Synthesis and Characterization of a Catalytic Cracking Y Zeolite

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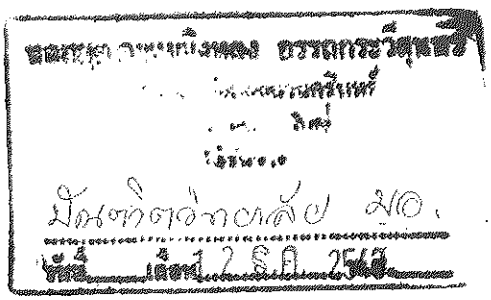

ชื่อวิทยานิพนธ์ การสังเคราะห์และศึกษาลักษณะเฉพาะของตัวเร่งปฏิกิริยาการแตกตัววายซีโอไลต์
ผู้เขียน นายจักรกฤษณ์ ตั้นตระกูล
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บทคัดย่อ

โซเดียมวายซีโอไลต์ได้ถูกสังเคราะห์โดยใช้วัตถุดิบหลักๆ ดังนี้ น้ำแก้ว โซเดียมอลูมิเนต อลูมิเนียมซัลเฟต และน้ำที่ปราศจากไอออน กระบวนการในการสังเคราะห์ประกอบด้วยพื้นฐานหลัก 4 ขั้นตอน คือ ขั้นตอนการเตรียมสารล่อผลึก[โมลขององค์ประกอบ (14-17)Na_2O : Al_2O_3 : (14-15) SiO_2 : (290-320)H_2O], ขั้นตอนการเตรียมเจล[โมลขององค์ประกอบ (4-6)Na_2O : Al_2O_3 : (9-11)SiO_2 : (190-200)H_2O], ขั้นตอนการตกผลึก และ ขั้นตอนการแยก

กราฟจลนศาสตร์อัตราการเติบโตของผลึกมีลักษณะเหมือนรูปตัวเอสและสามารถแยกออกได้เป็น 3 ช่วง ดังนี้คือ ช่วงการเหนี่ยวนำผลึก, ช่วงการเติบโตของผลึก และช่วงการเปลี่ยนวัฏภาคของผลึก

สภาวะที่ดีที่สุดในการสังเคราะห์ประกอบด้วย การใช้อุณหภูมิในขั้นตอนการกวนสารล่อผลึกและขั้นตอนการกวนเจลที่ 5 องศาเซลเซียส อุณหภูมิในการตกผลึกที่ 100 องศาเซลเซียส และเวลาในการตกผลึก 12 ชั่วโมง สมบัติสำคัญทางกายภาพของผลึกโซเดียมวายที่สังเคราะห์มีดังนี้คือ ความเป็นผลึกสัมพัทธ์ หน่วยเซลล์ และสัดส่วนซิลิกาต่ออลูมินา เป็น 98 เปอร์เซ็นต์ 24.65 อังสตรอม และ 5.26 ตามลำดับ ความเสถียรเชิงความร้อนของผลึกจะมีค่าประมาณ 939 องศาเซลเซียส ลักษณะของผลึกที่ปรากฏจะเป็นชนิดที่มีการเกาะกลุ่มกันของผลึกและมีขนาดของผลึกอยู่ในช่วง 0.5 ถึง 1.0 ไมโครเมตร พื้นที่ผิวทั้งหมดของผลึกมีค่าเท่ากับ 652 ตารางเมตรต่อกรัม และเมื่อไม่มีการเติมสารล่อผลึกในภาวะเดียวกันของการสังเคราะห์จะได้โซเดียมเอซีโอไลต์แทนโซเดียมวายซีโอไลต์

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Abstract

NaY zeolite was successfully synthesized by using four main raw materials such as, waterglass, sodium aluminate, aluminium sulphate and de-ionized water. The process consists of four fundamental steps as: seed preparation step [molar composition (14-17)Na_2O : Al_2O_3 : (14-15)SiO_2 : (290-320)H_2O], gel formation step [molar composition (4-6)Na_2O : Al_2O_3 : (9-11)SiO_2 : (190-200)H_2O], crystallization step and separation step.

The graph of kinetics crystal growth rate looks like S shape and can be divided into three periods as following; induction period, crystal growth period and decline period.

The best condition of our experiments was as following; the mixing temperature of seed preparation step and whole gel step at 5°C, the crystallization temperature at 100°C, and the crystallization time 12 hours. The physical properties of synthesized NaY zeolite such as: relative crystallinity, unit cell size and silica to alumina ratio were 98%, 24.65 Å and 5.26, respectively. The thermal stability was about 939°C. The crystals were an agglomerate type and had the size range of 0.5 to 1.0 μm. The BET surface area was 652 m^2/g. The NaA zeolite was synthesized when using no seed process.

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Jakkrit Tuntragul

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CHAPTER 1

INTRODUCTION

1.1 Introduction

Many academic and industrial research have been conducted in the field of zeolites as catalysis (Vaughan, 1988). The classification and structure of natural and synthetic zeolites have recently been reviewed by Break (Break, 1974). In the group of these many materials, the synthetic X and Y zeolites are very noticeable because catalytic and structural properties have been more extensively studies than those of any other. Faujasite zeolites are not only the synthetic X and Y zeolites having the same structure, but are also the rare mineral faujasite and a number of other synthetic zeolites (Rudham and Stolckwell,1972). Since faujasites were the first used in petroleum processing of cracking to convert the large petroleum molecules into smaller hydrocarbons of the gasoline range in the 1960s, zeolite catalysis has increased rapidly and dynamically advances because of four reasons as following (Vaughan, 1988):

1) new structures having a novel topology and define chemical,
2) expanded chemical compositions,
3) use of the method of activation and regenerating materials and
4) using new or known specific zeolites or group of zeolite in processes or applications.

The development of synthetic faujasite has made a powerful influence both technically and commercially catalytic cracking zeolite. An important advance in this application was ion-exchanged by rare earth cation. It increased not only cracking activity but also gasoline production as well because of its enhanced hydrogen transfer activity. Zeolite X type was

stability provided by the higher SiO_2/Al_2O_3 ratio. The use of high silica zeolites reduced both the rate of secondary cracking (coke formation) and the hydrogen transfer activity. The net outcome is that it produces more high-octane olefins than earlier rare earth exchanged catalysts. Hybrid rare earth exchanged high silica faujasite catalysts have recently become available such as HY, REY, USY, REUSY. The typical Fluid Catalytic Cracking(FCC) catalyst comprises of zeolite Y type dispersed in an amorphous matrix such as clay or silica-alumina from 10 to 40 wt %.

Faujasite can help the cracking reaction of crude oil to get high quantity of desirable gasoline products. The resultant saving from this improvement can be measured in billions of dollars per year. The estimation of the world consumption of zeolites for petroleum refining process was used about 305.8 Gg in the 1987s. Of this some 300 Gg were used for cracking (Chen and Degnon, 1988). These show that the development to synthetic zeolite containing catalyst, especially faujasite, are very important for petroleum refining industry.

The research area is to synthesize zeolite Y type by using basic preparation techniques from Research Institute of Petroleum Processing (RIPP) Sinopec, Beijing China. The further applications of experiments have been happened by understanding from some literature reviews and patents. Attempting on synthesis of zeolite Y type is to lay down a foundation for further scrutiny and modification in the field of catalyst development in Thailand.

1.2 Objectives

1. To use laboratory grade raw material for preparing working solution.
2. To synthesize NaY zeolite having SiO_2 / Al_2O_3 more than 4.0.
3. To study the effect of mixing temperature, crystallizing temperature and different types of seeds on the graph of kinetics crystal growth.
4. To examine the characteristics of synthesized NaY zeolite.

CHAPTER 2

LITERATURE REVIEWS

Linde Union Carbine Corporation was the first company producing synthetic faujasite in the 1956s and found that it had very high cracking activity. The commercial use of synthetic faujasite had dramatically changed in cracking catalyst introduced by Mobil Oil Corporation in the 1962s (Corma,1989). The progress of synthetic zeolite has been happened by many scientists and industrial researchers in order to modify the physical and chemical properties of it by effecting changes in pore size, cation species, silica to alumina ratio, and degree of hydration. These are great important to studies and modifies synthetic faujasite for desirable properties of zeolite-containing catalyst.

2.1 Summary of literature reviews

Strack and Kleinschmit (Strack and Kleinschmit,1989) reported that a process of the production of a seed mixture for faujasite synthesis having the objectives to produce economically and with a good production in the range of faujasite comprise the separate steps of reacting an amorphous, synthetic sodium aluminosilicate, in the form of a powder or filter cake, with an Na_2O-supplying compound in an aqueous system exhibited molar composition ratios of oxides as $(12\pm3)Na_2O : Al_2O_3 : (15\pm3)SiO_2 : (240\pm60)H_2O$ and allow it to age for at least 24 hours at temperature of 10°C to 35°C(room temperature). The seed mixture could be used in the synthesis of zeolite Y and/or zeolite X type. However, a slightly noticeable difference from the original plan caused well below the degree of crystallization.

Miyazaki and coworkers (Miyazaki et al.,1984) declared that the process for preparation of faujasite zeolite by using a transparent faujasite germ solution, having an oxide molar composition ratios to be like (7-30)M_2O : Al_2O_3 : (8-14)SiO_2 : (70-420)H_2O be synthesized by mixing a transparent faujasite germ solution 1 percent to 30 percent by weight as Al_2O_3 based on the resulting faujasite zeolite, an aqueous alkali metal silicate, an aqueous alkali metal aluminate and an alkali metal hydroxide and then the mixture be aged at the range of temperature from 20°C to 60°C.

Loechelt (Loechelt,1986) declared that a method of producing crystalline synthetic faujasite having the objectives to get rid of the necessity carrying out the reaction at cold temperatures, aging long times as well as using seed of zeolite Y type crystal comprise the separate steps of preparing a sodium silicate solution and a sodium aluminate solution, providing an activated sodium silicate system by mixing said sodium silicate solution at ambient temperature with finely ground dry seed synthetic faujasite of the zeolite Y type product desired in an amount of four percent of final product and then cooking at about 100°C for about four hours or more, cooling the activated sodium silicate system to about ambient temperature, mixing the sodium aluminate solution with the activated sodium silicate system to about ambient temperature to provide a reaction mixture having a molar composition ratios of oxides as (5.0-8.5)Na_2O : Al_2O_3 : (15.0-25.0)SiO_2 : (100-180)H_2O, heating the reaction mixture to about 100°C for about twelve hours or more with agitation until the desired crystalline synthetic faujasite was formed.

Sanders (Sanders,1984) mentioned that a method of producing a crystalline synthetic faujasite of the zeolite Y type having the objectives to meet current specifications of crystallinity for commercial application by utilizing an amount of reduced water together with to provide a process for producing a commercially acceptable and more economical than present processes comprise the separate steps of preparing a sodium silicate solution

and sodium aluminate solution, providing an activated system by mixing a sodium silicate solution with finely ground synthetic faujasite of the zeolite "Y" type at a temperature up to about 0°C for a period of at least about one-half hours, mixing the sodium aluminate solution with an activated system over period of time up to about five hours to provide a mixture having a molar composition ratios of oxides as $(4.4\text{-}8.5)Na_2O : Al_2O_3 : (10.1\text{-}16.0)SiO_2 : (145\text{-}200)H_2O$, allowing the mixture to stand for up to about 24 hours at temperature from about 0°C to ambient, heating the mixture to a temperature of about 90°C to 105°C and reacting at said temperature until the desired crystlline synthetic faujasite of the zeolite Y type was formed.

Elloit and McDanial (Elloit,Jr.et al.,1979) stated that a process for preparing crystalline aluminosilicates having the objectives to keep the final product silica to alumina ratios at or above about 4 as well as to use inexpensive raw materials to reduce the quantity of reactants comprise the separate steps of preparing a reaction slurry having a molar composition ratios of oxides as $(3\text{-}6)Na_2O : Al_2O_3 : (8\text{-}12)SiO_2 : (120\text{-}200)H_2O$ by mixing solution of sodium silicate, sodium aluminate, zeolitic nucleation center having an average particle size below about 0.1 micron prepared from a reaction mixture having a molar composition ratios of oxides as $(15\text{-}17)Na_2O : Al_2O_3 : (14\text{-}16)SiO_2 : (285\text{-}357)H_2O$ in an amount from 0.1 percent to 10 percent by weight of the reactant mixture and aluminium salt selected from the group consisting of the chloride, the sulfate, and the nitrate to provide about 10 percent to 90 percent by weight of the desired alumina, heating the mixture to about 100°C for a period of sufficient time to insure crystallization, washing, drying, and recovering the product.

Elliott (Elliott, Jr.,1972) wrote that a process for preparing zeolite Y type having the objectives to improve a process for preparing crystalline aluminosilicate zeolites and to use

the excess silicate in mother liquor to produce additional zeolite comprise the separate steps of preparing a reaction mixture containing a molar composition ratios of oxides as (3-6)Na_2O : Al_2O_3 : (8-12)SiO_2 : (120-200)H_2O, including in said reaction mixture zeolite nucleation center having a molar composition ratios of oxides as (15-17)Na_2O : Al_2O_3 : (14-16)SiO_2 : (285-357)H_2O, heating said mixture to obtain zeolite Y type and mother liquor which contains silicate separating said zeolite Y type from the mother liquor, reacting said mother liquor with sufficient aluminum sulfate to precipitate substantially all the silicate as silica-alumina hydrogel, recovering and washing said hydrogel to remove sodium sulfate to be part of the reaction mixture.

Vaughan and coworkers (Vaughan et al.,1979) maintained that a process for preparing type Y zeolite having the objectives to provide a commercially feasible by using inexpensive raw materials and minimum excess of reactants, hereby minimizing pollution problems and reducing the need for effluent purification facilities comprise the separate steps of preparing a slurry of zeolite nucleation centers having an average particle size below about 0.1 micron, said slurry having a molar composition ratios of oxides as (12-19)Na_2O : (0.7-9.0)Al_2O_3 : (12-19)SiO_2 : (220-900)H_2O, preparing an intermediate reaction mixture by combining the nucleation center with additional sources of Na_2O, Al_2O_3, SiO_2,and H_2O to obtain a mixture having a molar composition ratios of oxides as (2-6)Na_2O : Al_2O_3 : (4.5-11)SiO_2 : (30-200)H_2O, agitating and heating said intermediate reaction mixture at temperature of from about 30°C to 80°C, mixing an acid compound selected from the group comprising mineral acid, aluminum salt of mineral acids to obtain a final reaction mixture having a molar composition ratios of oxides as $Na_n(A)$: (1.2-3)Na_2O : Al_2O_3 : (4-7.5) SiO_2 : (40-200)H_2O, and heating the final reaction mixture in the range from about 2 hours to 40 hours to obtain zeolite Y type.

McDanial and coworkers (McDanial et al.,1979) reported that a method for preparing a crystalline aluminosilicate zeolite having the objectives to provide more rapidly and economically producing synthetic faujasite having a high silica-alumina ratio from relatively inexpensive raw materials comprise the separate steps of preparing an aqueous precursor mixture of silica, alumina, and alkaline metal hydroxide being those required to produce the desired zeolite by adding to said precursor mixture from about 0.1 percent to 10 percent by weight based on the weight of the theoretical yield of desired zeolite of amorphous aluminosilicate nucleation center having a molar composition ratios of oxides as $(0.9\pm0.1)Na_2O : Al_2O_3 : (2.3\text{-}2.7)SiO_2$, preparing an $Na_2O\text{-}Al_2O_3\text{-}SiO_2$ mixture from sodium aluminate, sodium silicate, sodium hydroxide, and water to provide a molar composition ratios of oxides as $(15\pm2)Na_2O : Al_2O_3 : (14\pm2)SiO_2 : (350\pm50)H_2O$, mixing vigorously at temperature of below 35°C, aging the mixture at a temperature of or below 25°C for at least 2 hours, reacting the mixture at a temperature of about 60°C to 150°C for a period of sufficient time to produce a substantially theoretical yield of crystalline zeolite.

Maher and coworkers (Maher et al.,1972) insisted that a preparation of high silica synthetic faujasite having the objectives to keep the silica to alumina ratios at or above 4 by using inexpensive raw materials and to decrease the quantity of reactants comprise the separate steps of having faujasite structure and a silica to alumina ratios above about 5 from a reactant mixture present in the following molar composition ratios of oxides as $(3.5\text{-}7)Na_2O : Al_2O_3 : (10\text{-}16)SiO_2 : (140\text{-}280)H_2O$ by preparing a sodium silicate solution in a quantity sufficient to provide the silica content in the reactant mixture, adding sulfuric acid to the silicate solution in an amount equal to 0.4 moles to 2 moles of acid per mole of alumina in the reactant mixture, preparing a sodium aluminate solution in a quantity sufficient to provide the desired alumina content in the reaction mixture, mixing the silicate and aluminate solutions and adding a quantity of zeolitic nucleation centers having an

average particle size below about 0.1 micron equal to about 0.1 percent to 10 percent by weight of the reactant mixture, heating to about 100°C for about 2 hours to 16 hours to insure crystallization, washing, drying and recovering the zeolite product.

Kasahara and coworkers (Kasahara et al., 1990) asserted that a clear aqueous nuclei solution using sodium hydroxide aqueous sole, sodium aluminate aqueous sole, sodium silicate aqueous sole as starting materials be effective to synthesize zeolite Y type by reducing a period of crystallization because it forms a great deal of aluminosilicate particles having a zeolitic structure of X.

Prabir and Bronic (Prabir and Bronic,1994) contented that the mechanism of zeolite formation: seed-gel interaction by designing specific reactor system in which both amorphous gel and seed be remained separate by membrane letting reactive species solution contact with both side of amorphous gel forming primary nucleation sites and side of seed forming secondary nucleation sites by using reactive species solution to be nutrients can be reorganized and grown as crystal of zeolite.

Ginter and coworkers (Ginter et al.,1992) insisted that the effects of gel aging on the synthesis of NaY zeolite from colloidal silica be formed by reaction between colloidal silica and sodium aluminate solution creating both a great deal of small nuclei and a large number of additional Si into the aluminosilicate solid on heating to obtain a higher yield of NaY zeolite.

Thompson and Ouden (Thompson and Ouden,1992) moved that the analysis of zeolite crystallization using the "crystallization curve" to measure the nucleation and crystallization rates show crystallization curve relating between the percentage of zeolite in solid phase and the crystallization time comprising of two important parts as following:

I) The induction time used to indicate the nucleation rate affected by the heat-transfer rate of differences in autoclave,

II) The slope of the crystallization curve used to indicate speed of the crystallization process relying on events happening in the nucleation phase and immediate linear growth rate.

Sender and Laurent (Sender and Laurent,1984) recommended that a method of producing a crystalline synthetic faujasite of the zeolite Y type through the process of preparing an activated low water system by mixing a sodium silicate solution with a seed amount up to about 10 percent by weight of the mixture of synthetic zeolite Y type compose the separate steps of preparing a reaction mixture having a molar composition ratios of oxides as (7-30)M_2O : Al_2O_3 : (8-14)SiO_2 : (70-420)H_2O, mixing sodium aluminate solution with an activated low water system about 24 hours at a temperature about 0°C to ambient followed by drying this mixture and slurry in water, heating the mixture to about 80°C to 120°C by spending the time more than 16 hours, and then crystalline synthetic faujasite of zeolite Y type be formed.

Miyanohara and coworkers (Miyanohara et al.,1983) declared that a process for producing a Y-type zeolite consist of two important steps. The first step incorporated an aqueous alkali silicate solution with an aqueous alkali aluminate solution to be mixture having a molar composition ratios of oxides as (7-30)M_2O : Al_2O_3 : (2-10)SiO_2, heated a mixture at the temperature from 40°C to 70°C in order to form gel having the following molar composition ratios of oxide as Al_2O_3 : (2.7-3.0)SiO_2 and then separated it from a mixture by using filtration, when maintained at that temperature for 20 minutes. The second step composed of the reaction between gel and an aqueous solution of an alkali silicate to be slurry having the following molar composition ratios of oxides as (24-40)M_2O : Al_2O_3 : (6-20) SiO_2 : (480-800)H_2O and then heated it to the temperature about 80°C to 110°C until the zeolite Y type crystals were formed at this temperature.

Kuehl (Kuehl,1990) maintained that a method for synthesis faujasite in the form of platelets having a particle size of 0.1 or less and a molar composition ratios of oxides as (6-15)Na_2O : Al_2O_3 : (4-20)SiO_2 : (72-2250)H_2O prepare by using water, alkali metal silicate at a temperature of at least 15°C. The gel was broke by using high shear agitation until a reaction mixture was converted to pour mixture and then aged for at least 6 hours. Sulfuric acid solution was added into aged mixture crystallizing by conducting at a temperature from 60°C to120°C for 2 hours to 24 hours.

Kostinko (Kostinko,1981) proposed that a method of producing zeolite Y type by using sodium silicate solution having SiO_2/Na_2O about 2.4 to 2.8 per 1 comprise the separate steps of preparing an activated sodium silicate solution by mixing alumina amount 50ppm to 2000ppm with sodium silicate solution at the temperature from 15°C to 100°C about 10 minutes, mixing an aqueous sodium aluminate about 30 seconds to form a reaction mixture having the following molar composition ratios of oxides as (3.5-30)Na_2O : Al_2O_3 : (7-30)SiO_2 : (35-2700)H_2O, heating to the temperature about 80°C to 120°C and then maintaining to this temperature until crystalline zeolite Y type was formed.

Dewaele and coworkers (Dewaele et al.,1985) claimed that an experiment studying the role of alkali chlorides affecting to the synthesis and characterization of faujasite - type zeolites be prepared from a reaction mixture having a molar composition ratios of oxides as 20Na_2O : Al_2O_3 : 20SiO_2 : 700H_2O : xKCl by mixing silica gel, sodium aluminate, sodium hydroxide and water and then adding alkali chlorides into the mixture. The reaction mixture was aged (static condition) at the temperature 20°C about 25 hours, and then it was heated to the temperature about 95°C to 100°C and kept at this temperature for 110 hours. The zeolite crystals were recovered and sent to analyze. As a result of this shown that the present of alkali chlorides in the reaction mixture have more effects to both zeolite products

and characterization of their products such as morphology, composition and size. Sodium cation favored to form a faujasite and sodalite.

Table 2-1 Summary list of literature reviews.

Inventor(s)	Type of nucleation	***Reaction mixture	Cryst[a]Temp	Reference
Loechelt,II	Synthesis zeolite Y (S)	(5.0-8.5)Na_2O:Al_2O_3:(15.0-25.0)SiO_2:(100-180)H_2O	100	US.P 4,576,807
Sender	Synthesis zeolite Y (S)	(5.0-8.5)Na_2O:Al_2O_3:(15.0-25.0)SiO_2:(100-180)H_2O	90 -105	US.P 4,436,708
Sender et al	Synthesis zeolite Y (S)	(5.0-15.0)Na_2O:Al_2O_3:(10.0-15.0)SiO_2:(85-450)H_2O	80-120	US.P 4,482,530
Maher, P.K et al.	*Zeolitic nucleation center (S)	(3.5-7.0)Na_2O:Al_2O_3:(10.0-16.0)SiO_2:(140-280)H_2O	100	US.P 3,671,191
Elliott, Jr. et al.	*Zeolitic nucleation center (S)	(3.0-6.0)Na_2O:Al_2O_3:(8.0-12.0)SiO_2:(120-200)H_2O	100	US.P 3,639,099
Miyanohara et al.	*Zeolitic nucleation center (S)	(24.0-40.0)Na_2O:Al_2O_3:(6.0-20.0)SiO_2:(480-200)H_2O	80-110	US.P 4,376,106
Kostinko	*Zeolitic nucleation center (S)	(3.5-30.0)Na_2O:Al_2O_3:(7.0-30.0)SiO_2:(35-2700)H_2O	80-120	US.P 4,264,562
Vaughan et al.	*Zeolitic nucleation center (S)	(0.5-2.5)Na_n(A):(1.2-3.0)Na_2O:Al_2O_3:(4.0-7.5)SiO_2:(40-200)H_2O	80-150	US.P 4,178,352
Kasahara et al.	*Clear aqueous nuclei solution (S)	3.0Na_2O:Al_2O_3:10.0SiO_2:105H_2O	92	J. Zeolite
Kuehl et al.	(P)	(6.0-15.0)Na_2O:Al_2O_3:(4.0-20.0)SiO_2:(72-2250)H_2O	60-120	EU.P 0435625A2
Dewaele, N et al.	Alkali chloride (S)	20.0Na_2O:Al_2O_3:20.0SiO_2:700H_2O.xMCl	95-100	Zeolite Tech.&appli.

Remark#:

Type of seed	Seed (Composition)	Range of seed composition
Synthesis zeolite Y	(0.7-1.1)Na_2O:Al_2O_3:(3.0-6.0)SiO_2:(0-9) H_2O	(0.7-1.1)Na_2O:Al_2O_3:(3.0-6.0) SiO_2:(0-9)H_2O
Amorphous aluminosilicate*	(15.0-17.0)Na_2O:Al_2O_3:(14.0-16.0)SiO_2: (285-357)H_2O**	(7-30)Na_2O: Al_2O_3:(8-18)SiO_2: (70-400)H_2O
	(9.0-15.0)Na_2O:Al_2O_3:(12.0-18.0)SiO_2: (180-300)H_2O**	
	15.3Na_2O:Al_2O_3:10.0SiO_2:183H_2O**	
	(7.0-30.0)M_2O:Al_2O_3:(8.0-14.0)SiO_2:(70-420)H_2O**	
	(12.0-17.0)N_2O:Al_2O_3:(12.0-16.0)SiO_2: (300-400)H_2O**	
Alkali chloride	NaCl	NaCl

* A small particle amorphous aluminosilicate

** Molar composition ratios of a reaction mixture for preparing seed

*** Molar composition ratios of a reaction mixture for preparing whole gel

P : Primary zeolitic nucleation center

S : Secondary zeolitic nucleation center

2.2 Analytical literature reviews

First, some technical term would be defined in order to understand in the same way with the author writer as following:

Seed is a small particle amorphous or crystal of a desiring substance added to a reaction mixture to induce crystallization.

Gel is a two-phase colloidal system consisting of a solid and a liquid in more solid form than a sol.

Second, there are three kinds of seed using in these thesis as following:

1) Synthetic zeolite Y type having the molar composition ratios as $(1.1\text{-}0.7)Na_2O : Al_2O_3 : (3\text{-}6)SiO_2 : (0\text{-}9)H_2O$,
2) Zeolitic nucleation centers having the molar composition ratios as $(7\text{-}30)Na_2O : Al_2O_3 : (8\text{-}18)SiO_2 : (70\text{-}400)H_2O$ and
3) Alkali chloride such as NaCl.

Third, the range of molar composition ratios of a reaction mixture using synthesis zeolite Y type shows like $(1.2\text{-}40)Na_2O : Al_2O_3 : (4\text{-}30)SiO_2 : (35\text{-}2700)H_2O$.

The quantity of molar composition ratios of both seed and reaction mixture depends on the process and condition to synthesis zeolite Y type; however, there are four main steps, which most of processes will be passed through in sequence.

1) Activated sodium silicate solution comprises of the reaction between seed and sodium silicate solution by mixing both of them and then aging for a period of time. At this step, a primary building block of zeolite Y type will be formed because seed provide sites for secondary nucleation to develop by using sodium silicate solution to be nutrient.
2) Gelation is happened by mixing sodium aluminate solution with activated sodium silicate solution for a period of time to form the whole gel of a reaction

mixture. At this step, a desired molar composition ratio of a reaction mixture is completed and provided a source of nutrients for nuclei growth.

3) Crystallization occurred by aging the whole gel at elevated temperature is about 60 to 120°C for a period of time until crystalline zeolite Y type is formed. At this step, faujasite structure is created by connecting a primary building block to form a crystalline structure of faujasite.

4) Separation is the process to recover crystal products from the system having the mother liquid and crystal particles. This step uses to stop further transformation of crystal in that system to be undesirable crystal products.

CHAPTER 3

THEORY

3.1 Introduction

The history of zeolites began with the discovery of stilbite in 1756 by the Swedish mineralogist Cronsted. The term "zeolite" was created by Cronsted from the Greek ζειν "to boil" and λιθος "stone" for minerals expelling water when heated and hence seem to boil (Dewael et al, 1985). The term of zeolite was originally used to describing many mineral groups of crystalline materials. Later the term was broadened to use a wide range, including all ion-exchange, naturally occurring and synthetic inorganic material as well as organic ones. In general, zeolites have eight important properties, namely (Break,1974);

1) high degree of hydration and the behavior of "zeolitic" water,
2) low density and large void volume when dehydrated,
3) stability of the crystal structure of many zeolites when dehydrated and when as much as 50 percent by volume of the dehydrated crystals are void,
4) cation exchange properties,
5) various physical properties such as electrical conductivity,
6) uniform molecular-sized channels in the dehydrated crystal,
7) adsorption of gases and vapors and
8) catalytic properties.

There are 40 known natural zeolites and about 96 zeolites have been synthesized. Of this large number of zeolites, only a few have found commercial application. They are mostly synthetic zeolites and synthetic-analog natural zeolites. Many of the known

structures have high thermal and chemical stability, making them useful materials in a wide range of important industrial processes such as catalysis, separation, purification, and ion-exchange.

3.2 Fundamental structure of zeolite

Smith (Smith,1976;Bhatia,1990) has defined a zeolite as a "crystalline aluminosilicate with a tetrahedral framework structure enclosing cavities occupied by cations and water molecules, both of which have enough freedom of movement to permit cation exchange and reversible dehydration". These crystalline aluminosilicate materials have uniform pore structure and minimum channel diameters of 0.1-0.3 nm. This size depends upon the types of zeolites (Tanabe et al., 1989). Zeolites have the structure of primary building unit (PBU) consisting of a three dimensional framework of $[SiO_4]$ and $[AlO_4]^-$ tetrahedra, each of which contains a silicon or aluminum atom in the center. These are shown in Figure 3-1. The oxygen at each tetrahedral corner is shared with an identical tetrahedron being present in various ratios and arrangement in a variety of ways. Thus pore, channels, and cages, or interconnected voids are obtained from the framework.

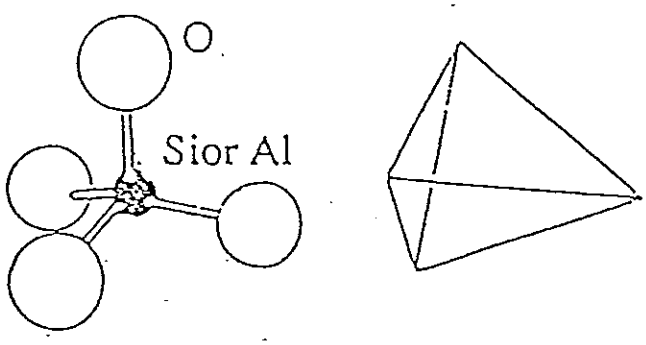


Figure 3-1 Primary building unit (PBU) of $[SiO_2]$ or $[AlO_4]^-$ tetrahedra (Dyer, 1988)

A secondary building unit (SBU) shown in Figure 3-2 consists of seven groups; within each group, zeolites have a common sub-unit of structure being a specific array of (Al, Si)O_4 tetrahedra. There are nine secondary building units used to describe all of known zeolite structures as follow: 4(S4R), 6(S6R), 8(S8R)-member single ring, 4-4(D4R), 6-6(D6R), 8-8(D8R)-member double rings, 4-1(T_5O_{10}), 5-1(T_8O_{16}), 4-4-1($T_{10}O_{20}$) branched rings.

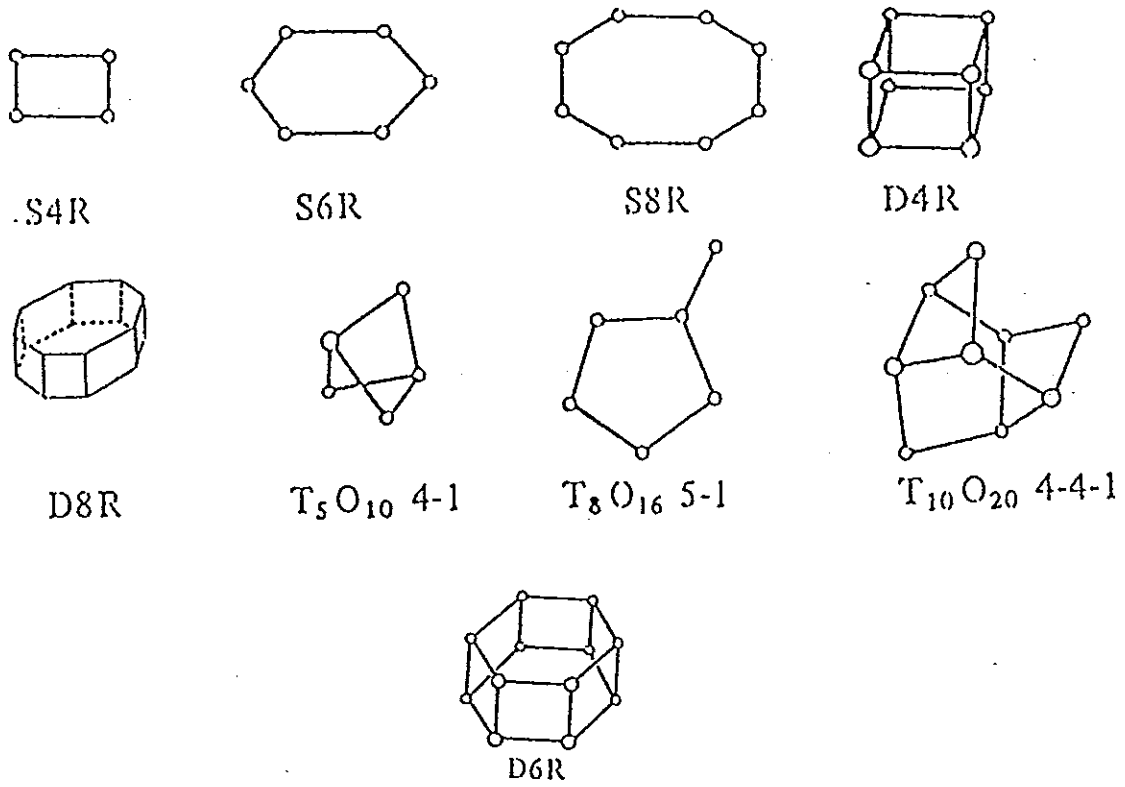


Figure 3-2 Secondary building units (SBU's) configurations in zeolite frameworks (Break,1974)

In some cases, the zeolite framework can be considered in the term of polyhedral units shown in Figure 3-3 such as 4-4(D4R), 6-6(D6R), 8-8(D8R)-member double rings, truncated octahedron

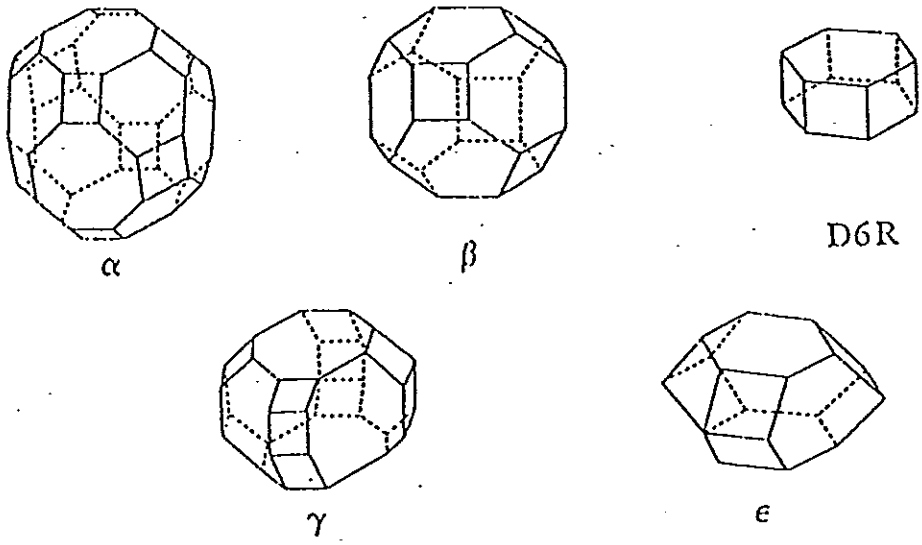


Figure 3-3 Polyhedral units configurations in zeolite frameworks (Break,1974).

Most zeolite framework can be generated from several different SBU's. Descriptions of known zeolite structures based on their SBU's are listed in Table 3-1.

Table 3-1 Zeolite and their secondary building units (Barrer,1978)

Zeolite	Secondary Building Units								
	4	6	8	4-4	6-6	8-8	4-1	5-1	4-4-1
Bikitaite								X	
Li-A(BW)	X	X	X						
Analcime	X	X							
Yugawaralite	X		X						
Episitbite								X	
ZSM-5								X	
ZSM-11								X	

Table 3-1 (Continuation)

Zeolite	Secondary Building Units								
	4	6	8	4-4	6-6	8-8	4-1	5-1	4-4-1
Ferrierite								X	
Dachiardite								X	
Brewsterite	X								
Laumonite		X							
Mordenite								X	
Sodalite	X	X							
Henulandite									X
Stilbite									X
Natrolite							X		
Thomsonite							X		
Edingtonite							X		
Cancrinite		X							
Zeolite L		X							
Mazzite	X								
Merlinoite	X		X			X			
Philipsite	X		X						
Losod		X							
Erionite	X	X		X					
Paulingite	X								
Offretite		X							

Table 3-1 (Continuation)

Zeolite	Secondary Building Units								
	4	6	8	4-4	6-6	8-8	4-1	5-1	4-4-1
TMA-E(AB)	X	X							
Gismondine	X		X						
Levyne		X							
ZK-5	X	X	X		X				
Chabazite	X	X			X				
Type A	X	X	X	X					
Faujasite	X	X			X				

This table shows that Brewsterite, Mazzite, Paulingite are generated by using only single 4-member rings along with Laumonite, Cancrinite, Zeolite L, Losod, Orifertite, and Levyne are generated by using only single 6-member rings. Natrolite, Thomsonite, and Edingtonite are generted by using only complex 4-1.Bikitaite, Episitbite, ZSM-5, ZSM-11, Ferrierite, Dachiardite and Mordenite are generated by using only complex 5-1. Both of Henulandite and Stilbite are generate by using only complex 4-4-1. The other zeolites are generated by using several building units such as Sodalite, Faujaite, Zeolite A type shown in Figure 3-4.

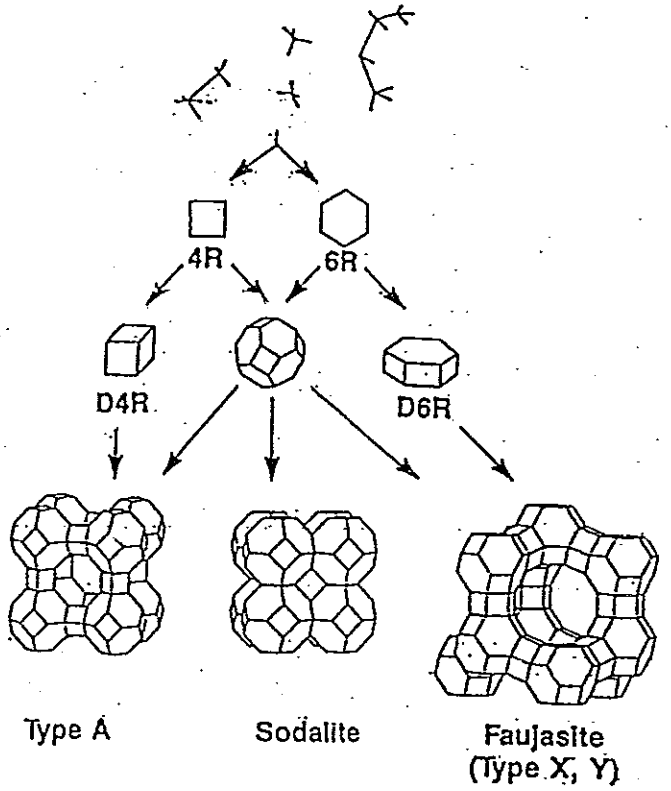


Figure 3-4 Framework structure of sodalite, faujasite, and zeolite A type (Vaughan, 1988)

The structure formula expressed for the crystallographic unit cell of zeolite is

$M_{x/n}[(AlO_4)_x(SiO_2)_y]wH_2O$, where

M is the cation of valence n,

w is the number of water molecules,

y/x has values of 1-5 formed in nature or synthesis, or in the term of empirical formula, $M_{2/n}O : Al_2O_3 : zSiO_2 : wH_2O$, where

z and w fall in a definite range.

The principle cations are sodium, potassium, mangnesium, calcium, strontium, and barium. These cations are loosely bound in the structure and may be exchanged to vary degree by each other (Kuehl,1990).

The pore size of zeolite is found by the number of tetrahedral units as well as the nature of the cations that are presented in or at the mouth of pore. As a result of this, zeolites are commonly accepted into three classes as following: small, medium, and large pore zeolites shown in Table 3-2.

Table 3-2 Classification group of zeolites (Barrer, 1982)

Pore size	Number of tetrahedra	Maximum free diameter
Small	6,8	4.3°A
Medium	10	6.3°A
Large	12	7.5°A

Small pore zeolites:

Eronite: The framework of this zeolite consist of double six-member rings and single six-member ring arranged in parallel planes perpendicular to the hexagonal axis. This produces cancrinite type cages linked by hexagonal prisms and these are cross-linked by single six-membered rings perpendicular to the hexagonal axis. This arrangement produces a three-dimension pore system containing cavities that have internal dimensions of 15.1x6.3 Å. The main apertures are formed by eight-member oxygen rings that have a free dimension of 3.6x5.2 Å; each cavity has six apertures shown in Figure 3-5 (Chen and Degnon, 1988).

Medium pore zeolites:

ZSM-5: The framework of ZSM-5 contains a configuration of linked tetrahedra consisting of eight, five-member rings. These units join through edges to form chains connected to form sheets and the linking of it lead to a three-dimension framework structure. The chain expands along the Z-axis. The straight channels have diameters of about 5.5x5.6 Å and sinusoidal channels are about 5.1x5.5 Å shown in Figure 3-5. (Bhatia, 1990)

Large pore zeolites:

Faujasite: The structure consists of truncated octahedra formed by single-4 ring and single-6 ring and joined by double-6 member rings. Having a large cavity called supercage, the structure surrounded by ten sodalite units has an inner diameter of 13°A. This creates interconnection among apertures of twelve-member oxygen rings having free diameter of about 7.4°A shown in Figure 3-5.(Botton, 1976)

3.3 Natural zeolite

The history of zeolites began with the discovery of stilbite in 1756 by Cronstedt. Zeolite minerals were considered as typically occurring in cavities of basaltic and volcanic rocks. During the last 50 years, zeolite occurrences are not restricted into basalt matrices and volcanic rocks. For example, Loew, in 1875, reported chabasite in a sedimentary tuff bed near Bowie, Arizona; Murray and Renard, in 1891, reported the present of zeolites in marine sediments; Johann, in 1914, reported that fine-grained zeolites comprised a substantial fraction of Eocene tuffs in Colorado, Wyoming, and Utha (Barrer, 1982). As a result of many geological explorations, zeolite formation is considered to six types of geological environments or hydrogical systems following: saline lake origin; soil and land surfaces; marine deposits; open flowing system; hydro thermal treatment; burial diagenesis.

These types of occurrences result in characteristic types of zeolite zoning shown in Figure 3-6. Zone A is characterized by alkali-rich zeolites, none-analcimic, zone B by analcime zone C by felspars.

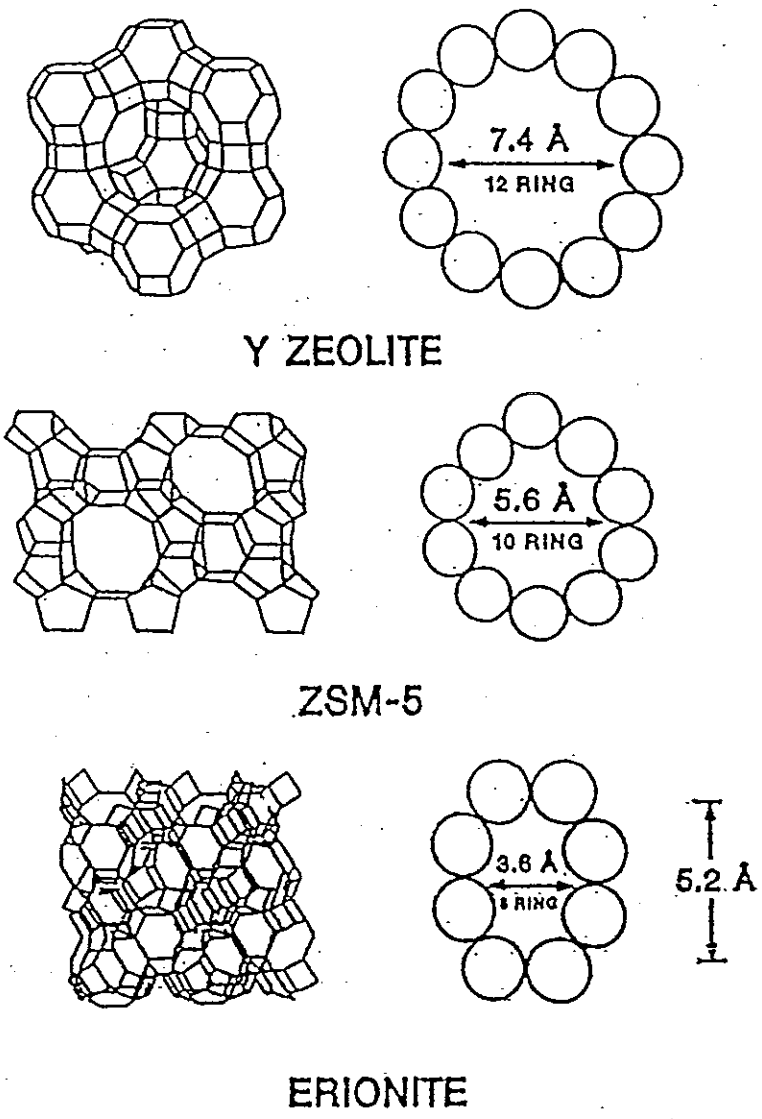


Figure 3-5 Framework structures and projections of zeolites(Chen and Degnon,1988)

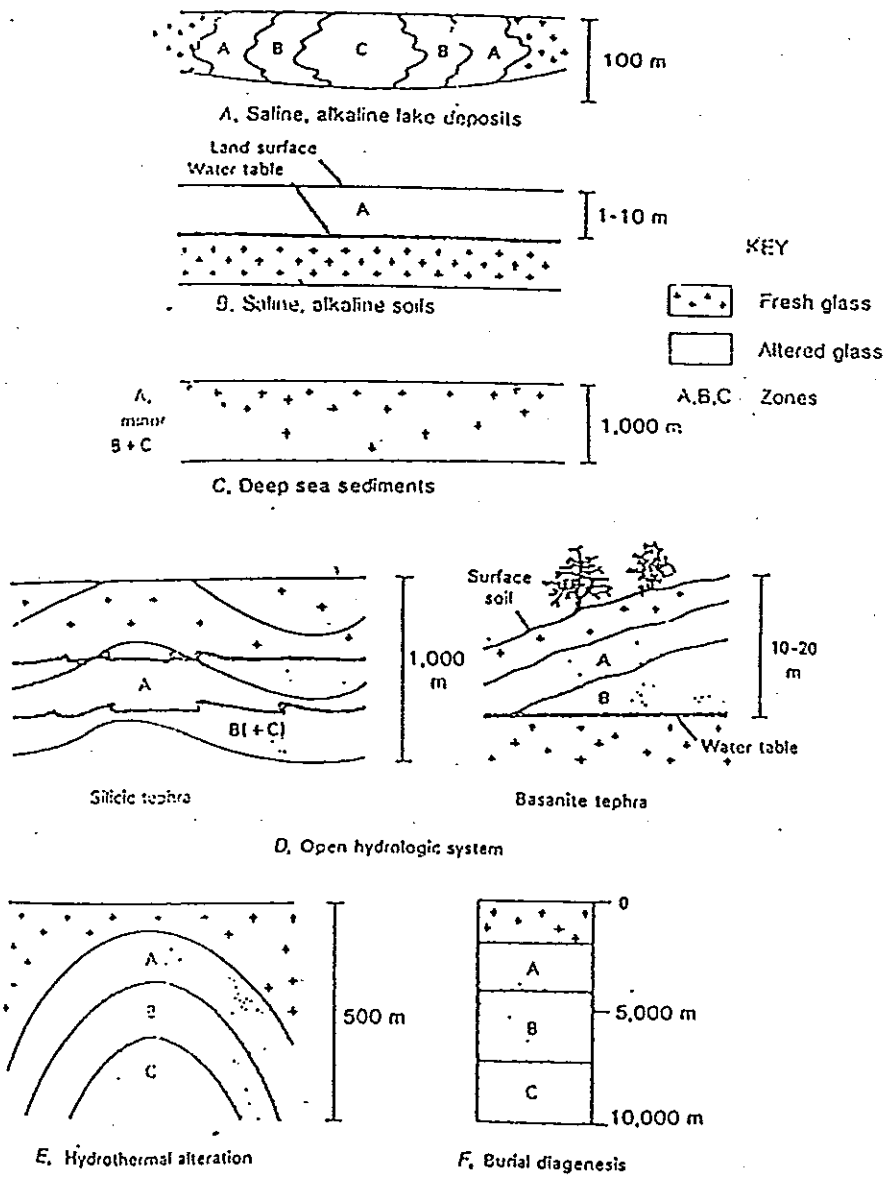


Figure 3-6 Patterns of authigenic zeolites and feldspars (Hay, 1978)

1) Zeolite of saline alkaline lake origin:

The creation of zeolites in a saline alkaline environment is represented in a typical closed basin of arid, or semi-arid regions in which is rich in dissolved sodium carbonate / bicarbonate and has gathered to produced a high pH of about 9.5. Zeolites are laid down from eactive materials deposited in the lack.

These materials are often "glass" of volcanic origin and described as "vitric tuffs". Other substances forming zeolites under these conditions are biogenic silica, clays, plagioclase (feldspar),neophelin and forms of quartz. Deposits of this type commonly contain phillipsite, clinoptilolite and eronite, but some include charbazite and mordernite. Zeolite locations of this sort are widespread in the Western of USA. The zonation of the mineral beds in the various saline, alkaline lakes deposits indicate the important reactions during diagenesis that produce patterns are (Hay, 1978):

Glass ⟶ alkalic, silicic zeolites

Alkalic, silicic zeolites ⟶ analcime

Analcime ⟶ K-feldspar

Alkalic, silicic zeolites ⟶ K-feldspar.

Some controlling chemical parameters on these reactions are the cation ratios, silicon-aluminium ratios, and the activity of the water dissolution of the glass is controlled by the salinity and pH (Surdam,1978).

2) Zeolite in soil and land surfaces:

Climate is the controlling factor in the formation of zeolites in the saline, alkaline soils. These deposit form in arid and semiarid regions, where evaporation causes sodium carbonate-bicarbonate concentrated in the soil surface. Rainwater percolating through the soils dissolves the sodium carbonate-bicarbonate and increases in pH allowing it to alter glasses and aluminosilicates present in soil. Zeolite deposits of this type can approach 18 meters in thickness and contain 15 to 40 percent zeolites. Analcime is the most abundant zeolite forming in these formations.(Hay, 1978) Minor amount of phillipsite, natrolite, and chabaszite are also occurred. Location of this environment has been observed in theOlduvai Gorge, Tanzania and other sites in Africa and in the Western United States. (Dyer, 1988)

3) Zeolite in marine deposits:

Zeolites form in marine sediments under low temperatures and moderate pH conditions. They seemed to have been principally formed the action of trapped salt solutions (pore fluids) on glasses of underwater volcanic origin. Clinoptilolite and phillipsite found abundant in regions of the Pacific Ocean and the Indian Ocean. This is shown in Figure 3-7.They probably forms when basaltic glass reacts with silica - rich pore waters. Analcime, eronite and mordernite were also present in these marine deposits.(Dyer, 1988) Phillipsite is associated with the low silica concentrations(less than 20ppm) typical of basaltic tephras, and clinoptilolite is associated with the high silica concantrations(20-40ppm) of siliceous tephras.(Hay, 1978)

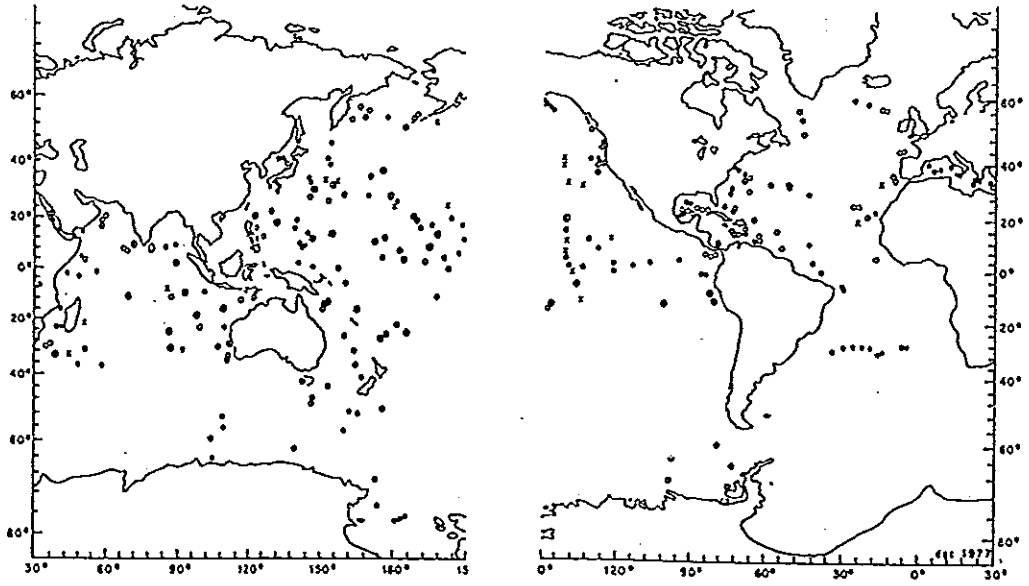


Figure 3-7 Distribution of phillipsite(x) and clinoptilolite(o) (Dyer,1988)

4) Zeolite from open flowing systems:

Zeolite can be formed when flowing waters of high pH and salt content interacts with vitric volcanic ash causing rapid crystal formation. The movement of the ground water downward through the system results in a vertical zonation of water composition and authigenic minerals, including zeolites. A silicic tephra may contain an upper zone of fresh glass, montmorillonite, and opal. The next bed can contain up to 90 percent of clinoptilolite, and underlying zone may contain analcime, feldspar, and quartz. Alternation of the glass can be occurred rapidly because of the high pH resulting from hydrolysis. For instance, the basanite vitric tuffs of Koko Crater, Oahu, Hawaii show the following vertical zonation: a) a zone of 1.5 to 12 meter thick with fresh glass, opal, and montmorillonite; b) a zone of 1.5 to 10 meter thick of palagonite tuffs with phillipsite and chabazite and c) a lower zone of 8 meter thick in which analcime is the dominant zeolite (Hay,1978).

5) Hydrothermally treated zeolite:

Zeolites precipitate into hydrothermal systems from alkaline to weakly acidic hot water. The assemblage observed that they are controlled by many factors such as temperature, host rock composition, host rock permeability and geothermal fluid composition. Often deposits occur in well-defined zones shown in Figure 3-8. Clinoptilolite and mordenite occur in the shallowest and coolest zone. Analcime, heulandite, laumontite and wairakite, the less hydrate forms, occur in the deeper and hotter zones. Hydrothermal zeolite deposits are found in Yellow stone Park, Wairakei(New Zealand), and Onikobi (Japan).(Hay, 1978)

6) Zeolite formed by burial diagenetic:

This classification relates to minerals formed as a result of depth of burial and the consequential geothermal gradient. In addition, it has strong association with deep-sea and hydrothermal conditions reflecting decrease in hydration with increased depth, so relatively

porous zeolites such as clinoptiolite and mordenite are found above those of a less open nature such as analcime, heulandite, and leumotite. Deposits of this nature have been described in the Green Tuff of Japan and in the John Day formation in Oregon, USA. (Dyer, 1988)

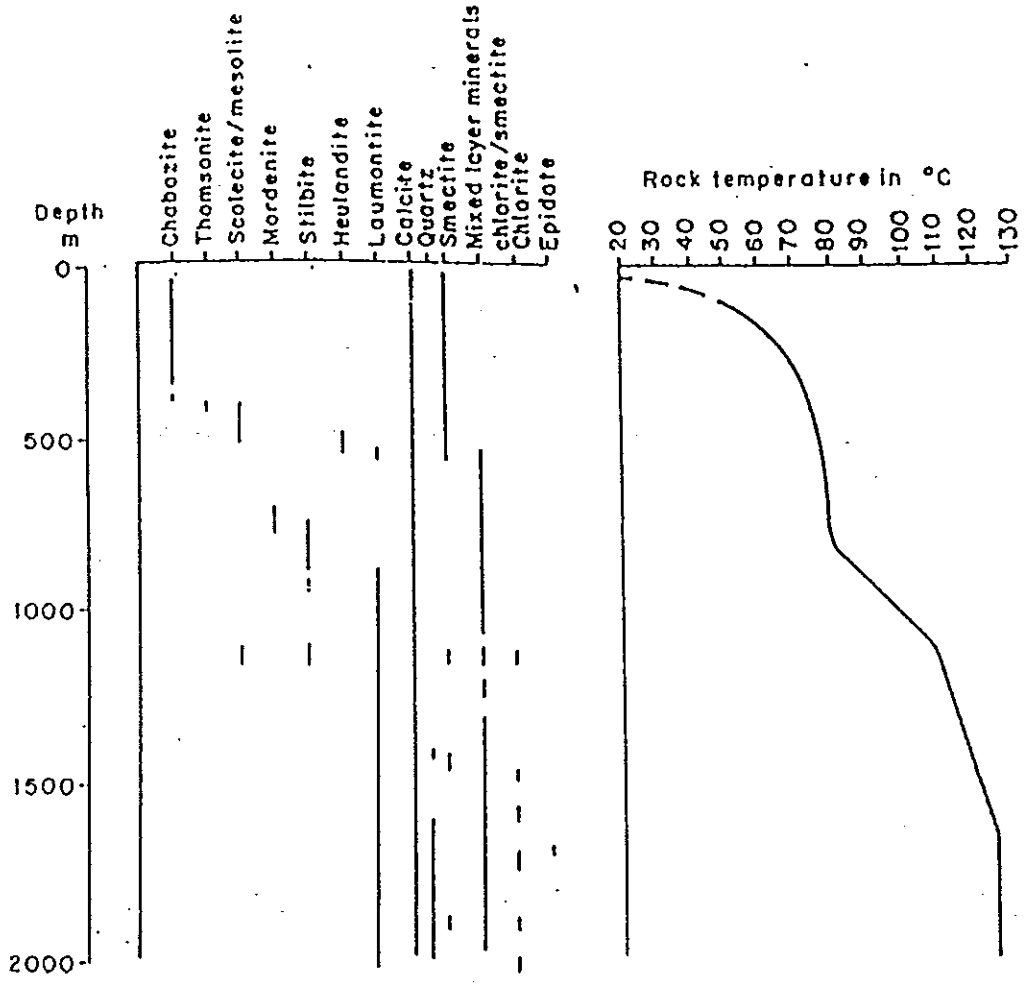


Figure 3-8 Zoning of zeolite with bore hole depth in a hydrothermal environment (Dyer,1988)

3.4 Synthesis zeolites

Zeolites are hydrate of aluminosilicates, formed under hydrothermal conditions. The term hydrothermal is used in a broad sense and includes the crystallization of zeolites from aqueous systems which contain the necessary chemical components. Levynite was the first synthetic zeolite synthesized by Deville in 1862, when aqueous solutions of potassium silicate and sodium aluminate were heated in glass tubes at 170°C. Additional synthesis of several "zeolites" were reported in the succeeding years; however, few of these reports can be substantiated due to the lack of essential data for identification.(Break,1974) In the 1940's, two factors made zeolite synthesis an exciting area in sequence (Robson,1978):

1) X-ray diffraction gave easy product identification.

2) R.M. Barrer developed the gel synthesis.

Many of natural zeolites of which structures were successfully duplicated from interaction of silica/alumina gels and alkali metal hydroxides in the process of synthesis shown in Table 3-3

Table 3-3 Synthetic counterparts of natural zeolite-gel synthesis (Robson,1978):

Zeolite	Alkali	Investigator	Date
Mordernite	Na	R.M. Barrer	1948
Analcime	Na	R.M. Barrer	1949
Phillipsite	Na	R.M. Barrer	1951
Cancrinite	Na	R.M. Barrer	1952
Natrolite	Na	R.M. Barrer	1952
Faujasite	Na	R.M. Milton	1956
Gmelinite	Na	R.M. Barrer	1959
Chabazite	Na	R.M. Milton	1960

Table 3-3 (Continuation)

Zeolite	Alkali	Investigator	Date
Erionite	K,Na	D.W. Breck	1960
Clinoptilolite	Li	L.L. Ames. Jr	1963
Ferrierite	Na	E.E. Senderov	1963
Gismondine	Na	A.M. Taylor&R.Roy	1964
Bikitaite	Li	D.J. Drysdale	1971

Early hydrothermal investigations were confined to temperature above 200°C and correspondingly elevated pressure. Most of the synthetic zeolites are produced under non-equilibrium conditions and considered in a thermodynamic sense as metastable phases in four component systems (Na_2O-Al_2O_3-SiO_2-H_2O). For example, at temperatures ranging 290°C to 700°C, 1000 atmosphere and excess water, synthetic phases related to albite, analcime, mordernite, hydroxy-cancrinite, natronite, nepheline hydrate, hydroxysodalite, and montmorillonite are formed. Milton initiated synthesis zeolite basing on starting with very reactive components in closed systems and employing low temperatures for crystallization in 1959. After that, many of the synthetic zeolites have synthesized at temperature ranging from about room temperature to boiling point of water. Conditions generally used in synthesis are:

1) Reactive starting materials such as freshly coprecipitate gels or amorphous solids,
2) Relatively high pH value introduced in the form of an alkali metal hydroxide or other strong base,
3) Low temperature hydrothermal conditions with concurrent low autogeneous pressure at saturated water vapor pressure levels,

4) A high degree of saturation of the components of the gel leading to the nucleation of a large number of crystals.(Break, 1974)

There are many sources of cations, alumina and silica summarized in Table 3-4; however, alkali metal hydroxide, soluble silicates and aluminates have frequently used to synthesized zeolite. Silica sols or silica gel have been common source of silica and aluminium trihydroxide is usually the source of alumina.(Barrer, 1982)

Amorphous aluminosilicate gels usually formed on mixing soluble silicate or colloidal silica and soluble aluminates. The crystallization of this gel, under carefully controlled conditions, gives the desired zeolite phase. The gel preparation and crystallization is presented schematically by using the Na_2O-Al_2O_3-SiO_2-H_2O system as shown in Figure 3-9.

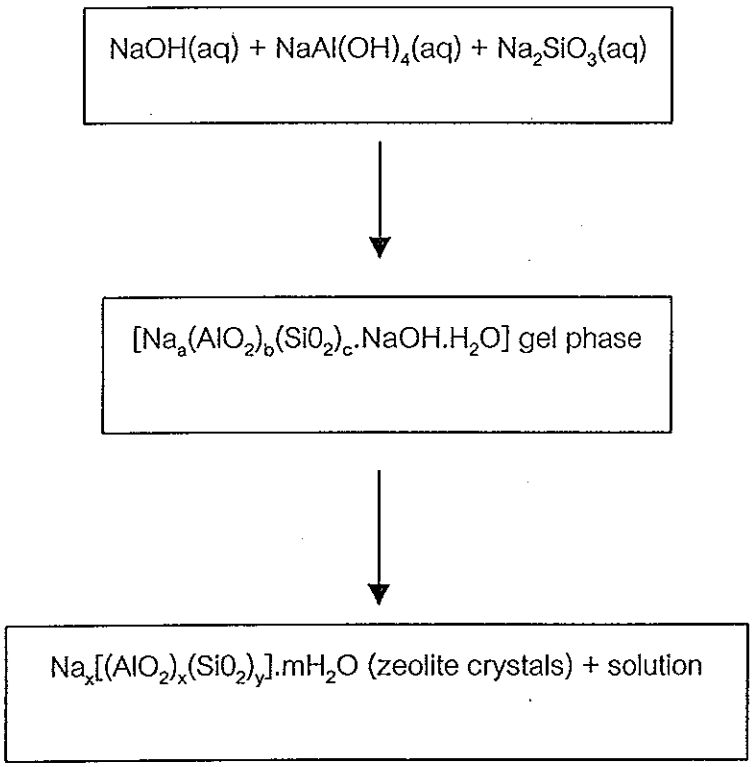


Figure 3-9 Scheme of gel preparation and crystallization (Break, 1974)

Table 3-4 Some sources of cations, aluminium, and silicon in zeolite crystallization (Barrer,1982)

Charge compensating cations	Aluminium	Silicon
Alkali metal hydroxides	Metal aluminate	Silicates and silicate hydrate
Alkaline earth hydroxides and oxides	$Al(OH)_3$, Al_2O_3, AlO.OH	Waterglass
Other oxides and hydroxides	Al alkoxides	Silica sols
Salts(fluorides, halides, Carbonates, phosphates, sulphates, etc.)	Al salts	Silica gels
Organic bases and ammonium hydroxide, especially quaternary base	Glasses	Silica and other synthetic glasses
Silicates and aluminates	Sediments	Silicon esters
Mixture of two or more of the above	Minerals, especially clay minerals, felspathoids, felspars and other zeolites	Minerals,including clay minerals, felsparthoids,felspars and other zeolites
		Basalts and mineral mixtures
		Sediment
		Tuff and volcanic glasses
		Combination of two or more of the above

The gel is probably produced by the copolymerization of the individual silicate and aluminate species by a condensation-polymerization mechanism. The gel compositions and structures appear to be controlled by the size and structure of polymerizing species. When solution of the aluminate anions and polysilicate anions are mixed to form the hydrous gel, they undoubtedly undergo a polymerization process. The gel structure thus produced amorphous and in a state of high simplexity. The composition and structure of this hydrous gel is controlled by the size and structure of the polymerizing species. Since the silicate may vary in chemical composition and molecular weight distribution, different silicate solutions may lead to differences in the gel structure. Therefore gelation controls the nucleation of the zeolite crystallites.

The resultant zeolite must be removed from the mother liquor at the proper time and must be thoroughly washed to remove sodium silicate from the pore structure. Properly washed zeolite should have an Na/Al ratio of 1.0. Zeolites are usually crystallized from alkaline aqueous gels at temperatures between 70°C and 300°C. The composition of the reaction mixture is suitably defined by a set of molar ratios following: SiO_2/Al_2O_3, H_2O/SiO_2, OH^-/SiO_2, M^+/SiO_2, where M^+ represents in most cases the Na ion,but it may also stand other alkali, alkaline earth, or ammonium ions.(Bhatia,1990)

During the crystallization of the gel, the aluminate and silicate components must undergo a rearrangement in order to form the crystalline structure. This occurs by depolymerization and solubilization of the gel. A schematic version of the crystallization of an amorphous aluminosilicate gel to a zeolite is given in Figure 3-10. The gel structure, represented in two-dimensions, is depolymerized by the hydroxyl ions producing soluble aluminosilicate species that may regroup to form the nuclei of the ordered zeolite structure. In this version the hydrated cation acts as a template. The representation presented, is for the formation of the zeolite Y structure, based upon the truncated octahedral unit. A similar scheme could be based on the use of other secondary building units such as the double 6-ring.(Break, 1974)

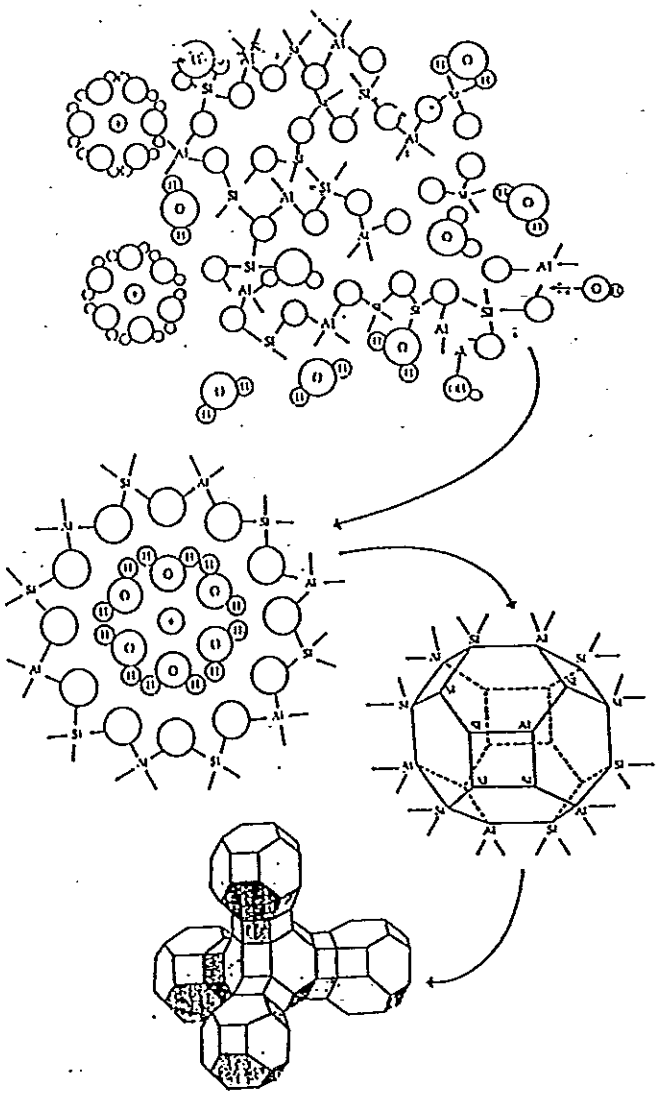


Figure 3-10 The schematic representation of zeolite crystal nuclei in a hydrous gel (Break, 1974)

3.5 The structure of Faujasitic Zeolites

The natural Faujasite, X zeolite, and Y zeolite have topologically similar structures. The silica and alumina tetrahedra are joined to form truncated octahedron (β-cage) ,with the 24 silicon or aluminium atoms(T atoms) tacking positions at the vertices. The 36 oxygen atoms are displaced from the midpoints of the edges joining the vertices to attain tetrahedral configuration around T atoms. The β-cage has a free diameter of the void 0.66 nm and has a diameter of opening ring of six oxygen atoms

0.22 nm. associated with each hexagonal face. Each β-cage is linked tetrahedrally across hexagonal faces by six bridge oxygen to four other β-cage units. The larger void spaces enclosed by β-cages and hexagonal prisms are termed α-cage, containing 26-hedron with a free diameter of 1.3 nm and 0.8 to 0.9 nm for four distorted twelve-member rings. Each α-cage is tetrahedrally joined to four others giving a complex system of void space extending throughout the zeolite structure.

The unit cell (a_o) of this structure is cubic, $a_o \sim$ 2.5 nm, and each contains 192 silicon- or aluminium-centred oxygen tetrahedra linked through shared oxygen atoms. Each unit cell contains an equivalent number of charge-balancing cations because of the net negative charge on each of the aluminium-centred tetrahedra. These are exclusively sodium ions in zeolite X and Y of their synthesized form, and a complex distribution between Sodium, Potassium, Magnesium, and Calcium in naturally- occurring faujasite. The unit cell contents for three zeolite in the hydrate form are :

faujasite $(Na_2, K_2, Mg, Ca)_{29.5}[(AlO_2)_{59}(SiO_2)_{133}].235H_2O$,

zeolite X $Na_{86}[(AlO_2)_{86}(SiO_2)_{106}].264H_2O$

zeolite Y $Na_{56}[(AlO_2)_{56}(SiO_2)_{136}].250H_2O$.

Zeolite X and Y are classified on the basis of the relative concentration of silicon and aluminium atoms, consequent effects on detailed structure and related chemical and physical properties such as cation composition, cation location, cation exchangeability, thermal stability, and sorptive and catalytic character. The aluminium atoms in the unit cell of zeolite X vary from 96 to 77 giving Si:Al ratios between 1 and 1.5, whereas for zeolite Y they vary from 76 to 48 giving a Si:Al ratio between 1.5 and 3.0. (Rudham, 1972)

In the form of empirical formula follows: $M_{2/n}.Al_2O_3.aSiO_2.bH_2O$, where

M is alkali or alkali earth cation of n valence,

a is number between 2 and 10,and

b is number between 2and 9.

Zeolite Y has an average value for "a" within the range 4.0 to 5.0, and "b" may be any volume up to 9.(Miyanohala et al., 1983)

The cations are loosely bound in the structure and the cation sites is shown in Figure 3-11 are:

Site I at the center of an hexagonal prism, 16 per unit cell;

Site I' in the β-cage adjacent to an hexagonal face shared by β-cage an hexagonal prism, 32 per unit cell;

SiteII' in the β-cage adjacent to an unshared hexagonal face of β-cage, 32 per unit cell;

SiteII in the α-cage adjacent to an unshared hexagonal face of β-cage, 32 per unit cell;

SiteII* as II, but further into the α-cage, 32 per unit cell;

SiteIII in the α-cage adjacent to a four-membered ring of β-cage, 48 per unit cell;

SiteV near the centre of the twelve -membered ring between α-cages, 16 per unit cell;

SiteU at the centre of a β-cage, 8 per unit cell.(Rudham, 1972)

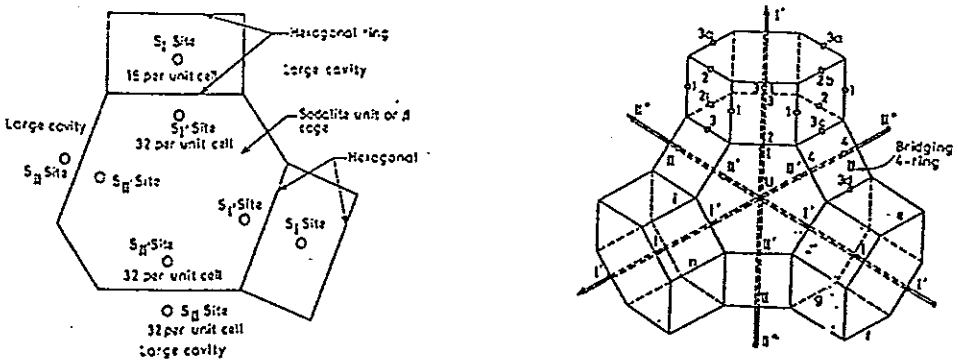


Figure 3-11 Location of cation sites in X and Y zeolites (Bhatia, 1990)

3.6 Physical Characterization of Zeolites

The physical characterization of a material such as a zeolite begins in principle by visual inspection. Such instrument may be: an ordinary microscope, an electron microscope or a scanning electron microscope. Crystalline materials may be often identified by the shape of a crystal which also may give information concerning the presence of crystalline impurities. Furthermore, from the shape of the crystal and their size distribution conclusion may even be drawn to render information concerning the condition of crystallization or later transformations which will take place and the color of the crystal reveals the presence of ionic impurities such as iron which occurs in natural or industrial zeolites.

The structure of crystalline lattice of zeolites may be obtained by X-ray diffraction methods. These methods range from simple powder patterns up to sophisticated single crystal methods allowing the localization of all atoms in a unit cell and the calculation of the electron distribution between these atoms.

The technique of thermal analysis shall now be mentioned by the force of interaction and the amount of sorbed molecules may be studied. The different mechanisms of thermal degradation may also be conventionally investigated by using this method which yields information on the intermediate states being often identical with the active catalytic species. Furthermore, information regarding the condition under which the zeolite is stable and where its crystalline structure is destroyed, can be obtained. Investigation of this kind are great importance for the description of the limit of stability of zeolite catalysts in technical processes.(Lechert,1984)

The principal method of measuring total surface area of porous structure of zeolite is occurred by adsorption of a particular molecular species from gas or liquid onto the surface. If the condition under which a complete adsorbed layer, averaging one molecule thick, can be established and the area covered per molecule is known, then

the quantity of adsorbed material gives directly the total surface area of the sample. (Satterfield,1980)

3.6.1 Principle of the Characterization of Zeolite by Diffraction Techniques

The most frequently used this method for identifying and describing a special zeolite structure. The primarily use for patent purposes, is the X-ray powder diffraction method producing a scattering pattern from the regular arrays of atoms(or ions) with the structure. It reflects the framework and non-framework symmetry of the constituents of each zeolite to produce a diagnostic fingerprint of 2θ(or "d") spacing according to the Bragg equation following(Dyer, 1988): $n\lambda = 2dSin\theta$, where

n = an integer

θ = the scattering angle

d = the value of the interlayer spacing of component atoms and ions

λ = the wavelength of the incident X-rays.

In practice, the pattern obtained from Debye-Scherrer-, a Guinier- or a diffractometer experiment are indexed and the spacing of the obtained (hkl) values are calculated from the angle of the respective peak. The intensity of the individual X-ray diffraction is given in a relative scale by using the abbreviation vs, s, ms, m, w, vw, and vvw meaning "very strong", "strong", "medium-strong", "medium", "weak", "very weak", and "very very weak". This is preferentially done when evaluating photographs. When inspecting diffractometer patterns usually the most intense peak is set to be 100 and the others are set relative to this. By this procedure in the most case an identification of the respective zeolite and of the most important impurities can be achieved. If the impurity has at least one strong reflection, it can be detected. Amorphous material can be detected by the nature of base line. A very board low base line absorption usually indicates amorphous material. Generally, by inspecting a powder pattern one can try to analyze the given structure. This has been done, particularly for synthetic zeolites shown in Table 3-5 with some success. The intensity obtained by the powder patterns may be

lost in the background or by an overlapping of reflections so that details concerning the structure, e.g. the exact positions of the cations can not be resolved. There are several methods reported in the literature for analyzing peak profiles and to avoid possible disadvantages. One advantage of the powder data is reduced secondary extinction which disturbs for single crystals, especially the strong reflexes so that in some cases powder data may be used as a supplement to single crystal data. For an exact determination of the crystal structure, single crystals of at least 20 - 50 μm are necessary and single crystal techniques need to be applied by using as many X-ray intensities as possible.(Lechert,1984)

Table 3-5 Some X-ray diffraction data for zeolite(Break,1974)

Structure Group:	4
Other Designation:	Acadialite, Haydenite, Phacolite, Glottalite
Typical Unit Cell Contents:	$Ca_2[(AlO_2)_4(SiO_2)_8] \cdot 13\ H_2O$
Variations:	Na and K; Ca > Na, K; Si/Al = 1.6-3; Si/Al = 3.2-3.8 reported in sedimentary mineral
Occurrence:	Ireland, Nova Scotia, Colorado; sedimentary in Italy, Africa, Arizona, California, Nevada
System:	Trigonal, a = 9.42 α = 94°28′ Hexagonal, a = 13.78, c = 15.06
Habit:	Rhombohedral
Twinning:	[0001] penetration
Cleavage:	[1011]
Density:	2.05 - 2.10
Hardness:	4½
Optical Properties:	Uniaxial (-), ε = 1.48-1.50, ω = 1.480-1.50; birefringence, δ = 0.002-0.005 mean index 1.46-1.47 in sedimentary chabazite·
Reference:	3, 4, 6, 38, 45-48

X-Ray Powder Data

hkl	d(A)	I	hkl	d(A)	I	hkl	d(A)	I
101	9.351	50	311	3.235	6	501	2.358	2
110	6.894	10	204	3.190	5	413	2.310	3
102	6.384	5	312	3.033	2	330	2.300	4
201	5.555	9	401	2.925	100	502	2.277	1
003	5.021	30	214	2.890	30	421	2.233	1
202	4.677	6	223	2.842	3	306	2.123	2
211	4.324	76	402	2.776	4	107	2.119	2
113	4.044	1	205	2.690	7	333	2.090	6
300	3.976	2	410	2.605	10	504	2.016	1
212	3.870	28	322	2.574	2	217	1.941	1
104	3.590	23	215	2.507	11	520	1.911	3
220	3.448	13	116	2.361	2	505	1.871	3

Table 3-5 (Continuation)

Structure Group:	I
Typical Unit Cell Contents:	$Na_{16}[(AlO_2)_{16}(SiO_2)_{32}] \cdot 16\,H_2O$
Variations:	$Si/Al = 1.8\text{-}2.8$; $H_2O/Al_2O_3 = 2\text{-}2.6$
Occurrence:	Igneous and sedimentary rocks; Iceland, Nova Scotia, New Jersey, Wyoming, Arizona, Utah, California, Nevada
System:	Cubic, a = 13.72 A
Habit:	Icositetrahedra, radiating aggregates
Twinning:	{001}, {110} lamellar
Cleavage:	{001} poor
Density:	2.24-2.29
Hardness:	5½
Optical Properties:	Isotropic, $n = 1.479\text{-}1.493$; birefringence, δ = slight, < 0.001
Reference:	3-6, 38-40

X-Ray Powder Data

hkl	d(A)	I	hkl	d(A)	I	hkl	d(A)	I
200[a]	6.87	< 10	631	2.022	10	842	1.498	20
211	5.61	80	543	1.940	< 10	761	1.480	20
220	4.86	40	640	1.903	50	664	1.463	10
321	3.67	20	633	1.867	40	754	1.447	10
400	3.43	100	642	1.833	< 10	932, 763	1.415	40
332	2.925	80	732, 651	1.743	60	941, 853	1.386	<10
422	2.801	20	800	1.716	30	860	1.372	10
431	2.693	50	741	1.689	40	1011	1.359	40
521	2.505	50	820	1.664	10	1031	1.308	10
440	2.426	30	822, 660	1.618	20	871	1.285	20
611, 532	2.226	40	831, 743	1.596	30	1033	1.263	20
620	2.168	< 10				963	1.220	30
541	2.115	< 10						

[a] (200) not in agreement with space group Ia3d

Structure Group:	7
Typical Unit Cell Contents:	$Na_6[(AlO_2)_6(SiO_2)_{30}] \cdot 24\,H_2O$
Variations:	Na, K ≫ Ca, Mg; $Si/Al = 4.25\text{-}5.25$; in sedimentary type $Si/(Al + Fe^{3+}) = 4.1\text{-}5.6$
Occurrence:	Wyoming; extensive sedimentary occurrences in western U. S.
System:	Monoclinic, a = 7.41 b = 17.89 c = 15.85 $\beta = 91°29'$
Habit:	Tabular, platy
Cleavage:	{010}
Density:	2.16
Optical Properties:	Biaxial (-), $\alpha = 1.476$, $\beta = 1.479$, $\gamma = 1.479$
Reference:	6, 38, 49-53

X-Ray Powder Data

hkl	d(A)	I	hkl	d(A)	I	hkl	d(A)	I
020	8.92	100	004	3.964	55	222	3.168	14
002	7.97	3	042	3.897	57	222	3.119	15
$10\bar{1}$	6.78	2	$14\bar{1}$	3.74	7	231	3.07	8
031	5.61	2	$21\bar{1}$	3.55	6	044	2.974	80
112	5.15	7	051, $11\bar{4}$	3.48	3	035	2.793	15
130	4.65	14				$12\bar{5}$	2.793	15
103	4.35	2	220	2.419	16	$16\bar{1}$	2.728	33
132	3.964	55	202	3.324	4			

Table 3-5 (Continuation)

Structure Group:	6
Typical Unit Cell Contents:	$Na_{1.5}Mg_2[(AlO_2)_{5.5}(SiO_2)_{30.5}]\cdot 18\ H_2O$
Variations:	Na, K in Nevada ferrierite Less Mg in Agoura ferrierite
Occurrence:	Kamloops, British Columbia, Vicenza, Italy; Agoura, California; sedimentary in Nevada.
System:	Orthorhombic, a = 19.16 b = 14.13 c = 7.49
Habit:	Blades, needles
Cleavage:	{100}
Density:	2.136-2.21
Hardness:	3 - 3½
Optical Properties:	Mean index = 1.484 in Na, K ferrierite; biaxial (+), $\alpha = 1.478, \beta = 1.479, \gamma = 1.482$; birefringence, $\delta = 0.004$, $2V\gamma = 50°$
Reference:	38, 52, 67 - 70

X-Ray Powder Data

hkl	d(A)	I	hkl	d(A)	I	hkl	d(A)	I
110	11.33	20	112, 040	3.54	80	350, 042, 701	2.58	30
200	9.61	100	202	3.49	80			
020, 101	7.00	30	501	3.42	20		2.49	20
011	6.61	20	240	3.31	20		2.43	20
310	5.84	50	600	3.20	10		2.37	40
121	4.96	10	141, 312	3.15	30		2.32	10
301, 400	4.80	10	521, 431	3.07	30		2.25	10
130	4.58	10	530	2.97	30		2.11	20
321, 031	3.99	90	620, 132	2.90	20		2.04	20
411	3.88	10	422	2.72	20		2.00	30
330, 510	3.79	20					1.94	30
	3.69	50					1.87	30
							1.78	40

Structure Group:	4
Typical Unit Cell Contents:	$Na_{12}Ca_{12}Mg_{11}[(AlO_2)_{59}(SiO_2)_{133}]\cdot 235\ H_2O$
Variations:	Si/Al = 2.1-2.3, also some K
Occurrence:	Kaiserstuhl, Germany; reported in Oahu, Hawaii
System:	Cubic, a = 24.67
Habit:	Octahedral
Cleavage:	{111}
Density:	1.91
Hardness:	5
Optical Properties:	Isotropic, $n = 1.48, 1.471$
Reference:	3, 38, 48, 66

X-Ray Powder Data

hkl	d(A)	I	hkl	d(A)	I	hkl	d(A)	I
111	14.418	100	533	3.779	32	751, 555	2.860	22
220	8.784	9	444	3.580	2			
311	7.487	5	711, 551	3.468	5	840	2.767	5
222	7.173	2				911, 753	2.719	3
331	5.695	30	642	3.311	16			
422	5.062	1	731, 553	3.227	5	664	2.641	7
333, 511	4.772	13				931	2.600	4
			733	3.025	6	10,2,2	2.382	5
440	4.387	32	822, 660	2.919	10	666		
620	3.915	4				880	2.189	3

3.6.2The Inspection of Crystal Size and Crystal Shape

The visual inspection of zeolite crystal and the inspection by using a weakly enlarging instrument, such as a magnifying glass are important for geologists out in the field. In the most case, especially when inspecting synthetic zeolites, a microscope is needed. A microscope is usually used as a first means of identification by looking at the crystal shape of some specific zeoloites. The shape of the crystal may sometime be misled because it depends on the condition of growth. More detailed information on the crystal classification may be obtained by using a polarization microscope. In the field of electron optical instrumentation, a wide range of techniques is available giving information concerning crystal habit, crystal size and other specific characteristics. The main techniques used in zeolite research are connected to transmission electron microscopy(TEM), whereby the technique yielding most information is connected with the use of the scanning electron microscope(SEM) accompanied by micro-probe analysis. With the transmission electron technique magnification up to about 10^6 can be obtained corresponding to a point to point resolution of about 3°A. Depending on the sample, this resolution can be improved by using special imaging technique known as bright-field, dark-field or lattice imaging. In the scanning electron technique a fine beam of electrons is scanned over the surface of the sample by using a system of deflection coils. The various signals produced by the interaction of the electron with the surface, such as secondary electrons, back scattered electrons or X-rays can be used to form an image. Magnifications in the range from 20 to 50,000 are available with a resolution of about 100°A. Non-metallic samples are usually covered with a thin film of carbon and gold to ensure a sufficient electric conductivity to prevent a surface charge which leads to distorted pictures. Another effect is the protection of heat sensitive material. The out put of the secondary electron varies according to the accelerating voltage of the beam (5-50 kV) and the structural characteristic of the sample as well as the particular angle of the incident beam with respect to the surface features. The change in the secondary

electron current are induced by these features exhibit. The back-scattered electron give a signal varying with the respective atomic number. Measuring the wavelength of the induced characteristic X-ray radiation with special detectives an elementary analysis of the area hit by the beam can be carried out. This technique is known as electron micro-probe analysis. In principle, this scanning technique and the analysis of the characteristic X-ray radiation can also be applied in transmissions. This method is usually called "Scanning Transmission Electron Microscopy" or STEM. This method has the advantage of better resolution as compared with the TEM, but has the disadvantage of difficult sample preparation. The most powerful method in the investigation of zeolite problem is the scanning electron microscopy (SEM). This method has above all the advantage of a simple preparation of the samples and gives quick information on the shape and the distribution of the size of the crystals and also of the present of amorphous material.(Lechert,1984)

3.6.3 Characterization of Zeolite by Thermal Analysis

Thermal analytical methods are among the most important tools of the characterization of zeolites. Generally, thermal analysis describes a group of methods whereby the dependence of the parameters of any physical property of a substance on temperature is measured. The two techniques measuring the change of heat and the change of weight are the methods used preferably for the characterization of zeolite properties. These methods are called differential thermal analysis(DTA)and thermogravimetric analysis(TGA). In both methods the sample and possibly a reference sample are heated or cooled at a controlled rate.

In the DTA technique the difference in temperature between a substance and a reference material against either time or temperature is recorded. If any heat releasing or heat consuming process takes place in the sample, the temperature of the sample increase or remains behind the temperature of the reference. If the process is finished the temperatures of both specimen become equal again. The peak, obtained in the

recorded curved can be evaluated to get the kinetics and the amount of the heat transfer.

In the thermalgravimetric analysis the weight of the sample is recorded in dependence on the temperature. The DTA method has a sensitivity of about 10^{-4} Joule. With the TGA method weight changes of about 10^{-8} g can be detected. In the typical behavior of a zeolite being heated and subjected to differential thermal analysis three typical regions can be distinguished. The first region begins slightly above room temperature, has its maximum mostly near 500 K and is finished at about 750 K. This region expresses itself as an endotherm in the DTA curve and is caused by the evolution of water and possibly other volatile substances in the zeolite cavities. Between about 900 and 1500 K often two exotherms can be observed which are associated with the collapse of the zeolite lattice and sometimes at much higher temperatures re-crystallization to a new phase. In the first region often a stepwise evolution of water can be observed. Figure 3-12 shows DTA curves for A zeolites containing different cations.

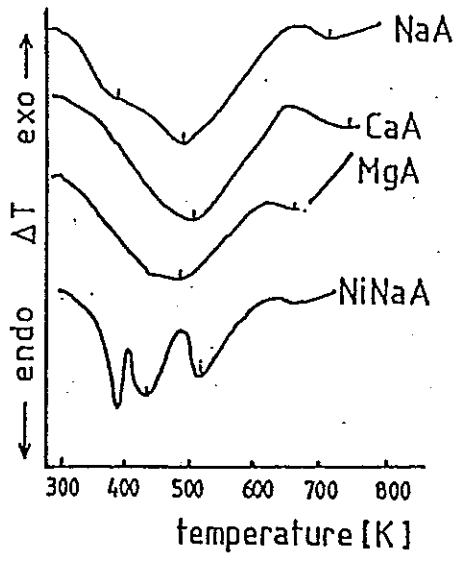


Figure 3-12 DTA curve on the region of the dehydration for A zeolite with different cations (Lochert, 1984)

3.6.4 Characterization of Zeolite by Brunauer-Emmett-Teller (BET)

This method developed by Brunauer, Emmett, and Teller is the most common use in catalyst studies in order to measure surface area. The Langmuir adsorption isotherm is applied to use for this method, especially in the case of multilayer adsorption. As in the Langmuir for the first layer, the rate of evaporation is considered to be equal to the rate of condensation, and the heat of adsorption is taken to be independent of coverage. For layer beyond the first, the rate of adsorption is taken to be proportional to the fraction of the lowest layer still vacant. The rate of de-sorption is taken to be proportional to the amount present in that layer. These assumption are made largely for mathematical convenience. The heat of adsorption for all layer except the first layer is assumed to be equal to the heat of liquefaction of the adsorbed gas. The summation over an infinite number of adsorbed layers gives the final expression as follows:

$$\frac{P}{V(P_o-P)} = \frac{1}{V_mC} + \frac{(C-1)P}{V_mC\,P_o} \qquad \text{------ 1}$$

where V : volume of gas adsorbed at pressure P

V_m : volume of gas adsorbed in monolayer, same unit as V

P_o: saturated pressure of adsorbated gas at the experimental temperature

C : a constant related exponentially to the heat of adsorption and liquefaction of the gas

$$C = e^{(q1-ql)/RT} \qquad \text{------ 2}$$

where q_1 : heat of adsorption on the first layer

q_l : heat of liquefaction of adsorbed gas on all other layers

R : the gas constant

If equation 1 is obeyed, a graph of $P/V(P_o-P)$ versus P/P_o should give a straight line, the slope and intercept of which can be used to evaluate V_m and C. Many adsorption data show very good agreement with the BET over values of the relative pressure P/P_o

between approximate 0.05 and 0.3 . This range is usually used for surface area measurements. At high P/P_o values, complexities associated with the realities of multilayer adsorption and/or pore condensation cause increasing deviation. With micropore substance such as zeolites, the linear region on a BET plot occurs at much lower volumes of P/P_o, typically around 0.01 or less. From equation 1, $V_m = 1/(S+I)$, where S is the slope, equal to $(C-1) / V_mC$ and I is the intercept, equal to $1/ V_mC$. This proceeds from the fact that

$$S+I = 1 / V_mC [(C-1) +1] = 1 / V_m \quad \text{----- 3}$$

The surface area of the catalyst may then be calculated from V_m if the average area occupied by an adsorbed molecule is known.

The inert vapor used in the BET method should be small and approximate spherical. In addition, the vapor should also be easy to handle at required temperatures. Liquid nitrogen is a readily available coolant ,and nitrogen is usually used as adsorbate since it is relatively cheap and readily available in high purity.(Satterfield,1980)

CHAPTER 4

EXPERIMENT

The experiments were mainly focused on the fundamental synthesized procedure of NaY zeolite and the characterization of the crystal product.

4.1 Crystals Synthesis

4.1.1 Equipment

a. Electric mixer with stirring rod (pitched blades turbine joined inside truncated cone) (Heidolph made in Germany)

The electric mixer type R2R1 with stirring rod shown in Figure 4-1 was used to mix working solutions. The speed was varied between 280 rpm and 2200 rpm.

b. Programming water bath (Eyela made in Japan)

The programming water bath model NCB-221 shown in Figure 4-2 was used to control the temperature of the initiating agent solution during the aging period.

c. Hot air oven (Eyela made in Japan)

The hot air oven model NDO-600N shown in Figure 4-3 was used to crystallize amorphous aluminosilicate gel or slurry.

d. Vacuum pump (Eyela made in Japan)

The vacuum pump model A-3S shown in Figure 4-4 was used for vacuum filtration of zeolite crystals and the mother liquid.

4.1.2 Reagents

The using reagents in our experiments were shown in Table 4-1 and appendix B.

Table 4-1 Synthetic Reagents

No	Reagent	Formula	Purposed	Grade	From
1.	Sodium silicate solution (water-glass)	Na_2SiO_3	Source of silicon ion	-	Oriental Silica Co,Ltd.
2.	Aluminium hydroxide	$Al(OH)_3$	Source of aluminum ion	LG	AJAX Chemicals
3.	Sodium hydroxide	NaOH	Source of sodium oxide	LG	AJAX Chemicals
4.	Aluminium sulphate	$Al_2(SO_4)_3$	Source of aluminum ion	AG	Carlo Erba
5.	Sodium chloride	NaCl	Source of sodium ion	AG	BDH Laboratory
6.	De-ionized water	H_2O	Make volume of solution into required concentration	-	Central instrument center of PSU

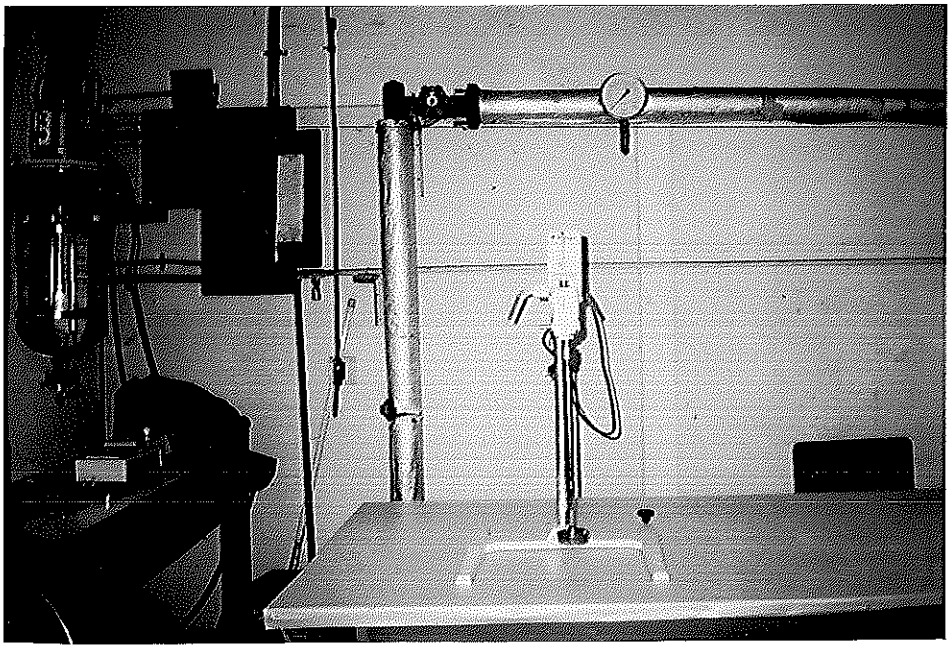


Figure 4-1 Electric mixer with stirring rod (pitched blades turbine joined inside truncated cone)

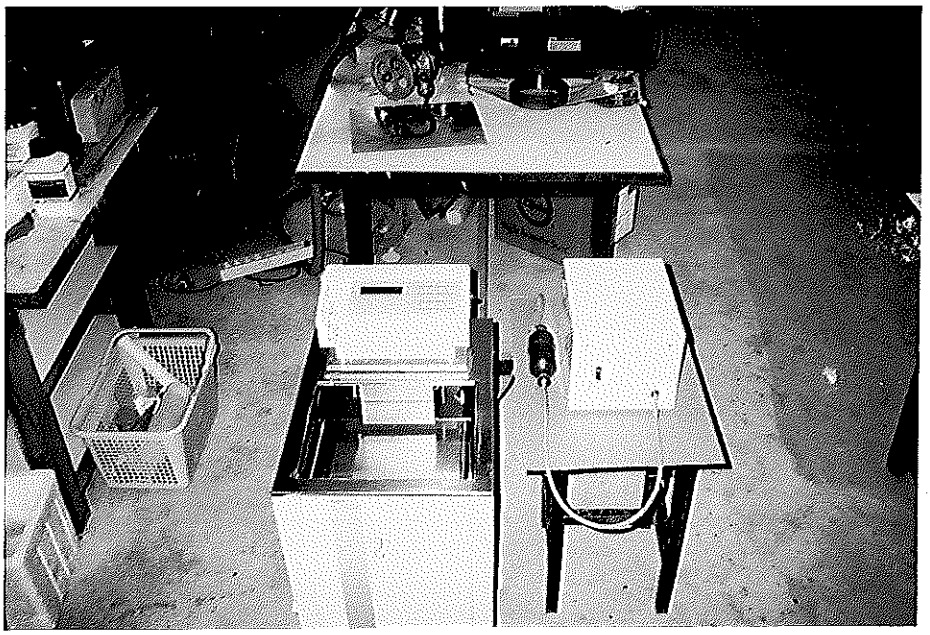


Figure 4-2 Programmable water bath

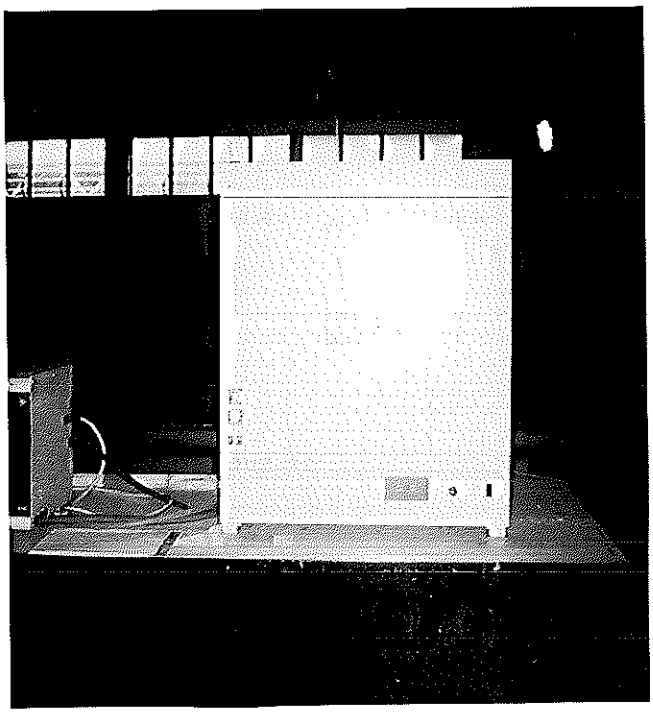


Figure 4-3 Hot air oven

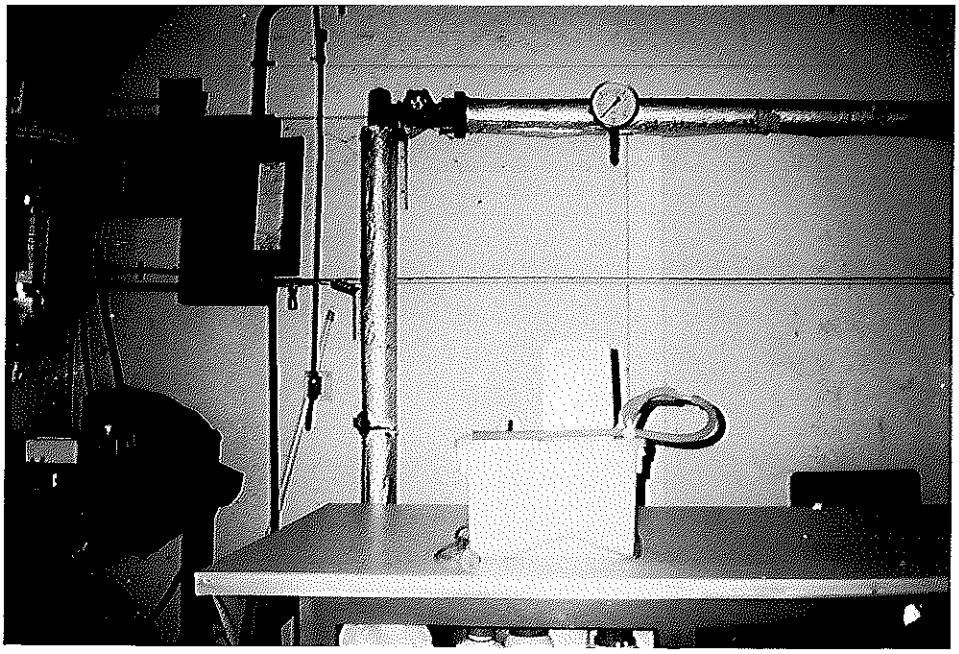


Figure 4-4 Vacuum pump

4.1.3 Synthesis of NaY zeolite

The synthetic catalytic NaY zeolite methods were shown in Chapter 2. The synthesis of NaY zeolite method that used in this research was simulated from the procedure of RIPP. The procedure was summarized in Figure 4-5 and appendix B. Details of prepared procedure as follows:

a. Preparation of working solution

The working solution is the most important factor in NaY zeolite synthesis process. In general process, there are three or four fundamental components, such as, reactive forms of silica, alumina templates, other forms of base solutions, and possibly a sources of seed and nuclei. The common reactants are: silica from sodium silicate (waterglass) or aqueous colloidal silica; aluminum from sodium aluminate, alum or a colloidal alumina (boehmite) and sodium or potassium hydroxides. There were four basic reactants used in this research that are sodium silicate (water glass), sodium aluminate, aluminium sulphate and deioniozed water. These working solutions were prepared and controlled the composition of the main components by using the method in appendix A.

b. Synthesis NaY zeolite

The first part of this work was emphasized on studying the fundamental NaY zeolite synthesis and the kinetics of crystal growth. There are four main steps in the NaY zeolite synthesized procedure as the following;

1). Preparation of initiating agent solution

The initiating agent is an amorphous aluminosilicate (disperse phase) fine particle in the solution preparing from the reaction between waterglass and sodium aluminate. The sodium aluminate solution was slowly added into waterglass solution, then the solution was agitated for 1 hour at 15°C. After that, the reaction mixture was statically aged for 6 hours at 35°C. This prepared initiating agent had the final molar composition ratios of oxides as:

$$14.22Na_2O:Al_2O_3:13.08SiO_2:271.3H_2O$$

Aluminium sulphate and deionized water were also added into the reaction mixture to adjust molar composition of the oxides to meet the required ratio .

2) Preparation of gel

The gel is the colloid of disperse phase (sodium aluminate, aluminium sulphate, and initiating agent) which combines to the continuous phase (waterglass) and become a viscous jelly-liked of aluminosilicate at 15°C. First, the initiating agent was added to the waterglass solution and the mixture was kept well agitation for 5 minutes. Next, aluminium sulphate was slowly added and continuous well agitated for 10 minutes. Then, sodium aluminate was added and mixed for 2 minutes. After that, de-ionized water was added and agitated for 15 minutes. Finally, the whole gel of the reaction mixture had the following molar composition ratios of oxides:

$$4.81Na_2O:Al_2O_3:9.74SiO_2:192.6\ H_2O$$

The gel was then poured into a plastic bottle and was placed in the hot air oven for crystallization process.

3) Crystallization

From figure 3-10, The formation of NaY zeolite crystal was started from the combination of the small molecular weight monomers (hydrated silica-alumina polymers) to be the "secondary building units " in the solution phase. The monomers may either directly set up on a growth nucleus or crystal face, or combine with the larger polyhedra before attachment. Many such building units may form in the solution, but only restricted species will successfully connect to the growth crystal. This aging stage was carried on in hot air oven at the designed time (4-14 hours) and temperature (100°C).

4) Separation

The vacuum filtration shown in Figure 4-4 was used for separation the crystal of NaY zeolite from the mother liquid to stop both the growth rate and the phase

transformation of NaY zeolite product. NaY zeolite crystals were washed by using deionized water to minimize the deposited impurities. At this step, samples were continuously taken every 2 hours to separate NaY zeolite crystal and washed.

b. Analysis

The crytals of NaY zeolites were dried in the hot air oven at 140°C for 2 hours to dehydrate free water from crystals, then ground, packed in small bottles and kept in the closed container containing saturated ammonium chloride solution. These samples were analyzed by using X-ray diffraction (XRD), scanning electron microscope (SEM), and differential thermal analysis (DTA).

Figure 4-5 Flow chart of catalytic NaY zeolite synthesis

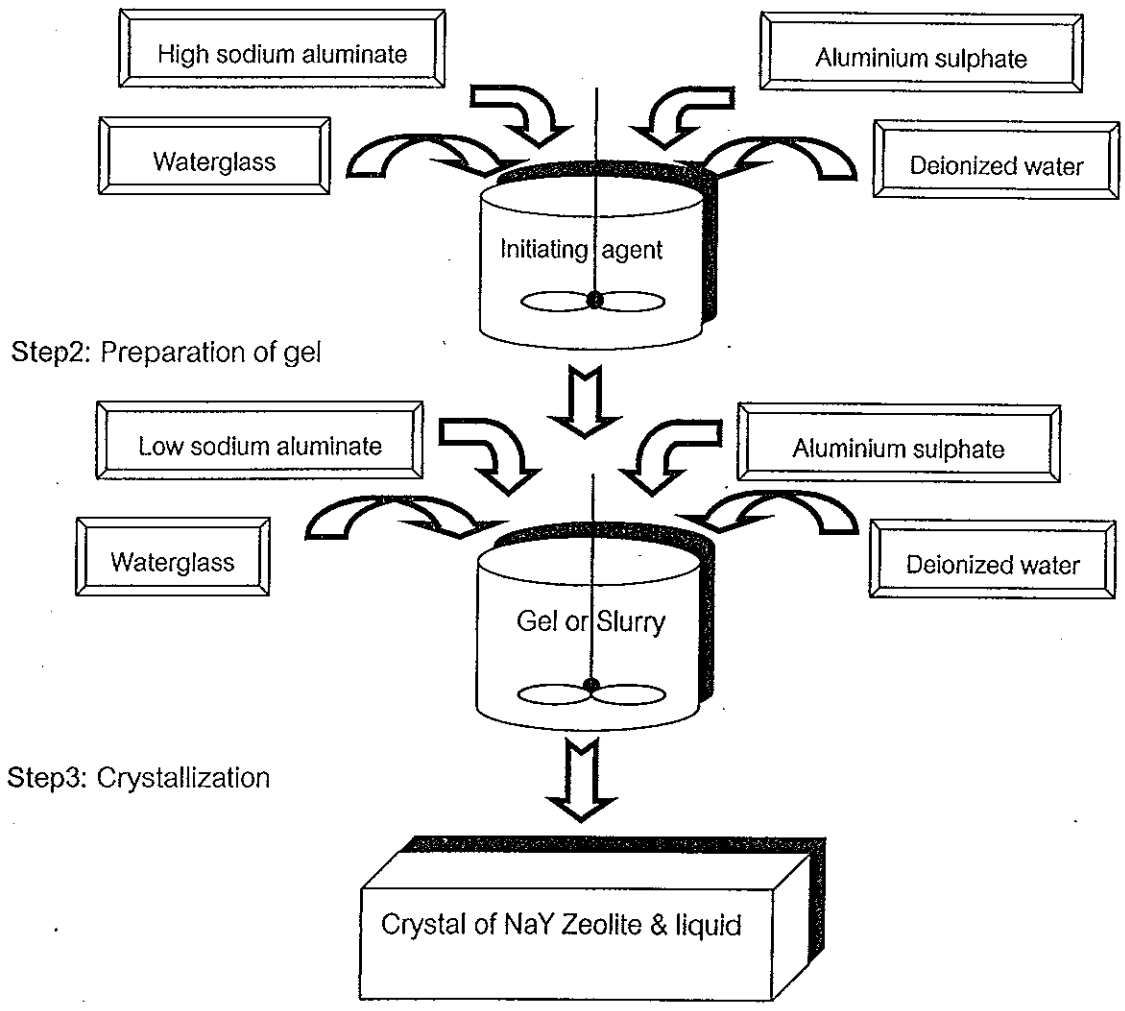
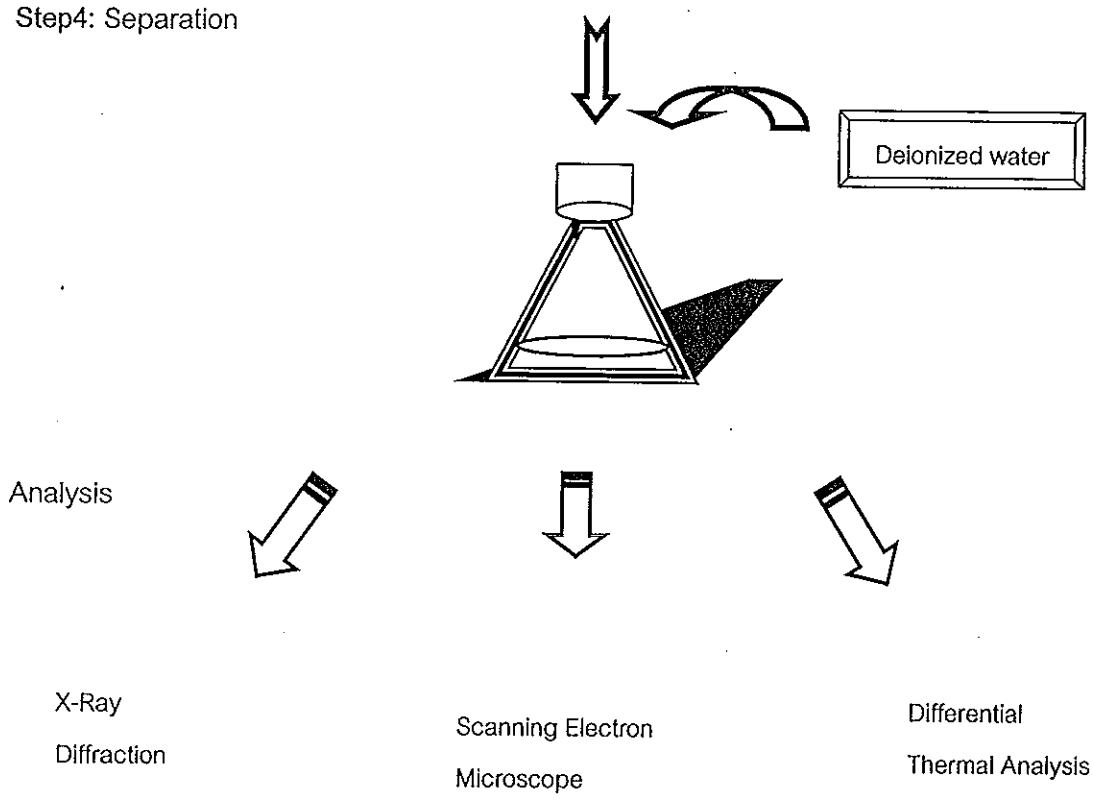


Figure 4-5 (Continuation)



The kinetics of crystal growth was observed by plotting a curve between crystallinity (y axis) and time (x axis). These were done by taking out the sample from hot air oven at different periods of time. The relative crystallinity was analyzed by using XRD.

The second part of our experiment was aimed to study the synthetic factors and conditions of the fundamental synthesis procedure by using the kinetics of crystal growth as an indicator. The factors and conditions of study were summarized in the following table;

Table 4-2.Effect of crystallization temperature

Step	Condition
1.The initiating agent step	
- Molar composition ratios of oxides	$16.62Na_2O:Al_2O_3:14.76SiO_2:321.26H_2O$
- Mixing temperature	15^oC
- Mixing time	1 hour
- Aging time	6 hours
2.The whole gel step	
- Molar composition ratios of oxides	$5.09Na_2O:Al_2O_3:10.17SiO_2:202.99H_2O$
- Mixing temperature	15^oC
- Mixing time	32 Minutes
3.Crystallization step	
- Crystallization temperature	70^o,85^o,$95^o$and 100^oC
- Crystallization time	
70^oC	39 - 49 hours
85^oC	12 - 24 hours
95^oC	10 - 18 hours
100^oC	4 - 16 hours
4. Separation step	
- pH(filtrate)	< 9

Table 4-3 Effect of mixing temperature in the initiating agent step

Step	Condition
1.The initiating agent step	
- Molar composition ratios of oxides	$15.96Na_2O:Al_2O_3:14.98SiO_2:312.28H_2O$
- Mixing temperature	5°,15°,$25^{\circ}C$
- Mixing time	1 hour
- Aging time	6 hours
2.The whole gel step	
- Molar composition ratios of oxides	$4.85Na_2O:Al_2O_3:9.82SiO_2:191.40H_2O$
- Mixing temperature	$15^{\circ}C$
- Mixing time	32 Minutes
3.Crystallization step	
- Crystallization temperature	$100^{\circ}C$
- Crystallization time	4 – 16 hours
4. Separation step	
- . pH(filtrate)	< 9

Table 4-4 Effect of mixing temperature at the whole gel step

Step	Condition
1.The initiating agent step	
- Molar composition ratios of oxides	$15.96Na_2O:Al_2O_3:14.98SiO_2:312.28H_2O$
- Mixing temperature	5^oC
- Mixing time	1 hour
- Aging time	6 hours
2.The whole gel step	
- Molar composition ratios of oxides	$4.85Na_2O:Al_2O_3:9.82SiO_2:191.40H_2O$
- Mixing temperature	5^o,15^o,20^o,25^oC
- Mixing time	32 Minutes
3.Crystallization step	
- Crystallization temperature	100^oC
- Crystallization time	4 – 16 hours
4. Separation step	
- pH(filtrate)	< 9

Table 4-5 Effect of seed

Step	Condition
1. Preparation of seed step	
1) The initiating agent	
- Molar composition ratios of oxides	$16.10Na_2O:Al_2O_3:15.00SiO_2:296.83H_2O$
- Mixing temperature	5^oC
- Mixing time	1 hour
- Aging time	6 hours
2) NaCl,	10 percent of final yield of synthetic crystal
3) NaY zeolite crystal(S01,S02,S03)	10 percent of final yield of synthetic crystal
4) No seed	-
2.The whole gel step	
- Molar composition ratios of oxides	$4.85Na_2O:Al_2O_3:9.82SiO_2:191.40H_2O$
- Mixing temperature	5^oC
- Mixing time	32 Minutes
3.Crystallization step	
- Crystallization temperature	100^oC
- Crystallization time	
Initiating agent	4 - 20 hours
NaY zeolite crystal	8 - 25 hours
NaCl crystal	95 hours
No seed	95 hours
4. Separation step	
- pH(filtrate)	< 9

4.2 Characterization of crystal product

Five characteristics of crystal product were examined, namely: crystallization analysis, external structure analysis, thermal stability analysis, particle size distribution and true density. The procedures to operate these instruments were shown in the appendix G.

4.2.1 Crystallinity analysis

The crystallinity of NaY zeolite crystal was determined by X-ray diffraction (XRD) spectroscopy (Figure 4-6) by using a reference database, complied by JPCDS. The XRD patterns of the zeolite containing sample and the reference sample (NaY) were obtained under the same conditions. Intensity of the 553 peak (23.5 deg with Cu Kα radiation) was compared to provide "%XRD intensity/NaY(533)". If the XRD pattern of the zeolite was sufficiently strong, a comparison of the sum of the intensities of eight peaks was used to give "%XRD intensity/NaY." This was referred as "% crystallinity". (ASTM, 1991)

4.2.2 Morphological analysis

The physical feature and particle size of NaY zeolite were examined by using scanning electron microscope (SEM) instrument (Jeol model JSH-35CF)(Figure 4-7).

From the SEM photograph, the external structure of the crystal is used to estimate size of the crystal by aiding of the micro length unit.

4.2.3 Thermal analysis

The Differential Thermal Analysis (DTA) instrument (Perkin Elmer model DTA 7, Figure 4-8) was used to measure the thermal stability of crystal. It measured the difference temperature between a sample cell and a thermally inert reference cell and then recorded this difference versus time or temperature.

4.2.4 Particle size analysis

The centrifugal particle size analyzer (Figure 4-9) was used to analyze particle size in the range of 0.1 to 150 μm by using Stoke' s law and the relation between absorbance of light and particle concentration.

4.2.5 True density analysis

The true density analysis (Figure 4-10) was used to measure the actual density of the sample

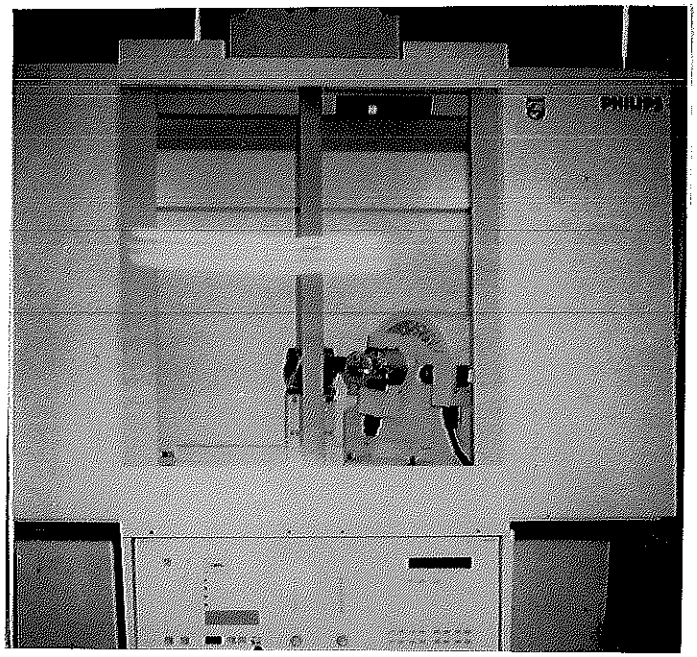


Figure 4-6 X - Ray Diffraction (XRD)

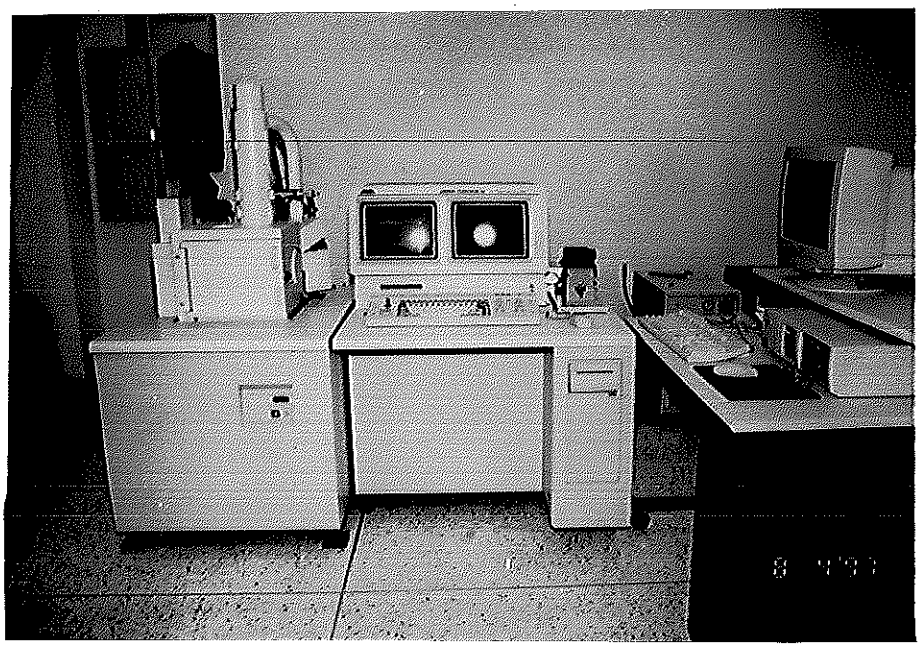


Figure 4-7 Scanning Electron Microscope (SEM)

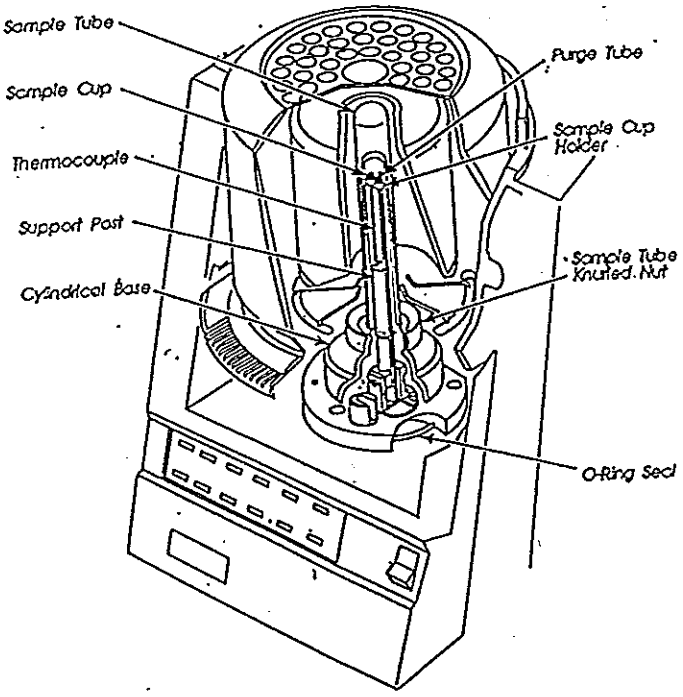


Figure 4-8 Differential Thermal Analysis (DTA)

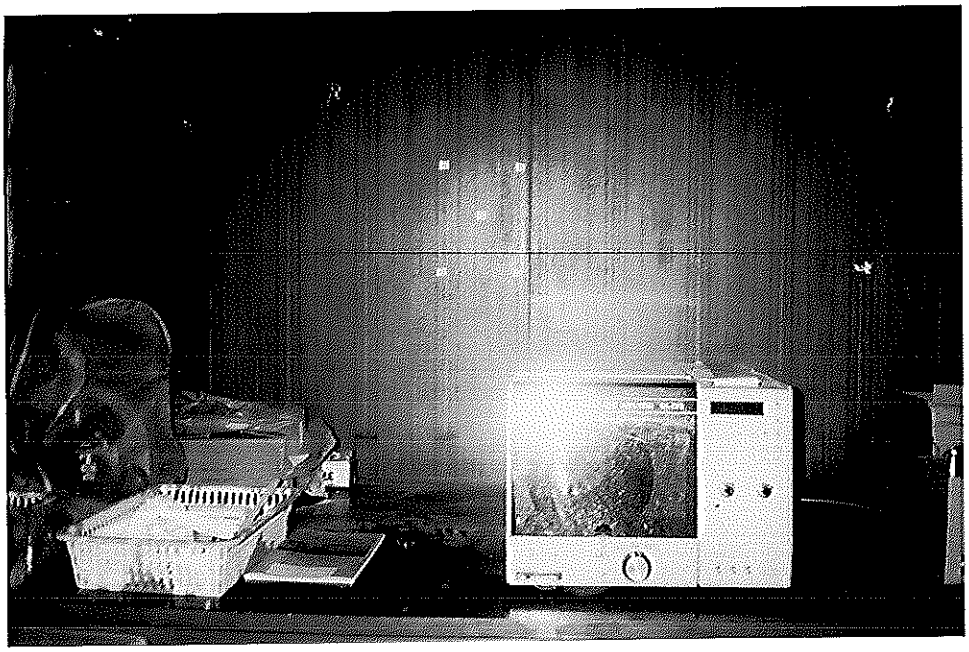


Figure 4-9 Centrifugal Particle Size Analysis (CPSA)

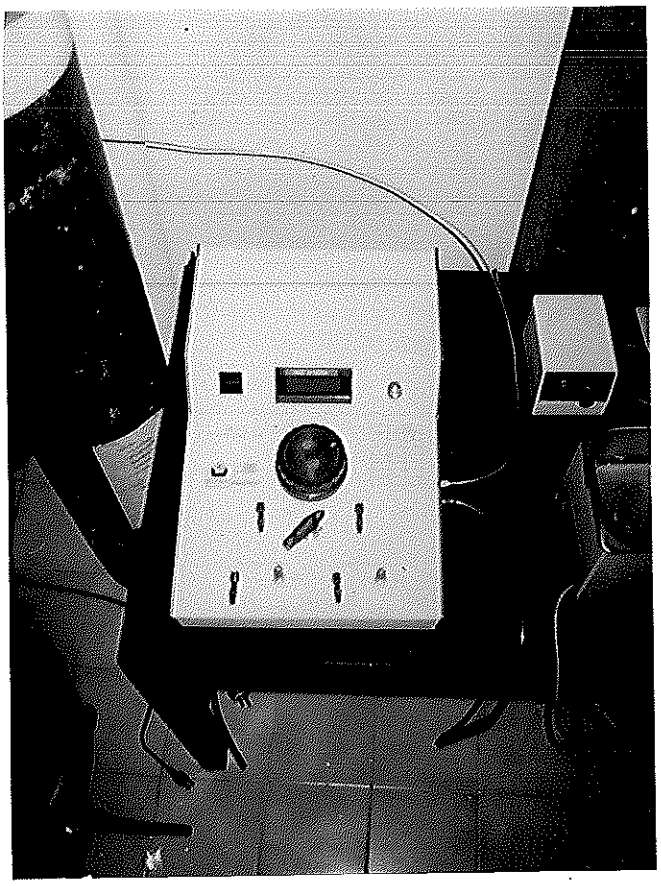


Figure 4-10 Multipycnometer

CHAPTER 5

RESULTS AND DISCUSSION

The results and discussion of our experiments were concentrated on our objective aims as the following: the fundamental synthesis of NaY zeolite, the kinetics of crystal growth, the effects of crystallization temperature, the effects of mixing temperature both at the initiating agent step and the whole gel steps, and the effects of some seeds.

5.1. Fundamental synthesis of NaY zeolite

The NaY zeolite was synthesized by using waterglass as a major source of silica and sodium oxide, and sodium aluminate as a source of alumina and sodium oxide. Aluminium sulfate and de-ionized water were used to balance the quantities of alumina and water in order to obtain the desired composition range. The process of synthesis NaY zeolite comprises of the four following steps:

1) The preparation initiating agent. The molar composition ratios of the oxides are as: (14-17)Na_2O:Al_2O_3:(14-15) SiO_2:(290-320) H_2O
2) The gel formation. The molar composition ratios of the oxides are as: (4-6)Na_2O:Al_2O_3:(9-11) SiO_2:(190 -200) H_2O
3) The crystallization, and
4) The separation.

The white powder produced from the synthesis step of test run 2 (see appendix B) by using initiating agent solution (15°C) as seed at the conditions of mixing temperature of whole gel step at 15°C and crystallization temperature 100°C for 8 hours was identified by X-ray diffraction (XRD) instrument and scanning electron microscope (SEM) instruments. The pattern of XRD peaks in Figure 5-1 identifies that the white

powder is the crystal of NaY zeolite having Si/Al and unit cell size as 2.30 and 24.70 respectively. The crystal is about 78 percent of relative crystallinity when compares with the standard crystal of NaY zeolite (Si/Al ratio 2.72, unit cell size 24.64, percentage crystallinity 90). Figure 5-2 shows that the morphology of the crystals which can be classified as the agglomerated type. The intergrowth seems to be occurred. The individual crystal has an average particle size in the range of 0.5 to 1.0 μm.

In this process, the initiating agent solution was used as seed in the reaction mixture and the gel was formed because of a condensation-polymerization reaction of polymeric aluminosilicate species between soluble silicon and aluminium species. During the crystallization of gel, aluminate and silicate species were rearranged by depolymerized and solubilized mechanisms in order to form NaY zeolite crystalline structure shown in Figure 3-10. Therefore, two phases of substance (solid and liquid) can be seen clearly.

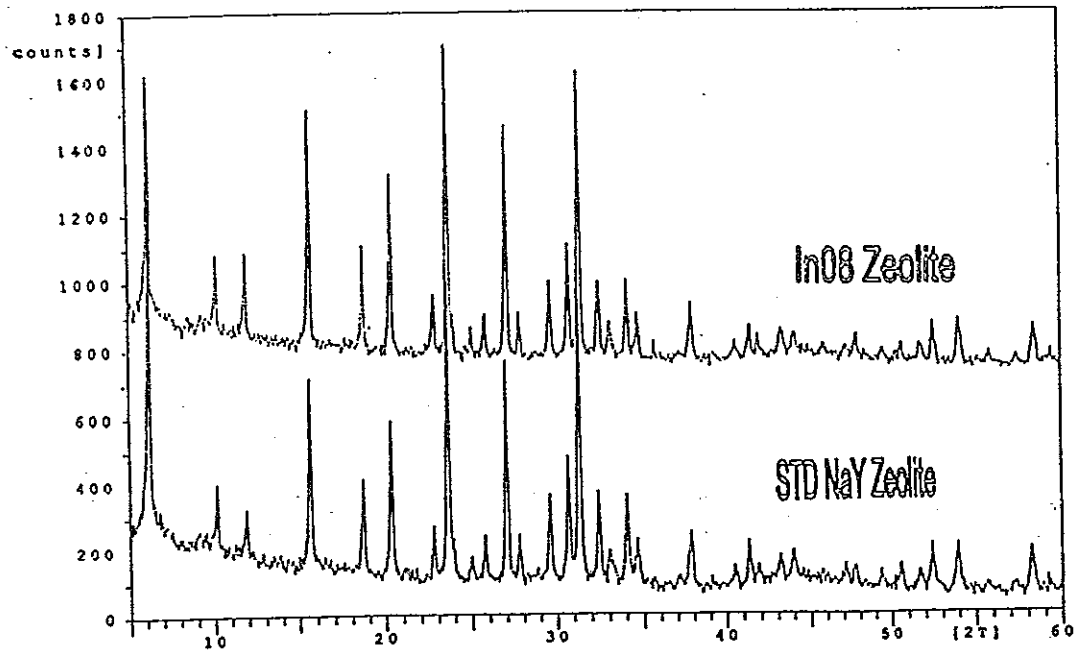


Figure 5-1 X - Ray Diffraction spectrum of standard NaY zeolite and synthesized zeolite (8 hours of crystallization, mixing temperature of initiating agent and whole gel step at 15°C)

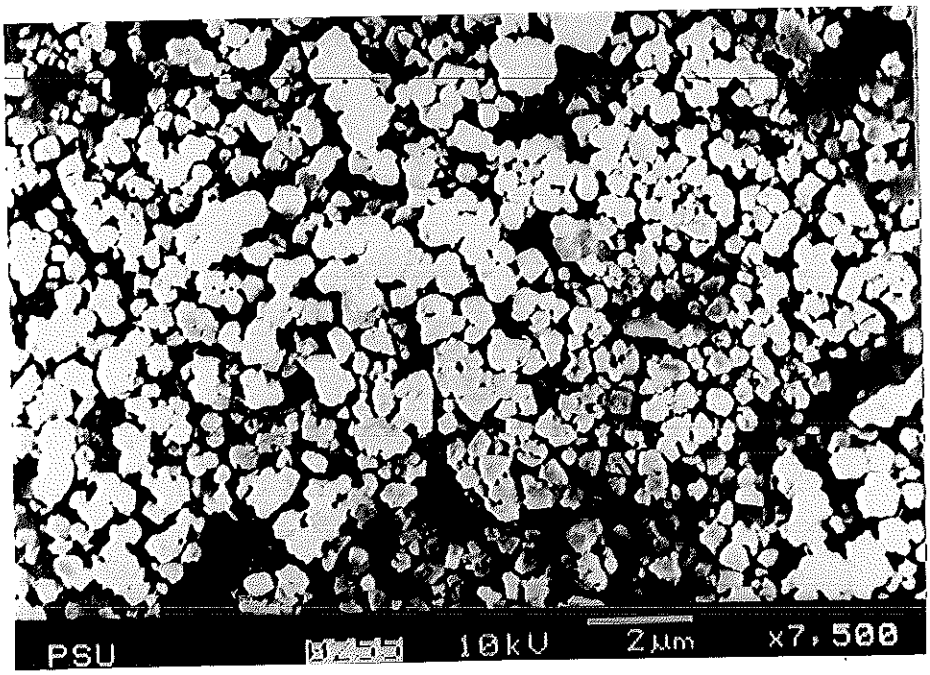


Figure 5-2 Morphology of synthesized zeolite (8 hours of crystallization, mixing temperature of initiating agent and whole gel step at 15°C)

5.2 The kinetics of crystal growth

The kinetics of crystal growth was investigated by examining the crystallinity of zeolite at different aging times (aging temperature 100°C). Figure 5-3 shows the XRD peaks of synthesized zeolite at different aging times. The synthesized zeolite was prepared at 15°C as the whole gel temperature with the initiating agent prepared at the same temperature. The change in relative crystallinity versus time was shown in Figure 5-4. The crystal growth rate curve looks like to be S shape and can be separated into three main periods as follows

1) Induction period (II) was identified in the range of 0.00 hours to 4.40 hours. During this interval time, the nucleation was developed and gradually

reorganized to be NaY zeolite. This period is very important for crystallization growth period because it represents the rate of nucleation.

2) Crystallization growth period. In Figure 5-4, this period is in the range of 4.40 to 12.00 hours. In the beginning of this period [4.40 to 6.00 hours (G1)], NaY zeolite growth increases rapidly as a result of the development of nucleation in the induction period and because of the suitable conditions such as excess of nutrient sources, a lot of useful primary and secondary building block. In the remaining time [6.00 to 12.00 hours (G2)], crystal growth slightly increases because of the depletion both of the nutrient sources and the nucleation particles.
3) Decline period (D). This period starts after 12.00 hours of aging time. The crystallization of NaY zeolite was decreased slowly because of the lacking of nutrient sources to create new NaY zeolite crystal and some of crystals were transformed to another kinds of zeolite such as Gmelinite, Garronite(NaP).

In this project, the kinetics growth was used as an important indicator to identify the optimum condition for obtaining the great benefit of the zeolitic crystal products.

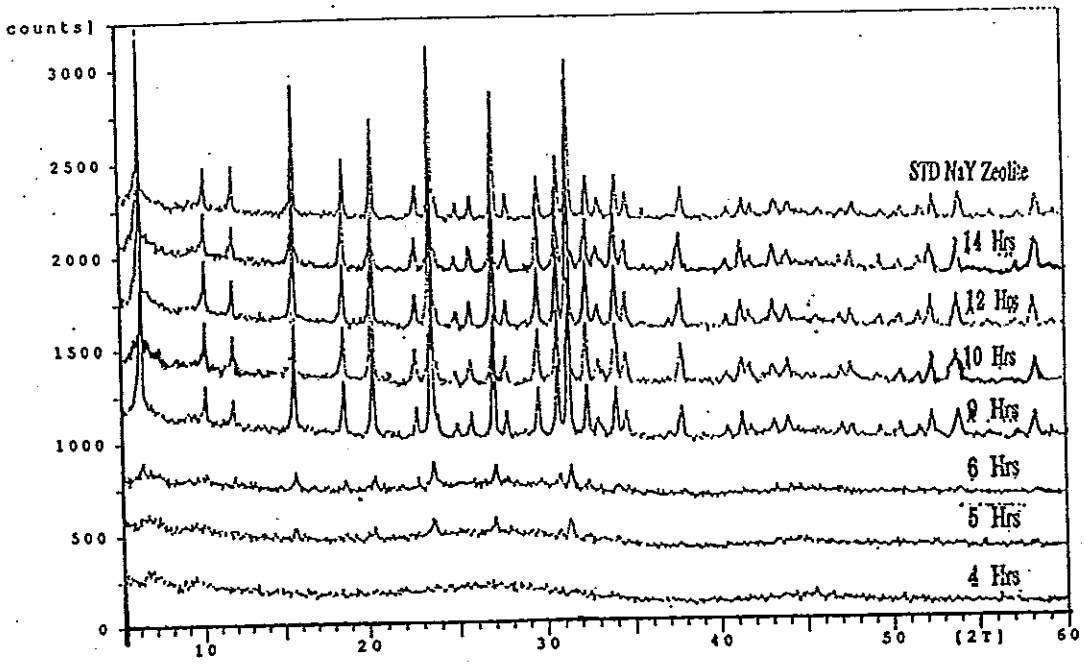


Figure 5-3 XRD spectrum of synthesized zeolite at different crystallization time.

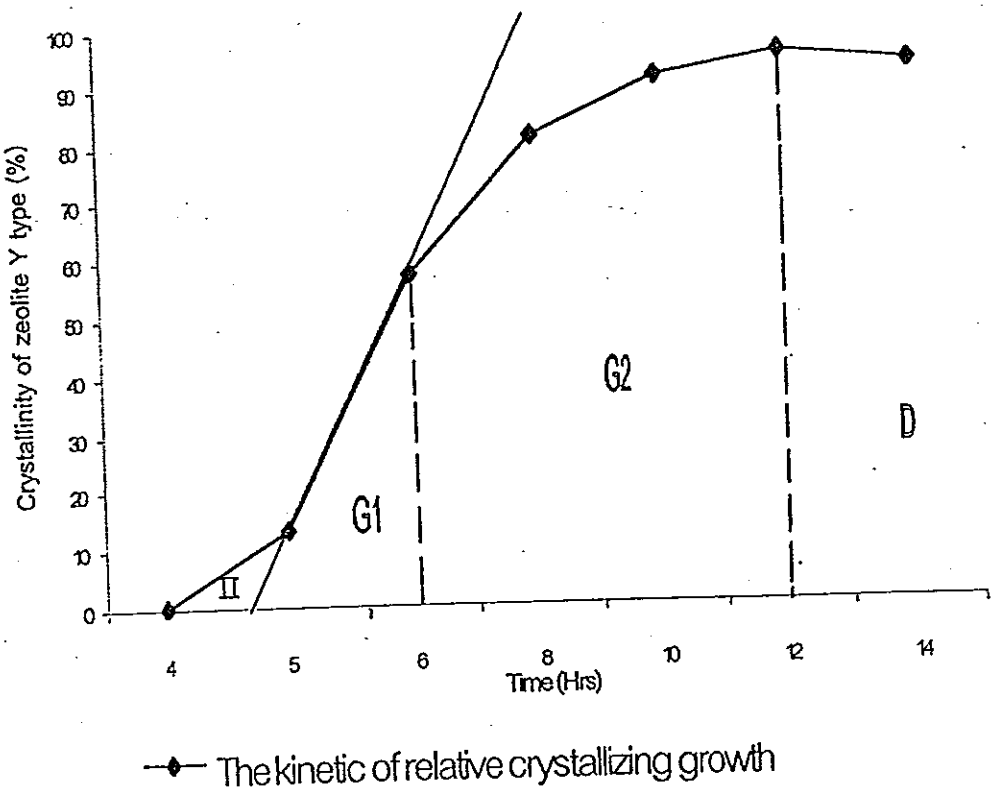


Figure 5-4 Kinetics of the crystal growth

5.3 The effects of crystallization temperature

The experiments were carried out by using the initiating agent prepared at 15°C and the whole gel mixing temperature was at 15°C. The crystallization temperatures were at 70°C, 85°C, 95°C and 100°C. The results of the experiments are shown in Figure 5-5. The crystallization temperature has a great influence on the retention time of the crystal growth. The experiments show that the retention times at the maximum relative crystallinity are at 45 hours, 24 hours, 14 hours and 12 hours according to 70°C, 85°C, 95°C and 100 °C, respectively. These indicate that the higher crystallization temperature the process used, the shorter retention time of the maximum relative crystallinity the product obtained. As the result of this, the temperature at 100°C was selected as aging temperature in the remaining studies.

Using the high crystallization temperature could increase the dissolution of gel in hot alkali media. This effects the production both the aluminosilicate species (aluminate and silicate ions) and the nuclei into the liquid phase as shown in Figure 5-6. On the other hand, it activates the supersaturated reaction of the liquid phase causing spontaneous nucleation and growth of zeolite particles by the deposition of aluminosilicate species that dissolved in the liquid phase.

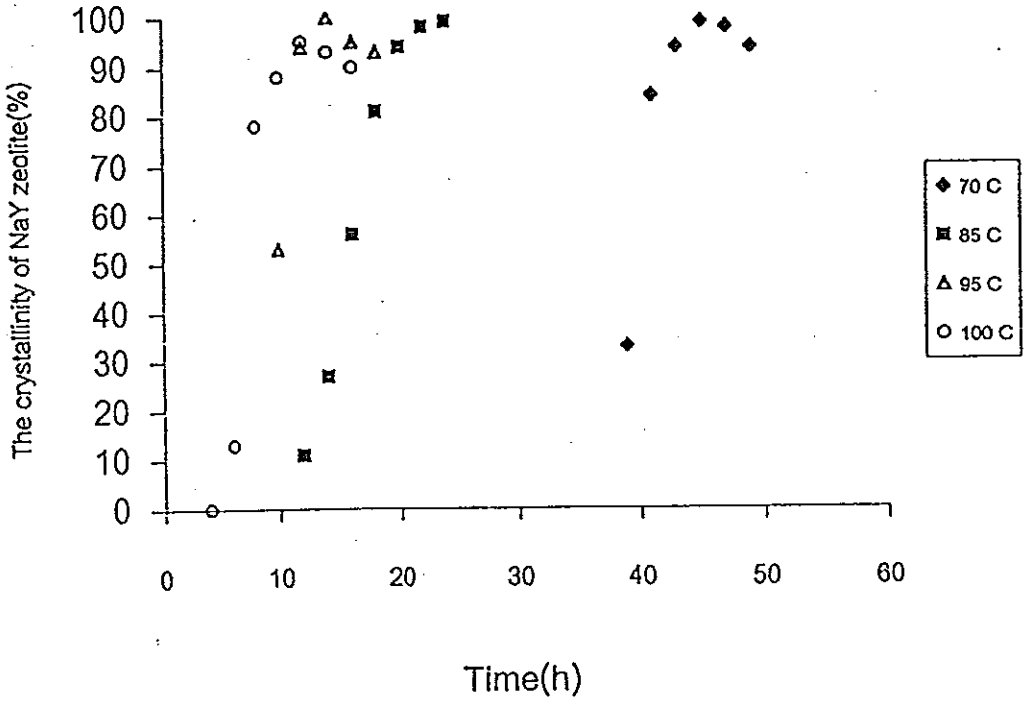
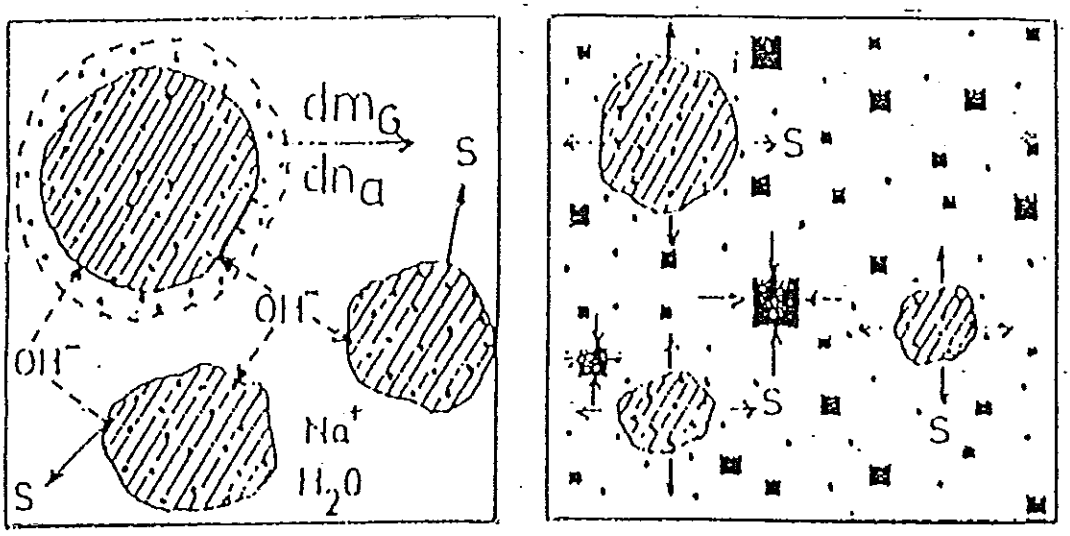


Figure 5-5 Kinetics of crystal growth of NaY zeolite (mixing temperature of the initiating agent step at 15 ^{o}C and the whole gel step at 15 ^{o}C) with various temperature of crystallization



Liquid phase Amorphous material Zeolite Nuclei of zeolite inside gel structure

Figure 5-6 Dissolution of gel in hot alkali medium

5.4 The effects of mixing temperature at the initiating agent step

In this study, we used the mixing temperature of whole gel step at 15°C and the aging temperature at 100°C, the mixing temperature of initiating agent step was varied namely, 5°C, 15°C and 25°C. The result of these experiments was shown in Figure 5-7. The kinetics of crystal growth had the retention time of maximum relative crystallinity at 12 hours. The specific peaks of NaY zeolite in Figure 5-8 and the relative crystallinity in Figure 5-7 indicates that the lower of mixing temperature at the initiating agent the process used, the higher of relative crystallinity the product obtained. As a consequence of this, the mixing temperature at 5°C of initiating agent step was used to study the mixing temperature of the whole gel step.

The mixing temperature of the initiating agent step effects on the quality of seed and the uniform of reactive species in gel formation. In the first case, The increasing mixing temperature could activate the reaction of reactive species to form amorphous

aluminosilicate particles and this make much more bigger amorphous aluminosilicate particles than when using at lower mixing temperature. As the result, lower mixing temperature of initiating agent step could create more fine particles than higher mixing temperature. This important effect may be the cause of the arrangement of the crystal growth and result on the relative crystallinity.

5.5 The effects of mixing temperature at the whole gel step

The mixing temperature of the whole gel step was varied as 5°C, 15°C, 20°C and 25°C by using the initiating agent prepared at 5°C and the aging temperature at 100°C. The result of these experiments was shown in Figure 5-9. The kinetics of the crystal growth had the same retention time of the maximum relative crystallinity at 12 hours. The specific peaks of NaY zeolite in Figure 5-10 show that the lower of the mixing temperature of the whole gel the process used, the higher of relative crystallinity the product obtained. The mixing temperature at 5°C of the whole gel step was used in studying the other factors of the process.

The lower mixing temperature of the whole gel step could inhibit the formation time of gel because of the lower reaction rate so that the reactive species had more times to mix and distribute to be an uniform gel. The uniformity of gel is an important factor on the crystallinity.

From the preceding results, the mixing temperature at the initiating agent step and the whole gel step had about the same retention time of the maximum relative crystallinity at 12 hours. The lower of mixing temperature gives the better relative crystallinity but does not influence on the retention time of crystallization. The retention time of crystallization seems to be effect only by aging temperature.

The morphology of the crystal from the best condition of the process mentioned above (5°C initiating agent step, 5°C whole gel step and 100°C aging step) was showed in Figure 5-11. Most of the crystals were agglomerated type and the

intergrowth seems to be occurred. The individual crystal has an average particle size in the range of 0.5 -1.0 μm. Thermal stability was showed in Figure 5-12. By using DTA instrument, the crystals were destroyed at 939°C. The BET specific surface shown in the Figure 5-13 was about 652 m^2/g.

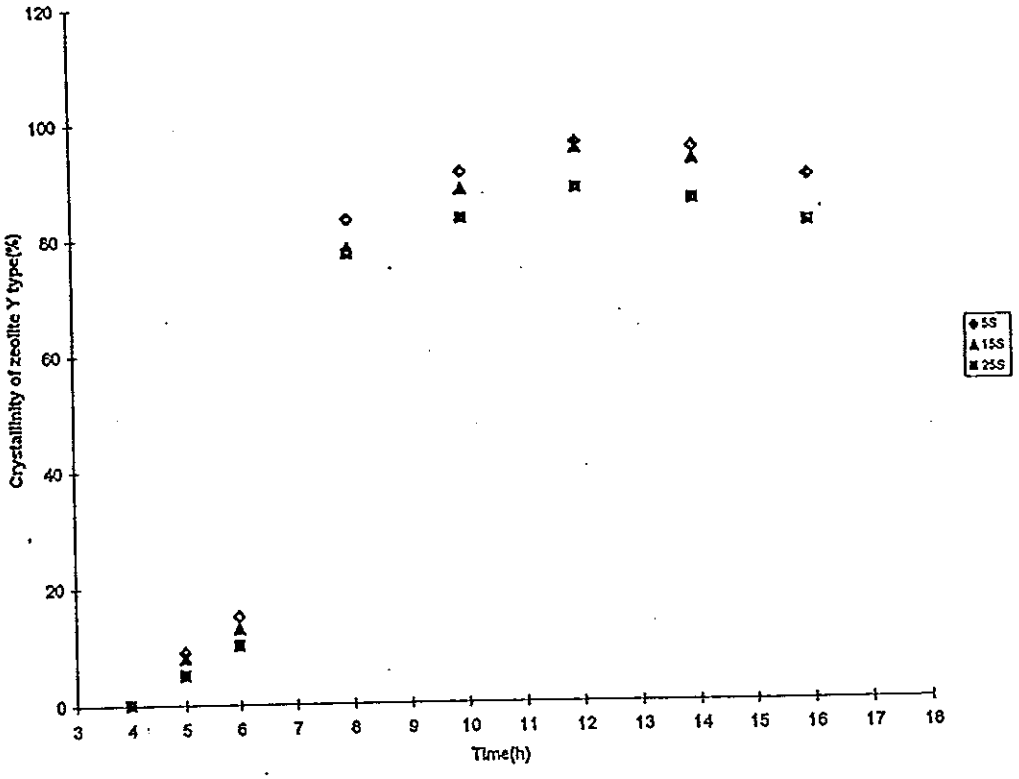


Figure 5-7 Kinetics of crystal growth of NaY zeolite (mixing temperature of whole gel step at 15°C and the crystallization temperature step at 100°C) with various mixing temperature of initiating agent step

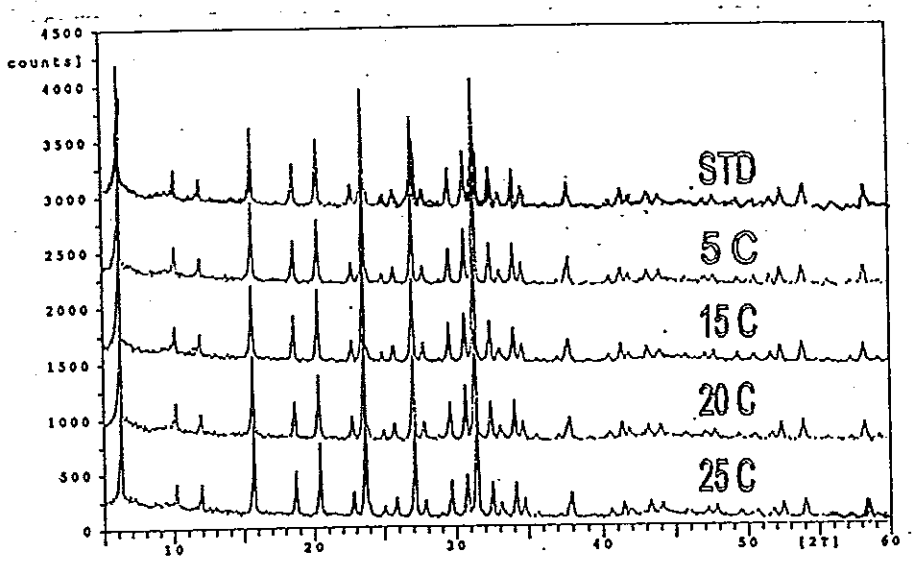


Figure 5-8 XRD spectrum of the synthesized zeolite for 12 hours (mixing temperature of whole gel step at 5°C and the crystallization temperature step at100°C) with various mixing temperature at initiating agent step

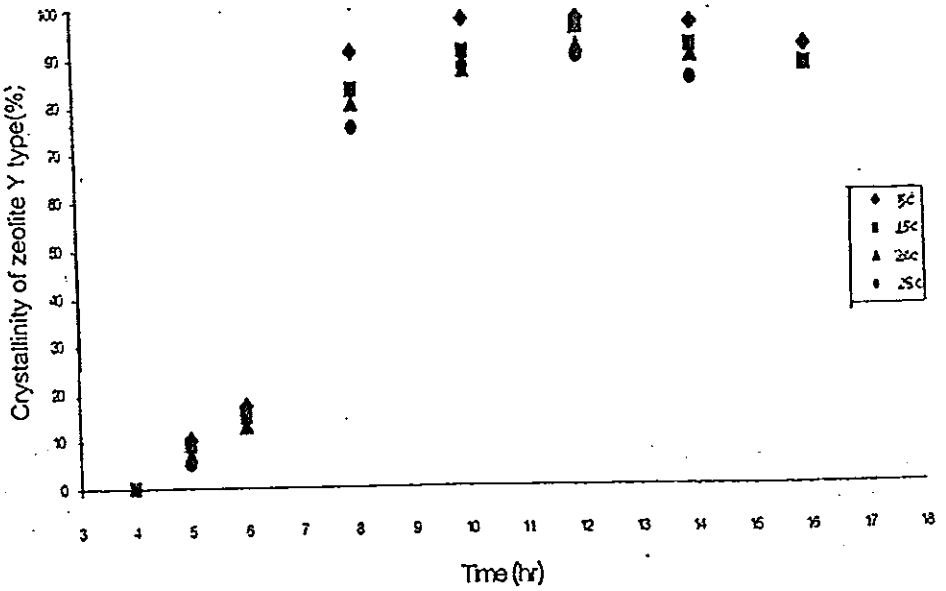


Figure 5-9 Kinetics of relative crystallization of NaY zeolite (mixing temperature of initiating agent step at 5°C and the aging temperature at 100°C) with various mixing temperature of the whole gel

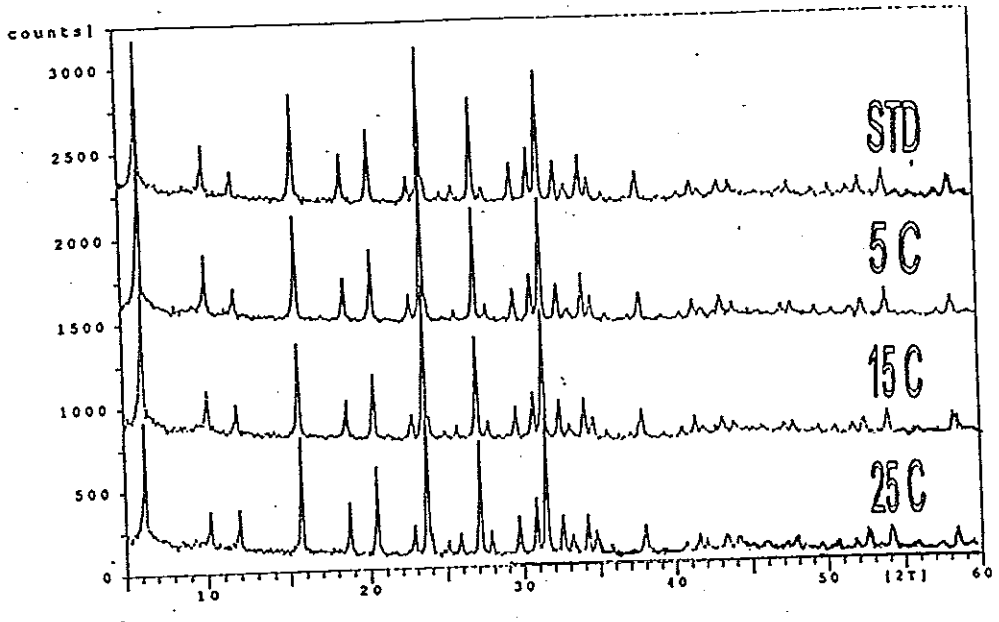


Figure 5-10 XRD spectrum of the synthesized zeolite for 12 hours (mixing temperature of initiating agent step at 5°C and crystallization temperature step at 100°C) with various mixing temperature of the whole gel

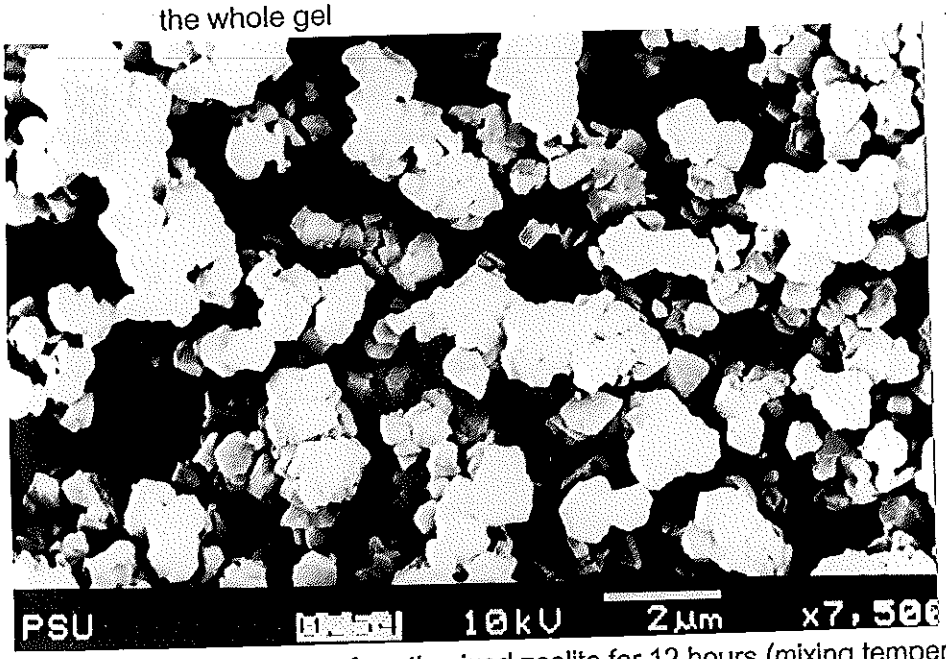


Figure 5-11 Morphology of synthesized zeolite for 12 hours (mixing temperature of initiating agent step at 5°C, whole gel step at 5°C and crystallization temperature step at 100°C)

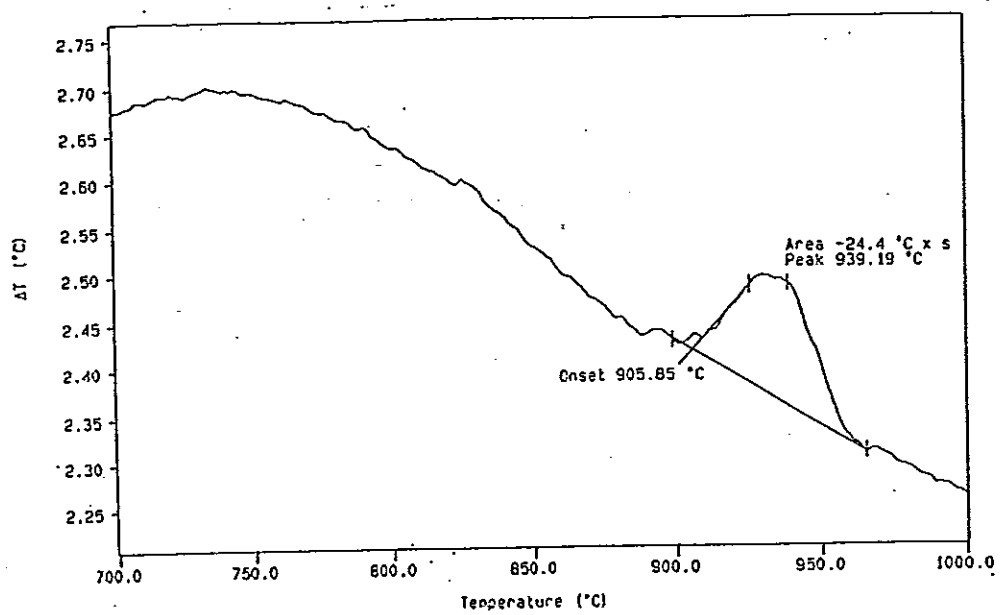


Figure 5-12 Thermal stability of synthetic zeolite (mixing temperature of initiating agent step at 5°C, whole gel step at 5°C and crystallization temperature step at 100°C)

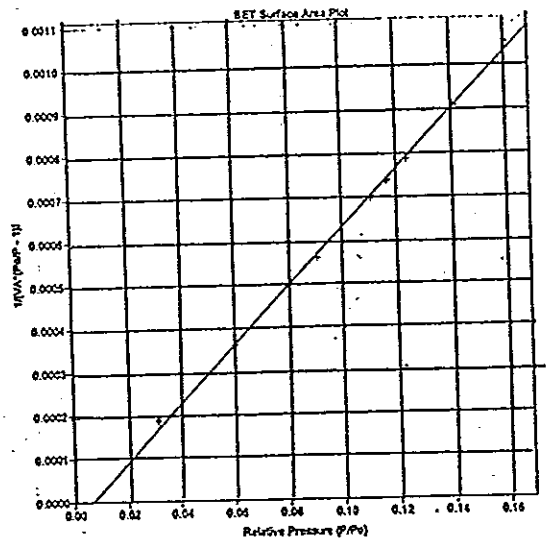


Figure 5-13 BET surface area of synthetic zeolite (mixing temperature of Initiating agent step at 5°C, whole gel step at 5°C and crystallization temperature step at 100°C)

5.6 The effects of seed

First, the experiment was designed to synthesize NaY zeolite by using no initiating agent and carried out the trail at our best conditions at the mixing temperature of whole gel step at 5°C and crystallization temperature at 100°C. The details in preparation of working solution and reaction mixture were shown in test run 3 of appendix B.

The induction period was very long and obtained the crystal product after 93 hours of crystallization. From the X- ray diffraction showed in Figure 5-14, the crystal was the NaA zeolite. The average particle size of NaA crystals was approximately 5.0–7.0 μm as shown in Figure 5-15. The characteristic of the crystal was similar to a ball.

Second, the experiment was designed to synthesize NaY zeolite by using NaCl crystals as a seed. The prepared conditions were the same as the first experiment, but NaCl crystals were added as a seed. The mole ratio of NaCl : alumina was about 10 in the reaction mixture of the whole gel step.

The crystals were completely developed after 96 hours. From the XRD analysis as shown in Figure 5-14, the NaY zeolite and NaA crystals were formed. The particle sizes were in the range of 1.0–1.5 μm and the shape of crystals were composed of cubic and ball shapes as shown in Figure 5-16. The thermal stability of these particles shown in Figure 5-17 was 771°C.

Third, the experiment was designed to synthesis NaY zeolite by using fine NaY zeolite crystal as a seed. The seed was the NaY zeolite crystal having particle size about 0.5 -1.0 μm, unit cell 24.65°A and relative crystallization about 90 percent as shown in Figure 5-18. This seed crystals were ground into 3 groups of particle size ranges (appendix D). The experiments were carried out as the same procedures as the two previous experiments. The details of the reagents and working solution were shown in the test run 3 of the appendix B. The amount of seed used was about 10 percent by weight of expected synthesized NaY zeolite.

Figure 5-20 shows the kinetics of crystal growth by using NaY zeolite and initiating agent as seed. The kinetics of crystal growth from the 3 different seed sizes seems to be the same. The maximum retention times were about 24 hours and the maximum relative crystallinity was at 98 percent. The XRD analysis shown in Figure 36 indicated the synthesized crystals were the true NaY zeolites. The NaY zeolite crystals had the particle sizes in the range of 1.0 to 1.5 μm as shown in Figure 5-20.The thermal stability and BET surface area shown in Figure 5-21 and 5-22 of these crystals were 935°C and 616 m^2/g respectively.

From our experiments, we can conclude that the NaY zeolite is difficult to synthesize without the initiating agent or seed. The NaA zeolite crystals may be formed instead of NaY zeolite. Inorganic cation such as Na^+ favor the formation of specific zeolitic structures by influencing the nature and configuration of the various silicious or aluminosilicate precursor species. From Figure 5-14, The comparison between XRD spectrum of with and without NaCl seed shows that Na^+ enhance the formation of NaY zeolite, so NaA formation is reduced. The sodium ions enhance the formation of NaY zeolite because of the hydrated cation species are served as a nucleation site for the polyhedral structure unit and influence the nucleation process.(Dewaele, 1985)

NaY zeolite fine crystals were used as a seed in our studies. The kinetics of relative crystal growth of the three groups of different sizes show that there are not much significance between them.

Amorphous aluminosilicate seed had very fine particles when compared with NaY zeolite crystal seed. The results of the kinetics of crystal growth in Figure 5-20 show clearly that the fine amorphous seeds could reduce both of the retention time of maximum relative crystallinity and the particle size of the crystal product than NaY zeolite crystal seed. The average size of NaY zeolite prepared from using amorphous aluminosilicate as seed is about 0.5-1 μm and the average size of NaY zeolite prepared from using fine NaY zeolite particles as seed is about 1.0-1.5 μm. These

results may come from the much more amounts of seed particles in aluminosilicate seed solution or others reasons.

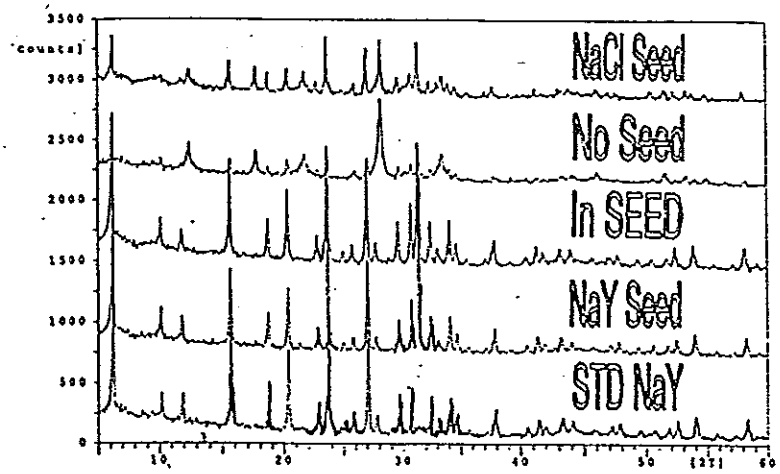


Figure 5-14 XRD spectrum of the synthesized zeolite (mixing temperature of Initiating agent step at 5°C, whole gel step at 5°C and crystallization temperature step at 100°C) with different types of seed

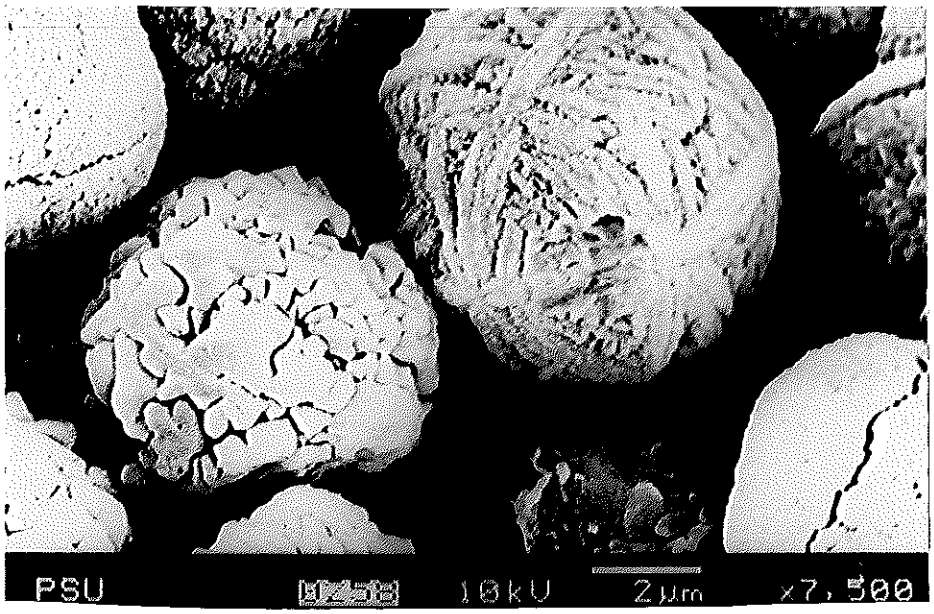


Figure 5-15 Morphology of synthesized zeolite without seed / (mixing temperature of initiating agent step at 5°C, whole gel step at 5°C and crystallization temperature step at 100°C)

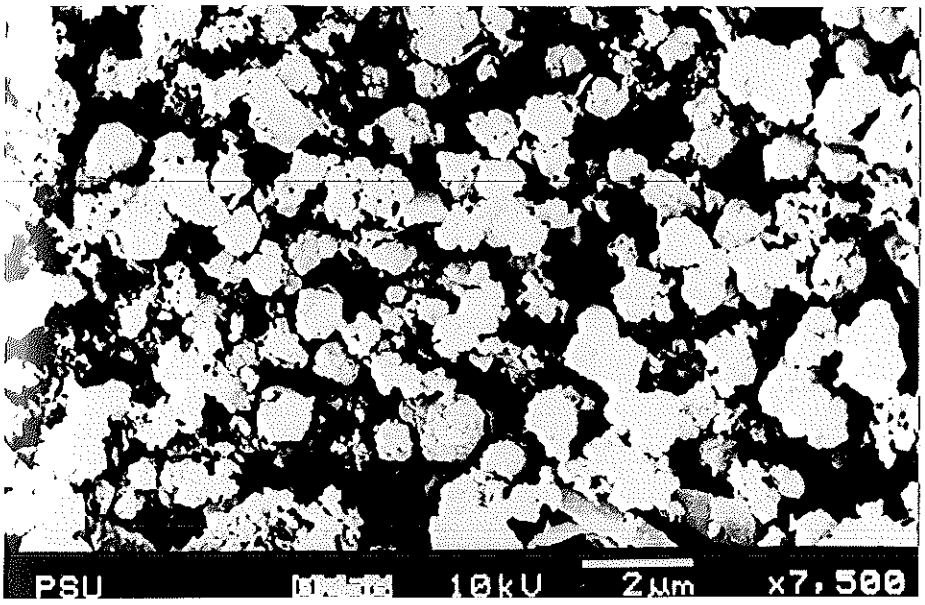


Figure 5-16 Morphology of synthesized zeolite using NaCl as seed (mixing temperature of initiating agent step at 5°C, whole gel step at 5°C and crystallization temperature step at 100°C)

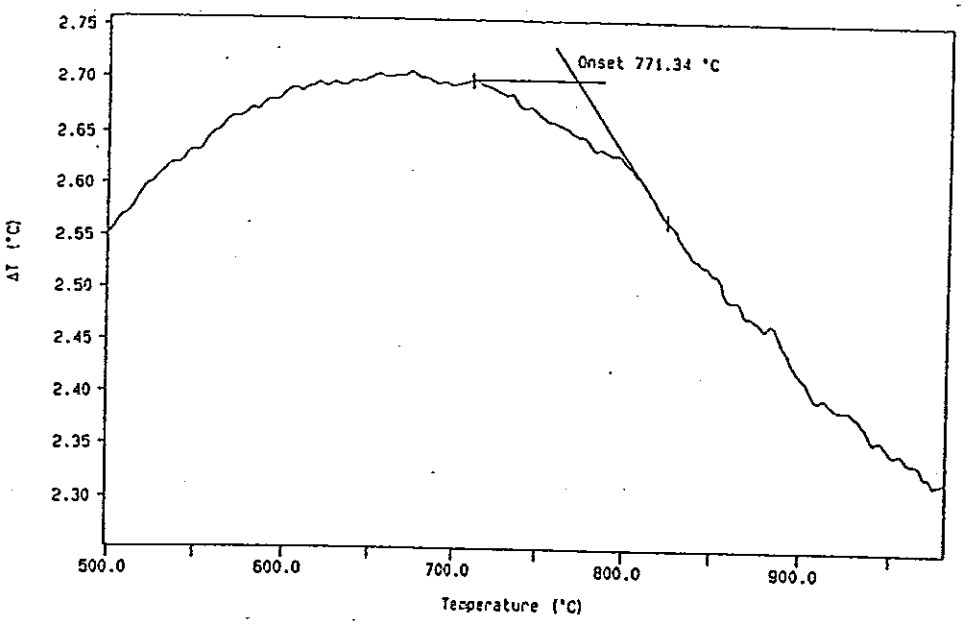


Figure 5-17 Thermal stability of synthetic zeolite using NaCl seed (mixing temperature of initiating agent step at 5°C, whole gel step at 5°C and crystallization temperature step at 100°C)

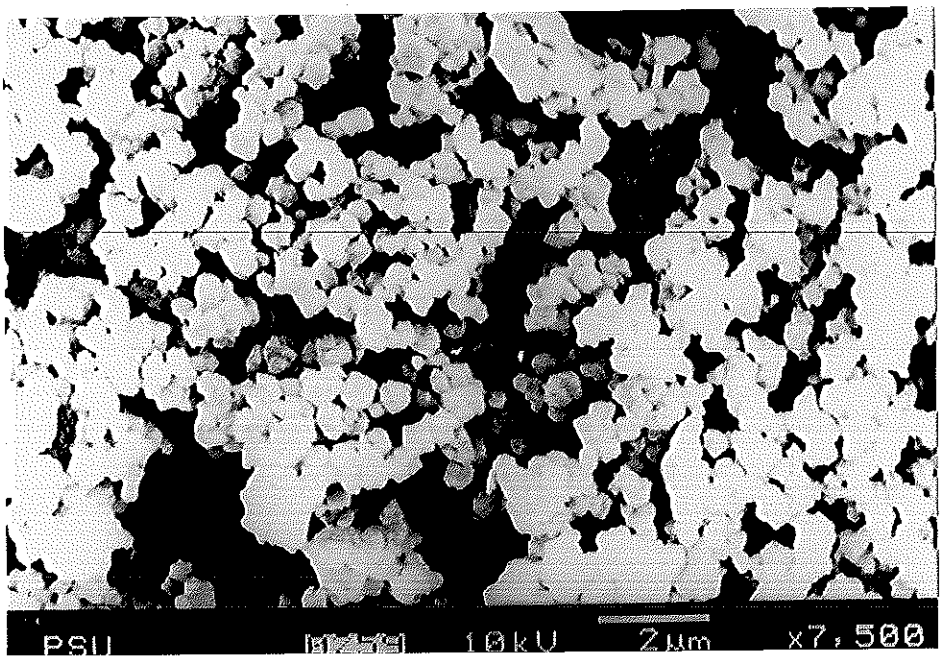


Figure 5-18 Morphology of synthesized zeolite (mixing temperature of initiating agent step at 5°C, whole gel step at 5°C and crystallization temperature step at 100°C) using initiating agent as seed

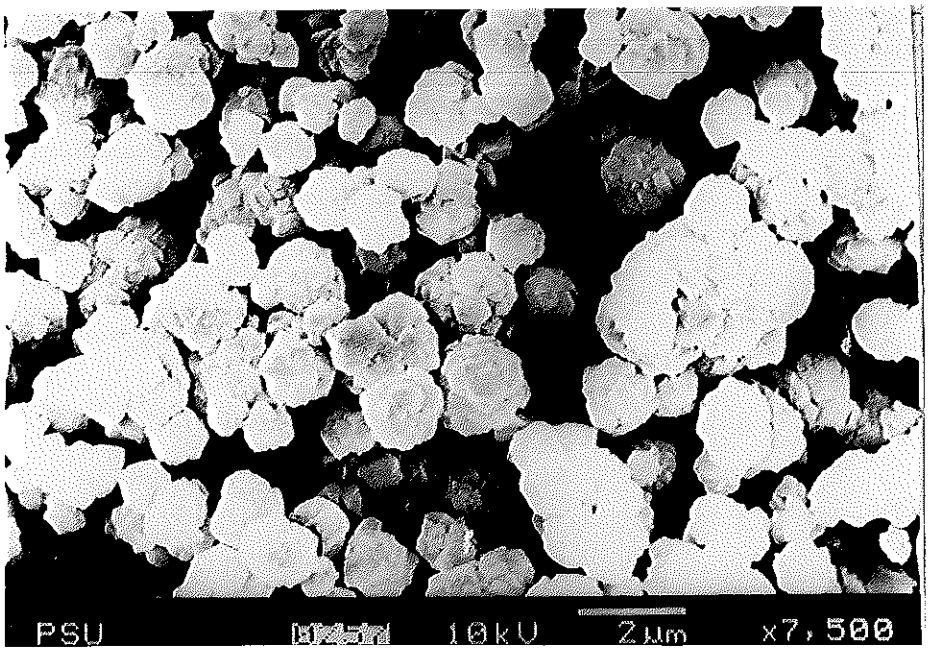


Figure 5-19 Morphology of synthesized zeolite (mixing temperature of whole gel step at 5°C and crystallization temperature at 100°C) using NaY zeolite crystal as seed

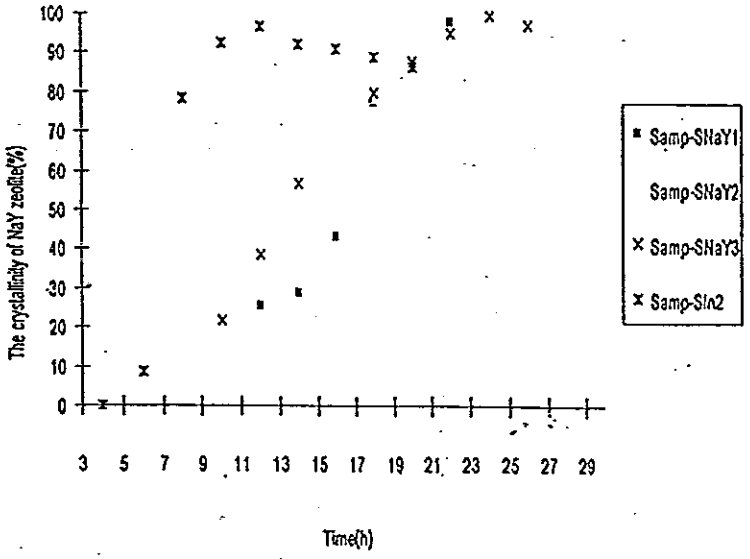


Figure 5-20 Comparison of the kinetics of crystal growth of NaY zeolite by using initiating agent and fine particles NaY zeolite (mixing temperature of initiating agent step at 5°C, whole gel step at 5°C and crystallization temperature step at 100°C)

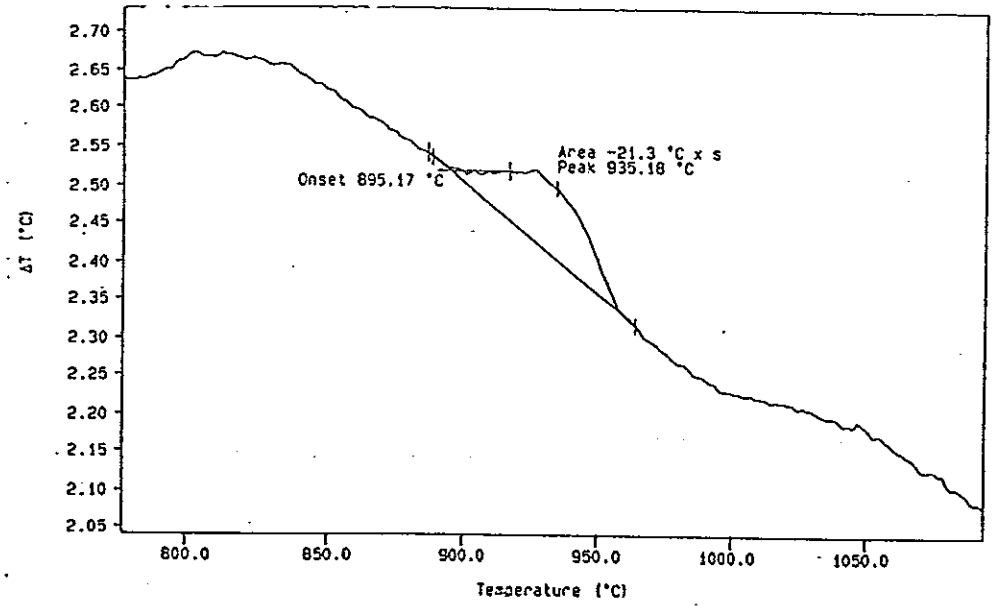


Figure 5-21 Thermal stability of synthetic zeolite (mixing temperature whole gel step at 5°C and crystallization temperature step at 100°C) using NaY zeolite crystals as seed

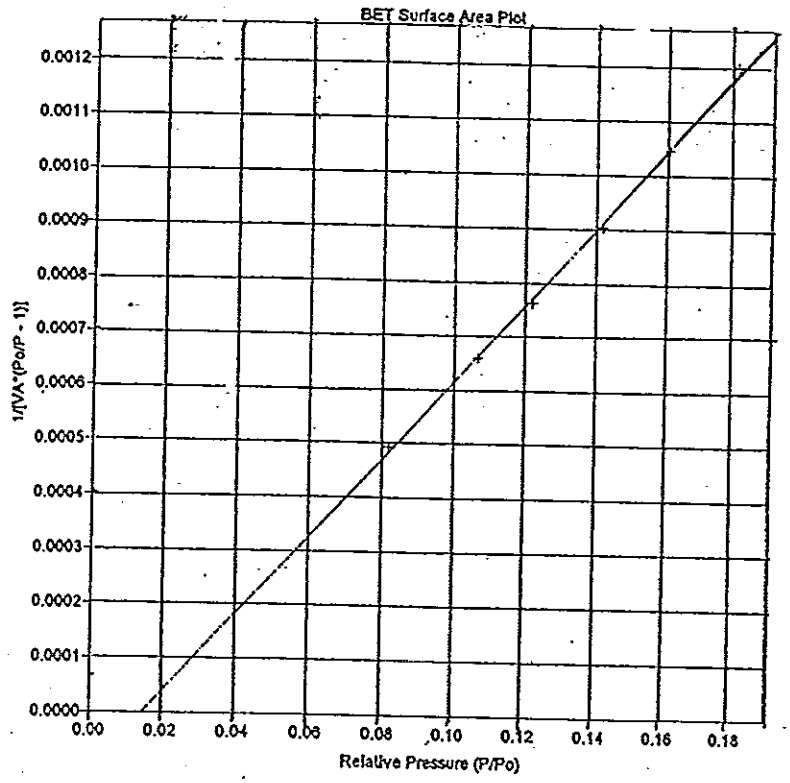


Figure 5-22 BET surface area of synthetic zeolite (mixing temperature of whole gel step at 5°C and crystallization temperature step at 100°C) using NaY zeolite crystals as seed

CHAPTER 6

CONCLUSION

This research was primarily studied the synthesis process of NaY zeolite. There are four main steps in process namely, seed preparation, gel preparation, crystallization and separation. The reaction mixture composition in the whole gel step was restricted in the form of oxide ratio in the range as following: (4-6)Na_2O : Al_2O_3 : (9-11)SiO_2 : (90-200)H_2O.

The kinetics of crystal growth looks likes the S shape and could separate into three parts as; 1) Induction period, 2) Crystal growth period and 3) Decline period.

The temperature is the very important parameter in synthesis process. There were three steps of process that must be carefully controlled as following: 1) amorphous aluminosilicate seed preparation, 2) whole gel preparation and 3) crystallization. In the first two steps, the higher temperature used in mixing, the lower relative crystallinity the crystal products received. The lower temperature in preparing the initiating agent makes the small amorphous aluminosilicate particles that will enhance the crystallinity. The lower temperature in the whole gel step inhibits the reaction and allows the reactive species distribution be more uniform. The uniformity of whole gel makes better crystallinity in the crystallization step. The temperature in the crystallization step gives the contrast effect of the two former steps. The higher temperature gives the higher dissolution of gel and higher formation rate of crystal. So, the induction period and growth period take the shorter time intervals. But the transformation rate to another type of zeolite is also rapid too. The aging temperature seems to have a little effect on relative crystallinity of NaY zeolite.

Seed plays a very important role on NaY zeolite synthesis. In this process, without seed, zeolite A type is formed instead of zeolite Y type. The amorphous aluminosilicate seed is the best when compares with the fine NaY zeolite particle and NaCl seed.

Some suggestions for the further study are:

1) Add some mineral acid to neutralize the excess of hydroxy ion to lower the pH and reduce the dissolution of silica species to liquid phase. This will make the higher silica/alumina ratio of zeolite Y.
2) Use organic seed such as polysaccharide, gelatin instead of inorganic seeds,
3) Continuously stir the initiating agent during the aging stage,
4) Study the effect of rate of heat transfer on the synthesis process.

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APPENDIX A

Analysis of raw materials

1. Waterglass

1.1 Sample pre-treatment:

1.1.1 Weigh accurately 12-13 grams of raw waterglass.

1.1.2 Transfer it into a 200ml volumetric flask.

1.1.3 Dilute it to the marked scale of the flask.

This solution is prepared for analysis sodium oxide (Na_2O) and silicon oxide(SiO_2).

1.2 Procedure:

1.2.1 Determination of Na_2O:

1.2.1.1 Pipette 10 ml of the pre-treatment waterglass solution into a 50 ml volumetric flask.

1.2.1.2 Dilute it to the marked scale of the flask.

1.2.1.3 Transfer it into a 250ml conical flask.

1.2.1.4 Add two drops of 0.1% p-dimethylamino-azo-benzene.

1.2.1.5 Add two drops of methyl blue.

At this time, the color of the solution reveals bright-green.

1.2.1.6 Titrate this solution by using the prepared 0.5N standard sulfuric acid (H_2SO_4) solution until the color of it changes to a red -violet color.

1.2.1.7 Record the volume of 0.5N standard H_2SO_4 solution.

1.2.1.7 The weight percent Na_2O of sample can be calculated by using following formula:

$$W\ \%Na_2O = \frac{(NV)H_2SO_4.62}{W}$$

where N = the normality of the standard H_2SO_4 solution in equivalent (N),

V = the volume of the standard H_2SO_4 solution in milliliter (ml),

W = the weight of raw waterglass sample in gram (g).

1.2.2 Determination of SiO_2:

1.2.2.1 Pipette 10 ml of the pre-treatment waterglass solution into a 300 ml of plastic beaker.

1.2.2.2 Add 10 ml of concentrated nitric acid (HNO_3).

1.2.2.3 Cool this solution down to the room temperature.

1.2.2.4 Add 2-3 grams solid of potassium chloride (KCl).

1.2.2.5 Stir the solution by using a plastic rod until the solid is fully dissolved.

1.2.2.6 Add 10 ml of potassium fluoride (KF) solution to form a white precipitation.

1.2.2.7 Filter it by using filter paper.

1.2.2.8 Wash the white precipitation with 10 ml (each time) of KF solution for several times.

1.2.2.9 Transfer the white precipitation and the paper into plastic beaker.

1.2.2.10 Add 12-15 ml of 5% by weight of KCl-Alcohol solution.

1.2.2.11 Add 20 drops of Phenolphthalein-Alcohol to be indicator.

1.2.2.12 Titrate this solution with 0.5N standard sodium hydroxide (NaOH) solution until the color of the solution changes to red.

1.2.2.13 Pour quickly 200 ml of hot distilled water in this beaker.

1.2.2.14 Titrate immediately by using a 0.5N standard NaOH solution until the color of solution appears to a slightly red.

1.2.2.15 Record the volume of 0.5N standard NaOH solution.

1.2.2.16 The weight percent Na_2O of sample can be calculated by using following formula:

$$\%W\ SiO2 = \frac{(NV)_{NaOH} \cdot 30}{W}$$

where N = the normality of the standard NaOH solution in equivalent (N),

V = the volume of the standard NaOH solution in millilitre (ml),

W = the weight of raw waterglass sample in gram (g).

2. Sodium Aluminate

2.1 Sample pre-treatment:

2.1.1 Pipette 5 ml of sodium aluminate ($NaAlO_2$) into a 200 ml of volumetric flask.

2.1.2 Dilute this solution by using water to the marked scale.

This solution is prepared for analysis Na_2O and aluminium oxide (Al_2O_3).

2.2 Procedure:

2.2.1 Determination of Al_2O_3

2.2.1.1 Pipette 5 ml of the pre-treatment sodium aluminate into a 250 ml conical flask.

2.2.1.2 Add 30 ml of 0.05 molars (M) standard ethylenediaminetetra-acetic acid (EDTA) solution.

2.2.1.3 Add 0.1 grams xylenol orange.

2.2.1.4 Drop 1:1 hydrochloric acid (HCl) solution until the color of solution changes to yellow.

2.2.1.5 Drop 1:1 ammonium hydroxide (NH_4OH) solution until the color of solution changes to purple-red.

2.2.1.6 Heat the solution until it boils for 1 minute.

2.2.1.7 Cool this solution down to room temperature.

2.2.1.8 Drop 1:1 HCl solution until the color of solution changes to lemon yellow.

2.2.1.9 Add 1.5 grams of hexamethylene-tetraamine.

2.2.1.9 Titrate the solution with 0.05N standard zince chloride ($ZnCl_2$) solution until the color of this solution changes to wine red.

2.2.1.11 Record the volume of the 0.05N standard $ZnCl_2$ solution.

2.2.1.12 The weight percent Al_2O_3 of sample can be calculated by using following formula:

$$\%W\,Al_2O_3 = \frac{((V1 - V2 \cdot K)).\ N.\ 40.8}{S_g}$$

where N = the normality of the standard EDTA solution in equivalent (N),

V_1 = the volume of the standard EDTA solution in milliliter (ml) (excess),

V_2 = the volume of the standard $ZnCl_2$ solution in milliliter (ml) (EDTA+Al_2O_3),

V_3 = the volume of the standard EDTA solution in milliliter (ml),

V_4 = the volume of the standard $ZnCl_2$ solution in milliliter (ml),

K = a volume coefficient , K = (V_3/V_4),

S_g = the specific gravity in gram per liter (g/l).

2.2.2 Determination of Na_2O

2.2.2.1 Pipette 5 ml of the pre-treatment sodium aluminate into a 250 ml conical flask.

2.2.2.2 Add 15 ml of 0.5N of H_2SO_4 solution.

2.2.2.3 Add 2 drops of methylene blue.

The color of this solution changes to violet (red-purple).

2.2.2.4 Titrate this solution with 0.5N of the standard NaOH solution.

The color of this solution changes from violet (red-purple) to blue-gray, colorless and light-green respectively.

2.2.2.5 The weight percent Na_2O of sample can be calculated by using following formula:

$$Na_2O \text{ mg/ml} = \left[\frac{(NV)_1 - (NV)_2 - A}{1/8} \right] \times \left[\frac{31}{17} \right]$$

where N_1 = the normality of the standard H_2SO_4 solution in equivalent (N),

V_1= the volume of the standard H_2SO_4 solution in milliliter (ml),

N_2= the normality of the standard NaOH solution in equivalent (N),

V_2 = the volume of the standard NaOH solution in milliliter (ml),

A = the quantity of Al_2O_3 in $NaAlO_2$ solution in gram per liter (g/l)

Appendix B

Composition Analysis

Table B-1 The experiment on NaY zeolite synthesis at the Research Institute of Petroleum processing (RIPP), Sinopec Bejing China

The compositions of working solution

Waterglass (g/ml)			
Na_2O:0.080	SiO_2:0.255	H_2O:0.937	ρ:1.272
High sodium aluminate (g/ml)			
Na_2O:0.296	Al_2O_3:0.040	H_2O:0.994	ρ:1.330
Low sodium aluminate (g/ml)			
Na_2O:0.156	Al_2O_3:0.104	H_2O:0.981	ρ:1.241
Aluminium sulfate (g/ml)			
$[SO_4]^{2-}$:0.254	Al_2O_3:0.090	H_2O:0.962	ρ:1.264

The quantities of working solution using to synthesize NaY-zeolite

Working Solution (ml)	
Initiating agent	
Waterglass	41
High sodium aluminate	30
Whole gel	
Waterglass	491
Initiating agent	70
Aluminium sulphate	100
Low sodium aluminate	120
Deionized water	70

Table B-1 (Continuation)

The mass balance derived from both of the compositions and the quantities of working solution using to synthesize NaY-zeolite

Preparation	Working Solution	SiO_2 (g)	Al_2O_3(g)	Na_2O (g)	H_2O (g)
Initiating agent	Waterglass	10.455	-	3.28	38.417
	High sodium aluminate	-	1.200	8.880	29.820
Total		10.455	1.200	12.160	68.237
Mole		0.1742	0.0118	0.1961	3.7909
Mole ratio		14.7627	1.0000	16.6186	321.2627
The molar composition ratios of initiating agent		$16.62Na_2O:Al_2O_3:14.76SiO_2:321.26H_2O$			
Whole gel	Waterglass	125.205	-	39.280	460.067
	Low sodium aluminate	-	12.480	18.720	117.720
	Aluminium sulphate	-	9.000	-	96.20
	Deionized water	-	-	-	70
Total		135.660	22.680	70.160	812.224
Mole		2.2610	0.2223	1.1316	45.1236
Mole ratio		10.1709	1.0000	5.0904	212.9852
The molar composition ratios of initiating agent		$5.09Na_2O:Al_2O_3:10.17SiO_2:202.99H_2O$			

Remark: The molecular weight of the reactants forming in the term of oxide are: SiO_2 : 60, Na_2O : 62, Al_2O_3 : 102, H_2O : 18, $[SO_4]^{2-}$: 96

Table B-2.1 The experiment on NaY zeolite synthesis at Department of Chemical Engineering,Prince of Songkla University, Thailand

The compositions of working solution

Waterglass (g/ml)			
Na_2O:0.081	SiO_2:0.259	H_2O:0.920	ρ:1.260
High sodium aluminate (g/ml)			
Na_2O:0.300	Al_2O_3:0.048	H_2O:0.988	ρ:1.336
Low sodium aluminate (g/ml)			
Na_2O:0.165	Al_2O_3:0.115	H_2O:0.973	ρ:1.253
Aluminium sulfate (g/ml)			
$[SO_4]^{2-}$:0.237	Al_2O_3:0.084	H_2O:0.976	ρ:1.258

The quantities of working solutions using to synthesize NaY-zeolite

Working Solution (ml)	
Initiating agent	
Waterglass	40
High sodium aluminate	28
Whole gel	
Waterglass	482
Initiating agent	68
Aluminium sulphate	113
Low sodium aluminate	111
Deionized water	76

Table B-2.1 (Continuation)

The mass balance derived from both of the compositions and the quantities of working solution using to synthesize NaY-zeolite

Preparation	Working Solution	SiO_2 (g)	Al_2O_3 (g)	Na_2O (g)	H_2O (g)
Initiating agent	Waterglass	10.360	-	3.240	36.800
	High sodium aluminate	-	1.344	8.400	27.664
Total		10.360	1.344	11.640	64.464
Mole		0.1727	0.0132	0.1877	3.5813
Mole ratio		13.0833	1.0000	14.2197	271.3131
The molar composition ratios of initiating agent		$14.22Na_2O:Al_2O_3:13.08SiO_2:271.31H_2O$			
Whole gel	Waterglass	124.838	-	39.042	443.440
	Low sodium aluminate	-	12.765	18.315	108.003
	Aluminium sulphate	-	9.492	-	110.288
	Deionized water	-	-	-	76.000
Total		135.198	23.601	68.997	802.195
Mole		2.2533	0.2314	1.1129	44.5664
Mole ratio		9.7377	1.0000	4.8094	192.5946
The molar composition ratios of initiating agent		$4.81Na_2O:Al_2O_3:9.74SiO_2:192.60H_2O$			

Remark: The molecular weight of the reactants forming in the term of oxide are: SiO_2 : 60, Na_2O :62, Al_2O_3 :102, H_2O :18, $[SO_4]^{2-}$: 96

Table B-2.2 The experiment on NaY zeolite synthesis at Department of Chemical Engineering, Prince of Songkla University, Thailand

The compositions of working solution

Waterglass (g/ml)			
Na_2O:0.091	SiO_2:0.272	H_2O:0.914	ρ:1.277
High sodium aluminate (g/ml)			
Na_2O:0.264	Al_2O_3:0.039	H_2O:0.997	ρ:1.300
Low sodium aluminate (g/ml)			
Na_2O:0.148	Al_2O_3:0.103	H_2O:0.994	ρ:1.245
Aluminium sulfate (g/ml)			
$[SO_4]^{2-}$:0.209	Al_2O_3:0.074	H_2O:0.982	ρ:1.230

The quantities of working solutions using to synthesize NaY-zeolite

Working Solution (ml)	
Initiating agent	
Waterglass	38
High sodium aluminate	30
Whole gel	
Waterglass	460
Initiating agent	68
Aluminium sulphate	152
Low sodium aluminate	107
Deionized water	51

Table B-2.2 (Continuation)

The mass balance derived from both of compositions and the quantities of working solution using to synthesize NaY-zeolite

Preparation	Working Solution	SiO_2 (g)	Al_2O_3 (g)	Na_2O (g)	H_2O (g)
Initiating agent	Waterglass	10.336	-	3.458	34.732
	High sodium aluminate	-	1.170	7.920	29.910
Total		10.336	1.170	11.378	64.642
Mole		0.1723	0.0115	0.1835	3.5912
Mole ratio		14.9826	1.0000	15.9570	312.2780
The molar composition ratios of initiating agent		$15.96Na_2O:Al_2O_3:14.98SiO_2:312.28H_2O$			
Whole gel	Waterglass	125.120	-	41.860	420.440
	Low sodium aluminate	-	11.021	15.836	106.358
	Aluminium sulphate	-	11.248	-	149.264
	Deionized water	-	-	-	51.000
Total		135.456	23.439	69.074	791.704
Mole		2.2576	0.2298	1.1141	43.9836
Mole ratio		9.8242	1.0000	4.8486	191.3995
The molar composition ratios of initiating agent		$4.85Na_2O:Al_2O_3:9.82SiO_2:191.40H_2O$			

Remark : The molecular weight of the reactants forming in the term of oxide as follows SiO_2 60, Na_2O : 62, Al_2O_3 : 102, H_2O : 18, $[SO_4]^{2-}$: 96

Table B-2.3 The experiment on NaY zeolite synthesis at Department of Chemical Engineering,Prince of Songkla University, Thailand

The compositions of working solution

Water-glass (g/ml)			
Na_2O:0.092	SiO_2: 0.294	H_2O: 0.906	ρ: 1.292
High Sodium aluminate (g/ml)			
Na_2O: 0.301	Al_2O_3: 0.037	H_2O: 0.997	ρ: 1.355
Low Sodium aluminate (g/ml)			
Na_2O: 0.173	Al_2O_3: 0.105	H_2O: 0.989	ρ: 1.270
Aluminium Sulphate (g/ml)			
$[SO_4]^{2-}$: 0.195	Al_2O_3: 0.069	H_2O: 0.959	ρ: 1.223

The quantities of working solution using to synthesize NaY-zeolite

Working Solution (mL)	
Initiating agent	
Water-glass	45
Aluminium sulphate	3
High Sodium aluminate	35
Whole gel	
Water-glass	460
Initiating agent	83
Aluminium sulphate	160
Low sodium aluminate	100
Deionized water	51

Table B-2.3 (Continuation)

The mass balance derived from both of the compositions and the quantities of working solution using to synthesize NaY-zeolite

Preparation	Working Solution	SiO_2 (g)	Al_2O_3 (g)	Na_2O (g)	H_2O (g)
Initiating agent	Water-glass	13.230	-	4.140	40.770
	Aluminium sulphate	-	0.207	-	2.877
	High Sodium aluminate	-	1.295	10.535	34.895
Total		13.230	1.502	14.675	78.542
Mole		0.2205	0.0147	0.2367	4.3634
Mole ratio		15.0000	1.0000	16.1020	296.8299
The mole composition ratios of initiating agent		16.10Na_2O:Al_2O_3:15.00 SiO_2:296.83 H_2O			
Whole gel	Water-glass	135.240	-	42.320	416.760
	Low Sodium aluminate	-	10.500	17.300	98.900
	Aluminium sulphate	-	11.040	-	153.440
	Deionized water	-	-	-	51.000
Total		148.470	23.042	74.295	796.642
Mole		2.4745	0.2259	1.1983	44.258
Mole ratio		10.954	1.0000	5.3046	195.9185
The mole composition ratios of initiating agent		5.30Na_2O:Al_2O_3:10.95 SiO_2:195.92 H_2O			

Remark : The molecular weight of the reactants forming in the term of oxide are: SiO_2 : 60, Na_2O : 62, Al_2O_3 : 102, H_20 : 18, $[SO_4]^2$: 96

Appendix C

The reaction of prepared raw materials and pattern of their oxide in water

1. Waterglass(Na_2SiO_3):

$$SiO_2 + Na_2CO_3 + H_2O \xrightarrow{\triangle} Na_2SiO_3 + CO_2 + H_2O$$

$$Na_2SiO_3 + 2H_2O \longrightarrow SiO_2 + Na_2O + 2H_2O$$

2. Sodium aluminate($NaAlO_2$):

$$2Al(OH)_3 \xrightarrow{\triangle} Al_2O_3 + 3\,H_2O$$

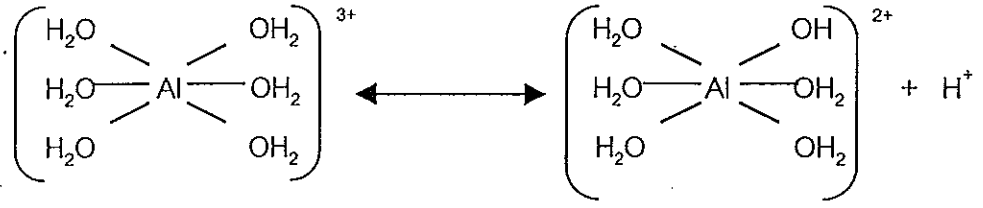
$$2NaOH \xrightarrow{\triangle} Na_2O + H_2O$$

$$Al(OH)_3 + NaOH + H_2O \xrightarrow{\triangle} NaAlO_2 + 3\,H_2O$$

$$2NaAlO_2 + 3H_2O \longrightarrow Al_2O_3 + Na_2O + 3H_2O$$

3. Aluminium sulphate($Al_2(SO_4)_3$):

$$Al_2(SO_4)_3 + \infty H_2O \longrightarrow 2Al^{3+} + 3SO_4^{2-} + \infty H_2O$$



Appendix D

Particle Size Distribution

Table D-1 The particle size distribution of NaY zeolite

Type of seed	Diameter (micron)	Cumulation (%)	R (%)
	20.0	16.6	***
NaY - S01	10.0	36.8	*******
P. DNST. (G/CC) : 1.86086	8.0	48.3	*********
L. DNST. (G/CC) : 0.99757	6.0	57.9	**********
VISCOSITY (CP) : 0.983	5.0	62.1	**********
DEPTH : 0	4.0	66.6	**********
ROTATION : 1000	3.0	71.5	**********
	2.0	77.4	**********
	1.0	87.8	**********
	0.8	91.1	**********
			WT. * : 5%
	20.0	15.1	***
NaY - S02	10.0	38.1	*******
P. DNST. (G/CC) : 1.82859	8.0	43.6	********
L. DNST. (G/CC) : 0.99757	6.0	49.6	*********
VISCOSITY (CP) : 0.983	5.0	53.4	**********
DEPTH : 0	4.0	57.3	**********
ROTATION : 1000	3.0	61.6	**********
	2.0	67.2	**********
	1.0	78.7	**********
	0.8	83.7	**********
	0.6	88.7	**********
	0.5	91.9	**********
			WT. * : 5%

Table D-1 (Continuation)

Type of seed	Diameter (micron)	Cumulation (%)	R (%)
NaY - S03 P. DNST. (G/CC) : 1.85629 L. DNST. (G/CC) : 0.99757 VISCOSITY (CP) : 0.983 DEPTH : 0 ROTATION : 1000	20.0	15.6	***
	10.0	33.4	******
	8.0	38.2	*******
	6.0	43.6	********
	5.0	46.7	*********
	4.0	50.4	**********
	3.0	55.1	**********
	2.0	60.9	**********
	1.0	73.2	**********
	0.8	78.2	**********
	0.6	85.0	**********
	0.5	89.0	**********
	0.4	93.3	**********
			WT. * : 5%

Appendix E

Data of the relative crystallization

Table E-1 The crystallization of zeolite Y type by mixing both the aqueous nuclei solution and the whole gel at 15°C with various temperature of crystallization.

Time (hr)	Relative crystallization (%)			
	Temperature (°C)			
	70	85	95	100
4	0	0	0	0
6	-	-	-	13
8	-	-	-	78
10	-	-	53	88
12	-	11	94	95
14	-	27	100	93
16	-	56	95	90
18	-	81	93	-
20	-	94	-	-
22	-	98	-	-
24	-	99	-	-
39	33	-	-	-
41	84	-	-	-
43	94	-	-	-
45	99	-	-	-
47	98	-	-	-
49	94	-	-	-

Table E-2 The crystallization of zeolite Y type by mixing an aqueous nuclei solution at 5°C with various mixing temperature of the whole gel

Time (hr)	Relative crystallization (%)			
	Temperature (°C)			
	5	15	20	25
3	-	-	-	-
4	0	0	0	0
5	10	9	7	5
6	17	15	13	15
8	91	83	80	75
10	98	91	87	88
12	98	96	92	90
14	97	92	90	85
16	92	88	88	-

Table E-3 The crystallization of zeolite Y type by mixing the whole gel at 15°C with various mixing temperature of an aqueous nuclei solution

Time (hr)	Relative crystallization (%)		
	Temperature (°C)		
	5	15	25
4	0	0	0
5	9	8	5
6	15	13	10
8	83	78	77
10	91	88	83
12	96	95	88
14	95	93	86
16	90	-	82

Appendix F

X - RAY Diffraction Data

1. The data from XRD analyzer of the synthesized zeolite (In08)

Philips Analytical — PW-APD, Diffraction soft-are

DI FILE:

Sample identification: In08

DI file name: IN08.DI
Input file name: IN08

Start angle [°2q]: 5.025
End angle [°2q]: 59.975
Start d-value [Å]: 17.57178
End d-value [Å]: 1.54119
Maximum number of counts: 912

Anode material: Cu
a1 Wavelength [Å]: 1.54060
a2 Wavelength [Å]: 1.54439

Intensities for FIXED slit

Peak positions defined by: Minimum of 2nd derivative of peak
Minimum peak tip width: 0.00
Maximum peak tip width: 1.00
Maximum peak base width: 2.00
Minimum significance: 0.75
Number of peaks: 36

DIFFRACTION LINES:

Angle [°2q]	d-value a1 [Å]	d-value a2 [Å]	T.width [°2q]	Height [counts]	Backgr. [counts]	Rel.int. [%]	Signific
5.190	14.26701	14.30211	0.150	353	231	94.1	2.79
10.125	8.72937	8.75084	0.100	252	204	22.1	7.45
11.870	7.44570	7.46803	0.100	146	180	16.1	3.34
✓15.625	5.66682	5.68076	0.200	565	151	62.1	5.93
✓18.655	4.75267	4.76436	0.150	282	130	30.9	1.55
✓20.325	4.36578	4.37652	0.200	471	113	51.6	5.38
22.750	3.90563	3.91521	0.150	161	106	17.7	1.04
✓23.605	3.76633	3.77533	0.150	912	104	100.0	3.04
24.395	3.55965	3.56842	0.200	74	102	8.1	0.75
25.760	3.45566	3.46416	0.150	142	100	15.5	5.05
✓27.005	3.29910	3.30722	0.150	708	98	77.6	2.94
27.735	3.21393	3.22181	0.200	149	98	16.3	1.94

Philips Analytical — PC-APD, Diffraction software

Angle [°2q]	d-value a1 [Å]	d-value a2 [Å]	T.width [°2q]	Height [counts]	Backgr. [counts]	Rel.int. [%]	Signific
29.600	3.01551	3.02293	0.150	286	94	31.3	1.46
✓30.710	2.90900	2.91616	0.150	396	92	43.4	1.35
✓31.355	2.85042	2.85763	0.150	906	90	99.3	3.13
32.410	2.76019	2.76698	0.150	292	88	32.1	1.58
32.975	2.71419	2.72035	0.150	104	86	11.4	1.75
✓34.040	2.63166	2.63813	0.150	286	85	31.3	1.36
34.625	2.58652	2.59439	0.200	151	85	16.6	1.23
37.065	2.42353	2.42949	0.300	26	81	2.9	0.95
37.870	2.37384	2.37968	0.250	166	81	18.2	2.79
40.450	2.22819	2.23365	0.250	48	88	5.2	1.26
41.315	2.18351	2.18888	0.200	123	92	14.0	1.75
41.830	2.15781	2.16312	0.200	56	94	6.2	0.81
43.185	2.09319	2.09834	0.200	79	100	8.7	1.45
43.945	2.05874	2.06380	0.200	85	104	9.3	1.03
47.160	1.92561	1.93035	0.150	41	92	4.5	0.88
47.680	1.90532	1.91050	0.250	55	88	6.0	1.43
49.290	1.84727	1.85181	0.250	30	77	3.3	0.88
50.565	1.80430	1.80874	0.200	66	74	7.2	1.32
51.650	1.76627	1.77262	0.200	50	69	5.5	2.09
52.350	1.74626	1.75056	0.200	135	67	14.8	1.42
53.910	1.69935	1.70353	0.200	151	62	16.6	1.47
55.660	1.65003	1.65405	0.300	27	58	3.0	1.39
57.255	1.60693	1.61094	0.250	29	58	3.2	0.81
58.175	1.58451	1.58841	0.250	132	62	14.5	2.64

2. The data from XRD analyzer of the standard zeolite (STD)

D I F F I L E :

Sample identification: stdNaY

DI file name: STDNAY.DI
Input file name: STDNAY

Start angle [°2q]: 5.025
End angle [°2q]: 59.975
Start d-value [Å]: 17.57179
End d-value [Å]: 1.54113
Maximum number of counts: 1102

Anode material: Cu
a1 Wavelength [Å]: 1.54060
a2 Wavelength [Å]: 1.54439

Intensities for FIXED slit

Peak positions defined by: Minimum of 2nd derivative of peak
Minimum peak tip width: 0.00
Maximum peak tip width: 1.00
Maximum peak base width: 2.00
Minimum significance: 0.75
Number of peaks: 37

D I F F R A C T I O N L I N E S :

Angle [°2q]	d-value a1 [Å]	d-value a2 [Å]	T.width [°2q]	Height [counts]	Backgr. [counts]	Rel.int. [%]	Signific
6.200	14.24403	14.27907	0.150	835	246	75.8	3.05
10.150	8.70792	8.72934	0.150	222	207	20.1	1.14
11.905	7.42788	7.44615	0.150	231	182	21.0	1.29
✓15.660	5.65423	5.66814	0.150	807	146	73.2	3.17
✓18.705	4.74007	4.75174	0.150	404	125	36.7	2.17
✓20.375	4.35518	4.36589	0.200	660	114	59.9	6.46
22.810	3.89546	3.90505	0.150	225	108	20.4	1.33
✓23.660	3.75740	3.76665	0.150	1102	106	100.0	3.97
25.025	3.55546	3.56421	0.150	86	102	7.8	2.30
25.915	3.44842	3.45690	0.150	172	100	15.6	1.20
✓27.070	3.29133	3.29942	0.150	784	98	71.1	3.23
27.795	3.20710	3.21499	0.150	146	96	13.3	1.00

Philips Analytical PC-APD, Diffraction software

Angle [°2q]	d-value a1 [Å]	d-value a2 [Å]	T.width [°2q]	Height [counts]	Backgr. [counts]	Rel.int. [%]	Signific
29.665	3.00905	3.01646	0.150	335	92	30.4	1.73
✓30.765	2.90393	2.91107	0.200	388	90	35.2	4.42
✓31.425	2.84442	2.85142	0.200	1063	88	96.4	8.23
32.475	2.75481	2.76159	0.200	317	86	28.7	4.10
33.080	2.70580	2.71246	0.150	139	86	12.6	0.92
✓34.115	2.62604	2.63250	0.150	320	85	29.1	1.43
34.705	2.58274	2.58909	0.150	177	83	16.0	1.16
35.670	2.51504	2.52123	0.150	49	81	4.4	0.76
37.920	2.37083	2.37666	0.200	225	77	20.4	2.30
40.530	2.22397	2.22944	0.200	71	79	6.4	0.84
41.460	2.17621	2.18156	0.200	104	85	9.4	1.82
41.970	2.15093	2.15623	0.250	69	86	6.2	1.21
43.265	2.08951	2.09465	0.200	135	92	12.2	1.51
44.040	2.05452	2.05957	0.200	74	96	6.7	0.92
47.215	1.92349	1.92823	0.150	72	88	6.6	0.92
47.940	1.89991	1.90449	0.200	98	83	8.9	1.40
49.510	1.83957	1.84410	0.200	37	74	3.4	0.86
50.650	1.80081	1.80524	0.200	55	71	5.0	0.84
51.785	1.76398	1.76832	0.200	72	67	6.6	1.01
52.480	1.74224	1.74653	0.200	142	66	12.8	1.41
54.005	1.69659	1.70076	0.250	169	61	15.3	3.05
55.185	1.66307	1.66716	0.100	18	56	1.7	0.77
55.785	1.64659	1.65064	0.150	46	55	4.2	1.04
57.385	1.60443	1.60838	0.250	34	53	3.1	0.88
58.325	1.58079	1.58468	0.250	164	55	14.9	3.14

Appendix G

Characterization Procedure

1. X-ray diffraction (XRD) spectroscopy(Crystallinity analysis)

   1) Place the sample and reference in the drying oven at 110°C for 1 hour.

   2) Cool the sample in the desiccator at 35 % relative humidity controlled by a saturated solution of ammonium chloride at room temperature for at least 16 hours.

   3) Grind the sample into very fine particles and pack the sample into XRD sample holder and put it into the goniometer.

   4) Close the XRD window.

   5) Start up the power source and adjust the detector speed.

   6) Set the starting angle at 5°.

   7) Turn on the goniometer and the recorder.

   8) The graph of 2θ eight peaks shown in Table 11 was used to calculate the area under each peak.

   9) Calculate % of crystallinity by using the formula:

   % crystallinity $= F \times 100 \times (S_X/S_R)$,

   where F = cofactor of crystallinity (100/90)

   S_X = Sum of peak areas for the sample

   S_R = Sum of peak areas for the reference (90%) NaY zeolite

   10) Calculate the unit cell size and silica to alumina ratio as the following equations,

   Unit cell size $(a_o) = 5.0509 / \sin(\theta)$

   Silica to alumina ratio $(SiO_2/Al_2O_3) = [(25.858 - a_o) / (a_o - 24.191)] \times 2$

Table.G-1 Diffraction angles 2θ hkl Miller Indices (ASTM D3906-80, 1991)

Peak	2θ	hkl
1	15.2 ± 0.2	331
2	18.7 ± 0.2	511, 333
3	20.4 ± 0.3	440
4	23.7 ± 0.4	533
5	27.1 ± 0.5	642
6	30.8 ± 0.5	822, 660
7	31.5 ± 0.5	555, 751
8	34.2 ± 0.6	664

2 Scanning Electron Microscope (SEM) (Morphological analysis)

1) Dry crystal at 110°C for 1 hour.

2) Put one side of the two-face tape on the copper stub and press the other side on the dry crystal.

3) Coat the sample as well as stub with gold and then put it into the chamber of SEM.

4) Switch on the system of SEM, chose the picture of crystal at optimum multiplication and take the SEM photograph.

3 Differential Thermal Analysis (DTA) (Thermal analysis)

1) Tare the DTA aluminium sample lid and pan.

2) Weigh the indium sample in the pan and put the lid on the pan.

3) Crimp the sample.

4) Record weight of sample

5) Place the sample in the left DTA cup and place an empty DTA aluminium sample pan and lid in the right DTA cup.

6) Make a run using the following criteria:

- Run a baseline, under analyzer parameter
- Scan rate = 10°C/min
- Temperature range = 500 – 1000°C
- Use the hard key "GO TO LOAD"
- End condition; use the hard key "GO TO LOAD"

4. Centrifugal Particle Size Analyzer (Particle size analysis)

Glass Cleaning

1) Place both of cells for measurement and balance in warm water with several drops of kitchen detergent.
2) Clean interior and exterior of cell using a soft cloth or brush. When cleaning the cell interiors, the ultrasonic cleaner is very helpful, if it is hard to clean the stains inside the cells. At the same time, clean the cell caps.
3) Rinse cells and caps thoroughly with clean warm water. Be careful so that no bubbles and stain remain inside the equipment.
4) Wipe cell with soft cloth such as gauze. At the same time, check that no stain remains.

Sample Preparation

1) Weigh Sample approximate 1 – 2 gram of sample powder without causing segregation.
2) Prepare approximate 100 ml of dispersion medium. If a dispersion agent was necessary, dissolve the agent in the dispersion medium to an appropriate concentration (normally 0.1 – 0.2 %).
3) Extract 50 ml of the dispersion medium and pour the sample powder into it. The appropriate concentration is less than 2 – 3 %. If the amount of the sample was less than it, reduced the amount of liquid.

4) Thoroughly agitate the suspension containing the sample with a mixer, magnetic stirrer or ultrasonic agitator or by hand, in order to fully disperse the sample in the liquid. When using a mixer or ultrasonic for agitation, the temperature of the solution might rise.

5) Use remaining dispersion medium as standard solution for sensitivity adjustment of the equipment before analyzing or as a solution to further dilute the suspension.

1) Adjust 0 %

1.1) Position of switches and dials

Check that switch and dials are at the following positions. If any is in the wrong position, correct in accordance with the following:

1.1.1) On main body

Cell speed : All close,

0 % dial : At approximate center of rotational range

100 % dial : Turn fully counterclockwise

Measurement mode selection knob : Lock,

Power : on

1.1.2) Microcomputer side

CPU on / off : On

1.2) Connect down transducer to power source and SA-CP2 power source cord to transducer. Activate down transducer switch and power switch on the main body.

1.3) Clean both of cells for measurement and balanced in accordance with procedure indicated in glass cell cleaning. Put same amount of standard liquid in both calls so that required sedimentation distance is attained.

1.4) Cape both cells. Any of solution that flowed out of cell must be wiped thoroughly.

1.5) Open the door of measurement chamber and rotate disc manually.(If it is difficult to rotate, turn measurement mode selecting knob to RELEASE. Disc would then rotate easily. After rotation, be sure to turn knob back to the lock side.) Then set the cell holder for the balance side at the 6 o'clock position.

1.6) Cell attachment procedure

1.6.1) Support rotation disc on one hand, and tilted cell holder for balance the right.

1.6.2) Then insert cell into cell holder, while pressing cell cap with fingers.

1.6.3) After insertion, return the cell holder to original position.(turn to thew left).

1.7) Rotate disc manually, and set cell holder on measurement side at the 6 o'clock position, following the same procedure as in 1.5.

1.8) Attach cell following the same procedure as in 1.6. When centrifugal sedimentation is used, the amount of liquid in balance and measurement cell must be the same.

1.9) Rotate disc manually, so that line mark on face of the disc aligned with the indicator on front upper position of measurement chamber. When cell reaches measurement position, lamp on the indication would activate. After positional adjustment, check that measurement mode selecting knobs is at Lock.

1.10) Watch value of display, adjusted displayed value at zero using 0% dial. In this case a $\pm$ 1.0 allowance is permit.

1.11) Open door of the measurement chamber and pulled out measurement cell from cell holder on measurement side. This procedure would be opposite that of 1.6

1.12) After agitating suspension adjusted sample, pour sample(or just a few drops) into measurement cell. Then cap cell and shook by hand.

1.13) Adjust liquid surface at the sedimentation distance and shook again. Thoroughly removed any solution remaining on exterior of cell.

1.14) Attach cell quickly and placed in measurement position.

2) Setting Measurement Conditions

2.1) Set Lift / Fall, Melt / Mono, Grav / Cent switchs at appropriate positions.

2.2) Press Go key. Display will indicate C_1 and printer would print out P DEST(G/CC).

2.3) Input particle density with numerical keys in g/cm^3 unit.

2.4) When displayed value is correct, pressed ENT key. Displayed value will be printed out. Then printer would print out L DNST (G/CC) and display would indicate C2.

2.5) Input density of dispersion medium with numerical key, in g/cm^3 units. Then press ENT key. Printer would print out value being input. Then VISCOSITY(CP) will be printed out and display will indicate C3.

2.6) When C3 is displayed, input viscosity of dispersion medium with numerical keys in CENTI POISE unit. Then press ENT key. Printer will print out the value input. The DEPTH (-) will be printed out and display will indicate C4.

2.7) Input position of liquid surface relative to sedimentation distance with numerical keys and press ENT key. The printer will print out value input.

2.8) When C5 is displayed, input cell speed with numerical keys in RPM units. Then press ENT key. Printer will print out value input and display will indicate 100% adjustment.

3) Adjust 100 %

3.1) Turn off cell speed switch, opened door of measurement chamber and remove cell.

3.2) Agitate suspension by shaking capped cell by hand. If solution surface does not coincide on both sides of disturbance eliminating plate, referring to cap once.

3.3) Thoroughly wipe of liquid on exterior of cell. Attach cell to holder quickly and adjust it to measurement position. Close door of the chamber.

3.4) Check the displayed value. If the display was not within 90.0-100.0%, adjusting value with 100% dial.

3.5) Set measurement mode selecting knob release in the case of lift measurement, or measurement by combination of natural and centrifugal sedimentation. Activated switch for chosen rate of revolution.

3.6) Press GO key and indicate maximum particle diameter (μm) to be measured on display.

5. True density analysis

Sample Preparation

1) Select the proper sample cell. The large cell is preferable, but if a limited amount of sample is available, the small cell can be used.

2) Weigh the sample cell.

3) Put the sample into the cell about approximately three quarters of the cell volume and weigh it.

4) Close Gas-In toggle valve (the toggle handle should be paralleled to the panel)

5) Close Gas-In-Control needle valve fully clockwise.

6) Make sure the SELECTOR VALVE is pointing to REF.

7) Open the Gas-Out toggle valve.

8) Turn Gas-out CONTROL needle valve fully counter-clockwise.

9) Set the Zero knob to get approximately Zero reading on the display.

10) Turn on the Helium tank and make sure that all valves in the line are opened and adjust the tank pressure to slightly between 20 and 25 psig.

11) Open the sample cell chamber and put sample cell in it. Slowly tighten the cap and do not over tighten it.

Purging

Purging is a general procedure to expel any contaminated gases or vapors from the sample. In some special case where the particle sample is very fine or highly porous (with micropores), a vacuum technique should be used instead.

1) Attach a hose to the VENT hose connection and immersed the other end in a beaker of water.

2) Turn selector switch to CELL

3) Open Gas-In toggle valve.

4) Adjust Gas-In CONTROL needle valve to give a slow rate of bubbling in the water.

5) Wait for 10-20 minutes.

6) Close Gas-In toggle valve.

Measurement Step

1) Turn Gas-Out needle valve fully clockwise(close) and then slightly open by turning it back about one-half turn.

2) Readjust the gauge to zero.

4) Close Gas-In toggle valve (the toggle handle should be paralleled to the panel)

5) Close Gas-In-Control needle valve fully clockwise.

6) Make sure the SELECTOR VALVE is pointing to REF.

7) Open the Gas-Out toggle valve.

8) Turn Gas-out CONTROL needle valve fully counter-clockwise.

9) Set the Zero knob to get approximately Zero reading on the display.

10) Turn on the Helium tank and make sure that all valves in the line are opened and adjust the tank pressure to slightly between 20 and 25 psig.

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6) Close Gas-In toggle valve.

Measurement Step

1) Turn Gas-Out needle valve fully clockwise(close) and then slightly open by turning it back about one-half turn.

2) Readjust the gauge to zero.

3) Turn the select valve to REF.

4) Close Gas-Out toggle valve. Momentarily pressed the tip of the toggle to release any excess pressure.

5) Open the Gas-Out toggle valve. Use the CONTROL needle valve to control the appropriate rate of helium flow and pressurize the system to slightly less than 20 psig. Stop the flow by closing Gas-In toggle valve when the pressure was approximately stabilized.

6) Record the pressure reading as "P2".

7) Turn the selector switch to CELL.

8) Record the new pressure reading as "P3" after it is stabilized.

9) Depressurize the system by opening As-Out toggle valve.

10) Calculate the true powder volume, V_P and true powder density using the equations:

$$V_P = V_C + (1 - P_2 / P_3) \text{ (unit : } cm^3)$$

$$\text{Density}(g/cm^3) = \frac{\text{Wt. of sample}(g)}{V_P(cm^3)}$$

11) Repeat steps 2 to 11 for the next measurement. These measurement are recommended for each sample.

VITAE

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B.Sc.(Agro-Industry)	Prince of Songkla University	1996