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Synthesis and Characterization ZSM-5 Based on Kaolin as a Catalyst for Catalytic Cracking of Heavy Distillate

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Abstract. This article describes the study of synthesis of ZSM-5 Zeolite based on kaolin as catalysts for catalytic cracking of heavy distillate. There are five types of formulas A, B, C, D, and E synthesized with varying the molar ratios of SiO_2/Al_2O_3, SiO_2/Na_2O, and H_2O/SiO_2 and characterized by chemical compound, microstructure and catalytic performance. Three methods conducted the catalytic cracking of heavy distillate such as without catalyst, Ni-Mo commercial catalyst, and bifunctional catalyst ZSM-5 from Formula E, which was impregnated with transition metals (Ni, Mo) to be Ni-Mo/HZSM-5. The catalytical performance test result shows that, under operational conditions (~350 °C, 1 MPa), middle distillate hydrocarbon is obtained by the catalytic cracking of heavy distillate using Ni-Mo commercial catalyst and Ni-Mo/HZSM-5 Formula E catalyst. When a Ni-Mo/HZSM-5 Formula E catalyst and Ni-Mo Commercial Catalyst were used in the cracking process, a light hydrocarbon fraction (C_3 - C_5) was formed.

Keywords: Catalytic Cracking; Formulation; Heavy Distillate; Zeolite

1. Introduction

Due to the scarcity and depletion of traditional light petroleum resources, low-quality heavy oils and or residues obtained by processing heavy crudes are considered a suitable alternate source for transportation fuels, energy, and petrochemicals to meet the needs of rapidly growing populations and civilizations. Furthermore, numerous statistical studies have revealed that heavy crude reservoirs are significantly larger than conventional oil reservoirs, necessitating deep upgrading of heavy crude for refining and petrochemicals (Corma et al., 2017).

The abundance of heavy crude oil reserves and the high demand for light olefins, particularly propylene, have created new opportunities to develop advanced catalyst and process technologies that efficiently convert asphaltene-enriched crudes to high-value chemicals. Indeed, many petrochemicals are produced as by-products of crude oil refining, as the primary goal of a crude oil refinery is to create transportation fuel (Alotaibi et al., 2018).

Catalytic cracking of hydrocarbons is important for industrial manufacturing because it has higher cracking conversion efficiency, higher light alkene selectivity, and less carbon deposition than thermal cracking (Sadrameli, 2016). ZSM-5 zeolite is the most commonly used catalyst for hydrocarbon catalytic cracking due to its acidity, unique pore structure,

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and high thermal and hydrothermal stability (Xue et al., 2017; Ahmed et al., 2017).

Zeolites are advanced chemical materials that are used in a variety of petrochemical applications. There has been a surge in research interest in improving and enhancing the effectiveness of ZSM-5 as a catalyst in recent years. There has been a lot of interest in finding less expensive, more environmentally friendly alternative starting materials for the synthesis of ZSM-5 (Agustina et al., 2020; Reddy et al., 2020). Because it contains the necessary constituents for an aluminosilicate zeolite material, kaolin has been extensively researched as a zeolite precursor; its ubiquitous nature and utility in zeolite synthesis are well known as a low-cost method of obtaining catalysts (Hartati et al., 2020; Nugraha et al., 2021).

The kaolin precursor influences physicochemical properties like morphology, porosity, and acidity, and optimal synthesis conditions are required for ZSM-5 synthesis from specific kaolin. However, studies of kaolin from different areas are critical because its varies depending on its geological occurrence. Chemical compositions of materials influence their properties, and variations in the structure and design of kaolin can thus influence its subsequent chemical reactivity (Pan et al., 2017; Krisnandi et al., 2019). The kaolin-based ZSM-5 catalyst showed good activity and selectivity to valuable fuel range hydrocarbons (Nugraha et al., 2021). Furthermore, significant efforts have been made to improve the catalytic activity of ZSM-5 catalysts by loading Ni and Mo on the supports. The shape of the XRD diffraction pattern of the ZSM-5 catalyst will be affected by the impregnation process of Ni and Mo metals at a specific concentration (Kedia & Zaidi, 2014; Ramasubramanian, et al. 2018).

The previous studies have reported the determination of physical-chemical characteristics of “Badau Belitung kaolin” and their dehydroxylation effect during metakaolinization and metakaolinization on the specific surface area (Ulfiati et al., 2020a; Ulfiati et al., 2020b). The current study aims to observe the physicochemical properties and catalytical performance of ZSM-5 catalyst based on kaolin produced. The catalyst is expected to be used in heavy distillate catalytic cracking. This study used a heavy distillate fraction of crude oil with a boiling point of more than350 °C as feedstock.

2. Methods

2.1. Materials

The kaolin used in this study was obtained from Badau Belitung, Indonesia, and was activated by 4 M NH_4NO_3 (E. Merck), NaOH (E. Merck), HCl (E. Merck), Na_2SiO_3 (E. Merck), $Ni(NO_3)_2.6H_2O$ (E. Merck), $(NH_4)_6Mo_7O_{24}.4H_2O$ (E. Merck) and distilled water. All of the chemicals used in this study were of analytical grade and were used as they were received, with no additional purification.

2.2. Synthesis

Kaolin-based ZSM-5 catalyst samples were synthesized with the hydrothermal method without organic molds with variations of molar ratios of SiO_2/Al_2O_3, SiO_2/Na_2O, and H_2O/SiO_2 (see Table 1) from activated kaolin, Na_2SiO_3, NaOH and H_2O. The molar composition of the mixture is as follows: $10Na_2O$: $120SiO_2$: $2Al_2O_3$: $1800H_2O$ and other molar ratio variations are shown in Table 1. In a typical synthesis, stoichiometric quantities of activated kaolin were dissolved in distilled water under magnetic stirring, then a specific amount of Na_2SiO_3 was poured into the mixture drop by drop. HCl was added dropwise until less than pH 9, then NaOH was added up to a pH of 11–12 and stirred for 4 h to obtain a gel solution. Finally, the mixture was transferred into an autoclave for hydrothermal reaction at 175 °C for 6 h. ZSM-5 catalysts products were neutralized using distilled water and then dried at 110 °C for 2 h.

Table 1 Formula ZSM-5 catalyst based on kaolin

Formula	Molar Composition	H_2O/SiO_2	SiO_2/Al_2O_3	SiO_2/Na_2O
A	$10Na_2O : 2Al_2O_3 : 120SiO_2 : 1800H_2O$	15	30	6
B	$10Na_2O : 2Al_2O_3 : 50SiO_2 : 1000H_2O$	20	12.5	2.5
C	$10Na_2O : 2Al_2O_3 : 30SiO_2 : 900H_2O$	30	7.5	1.5
D	$10Na_2O : 2Al_2O_3 : 76SiO_2 : 1000 H_2O$	13.16	19	3.8
E	$10Na_2O :2Al_2O_3 : 100SiO_2 : 1000 H_2O$	10	25	5

2.3. Impregnation and Calcination

The catalyst Ni-Mo/HZSM-5 was prepared for the five formulas A, B, C, D, and E, which were synthesized using the wet impregnation method (Hidayat et al., 2018). The metals impregnated on the catalyst were 4% Ni from $Ni(NO3)_2.6H2O$ and 8% Mo from $(NH_4)_6Mo_7O_{24}.4H_2O$ which dissolved in distilled water. The impregnation process was done in two stages. First, a 4% Ni metal solution was added to the kaolin-based ZSM-5 catalyst in amounts up to 1.5 times the part of the catalyst, with constant stirring, followed by 18 h of aging, followed by filtration and drying at 110 °C for 2 h. The second, 8% Mo metal solution was added in the same manner as the first, 4% Ni metal solution. After drying for 2 h at 110 °C, the samples were calcined for 6 h at 500 °C. (Kedia & Zaidi, 2014; Ramasubramanian et al., 2018; Machmudah, et al., 2019)

2.4. Characterization

Characterization methods such as x-ray diffraction (XRD), Breunauer-Emmett-Teller (BET), scanning electron microscope (SEM), and energy-dispersive-X-ray spectroscopy (EDX) were used to determine the morphology and structure properties of the catalyst materials produced. Powder X-ray diffraction patterns were observed using a Rigaku XRD instrument equipped with a Cu K node material X-ray radiation (1.5406 Å) and a scan rate of 5°/min. The degree of crystallinity was calculated by comparing the area of the crystal curve to the total area of amorphous and crystalline materials. The surface area and pore size were measured using the Brunauer-Emmett-Teller (BET) methods in the Quantachrome NovaWin 11.0 version at 77.3 K. Scanning electron microscopy (SEM) and EDX were performed using a JEOL-JSM-6390-SEM in low-voltage high-vacuum mode.

The liquid hydrocarbon products were analyzed using an Agilent 7890B Gas Chromatograph with flame ionize detector (FID), capillary column (30 m; 0.25 mm; 0.5m; 5% phenyl)-methylpolysiloxane. It was kept at nominal carrier gas helium (initial: 1mL/min maintain 22 min; Ramp 1: 5mL/min hold 200 min). Injector settings: 300 °C injector temperature, 100:1 split ratio, 0.2 ml injection volume. FID detector temperature: 350 °C, initial 35 °C hold 5 min. The oven temperature was set from 10 °C/min to 280 °C for 3.5 min, then increased to 10 °C/min to 325 °C for 90 min. The product compound calculations were based on GC and were classified as gasoline (C_6-C_{11}), kerosene (C_{12}-C_{20}), and gasoil (C_{21}-C_{30}).

2.5. Catalytic Activity Test

Figure 1 shows the illustration equipment used to vacuum fractional distillation for the heavy distillate catalytic cracking process, using Ni-Mo/HZSM-5 catalyst and compared with Ni-Mo-commercial catalyst. The catalytic cracking was carried out in a vacuum pressure batch reactor with a maximum volume of 2000 ml. A heating mantel was installed on the reactor. This process used a heavy fraction with a boiling point >360 °C as much as 500 – 600gram, as feed, and Ni-Mo/HZSM-5 catalyst as much as 1 gram. After preparthe oil and catalyst in the reactor, the catalytic cracking reaction process was set at ± 10 bar pressure (1 MPa). The reactor was heated to a maximum operating temperature of 360 °C. The reactor was cooled to 30 °C after the catalytic cracking reaction process was over.

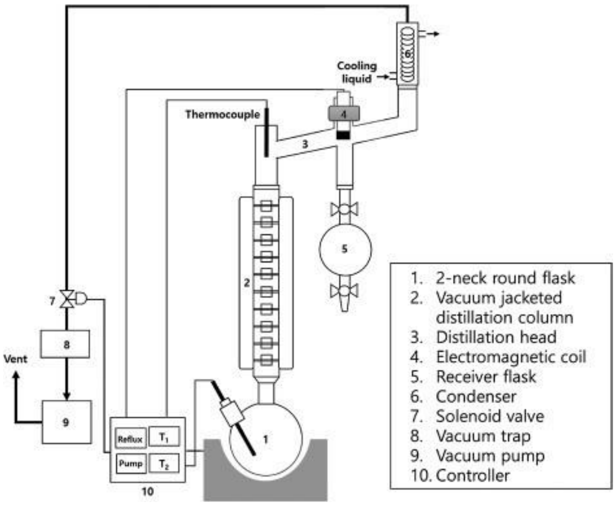

Figure 1 Vacuum Fractional distillation Unit

3. Results and Discussions

3.1. Synthesis Catalyst and XRD characterization

Zeolites are generally formed by combining sodium aluminosilicate gel with various commercial silica and alumina reagents. However, because of the rapid increase in zeolite consumption, commercial silica and alumina have cost constraints, which is undesirable for industries. As a result, less expensive raw materials are needed to redused the cost of manufacturing zeolites. One of these materials, fortunately, is natural aluminosilicate minerals.

The hydrothermal sol-gel method can be used to create kaolin-based ZSM-5 catalysts. This method is also superior to other methods to obtain a homogeneous solid composite by forming a colloid suspension in the form of a gel through the sol gelation process at room temperature. According to Ayodele and Abdullah (2019), raw kaolin is almost inactive because it is a naturally occurring mineral. It must be activated before being used as catalyst support through chemical (acid or base), thermal or mechanical treatments, or a combination of the two.

Kaolin must be activated through calcination or dehydroxylation before it can be used as catalyst support. Temperatures ranging from 500 °C to 900 °C are commonly used in this process via calcination methods (Kubliha et al., 2017; Maliwan et al., 2019). However, the calcination temperatures used in this study were 500 °C, 700 °C, and 800 °C). Diffraction pattern of calcined “Badau Belitung Kaolin” revealed that the kaolinite remained at 500 °C. The peak, which indicates the presence of SiO_2, was the only peak found at 700 °C, as shown in Figure 2. Kaolin is converted into metakaolin after it is calcined. Figure 2 shown XRD pattern of the highly amorphous metakaolin. As a result of the raw kaolin's calcining effect, the crystal structure disintegrates and turns into amorphous metakaolin.

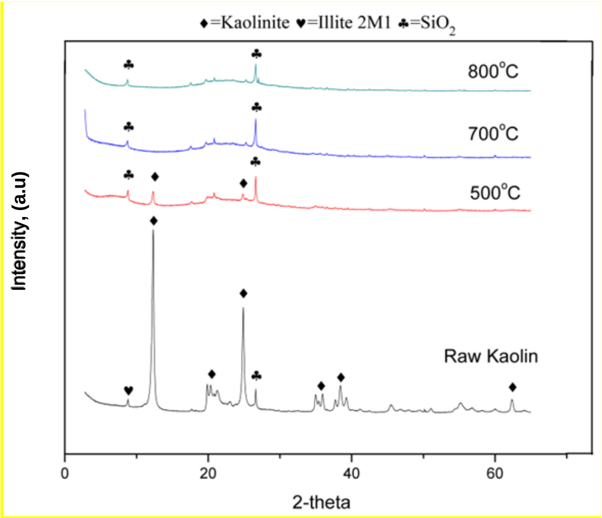

Figure 2 XRD Pattern of Calcined Kaolin

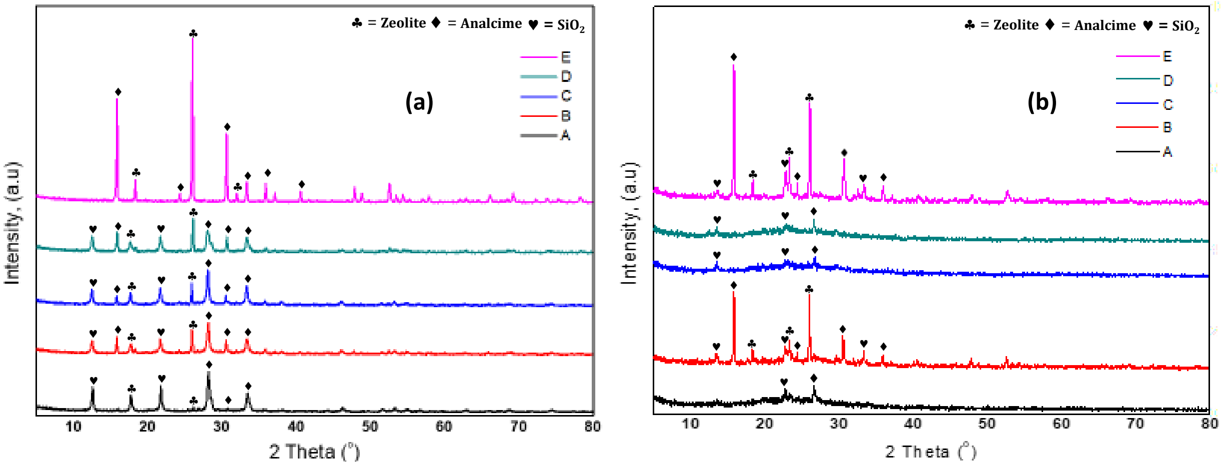

Figure 3 XRD Pattern of Kaolin-base ZSM-5 Formula A, B, C, D, and E: a) before impregnation: b) after impregnation

Figure 3 shows the diffraction pattern of the kaolin-based ZSM-5 catalysts product before and after impregnation with Ni and Mo. Figure 3(a) depicts the Formula E product with the highest degree of crystallinity, with a crystallinity degree of 73.31 %, and the peak is visible at $2\theta = 15.88, 18.36, 26.03, 30.62$, and 33.35. Meanwhile, the crystallinity levels in Formula A, B, C, and D were 70.81 %, 63.04 %, 69.62 %, and 72.33 %, respectively, with three dominant types of crystals zeolite, analcime, and silicon oxide. After impregnation with Ni and Mo metals to improve the catalytic performance of the catalyst, it was discovered that the stimuli of Formula B and E were still crystalline (Figure 3(b)), whereas the others were amorphous, resulting in a significant decrease in the degree of crystallinity, to 11.98 %, 40.96 %, 11.72 %, 11.45 %, and 51.89 % for Formula A, B, C, D, and E, respectively.

3.2. SEM characterization

Figure 4 depicts the SEM micrograph to examine the morphology of the synthesized product before and after Ni and Mo metal impregnation.

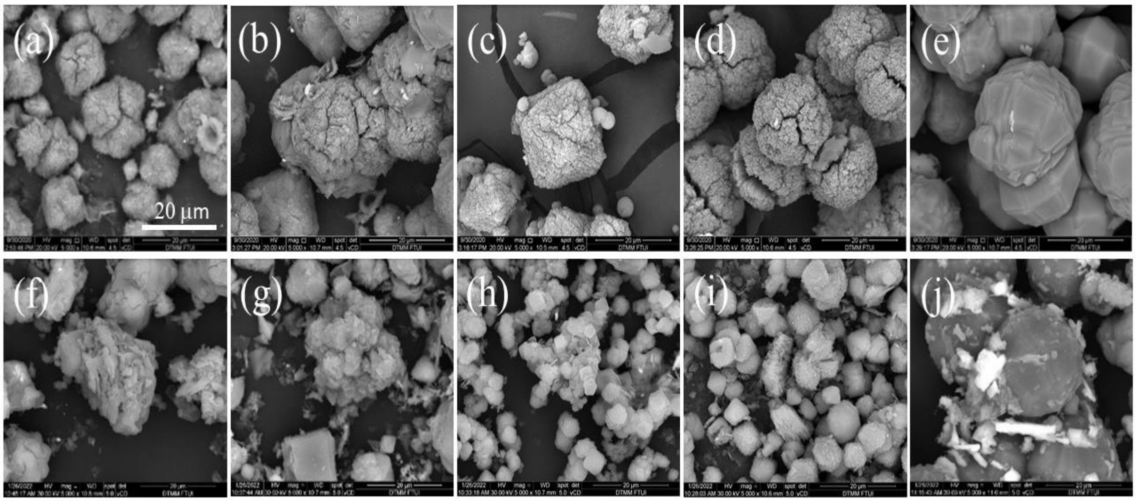

Figure 4 SEM images of Kaolin-based ZSM-5 formulas A, B, C, D, E before ((a) – (e)) and after ((f)-(j)) Ni/Mo impregnation

Figure 4 shows that the morphology of the ZSM5 catalyst differs before and after the impregnation of Ni and Mo metals. Before Ni and Mo metals impregnation, ZSM5 catalyst Formula A, B, C, and D had irregular spherical shapes with nearly the same size and sharp surfaces. The surface shape is smoother and more regular after impregnation, almost like a cube. The morphology of Formula E before and after Ni and Mo metals impregnation is nearly identical, consisting of particles with clear edges that appear like fragments of a uniform structure, with some particles having rounded edges, the same size, a flatter surface, and shaped like a dodecahedron. The presence of Ni and Mo metals adsorbed on the catalyst's surface after impregnation distinguishes it.

The EDX analysis results in Table 2 show that the composition of Si and Al is not the same as the value of the "Si/Al ratio (SAR)". The Si and Al compositions of commercial ZSM-5 with SAR 25 are 31.35 %wt and 18.47 %wt, respectively. As a result, differences in Si and Al composition can affect the morphology of the catalyst, as evidenced by the findings of Yan et al., (2016) discovered that when ZSM-5 catalysts with lower aluminum content are synthesized, they form different crystal sizes and morphology.

Table 2 Elemental composition of made sample Kaolin-base ZSM-5 by EDX analysis

Formula	O	Na	Al	Si
	%wt	%wt	%wt	%wt
A	41.65	11.27	15.62	31.36
B	41.54	12.25	16.65	29.57
C	39.37	13.37	18.47	28.73
D	37.53	10.85	17.20	34.43
E	39.73	10.83	14.67	34.76
ZSM-5(25)	43.30	06.89$^{*)}$	18.47	31.35

Note: $^{*)}$ = Carbon

3.3. Brunauer–Emmett–Teller (BET)

Table 3 shows the Brunauer-Emmett-Teller (BET) characterization results to determine the total surface area, pore volume, and pore radius of the kaolin-based ZSM-5 catalyst before and after Ni and Mo metal impregnation. The results of BET characterization of five kaolin-based ZSM-5 catalysts with formulas A, B, C, D, and E show that the values of total surface area, pore volume, and catalyst pore radius differ. The data in Table 3 show that variations in the Si/Al ratio (SAR) do not affect the catalyst surface area or pore structure.

The surface area and pore volume increased significantly after Ni and Mo metals impregnation for the catalysts Formula A, C and D. This is caused by a change in structure from crystalline to amorphous. While the formulas B and E, the surface area and pore volume are relatively stable. This can also be seen in the SEM micrograph, where Formula B and E are still crystals, whereas the others have formed small grains.

Based on the results of the Ni and Mo metal impregnation, the ZSM-5 catalyst based on kaolin formula E was evaluated for its catalytic performance in catalytic cracking heavy fraction of crude oil.

Table 3 BET test characteristics of Kaoline-base ZSM-5 Catalyst formulas A, B, C, D and E before and after impregnation

Formula	Surface Area (m^2/g)	Pore Volume (cc/g)	Pore Radius Dv(r) (Å)	Surface Area (m^2/g)	Pore Volume (cc/g)	Pore Radius Dv(r) (Å)
	Before Ni/Mo Impregnation			After Ni/Mo Impregnation		
A	16.655	0.036	15.249	24.145	0.050	17.043
B	22.064	0.055	15.335	23.011	0.065	15.358
C	21.363	0.075	17.081	26.604	0.088	17.542
D	14.375	0.022	15.367	26.214	0.105	21.629
E	40.051	0.079	15.263	41.157	0.089	15.465

3.4. Catalytic Performance

The impregnation of the kaolin-based ZSM-5 catalyst with specific amounts of Ni and Mo resulted in the formation of active sites that influenced the ZSM-5 catalyst's catalytic activity. Variations in the concentrations of Ni and Mo metals were studied by Kedia and Zaidi (2014) and Ramasubramanian et al., (2018). The effect of impregnation of the two metals significantly increased the activity of the catalyst with growing concentration of impregnated metal.

Furthermore, since the 1980s, ZSM-5-based additives have been used commercially in the FCC process to increase the octane number of gasoline. ZSM-5 is now used as a low-cost additive to boost the yield of C_2-C_5 olefins. The effectiveness of ZSM-5-based additives in increasing gasoline octane and light olefin selectivity has been demonstrated numerous times in the literature. The ideal additive content is around 25% of the total FCC catalyst composition (Gholami et al., 2021).

While Zhou et al., (2013) investigated catalytic cracking. The mass content of gasoline, diesel oil, and heavy oil was determined using a simulated distillation gas chromatogram, as described in ASTM standard D2887. The coke deposited on the catalyst is burned after splitting, and the CO_2 released is measured using gas chromatography.

In this study, the catalyst product tested for its catalytic performance is Formula E. This is because Formula E has the highest degree of crystallinity, and after impregnation with Ni and Mo metals, the morphology and molecular structure of Formula E remains relatively unchanged when compared to the other four formulas. Meanwhile, a commercial Ni-Mo catalyst was used to determine whether the ZSM-5 Formula E catalyst was of equal or higher quality than the commercial catalyst.

The results of the catalytic performance test of the Ni-Mo/HZSM-5 Formula E bifunctional catalyst are shown in Figure 5. In this study, the raw material for the reactor was heavy distillate (>350 ^oC), with the operating conditions of the catalytic cracking process and Gas Chromatography (GC) analysis as previously described. Based on GC test results, the hydrocarbon composition of vacuum distillation products was calculated and classified as gasoline (C_6-C_{11}), kerosene (C_{12}-C_{20}), and gasoil (C_{21}-C_{30}).

The GC analysis of the distillate fraction of the heavy distillate revealed that the cracking process was proceeding normally. A commercial Ni-Mo catalyst was used as a comparison or reference catalyst, and a test without a catalyst was used as a blank. GC then tested the resulting distillate product. It was discovered that the distillate from the non-catalyzed cracking process did not yield a light hydrocarbon fraction (C_3-C_5). Figures 5a and 5b show that when a bifunctional Ni-Mo/HZSM-5 Formula E catalyst was used, there was a light hydrocarbon fraction (C_3-C_5).

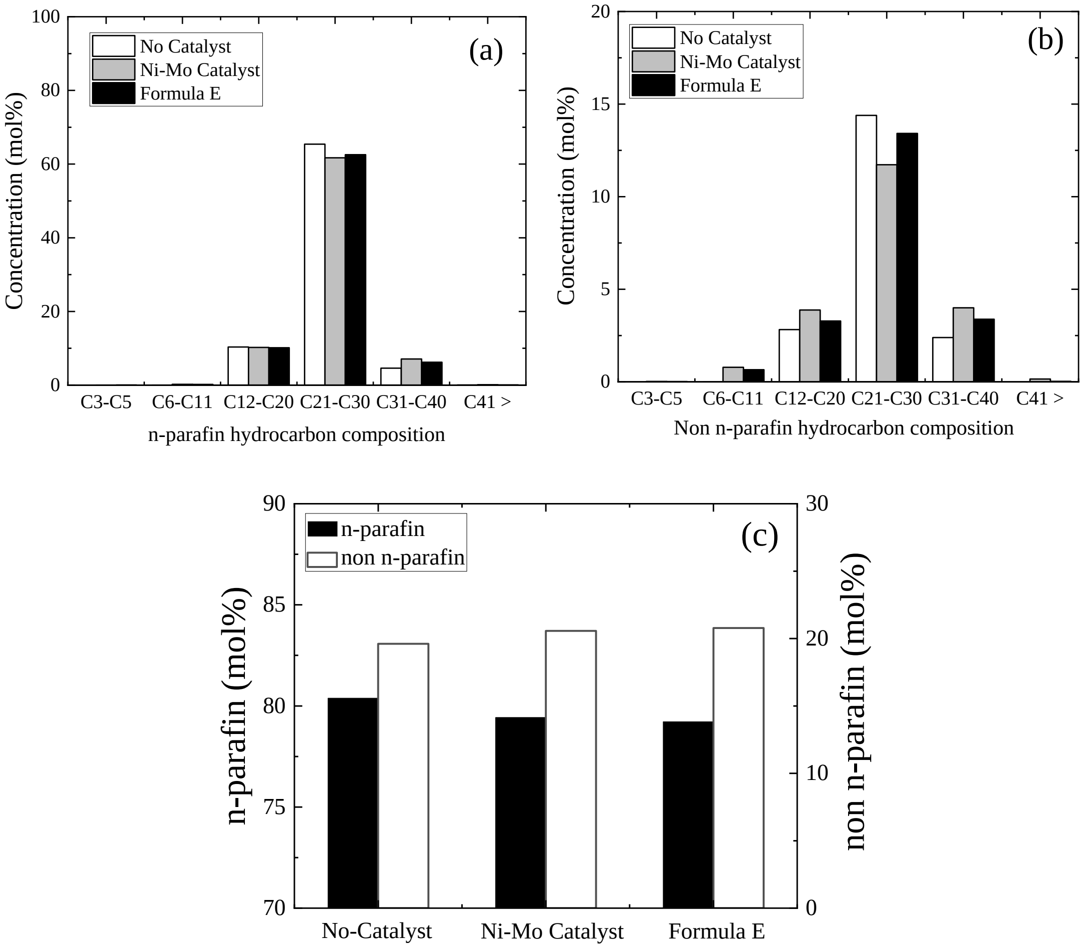

Figure 5 Hydrocarbon Composition: (a) n-Parafin (b) non n-Parafin (c) Total n-Parafin and Total non n-Parafin

4. Conclusions

The synthesis of bifunctional Ni-Mo/HZSM-5 for catalytic cracking of petroleum heavy fractions was carried out using “Badau Belitung kaolin” as raw material. There are five formulas: A, B, C, D, and E, with varying SiO_2/Al_2O_3, SiO_2/Na_2O, and H_2O/SiO_2 molar ratios. The surface area and pore volume of the catalysts Formula A, C and D increased significantly after Ni and Mo metals impregnation. The surface area and pore volume of the catalysts of formulas B and E remained relatively stable. This is due to a structural change from crystalline to amorphous. The result of performance test of the catalyst on the catalytic cracking process, where it does not use a catalyst, the yields did not produce a light hydrocarbon fraction (C_3-C_5), whereas when using a bifunctional catalyst Ni-Mo/HZSM-5 Formula E, it is seen that there is a fair amount of hydrocarbon fraction (C_3-C_5), as well as for the cracking process using Ni-Mo Commercial Catalyst. As a result, it is possible to conclude that the catalyst synthesized with Formula E has a fairly good cracking ability. When compared to the Ni-Mo commercial catalyst, the catalyst's performance test results showed roughly similar results in the catalytic cracking process of the heavy distillate fraction.

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