acid sites in zeolite crystals, reduce the effectiveness of zeolite catalysts. Furthermore, this limited mass transfer can also cause pore blockages by large molecules or by the formation of deposits such as coke which contribute to deactivation of the catalyst [9,10].

Table 1. Properties of Fe-Co/HZSM-5 catalyst.

Catalyst	Surface area (m ² /g)	Pore Volume (cm ³ /g)	Pore Size (nm)	Element wt. (%)	
				Fe	Co
HZSM-5	266.28	0.140	2.104	-	-
HZSM-5/ meso	526.03	0.486	3.029	-	-
Fe-Co/HZSM-5 (1:9)	284.90	0.699	4.906	1.49	7.21
Fe-Co/HZSM-5 (2:8)	278.70	0.695	4.987	5.52	13.08

After meso size had been formed, impregnation steps were carried out. Metal was the pores at the catalyst support. Table 4.2 shows the results of the BET analysis after the impregnation method was carried out. From these results it can be seen the impregnation of metal iron and cobalt salts dispersed on the surface of the catalyst, so that the surface area of the HZSM-5 oxide catalyst after the impregnation has decreased. As previously conducted by others, the addition of metals causes reduced surface area and pore volume of both metals to block micropores and clog the mesopores [11-15].

Characterization of catalysts with EDX aims to analyze the chemical elements or characteristics of the specimens. This characterization depends on research from the interaction of several X-ray excitation with specimens. Each element has a unique atomic structure and is characteristic of the atomic structure of an element, allowing X-rays to identify it. In this study an impregnation of Fe-Co metal salt with HZSM-5 support with a ratio of 1: 9 and 2: 8. From the three data shows that Fe and Co metals have been collected at the support of HZSM-5.

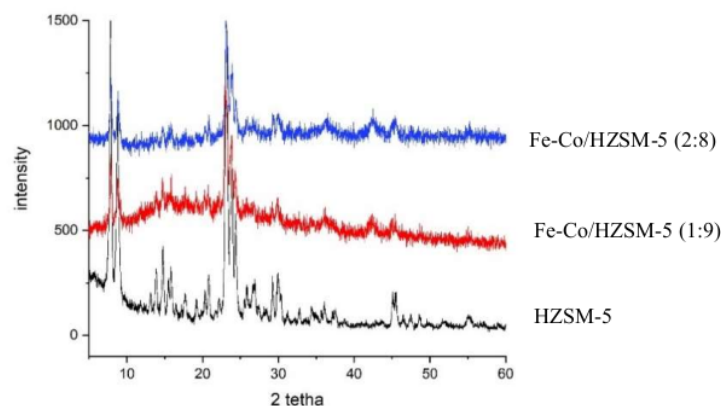


Figure 2. XRD Patterns of the HZSM-5, 1:9 Fe-Co/HZSM-5 and 2:8 Fe-Co/HZSM-5 catalyst.

Diffraction pattern of Fe-Co/HZSM-5 catalyst after impregnation with the composition of Fe-Co 1:9 and 2:8, the XRD results is presented in Figure 2. The catalyst consists of Fe-Co active metal and HZSM-5 supports. The XRD data readings of the samples were carried out by comparing the XRD diffractogram of the catalyst resulting from impregnation with the XRD database of Fe-Co impregnation carried out by other researchers. In the XRD analysis, the composition of impregnation of Fe-Co 1:9 and 2:8 were observed in 2θ of 36.11650, 42.33590, 44.93960, 45.20890. If adjusted to the previous XRD database, in that 2θ range, it correspond to Fe₂O₃, Co₃O₄, Fe metal, Co oxide phase and the combination of Fe-Co metal (which is in the range of 42.120, 45.240) is Co, 44.80 is Fe, 450 is a combination of Fe-Co metal and 36.80 is Co₃O₄ oxide. From the results of the XRD analysis it can be said that the incipient wetness of the impregnation of Fe-Co metal on the HZSM-5 support was successfully carried out.

3.2 Fischer-Tropsch Synthesis

The HZSM-5 catalyst activity test impregnated with Fe and Co. The research was conducted using Fischer Tropsch equipped with fixed bed reactor. Catalytic test begins with a reduction of 12 hours while flowing gas H₂ with a temperature of 400 °C. This reduction serves to remove the oxide group that is still present in the catalyst.

After the reduction is completed, it continued to the next process, namely the Fischer-Tropsch process, the temperature used was according to the variables, namely 250, 225 and 200°C. If the temperature was reached, the gas flow was then replaced with syngas with a flow rate of 20 ml/min. The Fischer-Tropsch process was carried out for 100 h in one run. This equipment was equipped with condensation which was maintained at a temperature below 100 °C during the running process. This was intended to condense the gas that has undergone a reaction out of the reactor. Every 24 hours, a gas sampling was further analyze by GC. After the running process was completed, it can be seen whether there are liquid products in the liquid product vacuum flask and under the reactor for wax products. Liquid products will be analyzed using GC-MS. Data from GC-MS analysis of liquid products with Fe-Co 1:9 and 2:8 catalyst variables loading 10% are presented in Figure 3 and Figure 4. From the data analysis, there are still many oxygenates, hydrocarbon compounds that cannot be detected.

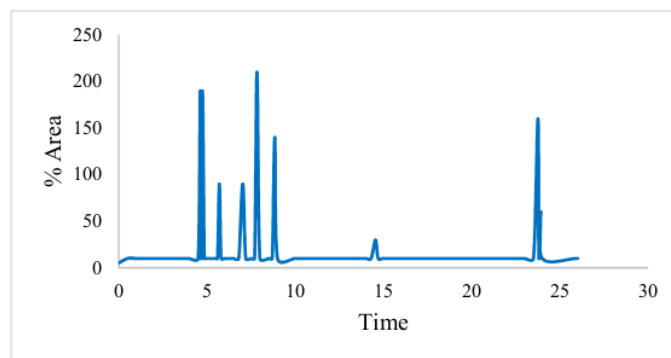


Figure 3. The results of analysis of GC-MS liquid products on Fe-Co 1:9 catalyst.

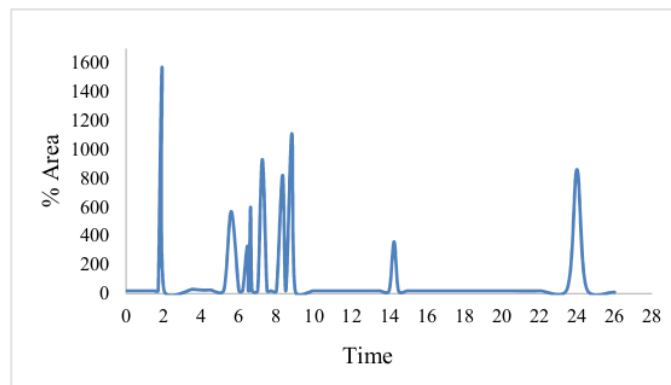


Figure 4. The results of analysis of GC-MS liquid products on Fe-Co 2:8 catalyst.

From the two results of the GC-MS results, there were no visible hydrocarbon compounds or aromatic compounds. Therefore, this result can be used as a basic information for further studies that will later be able to give better results.

Table 2. The results of GC-MS liquid products on Fe-Co 1:9 catalyst.

Compound	Chemical Formula	%area	RT
4-phthalimido Azobenzene	C ₁₂ H ₁₁ NO ₅	0.19	4.62
pyrimidinium hydroxide	C ₅ H ₇ NO	0.19	4.747
aminocarbonyl	C ₅ H ₂ N ₂ O ₂	0.09	5.705
5-methyl-3-n-propyl	C ₁₀ H ₂₀ O	0.09	7.027
methyl ester	C ₄ H ₁₀ ClNO	0.21	7.836
benzothiazole	C ₅ H ₇ NS	0.14	8.846
propane	C ₃ H ₈	0.03	14.547
5-methyl 1- propylcyclohexane	C ₁₀ H ₁₈	0.16	23.755
5-methyl-3-n-propyl-2-tetradeterio	C ₁₀ H ₂₀ O	0.06	23.924

Table 3. The results of GC-MS liquid products on Fe-Co 2:8 catalyst.

Compound	Chemical Formula	%area	RT
1 3-benzodioxole-5-carboxaldehyde	C ₈ H ₆ O ₃	1.57	1.907
1,3-benzenedicarboxylic acid	C ₈ H ₆ O ₄	0.57	5.594
2-pentanamine	C ₅ H ₁₃ N	0.33	6.456
8-bromo-3-oxooctanoate methyl	C ₉ H ₁₅ BrO ₃	0.6	6.620
pyridine	C ₅ H ₅ N	0.93	7.249
<i>N</i> -isobutyl-sec-butylamine	C ₈ H ₁₉ N	0.82	8.328
naphthalene	C ₁₀ H ₈	1.11	8.820
propane	C ₃ H ₈	0.36	14.262
benzaldehyde	C ₇ H ₆ O	0.86	24.003

4. Conclusion

Fe-Co/HZSM-5 catalysts has been prepared the incipient wetness impregnation method (the volume supplied is based on pore volume data supporting HZSM-5). The best surface area of the catalyst is shown on the Fe-Co/HZSM-5 metal ratio 1:9 metal ratio with 10% metal loading on the total catalyst weight which is 284.90 m²/gr.

The addition of Fe and Co metals to the HZSM-5 support causes a decrease in the surface area of the Fe-Co/HZSM-5 catalyst. The pore diameter and pore volume of the resulting Fe-Co/HZSM-5 catalyst are smaller than those of the HZSM-5 support. The XRD analysis also shows the peak of Fe and Co metal on all catalyst variables and is supported by EDX analysis data in the form of Fe and Co levels.

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