Characterization of Cr/Bentonite and HZSM-5 Zeolite as Catalysts for Ethanol Conversion to Biogasoline

Robert Ronal Widjaya
Material Sciences, Faculty of Mathematics and Natural Sciences, Universitas Indonesia, Jakarta 10430, Indonesia. Research Centre for Chemistry, Lembaga Ilmu Pengetahuan Indonesia, Tangerang 15314, Indonesia, rrw_83@yahoo.com

Bambang Soegijono
Material Sciences, Faculty of Mathematics and Natural Sciences, Universitas Indonesia, Jakarta 10430, Indonesia

Nino Rinaldi
Research Centre for Chemistry, Lembaga Ilmu Pengetahuan Indonesia, Tangerang 15314, Indonesia

Follow this and additional works at: https://scholarhub.ui.ac.id/science

Recommended Citation
Widjaya, Robert Ronal; Soegijono, Bambang; and Rinaldi, Nino (2012) "Characterization of Cr/Bentonite and HZSM-5 Zeolite as Catalysts for Ethanol Conversion to Biogasoline," Makara Journal of Science: Vol. 16: Iss. 1, Article 11.
DOI: 10.7454/mss.v16i1.1283
Available at: https://scholarhub.ui.ac.id/science/vol16/iss1/11

This Article is brought to you for free and open access by the Universitas Indonesia at UI Scholars Hub. It has been accepted for inclusion in Makara Journal of Science by an authorized editor of UI Scholars Hub.
Characterization of Cr/Bentonite and HZSM-5 Zeolite as Catalysts for Ethanol Conversion to Biogasoline

Robert Ronal Widjaya¹,²*, Bambang Soegijono¹, and Nino Rinaldi²

¹. Material Sciences, Faculty of Mathematics and Natural Sciences, Universitas Indonesia, Jakarta 10430, Indonesia
². Research Centre for Chemistry, Lembaga Ilmu Pengetahuan Indonesia, Tangerang 15314, Indonesia

*E-mail: rrw_83@yahoo.com

Abstract

The characterization on Cr/Bentonite and Zeolit HZSM-5 catalysts for ethanol catalytic process to biogasoline (equal to gasoline) has been done in this study. Cr/Bentonite has high acidity and resistant to a lot of moisture, in addition to being able to processing feed which a lot of moisture (>15%) from ethanol-water mixture, it is also not easy to deactivated. Cr/Bentonite which is then used as the catalyst material on the process of ethanol conversion to be biogasoline and the result was compared with catalyst HZSM-5 zeolite. Several characterization methods: X-ray diffraction, Brunauer Emmett Teller (BET), thermogravimetry analysis (TGA), and catalyst activity tests using catalytic Muffler instrument and gas chromatography-mass spectrometry (GC-MS) for product analysis were performed on both catalysts. From acidity measurement, it is known that acidity level of Cr/Bentonite is the highest and also from XRD result, it is known there is shift for 2theta in Cr/Bentonite, which indicates that Cr-pillar in the Bentonite can have interaction. It is also supported by BET data that shows the addition of specific surface area in Cr/Bentonite compared with natural Bentonite before pillarization. Furthermore catalyst activity test produced the results, analyzed by GC-MS, identified as butanol and also possibly formed hexanol, decane, dodecane, undecane, which are all included in gasoline range (C₄ until C₁₂).

Keywords: acidity, biogasoline, catalyst, Cr-pillars, ethanol

1. Introduction

Energy is one of the basic human needs of everyday life, for transportation, household and industrial needs. Energy needs are mainly met by converting natural resources such as non-renewable petroleum, natural gas and coal to obtain fossil fuels such as petrol (gasoline equivalent) and diesel. However, the demand for fuel is increasing every year. For example, in 2000, Indonesia's domestic demand on fossil fuels as much as 54.8 million
liters and that number continues to increase to 67.6 million liters in 2004, all of which is converted into energy to be used for daily needs [1]. To reduce dependence on petroleum as an energy source, it has been developed new and renewable energy sources, including the use of bioethanol as the fuel mix or replacement in gasoline.

The use of catalytic processes ethanol to gasoline (ETG) is very promising because regardless of the concentration of ethanol-water mixture produced from bioethanol processes, it can directly be used as a feed in ETG conversion process. So that the ethanol refining process using distillation or membrane can be eliminated. However, the challenge facing the use of catalytic processes ETG directly after the bioethanol process is deactivation of the catalyst in the ETG reaction. As is generally known that the ETG process uses a catalyst having high acidity (solid acid catalyst). And most of the catalysts that have been tested in the catalytic process ETG is a zeolite catalyst ZSM-5 because it has a level of acidity or the acidity is relatively high [2]. To be able to convert ethanol into bio-gasoline there are several reactions are involved, such as ethanol dehydration reaction to ethylene [3]. Then some reactions will occur from ethylene: oligomerization/isomerizaton,cracking and aromatization, so that from ethylene will be produced various kinds of good hydrocarbons, both paraffin (ethene, propene, butene, etc.) and aromatics (benzene, toluene, C8-10, gasoline). In general, the catalytic reaction mechanism of ethanol to gasoline is Figure 1 [4].

Zeolite is a mineral consisting of hydrated crystalline aluminosilicates containing alkali or alkaline earth cations inside three-dimensional framework. Besides having a high enough acidity so that it can provide high amount of a proton donor (H⁺ ions), ZSM-5 zeolite catalyst has a regular distribution of the pore structure. However, these catalysts are quickly deactivated or inactive if the ethanol-water mixture used as feed contains water concentrations >5% [4]. Therefore it is necessary for the development of other types of catalysts for the ETG process which has properties of high acidity and resistant to high water content, such as the Cr-pillared Bentonite, because natural bentonite is widely available in Indonesia with an abundant amount. There are several types of metal which is commonly used as a pillar that can increase the acidity of the catalyst with the type of clays [5]. Cr was chosen is because the type of metal will give large amount of the source of H⁺ ions [6].

The purpose of this study is to characterize and test the catalyst materials Cr/ Bentonite and HZSM-5 zeolite that are used to assist the process of Ethanol to Gasoline (ETG) as a renewable energy source.

2. Experiment

In this study, the materials used are bentonite from Trengalek that has been prepared as Cr/Bentonite with Si/Al ratio of 2:1 and HZSM-5 zeolite CBV3020E Lot No. 2200-28 from the International Zeolyst (3 g), ethanol 90% as a raw material to be converted, and nitrogen gas for flushing when running the catalyst activity test.

The acidity levels of the catalyst materials Cr/Bentonite and HZSM-5 that were used in the ETG were determined by the gravimetric method using pyridine [7].

Once the catalyst candidates were obtained, its specific surface area was measured using BET equipment. When the SA of Cr/Bentonite is larger, it would indicate that bentonite was pillared, as the space is wider. To find the distribution of oxide on the catalyst surface, X-ray diffraction (XRD) measurement was applied. While to know the resistance of the catalyst to high temperature, the catalyst material was tested by TGA. In addition, the weight and phase changes of the material can also identified. The flow chart in Figure 2 shows an outline of the experiment.

![Figure 1. Reaction Mechanism of Ethanol Conversion to Gasoline](image1)

![Figure 2. Implementation Flow Chart of the Experiment](image2)
Catalyst activity test is done by placing the catalyst in a fixed bed reactor electrically heated with adjustable temperature control. Before the catalyst used, it is first oxidized in situ with a flow of oxygen gas which is intended to allow the catalyst to be tested is completely free of water content [8]. The feed in the form of a mixture of ethanol and water was flowed into the reactor at a flow rate of 2 ml/min with HPLC pumps. The results of this process in the form of gas and liquid phases are separated prior analysis. Liquid products were analyzed off-line by GC-MS.

3. Results and Discussion

Acidity test was conducted on bentonite, Cr/Bentonite, SO₄/Bentonite and HZSM-5 which were dried in the oven or through calcination. The results of this acidity test using gravimetric method are shown in Figure 3.

The graph in Figure 3 shows that Cr/Bentonite has a higher acidity than HZSM-5. This is one indicator that the process of ion/cation exchange between the sheets of alumina-silicate well occurs because as shown in the periodic table, the oxidation number of Cr metal pillar also has higher acidity level. Therefore, for ETG process, catalyst Cr/Bentonite was used, because the material has higher Brønsted acidity containing plenty amount of H⁺ cations, which is expected to donate H⁺ cation and will produce biogasolin [9].

For comparison the acidity of calcined HZSM-5 with HZSM-5 which was dried in the oven at 120 °C for 12 hours (Figure 3), it can be seen that oven-dried HZSM-5 has a higher acidity, so oven-dried HZSM-5 was chosen as catalyst for this ETG process. The acidity of calcined HZSM-5 was lower, because the number of ions are released during calcination at high temperature (550 °C). During calcination, the H₂O molecules were released both physically and chemically, while drying in the oven will only remove H₂O physically, so that many H⁺ ions are still attached to the material. Thus, the material still has a fairly high level of acidity.

Differences in acidity level between bentonite and SO₄/Bentonite as shown the chart in Figure 3 can be explained as follows: SO₄/Bentonite is a natural bentonite that had been treated with H₃SO₄, that caused its acidity level increased, higher than that of natural bentonite. That is because the existing cations between the layers of alumina-silicate in natural bentonite is not homogeneous (there are other impurity cations such as Mg, Fe, Ca) that could be easily exchanged with H⁺ from sulphuric acid solution so that it becomes homogeneous. But for the ETG process material Cr/Bentonite was selected, because it has the highest level of acidity than others.

Pore size is defined as pore width (diameter) which is the distance between two opposite walls of the pore [10-11]. From Table 1, it can be seen that natural bentonite has a specific surface area (S.A) approximately 79.44 m²/gr. Because it has Cr polycations, there was a significant increased, so that the specific surface area becomes 153.03 m²/g for catalyst Cr/Bentonite. Besides S.A, it can also be seen that the pore width is also increased in Cr/Bentonite from 101.9 Å (in natural bentonite) to 102 Å, although it is not very significant. The pore volume increased from 0.03857 cc/g to 0.07436 cc/g, respectively from natural bentonite to Cr/bentonite. Based on these results, it can be said that the Cr metal is capable to interact.

When compared with HZSM-5 oven, the value of S.A of bentonite and Cr/Bentonite are far below the oven-HZSM-5. It is worth note-taking that HZSM-5 zeolite is a synthetic material (not natural zeolite), so HZSM-5 has been subjected tp specific activation treatment. Besides S.A, we also can compare the pore width of the Cr/Bentonite with oven-HZSM-5, 102 Å and 50.22 Å, respectively. So the value for the pore width is greater in Cr/Bentonite, which is very important because the wider the pores, the lesser deactivation (off) occurring in the Cr/Bentonite when it has adsorbed plenty amount of water. As for the oven-HZSM-5 having much smaller pores, as widely known, it is relatively easier deactivated when adsorbs plenty amount of water.

Table 1. The Results from BET Measurements

<table>
<thead>
<tr>
<th>Materials</th>
<th>Area (m²/gr)</th>
<th>Pore (Å)</th>
<th>Pore Volume (cc/gr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bentonit</td>
<td>79.4</td>
<td>101.9</td>
<td>3.857 x 10⁻²</td>
</tr>
<tr>
<td>Cr/Bentonite</td>
<td>153.0</td>
<td>102.0</td>
<td>7.436 x 10⁻²</td>
</tr>
<tr>
<td>SO₄/Bentonite</td>
<td>168.0</td>
<td>103.8</td>
<td>8.090 x 10⁻²</td>
</tr>
<tr>
<td>HZSM-5-Oven</td>
<td>289.1</td>
<td>50.2</td>
<td>14.94 x 10⁻²</td>
</tr>
<tr>
<td>HZSM-5-Calcination</td>
<td>301.7</td>
<td>62.5</td>
<td>15.36 x 10⁻²</td>
</tr>
</tbody>
</table>

Figure 3. The Acidity of the Materials Tested Using Gravimetric Method

Comparing the micro pore volume of Cr/Bentonite and oven-HZSM-5 is 7.436 x 10^{-2} cc/g and 14.94 x 10^{-2} cc/g, the value is very reasonable, because the micro pore volume is directly proportional to the value of the S.A of HZSM-5 which is almost twice that of Cr/Bentonite.

Based on the BET results, it can be seen that the surface area of SO4/Bentonit is slightly higher than the Cr/Bentonite, each 168.01 m²/g and 153.03 m²/g, respectively. This is because SO4 in bentonite is able to attract Fe impurities, in addition to the micro pore diameter and volume was also slightly higher at 103.8 Å and 102 Å, whereas the micro pore volume of each 8.090 x 10^{-2} cc/g and 7.436 x 10^{-2} cc/g, respectively. This is because S.A of SO4/Bentonite is slightly wider, but the pore diameter value is still higher in Cr/Bentonite, whereas if we compare the results of the BET measurement between SO4/Bentonite and calcined-HZSM-5, S.A of the later is much higher, 301.7 m²/g compared to 168.0 m²/g in SO4/Bentonite. However, the value of pore diameter of SO4/Bentonite is still higher, because during calcination on HZSM-5, ions or water content in the HZSM-5 were released physically and chemically. For the micro pore volume, the value is much higher in HZSM-5, because of HZSM-5 has specific surface area nearly double the specific surface area of SO4/Bentonite. In addition, it may be also due to structure differences between Bentonite and Zeolite. The two materials are compared because they have the same function in this study, as the catalyst for ETG process.

XRD characterization on bentonite materials aims to determine the basal spacing (d001) of natural bentonite and Cr/Bentonite. Measurement of basal space (d001) was performed on the diffraction angle 2θ ≤ 10° [12-13]. The information obtained from Figure 4 are (1) It was a shift in the d001 reflection peak at 2-theta angle of 6.065 to 4.756 in the bentonite that was intercalated with Cr metal pillars. This shift indicates an increase in basal spacing in Cr/Bentonite; (2) The change of peak intensity for d001 reflection. It is suggested that there has been interaction between one side of the bentonite framework with a solution of Cr as a polycationic pillar, in which some cations may also be attracted to the framework.

In addition, when observed more carefully it can be seen that there is a new peak at reflection d001 at 2θ = 7° for Cr/Bentonite. Based on the results of XRD characterization, it can be stated that Cr pillars between the sheets of alumina-silicate bentonite are able to interact.

Figure 5 is the result of XRD analysis at 10-80° 2-theta on natural bentonite catalyst and Cr/Bentonite. Although this XRD analysis does not directly represent the basal spacing (d001) on clay, but it can be seen from the results on the figure that there are increase in the intensity of the diffraction pattern at 2θ = 22°, 28° and 55° for the Cr-pillared clay pillars. This explains the occurrence of large enough exchange or interaction between the metal pillars, Cr, from CrCl3 with natural bentonite, which is indicated by a shift in (d001) basal spacing. In addition, there is an increased in acidity of the Cr/Bentonite, because the process of H⁺ cation exchange.

If we compare between Cr/Bentonite and HZSM-5 based on XRD results in Figure 6, it can be seen that HZSM-5 has a much higher peak intensity, because of HZSM-5 is more crystalline than Cr/Bentonite, which can be caused by the fact that HZSM-5 is synthetic material while bentonite is natural mineral.

TGA measurement was performed on bentonite to determine the damage to the material's structure after being heated at high temperature (over 400 °C). Figure 7 shows the TGA results.

From the TGA results on Cr/Bentonite as shown in Figure 7, it is obtained that the complete phase change occurs at 444 °C. The first change is the loss of molecular...
weight of water contained in the crystal structure. While the second significant weight change is indication of the structural changes in Cr/Bentonite and the chemically loss of water molecules. When the material was calcined at 550 °C, there are many molecules, present in the bentonite, were detached, including some parts of the pillar as well, that is shown by the XRD results in Figure 8.

In Figure 8 above, it can be seen that for the calcined Cr/Bentonite, the peak was shifted toward larger 2-theta, which is indicative of smaller pore size. This is one indicator of the removal of the existing pillars between the layers at the Cr/Bentonite as result of overheating.

From the TGA test results on HZSM-5 complete phase change occurs at a temperature of about 458.14 °C, so a little higher than the perfectly phase change in Cr/Bentonite. Just as in the Cr/Bentonite, which is the first weight change is the loss of water molecules contained in the crystal structure. While both a significant weight change is indicated on the material structure changes HZSM-5 and the loss of water molecules chemically. When done calcined at 550 °C temperature [14], then there are many molecules that are in the HZSM-5 apart, so it will affect the change in pore size.

After catalytic test using ethanol feedstock in Catalytic Muffler equipment, a liquid was produced, which was then analyzed using GC-MS and the obtained results are shown in Table 2.

Ethanol has chemical formula of C₂H₅OH, while the gasoline chemical formula fall into the range of C₄ to C₁₂, so from the results of analysis by GC-MS, ethanol has undergone a catalytic cracking process with assistance of Cr/Bentonite, so that two ethanol molecules were combined to become butanol (C₆H₁₄OH), or possibly to form other compounds such as decane (C₁₀H₂₂), hexanol (C₆H₁₃OH), undecane (C₁₁H₂₄), and dodecane (C₁₂H₂₆).

From Table 2 and 3, the gasoline compounds are identified from the peaks with retention time under 11 minutes,
Table 3. Data from GC-MS Analysis for Product from Catalytic Test Using HZSM-5

<table>
<thead>
<tr>
<th>Retention Time</th>
<th>Area (%)</th>
<th>Library/ID</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.311</td>
<td>13.49</td>
<td>1-Butanol, 3-methyl (impure)</td>
</tr>
<tr>
<td>8.693</td>
<td>0.32</td>
<td>Decane, n-Decane, n-C10H22</td>
</tr>
<tr>
<td>9.046</td>
<td>0.43</td>
<td>1-Hexanol, 2-Ethylhexanol</td>
</tr>
<tr>
<td>9.803</td>
<td>0.45</td>
<td>Undecane, n-Undecane, n-C11H24</td>
</tr>
<tr>
<td>10.861</td>
<td>0.29</td>
<td>Dodecane, n-Dodecane, n-C12H26</td>
</tr>
</tbody>
</table>

because gasoline has a low boiling point, while the retention time above 11 minutes the compounds could be excluded from gasoline compounds, because they have high boiling points and have C content higher than C12.

The catalytic test results using HZSM-5 is better than Cr/Bentonit. It can see in the Table 2 and 3. Cr/Bentonit has area 6.13% and HZSM-5 has area 13.49%. Because HZSM-5 is commercial zeolite and it has made with special treatment in the company, but the price is more expensive than Cr/Bentonit. The advantage of Cr/Bentonit is very cheap and easy to get it in Indonesia natural.

4. Conclusions

The Cr/Bentonite has a higher acidity than the bentonite and HZSM-5. Based on the results of BET measurements on specific surface area and pores, it is shown that HZSM-5 has the highest S.A compared with Cr/Bentonite, but Cr/Bentonite has a larger pore widths. From the XRD the difference in 2theta between natural bentonite and Cr/Bentonite, it indeed indicates the existence of Cr-pillars between the aluminosilicate sheets in the bentonite. From the TGA test it is known that the Cr/Bentonite was damage, if being heated above 450 °C, so for the catalytic activity test in the reactor for ETG was performed at a temperature of 400 °C. As for the ETG testing results analyzed by GC-MS, there has been conversion of ethanol into biogasoline, in which butanol and possibly also hexanol, decane, dodecane, undecane were form. Those compounds are included in the gasoline range (C4 to C12). The results obtained in the catalytic conversion in ETG process with Cr/Bentonite and HZSM-5 are not much different, but when compared to the economic side, Cr/Bentonite is cheaper than HZSM-5, and bentonite is widely available in nature Indonesia. So, to conclude, the use of Cr/Bentonite as catalyst in ETG process is promising.

Acknowledgements

The authors would like to acknowledge The Ministry of Research and Technology, Republic of Indonesia for funding this research through postgraduate scholarship program under contract number 218/M/Kp/VIII/2010.

References