

LEMBAR
HASIL PENILAIAN SEJAWAT SEBIDANG ATAU *PEER REVIEW*
KARYA ILMIAH : PROSIDING

Judul Karya Ilmiah (Prosiding) : Modification of Synthetic Zeolite from Bagasse Ash and Their Characterization
 Nama/ Jumlah Penulis : Sriatun, Taslimah, Linda Suyati
 Status Pengusul : Penulis pertama
 Identitas Prosiding : a. Judul Prosiding : Green Chemistry: Proceeding of 9th Joint Conference on Chemistry, 12-13 November 2014
 b. ISBN/ISSN : 978-602-285-049-6
 c. Thn Terbit, Tempat Pelaks. : 2015, Semarang
 d. Penerbit/Organiser : UNNES Press
 e. Alamat Repository/Web : https://jcc.undip.ac.id/24/the-proceeding-of-9th-jcc-semarang-2014.conf#post_detail
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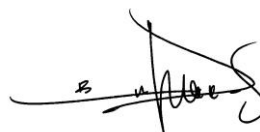
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Semarang, 3 April 2020
 Reviewer 1



Dr. Bambang Cahyono, MS
 NIP. 196303161988101001
 Unit Kerja : Departemen Kimia FSM UNDIP

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Drs. Gunawan, M.Si, Ph.D
 NIP.196408251991031001
 Unit Kerja : Departemen Kimia FSM UNDIP

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Semarang, 3 April 2020

Reviewer 2



Drs. Gunawan, M.Si, Ph.D
 NIP. 196408251991031001
 Unit Kerja : Departemen Kimia FSM UNDIP

Reviewer 1



Dr. Bambang Cahyono, MS
 NIP. 196303161988101001
 Unit Kerja : Departemen Kimia FSM UNDIP

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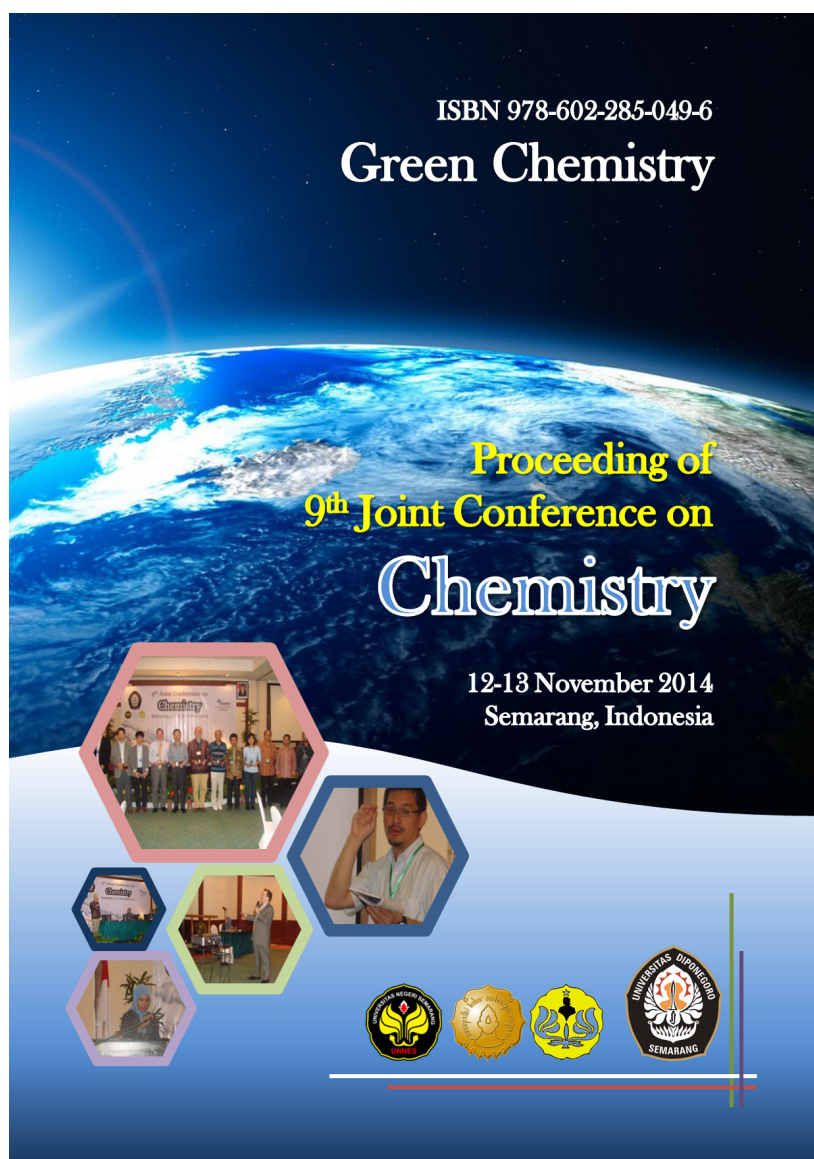
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Synthesis and Characterization of Nano Scale Zero-Valent Iron Supported on Mesoporous Silica

Atyaf Khalid Hammed^a, Nugroho Dewayanto^a, D. Dongyun^b, Mohd Ridzuan Nordin^a

Abstract

Nano scale zero-valent iron (NZVI) supported on mesoporous silica (MSN) was synthesized through liquid phase reduction route. In this method, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ solution was titrated with NaBH_4 as reduction agent. Various colours of products from black to light brown were formed from this process due to the different intensity of oxidation process. Mesoporous silica nanoparticles (MSNs) were prepared through the activation of fumed silica with concentrated hydrochloric acid (HCl). The mixture was refluxed at 90 °C with continuous stirring for 4 hours. This treatment increases the BET surface area from 61.0957 m^2/g to 125.8745 m^2/g . Preparation of NZVI supported by MSNs was conducted in alkaline solution. Amount of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in aqueous solution and activated silica in certain ratio was mixed at room temperature. NaBH_4 solution was added to the mixture in drop wise manner (3 ml/min) with vigorous stirring at room temperature. NZVI/MSN were characterized by XRD, BET, FTIR and FESEM. The capacity of NZVI/MSN in adsorption of methylene blue (MB) from aqueous solution was determined in series of batch experiments. Initial experiment showed the best performance of the adsorbent was achieved at $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ to MSN weight ratio of 0.4. The equilibrium was reached after 60 min of adsorption. The optimum adsorption condition was achieved at initial concentration 15 mg/L of MB and initial pH solution 7 under room temperature. NZVI/MSN is found to be an effective adsorbent for removing MB from aqueous solution.

^aFaculty of Industrial Science and Technology, Universiti Malaysia Pahang, Lebuhraya Tun Razak 26300 Kuantan, Pahang, Malaysia.

^bKey Laboratory for Catalysis and Materials Science of the State Ethnic Affairs Commissions & Ministry of Education, South Central University for Nationalities, Wuhan 430074, China.

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Introduction

The widespread application of dyes in textiles, printing, and food plants has produced a large amount of dye containing wastewater. Because some dyes and their degradation products may be carcinogens and toxic, the removal of dyes from wastewater becomes an important issue in environmental protection. Moreover, the colour that is generated by the presence of dyes in surface water causes great concern to the public. This urges an intensive search for the best available technology for the removal of dyes. Some physico-chemical methods, such as advanced oxidation and biological process, coagulants, oxidizing agents, membrane, electrochemical, and adsorption techniques have been proposed to satisfy the above requirements (Idris et al., 2007, Badruddoza et al., 2010, Kadirova et al., 2013). Among these methods, it was found that adsorption might be an efficient and economic process to remove dyes and also to control the biochemical oxygen demand (Ling et al., 2012).

Numerous studies have been done on dyes adsorption kinetics, equilibrium modelling, and mechanism as well

as to the factors that affect adsorption. Recently, mesoporous materials such as MCM-41 have also received a considerable recognition due to their large pore-space and special surface property (Petala et al., 2013). Porous materials have attracted the attention of scientists due to commercial interest related to their applications in separations, catalysts, and purification technologies. In the last decade, intensive scientific research efforts have been made in the areas of nanoporous materials (Zhu et al., 2009).

Nanostructures in the form of thin films, nanoparticles, nanocomposites and nanocrystalline materials are of interest for both fundamental scientific research and technological applications since some of their properties are controlled by their extremely large surface areas (Ray et al., 2010). Nanoporous and nanostructured materials are also considered ideal candidates for surface environment interactions, such as in gas-sensing, heterogeneous catalysis, and separation. Furthermore, scientists are still targeting new adsorbent with good property. In recent years, with the development of nanotechnology, various

Calcium Phosphate-Chitosan Composite as a Bone Cement CandidateTri Windarti^a and Benjamin Horrocks^b**Abstract**

A research about study of surface chemistry and morphology of bone cement from calcium phosphate-chitosan composite has been conducted. Surface chemistry and morphology of an artificial bone is directly influence to the osteoinductivity property. Calcium phosphate compounds as powder phase was reacted to liquid phase that contains of Na_2HPO_4 solution and chitosan. Analysis instruments such as XRD and SEM-EDS were used to identify surface chemistry, morphology and structural transformation of cement. Setting time and hardening time were tested to know the feasibility of cement when used in minimally invasive surgery technique. The results showed that setting time of calcium phosphate cement became shorter as well hardening time became longer by the increasing of liquid/powder (L/P) ratio and chitosan concentration. SEM image of calcium phosphate showed cuboid crystal shape. The transformation of calcium phosphate into CPC and composite were not changing its structure and morphology. The change only happen on calcium phosphate surface that caused by deposition of phosphate ions. It can be concluded that calcium phosphate – chitosan composite has osteoinductive property and can be used as bone cement.

Keywords: calcium phosphate, bone cement, composite^a) Chemistry Department, Diponegoro University, Indonesia^b) School of Chemistry, Newcastle University UKCorresponding author e-mail address: triwindarti@undip.ac.id**Introduction**

Calcium phosphate compounds (CP) are known as material that can accelerate recovery process of a damaged bone and formation of a new bone tissue (Ogose et al, 2006). The bioactivity and biocompatibility of CP are not only related to its chemical structure but also to the surface chemistry and morphology. Surface chemistry and morphology have strong effect to the ability of protein adsorption in vivo, cell adhesion and host response to implant (Ratner and Bryant, 2004). Generally, biomaterial for artificial bone is developed to have specific function and capacity to facilitate protein adsorption. Also, that biomaterial should be able to form composite with organic matrix such as chitosan, collagen or gelatine, because human bone is a composite of hydroxyapatite-collagen type I (Dee et al, 2002).

To improve the function of the CP as a biomaterial, calcium phosphate cement (CPC) has been developed. CPC are produced by chemical reaction of a solid phase (powder phase) and a liquid phase, which when mixed, form a paste which progressively hardens into a solid. The powder phase contain of one or several calcium phosphate compounds (CP) and the liquid phase is water or a calcium or phosphate containing solution. The dissolution of CP will produce oversaturation of

liquid phase, thus inducing the precipitation of crystals (Zang et al, 2014).

Beside the excellent biological behaviour, the other advantages of CPC is injectable and able to harden in vivo at body temperature. The viscous paste of CPC can be injected into damaged bone area and directly contact with the bone surface, so that CPC could be applied in minimally invasive surgery technique. This technique could reduce surgery duration, reduce the effect that caused by the opening of muscle tissue, reduce the wound and minimize pain (Ginebra et al, 2010). It is hoped that the patient will get a rapid recovery with lower costs.

In this research, chitosan was used as organic matrix to form calcium phosphate – chitosan composite. Chitosan is a biopolymer with chemical structure poly (2-amino-2-dioksi- β -D-Glucose) and has similarity with collagen structure. Chitosan has been widely used in medical field because of its properties such as biocompatible and biodegradable (Hargono et al, 2008). The addition of chitosan into CPC will affect to the surface structure and morphology of CPC that caused by interaction of powder phase-chitosan and liquid phase-chitosan.

Catalytic properties of bimetallic NiNP-M/AlOH (M = Sn, In, Ga, Ag, Nb, and Zr) on selective hydrogenation of furfural

Rodiansono^{a*}, M. D. Astuti^a, A. Ghofur^b, Shogo Shimazu^c

Abstract

A series of bimetallic NiNP-M/AlOH (M = Sn, In, Ga, Ag, Nb, and Zr) catalysts have been synthesised by a simple hydrothermal of the mixture of nickel nanoparticles supported aluminium hydroxide (NiNP/AlOH) and a salt solution containing those of the above metals at 423 K for 2 h. The synthesised catalysts were characterised by using ICP-AES, TG-DTA, XRD, N₂-adsorption, and H₂-chemisorption. The catalytic properties were evaluated on the selective hydrogenation of furfural (FFald) at 453 K for 90 minute. Reactant and products were characterised by GC, GC-MS, and ¹H NMR. The presence of the second metal remarkably reduced the crystallite sizes of Ni metal as indicated by the broadened diffraction peak of Ni(111) species compared to the former of NiNP/AlOH. H₂-uptake of Ni-M/AlOH also was lower than that of NiNP/AlOH. NiNP-Sn/AlOH and NiNP-In/AlOH catalysts showed extremely high selective hydrogenation towards furfuryl alcohol (FFalc) with almost 99% yield. We expect that the high activity and selectivity over Ni-Sn/AlOH and Ni-In/AlOH catalysts due to the formation of Ni-Sn or Ni-In alloys. On the other hand, NiNP-M/AlOH (M= Ga, Nb, Ag, Zr, and Ga) catalysts showed lower the catalytic activity than that of NiNP/AlOH catalyst. Therefore, further investigation of role of the second metal on the catalytic properties of NiNP-M/AlOH (M = Sn and In) catalysts is under progress.

Keywords: bimetallic catalysts, Ni-Sn alloy, Ni-In alloy, selective hydrogenation, furfural

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Introduction

Selective hydrogenation of furfural (FFald) to furfuryl alcohol (FFalc) is great industrial interest since it widely use in various applications[1]. Industrially, furfuryl alcohol was produced by liquid hydrogenation of furfural at the high temperature and H₂ pressure by using copper-chromite (Cu-Cr) catalysts which exhibits moderate in activity and selectivity. The main drawbacks of this catalyst system are toxicity and unrecyclable due to generated Cr₂O₃ and severe leaching of the metal into product[2-3]. Therefore, several attempts have been reported in order to replace Cu-Cr catalysts or to develop a new metallic catalyst system which have more efficient catalytic process and less severe of environmental problem.

Among developed metal catalysts, nickel-based catalyst with metal co-promotor or modified supports has been studied intensively due to its high activity for hydrogenation both of C=C and C=O. Several metal co-promoters were applied such as Cu [4, 8], Fe, Ce [5-7],

and Sn [10] in order to improve its chemoselectivity towards C=O rather than to C=C. In this advantage, system based on Ni modified with Fe, Ce or heteropolyacids have been proved to be successful, reaching 98% selectivity to FFA at almost total conversion [5-8]. However, in some cases these modified nickel catalysts cannot reuse [4] and also showed moderate in activity or selectivity [10]. Recently, Merlo et al. reported that tin modified of Pt/SiO₂ catalyst showed 96% selectivity to furfuryl alcohol and required 6 h to reach a complete reaction[9]. Moreover, the employing of noble metal catalyst is less favourable in economical advantageous. Therefore, the design less expensive the active and selective catalyst system for production furfuryl alcohol is an issue of interest, which still presents great challenges.

We recently have reported the chemoselective hydrogenation of FFald and various unsaturated carbonyl compounds over Ni-Sn catalysts both bulk and supported. The chemoselectivity of Ni-Sn alloy

Synthesis and Characterization of Nano Scale Zero-Valent Iron Supported on Mesoporous Silica

Atyaf Khalid Hammed^a, Nugroho Dewayanto^a, D. Dongyun^b, Mohd Ridzuan Nordin^a

Abstract

Nano scale zero-valent iron (NZVI) supported on mesoporous silica (MSN) was synthesized through liquid phase reduction route. In this method, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ solution was titrated with NaBH_4 as reduction agent. Various colours of products from black to light brown were formed from this process due to the different intensity of oxidation process. Mesoporous silica nanoparticles (MSNs) were prepared through the activation of fumed silica with concentrated hydrochloric acid (HCl). The mixture was refluxed at 90 °C with continuous stirring for 4 hours. This treatment increases the BET surface area from 61.0957 m^2/g to 125.8745 m^2/g . Preparation of NZVI supported by MSNs was conducted in alkaline solution. Amount of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in aqueous solution and activated silica in certain ratio was mixed at room temperature. NaBH_4 solution was added to the mixture in drop wise manner (3 ml/min) with vigorous stirring at room temperature. NZVI/MSN were characterized by XRD, BET, FTIR and FESEM. The capacity of NZVI/MSN in adsorption of methylene blue (MB) from aqueous solution was determined in series of batch experiments. Initial experiment showed the best performance of the adsorbent was achieved at $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ to MSN weight ratio of 0.4. The equilibrium was reached after 60 min of adsorption. The optimum adsorption condition was achieved at initial concentration 15 mg/L of MB and initial pH solution 7 under room temperature. NZVI/MSN is found to be an effective adsorbent for removing MB from aqueous solution.

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Introduction

The widespread application of dyes in textiles, printing, and food plants has produced a large amount of dye containing wastewater. Because some dyes and their degradation products may be carcinogens and toxic, the removal of dyes from wastewater becomes an important issue in environmental protection. Moreover, the colour that is generated by the presence of dyes in surface water causes great concern to the public. This urges an intensive search for the best available technology for the removal of dyes. Some physico-chemical methods, such as advanced oxidation and biological process, coagulants, oxidizing agents, membrane, electrochemical, and adsorption techniques have been proposed to satisfy the above requirements (Idris et al., 2007, Badruddoza et al., 2010, Kadirova et al., 2013). Among these methods, it was found that adsorption might be an efficient and economic process to remove dyes and also to control the biochemical oxygen demand (Ling et al., 2012).

Numerous studies have been done on dyes adsorption kinetics, equilibrium modelling, and mechanism as well

as to the factors that affect adsorption. Recently, mesoporous materials such as MCM-41 have also received a considerable recognition due to their large pore-space and special surface property (Petala et al., 2013). Porous materials have attracted the attention of scientists due to commercial interest related to their applications in separations, catalysts, and purification technologies. In the last decade, intensive scientific research efforts have been made in the areas of nanoporous materials (Zhu et al., 2009).

Nanostructures in the form of thin films, nanoparticles, nanocomposites and nanocrystalline materials are of interest for both fundamental scientific research and technological applications since some of their properties are controlled by their extremely large surface areas (Ray et al., 2010). Nanoporous and nanostructured materials are also considered ideal candidates for surface environment interactions, such as in gas-sensing, heterogeneous catalysis, and separation. Furthermore, scientists are still targeting new adsorbent with good property. In recent years, with the development of nanotechnology, various

Modification of Synthetic Zeolite from Bagasse Ash and Their Characterization

Sriatun^a, Taslimah^a, Linda Suyati^a

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 with NH_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 °C to 62.2-142.0 °C. The modification of zeolite with NiCl_2 the endothermic zone was shifted from 104.3 -16.6 °C 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 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 in Aida (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 by Kondrashova et al (2010). He has synthesized silica 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 time of 6, 24 and 72 hours. Wijayanti and Ediaty (2010) have synthesized MCM-41, Khan et al (2010) have synthesized Zeolite-A. Meanwhile Utcharyajit et al (2010) have synthesized SAPO-5 where silica powder as source of Si, and $\text{Al}(\text{OH})_3$ as source of Al, triethylamine (TEA) surfactant as pore forming agent. Yoon et al (2008) have synthesized organosilica.

In this research has been synthesized zeolite using bagasse ash as source of silica. On the process of synthesis required alkaline condition to obtain the materials target. The pH of solution should be higher than 10. It could be adjusted by means of adding NaOH solution. This led to the synthesis of products containing high 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 easy replaced sodium ion, (2) if ammonium was heated at temperature above 350 °C, therefore it would be decomposed into ammonia gas and H^+ ion. Exactly, this formation gave us an advantage since the acidity of materials would increase. The addition of NiCl_2 salt into materials product also 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 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 shaken 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) Synthesized zeolite was added NiCl_2 10% using impregnation method. The mixture was shaken for 24 hours at room temperature, then the solvent 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

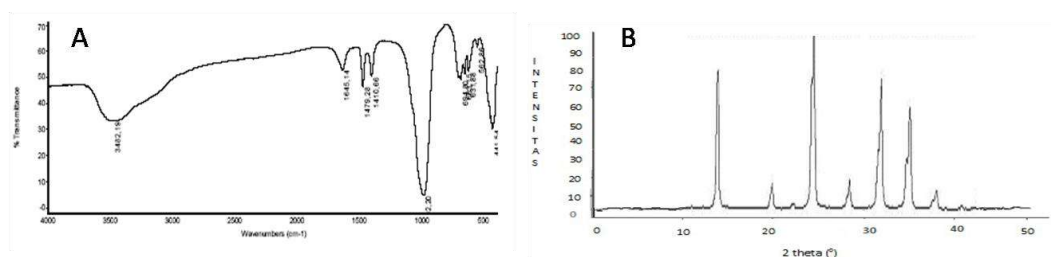


Figure 1. Characterization of synthesized zeolite (A) FTIR spectra (B) XRD Diffractogram

Modification of synthesized zeolite by NH_4Cl

The modification process aims to substitute Na^+ ion by NH_4^+ in synthesized zeolite. Indeed, substitution might occurred at several other cations, so not only on the Na^+ ion. Ammonium ion (NH_4^+) was selected as a cation exchange to Na^+ because it has high selectivity, i.e. $\text{NH}_4^+ > \text{Ag} > \text{Ba} > \text{Na} > \text{Sr} > \text{Ca} > \text{Li} > \text{Cu}$ (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.

The using of NaOH on the extraction process of silica from bagasse ashes caused it contains an assortment of metals oxides, meanwhile NaOH more selective to silica. Aqueous solution of NaOH was also used in the preparation of sodium aluminate. The high concentration of NaOH caused the solution were extremely alkaline. This condition was suitable for the synthesis process of zeolite because $\text{Si}_4\text{O}_8(\text{OH})_4^{4-}$ and $\text{Al}(\text{OH})_4^-$ 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 are symmetric 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 of high intensity peaks which were the main peaks at $2\theta = 24.58$; 14.11 and 31.91 which have an intensity 23110 counts, 18470 counts and 17276 counts respectively.

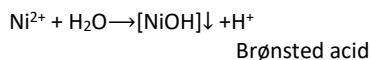
This way was expected more effective because there was no NiCl_2 was wasted. The concentration of precursor solution was 10%. We could observed that white colour of synthesized zeolite has been changed to light blue colour on modified zeolite by NiCl_2 .

The increasing of amount of NiCl_2 which was loaded into surface of supported materials/synthesized zeolite led to the surface area of materials also increased. The large of surface area has an important role in raising the catalytic activity.

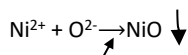
The formation of NiO crystals from solution containing Ni^{2+} ion covers several stages. First, dissolving the NiCl_2 crystal into the aquadest causing the occurrence of hydrolysis of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$.



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



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



Lewis acids as 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 decline significantly. 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 NH_4Cl 2 M gave 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 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 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 the surface morphology, particle shape and size homogeneity. Figure 1 shows surface 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 NH_4Cl could create a 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 addition, the size of particles increased to approximately 2 μm .

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 shows the increasing of surface area after modification process by NH_4Cl and NiCl_2 . The raising of surface area is 9 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) | 5.1×10^{-3} | 6.48×10^{-3} | 4.6×10^{-2} |
| Pore radius Size (\AA) | 1.8 | 1.8 | 1.83 |

Average pore radius of synthesized and modified zeolite were not change, they were about 1.8 \AA . 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 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 NH_4Cl and 39.3-106.8 °C by NiCl_2 .

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

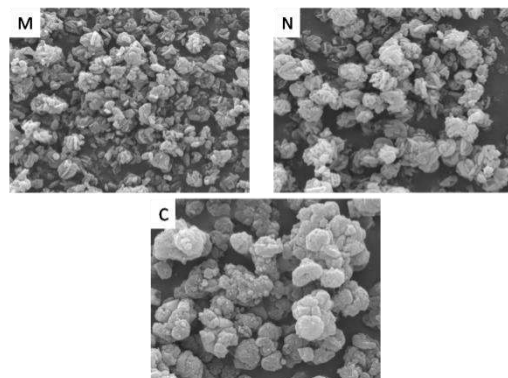


Figure 2. The SEM photographs at magnitude 20.000 x (M) synthesized zeolite/before modification, (H) Modified zeolite by NH_4Cl , (C) Modified zeolite by NiCl_2

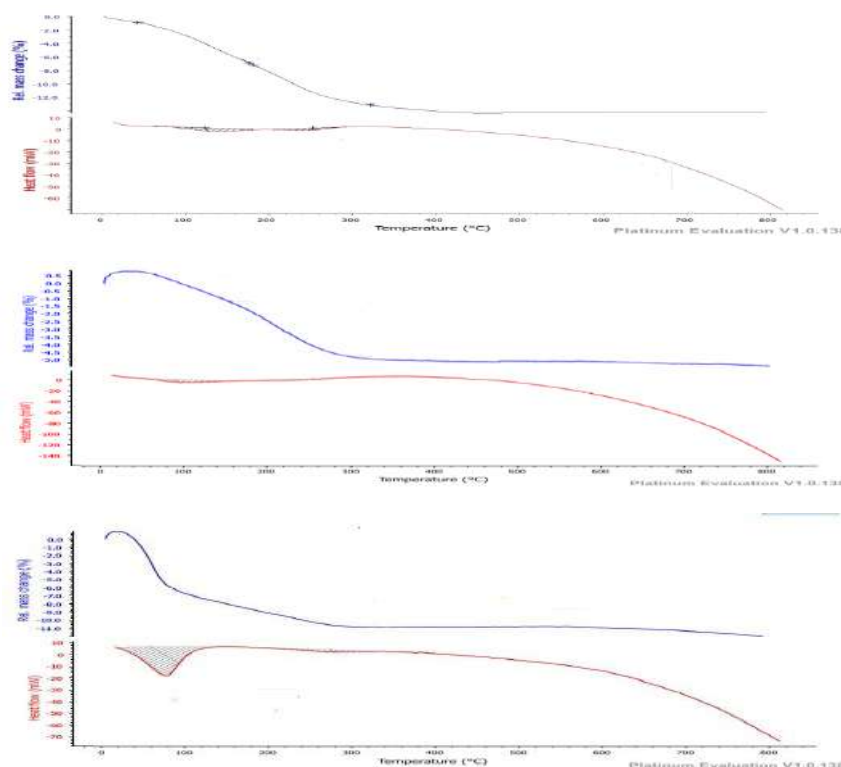


Figure 3. DTA-TGA curve (A) synthesized zeolite (B) Modified zeolite by NH_4Cl (C) Modified Zeolite by NiCl_2

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 included the content of constituent component, performance of surface, surface area and thermal stability. The characters just a slightly increased if using NH_4Cl but very tangible on using NiCl_2 .

Acknowledgements

This research is financially supported by DITLITABMAS DIKTI

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Modification of Synthetic Zeolite from Bagasse Ash and Their Characterization

by Sriatun Sriatun

Submission date: 25-May-2019 09:28AM (UTC+0700)

Submission ID: 1135658342

File name: ynthetic_Zeolite_from_Bagasse_Ash_and_Their_Characterization.pdf (899.95K)

Word count: 2708

Character count: 14629

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There were two modification procedures to synthesized zeolite (1) synthetic zeolite was added NH_4Cl 2 M then shaken 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) Synthesized zeolite was added NiCl_2 10% using impregnation method. The mixture was shaken for 24 hours at room temperature, then the solvent 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

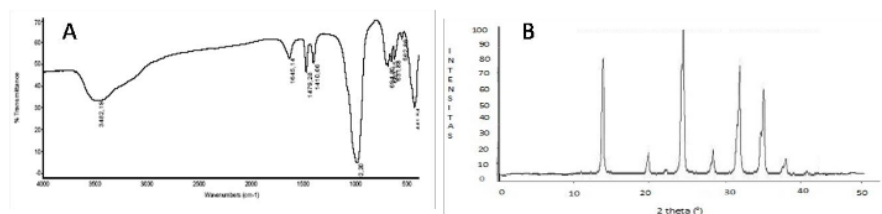


Figure 1. Characterization of synthesized zeolite (A) FTIR spectra (B) XRD Diffractogram

Modification of synthesized zeolite by NH_4Cl

The modification process aims to substitute Na^+ ion by NH_4^+ in synthesized zeolite. Indeed, substitution might occurred at several other cations, so not only on the Na^+ ion. Ammonium ion (NH_4^+) was selected as a cation exchange to Na^+ because it has high selectivity, i.e. $\text{NH}_4^+ > \text{Ag}^+ > \text{Ba}^{2+} > \text{Na}^+ > \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Li}^+ > \text{Cu}^{2+}$ (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.

The using of NaOH on the extraction process of silica from bagasse ashes caused it contains an assortment of metals oxides, meanwhile NaOH more selective to silica. Aqueous solution of NaOH was also used in the preparation of sodium aluminate. The high concentration of NaOH caused the solution were extremely alkaline. This condition was suitable for the synthesis process of zeolite because $\text{Si}_4\text{O}_8(\text{OH})_4^{4-}$ and $\text{Al}(\text{OH})_4^-$ 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 are symmetric 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 of high intensity peaks which were the main peaks at $2\theta = 24.58^\circ$; 14.11° and 31.91° which have an intensity 23110 counts, 18470 counts and 17276 counts respectively.

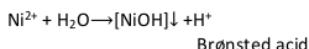
This way was expected more effective because there was no NiCl_2 was wasted. The concentration of precursor solution was 10%. We could observed that white colour of synthesized zeolite has been changed to light blue colour on modified zeolite by NiCl_2 .

The increasing of amount of NiCl_2 which was loaded into surface of supported materials/synthesized zeolite led to the surface area of materials also increased. The large of surface area has an important role in raising the catalytic activity.

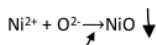
The formation of NiO crystals from solution containing Ni^{2+} ion covers several stages. First, dissolving the NiCl_2 crystal into the aquadest causing the occurrence of hydrolysis of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$.



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



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



Lewis acid as 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 decline significantly. 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 NH_4Cl 2 Mg gave 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 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 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 the surface morphology, particle shape and size homogeneity. Figure 1 shows surface 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 NH_4Cl could create a 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 addition, the size of particles increased to approximately 2 μm .

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 shows the increasing of surface area after modification process by NH_4Cl and NiCl_2 . The raising of surface area is 9 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) | 5.1×10^{-3} | 6.48×10^{-3} | 4.6×10^{-2} |
| Pore radius | 1.8 | 1.8 | 1.83 |
| Size (\AA) | | | |

Average pore radius of synthesized and modified zeolite were not change, they were about 1.8 \AA . 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 NH_4Cl and 39.3-106.8 °C by NiCl_2 .

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

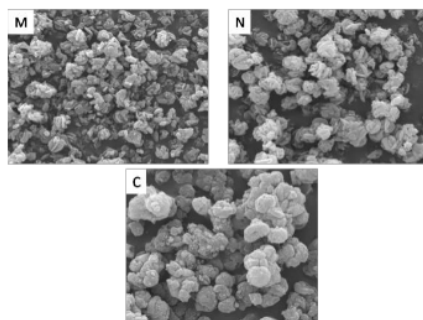


Figure 2. The SEM photographs at magnitude 20.000 x (M) synthesized zeolite/before modification, (H) Modified zeolite by NH_4Cl , (C) Modified zeolite by NiCl_2 .

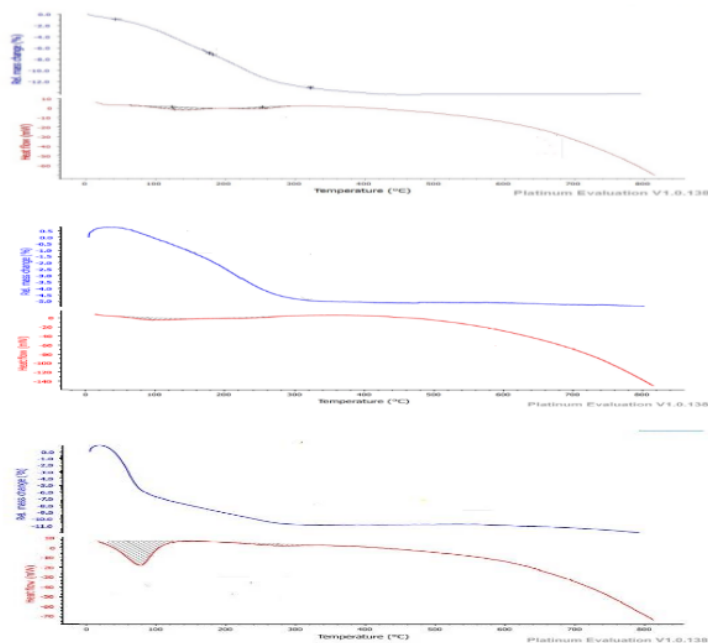


Figure 3. DTA-TGA curve (A) synthesized zeolite (B) Modified zeolite by NH_4Cl (C) Modified Zeolite by NiCl_2

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 included the content of constituent component, performance of surface, surface area and thermal stability. The characters just a slightly increased if using NH_4Cl but very tangible on using NiCl_2 .



Acknowledgements

This research is financially supported by DITLITABMAS DIKTI

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