SYNTHESIS AND CHARACTERIZATION OF ZEOLITE BETA

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ABSTRACT

SYNTHESIS AND CHARACTERIZATION OF ZEOLITE BETA

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Zeolite beta has been synthesized using hydrothermal methods. In order to synthesize zeolite beta an aqueous gel having a molar batch composition of 2.2 Na₂O· Al₂O₃· x SiO₂· 4.6 (TEA)₂O· 444 H₂O was utilized. The synthesis parameters were SiO₂/Al₂O₃ ratio ($20 \le x \le 50$) and crystallization time ($6 \le t \le 16$ days).

Pure zeolite beta was crystallized from the experiments which were performed with the batch composition having SiO_2/Al_2O_3 of 20 and 30 in 6 to 16 days period. For SiO_2/Al_2O_3 of 20 and 30, the highest yield was obtained for 12 days. Therefore, the rest of the experiments, in which SiO_2/Al_2O_3 was 40 and 50, were carried out keeping the synthesis time constant (12 days). Pure zeolite beta was

also synthesized for SiO_2/Al_2O_3 of 40 and 50. The highest yield and the most crystalline zeolite beta sample were obtained from the experiment performed at SiO_2/Al_2O_3 of 50 with a synthesis time of 12 days.

The morphology and crystal size of the zeolite beta samples were identified by using scanning electron microscope (SEM). It was observed that, zeolite beta samples had spheroidal morphology with the crystal size of about 0.5 μ m. According to the thermogravimetric analyses (TGA), it was found that template molecules and moisture constituted nearly 18 % by weight of the zeolite beta samples. The surface area of the calcined zeolite beta sample was determined by N₂ adsorption and was found to be 488 m²/g.

Gravimetric sorption analyses yield that, the limiting sorption capacity of Na-Beta for methanol, ethanol, isopropanol and n-butanol at 0°C was about the same with a value of 0.25 cm³/g. For o-xylene, m-xylene and p-xylene that value was $0.21 \text{ cm}^3/\text{g}$, $0.22 \text{ cm}^3/\text{g}$ and $0.24 \text{ cm}^3/\text{g}$, respectively.

Keywords: Zeolite Beta, Synthesis, Characterization, Sorption.

ZEOLİT BETA SENTEZİ VE KARAKTERİSAZYONU

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Zeolit beta hidrotermal yöntemler kullanılarak sentezlenmiştir. Zeolit beta sentezi için komposizyonu 2.2 Na₂O· Al₂O₃· x SiO₂· 4.6 (TEA)₂O· 444 H₂O olan sulu bir jel kullanılmıştır. Sentez parametreleri SiO₂/Al₂O₃ oranı ($20 \le x \le 50$) ve kristalleşme süresi ($6 \le t \le 16$ gün) olarak belirlenmiştir.

Başlangıç komposizyonundaki SiO_2/Al_2O_3 oranı 20 ve 30 olan, 6 ile 16 gün süresince gerçekleştirilen deneylerde, zeolit beta saf faz olarak elde edilmiştir. SiO_2/Al_2O_3 oranı 20 ve 30 olan bu deneylerde, en fazla verimin 12 gün sonunda elde edildiği saptanmıştır. Bu yüzden, bundan sonraki deneylerde kristalleşme süresi 12 gün olarak sabit tutulmuş ve başlangıç komposizyonundaki SiO_2/Al_2O_3 oranı 40 ve 50' ye çıkarılmıştır. Bu deneylerde de zeolit beta saf faz olarak sentezlenmiştir. Yapılan deneyler neticesinde en fazla verim ve en çok kristalleşme, SiO₂/Al₂O₃ oranı 50 olan ve 12 gün süren deney sonucunda elde edilmiştir.

Zeolit beta kristallerinin morfolojisi ve kristal büyüklükleri tarama elektron mikroskobu kullanılarak incelenmiştir. Buna göre zeolit beta kristallerinin morfolojisi küresel cisimler şeklinde olup, kristal büyüklükleri ise yaklaşık 0.5 μ m olarak gözlemlenmiştir. Termogravimetrik analizlere göre zeolit beta örneklerinin ağırlıkça % 18' ini şablon molekülleri ve nemin oluşturduğu tespit edilmiştir. N₂ gazı ile yapılan yüze tutunma deneyi kalsine edilmiş numunenin yüzey alanının 488 m²/g olduğunu göstermiştir.

Sodyum formundaki zeolit beta numunelerinin 0 °C 'de metanol, etanol, izopropanol ve n-bütanol sorpsiyon kapasiteleri hemen hemen aynı olup, 0.25 cm³/g olarak ölçülmüştür. Bu değer ksilen izomerleri olan o-ksilen, m-ksilen ve p-ksilen için sırasıyla 0.21 cm³/g, 0.22 cm³/g ve 0.24 cm³/g olarak tespit edilmiştir.

Anahtar Kelimeler: Zeolit Beta, Sentez, Karakterizasyon, Sorpsiyon.

To my mother, father and sister

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NOMENCLATURE

| SiO ₂ | : Silicon dioxide |
|-----------------------------|--|
| Al_2O_3 | : Aluminum oxide |
| TEAOH | : Tetraethylammonium hydroxide |
| TEABr | : Tetreethylammonium bromide |
| TEA | : Tetraethylammonium |
| XRD | : X-ray diffraction |
| SEM | : Scanning electron microscope |
| TGA | : Thermogravimetric analysis |
| AAS | : Atomic absorption spectroscope |
| DTA | : Differential thermal analysis |
| NMR | : Nuclear magnetic resonance |
| FTIR | : Fourier transform infrared |
| EDX | : Energy dispersive X-ray spectroscopy |
| BET | : Brunauer-Emmet-Teller |
| $\mathbf{P}_{\mathbf{f}}$ | : Final pressure of the system, mmHg |
| P ₀ | : Vapor pressure of the adsorbate, mmHg |
| PTFE | : Polytetrafluoroethylene |
| PSD | : Particle size distribution |
| σ | : Kinetic diameter, nm |
| Q | : Adsorbed gas quantity at STP, mol/g. |
| Qm | : Monolayer adsorbed gas quantity at STP, mol/g. |
| С | : BET constant |
| $\mathbf{S}_{\mathrm{BET}}$ | : BET surface area, m ² /g |
| α | : Analysis gas molecular cross sectional area, cm ² /molecule |
| Ν | : Avagadro's number, molecule/mole |
| Vm | : Molar volume of gas at STP, cm ³ /mol |
| ρ | : Density, g/cm ³ |
| $ ho_L$ | : Density of liquid sorbate at the temperature of adsorption, g/cm^3 |

CHAPTER 1

INTRODUCTION

1.1 Zeolites

Zeolites are crystalline, hydrated aluminosilicates. Their structure is a framework based on an infinitely extending three dimensional network of SiO_4 and AlO_4 tetrahedra linked to each other by sharing oxygen atoms. The framework contains channels or interconnected voids, which are in micropore range. These channels and voids are occupied by water molecules, and the cations; mainly alkali or alkaline earth metal ions, so as to balance the negative charge of the framework (Breck, 1974).

The general crystallographic unit cell formula of a zeolite is given as:

$$M_{x/m}[(AlO_2)_x (SiO_2)_y]$$
. z H₂O

where, M represents the non-framework metal cation, m is its charge, z is the number of water molecules and x and y are integers such that $y/x \ge 1$. The expression enclosed in the square brackets shows the anionic framework composition.

Zeolite was first discovered as a new type of mineral in 1756 by the Swedish mineralogist Cronstedt. The word "zeolite" derived from two Greek words "zeo"

and "lithos". They mean "to boil" and a "stone" because when gently heated, the mineral loses water rapidly and thus seems to boil (Elvers and Hawkins, 1996).

Zeolites can be grouped as; natural and synthetic zeolites. Today, about 50 species of zeolite minerals and numerous types of synthetic zeolites are known. Until the 1950's, when the synthetic zeolites became available as a new type of commercial adsorbents, zeolites did not have much significance. Since then, the utilization of zeolites as catalysts, adsorbents, and ion exchangers has been developed in the most fields of the chemical industry. Zeolites took place of the non-zeolite adsorbents, catalysts and ion exchangers as a result of the improved performance. Therefore, the consumption of zeolites in these fields has grown continuously (Bhatia, 1990).

Zeolites are formed in nature by the chemical reaction occurred between volcanic glass and saline water. This natural reaction is favored in temperatures between 27 °C to 55 °C, and the typical pH value is changing from 9 to 10. To complete this reaction nature requires 50 to 50000 years (Jacobs and Martens, 1987).

Natural zeolites are rarely phase-pure and they are contaminated to varying degrees by other minerals such as; quartz, other zeolites, amorphous glass etc. Thus, naturally occurring zeolites are not used in many important commercial applications where uniformity and purity are essential.

On the other hand, synthetic zeolites, which are often crystallized by nucleation from inhomogeneous supersaturated mother liquors are uniform and pure (Jacobs and Martens, 1987). The important point in the synthesis process is the preparation of the synthesis mixture. A variation occurred in process parameters changes the product properties, moreover the product. Therefore, the composition and the homogeneity of the synthesis mixture, chemical nature of the reactants, crystallization temperature and the period, the template molecule, and pH of the system are the main factors affecting the zeolite synthesis.

1.2 Zeolite Beta

One of the synthetic zeolites is Zeolite Beta. It is a high silica, large pore, and crystalline aluminosilicate. It was first synthesized hydrothermally from a reaction mixture containing silicon, aluminum and sodium oxides and tetraethylammonium hydroxide at a temperature of about 75 °C – 200 °C by Wadlinger et al. in 1967.

Zeolite beta is an intergrowth hybrid of two distinct structures and has a stacking disorder. These complexities hampered the structural characterization of zeolite beta until 1988. Newsam et al. (1988) determined the crystal structure of this zeolite by using high resolution electron microscopy, electron diffraction, computer assisted modeling and powder X-ray diffraction. It was reported that in zeolite beta structure, the ordered and disordered framework coexist and there are three mutually intersecting channels. The framework structure has two types of 12 membered ring pores. The channel system of zeolite beta has pore diameters of 5.6×5.6 Å and 7.7×6.6 Å (Bárcia et al., 2005). The framework structure and the channel system of zeolite beta are schematically shown in Figure 1.1 and Figure 1.2, respectively.

Because of its high Si/Al ratio and higher acidic strength zeolite beta is usually preferred rather than faujasite type zeolites in various hydrocarbon conversion reactions such as hydrodewaxing and pour point lowering of petroleum (Eapen et al., 1994). In addition, high Si/Al ratio makes zeolite beta hydrophobic and thermally stable even at high temperatures, therefore it can be utilized in separation and catalytic applications.



Figure 1.1 Framework Structure of Zeolite Beta (http://topaz.ethz.ch/IZA-SC/Atlas/data/pictures/BEA_mod.html)



Figure 1.2 Channel system of Zeolite Beta (Bárcia et al., 2005)

1.3 Scope of the Study

In this study, zeolite beta was synthesized in pure phase by changing synthesis parameters; SiO_2/Al_2O_3 ratio and crystallization period. Synthesized zeolite beta samples were to be further characterized in order to identify the phase, surface area, and investigate the morphology, hydration behavior and adsorption properties.

Zeolite beta samples were synthesized hydrothermally under autogenous pressure. In order to identify the phase of the synthesized products X-Ray diffraction (XRD) analyses were applied. In addition, morphology, hydration behavior and surface area of the zeolite beta samples were investigated by the characterization methods; scanning electron microscope (SEM), thermogravimetric analysis (TGA) and N_2 adsorption, respectively.

The sorption capacities of the samples against methanol, ethanol, isopropanol, nbutanol, o-xylene, m-xylene and p-xylene were determine by gravimetric sorption experiments. The effect of the temperature on the equilibrium adsorption capacities were examined by experiments at 0 °C, 23 °C and 50 °C by using the sample with the starting batch composition having SiO₂/Al₂O₃ ratio of 50.

CHAPTER 2

LITERATURE SURVEY

2.1 Synthesis and Characterization Studies

A detailed study on the synthesis of zeolite beta was performed by Newsam et al. (1988) in order to investigate the structure of zeolite beta and to understand the performance of the zeolite in applications as; a catalyst, ion exchanger and adsorbent. Crystallization was carried out under hydrothermal conditions at 78-180 °C in a period of 6 days to 60 days. They produced zeolite beta, using appropriate amounts of sodium aluminate and mixture of silica gel or sol and tetraethylammonium hydroxide (TEAOH) solution. The formulation used was [0.4 Na: 0.6 TEA] AlO₂: 10 SiO₂: w H₂O where, w \leq 4. To determine the structure, high resolution electron microscopy, electron diffraction, computer assisted modeling and powder X-ray diffraction (XRD) were applied. They found that the structure of zeolite beta was a highly faulted intergrowth of two distinct frameworks, polymorph A and polymorph B. Besides, zeolite beta had two sets of perpendicular channels, which intersect to form a three dimensional array of cages that have three 12 ring apertures.

The influence of, mixing sequence of the reagents, gel dilution, synthesis temperature and SiO_2/Al_2O_3 ratio of the gel on the synthesis efficiency of zeolite beta was explored by Perez-Pariente et al. (1988). Zeolite beta was synthesized from an aqueous gel composition of 1.5 Na₂O: 0.54 K₂O: 7.5 (TEA)₂O: Al₂O₃: 30 SiO₂: 360 H₂O. Two different procedures were used for the preparation of the

gel. In procedure A, first appropriate amount of sodium hydroxide, sodium aluminate and tetraethylammonium hydroxide were dissolved in water. Then, tetraethyl orthosilicate was added to that solution. In another procedure, procedure B, silica source was added to part of the tetraethylammonium hydroxide solution so as to obtain a TEA/Si ratio of 0.44. An aqueous solution of other reagents and the remaining tetraethylammonium hydroxide was added to the former solution. Crystallization was further carried out in the presence or absence of the ethanol formed upon hydrolysis of the tetraethyl orthosilicate. In order to characterize the products, XRD, atomic absorption spectroscopy (AAS) and thermogravimetric analysis (TGA) were performed. Depending on the gel preparation procedure the presence of ethanol influenced the crystallization kinetics of the gels in a different way. In the presence of ethanol, the samples prepared by procedure B, had 100 % crystallinity. However, the samples prepared by using procedure A had only about 20 % crystallinity. On the other hand, in the absence of ethanol, the preparation procedure was hardly of any influence on the kinetics of crystallization. When the effect of dilution of the gel was studied it was observed that there was no significant change on the length of the nucleation period or on the crystal growth rate, but it slightly improved the degree of crystallinity of the product. To determine the effect of SiO₂/Al₂O₃ ratio and synthesis temperature, crystallization was performed at 373, 393 and 423 K by using gels whose SiO₂/Al₂O₃ ratio were 30, 100, 300, 900 and 1000. As a result, 100 % crystalline zeolite beta was formed at 373 and 393 K from all gels with a SiO₂/Al₂O₃ ratio smaller than 1000. Whereas, at 423 K zeolite beta did not form, but denser phases such as; ZSM-5 and cristobalite appeared instead. The proportion of the latter two materials was a function of the SiO₂/Al₂O₃ ratio of the gel, with a more siliceous gel, more cristobalite was formed.

In the study that was performed by Bhat et al. (1990), the factors such as; reactivity of silica source, crystallization temperature, concentration of template, OH^- , Na^+ and H_2O in the starting gel, influencing the synthesis of zeolite beta was investigated. In order to crystallize zeolite beta, silica gel and

tetraethylammonium hydroxide containing gel was utilized. Synthesis was done at 130 °C, 150 °C and 170 °C, over 4–8 days under hydrothermal conditions. For characterization of the samples, XRD, scanning electron microscopy (SEM), differential thermal analysis (DTA), and infrared (IR) spectroscopy were performed. It was concluded that the nature of the final product was dependent on the reactivity of the source of silica. Zeolite beta was obtained by using silica gel whose surface area 400 m²/g. However, the formation of other zeolites ZSM-12 and ZSM-5 was favored with decreasing the surface area, namely the reactivity of the silica source, to 200 m^2/g and 120 m^2/g , respectively. Moreover, it was pointed out that the concentration of the template molecule and sodium ions were effective on the crystallinity of beta samples. The crystallinity of the products increased as the concentration of template molecule and sodium ions decreased. When the effect of alkalinity was investigated, it was found that an optimum value of the OH⁻ ion concentration that was sufficient to depolymerize the silica gel and to initiate the nucleation process was needed. Meanwhile; the chosen OH⁻ concentration should not dissolve the zeolite precursors and retard the crystallization. Besides, when the effect of the change of the water content in the gel on the synthesis process was examined it was observed that, the duration of induction period was not significantly influenced from the water content of the gel. However, crystallization was faster when the water amount decreased. In addition, 150 °C was seen to be the optimum temperature for obtaining high crystalline beta samples. ZSM-5 and cristobalite phases were also formed when the synthesis temperature was increased to 170 °C.

In another study, (Camblor et al., 1991) the effect of TEAOH/SiO₂, and SiO_2/Al_2O_3 ratios, concentration of the gel and agitation during crystallization on the rate of crystallization, average crystal size and crystal size distribution of zeolite beta was examined. For synthesis of samples, the gel containing sodium and potassium cations was utilized. Amorphous silica was used as the silica source. Experiments were carried out at 135 °C in PTFE lined stainless steel autoclaves. To determine the crystallinity and the crystal size of the solid product

XRD and SEM were performed, respectively. The atomic absorption spectroscopy and flame emission spectroscopy provided information about the concentration of aluminum and alkali cations in the solid phases. It was observed that although the average crystal sizes of the final crystalline phases was not affected so much from the agitation of the gel during crystallization, agitation led to a shorter crystallization time. Nevertheless, the particle size distributions (PSD) were rather different for the products obtained with and without agitation. PSD were broad and slightly bimodal for the sample obtained with agitation. As it was mentioned in the previous study, crystallization time decreased when the water content of the gel decreased. Accordingly, the zeolite obtained from the more concentrated gel had a lower average crystal size and a narrower PSD than that synthesized in a diluted gel. The effect of SiO₂/Al₂O₃ ratio on the average crystal size and PSD was as follows; when the ratio in the gel increased the former increased also and the latter became wider. Similarly, the PSD of the samples became wider when the TEAOH/SiO₂ ratio of the gel decreased. However, the average crystal size did not decrease continuously as TEAOH content of the gel decreased.

In most of the studies tetraethylammonium hydroxide were used as templating agents in the synthesis mixtures. Eapen et al. (1994), synthesized zeolite beta by using tetraethylammonium bromide (TEABr) in combination with ammonium hydroxide as an organic templating species and silica sol as a source of silica. The molar composition of the gel in terms of moles of oxides was $3.1 \text{ Na}_2\text{O}$: 15 (NH₄)₂O: 5.0 (TEA)₂O: 35 SiO₂: Al₂O₃: 656 H₂O and synthesis was performed in the temperature range of 100-140 °C. The products were characterized using XRD, SEM, DTA, and infrared techniques. According to the study, zeolite beta could be crystallized in the temperature range mentioned above within 6-13 days, using TEABr and NH₄OH as template with the SiO₂/Al₂O₃ = 15-58, H₂O/SiO₂ =19 and TEABr/SiO₂ = 0.25-0.50. The rate of crystallization increased with increasing the temperature. Temperature greater than 140 °C and the SiO₂/Al₂O₃ ratio in the gel above 58 favored the formation

of ZSM-12 instead of zeolite beta. Besides, sodium concentration higher than the optimum, $Na_2O/SiO_2 = 0.08-0.12$, led to the formation of ZSM-5. Replacement of part of Na^+ by the K^+ reduced the period needed to obtain fully crystalline zeolite beta. By achieving the synthesis of zeolite beta using TEABr as an organic template one more example was added to the literature to the list of templating agents.

Lohse et al. (1996) investigated the synthesis of zeolite beta using TEA^+ with addition of chelating agents; diethanolamine and triethanolamine. Silica sol, precipitated silica and amorphous silica were tested as silica source. The aluminum sources were sodium aluminate and pseudoboehmite. The reaction mixtures were prepared with the following templating agents; TEAOH, TEABrdiethanolamine and TEAOH-TEABr-triethanolamine. The temperature of crystallization was in the range of 95-170 °C. The samples were characterized using X-ray diffraction, micrographs, chemical, thermal analysis, and IR spectroscopy. It was stated that zeolite beta samples were formed from the gel consisted of TEABr-diethanolamine, only by rotating the autoclaves during the synthesis. Without rotation amorphous material was obtained. The ratio TEABr: diethanolamine in the gel was changed from 6:6 to 0:6. Zeolite beta crystallized at ratios greater than 3:6. The further decrease in the amount of TEA⁺ ions in the reaction mixture yielded mordenite and ZSM-5. With the addition of diethanolamine to the reaction mixture, the diameter of the crystallites reduced and the crystallite surface area increased in dependence on the TEABr/diethanolamine ratio. It was concluded that diethanolamine did not act as a templating agent and diethanolamine had not been incorporated into the pore system of zeolite beta. When the addition of triethanolamine to the reaction mixture was examined, it was observed that the properties of zeolite beta samples did not change in comparison with the samples synthesized by using TEA⁺ ions only. However, at a crystallization temperature of 95 °C, a structural transformation of zeolite beta into a SiO₂ layer structure was observed with increasing crystallization period over 100 days.

In their continuing study, Lohse et al. (1997) searched the formation of zeolite beta from a layer structure. For the preparation of the samples silica sol and amorphous silica were utilized as silica sources. The aluminum source was pseudoboehmite, and the templating agent was tetraethylammonium hydroxide. The formation of beta needed 19 to 50 days dependent upon the temperature of synthesis; 70-135 °C. Zeolite beta was obtained from a layered aluminosilicate, which formed spherical agglomerates. The transformation into the zeolite beta form occurred within the agglomerated particles. The agglomerates were preserved at a relatively low temperature of synthesis. As a result, a high intercrystalline volume was created. The conversion of zeolite beta into a layered SiO₂ was observed at low synthesis temperature and long times of synthesis. In addition, the well ordered SiO₂ structure formed regular plates. The structure collapsed above 200 °C with degradation of the template.

Mostowicz et al. (1997) studied the influence of alkali cations on the synthesis of zeolite beta in fluorine containing media. Synthesis experiments were performed at 170 or 190 °C, from a gel containing diaza-1,4 bicyclo [2,2,2] octane (DABCO), methylamine (MA), hydrofluoric acid (HF) and alkali cations. The molar composition of the gel was 12.5 DABCO: 12.5 MA: x HF: y MF: z Al₂O₃: 25 SiO₂: 500 H₂O. *M* shows the alkali cations; NH_4^+ , Li^+ , Na^+ , K^+ and Cs^+ . x + y = 25, and z = 1 and 2.5. Products were characterized by XRD, SEM, TGA and nuclear magnetic resonance (NMR). It was concluded that the best crystalline zeolite beta samples were obtained after 15 days of crystallization at 170 °C. When the cation content in the solution was 12.5 (y = 12.5) only NH₄, Li, and Cs led to zeolite beta. In the presence of Na and K fluorides, the amount of MF had to be decreased to synthesize pure zeolite beta. However, at 190 °C for the low MF ratios, the products were of lower crystallinity and/or MTN (ZSM-39) also co-crystallized. The crystal size of the samples obtained was about 1.5-3.0 µm. But the crystals obtained in the presence of sodium and potassium cations were smaller than those synthesized by NH₄⁺, Li⁺ and Cs⁺. In this study, by applying thermogravimetric analysis it was found that about 2-3 % weight loss was determined due to the elimination of water. The total weight loss for the samples was about 23 %. Moreover, by the analysis of both induction and crystallization rates it was seen that one of the main roles of the alkali cations was their electrostatic stabilization of the gel.

In the study performed by Vaudry et al. (1997) hydrothermal synthesis of zeolite beta in sodium-tetraethylammonium systems with aluminum content more than 6 atoms per unit cell was investigated. To crystallize zeolite beta precipitated silica and sodium aluminate were utilized as silica and alumina sources, and TEAOH and TEABr were the templating agents. Synthesis experiments were performed at 120 °C in a period of about four days. For the characterization of the products ²⁹Si NMR, AAS, SEM, electron probe microanalysis and XRD. thermogravimetric analysis were applied. It was stated that if no more than six tetraethylammonium molecules can enter a unit cell of zeolite beta, the insertion of more than six AlO₄, tetrahedra per unit cell requires the replacement of at least a fraction of TEA by smaller cations. As a result, the limiting factor in the synthesis of aluminum rich zeolite beta was the replacement of tetraethylammonium by a smaller cation. But such a cation strongly favored the formation of other zeolite phases. The sodium cation was well known as a template for analcime and gismondine formation. In addition, mordenite was formed in sodium-tetraethylammonium containing media. These zeolites, accommodate aluminum easier than zeolite beta. Therefore, their formation left less aluminum available for insertion into the zeolite beta lattice. So, the synthesis batches should be adjusted to obtain aluminum rich zeolite which contained more than 0.094*Al/(Si+Al). Another factor affected the synthesis of aluminum rich zeolite beta was the alkalinity. Lower alkalinity was required to avoid the formation of other zeolite phases because the decomposition of TEA in the alkaline solution was slower.

Camblor et al. (1998) studied the characterization of the nanocrystalline zeolite beta samples which were synthesized hydrothermally at 140 °C in basic medium and in the absence of alkali cations. The gel with the composition; x SiO₂: Al₂O₃: (0.52 x + 2) TEAOH: 15 x H₂O (x = 14-800) was utilized. So as to characterize the nanocrystalline samples, a combination of physicochemical techniques; N₂ adsorption, XRD, multinuclear MAS NMR, pyridine adsorption, FTIR and thermal analysis were applied. It was stated that the most important zeolite property, void volume of zeolite, varied with the composition. As the Si/Al ratio in the gel investigated in the range of 7-400, it was observed that the mesoporous volume increased as the Al content increased. In addition, void volume also decreased when the crystal size decreased below about 100 nm. For instance, when the crystal size decreased to 10 nm from 50 nm, unit cells per crystallite decreased from 16000 to 125.

The influence of alkalinity on particle size distribution and crystalline structure in synthesis of zeolite beta in a short crystallization period was explored by Xic et al. (2001). Zeolite beta samples were crystallized hydrothermally at 150 °C for 60 h under static conditions. Silica gel, TEAOH, sodium aluminate or pseudoboehmite were used as silica source, template and aluminum source, respectively. The alkalinity of the gel was adjusted by utilizing sodium hydroxide. The results indicated that the crystallinity of the samples, containing sodium aluminate did not change so much when the OH-/SiO₂ ratio was lower than 0.29 but increased suddenly when the alkalinity reached 0.29. The highest crystalline samples were obtained at $OH^{-}/SiO_{2} = 0.35$. When pseudoboehmite was the aluminum source, crystallinity increased as the alkalinity of the gel increased until the $OH^{-}/SiO_2 = 0.24$, at which the highest crystalline samples were obtained. Above this value crystallinity decreased and remained stable when the alkalinity of the gel was greater than 0.31. In addition, for the synthesis batches containing pseudoboehmite, the limit of the alkalinity ratio was 0.39. Above this ratio zeolite beta was not synthesized. It was noticed that the crystal morphology was independent of the alkalinity. When the particle size distributions (PSD) of the products were examined it was observed that as the alkalinity increased the PSD was narrowed. Besides, along with the increase of alkalinity, the average particle size was reduced from 1.4 to 0.7 µm.

Tosheva et al. (2001) synthesized zeolite beta spheres within the pores of strongly basic styrene-divinyl-benzene anion exchange resin beads from a solution with the molar composition of 0.31 Na₂O: 9 TEAOH: 0.5 Al₂O₃: 25 SiO₂: 295 H₂O. Synthesis was done at 170 °C in a period varying from 3 to 24 hours and the synthesis solution to resin weight ratio was changed from 2 to 10. According to the study, highly crystalline zeolite beta spheres synthesized within the resin beads after 18 hours of synthesis period. However, it was determined that after 16 hours; zeolite beta samples, crystallized in the bulk solution, were highly crystalline. Synthesized particles were in a size, similar to the resin beads. The interior of the spherical particles was built up by fine particles with a size of 0.1 µm. It was pointed out that for different synthesis time there was no difference in appearance of the interior particles. But differences were observed for the surface of spheres. Roughness of the surfaces was increasing with an increase in time of treatment. When the effect of synthesis solution to resin weight ratio investigated, it was seen that zeolite beta was formed in the beads when the ratio was 10. But zeolite beta was crystallized in the bulk solution at the ratio of 5. In conclusion, the presence of resin macrotemplates during synthesis influenced the crystallization process. In addition, when the products compared with the samples synthesized in the absence of resin beads, highly crystalline samples were synthesized in a shorter period in the bulk solution.

In the study performed by Akata et al. (2004) the effect of low gravity environment on the production of zeolite beta was explored. Products were obtained at 130 °C in microgravity environment from a batch of composition; 2.2 Na₂O: Al₂O₃: 30 SiO₂: 4.6(TEA)₂O: 444 H₂O. For characterization; XRD, field emission scanning electron microscopy (FE-SEM), energy dispersive X-ray spectroscopy (EDX), TGA and IR were applied. In addition, Lewis acid

(MPV) catalyzed Meerwein-Ponndorf-Verley reduction of 4-tertbutylcyclohexanone (4-TBCH) with 2-propanol to a mixture of cis- and tr- 4-tertbutylcyclohexanols (4-TBCHLs) had been utilized to asses the ease of dealumination, pore structure, and thermal stability of the zeolite beta crystals. It was concluded that the samples produced in the microgravity had the same morphology, identical surface and framework Si/Al ratio and unit cell dimensions as the terrestrially grown pure zeolite beta crystals. However, the average particle size was about 10 % larger for the flight products. Besides, the heat treated flight zeolite beta exhibited lower catalytic activity in the MPV reaction than identically heat treated terrestrially grown zeolite beta. By using the flight zeolite beta, higher tr-alcohol selectivity in the MPV reaction was determined. As a result, the samples produced in the low gravity environment had a higher degree of perfection and order.

2.2 Sorption Studies

Zeolites function as molecular sieves, due to their regular nature of pores and their apertures. This property is the outstanding property of zeolites which makes them useful as selective adsorbents for separating substances and as shape selective catalysts. Depending on the type and pore system of zeolites, molecules can penetrate into the channel network or be excluded from it. There are limited numbers of studies related with the sorption properties of zeolite beta in the literature.

On the zeolite beta samples of varying crystallinity, Bhat et al. (1990) studied the adsorption capacities of n-hexane, cyclohexane, m-xylene and water molecules having kinetic diameters of 0.43, 0.60, 0.68 and 0.26 nm, respectively. Experiments were performed at 20 °C, at a relative pressure $P/P_0 = 0.5$. It was concluded that as the crystallinity of the sample increased the adsorbed amount of the probe molecules increased. In addition, the pore volume of the 100 % crystalline sample was determined as 0.23 ml/g.

In the study performed by Eapen et al (1994), sodium forms of zeolite beta samples with different degrees of crystallinity were characterized by the adsorption of different probe molecules; n-hexane, water, benzene and cyclohexane at 25 °C. Samples utilized as adsorbents were activated at 400 °C under vacuum before the experiments and those activated samples was contacted with the sorbate vapors at $P/P_0 = 0.5$ for 2 hours. It was observed that there was a concurrence between the crystallinity and the equilibrium sorption. The average pore volumes for the adsorbates of 100 % crystalline sample were 0.24, 0.19, 0.22 and 0.21 cm³/g for n-hexane, water, benzene, and cyclohexane, respectively. The pore volume of the 100 % crystalline sample calculated from the adsorption of hydrocarbon molecules matched well with that reported in the study performed by Bhat et al. (1990). These results confirmed the large pore nature of the framework of zeolite beta.

Huddersman et al. (1996) studied the sorption capacities of Na-Beta and mordenite samples for 2,3-dimethylbutane and 3-methylpentane at room temperature. Ion exchange modification was performed on those zeolites. As a result, beta (H, Ba), mordenite(Na, K), mordenite(Na, Ba) were obtained. It was pointed out that the adsorption capacities of the zeolites for the probe molecules decreased in the following order; beta (H, Ba) > mordenite (Na, K) > mordenite (Na, Ba). This result confirmed that zeolite beta has larger pore sizes than mordenite. Besides, the amount of 2,3-dimethylbutane adsorbed was always less than that of 3-methylpentane due to the fact that parts of the zeolites were inaccessible to the more branched 2,3-dimethylbutane, and that the packing of this dibranched hexane isomer was less efficient. Pore volume of the hydrogen and barium forms of zeolite beta samples was found as 0.150 cm³/g, and 0.157 cm³/g by using 2,3-dimethylbutane and 3-methylpentane as probe molecules, respectively.

In 1998 Chu et al. measured the sorption capacities of a hydrogen form of zeolite beta for n-hexane, cyclohexane and water by using gravimetric apparatus. Sodium forms of zeolite beta samples were crystallized at different SiO₂/Al₂O₃ ratio and then ion exchanged with 1 N ammonium nitrate solution several times. As a result protonic form of zeolite beta was obtained. Products were calcined at 600 °C for 10 hours before the sorption experiments. Sorption studies were performed at 302 °C for 24 hours period. Zeolite was kept in contact with the vapor of the adsorbate at P/P₀ = 0.3. It was found that zeolite beta exhibited high cyclohexane and water sorption capacities at a SiO₂/Al₂O₃ ratio lower than 69. However, the water sorption capacity decreased with an increase in the SiO₂/Al₂O₃ ratio. Sorption capacity of n-hexane was observed to vary slightly with SiO₂/Al₂O₃ ratio. For the sample whose SiO₂/Al₂O₃ ratio was 25, the sorption capacities (wt %) of water, n-hexane and cyclohexane were found as; 20.29, 17.17 and 20.62 g/g_{zeolite}, respectively.

Adsorption equilibrium and kinetics of branched hexane isomers; n-hexane, 3-methylpentane, 2,3-dimethylbutane and 2,2-dimethylbutane in hydrogen form of zeolite beta samples were studied by Bárcia et al. (2005). It was observed that as the degree of branching increased, the accessibility of the molecules to the active sites of the channels decreased. As a result, it can be concluded that zeolite beta had affinity to the sorbate molecules decreasing in the order; n-hexane > 3-methypentane > 2,3-dimethylbutane > 2,2-dimethylbutane. In addition, macropore diffusion was the controlling mechanism for n-hexane and 3-methylpentane, but for 2,3-dimethylbutane and 2,2-dimethylbutane in the overall diffusion mechanism the micropore diffusion was of importance. It was found that n-hexane was the fastest component, on the other hand 2,3-dimethylbutane was the slowest.

CHAPTER 3

EXPERIMENTAL

3.1 Synthesis of Zeolite Beta

In order to synthesize pure and highly crystalline zeolite beta samples, crystallization was performed hydrothermally under autogenous pressure by using a gel with a molar composition of;

2.2 Na₂O: Al₂O₃: x SiO₂: 4.6 (TEA)₂O: 444 H₂O

where, $20 \le x \le 50$, (TEA = tetraethylammonium). Synthesis was carried out under static conditions at 150 °C for crystallization periods varying from 6 days to 16 days. These conditions were determined in the light of the study performed by Akata et al. (2004) in which SiO₂/Al₂O₃ ratio was selected as 30, and crystallization was done at 130 °C in 15 days period. Zeolite beta samples synthesized in the study are shown in Table 3.1 in a detailed form with the batch name, molar batch composition and crystallization periods.

| Table 3.1 Molar Batch Composition and Crystallization Periods of the |) |
|--|---|
| Synthesized Zeolite Beta Samples | |

| Batch | | Crystallization |
|--------|--|-----------------|
| Name | Molar Batch Composition | Time (Days) |
| NHT 37 | 2.2 Na ₂ O: Al ₂ O ₃ : 20 SiO ₂ : 4.6 (TEA) ₂ O: 444 H ₂ O | 6 |
| NHT 38 | 2.2 Na ₂ O: Al ₂ O ₃ : 20 SiO ₂ : 4.6 (TEA) ₂ O: 444 H ₂ O | 8 |
| NHT 39 | 2.2 Na ₂ O: Al ₂ O ₃ : 20 SiO ₂ : 4.6 (TEA) ₂ O: 444 H ₂ O | 10 |
| NHT 19 | 2.2 Na ₂ O: Al ₂ O ₃ : 20 SiO ₂ : 4.6 (TEA) ₂ O: 444 H ₂ O | 12 |
| NHT 21 | 2.2 Na ₂ O: Al ₂ O ₃ : 20 SiO ₂ : 4.6 (TEA) ₂ O: 444 H ₂ O | 14 |
| NHT 22 | 2.2 Na ₂ O: Al ₂ O ₃ : 20 SiO ₂ : 4.6 (TEA) ₂ O: 444 H ₂ O | 16 |
| NHT 25 | 2.2 Na ₂ O: Al ₂ O ₃ : 30 SiO ₂ : 4.6 (TEA) ₂ O: 444 H ₂ O | 6 |
| NHT 24 | 2.2 Na ₂ O: Al ₂ O ₃ : 30 SiO ₂ : 4.6 (TEA) ₂ O: 444 H ₂ O | 8 |
| NHT 28 | 2.2 Na ₂ O: Al ₂ O ₃ : 30 SiO ₂ : 4.6 (TEA) ₂ O: 444 H ₂ O | 10 |
| NHT 20 | 2.2 Na ₂ O: Al ₂ O ₃ : 30 SiO ₂ : 4.6 (TEA) ₂ O: 444 H ₂ O | 12 |
| NHT 40 | 2.2 Na ₂ O: Al ₂ O ₃ : 30 SiO ₂ : 4.6 (TEA) ₂ O: 444 H ₂ O | 14 |
| NHT 23 | 2.2 Na ₂ O: Al ₂ O ₃ : 30 SiO ₂ : 4.6 (TEA) ₂ O: 444 H ₂ O | 16 |
| NHT 34 | 2.2 Na ₂ O: Al ₂ O ₃ : 40 SiO ₂ : 4.6 (TEA) ₂ O: 444 H ₂ O | 12 |
| NHT 30 | 2.2 Na ₂ O: Al ₂ O ₃ : 50 SiO ₂ : 4.6 (TEA) ₂ O: 444 H ₂ O | 12 |

In the synthesis experiments, colloidal silica (Ludox HS-40, 40 wt. % SiO₂, Aldrich, lot no: 17726AD), sodium aluminate (anhydrous technical, Riedel-de Häen, lot no: 43380), sodium hydroxide (pearls, 97+%, J.T. Baker, lot no: 0504101014), tetraethylammonium hydroxide (35 wt. %, Aldrich, lot no: 05631AO-165), and deionized water (resistivity = 18.3 M Ω cm) were used as raw materials.

Zeolite beta formulation used in this study was prepared from two precursor solutions; sodium aluminate and silica containing solutions. The sodium aluminate precursor solution was prepared by dissolving sodium aluminate and sodium hydroxide in deionized water by stirring at room temperature for about 40 minutes. Then, this solution (named as Solution A), was heated in a convection oven at about 70 - 90 °C for 50 minutes. After cooling the solution down to room temperature, the template molecule; tetraethylammonium hydroxide was added. The silica containing precursor solution, Solution B, was prepared by mixing Ludox HS-40 colloidal silica with deionized water. As a next step, Solution B was added to the solution including Solution A and the template molecules. The resulting gel was shaken for 30 seconds and transferred into stainless steel or brass autoclaves with Teflon inserts of 15-20 ml capacity as shown in Figure 3.1. The autoclaves were then heated in an oven at 150 °C. After crystallization periods of $6 \le t \le 16$ days, the autoclaves were removed from the oven and quenched with cold water so as to stop the crystallization process. The solid product crystals were recovered by filtering the solution through Schleicher and Schuell blue ribbon (589/3) filter paper. Recovered solid product was washed with distilled water until obtaining a pH value, which was less or equal to 8. Finally, the products were dried at 75 °C in a day period. In Figure 3.2 the flow chart of the synthesis process is shown.



(a)



(b)

Figure 3.1 View of (a) Stainless Steel Autoclave and (b) Teflon Insert Used in Zeolite Beta Synthesis


Figure 3.2 Flow Diagram of Zeolite Beta Synthesis Procedure

3.2 X-Ray Diffraction (XRD) Analyses

Crystallinity and the phase purity of the zeolite beta samples were identified from their X-ray diffraction patterns. These patterns were obtained by a Philips PW 1840 diffractometer using Ni-filtered CuK α radiation. Analysis conditions are given in Table 3.2.

| Anode Tube | Cu |
|-----------------------------------|------|
| Filter | Ni |
| Radiation | CuKa |
| Voltage (kV) | 30 |
| Current (mA) | 24 |
| Bragg Angle (2θ) (Degree) | 5-40 |
| Scan Speed (Degree/ s) | 0.1 |
| Time Constant (s) | 1 |
| Slit (mm) | 0.2 |

 Table 3.2 Operating Conditions of X-Ray Diffractometer

Percent crystallinity of the samples was defined on the basis of the three characteristics peaks of Zeolite Beta at Bragg angles of 7.5, 21.3 and 22.4 shown with asterisks in Figure 3.3.

Percent crystallinity was calculated by using Equation 3.1.

%Crystallinity =
$$\frac{\sum_{i=1}^{3} \text{Intensity}_{i}}{\left[\sum_{i=1}^{3} \text{Intensity}_{i}\right]_{\text{Ref}}} \times 100$$
 (3.1)

Among all the synthesized zeolite beta samples, the one in which the sum of the diffraction intensities of these three peaks was highest was selected as the reference with 100 % crystallinity and the crystallinity of the other samples were calculated according to the reference.



Figure 3.3 The XRD Pattern of Zeolite Beta

To determine the percent yield of the synthesis, the solid product and the weight of the gel forming the batch were measured. Percent yield was calculated in dry basis by using the Equation 3.2. In Appendix B, sample calculation for % yield, is given in more detail.

% Yield =
$$\frac{\text{Weight of Solid}(g)}{\text{Weight of Batch in Dry Basis}(g)} \times 100$$
 (3.2)

3.3 Scanning Electron Microscope (SEM) Analyses

The morphologies and crystal sizes of the synthesized samples were observed by Leo 435VP (Variable Pressure Scanning) Zeiss-Leica Scanning Electron Microscope in Turkish Cement Manufacturers Association. The micrographs of SEM were taken in the magnification range of 3000 to 5000 times.

3.4 Thermogravimetric (TGA) Analyses

During the synthesis, the pores of the products were filled with the template molecules and these molecules must be removed in order to make the structure microporous. Therefore, the temperature at which the template molecules were removed from the pores of the zeolite beta and the hydration behavior of the samples were investigated by Thermogravimetric Analysis (TGA). Experiments were carried out by using Du Pont 951 thermal gravimetric analyzer. About 20-25 mg zeolite beta sample was heated at a rate of 10 °C/min within 30-1000 °C under nitrogen or air flow.

3.5 Nitrogen Adsorption Measurements

 N_2 adsorption and desorption isotherms of the zeolite beta sample were measured at - 196 °C with a Micromeritics Gemini V, surface area and pore size analyzer. About 0.2 mg zeolite beta sample which was previously calcined at 550 °C for 6 hours was utilized as the adsorbent. For the determination of the adsorption/desorption isotherm, the value of P/P₀ was increased from 0.080 to 0.985 and subsequently reduced to 0.14. In addition, the surface area was calculated by using the Brunauer-Emmett-Teller (BET) equation, given in Appendix C in more detail. For BET surface area measurements relative pressure was in the range of $0.08 \le P/P_0 \le 0.30$. Since, at higher relative pressures the BET equation is usually inaccurate as a result of capillary condensation effect; while at relative pressure values below 0.05 the amount of adsorbed gas is too small to be measured.

3.6 Gravimetric Sorption Analyses

With gravimetric sorption analyses, the amount of gas or vapor adsorbed on the sorbent was measured by weighing the sample in a closed system on a balance. Thus, sorption capacities and rates of sorption were determined by examining the change in mass as a function of time.

In gravimetric sorption experiments Na forms of zeolite beta samples, which were calcined at 550 °C for 6 hours, were utilized. Zeolite beta sample of which SiO₂/Al₂O₃ ratio is 50 and crystallized in 12 days period was selected as adsorbent. Sorbates used in these analyses were methanol (J.T. Baker, 99.8+%, lot no: 0417640002), ethanol (absolute, Gurup Deltalar, 99.5%, lot no: ASO 55-L 50), isopropanol (anhydrous, Acros, 99.8+%, lot no: A019329501), n-butanol (J.T. Baker, 99.4%, lot no: 0216510014), o-xylene (Fluka, puris pa., lot no: 247260), m-xylene (Fluka, puris pa., lot no: 225773) and p-xylene (Fluka, puris pa., lot no: 232507). Vapor pressures and liquid densities of the probe molecules are given in Appendix D in Table D.1 and D.2, respectively. The measurements were performed at 0 °C, 23 °C and 50 °C in a conventional gravimetric adsorption system which was used in the study of Öztin (1997). In Figure 3.4 gravimetric adsorption apparatus is shown.



Figure 3.4 Gravimetric Adsorption Apparatus (Öztin, 1997)

An electronic balance enclosed in a vacuum chamber, a high vacuum pump unit, an electronic manometer, a strip chart recorder, a thermostat, doser chambers and valves are the main units of this system.

For the operation of this system; the electrobalance was calibrated first. Then, about 30-40 mg zeolite beta sample was put into an aluminum sample pan attached to the electrobalance. By the help of high vacuum pump unit, system was evacuated and the pressure of the system was recorded by an electronic manometer. When the system reached the possible lowest pressure, about 3.8 mm Hg, the temperature of the thermostat was adjusted to the value at which the experiment was performed and then it was lifted up until the tube enclosing the sample pan was immersed into the thermostat. By means of that, the sample temperature was kept constant at adsorption condition. Next, the sorbate was

loaded with the help of doser chamber until the sorbate pressure reached to the desired value. At the same time when the sorbate was loaded to the system, the recorder was turned on and the change in the mass of the sorbent was recorded as a function of time with suitable chart speed and recorder range.

Since the rates of sorption and the amounts adsorbed are affected by the moisture, or other adsorbed species, before each experiment zeolite samples must be regenerated. To regenerate the samples an outgassing furnace and a temperature programmer was utilized. In addition, a digital thermometer was used to observe the temperature inside the furnace.

In order to regenerate the sample, the tube enclosing the zeolite beta was inserted into the outgassing furnace and by the temperature programmer heating was started. During regeneration, the temperature of the zeolite was increased to about 430 °C under vacuum. Heating rate was not constant during the process, and it was shown in Table 3.3. The operation continues for about 4 hours. After then, the furnace was removed and the sample was cooled down to the room temperature.

| Temperature Range (°C) | Heating Rate (°C/min) |
|---------------------------|-----------------------|
| ~20-50 | 1 |
| 50-100 | 3 |
| 100-300 | 6 |
| 300-375 | 4 |
| 375-400 | 2 |
| 400-~430 | 1 |

| Table 3.3 He | ating Rate in | n Regeneration |
|--------------|---------------|----------------|
|--------------|---------------|----------------|

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Synthesis of Zeolite Beta

In this study synthesis and characterization of zeolite beta was performed. Zeolite beta was synthesized under hydrothermal conditions and autogenous pressure from a sodium and tetraethylammonium hydroxide containing gel with a molar composition of 2.2 Na₂O: Al_2O_3 : x SiO₂: 4.6 (TEA)₂O: 444 H₂O. In order to synthesize pure zeolite beta samples, synthesis parameters were changed in the system. The parameters of the synthesis process were SiO₂/Al₂O₃ ratio and crystallization time.

In Figure 4.1 a sample XRD pattern of zeolite beta is shown. The characteristic peaks are observed at 2 theta values of 7.5°, 21.2° and 23.3°. The peaks of the XRD patterns obtained for the synthesized samples were compared with the pattern shown in Figure 4.1 in order to understand whether they were zeolite beta or not.



Figure 4.1 Sample XRD Pattern of Zeolite Beta (http://www.iza-online.org/synthesis/Recipes/ XRD/Zeolite%20Beta.jpg)

4.2 Crystallization Results

The experiments were carried out mainly in two groups. In the first group, syntheses were performed at 150 $^{\circ}$ C from gels having a SiO₂/Al₂O₃ ratio of 20 and 30. Crystallization period was changed in the range of 6 to 16 days for obtaining pure zeolite beta phase.

The aim in this group of experiments was to determine the effect of crystallization period on the yield and crystallinity of the zeolite beta samples, produced at 150 °C in the presence of tetraethylammonium hydroxide template. The values of the SiO₂/Al₂O₃ ratio and the crystallization time used in these experiments were planned by considering the previous studies on zeolite beta synthesis. For example, Perez-Pariente et al. (1993) offered a SiO₂/Al₂O₃ ratio range for zeolite beta synthesis between 30 and 900. Camblor et al. (1991) proposed a SiO₂/Al₂O₃ ratio of 50 for zeolite beta synthesis. Also Xic et al. (2001) noted this ratio as 50. The optimum SiO₂/Al₂O₃ ratio in the molar batch composition for synthesizing zeolite beta was estimated between 15 and 58 by Eapen et al. (1994). In addition, crystallization period range for zeolite beta synthesis was given from 5 to 8 days in the studies of Bhat et al. (1990) and Eapen at al. (1994). In the study of Akata et al. (2004) crystallization was carried out in 15 days period. Syntheses were accomplished in this study in a period varying from 6 to 16 days.

In the other group, crystallization period was fixed at 12 days and the behavior of crystallization and yield with respect to SiO_2/Al_2O_3 ratio was investigated by increasing the ratio to 40 and 50.

Temperature range for zeolite beta synthesis was given from 78 to 180 °C in the study of Newsam et al. (1988). In addition, Bhat et al. (1990) synthesized zeolite beta at temperatures varying from 130 to 170 °C. As well, in the study performed by Xic et al. (2001) crystallization temperature was selected as 150 °C. It should

be noted from the study performed by Bhat et al. (1990) that as the temperature decreases the time necessary for obtaining zeolite beta at higher crystallinity percent increases. From the previous studies mentioned above it was also observed that pure and highly crystalline zeolite beta products were obtained in the experiments performed at 150 °C. Thus, in this study 150 °C was determined as the synthesis temperature.

4.2.1 Crystallization Results of the Experiments Performed at Different Crystallization Periods

Table 4.1 and Table 4.2 show the results that were calculated for the first group of experiments performed with SiO_2/Al_2O_3 ratio of 20 and 30, respectively.

For all crystallization periods shown in these tables, the pure zeolite beta phase was synthesized successfully. A sample XRD pattern belonging to zeolite beta (NHT 19) of which SiO_2/Al_2O_3 ratio was 20 and crystallized in 12 days period is shown in Figure 4.2. It should be noted that, the peaks appeared were consistent with the peaks of the sample zeolite beta shown in Figure 4.1.

As seen in Table 4.1 and Table 4.2, yield % in dry basis slightly increases as the synthesis period increases, and the value reaches maximum in 12 days period for the samples crystallized from a gel having a SiO_2/Al_2O_3 ratio of either 20 or 30. After 12 days period, it was observed that yield decreases slightly with the crystallization time.



Figure 4.2 XRD Pattern of Zeolite Beta Sample Synthesized from a Molar Batch Composition of 2.2 Na₂O: Al₂O₃: 20 SiO₂: 4.6 (TEA)₂O: 444 H₂O in 12 Days.

| e 4.1 C | rystalliza | ation of 7 | Zeolite | Beta fi | rom a | Molar | Batch (| Composition | 1 of | able 4.1 Crystallization of Zeolite Beta from a Molar Batch Composition of | |
|---------|------------|------------------|--------------------------|----------------------------------|---|--|--|--|--|--|--|
| | e 4.1 C | e 4.1 Crystalliz | e 4.1 Crystallization of | e 4.1 Crystallization of Zeolite | e 4.1 Crystallization of Zeolite Beta f | e 4.1 Crystallization of Zeolite Beta from a | e 4.1 Crystallization of Zeolite Beta from a Molar | e 4.1 Crystallization of Zeolite Beta from a Molar Batch (| e 4.1 Crystallization of Zeolite Beta from a Molar Batch Composition | lda | |

| Crystallinity % | 85.25 | 85.89 | 87.01 | 89.32 | 17.19 | 92.76 |
|--------------------------------|--------------|--------------|--------------|--------------|--------------|--------------|
| Yield % | 39.43 | 40.14 | 44.09 | 44.88 | 44.82 | 39.15 |
| Weight of Product (g) | 1.5677 | 1.4862 | 1.5860 | 1.7202 | 1.4720 | 1.4995 |
| Weight of Batch (g) | 3.9764 | 3.7029 | 3.5969 | 3.8329 | 3.2844 | 3.8297 |
| Crystalline Phase | Zeolite Beta | Zeolite Beta | Zeolite Beta | Zeolite Beta | Zeolite Beta | Zeolite Beta |
| Crystallization Time (Days) | 9 | ∞ | 10 | 12 | 14 | 16 |
| Batch Name | NHT 37 | NHT 38 | NHT 39 | NHT 19 | NHT 21 | NHT 22 |

2.2 Na₂O: Al₂O₃: 20 SiO₂: 4.6 (TEA)₂O: 444 H₂O

| h: | 2.2 N Crystallization Time (Dave) | (a ₂ 0: Al ₂ 0 ₃ : 30 S Crystalline Dhase | Weight (TEA Weight of Batch (a) | V) ₂ O: 444 H ₂ O Weight of Product (a) | Yield % | Crystallinit % |
|----|--|--|---------------------------------------|---|------------|-------------------|
| 25 | 6 (5 (1) (1) (1) (1) (1) (1) (1) (1) (1) (1) | Zeolite Beta | 4.5183 | 1.9793 | 43.81 | 90.84 |

| Batch | Crystallization | Crystalline | Weight of | Weight of | Yield | Crystallinity |
|--------|-----------------|--------------|-----------|-------------|-------|---------------|
| Name | Time (Days) | Phase | Batch (g) | Product (g) | % | % |
| NHT 25 | 9 | Zeolite Beta | 4.5183 | 1.9793 | 43.81 | 90.84 |
| NHT 24 | 8 | Zeolite Beta | 4.5852 | 2.0418 | 44.53 | 91.42 |
| NHT 28 | 10 | Zeolite Beta | 4.5565 | 2.1850 | 47.95 | 92.35 |
| NHT 20 | 12 | Zeolite Beta | 4.3271 | 2.1564 | 49.83 | 93.29 |
| NHT 40 | 14 | Zeolite Beta | 4.5499 | 2.2218 | 48.83 | 93.98 |
| NHT 23 | 16 | Zeolite Beta | 4.1358 | 1.5609 | 37.74 | 94.33 |

Figure 4.3 and Figure 4.4 display the XRD patterns of the products synthesized at different time periods within the same batch composition having SiO_2/Al_2O_3 ratio of 20 and 30, respectively. From these figures the increase in crystallinity with the crystallization period is observed.



Figure 4.3 X-Ray Diffraction Patterns of the Samples Synthesized at Different
Time Periods in Days: (a) 6; (b) 8; (c) 10; (d) 12; (e) 14; (f) 16 from the Molar
Batch Composition of 2.2 Na₂O: Al₂O₃: 20 SiO₂: 4.6 (TEA)₂O: 444 H₂O.



Figure 4.4 X-Ray Diffraction Patterns of the Samples Synthesized at Different Time Periods in Days: (a) 6; (b) 8; (c) 10; (d) 12; (e) 14; (f) 16 from the Molar Batch Composition of 2.2 Na₂O: Al₂O₃: 30 SiO₂: 4.6 (TEA)₂O: 444 H₂O.

In Figure 4.5 and Figure 4.6, the effect of synthesis period on crystallinity of the samples can be observed better.



Figure 4.5 Effect of Synthesis Time on the Crystallization of Zeolite Beta from Molar Batch Composition of 2.2 Na₂O: Al₂O₃: 20 SiO₂: 4.6 (TEA)₂O: 444 H₂O.



Figure 4.6 Effect of Synthesis Time on the Crystallization of Zeolite Beta from Molar Batch Composition of 2.2 Na₂O: Al₂O₃: 30 SiO₂: 4.6 (TEA)₂O: 444 H₂O.

As seen from these figures, there is a continuous increase in crystallinity with the increase in time period. For SiO_2/Al_2O_3 ratio of 20, as the period changes from 6 days to 16 days, the crystallinity changes from 85.25 % to 92.76 %. However for the same change in the crystallization period results in change of crystallinity from 90.84 % to 94.33 % for the samples crystallized at SiO_2/Al_2O_3 ratio of 30.

The obtained results are consistent with the literature such that; in the studies performed by Bhat et al. (1990) and Eapen et al. (1994) it was reported that there is an increase in the crystallinity percent as the crystallization proceeds. According to Bhat et al. (1990), in periods of 4, 5, 6 and 8 days; the crystallinity values were reported as 20 %, 30 %, 60 % and 100 %, respectively. Similarly, Eapen et al. (1994) obtained the crystallinity values as 9 %, 41 %, 70 %, 90 % and 100 % for the synthesis time of 3, 5, 6, 7 and 8 days, respectively.

4.2.2 Crystallization Results of the Experiments Performed at Different SiO₂/Al₂O₃ Ratio

The results of the experiments that were performed in 12 days period with different SiO_2/Al_2O_3 ratios; 20, 30, 40 and 50 are tabulated in Table 4.3.

In the first group of experiments with SiO₂ /Al₂O₃ ratio of 20 and 30; as it was mentioned above, the highest yield was obtained in 12 days. As a result of this, the experiments with SiO₂ /Al₂O₃ ratio of 40 and 50 were carried out in 12 days. Results show that as the silica content increases, the yield also increases. For the SiO₂ /Al₂O₃ ratio of 20, the yield was 44.88 % and this value reaches to 62.29 % for the ratio of 50.

| Crystallinity % | 89.32 | 93.29 | 97.70 | 100.00 |
|--|--------|--------|--------|--------|
| Yield % | 44.88 | 49.83 | 55.99 | 62.29 |
| Weight of Product (g) | 1.7202 | 2.1564 | 2.8385 | 2.7643 |
| Weight of Batch (g) | 3.8329 | 4.3271 | 5.0695 | 4.4378 |
| SiO ₂ /Al ₂ O ₃ | 20 | 30 | 40 | 50 |
| Crystallization Time (Days) | 12 | 12 | 12 | 12 |
| Batch Name | NHT 19 | NHT 20 | NHT 34 | NHT 30 |

For the experiments performed in 12 days, when the effect of SiO_2/Al_2O_3 ratio on the crystallization was examined, it was determined that high crystallinity was obtained at high SiO_2/Al_2O_3 ratios.



Figure 4.7 Effect of SiO₂/Al₂O₃ Ratio on the Crystallization of Zeolite Beta Synthesized at 150 °C in 12 Days.

This result is also in agreement with the previous studies performed by Perez-Pariente et al. (1988) and Bhat et al. (1990). In these studies it was noted that, the products became more siliceous when the crystallinity increases.

4.3 Characterization by SEM

By using scanning electron microscope the morphology and the size of the synthesized zeolite beta crystals were observed. The sample micrographs are shown in Figure 4.8, Figure 4.9 and Figure 4.10.



Figure 4.8 SEM Micrograph of Sample NHT 34 of which SiO₂/Al₂O₃ Ratio was 40 and Crystallized in 12 Days.



Figure 4.9 SEM Micrograph of a Zeolite Beta Sample of which SiO₂/Al₂O₃ Ratio was 40 and Crystallized in 8 Days.



Figure 4.10 SEM Micrograph of Sample NHT 30 of which SiO₂/Al₂O₃ Ratio was 50 and Crystallized in 12 Days.

From Figure 4.8, it is seen that zeolite beta crystals were formed as spheroidal and their size were smaller than 1 μ m. The similar morphology with nearly the same crystal size; about 0.3-1.5 μ m was observed in zeolite beta sample synthesized in the study of Akata et al. (2004) where the SiO₂/Al₂O₃ ratio was 30 and synthesis time was 15 days.

In Figure 4.9 a micrograph of a zeolite beta sample crystallized from a gel having a molar batch composition of 2.2 Na₂O: Al₂O₃: 40 SiO₂: 4.6 (TEA)₂O: 444 H₂O in 8 days is shown.

When Figure 4.8 and Figure 4.9 were compared, it was observed that the morphology and the crystal size of zeolite beta samples, which were crystallized from the same molar batch composition in different synthesis duration, were very similar to each other. As a result, it can be pointed out that synthesis period does not affect the crystal morphology and crystal size.

Figure 4.10 belongs to a zeolite beta sample synthesized in 12 days with a SiO_2/Al_2O_3 ratio of 50. As in the cases above, the morphology and the crystal size of the sample did not change much, and the crystals were in spheroidal shape and they were smaller than 1 µm. The same result was obtained in the study performed by Camblor et al. (1991). According to that study the average crystal size of the zeolite beta was smaller than 1 µm and it was stated that when the SiO_2/Al_2O_3 ratio of the sample increased from 40 to 50 the crystal size of the product was not affected so much and remained almost constant.

4.4 Characterization by TGA

Thermogravimetric analysis was carried out to determine the temperature at which the template molecule can be removed from the synthesized zeolite beta samples. In addition, the water desorption amount and weight change due to heating was observed by applying TGA to the synthesized samples. The experiments were done under nitrogen or air flow in the temperature range of 30-1000 °C, with heating rate of 10 °C/min.

Figure 4.11 and Figure 4.12 show that TGA results of sample NHT 19, synthesized from a molar batch having a SiO_2/Al_2O_3 ratio of 20, under nitrogen and air flow, respectively.

It is seen from Figure 4.11 and Figure 4.12 that, between room temperature and 200 °C, a weight loss about 3.5 % occurs due to desorption of water. This value was reported as 3.9 % in the study of Bourgeat-Lami et al. (1992) and as 4 % in the study of Lohse et al. (1996).

The weight loss above 200 °C, which corresponds to 14-14.5 %, can be ascribed to desorption and/or decomposition of tetraethylammonium hydroxide from zeolite pores. Tetraethylammonium hydroxide left the zeolite beta structure at about 450 °C. This observation is in agreement with zeolite beta sample crystallized in the studies of Bourgeat-Lami et al. (1992) and Akata et al. (2004).

For the two temperature ranges indicated above, total weight loss was observed as about 18 %. This result was again almost in consistency with the study performed by Bourgeat-Lami et al. (1992), in which total weight loss was found to be around 20 %.

When the TGA results of the same sample under nitrogen and air flow are compared, it can be pointed out that in both cases similar results were observed for template removal temperature, water desorption amount and total weight loss. Under nitrogen flow two peaks belonging to water and tetraethylammonium hydroxide removal was observed at about 70 °C and 450 °C, respectively. However under air flow at about 600 °C a third peak was observed. This situation probably happened because of dehydroxilation. H_2O in the structure was removed under air atmosphere at about 600 °C.



Figure 4.11 TGA Graph of the Sample (NHT 19) under Nitrogen Flow



Figure 4.12 TGA Graph of the Sample (NHT 19) under Air Flow

In Figure 4.11, a weight loss was observed to continue at about 850 °C. This situation was clarified in Figure 4.12. Under nitrogen flow, water molecules in the structure of zeolite beta particles left the structure at higher temperatures than they did under air flow. On the other hand, in the case of under air flow, the weight loss almost stayed constant after the dehydroxilation at about 600 °C.

4.5 Nitrogen Adsorption Measurements Results



Figure 4.13 N₂ Adsorption and Desorption Isotherm at -196 °C of Zeolite Beta Synthesized from a Gel with the SiO₂/Al₂O₃ Ratio of 50 in 12 Days

The nitrogen adsorption and desorption isotherm for zeolite beta is shown in Figure 4.13. According to IUPAC classification (Brunauer et al., 1940), the isotherm is Type II, which is the same type of isotherm found by Tosheva et al., (2001) for calcined zeolite beta synthesized from a composition of 0.31 Na₂O: 9TEAOH: 0.5 Al₂O₃: 25 SiO₂: 295 H₂O. This type of isotherm describes the adsorption on microporous adsorbents with strong adsorbate-adsorbent interactions. Moreover, there was a continuous progression with increasing

loading from monolayer to multilayer and then to capillary condensation. A capillary condensation step at relative pressure P/P_0 of 0.94 on the isotherm for zeolite beta indicates the stage at which microporous adsorption was complete and the capillary condensation of the interparticle space was about to begin. As a result, zeolite beta can be considered to be a wide pore size zeolite. According to IUPAC, pore sizes can be grouped in three categories. Pores with diameters larger than 50 nm are called macropores, if the diameter size is between 2 and 50 nm these pores are named as mesopores. And finally micropores are the ones with pore diameter of less than 2 nm. Although, in this study the synthesized zeolite beta samples had wide pores they were in microporous range.

The total surface area of zeolite beta particles, evaluated by using BET theory, was $488 \pm 24 \text{ m}^2/\text{ g}$. In the previous study performed by Kubicek et al. (1998) the total surface area was found as 563 m²/ g for ammonium form of zeolite beta. In another study, Li et al. (2003) obtained 434 m²/g total surface area for pure silica zeolite beta. Then in the light of these studies, it can be concluded that the obtained result, $488 \pm 24 \text{ m}^2/\text{ g}$, was in the acceptable range when compared with these literature results.

4.6 Sorption Capacity Measurements

The uptake curves and equilibrium sorption capacities for methanol, ethanol, isopropanol, n-butanol, o-xylene, m-xylene and p-xylene on sodium (Na) form of zeolite beta were measured by gravimetric method using an electrobalance system at 0 $^{\circ}$ C, 23 $^{\circ}$ C and 50 $^{\circ}$ C.

During these sorption experiments, at first the system was evacuated. Then, the sorbate was loaded to the system. In experiments performed at 0 °C and 23 °C, system pressure was adjusted to about half of the vapor pressure of the probe molecule, whereas in the experiments which were carried out at 50 °C, the pressure was about the half of the vapor pressure of the sorbate at 23 °C. The

reason for this was to prevent the condensation of the probe molecule because the system was kept at room temperature. In addition, pressure was provided in a short time. Pressures were increased in a stepwise manner to observe the adsorption isotherms. The isotherms for methanol, ethanol, isopropanol and nbutanol are given in Figure 4.14, Figure 4.15, Figure 4.16 and Figure 4.17, respectively.



Figure 4.14 Methanol Adsorption Isotherms of Na-Beta



Figure 4.15 Ethanol Adsorption Isotherms of Na-Beta



Figure 4.16 Isopropanol Adsorption Isotherms of Na-Beta



Figure 4.17 n-Butanol Adsorption Isotherms of Na-Beta

As it is seen from the Figures 4.14-4.17 these isotherms are of Type I according to Brunauer's classification. Due to the nature of this type of isotherms, the adsorbed amount corresponds to limiting sorption volume.

The pore volume of a dehydrated zeolite and other microporous solids having Type I isotherms can be calculated by Gurvitsch rule (Breck, 1974). Densities of the sorbed molecules are different than those of normal liquids. However, Gurvitsch rule assumes that at the point of saturation (P/P₀ ~0.5-1.0) the sorbate fills the micropores of the solid as the normal liquid having a density of the liquid at the adsorption temperature.

As a result, the limiting volumetric equilibrium sorption capacities of the zeolite beta sample against different probe molecules were calculated by utilizing the adsorbed amount of the probe molecule and the liquid densities of the sorbates at the adsorption temperature.

In Table 4.4, the limiting volumetric equilibrium sorption capacities of the zeolite beta sample for methanol, ethanol, isopropanol, n-butanol, o-xylene, m-xylene and p-xylene are tabulated at different temperatures. In addition, kinetic diameters of the probe molecules (Bowen et al., 2003; Szostak, 1992) are presented. The values which are given in parentheses in Table 4.4 are the reproducibility results obtained at 0 °C by utilizing alcohols as the probe molecules.

As it is seen from Table 4.4 sorption capacities of zeolite beta sample against alcohols are about the same and are $0.25 \text{ cm}^3/\text{g}$ at 0 °C. For the xylene isomers; o-xylene, m-xylene and p-xylene at 0 °C these values are $0.21 \text{ cm}^3/\text{g}$, $0.22 \text{ cm}^3/\text{g}$ and $0.24 \text{ cm}^3/\text{g}$, respectively. Although these results are slightly larger than the results in literature, they are in good agreement with them. For example in one of the previous studies carried out by Bhat et al. (1990) the adsorption capacity of the zeolite beta at 20 °C for n-hexane, cyclohexane and m-xylene was

determined as $0.23 \text{ cm}^3/\text{g}$, $0.22 \text{ cm}^3/\text{g}$ and $0.22 \text{ cm}^3/\text{g}$, respectively. In addition, the sorption capacity values for the n-hexane and cyclohexane at 25 °C was calculated as $0.24 \text{ cm}^3/\text{g}$ and $0.21 \text{ cm}^3/\text{g}$, respectively in the study of Eapen at al. (1994).

Table 4.4 Sorption Capacities of Na-Beta at 0 °C, 23 °C and 50 °C AgainstMethanol, Ethanol, Isopropanol, n-Butanol, o-Xylene, p-Xylene and m-Xylene

| Zeolite | Temperature | | | Adsor | ption Capacity (| $cm^3/g)$ | | |
|---------|-------------|--------------------------------------|------------------------------------|--|--------------------------------------|-------------------------------------|-------------------------|---|
| Beta | () () | Methanol $\sigma = 0.385 \text{ nm}$ | Ethanol $\sigma = 0.43 \text{ nm}$ | Isopropanol $\sigma = 0.47 \text{ nm}$ | n-Butanol $\sigma = 0.50 \text{ nm}$ | o-Xylene $\sigma = 0.68 \text{ nm}$ | m-Xylene σ = 0.68 nm | p-Xylene $\sigma = 0.585 \text{ nm}$ |
| | 0 | 0.254 (0.253) | 0.250 (0.250) | 0.254 (0.255) | 0.254 (0.253) | 0.214 | 0.218 | 0.241 |
| Na form | 23 | 0.251 | 0.245 | 0.250 | 0.251 | 0.210 | 0.215 | 0.235 |
| | 50 | 0.223 | 0.235 | 0.241 | 0.243 | 0.206 | 0.208 | 0.225 |

Zeolite beta, as described in section 1.2, contains a 3-D channel system. This channel system consists of two types of 12 membered ring pores having dimensions of 5.6 x 5.6 Å and 7.7 x 6.6 Å (Bárcia et al., 2005). In Figure 4.18 the 12 membered ring pores along axis; [100] and [001] is shown.



Figure 4.18 12 Membered Ring Along Axis; (a) [100], (b) [001] (Bárcia et al., 2005)

It was seen from the Table 4.4 that, the kinetic diameters of all alcohols (methanol, ethanol, isopropanol and n-butanol) utilized in this study are smaller than the smallest pore diameter of zeolite beta, which is 5.6 Å. Therefore, they can fill in the pores of the zeolite beta, to a great extent and almost at the same amount. Hence, the sorption capacity of zeolite beta for these alcohols can be considered to be more or less the same.

On the other hand, when the kinetic diameters of xylene isomers were considered, it was seen that the diameters of o-xylene and m-xylene were wider

than 5.6 Å, which resulted in less sorption capacity of zeolite beta for these two xylene isomers than the alcohols. In addition, the packing density of zeolite beta could be effective on this case. Namely, the way of fitting of the sorbates in the zeolite beta pores would be important in terms of their conformation with the pore shapes and sizes.

Finally, the reason why p-xylene was adsorbed slightly greater than other two isomers could be again because of the effect of packing density. Also, its kinetic diameter (5.85 Å), which is closer to 5.6 Å, could be effective to a certain extent. Such a molecular size can make this xylene isomer to be adsorbed better than other two.

Uptake curves of the sorption of the probe molecules on sodium form of zeolite beta at different temperatures are shown in Figures 4.19 through 4.25. In these figures, the ratio of mg sorbate/g sorbent as a function of time is plotted.



Figure 4.19 Uptake Curves of Methanol on Na-Beta at Different Temperatures $(P_{f, 0 \circ C}=P_{o, 0 \circ C}/2 \text{ and } P_{f, 23 \circ C, 50 \circ C}=P_{o, 23 \circ C}/2)$



Figure 4.20 Uptake Curves of Ethanol on Na-Beta at Different Temperatures $(P_{f, 0 \circ C}=P_{o, 0 \circ C}/2 \text{ and } P_{f, 23 \circ C, 50 \circ C}=P_{o, 23 \circ C}/2)$



Figure 4.21 Uptake Curves of Isopropanol on Na-Beta at Different Temperatures $(P_{f, 0} \circ_C = P_{o, 0} \circ_C / 2 \text{ and } P_{f, 23} \circ_{C, 50} \circ_C = P_{o, 23} \circ_C / 2)$


Figure 4.22 Uptake Curves of n-Butanol on Na-Beta at Different Temperatures $(P_{f, 0 \circ C}=P_{o, 0 \circ C}/2 \text{ and } P_{f, 23 \circ C, 50 \circ C}=P_{o, 23 \circ C}/2)$



Figure 4.23 Uptake Curves of o-Xylene on Na-Beta at Different Temperatures $(P_{f, 0 \circ C}=P_{o, 0 \circ C}/2 \text{ and } P_{f, 23 \circ C, 50 \circ C}=P_{o, 23 \circ C}/2)$



Figure 4.24 Uptake Curves of m-Xylene on Na-Beta at Different Temperatures $(P_{f, 0 \circ C}=P_{o, 0 \circ C}/2 \text{ and } P_{f, 23 \circ C, 50 \circ C}=P_{o, 23 \circ C}/2)$



Figure 4.25 Uptake Curves of p-Xylene on Na-Beta at Different Temperatures $(P_{f, 0 \circ C}=P_{o, 0 \circ C}/2 \text{ and } P_{f, 23 \circ C, 50 \circ C}=P_{o, 23 \circ C}/2)$

The uptake curves indicate that, the time necessary for the system to reach equilibrium is affected by the temperature. The shortest time period for the system to reach equilibrium was observed at 50 °C. As the temperature increased, the time required for equilibrium decreased.

The results show that, the volumetric sorption capacities calculated at 0 °C are higher than those calculated at 23 °C and 50 °C. The temperature effect on the capacity values was explained only to the extent by the variation of the liquid molar volume of the adsorbed phase with temperature. Probe molecules in the sorption volume of a zeolite are usually mobile. They diffuse rapidly and hence are fluid-like. This fluid varies continuously in density with the equilibrium pressure of sorbate up to the approximate saturation capacity of the sorption volume. One property of a dense fluid is a covolume per molecule which increases with rising temperature. Therefore the saturation uptakes as judged from the flat tops of the isotherms decline slowly as the temperature at which the isotherm is measured increases (Barrer, 1978).

CHAPTER 5

CONCLUSIONS

In this study, zeolite beta were synthesized in autoclaves and characterized in terms of its phase purity, morphology, hydration behavior and surface area. In addition adsorption properties of Na-Beta were examined for some probe molecules: methanol, ethanol, isopropanol, n-butanol, o-xylene, m-xylene, and p-xylene at different temperatures. Based on the experimental studies the following conclusions can be drawn.

- Variation of the crystallization period or the SiO₂/Al₂O₃ ratio did not affect the phase purity of zeolite beta. In all cases, pure zeolite beta phase was obtained.
- Both the crystallization period and SiO₂/Al₂O₃ ratio were found to be effective on crystallinity of the product. High crystallinity was obtained at high SiO₂/Al₂O₃ ratios or at long crystallization periods.
- 3. An increase in the SiO₂/Al₂O₃ ratio in the gel resulted in slightly high yield percent. On the other hand, up to a certain crystallization period, the yield reached its maximum value. However, after this point, it started to decrease as the crystallization period further increased.

- SEM micrographs indicated that morphology and the crystal size of the zeolite beta products were not affected much from the synthesis duration and the SiO₂/Al₂O₃ ratio of the molar batch composition.
- 5. The volumetric sorption capacities for the alcohols were in good agreement with the theoretical pore volume reported for zeolite beta. The sorption capacities for xylene isomers are slightly less than those for alcohols.

CHAPTER 6

RECOMMENDATIONS

Based on the present study, for the future, some points can be recommended.

In this study zeolite beta was crystallized by changing the synthesis parameters; SiO_2/Al_2O_3 ratio and crystallization period. This synthesis procedure can further be extended by enlarging the parameters ranges or by applying different synthesis parameters, such as the template molecule, temperature or the alkalinity to see their effects on the synthesis of zeolite beta.

In addition, in this study, sorption behavior of methanol, ethanol, isopropanol, nbutanol, o-xylene, m-xylene, and p-xylene were observed. Since, methanol, ethanol, isopropanol or n-butanol may be transformed into liquid hydrocarbons (e.g. fuels) or gaseous compounds used for the production of plastics, monomers for polymer production. Furthermore, xylene isomers are of great importance to petrochemical industries, because these substances are bases for the synthesis of many organic compounds. For example, p-xylene is oxidized to teraphtalic or dimethylteraphtalic acid as the first stage in polyester production. According to the obtained results, yielding the same sorption amount for alcohols and nearly the same amount for xylene isomers, it can be recommended that zeolite beta should not be utilized as moleculer sieves for the separation of alcohol mixtures or xylene isomers. In many zeolite based catalyst applications, the temperature of reaction is very high. Therefore, sorption behavior of the probe molecules may be studied at higher temperatures in order to observe the effect of temperature. As well, hydrogen form of zeolite beta can be utilized in sorption capacity measurements so as to determine the capacity differences in sodium and hydrogen forms of zeolite beta.

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APPENDIX A

CALCULATION OF SYNTHESIS RECIPE FROM A BATCH COMPOSITION

Molar Batch Composition:

 $2.2 \text{ Na}_2\text{O}$: $Al_2\text{O}_3$: 20 SiO_2 : $4.6(\text{TEA})_2\text{O}$: $444 \text{ H}_2\text{O}$

Source Materials:

Sodium aluminate: Riedel-de Häen, 52.12 wt % Al₂O₃, 45.26 wt % Na₂O, Ludox HS-40 colloidal silica: Aldrich, 0.41 wt % Na₂O, 40 wt % SiO₂, Sodium hydroxide: J.T. Baker, 97 % NaOH, 3 wt. % H₂O, Tetraethyl ammonium hydroxide (TEAOH): Aldrich, 35 wt % TEAOH in water Deionized water

1 mole Al₂O₃
$$\times \frac{102 \text{ g}}{1 \text{ mole}} = 102 \text{ g} \text{ Al}_2\text{O}_3$$

For 102 grams of Al₂O₃,

 $102 \text{ g Al}_2\text{O}_3 \times \frac{100 \text{ g sodium aluminate}}{52.12 \text{ g Al}_2\text{O}_3} = 195.702 \text{ g sodium aluminate}$

In 195.702 g sodium aluminate,

 $195.702 \text{ g sodium alum.} \times \frac{45.26 \text{ g Na}_2 \text{O}}{100 \text{ g sodium alum.}} \times \frac{1 \text{ mole}}{61.98 \text{ g Na}_2 \text{O}} = 1.429 \text{ mol Na}_2 \text{O}$

So, compound formula of sodium aluminate is; 1.429 Na₂O·Al₂O₃

$$1 \text{ moleSiO}_{2} \times \frac{60.086 \text{ g}}{1 \text{ mole}} = 60.086 \text{ gSiO}_{2}$$

For 60.086 grams of SiO₂,
$$60.086 \text{ gSiO}_{2} \times \frac{100 \text{ g Ludox HS} - 40}{40 \text{ gSiO}_{2}} = 150.215 \text{ g Ludox HS} - 40$$

In 150.215 g Ludox HS-40,

 $150.215 \text{ g Ludox HS} - 40 \times \frac{0.41 \text{ g Na}_2 \text{ O}}{100 \text{ g Ludox HS} - 40} \times \frac{1 \text{ mole}}{61.98 \text{ g Na}_2 \text{ O}} = 0.01 \text{ mol Na}_2 \text{ O}$ $150.215 \text{ g Ludox HS} - 40 \times \frac{59.59 \text{ g H}_2 \text{ O}}{100 \text{ g Ludox HS} - 40} \times \frac{1 \text{ mole}}{18 \text{ g H}_2 \text{ O}} = 4.97 \text{ mol H}_2 \text{ O}$

Thus, compound formula of Colloidal Silica is; SiO₂·0.01 Na₂O·4.97 H₂O

$$1 \text{ mole NaOH} \times \frac{39.99 \text{ g}}{1 \text{ mole}} = 39.99 \text{ g NaOH}$$

For 39.99 grams of NaOH,
$$39.99 \text{ g NaOH} \times \frac{100 \text{ g sodium hydroxide}}{97 \text{ g NaOH}} = 41.227 \text{ g sodium hydroxide}$$

In 41.227 g sodium hydroxide,

 $41.227 \text{ g sodium hydroxide} \times \frac{3 \text{ g H}_2 \text{ O}}{100 \text{ g sodium hydroxide}} \times \frac{1 \text{ mole}}{18 \text{ g H}_2 \text{ O}} = 0.07 \text{ mol H}_2 \text{ O}$

As a result, compound formula of sodium hydroxide is; NaOH·0.07 H₂O

$$1 \text{ mole TEAOH} \times \frac{147.26 \text{ g}}{1 \text{ mole}} = 147.26 \text{ g TEAOH}$$

For 147.26 grams TEAOH,

 $147.26 \text{ g TEAOH} \times \frac{100 \text{ g TEAOH}(35\%)}{35 \text{ g TEAOH}} = 420.743 \text{ g TEOH}(35\%)$

In 420.743 g TEAOH (35%), 420.743 g TEAOH (35%) $\times \frac{65 \text{ g H}_2 \text{ O}}{100 \text{ g TEAOH} (35\%)} \times \frac{1 \text{ mole}}{18 \text{ g H}_2 \text{ O}} = 15.19 \text{ mol H}_2 \text{ O}$

The compound formula of tetraethylammonium hydroxide; TEAOH·15.19 H₂O

Pertinent Chemical Equations: 1 (1.429 Na₂O·Al₂O₃) = 1.429 Na₂O + Al₂O₃ 2 NaOH = Na₂O + H₂O 2 (NaOH·0.07 H₂O) = Na₂O + 1.14 H₂O 2 TEAOH = (TEA)₂O + H₂O 2 (TEAOH·15.19 H₂O) = (TEA)₂O + 31.38 H₂O

Calculations (see Table A.1 and Table A.2, respectively):

| $1 (1.429 \text{ Na}_2\text{O}\cdot\text{Al}_2\text{O}_3)$ | 195.702 g |
|---|------------|
| 20 (SiO ₂ ·0.01 Na ₂ O·4.97 H ₂ O) | 3004.300 g |
| 1.142 (NaOH·0.07 H ₂ O) | 47.081 g |
| 9.2 (TEAOH-15.19 H ₂ O) | 3870.836 g |
| 199.601 (H ₂ O) | 3592.818 g |
| + | |

10710.74 g

100 g Basis:

1.827 g Sodium aluminate

28.049 g Ludox Hs-40, colloidal silica

0.440 g Sodium hydroxide

36.140 g Tetraethylammonium hydroxide

33.544 g Deionized water

| Form |
|-------------|
| to |
| Necessary |
| of Reagents |
| Composition |
| Mole (|
| V.1 |
| Table ∤ |

Zeolite Beta Synthesis Mixture

| 1.0 Al ₂ O ₃ 20 1.0 Al ₂ O ₃ 20 0 Al ₂ O ₃ - 20 |
|---|
| 0 Al ₂ O ₃ |
| 0 Al ₂ O ₃ |
| 0 Al ₂ O ₃ |
| 0 Al ₂ O ₃ |

Table A.2 Mass Composition of Reagents Necessary to Form Zeolite Beta

 Synthesis Mixture

| Compound Formula | # of | Formula Weight | Mass (g) | |
|--|---------|----------------|------------|--|
| Compound Formula | Moles | (g/mol) | 1v1a55 (g) | |
| $1.429 \operatorname{Na_2O} \cdot \operatorname{Al_2O_3}$ | 1 | 195.702 | 195.702 | |
| SiO ₂ ·0.01 Na ₂ O·4.97 H ₂ O | 20 | 150.215 | 3004.300 | |
| NaOH·0.07 H ₂ O | 1.142 | 41.227 | 47.081 | |
| ТЕАОН-15.19 H ₂ O | 9.2 | 420.743 | 3870.836 | |
| H ₂ O | 199.601 | 18 | 3592.818 | |

APPENDIX B

YIELD CALCULATIONS

In the sample calculations of % yield, maximum yield, and % conversion, pure phase zeolite beta sample (Batch Name NHT 19) was used. It was synthesized from a molar batch composition, of which SiO_2/Al_2O_3 ratio is 20, in 12 days period at 150 °C.

% Yield = $\frac{\text{Weight of Solid}(g)}{\text{Weight of Batch in Dry Basis}(g)} \times 100$

Weight of Solid = 1.7202 g

Weight of Batch in Dry Basis = 3.8329 g

% Yield = $\frac{1.7202 \,\mathrm{g}}{3.8329 \,\mathrm{g}} \times 100 = \% \,44.88$

APPENDIX C

SURFACE AREA CALCULATIONS

BET theory is a well known rule for the physical adsorption of gas molecules on a solid surface. The concept of the theory is an extension of the Langmuir theory, which is a theory for monolayer molecular adsorption, to multilayer adsorption with the following hypotheses: (i) gas molecules physically adsorb on a solid in layers infinitely; (ii) there is no interaction between each adsorption layer; and (iii) the Langmuir theory can be applied to each layer. The resulting BET equation is expressed as;

$$\frac{1}{Q \times (P_0/P - 1)} = \frac{1}{Q_m \times C} + \frac{C - 1}{Q_m \times C} \times \frac{P}{P_0}$$
(C.1)

P and P_0 are the equilibrium and the saturation pressure of adsorbates at the temperature of adsorption, Q is the adsorbed gas quantity at STP, and Q_m is the monolayer adsorbed gas quantity at STP. C is the BET constant.

BET equation is an adsorption isotherm and it can be plotted as a straight line with 1 / Q [(P₀/P)-1] on the y-axis and P/P₀ on the x-axis according to the experimental results. BET surface area graph is shown in Figure C.1.

The value of the slope and the y-intercept of the line were used to calculate the monolayer adsorbed gas quantity Q_m and the BET constant; C.

$$C = \frac{\text{Slope} + Y_{\text{int}}}{Y_{\text{int}}}$$
(C.2)

$$Q_{\rm m} = \frac{1}{C \times Y_{\rm int}} \tag{C.3}$$



Figure C.1 BET Surface Area Plot

From the Figure C.1 the slope and the y-intercept of the line was found as; 0.205 g/mmol and -0.005 g/mmol, respectively.

Thus;

$$C = \frac{\text{Slope} + Y_{\text{int}}}{Y_{\text{int}}} = \frac{0.205 \,\text{g/mmol} - 0.005 \,\text{g/mmol}}{-0.005 \,\text{g/mmol}} = -40$$

$$Q_{m} = \frac{1}{C \times Y_{int}} = \frac{1}{-40 \times -0.005 \text{ g/mmol}} = 5 \text{ mmol/g} = 0.005 \text{ mol/g}$$

The BET method is widely used in surface science for the calculation of surface areas of solids by physical adsorption of gas molecules. A total surface area was evaluated by the following equation;

$$S_{BET} = \frac{Q_m \times M \times \alpha \times N}{v_m \times \rho \times 10^4 \text{ cm}^2/\text{m}^2}$$
(C.4)

α: analysis gas molecular cross sectional area

N: Avagadro's number

 v_m : molar volume of gas at STP

M: molecular weight of the adsorbate

 ρ : density of the adsorbate at STP

For spherical molecules arranged in close two dimensional packing

$$\alpha = 1.091 \times \left(\frac{M}{N \times \rho_L}\right)^{\frac{2}{3}}$$
 (C.5)

M: molecular weight of adsorbate

 ρ_L : density of liquid sorbate at the temperature of adsorption

N: Avagadro's number

For N₂; M = 28.014 g/mol $N = 6.023 \text{ x } 10^{23} \text{ molecule/mole}$ $\rho_L = 0.808 \text{ g/cm}^3 \text{ at } -196 \ ^\circ\text{C}$

$$\alpha = 1.091 \times \left(\frac{28.014 \text{ g/mol}}{6.023 \times 10^{23} \text{ molecule/mole} \times 0.808 \text{ g/cm}^3}\right)^{\frac{2}{3}} = 16.2 \times 10^{-16} \frac{\text{cm}^2}{\text{molecule}}$$

$$\mathbf{S}_{\text{BET}} = \frac{\mathbf{Q}_{\text{m}} \times M \times \alpha \times N}{\mathbf{v}_{\text{m}} \times \rho \times 10^4 \text{ cm}^2/\text{m}^2}$$

For N₂; M = 28.014 g/mol $\rho = 0.00125 \text{ g/cm}^3 \text{ at STP}$ $\alpha = 16.2 \times 10^{-16} \text{ cm}^2/\text{molecule}$ $N = 6.023 \times 10^{-23} \text{ molecule/mole}$ $v_m = 22414 \text{ cm}^3/\text{mol at STP}$

$$S_{BET} = \frac{\frac{0.005 \frac{\text{mol}}{\text{g}} \times 28.014 \frac{\text{g}}{\text{mol}} \times 16.2 \times 10^{-16} \frac{\text{cm}^2}{\text{molecule}} \times 6.023 \times 10^{23} \frac{\text{molecule}}{\text{mol}}}{22414 \frac{\text{cm}^3}{\text{mol}} \times 0.00125 \frac{\text{g}}{\text{cm}^3} \times \frac{10^4 \text{ cm}^2}{1 \text{ m}^2}}$$

 $S_{BET} = 488 \, m^2/g$

APPENDIX D

PHYSICAL PROPERTIES OF SORBATES

| Table D.1 | Vapor Pressures | of the Probe | Molecules a | at Different | Temperatures |
|-----------|-----------------|--------------|-------------|--------------|--------------|
| | (| Perry and Gr | een, 1999) | | |

| T (°C) P ₀ (torr) | 0 | 23 | 50 |
|---------------------------------|-------|--------|--------|
| Methanol | 29.32 | 112.75 | 414.49 |
| Ethanol | 11.85 | 52.45 | 220.49 |
| Isopropanol | 8.33 | 39.83 | 178.82 |
| N-Butanol | 0.96 | 5.99 | 34.30 |
| O-Xylene | 1.28 | 5.86 | 25.36 |
| M-Xylene | 1.68 | 7.43 | 31.05 |
| P-Xykene | 1.78 | 7.81 | 32.34 |

| $\frac{T (°C)}{\rho (g/cm^3)}$ | 0 | 23 | 50 |
|--------------------------------|-------|--------|--------|
| Methanol | 29.32 | 112.75 | 414.49 |
| Ethanol | 11.85 | 52.45 | 220.49 |
| Isopropanol | 8.33 | 39.83 | 178.82 |
| N-Butanol | 0.96 | 5.99 | 34.30 |
| O-Xylene | 1.28 | 5.86 | 25.36 |
| M-Xylene | 1.68 | 7.43 | 31.05 |
| P-Xykene | 1.78 | 7.81 | 32.34 |

Table D.2 Liquid Densities of the Probe Molecules at Different Temperatures(Perry and Green, 1999)