SYNTHESIS NANOZEOLITE A

NATSAREE MANUMAPHORN

POONSIRI RUAMMEK

ATITAYA MARASRI

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Student	Natsaree	Manumaphorn
	Poonsiri	Ruammek
	Atitaya	Marasri
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Advisor	Assoc. Prof. Tawan Sooknoi	

ABSTRACT

This special project is to study factors for synthesis of zeolite A nanoparticles and to study the properties of nanozeolite A as cation exchange or liquid surfactant carrier that is required for detergent industrial. The nanozeolite NaA was synthesized from various Si sources (fumed silica, sodium meta silicate, and Ludox AS40) and sodium aluminate. The gel with a molar composition of 1.80 SiO_2: 1.00Al_2O_3: 3.95Na_2O: 110.05H_2O, was aged at 0-20°C for 6-24 hours and then crystallized at 75-105°C for another 1-5 hours. From SEM & XRD images, zeolite A synthesized from fumed silica provided relatively small particle size and high crystallinity as compared with other sources. It was also found that the aging time effect to size distribution and relative crystallinity. In addition, aging temperature at 10-20°C gave the small particle size in range 200-400 nm, but the zeolite contained impurities. The result of decreased basicity showed that zeolite sample possessed high crystallinity with relatively large particles size. The crystallization temperature would not effect to zeolite particle size in this project. However, particle size would increase with increasing crystallized time. Cation exchange capacity became high when zeolite particle size is large. On the other hand, liquid carrying capacity increased when the particle size was decreased.

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Natasaree Manumaphorn

Poonsiri Ruammek

Atitaya Marasri

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CHAPTER 1

INTRODUCTION

1.1 Motivation

Zeolites and related crystalline microporous materials become currently more important and popular because of the great variety of applications. Their ion exchange properties enable applications in the purification of wastewater or as detergent builders.[1]

One of the main applications of zeolite A is as builder in detergents. Recently, environmental concerns of pollution from phosphate component have resulted in the replacement of it by zeolite A in detergent formulations without altering their softening characteristics. This has reduced environmental problems and capital consumption of detergent. The application and usage of this material can optimize the sewage treatment plant.[2]

However, zeolite that possess with large particle size (more than 1 micron) could not be used in liquid detergent because it would precipitate from the liquid during storage. Moreover the zeolite with large particle size also provided low liquid carrying capacity and left stain when used as powder detergent builders. Accordingly, the zeolite with nanoparticle may be able to solve the problems in both detergents. In case of liquid detergent, it would disperse well and remained stable during storage. On the other hands, nanozeolite would leave no stain on cloth and increased liquid carrying capacity for powder detergent.

In this project, nano-sized particles of zeolite A were prepared with various conditions. The influences of different parameters such as aging, crystallization time and temperature, and the initial gel composition on the quality of the final products were studied. The synthesis procedure for nanozeolite A was optimized with available quality control test, namely Cation Exchange Capacity (CEC) and Liquid Carrying Capacity (LCC).[3],[4]

1.2 Objectives

1.2.1 To obtain zeolite A with nanoparticle size and high crystallinity.

1.2.2 To understand the effect of silica sources, time and temperature of aging and crystallization on the zeolite particle size of the zeolite formed.

1.2.3 To understand the effect of zeolite particle size on Cation Exchange Capacity (CEC) and Liquid Carrying Capacity (LCC).

1.3 Scope of work

The scope of study on synthesizes zeolite NaA into nanosize is as follow:

1.3.1 Synthesis of zeolite A nanoparticles with certain gel compositions.

1.3.2 Synthesis zeolite A from different silica sources.

1.3.3 Study the effect of aging temperature and time.

1.3.4 Study the effect of crystallization temperature and time.

1.3.5 Characterization of zeolite A by XRD, SEM, and TGA.

1.3.6 Study on the properties for detergent builders; Cation Exchange Capacity (CEC) and Liquid Carrying Capacity (LCC).

1.4 Expected result

It is expected that the crystalline nanozeolite A could be further used in detergent manufacture as the liquid and powder detergent builders.

CHAPTER 2

Theory and Literal Reviews

2.1 Zeolites

Zeolites are crystalline aluminosilicates of group IA and group IIA elements, such as sodium, potassium, magnesium and calcium.[6] Structurally, zeolites are complex, crystalline inorganic polymers based on an infinitely extending three-dimensional, four-connected framework of $[AlO_4]^-$ and SiO_4 tetrahedra linked to each other by the sharing of oxygen ions. Each $[AlO_4]^-$ tetrahedron in the framework bears a net negative charge which is balanced by an extra-framework cation. The framework structure contains intracrystalline channels or interconnected voids that are occupied by the cations and water molecules. The cations are mobile and ordinarily undergo ion exchange. Zeolites are represented by the empirical formula:

$$M_{2/n}O \cdot Al_2O_3 \cdot xSiO_2 \cdot yH_2O$$

Where M is the charge balancing cations with the valance n, x is ≥ 2,and y is in range of 10 - 10000.

Different zeolites may have different Si/Al ratios and the tetrahedral SiO_4, $[AlO_4]^-$ can also be isostrucally by other elements such as Ga, Ge, Mn, Ti, and P, generating a molecular sieve.[7] The amount of Al within framework can vary over a wide range, with Si/Al = 1 to ∞ , the completely siliceous from being polymorphs of SiO_2. Lowenstein proposed that that lower limit of Si/Al = 1 of a zeolite arises because placement of adjacent $[AlO_4]^-$ tetrahedra is not favored of electrostatic repulsions between the negative charges. The framework composition depends on the synthesis conditions. Post synthesis modifications that insert Si or Al into framework have also been developed. As the Si/Al ratio of the frameworks increases, the hydrothermal stability as well as the hydrophobicity increases.

There are about 40 natural zeolites that have been identified during the past 200 years. The most common are analcime, chabazite, clinoptilolite, erionite, ferrierite, heulandite, laumontite, mordenite, and phillipsite. There are also more than 150 zeolites that have been synthesized and the most common are zeolites A, X, Y, and ZMS-5. Natural and synthetic zeolites are used

commercially because of their unique adsorption, ion-exchange, molecular sieve, and catalytic properties.[8]

2.1.1 Zeolite A (LTA)

Zeolite A is one of the most important industrial zeolites which is used as a builder in detergent powders and tablets for water softening in the washing process which exhibits the LTA (Linde Type A) structure. The secondary building units (SBU) of zeolite A are double 4-ring, the β-cage (sodalite cage) and the α-cage. The structure of zeolite A consider the arrangement of 24 primary building blocks, namely, SiO_4 and $[AlO_4]^-$ tetrahedral to form the tetrahedron cluster. This secondary building unit is called β-cage or sodalite cage (Figure2.1)

Figure 2.1 The cage structure of α-cage and β-cage (sodalite cage).

When the sodalite cages are connected by bridging oxygen ions between the four-membered oxygen rings. This structure has larger apertures than sodalite structure, shown in Figure 2, namely eight-membered oxygen rings and opening into cavity, called an α-cage, is arounded by eight sodalite cage. α-cage is characteristic of zeolite A, among other. Zeolite A has a void volume faction of 0.47, with Si/Al ratio of 1.0.

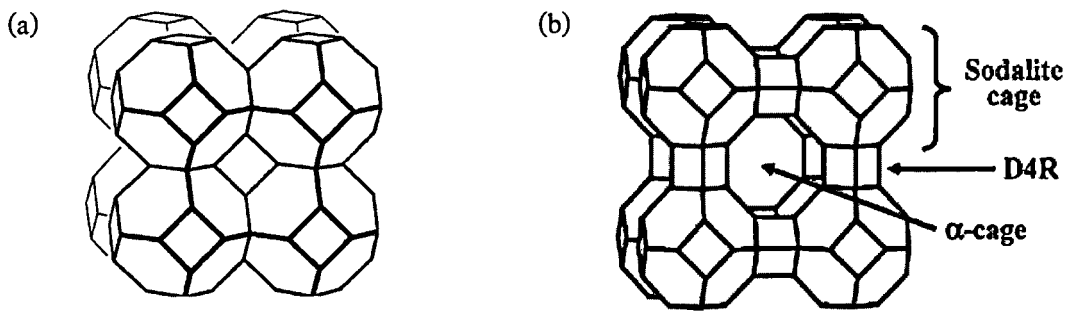


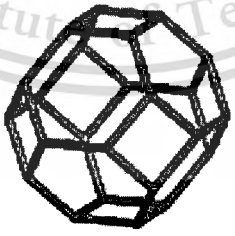
Figure 2.2 (a) Sodalite framework as an assembly of β-cages and (b) is Structure of zeolite A

Zeolite A has a three-dimensional pore system and molecules can diffuse in all three directions in space by moving across the 8-ring windows that connect the cavities. The windows have free diameter of approximately 4 Å. The composition of hydrated zeolite A as usually obtained from industrial is close to $[Na_{96}(H_20)_{216}][Al_{96}Si_{96}O_{384}]$-LTA.

2.1.2 Framework of Zeolite A (LTA)[9]

Space Group	:	Pm-3m
Cell Parameters	:	a = 11.919 Å b = 11.919 Å c = 11.919 Å
		α = 90.000° β= 90.000° γ= 90.000°
		Volume = 1693.24 Å^3
		R_{DLS} = 0.0026
Framework density(FD_{Si})	:	14.2 T/1000 Å^3
Ring sizes (# T-atoms)	:	8 6 4
Topological density	:	TD_{10} = 641 TD = 0.533333
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



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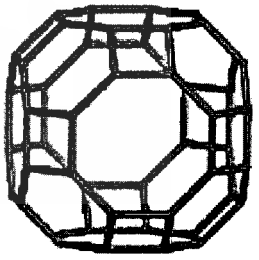


lta

2.1.3 Synthesis of zeolite[10]

Natural zeolites are found in volcanic or metamorphic rocks and their growth involves geological conditions (low temperature and pressure, low pH (8-9)) and time scale (thousands of years). Early efforts have been made by Saint Claire de Ville in 1862 to synthesize zeolites. The absence of reliable characterization methods made it impossible to verify that zeolites were indeed fabricated. The first precise confirmation of zeolite synthesis can be traced in 1948 when Barrer reported the synthesis of an analogue of mordenite. At the same time Milton and Beck succeeded in synthesizing other zeolite types using lower temperatures (≈100 °C) and a higher alkalinity. It led to the discovery of one of the most commercially successful zeolites, which has no natural counterpart, Linde A (LTA). Since then many new zeolite framework types have been attained thanks to important efforts by oil companies. In the early 1960s Barrer and Denny were the first to replace inorganic bases in the synthesis mixture with organic molecules. The use of quaternary ammonium salts resulted in an increase in the Si/Al ratio and the discovery of ZSM-5, being the most important new structure. The quest for higher Si/Al ratios ended in 1978 when Flanigen et al. reported the synthesis of silicalite-1which is the all-silica counterpart of ZSM-5. This material shows remarkable properties because of its hydrophobic and organophilic character. A new class of materials analogous to zeolites was introduced in the 1980s: microporous aluminophosphates. Nevertheless, poor thermal and hydrothermal stability of their metal substituted analogues hindered their commercial applications. The most noteworthy advance in crystalline microporous solids has recently been the synthesis of extra large pore zeolites with more than 12-ring apertures.

Zeolite synthesis has been extensively reviewed in several books and literature on this subject is abundant. The synthesis of zeolites is carried out under hydrothermal conditions. An aluminate solution and a silicate solution are mixed together in an alkaline medium to form a milky gel or in some instances, clear solutions. Various cations or anions

can be added to the synthesis mixture. Synthesis proceeds at elevated temperatures (60-200 °C) where crystals form through a nucleation step. The following sections give a general overview on

the parameters governing zeolite synthesis. Emphasis will be given to structure direction by organic molecules. A schematic representation of zeolite formation process is given in figure 2.3

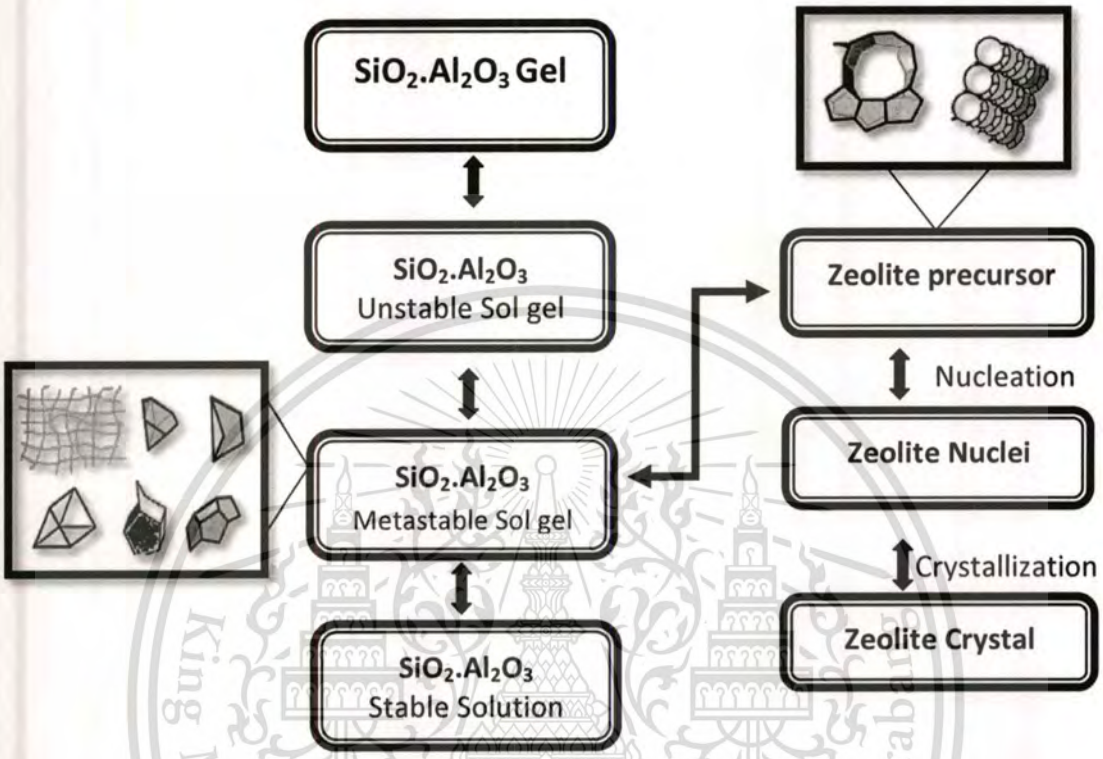


Figure 2.3 Simplified zeolite synthesis scheme.

a) Molar composition

Although this is not an independent parameter, every zeolite has a specific molar composition range often represented graphically in a ternary compositional phase diagram (Na_2O, Al_2O_3 and SiO_2). On the other hand, each structure will also impose constraints on the amount of Al it can incorporate. High-silica molecular sieves such as ZSM-5 can be synthesized over a wide range of Si/Al ratios (Si/Al from 7 to infinity35).

b) Mineralizer

A mineralizer is a species which enables the formation of a more stable solid phase from a less stable solid phase via dissolution and crystallization. Supersaturation can be reached by dissolution and these soluble species are then available for nucleation and crystal growth. In most

cases, hydroxyl ions act as mineralizing agents. Indeed, OH^- increases the solubility of silica by depolymerizing amorphous silica particles. Oligomeric species are then present in solution. Condensation of specific aluminosilicate species, facilitated by the presence of OH^-, occurs and leads to the appearance of the first crystals. In general high pH values increase crystal growth rates and shorten the nucleation period. Hydroxyl ion concentration can also influence crystal morphology, crystal yield and final zeolite structure.

Fluoride ions have been used as mineralizers. Silicalite-1 was the first zeolite synthesized from acidic F- medium. Fluoride anions act similarly to hydroxyl ions without contributing directly to the pH of the system. Nucleation and crystal growth rates are generally slowed down resulting in large and high quality crystals. The fluoride ion synthesis route has mostly been applied in the area of aluminophosphates mainly because it has led to the discovery of novel aluminophosphates and isomorphously substituted versions that cannot be obtained at high pH.

c) Inorganic cations

Inorganic cations have been regarded as an important parameter influencing the structure formed. They are involved in structure direction, solid yield, crystal morphology and purity. Most of the synthetic analogues of natural zeolites were obtained using alkali and alkaline earth metal cations. Nucleation and crystal growth can be optimized by the right choice of inorganic cations.

d) Temperature

Temperature can alter the zeolite structure as well as the induction period and crystal growth kinetics. The activation energies of zeolite synthesis are quite significant.

e) Silica and alumina sources

Nucleation and growth kinetics can depend on the dissolution of the solid reagents and formation of aluminosilicates precursors. Kuhl found that crystallization of some structures was dependent on the degree of prepolymerization of the silica source. Mintova and Valtchev recently investigated the colloidal distribution of silicalite-1 synthesis mixtures containing different silica

sources. Impurities in silica or alumina sources are likely to influence crystallization kinetics and framework composition.

Typical precursor materials are the listed below:

- Water content; since the composition of reaction mixture is given as ratio of oxide, any hydroxides employed to be considered as oxides plus water.
- Sources of Silica.
- Sources of Alumina.

2.1.4 Properties of Zeolites

Ion Exchange [11]

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 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 pored due to their size. Zeoites 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.

Adsorption and separation

Adsorption and separation are based on chromatographic processes which happen on the surface of zeolite crystals and are determined both by different migration speed of various compounds along the surface of adsorbent due to diversity in the intensity of their interactions with the surface and due to steric effects. The shape-selective properties of zeolites are the basis for their use in molecular adsorption. The ability preferentially to adsorb certain molecules, while excluding others, has opened up a wide range of molecular sieving applications. Sometimes it depends merely on the size and shape of pores controlling access into the zeolites; in other cases different types of molecule enter the zeolite, but some diffuse through the channels more quickly, leaving others stuck behind, as in the purification of para-xylene by the zeolites X or Y. [12] Cation containing zeolites are extensively used as desiccants due to their high affinity for water, and also

find applications in gas separation, where molecules are differentiated on the basis of their electrostatic interactions with the metal ions. Conversely, hydrophobic silica zeolites preferentially absorb organic solvents. Zeolites can thus separate molecules based on differences of size, shape and polarity.

Catalysts

Zeolites have the ability to act as catalysts for chemical reactions which take place within the internal cavities. Essentially, zeolites have two properties which make them particularly suitable as starting materials for the preparation of catalysts:[13]

(i) They are cation exchangers; hence it is possible to introduce a large variety of cations with different catalytic properties into their intracrystalline pore system, which in turn offers the opportunity to create different catalytic properties, e. g. in acid- or metal-catalyzed reactions

(ii) Zeolites are crystalline porous materials with pore dimensions in the same order as the dimensions of simple molecules; hence they possess molecular sieving properties when the shape and size of a particular pore system exert a steric influence on the reaction, controlling the access of reactants and products.

2.2 Nanoparticle[14]

In nanotechnology, a particle is defined as a small object that behaves as a whole unit in terms of its transport and properties. Particles are further classified according to size: in terms of diameter, coarse particles cover a range between 10,000 and 2,500 nanometers. Fine particles are sized between 2,500 and 100 nanometers. Ultrafine particles or nanoparticles are sized between 100 and 1 nanometers. The reason for this double name of the same object is that, during the 1970-80's, when the first thorough fundamental studies were running with "nanoparticle" in the USA (by Granqvistand Buhrman) and Japan, (within an ERATO Project) they were called "ultrafine particles" (UFP). However, during the 1990s before the National Nanotechnology Initiative was launched in the USA, the new name, "nanoparticle" had become fashionable (see, for example the same senior author's paper 20 years later addressing the same issue, lognormal distribution of sizes). Nanoparticles may or may not exhibit size-related properties that differ significantly from those observed in fine particles or bulk materials. Although the size of most molecules would fit into the above outline, individual molecules are usually not referred to

as nanoparticles. Nanoclusters have at least one dimension between 1 and 10 nanometers and a narrow size distribution. Nanopowders are agglomerates of ultrafine particles, nanoparticles, or nanoclusters. Nanometer-sized single crystals, or single-domain ultrafine particles, are often referred to as nanocrystals. Nanoparticle research is currently an area of intense scientific interest due to a wide variety of potential applications in biomedical, optical and electronic fields. The National Nanotechnology Initiative has led to generous public funding for nanoparticle research in the United States.

Uniformity

The chemical processing and synthesis of high performance technological components for the private, industrial, and military sectors requires the use of high purity ceramics, polymers, glass-ceramics, and material composites. In condensed bodies formed from fine powders, the irregular particle sizes and shapes in a typical powder often lead to non-uniform packing morphologies that result in packing density variations in the powder compact.

Uncontrolled agglomeration of powders due to attractive van der Waals forces can also give rise to in microstructural in homogeneities. Differential stresses that develop as a result of non-uniform drying shrinkage are directly related to the rate at which the solvent can be removed, and thus highly dependent upon the distribution of porosity. Such stresses have been associated with a plastic-to-brittle transition in consolidated bodies, and can yield to crack propagation in the unfired body if not relieved. In addition, any fluctuations in packing density in the compact as it is prepared for the kiln are often amplified during the sintering process, yielding inhomogeneous densification. Some pores and other structural defects associated with density variations have been shown to play a detrimental role in the sintering process by growing and thus limiting end-point densities. Differential stresses arising from inhomogeneous densification have also been shown to result in the propagation of internal cracks, thus becoming the strength-controlling flaws.

Inert gas evaporation and inert gas deposition are free many of these defects due to the distillation (c.f. purification) nature of the process and having enough time to form single crystal particles, however even their non-aggreated deposits have lognormal size distribution, which is typical with nanoparticles. The reason why modern gas evaporation techniques can produce a relatively narrow size distribution is that aggregation can be avoided. However, even in this case,

random residence times in the growth zone, due to the combination of drift and diffusion, result in a size distribution appearing lognormal.

It would therefore appear desirable to process a material in such a way that it is physically uniform with regard to the distribution of components and porosity, rather than using particle size distributions which will maximize the green density. The containment of a uniformly dispersed assembly of strongly interacting particles in suspension requires total control over interparticle forces. Monodisperse nanoparticles and colloids provide this potential.

Monodisperse powders of colloidal silica, for example, may therefore be stabilized sufficiently to ensure a high degree of order in the colloidal crystal or polycrystalline colloidal solid which results from aggregation. The degree of order appears to be limited by the time and space allowed for longer-range correlations to be established. Such defective polycrystalline colloidal structures would appear to be the basic elements of submicrometer colloidal materials science, and, therefore, provide the first step in developing a more rigorous understanding of the mechanisms involved in microstructural evolution in high performance materials and components.

2.3 Laundry Detergent

Laundry detergent, or washing powder, is a type of detergent (cleaning agent) that is added for cleaning laundry. In common usage, "detergent" refers to mixtures of chemical compounds including alkylbenzenesulfonates, which are similar to soap but are less affected by hard water[15]. In the early 70s, a systematic quest for phosphate substitutes led to research into zeolites as builders for detergents. All detergent zeolites are characterized by high aluminium content. According to Löwenstein's rule, not more than half the Si atoms in the crystal lattice can be replaced by Al atoms. In the case of detergent zeolites, a Si/Al ratio of 1 or virtually 1 is achieved. This in turn results in a maximum content of Na+ ions, which are necessary to neutralise the AlO_2- units. Since Na^+ ions are able to move in the zeolite pores, they can easily be exchanged for calcium ions, and sometimes other ions.

The zeolites available for detergents today (Zeolite A, Zeolite P, Zeolite X) have significantly different crystalline structures. The basic unit of the zeolite used in detergents since 1976, Zeolite A (x = y = 12, z = 27), often also referred to as Zeolite NaA or Zeolite 4A.[16]

2.3.1 Components

(i) Main components[17],[18]

There are two main components in the detergent, which are surfactant and water softener or Builders. Surfactants or service active agent is perhaps the most important ingredient used in every synthetic detergent formula. It has three primary roles: to improve the wetting ability of water; to loosen and remove the soils; and to emulsify, suspend, or eliminate the soils in the washing solution. Surfactants are organic compounds that wrap themselves around the soil particulates, break them up, and then force them away from the surface of the fabric. More importantly, they suspend the soil particles in water, prohibiting them from reattaching to the fabric.

Water softener or Builders are often used to enhance the surfactant effect. Their role is to lower the water hardness by scavenging the calcium and magnesium ions and adsorbing them or chelating them, such as Sodium tripolyphosphate (STPP), Zeolite, Nitriloacetic acid (NTA), Polycarboxylate, Phosphonate and Citrate. STPP which is the most effective builder available yet it is negatively perceived from an environmental stand point. The chemical formula is $Na_5P_3O_{10}$. Zeolite is more environmentally friendly and cheaper yet it provides less efficiency as builder.

(ii) Other components[5],[19]

1. Anti soil redisposition: aid in preventing loosened soil from redepositing on cleaned fabrics.
2. Corrosion Inhibitor: helps protect washer parts from corrosion.
3. Fluorescent Whitening Agents: adhere to fabrics to help maintain whiteness or brightness.
4. Colorants: contribute to product performance and help keep whites white.
5. Fragrances: cover the chemical odor of the detergent and other ingredients, and add a pleasant scent to the fabrics.
6. Opacifiers: provide a rich, creamy opaque appearance to liquid products.
7. Oxygen Bleach: provides detergents with an all-fabric bleaching agent for stain and soil removal; may be particularly effective if care labels specify not to use chlorine bleach.

8. Optical brightener: generally give clothes a bluish glow, giving the impression of whiteness. It is recommended that these be used cautiously as they can make dark clothing look faded.

9. Enzymes: aid in breaking down complex soils, especially proteins such as blood and grass, so they can be more easily removed from fabrics.

10. Suds Control Agents: help control the level of suds in the washing process.

11. Fabric Softening Agents: help control static cling and add softness to fabrics.

12. Bleach Alternative: is generally Sodium Perborate or Sodium Percarbonate. Both are milder than sodium hypochlorite (aka chlorine bleach), but they work.

2.4 Literature reviews

In the recent years, the properties of synthesized zeolites have been one of the most studied subjects. Investigations on the structural nature and properties of zeolites were especially intense.

Z. Ghasemi and H. Younesi was synthesized nanozeolite NaA by pure chemicals, rice husk which is an agricultural waste was used as silica source for the synthesis of nanozeolite NaA, because silica extracted from rice husk is cheap, less selective, and highly active.Amorphous extracted silica powder was composed of 87.988 wt%SiO_2.We have successfully synthesized nanometer-sized NaA nanozeolite with extracted silica at room temperature without using any organic additives. Also, the effect of alkalinity and Na_2O/SiO_2 ratio of initial system, as well as time of crystallization, on the properties of the final product was investigated. Zeolite NaA nanocrystals with crystallite size ranging from 50–120nm were obtained from a sodium aluminosilicate solution at room temperature in 3 days under Na_2O/SiO_2 = 6 conditions. Thus the aims to lower costs and to shorten crystallization time were both found possible through the study. To the best of our knowledge, this is the first report on the hydrothermal synthesis of zeolite NaA nanocrystals with rice husk as source of extracted silica, without using any organic additives during the whole crystallization process. Our

environmentally friendly process reduces the costs of synthesis effectively through the utilization of cheap raw materials and also by avoiding consumption of expensive chemical sources as template[15].

Mehdi Kamali use clinoptilolite, which is suitable and low cost Si source for preparing of zeolite A both in conventional and nano sizes. Different parameters such as temperature, time, pH, mass to volume ratio and alkaline concentration are affected by dissolving clinoptilolite. Aluminum sulfate was successfully used for preparing zeolite A both in powder and nano-sized particles for the first time. Since the latter source is rather cheaper and more available than the other Al sources, this study introduced a new convenient material for zeolite synthesis with considering its optimum conditions for related variables. Quality control tests (according ASTM) represent that the synthesized product, regarding to its efficient CEC and LOI, can be used as detergent builder in related industries[20].

CHAPTER 3

EXPERIMENTAL DETAILS

3.1 Reagents

Chemicals	Grade	Manufactures
1. Acetone	AR	Carlo Erba
2. Boric acid	-	-
3. Buffer pH10	-	-
4. Calcium carbonate	AR	APS AJAX Finechem
5. Calcium chloride dihydrate	AR	Carlo Erba
6. Distilled water	-	-
7. Eriochrom Black T indicator	AR	Carlo Erba
8. EDTA	AR	Carlo Erba
9. Fumed silica	Industrial	GBS
10. Hexane	Industrial	LAB-SYSTEM
11. Hydrochloric acid	AR	Carlo Erba
12. Ludox AS40	AR	ALDRICH Chemical
13. Sodium aluminate	AR	Riedel-de Haen
14. Sodium hydroxide	AR	Carlo Erba
15.Sodium metasilicate	AR	Fluka
16.Tergitol	-	-

3.2 Apparatus

1. Autoclave
2. Centrifuge and centrifuge tubes
3. Circulator with cooling unit
4. Clamp
5. Laboratory Plasticware and Glassware

6. Magnetic bar
7. Magnetic stirrer hot plate with temperature controller system (RCT basic, IKA)
8. Oven
9. pH meter
10. Scanning electron microscope (LEO 1455VP, LEO Electron Microscopy)
11. Sonicator
12. Spatula
13. Stirring rod
14. Stopwatch
15. Syringe with syringe filter
16. Thermogravimetric analyzer (Pyris 1 TG, Perkin Elmer)
17. Vials
18. Watch glass
19. X-ray diffractometer (D8 Advance, Bruker AG)
20. X-ray fluorescence spectrometer (SRS 3400, Bruker AG)

3.3 Experiment procedure

3.3.1 Synthesis of zeolite A

3.3.1.1 Effect of silica sources

3.3.1.2 Effect of aging temperature

3.3.1.3 Effect of aging time

3.3.1.4 Effect of crystallization temperature

3.3.1.5 Effect of crystallization time

3.3.2 Characterization of zeolite A

3.3.2.1 Crystal morphology using scanning electron microscope (SEM)

3.3.2.2 Zeolite structure using X-ray power diffractrometer (XRD)

3.3.2.3 Chemical composition of the zeolite using X-ray fluorescense spectrometer (XRF)

3.3.3 Study on zeolite properties for detergent builders

3.3.3.1 Cation Exchange Capacity (CEC) by titration method of EDTA

3.3.3.2 Liquid Carrying Capacity (LCC) using thermo gravimetric analysis (TGA)

3.4 Experiment Details

3.4.1 Synthesis of zeolite A

The synthesis of zeolite A were carried out using the homogenized mixture with the following molar composition: 1.80 SiO_2 : 1.00 Al_2O_3 : 3.95 Na_2O : 110.05 H_2O. Typically, 5 g of sodium aluminate was dissolved in 15% wt. sodium hydroxide solution (48 g) and 18 g of distilled water was added then mixed well in polypropylene (PP) bottle. Fumed silica (3.3 g) was slowly added into the PP bottle within 10 minutes. The final mixture was continually stirred at 0-5°C in a circulating bath containing ethylene glycol water coolant for 12 hours (aging). After 12 hours, the gel was stirred in 95°C for another 2 hours (crystallization). Then it was immersed in an ice bath to stop the reaction. The sample was made up with distilled water to 360 mL and shaked for 2 minutes. After achieving the cloudy mixture, it was divided equally into 8 tubes subjected to be centrifuged at 3000 rpm for 10 minutes. The sample was decanted and washed several times with distilled water until the pH value dropped to 10. The products were decanted and dried in an oven at 95°C overnight. The synthesized were varied in conditions of sources, aging time, aging temperature, crystallization time, and crystallization temperature which were obtained in the following Table 3.1.

Table 3.1 Condition of synthesis zeolite A

Condition	Source	Intention Ratio (Na_2O)	Aging Temperature (°C)	Aging Time (hours)	Crystallization Temperature (°C)	Crystallization time (hours)
Different Silica Sources	Sodium meta silicate	3.95	0-5	6	95	2
	Ludox AS40	3.95	0-5	6	95	2
	Fumed silica	3.95	0-5	6	95	2
Aging Time	Fumed silica	3.95	0-5	8	95	2
	Fumed silica	3.95	0-5	12	95	2
	Fumed silica	3.95	0-5	24	95	2
Aging Temperature	Fumed silica	3.95	10	12	95	2
	Fumed silica	3.95	20	12	95	2
	Fumed silica	3.00	20	12	95	2
Crystallization Time	Fumed silica	3.95	0-5	12	95	3
	Fumed silica	3.95	0-5	12	95	5
Crystallization Temperature	Fumed silica	3.95	0-5	12	75	2
	Fumed silica	3.95	0-5	12	85	2
	Fumed silica	3.95	0-5	12	105	2

3.4.2 Characterization of zeolite A

3.4.2.1 Crystal morphology of zeolite A

The zeolite A morphology and crystallize size were determined by scanning electron microscopy (SEM). The sample was prepared by dispersing 0.05 g of zeolite with 10 mL of acetone and sonicated 5 minute. The dispersed zeolite was dropped on SEM stub and allowed to dry.

3.4.2.2 Structure of zeolite A

The zeolite A structure was determined by X-ray diffraction (XRD). The sample was prepared by packing the zeolite powder in the sample holder. Cu-Kα X-ray beam is used for analysis at 45 kV, 30 mA. The sample was scanned over the angle ranged from 2-theta: 5 to 60 degrees, with 0.040 degrees/step, and detection time of 1 second/step. X-ray diffraction peak pattern of sample was compared to the X-ray diffraction peak pattern of commercial zeolite A obtained from PQ chemical for determining the relative crystallinity.

The relative crystallinity was calculated from the following equation.

$$\text{Relative crystallinity} = \frac{\text{Intensity at 2theta } 30^{\circ} \text{ (100plane)}}{\text{Standard Intensity at 2theta } 30^{\circ} \text{ (100plane)}} \times 100$$

3.4.2.3 Chemical composition of the zeolite A samples

The chemical composition of zeolite A could be determined by X-ray fluorescence (XRF). The sample was prepared by mixing 4.5 g of boric acid to 0.5 g of zeolite and grinded it. The mixer was packed onto sample holder then compressed at 150 kN and finally placed in the sample chamber. Rhodium was used as X-ray source for measuring at 50 kV, 60 mA.

3.4.3 Study on zeolite properties for detergent builders

3.4.3.1 Cation exchange capacity (CEC) by titration method of EDTA

3.4.3.1.1 Preparation of stock solutions

0.005 M Ethylenediaminetetraacetic acid was prepared by 1.86 g of EDTA diluted in 1,000 mL distilled water. The exchanged solution ($CaCl_2$) 0.01 M was prepared by dissolving 1.47 g of $CaCl_2 \cdot 2H_2O$ dilute in 1,000 mL distilled water. Primary standard $CaCO_3$ (0.005 M) was prepared by dissolving exactly 0.5 g of $CaCO_3$ with small amount of Conc. HCl. and diluted until $CaCO_3$ became clear solution. The solution was further made up to 1,000 mL with distilled water.

3.4.3.1.2 Determine exactly concentration of EDTA 0.005 M

Primary standard calcium solution ($CaCO_3$)was pipetted (10 mL) into Erlenmeyer flask then Buffer pH 10 (5 mL) was added with few drops of Eriochrome Black T (EBT). The solution was titrated with EDTA until the solution reached endpoint. The solution would change color from purple to dark blue.

3.4.3.1.3 Determine Cation Exchange Capacity (CEC)

The exchange solution was prepared by adding 250 mL of $CaCl_2$ solution into 0.5 g of zeolite at 21°C and rapidly stirred for 15 minutes. The resultant solution was filtrated with one time use filter paper (0.8 micron) and 10.0 mL of the solution (10.0 mL) were pipetted into Erlenmeyer flask. 5 mL of Buffer pH 10 was added in the flask as 2 drops of EBT indicator then the mixture was titrated with EDTA until the solution reached the endpoint. The solution would change color from purple to dark blue. Titration repeat 2 times (The different of data must not be higher than 0.05 mL, otherwise repeated).

From the experiment, the molarities of EDTA could be calculated from the following equation

$$\text{Molarities of EDTA} = \frac{\text{Weight of } CaCO_3}{\text{mL of EDTA} \times 100.09 \times 50}$$

After calculated the molarities of EDTA then calculate cation exchange capacity (CEC) can be calculated from the following equation.

$$CEC = \frac{(B-V)\times M\times 100.09\times 25}{W\times S}$$

B = Volume(mL) of EDTA titrated with Calcium Chloride solution

V = Volume (mL) of EDTA titrated with Sample solution

M = Molarities of EDTA

W = Sample weight (g)

100.09 = Molecular weight of $CaCO_3$

25 = Ca^{2+}Solution 250 (mL)/Volume of titrant 10 mL

S = Lost of ignitions (1- LOI)

To analyze the loss of ignition, TGA (thermo gravimetric analysis) method was used. 10-20 mg of zeolite A was loaded into sample holder and heated at temperature range 50-600°C, heating rate at 15°C/minute.

3.4.3.2 Liquid Carrying Capacity (LCC)

The surfactant that was used for absorb on zeolite A was 20%wt. of tergitol in hexane. Adsorbate was prepared by 20 g of tergitol mixing with 80 g of hexane. After that 5 g of adsorbate (20% wt. of tergitol in hexane) was added with 0.5 g of zeolite then sonicated for 5 minutes. The solution was stirred with magnetic stirrer for 30 minutes and washed by hexane. The mixture were finally centrifuged to separate the zeolite at 4000 rpm for 10 minutes and allowed it to dry for 30 minutes.

From TGA, Liquid carrying capacity (LCC) of zeolite A were determined by following equation

$$\frac{\text{Weight of zeolite adsorbed surfactant - Weight of zeolite}}{\text{Weight of zeolite}} \times 100$$

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Effect of silica sources

In this project, the effect of different silica sources used for preparing the synthesis gel were studied using aging time at 6 hours, aging temperature of 0-5°C, crystallization time of 3 hours, and crystallization temperature of 100°C. It was found that zeolite formation was very sensitive to the nature of the reactant in particular that of the silica sources. This factor was important in nucleation and growth kinetics.[21]

However, silica sources have no effect to crystallinity and composition as shown by XRD in Figure 4.1 and XRF in Table 4.1.

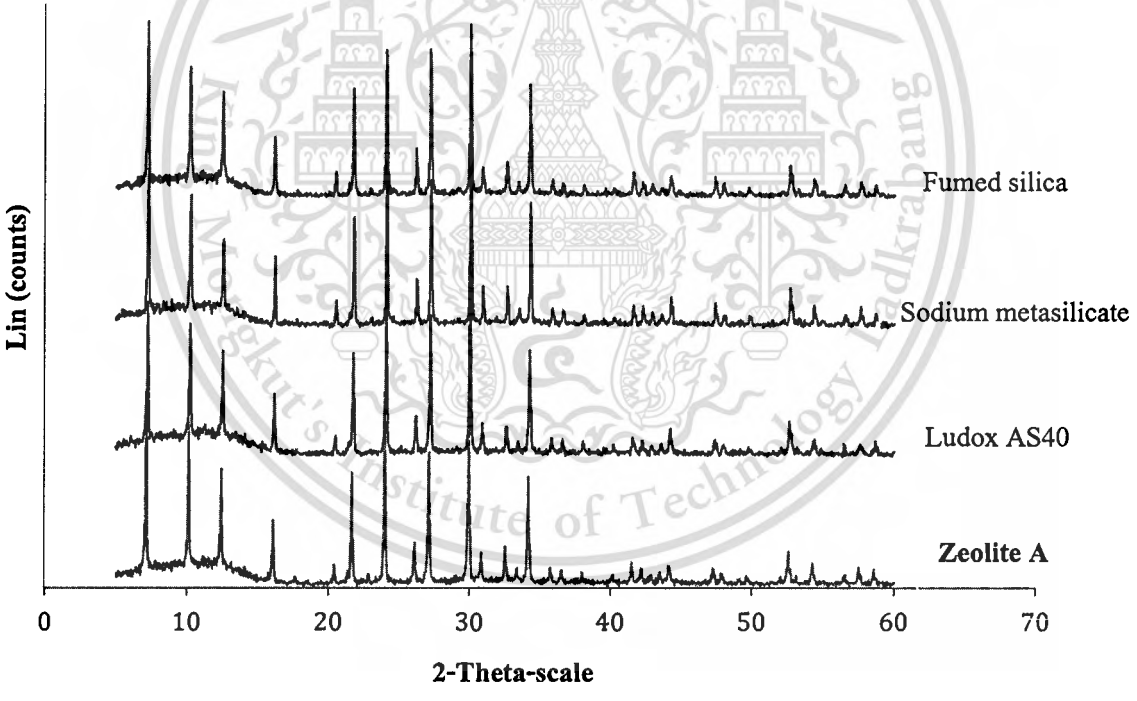


Figure 4.1 X-ray diffraction pattern of synthesized zeolite A compare with standard zeolite A.

Condition : 1.80 SiO_2 : 1.00 Al_2O_3 : 3.95 Na_2O : 110.05 H_2O, aging at 0°C for 6 hours, crystallization at 95°C for 2 hours.

From XRD (X-ray Diffraction) characterization, all silica sources provided peak pattern at 2θ = 7.08°, 10.08°, 12.36°, 15.98°, 21.58°, 23.9°, 27.02°, 29.86°, and 34.06, which were confirmed the formation of zeolite A.

Table 4.1 The composition of each source from XRF characterization.

Si Source / Composition*	Fumed silica	Sodium metasilicate	Ludox AS40
SiO_2	34.0%	36.6%	36.8%
Al_2O_3	26.0%	30.3%	29.7%
Na_2O	39.9%	33.0%	33.4%

* by weight

From Table 4.1 showed the similar composition of zeolite A. For example, 34-36%wt. composition of silicon dioxide (SiO_2) was obtained for all samples.

However, the silica source affected the relative crystallinity of zeolite A which can be calculated from XRD peak pattern. The calculation obtained from Appendix A and the results are shown in Table 4.2

Table 4.2 The comparison of particles size of different silica sources with their properties.

Sample	Size (nm)	Relative Crystallinity (%)	CEC (mg/g) *	LCC (% wt.) **	Yield (%)
Fumed silica	500-600	92.62	194	8.93	45.89
Ludox AS40	1300-1400	93.13	201	7.61	60.51
Sodium metasilicate	1100-1200	111.48	283	7.90	31.79
Commercial zeolite A	2,000	100.00	287	8.25	-

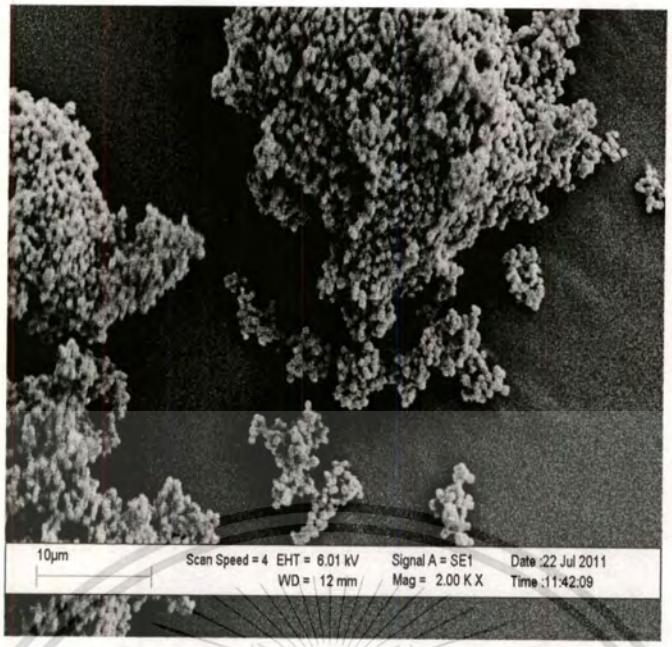
* mg $CaCO_3$ / g anhydrous zeolite

** surfactant / anhydrous zeolite

It can be seen that sodium metasilicate provided the higher relative crystallinity as compared to other silica sources. This is because sodium metasilicate was readily soluble in water and easily formed the zeolite precursors. The process is described in Chapter 2 (Figure 2.3). The zeolite A was synthesized by mixing silica source with alumina source to obtain aluminosilicate gel. As the time proceeds, the initial gel would rearrange into regular shape that was called "metastable gel". This step is very important because metastable gel can condense to an unstable gel or the secondary building unit of zeolite precursors. It could also be hydrolyzed to be stable primary building units, which caused the supersaturated solution. If the metastable gel occurred in large amount, there would have more chance to induce nucleation period. Since sodium metasilicate is high solubility so the nucleation and the growth step would occur rapidly and provided the large particle size with high crystallinity.

According to the discussion, Table 4.2 showed that the CEC result of the synthesized zeolite A from sodium metasilicate is higher than those two other sources. However it is similar to that of the commercial zeolite A in consistent with their crystallinity. As cation exchange capacity (CEC) showed the ability of internal ions exchange which was affected by relative crystallinity, the high relative crystallinity provides a complete structure with more sodalite cages. This is lead to more ion exchange inside the cages as observed. In addition to relative crystallinity and CEC, the silica sources affected to particle size as seen in SEM images (Figure 4.2).

(a) Fumed silica



(b) Ludox AS40

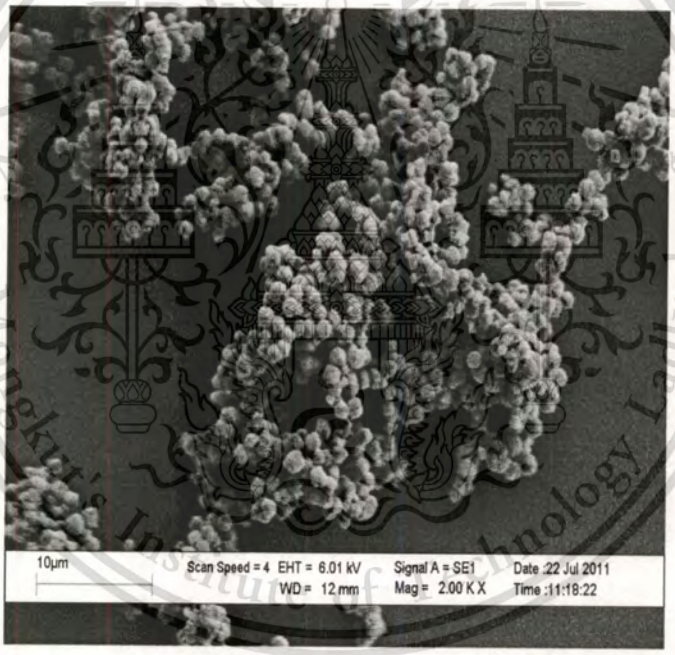


Figure 4.2 Scanning electron micrograph of zeolite A compared with different silica sources. (a) Fumed silica, (b) Ludox AS40, (c) Sodium metasilicate

Condition : 1.80 SiO_2 : 1.00 Al_2O_3 : 3.95 Na_2O : 110.05 H_2O, aging at 0°C for 6 hours, crystallization at 95°C for 2 hours.

(c) Sodium metasilicate

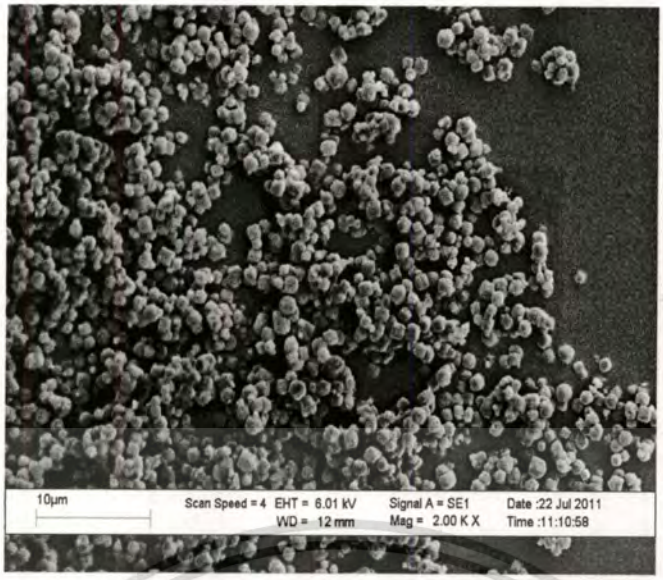


Figure 4.2 (Continued) Scanning electron micrograph of zeolite A compared with different silica sources.(a) Fumed silica, (b) Ludox AS40, (c) Sodium metasilicate

Condition : 1.80 SiO_2 : 1.00 Al_2O_3 : 3.95 Na_2O : 110.05 H_2O, aging at 0°C for 6 hours, crystallization at 95°C for 2 hours.

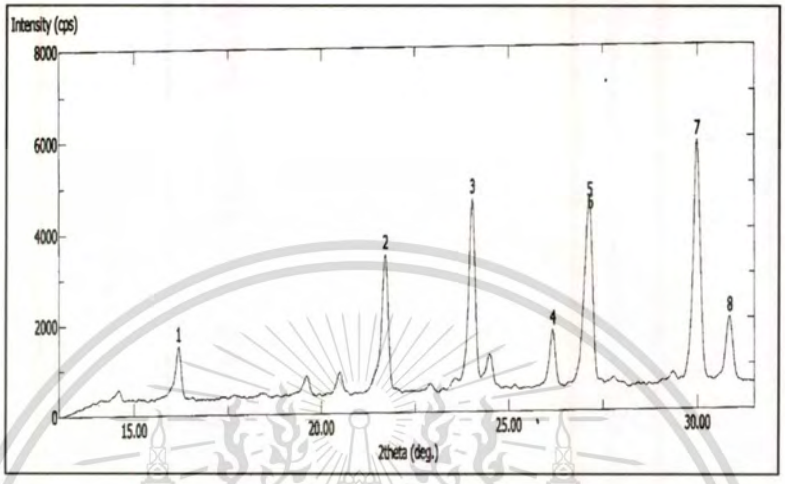
Sodium metasilicate possessed the large particle size in consistent with relative crystallinity and CEC as discussed earlier. However this project aims to produce small particle size and it can be seen that fumed silica give the smallest particle size as compared to other sources. Since the fumed silica source is a fine powder with an extremely low bulk density and high surface area so it provided a high viscosity gel, as compared to those with other sources. Due to the viscosity of fumed silica, it effected to the earlier process by retarding the nucleation and the growth step. Hence a large number of nuclei can be formed. However the stable solution that is known as the nutrient of nuclei is limited to feed all growing nuclei. Accordingly zeolite A with small particle size was obtained from the viscous synthesis gel using fumed silica as source.

Due to its small particle size, zeolite A using fumed silica as source also offered higher LCC result as compared to that of the two other sources and commercial zeolite A. Liquid carrying capacity (LCC) is the property that indicated the amount of liquid surfactant that zeolite A could absorb on external surface area. The small particle size possessed high surface area which could absorb large amount of liquid surfactant. As the zeolite A using sodium metasilicate and Ludox AS40 as source presented the large particle size as compared to that using fumed silica as source.

4.2 Effect of aging time

The effect of aging time used for preparing synthesis gel was studied using aging time of 8, 12, and 24 hours. After zeolite A was synthesized they were investigated by XRD as the peak pattern shown below;

(a) 8 hours



(b) 12 hours

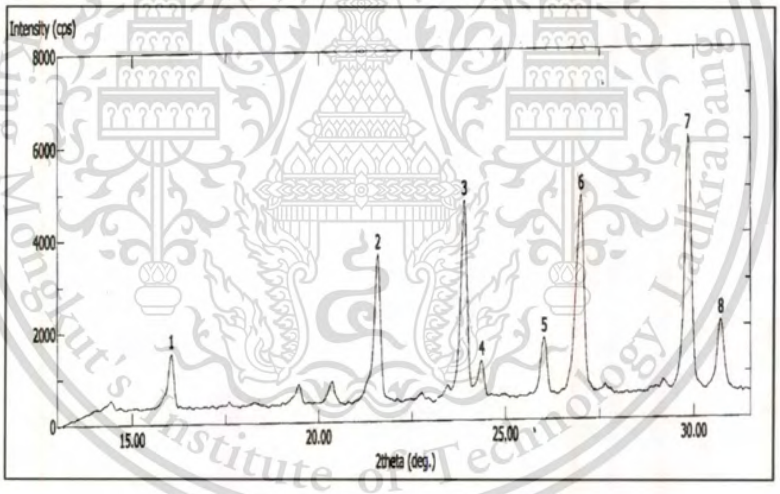


Figure 4.3 X-ray diffraction pattern of synthesized zeolite A compared with aging time. (a) 8 hours aged, (b) 12 hours aged, (c) 24 hours aged

Condition: 1.80 SiO_2 : 1.00Al_2O_3 : 3.95Na_2O : 110.05 H_2O, aging at 0°C, crystallization at 95°C for 2 hours. (fumed silica as Si source)

(c) 24 hours

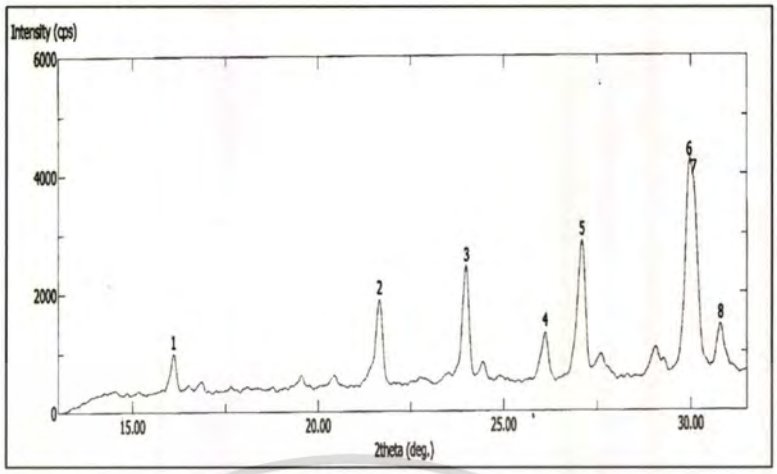


Figure 4.3(Continued) X-ray diffraction pattern of synthesized zeolite A compared with aging time. (a) 8 hours aged, (b) 12 hours aged, (c) 24 hours aged

Condition: 1.80 SiO_2 : 1.00Al_2O_3 : 3.95Na_2O : 110.05 H_2O, aging at 0°C, crystallization at 95°C for 2 hours. (fumed silica as Si source)

It can be seen that the samples are all zeolite A. Their relative crystallinty were obtained from comparing samples with the commercial zeolite A as shown in Table 4.3.

Table 4.3 The comparison of particle size of different aging time with their properties.

Sample	Size (nm)	Relative Crystallinity (%)	CEC (mg /g) *	LCC (% wt.) **	Yield (%)
Aging time 8 hours	550-650	111.48	245	9.50	53.28
Aging time 12 hours	500-600	109.15	211	10.54	52.93
Aging time 24 hours	300-400	75.34	192	9.77	53.78
Commercial zeolite A	2,000	100.00	287	8.25	-

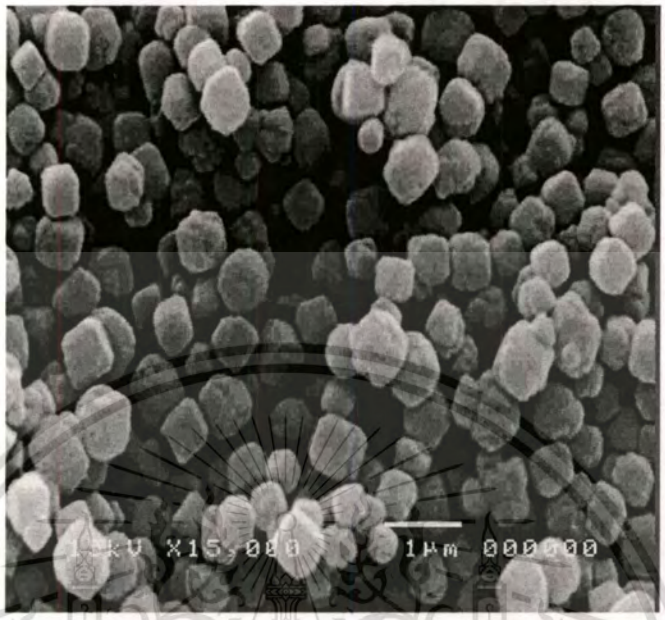
* mg $CaCO_3$ / g anhydrous zeolite

** surfactant / anhydrous zeolite

The relative crystallinity of zeolite A using 8 and 12 hours aging time is higher than that with 24 hours aging time. This value would decrease when the aging time is increased. It is because the longer time provided a lot of nuclei but the nutrient of nuclei is limited to feed all

growing nuclei. Hence the crystallinity of zeolite A with longer aging time would be decreased. Accordingly aging time also effected to particle size as shown in SEM images (Figure 4.4).

(a) 8 hours



(b) 12 hours

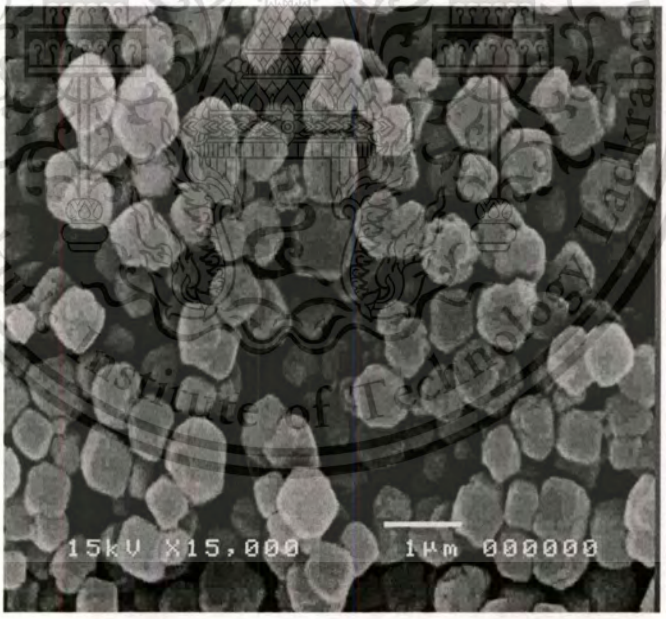


Figure 4.4 Scanning electron micrograph of zeolite A. (a) 8 hours aged, (b) 12 hours aged, (c) 24 hours aged

Condition : 1.80 SiO_2 : 1.00 Al_2O_3 : 3.95 Na_2O110.05 H_2O, aging at 0°C, crystallization at 95°C for 2 hours. (fumed silica as Si source)

(c) 24 hours

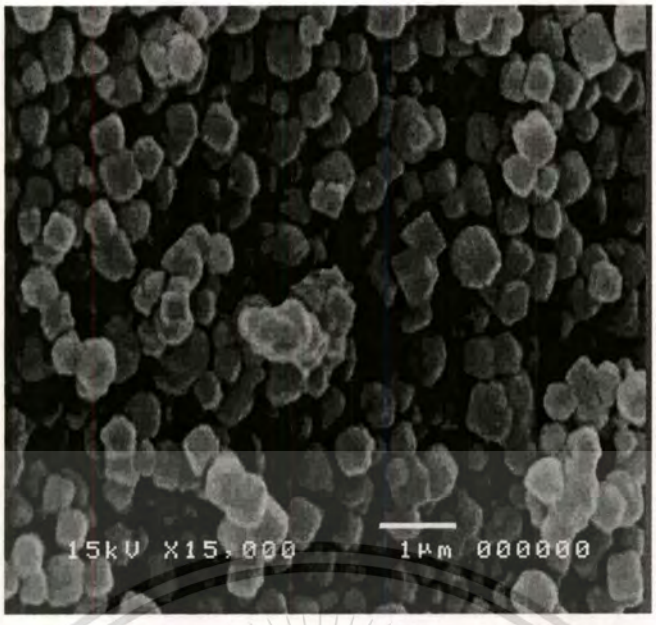


Figure 4.4 (Continued) Scanning electron micrograph of zeolite A. (a) 8 hours aged, (b) 12 hours aged, (c) 24 hours aged

Condition : 1.80 SiO_2 : 1.00 Al_2O_3 : 3.95 Na_2O110.05 H_2O, aging at 0°C, crystallization at 95°C for 2 hours. (fumed silica as Si source)

The mean particle size showed in Table 4.3 particle size of zeolite A of aging 8 and 12 hours is similar but it is larger than that with 24 hours. This is because the long time of aging generated a lot of nuclei as discussed earlier. Hence small particle size is result with good size distribution (narrow range of particle size).

From Table 4.3, it could be seen that the zeolite A with aging at 8 and 12 hours give larger particle size with higher relative crystallinity, as compared to 24 hours aged. The large particle size offered more sodalite cage that can exchange more cations and resulted in high CEC.

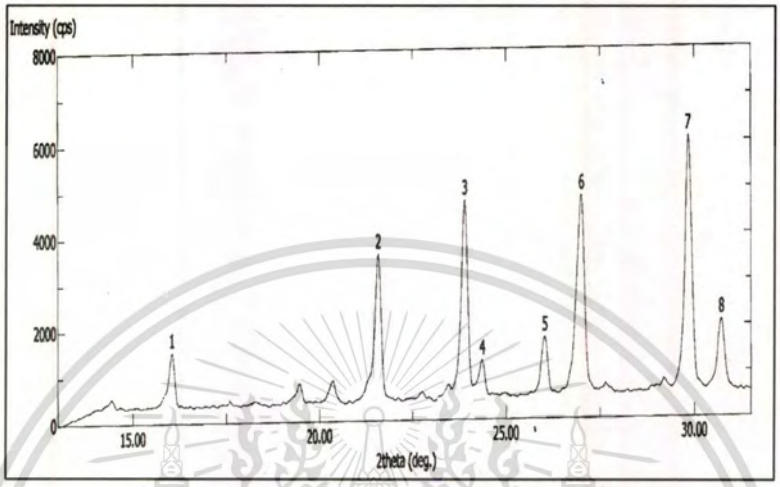
LCC of synthesized zeolite A with different aging time were resembled. This is because all samples gave particle size in nano region. It is worth noting that, LCC of synthesized zeolite A were higher than that of the commercial zeolite A which may well be benefit for use as powder detergent builders.

From the study, aging time at 12 hours provided small particle size with optimum relative crystallinity. Therefore, this condition was chosen for further study.

4.3 Effect of aging temperature

The effect of aging temperature were investigated using the temperature at 0-5°C, 10°C and 20°C. Synthesized zeolite A was characterized by XRD as peak pattern shown below.

(a) 0-5°C



(b) 10°C

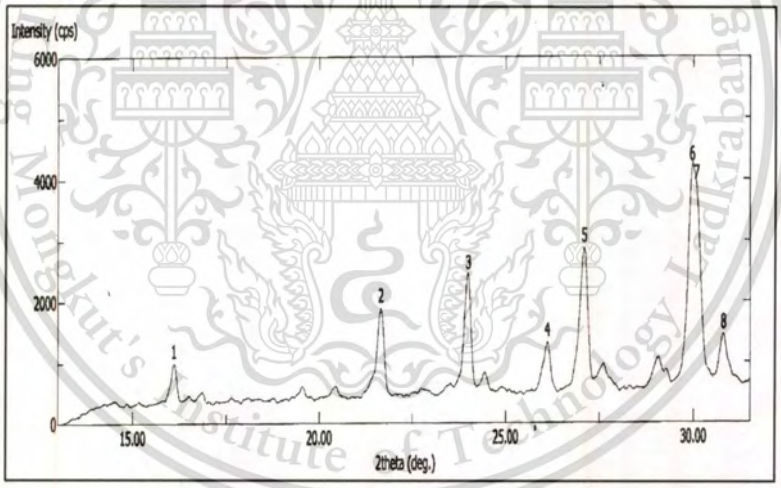


Figure 4.5 X-ray diffraction pattern of synthesized zeolite A compared with aging temperature. (a) 0-5°C aged, (b) 10°C aged, (c) 20°C aged

Condition : $1.80SiO_2 : 1.00Al_2O_3 : 3.95Na_2O : 110.05\ H_2O$, aging time 12 hours, crystallization at 95°C for 2 hours.(fumed silica as Si source)

(c) 20°C

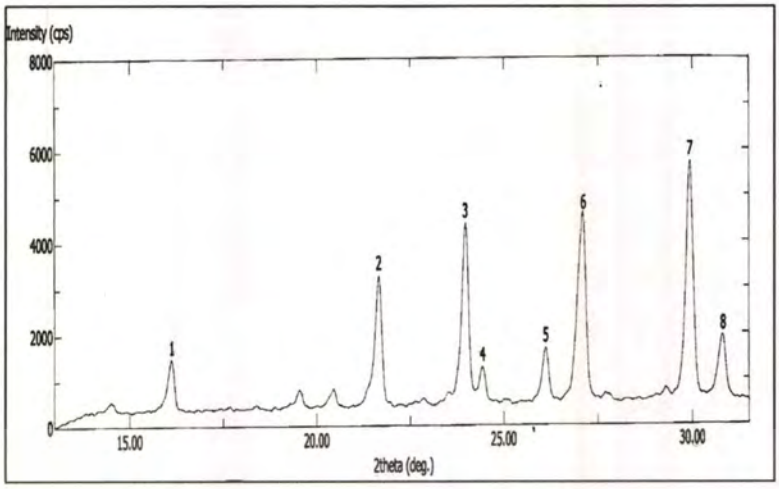


Figure 4.5(Continued) X-ray diffraction pattern of synthesized zeolite A compared with aging temperature. (a) 0-5°C aged, (b) 10°C aged, (c) 20°C aged

Condition : 1.80SiO_2 : 1.00Al_2O_3 : 3.95Na_2O : 110.05 H_2O, aging time 12 hours, crystallization at 95°C for 2 hours.(fumed silica as Si source)

The XRD peak pattern of all samples exhibited the zeolite A peak pattern which the relative crystallinity is calculated as shown in Table 4.4;

Table 4.4 The comparison of particles size of different aging temperature with their properties.

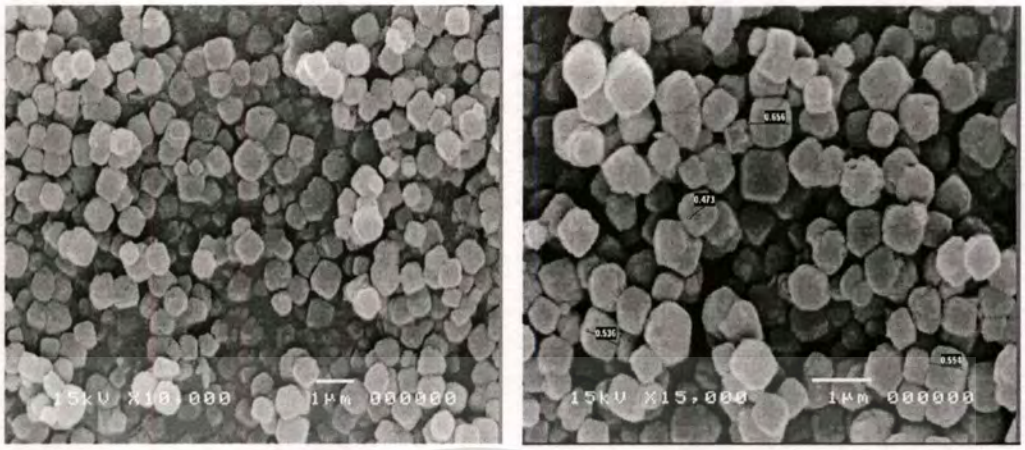
Sample	Size (nm)	Relative Crystallinity (%)	CEC (mg /g) *	LCC (% wt.) **	Yield (%)
Aging temperature 0-5°C	500-600	109.15	211	10.54	52.93
Aging temperature 10°C	200-400	107.22	157	7.70	51.22
Aging temperature 20°C	200-300	102.72	138	7.80	50.35
Commercial zeolite A	2,000	100.00	287	8.25	-

* mg $CaCO_3$ / g anhydrous zeolite

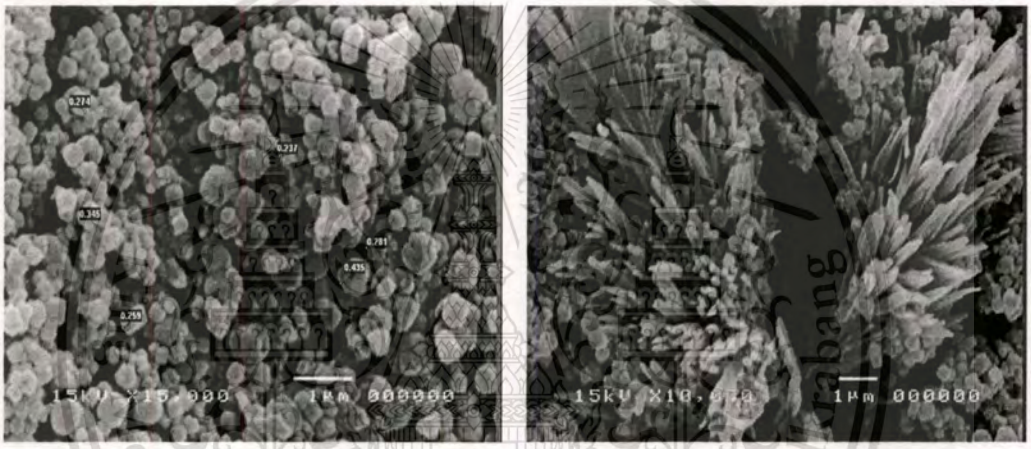
** surfactant / anhydrous zeolite

The results exhibited that zeolite A were form with high crystallinity for all samples. However, noticeably low CEC and LCC were particularly observed at aging temperature 10°C and 20°C. This is because the impurity phases are presented in samples as seen in SEM images (Figure 4.6).

(a) 0-5°C



(b) 10°C aged with impurities



(c) 20°C aged with impurities

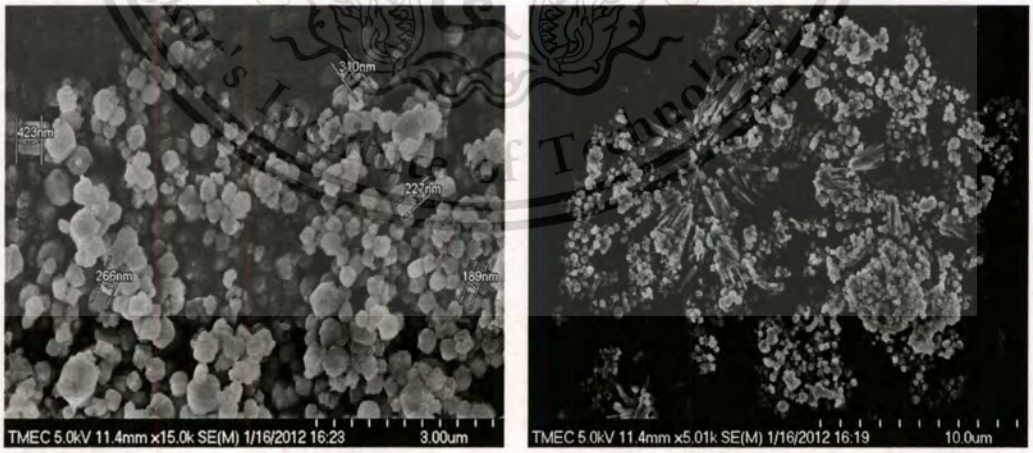


Figure 4.6 Scanning electron micrograph of zeolite A. (a) 0-5°C aged, (b) 10°C aged with impurities, (c) 20°C aged with impurities

Condition : 1.80SiO_2 : 1.00Al_2O_3 : 3.95Na_2O : 110.05 H_2O , aging time 12 hours, crystallization at 95°C for 2 hours. (fumed silica as Si source)

With the present synthesis condition, the small particle size occurred with impurities. This is due to too fast nucleation and crystallization. Zeolite A with low Si/Al ratio would have high free energy formation that rapidly decreased when the crystallization is progressed. Since the synthesis of zeolite A at aging temperature 10°C and 20°C possessed very high free energy of formation, a lot of nuclei with nano size can be largely generated. If such free energy rapidly decreased with the fast growing nuclei, large amounts of aluminosilicate species would be left in the mixture and that might be renucleated over the synthesis time. This can result in (i) zeolite A with very small particle size but wide size distribution, or (ii) even a change into new zeolite structure or (iii) other phases being formed as zeolite impurity. In this case, the impurities might be quartz as the high concentration of silica source left in the solution could be recrystallized.

In order to avoid impurities, decreasing in the rate of hydrolysis is needed. This can be done by reducing in alkalinity from $3.95Na_2O$ to $3.00\ Na_2O$. The alkalinity affected to the metastable gel growth and the crystallization kinetics.[21] In high basicity condition, the rate of nucleation is high hence a lot of nuclei is created. This leads to small particle size as shown in Figure 4.6. As the basicity was decreased, there was an increased in relative crystallinity as shown by XRD (Figure 4.7). This is because the rate of nucleation is lower providing complete crystallization and hence, large crystal size. CEC and LCC are also improved (Table 4.5) because no more impurities is founded as shown by SEM image (Figure 4.8)

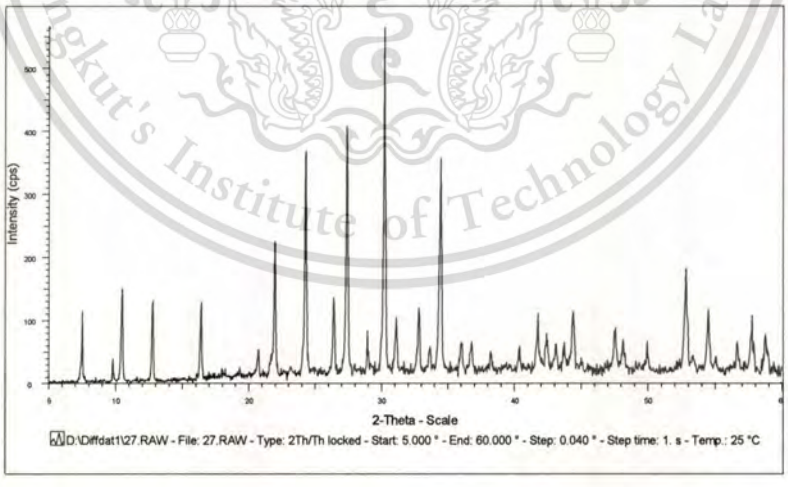


Figure 4.7 X-ray diffraction pattern of synthesized zeolite A, aging temperature 20°C based 3.00.
Condition : $1.80SiO_2 : 1.00Al_2O_3 : 3.00Na_2O : 110.05\ H_2O$, aging time 12 hours, crystallization at 95°C for 2 hours.(fumed silica as Si source)

The relative crystallinity, CEC and LCC are calculated as shown in Table 4.5;

Table 4.5 The comparison of particles size of different basicity with their properties.

Sample	Size (nm)	Relative Crystallinity (%)	CEC (mg /g) *	LCC (% wt.) **	Yield (%)
Aging temperature 20°C (3.95 Na_2O)	200-300	102.72	138	7.80	50.35
Aging temperature 20°C (3.00 Na_2O)	300-500	112.30	315	8.45	69.63
Commercial zeolite A	2,000	100.00	287	8.25	-

* mg $CaCO_3$ / g anhydrous zeolite

** surfactant / anhydrous zeolite

(a) 3.95 Na_2O

Figure 4.8 Scanning electron micrograph of zeolite A with different basicity. (a) 3.95 Na_2O, (b) 3.00 Na_2O

Condition : 1.80SiO_2 : 1.00Al_2O_3 : 110.05 H_2O , aging temperature at 20°C for 12 hours, crystallization at 95°C for 2 hours. (fumed silica as Si source)

(b) 3.00 Na_2O

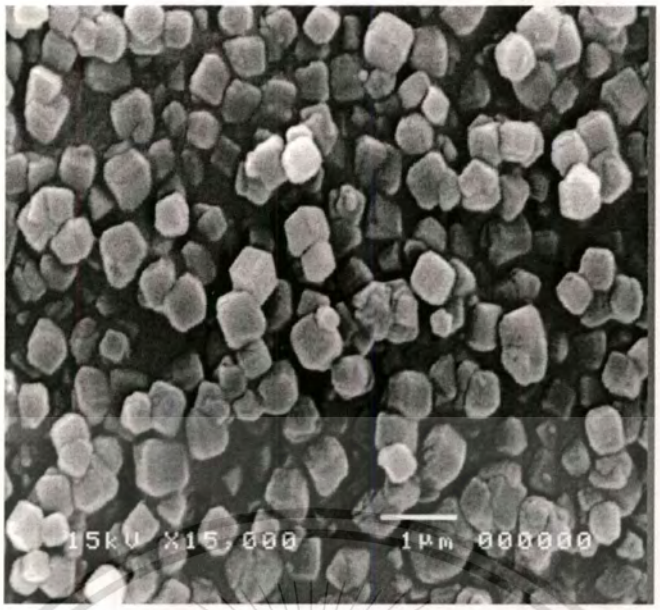


Figure 4.8 (Continued) Scanning electron micrograph of zeolite A with different basicity. (a) 3.95 Na_2O, (b) 3.00 Na_2O

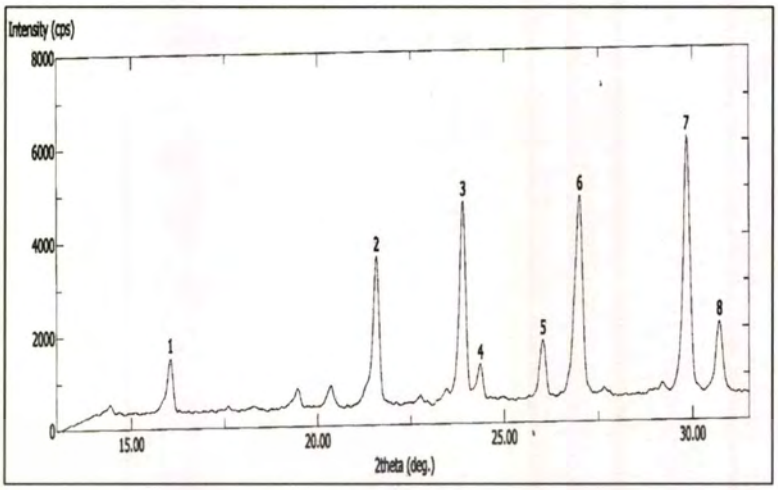
Condition : 1.80SiO_2 : 1.00Al_2O_3 : 110.05 H_2O , aging temperature at 20°C for 12 hours, crystallization at 95°C for 2 hours. (fumed silica as Si source)

The aging at 0-5°C is chosen as it provided the smallest particle size with no impurities. It also has high relative crystallinity with high CEC and LCC.

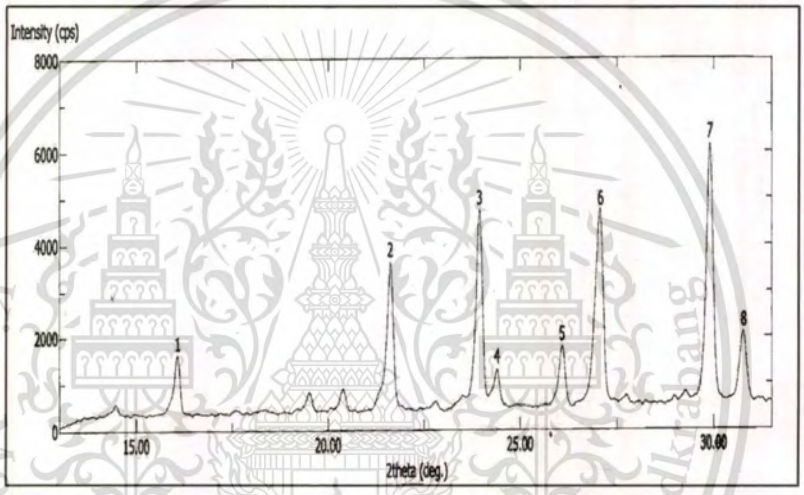
4.4 Effect of crystallization time

The synthesis of nanozeolite A with crystallization times of 2 hours, 3 hours, and 5 hours provides zeolite A with peak pattern as shown in Figure 4.9.

(a) 2 hours



(b) 3 hours



(c) 5 hours

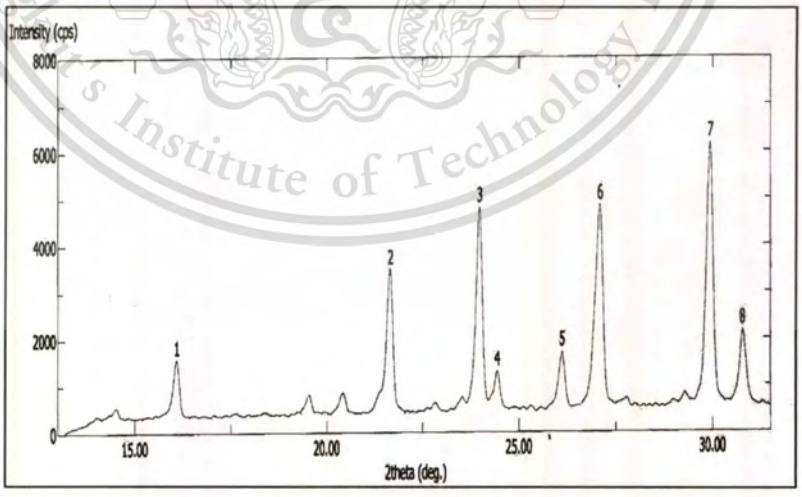


Figure 4.9 X-ray diffraction pattern of synthesized zeolite A compared with crystallization time. (a) 2 hours, (b) 3 hours, (c) 5 hours

Condition : $1.80SiO_2 : 1.00Al_2O_3 : 3.95Na_2O : 110.05\ H_2O$, aging temperature at 0-5°C for 12 hours, crystallization temperature at 95°C.(fumed silica as Si source)

The relative crystallinity is calculated from XRD peak pattern as shown in Table 4.6;

Table 4.6 The comparison of particles size of different crystallization time with their properties.

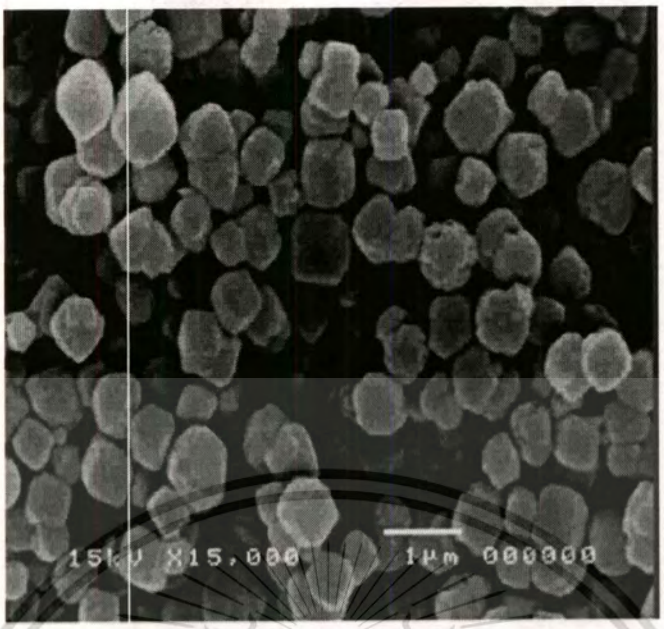
Sample	Size (nm)	Relative Crystallinity (%)	CEC (mg /g) *	LCC (% wt.) **	Yield (%)
Crystallization time 2 hours	500-600	109.15	211	10.54	52.93
Crystallization time 3 hours	500-700	110.28	231	9.81	62.29
Crystallization time 5 hours	800-1000	110.42	240	9.67	60.57
Commercial zeolite A	2,000	100.00	287	8.25	-

* mg $CaCO_3$ / g anhydrous zeolite

** surfactant / anhydrous zeolite

It can be noticed that at 2, 3 and 5 hours of crystallization time provided high relative crystallinity, as compared to that of commercial zeolite A. Refer to previous discussion, increasing in crystallization time resulted in more complete crystallization and larger particle size (Figure 4.10) which influenced to higher CEC. On the other hand, LCC could decrease with longer crysallaization time as shown in Table 4.6.

(a) 2 hours



(b) 3 hours

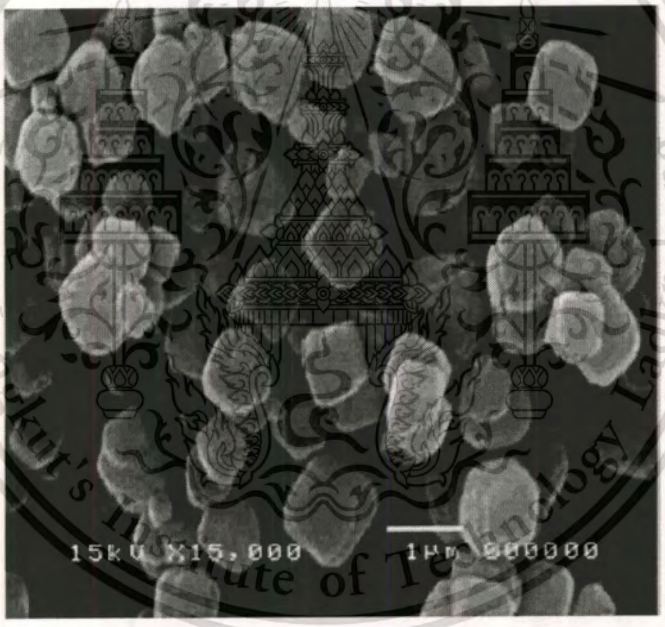


Figure 4.10 SEM images of synthesized zeolite A compared with crystallization time.

(a) 2 hours, (b) 3 hours, (c) 5 hours

Condition : $1.80SiO_2 : 1.00Al_2O_3 : 3.95Na_2O : 110.05\ H_2O$, aging temperature at 0-5°C for 12 hours, crystallization temperature at 95°C .(fumed silica as Si source)

(c) 5 hours

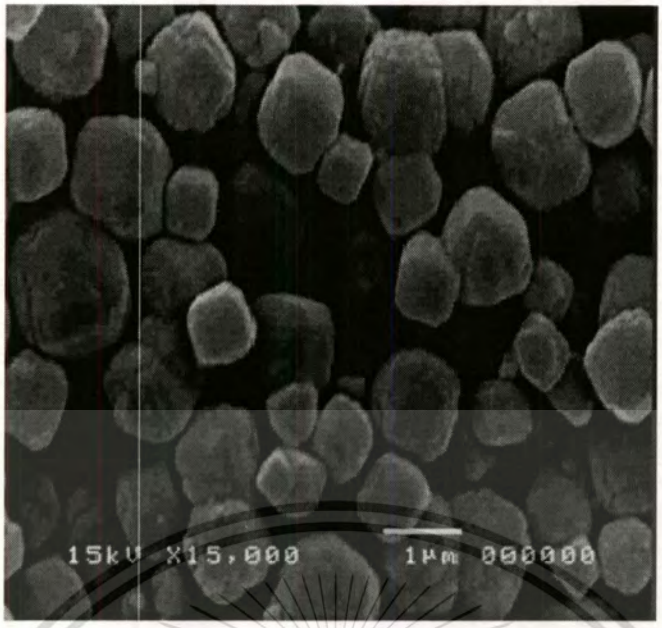


Figure 4.10(Continued) SEM images of synthesized zeolite A compared with crystallization time. (a) 2 hours, (b) 3 hours, (c) 5 hours

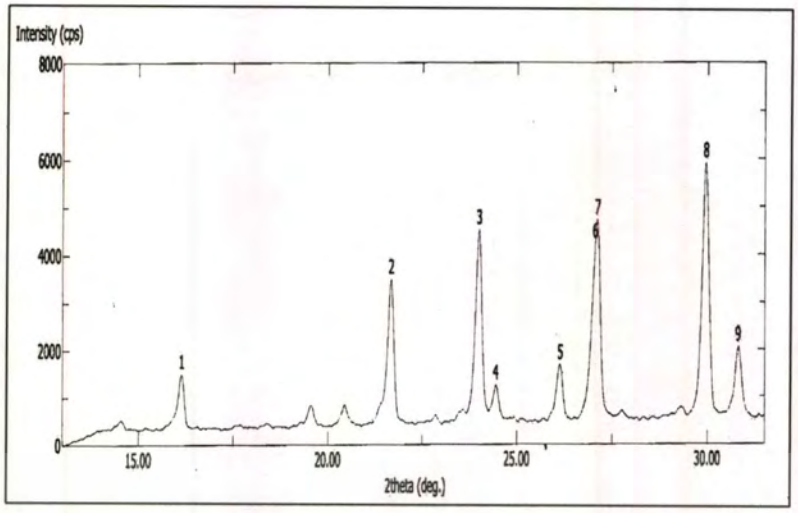
Condition : 1.80SiO_2 : 1.00Al_2O_3 : 3.95Na_2O : 110.05 H_2O, aging temperature at 0-5°C for 12 hours, crystallization temperature at 95°C .(fumed silica as Si source)

As the former results, it is found that 2 hours of crystallization time presented the smallest particle size (500-600 nm). It also showed optimum of crystallinity and CEC with high LCC. Therefore, 2 hours of crystallization time was chosen for further study.

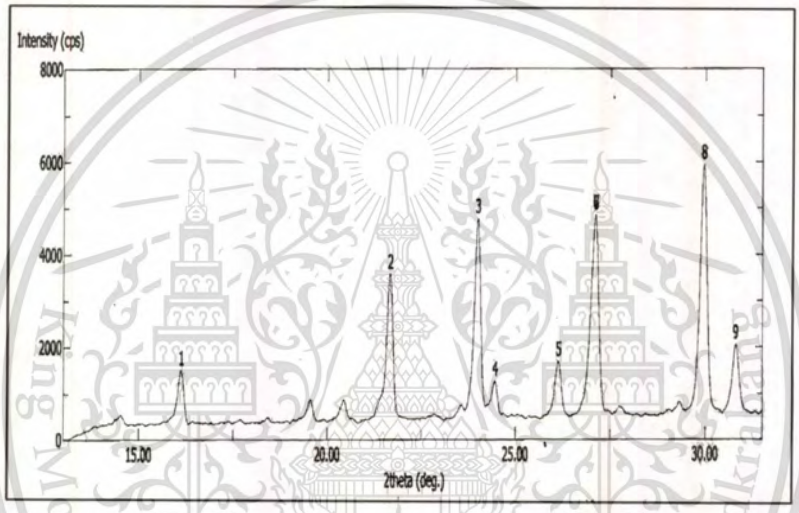
4.5 Effect of Crystallization temperature

Crystallization temperature at 75°C, 85°C, 95°C, and 105°C gave the zeolite A with the peak pattern as shown in Figure 4.11;

(a) 75°C



(b) 85°C



(c) 95°C

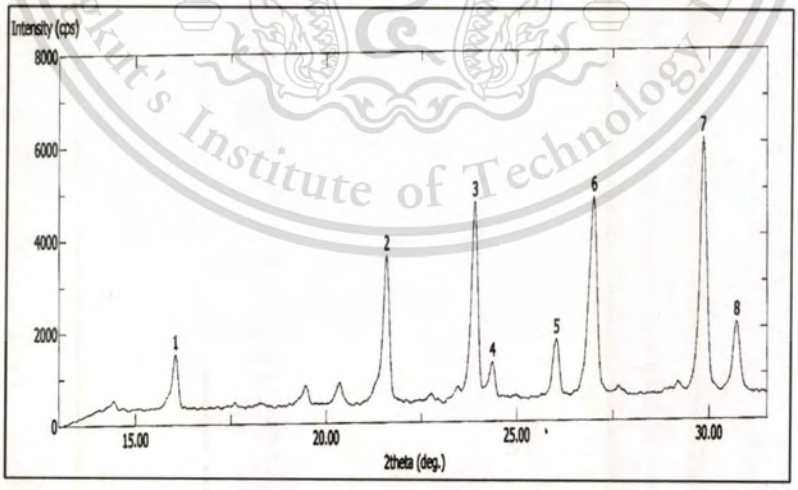


Figure 4.11 X-ray diffraction pattern of synthesized zeolite A compared with crystallization temperature. (a) 75°C, (b) 85°C, (c) 95°C, (d) 105°C

Condition : $1.80SiO_2 : 1.00Al_2O_3 : 3.95Na_2O : 110.05\ H_2O$, aging temperature at 0-5°C for 12 hours, crystallization time 2 hours. (fumed silica as Si source)

(d) 105°C

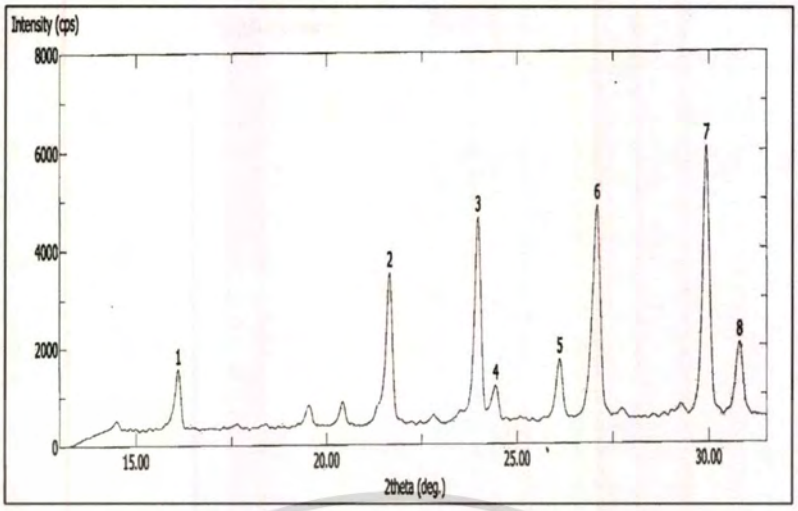


Figure 4.11(Conntinued) X-ray diffraction pattern of synthesized zeolite A compared with crystallization temperature. (a) 75°C, (b) 85°C, (c) 95°C, (d) 105°C

Condition : 1.80SiO_2 : 1.00Al_2O_3 : 3.95Na_2O : 110.05 H_2O, aging temperature at 0-5°C for 12 hours, crystallization time 2 hours. (fumed silica as Si source)

From above XRD, it can be seen that the peak patterns appeared as zeolite A which the calculated relative crystallinity are shown in Table 4.7;

Table 4.7 The comparison of particles size of different crystallization temperature with their properties.

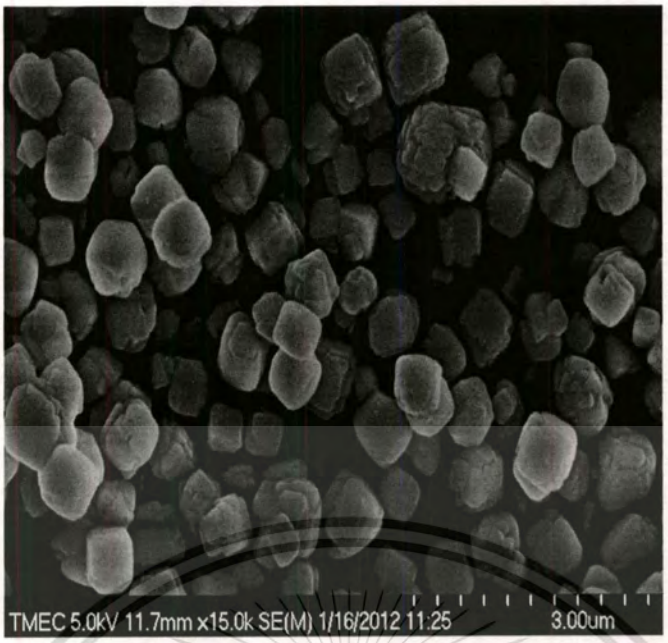
Sample	Size (nm)	Relative Crystallinity (%)	CEC (mg /g) *	LCC (% wt.) **	Yield (%)
Crystallization temperature 75°C	500-600	105.77	168	12.56	57.43
Crystallization temperature 85°C	600-800	106.52	172	11.20	53.38
Crystallization temperature 95°C	500-600	109.15	211	10.54	52.93
Crystallization temperature 105°C	500-600	109.09	255	9.45	51.51
Commercial zeolite A	2,000	100.00	287	8.25	-

* mg $CaCO_3$ / g anhydrous zeolite

** surfactant / anhydrous zeolite

The relative crystallinity of zeolite A synthesized at different crystallization temperatures are higher than that of commercial zeolite A. Nevertheless, the crystallization temperature rarely effect to particle size of zeolite in this experiment. Since the zeolite A was synthesized under the condition of long time aging (12 hours) and 2 hours crystallization time, 75°C crystallization temperature was high enough for activating the zeolite growth. So the zeolite particles are similar size as shown by SEM images (Figure 4.12).

(a) 75°C

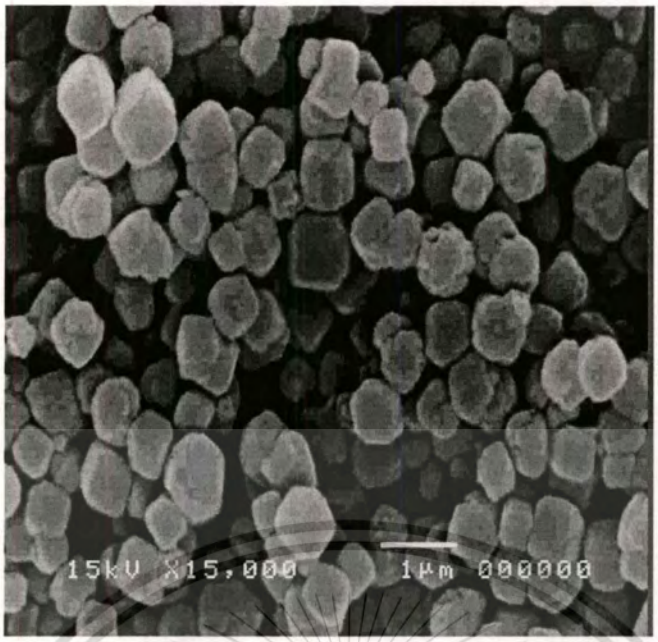


(b) 85°C

Figure 4.12 Scanning electron micrograph of synthesized zeolite A compared with crystallization temperature. (a) 75°C, (b) 85°C, (c) 95°C, (d) 105°C

Condition: 1.80SiO_2 : 1.00Al_2O3 : 3.95Na_2O : 110.05 H_2O, aging temperature at 0-5°C for 12 hours, crystallization time 2 hours. (fumed silica as Si source)

(c) 95°C



(d) 105°C

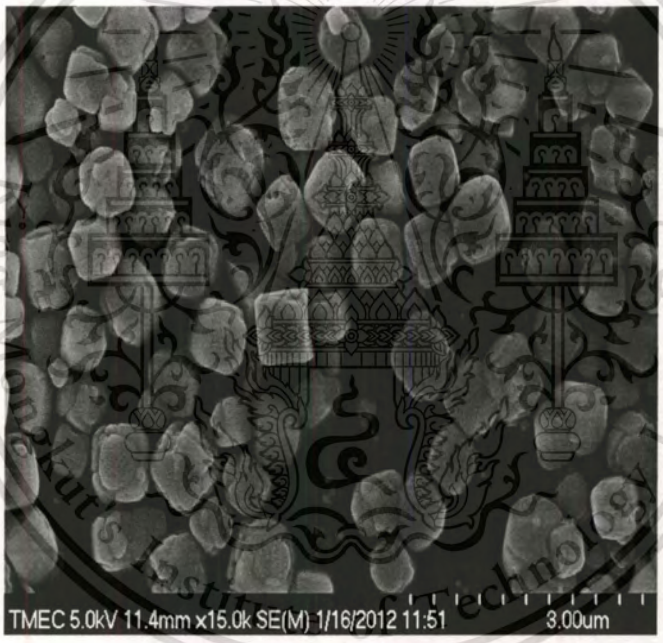


Figure 4.12(Continued) Scanning electron micrograph of synthesized zeolite A compared with crystallization temperature. (a) 75°C, (b) 85°C, (c) 95°C, (d) 105°C

Condition: 1.80SiO_2 : 1.00Al_2O3 : 3.95Na_2O : 110.05 H_2O, aging temperature at 0-5°C for 12 hours, crystallization time 2 hours. (fumed silica as Si source)

The relative crystallinity slightly increased with increasing crystallization temperature which effected to an increase in CEC and a decrease in LCC as observed. From the study crystallization temperature at 95°C provided zeolite A with high crystallinity and suitable CEC and LCC.

CHAPTER 5

CONCLUSION AND SUGGESTIONS

5.1 Conclusion

In this project, nanozeolite A was synthesized with the gel composition of 1.80 SiO_2: 1.00 Al_2O_3 : 3.95 Na_2O : 110.05 H_2O under different conditions.

To obtain nanozeolite A, the source and step of aging and crystallization have to be controlled. Zeolite A that using fumed silica as silica source provided the small particle size (500-600nm). Since fumed silica give high viscosity gel which retard the nucleation and growth step, so a lot of nuclei are created and leading to the formation of zeolite A with small particle size. In general, a small particle size zeolite would possess high liquid carrying capacity (LCC) independent to crystallinity. On the other hand, cation exchange capacity (CEC) depends on crystallinity and large particle size.

The aging step influenced the size distribution and particle size of zeolite A. The longer aging time lead to better size distribution along with the small particle size but, lower relative crystallinity. A large amount of metastable gel is promoted in this step to produce a number of nuclei. Since the nutrient is limited to feed all growing nuclei, small particle size is obtained. The gel that synthesized under high aging temperature also provided smaller particle size. At high temperature (10°C and 20°C), high energy of formation is obtained resulting in a number of nuclei with nano size. As the the free energy of formation decreased rapidly but left some aluminosilicate species in mixture. This leads to renucleation that results in impurity phases. Reducing the alkalinity of the gel would slower the rate of hydrolysis. This can eliminate the impurities and improve crystallinity, CEC, and LCC.

The particle size as well as CEC decreased with a decrease in crystallization time. However, this is inverse for LCC. The crystallization temperature had no effect to the particles size and relative crystallinity. Since zeolite A was synthesized through aging process before

crystallization, 75°C crystallization is high enough for activating the zeolite growth. Accordingly zeolite particles and relative crystallinity are similar for crystallization temperature at 75°C-105°C.

After the synthesis under various conditions, zeolite A using fumed silica as silica source, aging at 0-5°C for 12 hours and crystallization at 95°C for 2 hours provide the nanozeolite A (500-600nm particle size) with high relative crystallinity and optimum cation exchange capacity (CEC) and liquid carrying capacity (LCC).

5.2 Suggestions for future study

5.2.1 Aging time: The longer time of aging, the better size distribution. Therefore, stirring gel at low temperature for longer time (i.e. 3 days or longer) may reduce the particle size.

5.2.2 Surfactant: Addition of surfactant may enhance the rate of nucleation and increase amount of nuclei, which obtained zeolite A in smaller particle size.

5.2.3 Aging temperature: Aging at room temperature may obtain the small crystal size.

5.2.3 Increasing the centrifugation rate: The yield percentages of samples are similar in the range of 50-60%. Generally nanozeolite was separated by centrifugation higher than 10,000 rpm. Since the centrifugal in this project can provide only 3,000 rpm. There is some suspend in the water after the centrifugation. The nanozeolite may be gone by water as shown in low yield percentage.

REFERENCES

[1] W.M. Meire, "Molecular Sieve", Society of the Chemical Industry, London 1968, page 10

[2] P. Kurzendrfer, P.Kuhm, J.Steber, in: M.J. Schwuger (Ed.), Detergents in the Environment, Marcel Dekker, New York, 1997, page 127

[3] D.W. Breck, Zeolite Molecular Sieves: Structure, Chemistry and Uses, JohnWiley & Sons, New York, 1974, page 771

[4] R.M. Barrer, Hydrothermal Chemistry of Zeolites, Academic Press, London, 1982, page 360

[5] Mehdi Kamali, Sedigheh Vaezifar, Hamideh Kolahduzan, Akbar Malekpour, Mohammad Reza Abdi,"Synthesis of nanozeolite A from natural clinoptilolite and aluminum sulfate; Optimization of the method", Powder Technology, Volume 189, Issue 1, 25 January 2009, page 52-56

[6] Breck, D.W. (1974) "Zeolite Molecular Sieves, Structure, Chemistry and Use." John Wiley & Sons, Inc., New York; reprinted by Krieger, Malabar, Florida, 1984.

[7] Jia M. D., Noble R. D. and Fornoff L. L. "Ceramic Zeolite Composite Membranes and Use for Separation of Vapor/Gas Mixture." U.s patent no. 5464798, November 1995.

[8] Robert L. Virta "Zeolites"

[9] Framework of Zeolite A (LTA), From IZA Available on http://izasc.ethz.ch/fmi/xsl/IZA-SC/ftc_fw.xsl?-db=Atlas_main&-lay=fw&-max=25&STC =LTA&-find

[10] Christophe J.Y. Houssin. – Eindhoven, Nanoparticles in zeolite synthesis ,Technische Universiteit Eindhoven, 2003.

[11] F. Liebau, H. Gies, RP Gunawardne, B Marles. Zeolite Issue 6, page 373-377 ,1986

[12] Zeolites for Cleaner Technologies. (Eds.: M. Guisnet, J.-P. Gilson). Imperial College Press, London, 2002.

[13] Catalysis and zeolites: fundamentals and applications. (Eds.: J. Weitkamp, L. Puppe), Springer- Verlag, Berlin, 1999.

[14] Nanoparticle, From Wikipedia, the free encyclopedia Available on http://en.wikipedia.org/wiki/Nanoparticle

[15] Laundry Detergent, From Wikipedia, the free encyclopedia Available on http://en.wikipedia.org/wiki/Laundry_detergent

[16] Zeolites for Detergents - As nature intended, ZEODET Available on http://www.zeolites.eu /downloads/Zeolites.pdf

[17] Functions of different components of laundry detergents from CEEP Available on http ://www.ceep-phosphates.org/files/document/30/detergentcompwithfunct.pdf

[18] Laundry Detergents, From Texas 4-H and Youth Development Available on http://texas4-h.tamu.edu/files/2011/12/consumer_decision_making_guide_laundry_detergents_2011cdm.pdf

[19] Key Characteristics of Laundry Detergent Ingredients, From EPA Available on http://www.epa.gov/dfe/pubs/laundry/techfact/keychar.htm

[20] Zahra Ghasemi and Habibollah Younesi , "Preparation and Characterization of Nanozeolite NaA from Rice Husk at Room Temperature without Organic Additives" , Hindawi Publishing Corporation Journal of Nanomaterials Volume 2011, Article ID 858961, page 8

[21] F. Kleitz, F.Marlow, G. D. Stucky, and F. Sch¨uth, "Mesoporous silica fibers: synthesis, internal structure, and growth kinetics,"Chemistry of Materials, vol. 13, no. 10, page 3587–3595, 2001.

APPENDICES

APPENDIX A

CALCULATION

Example 1: Calculation of chemical composition

Gel composition

Example 2: Calculations of zeolite parameters

Yield, LCC, CEC, Relative crystallinity, and Particle size

Calculation of chemical composition

Gel composition

Gel composition of zeolite NaA

From this equation: $SiO_2(s) + 2NaOH(s) \rightarrow Na_2SiO_3(l) + H_2O(l)$

Synthesis Zeolite NaA from Sodium aluminate as Al source and Fumed silica as Si source

Gel composition is $0.055\ SiO_2 : 0.0305\ Al_2O_3 : 0.1205\ Na_2O : 3.36\ H_2O$

Gel composition is $1.80\ SiO_2 : 1.00\ Al_2O_3 : 3.95\ Na_2O : 110.05\ H_2O$

The amount of SiO_2 in Fumed silica was calculated by

SiO_2; SiO_2 = mole x MW

= 1 mole x 60 g/mole

= 60 g

For Fumed silica 3.3 g, which Fumed silica contains 100% of SiO_2

Thus; Mole of SiO_2 = $\dfrac{3.3 \text{ g of fumed silica} \times 1.0\ SiO_2}{60 \frac{g}{mole} SiO_2}$

= 0.055 mole of SiO_2

The amount of Al_2O_3 in Sodium aluminate (MW=164) was calculated by

Al_2O_3; Al_2O_3 = mole x MW

= 1 mole x 102 g/mole

= 102 g

For Sodium aluminate 5 g, Sodium aluminate contains 62.2% of Al_2O_3

$$\text{Thus;}\quad \text{Mole of } Al_2O_3 = \frac{5 \text{ g of Sodium aluminate} \times 0.622\ Al_2O_3}{102 \frac{g}{mole}\ Al_2O_3}$$

$$= 0.0305 \text{ mole of } Al_2O_3$$

The amount of Na_2O in Sodium aluminate (MW=164) was calculated by

Na_2O; Na_2O = mole x MW

= 1 mole x 62 g/mole

= 62 g

For Sodium aluminate 5 g, which Sodium aluminate contains 37.8% of Na_2O

$$\text{Thus;}\quad \text{Mole of } Na_2O = \frac{5 \text{ g of Sodium aluminate} \times 0.378\ Na_2O}{62 \frac{g}{mole}\ Na_2O}$$

$$= 0.0305 \text{ mole of } Na_2O$$

The amount of Na_2O in 15% wt. of NaOH (MW=40) was calculated by

Na_2O; Na_2O = mole x MW

= 1 mole x 62 g/mole

= 62 g

From 15% wt. of NaOH 48 g

In 100 g of NaOH 15% wt. has NaOH 15 g

Then 48 g of NaOH 15% wt. has NaOH 7.2 g

$$\text{Thus;}\quad \text{Mole of NaOH} = \frac{7.2 \text{ g of NaOH}}{40 \frac{g}{mole}\ NaOH}$$

$$= 0.18 \text{ mole of NaOH}$$

From equation: $2NaOH \longrightarrow Na_2O + H_2O$

As equation shows of Na_2O: 2NaOH

Thus; Mole of Na_2O $= \frac{0.18}{2} = 0.09$ mole of Na_2O

$\therefore$ Mole of Na_2O is 0.0305 + 0.09 $= 0.1205$ mole of Na_2O

From Step of Sodium aluminate preparation, add H_2O 18 g = 1 mole H_2O

In 100 g of 15% wt. of NaOH has H_2O 85 g

Then 48 g of 15% wt. of NaOH has H_2O 40.8 g = 2.27 mole H_2O

The amount of H_2O in 15% wt. of NaOH (MW=40) was calculated by

H_2O; H_2O = mole x MW

= 1 mole x 18 g/mole

= 18 g

From 15% wt. of NaOH 48 g

In 100 g of NaOH 15% wt. has NaOH 15 g

Then 48 g of NaOH 15% wt. has NaOH 7.2 g

Thus; Mole of NaOH $= \frac{7.2 \text{ g of NaOH}}{40 \frac{\text{g}}{\text{mole}} \text{ NaOH}}$

= 0.18 mole of NaOH

From equation: $2NaOH \longrightarrow Na_2O + H_2O$

As equation shows of H_2O : 2NaOH

Thus; Mole of H_2O $= \frac{0.18}{2} = 0.09$ mole of H_2O

$\therefore$ Mole of H_2O is 1.0 + 2.27 + 0.09 $= 3.36$ mole of H_2O

Synthesis Zeolite NaA from Sodium aluminate as Al source and LudoxAS40 as Si source

Gel composition is $0.055\ SiO_2 : 0.0305\ Al_2O_3 : 0.1205\ Na_2O : 3.36\ H_2O$

Gel composition is $1.80\ SiO_2 : 1.00\ Al_2O_3 : 3.95\ Na_2O : 110.05\ H_2O$

From LudoxAS40

In 100 g of Ludox has SiO_2 40 g

Then 3.3 g of Ludox has SiO_2 1.32 g

$\therefore$ We must add 8.25 g of Ludox to get SiO_2 3.3 g

For LudoxAS40 8.25g, which LudoxAS40 contains 100% of SiO_2

Thus; Mole of SiO_2 $= \dfrac{3.3\text{ g of } SiO_2 \times 1.0\ SiO_2}{60\ \frac{g}{mole}\ SiO_2}$

$= 0.055$ mole of SiO_2

The amount of Al_2O_3 in Sodium aluminate (MW=164) was calculated by

Al_2O_3; $Al_2O_3 =$ mole x MW

$=$ 1 mole x 102 g/mole

$=$ 102 g

For Sodium aluminate 5 g, which Sodium aluminate contains 62.2% of Al_2O_3

Thus; Mole of Al_2O_3 $= \dfrac{5\text{ g of Sodium aluminate} \times 0.622\ Al_2O_3}{102\ \frac{g}{mole}\ Al_2O_3}$

$= 0.0305$ mole of Al_2O_3

The amount of Na_2O in Sodium aluminate (MW=164) was calculated by

Na_2O; Na_2O = mole x MW

= 1 mole x 62 g/mole

= 62 g

For Sodium aluminate 5 g, which Sodium aluminate contains 37.8% of Na_2O

Thus; Mole of Na_2O = $\dfrac{5 \text{ g of Sodium aluminate} \times 0.378\ Na_2O}{62 \frac{g}{mole}\ Na_2O}$

= 0.0305 mole of Na_2O

The amount of Na_2O in 15% wt. of NaOH (MW=40) was calculated by

Na_2O; Na_2O = mole x MW

= 1 mole x 62 g/mole

= 62 g

From 15% wt. of NaOH 48 g

In 100 g of NaOH 15% wt. has NaOH 15 g

Then 48 g of NaOH 15% wt. has NaOH 7.2 g

Thus; Mole of NaOH = $\dfrac{7.2 \text{ g NaOH}}{40 \frac{g}{mole}\ NaOH}$

= 0.18 mole of NaOH

From equation; $2NaOH \longrightarrow Na_2O + H_2O$

As equation shows of Na_2O : 2NaOH

Thus; Mole of Na_2O = $\dfrac{0.18}{2}$ = 0.09 mole of Na_2O

$\therefore$ Mole of Na_2O is 0.0305 + 0.09 = 0.1205 mole of Na_2O

From Step Sodium aluminate preparation, add H_2O 13.05 g = 0.725 mole H_2O

From 100 g of 15% wt. of NaOH has H_2O 85 g

Then 48 g of 15% wt. of NaOH has H_2O 40.8 g = 2.27 mole H_2O

The amount of H_2O in 15% wt. of NaOH (MW=40) was calculated by

H_2O; H_2O = mole x MW

= 1 mole x 18 g/mole

= 18 g

From 15% wt. of NaOH 48 g

In 100 g of NaOH 15% wt. has NaOH 15 g

Then 48 g of NaOH 15% wt. has NaOH 7.2 g

Thus; Mole of NaOH $= \dfrac{7.2 \text{ g NaOH}}{40 \frac{\text{g}}{\text{mole}} \text{ NaOH}}$

= 0.18 mole of NaOH

From equation: $2NaOH \longrightarrow Na_2O + H_2O$

As equation shows of H_2O : 2NaOH

Thus; Mole of H_2O $= \dfrac{0.18}{2}$ = 0.09 mole of H_2O

From LudoxAS40

In 100 g of Ludox has H_2O 60 g

Then 8.25 g of Ludox has H_2O 4.95 g = 0.275 mole of H_2O

$\therefore$ Mole of H_2O is 0.725 + 2.27 + 0.09 + 0.275 = 3.36 mole of H_2O

Synthesis Zeolite NaA from Sodium aluminate as Al source and Sodium metasilicate as Si source

Gel composition is $0.055\ SiO_2 : 0.0305\ Al_2O_3 : 0.1205\ Na_2O : 3.36\ H_2O$

Gel composition is $1.80\ SiO_2 : 1.00\ Al_2O_3 : 3.95\ Na_2O : 110.05\ H_2O$

From Sodium metasilicate

In 122 g of Sodium metasilicate has SiO_2 60 g

Then 6.71 g of Sodium metasilicate has SiO_2 3.3 g

For Sodium meta silicate 6.71 g, which Sodium metasilicate contain 100% of SiO_2

Thus; Mole of SiO_2 $= \dfrac{3.3 \text{ g of } SiO_2 \times 1.0\ SiO_2}{60 \frac{g}{mole} SiO_2}$

$= 0.055$ mole of SiO_2

The amount of Al_2O_3 in Sodium aluminate (MW=164) was calculated by

Al_2O_3; $Al_2O_3 =$ mole x MW

$=$ 1 mole x 102 g/mole

$=$ 102 g

For Sodium aluminate 5 g, which Sodium aluminate contains 62.2% of Al_2O_3

Thus; Mole of Al_2O_3 $= \dfrac{5 \text{ g of Sodium aluminate} \times 0.622\ Al_2O_3}{102 \frac{g}{mole} Al_2O_3}$

$= 0.0305$ mole of Al_2O_3

The amount of Na_2O in Sodium aluminate (MW=164) was calculated by

Na_2O; Na_2O = mole x MW

= 1 mole x 62 g/mole

= 62 g

For Sodium aluminate 5 g, which Sodium aluminate contains 37.8% of Na_2O

Thus; Mole of Na_2O = $\frac{5 \text{ g of Sodium aluminate} \times 0.378\ Na_2O}{62 \frac{g}{mole} Na_2O}$

= 0.0305 mole of Na_2O

From Sodium metasilicate

In 122 g of Sodium metasilicate has Na_2O 62 g

Then 6.71 g of Sodium metasilicate has Na_2O 3.41 g = 0.055

The amount of Na_2O in 15% wt. of NaOH (MW=40) was calculated by

Na_2O; Na_2O = mole x MW

= 1 mole x 62 g/mole

= 62 g

From 15% wt. of NaOH 18.67 g

In 100 g of NaOH 15% wt. has NaOH 15 g

Then 18.67 g of NaOH 15% wt. has NaOH 2.8 g

Thus; Mole of NaOH = $\frac{2.8 \text{ g NaOH}}{40 \frac{g}{mole} NaOH}$

= 0.07 mole of NaOH

From equation: $2NaOH \longrightarrow Na_2O + H_2O$

As equation showed of Na_2O : 2NaOH

Thus; Mole of Na_2O = $\frac{0.07}{2}$ = 0.0350 mole of Na_2O

$\therefore$ Mole of Na_2O is 0.0305 + 0.055 + 0.0350 = 0.1205 mole of Na_2O

From Step of Sodium aluminate preparation, add H_2O 21.96 g = 1.22 mole H_2O

From step of Sodium meta silicate preparation, add H_2O 21.96 g = 1.22 mole H_2O

From 100 g of 15% wt. of NaOH has H_2O 85g

Then 18.67 g of 15% wt. of NaOH has H_2O 15.87 g = 0.88 mole H_2O

The amount of H_2O in 15% wt. of NaOH (MW=40) was calculated by

H_2O; H_2O = mole x MW

= 1 mole x 18 g/mole

= 18 g

From 15% wt. of NaOH 48 g

In 100 g of NaOH 15% wt. has NaOH 15 g

Then 18.67 g of NaOH 15% wt. has NaOH 2.8 g

Thus; Mole of NaOH = $\frac{2.8 \text{ g NaOH}}{40 \frac{\text{g}}{\text{mole}} \text{NaOH}}$

= 0.07 mole of NaOH

From equation: $2NaOH \longrightarrow Na_2O + H_2O$

As equation showed of H_2O : 2NaOH

$$\text{Thus; Mole of } H_2O = \frac{0.07}{2} = 0.035 \text{ mole of } H_2O$$

$$\therefore \text{ Mole of } H_2O \text{ is } 1.22 + 1.22 + 0.88 + 0.035 = 3.36 \text{ mole of } H_2O$$

Synthesis Zeolite NaA from Sodium aluminate as Al source and Fumed silica as Si source **at base 3.00**

Gel composition is $0.055\ SiO_2 : 0.0305\ Al_2O_3 : 0915\ Na_2O : 3.36\ H_2O$

Gel composition is $1.80\ SiO_2 : 1.00\ Al_2O_3 : 3.00\ Na_2O : 110.05\ H_2O$

The amount of SiO_2 in Fumed silica was calculated by

SiO_2; SiO_2 = mole x MW

= 1 mole x 60 g/mole

= 60 g

For Fumed silica 3.3 g, which Fumed silica contains 100% of SiO_2

$$\text{Thus; Mole of } SiO_2 = \frac{3.3 \text{ g of Fumed silica} \times 1.0\ SiO_2}{60 \frac{\text{g}}{\text{mole}}\ SiO_2}$$

= 0.055 mole of SiO_2

The amount of Al_2O_3 in Sodium aluminate (MW=164) was calculated by

Al_2O_3; Al_2O_3 = mole x MW

= 1 mole x 102 g/mole

= 102 g

For Sodium aluminate 5 g, which Sodium aluminate contains 62.2% of Al_2O_3

Thus; Mole of Al_2O_3 = $\dfrac{5\text{ g of Sodium aluminate} \times 0.622\ Al_2O_3}{102\ \frac{g}{mole}\ Al_2O_3}$

= 0.0305 mole of Al_2O_3

The amount of Na_2O in Sodium aluminate (MW=164) was calculated by

Na_2O; Na_2O = mole x MW

= 1 mole x 62 g/mole

= 62 g

For Sodium aluminate 5 g, which Sodium aluminate contains 62.2% of Na_2O

Thus; Mole of Na_2O = $\dfrac{5\text{ g of Sodium aluminate} \times 0.378\ Na_2O}{62\ \frac{g}{mole}\ Na_2O}$

= 0.0305 mole of Na_2O

The amount of Na_2O in 15% wt of NaOH (MW=40) was calculate by

Na_2O; Na_2O = mole x MW

= 1 mole x 62 g/mole

= 62 g

From 15% wt. of NaOH 32.53 g

In 100 g of NaOH 15% wt. has NaOH 15 g

Then 32.53 g of NaOH 15% wt. has NaOH 4.88 g

Thus; Mole of NaOH = $\dfrac{4.88\text{ g NaOH}}{40\ \frac{g}{mole}\ NaOH}$

= 0.122 mole of NaOH

From equation: $2NaOH \longrightarrow Na_2O + H_2O$

As equation showed of Na_2O : 2NaOH

Thus; Mole of Na_2O = $\frac{0.122}{2}$ = 0.061 mole of Na_2O

$\therefore$ Mole of Na_2O is 0.0305 + 0.061 = 0.0915 mole of Na_2O

From Step to prepare Sodium aluminate add H_2O 31.672 g = 1.76 mole H_2O

From 100 g of 15% wt. of NaOH has H_2O 85 g

Then 32.53 g of 15% wt. of NaOH has H_2O 27.65 g = 1.54 mole H_2O

The amount of H_2O in 15% wt. of NaOH (MW=40) was calculated by

H_2O; H_2O = mole x MW

= 1 mole x 18 g/mole

= 18 g

From 15% wt. of NaOH 32.53 g

In 100 g of NaOH 15% wt. has NaOH 15 g

Then 32.53 g of NaOH 15% wt. has NaOH 4.88 g

Thus; Mole of NaOH = $\frac{4.88 \text{ g NaOH}}{40 \frac{\text{g}}{\text{mole}} \text{ NaOH}}$

= 0.122 mole of NaOH

From equation: $2NaOH \longrightarrow Na_2O + H_2O$

As equation showed of H_2O : 2NaOH

Thus; Mole of H_2O = $\frac{0.122}{2}$ = 0.061 mole of H_2O

$\therefore$ Mole of H_2O is 1.76 + 1.54 + 0.061 = 3.36 mole of H_2O

Calculations of zeolite parameters

Yield

%Yield can be obtained from the following equation

$$\%\text{Yield} = \frac{\text{actual weight of zeolite}(g)}{\text{theoretical weight}(g)} \times 100$$

Theoretical weight can calculate from gel composition of zeolite without H_2O

0.0549 SiO2 : 0.0305 Al2O3 : 0.1205 Na2O

For example weight of zeolite from crystallization time 1hr is 7.353 g and theoretical weight of zeolite is 13.876 g

$$\%\text{Yield} = \frac{7.353g}{13.876\ g} \times 100$$

$$= 52.99\ \%$$

Liquid carrying capacity (LCC) of Zeolite A

From TGA, Liquid carrying capacity (LCC) of zeolite A were determined by following equation

$$\frac{\text{Weight of zeolite adsorbed surfactant - Weight of zeolite}}{\text{Weight of zeolite}} \times 100$$

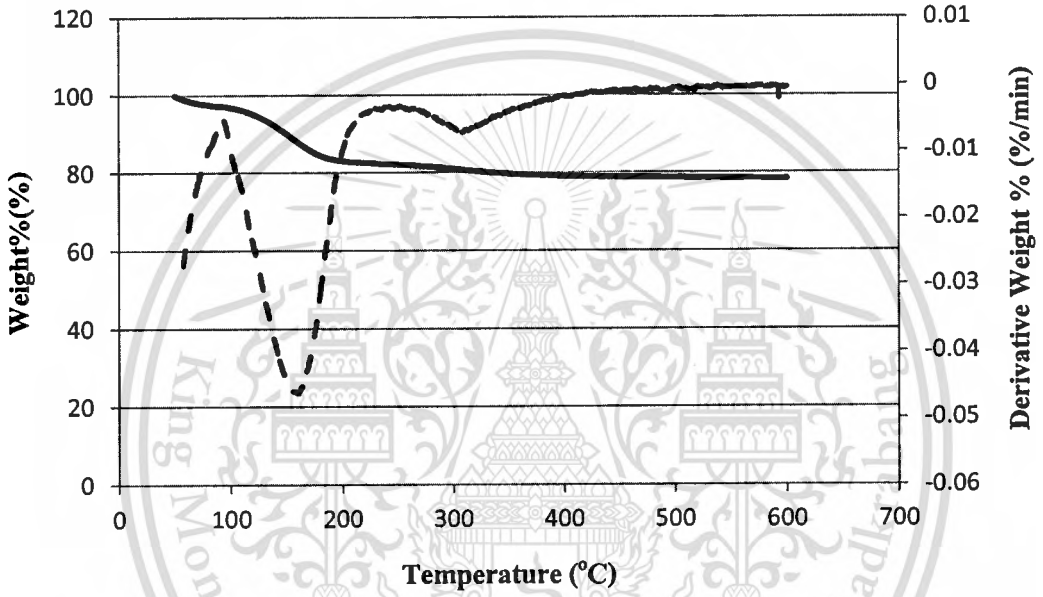


Figure A1 TGA/DTG of zeolite A

Condition : : 1.80 SiO_2 : 1.00 Al_2O_3 : 3.95 Na_2O : 110.05 H_2O ,Aging time 8 hours, Aging temperature 0-5°C, Crystallization time 2 hours, and Crystallization temperature 95°C. (fumed silica as Si source)

From the TGA graph; the weight of zeolite adsorbed surfactant start at temperature ~ 163°C and weight of zeolite is at the end point of temperature 600°C

Table A1 Example from TGA data

TGA Temp.	Time	Unsubtracted Weight	Baseline Weight	Program Temp.	Sample Temp.	Approx. Gas flow
	8.066667	18.837957	0.000000	171.006000	162.554000	0.000000
	8.083333	18.828683	0.000000	171.256000	162.858000	0.000000
	8.100000	18.819538	0.000000	171.506000	*163.153000	0.000000
	8.116667	18.810155	0.000000	171.756000	163.454000	0.000000
	36.333333	17.182231	0.000000	595.006000	599.998000	0.000000
	36.350000	17.182172	0.000000	595.256000	*600.250000	0.000000
	36.366667	17.181727	0.000000	595.506000	600.496000	0.000000
	36.383333	17.181323	0.000000	595.756000	600.75000	0.000000

For example;

From the reported data at temperature 163.153°C, the unsubtracted weight = 18.819538

From the reported data at temperature 600.250°C, the unsubtracted weight = 17.182172

$$\frac{\text{Weight of zeolite adsorbed surfactant - Weight of zeolite}}{\text{Weight of zeolite}} \times 100$$

$$\frac{18.819 - 17.182}{17.182} \times 100 = 9.52$$

Cation Exchange Capacity

From the experiment, the molarities of EDTA could be calculated from the following equation ;

$$\text{Molarities of EDTA} = \frac{\text{Weight of } CaCO_3}{\text{mL of EDTA} \times 100.09 \times 50}$$

For example, weight of $CaCO_3$ is 0.502 mg and the amount of EDTA used is 8.3 ml $CaCO_3$

$$\text{Molarities of EDTA} = \frac{502}{8.3 \times 100.09 \times 50}$$

$$= \quad 0.01$$

After calculate the molarities of EDTA then calculate cation exchange capacity (CEC) can be calculated from the following equation.

$$CEC = \frac{(B\text{-}V)\times M\times 100.09\times 25}{W\times S}$$

B = Volume (mL) of EDTA titrated with Calcium Chloride solution

V = Volume (mL) of EDTA titrated with Sample solution

M = Molarities of EDTA

W = Sample weight (g)

100.09 = Molecular weight of $CaCO_3$

25 = Ca^{2+}Solution 250(mL)/Volume of titrant 10 mL

S = Lost of ignitions (1- LOI)

To analyze the loss of ignition, TGA (thermo gravimetric analysis) method was used. 10-20 mg of zeolite A was loaded into sample holder and heated at temperature range 50-600°C, heating rate at 15°C/minute.

For example Volume (ml) of EDTA titrated with Calcium Chloride solution is 16 mL, Volume (mL) of EDTA titrated with Sample solution is 9.23 mL, Weight of sample is 0.5 g, Lost of ignitions is 0.8.

$$CEC = \frac{(16\text{-}9.2)\times 0.005\times 100.09\times 25}{0.5\times 0.8}$$

$$= \quad 212 \text{ mg } CaCO_3\text{/gram of anhydrous zeolite}$$

Relative crystallinity

The relative crystallinity was calculated from the following equation.

$$\text{Relative crystallinity} = \frac{\text{Intensity at 2 theta } 30^{\circ} \text{ (100plane)}}{\text{Standard Intensity at 2 theta } 30^{\circ} \text{ (100plane)}} \times 100$$

For example; the relative crystallinity of aging time 12 hours

$$\frac{\text{Intensity at 2theta30 (100plane)}}{\text{Standard Intensity at 2thata 30 (100plane)}} \times 100 = \frac{6092}{5581} \times 100 = 109.15$$

Particle size

Table A2 Particle size and standard deviation

Condition	Time/ Temp.	Particle size(nm)	No. of particles	Particle size average (nm)	Standard deviation
Fumed Silica	Aging at 0-5°C for 6 hours, Crystallization at 95°C for 2 hours	401-500	15	557.68	64.78
		501-600	31		
		601-700	4		
Ludox AS40		1201-1300	6	1312.98	80.81
		1301-1400	16		
		1401-1500	8		
Sodium metasilicate		1201-1300	31	1277.76	42.08
		1301-1400	9		
Aging time	8 hours	301-400	6	504.90	96.33
		401-500	6		
		501-600	20		
		601-700	8		
	12 hours	401-500	11	541.33	65.42
		501-600	16		
		601-700	3		

Condition	Time/ Temp.	Particle size(nm)	No. of particles	Particle size average (nm)	Standard deviation
Aging time	24 hours	301-400	17	437	72.13
		401-500	11		
		501-600	2		
Aging temperature	10°C	201-300	4	353.50	101.22
		401-500	2		
	20°C	101-200	6	262.33	64.48
		201-300	17		
		301-400	5		
	20°C ($3.00\ Na_2O$)	301-400	15	497	131.58
		401-500	3		
		501-600	3		
		601-700	4		
Crystallization time	3 hours	301-400	3	592.50	161.76
		401-500	2		
		501-600	6		
		601-700	4		
		701-800	6		
		801-900	4		
	5 hours	500-600	4	805.33	227.43
		601-700	2		
		701-800	2		
		801-900	4		
		901-1000	2		
		1001-2000	6		

Condition	Time/ Temp.	Particle size(nm)	No. of particles	Particle size average (nm)	Standard deviation
Crystallization temperature	75°C	401-500	7	607	91.01
		501-600	9		
		601-700	12		
		701-800	2		
	85°C	401-500	2	650	136.93
		501-600	5		
		601-700	5		
		701-800	11		
		801-900	9		
	105°C	401-500	6	584.50	99.45
		501-600	10		
		601-700	12		
		701-800	6		

For Aging temperature at 0-5°C, Crystallization time 2 hours and Crystallization temperature at 95°C the data similar to aging time 2 hours.

The Standard deviation calculate from

$$SD = \sqrt{\frac{\sum_{i=1}^{k} f_i\left(X_i - \overline{X}\right)^2}{N}}$$

f = the frequency of particle size

X = middle point particle size range

$\overline{X}$ = average particle size

N = number of data.

APPENDIX B

SCANNING ELECTRON MICROSCOPE IMAGES

2000X 5000X

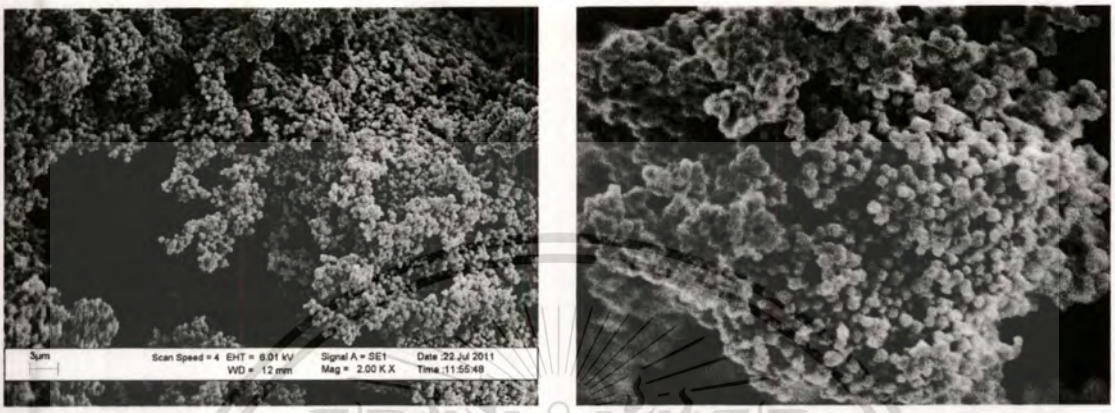


Figure B1 Fumed silica source scanning at 2000x and 5000x magnification.

Condition : 1.80 SiO_2 : 1.00 Al_2O_3 : 3.95 Na_2O : 110.05 H_2O ,Aging at 0°C for 6 hours, Crystallization at 100°C for 2 hours.

2000X 5000X

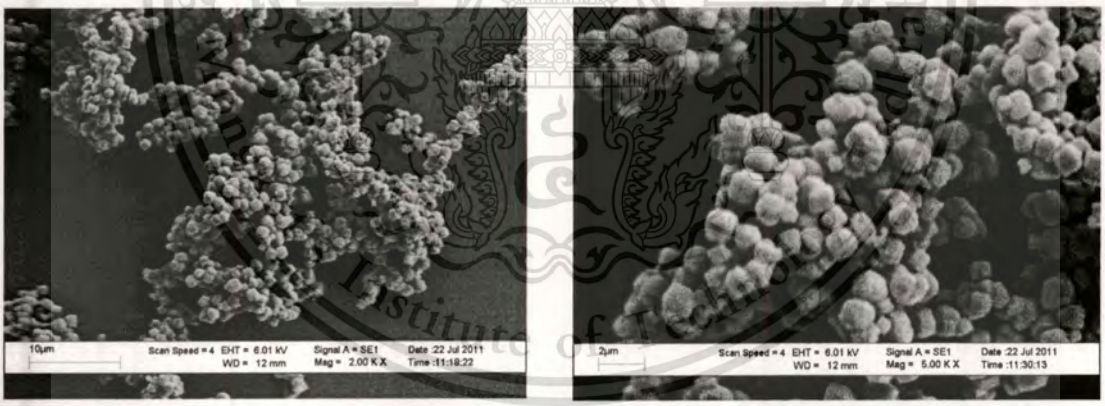


Figure B2 LudoxAS40 source scanning at 2000x and 5000x magnification.

Condition : 1.80 SiO_2 : 1.00 Al_2O_3 : 3.95 Na_2O : 110.05 H_2O ,Aging at 0°C for 6 hours, Crystallization at 100°C for 2 hours.

2000X 5000X

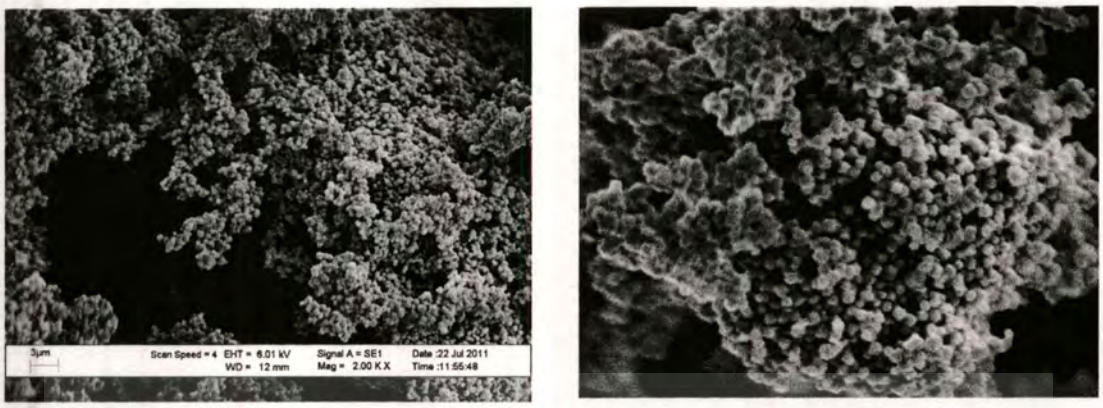


Figure B3 Sodium metasilicate source scanning at 2000x and 5000x magnification.

Condition : 1.80 SiO_2 : 1.00 Al_2O_3 : 3.95 Na_2O : 110.05 H_2O ,Aging at 0°C for 6 hours, Crystallization at 100°C for 2 hours.

5000X 10000X 15000X

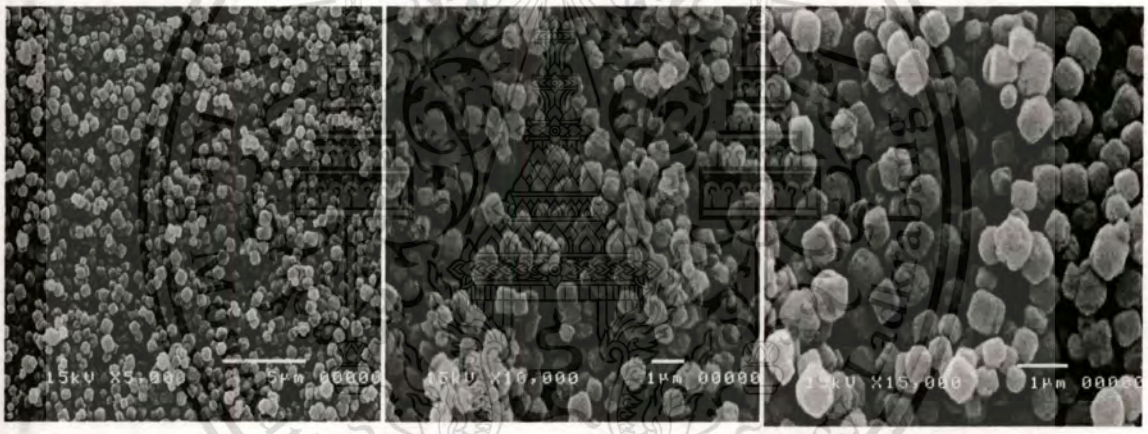


Figure B4 Fumed silica ,8 hours aging time scanning at 5000x, 10000x, and 15000x magnification.

Condition : 1.80 SiO_2 : 1.00 Al_2O_3 : 3.95 Na_2O : 110.05 H_2O ,Aging at 0°C ,Crystallization at 95°C for 2 hours.

5000X 10000X 15000X

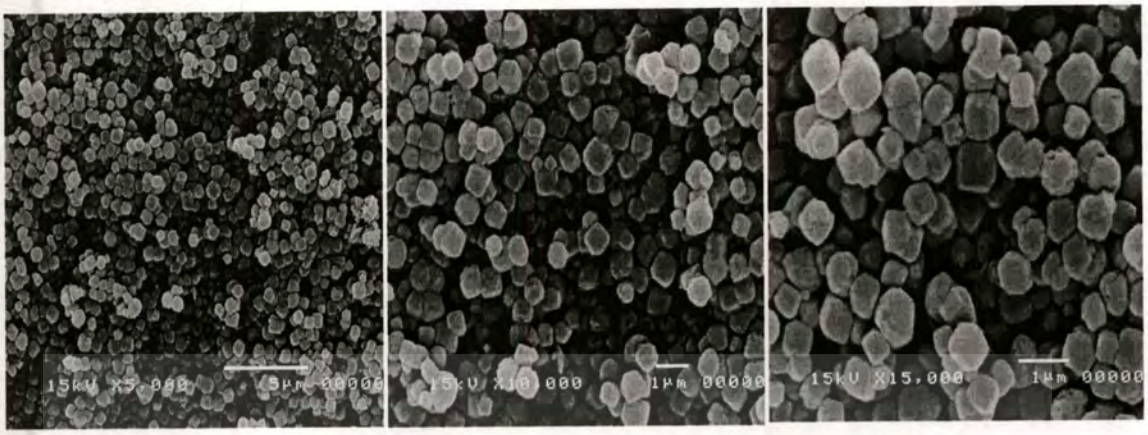


Figure B5 Fumed Silica ,12 hours aging time scanning at 5000x, 10000x, and 15000x magnification.

Condition : 1.80 SiO_2 : 1.00 Al_2O_3 : 3.95 Na_2O : 110.05 H_2O,Aging at 0°C , Crystallization at 95°C for 2 hours.

5000X 10000X 15000X

Figure B6 Fumed Silica ,24 hours aging time scanning at 5000x, 10000x, and 15000x magnification.

Condition : 1.80 SiO_2 : 1.00 Al_2O_3 : 3.95 Na_2O :110.05 H_2O,Aging at 0°C ,Crystallization at 95°C for 2 hours.

5000X 10000X 15000X

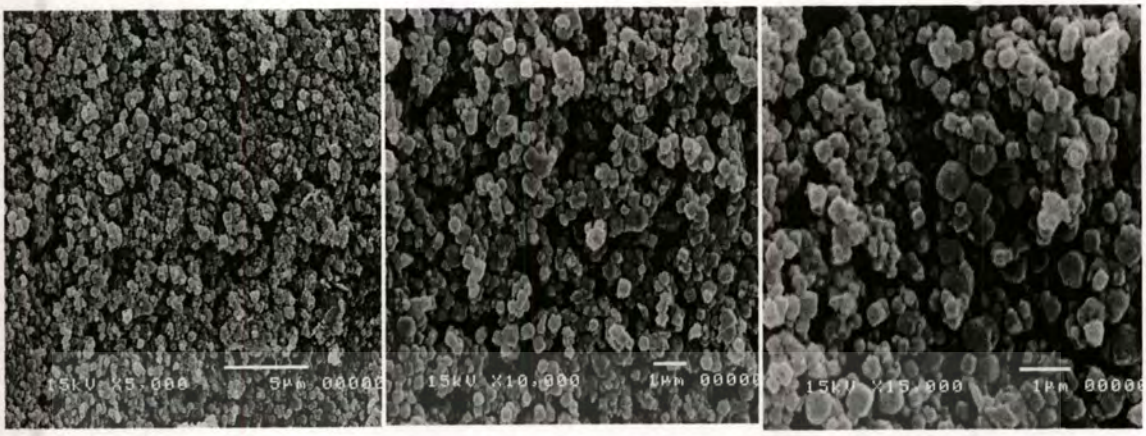


Figure B7 Fumed Silica, 10°C aging temperature scanning at 5000x, 10000x, and 15000x magnification.

Condition : 1.80 SiO_2 : 1.00 Al_2O_3 : 3.95 Na_2O :110.05 H_2O ,Aging time 12 hours, Crystallization at 95°C for 2 hours.

10000X 10000X 10000X

Figure B8 Fumed Silica impurities,10°C aging temperature scanning at 10000x magnification.

Condition : 1.80 SiO_2 : 1.00 Al_2O_3 : 3.95 Na_2O :110.05 H_2O ,Aging time 12 hours, Crystallization at 95°C for 2 hours.

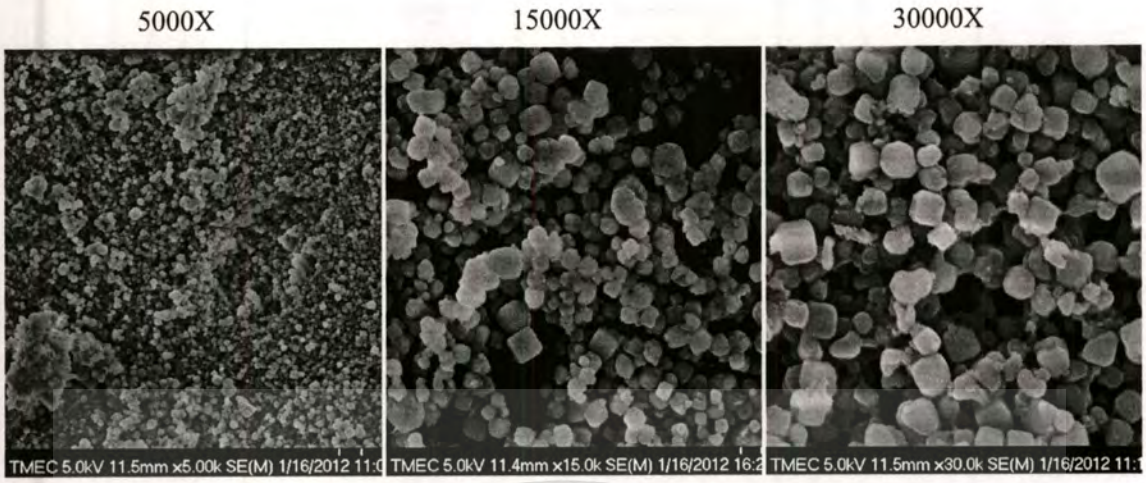


Figure B9 Fumed Silica, 20°C aging temperature scanning at 5000x, 10000x, and 15000x magnification.

Condition : 1.80 SiO_2 : 1.00 Al_2O_3 : 3.95 Na_2O :110.05 H_2O ,Aging time 12 hours, Crystallization at 95°C for 2 hours.

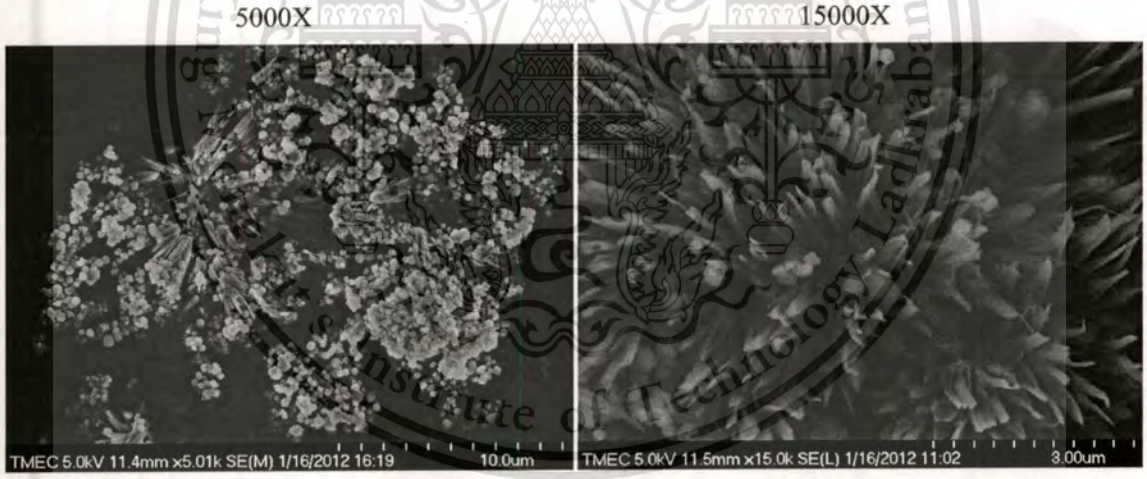


Figure B10 Fumed Silica impurities,20°C aging temperature scanning at 5000x, and 15000x magnification.

Condition : 1.80 SiO_2 : 1.00 Al_2O_3 : 3.95 Na_2O :110.05 H_2O ,Aging time 12 hours, Crystallization at 95°C for 2 hours.

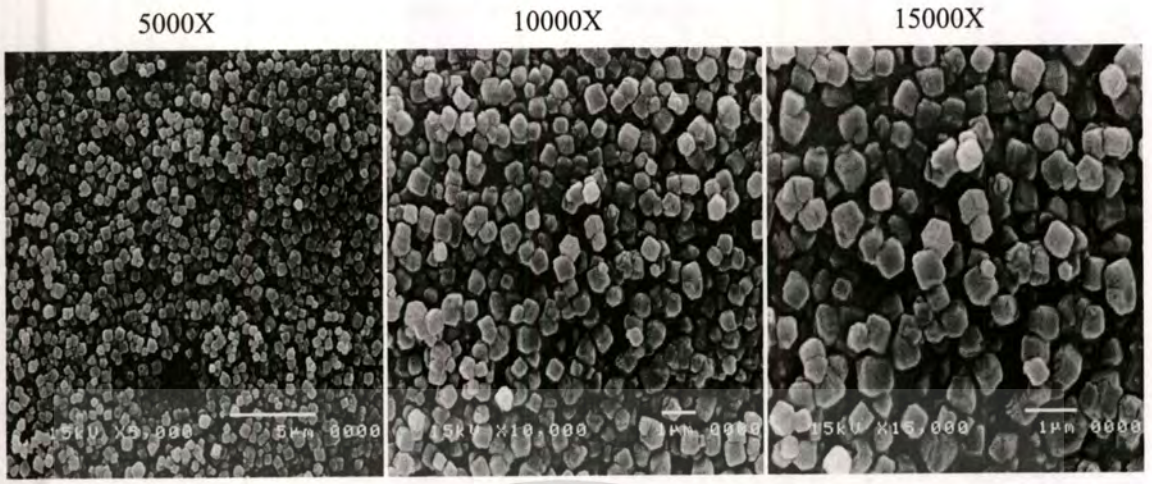


Figure B11 Fumed Silica 3.00 Na_2O, 20°C aging temperature scanning at 5000x, 10000x, and 15000x magnification.

Condition : 1.80 SiO_2 : 1.00 Al_2O_3 : 3.95 Na_2O :110.05 H_2O ,Aging time 12 hours, Crystallization at 95°C for 2 hours.

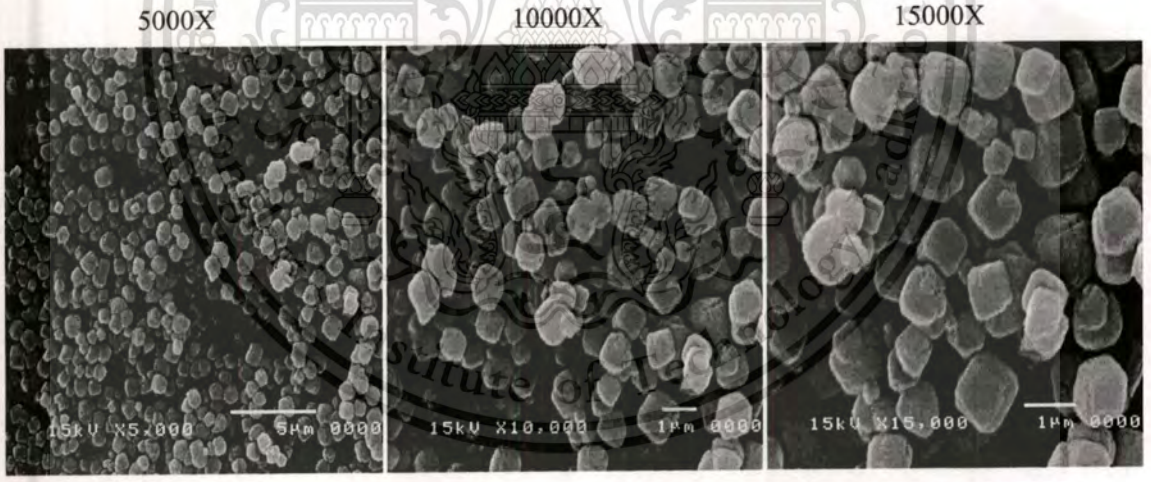


Figure B13 Fumed Silica, 3 hours crystallization time, scanning at 5000x, 10000x, and 15000x magnification.

Condition : 1.80 SiO_2 : 1.00 Al_2O_3 : 3.95 Na_2O :110.05 H_2O , Aging at 0°C for 12 hours, Crystallization at 95°C for 3 hours.

5000X 10000X 15000X

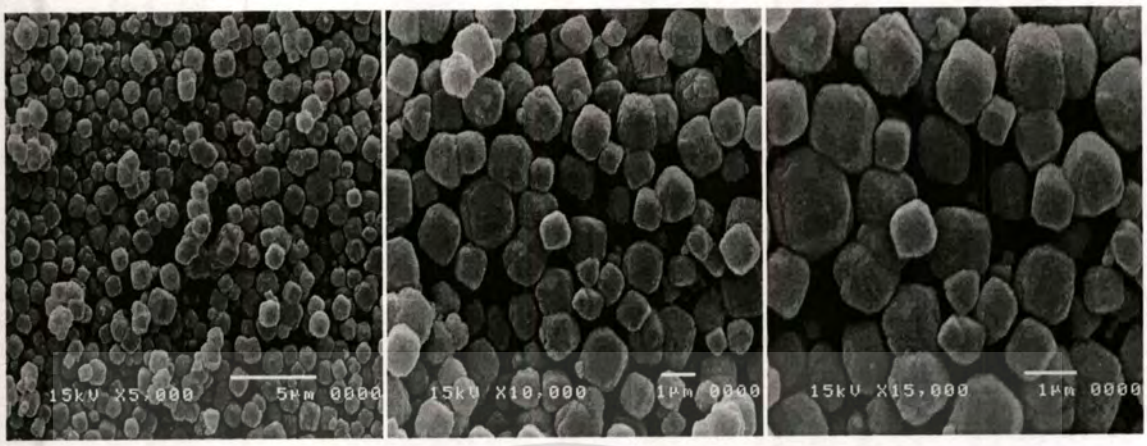


Figure B14 Fumed Silica, 5 hours crystallization time, scanning at 5000x, 10000x, and 15000x magnification.

Condition : 1.80 SiO_2 : 1.00 Al_2O_3 : 3.95 Na_2O :110.05 H_2O ,Aging at 0°C for 12 hours, Crystallization at 95°C for 5 hours.

5000X 15000X 15000X

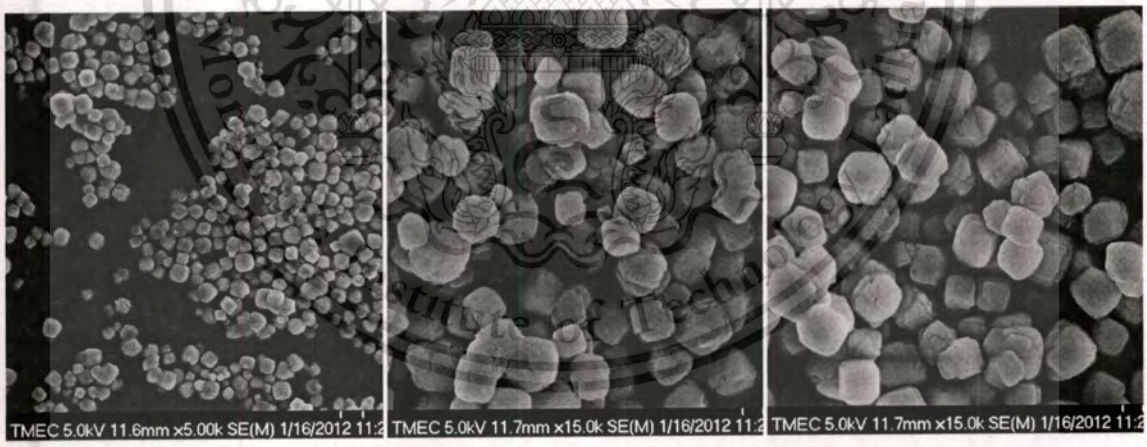


Figure B15 Fumed Silica, 75°C crystallization temperature, scanning at 5000x, and 15000x magnification.

Condition : 1.80 SiO_2 : 1.00 Al_2O_3 : 3.95 Na_2O :110.05 H_2O ,Aging at 0°C for 12 hours, Crystallization at 75°C for 2 hours.

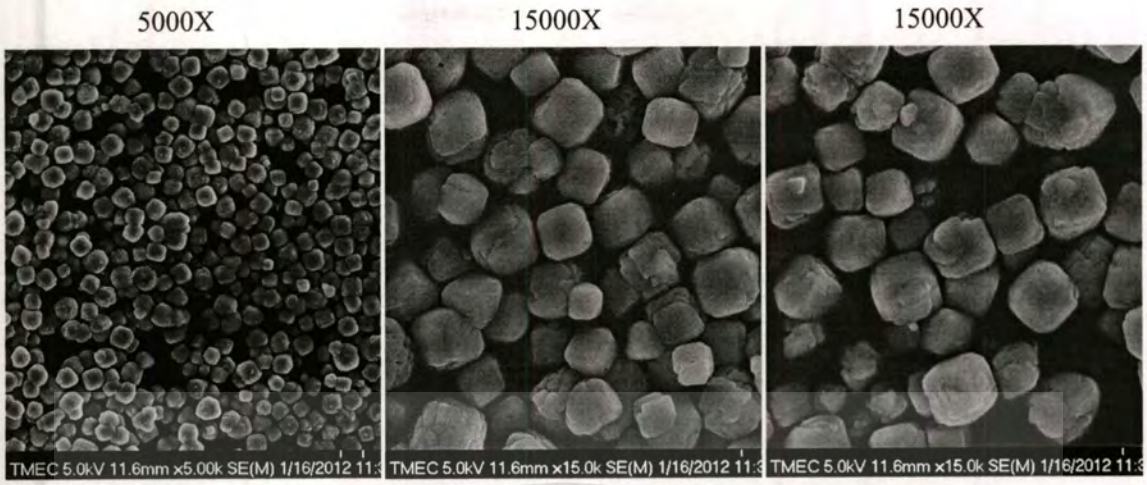


Figure B16 Fumed Silica, 85°C crystallization temperature, scanning at 5000x, and 15000x magnification

Condition : 1.80 SiO_2 : 1.00 Al_2O_3 : 3.95 Na_2O :110.05 H_2O ,Aging at 0°C for 12 hours, Crystallization at 85°C for 2 hours.

Figure B17 Fumed Silica, 105°C crystallization temperature, scanning at 5000x, and 15000x magnification.

Condition : 1.80 SiO_2 : 1.00 Al_2O_3 : 3.95 Na_2O :110.05 H_2O ,Aging at 0°C for 12 hours, Crystallization at 105°C for 2 hours.

APPENDIX C

THERMOGRAVIMETRIC ANALYSIS DATA

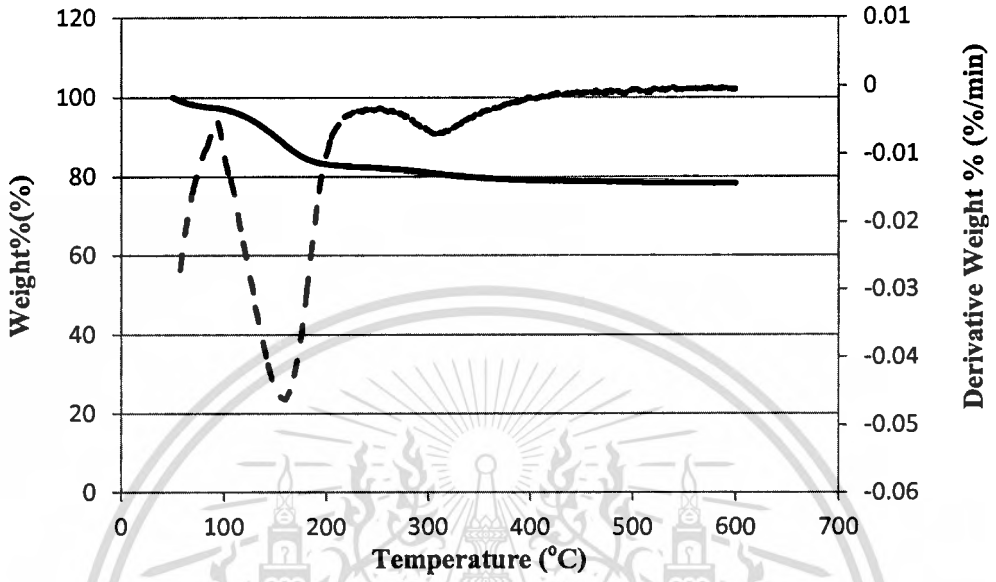


Figure C1 TGA/DTG of zeolite A

Condition : 1.80 SiO_2 : 1.00 Al_2O_3 : 3.95 Na_2O : 110.05 H_2O ,Aging at 0°C for 8 hours, Crystallization at 95°C for 2 hours. (fumed silica as Si source)

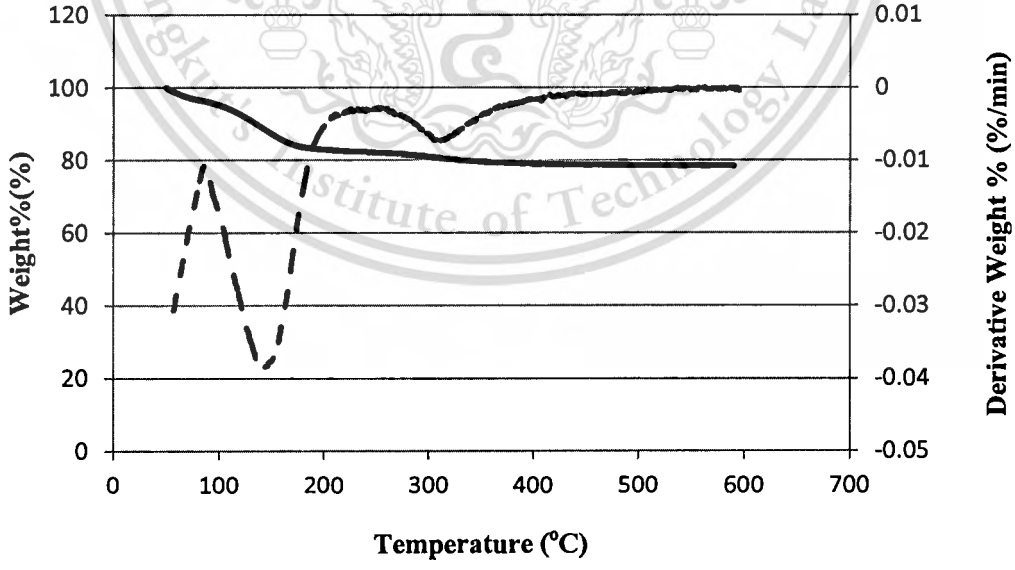


Figure C2 TGA/DTG of zeolite A

Condition : 1.80 SiO_2 : 1.00 Al_2O_3 : 3.95 Na_2O : 110.05 H_2O ,Aging at 0°C for 12 hours, Crystallization at 95°C for 2 hours. (fumed silica as Si source)

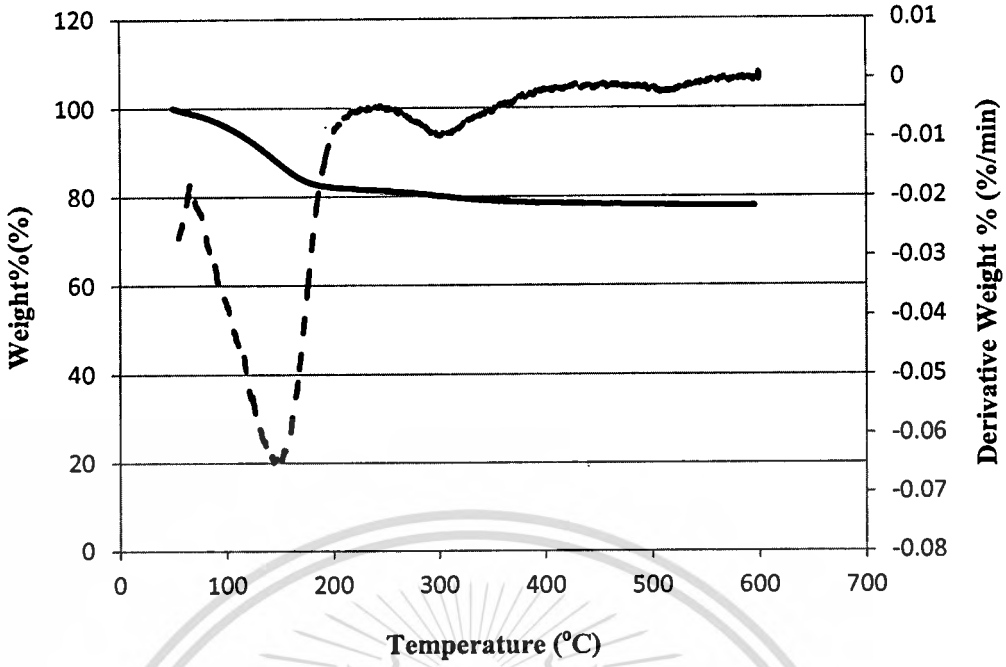


Figure C3 TGA/DTG of zeolite A

Condition : 1.80 SiO_2 : 1.00 Al_2O_3 : 3.95 Na_2O : 110.05 H_2O ,Aging at 0°C for 24 hours, Crystallization at 95°C for 2 hours. (fumed silica as Si source)

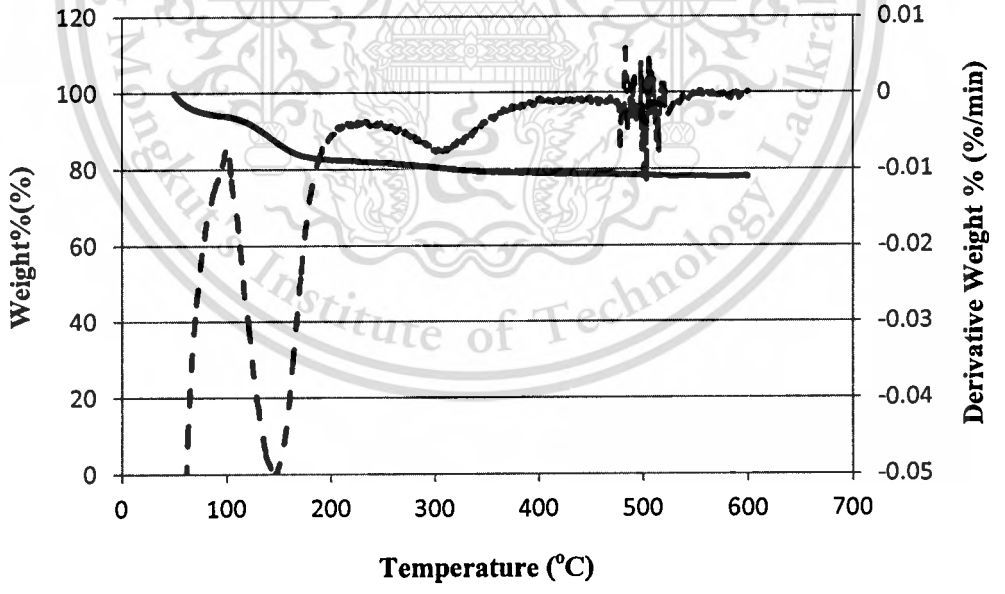


Figure C4 TGA/DTG of zeolite A

Condition : 1.80 SiO_2 : 1.00 Al_2O_3 : 3.95 Na_2O : 110.05 H_2O ,Aging at 10°C for 12 hours, Crystallization at 95°C for 2 hours. (fumed silica as Si source)

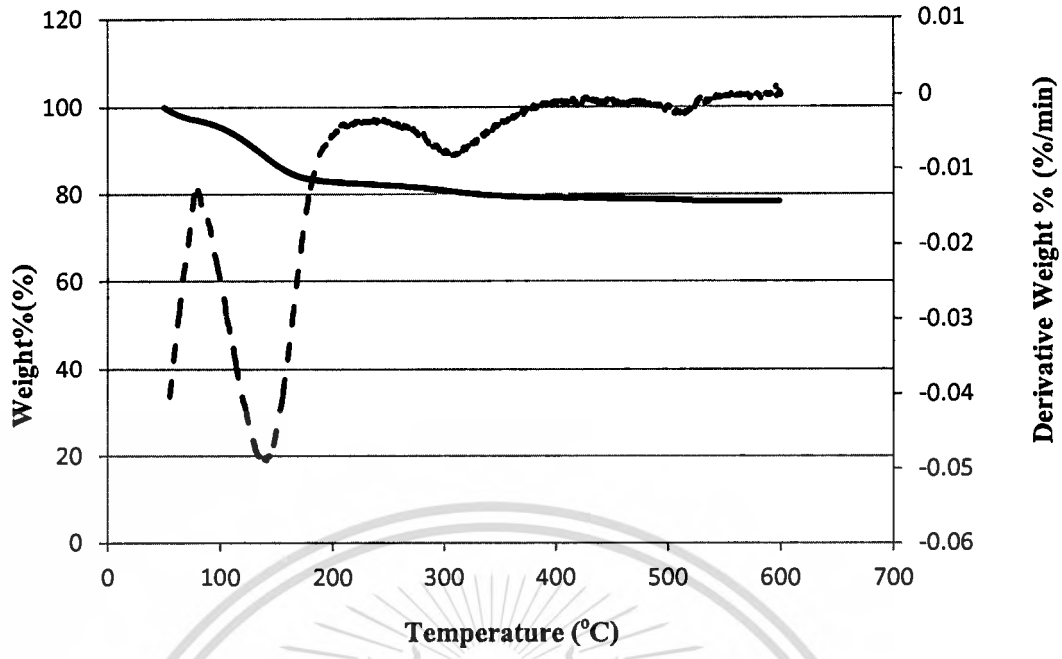


Figure C5 TGA/DTG of zeolite A

Condition : 1.80 SiO_2 : 1.00 Al_2O_3 : 3.95 Na_2O : 110.05 H_2O ,Aging at 20°C for 12 hours, Crystallization at 95°C for 2 hours. (fumed silica as Si source)

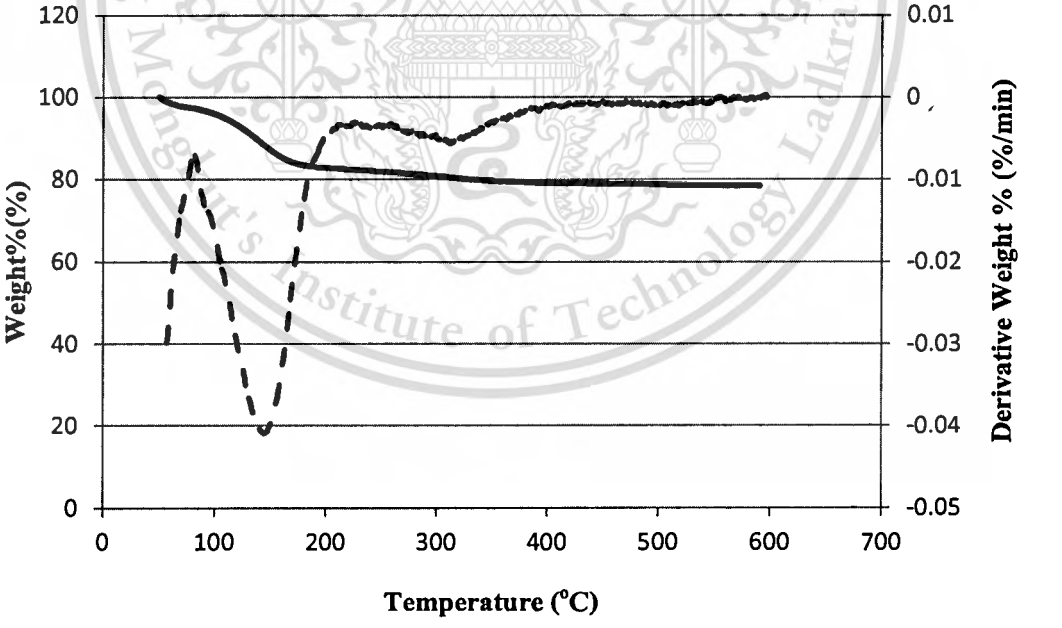


Figure C6 TGA/DTG of zeolite A

Condition: 1.80 SiO_2 : 1.00 Al_2O_3 : 3.95 Na_2O : 110.05 H_2O ,Aging at 0°C for 12 hours, Crystallization at 75°C for 2 hours. (fumed silica as Si source)

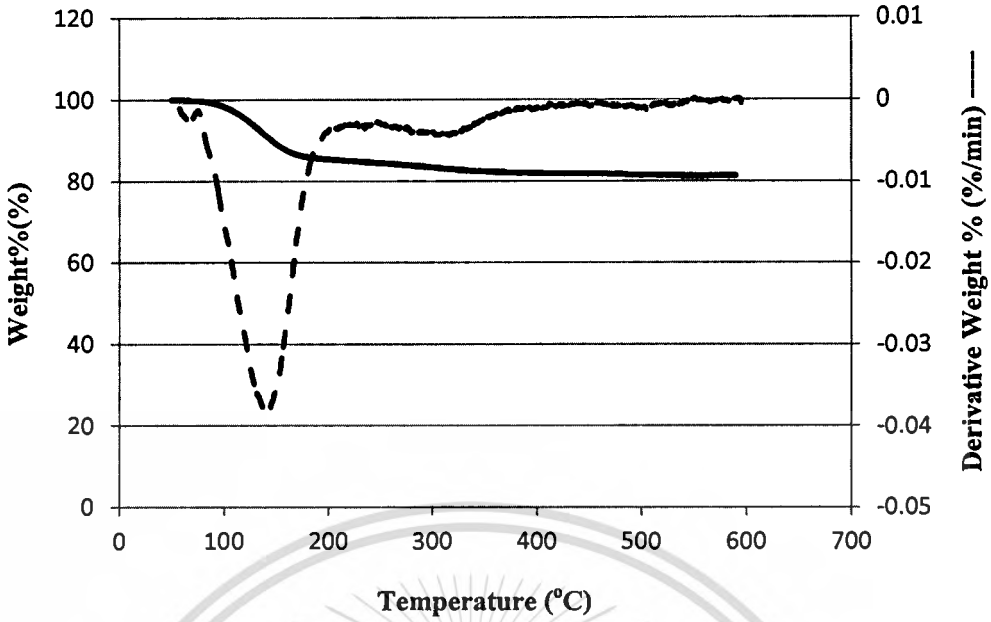


Figure C7 TGA/DTG of zeolite A

Condition : 1.80 SiO_2 : 1.00 Al_2O_3 : 3.95 Na_2O : 110.05 H_2O ,Aging at 0°C for 12 hours, Crystallization at 85°C for 2 hours. (fumed silica as Si source)

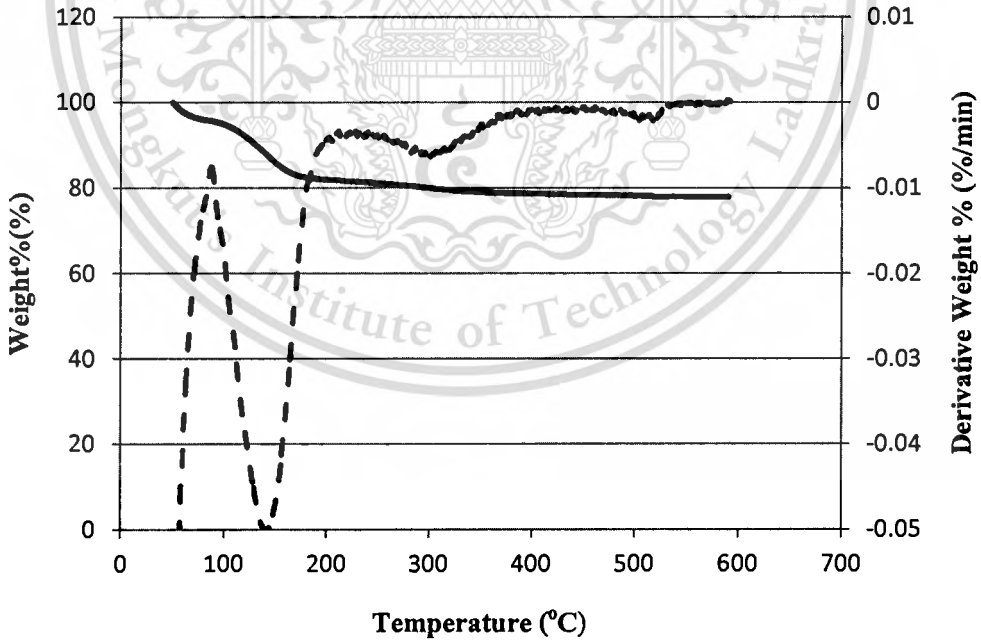


Figure C8 TGA/DTG of zeolite A

Condition : 1.80 SiO_2 : 1.00 Al_2O_3 : 3.95 Na_2O : 110.05 H_2O, Aging at 0°C for 12 hours, Crystallization at 105°C for 2 hours. (fumed silica as Si source)

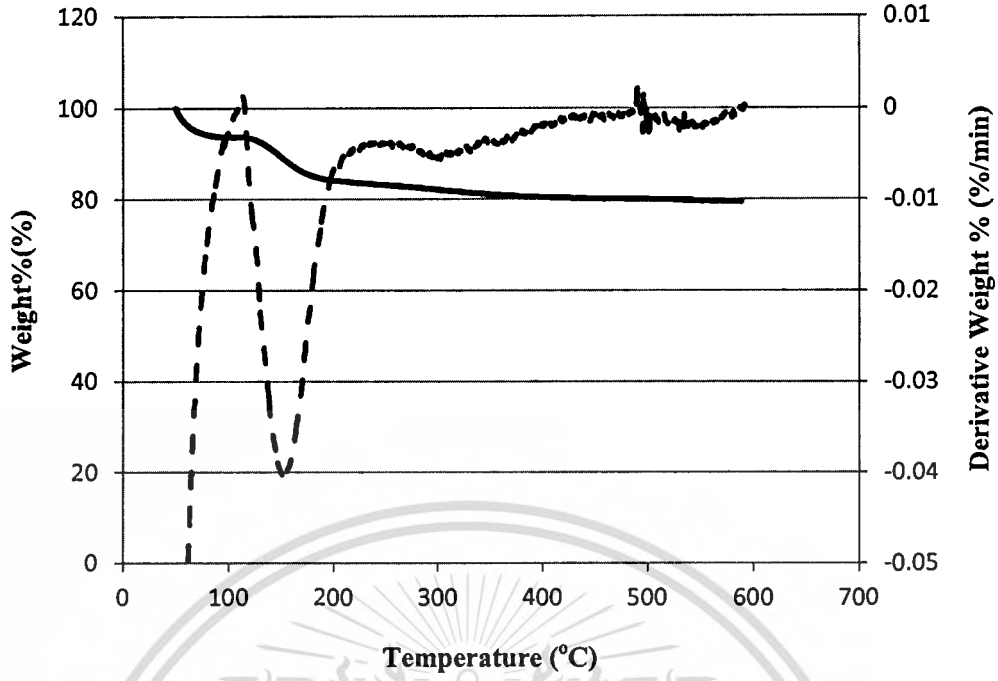


Figure C10 TGA/DTG of zeolite A

Condition : 1.80 SiO_2 : 1.00 Al_2O_3 : 3.95 Na_2O : 110.05 H_2O , Aging at 0°C for 12 hours, Crystallization at 95°C for 3 hours. (fumed silica as Si source)

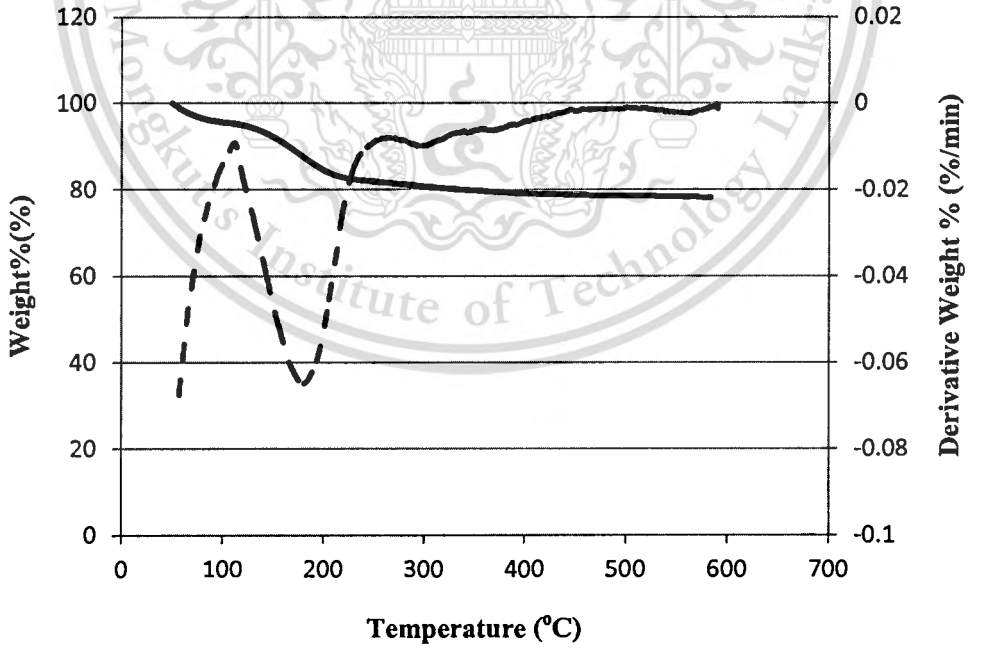


Figure C11 TGA/DTG of zeolite A

Condition : 1.80 SiO_2 : 1.00 Al_2O_3 : 3.95 Na_2O : 110.05 H_2O, Aging at 0°C for 12 hours, Crystallization at 95°C for 5 hours. (fumed silica as Si source)

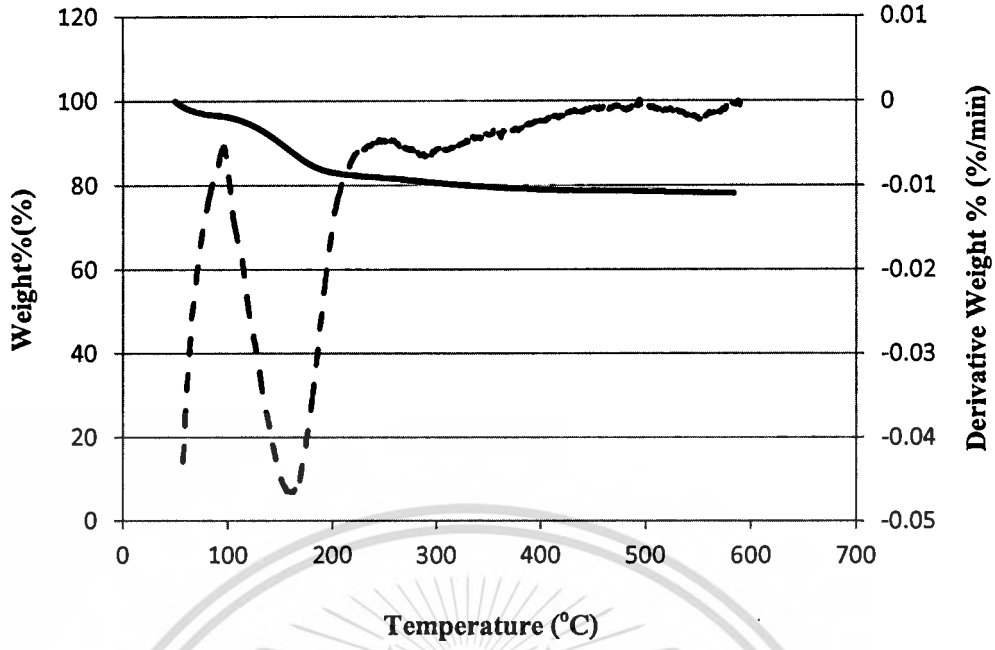


Figure C12 TGA/DTG of zeolite A

Condition : 1.80 SiO_2 : 1.00 Al_2O_3 : 3.95 Na_2O : 110.05 H_2O, Aging at 0°C for 6 hours, Crystallization at 95°C for 2 hours. (fumed silica as Si source)

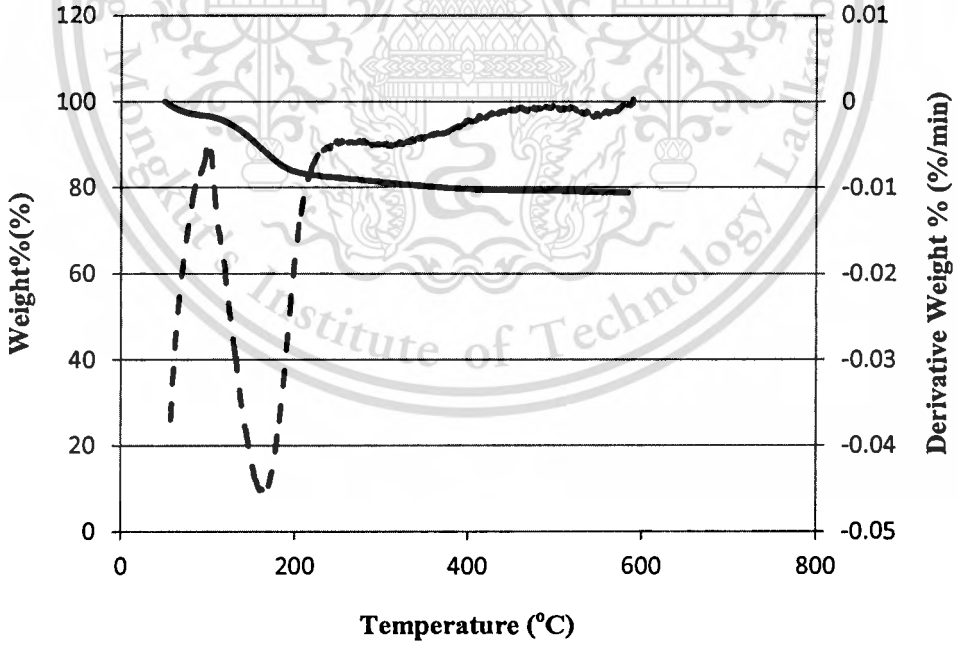


Figure C13 TGA/DTG of zeolite A

Condition : 1.80 SiO_2 : 1.00 Al_2O_3 : 3.95 Na_2O : 110.05 H_2O ,Aging at 0°C for 6 hours, Crystallization at 95°C for 2 hours. (Ludox AS40 source)

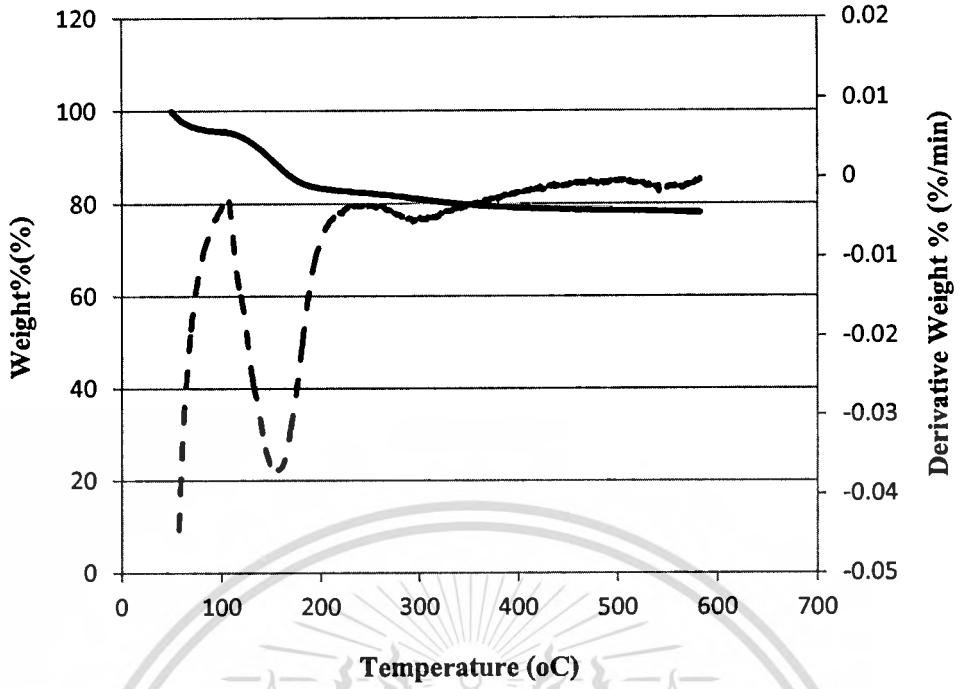


Figure C14 TGA/DTG of zeolite A

Condition : 1.80 SiO_2 : 1.00 Al_2O_3 : 3.95 Na_2O : 110.05 H_2O , Aging at 0°C for 6 hours, Crystallization at 95°C for 2 hours. (Sodium metasilicate source)

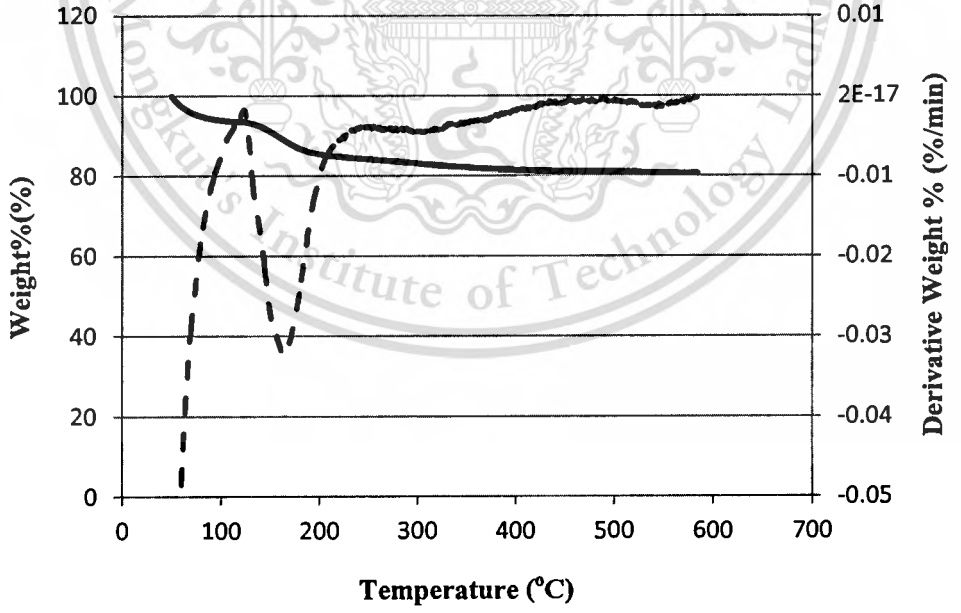


Figure C15 TGA/DTG of zeolite A

Condition : 1.80 SiO_2 : 1.00 Al_2O_3 : 3.00 Na_2O :110.05 H_2O ,Aging at 0°C for 8 hours, Crystallization at 95°C for 2 hours. (fumed silica as Si source)

APPENDIX D

X-RAY DIFFRACTION PATTERN

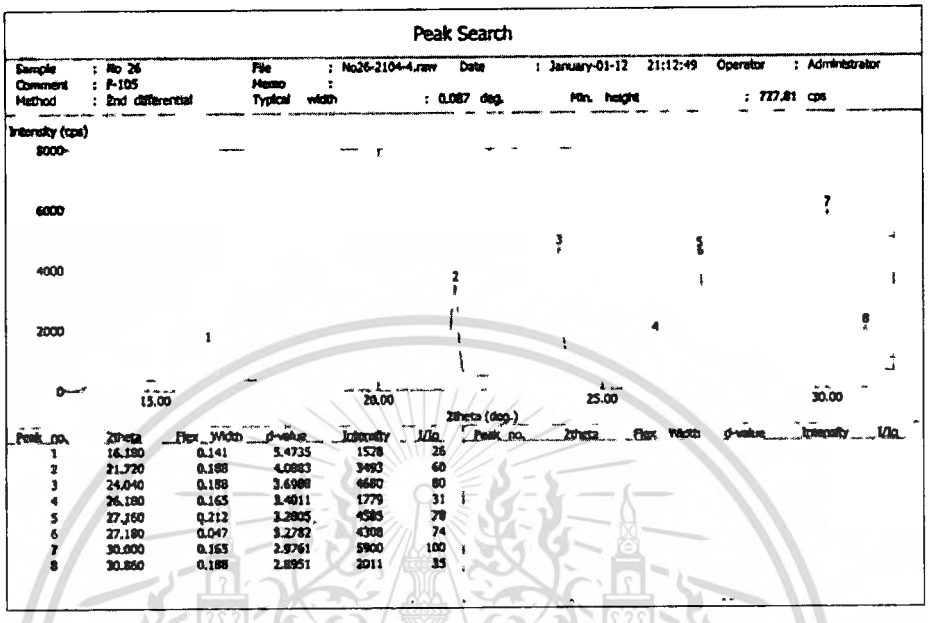


Figure D1 X-ray diffraction pattern of zeolite A Condition : 1.80 SiO_2 : 1.00 Al_2O_3 : 3.95 Na_2O : 110.05 H_2O, Aging at 0°C for 8 hours, Crystallization at 95°C for 2 hours.(fumed silica as Si source)

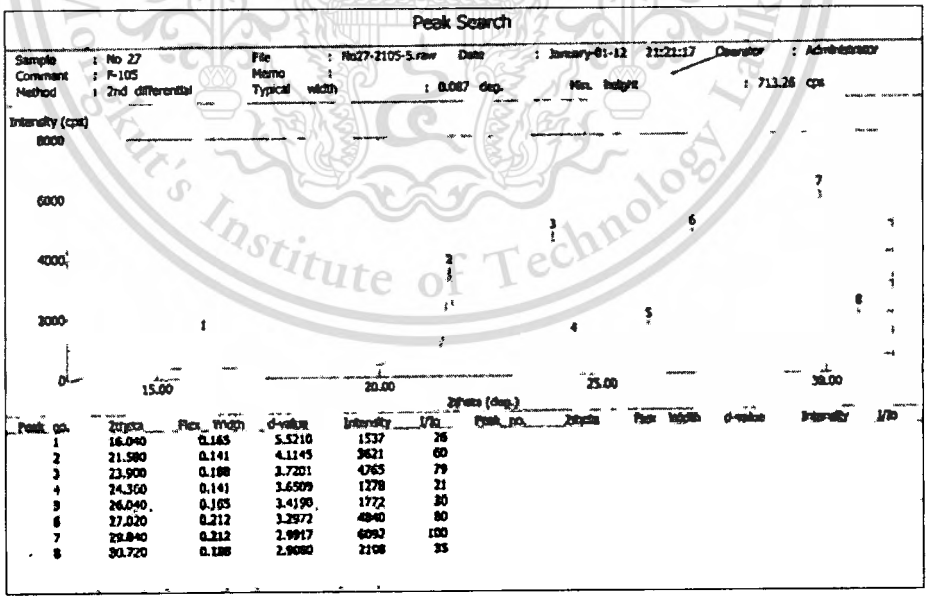
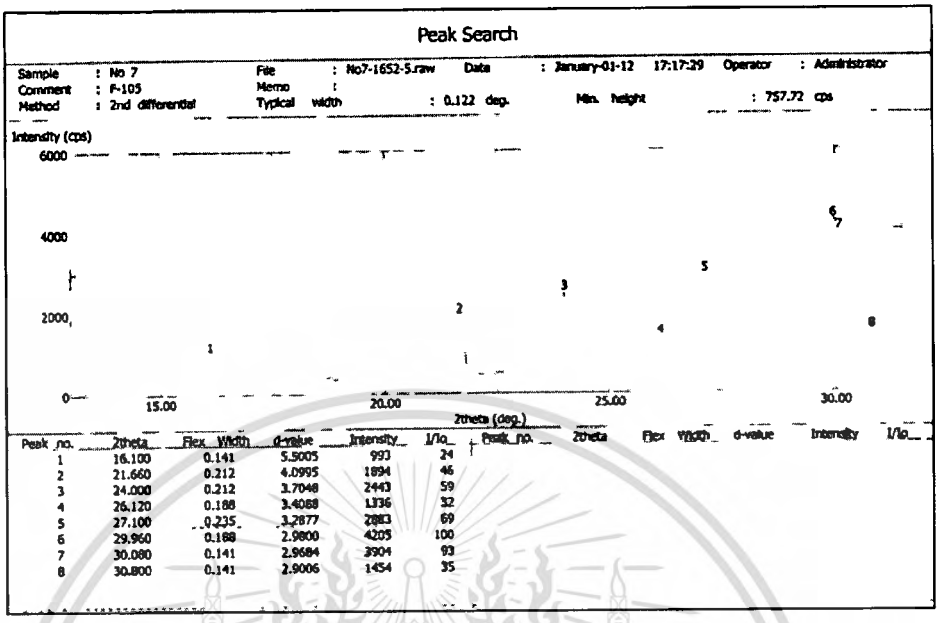
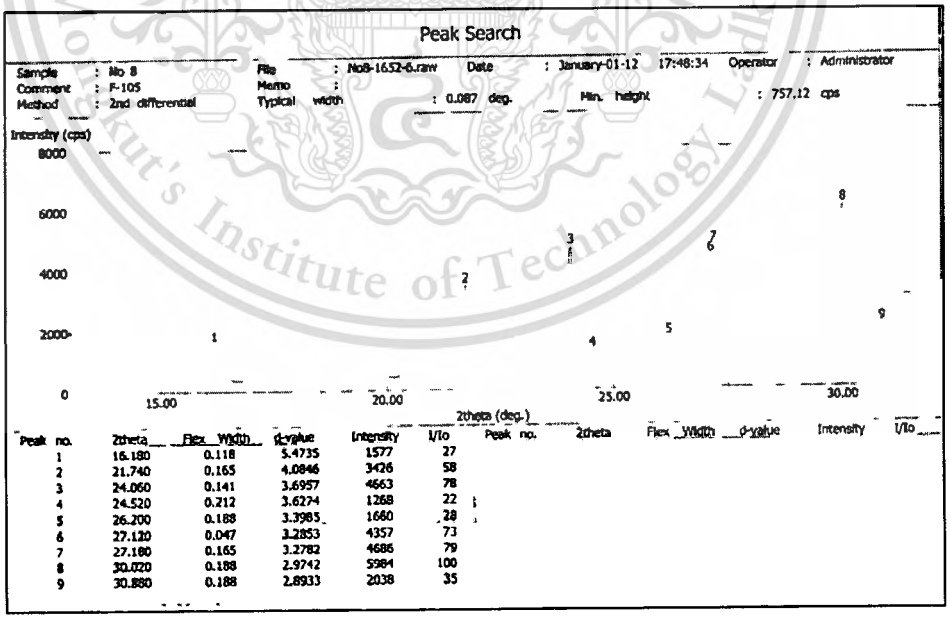


Figure D2 X-ray diffraction pattern of zeolite A Condition : 1.80 SiO_2 : 1.00 Al_2O_3 : 3.95 Na_2O : 110.05 H_2O ,Aging at 0°C for 12 hours ,Crystallization at 95°C for 2 hours.(fumed silica as Si source)



Peak no.	2theta	Flex	Width	d-value	Intensity	I/Io
1	16.100		0.141	5.5005	993	24
2	21.660		0.212	4.0995	1894	46
3	24.000		0.212	3.7048	2443	59
4	26.120		0.188	3.4088	1336	32
5	27.100		0.235	3.2877	2883	69
6	29.960		0.188	2.9800	4203	100
7	30.080		0.141	2.9684	3904	93
8	30.800		0.141	2.9006	1454	35

Figure D3 X-ray diffraction pattern of zeolite A Condition : 1.80 SiO_2 : 1.00 Al_2O_3 : 3.95 Na_2O :110.05 H_2O ,Aging at 0°C for 24 hours, Crystallization at 95°C for 2 hours.(fumed silica as Si source)



Peak no.	2theta	Flex	Width	d-value	Intensity	I/Io
1	16.180		0.118	5.4735	1577	27
2	21.740		0.165	4.0846	3426	58
3	24.060		0.141	3.6957	4663	78
4	24.520		0.212	3.6274	1268	22
5	26.200		0.188	3.3985	1660	28
6	27.120		0.047	3.2853	4357	73
7	27.180		0.165	3.2782	4686	79
8	30.020		0.188	2.9742	5984	100
9	30.880		0.188	2.8933	2038	35

Figure D4 X-ray diffraction pattern of zeolite A Condition : 1.80 SiO_2 : 1.00 Al_2O_3 : 3.95 Na_2O : 110.05 H_2O ,Aging at 10°C for 12 hours, Crystallization at 95°C for 2 hours.(fumed silica as Si source)

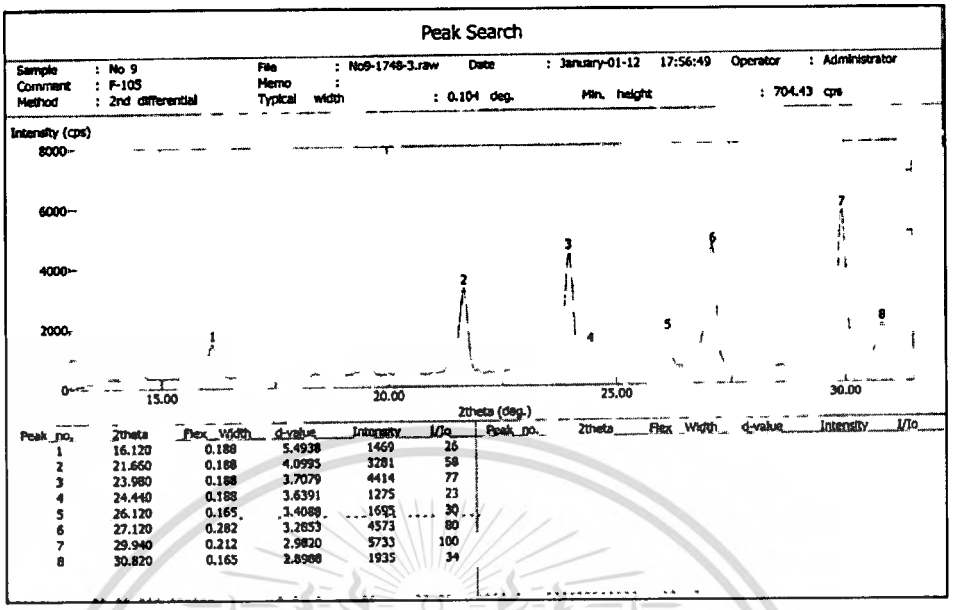


Figure D5 X-ray diffraction pattern of zeolite A Condition : 1.80 SiO_2 : 1.00 Al_2O_3 : 3.95 Na_2O, : 110.05 H_2O ,Aging at 20°C for 12 hours, Crystallization at 95°C for 2 hours.(fumed silica as Si source)

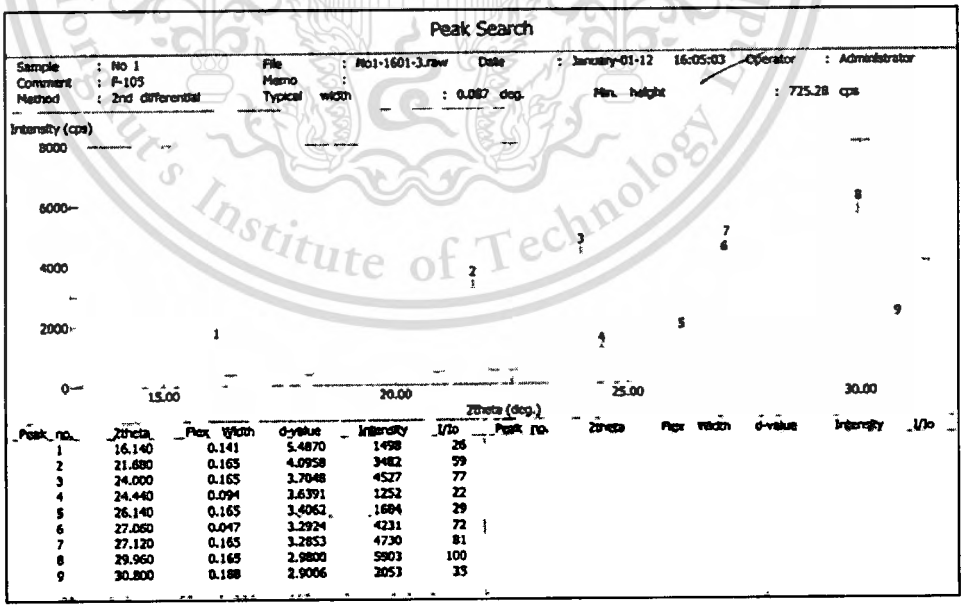
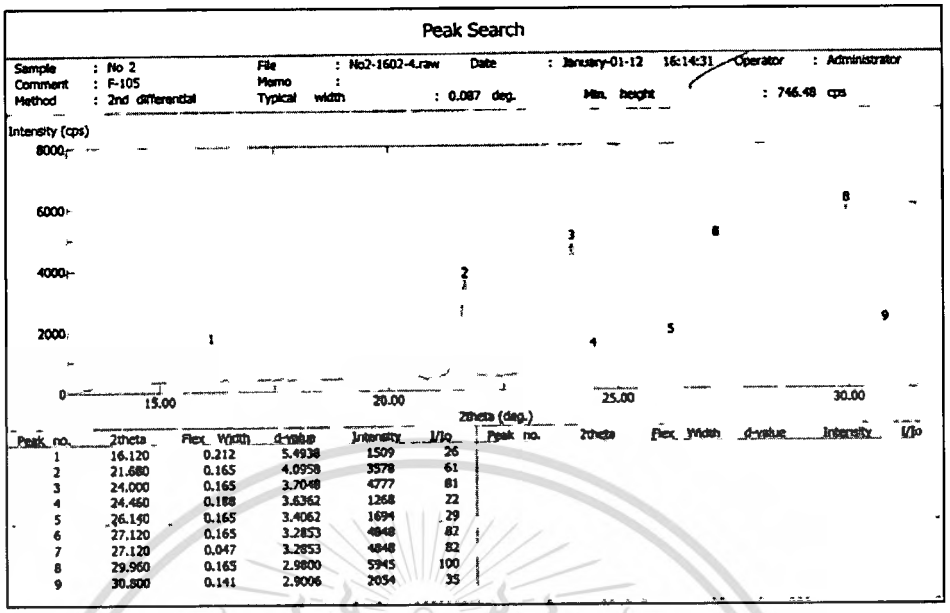
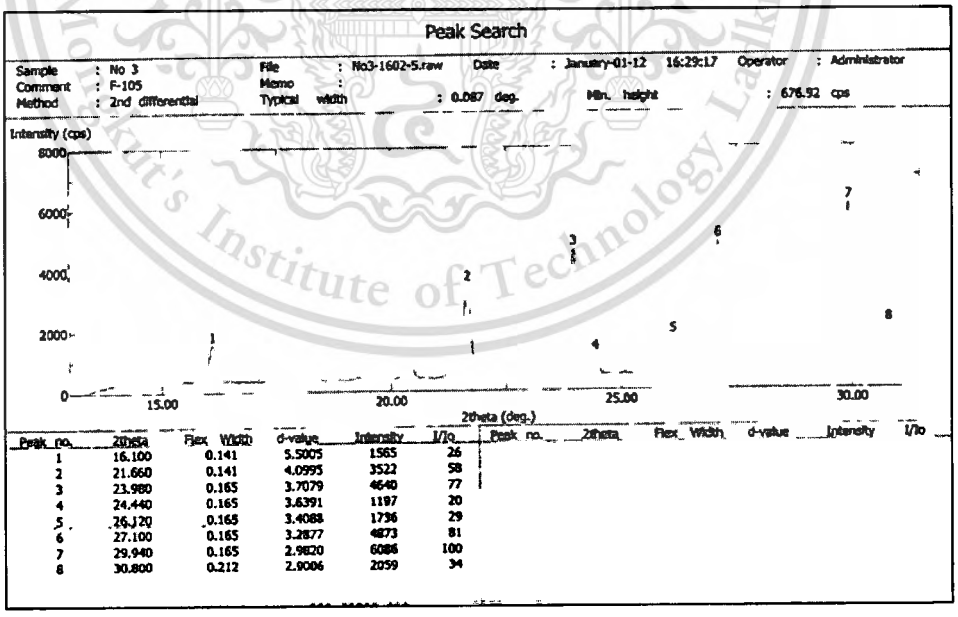


Figure D6 X-ray diffraction pattern of zeolite A Condition : 1.80 SiO_2 : 1.00 Al_2O_3 : 3.95 Na_2O : 110.05 H_2O : 110.05 H_2O ,Aging at 0°C for 12 hours ,Crystallization at 75°C for 2 hours. (fumed silica as Si source)



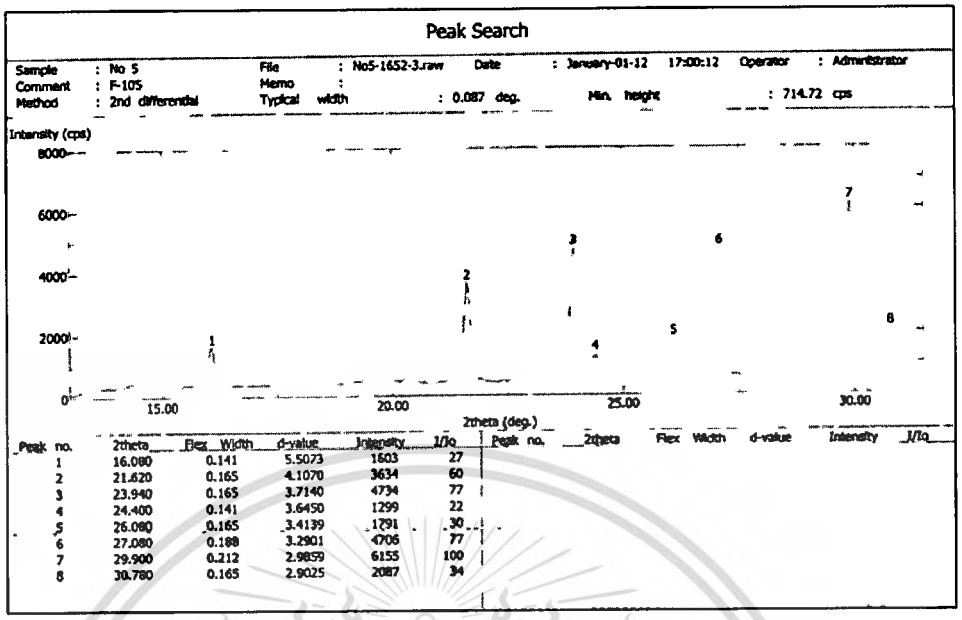
Peak no.	2theta	Flex. Width	d-value	Intensity	I/Io
1	16.120	0.212	5.4938	1509	26
2	21.680	0.165	4.0958	3578	61
3	24.000	0.165	3.7048	4777	81
4	24.460	0.188	3.6362	1268	22
5	26.140	0.165	3.4062	1694	29
6	27.120	0.165	3.2853	4848	82
7	27.120	0.047	3.2853	4848	82
8	29.960	0.165	2.9800	5945	100
9	30.800	0.141	2.9006	2054	35

Figure D7 X-ray diffraction pattern of zeolite A Condition : 1.80 SiO_2 : 1.00 Al_2O_3 : 3.95 Na_2O : 110.05 H_2O ,Aging at 0°C for 12 hours ,Crystallization at 85° for 2 hours. (fumed silica as Si source)



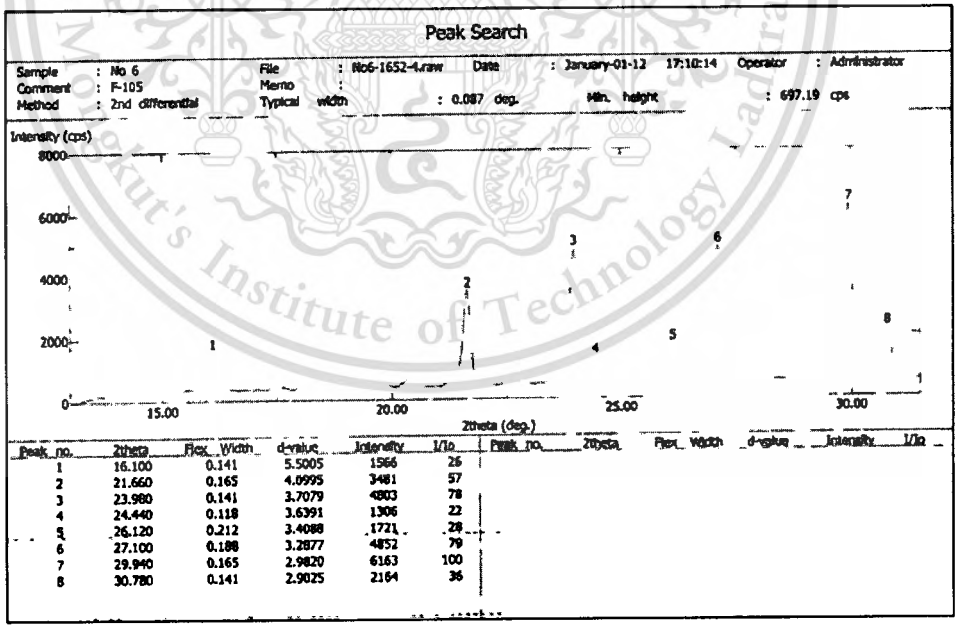
Peak no.	2theta	Flex. Width	d-value	Intensity	I/Io
1	16.100	0.141	5.5005	1565	26
2	21.660	0.141	4.0995	3522	58
3	23.980	0.165	3.7079	4640	77
4	24.440	0.165	3.6391	1197	20
5	26.120	0.165	3.4088	1736	29
6	27.100	0.165	3.2877	4873	81
7	29.940	0.165	2.9820	6086	100
8	30.800	0.212	2.9006	2059	34

Figure D8 X-ray diffraction pattern of zeolite A Condition : 1.80 SiO_2 : 1.00 Al_2O_3 : 3.95 : Na_2O : 110.05 H_2O ,Aging at 0°C for 12 hours, Crystallization at 105°C for 2 hours. (fumed silica as Si source)



Peak no.	2theta	Flex	Width	d-value	Intensity	I/Io
1	16.080		0.141	5.5073	1603	27
2	21.620		0.165	4.1070	3634	60
3	23.940		0.165	3.7140	4734	77
4	24.400		0.141	3.6450	1299	22
5	26.080		0.165	3.4139	1791	30
6	27.080		0.188	3.2901	4706	77
7	29.900		0.212	2.9859	6155	100
8	30.780		0.165	2.9025	2087	34

Figure D10 X-ray diffraction pattern of zeolite A Condition : 1.80 SiO_2 : 1.00 Al_2O_3 : 3.95 Na_2O : 110.05 H_2O ,Aging at 0°C for 12 hours ,Crystallization at 95°C for 3 hours. (fumed silica as Si source)



Peak no.	2theta	Flex	Width	d-value	Intensity	I/Io
1	16.100		0.141	5.5005	1566	26
2	21.660		0.165	4.0995	3481	57
3	23.980		0.141	3.7079	4803	78
4	24.440		0.118	3.6391	1306	22
5	26.120		0.212	3.4088	1721	28
6	27.100		0.188	3.2877	4852	79
7	29.940		0.165	2.9820	6163	100
8	30.780		0.141	2.9025	2164	36

Figure D10 X-ray diffraction pattern of zeolite A Condition : 1.80 SiO_2 : 1.00 Al_2O_3 : 3.95 Na_2O : 110.05 H_2O ,Aging at 0°C for 12 hours, Crystallization at 95°C for 5 hours. (fumed silica as Si source)

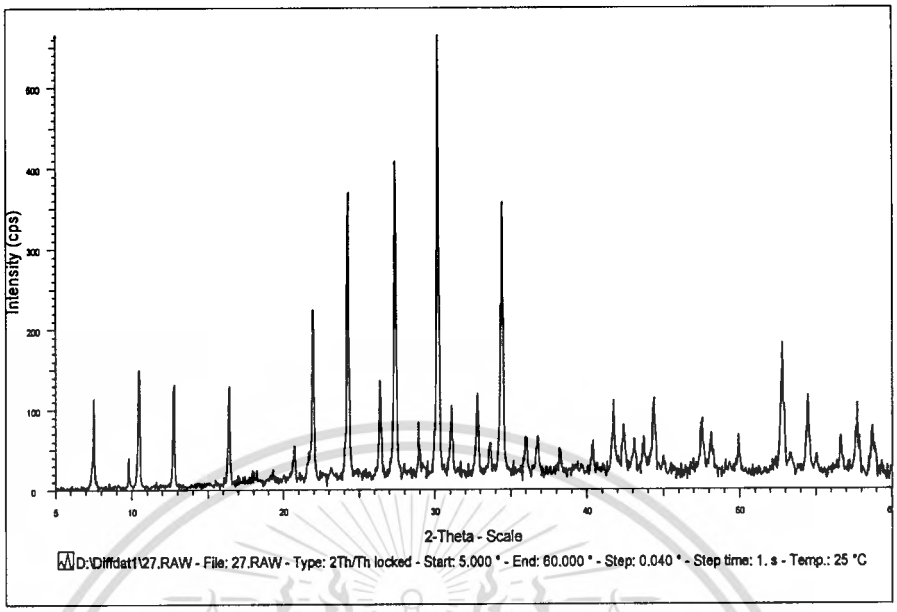


Figure D11 X-ray diffraction pattern of zeolite A Condition : 1.80 SiO_2 : 1.00 Al_2O_3 : 3.00 Na_2O : 110.05 H_2O , Aging at 20°C for 12 hours, Crystallization at 95°C for 2 hours. (fumed silica as Si source)