Fe-Cr pillared clay as catalysts for the ethanol to gasoline conversion

Robert R Widjaya1*, Nanda Saridewi2, Alda A Putri2, Nino Rinaldi1 and Adid A Dwiatmoko1

1Research Center for Chemistry Indonesian Sciences, Kawasan PUSPIPTEK Serpong, Tangerang Selatan 15314, Indonesia
2Department of Chemistry, UIN Syarif Hidayatullah Jakarta, Indonesia

*Corresponding author: robert.ronal.widjaya@lipi.go.id

Abstract. Bentonite is a clay mineral type of montmorillonite that can be used as a catalyst. The use of bentonite as a catalyst has weaknesses, namely small surface area, pore volume and low thermal stability, so it is necessary to modify the structure. Modification of bentonite structure carried out in this research used the pillarization method (Pillared Clay or PILC) with the addition of Fe and Cr metals to form Cr/PILC, Fe/PILC, and Fe-Cr/PILC catalysts. The PILC catalysts can be used as a catalyst in the ethanol to gasoline conversion process for alternative fuels. The XRD result shows that the pillarization process with the addition of Fe and Cr metals was succeeded so it can increase the interlayer spacing by 22.03 Å, 15.79 Å, and 15.85 Å on the Cr/PILC, Fe/PILC, and Fe-Cr/PILC catalysts. The SAA result shows an increase in surface area and pore volume in the Cr/PILC, Fe/PILC, and Fe-Cr/PILC catalysts structure. The presence of Brønsted acid type is indicated through the absorption peaks at 1515-1640 cm\(^{-1}\) and Lewis acid type at 1435-1470 cm\(^{-1}\) from the FTIR result. The TGA result shows an increase in thermal stability on the Cr/PILC, Fe/PILC, and Fe-Cr/PILC catalysts. The Fe-Cr/PILC catalyst shows the best activity results on the ethanol to gasoline conversion process with the acquisition of percent conversion and selectivity by 43.30% and 87.15% respectively.

1. Introduction

Clays are rocks that contain minerals and are composed of alumina-silica. Minerals in clay are a group of mineral constituents of sedimentary rocks and also as the main element of soil [1]. Clay or bentonite is generally used as an ion-exchange, adsorbent, and catalyst in the paper, paint, and rubber industries, so clay is often referred to as a multipurpose material. The type of clay that has become a concern in recent years is bentonite. Bentonite can be used as a catalyst buffer because it has advantages, namely having a pore volume that is easy to modify and a flexible structure [2]. The use of bentonite as a buffer on the catalyst has disadvantages, its thermal and hydrothermal stability is low, which is below 400°C [3]. The catalytic activity of bentonite as a catalyst buffer can be increased by modifying the bentonite structure.

Bentonite engineering methods can be done by pillarization (Pillared Clay or PILC). The pillarization method is carried out by an intercalation process using a pillaring agent in the form of a metal hydroxide cation into a bentonite alumina-silica interlayer that is useful as a pillar or pillar between its layers [4]. The bentonite structure will dehydrate and dehydroxylate during the intercalation process, resulting in metal oxides between the alumina-silica layers. Bentonite which has been successfully polarized will have high thermal stability and produce interlayer space in molecular dimensions [3]. The pillarization
method was chosen in this study because the pillarization method has the advantages of not changing the basic structure of the bentonite after an intercalation process and is easy to do. Metal polyhydroxy which is commonly used in the modification of pillared bentonite is Fe, Cr, Ti, Zr, and Al. Some previous studies that have used metals in the manufacture of PILC catalysts include Fe metals [5-7].

Research that uses variations of two metal oxides (bi-oxide metals) on the PILC catalyst is still rarely done. The use of two different metal oxides will complement each other’s shortcomings. An alloy of two metal oxides used in the synthesis of the PILC catalyst can affect the acidity of the catalyst surface which will be used for the reaction in the conversion of ethanol to gasoline. Previous research has been carried out by Widjaya et al. (2012) using Cr metal in the production of Cr/PILC catalysts. The presence of Cr metal in the production of Cr/PILC catalysts can increase the interlayer distance of bentonite up to 19.25 Å, besides there is also an increase in specific surface area and pore volume after the pillarization process using Cr polycation. The increase that occurs in the Cr/PILC catalyst makes the catalyst not easily deactivated when tested for catalytic activity.

PILC catalyst using Fe metal in a study that there is an increase in acidity on bentonite surfaces due to the influence of the presence of Fe metal combined with Zr metal in the manufacture of Zr-Fe/PILC catalysts [8]. Based on the results of research on the synthesis of Cr/PILC and Fe/PILC catalysts, bentonite catalysts polarized by Fe and Cr metals are needed in conducting this research. The use of Fe and Cr metal alloys in the synthesis of Fe-Cr/PILC catalysts is expected to increase surface area, pore-volume, and acidity on the catalyst surface.

In this research, catalyst Fe/PILC, Cr/PILC, and Fe-Cr/PILC catalysts are made at a ratio of 1: 1, then the catalytic activity is tested through the process of converting ethanol to gasoline. The process of converting ethanol to gasoline using an Sn-Cr/PILC catalyst at a ratio of 1: 1 and obtained ethanol products which have been converted to benzene, toluene, octane, and naphthalene similar to commercial gasoline [6]. The catalytic process used in the conversion of ethanol to gasoline requires an acidic catalyst. The process of pillarization in bentonite will increase the comparison of Brønsted and Lewis acid sites where the formation of metal oxide pillars will dominate the surface properties of bentonites [9]. The synthesized Fe/PILC, Cr/PILC, and Fe-Cr/PILC catalysts were characterized by physical and chemical characteristics including increased interlayer distances, elemental distribution, acidity, specific surface area, and pore volume, thermal stability, and clusters functional contained in the catalyst. The products produced from the catalytic activity test used Fe/PILC, Cr/PILC, and Fe-Cr/PILC catalysts and then analyzed using GC/FID.

2. Experimental

2.1. Preparation Materials
Bentonite was obtained from commercial product Bentonite (From Sigma Aldrich 285234) and CrCl₃.6H₂O, FeCl₃.6H₂O, NaOH, (AgNO₃) 0.1 M from Merck. Ethanol with a concentration of 99.8% from Smart Lab A-1035 and distilled water. The nano-sized Sn-Bentonite was prepared by a pillarization method.

2.2. Single metal pillared clay synthesis (Fe/PILC and Cr/PILC)
One a half litter of distilled water was put into a 5L beaker glass, then 81.099 gr of FeCl₃.6H₂O powder was added slowly while stirring with a magnetic stirrer for 2 hours. Next, 3 L of distilled water was put into a 5L beaker glass then added 24 gr of NaOH pellets slowly while stirring with a magnetic stirrer for 2 hours. Fe polycation solution was prepared by adding 3L of 0.2 M NaOH solution slowly into 1.5L of FeCl₃.6H₂O 0.2 M solution using a peristaltic pump at a speed of 0.25 mL/min while stirring rapidly for ± 12 hours at room temperature.

Distilled water (2L) was put into a 5L beaker glass, then 53.29 grams of CrCl₃.6H₂O powder was added slowly while stirring with a magnetic stirrer for 2 hours. Next, 2L of distilled water was put into a 5L beaker glass then added 16 gr of NaOH pellets slowly while stirring with a magnetic stirrer for 2 hours. Cr polycation solution was prepared by adding 2L of 0.2 M NaOH solution slowly to 2L of 0.1
M \text{CrCl}_3.6\text{H}_2\text{O} \text{ solution} \text{ using a peristaltic pump at a speed of 0.25 mL/min while stirring rapidly for ± 12 hours at temperature room.}

Five grams of bentonite were dissolved into 500 mL of distilled water, then heated to a temperature of 60 °C while stirring using a magnetic stirrer for 2 hours to obtain a 1% bentonite suspension. The preparation results of each Fe polycation solution was 4.5L and further 4L polycation solution was added little by little to a 1% bentonite suspension in a stirred state. Furthermore, after the addition of the polycation solution, the solution was mixed for 24 hours at the room temperature. The Fe / PILC and Cr / PILC suspensions were centrifuged at 7000 rpm for 5 minutes at 20 °C. The precipitate was washed using distilled water at 60 °C until the solution showed a negative reaction with no white precipitate formed when a 0.1 M AgNO\textsubscript{3} solution was dropped. Fe / PILC suspension and Cr/PILC were re-centrifuged, then the precipitate was dried in an oven at 100 °C for 12 hours later weighed and put in a sample bottle.

2.3. \textit{Bimetallic pillared clay synthesis (Fe-Cr/PILC)}

Nine hundred mL of distilled water was put into a 5L beaker glass, then added 48.6594 grams of FeCl\textsubscript{3}.6H\textsubscript{2}O powder slowly while stirring with a magnetic stirrer for 2 hours. 1.8L of distilled water was put into a 5L beaker glass, then added 47.961 gr of CrCl\textsubscript{3}.6H\textsubscript{2}O powder slowly while stirring with a magnetic stirrer for 2 hours.

Nine hundred mL of Fe polycation solution was put into the beaker glass and 1.8L of polycation solution was added then stirred with a magnetic stirrer for 2 hours. Next, 1.8 L of distilled water was put into a 5L beaker glass and then added 14.4 gr NaOH pellets slowly while stirring with a magnetic stirrer for 2 hours. Fe/Cr polycation solution was prepared by adding 1.8L of 0.2 M NaOH solution slowly to 2.7L of Fe/Cr metal solution using a peristaltic pump at a speed of 0.25 mL/min while stirring rapidly for ± 12 clock at room temperature.

Three grams of bentonite are dissolved into 300 mL distilled water, then heated to 60 °C while stirring using a magnetic stirrer for 2 hours to obtain a 1% bentonite suspension. The results of the preparation of 4.5L Fe/Cr polycation solution were added little by little to the 1% bentonite suspension in a stirred state. Then, after the addition of the polycation solution, the solution remains stirred for 24 hours at room temperature. The Fe-Cr/PILC suspension was then centrifuged at 7000 rpm for 5 minutes at 20 °C. The precipitate was washed using distilled water at 60 °C until the solution showed a negative reaction with no white precipitate formed when a 0.1 M AgNO\textsubscript{3} solution was dropped. Fe-Cr/PILC suspension was re-centrifuged, then the precipitate was dried in an oven at 100 °C for 12 hours then weighed and put in a sample bottle.

2.4. \textit{Characterization Materials}

The catalysts were analyzed by X-Ray Diffraction (XRD) from Pananalytical Varian AERIS using Cu-K\textalpha, scan speed 2 deg/min, λ Cu 1.54Å, and step width 0.01 deg, radiation on generated 40 kV, 15 mA, it aims to determine the interlayer distance in the reflection field (d001) and crystallinity so that the composition of the composition is known in the catalyst matches the typical crystal diffraction pattern. Fe and Cr content in PILC is measured by X-Ray Fluorescence (XRF) from Brucker, under a flowing Helium gas. Surface Area Analyzer based on the Brunauer-Emmet-Teller (BET) method from TriStar II 3020 Version 2.00 manufactured by N\textsubscript{2} analysis adsorptive and equilibration interval 10 s, sample mass 0.35 gr, cold free space 32.81 cm\textsuperscript{3}, sample density 1 gr/cm\textsuperscript{3}, Barret-Joyner-Halenda (BJH) method. Fourier Transform Infra-Red (FTIR) from shimadzu and used KBr phase method, prestige-21 with ATR 4000 attached to an automatic data acquisition center. The Thermogravimetric analysis (TGA) was performed by the LINSEIS STA Platinum Series apparatus, the temperature was increased at a rate of 10 °C/min from 10 to 1000 °C underflow of the nitrogen. Product analysis with GC-FID Carbowax/20M columns (30 m x 320 µm, 25 µm).
3. Results and Discussion

3.1. Comparison of XRD results for Bentonite and Sn-Bentonite

X-ray diffraction analysis using XRD (X-Ray Diffraction) on bentonite, Cr/PILC, Fe/PILC, and Fe-Cr/PILC measurement of the distance between layers (interlayer) was carried out at a diffraction angle of 20 low angle between 2-10°. The results of XRD diffraction characterization of 20 low angle can be seen in figure 1.

Figure 1. XRD low angle patterns of (a) bentonite, (b) Cr/PILC, (c) Fe/PILC, and (d) Fe-Cr/PILC.

The low angle X-ray diffraction pattern in Figure 1 shows that there has been a 20 shift of the reflection peak d001 to the left (in the smaller direction) of the bentonite sample after the pillarization process. The peak of reflection d001 in bentonite before pillarization shows 20 at 7.01°. This is consistent with the low angle X-ray diffraction pattern of bentonite which has a main peak at an angle of 20 = 7° [5]. The shift of reflection peak d001 that occurs in bentonite after pillarization with Cr metal on the Cr/PILC catalyst shows an angle of 20 of 4.01°. Based on research conducted by Widjaya et al., the Cr/PILC catalyst has a reflection peak d001 at 20 = 4.76°. The same thing happened to bentonite after pillarization with Fe metal on Fe/PILC catalyst which showed an angle of 20 at 5.59°. Sekewael (2008) has made montmorillonite iron oxide composites with the results of low angle X-ray diffraction patterns at 20 = 5.24°. Bentonite which has been pillarized with Fe and Cr metals at a ratio of 1:1 in Fe-Cr/PILC also shows a shift of angle of 20 to 5.57°. The low angle X-ray diffraction pattern on the Fe-Cr/PILC catalyst has an angle of 20 which is similar to the Fe/PILC catalyst, this can be indicated by the presence of a more dominant Fe metal than the Cr metal on the Fe-Cr/PILC catalyst.

Shifting peak 20 reflection d001 shows an increase in the distance between layers (interlayer) on the bentonite that has been carried out the pillarization process. The increase that occurred due to the exchange of cations that exist in the interlayer of bentonite with polycation of Fe and Cr, thus causing the expansion of the distance between layers in bentonite. The interlayer distance of the bentonite before the pillarization process is 12.60 Å. The bentonite has a distance between layers between 12.0-15.0 Å. Bentonite which has been carried out by the pillarization process using Fe and Cr metal has increased the interlayer distance to 22.03 Å for Cr/PILC, 15.79 Å for Fe/PILC, and 15.85 Å for Fe-Cr/PILC. Cr/PILC catalyst has the highest interlayer distance compared to Fe/PILC and Fe-Cr/PILC catalysts, this is because in the pillarization process using Cr metal can make the molecular size larger [10]. The Fe-Cr/PILC catalyst has decreased interlayer when compared to the Cr/PILC catalyst. The decrease occurred due to diffusion barriers by the number of molecules of one of the most intercalated metal
pillars, namely Fe metal so that the Fe-Cr/PILC catalyst has a similarity between the interlayer and the Fe/PILC catalyst [11].

The increased interlayer distance is caused by the exchange of hydrated cations on the surface between bentonite layers and larger cations, namely Cr\(^{3+}\) and Fe\(^{3+}\). An increase in the distance between layers is one of the success factors in the process of pillarization due to the intercalation of the pillaring agent in the form of Fe and Cr metal into the interlayer of the bentonite. The increase in interlayer distance can be concluded that the pillarization process using Fe and Cr metals in the synthesis of Cr/PILC, Fe/PILC, and Fe-Cr/PILC catalysts has been successfully carried out. The composition of the catalyst can be determined through crystallinity with a 2-high angle X-ray diffraction pattern between 10-80°. The results of the XRD analysis showed typical peaks which were then compared with data from the JCPDS (Joint Committee of Powder Diffraction Standards).

The high angle X-ray diffraction pattern of 2θ can be seen in Figure 2. High angle X-ray diffraction patterns in bentonite produce peak angles of 2θ = 19.48°; 21.65°; 26.3°; 35.14°; 54.11°; and 61.48°. These results are following JCPDS No. 29-1499 which shows that these peaks are typical peaks for montmorillonite type. Research conducted by Dewi et al. states that montmorillonite X-ray diffraction patterns are at 2θ = 19.58°; 20.64°; and 26.33°. Based on these results, the bentonite structure is a montmorillonite type [12]. Bentonite with montmorillonite type is distinguished through alumina-silica composition which has a 2:1 configuration ratio with the characteristic of swelling in the bentonite framework. The high angle X-ray diffraction pattern on the Cr/PILC catalyst results in a peak angle of 2θ = 19.72°; 20.71°; 26.52°; 34.61°; and 61.79°. Peak 2θ = 34.61° indicates that the Cr\(_2\)O\(_3\) compound that was successfully interpreted had a rhombohedral crystal system. These results are following JCPDS No. 84-1616 which shows typical Cr\(_2\)O\(_3\) peaks at 2θ = 24.52°; 34.6°; and 36.5°. Based on research by Rahmani et al., typical peaks of the rhombohedral Cr\(_2\)O\(_3\) phase appear at 2θ = 24.5°; 34.6°; 36.2°; 41.5°; and 50.2°. Figure 2 shows the peak shift 2 peaks and the change in intensity which proves that the addition of Cr\(_2\)O\(_3\) into the interlayer of the bentonite was successfully carried out and formed a crystalline phase [13].

The high angle X-ray diffraction pattern on the Fe/PILC catalyst produces a peak angle of 2θ = 19.94°; 26.75°; 35.3°; and 55.73°. The peak of X-ray diffraction that appears in the region 2θ = 35.3° indicates that the Fe\(_2\)O\(_3\) compound with the hematite phase was successfully synthesized. These results are following JCPDS No. 13-5340 which shows the typical peaks of Fe\(_2\)O\(_3\) at 2θ = 24.19°; 35.3°; and 62.47°. The peak indicating the presence of Fe\(_2\)O\(_3\) was at 2θ = 24.02°; 33.36°; 35.3°; and 54.02 [14]. Based on these results, Fe\(_2\)O\(_3\) which was intercalated into the interlayer of the bentonite was successfully carried out. The high angle X-ray diffraction pattern on the Fe-Cr/PILC catalyst produces an angle peak of 2θ = 19.77°; 22.47°; 26.65°; 35.3°; 36.5°; and 61.93°. The typical peaks that appear in the region 2θ = 35.3° and 36.5° indicate that there are Fe\(_2\)O\(_3\) compounds with hematite phase and Cr\(_2\)O\(_3\) compounds with the rhombohedral phase. These results are following JCPDS No. 13-5340 which shows the typical peaks of Fe\(_2\)O\(_3\) at 2θ = 24.19°; 35.3°; and 62.47° and JCPDS No. 84-1616 which shows typical Cr\(_2\)O\(_3\) peaks at 2θ = 24.52°; 34.6°; and 36.5°.

3.2. Measurement with X-Ray Fluorescence (XRF)

The results of XRF characterization on bentonite, Cr/PILC, Fe/PILC, and Fe-Cr/PILC can be seen in Table 1. The XRF analysis results in Table 3 show that the main components of bentonite are SiO\(_2\) and Al\(_2\)O\(_3\). This is because SiO\(_2\) and Al\(_2\)O\(_3\) in bentonite have the largest percentage composition compared to other metal oxide components, such as Fe\(_2\)O\(_3\), Cr\(_2\)O\(_3\), MgO, CaO, and K\(_2\)O. The content of SiO\(_2\) and Al\(_2\)O\(_3\) in bentonite before the pillarization process was 60.51% and 19.12%, respectively.

| Catalysts     | Elements (% wt) |
|---------------|-----------------|
|               | SiO\(_2\) | Al\(_2\)O\(_3\) | Fe\(_2\)O\(_3\) | Cr\(_2\)O\(_3\) | MgO | CaO | K\(_2\)O |
| Bentonite     | 60.51 | 19.12 | 4.84 | 0.01 | 12.2 | 1.59 | 0.41 |
| Cr/PILC       | 46.78 | 13.7 | 3.01 | 17.67 | 14.51 | 2.96 | 0.25 |
Modification of the structure of bentonite by performing the pillariization process using metal oxides Fe and Cr showed an increase in the percentage of composition in Fe\(_2\)O\(_3\) and Cr\(_2\)O\(_3\) on each catalyst Cr/PILC, Fe/PILC, and Fe-Cr/PILC. Cr/PILC catalyst showed an increase in Cr\(_2\)O\(_3\) composition which was originally in bentonite before the pillariization process was 0.01% to 17.67%, whereas in Fe/PILC catalyst there was an increase in Fe\(_2\)O\(_3\) composition from 4.84% to 44.5%. Alloys of bimetallic oxides Fe and Cr which were interpreted in the Fe-Cr/PILC catalyst showed the presence of Fe\(_2\)O\(_3\) and Cr\(_2\)O\(_3\) content of 31.89% and 5.42%, respectively. Based on the results of the XRF analysis, before the pillariization process using two metal oxides of Fe and Cr, the composition of Fe\(_2\)O\(_3\) on the Cr/PILC catalyst was 3.01% and the composition of Cr\(_2\)O\(_3\) on the Fe/PILC catalyst was 0.03%. The composition of the element content when the process of pillariization using bimetallic Fe and Cr on the Fe-Cr/PILC catalyst indicates that the elements of Fe and Cr are bonded to each other in interlayer bentonite [6]. A comparison of the composition of Fe\(_2\)O\(_3\) is greater when compared to the composition of Cr\(_2\)O\(_3\) on the Fe-Cr/PILC catalyst. This confirms the results of the low angle XRD analysis of diffusion barriers by the number of molecules of one of the most intercalated pillars of the metal oxide Fe, so the XRF analysis results show that the composition of Fe\(_2\)O\(_3\) has a greater percentage content than the composition of Cr\(_2\)O\(_3\) (Gil et al., 2000).

### 3.3. Measurement with Surface Area Analyzer (SAA)

Table 2 showed the results of surface area and pore volume analysis of bentonite, Cr/PILC, Fe/PILC, and Fe-Cr/PILC using SAA. Bentonite before being modified through the pillariization process showed a surface area of 26.48 m\(^2\)/g and a pore volume of 0.08 cm\(^3\)/g. After the pillariization process, there was an increase in surface area and pore volume respectively to 158.79 m\(^2\)/g and 0.15 cm\(^3\)/g for the Cr/PILC catalyst and 184.24 m\(^2\)/g and 0.31 cm\(^3\)/g for the Fe/PILC. The increase in surface area that occurs indicates that the insertion of the Fe\(^{3+}\) and Cr\(^{3+}\) cations has been stably bound in the interlayer of the bentonite in the Fe/PILC and Cr/PILC catalysts. The addition of transition metals, Fe and Cr can cause an increase in the surface area of the catalyst, this occurs because the Fe and Cr metals that are embodied through the pillariization process may have been distributed to the interlayer of the bentonite, thereby increasing the surface area and volume of the portion.

#### Table 2. Results of SAA analysis.

| Material     | SSA (m\(^2\)/g) | Pore Volume (cm\(^3\)/g) |
|--------------|-----------------|--------------------------|
| Bentonite    | 26.48           | 0.08                     |
| Cr/PILC      | 158.79          | 0.15                     |
| Fe/PILC      | 184.24          | 0.31                     |
| Fe-Cr/PILC   | 174.11          | 0.26                     |

The SAA analysis graph in Table 2 showed that the Fe-Cr / PILC catalyst has a surface area and pore volume of 174.11 m\(^2\)/g and 0.26 cm\(^3\)/g. These results show an increase in surface area and pore volume in the interlayer of the bentonite after the pillariization process using Fe and Cr metal on the Fe-Cr/PILC catalyst, but when compared with the Fe/PILC catalyst, the Fe-Cr/PILC catalyst has decreased surface area and volume of the portion. The presence of Cr metal affects the decrease in surface area and pore volume in the Fe-Cr/PILC catalyst. The Cr metal cannot increase surface area and pore volume that is too large in bentonite, this is in accordance with the results of surface area and pore volume analysis in Cr/PILC catalysts which are smaller when compared to Fe/PILC. The decrease occurred due to Cr metal trapped interlayer (interlayer) and on the surface of pillared bentonite, thus covering the pores of bentonite. The surface area is one of the factors that determine how the catalyst activity takes place in the catalysis reaction process, so with an increased surface area from 26.48 m\(^2\)/g to 174.11 m\(^2\)/g making...
the site of the reaction bigger [15]. A large surface area will provide a large contact area between the reactants and the catalyst, so the size of the contact will affect the overall catalysis process. The reactant molecule will move freely before undergoing adsorption on the surface of the catalyst which will then be activated and react to produce a product.

3.4. Measurement with Thermogravimetric Analysis (TGA)

Figure 3 shows a decrease in the relative mass percent curve in bentonite, Cr/PILC, Fe/PILC, and Fe-Cr/PILC as the heating temperature increases to 1000°C. Decrease in mass percent of total thermal decomposition of bentonite, Cr/PILC, Fe/PILC, and Fe-Cr/PILC catalysts respectively by 19.07%; 33.13%; 31.07%; and 32.04%. The results of measurements by TGA in the first stage show the release of physically bound water molecules (dehydration) on the surface of the catalyst structure. Bentonite shows a mass change of 7.65% at temperatures between 76 ˚C to 140 ˚C. The bentonite material is very stable to heat-stable to temperatures below 73°C [6]. The process of pillarization using metals and Fe and Cr on Cr/PILC, Fe/PILC, and Fe-Cr/PILC catalysts affects the release of water molecules in the temperature range 74-225˚C with changes in mass with a range of 17.19-18.58%. This finding indicated by changes in molecular structure due to the addition of Fe and Cr metals to the bentonite so that the decomposition temperature increases.

Figure 3. TGA Curve of (a) Bentonite, (b) Cr/PILC, (c) Fe/PILC, and (d) Fe-Cr/PILC.

Bentonite in the second stage showed a change in mass at a temperature of 140-200˚C of 1.35%, while bentonite pillarized metals Fe and Cr on catalyst Cr/PILC, Fe/PILC, and Fe-Cr/PILC experienced mass changes with a range of 8.28-8.58% at temperature 210-520°C. The temperature there is a release of water molecules (dehydration) and changes in the structure of salt (Mg, Na, Ca, and K) in the cation oligomer in the interlayer (interlayer) bentonite [15]. The third step shows the chemical decomposition. Third stage mass changes in bentonite occur at temperatures of 200-686˚C of 10.05%. The results of the third stage TGA measurements, catalyst Cr/PILC, Fe/PILC, and Fe-Cr/PILC showed a change in mass percent with a range of 5.01-6.25% at temperatures between 500-710°C. The temperature range of 500-680˚C occurs maximum dehydroxylation of pillared metals in interlayer bentonite which results in damage to the proton structure on bentonite alumina-silica sheets [16].

The results of measurements with TGA at temperatures above 710°C indicate the maximum temperature limit that can be accepted by bentonite material before the total damage caused by the process in the first to third stages. The addition of metals, namely Fe and Cr metals to Cr/PILC, Fe/PILC, and Fe-Cr/PILC catalysts, provides physical property resistance to the bentonite structure thereby resulting in increased thermal stability compared to bentonite which has not been carried out by the pillarization process [17].
3.5. Measurement with Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectrum results in Figure 4 showed that bentonite has 6 characteristic absorption peaks detected at a wavelength of 453.7 cm\(^{-1}\); 524.38 cm\(^{-1}\); 1081.41 cm\(^{-1}\); 1635.64 cm\(^{-1}\); 3433.29 cm\(^{-1}\); and 3630.03 cm\(^{-1}\). The absorption peak at the wave number 453.7 cm\(^{-1}\) is the bending vibration of Si-O-Si in the bentonite silicate aluminum framework, while the absorption peak at the wavenumber area 1081.41 cm\(^{-1}\) shows the existence of stretch vibration (stretching) Si-O-Si. The bending vibrations and stretching of Si-O-Si occur in each of the absorption bands 470 cm\(^{-1}\) and 1008.7 cm\(^{-1}\). The existence of Si-O-Si buckling vibrations and shows the formation of an aluminosilicate framework on the catalyst [18].

**Figure 4.** FTIR Results analysis of (a) bentonite, (b) Cr/PILC, (c) Fe/PILC, and (d) Fe-Cr/PILC.

FTIR analysis showed that the success of the pillarization process using Fe and Cr metals with a shift in absorption peaks which indicates the addition of compounds derived from metals that are intercalated into the interlayer of bentonite. Figure 4 shows the shifts in 6 typical bentonite absorption peaks after pillarization of the Cr/PILC, Fe/PILC, and Fe-Cr/PILC catalysts. Also, there is a new absorption peak in the Cr/PILC catalyst in the wavelength region of 920.05 cm\(^{-1}\) which shows the bending vibration of -OH with the Cr\(^{3+}\) cation. The bend -OH vibrations with cations occur in the region of 918.88 cm\(^{-1}\). New absorption peaks on the Fe/PILC catalyst also appear at wavelengths of 794.67 cm\(^{-1}\) due to the presence of a stretching -OH vibration which indicates the binding of the Fe\(^{3+}\) cation to the interlayer of the bentonite. The Fe-Cr/PILC catalyst showed new absorption peaks in the region of 794.67 cm\(^{-1}\) and 921.97 cm\(^{-1}\) indicating the presence of both Cr\(^{3+}\) cations from Cr and Fe\(^{3+}\) metals from Fe.

**Figure 5.** GC-FID Results analysis of (a) Cr/PILC, (b) Fe/PILC, and (c) Fe-Cr/PILC.

FTIR analysis results were useful to find out the type of acidity the catalyst has. There are two types of acidity that catalysts have, namely Bronsted and Lewis acids. Bronsted acid type is at a wavelength of 1515-1640 cm\(^{-1}\) and Lewis acid type is at a wavelength of 1435-1470 cm\(^{-1}\) [19]. The Bronsted acid site tends to donate protons or H\(^{+}\) ions, while the Lewis acid site tends to capture or accept electrons. The peak yield of FTIR uptake in bentonite before and after pillarization the Cr/PILC, Fe/PILC, and Fe-Cr/PILC catalysts have both acidity types, both Bronsted and Lewis acid types.

3.6. Measurement with Gas Chromatography- flame ionization detector (GC-FID)

The success of ethanol compounds that have been converted to gasoline compounds in Figure 5 showed that the Fe-Cr/PILC catalyst is able to produce the highest percent conversion, which is 43.3% compared to both Cr/PILC and Fe/PILC catalysts. The results of GC/FID analysis of gasoline compound products...
formed from the results of ethanol conversion determined each percent of selectivity which can be seen in Table 3. Table 3 shows that the gasoline compound resulting from the conversion of ethanol produces product components with a range of C6 to C12 hydrocarbon bonds in the form of paraffin and aromatic compounds. Product compounds produced from the conversion reaction of ethanol into gasoline are the main components contained in gasoline or commercial gasoline. The total selectivity of gasoline in Table 3 shows the highest selectivity results obtained from the use of Fe-Cr/PILC catalysts with a percent selectivity of 87.15% in which the highest percentage of product selectivity is produced in benzene compounds (C6H6), which is 48.52%. The benzene is one of the most important compounds in the gasoline component. The use of the Fe-Cr/PILC catalyst in the activity of the catalyst to the conversion process of ethanol to gasoline produces the highest percent conversion and selectivity values [6].

| No. | Product                | Selectivity (%) | Cr/PILC | Fe/PILC | Cr-Cr/PILC |
|-----|------------------------|-----------------|---------|---------|------------|
| 1.   | n-Heptane (C7H16)      | 4.97            | 2.29    | 1.21    |
| 2.   | Cyclohexane (C6H12)    | 3.07            | 2.29    | 31.87   |
| 3.   | Toluene (C7H8)         | 1.30            | 1.19    | 1.52    |
| 4.   | Benzene (C6H6)         | 15.02           | 28.18   | 48.52   |
| 5.   | n-Dodecane (C12H26)    | -               | 1.92    | -       |
| 6.   | Fenol (C6H6O)          | 3.79            | 1.54    | 0.42    |
| 7.   | n-Hexane (C6H14)       | 19.35           | 15.66   | 3.61    |
| Total Selectivity Product | 47.48           | 53.07           | 87.15 |

The Fe-Cr/PILC catalyst has a good surface area and pore volume and acidity of the catalyst although the results are lower than the Fe/PILC catalyst for surface area and pore volume and with the Cr/PILC catalyst as seen from the measurement results of SAA. Fe metal alloy as an active component with Cr metal as a promoter on Fe-Cr/PILC catalyst can influence the catalytic reaction so that it can produce the best percent conversion and selectivity of the catalyst in the catalyst activity test of the conversion process of ethanol to gasoline.

4. Conclusion

Based on the results of the characterization, modification of the bentonite structure using the pillarization method in the synthesis of Cr/PILC, Fe/PILC, and Fe-Cr/PILC catalysts increased physical and chemical properties possessed by the catalyst, namely increased surface area, pore-volume, thermal stability and acidity in the catalyst to increase the activity of the catalyst in the process of converting ethanol to gasoline. The best results on the catalyst activity test on the process of converting ethanol to gasoline are obtained from the use of the Fe-Cr/PILC catalyst which results in percent conversion, and selectivity of 43.30%, 87.15% respectively.

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