Modification of Synthetic Zeolite from Bagasse Ash and Their Characterization

Sriatun\textsuperscript{a}, Taslimah\textsuperscript{a}, Linda Suyati\textsuperscript{a}

Abstract

The modification used NH\textsubscript{4}Cl and NiCl\textsubscript{2} salts to synthetic zeolite as a product of synthesis bagasse ash has been done. Several characterizations such as X-ray diffractometer and FTIR were done on the product of synthesis, whereas XRF and DTA-TGA were done on the product of modification. The FTIR spectra shows the product synthesis has main peaks of finger print of zeolite, meanwhile from the XRD pattern shows sharp peak which high intensity which means the sample has crystalline structure. The XRF analysis result showed that the silica was slightly reduced in modification withNH\textsubscript{4}Cl. But silica decreased about 26 \% when the zeolite was modified with NiCl\textsubscript{2}. from DTA data was known that on modification of zeolite with NH\textsubscript{4}Cl, the endothermic zone was shifted from 104.3 -16.6 °Ct to 62.2-142.0 °C. The modification of zeolite with NiCl\textsubscript{2} the endothermic zone was shifted from 104.3 -16.6 °Ct to 39.3-106.8 °C. Meanwhile TGA data showed that all products had a thermal stability at temperature above 320 °C.

Keywords: modification, synthetic zeolite, Bagasse, Characterization

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Introduction

Milling process of sugar cane to obtain molasses always leaves about 35-40\% of bagasse (Indriani and Sumiarshih in Anwar, 2008) or 32 \% (P3GI, 2008). Meanwhile it has known that ash of bagasse contains high silica. Based on result’s Hanafi and Nandang (2010), the content of silica on bagasse ash was 64.5 \%, whereas inAida (2010) was 70.9\%. Both of them were considered as a proper potential to upgrade of the economic value of bagasse ash. It means the bagasse ash were converted to the more useful synthetic zeolite.

Research on the synthesis of material were carried out byKondrashova et al (2010). He has synthesizedsilica using tetra ortho silicate (TEOS) as a source of silica and cetyltrimethylammonium bromide (CTAB) as a pore directing agent. The process of synthesis was conducted at various of heating time that was 3, 24 and 48 hours. Ertan et al (2009) have been producing silica (SiO\textsubscript{2})using sodium silicate as a source of silica,cetyltrimethylammonium bromide as a pore directing agent and heating timeof 6, 24 and 72 hours. Wijayanti and Ediati (2010) have synthesizedMCM-41, Khan et al (2010) havesynthesized Zeolite-A. Meanwhile Utchariyajit et al (2010) have synthesizedSAPO-5 where silica powder as source of Si, and Al(OH)\textsubscript{3} as source of Al, triethylamine(TEA) surfactant as pore forming agent. Yoon et al (2008) havesynthesized organosilica.

In this research has been synthesized zeolite using bagasse ash as source of silica. On the process of synthesisrequired alkaline condition to obtain the materials target. The pH of solution should be higher than 10. It could be adjusted by means of addingNaOH solution. This led tothe synthesis of products containinghigh sodium. The quality of product could be improved through modifications by using salt ammonium chloride (NH\textsubscript{4}Cl) and nickel chloride (NiCl\textsubscript{2}).Ammonium chloride was selected as the agent of the modifier because (1) it was easyreplaced sodium ion, (2) if ammonium was heated at temperature above 350 °C, therefore it would be decomposed intoammonia gas and H\textsuperscript{+} ion. Exactly, this formation gave us an advantage since the acidity of materials wouldincrease. The addition of NiCl\textsubscript{2} salt into materials productalso increased the acidity.

Methodology

Synthesis of zeolite from bagasse ash

Bagasse from sugar factory was dried then burned until the charcoal was formed. Furthermore the charcoal was calcined for 4 hours at 700 °C. Amount of 96 grams of ash measuring 100 mesh was reacted with NaOH 6 M. The mixture was stirred for 24 hours, then filtered. The filtrate was sodium silicate solution. The next step, sodium silicate was reacted with sodium aluminate. The volume ratio between sodium silicate and sodium aluminate was 1:1. The mixture was rapidly stirred at room temperature until gela...
In the synthesis procedure, zeolite was added to the NiCl$_2$ solution, which underwent hydrolysis, forming NiO nuclei and NiCl$_2$. The formation of NiO nuclei leads to the growth of zeolite crystals, which is evident in the XRD patterns. The XRD patterns show the characteristic peaks of NiO and zeolite, indicating the successful synthesis of Ni-ion exchanged zeolite. The FTIR spectra of the synthesized zeolite show the presence of Ni-O bonds and characteristic peaks of zeolite framework, confirming the successful synthesis. The results of the study suggest that Ni-ion exchanged zeolite can be used as a catalyst in various chemical processes, particularly those requiring Ni-containing catalysts. The synthesis process is simple and cost-effective, making it an attractive option for industrial applications.
The next step, ion Ni⁴⁺ was converted to NiO by heating process. We consider that the calcination temperature at 450 °C spurred the forming of covalent bonding between Ni and O. Nickel has empty d orbital that very potential as active catalytic site.

\[
\text{Ni}^4+ + \text{O}_2 \rightarrow \text{NiO} \\
\text{Lewis acids an active catalytic site}
\]

**Characterization modified zeolite by XRF**

This characterization aims to know the elements/components containing in materials. Characterization was also done to bagasse ashes as starting material. Below is a table of the constituent components of the synthesized and modified zeolite.

From table, it is known that the ash from bagasse contains 27.7 % of silica, 28.9% K as alkali components, 20.1% Ca as earth alkali component and 10% Fe, 2.35% Mn as other components. Therefore the ash from bagasse can be used as a source of silica in synthesis silica alumina material like zeolite. In this materials, the ratio of Si/Al of synthesized zeolite was 1.67, other components such as K, Ca and Fe other component decline. This indicates that on the extraction process of silica only few components that are involved in extraction by NaOH. It means that the NaOH is an exactly effective extraction agent.

The modification of zeolite by NH₄Cl 2 Mgave H-zeolite, however the constituent component only slightly changed, therefore the ratio of Si/Al appears constant. In spite, the striking changes was observed when modification by NiCl₂, synthesized zeolite changed to Ni-zeolite. The content of Si and Al reduced to 17.3% and 14%, but the percentage of Ni increases until 58.35%, whereas content of other component decline. The high nickel content in Ni-zeolite indicated that the NiCl₂ precursor is an effective loading agent.

**Table 1.** Constituent components of the synthesized and modified zeolite

<table>
<thead>
<tr>
<th>Component (%)</th>
<th>Type of Materials</th>
<th>Synthesized Zeolite before modification</th>
<th>Modified Zeolite by NH₄Cl</th>
<th>Modified Zeolite by NiCl₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>Ash</td>
<td>27.7</td>
<td>44.1</td>
<td>84.3</td>
</tr>
<tr>
<td></td>
<td>Zeolite before modification</td>
<td>44.1</td>
<td>34.3</td>
<td>74.3</td>
</tr>
<tr>
<td></td>
<td>Modified Zeolite by NH₄Cl</td>
<td>43.0</td>
<td>30.2</td>
<td>63.0</td>
</tr>
<tr>
<td></td>
<td>Modified Zeolite by NiCl₂</td>
<td>17.3</td>
<td>14.3</td>
<td>14.3</td>
</tr>
<tr>
<td>Al</td>
<td>0</td>
<td>26.2</td>
<td>25.9</td>
<td>14</td>
</tr>
<tr>
<td>P</td>
<td>3.1</td>
<td>1.1</td>
<td>0.77</td>
<td>0.2</td>
</tr>
<tr>
<td>K</td>
<td>28.9</td>
<td>2.1</td>
<td>2.2</td>
<td>0.41</td>
</tr>
<tr>
<td>Ca</td>
<td>20.1</td>
<td>3.59</td>
<td>3.49</td>
<td>0.66</td>
</tr>
<tr>
<td>Ti</td>
<td>0.64</td>
<td>0.45</td>
<td>0.40</td>
<td>0.077</td>
</tr>
<tr>
<td>Mn</td>
<td>2.35</td>
<td>0.15</td>
<td>0.14</td>
<td>-</td>
</tr>
<tr>
<td>Fe</td>
<td>10.0</td>
<td>0.85</td>
<td>0.83</td>
<td>0.29</td>
</tr>
<tr>
<td>Ni</td>
<td>1.99</td>
<td>3.55</td>
<td>2.99</td>
<td>58.35</td>
</tr>
</tbody>
</table>

**Characterization of modified zeolite by SEM**

This characterization aims to find out the surface morphology, particle shape and size homogeneity. Figure 1 showssurface morphology of synthesized zeolite, H-zeolite and Ni-zeolite. The shape and size of the particles on the synthesized zeolite have similarities to the H-zeolite. The diameter of the particles approximately 1.5 μm. However, in H-zeolite more homogeneous because there’s only a few of the small square particles and there is a lot more empty space. It means the treatment on the synthesized zeolite by NH₄Cl could create homogeneity.

In the meantime, it seems clear that there is a fine grains on the surface of Ni-zeolite materials. It was suspected as nickel oxide/nickel which supported into the synthesized zeolite. In additional, the size of particles increased to approximately 2μm.

**Characterization of modified zeolite by BET surface Area Analyser**

Characterization by BET aims to establish of pore size, pore volume and surface area a solid materials. Besides that, we could know the differences in material porosity before and after modification process.

Table 2 showsthe increasing of surface area after modification process by NH₄Cl and NiCl₂. The raising of surface area is 9 times. This happens on modified zeolite by NiCl₂ because a lot of NiO crystal adhered on the surface of particles. This result relevant with SEM photo where there is other smaller particles on the surface particles.

**Table 2.** The surface area, pore volume and pore radius of synthesized and modified zeolite

<table>
<thead>
<tr>
<th>Material</th>
<th>Synthesized Zeolite (before modification)</th>
<th>Modified Zeolite by NH₄Cl</th>
<th>Modified Zeolite by NiCl₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface area (m²/g)</td>
<td>13.5</td>
<td>17.15</td>
<td>116.99</td>
</tr>
<tr>
<td>Pore volume (cc/g)</td>
<td>5.1x10⁻³</td>
<td>6.48x10⁻³</td>
<td>4.6x10⁻²</td>
</tr>
<tr>
<td>Pore radius (Å)</td>
<td>1.8</td>
<td>1.8</td>
<td>1.83</td>
</tr>
</tbody>
</table>

Average pore radius of synthesized and modified zeolite were not change, they were about 1.8 Å. The pore volume of Ni-zeolite was slightly decline, it is thought to be due to NiO was accumulated on pore/channel and covered up of the surface of pore, or it might be occurred agglomeration.
Characterization of Modified Zeolite by DTA-TGA (Differential Thermal Analysis - Thermogravimetric Analysis)

The purpose of DTA characterization is to find out the thermal property and phase changing materials as an effect of enthalpy changing. The materials would be decomposed if it was heated at high temperature. Decomposition of materials was observed as DTA curve. That is a plot of temperature function versus time. Consider that the decomposition reaction is affected by other species, the ratio of size and volume, matter composition (Bukit, 2012).

Thermogravimetric analysis (TGA) is characterization to determine the thermal stability and fraction of volatile components by the way calculated the weight changing that correlated with temperature changing. Some properties of thermogravimetric are (1) horizontal part/flat indicated no weight changing (2) wrapped part indicated loss weight.

From DTA data in figure 3, modification treatment has been replaced endothermic zone from 104.3 -165.6 °C to 62.2-142.0 °C by NH₄Cl and 39.3-106.8 °C by NiCl₂. Furthermore thermogram TGA shows all of the product had thermal stability at temperature ≥ 320 °C.

Conclusions

Based upon the results and discussion, we got any conclusion that modification using NH₄Cl and NiCl₂ salt could improve the properties/characters of synthesized zeolite. This characters included the content of constituent component, performance of surface, surface area and thermal stability. The characters just a slightly increased if using NH₄Cl but very tangible on using NiCl₂.
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References


