SYNTHESIS ZEOLITE A MEMBRANE FROM RICE HUSK ASH

MR. CHALERMCHAI RUNGPHAEN

MR. CHAYAKORN BHAVORNTHANAYOD

MISS. ANGSARAT THONGTUB

A SPECIAL PROJECT SUBMITTED IN PARTIAL FULFILLMENT OF THE

REQUIREMENTS FOR THE DEGREE OF BACHELOR OF SCIENCE

INTERNATIONAL PROGRAMS, FACULTY OF SCIENCE

KING MONGKUT'S INSTITUTE OF TECHNOLOGY LARDKRABANG

2008

Title of Special Project	Synthesis Zeolite A membrane from Rice Husk Ash
Students	Mr. Chalermchai Rungphaen ID: 48050442
	Mr. Chayakorn Bhavornthanayod ID: 48050469
	Miss. Angsarat Thongtub ID: 48050476
Degree	Bachelor of Science
Program	Petrochemical Technology (International Program)
Academic Year	2008
Special Project Advisor	Dr. Pesak Rungrojchaipon

Abstract

The rice husk ash was used as raw materials for synthesized zeolite NaA. It was demonstrated that the SiO_2 can be synthesized directly from RHA. Fisrt, Silica was reacted with hydrochloric acid and then reacted with base (NaOH). The Na_2SiO_3 was formed. After that zeolite NaA was synthesized by the composition of Na_2O:Al_2O_3:SiO_2:H_2O in various ratio, time and temperature. When the zeolite NaA was formed, the zeolite NaA was coated on the substrate surface (Al_2O_3) to become zeolite membrane. The experimental results show the quality and characteristic of zeolite A in each condition.

ACKNOWLEDGEMENTS

This special project was carried out and completed with a reasonable suggestion for solving riddles and all suggestion are given us to walk to the right direction.

We would like to thank our respected advisor, Dr. Pesak Rungrojchaiyapon for all suggestion and answering all question until we finished this special project.

We would like to thank Assoc. Prof. Dr. Somsak Woramongkolchai and Dr. Samart Kongtaweelert for all comments and suggestions. We would like to thank Asst. Prof. Dr. Pachernchai Chaiyasith and Miss Supalak Changangam for great attitude to us until this special project completed.

We would like to thank Centre of international staffs for necessary information. Special thanks to staffs of the Department of Chemistry, KMITL and Scientific Instruments Service Center (SISC) for suggestion and helping us about scientific instruments. In addition, thanks also to Faculty of Science, KMITL for instrument process and instrument analysis.

Finally, we would like to thank our family for giving us wisdom to pass on all questions.

Mr. Chalermchai Rungphaen

Mr. Chayakorn Bhavornthanayod

Miss. Angsarat Thongtub

TABLE OF CONTENTS

TABLE OF CONTENTS (CONTINUED)

TABLE OF CONTENTS (CONTINUED)

LIST OF TABLES

LIST OF FIGURES

LIST OF FIGURES (CONTINUED)

LIST OF FIGURES (CONTINUED)

LIST OF FIGURES (CONTINUED)

LIST OF FIGURES (CONTINUED)

Figures Page

Chapter 1

INTRODUCTION

1.1 Motivation

Rice husk is a major by-product of the rice-processing industries and like most of the other rural biomass materials (e.g. sugar, cane leaf, corn leaf) is recognized as a potential source for energy generation from gasification or incineration processes. The burning of rice husk in air results in the formation of rice husk ash (RHA) with a content in SiO_2 that 2 varies from 85 to 98% depending on the burning conditions, the furnace type, the rice variety, the rice husk moisture content, the climate and the geographic area. Some small amounts of inorganic impurities are always present in the ash along with unburned carbon. The unburned carbon can be removed from the ash by further heating treatments at high temperatures, but this usually leads to the crystallization of the amorphous silica to cristobalite and/or tridymite. The crystallization of the contained silica of the ash also occurs when the burning conditions of husk are uncontrolled. This crystallization is a disadvantage towards the preparation of silicon based materials, because the silica ash is rendered inactive in its crystalline form.

RHA can be used as an alternative cheap source of amorphous silica for the production of silicon based materials with industrial and technological interests. Among the various utilizations of RHA, there is a significant interest in its use in the preparation of zeolites due to the widespread industrial use of zeolites in separation processes as sorbents, as well as in catalytic refinery and petrochemical processes [1].

Zeolites are hydrated crystalline aluminosilicates with open three-dimensional framework structures, made up of SiO_4 and AlO_4 tetrahedral linked by sharing their oxygen atom to form regular intracrystalline cavities and channels of atomic dimensions. Zeolites are conventionally prepared by the hydrothermal method of the gel containing silica, alumina, cation, template and water. Different types of silica are known to produce different types of zeolites from the same gel mixture. Most of the silica sources used in the synthesis of zeolite are commercially available in the form of a solution, a gel, a fumed solid, a colloid, and an organic derivative such as tetraethyl-orthosilicate. Zeolites have been developed into key materials in the chemical industry for wide field of applications ranging from ion exchange to the catalysis of petrochemical processes. One of them is NaA zeolite. By far the greatest amount of NaA zeolite is consumed in the manufacturing of detergents [2, 3].

Zeolite membranes could either be self supported zeolite films or a thin film of zeolite on a porous and mechanically stable support. This support is commonly referred to as substrate in the literature. A large disadvantage with self supported membranes is the low mechanical strength. A substantial film thickness is necessary for mechanical reasons. The mass transport resistance will be large in the narrow zeolite pores and a low flux though the unsupported membrane will result. The synthesis of Zeolite as films is traditionally of great scientific and industrial importance in the area of catalyst, adsorption and ion-exchange. Zeolite A membranes offer the advantage of highly selectivity towards water separation and chemical engineering owing to their potential applications as membrane separators, catalytic membrane reactor, selective sensor and components in micro-electronic devices [4].

1.2 Objective

1. To obtain the synthesis zeolite A from rice husk ash.
2. To obtain the synthesis zeolite A membrane with high water selectivity.
3. To obtain the preferable methodology for the synthesis of zeolite A membrane.

1.3 Scope of study

1. To prepare and characterize the zeolite A membrane from rice husk ash.
2. To investigate the effect of the synthesis time, temperature of zeolite A.
3. To investigate the separation of ethanol/water mixture using zeolite A membrane.

1.4 Expected results

1. The preferable methodology for synthesis of zeolite A membrane from rice husk ash.
2. The zeolite A membrane can be used to remove the water from ethanol/water mixture

Chapter 2

THEORY AND LITERATURE REVIEW

2.1 Zeolite [5].

Zeolites are microporous crystalline aluminosilicates, composed of TO_4 tetrahedral (T=Si, Al) with O atoms connecting neighboring tetrahedral. For a completely siliceous structure, combination of TO_4 (T=Si) units in this fashion leads to silica (SiO_2), which is an uncharged solid. Upon incorporation of Al into the silica framework, the +3 charge on the Al makes the framework negatively charged, and requires the presence of extra framework cations (inorganic and organic cations can satisfy this requirement) within the structure to keep the overall framework neutral. The zeolite composition can be best described as having thee components:

$$M_{n/m}^{m+} \cdot [Si_{1-n}Al_nO_2] \cdot nH_2O$$

extra framework cations ▪ framework ▪ sorbed phase

The extra framework cations are ion exchangeable and give rise to rich ion-exchange chemistry of these materials. The novelty of zeolites stems from their micro porosity and is a result of the topology of the framework.

The amount of Al within the framework can vary over a wide range, with Si/Al=1 to ∞, the completely siliceous from being polymorphs of SiO_2. Lowenstein proposed that the lower limit of Si/Al=1 of a zeolite framework arises because placement of adjacent AlO_4^- tetrahedra is not favored because of electrostatic repulsions between the negative charges. The

framework composition depends on the synthesis conditions. Post synthesis modifications that insert Si or Al into the framework have also been developed. As the Si/Al ratio of the framework increases, the hydrothermal stability as well as the hydrophobicity increases.

2.2 Zeolite structure

The primary building unit of zeolites is cations coordinated tetrahedrally by oxygen. These tetrahedral are connected via corners, thus forming the crystal structure of the specific zeolite. Figure 2.1 shows an example of structure of the zeolite.

Figure 2.1 Structure of Zeolites [7]

The best criteria for distinguishing zeolites and zeolite-like materials (porous tectosilicates) from denser tectosilicates are the number of tetrahedrally coordinated atoms per 1000 $Å^3$. This number, known as the framework density, is less than 21 T atoms per 1000 $Å^3$ for porous tectosilicates. The angles connecting the tetrahedral can vary over a wide range ~125° to ~180°. Liebau and coworkers have proposed a classification for porous tectosilicates that distinguishes between aluminous (porolites) and siliceous (porosils) frameworks as well as frameworks that do (zeolites/zeosils) and do not (clathalites/clathasils) allow exchange of guest specie [6]. Table 2.1 shows classification of porous tectosilicates.

Table 2.1: Classification of Porous Tectosilicates [7]

Porosils (SiO_2 based)		Porolites (aluminosilicates)	
Clathasils	Zeosils	Clathalites	Zeolites
Silica sodalite	Silicalite	Sodalite	Faujasite
	Silica ZSM-22		Mordenite
Dodecasil	SSZ-24		ZSM-5
			Zeolite A

By now, about 140 different zeolite structures are known of which about 40 are found in natural zeolites. The nomenclature of zeolites is rather confusing since every company is using its own names and abbreviations. To overcome this problem, a thee-letter code system has been developed. These codes are assigned to specific structure types independent of their actual chemical compositions, e.g., the code LTA is used for Zeolite A and is derived from the name *L*inde *T*ype *A*. This structure type is found in various materials, as for example in aluminosilicates, aluminogermanates, gallophosphates or silicoaluminophosphates. A collection of all known zeolite structures can be found in the atlas of zeolite framework types or on the wep page of the international zeolite association [7].

2.2.1 Zeolite A (LTA) [5].

Zeolite A is one of the most important industrial zeolites. Hundreds of thousands of tons of this zeolite are produced every year for application as diverse as water softening in detergents, additive in polyvinyl chloride (PVC) thermoplastics, industrial gas drying, separation of linear and branched hydrocarbon, etc. The CBUs of Zeolite A (LTA) are the double 4-ring, the β cage, and the α cage. This last CBU is formally a cavity but is also known as an α cage for historical reasons. Zeolite A has a three-dimensional pore system and

molecules can diffuse in all thee directions in space by moving across the 8-ring windows that connect the cavities. The windows have a free diameter of approximately 4 Å. The composition of hydrated zeolite A as usually obtained from industrial manufacturers is close to $|Na_{96}(H_2O)_{216}|[Al_{96}Si_{96}O_{384}]$—LTA.

The crystal structure belongs to space group Fm3c (a=24.6Å) and contains 8 large cages per unit cell. This large unit cell is the consequence of the ordering of the Si and Al atoms in the framework (i.e., the Loewenstein rule). When Si and Al atoms are not discriminated, the average symmetry of the structure is Pm3-m and the cell parameter halves (á=12.3Å). In addition to this particular composition, materials with many different Si/Al ratios have been prepared; gallophosphate and other silicoaluminophosphate varieties have been reported. Figure 2.2 show the structure of zeolites A.

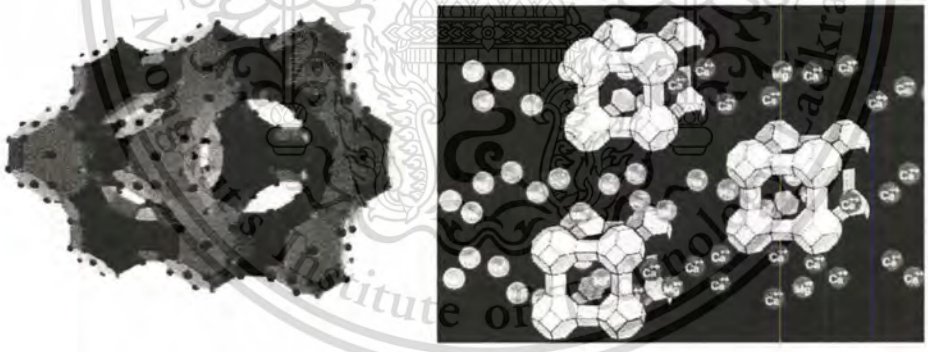


Figure 2.2 Structure of zeolites A(LTA)

2.2.2 Framework of Zeolites A (LTA) [7]

Space Group : Pm-3m

Cell Parameters : a = 11.919Å b = 11.919Å c = 11.919Å

$\alpha = 90.000°$ $\beta = 90.000°$ $\gamma = 90.000°$

Volume = 1693.24 $Å^3$

R_{DLS} = 0.0026

Framework density (FD_{Si}) : 14.2 T/1000 $Å^3$

Topological density : TD_{10} = 641 TD = 0.533333

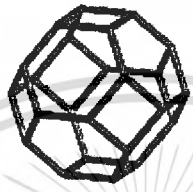
Ring sizes (# T-atoms) 8 6 4

Channel system : 3-dimensional

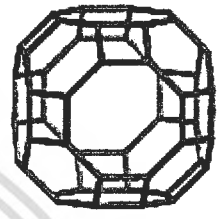
Secondary Building Units : 8 or 4-4 or 6-2 or 6 or 1-4-1 or 4

Composite Building Units :

d4R



sod



ita

2.3 Synthesis of Zeolites [8]

Zeolite formation is a kinetically controlled process. Zeolites are reaction intermediates during the formation of dense phases from silica precursors. Provided the reaction time is long enough (up to some million years in nature) or the reaction rate is enhanced, e.g. due to high temperature, dense silica or silicon oxide phases are the thermodynamically stable products. In zeolite synthesis, the reaction is stopped when the thermodynamically meta-stable zeolite has formed. Extended reaction time at high temperature and/or high pressure usually results in dense phases. Most aluminosilicate zeolites probably could be obtained at temperatures below 100°C in alkaline solutions. This is generally the case for zeolites with a low Si/Al ratio. However, in order to reduce the reaction time (especially for zeolites with a high Si/Al ratio) and to control crystallite sizes, morphologies, and compositions, some syntheses are performed at temperatures above 100°C under autogeneous pressure in autoclaves. The composition of the reaction mixture (= often called reaction gel) as well as the kind of precursor materials used in the reaction mixture are

very important parameters. They determine the properties of the resulting material, like for example its structure, morphology, particle sizes, particle size distribution, homogeneity of elements within the crystallites and many more. Typical precursor materials are listed below.

- Water Content; since the composition of a reaction mixture is given as ratio of oxides, any hydroxides employed are to be considered as oxides plus water, for example, $NaOH = 1/2Na_2O + 1/2H_2O$ (22.5 wt. % H_2O). Additionally, a small percentage of free water may be present, for example, sodium hydroxide pellets may contain about 97 or 98% NaOH. Similarly, an 85% H_3PO_4 contains 61.6 wt. % P_2O_5 and 38.4 wt. % H_2O. The water content of source materials may or may not constitute an important fraction of the total water content, and it is recommended that the water contained in these chemicals always be considered when the amount of water to be added in the preparation of the reaction mixture is calculated. [9]
- Sources of Aluminum; Some aluminum sources have been mentioned above. A disadvantage of using salts is that, after pH adjustment or addition of alkali silicate solutions, alkali salts are formed which have a strong electrolytic effect on gel formation. For example, such salts may cause sodality to be crystallized instead of zeolite A type materials. For this reason, it is advantageous, particularly for reaction mixtures of low SiO_2/Al_2O_3 ratios, to introduce aluminum in the anionic form, that is, as sodium aluminate. [9]
- Source of Silica; a widely used silica source is aqueous sodium silicate, such as water glass. Tetra methyl- and tetraethylorthosilicate are available in high purity and yield the highest SiO_2/Al_2O_3 ratios. Any noticeable aluminum contamination is likely brought in from other sources. Another sources of silica such as Aerosol, Ludox, Siloxane, fly ash. [9]

For the synthesis of some materials, an organic template molecule has to be added to the reaction mixture. These structure directing agents (usually amines, alkyl ammonium salts or alcohols) are essential for the formation of a large number of zeolitic materials. However,

the role of the template molecules during the crystallization is not absolutely clear and a number of possible mechanisms for its interaction with the forming zeolite are discussed. The most accepted ones are:

1) The true template effect, where the zeolite is formed around the organic molecule (= template) which determines the pore topology due to its own shape.

2) A pore filling effect, where the template stabilizes the micropores of the zeolite by filling them and, thus, preventing a collapse of the pores.

3) A pH-stabilizing effect, due to the functionality of the organic molecules.

2.4 Properties of Zeolites

2.4.1 Ion Exchange [4, 8]

Zeolite usually contains cations (e.g., Na^+, K^+, or NH_4^+) after the synthesis. These cations are required to balance the negative net-charge caused by trivalent aluminum cations which are coordinated tetrahedrally by oxygen anions. By exposing a sodium containing zeolite to a solution containing other cations, the sodium ions can be exchanged by these other cations provided they are not excluded from the pores due to their size (including the water molecules coordinating the respective cations). Zeolites are used on a large scale as ion exchangers in many fields; most notable are their use as 'builders' or water softeners for laundry detergents, and their use in the decontamination of various types of waste streams. Additionally, the ion exchange capability of zeolites can be used as a tool to modify their catalytic and sorptive properties. Some attention will be paid to structural parameters which influence the ion exchange properties of zeolites in the following paragraphs.

- the structure of the zeolite, particularly the diameters of the windows allowing access to the pores and cavities
- The location of the ion exchange sites; different cation environments lead to different ion exchange properties. The number of charge-balancing cations required for an electroneutral material is often less than the number of available ion exchange sites, thus partial occupancy of sites is common. Some of the possible cation positions in zeolites A and X (two of the most widely used synthetic zeolite ion exchangers) are indicated in Figure 2.3 below.

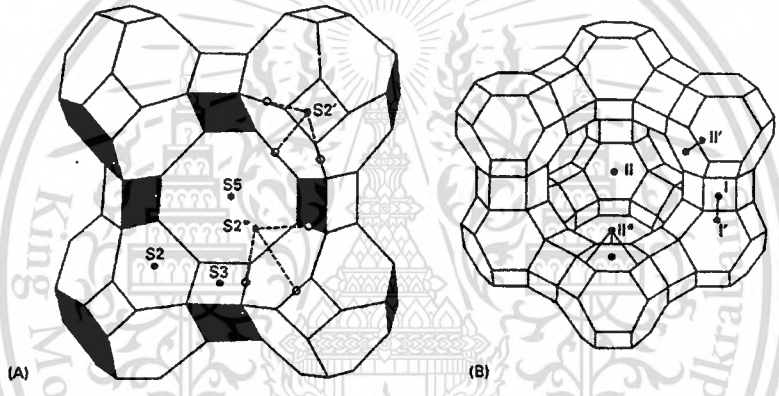


Figure 2.3 A representation of the possible positions of exchangeable cations in the zeoliteA (A) and X (B)

- The composition of the zeolite framework; varying the Si: Al ratio or changing the framework substituent elements may change, for example, the density of exchange sites, the electric field strength or the hydrophobicity of the sample as a whole.

2.4.2 Molecular Sieves. [8]

The pore sizes of zeolites are determined by their structures and may be varied slightly by ion-exchanging the zeolite. By this process smaller captions can be positioned in windows making them wider. Specific captions may also be positioned on other sites than in the windows, thus leading to even larger open windows. The window sizes determine the accessibility of the zeolite pore system for other (e.g. organic) molecules. Molecules which can penetrate the pore system are usually strongly adsorbed in the micropores. Thus,

molecules which may pass though the pore windows of zeolites are "trapped" in these pores. A phenomenon which is taken advantage of in gas separation processes (e.g. pressure swing process) or removal of water molecules from organic solvents.

2.4.3 Acidity [8]

As already mentioned protonated zeolites have acidic properties. The protons which balance the negative charge of a zeolite framework are not strongly bound to the framework and are able to move within the pores and react with molecules which penetrate into the zeolite pore system. A protonated zeolite thus can act as a Bronsted acid. Furthermore, Lewis acidity can be caused by cations within the pores. The different between Bronsted acidity and Lewis acidity shows in the Figure 2.4 below.

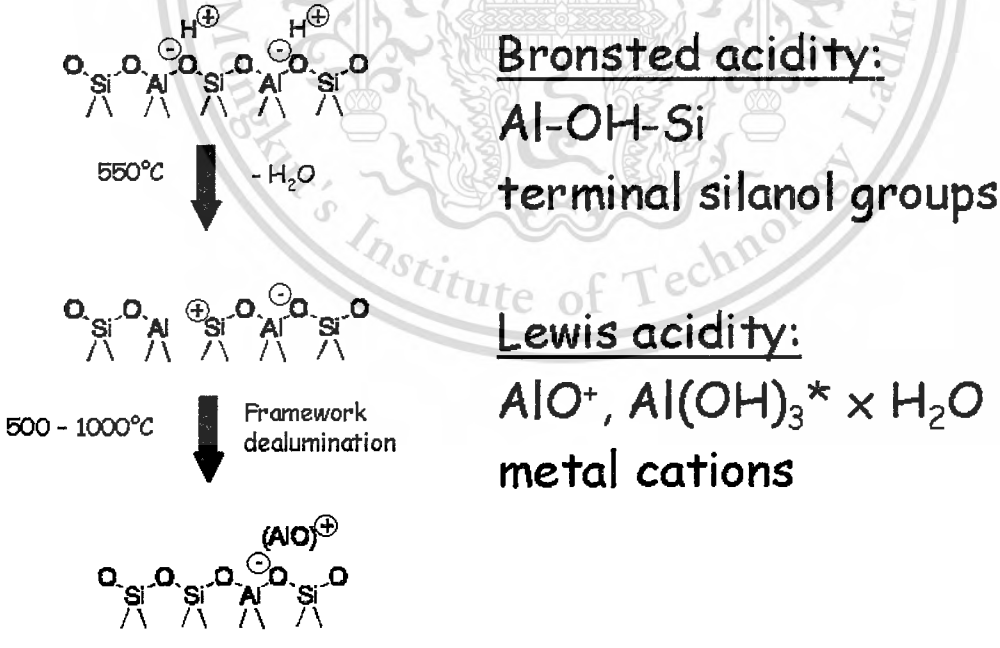


Figure 2.4 The different between Bronsted acidity and Lewis acidity

2.5 Rice husk ash [10]

Rice milling generates a byproduct know as husk. This surrounds the paddy grain. During milling of paddy about 78 % of weight is received as rice, broken rice and bran .Rest 22 % of the weight of paddy is received as husk. This husk is used as fuel in the rice mills to generate steam for the parboiling process. This husk contains about 75 % organic volatile matter and the balance 25 % of the weight of this husk is converted into ash during the firing process, is known as rice husk ash (RHA). This RHA in turn contains around 85 % - 90 % amorphous silica. So for every 1000 kgs of paddy milled , about 220 kgs (22 %) of husk is produced , and when this husk is burnt in the boilers , about 55 kgs (25 %) of RHA is generated. The compositions of RHA was examined by XRF which the results was reported below in table 2.2.

Table 2.2 The compositions of RHA [11]

Compositions		The perccentage of compositions
Silicon dioxide	(SiO_2)	94.23
Aluminium oxide	(Al_2O_3)	1.97
Ferric oxide	(Fe_2O_3)	0.91
Calcium oxide	(CaO)	0.86
Magnesium oxide	(MgO)	0.77
Potassium oxide	(K_2O)	1.93
Sodium oxide	(Na_2O)	0.05
Sulfer trioxide	(SO_3)	0.28
Phosphorus pentaoxide	(P_2O_5)	-
Titanium oxide	(TiO_2)	0.17

2.6 Literature about NaA and synthesis NaA membrane.

2.6.1 Synthesis of NaA zeolite membrane on a ceramic hollow fiber [12].

Xiaochun Xua, Weishen Yang, Jie Liu, Liwu Lin, Norbert Stroh, Herwig Brunner were successfully synthesized NaA zeolite membrane on a ceramic hollowfiber with an outer diameter of 400 μm, a thickness of 100 μm and an average pore radius of 0.1 μm. The as-synthesized membranes were characterized by XRD, SEM as well as gas permeation. A continuous NaA zeolite membrane formed after a three-stage synthesis. The membrane thickness was ~5 μm. Gas permeation data indicated that a relatively high quality NaA zeolite membrane formed on the ceramic hollow fiber support

2.6.2 Direct synthesis of NaA zeolite from rice husk and carbonaceous rice husk ash [13].

Hadi Nur was used rice husk (RH) and carbonaceous rice husk ash (CRHA) as source of silica for the synthesis of NaA zeolite. It was demonstrated that the NaA zeolite can be synthesized directly from RH and CRHA. First, RH and CRHA samples were submitted to a chemical pre-treatment using NaOH solution and then followed by mixing with aluminates solutions, and maintaining the mixture at temperature of 100 ^{o}C for 5 hours. The experimental results show that the quality of NaA zeolite from CRHA is higher than that of RH, because there is the tendency the formation of amorphous phases in NaA zeolite from RH.

2.6.3 Zeolite NaA from Brazilian chysotile and rice husk [14].

Diego Ivan Petkowicz, Reus Tiago Rigo, Cláudio Radtke, Sibele B. Pergher, Joao H.Z. dos Santos were reported natural form and after acid leaching, and rice husk, submitted to calcinations and to acid leaching of brazilian chysotile, were used as a silica source for zeolite NaA synthesis. For comparative reasons, commercial pyrogenic silica was also employed as a silicon source. The raw and chemically modified materials, as well as the resulting zeolites were characterized by X-ray diffraction, infrared spectroscopy, scanning electron microscopy, X-ray photoelectron spectroscopy and thermal analysis. Zeolite NaA,

with high crystallinity and purity, was obtained with all the natural sources, excepting in the case of natural chysotile. High specific area materials were obtained after Ca2+ exchange. Bigger crystals were observed in the case of natural silicon source.

2.6.4 Layer development and growth history of polycrystalline zeolite A membranes synthesised from a clear solution [15].

Jaco Zah, Henning M. Krieg, Jaco C. BreytenbachA was presented on the specific layer growth history of an a-Al2O3 supported NaA zeolite membrane synthesised from a clear solution. Using a defined set of synthesis parameters, the layer development over time (1.0–4.0 h) was described in terms of morphology, growth rate and elemental composition. It was shown that membrane growth proceeds along two distinct morphological pathways over the duration of synthesis – an initial layer of semicrystalline, hemisphere-shaped grains transforming into a fully crystalline layer with cubic morphology at the end of the growth process. A two-step growth rate trend was observed and could be correlated to the respective growth phases within the two underlying morphology types. The development of the hemisphere-shaped grains was associated with a period of accelerated growth during the first 2.5 h of synthesis (3.3×10^{-10} m•s^{-1}), followed by a period of slower growth for the formation of the cubic morphology (1.9×10^{-10} m•s^{-1}). Localised changes in supersaturation, combined with the possible effects of grain crowding, were offered as feasible explanations for the observed morphology and growth rate tendencies. Following the elemental make-up of the developing membrane showed a gradual decrease in the Na/Si ratio with increasing crystallisation times, which was explained by the consumption of the amorphous content in the membrane as growth proceeds. The solid phase compositions (Na/Si ratio) could however not explain the observed morphology and growth rate changes.

2.7 Characteristic of Zeolites

2.7.1 X-ray Diffraction ; XRD

Figure 2.5 X-ray Diffraction (XRD)

X-ray diffraction is a versatile analytical technique for examining crystalline solids, which include ceramics, metals, electronic materials, geological materials, organics, and polymers. These materials may be powders single crystals, multilayer thin films, sheets, fibers, or irregular shapes, depending on the desired measurement. X-ray diffractometers fall broadly into two classes: single-crystal and powder. Single-crystal diffractometers are most often used to determine the molecular structure of new materials. Powder diffractometers are routinely used for phase identification and quantitative phase analysis but can be conFigured for many applications, including variable-temperature studies, texture and stress analysis, grazing

incidence diffraction, and reflectometry. The operative equation in X-ray diffraction is the Bragg equation : $n\lambda = 2d\sin\theta$

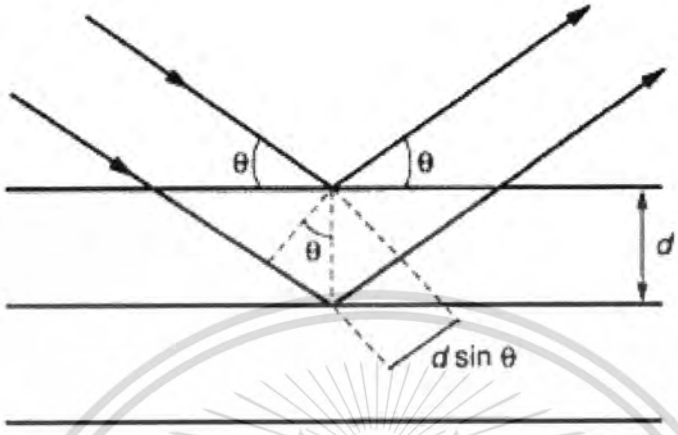


Figure 2.6 Illustration of Bragg's Law.

Where n is the order of a reflection ($n \in \{1,2,3 \ldots\}$), λ the wavelength, d the distance between parallel lactice planes, and θ the angle between the incident beam and a lacttice plane, known as the Bragg angle (Figure 2.6). When the pathlength in the crystal ($2d\sin\theta$) is a multiple of wavelength, constructive interference occurs and diffracted intensity is obtained. In general, the d-spacing is a function of the lattice parameters (a,b,c) and angles (α,β,γ) defining the unit cell, and the Miller indices (h,k,l) denoting a particular reflection. As such, it is the geometry of the crystal lattice that determines the positions of the peaks in an X-ray diffraction pattern. In general, the more symmetrical the material, the fewer peaks in its diffraction pattern. The diffracted intensities associated with those peaks are determined by the type and arrangement of atoms within the crystal lattice [16].

A crystal lattice is a regular three-dimensional distribution (cubic, rhombic, etc.) of atoms in space. These are arranged so that they form a series of parallel planes separated from one another by a distance d, which varies according to the nature of the material. For any crystal, planes exist in a number of different orientations - each with its own specific d

-spacing. When a monochomatic X-ray beam with wavelength λ is projected onto a crystalline material at an angle θ, diffraction occurs only when the distance traveled by the rays reflected from successive planes differs by a complete number n of wavelengths [17].

X-ray diffraction techniques are based on the elastic scattering of x-rays from structures that have long range order. The most comprehensive description of scattering from crystals is given by the dynamical theory of diffraction.

- Single-crystal X-ray diffraction is a technique used to solve the complete structure of crystalline materials, ranging from simple inorganic solids to complex macromolecules, such as proteins.
- Powder diffraction (XRD) is a technique used to characterize the crystallographic structure, crystallite size (grain size), and preferred orientation in polycrystalline or powdered solid samples. Powder diffraction is commonly used to identify unknown substances, by comparing diffraction data against a database maintained by the International Centre for Diffraction Data. It may also be used to characterize heterogeneous solid mixtures to determine relative abundance of crystalline compounds and, when coupled with lattice refinement techniques, such as Rietveld refinement, can provide structural information on unknown materials. Powder diffraction is also a common method for determining strains in crystalline materials.
- Thin film diffraction and grazing incidence x-ray diffraction may be used to characterize the crystallographic structure and preferred orientation of substrate-anchored thin films.
- High-resolution x-ray diffraction is used to characterize thickness, crystallographic structure, and strain in thin epitaxial films. It employs parallel-beam optics.
- X-ray pole Figure analysis enables one to analyze and determine the distribution of crystalline orientations within a crystalline thin-film sample.
- X-ray rocking curve analysis is used to quantify grain size and mosaic spread in crystalline materials [18, 19].

2.7.2 Scanning Electron Microscope; SEM [20, 21, 22]

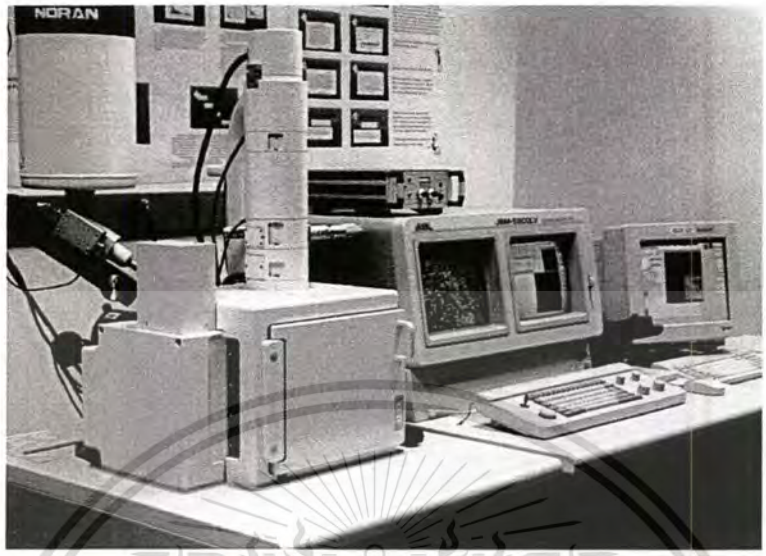


Figure 2.7 Scanning Electron Microscope (SEM)

The Scanning Electron Microscope (SEM) is a microscope that uses electrons rather than light to form an image. There are many advantages to using the SEM instead of a light microscope. The SEM has a large depth of field, which allows a large amount of the sample to be in focus at one time. The SEM also produces images of high resolution, which means that closely spaced features can be examined at a high magnification. Preparation of the samples is relatively easy since most SEMs only require the sample to be conductive. The combination of higher magnification, larger depth of focus, greater resolution, and ease of sample observation makes the SEM one of the most heavily used instruments in research areas today.

The Electron source; the electron beam comes from a filament, made of various types of materials. The most common is the Tungsten hairpin gun. This filament is a loop of tungsten which functions as the cathode. A voltage is applied to the loop, causing it to heat up. The anode, which is positive with respect to the filament, forms powerful attractive forces for electrons. This causes electrons to accelerate toward the anode. Some accelerate right by the anode and on down the column, to the sample. Other examples of filaments are Lanthanum Hexaboride filaments and field emission guns.

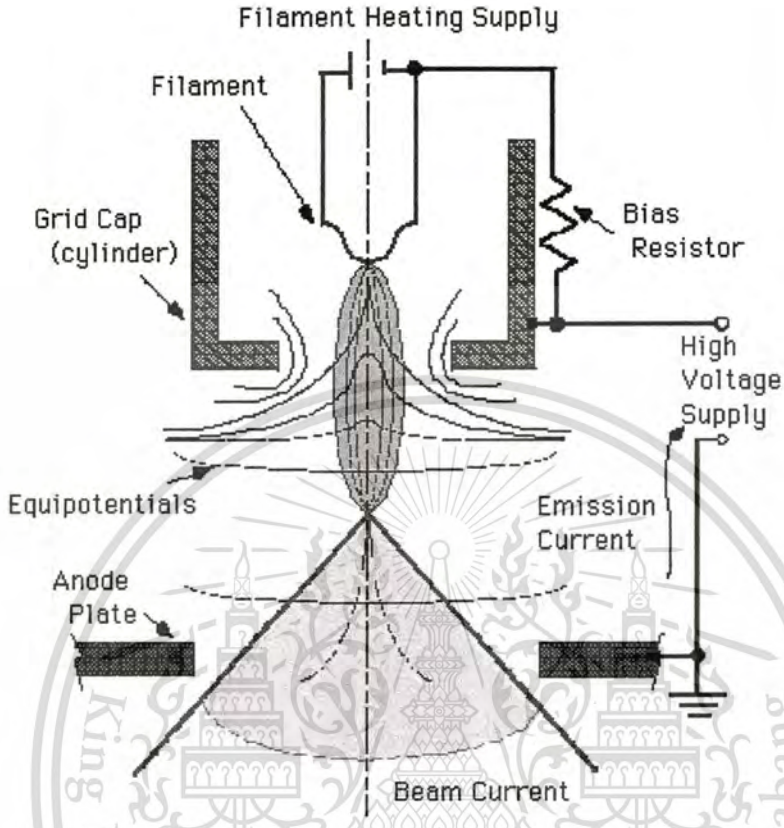


Figure 2.8 The electron sources

A beam of electrons is generated in the electron gun, located at the top of the column, which is pictured to the left. This beam is attracted though the anode, condensed by a condenser lens, and focused as a very fine point on the sample by the objective lens. The scan coils are energized (by varying the voltage produced by the scan generator) and create a magnetic field which deflects the beam back and forth in a controlled pattern. The varying voltage is also applied to the coils around the neck of the Cathode-ray tube (CRT) which produces a pattern of light deflected back and forth on the surface of the CRT. The pattern of deflection of the electron beam is the same as the pattern of deflection of the spot of light on the CRT.

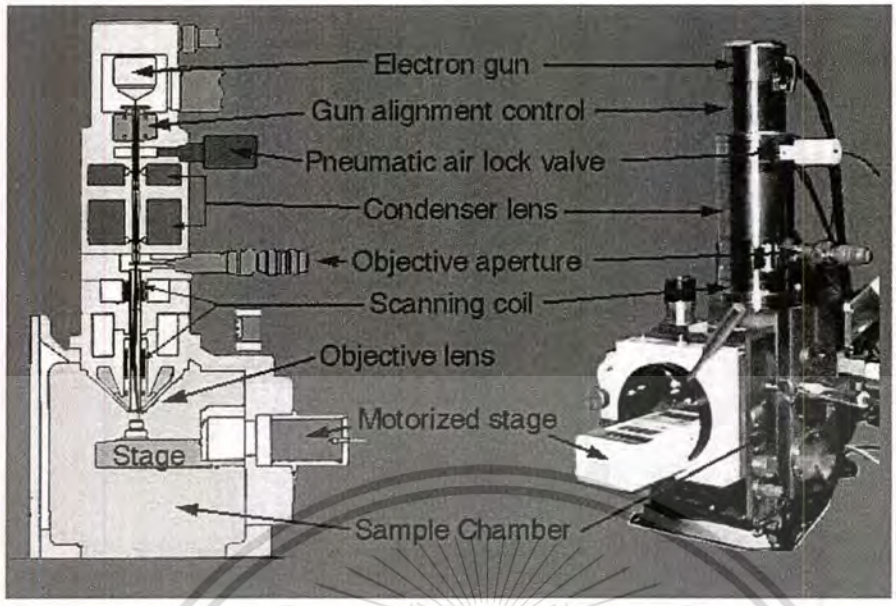


Figure 2.9 The electron beam path though the column

In a typical SEM, electrons are thermonically emitted from a tungsten or lanthanum hexaboride (LaB_6) cathode and are accelerated towards an anode; alternatively, electrons can be emitted via field emission (FE). Tungsten is used because it has the highest melting point and lowest vapour pressure of all metals, thereby allowing it to be heated for electron emission. The electron beam, which typically has an energy ranging from a few hundred eV to 100 keV, is focused by one or two condenser lenses into a beam with a very fine focal spot sized 0.4 nm to 5 nm. The beam passes though pairs of scanning coils or pairs of deflector plates in the electron optical column, typically in the objective lens, which deflect the beam horizontally and vertically so that it scans in a raster fashion over a rectangular area of the sample surface. When the primary electron beam interacts with the sample, the electrons lose energy by repeated scattering and absorption within a teardrop-shaped volume of the specimen known as the interaction volume, which extends from less than 100 nm to around 5 μm into the surface. The size of the interaction volume depends on the electrons' landing energy, the atomic number of the specimen and the specimen's density. The energy exchange between the electron beam and the sample results in the emission of electrons and electromagnetic radiation, which can be detected to produce an image

X-ray Diffraction sample Preparation; Metal specimens require no special preparation for SEM, except for trimming to appropriate size to fit in a specimen chamber, and make appropriate sectioning if necessary. Nonconductive solid specimens should be coated with a layer of conductive material, except when observed with Variable Vacuum or Environmental SEM. An ultrathin coating of electrically-conducting material is deposited either by high vacuum evaporation or by low vacuum sputter coating of the sample. This is done to prevent the accumulation of static electric fields at the specimen due to the electron irradiation during imaging. Such coatings include gold, gold/palladium, platinum, tungsten, graphite etc. Another reason for coating, even when there is more than enough conductivity, is to improve contrast, a situation more common with the operation of a FESEM (field emission SEM). Embedding in a resin with further polishing to a mirror-like finish could be beneficial for both biological and materials specimens, especially when imaging in backscattered electrons or X-ray microanalysis are performed. A biological specimen requires fixation to preserve its structure, which is usually performed by incubation of specimen in solution of fixative, such as gluteraldehyde or formalin. If not used in ESEM, biological specimen then should be dehydrated, usually by replacing water with organic solvents such as ethanol or acetone, and then removing solvents. If SEM is equipped for cryo-microscopy, then cryofixation could be used. Cryofixation – freezing a specimen so fast, to liquid nitrogen or even liquid helium temperatures, that the water forms vitreous (non-crystalline) ice. This preserves the specimen in a snapshot of its solution state. An entire field called cryo-electron microscopy has branched from this technique. With the development of cryo-electron microscopy of vitreous sections (CEMOVIS), it is now possible to observe virtually any biological specimen close to its native state. Another cryo-technique for biological specimens is cryo-fracture, when frozen specimen is fractured in special apparatus, sputter coated and transferred into SEM cryo-holder while still frozen. Freeze-fracturing, freeze-etch or freeze&break is a preparation method particularly useful for examining lipid membranes and their incorporated proteins in "face on" view. The preparation method reveals the lipids embedded in the protein bilayer. Freeze-fracturing where called, at the university of Harvard, for one of the most important

discoveries in the world in 1967. Due to the loss of information, gold coating is often a semi-destructive process since removing a gold coating chemically requires aggressive chemicals like potassium cyanide or aqua regia. Alternative techniques, for example the low-vacuum environmental SEM, allow samples to be imaged without such plating and without the loss of natural contrast arising from the beam-specimen interaction. Gold has a high atomic number and produces high topographic contrast and resolution but the information thus produced can obscure the underlying fine detail of the specimen under examination.

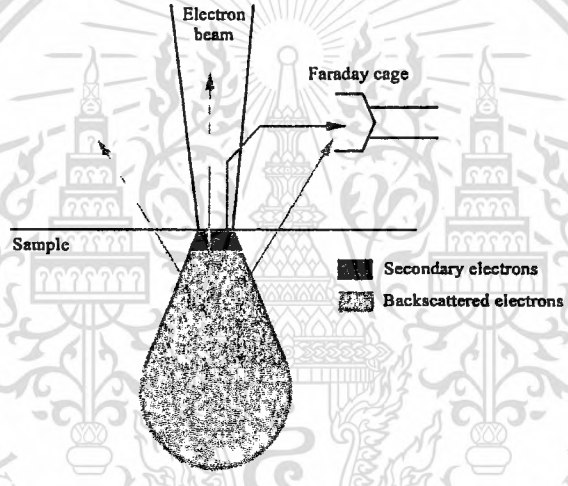


Figure 2.10 Secondary electron & Backscattered electron

Detection of secondary electron; the most common imaging mode monitors low energy (<50 eV) secondary electrons. Due to their low energy, these electrons originate within a few nanometers from the surface. The electrons are detected by an Everhart-Thornley detector which is a type of scintillator-photomultiplier device and the resulting signal is rendered into a two-dimensional intensity distribution that can be viewed and saved as a Digital image. This process relies on a raster-scanned primary beam. The brightness of the signal depends on the number of secondary electrons reaching the detector. If the beam enters

the sample perpendicular to the surface, then the activated region is uniform about the axis of the beam and a certain number of electrons "escape" from within the sample. As the angle of incidence increases, the "escape" distance of one side of the beam will decrease, and more secondary electrons will be emitted. Thus steep surfaces and edges tend to be brighter than flat surfaces, which results in images with a well-defined, thee-dimensional appearance. Using this technique, resolutions less than 1 nm are possible.

Detection of backscattered electrons; Backscattered electrons consist of high-energy electrons originating in the electron beam that are reflected or back-scattered out of the specimen interaction volume. Backscattered electrons may be used to detect contrast between areas with different chemical compositions, especially when the average atomic number of the various regions is different, since the brightness of the BSE image tends to increase with the atomic number. Backscattered electrons can also be used to form electron backscatter diffraction (EBSD) image. This image can be used to determine the crystallographic structure of the specimen. There are fewer backscattered electrons emitted from a sample than secondary electrons. The number of backscattered electrons leaving the sample surface upward might be significantly lower than those that follow trajectories toward the sides. Additionally, in contrast to the case with secondary electrons, the collection efficiency of backscattered electrons cannot be significantly improved by a positive bias common on Everhart-Thornley detectors. This detector positioned on one side of the sample has low collection efficiency for backscattered electrons due to small acceptance angles. The use of a dedicated backscattered electron detector above the sample in a "doughnut" type arrangement, with the electron beam passing though the hole of the doughnut, greatly increases the solid angle of collection and allows for the detection of more backscattered electrons.

Conventional SEM requires samples to be imaged under vacuum, which means that samples that would produce a significant amount of vapour, e.g. biological samples, need to be either dried or cryogenically frozen. This means that processes involving transitions to or from liquids or gases, such as the drying of adhesives or melting of alloys, liquid transport,

chemical reactions and solid-air-gas systems in general could not be observed. The first commercial development of the Environmental SEM (ESEM) in the late 1980s allowed samples to be observed in low-pressure gaseous environments (e.g. 1-50 Torr) and high relative humidity (up to 100%). This was made possible by the development of a secondary-electron detector capable of operating in the presence of water vapour and by the use of pressure-limiting apertures with differential pumping in the path of the electron beam to separate the vacuum regions around the gun and lenses from the sample chamber. ESEM is especially useful for non-metallic and biological materials because coating with carbon or gold is unnecessary. Plastics and Elastomers can now be routinely examined, as can biological samples. Coating can be difficult to reverse, and may reduce the value of the results obtained. For example very small details on the surface of the sample may be concealed by the coating, let alone that coating is done under vacuum, which drastically alters hydrated specimens.

Chapter 3

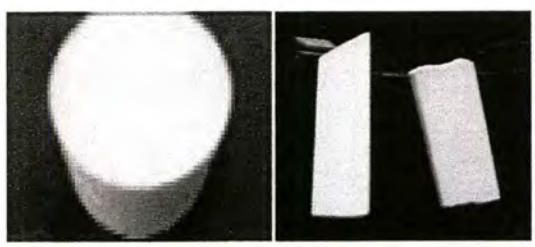
Experimental details

3.1 Chemicals

1. Sodium hydroxide (NaOH) Carlo Erba co.,Ltd.
2. Sodium aluminate ($Na_2Al_2O_4$) Riedel-de Haen co.,Ltd.
3. Hydrochloric acid solution (HCl) 37% Carlo Erba
4. Ammonia solution (NH_3) 25% Fisher chemicals
5. Sodium metasilicate ($Na_2O_3Si{\cdot}5H_2O$) Rankem
6. Deionized water (DI water)
7. Rice husk ash (RHA)

Figure 3.1 Rice husk ash

8. The porous substrate of aluminum oxide (Al_2O_3)



(a) (b)

Figure 3.2 The Aluminum oxide substrate (a) which clean and cut in to small pieces (b)

3.2 Equipments

1. Furnace
2. Digital balance
3. Magnetic bar and stirrer
4. Vacuum Filter
5. Filter paper
6. X-ray Diffraction; XRD (Siemens: D8 Advance)
7. Scanning Electron Microscope; SEM (LEO 1455 VP)
8. Fourier Transform Infrared spectrometer; FTIR (PerkinElmer: spectrum GX)
9. 100-150 ml High-density polyethylene(HDPE) bottle

3.3 Experimental.

1. The synthesis of silica from rice husk ash.

This process aim to synthesized silica which become a silica solution for synthesis zeolite NaA by using RHA as raw materials react with acid and base. The silica source was prepared from the equation;

$$SiO_2\ (s) + 2NaOH\ (s) \rightarrow Na_2SiO_3\ (l) + H_2O\ (l) \qquad (3.1)$$

At first, RHA was ground and weighted. The ground RHA was mixed with 0.1M HCl and stirred for an hour. After one hour, the solution was filtered and the remained RHA was discarded. The RHA was heated in an oven at 100 °C for overnight. The RHA was weighted and mixed with NaOH solution. The concentration of NaOH calculated from the equation:

$$NaOH = \left(\frac{X\left(\frac{Y\%}{100}\right)}{M.W._{SiO_2}}\right) \times 2(M.W._{NaOH}) \qquad (3.2)$$

Where; X = weight of RHA and Y = percentage of SiO_2 in RHA

NaOH was dilute to 10% wt. Next, RHA was mixed with NaOH, RHA was heated at 80 °C for an hour. After, an hour the solution was cool down to room temperature and then filtered. At this point we get the light-brown solution which is Na_2SiO_3 solution was left for a week to make the solution clear.

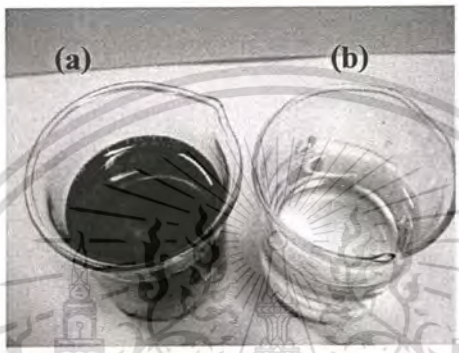


Figure 3.3 The light-brown solution which filtered (a) and left for a week (b)

Finally, the solution was characterized by FTIR and XRD. The solution was recovered to solid of SiO_2 describe by the equations below.

$$Na_2SiO_3\,(aq) + HCl \xrightarrow{ph7} NaCl\,(aq) + Si(OH)_n\,(s) \quad (3.3)$$

$$Si(OH)_n\,(s) + HCl \xrightarrow{ph1} SiO_2 + H^+ \quad (3.4)$$

$$SiO_2 + H^+ + NH_4OH \xrightarrow{ph7} SiO_2\,(s) \quad (3.5)$$

The light brown solution was recovered to sodium dioxide by adjusted pH to 1 by 1 M HCl. Subsequently, the white precipitation was formed and then neutralized by ammonium solution. Next, the white precipitation was filtered by vacuum filter and then heated at 100 °C overnight. Sodium dioxide was characterized by FTIR and XRD.

Figure 3.4 The picture of Silicon dioxide.

2. Synthesis of Zeolite NaA

As zeolite NaA consists of aluminum source and silica source, there are 2 ratios that we investigated for zeolite NaA synthesis.

2.1 The composition $3.165Na_2O : Al_2O_3 : 1.926SiO_2 : 128H_2O$ [9]

2.1.1 Use silica source from commercial

First, 0.723 g sodium hydroxide was mixed gently with 80 ml DI water until NaOH is completely dissolved then divide into two equal volumes in high density polyethylene(HDPE) bottles. Next, the aluminate solution was prepared by mixed 8.285 g sodium aluminate with sodium hydroxide solution. The silicate solution was prepared by mixed 15.48 g sodium metasilicate with sodium hydroxide solution. The solution of aluminate and silicate were mixed in capped bottles until the solutions become clear and these could take about 10-20 minutes. The mixtures should cap tightly and mixed until homogenized which may be done with stirrer or vigorously by hand for 5-10 minutes. After that, the homogenized solution was heated 100 °C with various synthesis time at 15mins, 30mins, 1h, 2h and 4h. Then the solution was removed from heat source leave it cools to below 30 °C. Then, the sample was filtered to

recovery solids and wash with DI water until filtrate pH is below 9; one- half liter should be sufficient. Finally, the product was dried on filter paper and watch glass at 80-100 ℃ overnight.

2.1.2 Use silica source from stock

First, the concentration of stock solution which is a silicate solution was calculated. Then, the composition of aluminate solution that consists of sodium hydroxide, sodium aluminate and DI water was calculated and mixed in capped bottle until clear. This could take 10-20 minutes. Next, silicate solution was quickly poured into aluminate solution suddenly a thick gel should form. The mixer should cap tightly and mixed until homogenized which may be done with stirrer or vigorously by hand for 5-10 minutes. After that, the mixture solution was heated at 100 ℃ with various synthesis time at 15mins, 30mins, 1h, 2h and 4h. Then the solutions were removed from heat source and allow cooling down to room temperature. Next, the sample was filtered and washed with DI water until the filtrate pH is below 9; one- half liter should be sufficient. Finally, the product was dried at 80-100 ℃ overnight.

2.2 The composition $49Na_2O : Al_2O_3 : 5SiO_2 : 980H_2O$ [15]

Initially, the silicate solution was prepared by mixed 2.628 g sodium metasilicate with 3.481 sodium hydroxide and 20 ml DI water. The aluminate solution was prepared by mixed 0.452 sodium aluminate with 4.807 sodium hydroxide and 20 ml DI water. After, aging both solutions for an hour they were combined by slow addition of the aluminate to the silicate solution under continuous stirring, and aged further for 1 h at room temperature. Next, the synthesized solution was heated at 100 ℃ for 4 h.

3. **Coating of zeolite on substrate (Al_2O_3) by direct synthesis.**

In this part we use the porous substrate of aluminum oxide (Al_2O_3) for growth of zeolite membrane. At first, the substrate was cleaned with DI water prior the substrate was transferred into capped HDPE bottle which contained the synthesized solution of zeolite A and heated at 100 °C with various synthesis times at 15mins, 30mins, 1h, 2h and 4h. Finally, the substrate was rinsed with DI water and then heat at 100 °C overnight.

Figure 3.5 The substrate which zeolite A successfully growth.

4. **Characterization metasilicate and zeolite A**

- XRD was used to characterize zeolite A and zeolite A membrane.
- Metasilicate solution was characterized by FTIR.
- SEM was used to characterize zeolite A and zeolite A membrane.

Chapter 4

Results and Discussion

4.1 Synthesis silica from Rice husk ash.

4.1.1 Characteristic of rice husk ash

As mentioned before, RHA contained silica and also organic compounds. RHA was characterized by FTIR and XRD before synthesized to sodium metasilicate which appeared as light-brown solution. The FTIR result was shown in Figure 4.1.

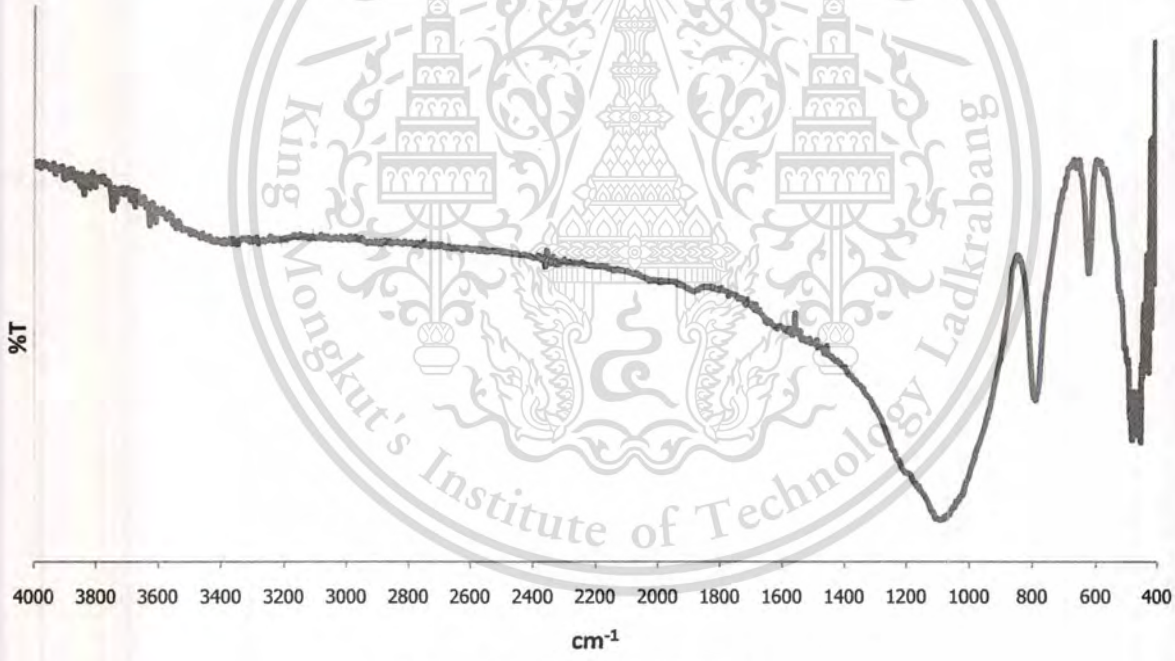


Figure 4.1 FTIR spectrum for RHA

According to Figure 4.1, FTIR was analyzed and found 3 functional groups that was silica or silicate was described by the region 1130-1000 and 800-400 cm^{-1} which basic functional group was –O–Si–O– and typical structures were SiO_2 which was silica, $(SiO_2)_n \cdot xH_2O$ which was silica gel and $M^{2+}[SiO_4]^{2-}$ which was metal silicate [23]. The region 1100-950 cm^{-1} was presented significant interferences from silicates and silica derivatives. As RHA

contains carbon compounds FTIR result was presented functional of polyhalogenated carbon compound inorganic oxide or oxyanoin by the regions 1160-1095 cm^{-1} [24, 25]. Some simple halogenated compounds containing C-H bonds may also described by this region and the most prominent inorganic compounds to appear with this region are silicates or silica based samples and sulphates. Figure 4.2 was shown XRD result of RHA scan from 10 to 70 2theta, and the asterisk shown peaks which presented distinctive characteristic of cristobalite and tridymite [13].

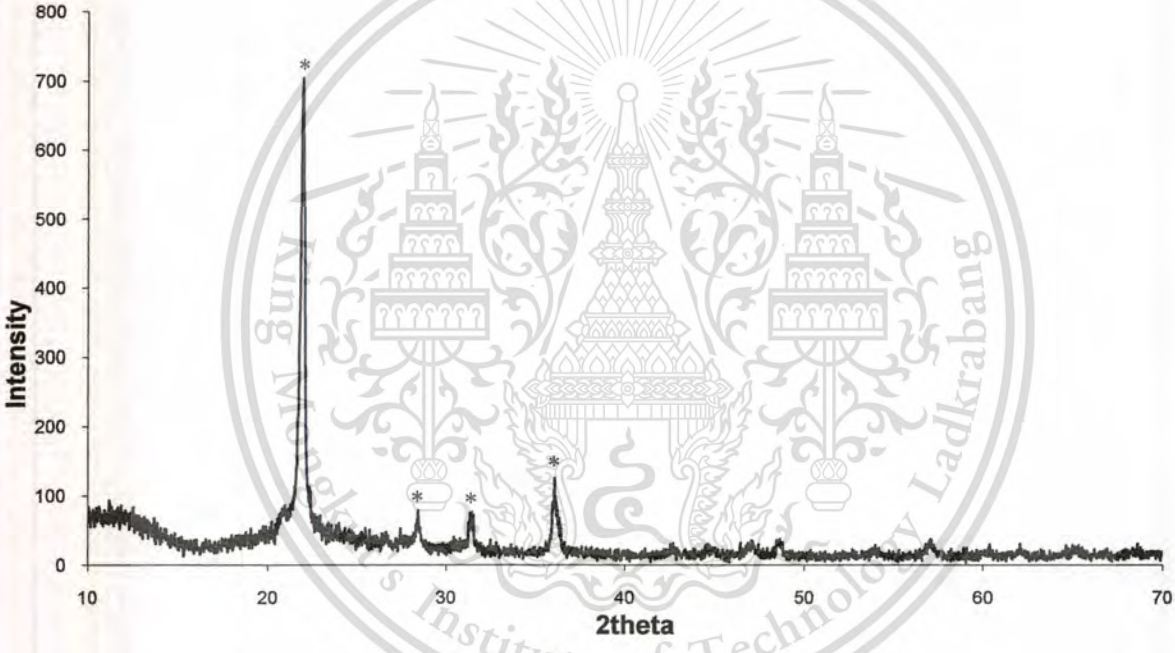


Figure 4.2 The XRD spectrum of RHA

4.1.2 Characteristic of silica source.

As mentioned before, this special project aims to synthesis zeolite A from rice husk ash. Silica source from RHA was characterized by XRD and FTIR. As the light brown solution contains both sodium metasilicate and water so, the light brown solution was recovery to solids. The results of XRD and FTIR were shown in Figure 4.3-4.5 below.

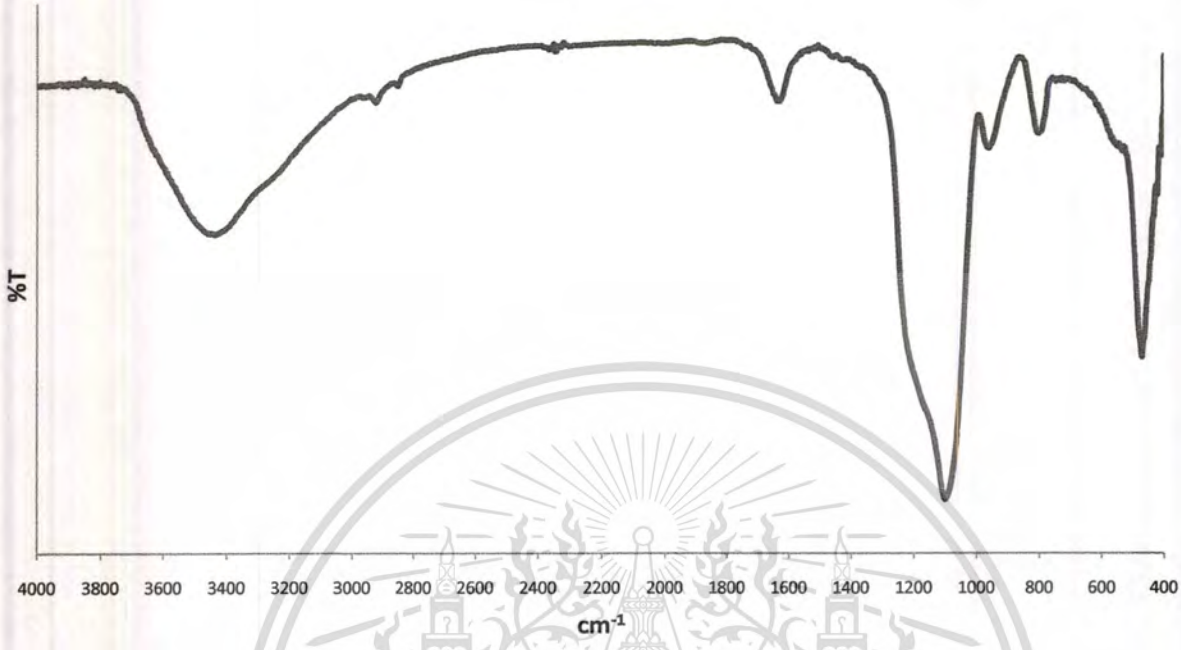


Figure 4.3 The FTIR spectrum of Silicon dioxide.

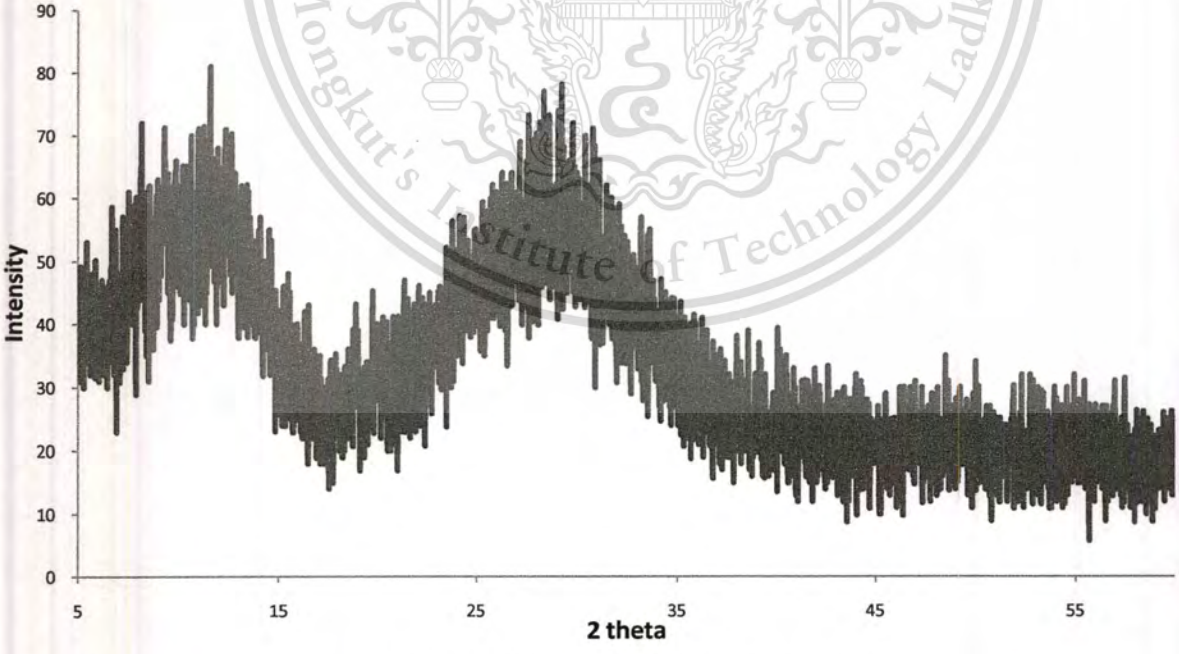


Figure 4.4 The XRD spectrum of Silicon dioxide.

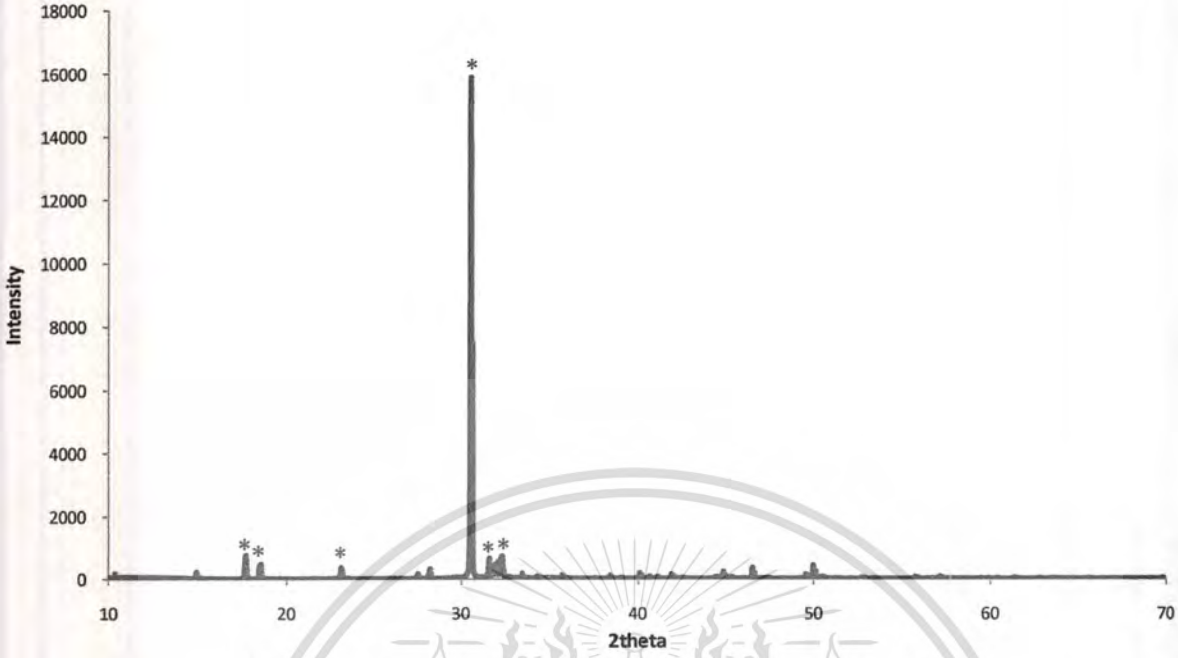


Figure 4.5 The XRD spectrum of Sodium metasilicate ($Na_2O_3Si{\cdot}9H_2O$) Rankem

Regarding to Figure 4.3, FTIR results showed significant peaks at 3437, 1631, 1113, 959, 802 and 470 which mean the sample consists of 3 functional groups which was silica or silicate groups that was presented at the region 1130-1000 and 800-400 cm^{-1}, hydrated metal salt or oxide which under certain circumstances organic compounds containing silicate, phosphate or polyether groups in conjunction with amino and/or hydroxyl groups could occur was presented at the region 3550-3145, 1665-1595 and 1200-600 cm^{-1}. The region 1100-950 cm^{-1} was presented significant interferences from silicates and silica derivatives. The sample was SiO_2. The XRD result of silicon dioxide in Figure 4.4 which the area between 15 - 30 2theta reported SiO_2 amorphous with board and no peaks while sodium metasilicate in Figure 4.5 the significant peak was shown.

4.2 Synthesis zeolite A

4.2.1 The composition 3.165 Na_2O : Al_2O_3 : 1.926SiO_2 : 128H_2O by using the silica source from commercial.

The synthesis zeolite A which various synthesis time from 15mins, 30mins, 1 h, 2 h and 4 h was characterized by XRD and FTIR. The Figure 4.6 showed significant peak of zeolite A at 7.2, 10.2, 12.5, 16.14, 21.7, 24.02, 26.14, 27.16, 29.98, 30.86, 32.58 and 34.22 2theta which normally found only zeolite A

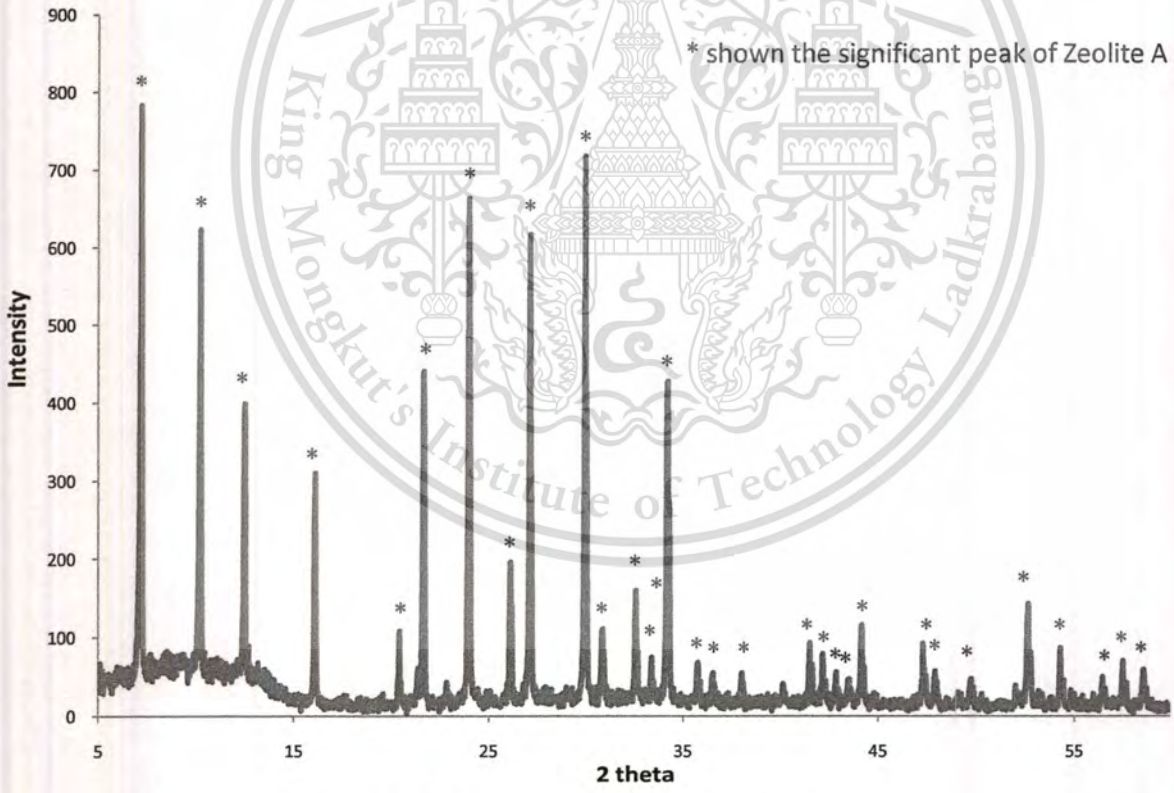


Figure 4.6 The XRD spectrum of zeolite A powder.

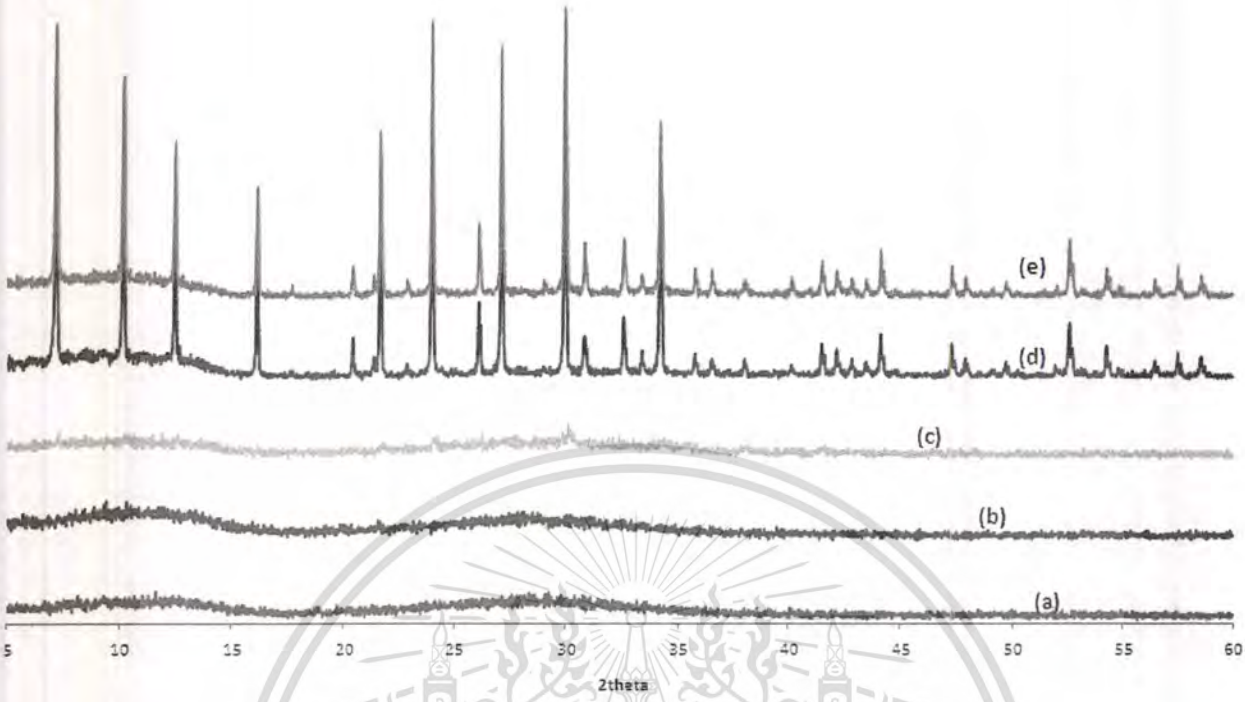


Figure 4.7 The XRD spectrum of zeolite A powder synthesis by procedure 2.1.1 (The composition $3.165Na_2O : Al_2O_3 : 1.926SiO_2 : 128H_2O$) varies time from 15mins (a), 30mins(b), 1h (c), 2h (d), 4h (e).

According to the XRD results in Figure 4.7, At 15mins, 30mins and 1 h synthesis times appeared amorphous phases but at 2 h and 4 h synthesis times showed significant peak of zeolite A and the XRD peaks were attributed to sodium aluminum silicate hydrate zeolite A according to asterisk shown in Figure 4.6. Figure 4.8 showed the result of FTIR various from 15mins to 4 h. The FTIR results of zeolite A normally contains 4 functional groups which is hydroxy group presented by the regions 3540-3200 and 1205-885 cm^{-1}, silica or silicate which presented by the regions 1130-1000 and 800-400 cm^{-1}, hydrated metal salt or oxide that presented by the regions 3550-3145, 1665-1595 and 1200-600 cm^{-1} and silicate which presented by the region 1100-950 cm^{-1}. At 2h and 4h synthesis time were represented the distinctive peaks of zeolite A at 800-400 cm^{-1} which is not represented at 15mins, 30mins and 1h synthesis times, respectively.

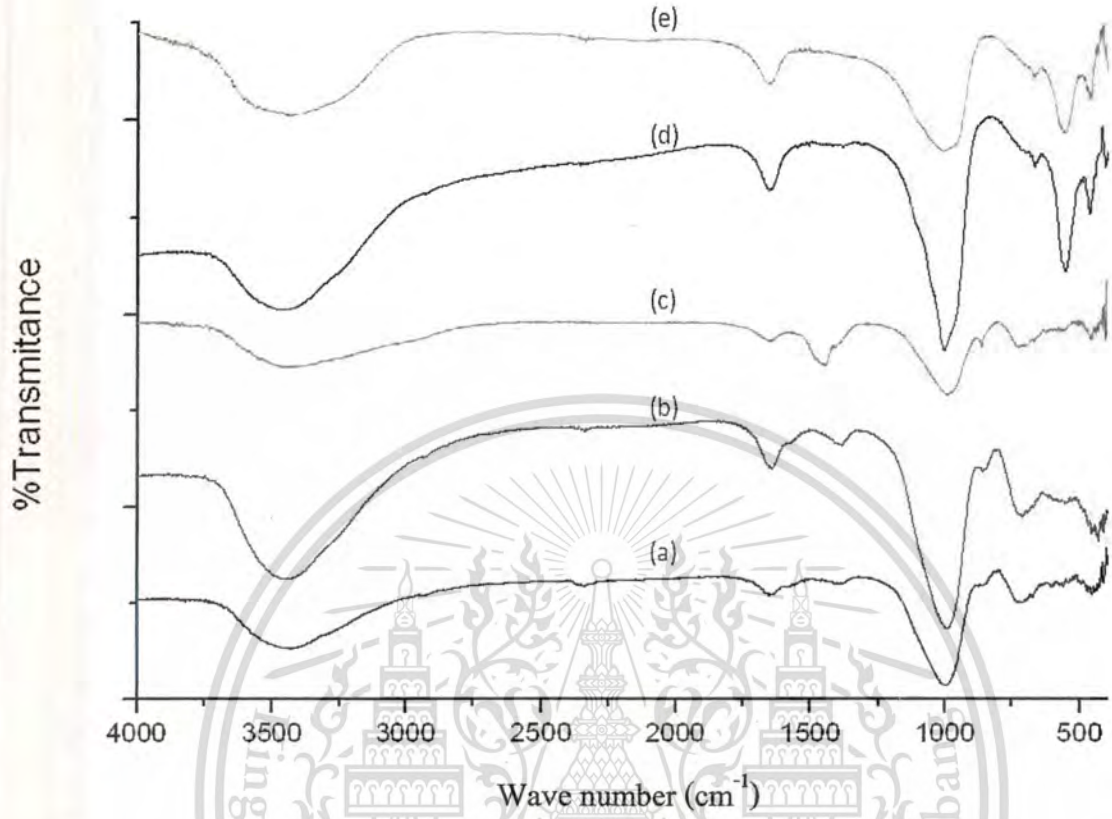


Figure 4.8 The FTIR spectrum of zeolite A powder synthesis by procedure 2.1.1 (The composition $3.165Na_2O : Al_2O_3 : 1.926SiO_2 : 128H_2O$) varies time from 15mins (a), 30mins(b), 1h (c), 2h (d), 4h (e).

4.2.2 The composition $3.165Na_2O : Al_2O_3 : 1.926SiO_2 : 128H_2O$ by using the silica source from stock solution.

The synthesis Zeolite A was checked by various the synthesis times. Figures 4.9 show the XRD spectrum of 15mins, 30mins and 1h synthesis times. Figures 4.10 show the FTIR spectrum of 15mins, 30mins and 1h synthesis times.

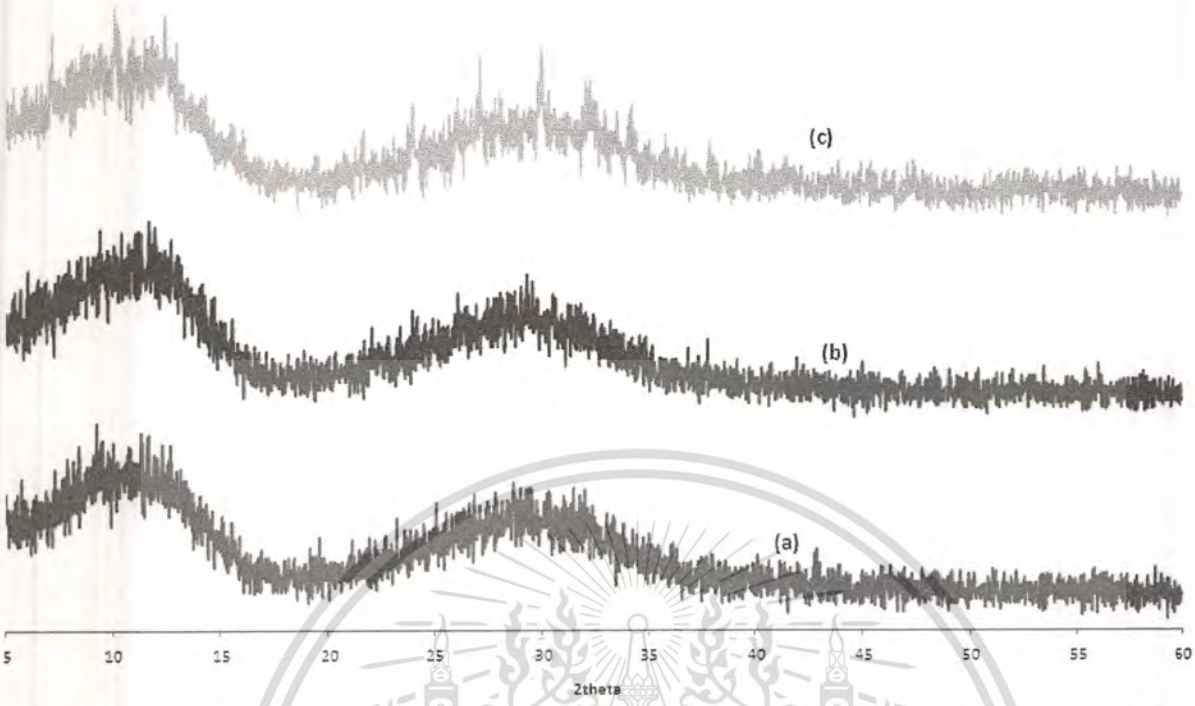


Figure 4.9 The XRD spectrum of zeolite A powder synthesis by procedure 2.1.2 (The composition $3.165Na_2O : Al_2O_3 : 1.926SiO_2 : 128H_2O$) varies time from 15mins (a), 30mins(b) and 1h (c)

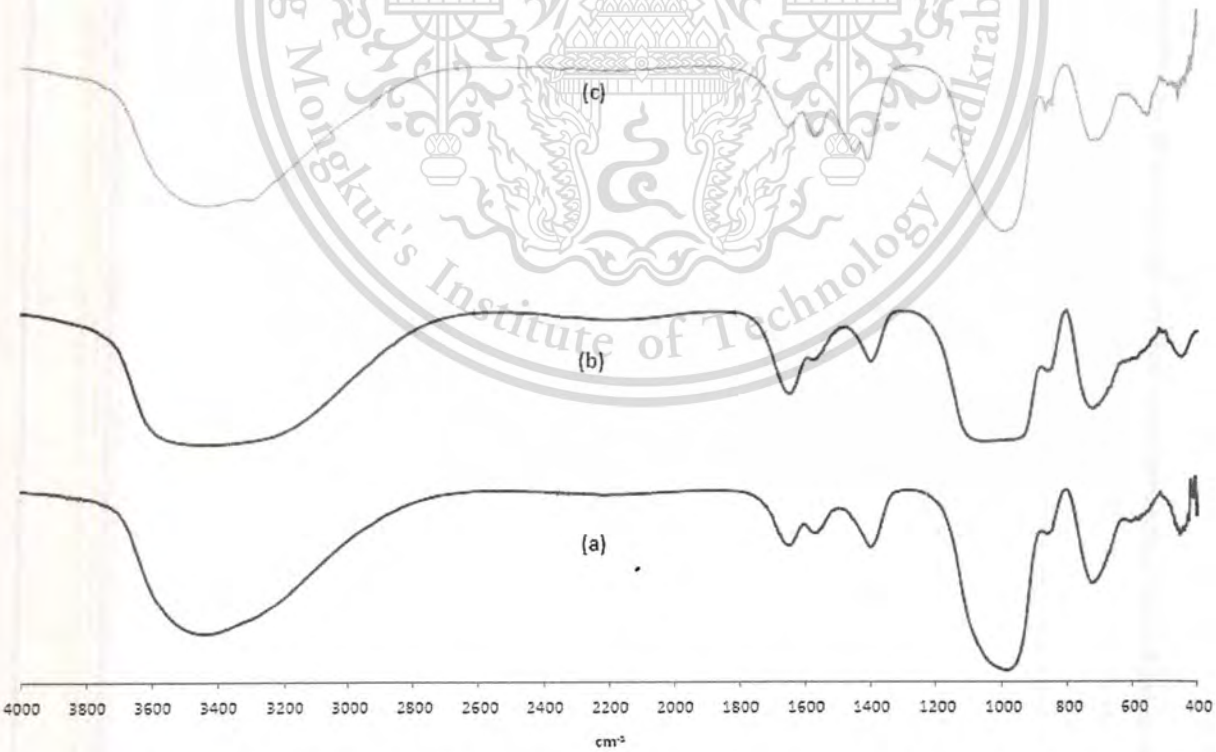


Figure 4.10 The FTIR spectrum of zeolite A powder synthesis by procedure 2.1.2 (The composition $3.165Na_2O : Al_2O_3 : 1.926SiO_2 : 128H_2O$) varies time from 15mins (a), 30mins(b), 1h (c)

According to Figure 4.9, precursors were begun to formed zeolite A at 15mins, 30mins and 1 h synthesis times. However, the XRD results showed that there were amorphous phase. When more synthesis time was used, the product showed increasing in crystallinity of zeolite A and the amorphous phase were decrease. At 1 h synthesis time, the significant peaks of zeolite A appeared and become more 15mins and 30mins. While FTIR results show in Figure 4.10 were reported only 2 functional groups there were hydroxyl compound which described by 3540-3200 and 1205-885 cm^{-1} regions and hydrated metal salt that represented by 3550-3145, 1665-1595 and 1200-600 cm^{-1} regions.

Figure 4.11 showed the XRD results of 2h and 4h synthesis times which the result contains most significant peaks respectively. Figure 4.12 showed the FTIR results of 2h and 4h which reported important functional groups and peaks in zeolite A. The functional groups found in Figure 4.12 were hydroxyl compounds, silica and silicate, hydrated matal salt or oxide and silicate. Thus, at 2h and 4 h synthesis times the zeolite A were formed.

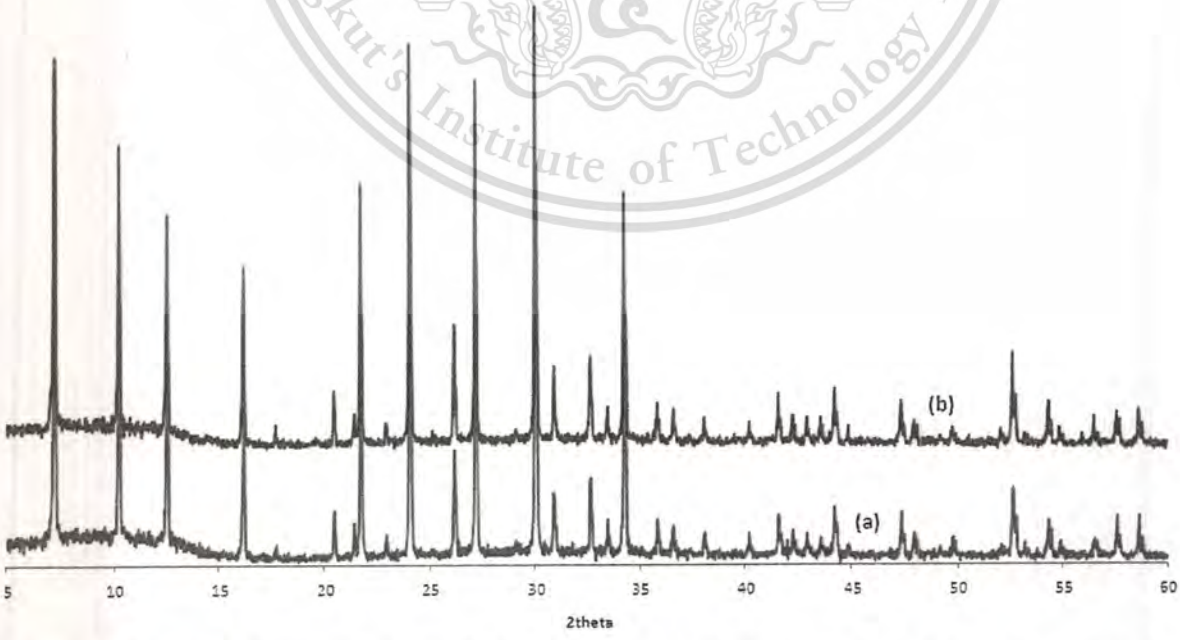


Figure 4.11 The XRD spectrum of zeolite A powder synthesis by procedure 2.1.2 (The composition $3.165Na_2O : Al_2O_3 : 1.926SiO_2 : 128H_2O$) at 2h (a) and 4h (b) synthesis times

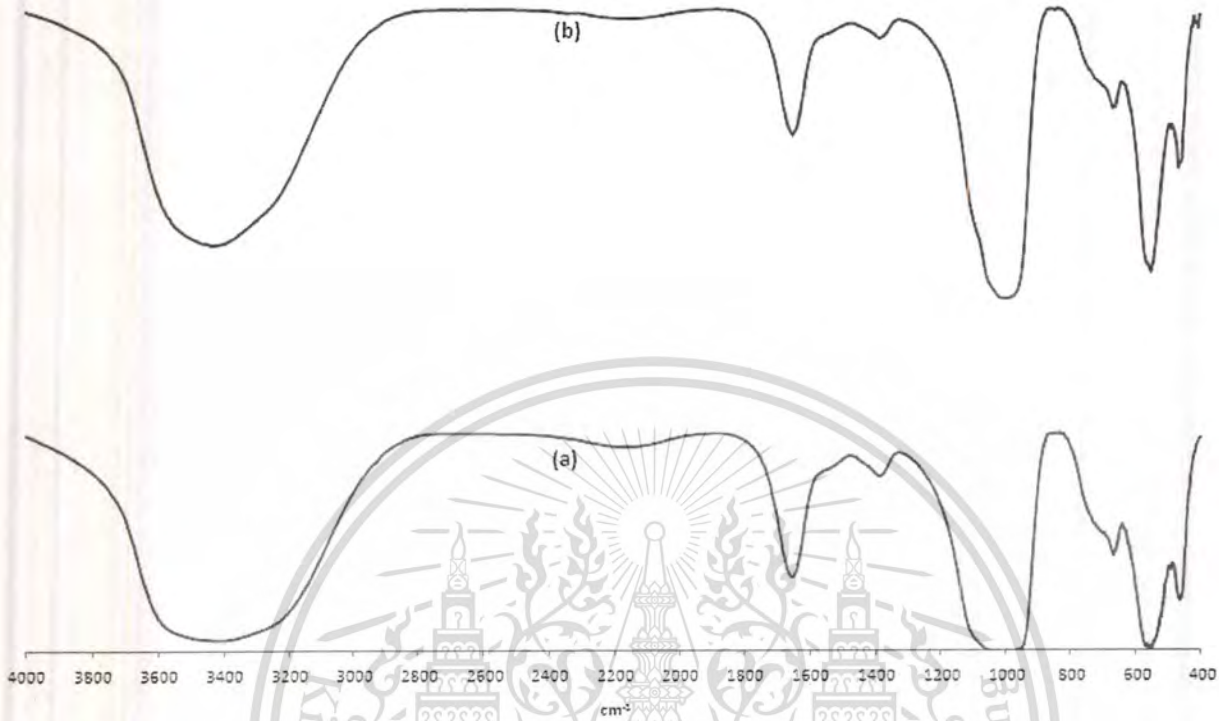


Figure 4.12 The FTIR spectrum of zeolite A powder synthesis by procedure 2.1.2 (The composition $3.165Na_2O : Al_2O_3 : 1.926SiO_2 : 128H_2O$) at 2h (a) and 4h (b) synthesis times

4.2.3 The composition $49Na_2O : Al_2O_3 : 5SiO_2 : 980H_2O$

The XRD results for this synthesis show in Figure 4.13 below. In this composition 4h synthesis time was used. The XRD results did not show significant peaks of zeolite A while FTIR result in Figure 4.14 did not report distinctive characterize of zeolite A. So, the sample was surely not zeolite A.

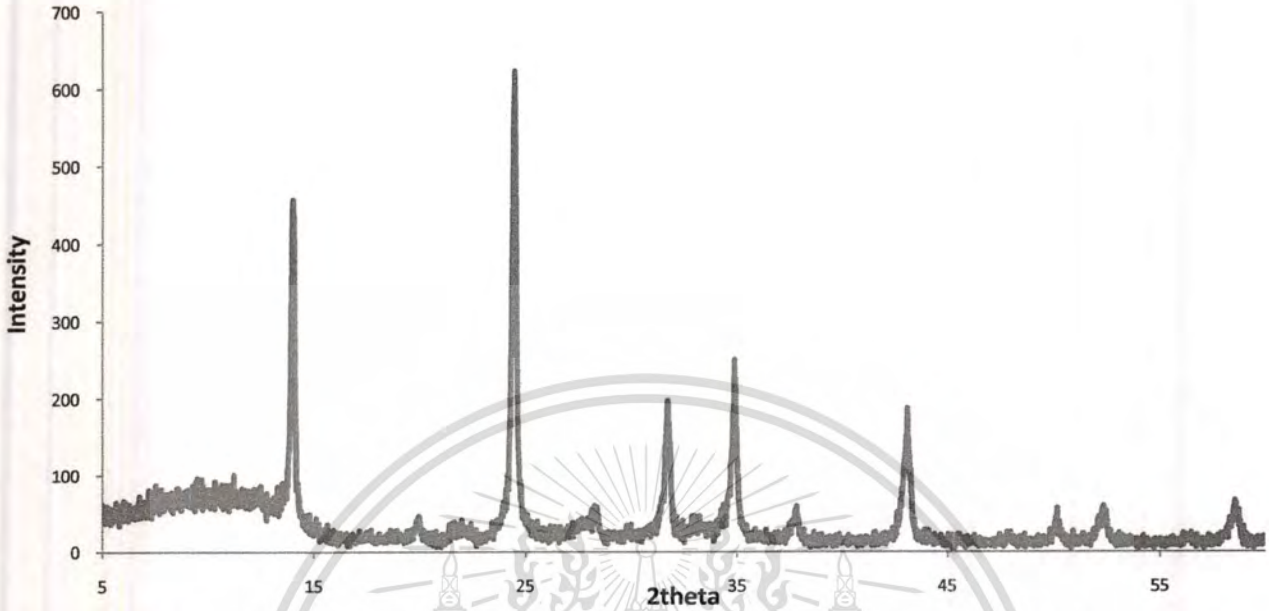


Figure 4.13 The XRD spectrum of zeolite A powder at 4 h synthesis time by procedure 2.2 (The composition $49Na_2O : Al_2O_3 : 5SiO_2 : 980H_2O$)

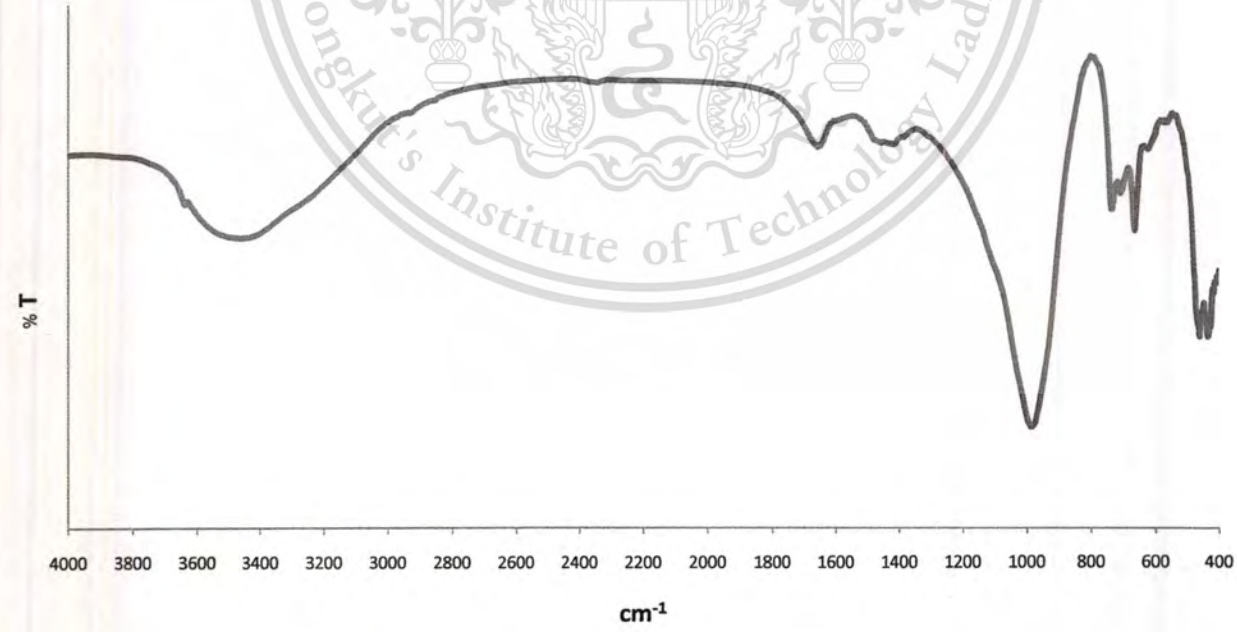


Figure 4.14 The FTIR spectrum of zeolite A powder at 4 h synthesis time by procedure 2.2 (The composition $49Na_2O : Al_2O_3 : 5SiO_2 : 980H_2O$)

4.3 Coating of zeolite on the porous aluminum substrate (Al_2O_3) by direct synthesis.

4.3.1 The composition $3.165Na_2O : Al_2O_3 : 1.926SiO_2 : 128H_2O$ by using the silica source from commercial.

At first, the substrate (Al_2O_3) was charactirized by XRD. The XRD result show in Figure 4.15 was reported significant peaks which XRD reported that was aluminum oxide (Al_2O_3) respectively.

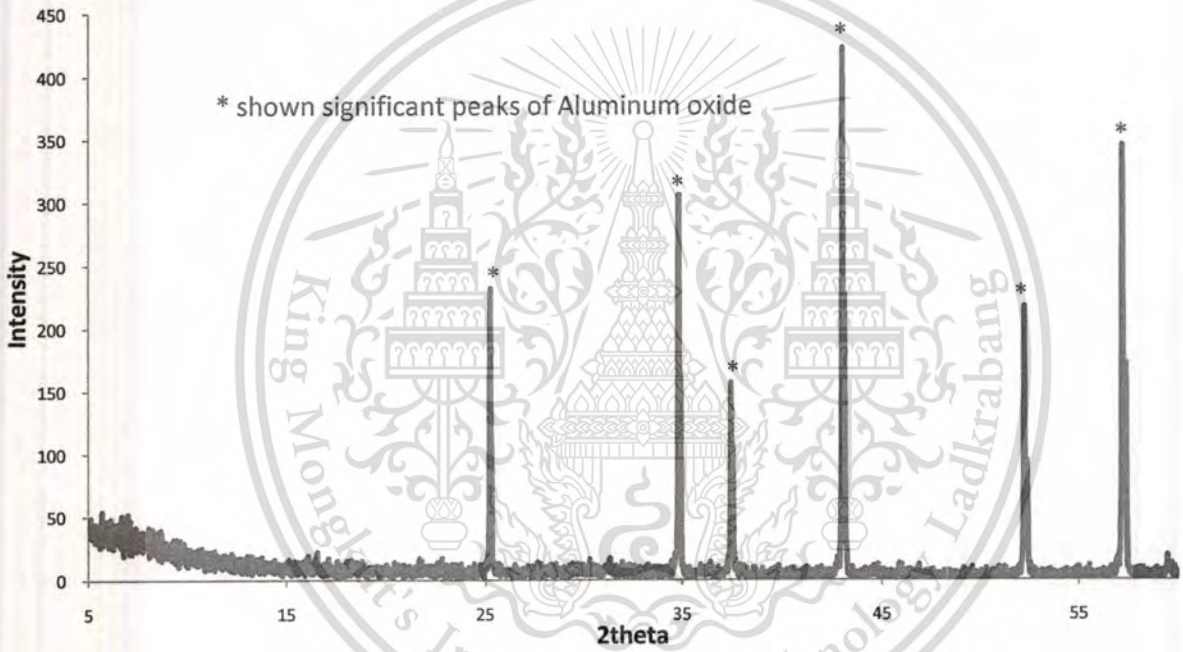


Figure 4.15 The XRD spectrum of substrate (Al_2O_3).

The substrate (Al_2O_3) was transferred into HDPE bottles which contained precursors of zeolite A and varied synthesis times from 15mins, 30mins, 1 h, 2 h and 4 h. Figure 4.16 show the XRD results of each synthesis times.

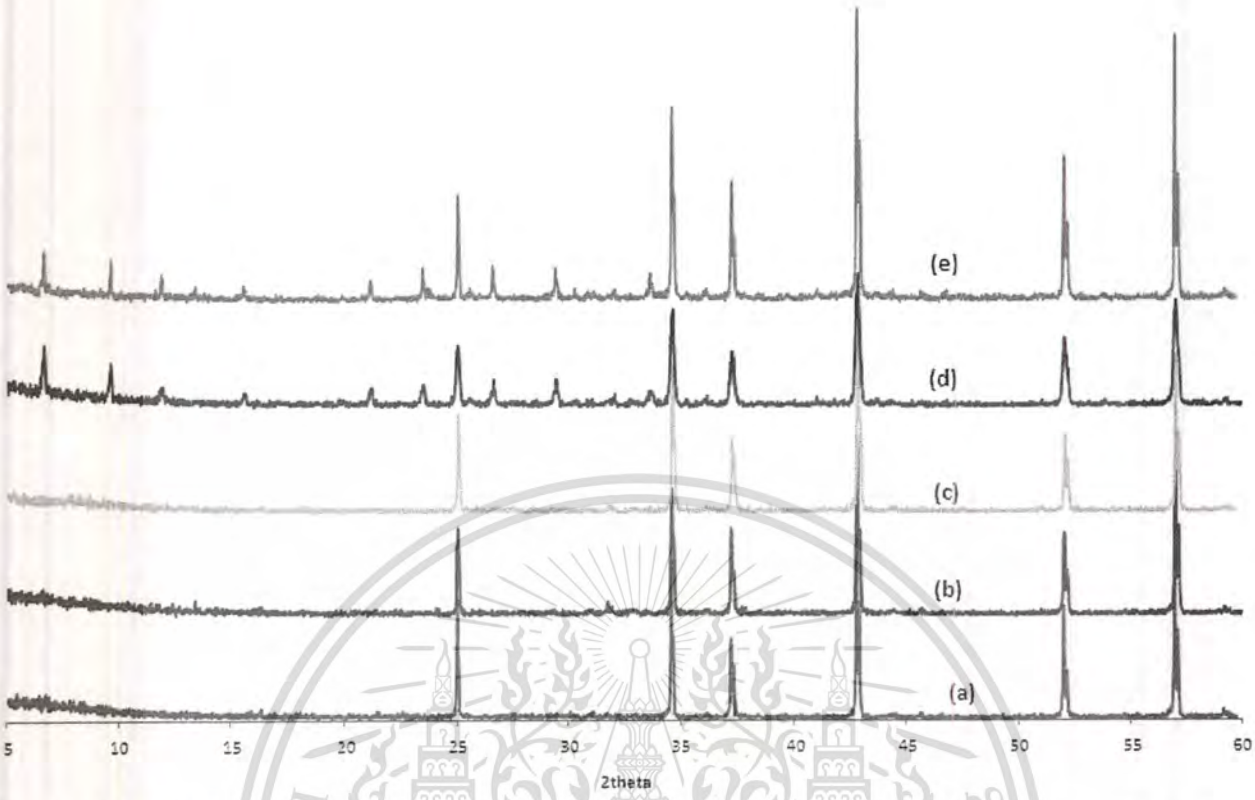


Figure 4.16 The XRD spectrum of zeoliteA membrane synthesis by procedure 2.1.1 (The composition $3.165Na_2O : Al_2O_3 : 1.926SiO_2 : 128H_2O$) varies time from 15mins (a), 30mins(b), 1h (c), 2h (d), 4h (e).

According to Figure 4.16, at 15mins, 30mins and 1 h synthesis times the XRD results reported the significant peaks the same as the substrate (Al_2O_3) that means in these interval time (15mins, 30mins and 1h) zeolite A membrane did not grow on surface of substrate (Al_2O_3). At 2 h and 4 h synthesis times, the XRD results showed significant peaks of zeolite A that grew on substrate at 2h and 4 h, when compared distinctive characteristic of both zeolite A and substrate. The growth of zeolite A membrane at 2 h synthesis time was not completely because the results reported some amorphous phase while zeolite A membrane at 4h synthesis time showed higher crystalline than 2 h synthesis time.

4.3.2 The composition $3.165Na_2O : Al_2O_3 : 1.926SiO_2 : 128H_2O$ by using the silica source from stock.

The substrate (Al_2O_3) was transferred into HDPE bottles which contained precursors of zeolite A and various synthesis times from 15mins, 30mins, 1 h, 2 h and 4 h. Figure 4.34-4.38 showed the XRD results of each synthesis times.

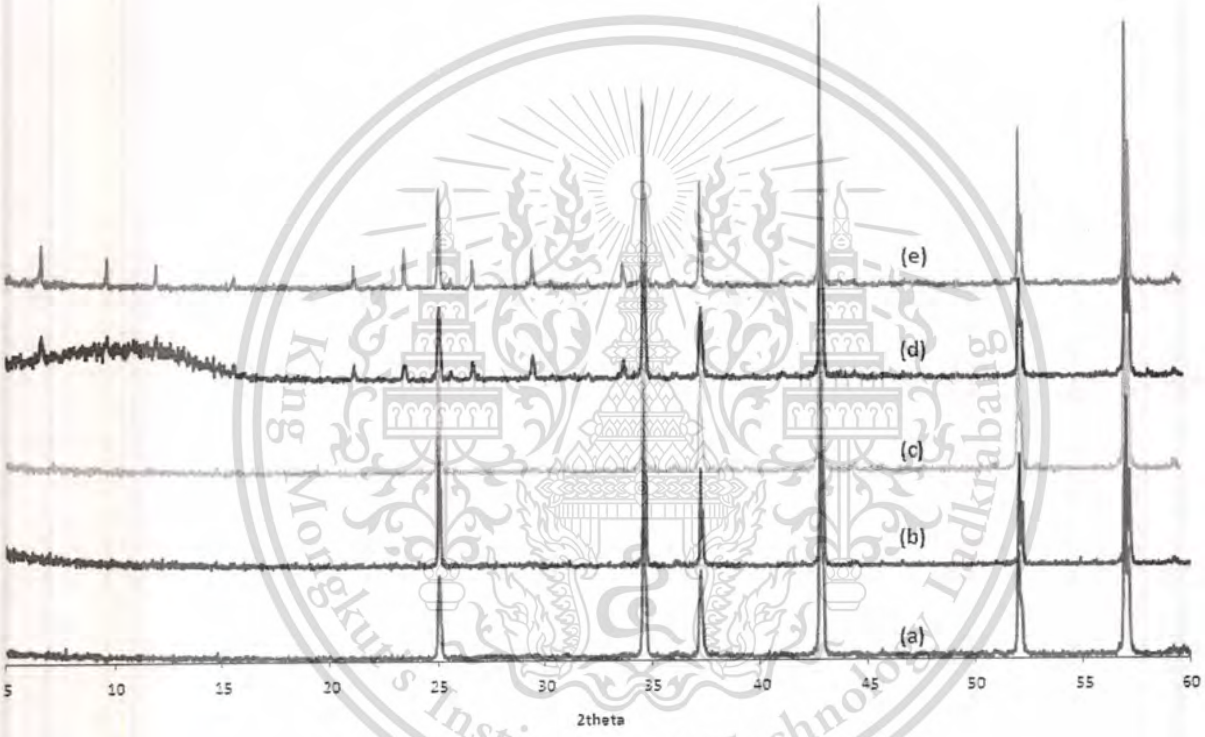


Figure 4.17 The XRD spectrum of zeolite A membrane synthesis by procedure 2.1.2 (The composition $3.165Na_2O : Al_2O_3 : 1.926SiO_2 : 128H_2O$) varies time from 15mins (a), 30mins(b), 1h (c), 2h (d), 4h (e).

The results of synthesis zeolite A membrane by used silica source from stock solution reported the same trends as synthesis zeolite A membrane by used silica source from commercial. The results of zeolite A membrane at 2h and 4 h synthesis times was presented distinctive characteristic of both zeolite A and substrate while at 15mins, 30mins and 1h synthesis times was presented amorphous phase same as previous method which used silica source from commercial.

4.3.3 The composition $49Na_2O : Al_2O_3 : 5SiO_2 : 980H_2O$

The results show in Figure 4.39, was appeared significant peaks of substrate only, thus it is indicated that the zeolite A sample did not grown on substrate.

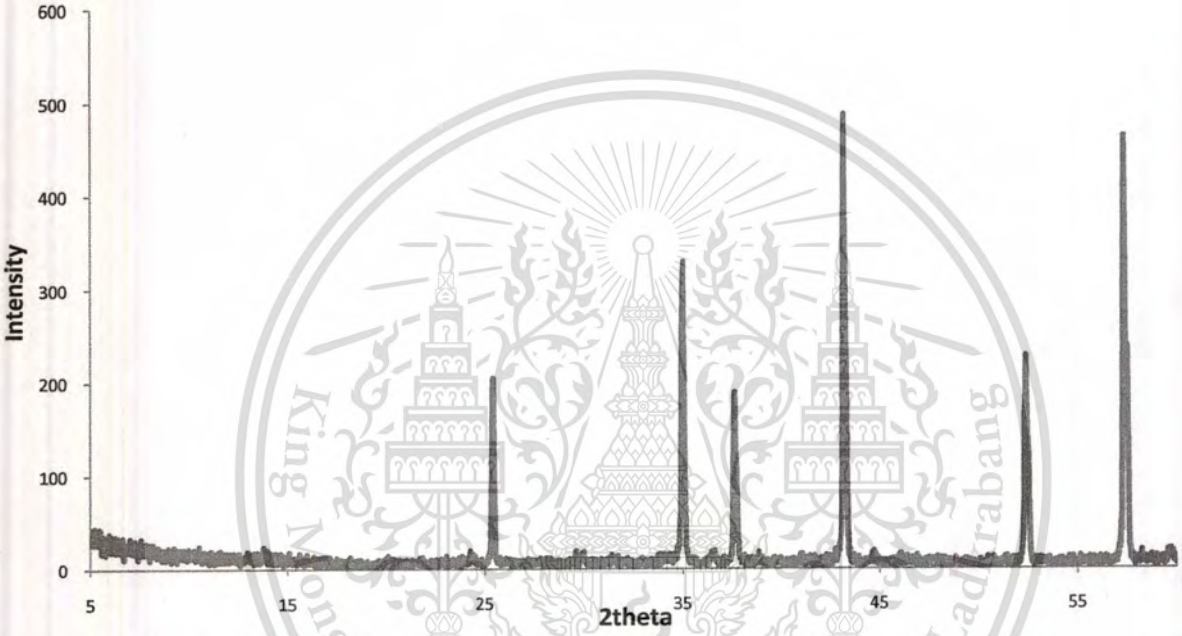
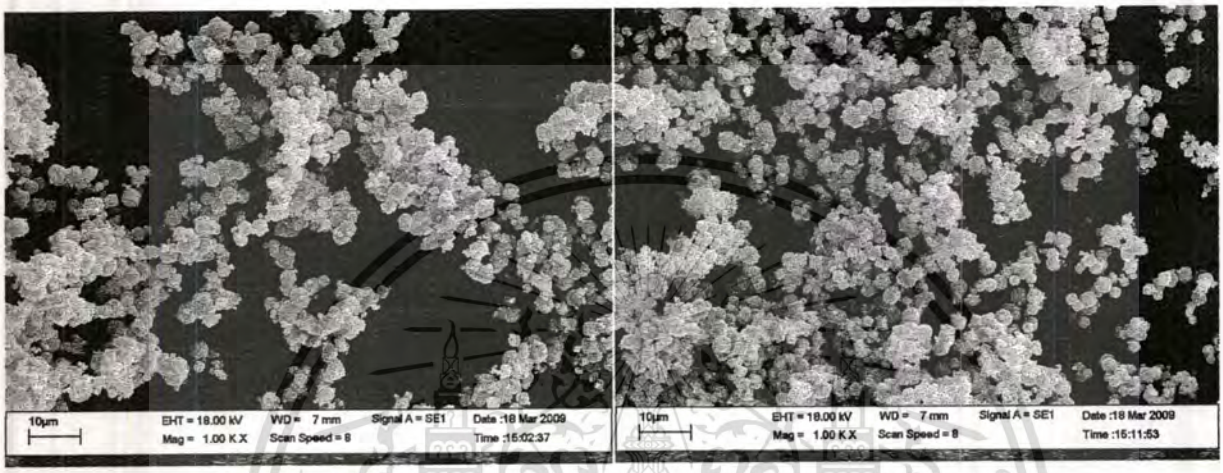


Figure 4.18 The XRD spectrum of zeolite A membrane at 4 h synthesis time by procedure 2.2 (The composition $49Na_2O : Al_2O_3 : 5SiO_2 : 980H_2O$)

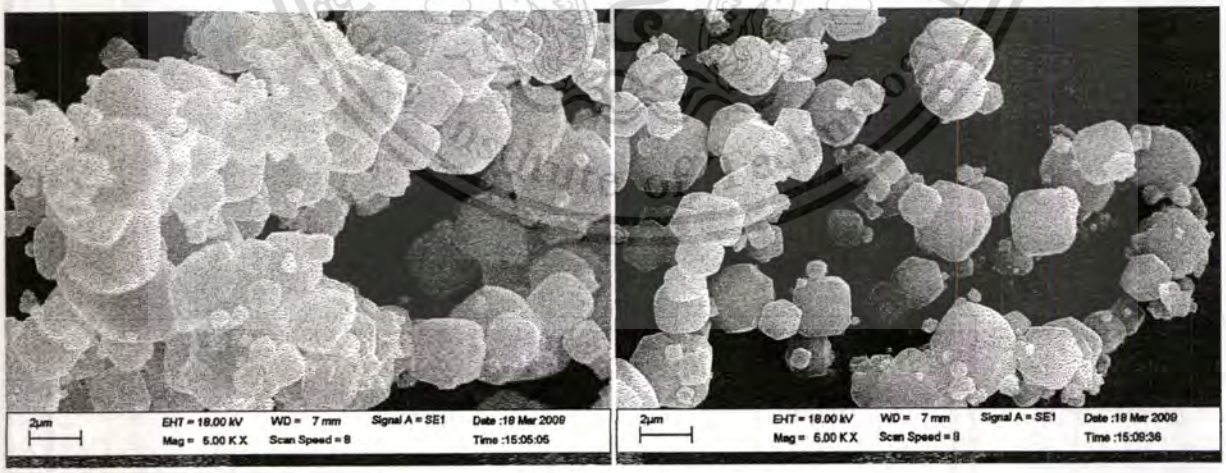
4.4 Characterize zeolite A and zeolite A membrane by SEM.

4.4.1 Zeolite A powder synthesized from the composition $3.165Na_2O : Al_2O_3 : 1.926SiO_2 : 128H_2O$ at 2 h and 4 h synthesis time by used silica from commercial



(a) (b)

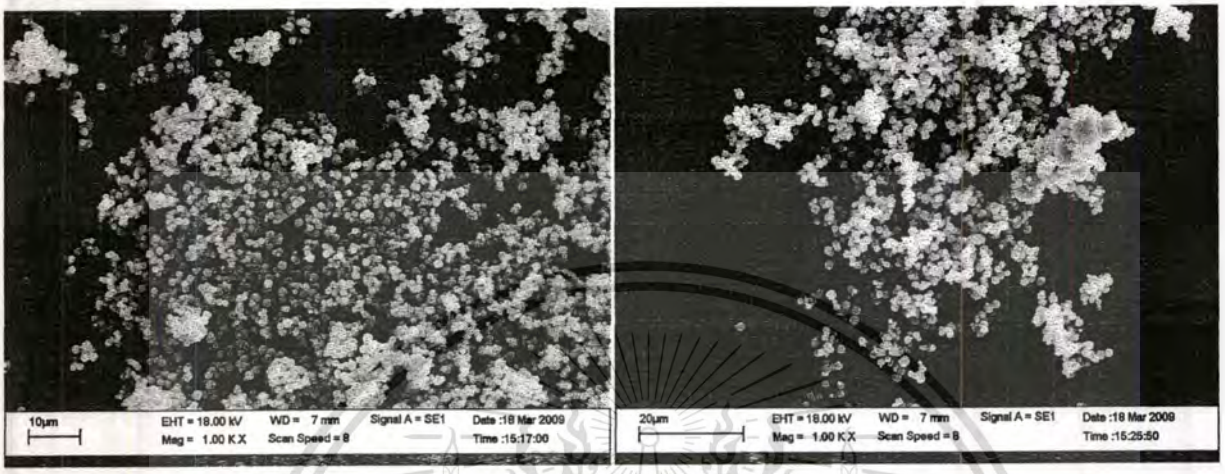
Figure 4.19 SEM picture of zeolite A powder at 2 h (a)and 4 h (b) synthesis time with magnification 1k by using silica from commercial (The composition $3.165Na_2O : Al_2O_3 : 1.926SiO_2 : 128H_2O$)



(a) (b)

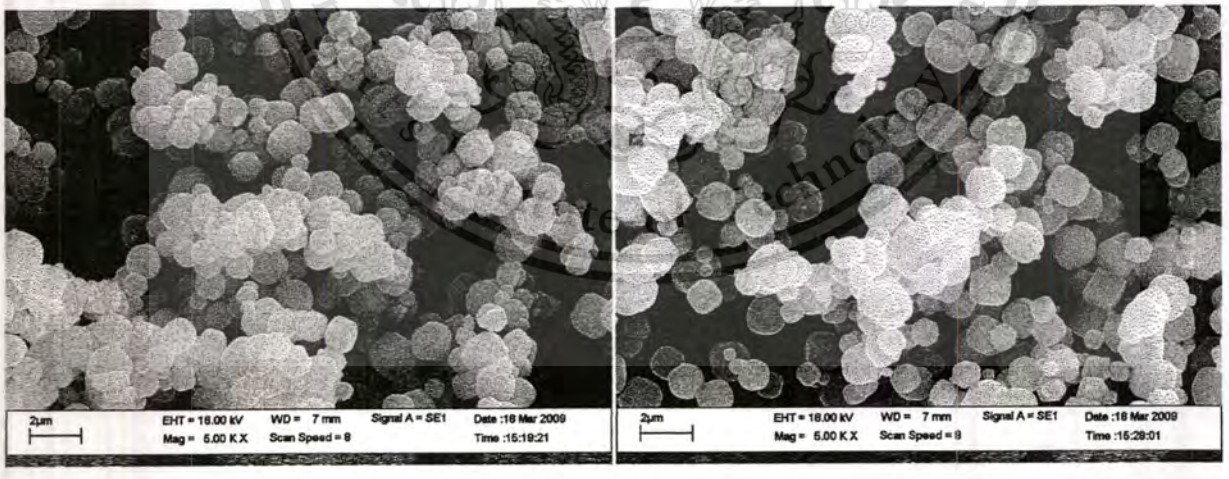
Figure 4.20 SEM picture of zeolite A powder at 2 h (a) and 4 h (b) synthesis time with magnification 5k by using silica from commercial (The composition $3.165Na_2O : Al_2O_3 : 1.926SiO_2 : 128H_2O$)

4.4.2 Zeolite A powder synthesized from the composition $3.165Na_2O : Al_2O_3 : 1.926SiO_2 : 128H_2O$ at 2 h and 4 h synthesis time by used silica source from stock solution



(a) (b)

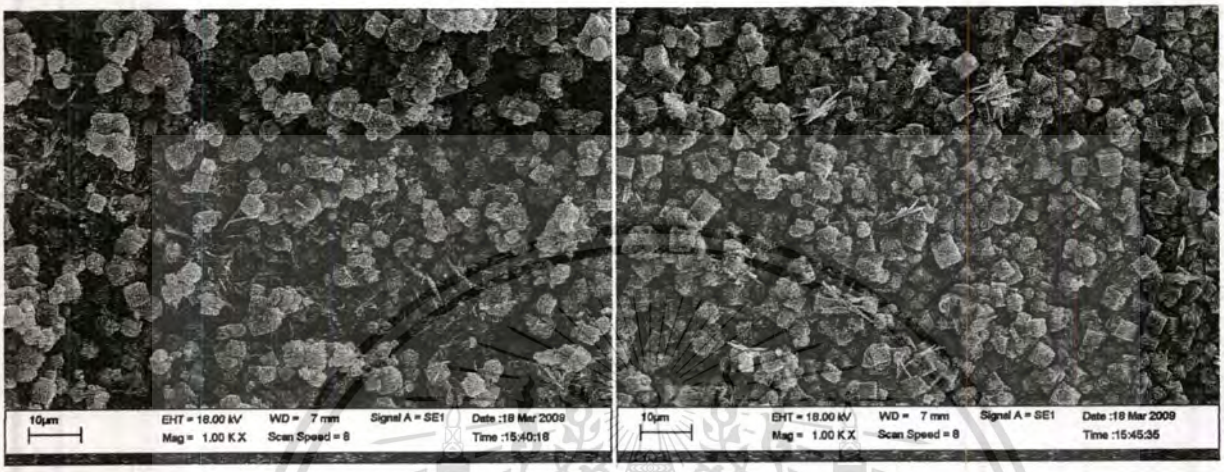
Figure 4.21 SEM picture of zeolite A powder at 2 h (a) and 4 h (b) synthesis time with magnification 1k by using silica from stock solution (The composition $3.165Na_2O : Al_2O_3 : 1.926SiO_2 : 128H_2O$)



(a) (b)

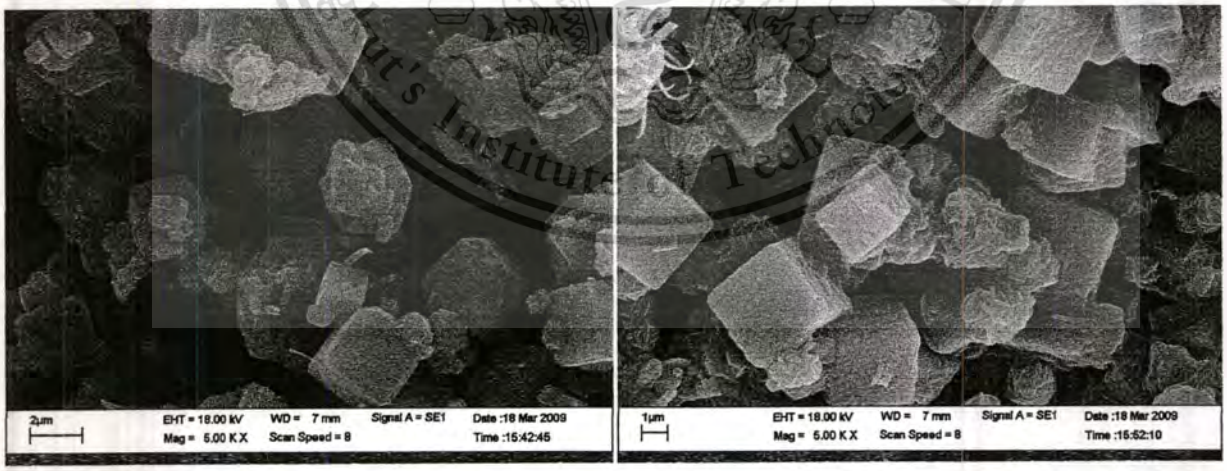
Figure 4.22 SEM picture of zeolite A powder at 2 h (a) and 4 h (b) synthesis time with magnification 5k by using silica from stock solution (The composition $3.165Na_2O : Al_2O_3 : 1.926SiO_2 : 128H_2O$)

4.4.3 Zeolite A membrane synthesized from the composition $3.165Na_2O : Al_2O_3 : 1.926SiO_2 : 128H_2O$ at 2 h and 4 h synthesis time by used silica from commercial



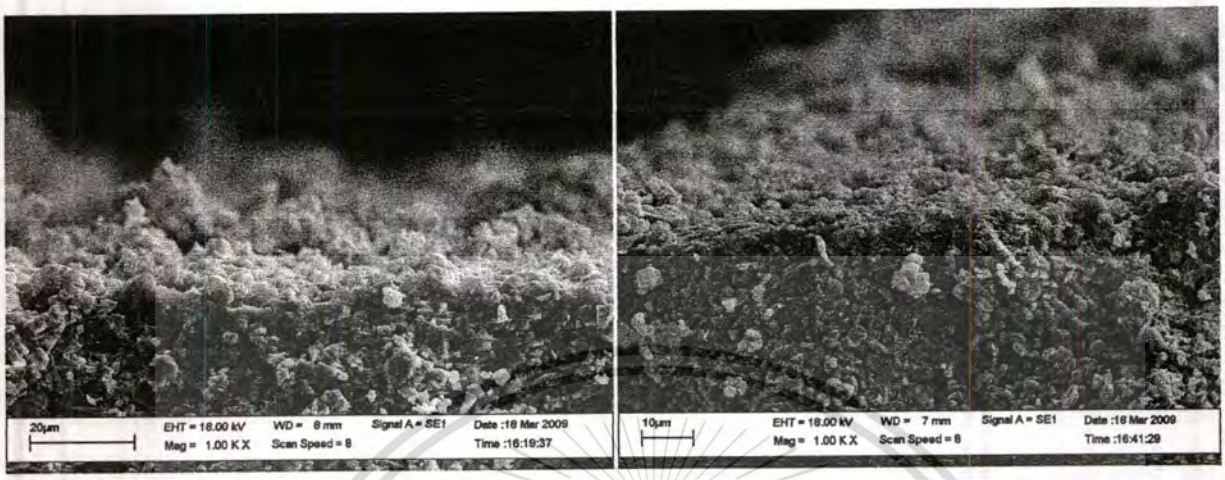
(a) (b)

Figure 4.23 SEM surface picture of zeolite A membrane at 2 h (a) and 4 h (b) synthesis time with magnification 1k by using silica from commercial (The composition $3.165Na_2O : Al_2O_3 : 1.926SiO_2 : 128H_2O$)



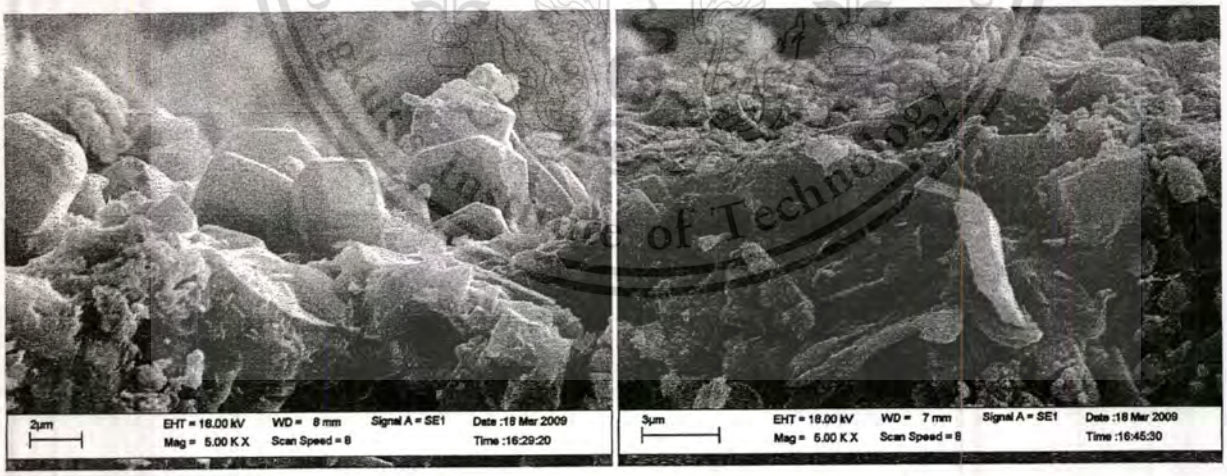
(a) (b)

Figure 4.24 SEM surface picture of zeolite A membrane at 2 h (a) and 4 h (b) synthesis time with magnification 1k by using silica from commercial (The composition $3.165Na_2O : Al_2O_3 : 1.926SiO_2 : 128H_2O$)



(a) (b)

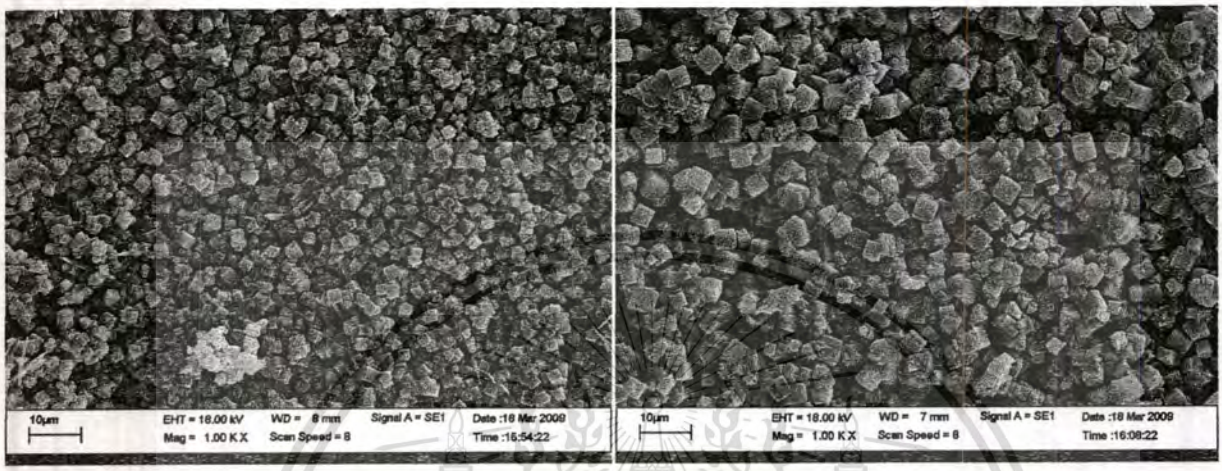
Figure 4.25 SEM cross sectional area of zeolite A membrane at 2 h (a) and 4 h (b) synthesis time with magnification 1k by using silica from commercial (The composition $3.165Na_2O : Al_2O_3 : 1.926SiO_2 : 128H_2O$)



(a) (b)

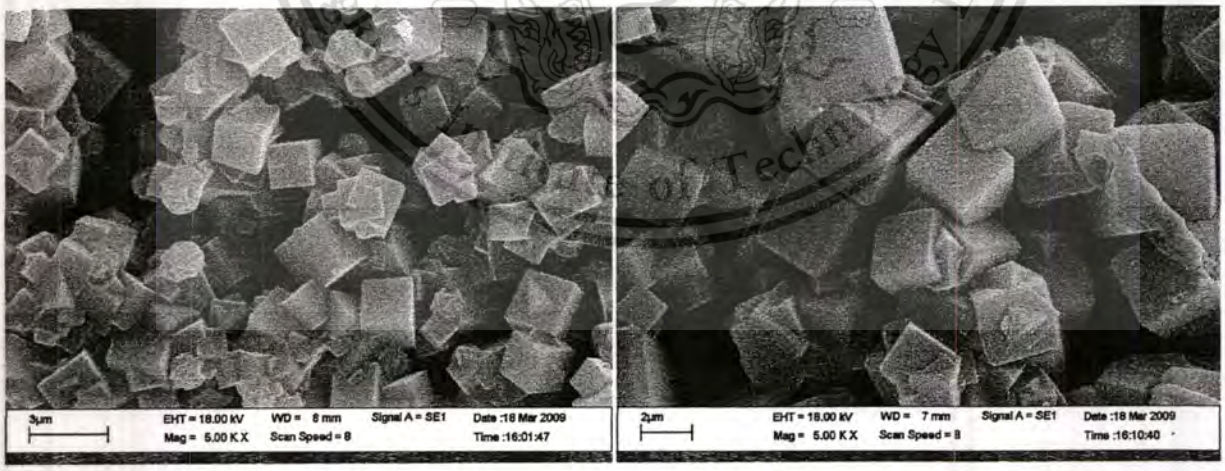
Figure 4.26 SEM cross sectional area of zeolite A membrane at 2 h (a) and 4 h (b) synthesis time with magnification 5k by using silica from commercial (The composition $3.165Na_2O : Al_2O_3 : 1.926SiO_2 : 128H_2O$)

4.4.4 Zeolite A membrane synthesized from the composition $3.165Na_2O : Al_2O_3 : 1.926SiO_2 : 128H_2O$ at 2 h and 4 h synthesis time by used silica from stock solution.



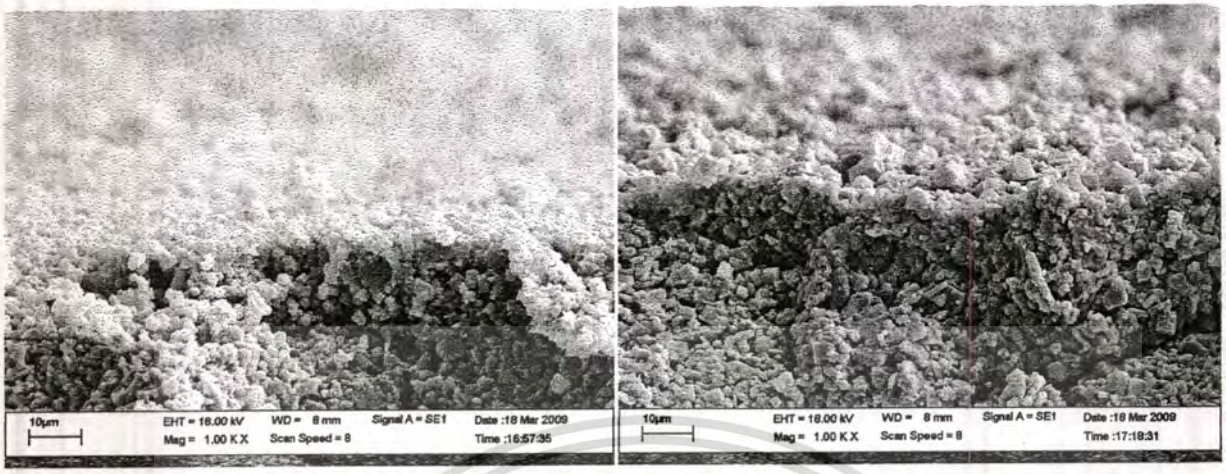
(a) (b)

Figure 4.27 SEM surface picture of zeolite A membrane at 2 h (a) and 4 h (b) synthesis time with magnification 1k by using silica from stock solution (The composition $3.165Na_2O : Al_2O_3 : 1.926SiO_2 : 128H_2O$)



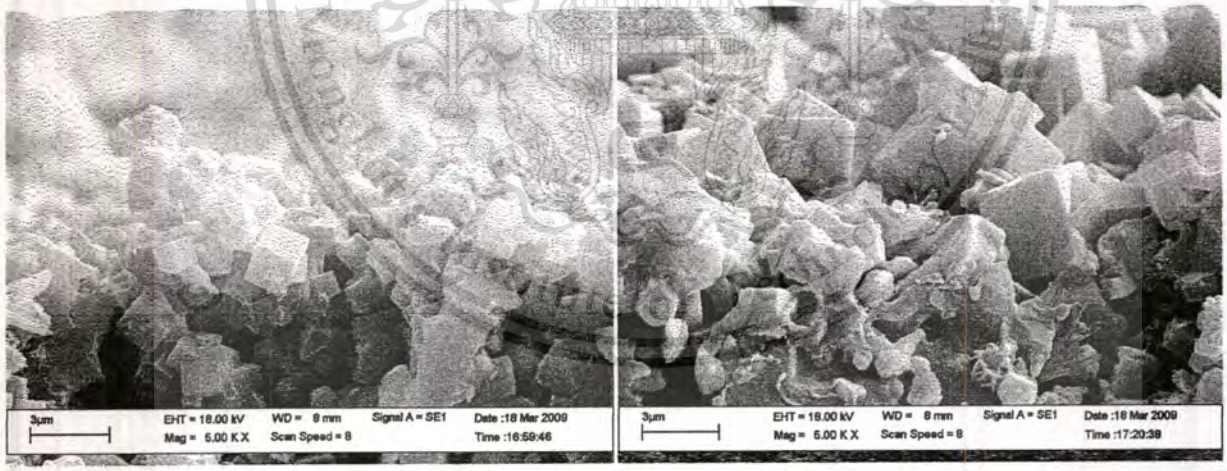
(a) (b)

Figure 4.28 SEM surface picture of zeolite A membrane at 2 h (a) and 4 h (b) synthesis time with magnification 5k by using silica from stock solution (The composition $3.165Na_2O : Al_2O_3 : 1.926SiO_2 : 128H_2O$)



(a) (b)

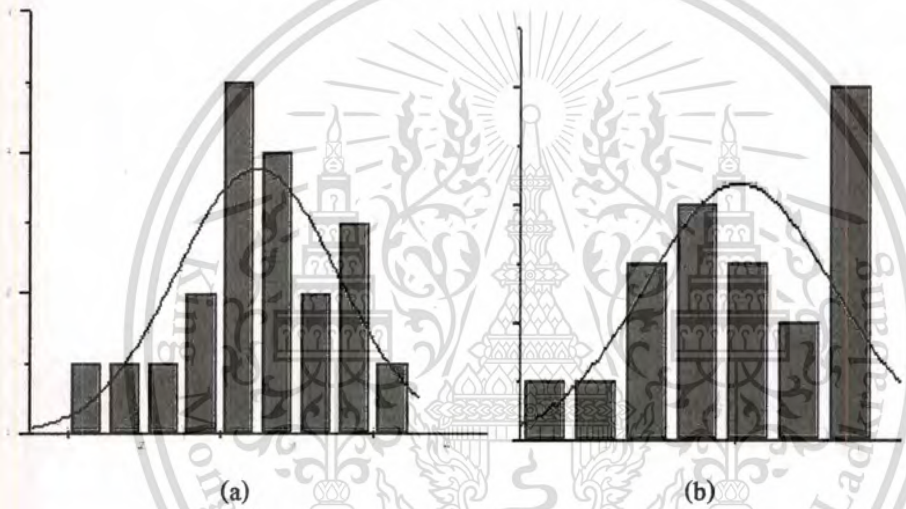
Figure 4.29 SEM cross sectional area of zeolite A membrane at 2 h (a) and 4 h (b) synthesis time with magnification 1k by using silica from stock solution (The composition $3.165Na_2O : Al_2O_3 : 1.926SiO_2 : 128H_2O$)



(a) (b)

Figure 4.30 SEM cross sectional area of zeolite A membrane at 2 h (a) and 4 h (b) synthesis time with magnification 5k by using silica from stock solution (The composition $3.165Na_2O : Al_2O_3 : 1.926SiO_2 : 128H_2O$)

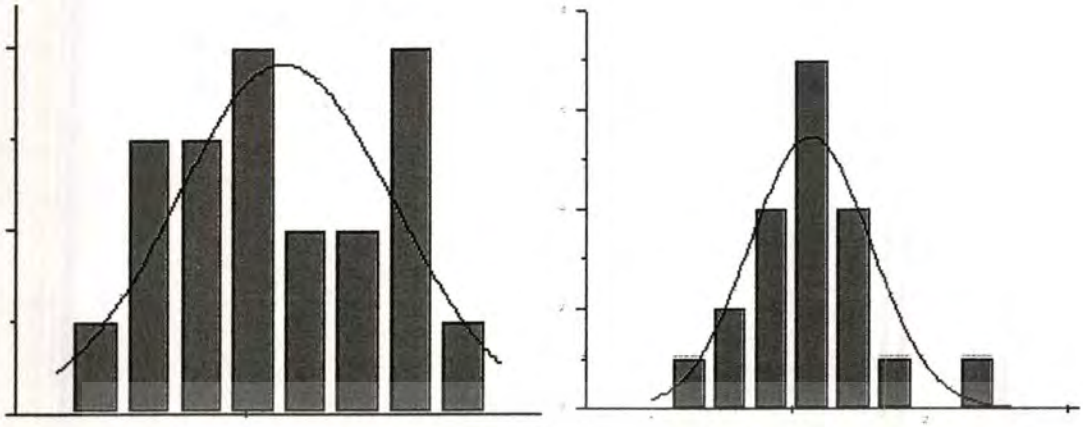
Figures 4.19 and 4.20, the SEM pictures showed the morphology of crystalline zeolite A at 2 h and 4 h synthesis times by the composition $3.165Na_2O : Al_2O_3 : 1.926SiO_2 : 128H_2O$ used silica from commercial and the crystalline look like cubic-shaped. The particle sizes obtained from the imageJ program was showed in Figure 4.31. At 2 h synthesis time the particle size was approximately 2.756 ± 0.53. At 4 h synthesis time the particle size of 2.514 ± 0.367 shown in the Figure 4.31.



(a) (b)

Figure 4.31 The histogram particles sizes of zeolite A powder at 2 h (a) and 4 h (b) synthesis time by using silica from commercial (The composition $3.165Na_2O : Al_2O_3 : 1.926SiO_2 : 128H_2O$)

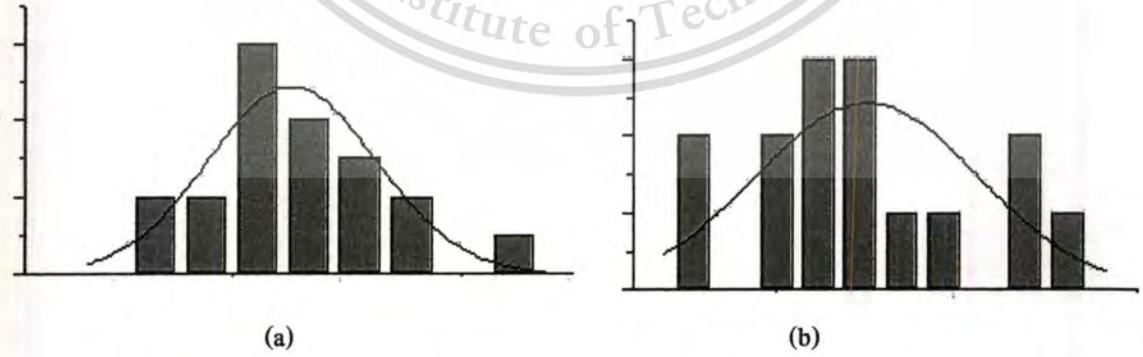
And Figures 4.21 and 4.22 the SEM pictures showed the morphology of crystalline zeolite A at 2 h and 4 h synthesis times by the composition $3.165Na_2O : Al_2O_3 : 1.926SiO_2 : 128H_2O$ used silica from stock solution and the crystalline look like cubic-shape. The particle sizes obtained from the imageJ program was showed in Figure 4.32. At 2 h synthesis time the particle size was approximately 1.556 ± 0.167. At 4 h synthesis time the particle size of 1.566± 0.219 shown in Figure 4.32.



(a) (b)

Figure 4.32 The histogram particles sizes of zeolite A powder at 2 h (a) and 4 h (b) synthesis time by using silica from stock solution (The composition $3.165Na_2O : Al_2O_3 : 1.926SiO_2 : 128H_2O$)

Figure 4.23 and 4.24, the SEM picture showed the surface morphology of crystalline zeolite A on the alumina substrate at 2 h and 4 h synthesis time by using silica from commercial (The composition $3.165Na_2O : Al_2O_3 : 1.926SiO_2 : 128H_2O$). The crystalline zeolite A membrane was successfully growth and fully covered on the alumina substrate which particle size of 3.761 μm at 2 h synthesis time and 3.749 μm at 4 h synthesis time as shown in Figure 4.33.



(a) (b)

Figure 4.33 The histogram particles sizes of zeolite A membrane at 2 h (a) and 4 h (b) synthesis time by using silica from commercial (The composition $3.165Na_2O : Al_2O_3 : 1.926SiO_2 : 128H_2O$)

Figure 4.25 and 4.26, the SEM picture showed the cross-sectional morphology of crystalline zeolite A on the alumina substrate at 2 h and 4 h synthesis time by using silica from commercial (The composition $3.165Na_2O : Al_2O_3 : 1.926SiO_2 : 128H_2O$). The membrane has the thickness around of 6.053 μm ± 0.689 at 2 h synthesis time and 7.623 μm ± 0.426 at 4 h synthesis time as shown Figure 4.34.

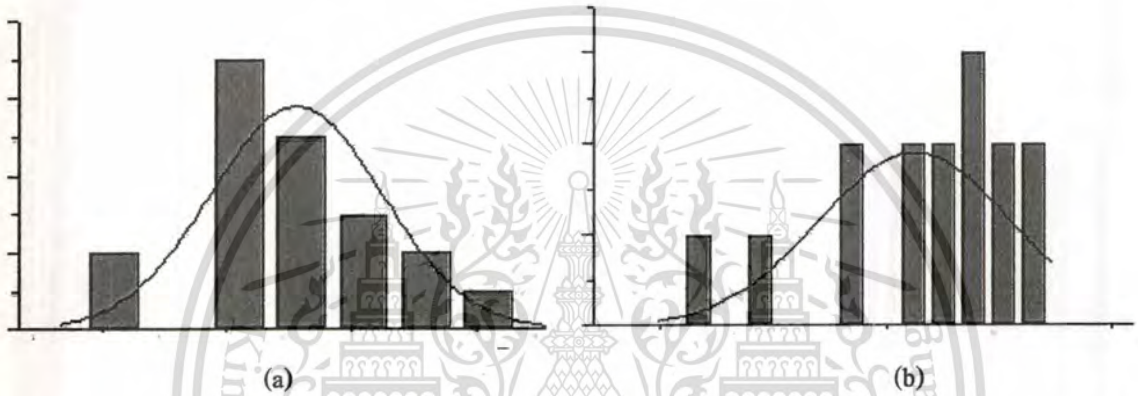
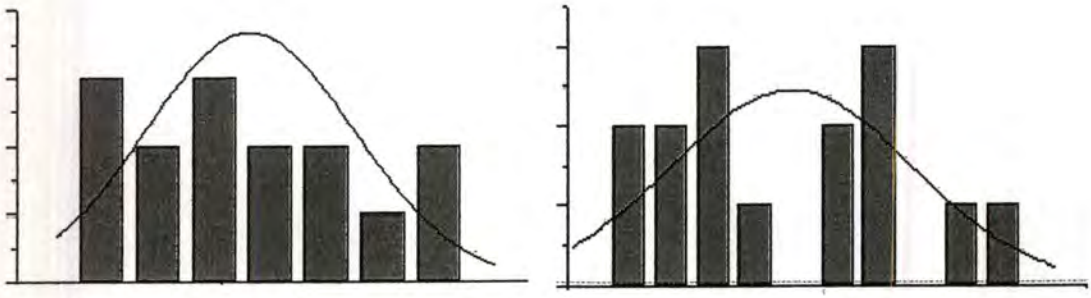


Figure 4.34 The histogram thickness of zeolite A membrane at 2 h (a) and 4 h (b) synthesis time by using silica from commercial (The composition $3.165Na_2O : Al_2O_3 : 1.926SiO_2 : 128H_2O$)

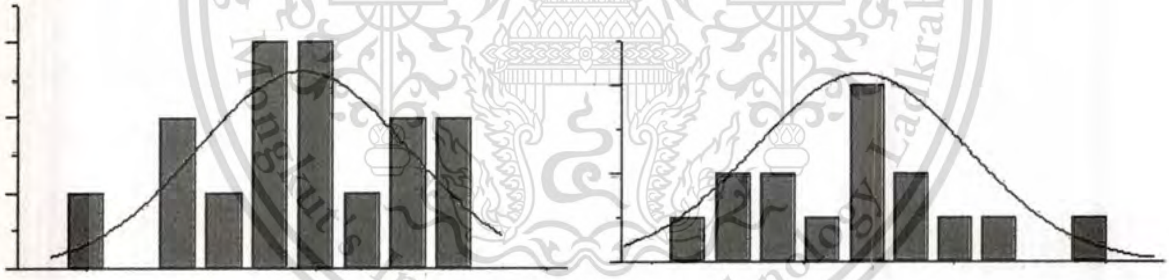
Figure 4.27 and 4.28, the SEM picture showed the surface morphology of crystalline zeolite A on the alumina substrate at 2 h and 4 h synthesis time by using silica from stock solution (The composition $3.165Na_2O : Al_2O_3 : 1.926SiO_2 : 128H_2O$). The crystalline zeolite A membrane was successfully growth and fully covered on the alumina substrate which particle size of 2.554 μm at 2 h synthesis time and 3.93 μm at 4 h synthesis time as shown in Figure 4.35.



(a) (b)

Figure 4.35 The histogram particle sizes of zeolite A membrane at 2 h (a) and 4 h (b) synthesis time by using silica from stock solution (The composition $3.165Na_2O : Al_2O_3 : 1.926SiO_2 : 128H_2O$)

Figure 4.29 and 4.30, the SEM picture showed the cross-sectional morphology of crystalline zeolite A on the alumina substrate at 2 h and 4 h synthesis time by using silica from stock solution (The composition $3.165Na_2O : Al_2O_3 : 1.926SiO_2 : 128H_2O$). The membrane has the thickness around of 3.441 μm ± 0.457 at 2 h synthesis time and 7.88 μm ± 0.705 at 4 h synthesis time as shown Figure 4.36.



(a) (b)

Figure 4.36 The histogram thickness of zeolite A membrane at 2 h (a) and 4 h (b) synthesis time by using silica from stock solution (The composition $3.165Na_2O : Al_2O_3 : 1.926SiO_2 : 128H_2O$)

Regarding to Figure 4.31-4.36, both procedures were reported in the same way. The particles size of zeolite A at 2 h synthesis time was larger than 4 h synthesis time. From cross sectional area picture at 4 h synthesis time was thicker than 2 h synthesis time. At the surface of substrate zeolite A was successfully growth.

Chapter 5

Conclusion and Recommendations

5.1 Conclusion

The rice husk ash was used as raw materials for synthesized zeolite NaA. It was demonstrated that the SiO_2 can be synthesized directly from RHA. Fisrt, Silica was reacted with hydrochloric acid to eliminated organic compounds contained in RHA and then reacted with base (NaOH) where Na_2SiO_3 was formed.

The zeolite A powder was synthesized using silica source from commercial and stock solution. From the XRD and FTIR results, with the synthesis time at 15mins, 30mins and 1 h there were no indication of zeolite A. However, with the synthesis times at 2 h and 4 h the zeolite A powder were presented which can be characterized by XRD and FTIR.

The zeolite A membrane grew on the aluminium oxide substrate by direct synthesis method which the substrate was transferred directly into the mixture solution of zeolite A using HDPE bottles. The thickness of zeolite A was directly affected by the synthesis time. At 2 h synthesis time the thickness of zeolite A grew on the surface around 3.749±0.038 μm whereas, the thickness of zeolite A grew on the surface at 4 h synthesis time around 7.623±0.426 μm. According to expected results, the layer thickness of zeolite A at 4 h synthesis time was thickness than zeolite A at 2 h synthesis time. SEM surface picture at 2 h synthesis time showed that particles of zeolite A was round-shaped but 4 h synthesis time particles showed cube-shaped.

There were 3 procedures used to synthesis zeolite A and zeolite A membrane. The procedure 2.1.1 and 2.2.2 (the composition $3.165Na_2O : Al_2O_3 : 1.926SiO_2 : 128H_2O$ which

using silica from commercial or stock solution) were preferable methods to synthesis zeolite A and zeolite A membrane. However, the procedure 2.2 can not synthesize zeolite A. The procedures 2.1.1 and 2.2.2 was used the composition $3.165Na_2O_3 : Al_2O_3 : 1.926SiO_2 : 128H_2O$ for synthesis zeolite A and zeolite A membrane. The procedure 2.2 was used the composition $49Na_2O_3 : Al_2O_3 : 5SiO_2 : 980H_2O$ for synthesis but the results did not show the zeolite A.

5.2 Recommendations

The experimenter must keep an eye on temperature and times carefully. There are many compositions ratios to prepare precursors of zeolite NaA and zeolite NaA membrane if high pressure require autoclaves was recommended because HDPE bottles can not resist high pressure.

REFERENCES

[1] Didik Prasetyoko, Zainab Ramli, Salasiah Endud, Halimaton Hamdan, Bogdan Sulikowski "Conversion of rice husk ash to zeolite beta" Waste Management 26(2006) 1173-1179

[2] K. Kordatos, S. Gavela, A. Ntziouni, K.N. Pistiolas, A. Kyritsi, V. Kasselouri-Rigopoulou. "Synthesis of highly siliceous ZSM-5 zeolite using silica from rice husk ask". Microporous and mesoporous materials, ELSEVIER 2007

[3] Scott M. Averbach, Kathleen A. Carrado, Prabir K. Dutta "Handbook of zeolite Science and Technology", Marcel Dekker;2003.

[4] F. Liebau, H. Gies, RP Gunawardne, B Marles. Zeolite6:373-377 , 1986

[5] Marc Pera-Titus, Marta Bausach, Joan Llorens, Fidel Cunill, "Preparation of inner-side tubular zeolite NaA membranes", Chemical Engineering Department, University of Barcelona; http://www.sciencedirect.com

[6] Xiongfu Zhang, Haiou Liu and King Lun Yeung, "Novel two-layered zeolite NaA-silicalite-1 membranes"; http://www.sciencedirect.com

[7] http://www.iza-structure.org

[8] Huanting Wang, Limin Huang, Brett A. Holmberg and Yushan Yan "Nanostructured zeolite 4A molecular sieving air separation membranes" Department of Chemical and Environmental Engineering, University of California; http://www.rsc.org/chemcomm

[9] Harry Robson and Karl Petter Lillerud, "Verified Syntheses of Zeolitic Materials 2nd edition" Elsevier Science B.V.(2001)

[10] http://www.ricehuskash.com/details.htm

[11] Burachat Chatveera, "Properties of Rice husk ash brick" Faculty of Engineering, Thammasat University

[12] Xiaochun Xu, Weishen Yang, Jie Liu, Liwu Lin, Norbert Stroh and Herwig Brunner "Synthesis of NaA zeolite membrane on a ceramic hollow fiber" Fraunhofer Institute for Interfacial Engineering and Biotechnology; http://www.sciencedirect.com

[13] Hadi Nur "Direct synthesis of NaA zeolite from rice husk and carbonaceous rice husk ash" Catalysis Research Center, Hokkaido UniversityCatalysis Research Center, Hokkaido University; http://www.sciencedirect.com

[14] Diego Ivan Petkowicz, Reus Tiago Rigo, Cláudio Radtke, Sibele B. Pergher and João H.Z. dos Santos, "Zeolite NaA from Brazilian chysotile and rice husk" Microporous and Mesoporous Materials; http://www.sciencedirect.com

[15] Jaco Zah, Henning M. Krieg and Jaco C. Breytenbach, "Layer development and growth history of polycrystalline zeolite A membranes synthesised from a clear solution" North-West University, South Africa; http://www.sciencedirect.com

[16] PANalytical's website http://www.panalytical.com/index.cfm?pid=135

[17] Azaroff, L.V. ; R. Kaplow, N. kato, R.J. Weiss, A.J.C. Wilson, R.A. Young(1974). X-ray diffraction. Mc Graw-Hill.

[18] Glatter, O. Kratky(1982). Small Angle x-ray Scattering. Academic Press.

[19] Frank A.Settle, "Handbook of Instrumental Techniques For Analytical Chemistry"; Prentice-Hall Inc. (1997)

[20] Iowa State University Material Science & Engineering Dept. "http://mse.iastate.edu/microscopy/home.html"

[21] von Andenne, Manfred(1938). "Das Elektronen-Rastermikroskop Theoretische Grundlagen" Lin German. Zeitschrift fur Physik 108:553-572

[22] Danilatos, GD (1990) "Theory of the Gaseous Detector Device in the SEM" Advance in Electronics and Electron Physics 73:1-102

[23] K.D.O. Jackson, M.J.R. Loadman, C.H. Jones and G. Ellis, "Spectrochim. Acta" 46A, 217 (1990)

[24] K.D.O. Jackson and P.J. Hendra, "Spectrochim.Acta" 50A, 1987 (1994)

[25] C.V. Raman, Nature 21, 619 (1928)

Appendix

Calculations the composition of zeolite NaA

1. Synthesis silicon dioxide from RHA.

From this equation :

$$SiO_2\,(s) + 2NaOH\,(s) \rightarrow Na_2SiO_3\,(l) + H_2O\,(l)$$

The amount of SiO_2 in the RHA was calculated by

SiO_2; SiO_2 = mole × MW.

= 1 mole × 60 g/mole

= 60 g

For RHA 15 g, which RHA contain 90% of silica.

Thus; Mole of SiO_2 $= \left(\frac{15\text{ g RHA} \times 0.9\ SiO_2}{60\frac{g}{mole}\ SiO_2}\right)$

= 0.225 mole of SiO_2

The amount of NaOH used to formed sodium metasilicate by

NaOH; NaOH = mole × MW.

= 1 mole × 40 g/mole

= 40 g NaOH

As equation showed the ratio of $1\ SiO_{2\,(s)} : 2\ NaOH_{\,(s)}$

Weight of NaOH $= 0.225\text{ mole } SiO_2 \times \frac{2\text{ mole of NaOH}}{1\text{ mole of } SiO_2} \times \frac{40\text{ g of NaOH}}{1\text{ mole of NaOH}}$

= 18 g of NaOH

NaOH was diluted to 10% wt/volume;

10 g of NaOH was diluted to 100 ml

If 18 g 0f NaOH used was diluted to $\frac{100\text{ ml}}{10\text{ g of NaOH}} \times 18\text{ g of NaOH}$

= 180 ml

2. Synthesis zeolite A and zeolite A membrane by used silica source form commercial.

BATCH :	Na_2O	Al_2O_3	SiO_2	H_2O
COMPOSITION :	3.165	1	1.926	128

In these method sodium aluminate, sodium metasilicate, sodium hydroxide and water were used to synthesized which molecular weights of each compounds show below;

Sodium aluminate	$Na_2Al_2O_4 \cdot 3H_2O$	218	g/mol
Sodium metasilicate	$Na_2SiO_3 \cdot 9H_2O$	284.2	g/mol
Sodium hydroxide	NaOH	40	g/mol
DI water	H_2O	18	g/mol

From batch compositions Al_2O_3 was prepared by the amount of $Na_2Al_2O_4$ used as equation below;

$$Na_2Al_2O_4 \cdot 3H_2O \rightarrow Al_2O_3 + Na_2O + 3H_2O$$

The $Na_2Al_2O_4$ 1 mol presented 1mol of Al_2O_3 and 1 mol of Na_2O

Al_2O_3; Al_2O_3 = mole × MW.

= 1 mole × 102 g/mole

= 102 g

Na_2O; Na_2O = mole × MW.

= 1 mole × 62 g/mole

= 62 g

Molecular weights of $Na_2Al_2O_4$ = 164 g

∴ 218 g of $Na_2Al_2O_4 \cdot 3H_2O$ was prepared.

As equation below, Na_2SiO_3 presented 1 mol of SiO_2 and 1 mol of Na_2O.

$$Na_2SiO_3 \cdot 9H_2O \rightarrow SiO_2 + Na_2O + 9H_2O$$

SiO_2; SiO_2 = mole × MW.

= 1.916 mole × 60 g/mole

= 115.56 g

Molecular weights of Na_2SiO_3 = 122.2 g

Molecular weights of $Na_2SiO_3 \cdot 9H_2O$ = 284.2 g

$$1.926 \text{ mol } Na_2SiO_3 \cdot 9H_2O = \frac{284.2 \text{ g } Na_2SiO_3 \cdot 9H_2O \times 1.926 \text{ mol}}{1 \text{ mol } Na_2SiO_3 \cdot 9H_2O}$$

= 547.3692 g of $Na_2Si_2O_3$

From 284.2 g $Na_2SiO_3 \cdot 9H_2O$ have 62 g Na_2O

$$547.3692 \text{ g } Na_2Si_2O_3 = \frac{547.3692 \text{ g } Na_2SiO_3 \times 62 \text{ g } Na_2O}{284.2 \text{ g } Na_2SiO_3 \cdot 9H_2O}$$

= 119.412 g of Na_2O

∴ 218 g of $Na_2SiO_3 \cdot 9H_2O$ was prepared.

As 2 mol of NaOH presented 1 mol of Na_2O and 1 mol of H_2O as show in equation below.

$$2NaOH \rightarrow Na_2O + H_2O$$

Molecular weights of Na_2O = 62 g

Molecular weights of NaOH = 40 g

$$3.165 \text{ mol } Na_2O = \frac{3.165 \text{ mol } Na_2O \times 62 \text{g} Na_2O}{1 \text{ mol } Na_2O}$$

= 196.23 g of Na_2O

Calculate Na_2O from Na_2SiO_3 and $Na_2Al_2O_4$ = 62 g Na_2O +119.412 g Na_2O

= 181.412 g of Na_2O

Thus; 196.3 g Na_2O – 181.412 g Na_2O = 14.818 g Na_2O

$$\frac{14.818 \text{ g } Na_2O \times 1 \text{ mol } Na_2O}{62 \text{ g } Na_2O} \cdot 80 \text{ g } 2NaOH = 19.12 \text{ g of NaOH}$$

∴ 19.12 g of NaOH was prepared.

Calculate volume 128 mol of H_2O

H_2O = mole × MW.

= 128 mole × 18 g/mole

= 2304 g of H_2O

From volume of H_2O in Na_2SiO_3 = 162 g H_2O

From volume of H_2O in $Na_2Al_2O_4$ = 54 g H_2O

Thus; volume of H_2O = 2304 g H_2O - 54 g H_2O - 162 g H_2O

= 2160 g H_2O

As we want to prepare 80 ml of mixture.

divide by 27; NaOH $= \frac{19.12}{27}$ = 0.7081 g NaOH

$Na_2Al_2O_4 \cdot 3H_2O$ $= \frac{218}{27}$ = 8.07407 g $Na_2Al_2O_4$

$Na_2SiO_3 \cdot 9H_2O$ $= \frac{196.23}{27}$ = 20.2729 g $Na_2Si_2O_3$

H_2O $= \frac{2160}{27}$ = 80 g H_2O **Ans**

3. Synthesis zeolite A and zeolite A membrane by used silica source form stock solution

As this procedure use the same composition as in part 2 and the composition was calculated in part 2 showed below;

19.12 NaOH : 218 $Na_2Al_2O_4$: 547.3692 Na_2SiO_3 : 2160 H_2O

We want to calculate at 80 ml so; the composition was divided by 43.2

NaOH $= \frac{19.12}{43.2}$ = 0.44157 g of NaOH

$Na_2Al_2O_4$ $= \frac{218}{43.2}$ = 5.0346 g of $Na_2Al_2O_4$

$Na_2Si_2O_3$ $= \frac{196.23}{43.2}$ = 12.64132 g of $Na_2Si_2O_3$

H_2O $= \frac{2160}{43.2}$ = 50 g of H_2O

Calculate the concentration stock solution which consists of 15 g of RHA, 17.55 g of NaOH and dilute to 180 ml;

$$\frac{\frac{g}{Mw}}{\frac{(17.55+14.7)}{122.2}} = \frac{\frac{CV}{1000}}{\frac{C \cdot 180}{1000}}$$

$$C = 1.457\ M$$

Calculate SiO_2;

Calculate concentration of $Na_2Si_2O_3$ at 50 ml

$$\frac{12.67058\ g\ of\ Na_2SiO_3}{284\ g\ of\ Na_2SiO_3} = \frac{C \cdot 50\ ml}{1000}$$

$$C = 0.891667\ M$$

Find volume of SiO_2

$$C_1V_1 = C_2V_2$$

$$0.891667 \times 50\ ml = 1.457 \times V_2$$

$$V_2 = 19.40059\ ml$$

Thus; volume of stock solution $= 19.40059\ ml \approx 19.5\ ml$

∴ The volume of aluminate solution was prepared by 0.44157 g of NaOH, 5.0346 g of $Na_2Al_2O_4$ and 30.5 ml of DI water.