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Modification of Synthetic Zeolite from Bagasse Ash and Their Characterization

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Abstract

The modification used NH_4Cl and $NiCl_2$ 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_4Cl. But silica decreased about 26 % when the zeolite was modified with $NiCl_2$. from DTA data was known that on modification of zeolite with NH_4Cl, the endothermic zone was shifted from 104.3 -16.6 °Cto 62.2-142.0 °C. The modification of zeolite with $NiCl_2$ the endothermic zone was shifted from 104.3 -16.6 °Cto 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 Sumiarsih 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_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 $Al(OH)_3$ 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 behigher 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_4Cl) and nickel chloride ($NiCl_2$).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^+ ion. Exactly, this formation gave us an advantage since the acidity of materials wouldincrease. The addition of $NiCl_2$ 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, thenfiltered.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 stirredat room temperature until gelatinous

materials were formed. Furthermore gelatinous materials were heated at 100 °C during 3 days. The obtained product was dried and characterized by FTIR (*Fourier Transform Infrared*), XRD (*X-ray Diffraction*).

Modification on Synthesized Zeolite by NH_4Cl and $NiCl_2$

There were two modification procedures to synthesized zeolite (1) synthetic zeolite was added NH_4Cl 2 M then shaked for 24 hours, filtered and dried, the last procedure for this step was calcined at 350 °C to remove NH_3 gas so only H^+which remains in modified materials. (2) Synthesizedzeolite was added $NiCl_2$ 10% using impregnation method. The mixture was shaked for 24 hours at room temperature, then thesolvent was evaporated. Furthermore, the modified materials were dried and calcined at 500 °C, so NiO or Ni would be formed in the materials. Finally, the properties of modified materials were characterized by XRF (*X-ray Fluorescence*, SEM *(Scanning Electron Microscope)*, surface area analyser and DTA-TGA (*Differential thermal analysis-Thermogravimetric analysis*)

Results and Discussion

The using ofNaOH on the extraction process of silica from bagasse ashescaused it contains an assortment of metals oxides, meanwhile NaOHmoreselective to silica. Aqueous solution of NaOH was also used in the preparation of sodium aluminate. The highconcentration of NaOH caused the solution were extremely alkaline. This condition was suitable for the synthesis process of zeolite because $Si_4O_8(OH)_4^{4-}$ and $Al(OH)_4^-$ anions would be appears in solution. Those anions would interacted to form silica alumina polymers as a zeolite material.So they had an important role play in the rate of growth of crystal nuclei (Hamdan, 1992).

FTIR spectra showed that Si-O-Al or Si-O-Si frameworks has been formed at wavenumber 992 cm^{-1}. It is an asymmetric stretching vibration. The following peaks aresymmetric stretching vibration at 663 cm^{-1}, double ring at 562 cm^{-1}, bending vibration of T-O at 441 cm^{-1}, and may pore opening.

Based on XRD data revealed that the obtained product has a crystal structure. This was showed by the advent ofhigh intensity peaks which were the main peaks at 2θ = 24.58; 14.11 and 31.91 which have an intensity 23110 counts, 18470 counts and 17276 counts respectively.

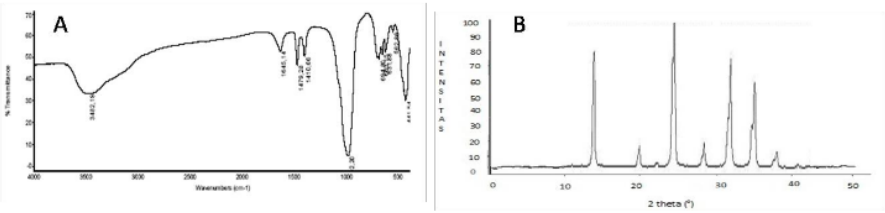

Figure 1. Characterization of synthesized zeolite (A) FTIR spectra (B) XRD Diffractogram

Modification of synthesized zeolite by NH_4Cl

The modification process aims to substituteNa^+ ion by NH_4^+ in synthesized zeolite. Indeed, substitution might occurred at several other cations, so not onlyon the Na^+ ion. Ammonium ion (NH_4^+) was selected as a cation exchange to Na^+because it has high selectivity, i.e.NH_4> Ag > Ba > Na > Sr > Ca > Li > Cu (Tsitsishvili et al, 1992). in addition,NH_4^+ ion easy to form acidic zeolite (H-zeolite) because the heating at 350 °C,NH_4^+ was decomposed and released NH_3 gas so it formed H-zeolite. Physically, there were not any changing on both of colour and texture of synthesized and modified zeolite.

Modification of synthesized zeolite by $NiCl_2$

This process used $NiCl_2$ as a precursor, because it was known that $NiCl_2$ has trans esterification catalytic activity. The$NiCl_2$ precursor was loaded into synthesized zeolite by the way impregnation method. This way was expected more effective because there was no$NiCl_2$ was wasted. The concentration of precursor solution was 10%.We could observed thatwhite colour of synthesized zeolite has been changed to light blue colour onmodified zeolite by $NiCl_2$.

The increasing of amount of $NiCl_2$ which was loaded into surface of supported materials/synthesized zeolite led tothe surface area of materialsalso increased. The large of surface area has an important role inraising the catalytic activity.

The formation ofNiO crystals from solution containing Ni^{2+} ion covers several stages. First, dissolving the $NiCl_2$ crystal into the aquadest causing the occurrence of hydrolysis of $NiCl_2.6H_2O$.

$$NiCl_2.6H_2O_{(s)} + H_2O_{(l)} \rightleftharpoons Ni^{2+}_{(aq)} + 2\ Cl^-_{(aq)} + 7\ H_2O$$

Hydrolysis reaction of Ni^{2+} ion would generated active catalytic site as a Brønsted acid.

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$Ni^{2+} + H_2O \longrightarrow [NiOH]\downarrow + H^+$

Brønsted acid

The next step, ion $Ni^{2+}$was convertedtoNiO 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.

$Ni^{2+} + O^{2-} \longrightarrow NiO \downarrow$

Lewis acidas 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 ofsynthesized zeolite was 1.67,other components such as K, Ca and Fe decline significantly. This indicates that on theextraction process of silica onlyfewcomponents that are involved in extraction by NaOH. It means that the NaOH is an exactly effective extraction agent.

The modification of zeolite by NH_4Cl 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 $NiCl_2$, synthesized zeolite changed to Ni-zeolite. The content of Si andAl reduced to 17.3% and 14%, but the percentage of Ni increases until 58.35%, whereas content of other component decline. The high nickel contentin Ni-zeolite indicated that the $NiCl_2$ precursor is an effective loading agent.

Table 1. Constituent components of the synthesized and modified zeolite

Component (%)	Type of Materials			
	Ash	Zeolite before modification	Modified Zeolite by NH_4Cl	Modified Zeolite by $NiCl_2$
Si	27.7	44.1	43.0	17.3
Al	0	26.2	25.9	14
P	3.1	1.1	0.77	0.2
K	28.9	2.1	2.2	0.41
Ca	20.1	3.59	3.49	0.66
Ti	0.64	0.45	0.4	0.077
Mn	2.35	0.15	0.14	-
Fe	10.0	0.85	0.83	0.29
Ni	1.99	3.55	2.99	58.35

Characterization of modified zeolite by SEM

This characterization aims to find out thesurface 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 thesynthesized zeolite have similarities to theH-zeolite. The diameter of the particles approximately 1.5 µm. However, in H-zeolitemore 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 NH_4Cl could create ahomogeneity.

In the meantime, it seems clearthat there is a fine grains on the surface ofNi-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 materialsporosity before and after modification process.

Table 2 showsthe increasing of surface area after modification process by NH_4Cl and $NiCl_2$.The raising of surface area is9 times. This happens on modified zeolite by $NiCl_2$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

Material	Synthesized Zeolite (before modification)	Modified Zeolite by NH_4Cl	Modified Zeolite by $NiCl_2$
Surface area (m^2/g)	13.5	17.15	116.99
Pore volume (cc/g)	$5.1x10^{-3}$	$6.48x10^{-3}$	$4.6x10^{-2}$
Pore radius Size (A°)	1.8	1.8	1.83

Average pore radius of synthesized and modified zeolite were not change, they were about 1.8°A. The pore volume of Ni-zeolite was slightly decline, it is thought to be due to NiO was accumulated onpore/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 ofDTAcharacterizationfind out the thermal property and phase changingmaterials 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 temperaturefunctionversus 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 thermogravimmetric are (1) horizontal part/flat indicated no weight changing(2) wrapped part indicated loss weight.

From DTA data in figure 3, modification treatmenthas been replaced endothermic zone from 104.3 -165.6 °C to 62.2-142.0 °C by NH_4Cl and 39.3-106.8 °C by $NiCl_2$.

Furthermore thermogram TGA shows all ofthe product had thermal stability at temperature ≥ 320 °C.

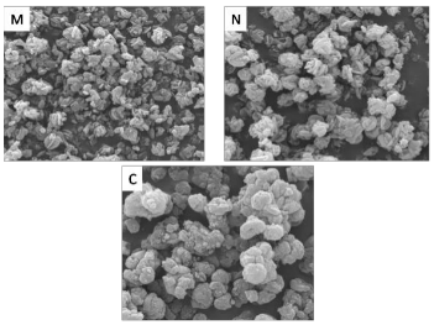

Figure 2. The SEM photographs at magnitude 20.000 x (M) synthesized zeolite/before modification, (H) Modified zeolite by NH_4Cl, (C) Modified zeolite by $NiCl_2$

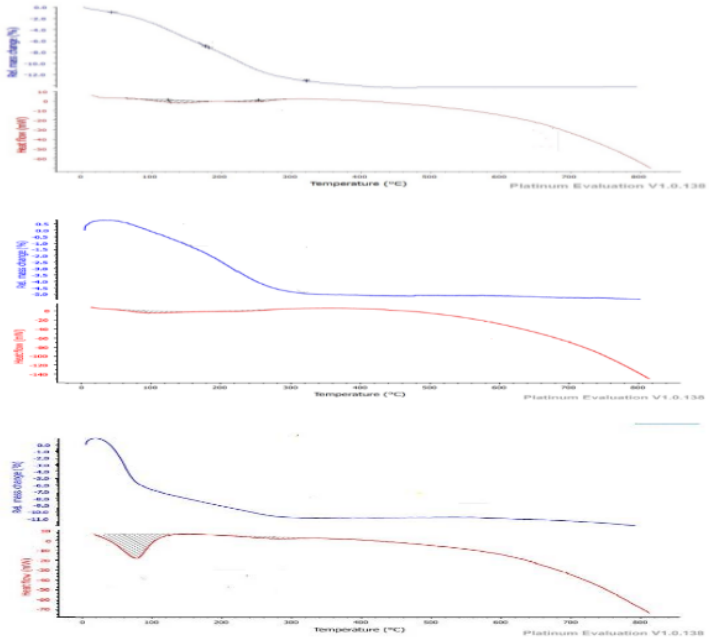

Figure 3. DTA-TGA curve (A) synthesized zeolite (B) Modified zeolite by NH_4Cl (C) Modified Zeolite by $NiCl_2$

Conclusions

Based upon the results and discussion, we got any conclusion that modification using NH_4Cl and $NiCl_2$ salt could improve the properties/characters of synthesized zeolite. This characters includedthe content of constituent component, performance of surface, surface area and thermal stability. The characters just a slightly increased if usingNH_4Cl but very tangible on using $NiCl_2$.

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