SYNTHESIS OF ZEOLITE BETA FOR COMPOSITE MEMBRANES

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NADİYE GÜR

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Prof. Dr. Canan ÖZGEN
Director

I certify that this thesis satisfies all the requirements as a thesis for the degree of Master of Science.

Prof. Dr. Nurcan BAÇ
Head of Department

This is to certify that we have read this thesis and that in our opinion it is fully adequate, in scope and quality, as a thesis for the degree of Master of Science.

Dr. Burcu (AKATA) KURÇ Co-Supervisor	Prof. Dr. Nurcan BAÇ Supervisor

Examining Committee Members

Prof. Dr. Güniz GÜRÜZ	(METU, CHE)	
Prof. Dr. Nurcan BAÇ	(METU, CHE)	
Instr. Dr. Burcu (AKATA) KURÇ	(METU, TVSHE)	
Prof. Dr. İnci EROĞLU	(METU, CHE)	
Prof. Dr. Hayrettin YÜCEL	(METU, CHE)	

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Name, Last Name	: Nadiye GÜR
Signature	:

ABSTRACT

SYNTHESIS OF ZEOLITE BETA FOR COMPOSITE MEMBRANES

Gür, Nadiye
M.S., Department of Chemical Engineering
Supervisor: Prof. Dr. Nurcan Baç
Co-supervisor: Dr. Burcu (Akata) Kurç

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In this work, zeolite Beta was synthesized experimentally in order to be used as filler in fuel cell membranes in order to assess the proton conductivity of composite membranes. Effects of the Si/Al ratio, and synthesis time on yield, relative crystallinity, crystal size, and proton conductivity were investigated.

Zeolite Beta with Si/Al ratio between 10 and 30 was synthesized with a batch formulation of $2.2Na_2O:1Al_2O_3:ySiO_2:4.6(TEA)_2O:tH_2O$ (where TEA≡ tetraethyl-ammonium) at 150°C for 5-15 days of synthesis time. Sodium aluminate, tetraethylammonium hydroxide (TEAOH) solution, sodium hydroxide pellets (NaOH), and deionized water were used for the preparation of the batch solution. Zeolite Na-Beta was calcined and treated with sulfuric acid solution at different concentrations in order to have zeolite H-Beta. Polyetherether ketone (PEEK) was sulfonated in order to have a proton conductive membrane and than zeolite H-Beta was incorporated resulting in a composite or nanocomposite membrane.

X-ray diffraction (XRD) analysis helped to understand whether the synthesized material was zeolite Beta or not. The morphology and the crystal size of the crystals were observed as a result of the scanning electron microscopy (SEM) analysis. In order to see the effect of sulfuric acid treatment on the sodium (Na) content of the zeolite Beta, inductively coupled plasma (ICP) analysis was performed. Synthesis results indicate that as Si/Al ratio and synthesis time increased the yield of zeolite Beta increased. It was observed that Si/Al ratio from 10 to 30, and synthesis time between 5 to 15 days did not affect the crystal size significantly.

For the sulfonation of PEEK, sulfuric acid was used. Sulfonated polyetherether ketone (SPEEK) was dissolved in a solvent that was dimethyl acetamide (DMAC), incorporated with zeolite Beta, and then solvent was removed in the vacuum oven. The proton conductivity was measured with a 2-probe impedance spectrometer. Initial results indicate that zeolite Beta at 10 and 20 wt % loadings did not affect the proton conductivity of the SPEEK membrane at 100 % relative humidity and room temperature.

Keywords: Zeolite Beta, SPEEK, composite membrane, proton conductivity

ÖZ

KOMPOZİT MEMBRANLAR İÇİN ZEOLİT BETA SENTEZİ

Gür, Nadiye
Yüksek Lisans, Kimya Mühendisliği Bölümü
Tez Yöneticisi: Prof. Dr. Nurcan Baç
Yardımcı Tez Yöneticisi: Dr. Burcu (Akata) Kurç

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Bu tez çalışmasında, kompozit yapıdaki yakıt pili membranlarında proton transferini incelemek amacıyla kullanılacak olan zeolit Beta sentezlenmiştir. Zeolit Beta'nın Si/Al oranının ve sentez süresinin, sentez verimine, ürünün bağıl kristalinitesine, ve proton transferine olan etkisi araştırılmıştır.

Si/Al oranı 10 ve 30 arasında olan, 5 günden 15 güne kadar farklı zamanlarda ve 150 ºC'de sentezlenen zeolit Beta, $2.2Na_2O:1Al_2O_3:ySiO_2:4.6(TEA)_2O:tH_2O$ (TEA≡tetraetilamonyum) formülü içeren çözeltilerden sentezlenmiştir. Bu sentez çözeltisinin hazırlanması için sodyum aluminat, tetraetilamonyum hidroksit (TEAOH) çözeltisi, sodyum hidroksit (NaOH), ve deionize su kullanılmıştır. Bu şekilde sentezlenen zeolit sodyum Beta (Na-Beta) 550°C'de 6 saat boyunca kalsinasyon işlemine tabi tutularak yapı düzenleyici organik maddenin ($(TEA)_2O$) kristal yapıdan uzaklaştırılması sağlanmıştır. Böylece organik düzenleyici maddesi uzaklaştırılmış olan zeolit Na-Beta'nın iyon değişimine uğrayarak zeolit H-Beta'ya dönüşmesi için zeolit Na-Beta farklı konsantrasyonlarda (konsantre (%98) ve 1 M) sülfürik asitte bekletilmiştir (4, 18, 24 saat). Bu zeolit H-Beta'lar sülfonlanmış polietereter ketona (SPEEK) eklenerek kompozit yapıda membranlar oluşturulmuştur.

X-ışını kırınımı (XRD) analizleri sonuçları ile sentezlenen maddenin zeolit Beta olup olmadığı anlaşılmıştır. Ayrıca bağıl kristalinite değerleri de XRD desenindeki en yüksek pikin altında kalan alanlardan yararlanılarak bulunmuştur. Kristal yapısı ve boyutunun tespiti için taramalı elektron mikroskobu (SEM) kullanılmıştır. Zeolit Na-Beta'nın sülfürik asite tabi tutulması sonucu yapısındaki sodyumun değişimi ile ilgili bilgi sahibi olunabilmesi için ICP (Inductively Coupled Plasma) kullanılmıştır. Zeolit Beta sentezi deneylerinin sonucunda, Si/Al oranının 10'dan 30'a kadar ve sentez süresinin 5 günden 15 güne kadar zeolit Beta verimi üzerine olumlu etkisi olduğu görülmüştür. Diğer bir deyişle Si/Al oranı ve kristallenme zamanı arttıkça elde edilen zeolit Beta miktarı da artmıştır. Si/Al oranının 10 ile 30 arasında ve sentez zamanının kristal boyutu üzerine belirgin bir etkisi olmadığı görülmüştür.

Polietereter ketonun (PEEK) sülfonasyonu için sülfirik asit kullanılmıştır. SPEEK dimetil asetamitte (DMAC) çözülerek zeolit H-Beta eklenir ve vakumlu fırında kurutularak çözücü uçurulmuştur. Bu şekilde oluşturulan kompozit yapıdaki membranların proton iletkenlikleri 2 uçlu empedans spektrometre ile ölçülmüştür. Proton transferi sonuçları sonucunda ağırlıkça % 10 ve % 20 oranında zeolit Beta eklemenin % 100 bağıl nemlilik ve oda sıcaklığında proton transferine belirgin bir etkisi bulunmadığı görülmüştür.

Anahtar kelimeler: Zeolit Beta, SPEEK, kompozit membran, proton transferi

To My Family

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INTRODUCTION

1.1 Zeolite Beta

Zeolites are hydrated, crystalline tectoaluminosilicates that are constructed from TO_4 tetrahedra (T= tetrahedral atom, e.g., Si, Al, P, Ga, Ge, As, B, Be); each apical oxygen atom is shared between two adjacent tetrahedra giving a framework ratio of O/T= 2. The term tectoaluminosilicate means that all the oxygen atoms bridges two tetrahedral atoms [1]. Zeolites have many uses in industrial applications and fine chemical industry. Their incorporation into different materials, such as polymers, is making zeolites even more beneficial for different applications. Zeolites can be incorporated into polymeric membranes forming a nanocomposite or composite structure in order to improve the permeability, and thermal stability of polymeric membranes. The “molecular sieve” character of zeolites is believed to give an improved ability to the final improved composite membrane for the discrimination between molecules of different sizes and shapes [2].

Zeolites having Si/Al ratios between 2 and 4 are called low-silica zeolites, 4 and 10 are called intermediate-silica zeolites, and higher than 10 are called high silica zeolites. Zeolite Beta is a high-silica, large-pore crystalline aluminosilicate material first synthesized by Wadlinger et al. in 1964. The framework structure of zeolite Beta possesses three-dimensional 12-membered ring pores with an interconnected channel system (Figure 1.1) [3].

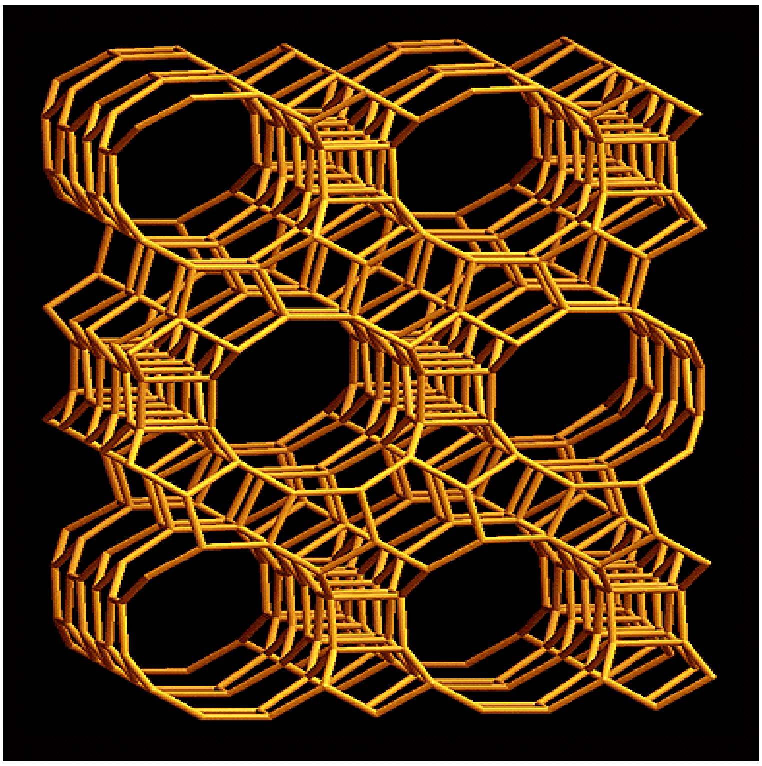

Figure 1.1 Zeolite Beta framework structure [4]

Incorporating zeolite Beta into polymeric membranes that are used in the polymer electrolyte membrane (PEM) fuel cell improves the thermal and mechanical properties as well as the proton conductivity. The synthesis of zeolite Beta with high yield and purity can be very important to achieve the desired performance from the final composite membrane. In the current study, aim was to synthesize pure zeolite Beta with high synthesis yield, and incorporate it into polyetherether ketone (PEEK) polymer to form composite membranes. Proton conductivities of resulting composite membranes were measured. Several different synthesis parameters can be studied in order to obtain the zeolite Beta with high yield [3]. In this study, effects of the silica to alumina (Si/Al) ratios, and crystallization time on the yield and crystallinity of zeolite Beta were investigated.

1.2 Polyetherether Ketone (PEEK)

Polyetherether ketone (PEEK) is one of the new generations of engineering thermoplastics. It is a kind of polyaryletherketone polymer which is suitable for use at high temperatures. The polyetherether ketones have repeating monomers of two ether and ketone groups [5] [6] (Figure 1.2). The materials have excellent chemical resistance, high strength and good resistance to burning but equally the high cost of these materials makes applications limited to those where the properties are very necessary.

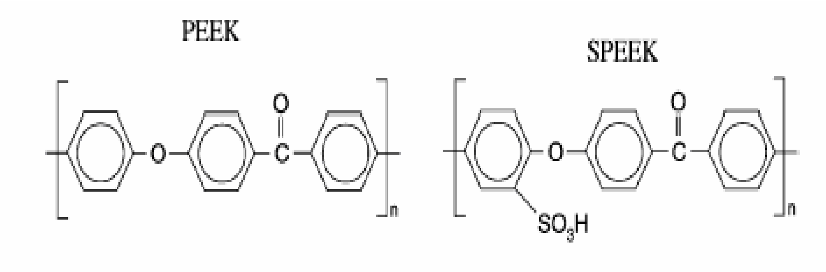

Figure 1.2 Structures of PEEK and SPEEK [6].

Recently, PEEK has been found to have a good thermal stability, appropriate mechanical properties, cost advantages, and some conductivity when sulfonated. The proton conductivity of SPEEK depends on the degree of sulfonation (DS). As DS increases proton conductivity of the SPEEK membrane gets close to the value of the Nafion membrane. Nafion is the most widely employed proton exchange membrane (PEM) for fuel cell applications. As shown in Figure 1.3, Nafion is a perfluorinated polymer containing small proportions of sulfonic or carboxylic ionic functional groups [6], [7], [8].

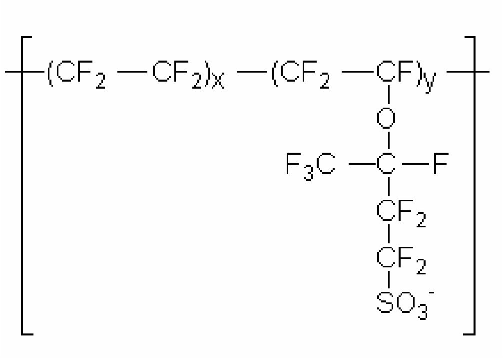

Figure 1.3 Structure of Nafion [8].

On the other hand, DS also affect mechanical stability of the membrane. The highly sulfonated membranes swell under the humidified conditions of fuel cell environment and lose their dimensional stability. The membranes with DS in the range 45–55 % can have satisfactory mechanical properties. However proton conductivity is not sufficient enough for a good fuel cell performance at this DS range. The proton conductivity of SPEEK membranes can be improved by incorporating proton conductor additives into the polymer matrix [6], [7].

1.3 Fuel Cells

Fuel cell is an electrochemical device that directly converts the chemical energy of fuel into electrical energy and heat. Fuel cells have many advantages like high efficiency, low or zero emissions, no noise, having no moving parts, modularity, and simplicity when compared with the conventional energy conversion technologies. The efficiency of the fuel cell is much higher than the efficiency of internal combustion engines; so fuel cells are attractive for automobile applications. Also, the efficiency of the fuel cell is higher than the efficiency of conventional power plants that makes fuel cells suitable for decentralized power generation. Since the outputs of the fuel cells are air and water, fuel cells are environmentally friendly devices. Hydrogen is used in the fuel cells as fuel. If hydrogen is produced from methanol some emissions are generated; but these emissions are lower than the conventional energy conversion technologies. Additionally, fuel cells exhibit a long life since there are no moving parts [9].

Polymer electrolyte membrane is the most important part of the PEM fuel cells. It conducts protons. However it is impermeable to gases. The membrane acts as the electrolyte. It is squeezed between the two porous, electrically conductive electrodes that are made from either carbon cloth or carbon fiber paper (Figure 1.4). There is a catalyst layer between the membrane and the electrodes. Catalyst layer consists of platinum supported on carbon. Electrochemical reactions occur at the surface of the catalyst. Hydrogen (H_2) consisting of one electron and one proton is fed on one side of the membrane. It splits into a proton (H^+) and an electron (e^-):

$$H_2 \rightarrow 2H^+ + 2e^- \qquad (1.1)$$

Electrons travel through the electrodes, and protons pass through the membrane. On the other side of the membrane protons passed through the membrane meet with the oxygen (O_2) fed on that side of the membrane. Electrochemical reaction occurs and water (H_2O) is produced:

$$½O_2 + 2H^+ + 2e^- \rightarrow H_2O + \text{heat} \qquad (1.2)$$

The water is removed from the cell by excess oxygen. The net result of these simultaneous reactions is current of electrons through an external circuit. The hydrogen side of the membrane is negative and it is called anode. The oxygen side of the membrane is positive and it is called cathode [10].

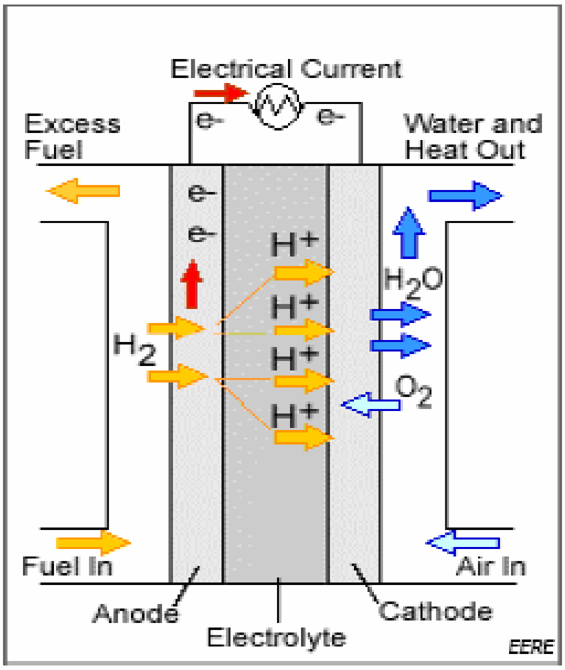

Figure 1.4 PEM Fuel Cell [10]

PEM fuel cells have various advantages among the other types of fuel cells. Compared to other types of fuel cells PEM fuels have low volume and weight. They also have an advantage of fast start up since the operating temperatures are relatively low (typically, 353 to 393 K). They operate with zero emissions of environmental pollutants; so they are clean energy devices. Since for the operation of a PEM fuel cell hydrogen and oxygen is needed and water is produced, they do not require any corrosive fluids. However current use of PEM is limited with a very narrow operation temperature of about 80 °C due to the current perfluorosulfonic acid based Nafion membrane. The operation temperatures of 80 °C cause the platinum (Pt) anode electro catalysts to be poisoned by the CO even if its concentration in the hydrogen is at the 5-10 ppm level [4] [5]. Moreover, hydrogen storage is another problem for PEM fuel cells [7] [9].

CHAPTER 2

REVIEW OF PREVIOUS WORKS

2.1 Synthesis of Zeolite Beta

Zeolite Beta is an important crystalline material that is used in many industrial applications and fine chemical industry. The “molecular sieve” character of zeolite Beta allows it to discriminate between molecules of different sizes and shapes; so it is also beneficial for incorporation with different materials such as polymers [2]. In the current study, it is aimed to synthesize zeolite Beta with high synthesis yield and purity; investigate the effects of Si/Al ratio, and synthesis time on yield. Additionally, synthesized zeolite Beta is aimed to be incorporated into polyetherether ketone (PEEK) in order to have a composite membrane. The proton conductivities of the composite membranes were measured. For that purpose, previous studies about synthesis of zeolite Beta were presented and membrane studies for fuel cell applications in the literature were mentioned.

Schoeman et al. [11] synthesized zeolite Beta for the thin film preparations. They used a colloidal silica suspension as a silica source. The suspension was freeze dried to a powder form. Sodium aluminate or aluminum isopropylate was the sources of alumina. As an organic templating agent, tetraethyl ammonium hydroxide (TEAOH) was used. Sodium hydroxide was the additional sodium source. Double distilled water was used for all experiments. For the synthesis, freeze dried silica was dissolved in a portion of the TEAOH solution by heating. Remaining TEAOH solution was used to dissolve sodium aluminate and sodium hydroxide. Then, aluminate solution was slowly added to silica solution with stirring, and finally that solution was put into the polypropylene reactor submerged in a silicone oil bath that was at 100 °C. The synthesized zeolite Beta was filtered by centrifuge. The organic template was removed by calcination in air at 600 °C.

Zeolite Beta product was analyzed by dynamic light scattering in order to find the particle size; plasma-emission spectrometry (ICP-AES) in order to find the Si/Al ratio of the zeolite products; scanning electron microscopy (SEM) to determine the morphology of the crystals; X-ray diffractometer (XRD) to analyze the calcined and non-calcined samples; N_2 adsorption according to BET method to find the specific surface areas of the samples. As shown in the Figure 2.1, characteristic peaks of zeolite Beta are at 2θ≈ 7.8°, and 2θ≈ 22.4°.

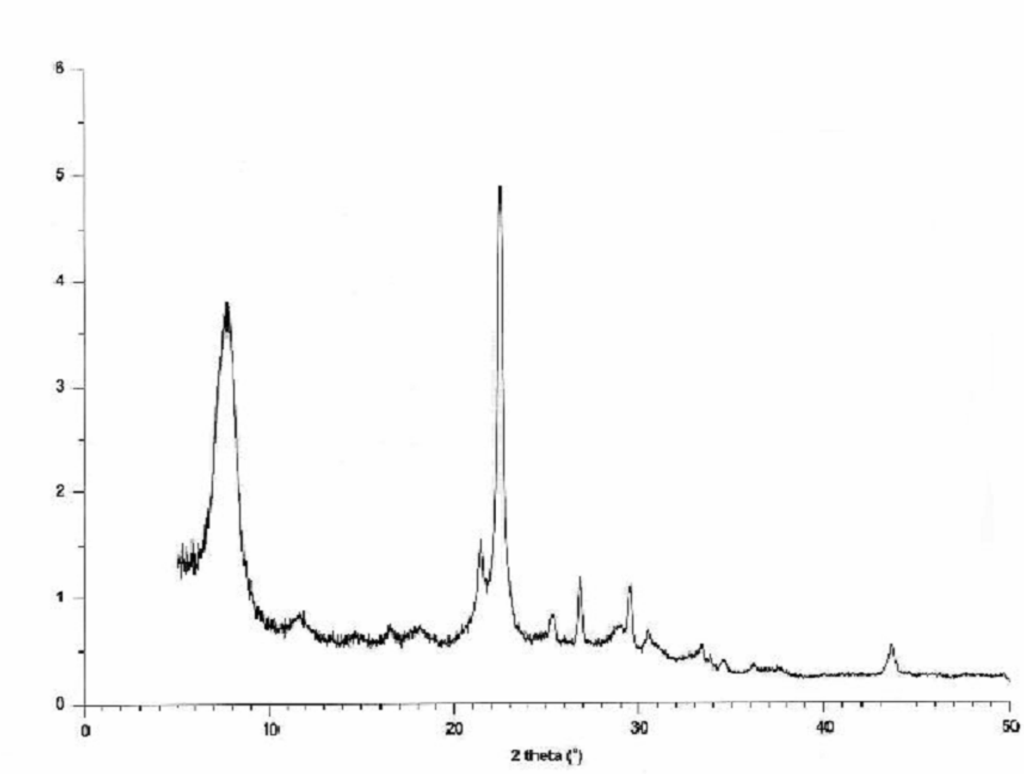

Figure 2.1 Powder X-Ray diffraction patterns of zeolite Beta with a batch formula of $1.97Na_2O$: $1.00K_2O$: $12.5(TEA)_20$: Al_2O_3: $50SiO_2$: $750H_2O$: 2.9HCl for 16 days [12]

They obtained zeolite Beta in crystalline phase only for Si/Al ratios between 12.5 and 25 (Table 2.1). They observed that the crystal size did not appear to be affected by the alumina content for Si/Al ratios of 12.5 to 25. They found the average crystal size within a range of 150 to 175 nm. From the SEM micrographs it was determined that the crystal size distribution was narrow and the crystals were slightly cubical with a grainy surface. When it comes to the effect of aluminum on the zeolite Beta yield (g zeolite Beta/100 g suspension), as the alumina content of the synthesis mixture increased, yield also increased (Table 2.1).

Table 2.1 Data collected from runs following hydrothermal treatment of mixtures with the molar composition 1.33Na_2O: 7.5TEAOH: xAl_2O_3: 25SiO_2: 363H_2O [11]

Run	**x**	**Crystal size (nm)**	**Crystalline phase**	**Zeolite yield (g/100 g sol)**	**Crystallization time (days)**
B1	0	>500	S	Very low	49
B2	0.025	>500	S + B	-	45
B3	0.063	>500	S + B	Very low	14
B4	0.100	175	B	0.7	11
B5	0.125	152	B	2.2	10
B6	0.250	160	B	9.4	6
B7	0.400	170	B	-	7
B8	0.500	161	B	20.6	8

where;
B: Zeolite Beta
S: Silicalite-1

Knowledge of the zeolite yield and the composition may be helpful to understand the growth limiting nutrient. In the study of Schoeman et al. [11], it was observed that the crystallization was terminated at a point when the alumina content of the solution reached an equilibrium level. For the runs with low alumina contents very little alumina was available for the incorporation into the crystal lattice. For example, only 4 % of the silica and the 23 % of the alumina in the solution was consumed by crystal growth in run B4. On the other hand, in run B8 more than 90 % of the silica and alumina was consumed by crystal growth. The remaining aluminum content was enough to supply the solution phase with equilibrium concentration. As stated earlier, the crystal size distribution was nearly the same for all alumina contents. This result indicates that as alumina content of the solution increased, number of crystals increased also. It could be thought that, as alumina content of the solution increased zeolite Beta crystallization became easier. In other words, the rate of nucleation was higher for solutions with higher alumina content. The time that was necessary to have an ultimate crystal size decreased from 11 days to 8 days in run B4 to B8. Additionally, zeolite Beta crystals were stable in their mother liquor for extended periods of time such as 3 weeks.

Schmidt et al. [13] investigated the influence of different silica sources on the crystallization kinetics of zeolite Beta. The batch composition was the same for all syntheses: 23TEAOH: $2Na_2O$: $1Al_2O_3$: $50SiO_2$: $900H_2O$. For the preparation of the synthesis batch, firstly sodium aluminate was dissolved in distilled water first. Then the TEAOH solution was added with the mixture being stirred, and finally the silicon source was added. In order to investigate the effect of the temperature, the solutions were kept at 110 °C, 140 °C, and 170 °C. Also time changed from 40 to 250 hours. XRD, thermogravimetric analysis (TGA/DTA), solid state nuclear magnetic resonance spectrometer (NMR), and transmission electron microscopy (TEM) analysis were performed in order to characterize the synthesized zeolite Beta samples.

As a result of the experiments pure zeolite Beta was obtained at all temperatures. However crystallization rate of zeolite Beta was not the same for the batches that had different sources of silicon. The degree of conversion of the silicon source was calculated from the amount of silicon source in the starting gel and from the amount of silicon in the resulting. At 110 °C, the silica sol reacted fastest especially after 80 hours. There were no further new zeolite Beta crystals formed after 250 hours. The conversion of the silica sol had a maximum value of 0.8 and the conversion factor of aluminum was 1. This result suggested that, after all the aluminum was incorporated into the zeolite frame work, no more silica was added. Silica sol was the silicon source reacted fastest at 140 °C. Moreover, the synthesis occurred until 130 hours at that temperature, and the conversion of silica sol was 0.6. At 170 °C, the crystallization of zeolite beta proceeded very fast for all batches with different silicon sources. Tetraethyl orthosilicate (TEOS and fumed silica (AERO) reacted much faster compared with the reactions at 110°C and 140°C. Pure zeolite Beta was obtained in good yields with all silicon sources after only 40 hours. When it came to the morphology of the synthesized zeolite Beta, the crystals were larger spherical aggregates. The size of the zeolite Beta was the largest (350-450 nm) when synthesized from the solution with silica sol.

Camblor et al. [14], studied the effects of TEAOH/SiO_2 ratio, SiO_2/Al_2O_3 ratio, concentration of the gel, and agitation on the crystallization rate, average crystal size and crystal size distribution of zeolite Beta. For the batch solution they used amorphous silica, tetraethylammonium hydroxide, sodium aluminate, aluminum, sodium hydroxide, potassium hydroxide, sodium chloride, and potassium chloride. The gels had a molar composition of xNa_2O: yK_2O: $v(TEA)_2O$: Al_2O_3: $wSiO_2$: uH_2O: zHCl where w/(x+y)= 17, u/w=30 and 15, v/w= 0.25, 0.2, and 0.15; y/(x+y)= 0.33 and 0.47. They used tetraethyl orthosilicate, colloidal silica, and fumed silica as silicon sources. The batch solutions were prepared with sodium aluminate as alumina and sodium sources; and either tetraethyl orthosilicate (TEOS), silica sol, or fumed silica (AERO) as silicon sources.

XRD analysis was used to determine the crystallinity of the zeolite Beta by measuring the area of the peak at $2\theta \approx 22.4°$. Atomic absorption and flame emission spectroscopy were used to determine the concentration of the aluminum and the alkali cations in the solid phase. SEM was used to determine the crystal morphology.

The experiments resulted in only crystalline phase. The crystal size distributions (CSD) were always quite narrow but became wider as the SiO_2/Al_2O_3 in the gel was increased. It was found that higher the SiO_2/Al_2O_3 ratio, lower were the number of crystals produced per unit mass of gel. The efficiency of the silicon incorporation into the zeolite was shown to decrease progressively with the decrease of the aluminum content of the initial gel.

Eapen et al. [15] synthesized zeolite Beta by using tetraethylammonium bromide (TEA-Br) as an organic template under static and stirred conditions in the temperature range of 100-170 °C. They investigated the effects of SiO_2/Al_2O_3 ratio, alkalinity, gel dilution, amount of the seed crystals and alkali metal, nature of the organic template, time, and temperature of the synthesis. For the batch preparation they used tetraethylammonium bromide, sodium aluminate, sodium hydroxide, ammonium hydroxide solution, and seed crystals of previously synthesized batches. TEA-Br was selected as an organic template instead of TEAOH because of the high price of the TEAOH. However solubility of silica was known to be higher with TEAOH template. As the first step in synthesis, firstly, ammonium hydroxide was mixed with a solution of 16 g of TEA-Br and deionized water. Sodium aluminate and NaOH was added to that mixture. Finally, silica sol and seed crystals were added. The molar composition of the batch solution was $3.1Na_2O$: $15(NH_4)_2O$: $5(TEA)_2O$: $35SiO_2$: Al_2O_3: $656H_2O$. Zeolite Beta was characterized by XRD, SEM, framework I.R. techniques, atomic absorption, ICP, and sorption of different molecules. Percent crystallinity of the zeolite Beta was found by comparing the area under the peak $2\theta = 22.4°$ to that of the most crystalline sample obtained in their study.

As a result of the experiments it was determined that as the crystallization time increased to 8 days at 140 °C, crystallinity of the zeolite Beta also increased. SEM pictures of zeolite Beta samples indicated that there are no amorphous material and impurities. The size of the crystals was 0.5-0.7 µm with a cubical shape. It was seen that the crystal morphology changed with changing synthesis parameters. Dissolution of silica was known to be the first step for crystallization of zeolite Beta and hydrothermal crystallization of zeolite Beta follows liquid phase transformation; so the influence of the silica source on crystallization was studied. Maximum synthesis yield was obtained with silica sol. Also the effect of gel dilution (H_2O/SiO_2) was determined and it was found that the crystallization rate was enhanced in more concentrated systems. In fact for H_2O/SiO_2 value up to 55 the crystallization time increased up to 24 days to have a fully crystalline phase and for the H_2O/SiO_2 value below 19 the water content was not enough to prepare a homogenous gel.

Eapen et al. [15] also investigated the effect of SiO_2/Al_2O_3 on the crystallization of zeolite Beta. The values of the SiO_2/Al_2O_3 ratio of the synthesis mixture and the SiO_2/Al_2O_3 ratio of the synthesized zeolite Beta were close to each other (Table 2.2). They could obtain pure zeolite Beta only for a SiO_2/Al_2O_3 ratio within the 15 and 58 at 140 °C. As synthesis temperature increased to 170°C with a SiO_2/Al_2O_3 ratio of 60, zeolite ZSM-12 was seen with zeolite Beta. They also observed that as the aluminum content of the batch solution increased the incorporation of the silica into the zeolite framework was more efficient. In other words, as aluminum content of the synthesis mixture increased the zeolite Beta yield also increased.

Table 2.2 Unit cell composition of zeolite Beta by chemical analysis [15]

SiO_2/Al_2O_3 mole ratio	
In gel	**In product**
57.7	56.8
47.0	46.2
35.3	34.8
20.0	19.2

Influence of the aluminum source was another factor studied by Eapen et al. [15]. Aluminum sulfate, aluminum isopropoxide, and sodium aluminate were used as aluminum sources. It was found that the sodium aluminate had the highest synthesis yield. That may be due to the fact that sodium aluminate favored faster crystallization.

Guisnet et al. [16] studied the concentration of acid sites of non-dealuminated (Si/Al= 10), and dealuminated (Si/Al=20-90) zeolite Beta. They did not synthesize zeolite Beta. They used a commercial Beta synthesized by PQ Zeolites. Dealumination was done by treatment with HCl solution. The concentration of HCl was varied between 0.1-1.5 M at temperatures 30-100 °C. Zeolite Beta samples with different Si/Al ratios were obtained. The parent zeolite Beta was Na-Beta. After the acid treatment the zeolite Na-Beta became H-Beta. The concentration of acid sites was determined by IR studies of pyridine sorption. It was found that the dealumination removed both Brønsted and Lewis sites. The increase of the Si/Al ratio from 10 to 35 caused a two fold decrease in Brønsted sites, and a five fold decrease in Lewis sites. As shown in Table 2.3, the increase in Si/Al ratio by acid treatment caused the acid sites of the zeolite H-Beta to decrease.

Table 2.3 Concentrations of framework Al, Brønsted and Lewis acid sites of zeolite Beta [16]

Zeolite	**$Al_{framework}$ (per unit cell)**	**Brønsted sites (per unit cell)**	**Weak Brønsted sites (%)**	**Lewis sites (per unit cell)**
HB-10	3.88	2.0	32	1.49
HB-20	2.72	1.9	24	0.82
HB-35	1.69	1.0	13	0.27
HB-40	1.54	1.1	13	0.17
HB-70	0.84	0.62	12	0.05
HB-90	0.73	0.40	17	0.05

where;

10, 20, 35…90 represents the Si/Al ratio of the zeolite Beta.

Verhoef et al. [17] synthesized zeolite Beta in order to use as a solid acid catalyst in liquid and gas phase esterification reactions. They also investigated the influence of the hydrophobicity of the catalyst. They synthesized zeolite Beta with Si/Al ratios of 10 (H-Beta 10) and 5 (H-Beta 5), and all silica Beta (H-Beta ∞) [18], [19]. Dealumination was done by treating 10 g of zeolite H-Beta 10 with a 50 ml of 0.1 or 1 M HCl solution. The zeolites were characterized by ICP, XRD, and MAS-NMR. The acidity of the zeolites was obtained by NH_3-TPD measurement. In order to find the hydrophobicity index (HI) of the zeolites, water and toluene vapor mixture was passed through a fixed bed adsorber at 35°C. Nitrogen was used as a carrier gas. It was observed that as Si/Al ratio increased the hydrophobicity of the zeolite Beta increased (Table 2.4).

Table 2.4 Zeolites with their hydrophobicity index (HI) [17]

Zeolite	**Si/Al**	**HI**
H-Beta	5	0.8
H-Beta	10	2.3
H-Beta	45	4.8
H-Beta	100	5.4
H-Beta	∞	10.8

Holmberg et al. [20] synthesized zeolite Beta and investigated the proton conductivity of sulfonic acid functionalized zeolite Beta nanocrystals. Additionally they synthesized phenethyl functionalized zeolite Beta (PE-BEA) with two different methods. The first method was the same with the method reported by Schoeman et al. [11]. Distilled water, 35 wt % aqueous tetraethylammonium hydroxide solution, and aluminum isopropoxide, were mixed first. Then 30 wt % colloidal silica was added. Finally, phenethyl trimethoxysilane (PETMS) was added. Molar composition of any given synthesis solution was $1Al_2O_3:(100*(1-w))SiO_2:100*(w)SiO_2(PETMS)$: 18 $(TEA)_2O(2OH)$: $1.11Na_2O$: $1.330H_2O$ where w could be varied between 1 and 0. The second method was applied according to the composition published by Camblor et al. [21]. Two precursor solutions were prepared for each batch solution. One of them was composed of Al powder and half of the required TEAOH. The other was composed of the remaining half of the recipe's TEAOH, distilled H_2O fumed silica, and PETMS. The solutions were mixed and then put into teflon lined stainless steel autoclaves. The composition of that solution was $1Al_2O_3:(v*(1-w))SiO_2$: $(v*w)SiO_2(PETMS):(0.26*v+1)(TEA)_2O(2OH^-):(15*v)H_2O$ where w was between 0 and 1, v changed from 25 to infinity. The total SiO_2/Al_2O_3 ratio was represented by the symbol v. After the synthesis, the zeolite PE-BEA samples were dispersed in 96 wt% concentrated sulfuric acid. The zeolite Beta was 2 wt % suspension in sulfuric acid. Treatment with sulfuric acid caused to structure directing agent to be removed and the sulfonation of the organic groups in the nanocrystals. Acid treated PE-BEA samples were called sulfonic acid phenethyl functionalized zeolite Beta (SAPE-BEA).

The zeolite Beta samples were characterized by dynamic light scattering (DLS), powder XRD, Fourier transform infrared spectroscopy (FT-IR), NMR, and TGA analysis. Proton conductivity of the samples was measured by two-probe electrode impedance spectroscopy. The XRD patterns of the parent and acid treated zeolite Beta showed that the characteristic peaks of the zeolite Beta were still very strong even after the strong acid treatments (Figure 2.2). It was observed that the 96 wt% sulfuric acid treatment most effectively removed the structure directing agent from the framework of the zeolite Beta nanocrystals (Figure 2.3).

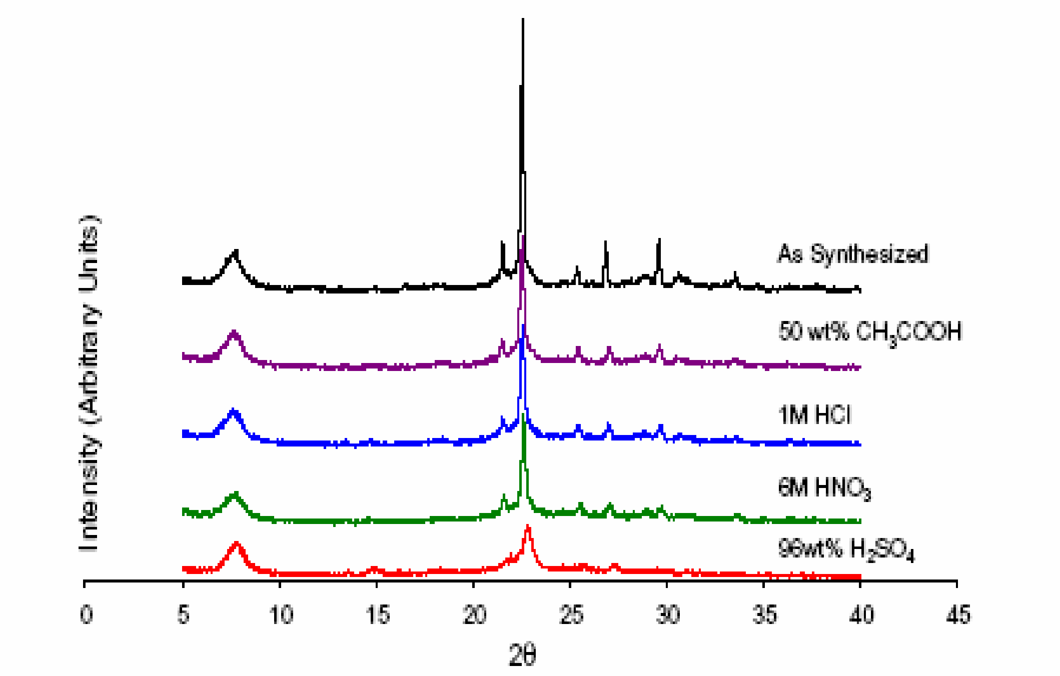

Figure 2.2 XRD patterns of as synthesized Beta nanocrystals according to the first method after 50 wt% acetic acid (CH_3COOH), 1M hydrochloric acid (HCl), 6M nitric acid (HNO_3), and concentrated sulfuric acid (96 wt% H_2SO_4) treatments [20].

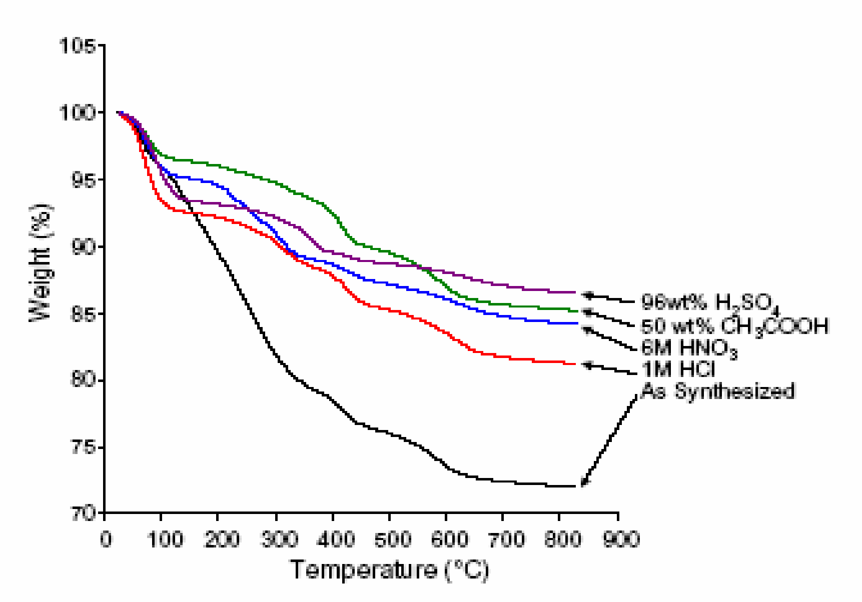

Figure 2.3 TGA curves of as synthesized BEA nanocrystals from the first method after 50 wt% acetic acid (CH_3COOH), 1M hydrochloric acid (HCl), 6M nitric acid (HNO_3), and concentrated sulfuric acid (96 wt% H_2SO_4) treatments [20].

Holmberg et al. [20] could obtain crystalline products from all synthesis mixtures. Fourteen days were required to have crystalline samples with a Si/Al ratio of 25. On the other hand 6 days were enough for Si/Al ratios of 50, 100, 200, and 400. The dimensions of the zeolite Beta nanocrystals were shown in the Table 2.5. It was easily seen that for smaller Si/Al ratios, the size of crystals was smaller.

Table 2.5 Mass median diameters of BEA, PE-BEA, SAPE-BEA nanocrystals synthesized with the second method [20].

Synthesis SiO_2/Al_2O_3	**Post synthesis treatment**	**Mass median diameter (nm)**
400	As synthesized	460
200	As synthesized	320
200	Acid treated	117
100	As synthesized	86
100	Acid treated	89
50	As synthesized	52
50	Acid treated	79
25	As synthesized	46
25	Acid treated	88

It was found that the proton conductivity of the phenethyl functionalized zeolite Beta was higher than the zeolite Beta (Table 2.6). Also proton conductivity was approximately doubled when Si/Al ratio was halved. The reason for the difference in proton conductivity might have been the decrease in crystal size with decreasing Si/Al ratios and the increase of the concentration of silanol nest defects caused by dealumination during treatment with sulfuric acid.

Table 2.6 Proton conductivity results for BEA, PE-BEA and SAPE-BEA nanocrystals synthesized with the second method [20].

Sample	**Average proton conductivity (S/cm)**	**Standard deviation**
BEA, v=50	1.47E-04	5.2E-06
BEA, v=50, after 80°C H_2SO_4	1.59E-04	2.14E-05
PE-BEA, v=50	1.86E-04	7.12E-06
SAPE-BEA, v=100, after 80°C H_2SO_4	1.17E-03	6.24E-05
SAPE-BEA, v=50, after 80°C H_2SO_4	2.96E-03	4.11E-04
SAPE-BEA, v=25, after 80°C H_2SO_4	1.15E-02	1.80E-04

2.2 Sulfonation of PEEK

Huang et al. [22] investigated the sulfonation of polyetherether ketone (PEEK) at different temperatures (22, 36, 45, and 55°C) and time by using concentrated sulfuric acid as solvent. Additionally, kinetic study of sulfonation reaction was studied. For sulfonation of PEEK, concentrated sulfuric acid, PEEK in powder form, dimethyl-formamide, dimethyl-acetamide and acetone were used.

For sulfonation, PEEK was dissolved in concentrated sulfuric acid at room temperature to suppress the heterogeneous sulfonation. After PEEK dissolved completely (1 h), the polymer solution was brought to the reaction temperature. After keeping the reaction solution for different durations (1-24 h), the sulfonated PEEK solution was quenched in deionized water under mechanical agitation to recover the modified polymer. Sulfonated PEEK was then washed with deionized water to remove the residual sulfuric acid until the pH value of the wash water was 5. After washing, sulfonated PEEK was immersed in an aqueous acetone solution and then in pure acetone in order to remove the water in the SPEEK–H. Samples were dried and then neutralized in a sodium hydroxide solution to be converted into its sodium salt form, SPEEK–Na.

The sulfonated PEEK samples were characterized in terms of ion-exchange capacity (IEC), H-NMR, contact angle, and solubility. The NMR spectra of SPEEK samples of different known sulfonation degrees were obtained (Figure 2.4). The intensity of the signals enhances expectedly as more sulfonic groups were attached to the aromatic ring in the PEEK repeat unit. The sulfonation degree (SD) of the SPEEK samples was quantitatively determined with Equation 2.1 by evaluating the intensity or peak area represented by all these protons as shown in Figure 2.5. As a result of the experiments it was observed that the sulfonation degree of PEEK could be well controlled by reaction time and temperature.

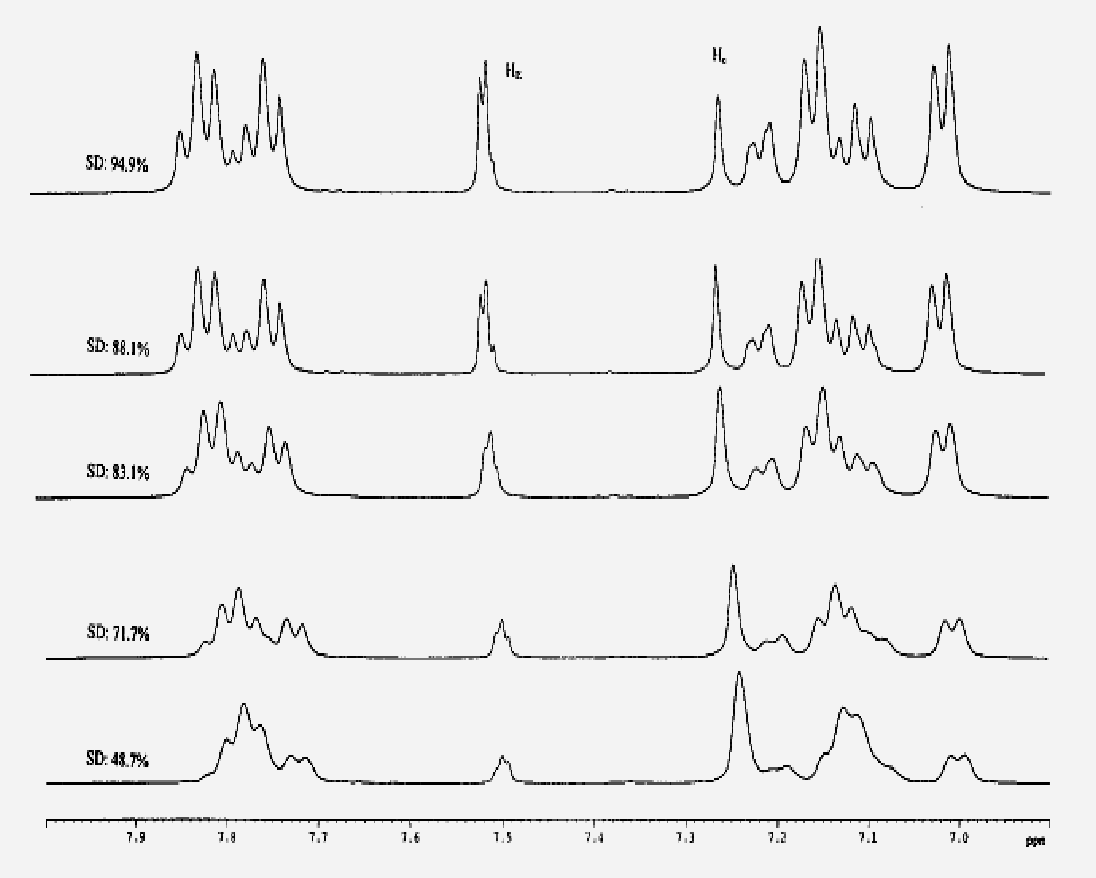

Figure 2.4 H-NMR spectra of the SPEEK samples of different sulfonation degrees [22].

$$\frac{n}{12-n} = \frac{A_{H_E}}{\sum A_{H_{AA'BB'CDE}}} \qquad (0 \le n \le 1) \qquad (2.1)$$

$$SD = n * 100\,\% \qquad (2.2)$$

where;

A_{HE}: The area of the signal, and the integrated peak area of the signals corresponding to all the other aromatic protons.

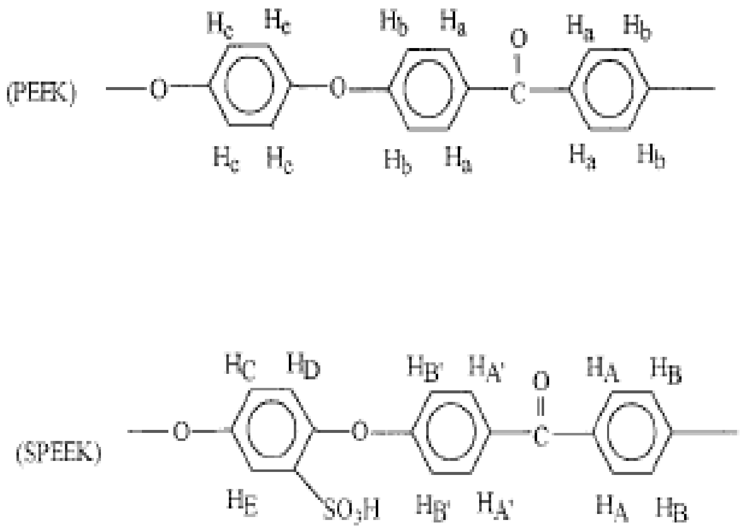

Figure 2.5 Nomenclature of the aromatic protons for PEEK and SPEEK repeat unit [22].

2.3 Incorporation of Inorganic Fillers into Membranes

Bac et al. [23] investigated the effect of incorporation of zeolites (4A and Beta) and fumed silica with Nafion and sulfonated poly(arylene ether)sulfone (SPES-40) membranes. SPES-40 polymer was dissolved in the solvent dimethyl acetate, DMAc. The inorganic additives were incorporated into the Nafion and SPES-40 solutions using ultrasonication and the solutions cast on glass surface to form the composite membranes. The loadings of the inorganic materials were kept constant at 15 weight percent. The proton conductivities of the membranes were found by four probe impedance spectrometer.

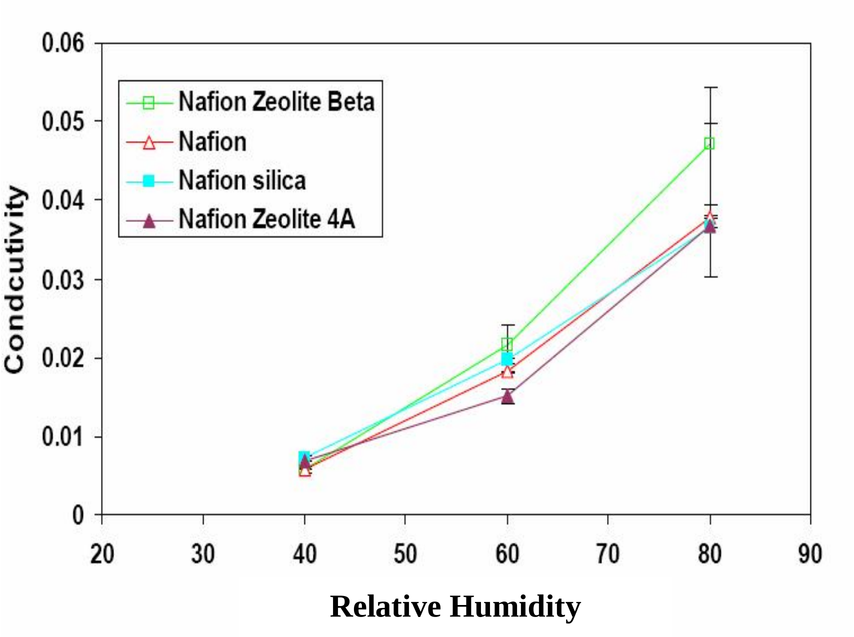

Figure 2.6 Conductivity of Nafion based composite membranes as a function of relative humidity at room temperature [23].

As a result of the experiments, they found that addition of zeolite Beta increased the proton conductivity of the Nafion membrane especially at high relative humidity ranges (Figure 2.6). Additionally, zeolite H-Beta was found to improve proton conductivity better than zeolite Na-Beta [23]. In the current study synthesized zeolite Na-Beta was converted to zeolite H-Beta since Bac et al. [23] had found that zeolite H-Beta improved proton conductivity better than zeolite Na-Beta. Moreover, polyarylene ether sulfone (SPES-40) was found that it could be an alternative membrane to Nafion when zeolite Beta was incorporated (Figure 2.7) [23].

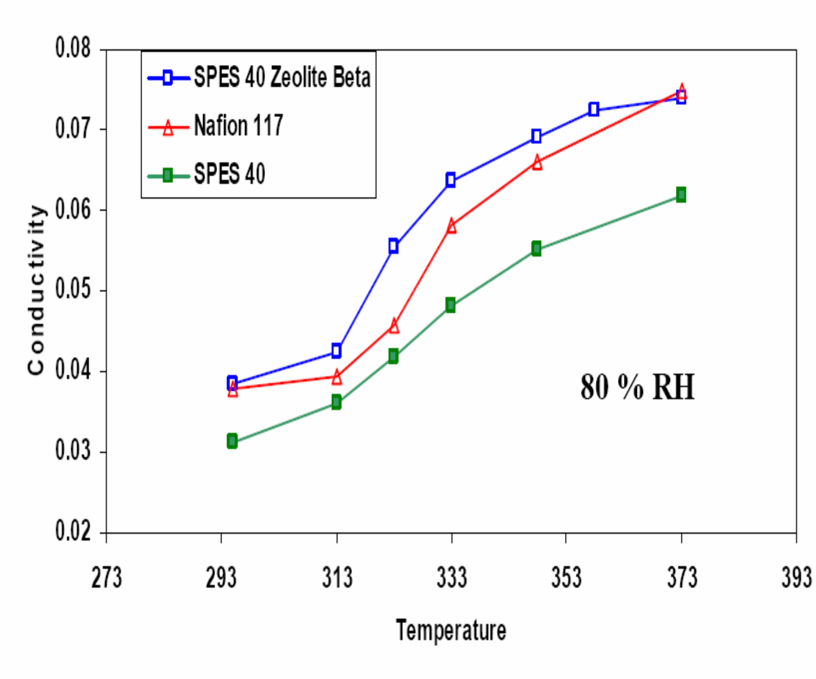

Figure 2.7 Conductivity of SPES-40 composite membranes as a function of temperature [23].

Thampan et al. [24] incorporated inorganic additives into Nafion membrane. The effects of particle size, chemical treatment, additive loading, and alternate processing methodologies were obtained. For the synthesis of inorganic additive (SO_4^{2-}/ZrO_2) the method explained in Arata’s work on metal oxides was applied [25]. Composite membranes were obtained with two different methods by mixing Nafion gel and inorganic particles followed by membrane casting, and synthesizing of nanoparticles with sol-gel processing in precast or commercial Nafion membranes.

The conductivity measurements were made with a perturbation voltage of 10 mV in the frequency range 0.01 Hz to 106 Hz using a Solartron SI 1260 FRA (Solartron, Hampshire, UK). As described by Schimidt et al. [26], real and imaginary components of the impedance were measured and the real *z* axis intercept was closely approximated to provide an estimate of the membrane resistance, and conductivity. In order to measure the conductivity a composite membrane sample was sandwiched between two electrodes as described by Johnson et al. [27]. After that, it was put in a humidity-controlled chamber. The humidity of the chamber was monitored utilizing a dew point/temperature probe. An air stream was saturated with water by bubbling through a humidifier. Also that air stream was heated in order to avoid the condensation in the chamber. The proton conductivity of the PEM was measured in the RH range from 10 to 90% at 90°C and in the RH range from 10 to 40% at 120°C.

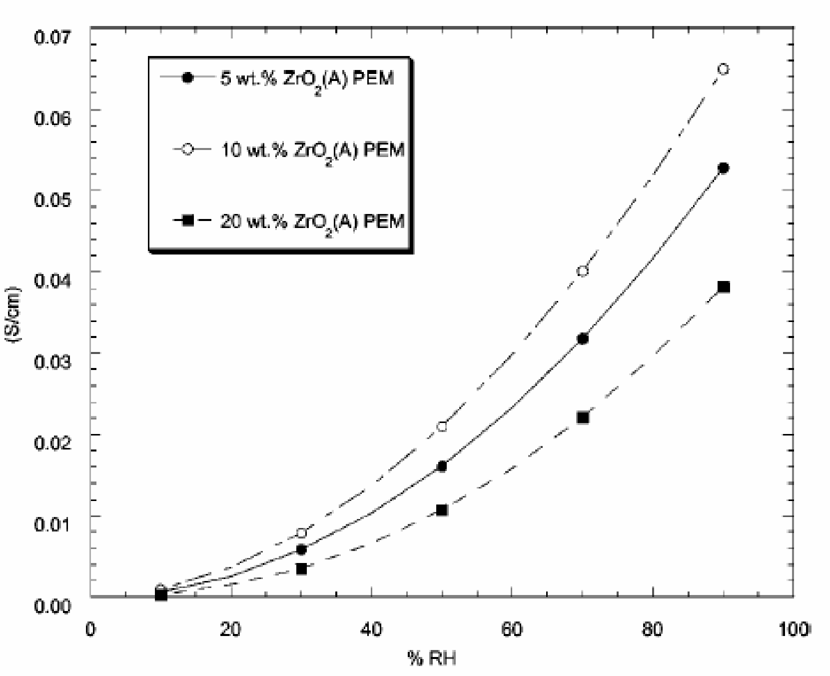

Figure 2.8 The conductivity of loaded composites PEMs at 120 °C vs. RH. [24]

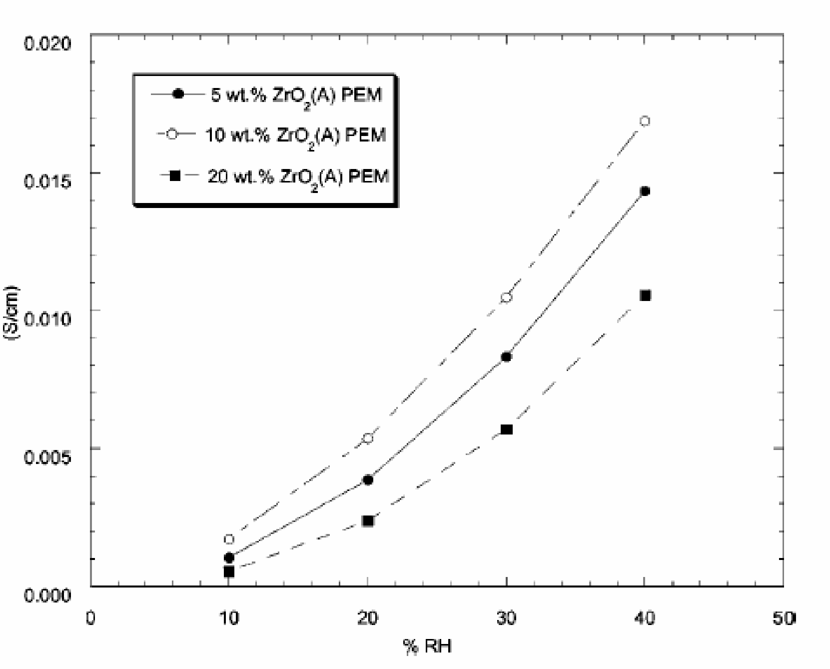

Figure 2.9 The conductivity of loaded composites PEMs at 90 °C vs. RH. [24]

As shown in Figures 2.8 and 2.9, the proton conductivity of loaded membranes was found to be optimum at 10 wt % loading. Additionally it was determined that the proton conductivity of the loaded membranes was higher at 120 °C than the proton conductivity at 90 °C. An increase in proton conductivity at higher temperature and lower RH conditions appeared to be an attractive candidate for incorporation into a membrane-electrode assembly for improved performance under these hot and dry conditions.

Krishnan et al. [7] prepared the solid proton conductor zirconium phosphate sulfophenylenphosphonate ((ZrSPP)x) with a composition of $Zr(HPO_4)_{0.65}(SPP)_{1.35}$ where SPP denoted metasulfophenylenphosphonate and incorporated with SPEEK. For the sulfonation procedure they added 25 g of PEEK into 500 ml of 95 wt % H_2SO_4. PEEK polymer was dissolved in an hour and the sulfonation reaction was continued for five hours. In order to stop the reaction they dropped the solution over ice-cold demineralised (DM) water. The fibers were washed with DM water until having a neutral pH value and stirred overnight to remove the residual acid. Sulfonated PEEK (SPEEK) was dried at 60 °C for 12 h followed by overnight drying at 110 °C under vacuum. Then, they dissolved SPEEK in dimethyl formamide (DMF) and mixed with required amount of zirconium phosphate sulfophenylenphosponate. The resulting mixture was stirred with magnetic stirrer and ultrasonication for an hour. The homogenous gel was finally poured to the petri dishes and the solvent was removed at 60 ºC for 12 h followed by further drying at 120 ºC under vacuum.

The composite membranes were characterized using FT-IR, powder X-ray diffraction, SEM, and DSC/TGA. The DSC graphs for SPEEK and the composite membranes are shown in Figure 2.10. The DSC curve for SPEEK showed glass transition temperature (Tg) around 195 °C. The Tg of the composite membranes increased by about 25 °C. This was due to restrictive segmental motion of the polymer chains in the composite membranes as the result of strong ionic interaction between SPEEK and (ZrSPP)x. As a result of the TGA analysis it was observed that the composite membranes had better thermal stability compared to that of SPEEK. The onset temperature for the thermal degradation was shifted to higher temperature with increase in concentration of Zr(SPP)x up to 30 wt. %. Thermal stability decreased at higher concentrations. The reason for that might have been the formation of bigger aggregates. But still decomposition temperature of composite membrane with even 50 wt % of (ZrSPP)x was slightly higher than that of SPEEK.

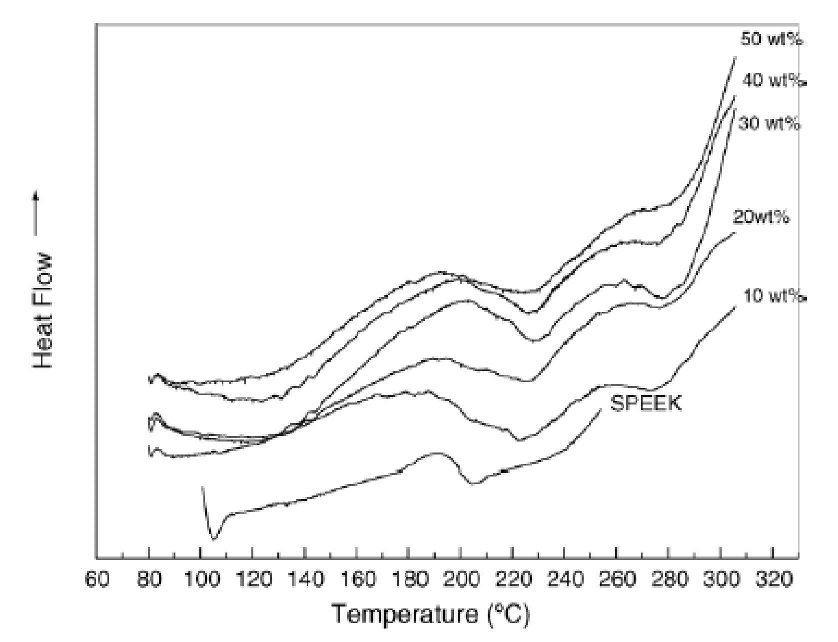

Figure 2.10 DSC curves for SPEEK and composite membranes [7]

The proton conductivity of the membranes was measured under 100 % relative humidity up to 70 ºC. The conductivity of the composite membrane with 10 wt % (ZrSPP)x was always found lower than that of SPEEK (Figure 2.11). They observed that the concentration of proton conductor at this level was not sufficient enough to establish continuous conduction pathway for proton transfer. However, the conductivity increased with increase in concentration of proton conductor up to 50 wt %. A three-fold increase in conductivity was observed for the composite membrane with 50 wt % (ZrSPP)x.

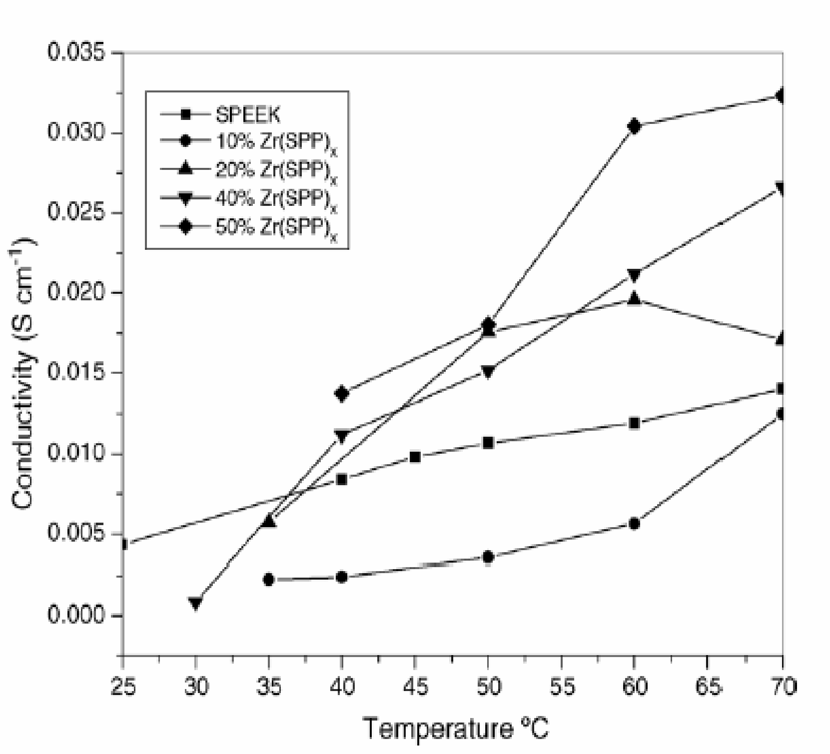

Figure 2.11 Proton conductivity of SPEEK and SPEEK + Zr(SPP)x composite membranes at different temperatures under 100 % relative humidity [7].

CHAPTER 3

EXPERIMENTAL PROCEDURE

3.1 Synthesis of Zeolite Beta

Zeolite Beta was synthesized with a formulation of $2.2Na_2O$: $1Al_2O_3$: $ySiO_2$: $4.6(TEA)_2O$: tH_2O (where TEA≡ tetraethylammonium) from two precursor solutions. Calculations made for the determination of the necessary amounts of sodium aluminate, deionized water, tetraethyl ammonium hydroxide, sodium hydroxide, and colloidal silica was shown in Appendix A. A sodium aluminate precursor solution were prepared first by dissolving sodium aluminate (52.9 wt % Al_2O_3, 45.3 wt % Na_2O, Riedel de Haën) in deionized water and tetraethylammonium hydroxide (TEAOH) solution (20 or 35wt % in water, Aldrich). Additional sodium was supplied from sodium hydroxide pellets (J.T. Baker, NaOH). The first precursor solution was kept in a HDPE (high density poly ethylene) bottle at 60°C for 15 minutes and then stirred by shaking the bottle until the solid particles were completely dissolved. To this solution, colloidal silica (40 wt % suspension in water, Sigma Aldrich, SiO_2) was added and the resulting solution was again kept at 60°C for 30 minutes in order to increase the solubility of the solid particles. The final gel was stirred until a homogenous gel was obtained and then it was placed into the teflon-lined autoclaves (Figure 3.1). The autoclaves were kept at constant temperature (150ºC) under static conditions for 5-15 days.

Figure 3.1 The addition of the batch solution into the teflon-lined autoclaves.

After keeping the autoclaves in the oven at the desired temperature and time, they were taken out from the oven and kept in a water bath. Then the zeolite crystals were filtered by vacuum filtration or centrifuge. The zeolites were washed with deionized water in order to decrease the pH of the samples and to remove impurities coming from the residual solution. The samples were dried at 80°C. These zeolite samples also include the organic template as well. In order to remove the organic template from the zeolite Beta crystals, the samples were calcined at 550ºC for 6 hours. Synthesized zeolite Beta was also called Zeolite Na-Beta since it contained sodium (Na) as an extra framework cation.

In order to convert the zeolite Na-Beta into zeolite H-Beta, ion exchange was applied by treating the samples with sulfuric acid (H_2SO_4) by the procedure proposed by Nadirler S. [28]. It is assumed that the treatment increases the surface acidity of the material by replacing Na^+ with H^+. Firstly, two grams of zeolite Beta were weighed and placed in a small beaker. 98 percent H_2SO_4 from Fisher Scientific and 1 M H_2SO_4 was added into the beaker in order to cover the surface of the material. The zeolites were allowed to remain in the solution for 24 hours in order to reassure the ion exchange to be completed. After the treatment, zeolites were filtered and washed in order to remove the excess sulfuric acid from the zeolites with deionized water until having a neutral pH value. The H-Beta crystals were dried at 65°C for 2 hours and stored in closed bottles.

3.2 Characterization of Zeolite Beta

Synthesized zeolite Na-Beta was characterized by X-Ray Powder Diffraction (XRD), Scanning Electron Microscopy (SEM)/ Energy Dispersive X-Ray Analysis (EDX), Thermogravimetric Analysis (TGA), and Inductively Coupled Plasma (ICP) Analysis. X-Ray Powder Diffraction (XRD) data were collected on a Philips PW1840 X-Ray Diffractometer using CuKα radiation. XRD was applied for all of synthesized zeolites before calcination. If the XRD peaks belonged to the zeolite Beta, calcined zeolite Na-Beta was also analyzed by XRD. After the acid treatment zeolite H-Beta was also analyzed by XRD. Zeolite Na-Beta samples synthesized with different Si/Al ratios and synthesis times were also analyzed by SEM and EDX. Thermogravimetric Analysis (TGA) was carried out on a 951 Dupont Thermogravimetric Analyzer. Samples were heated from 25 to 550°C at a rate of 5 °C/min under dry air flow (200 ml/min, NTP) in 150 μL crucibles. TGA was not applied for all of the synthesized samples but applied to the first ones. ICP analyses were applied in order to obtain the percents of Na, Si, and Al in the non calcined, calcined, and acid treated zeolite Beta.

3.3 Sulfonation of PEEK

PEEK was dried at 100 °C and ground before sulfonation. Dried PEEK was dissolved in H_2SO_4 at room temperature for 2.5 hours (Figure 3.2). The initial ratio of PEEK/H_2SO_4 concentration was maintained as 0.04 (g PEEK/ml H_2SO_4) for all experiments. After that, the solution was heated to 55 °C in the heated water bath. Solution was kept at this reaction temperature for 4 hours for sulfonation of PEEK. After 4 hours, the reaction was stopped by pouring it slowly into ice-cold distilled water (Figure 3.3). SPEEK was washed with distilled water until a pH value greater than 5 was reached. SPEEK was kept at room temperature for 24 hours and then completely dried in the oven at 100°C. After drying, SPEEK was stored in a dessicator to prevent moisture uptake from air.

Figure 3.2 Addition of PEEK into H_2SO_4

Figure 3.3 Sulfonation of PEEK is stopped by pouring into the distilled water.

3.4 Characterization of PEEK and SPEEK

PEEK and SPEEK were characterized by Nuclear Magnetic Resonance Spectrometer (NMR) and Differential Scanning Calorimeter (DSC) analysis. NMR was used for the determination of the sulfonation degree. DSC analysis helped to observe the glass transition temperature of the membranes. Additionally, proton conductivity of SPEEK membrane was found by 2-probe impedance spectrometer.

3.5 Membrane Preparation and Incorporation of Zeolite Beta

SPEEK was dissolved in a solvent dimethyl-acetamide (DMAC) and stirred with ultrasonication for 2 hours. For all of the membrane preparation 10 ml DMAC was used to dissolve 0.5 gr SPEEK. Zeolite H-Beta samples were added to DMAC and SPEEK solution at desired loadings. Then, the solution was poured over flat bottom petri dish (Figure 3.4). The solvent was removed by keeping the dishes in the vacuum oven at 80°C for 18 hours followed by further drying at 120 °C. Finally, SPEEK membranes were taken from the dishes and characterized. Membranes were characterized by proton conductivity measurements.

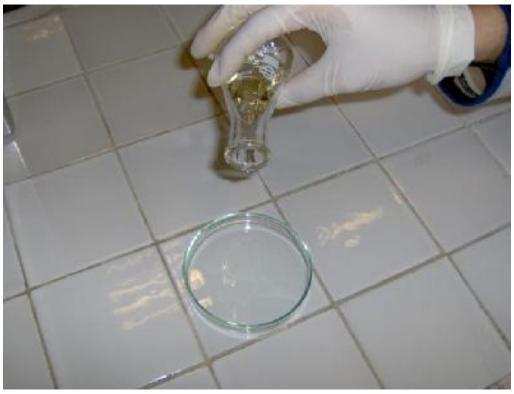

Figure 3.4 Pouring SPEEK loaded with zeolite H-Beta and dissolved in DMAC into the Petri dishes.

CHAPTER 4

RESULTS AND DISCUSSION

The experimental data obtained from synthesis of zeolite Beta, sulfonation of PEEK, and incorporation of zeolite Beta into the SPEEK are presented in this chapter. Zeolite Beta crystals with different Si/Al ratios, and synthesis times were synthesized. PEEK was sulfonated by treating with sulfuric acid. Zeolite Beta loaded SPEEK membranes were prepared. The results were discussed and compared with results reported in literature.

4.1 Results of Synthesis of Zeolite Beta

XRD peak spectrum of zeolite Beta synthesized with Si/Al ratio of 30 and synthesis time of 10 days is shown in the Figure 4.1. Calcination was observed to cause decrease in the crystallinity of the zeolite Beta since the area of the peak at $2\theta = 22.4°$ decreased (Figure 4.2). In the literature Schoeman et al. [11] also found similar XRD patterns upon the application of calcination. XRD peaks of zeolite Beta synthesized with Si/Al ratio of 30 and synthesis time of 7 days, calcined for 6 hours at 550ºC, and treated with 1 M H_2SO_4 for 4 hours showed that treatment with sulfuric acid solution caused a further decrease in the crystallinity of the samples (Figure 4.3). Holmberg et al. [20] also reported similar results (Figure 2.2).

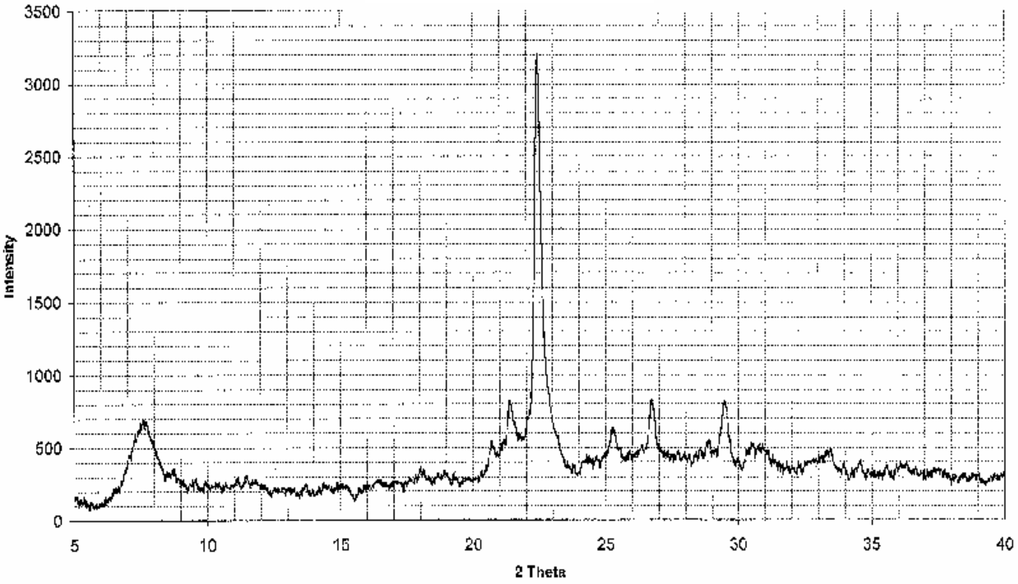

Figure 4.1 XRD peaks of zeolite Beta (BEA-9) synthesized with a Si/Al ratio of 30 in 10 days

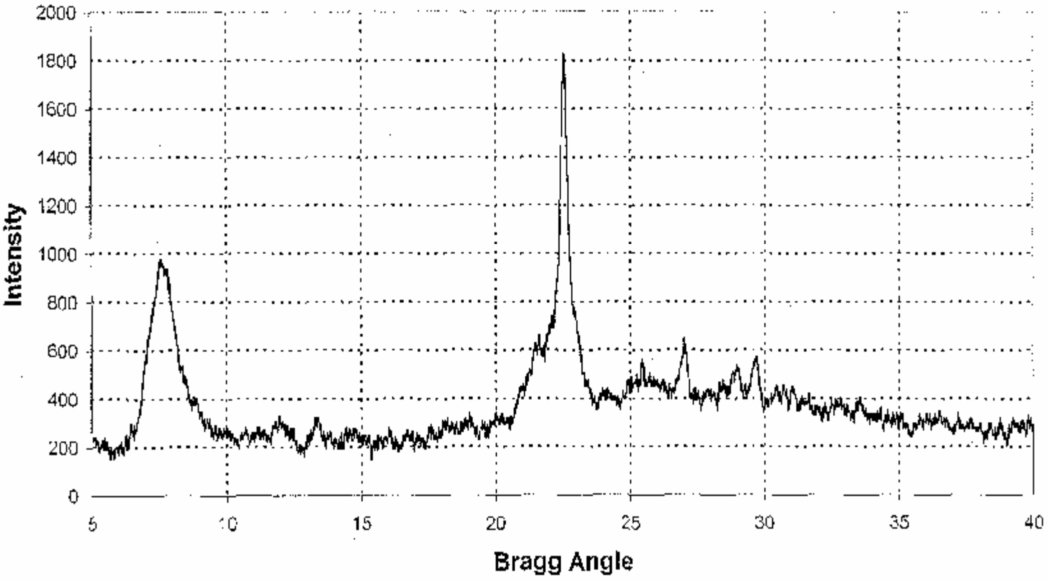

Figure 4.2 XRD peaks of zeolite Beta (BEA-9 calcined) synthesized with a Si/Al ratio of 30 in 10 days and calcined for 6 hours at 550ºC

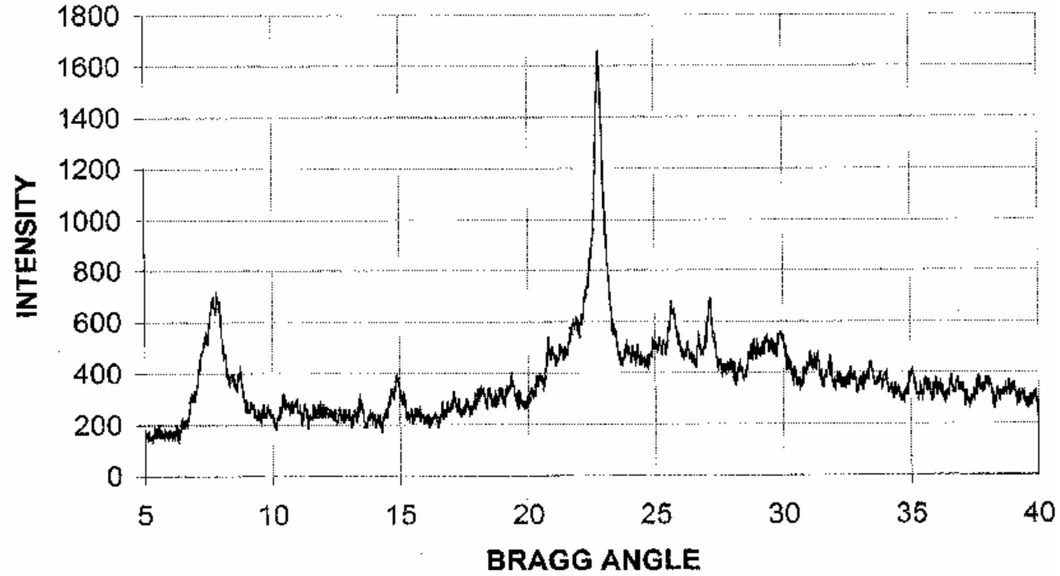

Figure 4.3 XRD peaks of zeolite Beta (BEA-11) synthesized with a Si/Al ratio of 30 in 7 days, calcined for 6 hours at 550ºC, and treated with 1 M H_2SO_4 for 4 hours

Zeolite Beta could be synthesized with Si/Al= 10-30 for 5-15 days of synthesis time with a batch formulation of $2.2Na_2O$: $1Al_2O_3$: $ySiO_2$: $4.6(TEA)_2O$: tH_2O. The list of experiments resulted with pure zeolite Beta phase are shown in the Table B.1 in Appendix B. When the Si/Al ratio in the batch solution was 5, XRD patterns did not give the characteristic $2\theta \approx 7.8°$ and $2\theta \approx 22.4°$ peaks of zeolite Beta (Figure 4.4). In addition, when the alumina content of the batch solution was changed to 0.5, 0.3, and 0 instead of 1, with SiO_2 kept at 60, zeolite Beta could not be obtained.

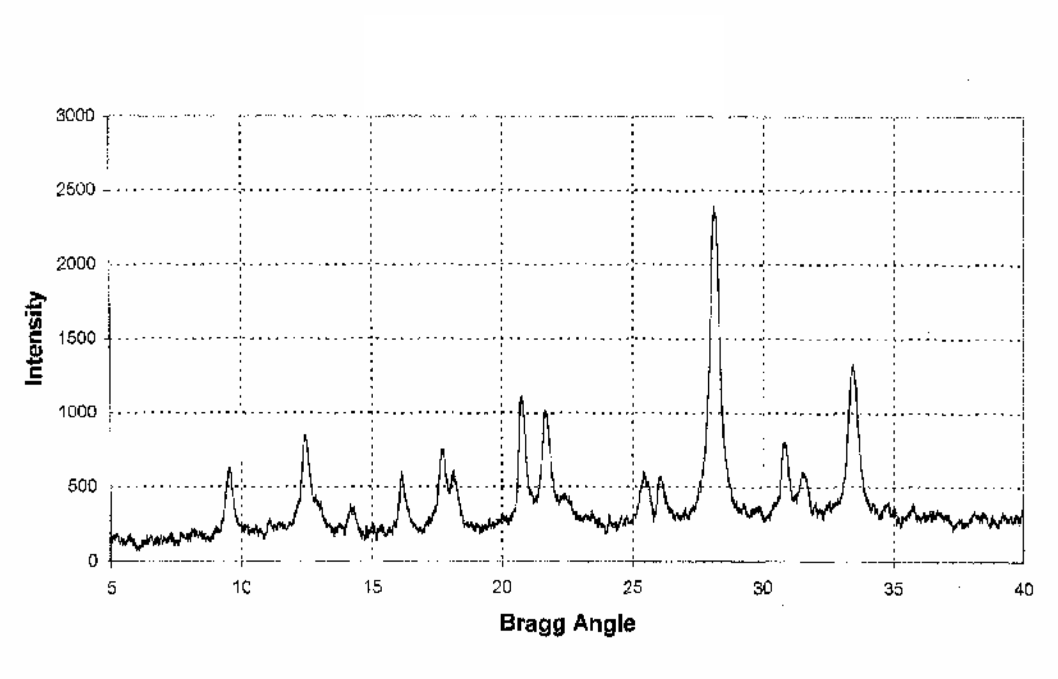

Figure 4.4 XRD peaks of inorganic material (BEA-17) synthesized with Si/Al ratio of 5

In the literature, Schomean et al. [11] could synthesize zeolite Beta with a batch formulation of $13.3Na_2O$: 75TEAOH: $1Al_2O_3$: $250SiO_2$: $3630H_2O$ at 100 ºC. In the current study, with a batch formulation of $2.2Na_2O$: $60SiO_2$: $0.3Al_2O_3$: $4.6(TEA)_2O$: $446.8H_2O$ or $7.33Na_2O$: $200SiO_2$: $1Al_2O_3$: $15.33(TEA)_2O$: $1488.33H_2O$ zeolite Beta could not be obtained at 150 ºC. The reason for that may be the higher TEAOH content (SiO_2/TEAOH= 3.3) of the batch solution of the Schoemean's. In the current study, for $7.33Na_2O$: $200SiO_2$: $1Al_2O_3$: $15.33(TEA)_2O$: $1488.33H_2O$ batch composition SiO_2/TEAOH ratio was 6.5. Consequently, with a $2.2Na_2O$: $60SiO_2$: xAl_2O_3: $4.6(TEA)_2O$: $446.8H_2O$ batch composition, zeolite Beta could not be obtained for x=0.5, and 0.3.

As a result of the EDX analysis it was found that the Si/Al ratio in the structure of the as-synthesized zeolite Na-Beta is close to the value of Si/Al ratio in the batch solution (Table 4.1). Detailed information about EDX results are shown in Appendix C3. As shown in Table 2.2, Eapen et al. [14] also found close values for the Si/Al ratios (20 and 57.7) in gel and in the product.

Table 4.1 Si/Al ratio in the batch solution and in the zeolite Beta structure.

Sample Name	Si/Al ratio in the Batch Solution	Si/Al ratio measured by EDX
BEA-3	10	9.5
BEA-7	20	20.5
BEA-9	30	33.7
BEA-11	30	37.1

As a result of the TGA analysis it was found that the weight loss of the zeolite Beta was about 20 percent at about 465 ºC for zeolite Beta synthesized with Si/Al ratio of 20 and a synthesis time of 10 days (Figure 4.5). Weight loss at that temperature is due to the removal of the organic template. Some other examples of TGA are shown in the Appendix C2.

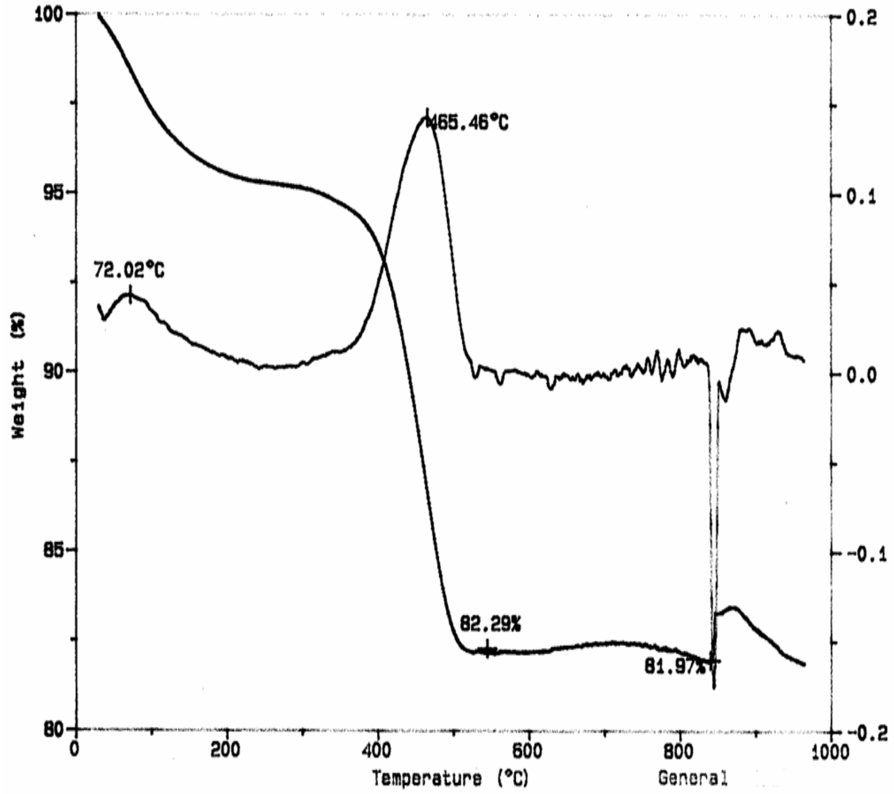

Figure 4.5 TGA of zeolite Beta (BEA-7) synthesized with Si/Al ratio of 20 for 10 days

SEM images of zeolite Beta are as shown in Figures 4.6, 4.7, 4.8, and 4.9. The crystal sizes of the as-synthesized zeolite Na-Beta crystals are given in Table 4.2. There was not a significant change in the crystal sizes for zeolite Beta samples with Si/Al ratios of 10, 20, 30, and synthesis durations of 7, 8, and 10 days. Schoeman et al. also observed that the crystal size did not appear to be affected by the alumina content for Si/Al ratios of 12.5 to 25 [11]. However, Holmberg et al. found that as Si/Al ratio decreased, the size of the zeolite Beta crystals also decreased [22].

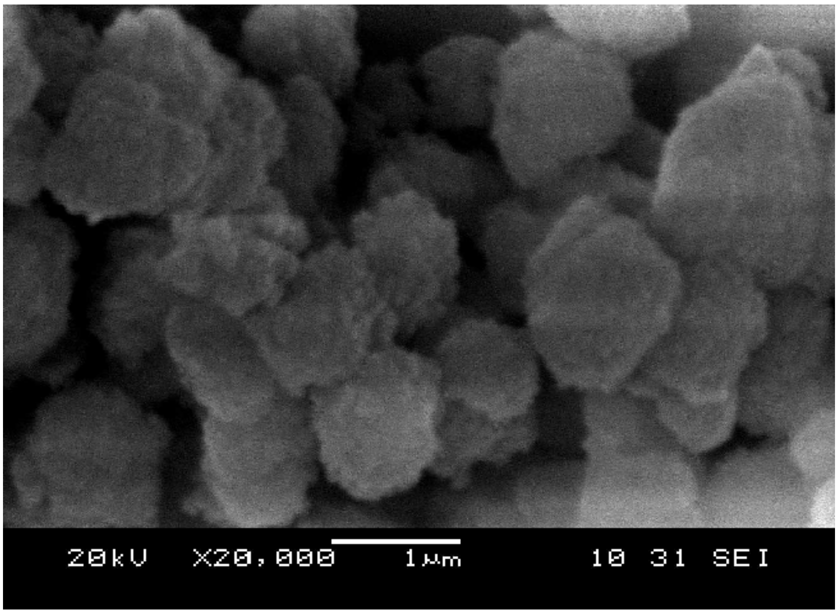

Figure 4.6 SEM image of zeolite Na-Beta synthesized in 8 days with a Si/Al ratio of 10.

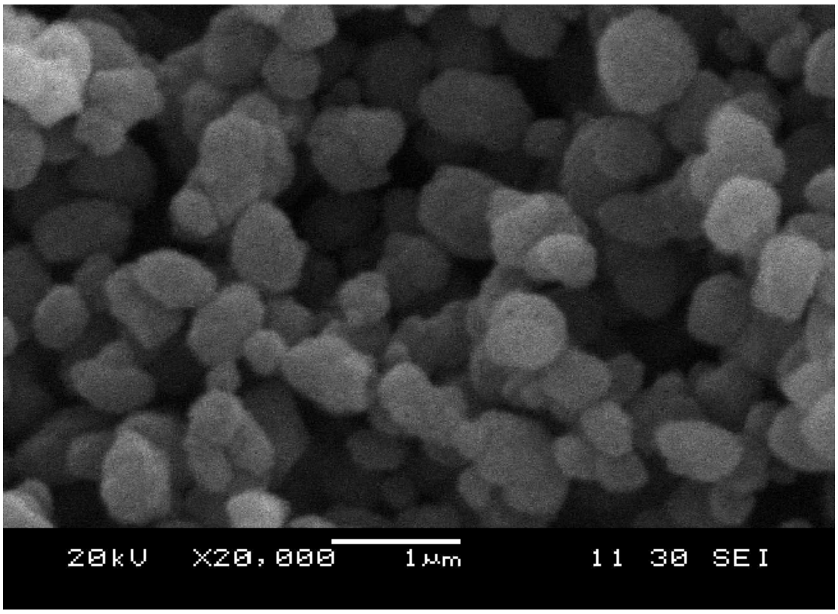

Figure 4.7 SEM image of zeolite Na-Beta synthesized in 10 days with a Si/Al ratio of 20.

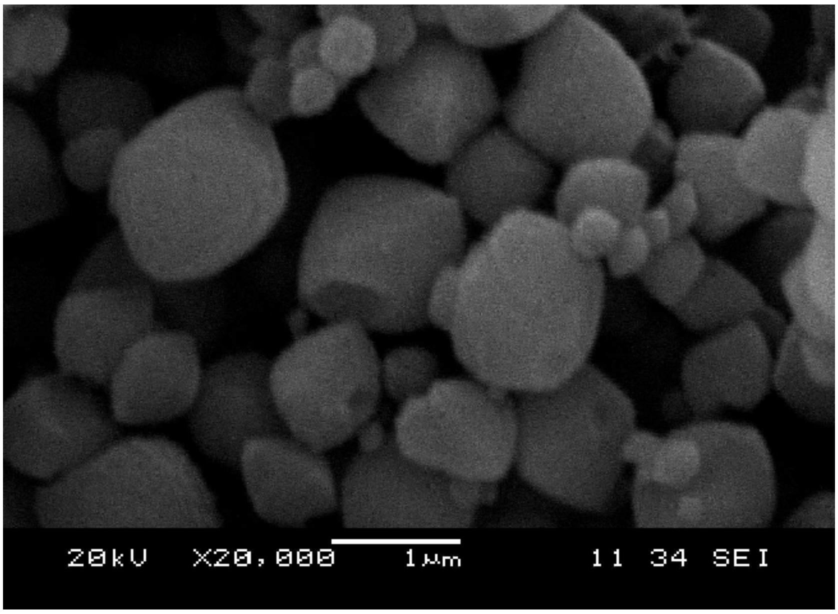

Figure 4.8 SEM image of zeolite Na-Beta synthesized in 10 days with a Si/Al ratio of 30.

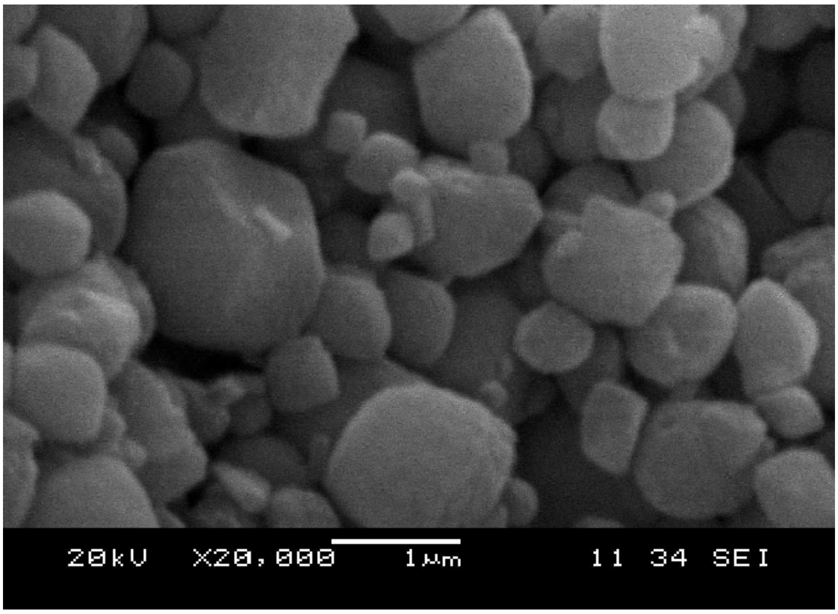

Figure 4.9 SEM image of zeolite Na-Beta synthesized in 7 days with a Si/Al ratio of 30.

Table 4.2 Effects of Si/Al ratio and synthesis time on the crystal size.

Experiment Number	**Si/Al Ratio**	**Synthesis Time (days)**	**Average Crystal Size (µm)**
BEA-3	10	8	0.9
BEA-7	20	10	0.6
BEA-9	30	10	0.7
BEA-11	30	7	0.8

As a result of the ICP analyses Na, Si and Al percents of the zeolite Beta samples were obtained (Table 4.3). It was seen that H_2SO_4 treatment caused the Na percent of the samples to decrease that showed Na ions were exchanged with H ions during acid treatment. Na quantities of the calcined samples (BEA-23 and BEA-25) were observed to increase (from 0.92 to 1.065 % and from 0.95 to 1.15). The reason for the increase in the Na percent of the zeolite Beta sample by calcination was the removal of the organic template ($(TEA)_2O$) from the zeolite structure. Treatment of calcined BEA-23 sample with 1 M H_2SO_4 solution for 4 hours and 18 hours decreased the Na percent from 1.065 to 0.0357 % and 0.012 %. These results indicated that longer treatment times cause further exchange of Na ions with H ions. Treatment of non-calcined zeolite Beta (BEA-25) with 1 M H_2SO_4 solution for 18 hours caused the Na percent to decrease from 0.95 to 0.245 % that showed that Na of non-calcined zeolite Beta samples could also be exchanged with H ions.

It was additionally observed that treatment of zeolite Beta with acid solution caused the Si/Al ratio of the zeolite Beta samples to increase. The increase in Si/Al ratios was predominantly due to the decrease in Al % of the zeolite Beta; so it could be said that acid treatment caused dealumination of zeolite Beta. Guisnet et al. [16] similarly found that acid treatment of zeolite Na-Beta caused it to be converted to H-Beta and to be dealuminated. They found that the dealumination removed both Brønsted and Lewis sites. In the current study, it was observed that calcination had an effect also on the Si/Al ratio. For BEA-23 sample calcination was seemed to have no effect on the Si/Al ratio. On the other hand, for BEA-25 sample calcination increased the Si/Al ratio from 14.42 to 26.28. Consequently, the effect of calcination on the Si/Al ratio of the zeolite Beta could not be explained by these values. Additionally, acid treatment of calcined samples was observed to cause more dealumination than the acid treatment of non-calcined samples.

Table 4.3 ICP analysis results for zeolite Beta samples.

Sample	**Si/Al in Batch Solution**	**Si %**	**Al %**	**Na %**	**Si/Al in Zeolite Beta**
BEA-23 (as synthesized)	15	30.08± 0.51	2.87± 0.04	0.92± 0.02	10.48
BEA-23 (calcined)	15	32.61± 0.21	3.44± 0.003	1.065± 0.007	9.48
BEA-23 (calcined and treated with 1 M H_2SO_4 for 4 hours)	15	34.89±0.34	0.6± 0.01	0.0357± 0.0003	58.15
BEA-23 (calcined and treated with 1 M H_2SO_4 for 18 hours)	15	34.15±0.15	0.61± 0.01	0.0120± 0.0001	55.98
BEA-25 (as synthesized)	20	29.56±0.21	2.05± 0.01	0.95± 0.01	14.42
BEA-25 (calcined)	20	35.74±0.49	1.36± 0.01	1.15± 0.01	26.28
BEA-25 (as synthesized and treated with 1 M H_2SO_4 for 18 hours)	20	33.36±0.49	1.254± 0.005	0.0245± 0.0005	26.60

4.2 Effects of Synthesis Time and Si/Al Ratio on the Yield of the Zeolite Beta

Figure 4.10 shows that as synthesis time increases from 5 to 10 days, zeolite Beta yield also increases from 39 to 46 with a ± 5 standard deviation, for zeolite Beta synthesized at 150 °C with a Si/ Al ratio of 10.

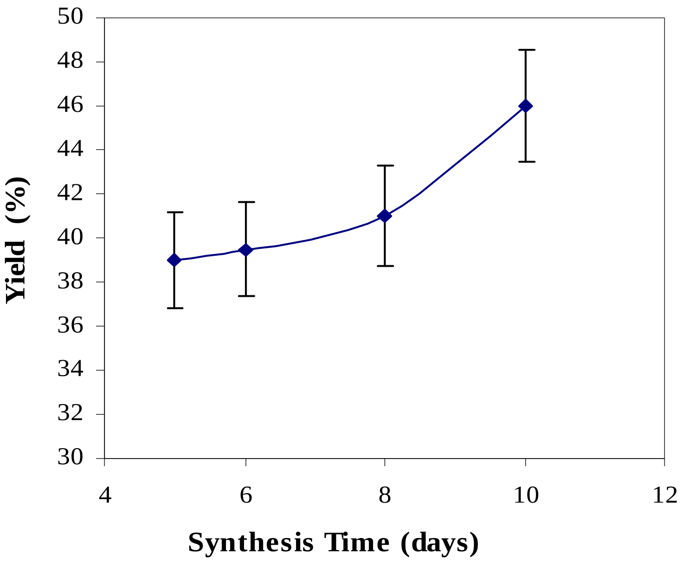

Figure 4.10 Yield vs. synthesis time of zeolite Beta synthesized at 150ºC with a Si/ Al ratio of 10.

In Figures 4.11 and 4.12, it was shown that as the Si/Al ratio of the zeolite Beta increases from 10 to 30, the yield of zeolite Beta is also increased for zeolite Beta synthesized at 150 ºC in 10 days, and zeolite Beta synthesized at 150 ºC in 8 days.

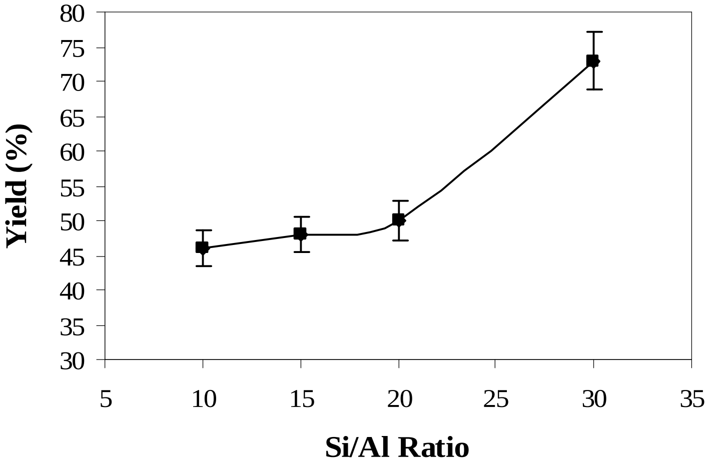

Figure 4.11 Yield vs. Si/ Al ratio of the zeolite Beta synthesized at 150 ºC in 10 days.

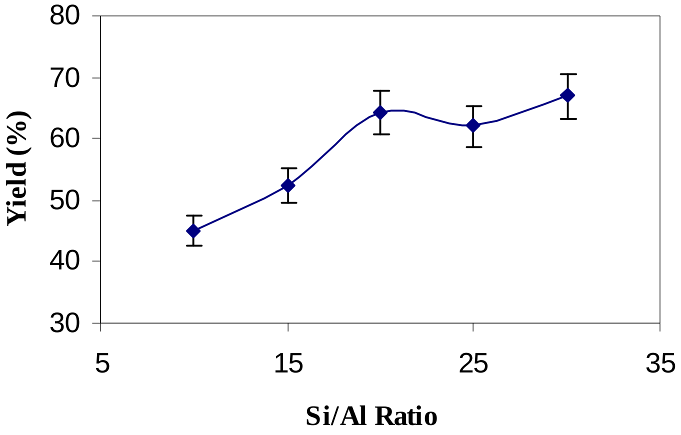

Figure 4.12 Yield vs. Si/ Al ratio of the zeolite Beta synthesized at 150 °C for 8 days.

The relative crystallinity of the zeolite Beta decreases from Si/Al ratio of 10 to 15 and then increases from 15 to 30 synthesis at 150 °C for 10 and 8 days (Figures 4.13 and 4.14). Relative crystallinity of the samples is found by using the XRD graphs, and comparing the area of the peak at 22.4° for each sample with the one which has highest area. It was expected that crystallinity would increase with increasing Si/Al ratios.

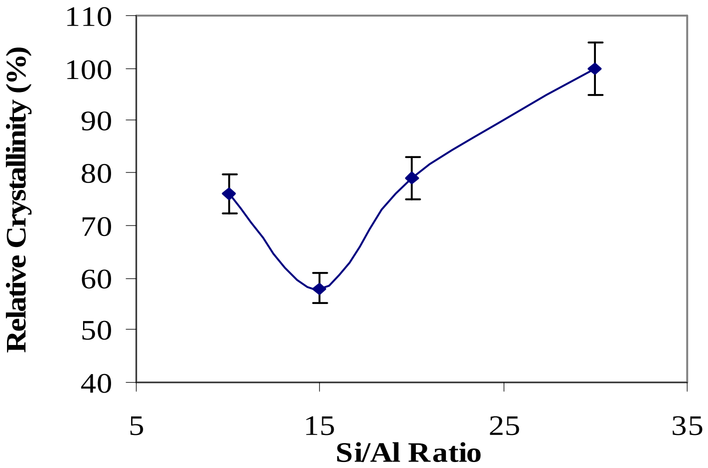

Figure 4.13 Relative crystallinity vs. Si/ Al ratio of the zeolite Beta synthesized at 150 °C in 10 days

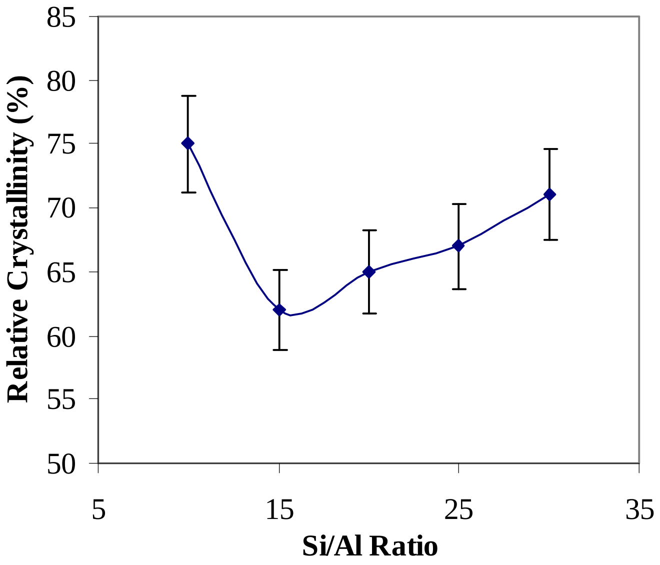

Figure 4.14 Relative crystallinity vs. Si/ Al ratio of the zeolite Beta synthesized at 150 ºC in 8 days.

4.3 Results of Sulfonation of PEEK and Incorporation of Zeolite Beta into SPEEK

Degree of sulfonation (DS) of the SPEEK was found as described by Huang et al. [22] as 72 %. The glass transition temperature of SPEEK was found as approximately 200 ºC. The NMR and DSC graphs of the SPEEK are shown in the Appendix D.

Three composite membranes (shown with numbers 4, 5, and 6 in Table 4.4) were made with incorporating zeolite Beta synthesized with Si/Al ratio of 30 for 15 days and treated with sulfuric acid for 24 hours. The standard deviation for the conductivities of these composite membranes was found as ± 0.02; so for all of the conductivity measurements standard deviation was accepted as ± 0.02. As a result of the incorporation of zeolite H-Beta into the SPEEK membranes sulfonated with the procedure as described in the Chapter 3.5, it was found that incorporation of zeolite H-Beta at 10 and 20 % loadings did not affect the proton conductivity significantly (Table 4.4). These measurements were from a two-probe cell which is known to yield approximate results.

Table 4.4 Electrical resistance and proton conductivity of the composite membranes SPEEK incorporated with zeolite Beta at 27 °C

Number	**Loading (%)**	**Average Thickness (µm)**	**Resistance (Ω)**	**Conductivity (S/cm)**
1	0	107.7 ± 3.2	6905	0.027 ± 0.02
2 (Si/Al=30,15 days, NaB)	10	64.7 ± 15.0	23340	0.013 ± 0.02
3 (Si/Al=30,15 days, 24 h H_2SO_4)	10	53.0 ± 2.6	70000	0.005 ± 0.02
4 (Si/Al=30,15 days, 24 h H_2SO_4)	10	73.5 ± 5.6	12958	0.021 ± 0.02
5 (Si/Al=30,15 days, 24 h H_2SO_4)	10	71.7 ± 8.1	23400	0.012 ± 0.02
6 (Si/Al=15, 8 days, 1M H_2SO_4 4 h, 30°C)	10	131.3 ± 7.0	5404	0.028 ± 0.02
7 (Si/Al= 10, 8 days, 1M H_2SO_4 4 h, 30°C)	10	93.7 ± 4.0	19850	0.011 ± 0.02
8 (Si/Al=15, 8 days, 1M H_2SO_4 18 h)	10	84.8 ± 13.3	41000	0.006 ± 0.02
9 (Si/Al=15, 8 days, 1M H_2SO_4 18 h)	20	76.8 ± 10.1	48000	0.006 ± 0.02

Bac et al. made a similar study and incorporated zeolite H-Beta into Nafion and SPES 40 membranes and they found that this lead to an increase in the proton conductivity. However, the conductivity was observed to be higher especially at higher temperatures (about 100ºC) and relative humidity ranges (80%). In their study, the proton conductivity of Nafion was measured as 0.04 S/cm, and the proton conductivity of SPES 40 was measured as 0.03 S/cm at room temperature and 80 % relative humidity [23]. The conductivities measured in the current study, as shown in the Table 4.5, are close to the values of SPES 40 membrane.

Thampan et al. [24] again found that addition of inorganic additives (SO_4^{2-}/ZrO_2) into Nafion membranes increased the proton conductivity again especially at high relative humidity ranges at 120 and 90 ºC. Krishnan et al. [7] made a composite membrane by incorporating zirconium phosphate sulfophenylenphosphonate ((ZrSPP)x) into SPEEK. They found that the proton conductivity of the composite membrane with 10 wt % of SPEEK was always lower than SPEEK and the conductivity increased with increase in concentration of proton conductor up to 50 wt % (Figure 2.11). In the current study, composite membrane, which had 10 and 20 wt % zeolite H-Beta loadings, did not cause the proton conductivity to increase similar to the result of the study of Krishnan et al. [7].

Holmberg et al. [20] found that as Si/Al ratio decreased, the crystal size decreased and the average proton conductivity of zeolite Beta increased. Verhoef et al. [17] found that hydrophobicity of zeolite Beta decreased with decreasing Si/Al ratio. This suggested that as Si/Al ratio decreased proton conductivity should increase because of low hydrophobicity index. When the inorganic additive of the membrane was hydrophilic it tends to take more water and so it helps to increase proton conductivity by increasing relative humidity. Consequently, low Si/Al ratio of the zeolite Beta cause low hydrophobic effect and so higher proton conductivity. Guisnet et al. [16] suggested that as the Si/Al ratio decreases, the number of acid sites increases. All of these literature results show that as Si/Al ratio of zeolite Beta decreases the proton conductivity increases so proton conductivity changes with changing Si/Al ratio and hydrophobicity and number of the acid sites. However, the current study suggests that zeolite Beta into SPEEK did not affect the proton conductivity significantly at room temperature and 100 % relative humidity. The reason for this might be that addition of zeolite H-Beta into SPEEK with 10 and 20 wt % loadings does not have any significant effect at room temperature.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

In the current study, zeolite Beta was synthesized at various Si/Al ratios and then incorporated into SPEEK membrane in order to have a composite membrane. The experiment with Si/Al ratio of 10, and synthesis time of 8 days at 150 °C were repeated four times and ± 5 % standard deviation was found. The yield was observed to increase with increasing Si/Al ratio from 10 to 30 for the same synthesis times and temperatures. Also by keeping the Si/Al ratio and temperature constant, it was found that increase in synthesis time from 5 to 10 days caused an increase in the zeolite Beta yield. For Si/Al ratios lower than 10 and higher than 30, pure zeolite Beta could not be obtained. When it comes to the effect of Si/Al ratio on relative crystallinity, again the relative crystallinities of samples synthesized at the same conditions were calculated by comparing the area of the XRD peak at 22.4°, and the standard deviation was found as ± 5 %. It was observed that the crystallinity decreased from Si/Al ratio of 10 to 15, then increased from Si/Al ratio of 15 to 30.

It was observed that Na content of the zeolite Beta decreased as treatment time increased from 4 to 28 hours. XRD analysis showed that treatment did not destroy the structure of the samples but decreased the crystallinity. ICP analysis also showed that sulfuric acid treatment increased the Si/Al ratio that means it caused dealumination also.

SEM and EDX analysis helped to understand the morphology and the Si/Al ratio of the synthesized zeolite Beta. It was observed that Si/Al ratio did not affect the average crystal size significantly. Si/Al ratio of the synthesized zeolite Beta samples were near the value of the Si/Al ratio of the experimental batch solution. XRD analysis helped to understand whether the synthesized sample was zeolite Beta or not. In addition, relative crystallinity of the samples was found by XRD peaks. TGA analysis showed that weight of the zeolite Beta decreased about 20 percent at about 455 °C. The reason for that weight loss is the removal of organic template from the structure. Zeolite Beta samples calcined at 550 °C for 6 hours were also analyzed by XRD and it was observed that the structure was not destroyed. By the combination of TGA and XRD analysis it can be said that, organic template of zeolite Beta can be removed by calcination without destroying the structure but causing the crystallinity of the samples to decrease.

Synthesized, and calcined zeolite Na-Beta samples were treated with concentrated and diluted sulfuric acid. The XRD analyses again helped to assess whether the structure was destroyed by acid treatment or not. Na content of the acid treated zeolite Beta was found to decrease by ICP analyses. That showed Na ions were ion exchanged with H ions by acid treatment. On the other hand, acid treatment was observed to cause the zeolite Beta to be dealuminated also. Additionally, acid treatment decreased the crystallinity of the zeolite Beta.

In order to see the effect of incorporation of zeolite Beta on the proton conductivity of the composite membrane, PEEK polymer was sulfonated. After sulfonation of PEEK, zeolite H-Beta was incorporated and the proton conductivities of the membranes were measured by 2-probe impedance spectrometer. Results of the preliminary proton conductivity measurements indicated that the incorporation of 10 and 20 wt % zeolite Beta into SPEEK did not change significantly the proton conductivity of the composite membrane at room temperature and 100 % relative humidity.

5.2 Future Work Recommendations

As a future work, the following recommendations can be taken into consideration.

Further investigations in the area of proton conductivity measurement are needed. Besides the proton conductivity measurements at room temperature and 100% relative humidity, measurements at higher temperatures and lower relative humidity levels can be done. So the effect of zeolite Beta incorporation into SPEEK on the proton conductivity can be investigated for higher temperatures and lower relative humidity levels. For these investigations, a new test set-up can be designed and constructed. Also, proton conductivities can be measured with a 4-probe measurement device instead of 2-probe impedance spectrometer since Lee et al. [29] found that the values of proton conductivities measured using the four-probe method were always higher (2-5 times) than those measured using the two-probe method at ambient humidity and temperature.

Zeolite Beta, with different compositions, synthesis methods, and chemical sources can be synthesized and the results of incorporation of these zeolite Beta samples on the proton conductivity can be observed. In addition, the sulfonation procedure can be changed and incorporated with zeolite Beta. Polymers other than PEEK can be used to cast composite membranes, and the proton conductivities of these different zeolite Beta nanocomposites can be compared.

The results of this study can be extended to the more general case of zeolite Beta synthesis. Experiments can be planned to use zeolite Beta for different applications. Development in a mathematical model for the proton conductivity and visualization of the proton conductivity will provide a better understanding of the proton conductivity.

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APPENDIX A

PREPERATION OF THE BATCH SOLUTION FOR THE SYNTHESIS OF ZEOLITE BETA

Calculations of the amounts of the tetraethyl ammonium hydroxide, colloidal silica, sodium aluminate, sodium hydroxide, and de-ionized water that were used for the preparation of the of batch solution are presented in this part. Calculations were firstly done by hand calculation and then by using Excel program formulas were written. The batch preparation calculations for the experiments BEA-1 and BEA-2 are shown as an example.

A.1 Calculation of the Necessary Amounts of the Reagents for Batch Preparation

Batch (Molar) Composition:

2.2 Na_2O: 20SiO_2: Al_2O_3: 4.6 $(TEA)_2O$: 440 H_2O

Source Materials:

- Tetraethyl ammonium hydroxide (TEAOH=$(C_2H_5)_4NOH$), 20 wt.% TEAOH in water,

MW $_{TEAOH}$ = 147.26 g/mol

- Colloidal silica, 40 wt.% SiO_2 suspension in water, MW $_{SiO2}$ = 60.08 g/mol
- Sodium aluminate, 52.9 wt.% Al_2O_3 and 45.3 wt.% Na_2O, MW $_{Al2O3}$ = 102 g/mol,

MW $_{Na2O}$ = 62 g/mol

- Sodium hydroxide (NaOH), MW $_{NaOH}$ = 40 g/mol
- De-ionized water

Batch Preparation

- Amount of TEAOH solution:

$2\ TEAOH + H_2O \rightarrow (TEA)_2O + 2\ H_2O$

-9.2 mol -4.6 mol 4.6 mol 9.2 mol

9.2 mol TEAOH (147.26 g/mol) = 1354.792 g TEAOH

1354.792 g TEAOH (100 g solution /20 g TEAOH) = 6773.96 g TEAOH solution

- Amount of colloidal silica:

20 mol SiO_2 (60.08 g/mol) = 1201.6 g SiO_2

1201.6 g SiO_2 (100 g colloidal silica/ 40 g SiO_2) = 3004 g colloidal silica

- Amount of sodium aluminate:

45.3 wt. % Na_2O, 55 wt. % Al_2O_3

There is 1 mol Al_2O_3 in the batch;

1 mol (102 g/mol) = 102 g Al_2O_3

102(45.3/52.9) = 87.3459 g Na_2O

87.3459 g Na_2O / (62 g/mol) = 1.4088 mol Na_2O comes from the sodium aluminate

Amount of sodium aluminate = 102 + 87.3459 = 189.3459 g

- Amount of sodium hydroxide:

Na_2O in the batch= 2.2 mol

Na_2O in sodium aluminate = 1.4088 mol

Na_2O comes from the sodium hydroxide = 2.2 – 1.4088= 0.7912 mol

$2\ NaOH + H_2O \rightarrow Na_2O + 2\ H_2O$

-1.5824 mol -0.7912 mol 0.7912 mol 1.5824 mol

1.5824 mol NaOH (40 g/mol) = 68.296 g NaOH

- Amount of water:

H_2O from TEAOH solution = 6773.96 g (0.8 g water/g TEAOH soln.)= 5419.168 g
5419.168 g (1 mol/18 g) = 301.06 mol
H_2O from TEAOH= 9.2- 4.6= 4.6 mol
H_2O from colloidal silica = 3004 g (0.6 g water/ g colloidal silica) = 1802.4 g
1802.4 g (1 mol/ 18 g) = 100.13
H_2O from NaOH = 1.5824-0.7912= 0.7912 mol

So; total H_2O comes from the TEAOH solution, colloidal silica, and NaOH is:
301.06 + 4.6 + 100.13 + 0.7912= 407.1212 mol

H_2O in the batch composition is 440 mol; 440 – 407.1212= 32.8788 mol= 591.8184 g water must be added.

Sodium aluminate = 189.3459 g
Colloidal silica= 3004 g
Sodium hydroxide= 68.296 g
Tetraethyl ammonium hydroxide= 6773.96 g
De-ionized water= 591.8184 g

So for a total 10627.42 g batch solution the necessary chemicals are shown as above. For 100 g batch solution, they can be recalculated in proportion as:

Sodium aluminate = 1.7817 g
Colloidal silica= 28.2655 g
Sodium hydroxide= 0.6426 g
Tetraethyl ammonium hydroxide= 12.7481 g
De-ionized water= 5.5688 g

A.2 Calculation of the Necessary Amounts of the Reagents for Batch Preparation by Excel Program

Batch (Molar) Composition:

2.2 Na_2O: 20SiO_2: Al_2O_3: 4.6 $(TEA)_2O$: 440 H_2O

Source Materials:

- Sodium aluminate, 52.9 wt.% Al_2O_3 and 45.3 wt.% Na_2O, Compound Formula

(Al_2O_3 1.346 Na_2O), FW= 185.4545 g/mol

- Colloidal silica, 40 wt.% SiO_2 suspension in water, Compound Formula (SiO_2.5.0067 H_2O), FW= 150.2006 g/mol
- Sodium hydroxide (NaOH.0.07 H_2O), FW= 41.26 g/mol
- Tetraethyl ammonium hydroxide (TEAOH=$(C_2H_5)_4NOH$), 20 wt.% TEAOH in water, Compound Formula (TEAOH.32.72 H_2O), FW=736.22 g/mol
- De-ionized water (H_2O), FW=18 g/mol

Pertinent Chemical Equations:

Al_2O_3 1.346 Na_2O= Al_2O_3 + 1.346 Na_2O

2 NaOH.0.07 H_2O + H_2O= Na_2O + 2.14 H_2O

2 TEAOH = $(TEA)_2O$ + H_2O

2(TEAOH.32.72 H_2O) = $(TEA)_2O$ + H_2O + 65.44 H_2O

Calculations (see Tables 1 and 2, below):

Al_2O_3 1.346 Na_2O = 185.45 45 g

20(SiO_2.5.0067 H_2O) = 3004.012 g

1.708 NaOH= 68.32 g

9.2(TEAOH.32.72 H_2O) = 6773.224 g

Table A-1 Mole composition of reagents necessary to form zeolite Beta synthesis mixture

Moles	Compound Formula	Na_2O	Al_2O_3	SiO_2	$(TEA)_2O$	H_2O
		2.2	**1**	**20**	**4.6**	440
1	Al_2O_3.1.407 Na_2O	**1.407**	**1**	**0**	**0**	**0**
20	SiO_2.5.0067 H_2O	**0.854**	**0**	**20**	**4.6**	**440**
		0	0	20	0	100.134
1.708	NaOH.0.07	**0.854**	**0**	**0**	**4.6**	**339.866**
		0.854	0	0	0	0.97356
9.2	TEAOH.32.72 H_2O	**0**	**0**	**0**	**4.6**	**338.8924**
		0	0	0	4.6	305.624
33.388	H_2O	**0**	**0**	**0**	**0**	**33.26844**

After Scaling Down by a factor of 106.3199 for 100 g batch (see Table A.2, below):

Sodium aluminate = 1.7449 g

Colloidal silica= 28.2645 g

Sodium hydroxide= 0.5969 g

Tetraethyl ammonium hydroxide= 63.7287 g

De-ionized water= 5.6649 g

Table A.2 Necessary amounts of the chemicals for the batch preparation

Moles	Compound Formula	FW	Mass	BATCH
1	Al_2O_3.1.407 Na_2O	**185.4545**	185.4545	**1.744927**
20	SiO_2.5.0067 H_2O	**150.2006**	3004.012	**28.26451**
1.708	NaOH.0.07	**40**	63.44	**0.596902**
9.2	TEAOH.32.72 H_2O	**736.22**	6773.224	**63.72872**
33.388	H_2O	**18**	602.082	**5.664941**

Procedure:

1- Preparation for the experiment
2- Weigh TEAOH solution
3- Weigh sodium hydroxide and put into TEAOH solution (2)
4- Weigh sodium aluminate, then put into sodium hydroxide and TEAOH solution (3)
5- Stir sodium aluminate, sodium hydroxide, and TEAOH solution (4) with magnetic stirrer bar for 5 minutes
6- Weigh colloidal silica
7- Keep colloidal silica (6) and sodium aluminate, sodium hydroxide, and TEAOH solution (5) at 60°C for 30 minutes
8- Stir sodium aluminate, sodium hydroxide, and TEAOH solution for 15 minutes
9- Add colloidal silica into sodium aluminate, sodium hydroxide, and TEAOH solution (8)
10- Heat the batch at (9) at 60°C for 30min
11- Stir (10) by hand shake for 15 minutes
12- Put (11) into autoclaves and into the oven
13- Clean the work space

Timeline Approximately 175 minutes

1-	25 minutes
2-4-	25 minutes
5-	5 minutes
6-	Carried out when (5) occurs
7-	30 minutes
8-	15 minutes
9-10-	30 minutes
11-	15 minutes
12-13-	25 minutes

APPENDIX B

EXPERIMENTS FOR THE SYNTHESIS OF ZEOLITE BETA

The batch compositions of all the experiments by which zeolite Beta could be obtained, experiment numbers, Si/Al ratios, synthesis time, and yield are shown in Table B.1. Additionally the experiments by which zeolite Beta could not be synthesized are presented in Table B.2. Then, the results for the effects of synthesis time and Si/Al ratio on yield and crystallinity are given in Tables B.3, B.4, B.5. The graphs corresponding to the effects of Si/Al ratio, and synthesis time were given in Chapter 4 in Figures 4.10, 4.11, 4.12, 4.13, and 4.14.

Table B.1 The compositions of the experiments by which zeolite Beta could be obtained at 150°C, synthesis time, and yield values

Batch Formula	**Experiment Number**	**Si/Al ratio in**	**Synthesis Time**	**Yield**
$2.2Na_2O$: $20SiO_2$: Al_2O_3: $4.6(TEA)_2O$: $440H_2O$	BEA-1 (07.27.05.1)	10	5	39
$2.2Na_2O$: $20SiO_2$: Al_2O_3: $4.6(TEA)_2O$: $440H_2O$	BEA-2 (07.27.05.2)	10	6	39.5
$2.2Na_2O$: $20SiO_2$: Al_2O_3: $4.6(TEA)_2O$: $440H_2O$	BEA-3 (08.12. 05.3)	10	8	41
$2.2Na_2O$: $20SiO_2$: Al_2O_3: $4.6(TEA)_2O$: $440H_2O$	BEA-4 (08.12. 05.4)	10	10	46
$2.2Na_2O$: $30SiO_2$: Al_2O_3: $4.6(TEA)_2O$: $456.7H_2O$	BEA-5 (08.12. 05.1)	15	8	42.5
$2.2Na_2O$: $30SiO_2$: Al_2O_3: $4.6(TEA)_2O$: $456.7H_2O$	BEA-6 (08.12. 05.2)	15	10	48
$2.2Na_2O$: $40SiO_2$: Al_2O_3: $4.6(TEA)_2O$: $440H_2O$	BEA-7 (09.29. 05.3)	20	10	50
$2.2Na_2O$: $40SiO_2$: Al_2O_3: $4.6(TEA)_2O$: $440H_2O$	BEA-8 (09.29. 05.4)	20	15	34
$2.2Na_2O$: $60SiO_2$: Al_2O_3: $4.6(TEA)_2O$: $445.7H_2O$	BEA-9 (09.29. 05.1)	30	10	73
$2.2Na_2O$: $60SiO_2$: Al_2O_3: $4.6(TEA)_2O$: $445.7H_2O$	BEA-10 (09.29. 05.2)	30	15	57
$2.2Na_2O$: $60SiO_2$: Al_2O_3: $4.6(TEA)_2O$: $445.7H_2O$	BEA-11 (11.10.05.2)	30	7	61
$2.2Na_2O$: $50SiO_2$: Al_2O_3: $4.6(TEA)_2O$: $440H_2O$	BEA-16 (01.30.06.3)	25	8	62
$2.2Na_2O$: $20SiO_2$: Al_2O_3: $4.6(TEA)_2O$: $440H_2O$	BEA-19 (02.27.06.2)	10	8	42.5
$2.2Na_2O$: $20SiO_2$: Al_2O_3: $4.6(TEA)_2O$: $440H_2O$	BEA-20 (02.27.06.3)	10	8	45
$2.2Na_2O$: $20SiO_2$: Al_2O_3: $4.6(TEA)_2O$: $440H_2O$	BEA-21 (02.27.06.4)	10	8	53.3
$2.2Na_2O$: $30SiO_2$: Al_2O_3: $4.6(TEA)_2O$: $456.7H_2O$	BEA-22 (02.13.06.3)	15	8	52.3
$2.2Na_2O$: $30SiO_2$: Al_2O_3: $4.6(TEA)_2O$: $456.7H_2O$	BEA-23 (02.13.06.4)	15	8	53.3
$2.2Na_2O$: $40SiO_2$: Al_2O_3: $4.6(TEA)_2O$: $440H_2O$	BEA-24 (03.13.06.1)	20	8	64.3
$2.2Na_2O$: $40SiO_2$: Al_2O_3: $4.6(TEA)_2O$: $440H_2O$	BEA-25 (03.13.06.2)	20	8	66.3
$2.2Na_2O$: $60SiO_2$: Al_2O_3: $4.6(TEA)_2O$: $445.7H_2O$	BEA-26 (03.13.06.3)	30	8	71
$2.2Na_2O$: $60SiO_2$: Al_2O_3: $4.6(TEA)_2O$: $445.7H_2O$	BEA-27 (03.13.06.3)	30	8	67

Table B.2 The experiments that did not yield zeolite Beta

Experiment Number	**Batch Formula**
BEA-12 (12.19.05.1)	5.56 SiO_2:$(TEA)_2O$: 31.4 H_2O
BEA-13 (12.19.05.2)	5.56 SiO_2:$(TEA)_2O$: 31.4 H_2O
BEA-14 (12.19.05.3)	2.2Na_2O: 60SiO_2: 0.3Al_2O_3: 4.6$(TEA)_2O$: 446.8H_2O
BEA-15 (12.19.05.4)	2.2Na_2O: 60SiO_2: 0.5Al_2O_3: 4.6$(TEA)_2O$: 446.8H_2O
BEA-17 (02.13.06.1)	2.2Na_2O: 10SiO_2: Al_2O_3: 4.6$(TEA)_2O$: 440H_2O
BEA-18 (02.13.06.2)	2.2Na_2O: 10SiO_2: Al_2O_3: 4.6$(TEA)_2O$: 440H_2O
BEA-28 (01.19.05.4)	2.2Na_2O: 60SiO_2: 0.3Al_2O_3: 4.6$(TEA)_2O$: 446.8H_2O

Table B.3 The effect of the synthesis time on yield for zeolite Beta synthesized with 2.2Na_2O: 20SiO_2: Al_2O_3: 4.6$(TEA)_2O$: 440H_2O batch composition at 150 °C

Experiment Number	**Si/Al ratio in the Batch Solution**	**Synthesis Time**	**Yield**
BEA-1 (07.27.05.1)	10	5	39
BEA-2 (07.27.05.2)	10	6	39.5
BEA-3 (08.12. 05.3)	10	8	41
BEA-4 (08.12. 05.4)	10	10	46
BEA-19 (02.27.06.2)	10	8	42.5
BEA-20 (02.27.06.3)	10	8	45
BEA-21 (02.27.06.4)	10	8	53.3

Table B.4 The effect of the Si/Al ratio on yield and crystallinity for zeolite Beta synthesized at 150°C for 10 days

Experiment Number	Si/Al ratio in the Batch Solution	Synthesis Time	Yield	Crystallinity
BEA-4 (08.12. 05.4)	10	10	46	76
BEA-6 (08.12. 05.2)	15	10	48	58
BEA-7 (09.29. 05.3)	20	10	50	79
BEA-9 (09.29. 05.1)	30	10	73	100

Table B.5 The effect of the Si/Al ratio on yield and crystallinity for zeolite Beta synthesized at 150°C in 8 days

Experiment Number	Si/Al ratio in the Batch Solution	Synthesis Time	Yield	Crystallinity
BEA-20 (02.27.06.3)	10	8	45	75
BEA-22 (02.13.06.3)	15	8	52.3	62
BEA-24 (03.13.06.1)	20	8	64.3	65
BEA-16 (01.30.06.3)	25	8	62	67
BEA-27 (03.13.06.3)	30	8	67	71

APPENDIX C

XRD PATTERNS, TGA GRAPHS, and EDX ANALYSIS of the EXPERIMENTS

The XRD patterns, TGA graphs, and EDX analysis results of the experiments performed in the current study are shown. Important XRD patterns, results of the EDX analysis were given in Chapter 4.

C.1 XRD PATTERNS

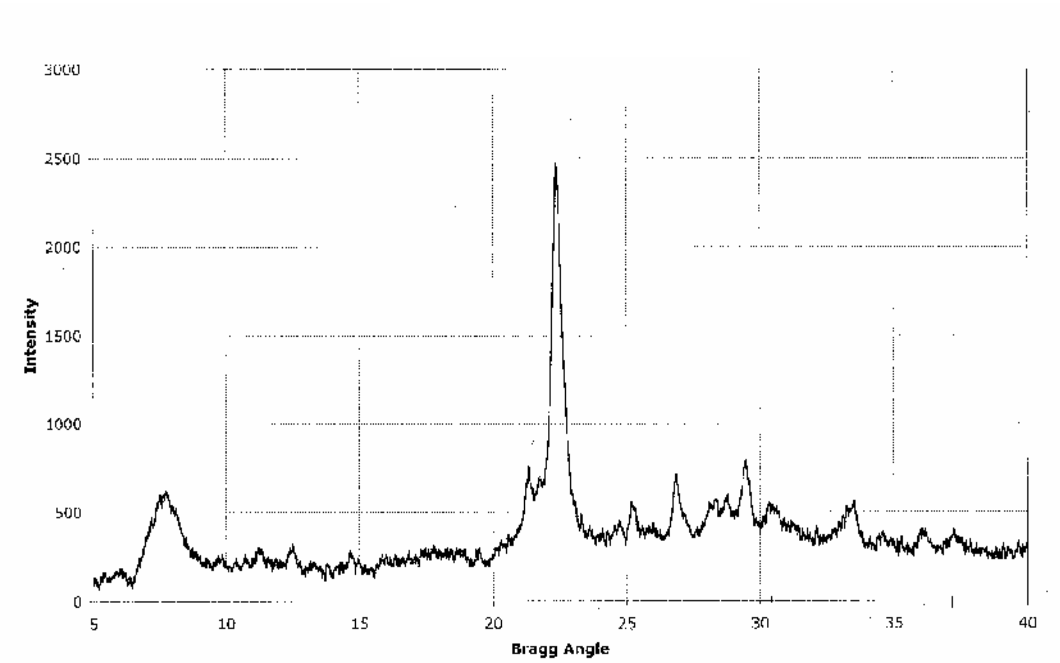

Figure C.1 XRD pattern of zeolite Beta synthesized with $2.2Na_2O$: $20SiO_2$: Al_2O_3: $4.6(TEA)_2O$: $440H_2O$ batch formula at 150 °C in 5 days (BEA-1)

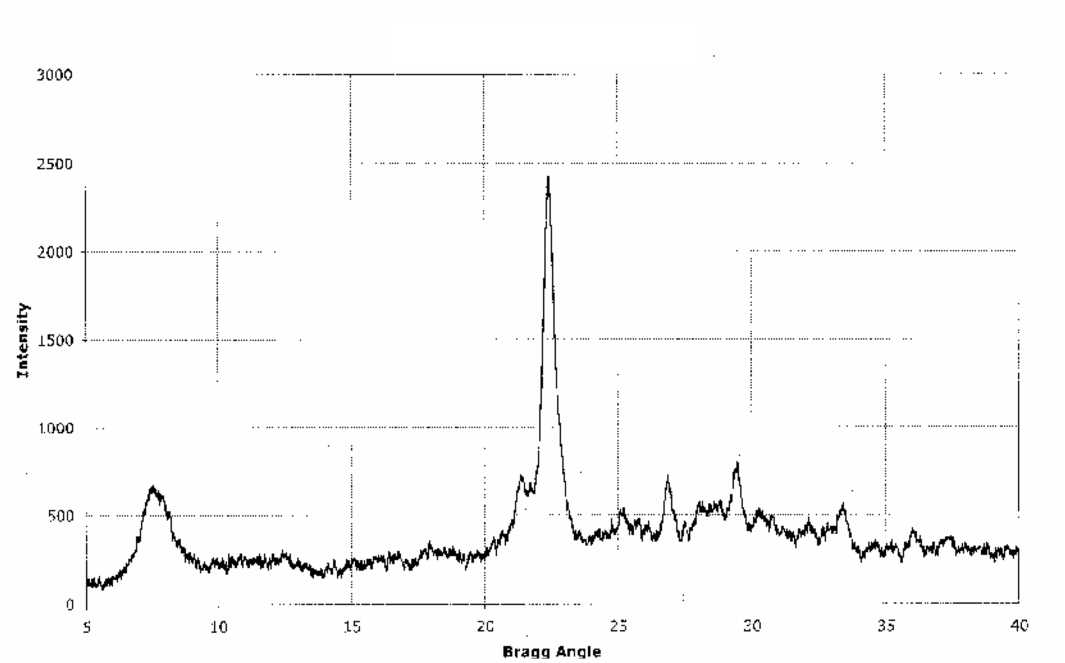

Figure C.2 XRD pattern of zeolite Beta synthesized with $2.2Na_2O$: $20SiO_2$: Al_2O_3: $4.6(TEA)_2O$: $440H_2O$ batch formula at 150 °C in 6 days (BEA-2)

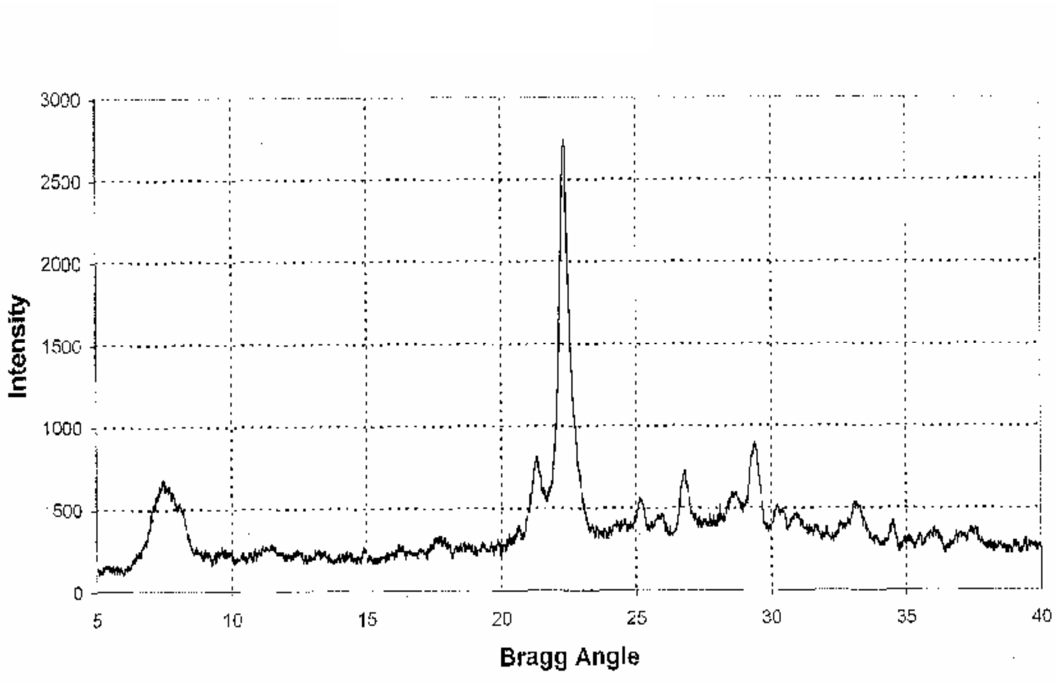

Figure C.3 XRD pattern of zeolite Beta synthesized with $2.2Na_2O$: $20SiO_2$: Al_2O_3: $4.6(TEA)_2O$: $440H_2O$ batch formula at 150 °C in 8 days (BEA-3)

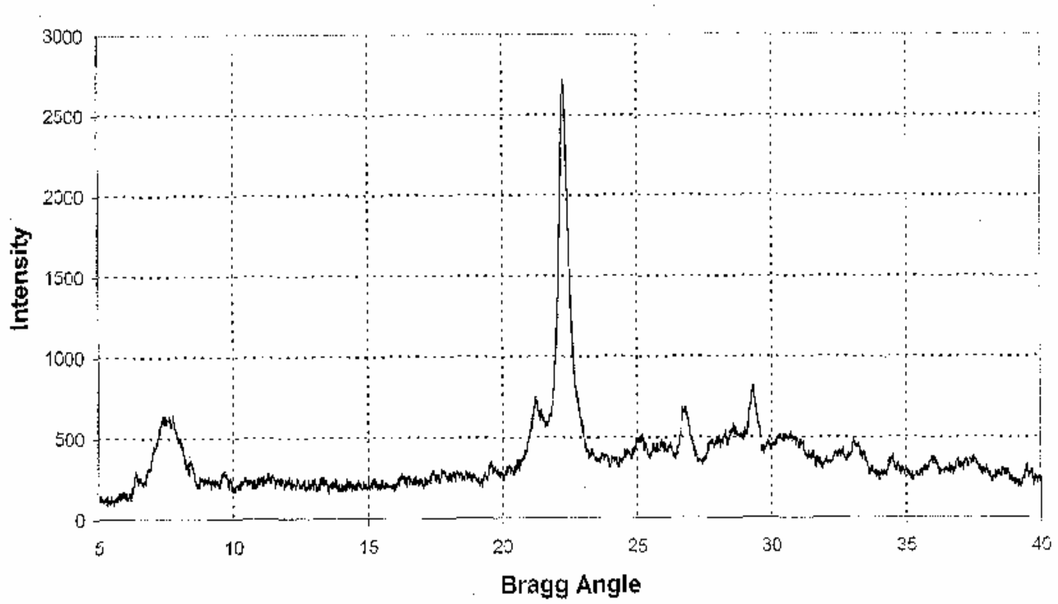

Figure C.4 XRD pattern of zeolite Beta synthesized with $2.2Na_2O$: $20SiO_2$: Al_2O_3: $4.6(TEA)_2O$: $440H_2O$ batch formula at 150 °C in 10 days (BEA-4)

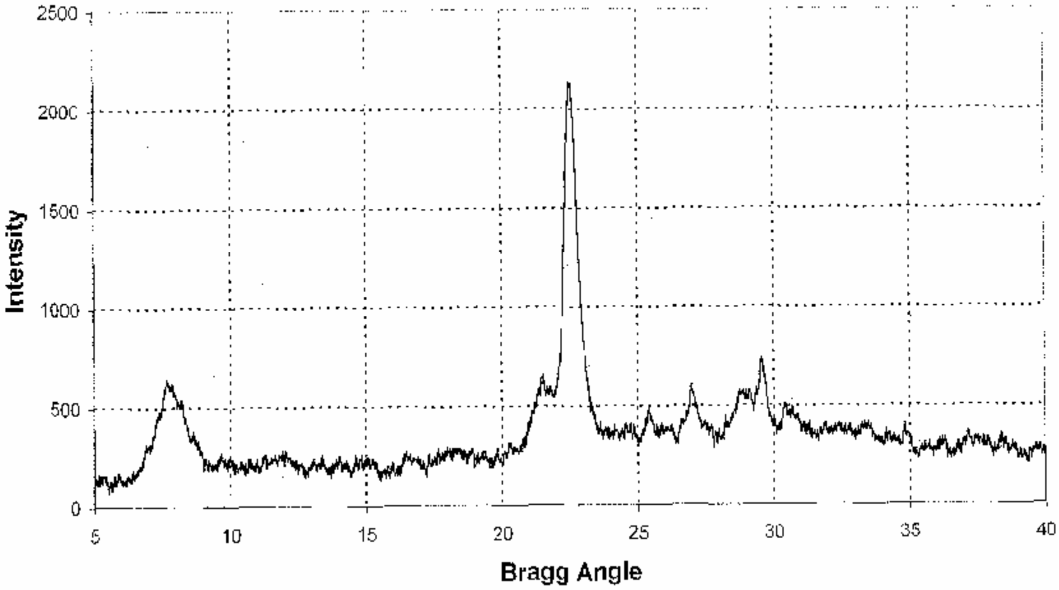

Figure C.5 XRD pattern of zeolite Beta synthesized with $2.2Na_2O$: $30SiO_2$: Al_2O_3: $4.6(TEA)_2O$: $456.7H_2O$ batch formula at 150 °C in10 days (BEA-6)

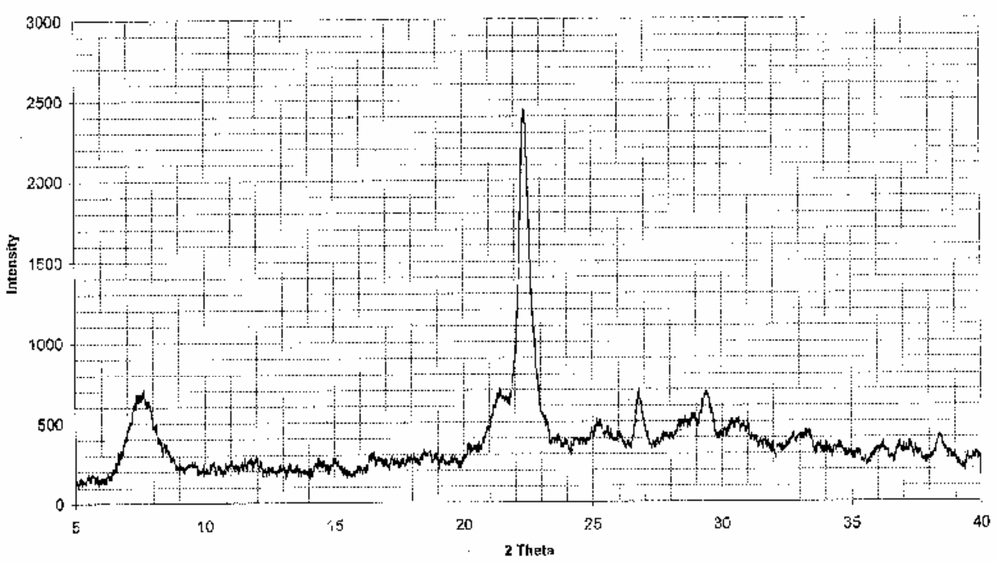

Figure C.6 XRD pattern of zeolite Beta synthesized with $2.2Na_2O$: $30SiO_2$: Al_2O_3: $4.6(TEA)_2O$: $456.7H_2O$ batch formula at 150 °C in 10 days (BEA-7)

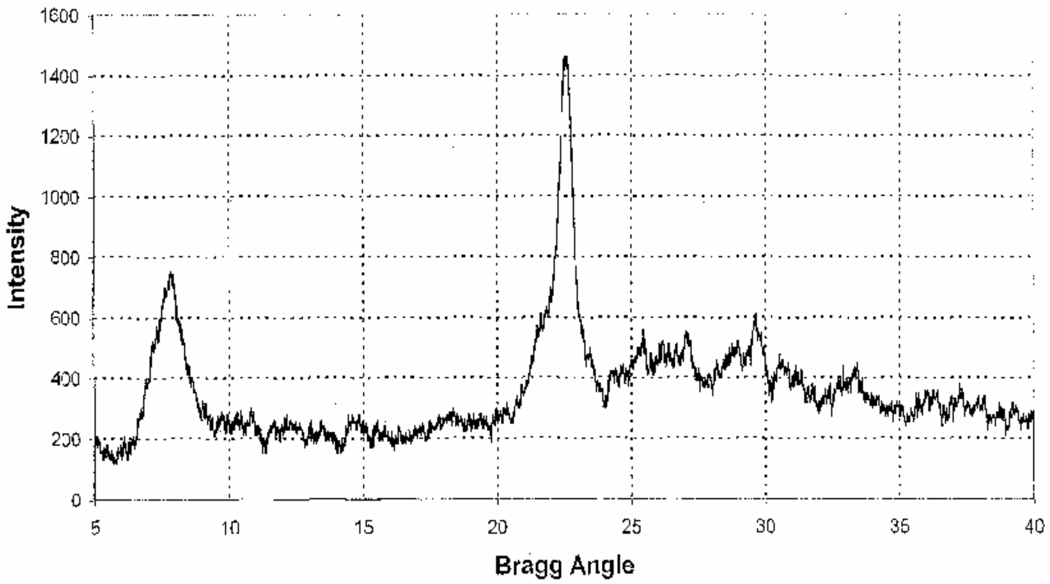

Figure C.7 XRD pattern of calcined zeolite Beta synthesized with $2.2Na_2O$: $40SiO_2$: Al_2O_3: $4.6(TEA)_2O$: $440H_2O$ batch formula at 150 °C in 15 days (BEA-8 calcined)

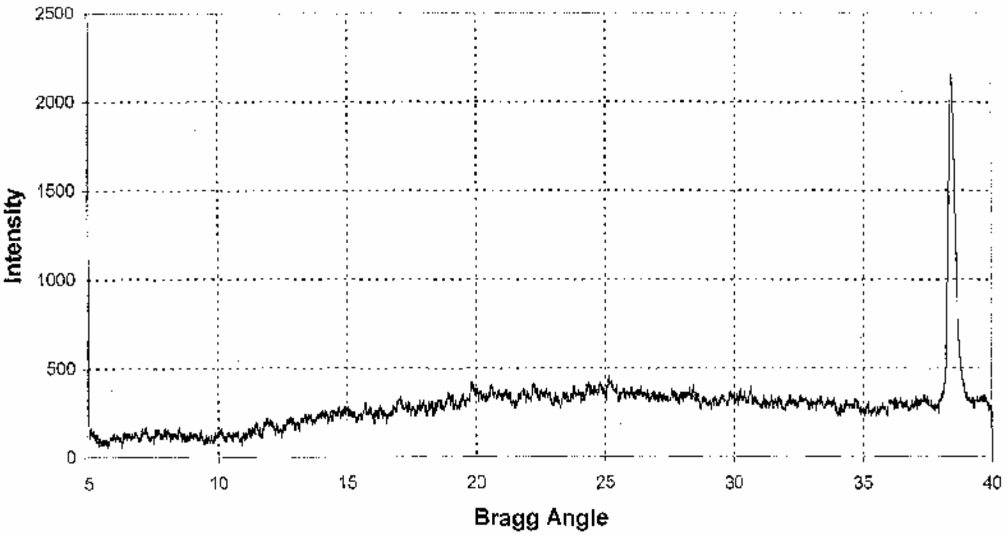

Figure C.8 XRD pattern of the sample synthesized with 5.56 SiO_2:$(TEA)_2O$: 31.4 H_2O batch formula at 150 °C in 8 days (BEA-12)

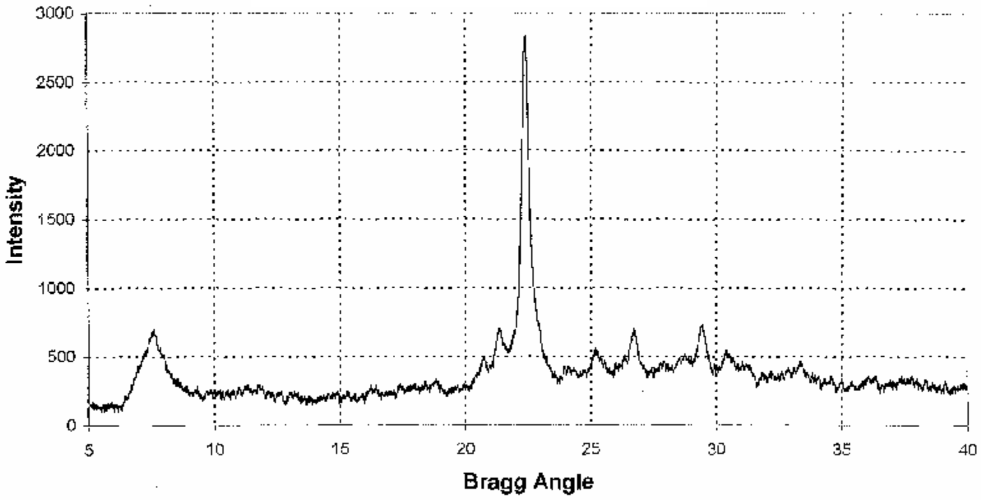

Figure C.9 XRD pattern of the zeolite Beta synthesized with $2.2Na_2O$: $50SiO_2$: Al_2O_3: $4.6(TEA)_2O$: $440H_2O$ batch formula at 150 °C in 8 days (BEA-16)

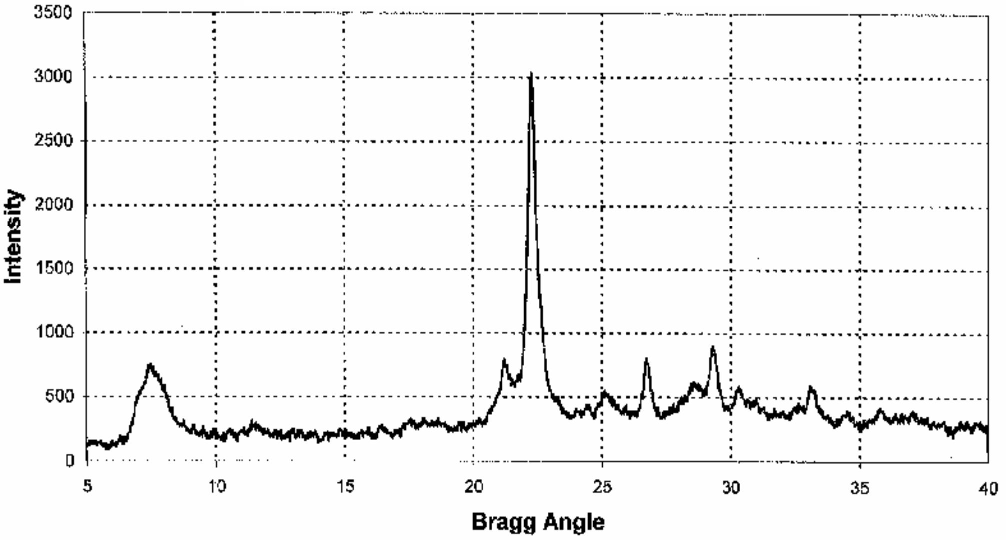

Figure C.10 XRD pattern of the zeolite Beta synthesized with $2.2Na_2O$: $20SiO_2$: Al_2O_3: $4.6(TEA)_2O$: $440H_2O$ batch formula at 150 °C in 8 days (BEA-19)

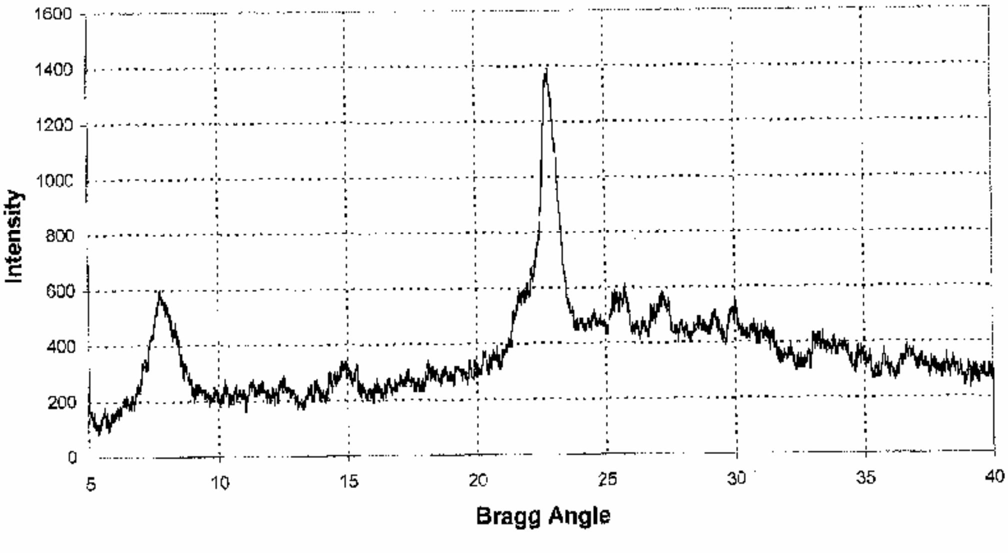

Figure C.11 XRD pattern of the zeolite Beta synthesized with $2.2Na_2O$: $30SiO_2$: Al_2O_3: $4.6(TEA)_2O$: $456.7H_2O$ batch formula at 150 °C in 8 days (BEA-23)

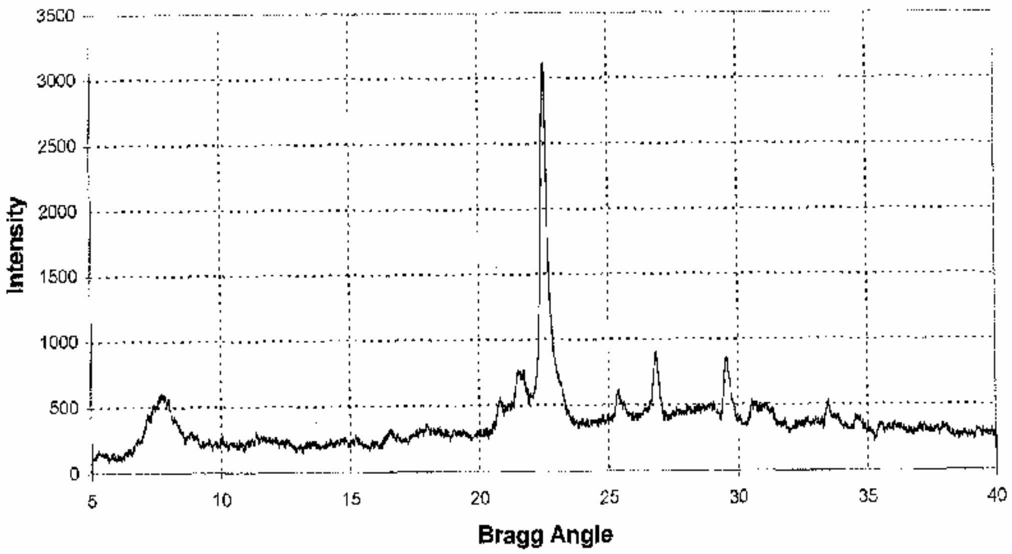

Figure C.12 XRD pattern of the zeolite Beta synthesized with $2.2Na_2O$: $40SiO_2$: Al_2O_3: $4.6(TEA)_2O$: $440H_2O$ batch formula at 150 °C in 8 days (BEA-24)

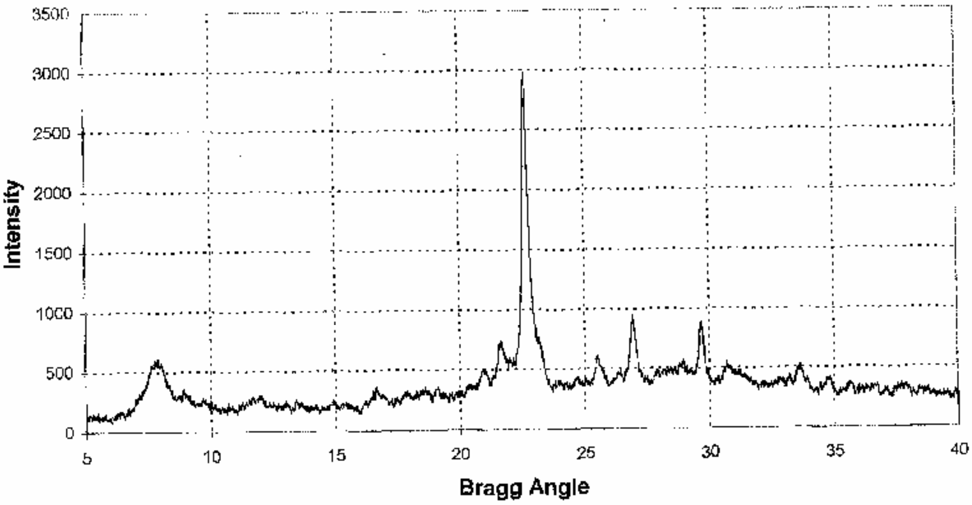

Figure C.13 XRD pattern of the zeolite Beta synthesized with $2.2Na_2O$: $60SiO_2$: Al_2O_3: $4.6(TEA)_2O$: $445.7H_2O$ batch formula at 150 °C in 8 days (BEA-26)

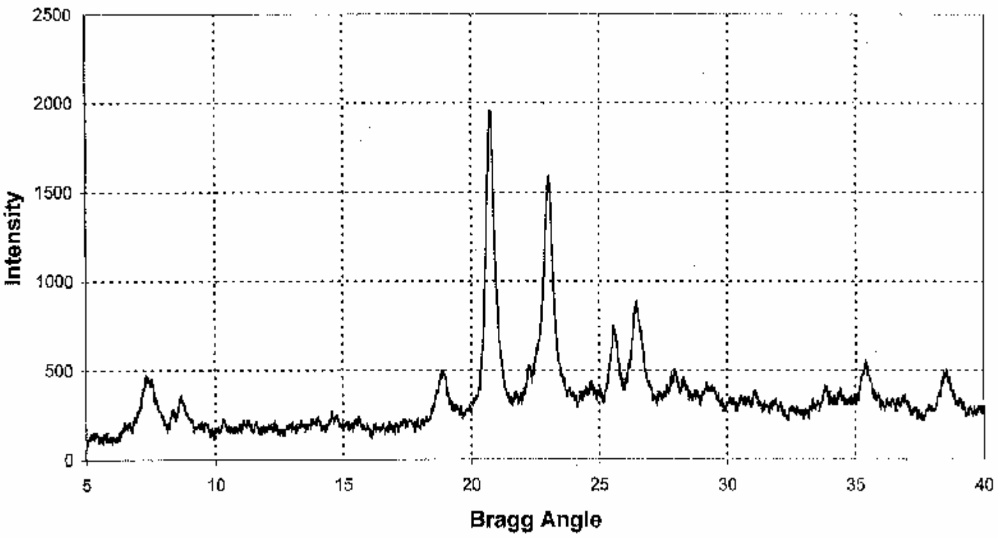

Figure C.14 XRD pattern of the sample synthesized with $2.2Na_2O$: $60SiO_2$: $0.3Al_2O_3$: $4.6(TEA)_2O$: $446.8H_2O$ batch formula at 150 °C in 8 days (BEA-28)

C.2 TGA ANALYSES

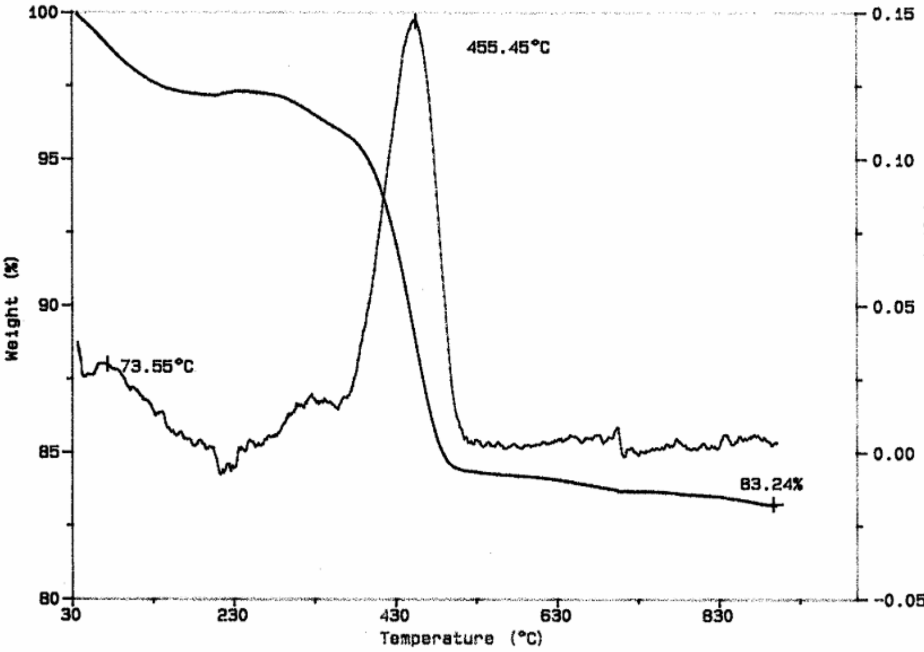

Figure C.15TGA graph of the zeolite Beta synthesized with $2.2Na_2O$: $40SiO_2$: Al_2O_3: $4.6(TEA)_2O$: $440H_2O$ batch formula at 150 °C in 15 days (BEA-8)

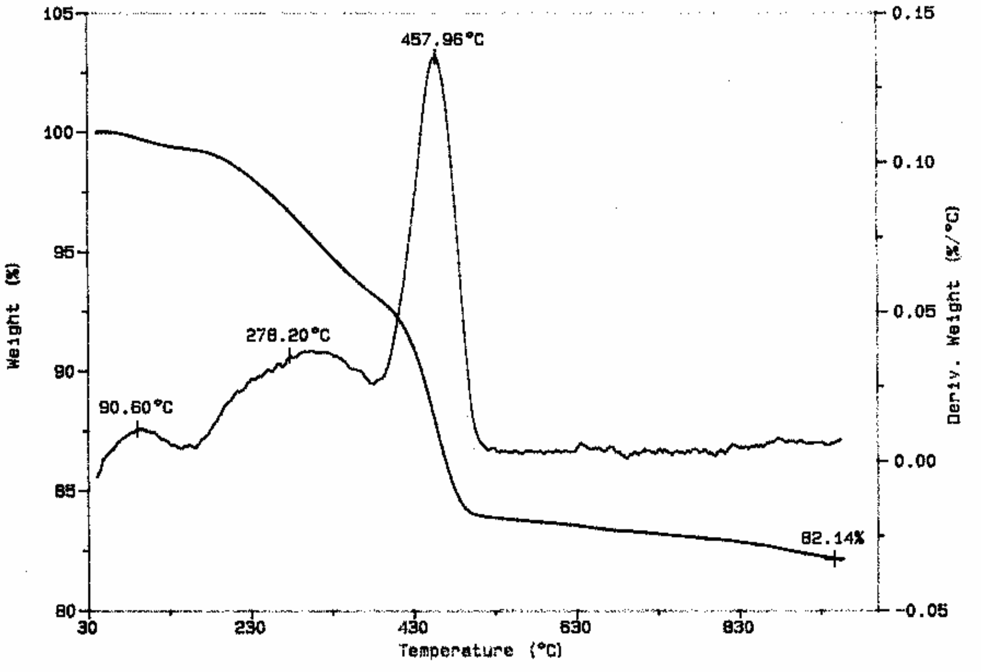

Figure C.16 TGA graph of the zeolite Beta synthesized with 2.2Na_2O: 60SiO_2: Al_2O_3: 4.6$(TEA)_2O$: 445.7H_2O batch formula at 150 °C in 15 days (BEA-9)

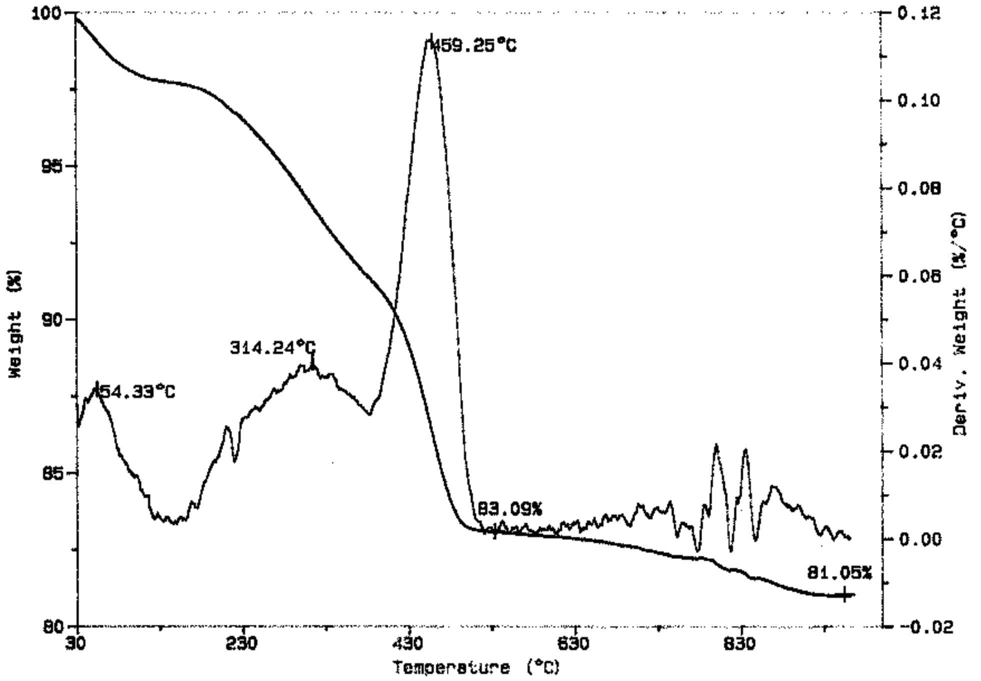

Figure C.17 TGA graph of the zeolite Beta synthesized with 2.2Na_2O: 60SiO_2: Al_2O_3: 4.6$(TEA)_2O$: 445.7H_2O batch formula at 150 °C in 15 days (BEA-10)

C.3 EDX ANALYSIS

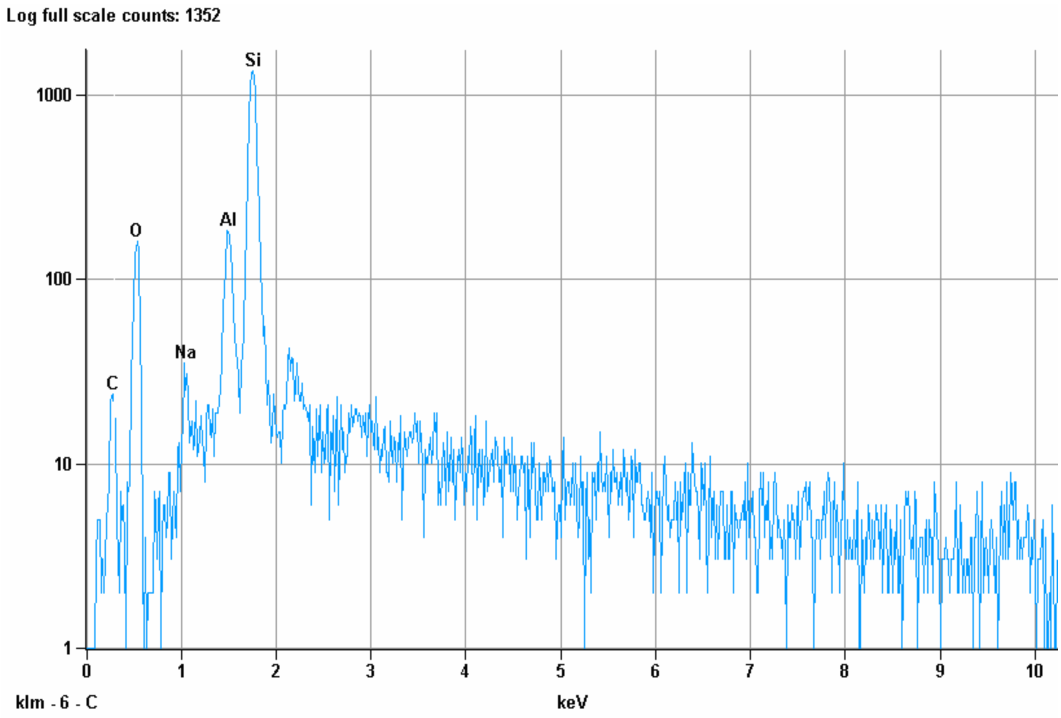

Figure C.18 EDX (Accelerating Voltage: 2000 Live Time: 31.79) result of the zeolite Beta synthesized with $2.2Na_2O$: $20SiO_2$: Al_2O_3: $4.6(TEA)_2O$: $440H_2O$ batch formula at 150 °C in 8 days (BEA-3)

Table C.1 EDX (Accelerating Voltage: 2000 Live Time: 31.79) result of the zeolite Beta synthesized with $2.2Na_2O$: $20SiO_2$: Al_2O_3: $4.6(TEA)_2O$: $440H_2O$ batch formula at 150 °C in 8 days (BEA-3)

Element	***Weight Conc %***	***Compnd Conc %***	***Formula***
C	6.89	25.24	CO_2
O	57.40	0.00	
Na	0.89	1.20	Na_2O
Al	3.71	7.02	Al_2O_3
Si	31.11	66.55	SiO_2

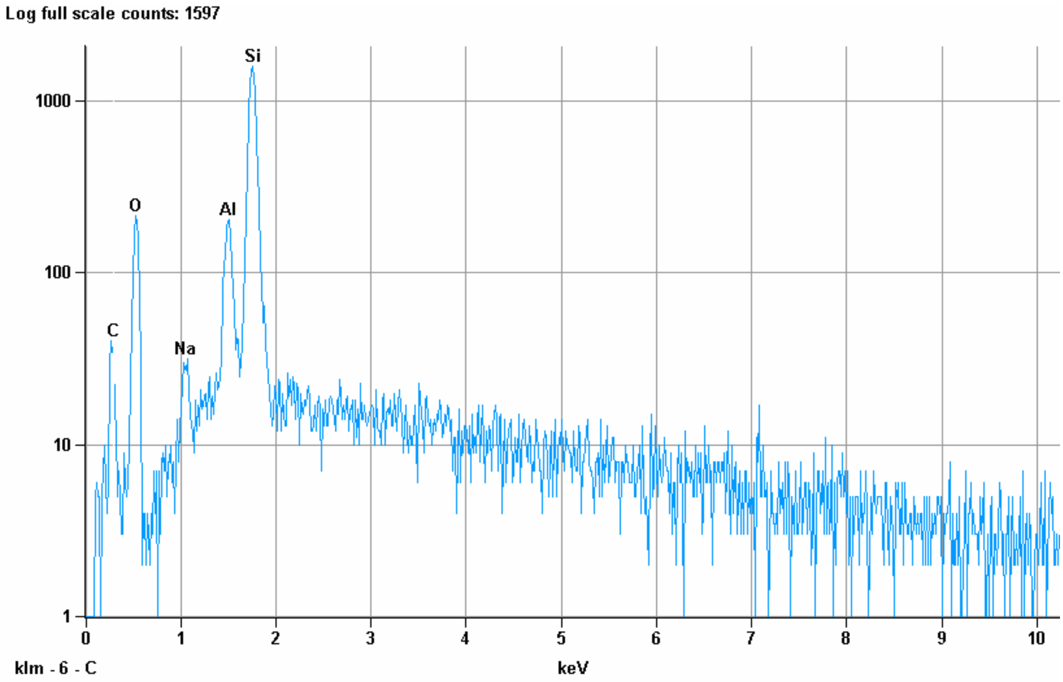

Figure C.19 EDX (Accelerating Voltage: 20.00 Live Time: 37.65) result of the zeolite Beta synthesized with $2.2Na_2O$: $20SiO_2$: Al_2O_3: $4.6(TEA)_2O$: $440H_2O$ batch formula at 150 °C in 8 days (BEA-3)

Table C.2 EDX (Accelerating Voltage: 20.00 Live Time: 37.65) result of the zeolite Beta synthesized with $2.2Na_2O$: $20SiO_2$: Al_2O_3: $4.6(TEA)_2O$: $440H_2O$ batch formula at 150 °C in 8 days (BEA-3)

Element	***Weight Conc %***	***Compnd Conc %***	***Formula***
C	8.43	30.87	CO_2
O	58.56	0.00	
Na	0.80	1.08	Na_2O
Al	3.42	6.47	Al_2O_3
Si	28.78	61.57	SiO_2

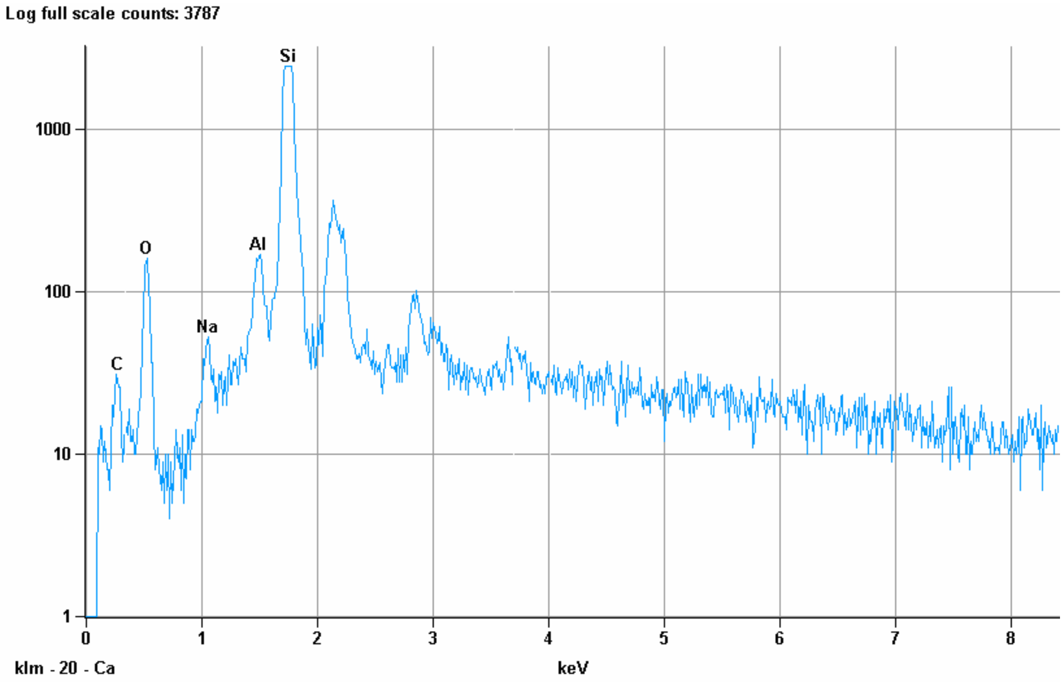

Figure C.20 EDX (Accelerating Voltage: 20.00 Live Time: 61.70) result of the zeolite Beta synthesized with 2.2Na_2O: 60SiO_2: Al_2O_3: 4.6$(TEA)_2O$: 445.7H_2O batch formula at 150 °C in 7 days (BEA-11)

Table C.3 EDX (Accelerating Voltage: 20.00 Live Time: 61.70) result of the zeolite Beta synthesized with 2.2Na_2O: 60SiO_2: Al_2O_3: 4.6$(TEA)_2O$: 445.7H_2O batch formula at 150 °C in 7 days (BEA-11)

Element	***Weight Conc %***	***Compnd Conc %***	***Formula***
C	3.04	11.13	CO_2
O	55.01	0.00	
Na	0.72	0.98	Na_2O
Al	1.24	2.33	Al_2O_3
Si	39.99	85.56	SiO_2

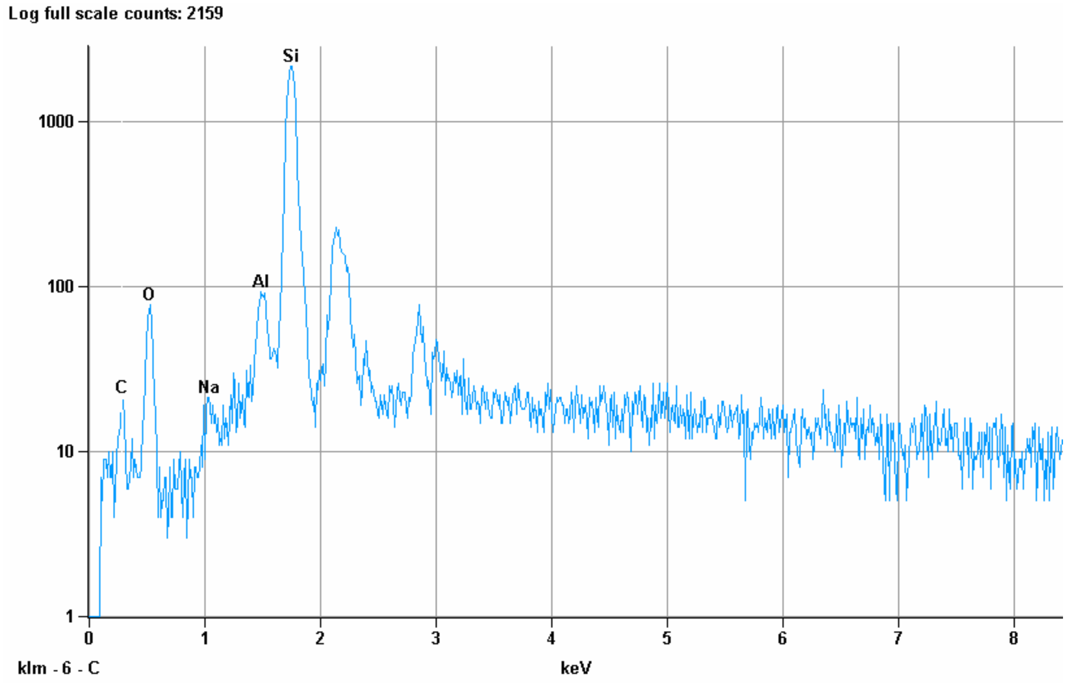

Figure C.21 EDX (Accelerating Voltage: 20.00 Live Time: 50.63) result of the zeolite Beta synthesized with $2.2Na_2O$: $60SiO_2$: Al_2O_3: $4.6(TEA)_2O$: $445.7H_2O$ batch formula at 150 °C in 7 days (BEA-11)

Table C.4 EDX (Accelerating Voltage: 20.00 Live Time: 50.63) result of the zeolite Beta synthesized with $2.2Na_2O$: $60SiO_2$: Al_2O_3: $4.6(TEA)_2O$: $445.7H_2O$ batch formula at 150 °C in 7 days (BEA-11)

Element	***Weight Conc %***	***Compnd Conc %***	***Formula***
C	2.05	7.53	CO_2
O	54.40	0.00	
Na	0.47	0.64	Na_2O
Al	1.27	2.41	Al_2O_3
Si	41.80	89.43	SiO_2

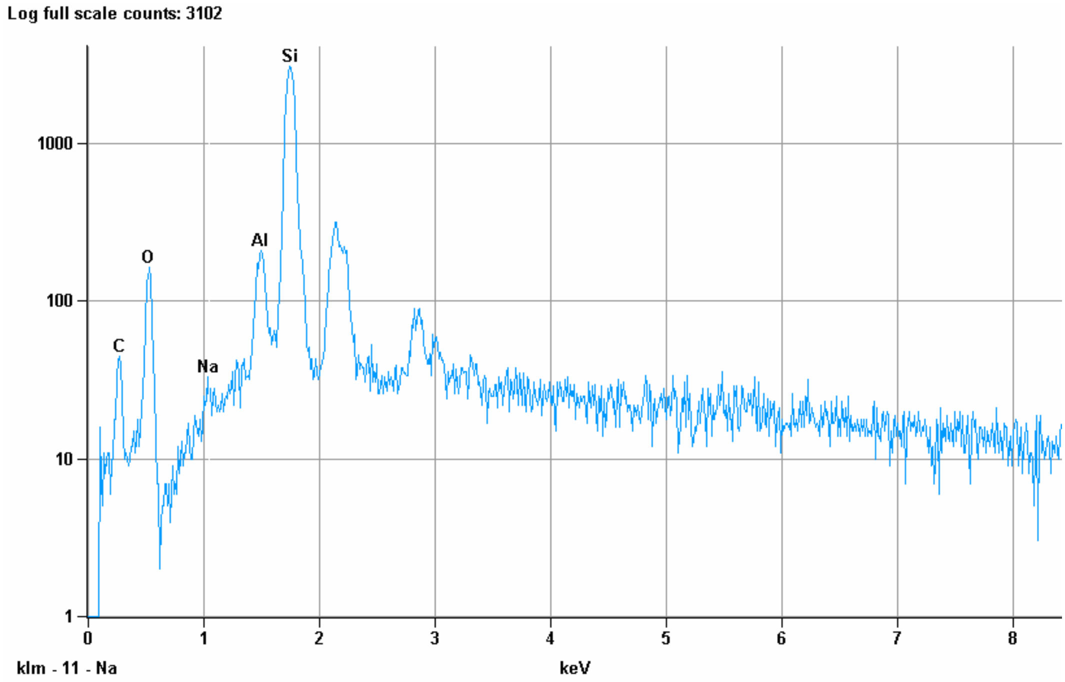

Figure C.22 EDX (Accelerating Voltage: 20.00 Live Time: 59.14) result of the zeolite Beta synthesized with $2.2Na_2O$: $40SiO_2$: Al_2O_3: $4.6(TEA)_2O$: $440H_2O$ batch formula at 150 °C in 10 days (BEA-7)

Table C.5 EDX (Accelerating Voltage: 20.00 Live Time: 59.14) result of the zeolite Beta synthesized with $2.2Na_2O$: $40SiO_2$: Al_2O_3: $4.6(TEA)_2O$: $440H_2O$ batch formula at 150 °C in 10 days (BEA-7)

Element	***Weight Conc %***	***Compnd Conc %***	***Formula***
C	4.90	17.96	CO_2
O	56.42	0.00	
Na	0.27	0.37	Na_2O
Al	1.95	3.68	Al_2O_3
Si	36.45	77.99	SiO_2

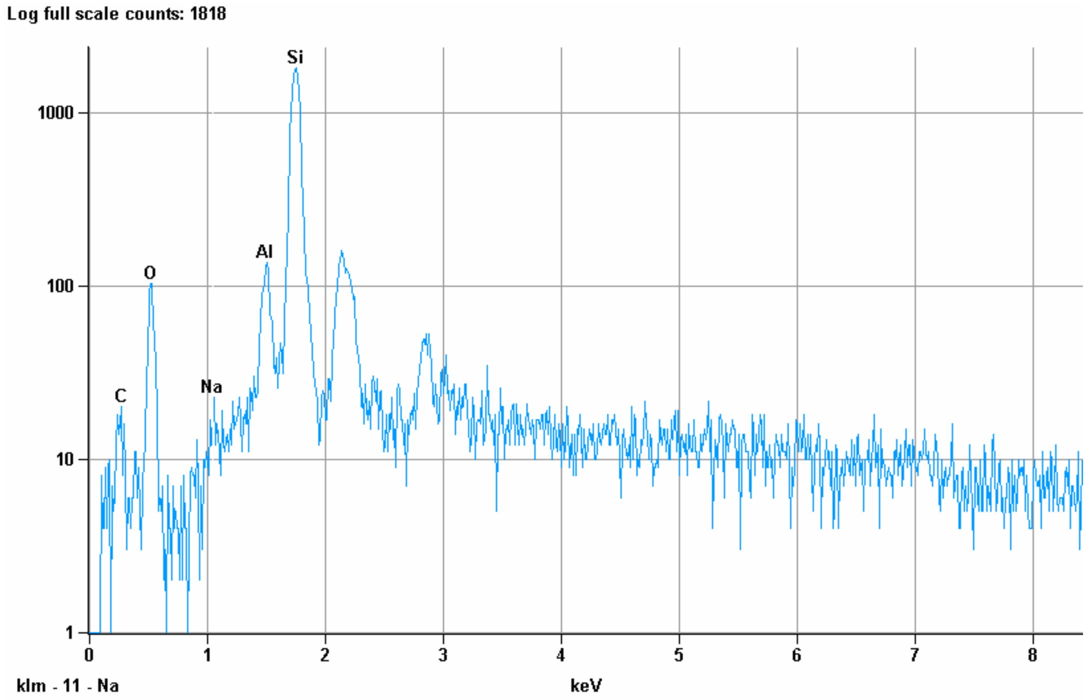

Figure C.23 EDX (Accelerating Voltage: 20.00 Live Time: 34.28) result of the zeolite Beta synthesized with 2.2Na_2O: 40SiO_2: Al_2O_3: 4.6$(TEA)_2O$: 440H_2O batch formula at 150 °C in 10 days (BEA-7)

Table C.6 EDX (Accelerating Voltage: 20.00 Live Time: 34.28) result of the zeolite Beta synthesized with 2.2Na_2O: 40SiO_2: Al_2O_3: 4.6$(TEA)_2O$: 440H_2O batch formula at 150 °C in 10 days (BEA-7)

Element	***Weight Conc %***	***Compnd Conc %***	***Formula***
C	3.57	13.06	CO_2
O	55.42	0.00	
Na	0.35	0.47	Na_2O
Al	2.13	4.02	Al_2O_3
Si	38.53	82.44	SiO_2

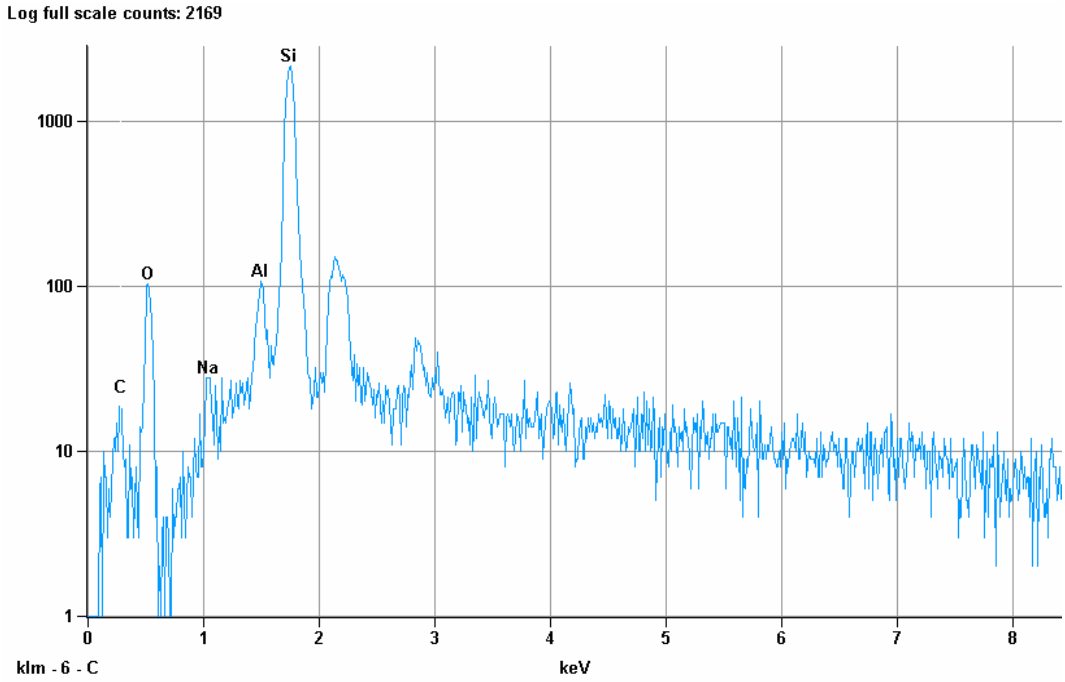

Figure C.24 EDX (Accelerating Voltage: 20.00 Live Time: 36.53) result of the zeolite Beta synthesized with $2.2Na_2O$: $60SiO_2$: Al_2O_3: $4.6(TEA)_2O$: $445.7H_2O$ batch formula at 150 °C in 10 days (BEA-9)

Table C.7 EDX (Accelerating Voltage: 20.00 Live Time: 36.53) result of the zeolite Beta synthesized with $2.2Na_2O$: $60SiO_2$: Al_2O_3: $4.6(TEA)_2O$: $445.7H_2O$ batch formula at 150 °C in 10 days (BEA-9)

Element	*Weight Conc %*	*Compnd Conc %*	*Formula*
C	3.37	12.34	CO_2
O	55.28	0.00	
Na	0.61	0.82	Na_2O
Al	1.32	2.50	Al_2O_3
Si	39.43	84.34	SiO_2

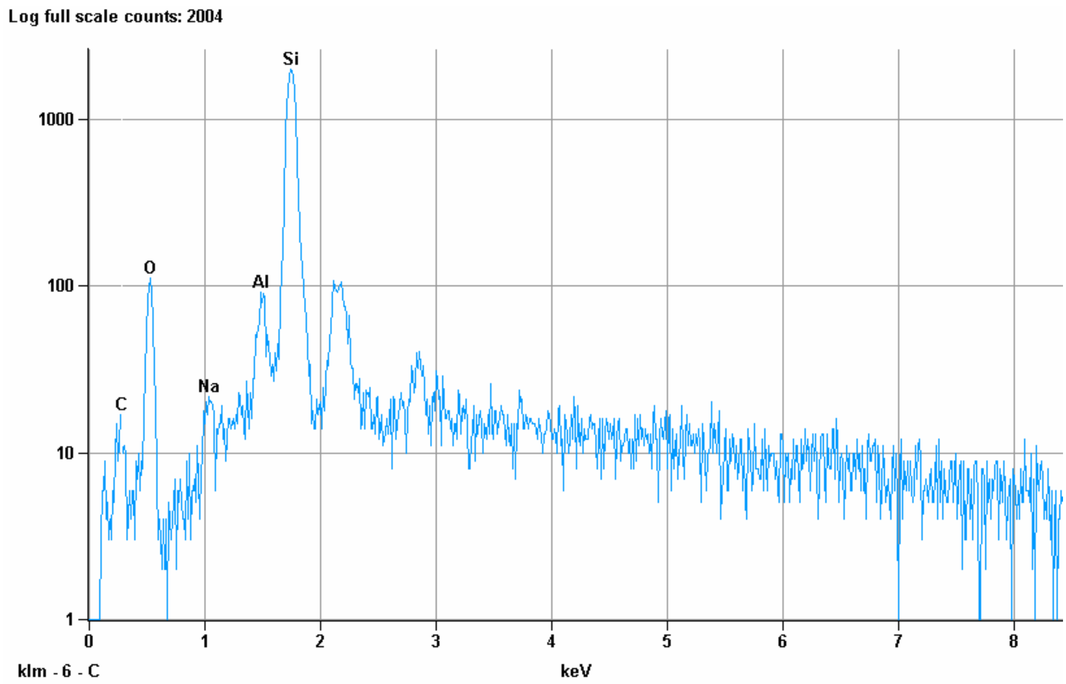

Figure C.25 EDX (Accelerating Voltage: 20.00 Live Time: 31.06) result of the zeolite Beta synthesized with $2.2Na_2O$: $60SiO_2$: Al_2O_3: $4.6(TEA)_2O$: $445.7H_2O$ batch formula at 150 °C in 10 days (BEA-9)

Table C.8 EDX (Accelerating Voltage: 20.00 Live Time: 31.06) result of the zeolite Beta synthesized with $2.2Na_2O$: $60SiO_2$: Al_2O_3: $4.6(TEA)_2O$: $445.7H_2O$ batch formula at 150 °C in 10 days (BEA-9)

Element	***Weight Conc %***	***Compnd Conc %***	***Formula***
C	2.96	10.84	CO_2
O	55.01	0.00	
Na	0.55	0.75	Na_2O
Al	1.27	2.39	Al_2O_3
Si	40.21	86.02	SiO_2

APPENDIX D

NMR and DSC RESULTS OF SPEEK(220206)

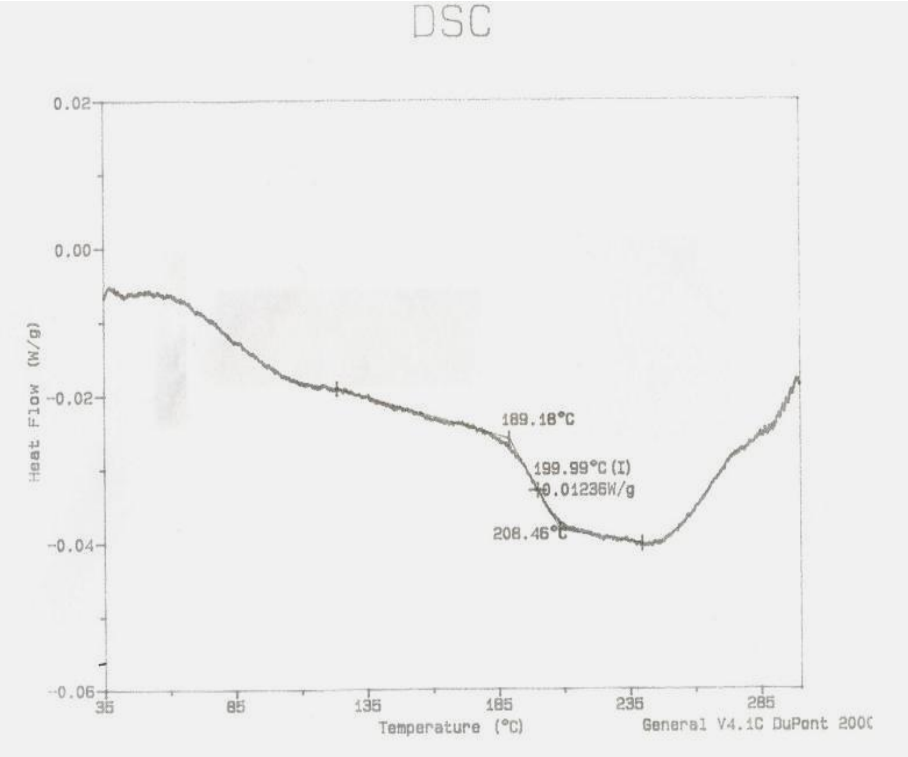

Figure D.1 DSC graph of SPEEK

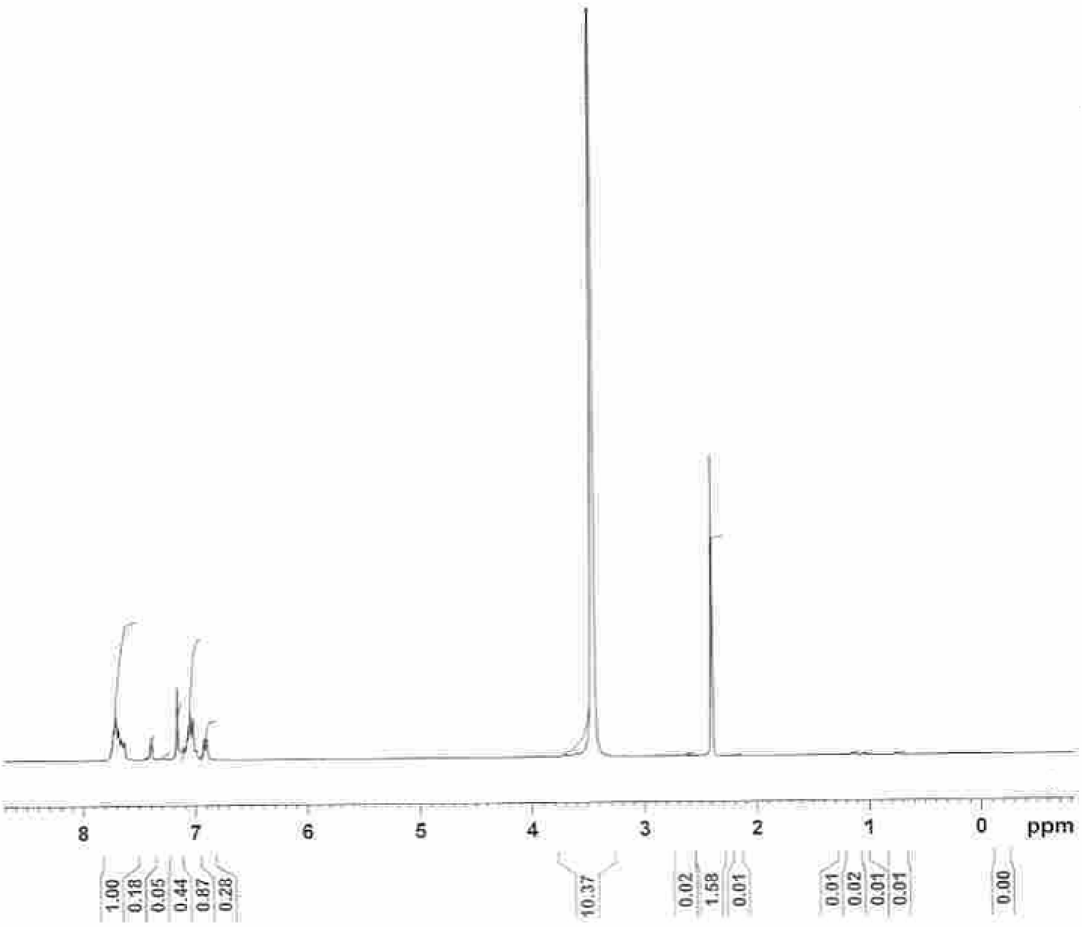

Figure D.2 NMRgraph of SPEEK(220206)

APPENDIX E

MEASUREMENT of CONDUCTIVITY

Impedance and phase angle are measured as a function of frequency. Since impedance is constant as a function of frequency, it implies that the measured value is the resistance of the membrane [27], [28].

$$\text{Conductivity} = \frac{L}{W * \delta * R} \tag{E.1}$$

where;
L= Distance between the two probes (cm)
W= width of membrane test sample (cm)
δ= thickness of membrane test sample (cm)
R= resistance through membrane (ohm)

For example, when the thickness of the membrane was 104, 110, and 109 µm average thickness became 108 µm. The resistance was measured as 6905 ohm by two-probe impedance spectrometer. Length of the membrane was 2 cm, and the width of the membrane was 1 cm. Proton conductivity was calculated as:

$$\text{Conductivity} = \frac{2}{1 * 6905 * 0.0108} = 0.0268 \text{ S/cm} \approx 0.27 \text{ S/cm}$$