SYNTHESIS AND CHARACTERIZATION OF CLINOPTILOLITE

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ABSTRACT

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Clinoptilolite is the most abundant zeolite mineral in nature. In this study a reproducible synthesis recipe for clinoptilolite was established and the limits of the crystallization field were developed by changing synthesis parameters such as temperature, composition and the nature of reactants.

Clinoptilolite was reproducibly synthesized as a pure phase and in high yield at 140^oC using a benchmark batch composition of 2.1 Na_2O:Al_2O_3:10SiO_2:110.1 H_2O. Clinoptilolite was crystallized from 10wt% or 28wt% seeded systems while it was not formed if no seeds were present. Clinoptilolite was also crystallized as a pure phase when the cation in the benchmark batch composition was Na,K mixture, or when alkali salts such as carbonates or chlorides were used besides alkali hydroxides, or when the SiO_2/Al_2O_3 ratio was in the range of 10-12. Clinoptilolite was still crystallized as a single phase when alkali hydroxides in the batch were reduced by 20%.

With the benchmark batch composition, clinoptilolite was crystallized in pure phase form at 100°C, 120°C, 140°C and 160°C while synthesis at 175°C resulted in the formation of pure mordenite. At 140°C clinoptilolite was crystallized together with Linde L when cation in the benchmark composition is only potassium. Phillipsite crystallized together with clinoptilolite at SiO_2/Al_2O_3 ratio of 8 to 9. At SiO_2/Al_2O_3 ratios of 6 or 4, phillipsite or analcime was formed as pure phase respectively. When the alkali hydroxides in the batch was increased by 20%, sanidine was formed. Use of reactive aluminosilicate gels enhanced the formation of clinoptilolite while attempts to use mineral raw materials were unsuccessful.

For both Na and (Na,K)-clinoptilolite, Si/Al ratio of products were greater than four. Thermal stability of synthetic clinoptilolites were comparable with natural clinoptilolite and potassium ion increased thermal stability of clinoptilolite.

Keywords: Zeolite; Natural zeolite; Clinoptilolite; Synthesis of clinoptilolite

ÖZ

KLİNOPTİLOLİT SENTEZİ VE KARAKTERİZASYONU

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Klinoptilolit doğada en çok bulunan mineral zeolittir. Bu çalışmada klinoptilolit için tekrarlanabilir bir sentez reçetesi oluşturulmuştur ve sıcaklık, kompozisyon ve hammadde kaynağının türü gibi sentez parametreleri değiştirilerek, kristalleşme alanının sınırları belirlenmiştir.

Klinoptilolit $2.1Na_2O$: Al_2O_3: $10SiO_2$: $110.1H_2O$ standart başlangıç bileşimi kullanılarak, 140^oC'de saf faz olarak ve yüksek verimde, tekrarlanabilir olarak sentezlenmiştir. Klinoptilolit ağırlıkça %10 veya % 28 tohumlanmış sistemlerde kristalleşirken, tohum kristali kullanılmadığında oluşmamıştır. Standart başlangıç bileşimindeki katyon türü Na,K karışımı olduğunda veya karbonatlar ve klorürler gibi alkali tuzları alkali hidroksitler yanında kullanıldığında veya SiO_2/Al_2O_3 oranı 10-12 aralığında olduğunda da klinoptilolit saf faz olarak kristalleşmiştir. Alkali hidroksitlerin başlangıç bileşimindeki miktarı % 20 azaltıldığında da klinoptilolit tek faz olarak kristalleşmiştir.

Klinoptilolit 100^{o}C, 120^{o}C, 140^{o}C ve 160^{o}C'de standart başlangıç bileşimi kullanılarak saf faz olarak sentezlenirken, 175^{o}C'de saf faz olarak mordenit oluşmuştur. Standart başlangıç bileşimindeki katyon türü sadece potasyum olduğunda, klinoptilolit Linde L ile birlikte kristalleşmiştir. SiO_2/Al_2O_3 oranı 8 ve 9 arasında olduğunda klinoptilolit filipsit ile birlikte kristalleşmiştir. SiO_2/Al_2O_3 oranı 6 veya 4 olduğunda, sırasıyla filipsit veya analsim saf faz olarak oluşmuştur. Başlangıç bileşimdeki alkali hidroksit miktarı % 20 arttırıldığında sanidine oluşmuştur. Reaktif aluminosilikat jellerin kullanılması klinoptilolitin oluşmasını sağlarken doğal hammaddelerin kullanıldığı denemeler başarısız olmuştur.

Na ve (Na,K)-klinoptilolitin her ikisi için de ürünlerin SiO_2/Al_2O_3 oranı dörtten büyüktür. Yapay klinoptilolitlerin ısıl dayanımları doğal klinoptilolit ile benzer düzeydedir ve potasyum iyonu klinoptilolitin ısıl dayanımını arttırmaktadır.

Anahtar sözcükler: Zeolit; Doğal zeolit; Klinoptilolit; Klinoptilolit sentezi

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NOMENCLATURE

Clino. : Clinoptilolite

W_b : Weight of batch

W_s : Weight of seed

W_p : Weight of product

W_c : Weight of clinoptilolite

X_c : Clinoptilolite fraction in the solid product

$(\%\ \text{Yield})_{sfb}$: % yield for seed free batch

$(\%\ \text{Conversion})_{sfb}$: % Conversion for seed free batch

DCP : Decomposed product

CHAPTER 1

INTRODUCTION

1.1 Zeolites and Clinoptilolite

Zeolites are crystalline hydrated aluminosilicates with a framework structure. The framework of zeolites consists of three dimensional network of SiO_4 and AlO_4 tetrahedra linked to each other via sharing oxygen atoms. This framework contains voids and channels occupied by water molecules and cations to balance the charge of whole framework. Cations in the structure are mobile and may be exchanged by other cations.

Zeolites can be naturally occurring or synthetically obtained. Synthetics are mostly crystallized from amorphous alkali aluminosilicate gels under hydrothermal conditions. Temperatures varying from room temperature to 200^oC are widely used for hydrothermal synthesis of zeolites. Synthesis pressure is generally autogenous pressure which is equivalent to saturated vapor pressure of water at synthesis temperature. Main variables in the zeolite synthesis are composition of reactant mixture, nature of reactants, temperature, pH of the reaction medium and synthesis time. Another important synthesis parameter is the addition of seed crystals to the reactant gel.

A zeolite can be synthesized from more than one composition and at various reaction conditions, however some changes in the reaction composition or conditions may yield undesired zeolitic phase or phases. For this reason fine tuning of synthesis variables is the most important step in zeolite synthesis.

Clinoptilolite is the most abundant and widely distributed natural zeolite in the world. It is silica the rich member of heulandite family of zeolites having a Si/Al ratio greater than 4. It occurs most commonly in sedimentary rocks.

Nowadays large portions of mineral clinoptilolite are used as construction material, animal feed additive or fertilizer additive in the world. Clinoptilolite can also be used in ion exchange and adsorption applications including waste water treatment and SO_2 removal. Although these are environmentally and industrially more important than bulk applications, impurities and compositional variations in clinoptilolites of different origin limit its use in these applications .

In the literature there are only a few works related with clinoptilolite synthesis whose reproducibility is questionable. Chi and Sand's [1] work reported in Nature at 1983 is one of the main contributions to clinoptilolite synthesis. In this work single phase clinoptilolite was synthesized in some experimental runs, however Williams (1997) [2] could not reproduce Chi and Sand's results. Despite its abundance in nature, it was reported that clinoptilolite synthesis in laboratory conditions reproducibly is not a simple task.

Considering reproducible clinoptilolite synthesis is under debate, any contribution related with reproducible clinoptilolite synthesis will be important for zeolite science.

Moreover as a prospective application, synthetic clinoptilolite can be used as a material for comparison in ion exchange or adsorption applications of mineral clinoptilolite.

1.2 Scope of The Study

Development of a reproducible synthesis recipe for pure clinoptilolite is the main objective of this work. As a starting point, a benchmark composition yielding pure clinoptilolite was obtained by reproducing Chi and Sand's [1] work. Then this composition was modified via changing cation type, anion type, SiO_2/Al_2O_3 ratio, alkalinity, nature of reactants and temperature to see the effect of these parameters on clinoptilolite crystallization. Products were characterized by XRD, SEM, TGA and XRF to define their purity, crystallinity, morphology, thermal behavior and chemical composition.

CHAPTER 2

LITERATURE SURVEY

2.1 Structure and Properties of Clinoptilolite Mineral

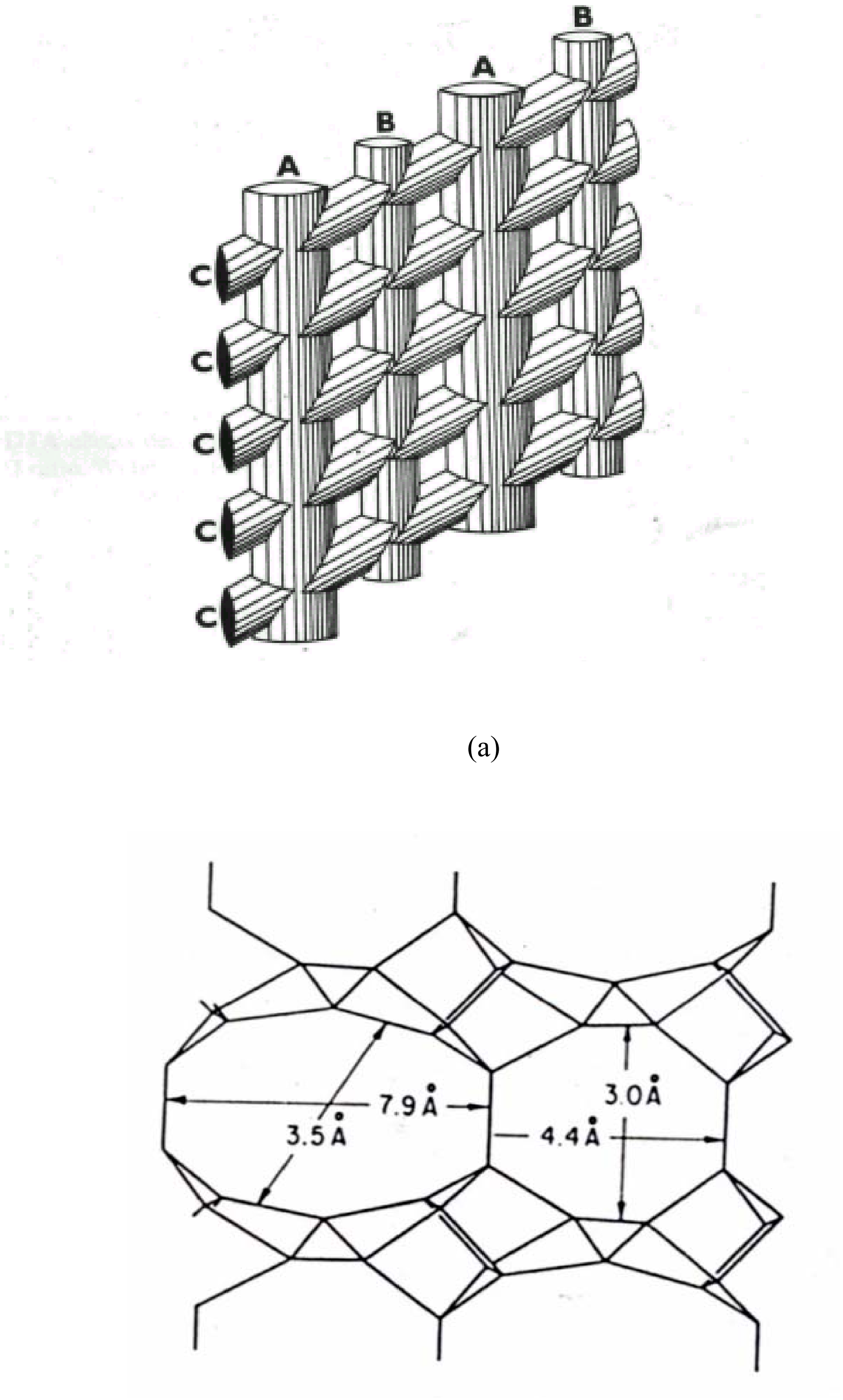
Clinoptilolite is the most common and widely distributed zeolite mineral found in nature. It is a member of heulandite family of zeolites consisting of clinoptilolite and heulandite which are isostructural with each other.

2.1.1 Crystal Structure and Chemistry of Clinoptilolite Mineral

Clinoptilolite is silica rich member of heulandite family of zeolites. Its Si/Al ratio is greater than 4 while for heulandite this ratio is lower than 4. Clinoptilolite species are mostly enriched with potassium and sodium [3]. Chemical composition of clinoptilolite is $(Na,K)_6\ (Al_6Si_{30}O_{72})\ 20H_2O$ [8].

In the structure of clinoptilolite crystals, $(Si,Al)O_4$ tetrahedra are linked through oxygen atoms in layers [4]. Secondary building unit (SBU) for clinoptilolite is the 4-4-1 unit.The connection of SBU's forms the framework with monoclinic symmetry with unit cell constants a=7.41Å, b=17.89Å, c=15.85 Å and $\beta=91^{o}29'$ (3].

The channel system of clinoptilolite is two dimensional consisting of ten membered (7.9x 3.5 Å) and eight membered (4.4 x 3 Å) tetrahedral rings (Figure 2.1-b). There is an additional eight membered channel cross-linked to these channels which is responsible for the two dimensional layer-like structure (Figure 2.1-a) [4].



(a)

(b)

Figure 2.1 (a) Schematic representation of two dimensional channel system of clinoptilolite [4] (b) Schematic representation of ten and eight membered channels of clinoptilolite with their size [7]

A crystalline substance can be identified from its XRD pattern since powder pattern of a substance is characteristic of that substance and forms a kind of fingerprint by which the substance can be identified.

Published X-ray diffraction data for several natural clinoptilolite samples, a heulandite sample and a synthetic clinoptilolite sample are given on Figure 2.2 in the form of bar charts. In this figure mineral clinoptilolites from different sources were given. Among these, pattern of Wise W., Nokleberg W, Kokinos M. [5] is the one which is given in 'Powder Diffraction File' and in 'Zeolite Molecular Sieves' [3] as the pattern of natural clinoptilolite. Also synthetic clinoptilolite pattern of Chi and Sand was given for comparison with mineral clinoptilolites.

As can be seen on Figure 2.2 clinoptilolite and heulandite cannot be distinguished from one another on the basis of their XRD pattern. Clinoptilolite is distinguished from its group member heulandite mainly by Si/Al ratio, dominant cation types and thermal behavior.

2.1.2 Distinctions between Clinoptilolite and Heulandite

Distinctions between clinoptilolite and heulandite are dominant cation type, Si/Al ratio and thermal stability as proposed by many researchers previously. Mumpton suggested that difference between the thermal behavior of clinoptilolite and heulandite can be used to distinguish clinoptilolite from heulandite. As it was proposed by Mumpton [6] heulandite converts to 'heulandite B' at $230^oC \pm 10^oC$. An overnight heating at 450 ^oC results in complete destruction of heulandite lattice. On the other hand no transitions or reactions were observed in clinoptilolite up to 750^oC, heating at higher temperatures resulted in the complete disappearance of peaks in the X-ray diffraction pattern and formation of an amorphous product.

DTA curves of heulandite and clinoptilolite are also different from each other as stated by Mumpton . DTA patterns of clinoptilolite show only dehydration

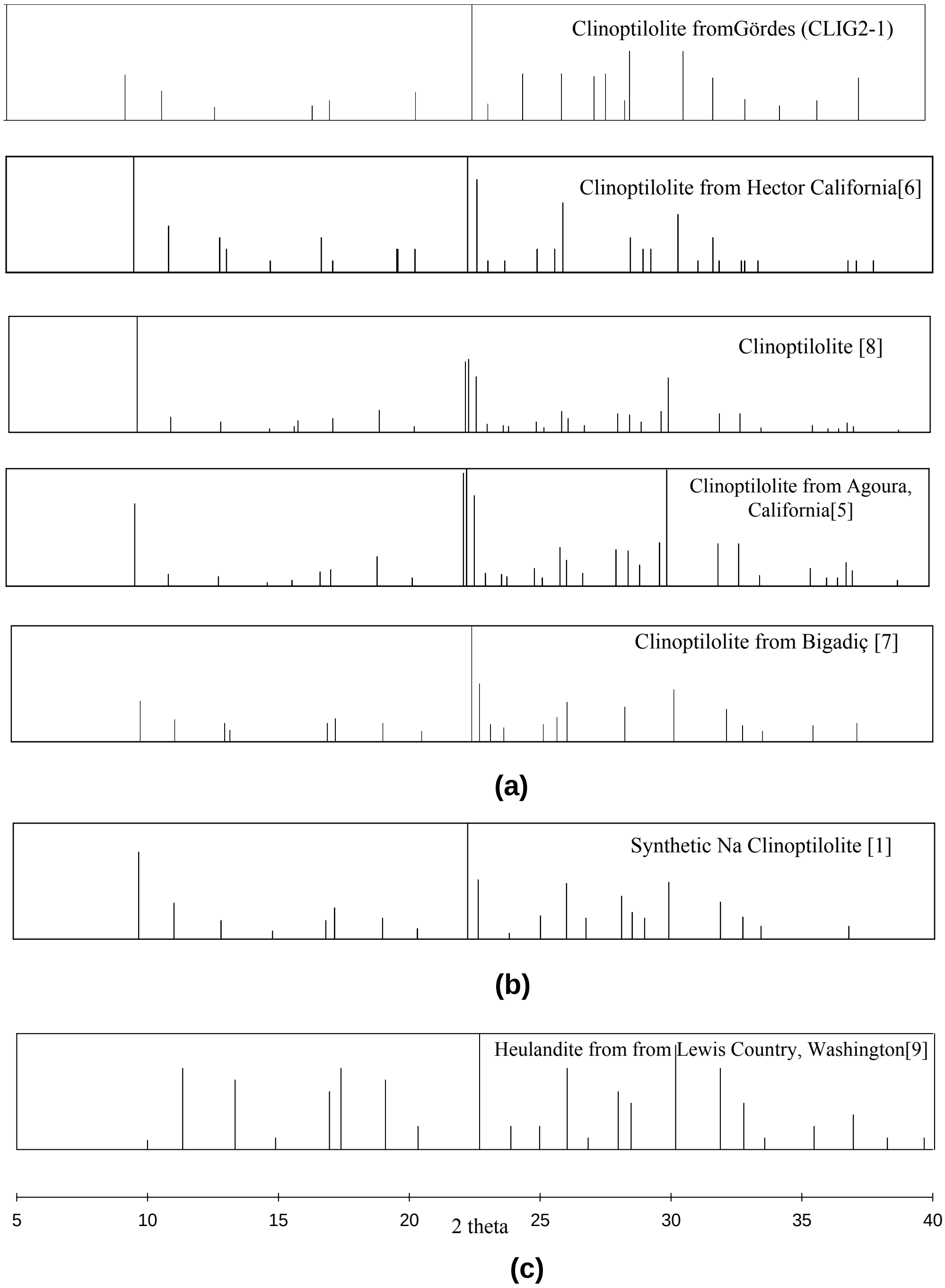


Figure 2.2 X-ray Diffraction Data of (a) Natural clinoptilolites from various sources (b) Synthetic Na clinoptilolite (c) Natural heulandite

endotherm at temperatures lower than 300^oC while heulandite contains a dehydration endotherm at temperatures lower than 300^oC followed by a sharp endotherm in the vicinity of 300^oC.

Beside thermal behavior, Si/Al ratio and dominant cation type for clinoptilolite and heulandite are different. By using chemical data in the literature Mumpton [6] stated that clinoptilolite has SiO_2/Al_2O_3 ratio of about 8.5 to 10.5 and contains predominantly monovalent over divalent cations while for heulandite SiO_2/Al_2O_3 ratio is about 5.4 to 6.7 and divalent cations are dominant. High thermal stability of clinoptilolite was explained by Mumpton in terms of SiO_2/Al_2O_3 ratio.

Mason and Sand [10] showed that clinoptilolite is a distinct zeolite species with heulandite structure in which (Na+K) atoms per unit cell are predominant over Ca. In contrast to Mumpton [6] they stated that content of sodium and potassium that exceeds calcium is a more significant difference than SiO_2/Al_2O_3 ratio to distinguish clinoptilolite from heulandite.

Alietti (1972) and Boles (1972) investigated the relationships between thermal stability and chemical composition to clarify the definitions of Mumpton [6] and Mason and Sand [10]. According to the definition of Boles(1972), heulandite is a zeolite species having a Si/Al ratio less than 4 and clinoptilolite with the same framework topology is a zeolite species having a Si/Al ratio greater than 4 [11].

Consequently among heulandite family of zeolites, clinoptilolite is silica rich one (Si/Al>4) usually containing monovalent cations rather than divalent cations, (Na+K) > (Ca+Sr+Ba) and also thermally more stable than heulandite due to its high SiO_2/Al_2O_3 ratio.

Clinoptilolite-heulandite nomenclature is not very clear. Within distinctive properties, Si/Al ratio is more appropriate one as compared to thermal stability because thermal stability is a derivative property which is also related with this ratio.

2.2 Attempts to Synthesize Clinoptilolite

Only a few contributions have been reported about clinoptilolite synthesis since its first synthesis by Ames [12] in 1963. In the view of previous studies crystallization conditions of single phase clinoptilolite is still not clear or a composition diagram is not available. Also any recipe for single phase clinoptilolite synthesis is not available in 'International Zeolite Association's Verified Syntheses Compilation' which includes synthesis recipes for many zeolites [13].

In the study of Ames [12] clinoptilolite was synthesized in lithium-alumina-silica-water system at temperatures between 250°C-300°C from gel mixtures with composition of Li_2O: Al_2O_3: 8 Si_2O: 8.5 H_2O for 2-5 days under autogenous pressure. In this study it was claimed that clinoptilolite can not be synthesized from Na,K including systems.

Hawkins et al. [14] synthesized clinoptilolite from rhyolitic glass (Mg-Fe poor Na-K rich glass), treated with alkali carbonate solutions of 2 M (K/Na = 0 to 5) at 130°C-150°C under the pressure of 1 kbar for 7 to 12 days. Natural clinoptilolite was used as seed crystals. Clinoptilolite was obtained in the range of 3:2 K/Na to 2:3 K/Na at 1 kbar and at 145 °C. Clinoptilolite synthesis was achieved only by using rhyolitic glass, co-precipitated gels of the approximate composition did not yield clinoptilolite.

Goto [15] synthesized clinoptilolite co-existing with mordenite under hydrothermal conditions at 200°C from a starting material of composition $(Na,K)_2 Al_2Si_7O_{18}$ in a weakly basic solution, pH=7.9. Composition of the starting material, $Na_{2-x} Al_{2-x}Si_{7+x}O_{18}$, was altered due to changing x value ranging from 0 to 1. In this study presence of K besides Na in the starting material and weakly basic reaction medium was indicated to be important for clinoptilolite crystallization. In this study clinoptilolite was synthesized by using co-precipitated gels prepared by chemical reagents as opposed to Hawkins et al.[14].

After these early investigations, Chi and Sand's [1] work is one of the main contributions on clinoptilolite synthesis. Single phase Na-clinoptilolite and K-clinoptilolite were synthesized in this study for the first time while Na,K clinoptilolite synthesis was achieved in previous studies. Clinoptilolite was synthesized as a single phase from a molar batch composition of $2.1M_2O: Al_2O_3: 10SiO_2: 110.1\ H_2O$ where M is Na or K and at temperatures between 120-195^oC with the addition of 1-10 wt% of seed crystals. Na-clinoptilolite was synthesized with seed crystal addition while K and Na,K clinoptilolite was synthesized with or without seed crystals and it was observed that addition of seed crystals improve both degree and rate of crystallization of clinoptilolite.

In the study of Chi and Sand [1] kinetics of both Na and K clinoptilolite were investigated and crystallization of K clinoptilolite was found to be two or four times slower than Na clinoptilolite for the same temperature and pressure. Crystallization was performed for various temperatures and dependence of rate on temperature was expressed by Arrhenius equation to calculate apparent activation energies. Activation energies were calculated as 13.8 kcal/gmol and 14.5 kcal/gmol for Na and K clinoptilolite, respectively. These values were noted to be very close to activation energy for mordenite crystallization (15 kcal/gmol) which widely occurs with clinoptilolite in nature. It was stated that clinoptilolite is the lower temperature phase and mordenite having a higher activation energy with a similar composition is the higher temperature phase. In this study, many novel findings on clinoptilolite synthesis was mentioned on crystallization kinetics or seed addition effect, on the other hand it was concluded that clinoptilolite synthesis was surprisingly difficult due to its limited crystallization conditions.

Satokawa and Itabashi [16] were reported crystallization of single phase clinoptilolite with and without using seed crystals. Synthesis was performed hydrothermally from aluminosilicate gel with Si/Al =5.5, (Na+K)/Si =0.3, K/(Na+K)= 0.5 through homogeneous mixing conditions (revolving autoclaves at 35 rpm) for 144 h at 150^oC. As opposed to Chi and Sand's work, clinoptilolite synthesis was achieved only when both Na and K ions exist in the synthesis gel and when synthesis mixture was homogeneously mixed.

Williams [2] tried to re-examine work done by Chi and Sand [1] and the work done by Satokawa and Itabashi [16] to obtain pure clinoptilolite in unseeded systems. Hydrothermal syntheses were performed at temperatures between 150°C -175°C under autogenous pressure. Clinoptilolite was synthesized from a molar batch composition of 1.07 Na_2O : 1.07 K_2O : 8.4 SiO_2 : Al_2O_3 : 210 H_2O at 150°C after 336 h of hydrothermal treatment without using seed crystals as Satokawa and Itabashi stated. According to the recipe of Chi and Sand, syntheses were performed for molar batch composition 2.1 K_2O: 10 SiO_2: Al_2O_3: 105 H_2O in 1-10% seeded and unseeded systems, but merlionite, sanidine or potassium feldspar were crystallized instead of clinoptilolite. Reproducibility of Chi and Sand's work was considered suspect. Like many previous studies, it was proposed that It is difficult to synthesize clinoptilolite free from co-existing phases in laboratory conditions.

In the study of Zhao et al. [17] effect of cation type and Si/Al ratio of the reactant mixture on the crystallization of heulandite-type zeolites were investigated. For this purpose syntheses were performed in the presence of Li^+, (Li^+,K^+) or (Na^+,K^+) alkali cations and for various Si/Al ratios of the reactant mixture. It was found that clinoptilolite can be synthesized from gels having Si/Al ratios of 3~5 with the addition of ~10 wt% seed crystals after 7-8 days of hydrothermal treatment from Na, K, (Na,K) and (K,Li) including systems. (Na,K)-clinoptilolite was synthesized from unseeded systems also. On the other hand heulandite was formed if Si/Al ratio was 2.5~3. Mordenite was formed if Si/Al ratio>6 in the gel. With Si/Al ratio of 5.0 to 6.0 mordenite and phillipsite coexist with clinoptilolite.

Zhao et al. [18] investigated the characteristics of synthetic heulandite-clinoptilolite family of zeolites synthesized in their previous work [18]. Thermal stability tests showed that thermal stability was low at low Si/Al ratios. Effect of cation type on the thermal stability of clinoptilolite was investigated by thermal stability tests. It was found that cation type does not have a significant effect on thermal stability of synthetic clinoptilolite. As opposed to this finding Vaughan [19] proposed for natural clinoptilolites that potassium form is thermally more stable. It was also stated that the nature of the cation used in the synthesis affects the type of crystallized phase such that presence of sodium, potassium or their mixture favors the formation of clinoptilolite while presence of lithium increases the tendency to form heulandite, which is the phase with lower Si/Al ratio.

Tanaka et al. [20] synthesized (Na,K) clinoptilolite from an aluminosilicate gel with a composition of 1.26 Na_2O : 1.26 K_2O : 12 SiO_2 : Al_2O_3 : 105 H_2O with the addition of 5 wt% of seed crystals at 140°C for 14 days under homogenous mixing conditions. In this study formation process of clinoptilolite was investigated. It was stated that amorphous aluminosilicate gel crystallizes as clinoptilolite completely after hydrothermal treatment for 8 days. Crystallization was followed by using SEM images and it was observed that amorphous irregular particles turns to platy like crystals by hydrothermal treatment.

2.2.1 Characterization of Synthetic Clinoptilolites

In the field of clinoptilolite synthesis, XRD was used for both qualitative and quantitative description in the previous studies. Natural clinoptilolite was used for comparison to determine whether the product is single phase clinoptilolite or includes any other crystalline phase [14, 16, 18]. Quantitative information for crystallization degree of synthesized clinoptilolites was obtained by intensity summation method for selected peaks in the XRD pattern of natural clinoptilolite [14, 16, 20].

Scanning electron microscope was employed for the morphology determination. Clinoptilolite crystals synthesized in the previous studies were in the form of plates and aggregation of plates independent of synthesis condition or composition [1], [14, 16, 20]. Whereas SEM images of natural clinoptilolite in sedimentary rocks show that crystals generally occur as plates and laths, several micron in length and

1-2μm thick. Naturally most crystals are coffin shaped [21]. Lath like morphology similar with natural minerals was not observed for synthetic clinoptilolites.

Thermal stability tests were widely employed to classify synthesized products as clinoptilolite or heulandite. Products were defined as clinoptilolite according to the definition of Mumpton [6] such that if their XRD pattern did not disappear by thermal treatment at 450^{o}C or below [14, 16, 18, 20].

DTA and chemical analyses were also employed. According to DTA curve of a product, if a broad continuous endothermic peak was observed like their natural counterparts [16], since natural clinoptilolites show a broad continuous endothermic peak while heulandite shows two successive peaks [6]. According to chemical analyses results, if Si/Al ratio of a product was greater than 4, it was defined as clinoptilolite [14, 16, 18].

CHAPTER 3

EXPERIMENTAL

3.1 Synthesis of Clinoptilolite

3.1.1 Batch Composition Selection

In this study synthesis of clinoptilolite was performed from aluminosilicate gels of various compositions and temperatures under hydrothermal conditions at autogenous pressure. Syntheses were performed for both seeded and unseeded systems.

As a starting point, experiments were performed from a molar batch composition of $2.1Na_2O$: $10SiO_2$: Al_2O_3: $110.1H_2O$ at 140°C as outlined by Chi and Sand (1] with the addition of seed crystals. The amount of seed added was 10 wt% or 28 wt% of dry material in the batch. Then this recipe was modified and various batch compositions and conditions were examined to synthesize clinoptilolite. Table 3.1 summarizes molar batch compositions of all experiments performed in this study with their batch codes. Amounts of reactants used for the preparing these batches are given in Table A.1.1 in Appendix A.

3.1.2 Raw materials

Raw materials used for clinoptilolite synthesis in this study can be classified as chemical reagents and natural raw materials including thermal decomposition products of natural clinoptilolite. In seeded syntheses natural clinoptilolite originated from Gördes in Western Anatolia (CLIG2-1) was used as seed crystals.

Table 3.1 Molar Batch Compositions Used for Clinoptilolite Synthesis

Batch Code*	Molar Batch Composition
BC 1	$2.1Na_2O : 10SiO_2 : Al_2O_3 : 104.8H_2O$
BC 2	$2.1Na_2O : 10SiO_2 : Al_2O_3 : 110.1H_2O$
BC 2-1	$2.1Na_2O : 10SiO_2 : Al_2O_3 : 110.1H_2O$
BC 3	$2.1K_2O : 10SiO_2 : Al_2O_3 : 110.1H_2O$
BC 3-1	$2.1K_2O : 10SiO_2 : Al_2O_3 : 110.1H_2O$
BC4	$2.1Na_2O : 10SiO_2 : Al_2O_3 : 97.01H_2O$
BC 5-1	$1.05K_2O : 1.05\ Na_2O : 10SiO_2 : Al_2O_3 : 110.1H_2O$
BC 6-1	$2.1\ Na_2O : 10SiO_2 : Al_2O_3 : 110.1H_2O : 0.7\ CO_2$
BC 7-1	$1.05K_2O : 1.05\ Na_2O : 10SiO_2 : Al_2O_3 : 110.1H_2O : 0.7CO_2$
BC 8-1	$1.4\ Na_2O : 10SiO_2 : Al_2O_3 : 110.1H_2O$
BC 9-1	$2.1\ Na_2O : 10SiO_2 : Al_2O_3 : 110.1H_2O : 0.7Cl^-$
BC 10-1	$1.05Li_2O : 1.05\ Na_2O : 10SiO_2 : Al_2O_3 : 110.1H_2O$
BC 12-1	$2.1Na_2O : 9SiO_2 : Al_2O_3 : 110.1H_2O$
BC 13-1	$2.1Na_2O : 11SiO_2 : Al_2O_3 : 110.1H_2O$
BC 14-1	$2.1Na_2O : 8SiO_2 : Al_2O_3 : 110.1H_2O$
BC 15-1	$2.1Na_2O : 6SiO_2 : Al_2O_3 : 110.1H_2O$
BC 16-1	$2.1Na_2O : 4SiO_2 : Al_2O_3 : 110.1H_2O$
BC 17-1	$2.1Na_2O : 12SiO_2 : Al_2O_3 : 110.1H_2O$
BC 18	$2.1Na_2O : 15SiO_2 : Al_2O_3 : 110.1H_2O$
BC 19-1	$1.26\ K_2O : 1.26\ Na_2O : 10SiO_2 : Al_2O_3 : 110.1H_2O$
BC 20-1	$1.084\ K_2O : 0.84\ Na_2O : 10SiO_2 : Al_2O_3 : 110.1H_2O$

* Silica source was Ludox HS-40 for the batch composition BC 1, BC 2,BC 3, BC 4, and BC 18. For all others, silica source was Ludox AS-30

XRD pattern, SEM image and chemical analyses results of Gördes clinoptilolite (CLIG2-1) were given in Appendix B3.

Chemical reagents were obtained commercially and summarized in Table 3.2 with their manufacturers, lot/batch no and contents. Natural raw materials were prepared in laboratory by thermal treatment of Gördes clinoptilolite. They were classified as completely or partly decomposed products according to their clinoptilolite percentage determined by XRD calibration curve whose preparation details are given in section 3.2.2. If thermal decomposition product is totally amorphous according to its XRD result it was defined as completely decomposed product. If clinoptilolite peaks are still observable in the XRD pattern of thermal decomposition product, it was defined as partly decomposed product.

Completely decomposed product was prepared by thermal treatment of Gördes clinoptilolite at $900^{o}C$ for 2 h. For the preparation, 60 g of natural clinoptilolite sample was placed in a furnace within a porcelain crucible then the furnace was programmed to increase temperature from room temperature to $900^{o}C$ in 1 h and stay there for 2h. After thermal treatment completely decomposed product was characterized with XRD and defined as an amorphous material including trace amount of quartz in it.

Partly decomposed product was prepared in a similar way with completely decomposed product. However decomposition temperature was selected to be $785^{o}C$ to avoid complete decomposition of the product. According to XRD pattern, partly decomposed product contained 11wt% clinoptilolite, the remainder being an amorphous material with a trace amount of quartz in it.

3.1.3 Batch Preparation

In a typical synthesis calculated amounts of sodium and/or potassium source (e.g. hydroxides or carbonates of sodium and potassium), aluminum source and distilled

Table 3.2 Chemical Reagents used for the Batch Preparation

	Raw material	**Manufacturer**	**Contents**
Cation Sources	NaOH pellets	Merck (Lot no: 102362)	97 % NaOH 1.98 % H_2O
	KOH pellets	Merck (Lot no: 6376451)	84 % KOH 13.97 % H_2O
	Na_2CO_3	Merck (Lot no:A310598110)	Pure powder
	K_2CO_3	Riedel de Häen (Batch no:12609)	98.5% K_2CO_3
	NaCl	Merck (Lot no: K91077400810)	Pure powder
Alumina Sources	$Al(OH)_3$	Merck (Lot no: K 24826491817)	99.66% $Al(OH)_3$
	Sodium Aluminate	Riedel de Häen (Batch no:13404)	55 %Al_2O_3 44 % Na_2O 1%H_2O
Silica Sources	Ludox AS-30	Aldrich (Lot no :04319NH)	30 % SiO_2 70 %H_2O
	Ludox HS- 40	Aldrich (Lot no :03616MO)	40 % SiO_2 60 %H_2O

water were mixed and magnetically stirred on a hot plate until a clear solution was obtained. To obtain clear solution, heating and stirring gently for 15 minutes was enough if sodium aluminate was used as aluminum source. However if $Al(OH)_3$ used as aluminum source heating up to ~ 80-90°C and vigorous stirring for ~1 h required to dissolve $Al(OH)_3$. When Al chips or Al powder was used, they dissolved in NaOH solution to prepare sodium aluminate solution. After clear solution was obtained, evaporated amount of water was added to the solution to adjust the water content of the composition. Next colloidal silica was added slowly with stirring into the clear solution. Ludox AS-30 or Ludox HS-40 was used as colloidal silica. With the addition of colloidal silica gelation occurred immediately and a gel with snow like consistency was obtained. This gel was vigorously stirred for 1 h at room temperature for homogenization until its consistency turned to creamy-like consistency. At this stage seed crystals (Gördes clinoptilolite, CLIG2-1) were added into gel and stirring was continued for ~4-5 min. The amount of seed added is 10wt %-30 wt % of dry material in batch. A sample calculation for batch preparation will be given in Appendix A1.

For the syntheses performed with decomposed products, calculated amounts of thermal decomposition product of natural clinoptilolite was mixed with appropriate amount of sodium and potassium hydroxide solution and stirred on a magnetic stirrer for 24 h on hot plate. For the syntheses performed with completely decomposed product, the amount of seed added is 10 wt% of dry material in batch. When partly decomposed product of clinoptilolite was used, no extra seed were added to the synthesis mixture. A sample calculation for batch preparation from decomposed products will be given in Appendix A2.

For each synthesis procedure the synthesis mixture was poured into PTFE inserts of stainless steel autoclaves with 8-10 ml or 30-35 ml capacity. Approximately 80% of each insert were filled with reactant mixture. Teflon inserts were weighed when they are empty and filled with reactant mixture. The difference between empty and filled inserts was noted as weight of batch (W_b).

3.1.4 Crystallization and Product Recovery

Syntheses were carried out in stainless steel autoclaves with PTFE inserts, at temperatures 100°C, 120°C, 140°C, 160°C and 175°C and at autogenous pressure which is equivalent to the vapor pressure of water at that temperature. Reaction times were varied between 20 h to 80 days.

Autoclaves were taken out of oven after desired reaction time and immediately quenched with tap water to cool. After cooling the contents to the autoclaves were transferred into a mortar and ground with some distilled water smoothly. Next solid products were recovered by filtration and washed with demineralized water up to pH=8 and dried at 80-100°C in an oven. Dried products were equilibrated at a desiccator containing saturated $CaCl_2$ solution for at least 24 h to provide constant humidity. After 24 h of equilibration products were weighted (W_p).

3.2 Characterization of Products by X-Ray Diffraction (XRD)

Phase identification and clinoptilolite percentage determination in the solid products were done by X-Ray diffraction. For this purpose Phillips PW1840 diffractometer was used. The scanning conditions are given in Table 3.3.

Table 3.3 Scanning conditions of XRD

Anode	Cu
Filter	Ni
Radiation	CuKα (λ=1.5405)
Tube Potential	30 kV
Tube Current	24 mA
Step Size	0.01°
Angle Range (2 theta)	5-50°
Scan Speed	0.1° /sec
Intensity Range	10000 counts/s
Time Constant	1 sec
Slit	0.2 mm

3.2.1 Phase Identification

A crystalline substance always produces a characteristic diffraction pattern and this pattern forms a kind of fingerprint by which the substance could be identified. In the view of this fact as a general procedure, for identification of solid products first XRD patterns of products were investigated to determine whether all peaks belong to clinoptilolite or not by comparing product patterns with the pattern of natural clinoptilolites from literature [5, 6-8].

For this purpose main reference for XRD pattern of natural clinoptilolite was chosen to be the pattern of Wise W., Nokleberg W, Kokinos M.[5] which is also given in 'Powder Diffraction File, PDF 39-1383' and in the book of 'Zeolite Molecular Sieves' [3]. This pattern was also compared with some other patterns from literature because XRD patterns of clinoptilolites from different origins are slightly different from each other. Some selected patterns for natural clinoptilolite were given in Figure 2.2 in the form of bar charts. By this comparison 21 characteristic peaks were selected for clinoptilolite from the pattern of Wise W., Nokleberg W, Kokinos M.[5]. These peaks are given in Table 3.4 together with the complete pattern of Wise W., Nokleberg W, Kokinos M.

To decide whether the product is clinoptilolite or not, first 2θ values corresponding to these 21 most intense peaks were searched in the product pattern. After all these peaks were found in the product pattern less intense peaks were investigated either they are found in the other XRD patterns of natural clinoptilolite patterns given in Appendix F.1 or not. Finally if still unmatched peaks were observed they were defined as peaks of a crystalline phase other than clinoptilolite. Identification of these coexisting crystalline phases was also performed by searching from PDF cards. Phases which were not identified by searching from PDF cards were named as unidentified phase. In Appendix F.2 X-ray data of coexisting phases synthesized in this study were given.

Table 3.4 d-spacing , Bragg Angle and Relative Intensity Data of 21 Major Peaks of Sample XRD pattern of Natural Clinoptilolite from Agoura, California [5]

Peak no	2 θ	d	I/I_o
1	9.875	8.950	70
2	11.149	7.930	10
3	13.047	6.780	8
	14.902	5.940	3
	15.841	5.590	5
	16.907	5.240	12
4	17.306	5.120	14
5	19.071	4.650	25
	20.399	4.350	7
6	22.342	3.976	96
7	22.462	3.955	100
8	22.754	3.905	77
	23.175	3.835	11
	23.785	3.738	10
	23.986	3.707	8
20	25.035	3.554	15
	25.332	3.513	7
9	26.002	3.424	33
	26.252	3.392	22
10	26.865	3.316	11
11	28.127	3.170	31
12	28.587	3.120	30
13	29.024	3.074	18
	29.777	2.998	37
14	30.054	2.971	99
15	31.995	2.795	36
16	32.778	2.730	36
	33.575	2.667	9
21	35.496	2.527	15
	36.116	2.485	7
	36.527	2.458	7
17	36.853	2.437	20
18	37.089	2.422	13
	38.801	2.319	5
	43.276	2.089	9
	44.006	2.056	6
	44.927	2.016	6
19	45.937	1.974	12

3.2.2 Clinoptilolite Percentage Determination in Solid Products

If a solid product was defined as single phase clinoptilolite with XRD according to the procedure in Section 3.2.1, then percent clinoptilolite in solid product was also calculated by using XRD. Considering the fact that intensities of diffraction lines due to one phase of a mixture depend on the proportion of that phase in the sample [22], for amorphous clinoptilolite mixtures a calibration curve based on intensity summation of selected peaks can be constructed to determine clinoptilolite content.

In our study calibration plot given in Figure 3.1 was used to determine clinoptilolite fraction (x_c) in amorphous clinoptilolite mixtures. To construct the calibration plot, mixtures were prepared by mixing mineral clinoptilolite originated from Bigadiç in Western Anatolia (CLI 11) with amorphous substrate with clinoptilolite composition (Table 3.1, BC 2-1) at definite amounts (10%, 25%, 50%, 65%, 75%, 90% and 100% of CLI-11). XRD analyses were performed for each mixture and peak intensity summation was calculated for 3 characteristic peaks (2θ=22.34, 30.05, 31.99) of clinoptilolite. One of the products, OG 70, synthesized in this study and having the highest intensity summation was selected as 100% clinoptilolite.

Clinoptilolite fraction in CLI 11 with respect to OG 70 was found as 0.72 from the ratio of intensity summation of CLI 11 to intensity summation of OG 70. Clinoptilolite fractions in CLI 11-amorphous mixtures were also calculated by considering CLI 11 is 72% clinoptilolite.

By calculating clinoptilolite fraction (x_c) in the solid products obtained at various stages of crystallization, clinoptilolite crystallization from amorphous material by time was followed.

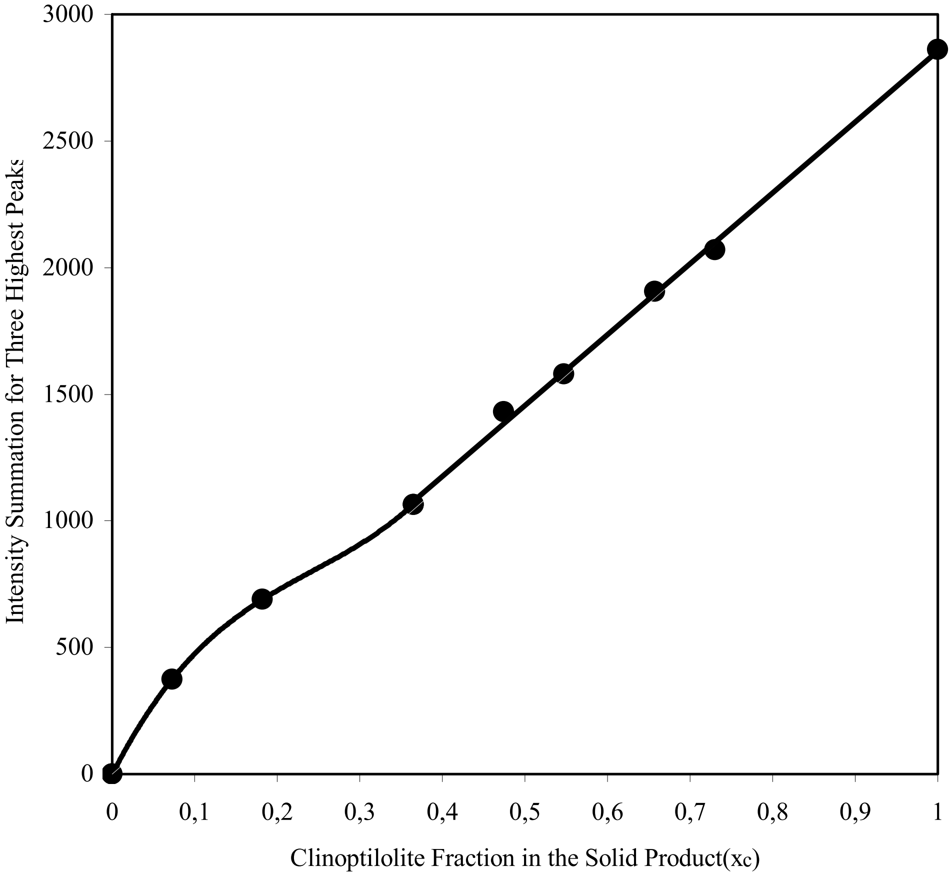


Figure 3.1 Peak intensity summation as a function of corrected clinoptilolite fractions of mineral clinoptilolite (CLI-11) with respect to a highly crystalline product (OG 70) in mixtures including amorphous substrate used for clinoptilolite synthesis.

3.2.2.a Precision Determination for Quantitative Analysis with XRD

XRD analyses of some selected products and natural clinoptilolite samples were performed at the same conditions for at least two times, for the precision determination of XRD analyses. By using the calibration plot given in Figure 3.1, clinoptilolite fractions in these products were determined separately for the two analyses. Then average of clinoptilolite fractions for each product was calculated. Deviation of clinoptilolite fractions from this average value was determined. Finally an average deviation value for clinoptilolite fraction in the solid products was calculated as ±0.02. Calculation of this average deviation was given in Appendix B.1.

3.3 Characterization with Scanning Electron Microscope (SEM)

The morphology of samples were determined by scanning electron microscope (SEM Jeol 840-A). For this purpose pellet form were given to powder samples by pressing. Then small pieces of product pellets were mounted on brass pegs to be coated with gold to provide an electrically conductive layer.

3.4 Characterization with TGA and Thermal Stability Test

Thermogravimetric analyses of samples were made by Dupont 2000 TG analyzer to determine weight change of zeolite due to water desorption. The samples were heated with a rate of $10^{o}C/min$ under N_2 atmosphere. The N_2 flow rate was 100 cm^3/min.

Thermal stability of products were determined by heating products in an oven programmed to reach maximum desired temperature (e.g. $450^{o}C$, $800^{o}C$) in 1 h, stay there for 2h and cooling to room temperature. After decomposition, XRD patterns of products were obtained and clinoptilolite content in the products were determined by the calibration plot shown in Figure 3.1

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Development of a Benchmark Composition

A significant portion of this work was devoted to the development of a reproducible benchmark composition to be modified in order to investigate the effect of synthesis parameters such as cation type, anion type, temperature etc. For this purpose as a starting point clinoptilolite was tried to be synthesized according to a recipe outlined by Chi and Sand [1].

Syntheses were performed for both seeded and unseeded systems. For seeded syntheses natural clinoptilolite originated from Gördes in Western Anatolia was used as seed crystals. Crystallinity of Gördes clinoptilolite was found to be 58% crystalline with respect to the most crystalline product (OG 70) synthesized in this study by using the calibration plot. Two different seed amount (10 wt% and 28 wt% of dry material in batch) were used to see the effect of seed amount on clinoptilolite crystallization.

Results of experiments performed from molar batch composition of $2.1Na_2O$: Al_2O_3: $10SiO_2$: 110.1 H_2O at 140°C with the addition of 28 wt % seed crystals were given in Table 4.1. Following tables Table 4.2 and 4.3 gives the results of experiments performed in 10 wt % seeded and unseeded systems for the same batch composition and temperature, respectively.

Table 4.1 Crystallization of Clinoptilolite from a Molar Batch Composition of $2.1Na_2O: 10SiO_2: Al_2O_3: 110.1H_2O$ at 140°C with seeding. (The amount of seed added is 28% of dry material in batch, % maximum yield for seed free batch = 32.46 %)

Batch Code	Sample code	Time (h)	Weight of Batch (W_b) (g)	Weight of Seed (W_s) (g)	Weight of Product (W_p) (g)	% Yield of product (%Yield)	Crystalline Phase(s)	Clino. Fraction in the Product (x_c)	Weight of Clino. in the Product (W_c) (g)	% Yield of clino. $(\%Yield)_{sfb}$	$(\%Conversion)_{sfb}$
BC 2-1	OG 42	21	7.21	0.72	2.71	37.6	Clinoptilolite	0.17	0.46	0.6	2
	OG 43	45	31.93	3.19	11.6	36.3	Clinoptilolite	0.42	4.87	10.0	31
	OG 44	69	7.86	0.79	2.51	31.9	Clinoptilolite	0.87	2.18	23.2	72
	OG 32	118	6.13	0.61	2.00	32.6	Clinoptilolite	0.91	1.82	25.4	78
	OG 45	163	31.53	3.15	11.35	36.0	Clinoptilolite	0.89	10.10	27.9	86

Table 4.2 Crystallization of Clinoptilolite from a Molar Batch Composition of $2.1Na_2O$: $10SiO_2$: Al_2O_3: $110.1H_2O$ at 140°C with seeding. (The amount of seed added is 10 wt % of dry material in batch, % maximum yield for seed free batch = 32.46 %)

Batch Code	Sample code	Time (h)	Weight of Batch (W_b) (g)	Weight of Seed (W_s) (g)	Weight of Product (W_p) (g)	% Yield of product (%Yield)	Crystalline Phase(s)	Clino. Fraction in the Product (x_c)	Weight of Clino. in the Product (W_c) (g)	% Yield of clino. $(\%Yield)_{sfb}$	$(\%Conversion)_{sfb}$
BC2-1	OG 68	23	8.00	0.25	2.51	31.4	Clinoptilolite	0.08	0.20	0.8	2
	OG 69	70	37.89	1.21	11.10	29.3	Clinoptilolite	0.89	9.88	24.7	76
	OG 70	141	8.28	0.26	2.40	29.0	Clinoptilolite	1.00	2.40	27.7	85

Table 4.3 Crystallization results of experiments performed from a Molar Batch Composition of $2.1Na_2O: 10SiO_2: Al_2O_3: 110.1H_2O$ at 140°C for unseeded systems (% Maximum yield for seed free batch = 32.46 %)

Batch Code	Sample code	Time (h)	Weight of Batch (W_b) (g)	Weight of Seed (W_s) (g)	Weight of Product (W_p) (g)	% Yield of Product (%Yield)	Crystalline Phase(s)	Clino. Fraction in the Product (x_c)	% Yield of clino. $(\%Yield)_{sfb}$	$(\%Conversion)_{sfb}$
BC2-1	OG 55	20	7.20	0	2.03	28.2	Amorphous	0	0	0
	OG 56	45	37.89	0	11.52	30.4	Amorphous	0	0	0
	OG 57	68	6.74	0	1.93	28.6	Amorphous	0	0	0
	OG 58	116	7.16	0	1.98	27.6	Amorphous	0	0	0
	OG 59	163	33.71	0	9.61	28.5	Amorphous	0	0	0

In these tables; weight of batch (W_b) consists of seed crystals and reactant gel with the given molar batch composition together. Weight of seed crystals (W_s) is the amount of seed crystal added to the reactant gel initially. In our study W_s is 10% or 28% of the weight of dry material in the reactant mixture. Here dry material was defined as all components of a molar batch composition other than water. Weight of product (W_p) is the amount of solid product obtained after washing, drying and equilibration in the desiccators.

When the products were found to contain clinoptilolite as the only crystalline phase by XRD as explained in Part 3.2.1, clinoptilolite fraction in the solid (x_c) products was determined by using the calibration plot given in Figure 3.1. Details of construction of this plot are given in Part 3.2.2. Weight of clinoptilolite in the solid product (W_c) was calculated by using weight of product (W_p) and clinoptilolite fraction (x_c) in this solid product by Equation 4.1.

$$W_c = W_p \; x_c \qquad (4.1)$$

Yield for a product is the actual amount of product of a certain batch. Percent yield for a certain batch was calculated from weight of batch (W_b) and weight of product (W_p) by Equation 4.2.

$$\%\text{Yield} = \frac{W_p}{W_b} \text{x}\, 100 \qquad (4.2)$$

Maximum yield of a zeolite is the amount of zeolite in the solid product when the concentration of the limiting reactant in the liquid phase reaches to zero. This is the maximum amount of zeolite that can be produced from a certain batch. For the calculation of maximum yield, a composition for clinoptilolite was selected as $(Na_2O)\ (Al_2O_3)\ (SiO_2)_{10}\ (H_2O)_8$ from literature (5] then SiO_2/Al_2O_3 ratio of the all products synthesized in this study were accepted to be 10 just like this formula. Formula weight of clinoptilolite (FW_c) was calculated by using this one mole Al_2O_3 based formula. For most of the batch compositions in this study, Al_2O_3 was used as the limiting reactant. All batch compositions were expressed as one mole Al_2O_3 basis. Formula weight of molar batch compositions which are expressed on one mole Al_2O_3 and seed free basis was called formula weight of seed free batch (FW_{sfb}).

For seeded systems percent maximum yield for seed free batch ((% Maximum Yield)$_{sfb}$) was calculated by Equation 4.3. For this calculation it was assumed that all limiting reactant in seed free batch is consumed to form clinoptilolite and seed crystals are not consumed or destroyed throughout the reaction.

$$(\%\ \text{Maximum Yield})_{sfb} = \frac{(FW)_c}{(FW)_{sfb}} x100 \qquad (4.3)$$

(% Maximum Yield)$_{sfb}$ for different batch compositions were given in table headings in this chapter showing clinoptilolite crystallization from various composition and conditions.

For seeded syntheses, percent yield of clinoptilolite was also calculated on the basis of seed free batch ((% Yield)$_{sfb}$). By calculating this, clinoptilolite synthesized other than seed crystals initially added to the batch was considered. However this definition is valid when seed crystals are 100% clinoptilolite. Otherwise clinoptilolite fraction of seed crystal ($x_{c,s}$) should be considered and weight of seed (W_s) should be multiplied by this fraction ($x_{c,s}$) to calculate clinoptilolite amount in the seed crystals. Remaining fraction of seed crystals ($1\text{-}x_{c,s}$) is amorphous material which can also react to form clinoptilolite. Amorphous part of seed has SiO_2/Al_2O_3 ratio of 10 which is the same as the synthesis composition. Thus batch composition will not be affected appreciably. Consequently % yield for seed free batch ((% Yield)$_{sfb}$) can be expressed by Equation 4.4;

$$(\%\text{Yield})_{sfb} = \frac{[W_c - W_s\ x_{c,s}]}{[W_b - W_s\ x_{c,s}]} x\,100 \qquad (4.4)$$

In Equation 4.4, if seed crystals are 100% clinoptilolite $x_{c,s}$ will be equal to 1. In our case clinoptilolite fraction in seed crystals ($x_{c,s}$) is 0.58 according to the calibration plot given in Figure 3.1.

Percent conversion is the degree of how much a reaction has progressed to form the product by the consuming limiting reactant. It can be expressed by the ratio of percent yield to percent maximum yield achieved for a certain batch. It should be equal to 100% when the reaction progressed to consume all of the limiting reactant. In our case % conversion of the limiting reactant was calculated on the basis of seed free batch ((%conversion)$_{sfb}$) by using (% Yield)$_{sfb}$ and (% Maximum Yield)$_{sfb}$ as given in Equation 4.5.

$$(\%\,\text{Conversion})_{\text{sfb}} = \frac{(\%\text{Yield})_{\text{sfb}}}{(\,\%\,\text{Maximum Yield})_{\text{sfb}}} \text{ x } 100 \qquad (4.5)$$

A sample calculation for (% Yield), (% Maximum Yield)$_{sfb}$, (% yield)$_{sfb}$ and (%conversion)$_{sfb}$ is given in Appendix C.

As can be seen on Table 4.1 and Table 4.2, single phase and highly crystalline clinoptilolite was synthesized reproducibly as it was claimed by Chi and Sand (1], for both 28% seeded and 10% seeded systems. XRD pattern of single phase clinoptilolite (OG 70) synthesized from 10% seeded system was given in Figure 4.1. XRD patterns of products in these tables are given in Appendix D, Figure D.5 and Figure D.6 also.

According to the data in Table 4.1 and Table 4.2, it is clear that as reaction proceeds, % clinoptilolite in the solid product increases so does the (%yield)$_{sfb}$ and (%conversion)$_{sfb}$ values. Ultimately high crystallinity, (%yield)$_{sfb}$ and (%conversion)$_{sfb}$ were achieved for both. Also % yield for each product were found to be similar.

For unseeded systems clinoptilolite was not synthesized as given in Table 4.3. Even after 163 h product is totally amorphous while for 10 % seeded system product is 100% clinoptilolite at this time (see Table 4.2). Percent yield is nearly constant for each product too.

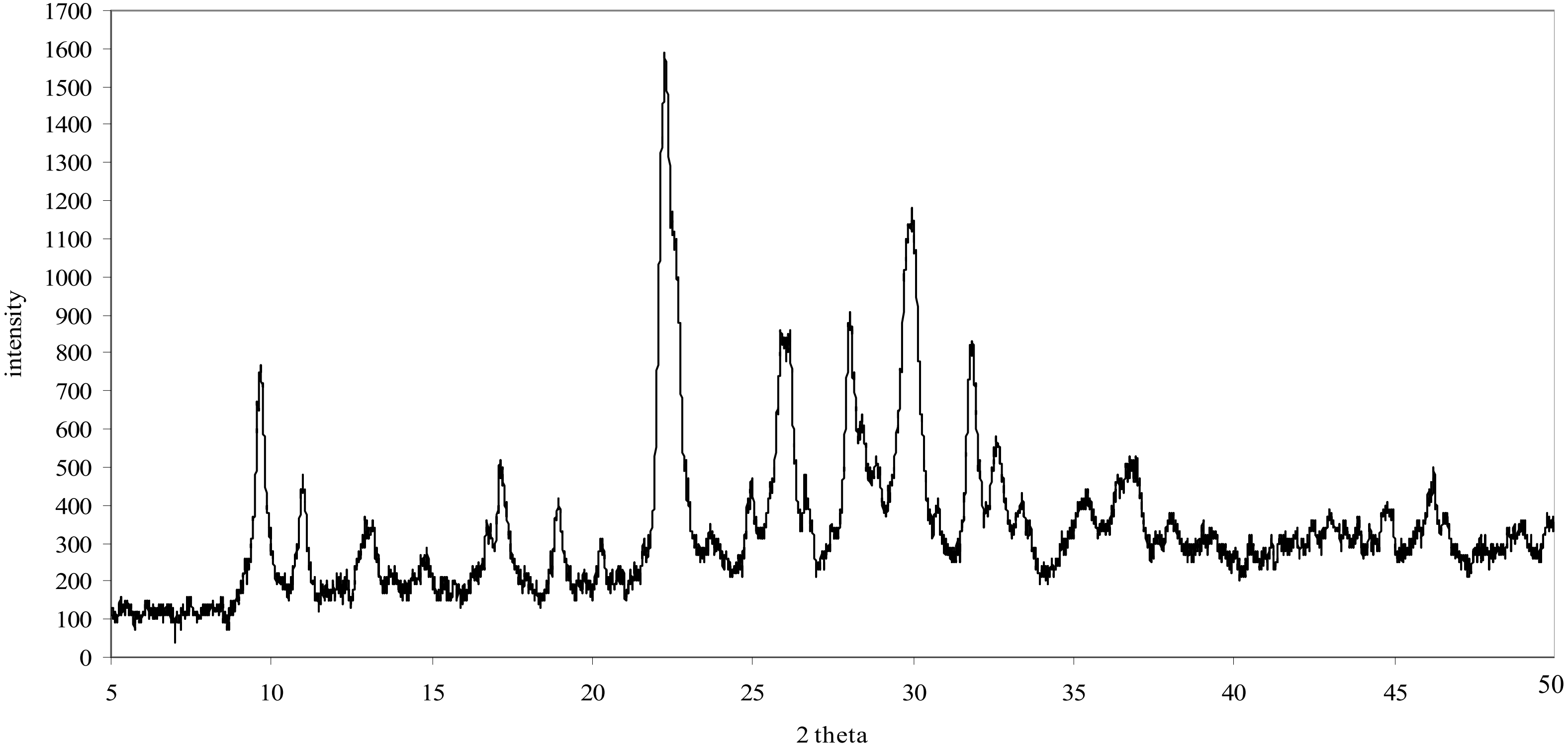
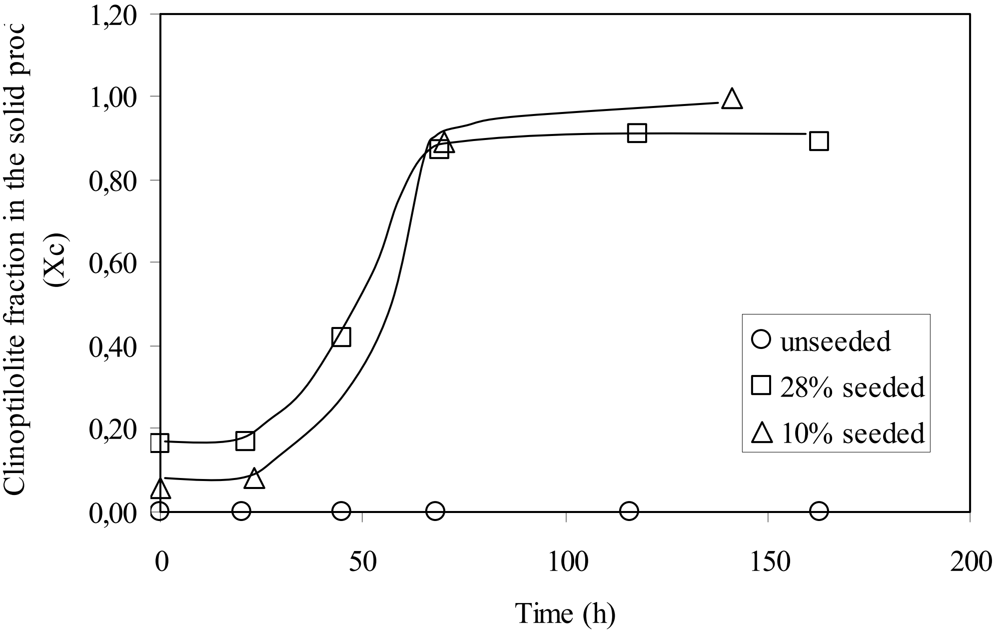


Figure 4.1 XRD Pattern of clinoptilolite (OG 70) synthesized from a molar batch composition of 2.1 Na_2O: $10SiO_2$: Al_2O_3: $110.1H_2O$ at 140°C for 141 h with seeding (The amount of seed added is 10 wt % of dry material in batch).

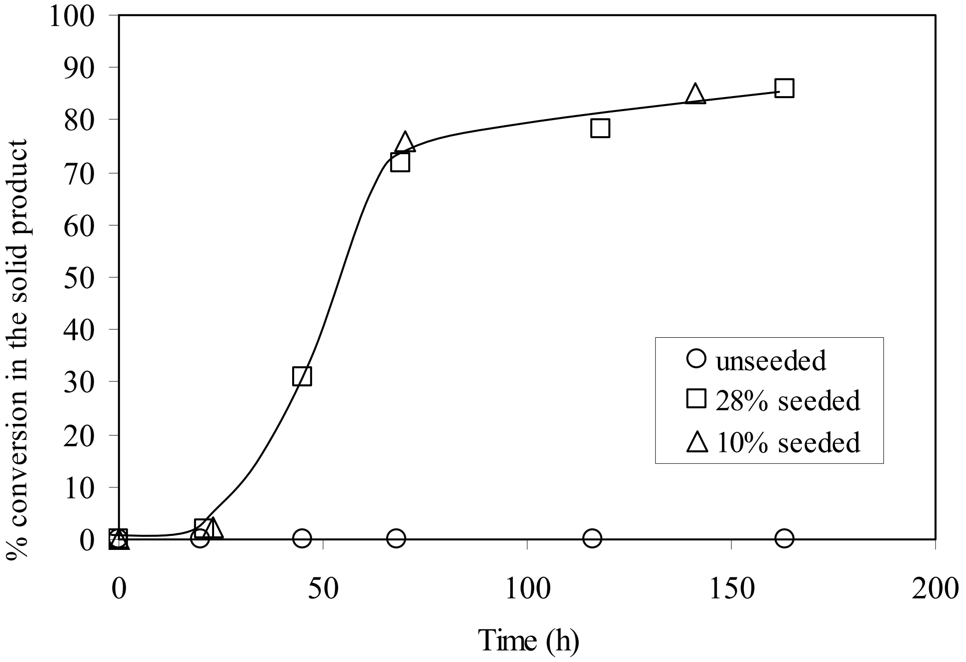
Effect of seed amount on clinoptilolite fraction in solid product and percent conversion were given in Figure 4.2 (a) and (b). As can be seen on both figure crystallization curve is S-shaped which is typical for zeolite synthesis. At early stages of crystallization clinoptilolite fraction in the solid product is nearly constant and in this part, $(\%\text{conversion})_{\text{sfb}}$ is nearly zero which shows no new clinoptilolite crystals were synthesized. This part of crystallization which elapsed up to new crystals formed is called nucleation period. At time is equal to zero, clinoptilolite fraction is not zero because of seed crystals added initially. At this time for 28 % and 10% seeded system clinoptilolite fractions are 0.16 and 0.06 respectively since clinoptilolite fraction of seed crystals is 0.58. By proceeding reaction both clinoptilolite fraction in the solid product and $(\%\text{conversion})_{\text{sfb}}$ increases then new crystals are forming. This period is called crystallization. After a certain time crystallization stops and clinoptilolite fraction and $(\%\text{conversion})_{\text{sfb}}$ does not increase any more.

As can be seen on Figure 4.2 (b) % conversion for products obtained at similar times are similar for 28% and 10% seeded systems then a single plot can be constructed for both. This shows conversion of limiting reactant to clinoptilolite does not depend on the amount of seed in this range. On the other hand without any seeds conversion was not observed. Consequently perhaps longer crystallization period is required for crystallization without seed crystals or seed crystal addition is inevitable for clinoptilolite synthesis.

At early stages of crystallization product was highly amorphous (e.g. see Table 4.1, OG 42) including clinoptilolite just originated from seed crystals for this reason at this time, $(\%\text{yield})_{\text{sfb}}$ and $(\%\text{conversion})_{\text{sfb}}$ is expected to be zero. However these values are slightly greater than zero. This slight difference may be a result of precision uncertainty of XRD analyses used for quantitative analyses of products or weighting the product, batch or seed.



(a)



(b)

Figure 4.2 Effect of seed amount on (a) percent clinoptilolite in the solid product (b) % conversion for seed free batch for the batch composition $2.1Na_2O$: $10SiO_2$: Al_2O_3: $110.1H_2O$ at 140^oC

Constant % yield for products synthesized from the same molar batch composition is an expected result since percent yield is related with molar batch composition and solubility of components of that molar batch composition.

As a result of these preliminary experiments, single phase and highly crystalline clinoptilolite was synthesized reproducibly from molar batch composition of $2.1Na_2O$: Al_2O_3: $10SiO_2$: 110.1 H_2O at 140°C with the addition of seed crystals. The amount of seed added was either 10 wt % or 28 wt% of dry material in batch. Thus a benchmark composition was obtained in order to use for further studies.

4.1.1 Evaluation of Results with XRD Precision

Precision of quantitative analyses performed with XRD was considered to evaluate our results more critically. An average deviation for clinoptilolite fraction in the solid products (x_c) was calculated as ±0.02. Determination procedure of this value is given in part 3.2.2-a and Appendix B1 According to this result, if clinoptilolite fraction in this solid product is calculated as 0.20, it can be 0.22 or 0.18 within precision uncertainty of quantitative analyses with XRD.

Table 4.4 shows crystallization results given in Table 4.1 by considering ±0.02 deviation for clinoptilolite fraction in the solid product. In this table a range was calculated for weight of clinoptilolite in the solid product (W_c), percent yield for seed free batch ($(\%Yield)_{sfb}$) and percent conversion for seed free batch ($(\%Conversion)_{sfb}$) according to this deviation. To demonstrate these results, columns including these were divided to three rows. Exact values of x_c, W_c, $(\%Yield)_{sfb}$ and $(\%Conversion)_{sfb}$ were given by bold style. Results calculated by considering ±0.02 deviation were given on and under these exact values.

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Table 4.4 Crystallization Results Calculated by Considering ±0.02 XRD Precision Uncertainty for Clinoptilolite Synthesized from a Molar Batch Composition of $2.1Na_2O$: $10SiO_2$: Al_2O_3: $110.1H_2O$ at 140°C with seeding. (The amount of seed added is 28 wt% of dry material in batch, % maximum yield for seed free batch = 32.46 %)

Batch Code	Sample code	Time (h)	Weight of Batch (W_b) (g)	Weight of Seed (W_s) (g)	Weight of Product (W_p) (g)	Crystalline Phase(s)	Clino. Fraction in the Product (x_c)	Weight of Clino. in the Product (W_c) (g)	% Yield of clino. $(\%Yield)_{sfb}$	$(\%Conversion)_{sfb}$
BC 2-1	OG 42	21	7.21	0.72	2.71	Clinoptilolite	0.15	0.41	-0.2	-1
							0.17	**0.46**	**0.6**	**2**
							0.19	0.51	1.3	4
	OG 43	45	31.93	3.19	11.6	Clinoptilolite	0.40	4.64	9.3	29
							0.42	**4.87**	**10.0**	**31**
							0.44	5.10	10.8	33
	OG 44	69	7.86	0.79	2.51	Clinoptilolite	0.85	2.13	22.6	70
							0.87	**2.18**	**23.2**	**72**
							0.89	2.23	23.9	74
	OG 32	118	6.13	0.61	2.00	Clinoptilolite	0.89	1.78	24.7	76
							0.91	**1.82**	**25.4**	**78**
							0.93	1.86	26.1	80
	OG 45	163	31.53	3.15	11.35	Clinoptilolite	0.87	9.87	27.1	83
							0.89	**10.10**	**27.9**	**86**
							0.91	10.33	28.6	88

At early stages of crystallization, it is expected to obtain $(\%\text{Yield})_{sfb}$ and $(\%\text{Conversion})_{sfb}$, equal to zero since at these stages no new clinoptilolite crystals is expected to grow. Slightly greater or lower results than zero is due to precision uncertainty of XRD. For example for OG 42 synthesized for 21 h, $(\%\text{Yield})_{sfb}$ and $(\%\text{Conversion})_{sfb}$ is slightly greater than zero. Within ±0.02 XRD precision uncertainty for this product $(\%\text{Yield})_{sfb}$ can be in between -0.2 and 1.3 and $(\%\text{Conversion})_{sfb}$ can be in between -1 and 4.

4.2 Effect of Aluminum Source, Stirring Period, Water content and Colloidal Silica Type on Crystallization of Clinoptilolite

Molar batch composition $2.1Na_2O$: Al_2O_3: $10SiO_2$: 110.1 H_2O was modified by changing aluminium source, silica source, water content and stirring period before hydrothermal synthesis. These were investigated to determine the effect of these on phase purity, clinoptilolite fraction in the solid product (x_c) and percent conversion for seed free batch $(\%\text{ conversion})_{sfb}$.

Aluminium powder and aluminium chips dissolved in sodium hydroxide solution were used as aluminium source instead of sodium aluminate. Colloidal silica type was changed by using Ludox AS-30 which is ammonium stabilized and Ludox HS-40 which is sodium stabilized. Water content of batch composition was decreased from 110.1 moles to 97 moles and synthesis was performed from molar batch composition $2.1Na_2O$: Al_2O_3: $10SiO_2$: 97 H_2O. For another trial, reactant gel was stirred for 22 h instead of 1 h before hydrothermal synthesis.

Results of experiments performed in this part were given in Table 4.5. For all products synthesized from different conditions single phase clinoptilolite was obtained. High crystallinity was observed for all. $(\%\text{ Conversion})_{sfb}$ data were also similar for all, only synthesis performed with dissolved Al chips it is slightly higher. Similar percent yield of products were obtained except OG 33 and OG 34 synthesized from a different batch composition (BC 4) including lower amount of water.

Table 4.5 Crystallization of Clinoptilolite from a Molar Batch Composition of $2.1Na_2O: 10SiO_2: Al_2O_3: 110.1H_2O$ (BC 2-1) and $2.1Na_2O: 10SiO_2: Al_2O_3: 97\ H_2O$ (BC 4) at 140°C with Seeding. (The amount seed added is 28 wt% of dry material in batch, % maximum yield for seed free batch = 32.46 for BC 2-1, % maximum yield for seed free batch = 35.22 for BC 4)

Batch Code	Sample code	Time (h)	Weight of Batch (W_b) (g)	Weight of Seed (W_s) (g)	Weight of Product (W_p) (g)	% Yield of product (%Yield)	Crystalline Phase(s)	Clino. Fraction in the Product (x_c)	Weight of Clino. in the Product (W_c) (g)	% Yield of clino. $(\%Yield)_{sfb}$	$(\%Conversion)_{sfb}$
BC 2	OG 29[1]	68	30.42	3.04	10.05	0.33	clinoptilolite	0.86	8.64	24.0	68
	OG 30[1]	118	29.63	2.96	10.10	0.34	clinoptilolite	0.86	8.69	25.0	71
BC 2-1	OG 31[2]	68	7.42	0.74	2.70	0.36	clinoptilolite	0.86	2.32	27.0	77
	OG 32[2]	118	6.13	0.61	2.00	0.33	clinoptilolite	0.88	1.82	25.4	78
	OG 129[3]	119	34.11	1.13	9.60	0.28	clinoptilolite	0.94	9.02	25.0	71
	OG 130[4]	119	33.63	1.11	9.92	0.29	clinoptilolite	1.03	9.92	28.1	80
BC 4	OG 33[5]	68	6.36	0.63	2.30	0.36	clinoptilolite	0.82	1.89	25.5	72
	OG 34[5]	118	7.43	0.74	2.70	0.36	clinoptilolite	0.88	2.38	27.8	79

1- Ludox HS-40, 22 h of stirring period, 110.1 moles of H_2O, sodium aluminate
2- Ludox AS-30, 1 h of stirring period, 110.1 moles of H_2O, sodium aluminate
3- Ludox AS-30, 1 h of stirring period, 110.1 moles of H_2O, Al powder dissolved in sodium hydroxide solution
4- Ludox AS-30, 1 h of stirring period, 110.1 moles of H_2O, Al chips dissolved in sodium hydroxide solution
5- Ludox HS-40, 1 h of stirring period, 97 moles of H_2O, sodium aluminate

Clinoptilolite fraction in the solid product (x_c) and (% conversion)$_{sfb}$ with respect to time for all products is given in Figure 4.3 for all syntheses with the benchmark batch composition (BC 2-1). By using all data obtained in this part a single curve was constructed since clinoptilolite fractions and conversion for seed free batch at similar times is nearly the same within XRD precision. For Al chips dissolved in sodium hydroxide solution clinoptilolite fraction in the solid product (x_c) is slightly higher so that it was demonstrated with dotted line.

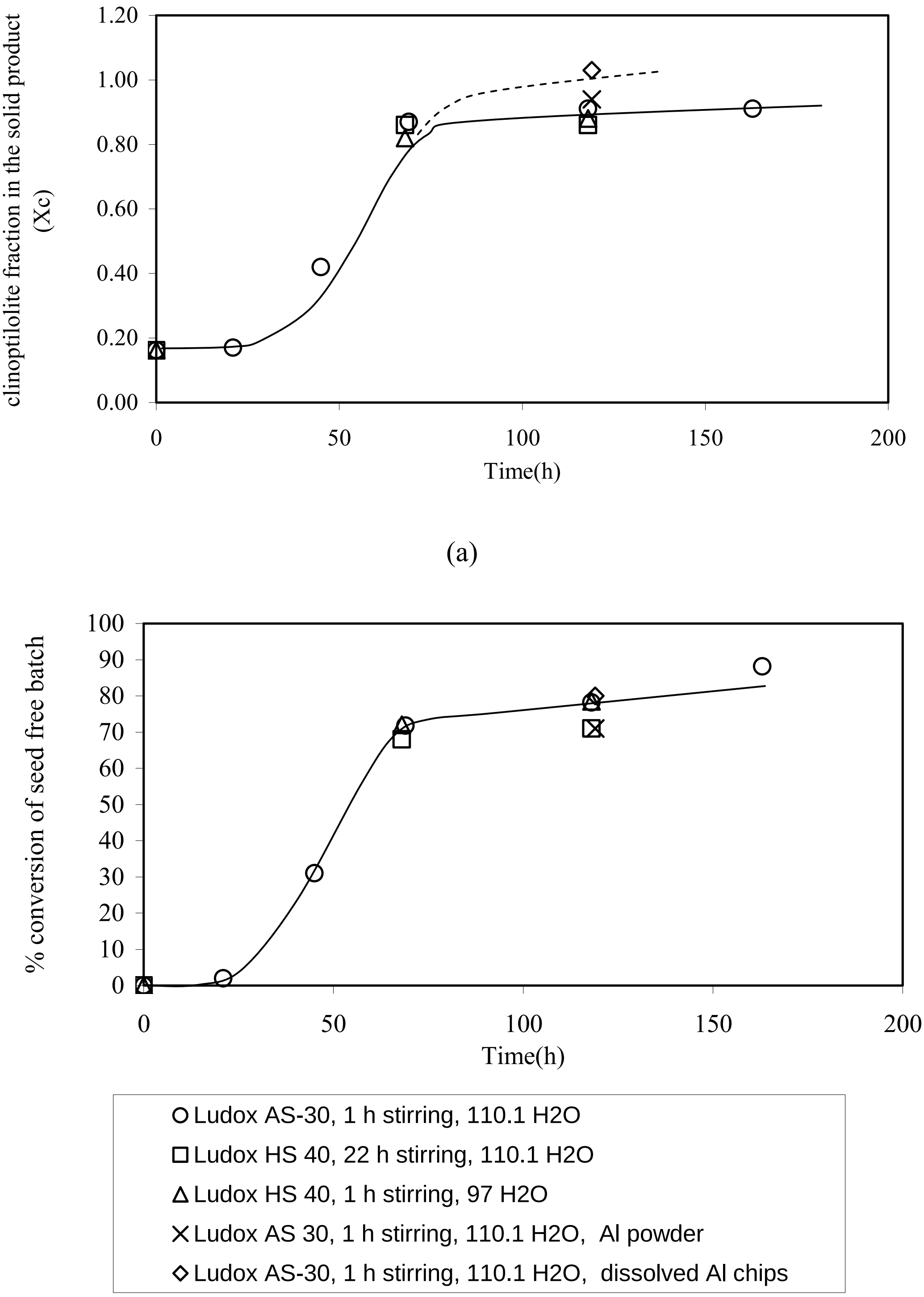
As can be seen on Table 4.5 type of silica source, stirring period, water content decrease within the given range and usage of aluminium powder or chips does not have a significant effect on phase purity. Single phase clinoptilolite was synthesized for each case. Then this shows tolerance of our benchmark composition to these modifications.

For further experiments usage of sodium aluminate powder rather than aluminium chips or aluminium powder should be preferred since it is more practical to prepare sodium aluminate solution with it.

Consequently in this part it was demonstrated that despite making modifications on reactant types, preparation route or water content of our benchmark composition single phase clinoptilolite can be synthesized. Additionally results are so reproducible that clinoptilolite fractions or (% conversion)$_{sfb}$ for each product are similar within the precision limits of XRD.

4.3 Crystallization Results of Experiments Performed with Cations Na, K and Mixture of Na and K

In this part of the experiments, our benchmark composition, 2.1 Na_2O: Al_2O_3: 10SiO_2: 110.1 H_2O was modified by using potassium and sodium potassium mixture (1:1) instead of sodium. Effect of cation type on phase purity and conversion rate were investigated.



(a)

(b)

Figure 4.3 Effect of silica source, stirring period, water content and aluminum source on (a) clinoptilolite fraction in the solid product and (b) % conversion for seed free batch for the batch composition $2.1Na_2O$: $10SiO_2$: Al_2O_3: x H_2O where x=110.1 or 97 at 140°C with 28% seed crystals.

Alkali cations were preferred rather than alkaline earth because natural clinoptilolite consists of monovalent cations rather than divalent cations [6]. (Na,K) mixture was examined because natural samples are generally rich with both of these cations [10].

In the experiments, clinoptilolite synthesis was carried out from synthesis gels with composition of $1.05\ Na_2O$: $1.05\ K_2O$: $10\ SiO_2$: Al_2O_3: $110.1H_2O$ and $2.1K_2O$: $10SiO_2$: Al_2O_3: $110.1\ H_2O$ at 140^oC with seeding at autogenous pressure. The amount of seed added is 10 wt % or 28 wt % of dry material in batch.

Table 4.6 and Table 4.7 shows the crystallization results that were calculated from this group of experiments performed for 10 wt% seeded (Na,K) and K including systems. Table 4.8 and Table 4.9 shows the crystallization results of experiments performed for 28 % seeded Na,K and K including systems respectively. The experimental conditions for each synthesis were given in table headings. Phases in the products were listed with respect to their abundance.

Figure 4.4 and Figure 4.5 show clinoptilolite fraction in the solid product and $(\%\text{conversion})_{\text{sfb}}$ with respect to time for 28% and 10% seeded Na, (Na,K) and K including systems.

As can be seen in Table 4.6 clinoptilolite was crystallized as a single phase for Na,K including system for 10% seeded system. After 70 h of hydrothermal treatment crystallization was nearly completed and high crystallinity and conversion was achieved. Figure 4.6 shows XRD pattern of single phase clinoptilolite, OG 74, synthesized from (Na,K) including system. Results are not similar for 28% seeded (Na,K) included system since after 68 h of hydrothermal treatment, trace amount of an unidentified phase was appeared coexisting with clinoptilolite (Table 4.8).

Table 4.6 Crystallization of Clinoptilolite from a Molar Batch Composition of $1.05Na_2O: 1.05K_2O : 10SiO_2 : Al_2O_3: 110.1H_2O$ at 140°C with Seeding (The amount of seed added is 10wt% of dry material in batch, % maximum yield for seed free batch = 32.41 %)

Batch Code	Sample code	Time (h)	Weight of Batch (W_b) (g)	Weight of Seed (W_s) (g)	Weight of Product (W_p) (g)	% Yield of product (%Yield)	Crystalline Phase(s)	Clino. Fraction in the Product (x_c)	Weight of Clino. in the Product (W_c) (g)	% Yield of clino. $(\%Yield)_{sfb}$	$(\%Conversion)_{sfb}$
BC 5-1	OG 72	24	7.07	0.23	2.16	30.6	Clinoptilolite	0.05	0.11	-0.3	-1
	OG 73	48	7.68	0.25	2.31	30.1	Clinoptilolite	0.18	0.42	3.7	11
	OG 74	70	38.54	1.26	11.08	28.7	Clinoptilolite	0.78	8.64	20.9	64
	OG 75	166	7.50	0.25	2.16	28.8	Clinoptilolite	0.79	1.71	21.3	66

Table 4.7 Crystallization of Clinoptilolite from a Molar Batch Composition of 2.1K_2O: 10SiO_2: Al_2O_3: 110.1H_2O at T=140°C with Seeding (The amount of seed added is 10wt% of dry material in batch, % maximum yield for seed free batch = 32.62 %)

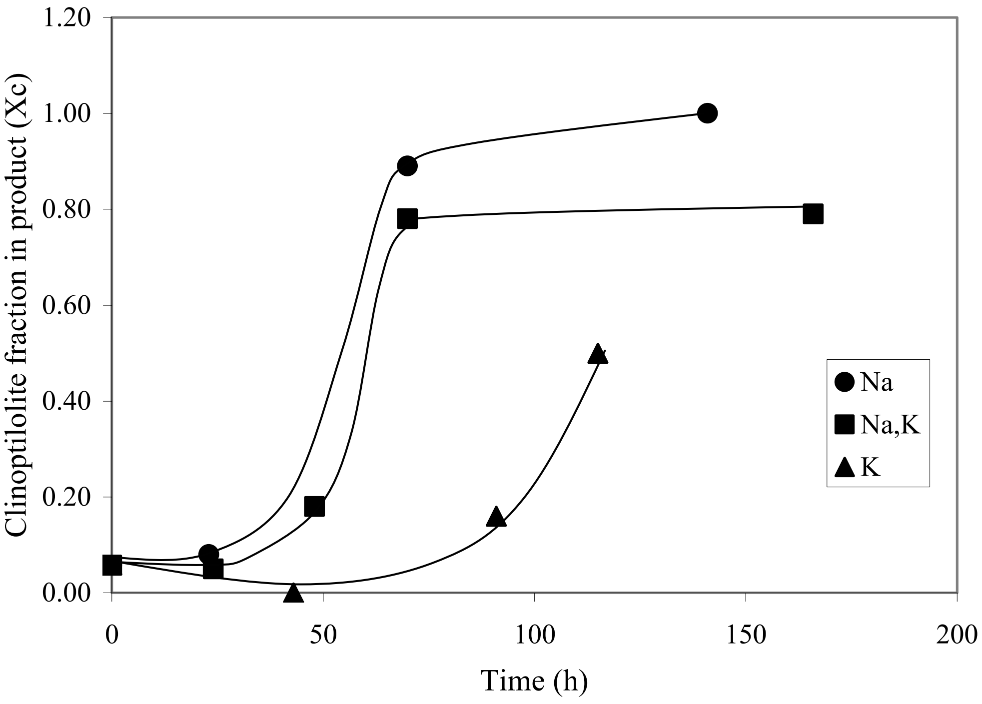
Batch Code	Sample code	Time (h)	Weight of Batch (W_b) (g)	Weight of Seed (W_s) (g)	Weight of Product (W_p) (g)	% Yield of product (%Yield)	Crystalline Phase(s)	Clino. Fraction in the Product (x_c)	Weight of Clino. in the Product (W_c) (g)	% Yield of clino. $(\%Yield)_{sfb}$	$(\%Conversion)_{sfb}$
BC 3-1	OG 141	43	7.76	0.23	2.44	30.6	----	0.00	0.00	-1.7	-5
	OG 142	91	8.41	0.25	2.48	30.1	Clinoptilolite Linde L	0.16	0.40	3.1	9
	OG 143	115	7.39	0.22	2.03	28.7	Clinoptilolite Linde L	0.50	1.01	12.1	37

Table 4.8 Crystallization of Clinoptilolite from a Molar Batch Composition of $1.05Na_2O: 1.05K_2O: 10SiO_2: Al_2O_3: 110.1H_2O$ at 140°C with Seeding. (The amount of seed added is 28 wt % of dry material in batch, % maximum yield for seed free batch =32.41 %)

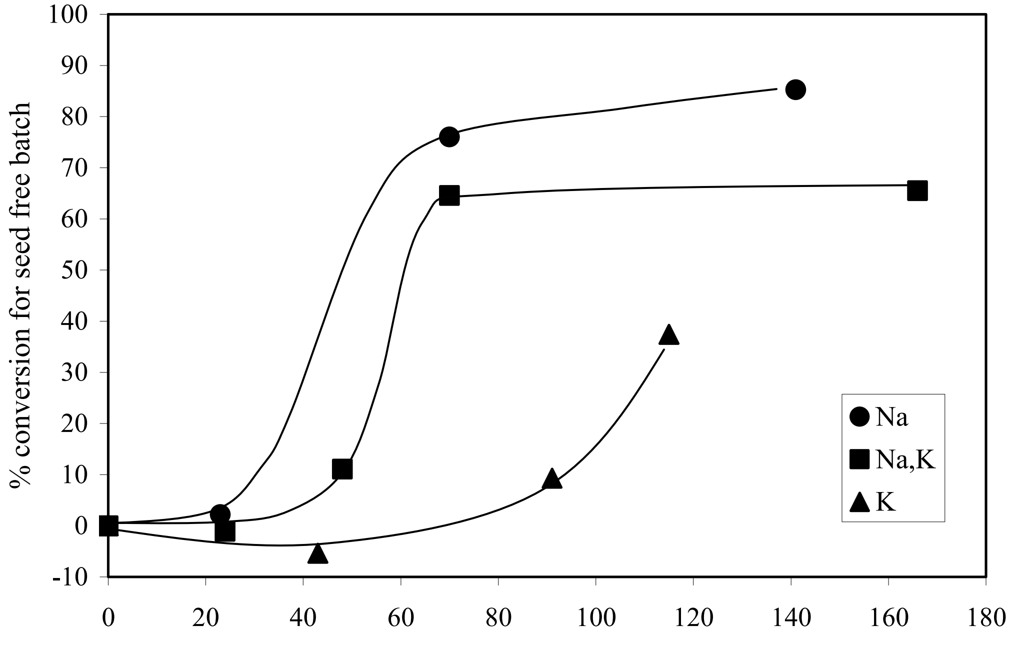
Batch Code	Sample code	Time (h)	Weight of Batch (W_b) (g)	Weight of Seed (W_s) (g)	Weight of Product (W_p) (g)	% Yield of product (%Yield)	Crystalline Phase(s)	Clino. Fraction in the Product (x_c)	Weight of Clino. in the Product (W_c) (g)	% Yield of clino. $(\%Yield)_{sfb}$	$(\%Conversion)_{sfb}$
BC 5-1	OG 63	20	7.99	0.80	2.80	35.0	Clinoptilolite	0.18	0.50	0.5	2
	OG 64	38	34.34	3.43	12.29	35.8	Clinoptilolite	0.32	3.93	6.00	19
	OG 47	46	7.19	0.72	2.50	34.8	Clinoptilolite	0.58	1.45	15.2	47
	OG 48	68	7.30	0.73	2.35	32.2	Clinoptilolite Unidentified phase	0.75	1.76	19.5	60
	OG 49	113	7.27	0.72	2.42	33.3	Clinoptilolite Unidentified phase	0.65	1.57	16.8	52
	OG 50	163	32.68	3.27	11.02	33.7	Clinoptilolite Unidentified phase	0.65	7.16	17.1	53
	OG 66	212	7.37	0.74	2.73	37.0	Clinoptilolite Unidentified phase	0.70	1.91	21.3	66

Table 4.9 Crystallization of Clinoptilolite from a Molar Batch Composition of $2.1K_2O: 10SiO_2: Al_2O_3: 110.1H_2O$ at 140°C with the addition of 28 % of seed crystals, %maximum Yield for Seed Free Batch= 32.62)

Batch Code	Sample code	Time (h)	Weight of Batch (W_b) (g)	Weight of Seed (W_s) (g)	Weight of Product (W_p) (g)	% Yield of product (%Yield)	Crystalline Phase(s)	Clino. Fraction in the Product (x_c)	Weight of Clino. in the Product (W_c) (g)	% Yield of clino. $(\%Yield)_{sfb}$	$(\%Conversion)_{sfb}$
BC 3-1	OG 51	20	7.80	0.78	2.70	34.6	Clinoptilolite	0.18	0.49	0.5	1
	OG 52	46	7.52	0.75	2.69	35.8	Clinoptilolite	0.18	0.48	0.7	2
	OG 53	68	6.80	0.68	2.44	35.9	Clinoptilolite	0.19	0.46	1.1	3
	OG 54	118	37.42	3.74	12.37	33.1	Clinoptilolite Unidentified phase	0.60	7.42	14.9	46

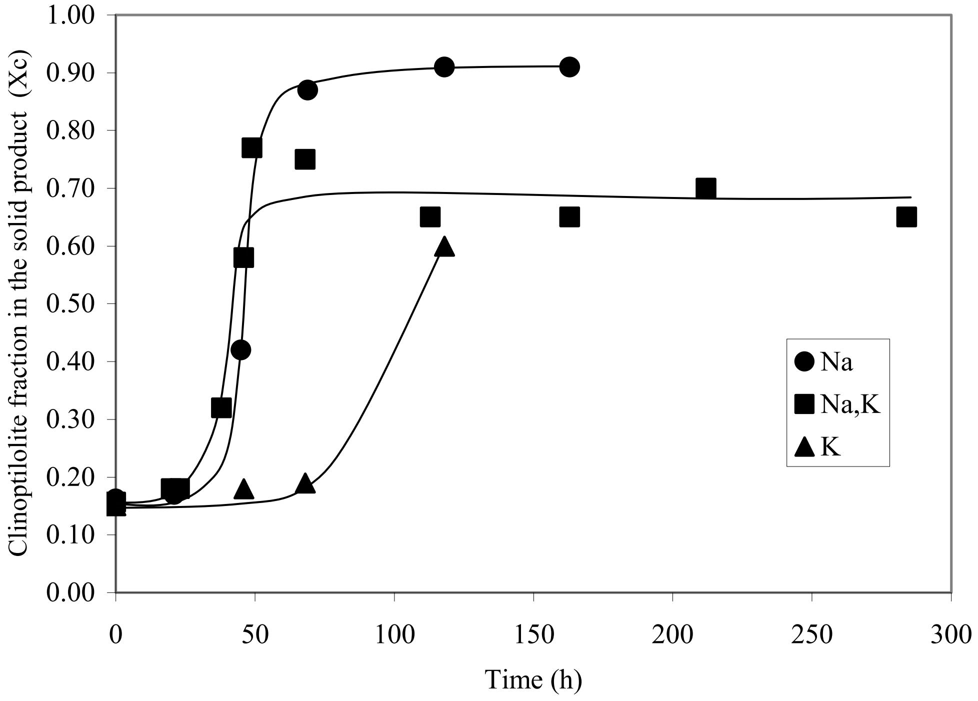


(a)

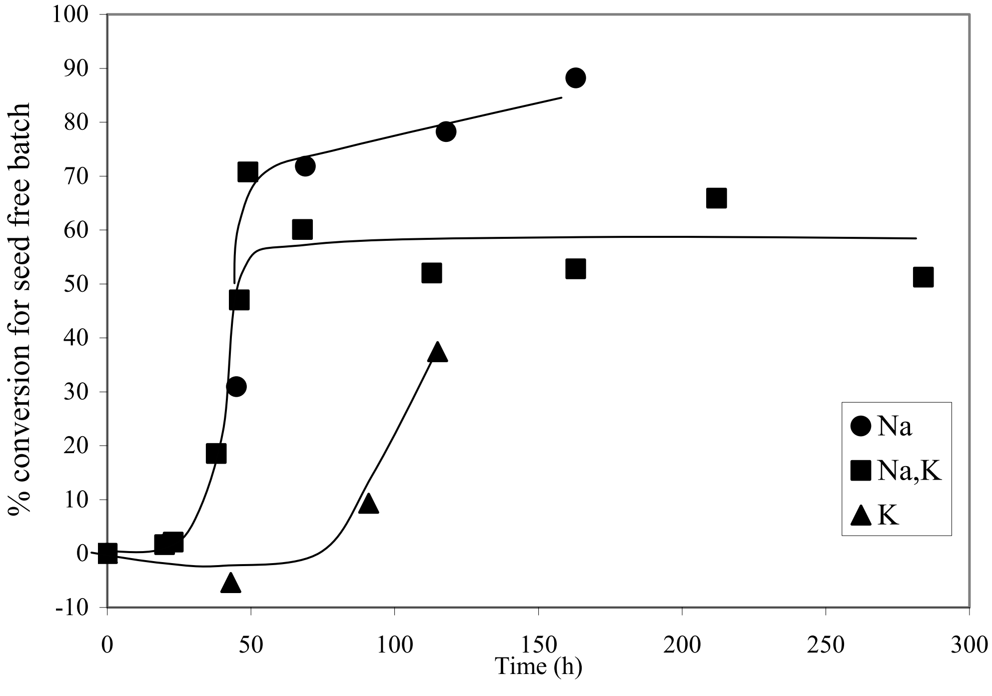


(b)

Figure 4.4 Effect of cation type on (a) clinoptilolite fraction in the solid product (b) % conversion for seed free batch for the batch composition $2.1M_2O$: Al_2O_3: $10SiO_2$: $110.1H_2O$ where M is Na or K or Na,K mixture (1:1) at 140°C with 10% seed crystals



(a)



(b)

Figure 4.5 Effect of cation type on (a) clinoptilolite fraction in the solid product (b) % conversion for seed free batch for the batch composition $2.1M_2O$: Al_2O_3: $10SiO_2$: $110.1H_2O$ where M is Na or K or Na,K mixture (1:1) at 140°C with 28% seed crystals

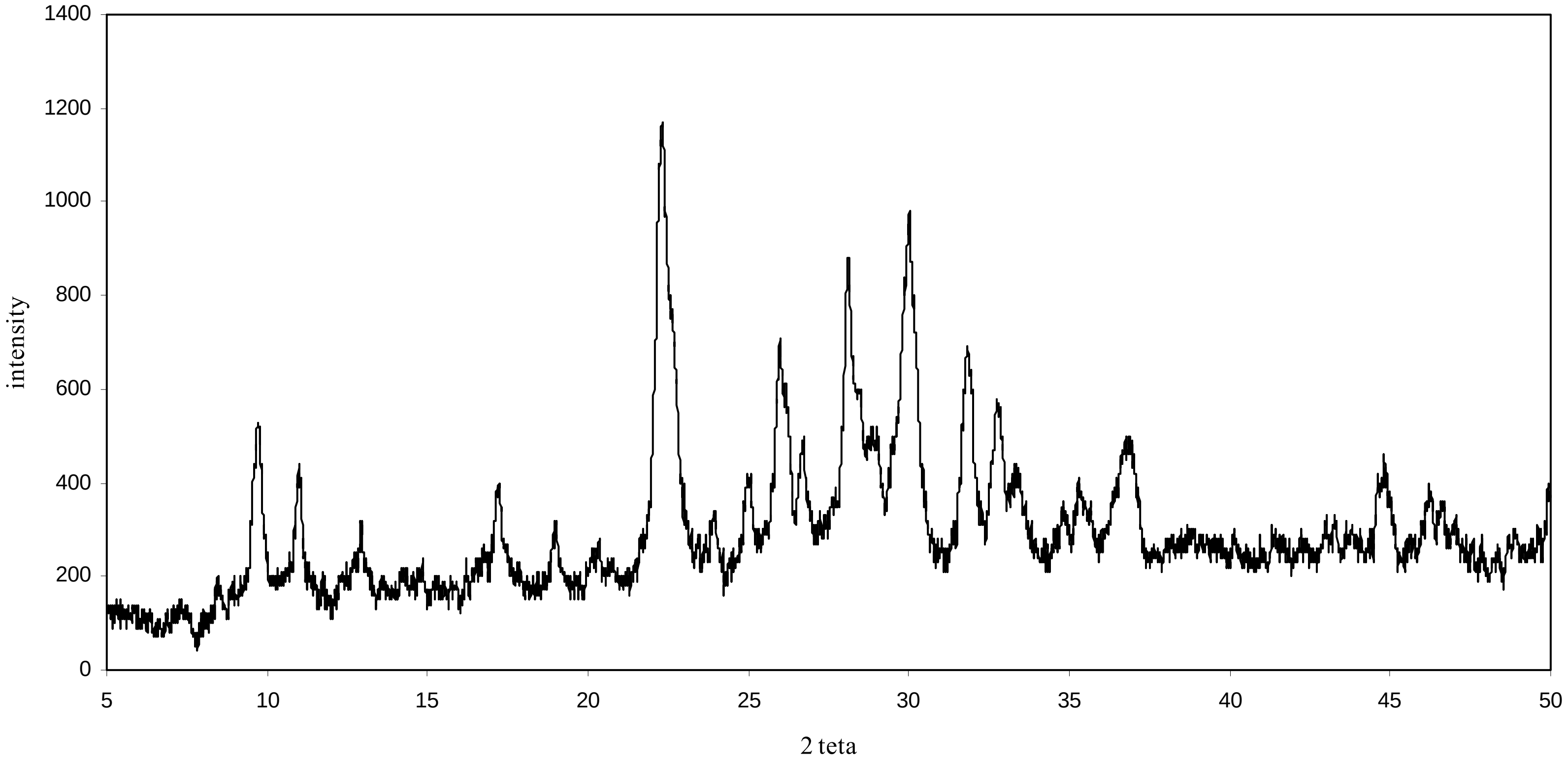


Figure 4.6 XRD Pattern of clinoptilolite (OG 74) synthesized from a molar batch composition of $1.05Na_2O$: $1.05K_2O$: Al_2O_3: $10SiO_2$: $110.1H_2O$ at 140°C for 68h with 10 wt% of seed crystals

For K including and 10% seeded systems clinoptilolite was crystallized with minor amount of Linde-L (Table 4.7). Figure 4.7 shows XRD pattern of the product OG 143 synthesized from K including systems. For 28% seeded systems, it was crystallized with an unidentified phase (Table 4.9). X-ray powder diffraction data used for the identification of Linde-L is given in Appendix F2.

Rate of conversion can be defined as the slope at 50% of maximum conversion. According to this definition, as can be seen on Figure 4.4 and 4.5 rate of conversion to clinoptilolite is 3 times faster for Na including system than K including system approximately. Similar finding was also reported by Chi and Sand previously. For Na,K including system rate of crystallization is also faster than K including system whereas within Na and Na,K including systems significant difference in rate of crystallization was not observed. In fact this is not an expected result because if K ion decreases crystallization rate, crystallization rate should also be decreased for (Na,K) including system as compared to Na including system. May be up to a critical amount of K^+ ion in the reactant mixture, a significant effect on crystallization rate can not be observed and this amount is more than half of the total cation content.

Consequently cation type in the reaction system was found to affect both phase purity of the products and rate of clinoptilolite crystallization. Clinoptilolite can be synthesized as a single phase with the use of Na or Na,K mixture. Sodium ion favors the formation of clinoptilolite as a single phase either solely or mixed with potassium however replacement of sodium with potassium completely results formation of coexisting phases.

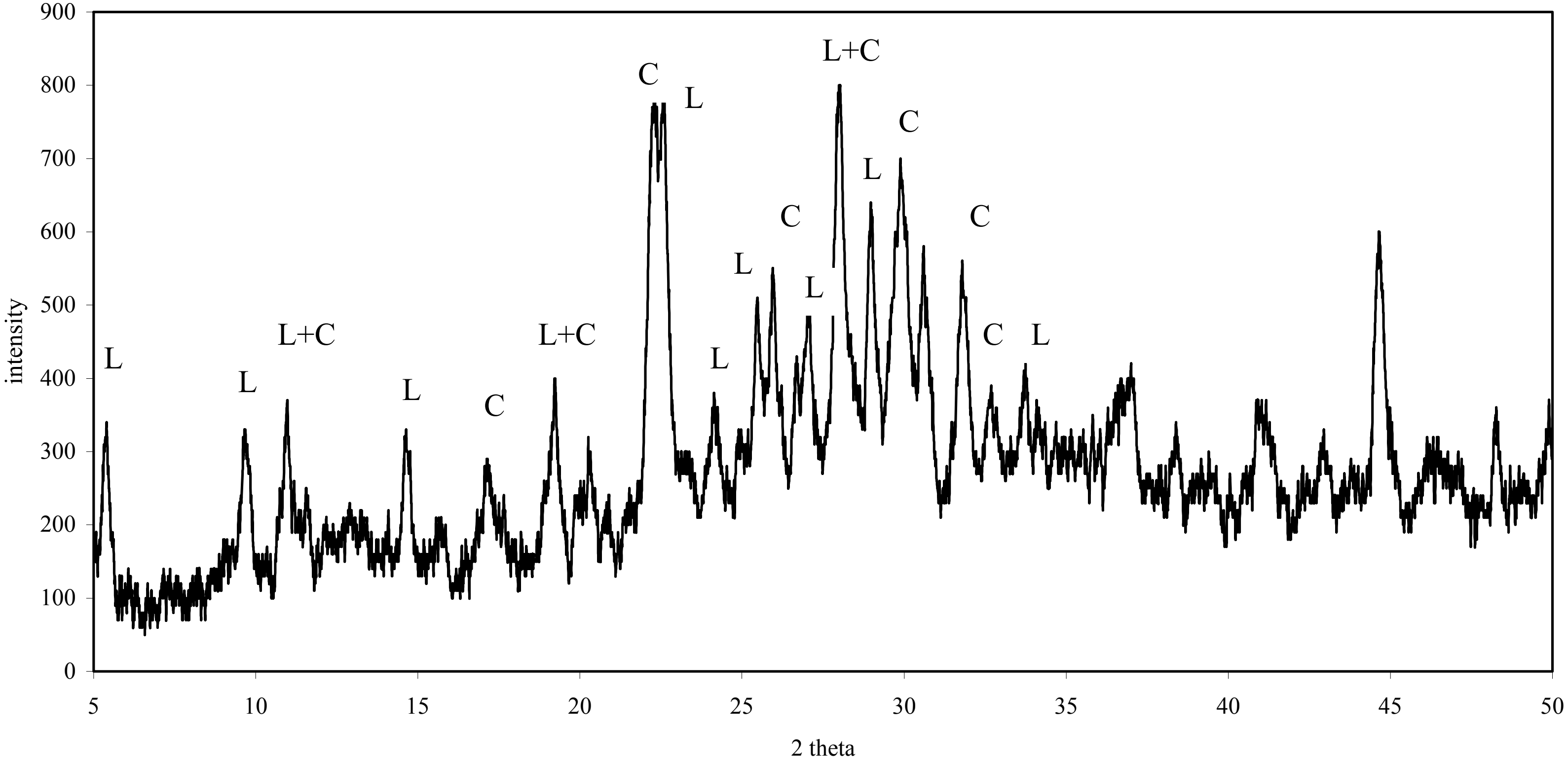


Figure 4.7 XRD Pattern of OG 143 synthesized from a molar batch composition of 2.1K_2O : Al_2O_3: 10SiO_2 : 110.1H_2O at 140^oC for 115 h with 10 wt% of seed crystals (L:Linde L, C: Clinoptilolite)

4.4 Crystallization Results of Experiments Performed with the Addition of Na_2CO_3, K_2CO_3 and NaCl Salts to the Reactant Systems

In this part of the experiments alkali carbonates and chlorides were used for the syntheses of clinoptilolite. Considering alkali carbonates and chlorides are naturally more abundant than alkali hydroxides, usage of carbonates and chlorides seems to be worthwhile for the synthesis of such a naturally abundant mineral.

Benchmark composition, $2.1Na_2O$: $10SiO_2$: Al_2O_3: $110.1H_2O$, was prepared by using Na_2CO_3 and NaCl salts besides NaOH. Molar batch composition 1.05 Na_2O: 1.05 K_2O: 10 SiO_2 : Al_2O_3: $110.1H_2O$ was also prepared by using Na_2CO_3, K_2CO_3 salts besides NaOH and KOH to investigate the effect of cation type and anion type together. Syntheses were performed at 140^oC with the addition of seed crystals at autogenous pressure. The amount of seed added was 10wt% of dry material in batch.

To prepare synthesis gel with a composition $2.1Na_2O$: $10SiO_2$: Al_2O_3: $110.1H_2O$: 0.7 (CO_2, Cl_2), 1.4 moles of Na_2O was provided from NaOH while 0.7 moles Na_2O from Na_2CO_3 or NaCl. To prepare gel with a composition 1.05 Na_2O: 1.05 K_2O : 10 SiO_2 : Al_2O_3: $110.1H_2O$:0.7 CO_2 , 0.7 moles Na_2O was provided from sodium hydroxide while 0.35 moles Na_2O from sodium carbonate and 0.7 moles K_2O was provided from potassium hydroxide while 0.35 moles K_2O from potassium carbonate.

Table 4.10, Table 4.11 and Table 4.12 shows crystallization results of experiments performed with Na_2CO_3, NaCl and Na_2CO_3, K_2CO_3 mixture. From the data it is clear that single phase and highly crystalline clinoptilolite was synthesized from both chloride and carbonate including systems. High clinoptilolite fractions, $(\%\text{yield})_{sfb}$ and $(\%\text{conversion})_{sfb}$ were achieved for each.

Table 4.10 Crystallization of Clinoptilolite from a Molar Batch Composition of $2.1Na_2O : 10SiO_2 : Al_2O_3 : 110.1H_2O : 0.7\ CO_2$ at 140°C with seeding. (The amount of seed added is 10 wt% of dry material in batch, % maximum yield for seed free batch = 31.92 %)

Batch Code	Sample code	Time (h)	Weight of Batch (W_b) (g)	Weight of Seed (W_s) (g)	Weight of Product (W_p) (g)	% Yield of product (%Yield)	Crystalline Phase(s)	Clino. Fraction in the Product (x_c)	Weight of Clino. in the Product (W_c) (g)	% Yield of clino. $(\%Yield)_{sfb}$	$(\%Conversion)_{sfb}$
BC 6-1	OG 79	45	7.65	0.25	2.46	32.2	Clinoptilolite	0.06	0.15	0.1	0
	OG 80	75	7.32	0.24	2.40	32.8	Clinoptilolite	0.10	0.24	1.4	4
	OG 81	139	35.56	1.16	11.15	31.4	Clinoptilolite	0.18	2.01	3.8	12
	OG 82	172	6.57	0.22	2.15	32.7	Clinoptilolite	0.23	0.49	5.6	18
	OG 83	262	6.95	0.23	2.03	29.2	Clinoptilolite	0.99	2.01	27.6	86
	OG84	309	32.90	1.07	10.54	32.0	Clinoptilolite	0.91	9.59	27.8	87
	OG 85	404	32.85	1.07	10.55	32.1	Clinoptilolite	0.99	10.44	30.5	96

Table 4.11 Crystallization of Clinoptilolite from a Molar Batch Composition 1.05 Na_2O: 1.05 K_2O : 10 SiO_2 : Al_2O_3: 110.1H_2O: 0.7 CO_2 at 140°C with Seeding. (The amount of seed added is 10 wt% of dry material in batch, % maximum yield for seed free batch = 30.67 %)

Batch Code	Sample code	Time (h)	Weight of Batch (W_b) (g)	Weight of Seed (W_s) (g)	Weight of Product (W_p) (g)	% Yield of product (%Yield)	Crystalline Phase(s)	Clino. Fraction in the Product (x_c)	Weight of Clino. in the Product (W_c) (g)	% Yield of clino. $(\%Yield)_{sfb}$	$(\%Conversion)_{sfb}$
BC7-1	OG 86	74	8.02	0.21	2.58	32.2	Clinoptilolite	0.10	0.26	1.8	6
	OG 99	100	33.43	1.18	10.24	30.6	Clinoptilolite	0.10	1.02	1.0	3
	OG87	187	7.63	0.27	2.42	31.7	Clinoptilolite	0.80	1.94	23.9	78
	OG 100	188	31.90	1.13	10.07	31.6	Clinoptilolite	0.86	8.66	25.6	83
	OG 88	259	7.74	0.27	2.48	32.0	Clinoptilolite	0.93	2.31	28.4	93
	OG 101	260	31.40	1.11	9.71	30.9	Clinoptilolite	0.85	8.25	24.7	81

4.12 Crystallization of Clinoptilolite from a Molar Batch Composition of $2.1\ Na_2O : 10SiO_2 : Al_2O_3 : 110.1H_2O : 0.7\ Cl_2$ at 140°C with Seeding. (The amount of seed added is 10 wt% of dry material in batch, % maximum yield for seed free batch = 32.39 %)

Batch Code	Sample code	Time (h)	Weight of Batch (W_b) (g)	Weight of Seed (W_s) (g)	Weight of Product (W_p) (g)	% Yield of product (%Yield)	Crystalline Phase(s)	Clino. Fraction in the Product (x_c)	Weight of Clino. in the Product (W_c) (g)	% Yield of clino. $(\%Yield)_{sfb}$	$(\%Conversion)_{sfb}$
BC 9-1	OG 102	48	8.15	0.28	2.67	32.8	Clinoptilolite	0.04	0.11	-0.6	-2
	OG 103	70	7.77	0.27	2.50	32.2	Clinoptilolite	0.07	0.18	0.3	1
	OG 104	140	8.05	0.28	2.53	31.4	Clinoptilolite	0.04	0.10	-0.8	-2
	OG 105	336	7.97	0.28	2.70	33.9	Clinoptilolite	0.47	1.27	14.2	44
	OG 106	474	8.20	0.29	2.39	29.1	Clinoptilolite	0.98	2.34	27.0	83

Figure 4.8 gives sample XRD pattern of clinoptilolite (OG 84) synthesized from Na_2CO_3 including systems. XRD patterns of products synthesized from NaCl and Na_2CO_3,K_2CO_3 including systems is shown in Appendix D1.

Figure 4.9 (a) and (b) show the effect of anion type on clinoptilolite fraction in the solid product and conversion to clinoptilolite for Na including system. Nucleation period can be defined as time elapsed before crystals start to appear. Rate of conversion is the slope at 50% of maximum conversion. As can be seen on Figure 4.9, anion type has significant effect on both rate of conversion and nucleation period. Rate of conversion to clinoptilolite for hydroxyl including system is approximately 10 times faster than chloride including system and 3 times faster than carbonate including system. Nucleation period is the shortest for hydroxyl including system and longest for chloride including system. One possible explanation of this is the alkalinity decrease with the use of carbonates and chloride. Comparing alkalinities of Na_2CO_3, NaCl and NaOH aqueous solutions can give an idea about their behaviour in the synthesis mixture. NaOH is a strong base then its aqueous solution is highly alkaline, Na_2CO_3 is a salt of a strong base (NaOH) and weak acid (H_2CO_3) then aqueous solution of Na_2CO_3 is also alkaline but not as much as NaOH and NaCl is a salt of a strong base (NaOH) and a strong acid (HCl) then aqueous solution of NaCl is neutral. Within NaOH, Na_2CO_3 and NaCl highest alkalinity in the reaction mixture can be achieved by NaOH and lowest by NaCl addition.

By the additon of alkali salts besides alkali hydroxyls alkalinity of the system decreseases as compared to when all cations are supplied in the form of hydroxyls.

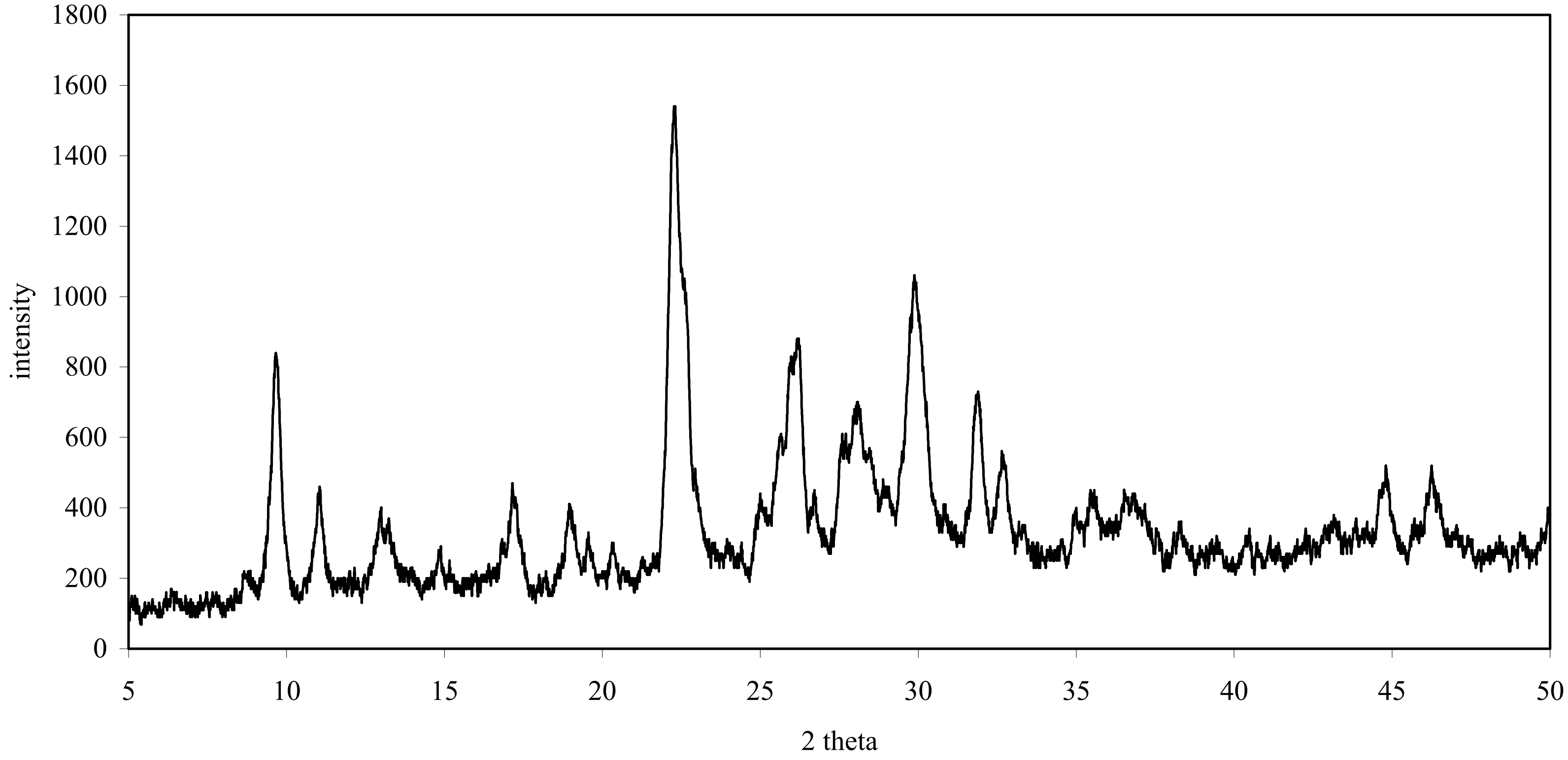
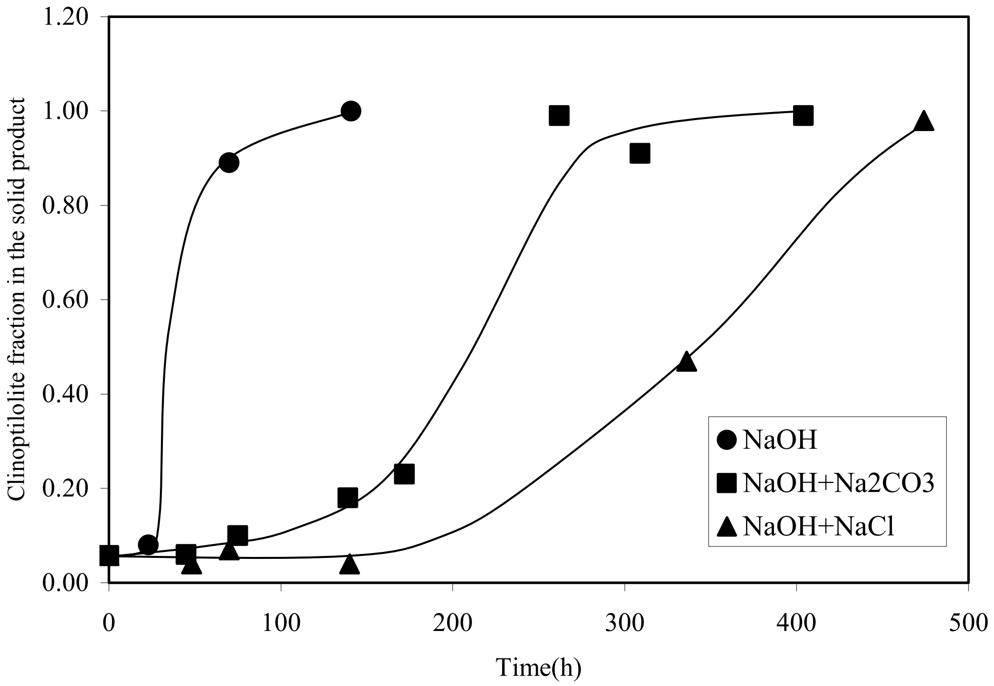
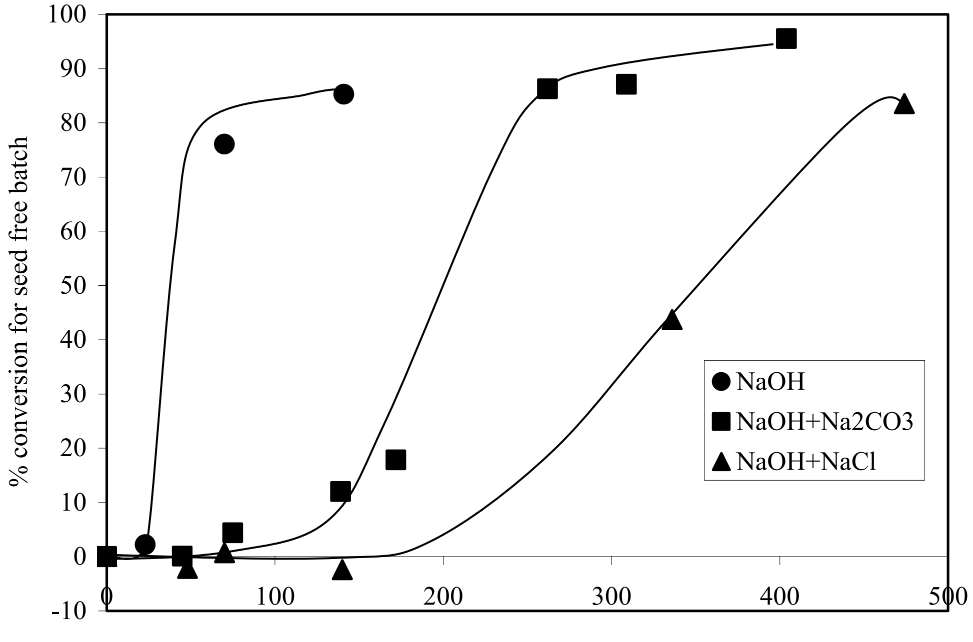


Figure 4.8 XRD pattern of clinoptilolite (OG 84) synthesized from $2.1Na_2O: Al_2O_3 : 10SiO_2: 110.1H_2O: 0.7\ CO_2$ at 140^oC for 309 h with the addition of 10 wt% of seed crystals



(a)



(b)

Figure 4.9Effect of anion type on (a) clinoptilolite fraction in the solid product (b)% conversion for seed free batch for the batch composition 2.1 Na_2O: Al_2O_3: $10SiO_2$:110.1 H_2O at 140°C with 10 wt% seed crystals

Consequently single phase and highly crystalline clinoptilolite was synthesized by using sodium and/or potassium carbonate, sodium chloride as well as by using sodium hydroxide. Previously Hawkins et al. [14] synthesized clinoptilolite by using carbonates of Na and K and volcanic glass at 1 kbar pressure. Synthesis of clinoptilolite by using alkali salts at autogenous pressure was not reported previously but achieved for the first time in this study.

4.5 Effect of Alkalinity of the Reactant Mixture on Clinoptilolite Crystallization

In this part of the experiments, alkalinity of reactant gel with a molar batch composition of 1.05 Na_2O: 1.05 K_2O: Al_2O_3: 10SiO_2: 110.1 H_2O (BC 5-1) was modified by increasing and decreasing Na_2O and K_2O contents by 20% keeping all other variables constant. In this way it was intended to investigate the effect of alkalinity change on the phase purity and rate of clinoptilolite crystallization.

Table 4.13 and Table 4.14 shows crystallization results of experiments performed for a molar batch composition of 0.84 Na_2O: 0.84 K_2O: Al_2O_3: 10SiO_2: 110.1 H_2O and 1.26 Na_2O: 1.26 K_2O: Al_2O_3: 10SiO_2: 110.1 H_2O at 140^{o}C with seeding. The amount of seed added was 10 wt % of dry material in batch.

Figure 4.10 (a) and (b) shows effect of alkalinity decrease on clinoptilolite fraction in the solid product (x_c) and %conversion for seed free batch ($(\%conversion)_{sfb}$) comparatively with carbonate including system. Such a comparison with carbonate including system was given since alkalinity decrease is also provided by the addition of alkali salts.

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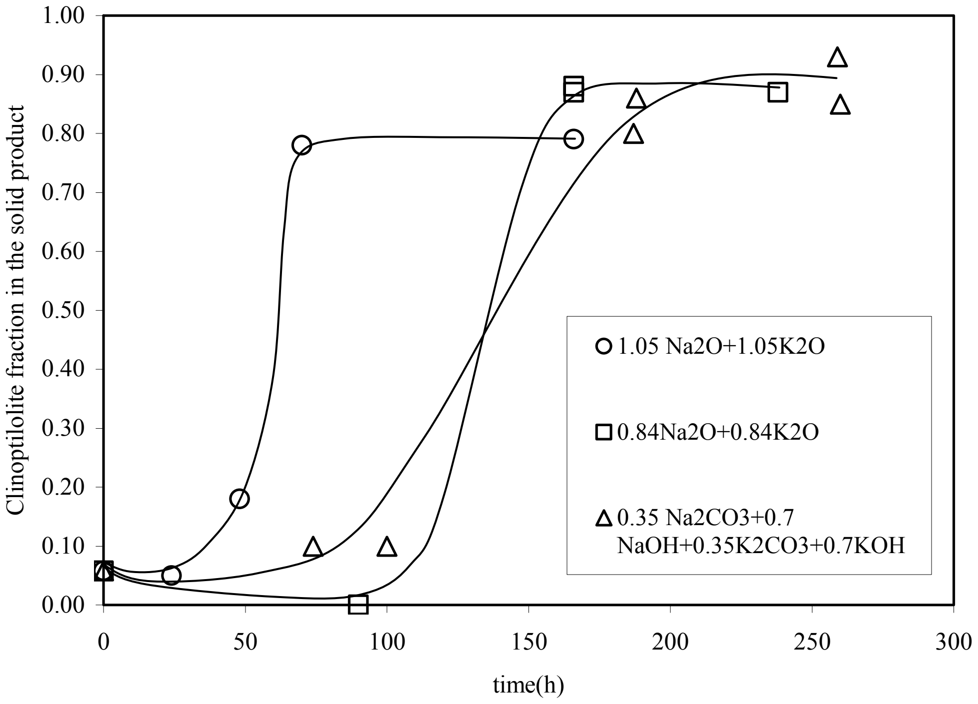
Table 4.13 Crystallization of Clinoptilolite from a Molar Batch Composition of $0.84\ K_2O\ 10SiO_2: Al_2O_3: 110.1H_2O$ at 140°C with seeding. (The amount of seed added is 10 wt % of dry material in batch, % maximum yield for seed free batch = 33.00)

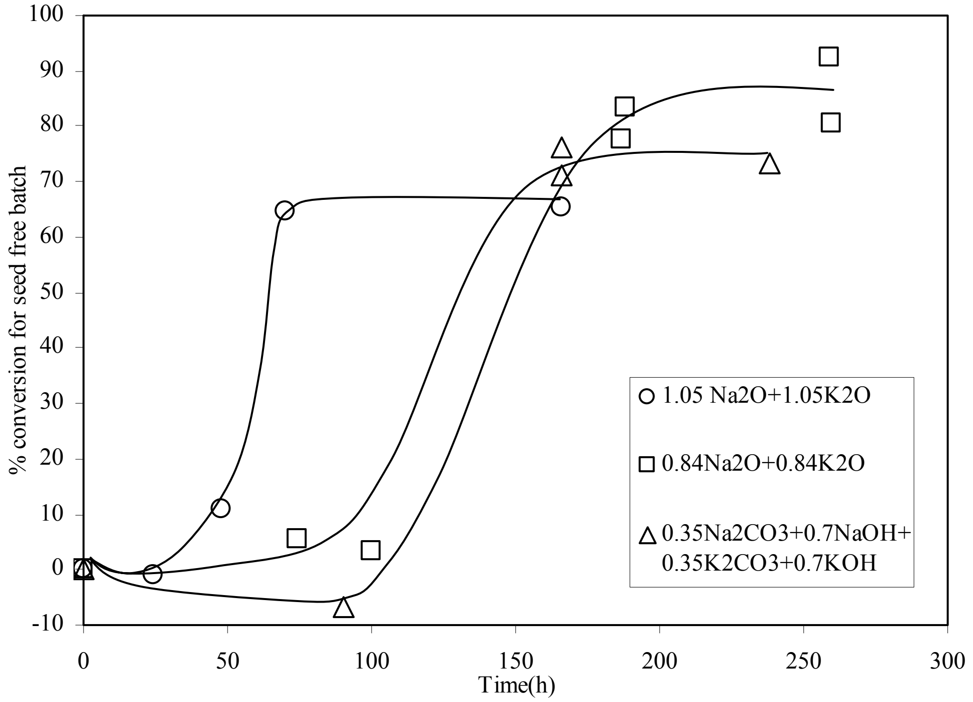
Batch Code	Sample code	Time (h)	Weight of Batch (W_b) (g)	Weight of Seed (W_s) (g)	Weight of Product (W_p) (g)	% Yield of product (%Yield)	Crystalline Phase(s)	Clino. Fraction in the Product (x_c)	Weight of Clino. in the Product (W_c) (g)	% Yield of clino. $(\%Yield)_{sfb}$	$(\%Conversion)_{sfb}$
BC 20-1	OG 150	90	7.56	0.28	2.13	28.2	---	0.00	0.00	-3.8	-12
	OG 151	166	7.68	0.29	2.20	28.6	Clinoptilolite	0.88	1.94	23.6	71
	OG 156	166	7.58	0.28	2.33	30.7	Clinoptilolite	0.87	2.03	25.2	76
	OG 157	238	7.80	0.29	2.32	29.7	Clinoptilolite	0.87	2.02	24.2	73

Table 4.14 Crystallization results of experiments performed from a Molar Batch Composition of $1.26\ K_2O\ 10SiO_2: Al_2O_3: 110.1H_2O$ at 140°C with seeding. (The amount of seed added is 10 wt % of dry material in batch, % maximum yield for seed free batch = 30.39)

Batch Code	Sample code	Time (h)	Weight of Batch (W_b) (g)	Weight of Seed (W_s) (g)	Weight of Product (W_p) (g)	% Yield of product (%Yield)	Crystalline Phase(s)
BC 19-1	OG 158	94	7.48	0.28	2.07	27.7	Sanidine Clinoptilolite
	OG 148	166	34.89	1.30	8.93	25.6	Sanidine Clinoptilolite Unidentified phase
	OG 149	196	30.22	1.13	7.75	25.6	Sanidine Clinoptilolite
	OG 159	334	7.06	0.26	1.69	23.9	Sanidine



(a)



(b)

Figure 4.10 Effect of alkalinity of the reactant mixture on (a) % clinoptilolite in the solid product (b) % conversion for seed free batch for the batch compositions $1.05Na_2O:1.05K_2O:Al_2O_3:10\ SiO_2:110.1H_2O$ and $0.84Na_2O: 0.84K_2O:Al_2O_3:10\ SiO_2:110.1H_2O$ at 140°C with 10wt% seed crystals

As can be seen on Table 4.13 single phase and highly crystalline clinoptilolite was synthesized from a molar batch composition of 0.84 Na_2O: 0.84 K_2O Al_2O_3: 10SiO_2: 110.1 H_2O. Consequently reduction of alkali content by 20% of the benchmark composition still resulted the formation of single phase clinoptilolite. Considering addition of alkali salts decreases the alkalinity of the reactant mixture, similar conclusion was also given for carbonate and chloride including systems too (see part 4.4). On the other hand, for 1.26 Na_2O: 1.26 K_2O: Al_2O_3: 10SiO_2: 110.1 H_2O clinoptilolite was not synthesized either single or major phase. Alkalinity increase of reactant mixture results formation of sanidine.

As can be seen on Figure 4.10 (a) and (b), by the decrease in alkalinity, nucleation period increases. Also slower completition of crystallization was observed with reduced alkalinity. These results are similar to the results obtained when alkali salts were used.

To sum up clinoptilolite was synthesized as a single phase by decreasing alkali content of our benchmark composition by 20%. Nucleation period was increased by the decrease of alkali content.

4.6 Crystallization Results of Experiments Performed at Different Temperatures

Limits of clinoptilolite crystallization in terms of temperature were investigated by performing syntheses at temperatures 100°C, 120°C, 140°C, 160°C and 175°C. Syntheses were carried out from synthesis gels with composition of 2.1Na_2O: 10SiO_2: Al_2O_3: 110.1 H_2O and 1.05 Na_2O: 1.05 K_2O: 10 SiO_2: Al_2O_3: 110.1H_2O with seeding at autogenous pressure. The amount of seed added is 10 wt % or 28wt% of seed crystals of dry material in batch.

Crystallization results of experiments performed at 100°C, 120°C, 160°C and 175°C were tabulated at Table 4.15, Table 4.16, Table 4.17 and Table 4.18,

Table 4.15 Crystallization of Clinoptilolite from a Molar Batch Composition of $2.1Na_2O: 10SiO_2: Al_2O_3: 104.8\ H_2O$ at 100°C with seeding. (The amount of seed added is 28 wt% of dry material in batch, % maximum yield for seed free batch =33.40 %)

Batch Code	Sample code	Time (h)	Weight of Batch (W_b) (g)	Weight of Seed (W_s) (g)	Weight of Product (W_p) (g)	% Yield of product (%Yield)	Crystalline Phase(s)	Clino. Fraction in the Product (x_c)	Weight of Clino. in the Product (W_c) (g)	% Yield of clino. $(\%Yield)_{sfb}$	$(\%Conversion)_{sfb}$
BC 1	OG 36	167	7.04	0.70	2.62	37.2	Clinoptilolite	0.18	0.47	0.9	3
	OG 37	336	8.14	0.81	3.17	38.9	Clinoptilolite	0.18	0.57	1.3	4
	OG 38	432	6.98	0.70	2.75	39.4	Clinoptilolite	0.19	0.52	1.7	5
	OG 60	648	9.06	0.91	4.49	49.6	Clinoptilolite	0.59	2.65	24.9	75
	OG 40	1918	8.29	0.83	2.99	36.1	Clinoptilolite	0.92	2.75	29.1	87

Table 4.16 Crystallization of Clinoptilolite from a Molar Batch Composition 1.05 Na_2O: 1.05 K_2O : 10 SiO_2 : Al_2O_3: 110.1H_2O at 120°C with seeding. (The amount of seed added is 10 wt% of dry material in batch, % maximum yield for seed free batch = 33.41%)

Batch Code	Sample code	Time (h)	Weight of Batch (W_b) (g)	Weight of Seed (W_s) (g)	Weight of Product (W_p) (g)	% Yield of product (%Yield)	Crystalline Phase(s)	Clino. Fraction in the Product (x_c)	Weight of Clino. in the Product (W_c) (g)	% Yield of clino. $(\%Yield)_{sfb}$	$(\%Conversion)_{sfb}$
BC 5-1	OG 152	94	7.48	0.25	2.02	27.0	Clinoptilolite	0.25	0.51	5.0	15
	OG 153	166	7.30	0.24	2.05	28.1	Clinoptilolite	0.20	0.41	3.8	11
	OG 154	266	7.51	0.25	1.68	22.4	Clinoptilolite	0.44	0.74	8.1	24
	OG 155	578	7.09	0.24	1.92	27.1	Clinoptilolite	0.62	1.19	15.1	45

Table 4.17 Crystallization of Clinoptilolite from a Molar Batch Composition 1.05 Na_2O: 1.05 K_2O : 10 SiO_2 : Al_2O_3: 110.1H_2O at 160°C with seeding. (The amount of seed added is 10 wt % of dry material in batch, % maximum yield for seed free batch = 33.41%)

Batch Code	Sample code	Time (h)	Weight of Batch (W_b) (g)	Weight of Seed (W_s) (g)	Weight of Product (W_p) (g)	% Yield of product (%Yield)	Crystalline Phase(s)	Clino. Fraction in the Product (x_c)	Weight of Clino. in the Product (W_c) (g)	% Yield of clino. $(\%Yield)_{sfb}$	$(\%Conversion)_{sfb}$
BC 5-1	OG 161	22	6.66	0.22	1.22	18.3	Clinoptilolite	0.87	1.06	14.2	42
	OG 162	46	8.11	0.27	1.57	19.4	Clinoptilolite	0.89	1.4	15.6	47
	OG 163	72	6.92	0.23	1.79	25.8	Clinoptilolite Sanidine	---	---	---	---
	OG 164	164	7.49	0.25	1.92	25.6	Sanidine Clinoptilolite	---	---	---	---

Table 4.18 Crystallization Results of Experiments Performed From a Molar Batch Composition of $2.1Na_2O: 10SiO_2: Al_2O_3: 110.1 H_2O$ and $1.05 Na_2O: 1.05 K_2O : 10 SiO_2 : Al_2O_3: 110.1H_2O$ at 175°C with seeding.(The amount of seed added is 10 wt% of dry material in batch)

Batch Code	Sample code	Time (h)	Weight of Batch (W_b) (g)	Weight of Seed (W_s) (g)	Weight of Product (W_p) (g)	% Yield of product (%Yield)	Crystalline Phase(s)
BC 2-1	OG 111	42	31.31	0.96	9.06	28.9	Mordenite Clinoptilolite
	OG 112	115	33.32	1.02	9.18	27.5	Mordenite
	OG 113	163	31.37	0.96	8.88	28.3	Mordenite
BC 5-1	OG 118	45	30.94	1.01	9.99	32.3	Mordenite Clinoptilolite
	OG 119	117	31.29	1.02	9.46	30.2	Mordenite
	OG 120	165	29.70	0.96	9.57	32.2	Mordenite

respectively. XRD patterns of products synthesized at 120°C, 160°C and 175°C were given on Figures D.15, D.16 and D.17, recpectively. XRD pattern of clinoptilolite synthesized at 100°C (OG 40) and mordenite (OG 112) synthesized at 175°C was given on Figures D.3 and D.4 in Appendix D1 .

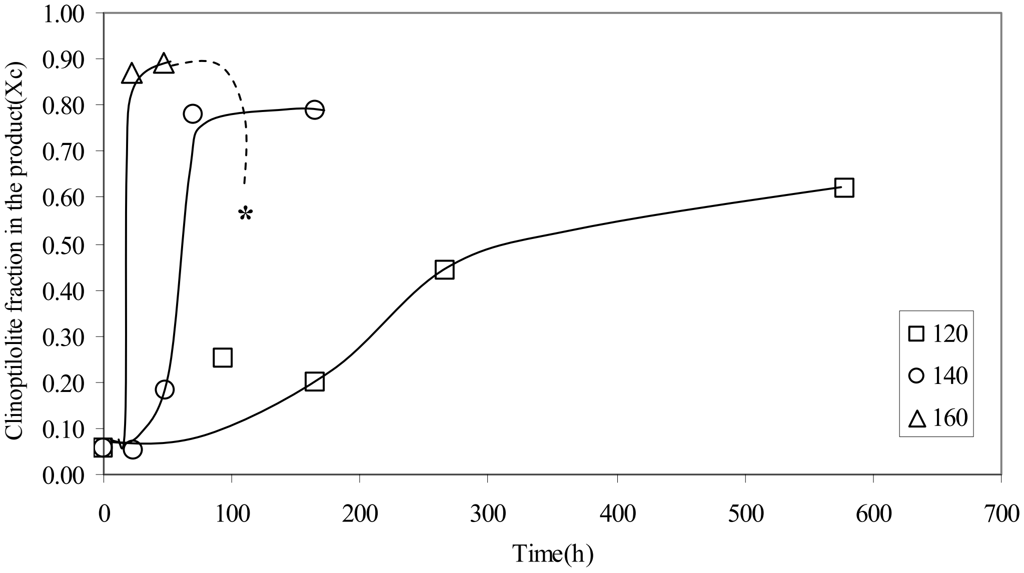
As can be seen from Table 4.15, Table 4.16 and Table 4.17 single phase clinoptilolite was synthesized at 100°C, 120°C and 160°C. At 160°C clinoptilolite first formed, by proceeding crystallization it converted into sanidine. At 175 °C single phase mordenite was formed with either Na or Na,K mixture (Table 4.18).

Clinoptilolite fraction in the solid product and % conversion for seed free batch is plotted versus time for 120°C, 140°C, 160°C for Na,K including system on Figure 4.11. It was observed that decrease of temperature decreases crystallization rate.

Synthesis of clinoptilolite at 100°C is worthwhile to mention because this temperature is the lowest one examined within the literature. This shows that clinoptilolite may be synthesized at lower temperatures similar to naturally achievable ones.

As can be seen on Table 4.18, in experiments performed with either Na or Na,K mixture at 175°C, at early stages of crystallization mordenite coexists with clinoptilolite that is probably coming from seed crystals. However at later stages of crystallization clinoptilolite was not observed such that product was single phase mordenite. This shows dissolution of seed crystals in the reactant mixture throughout the crystallization of a phase other than clinoptilolite.

Crystallization of mordenite at 175°C provided findings on literature. According to Hawkins et al. [14] within clinoptilolite and mordenite, clinoptilolite tends to form at lower temperatures and at high temperatures clinoptilolite is unstable with respect to mordenite.



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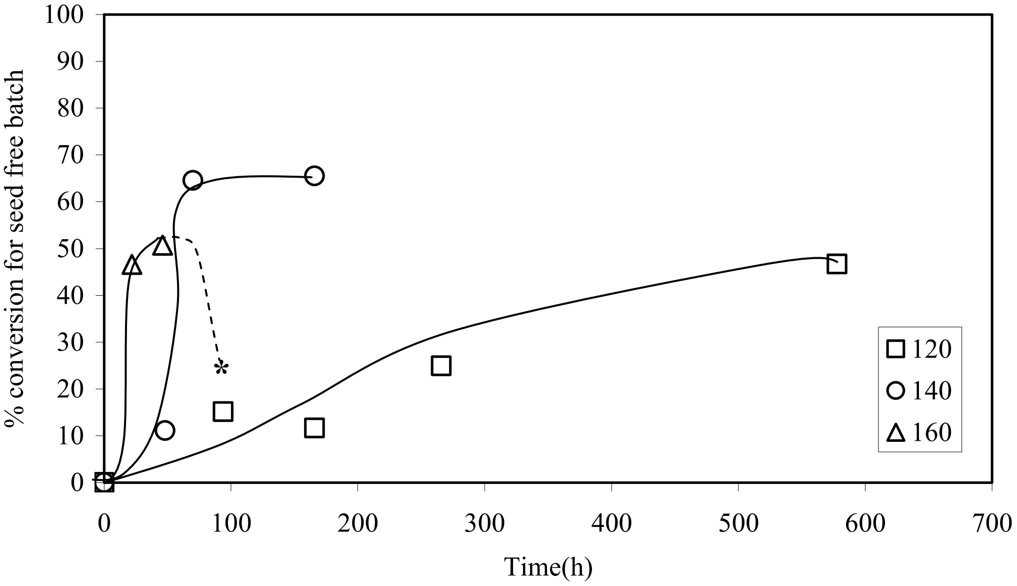

(b)

Figure 4.11 Effect of temperature on (a) clinoptilolite fraction in the solid product (b) % conversion for seed free batch for the batch composition 1.05Na_2O: 1. 05 K_2O : 10SiO_2 : Al_2O_3: 110.1H_2O with 10 wt% seed crystals

(*Clinoptilolite decomposes partly to form sanidine)

Clinoptilolite was also tried to be synthesized from molar batch composition $2.1K_2O: Al_2O_3: 10SiO_2: 110.1\ H_2O$ either at 175 or 195°C. For the two cases synthesized crystalline products were Linde L and gismondine.

Consequently single phase clinoptilolite synthesis was achieved at temperatures 100°C, 120 °C,140°C and 160°C. Crystallization of clinoptilolite at 100°C was not reported previously but achieved in this study for the first time. From the same batch composition, mordenite crystallized at 175°C as a single phase and clinoptilolite seed crystals dissolved completely.

4.7 Crystallization Results of Experiments Performed at Different SiO_2/Al_2O_3 Ratios

In this part of experiments, limits of clinoptilolite crystallization were investigated in terms of SiO_2/Al_2O_3 ratio. In all experiments mentioned in previous parts SiO_2/Al_2O_3 ratio was equal to 10. In this part syntheses were performed from molar batch composition, $2.1Na_2O: x\ SiO_2: Al_2O_3: 110.1\ H_2O$ where x= 4, 6, 8, 9, 11, 12. at 140°C with seeding at autogenous pressure. The amount of seed added is 10 wt % of dry material in batch.

Figure 4.12 shows XRD patterns of products synthesized for different SiO_2/Al_2O_3 ratios at 140°C with the addition of 10 wt% of seed crystals for 144 h. X-ray powder diffraction data used for the identification of phases other than clinoptilolite are given in Appendix F2.

Synthesis conditions and crystallization results of experiments performed at different SiO_2/Al_2O_3 were tabulated at Table 4.19. Figure 4.13 (a) and (b) shows effect of SiO_2/Al_2O_3 ratio on clinoptilolite fraction in the solid product and % conversion for seed free batch.

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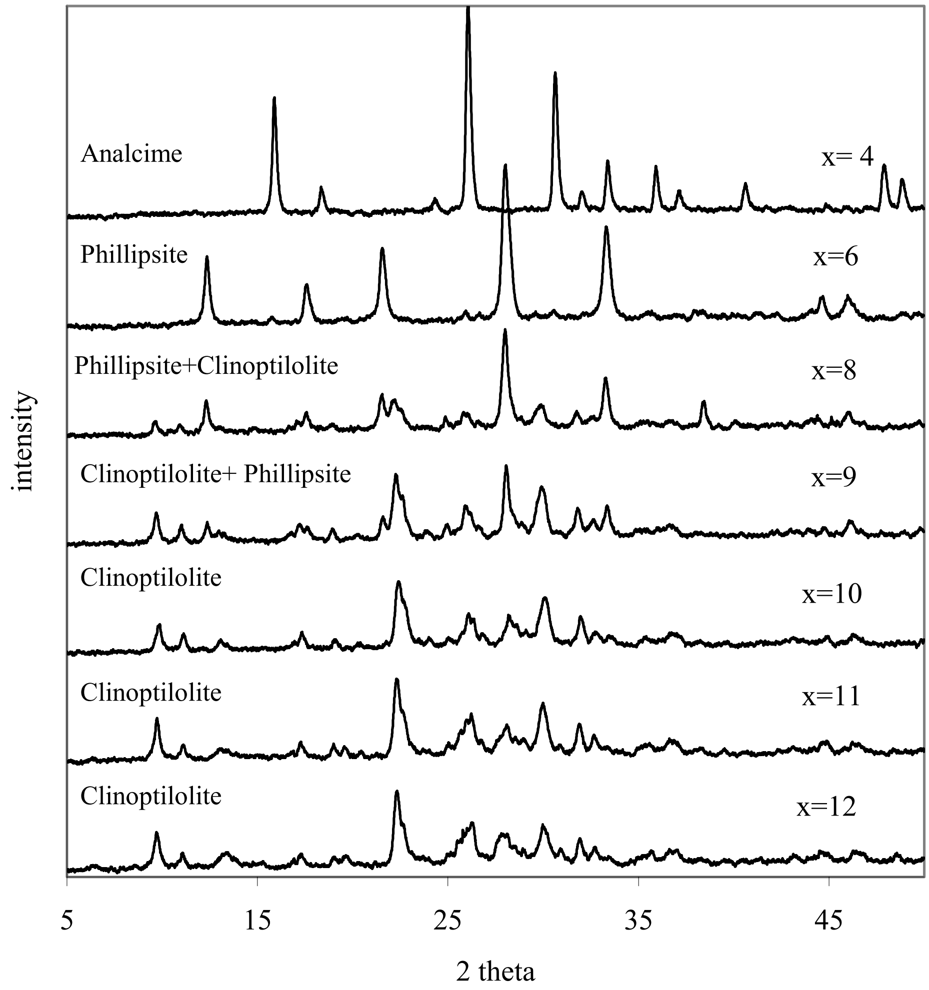
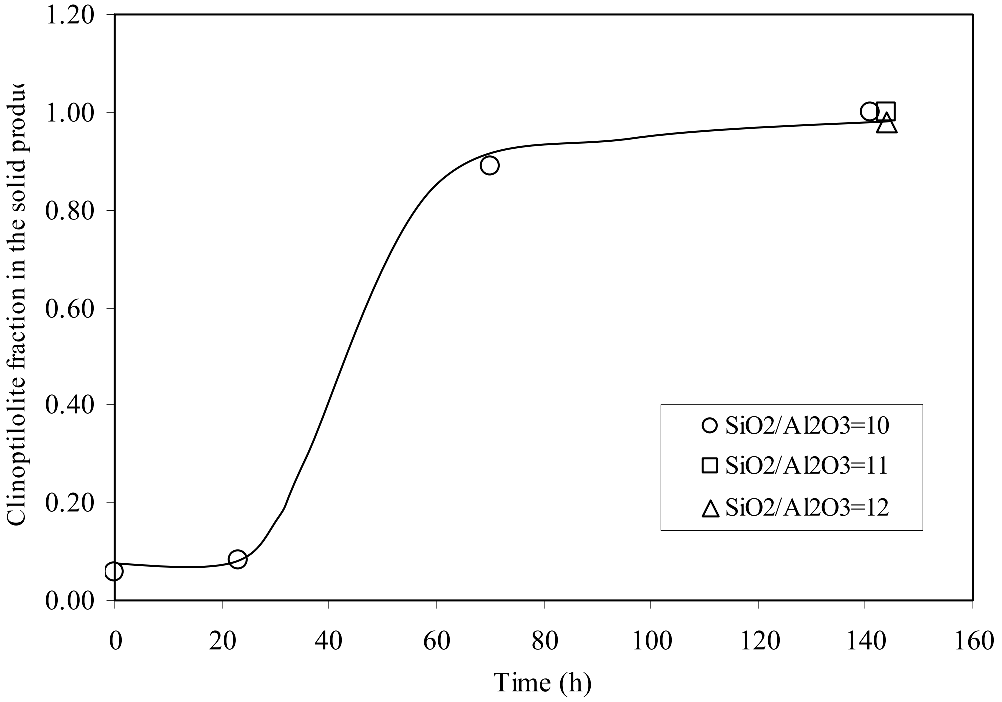


Figure 4.12 XRD patterns of products synthesized from molar batch composition of $2.1Na_2O : x\ SiO_2 : Al_2O_3 : 110.1H_2O$ where x is equal to 4, 6, 8, 9, 10, 11, 12 after 144 h of hydrothermal treatment with seeding. The amount of seed added is 10 wt% of dry material in batch.

Table 4.19 Crystallization Results of Experiments for Molar Batch Composition $2.1Na_2O$: x SiO_2 : Al_2O_3: $110.1H_2O$ where x=12, 11, 10, 9, 8, 6 at 140^{o}C with seeding. (The amount of seed added is 10wt% of dry material in batch], (% Maximum yield for seed free batch 17-1 =31.35 %, % Maximum yield for seed free batch 13-1 = 32.00 %]

Batch Code	Sample code	SiO_2/Al_2O_3	Time (h)	Weight of Batch (W_b) (g)	Weight of Seed (W_s) (g)	Weight of Product (W_p) (g)	% Yield of product (%Yield)	Crystalline Phase(s)	Clino. Fraction in the Product (x_c)	Weight of Clino. in the Product (W_c) (g)	% Yield of clino. $(\%Yield)_{sfb}$	$(\%Conversion)_{sfb}$
BC 17-1	OG 136	12	144	34.68	1.26	10.79	31.1	Clinoptilolite	0.98	10.57	29.0	93
BC 13-1	OG 132	11		34.08	1.19	10.49	30.8	Clinoptilolite	1.00	10.49	29.4	92
BC 2-1	OG 70	10		8.28	0.26	2.40	29.0	Clinoptilolite	1.00	2.40	27.7	85
BC 12-1	OG 131	9		34.63	1.09	9.85	28.4	Clinoptilolite Phillipsite	---	---	---	---
BC 14-1	OG 147	8		36.18	1.08	9.1	25.1	Phillipsite Clinoptilolite	---	---	---	---
BC 15-1	OG 134	6		7.22	0.19	1.41	19.5	Phillipsite	---	---	---	---
BC 16-1	OG 135	4		7.27	0.16	1.25	17.2	Analcime	---	---	---	---



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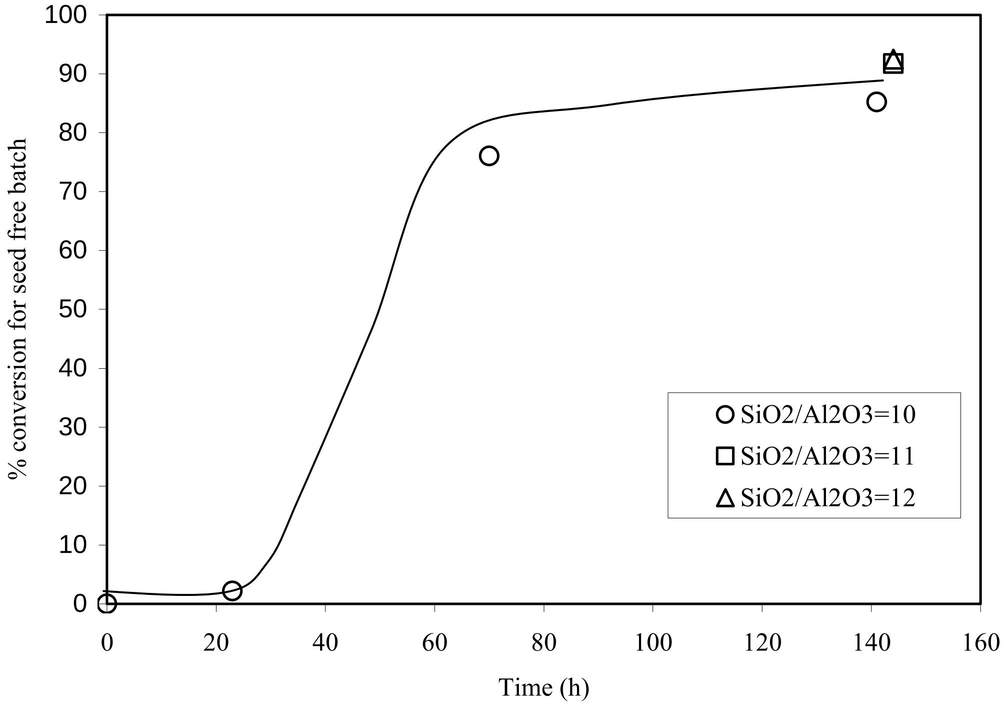


(b)

Figure 4.13 Effect of SiO_2/Al_2O_3 ratio on (a) clinoptilolite fraction in the solid product (b) % conversion for seed free batch for the batch composition $2.1Na_2O$: x SiO_2 : Al_2O_3: $110.1H_2O$ where x=10, 11 and 12 at 140°C with 10wt% seed crystals

Single phase clinoptilolite was synthesized if the SiO_2/Al_2O_3 ratio of the reactant mixture is in between 10 and 12 as can be seen on Figure 4.12. According to Table 4.19 synthesized clinoptilolites are all highly crystalline, and (%conversion)$_{sfb}$ values are high and similar to each other for different SiO_2/Al_2O_3 ratios

At lower values of this ratio, first phillipsite appears as a coexisting phase with clinoptilolite then becomes single phase and at still lower values of SiO_2/Al_2O_3 ratios and analcime forms as a single phase.

As can be seen on Figure 4.13, data for SiO_2/Al_2O_3 ratios of 11 and 12 were also shown on the curve for SiO_2/Al_2O_3 ratios of 10 since ultimate clinoptilolite fraction and (% conversion)$_{sfb}$ are similar.

Similar with our findings, Tanaka et al.[20] synthesized clinoptilolite with trace amount of an impurity from a molar batch composition of 1.26 Na_2O: 1.26 K_2O: Al_2O_3: 12SiO_2: 105 H_2O in which SiO_2/Al_2O_3=12. Satokawa and Itabashi [16] synthesized clinoptilolite from a molar batch composition of 0.825 Na_2O: 0.825 K_2O: Al_2O_3: 11SiO_2: 275 H_2O in which SiO_2/Al_2O_3=11.

Our benchmark composition with SiO_2/Al_2O_3 ratio of 10 is probably at the lower bound of SiO_2/Al_2O_3 range that clinoptilolite can be synthesized because lowering this ratio to 9 results formation of phillipsite as a coexisting phase. For this reason any experimental error that causes the decrease of Si/Al ratio may result the formation of phillipsite. As can be seen on Table G.1 in Appendix G showing crystallization conditions of products synthesized in this study, for OG 2, OG 3, OG 4, OG 5, OG 8, OG 9 phillipsite was coexisting with clinoptilolite in the products. Although crystallization composition and conditions were suitable for clinoptilolite crystallization phillipsite impurity is probably formed due to experimental errors decreasing SiO_2/Al_2O_3 ratio. Consequently great care is required to prepare the synthesis mixture.

On Figure 4.12, no clinoptilolite peaks were observed when SiO_2/Al_2O_3 ratio is 6 and 4, phillipsite and analcime was obtained as a single phase although 10wt% of seed crystal was added to the reaction systems. This is also an evidence for seed dissolution in the reactant mixture completely throuhout the crystallization if clinoptilolite is not formed from that batch composition.

Consequently single phase clinoptilolite was synthesized when SiO_2/Al_2O_3 ratio is in between 10 and 12. Moreover an evidence for dissolution of seed crystals in the reactant mixture was obtained.

4.8 Crystallization Results of Experiments Performed by Using Thermally Decomposed Products of Mineral Clinoptilolite

In this part of experiments clinoptilolite synthesis was tried to be performed by using thermally decomposed products of mineral clinoptilolite as raw materials. By the usage of decomposition products of clinoptilolite it was intended to propose a new approach to the synthesis of clinoptilolite and to provide a comparison for natural raw materials and standard chemical reagents.

Decomposition results of mineral clinoptilolite and crystallization results of experiments performed by using thermally decomposed products will be given in the following sections separately (4.8.1 and 4.8.2).

4.8.1 Decomposition Results of Clinoptilolite Mineral

Clinoptilolite mineral from a deposit in Gördes, located in Western Anatolia was used for the preparation of partly or completely decomposed products. XRD pattern, SEM image and chemical analyses results of Gördes clinoptilolite (CLIG2-1) are given in Appendix B3. Decomposition of mineral clinoptilolite was performed thermally to collapse the structure either partly or completely. Clinoptilolite fraction in the decomposed products were determined by the calibration plot given in Figure 3.1. For thermal decomposition, clinoptilolite samples were treated at different temperatures. XRD patterns of decomposition products at temperatures 500 to 900^{o}C were given in Figure 4.14.

As it is seen on Figure 4.14, crystallinity of mineral clinoptilolite was reduced by increasing temperature. Up to 800^{o}C clinoptilolite was not decomposed completely. At 900^{o}C clinoptilolite pattern was completely destroyed. Quartz appears in the products with the increase of temperature which is probably a minor impurity in the original clinoptilolite sample.

As a result of thermal decomposition experiments, completely decomposed clinoptilolite at 900^{o}C (CLIG2-900) and partly decomposed clinoptilolite at 785^{o}C (CLIG2-785) were obtained to be used as raw materials for the syntheses. Clinoptilolite fraction in partly decomposed product was found as 0.11 by the calibration plot given in Figure 3.1.

4.8.2 Crystallization Results of Syntheses Performed with Decomposed Products

Decomposed product was an amorphous material with Gördes clinoptilolite composition. Chemical composition of Gördes clinoptilolite was obtained from an earlier work [24] (see Appendix E 1) and converted to oxide formula as 0.176 Na_2O: 0.405 K_2O: Al_2O_3: 10.1SiO_2: 7.11H_2O+others (MgO, Fe_2O_3, CaO, MnO, TiO_2). It was assumed that composition of clinoptilolite remains constant except water content after thermal decomposition

Molar batch composition 1.05Na_2O: 1.05K_2O: 10SiO_2: Al_2O_3: 110.1H_2O which yields pure clinoptilolite (Table 4.7) was prepared by using partly (CLIG2-785) or completely decomposed (CLIG2-900) products of Gördes

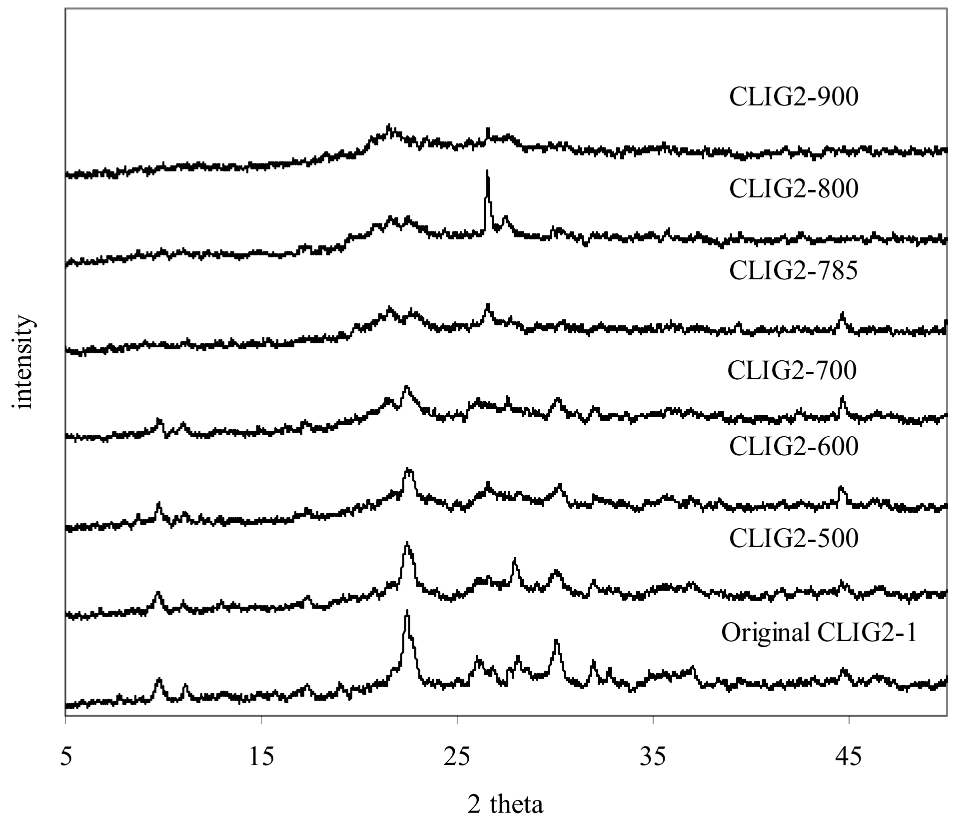


Figure 4.14 XRD patterns of decomposed Gördes clinoptilolite (CLIG2-1) at temperatures 500, 600, 700, 785, 800, 900 with original CLIG2-1

clinoptilolite. By adding required amounts of Na, K and water to decomposed clinoptilolite, synthesis mixture with desired composition was prepared. Syntheses were performed at 140°C. 10 wt% of seed crystals were added to the reaction system for syntheses performed with completely decomposed product. No extra seed crystals were added to the reaction system for syntheses performed with partly decomposed product. Required amounts of reactants were calculated as it is shown in Appendix A2.

Crystallization results of experiments were given on Table 4.20 for completely or partly decomposed products. A sodium potassium aluminosilicate phase sanidine was obtained as a major phase with minor amount of clinoptilolite and quartz from either partly or completely decomposed products for the same composition and conditions that clinoptilolite was crystallized with standard chemicals. This result was probably observed because when decomposed products were used, a gel formation was not observed and a homogenous synthesis mixture was not obtained although it was stirred for 24 h before hydrothermal treatment.

By performing clinoptilolite synthesis with natural raw materials beside standard chemicals, a comparison was given within natural raw materials and chemicals. It can be concluded that standard chemical reagents should be used for single phase clinoptilolite crystallization because they are more soluble and ready to react.

Table 4.20 Crystallization Results of Experiments Performed by Using Completely and Partly Decomposed Products of Clinoptilolite for Molar Batch Composition $1.05Na_2O$: $1.05K_2O$: $10SiO_2$: Al_2O_3: $110.1H_2O$ at 140°C with seeding. (The amount of seed added is 10 wt % of dry material in batch, % maximum yield for seed free batch =32.41 %)

Batch Code	Raw Material	Sample code	Time (h)	Weight of Batch (W_b) (g)	Weight of Seed (W_s) (g)	Weight of Product (W_p) (g)	Crystalline Phase(s)
BC5-1	Completely Decomposed Products of Clinoptilolite	OG 94	96	8.08	0.25	2.48	Sanidine Clinoptilolite Quartz
		OG 95	124	7.99	0.25	2.95	Sanidine Clinoptilolite Quartz
		OG 97	214	8.77	0.27	2.44	Sanidine Clinoptilolite Quartz
BC5-1	Partly Decomposed Products of Clinoptilolite	OG 114	45	7.03	0.54	2.49	Amorphous Sanidine Clinoptilolite
		OG 116	141	6.98	0.54	2.19	Sanidine Clinoptilolite
		OG 117	264	7.24	0.56	2.35	Sanidine Clinoptilolite

4.9 X-Ray Powder Diffraction Data For Synthetic Clinoptilolite

Within previous studies on clinoptilolite synthesis, only Chi and Sand's [1] work includes X-ray powder diffraction data for synthetic Na and K clinoptilolite. Then an additional contribution in this field in comparison with Chi and Sand's work will be worthwhile.

Table 4.21 shows d-spacing and intensity data of OG 70, a Na-clinoptilolite (See Table 4.2) and OG 100, a (Na,K)-clinoptilolite (See Table 4.11) synthesized in this study with the addition of 10 wt% of seed crystals. Table 4.21 also includes XRD data for synthetic Na and K clinoptilolite of Chi and Sand [1] for comparison. XRD results of OG 70 and OG 100 were obtained at the analysis conditions of; speed = 0.02 and time constant= 2. Determination of X-ray powder diffraction data for OG 70 and OG 100 was performed by using the computer program JADE and details of this determination was mentioned in Appendix B3.

Figure 4.15 shows X-ray diffraction data for OG 70, OG 100, Na and K clinoptilolite of Chi and Sand and natural clinoptilolite from Agoura, California of Wise, Nokleberg and Kokinos [5] in the form of bar charts.

Comparing our data with the data reported by Chi and Sand, as can be seen on Table 4.21 for Na and Na,K clinoptilolite, d-spacing values are nearly the same. In terms of intensity, for some of the peaks for both Na and Na,K clinoptilolite slight differences was observed.

On Table 4.21, it was observed that for Na clinoptilolite some of d-spacing values are slightly greater than (Na,K)-clinoptilolite. This is similar in the study of Chi and Sand, within Na and K clinoptilolite, d-spacings for Na clinoptilolite are greater than K clinoptilolite mostly.

As can be seen on Figure 4.15 XRD patterns of OG 100 and OG 70 are similar with XRD patterns of Na and K clinoptilolite of Chi and Sand and natural clinoptilolite reported by Wise, Nokleberg and Kokinos [5].

Consequently in this part X-ray powder diffraction data for Na and Na,K clinoptilolite synthesized in this study were given. XRD data has been reported for the first time for a synthetic (Na,K)-clinoptilolite in this study .

4.10 SEM Results

Morphology of the synthesized clinoptilolites was investigated by scanning electron microscope (SEM). Micrographs of sample products synthesized at different batch compositions were demonstrated in Figure 4.15. SEM photomicrographs for further products are given in Appendix D2.

Figure 4.16 (a) belongs product OG 69 (Batch Code 2-1, part 3) synthesized from a molar batch composition of $2.1Na_2O$: $10SiO_2$: Al_2O_3: $110.1H_2O$ at 140^oC with the addition of 10 wt% of seed crystals for 70 h. Percent clinoptilolite in the solid product was calculated as 89% by using the calibration plot given in Figure 3.1.

Figure 4.16 (b) belongs product OG 74 (Batch Code 5-1, part 3) synthesized from molar batch composition 1.05 Na_2O: 1.05 K_2O: 10 SiO_2: Al_2O_3: $110.1H_2O$ at 140^oC with the addition of 10 wt% of seed crystals for 70 h. Percent clinoptilolite in the solid product was calculated as 78%.

Table 4. 21 X-ray powder diffraction data of OG 70, a Na clinoptilolite, and OG 100, a (Na,K) clinoptilolite, synthesized in this study in comparison with the data of Chi and Sand [1] for synthetic Na and K clinoptilolite.

Chi and Sand (Na clino)		**OG 70 (Na clino)**		**Chi and Sand (K clino)**		**OG 100 (Na;K clino)**	
d spacing	**I/Io**	**d spacing**	**I/Io**	**d spacing**	**I/Io**	**d spacing**	**I/Io**
9.05	75	9.09	48	9.00	100	9.16	37
7.96	31	8.04	25	7.96	26	8.06	34
6.86	16	6.88	15	6.85	10	6.86	12
5.96	7	6.03	4	5.97	8	5.98	9
5.25	16	5.30	12	5.24	8	5.28	9
5.15	27	5.17	25	5.15	19	5.15	27
4.66	18	4.68	14	4.66	14	4.65	8
4.36	9	4.39	8	4.36	6	4.32	4
3.99	100	3.99	100	3.98	68	3.99	100
3.92	51	3.94	53	3.912	40	3.933	53
3.729	5	3.734	8	3.729	7	3.757	6
3.555	20	3.556	12	3.552	14	3.565	20
3.422	48	3.433	42	3.422	29	3.431	44
3.329	18	3.336	12	3.326	17	3.335	21
3.172	37	3.187	46	3.167	24	3.176	42
3.128	23	3.125	17	3.125	18	3.14	22
3.078	18	3.091	20	3.074	15	3.084	24
2.985	49	2.979	52	2.978	49	2.977	51
2.806	32	2.817	44	2.807	20	2.808	45
2.735	19	2.749	25	2.733	19	2.735	21
2.68	11	2.697	10	2.684	6	2.686	10
2.444	11	2.444	15	2.445	12	2.448	20

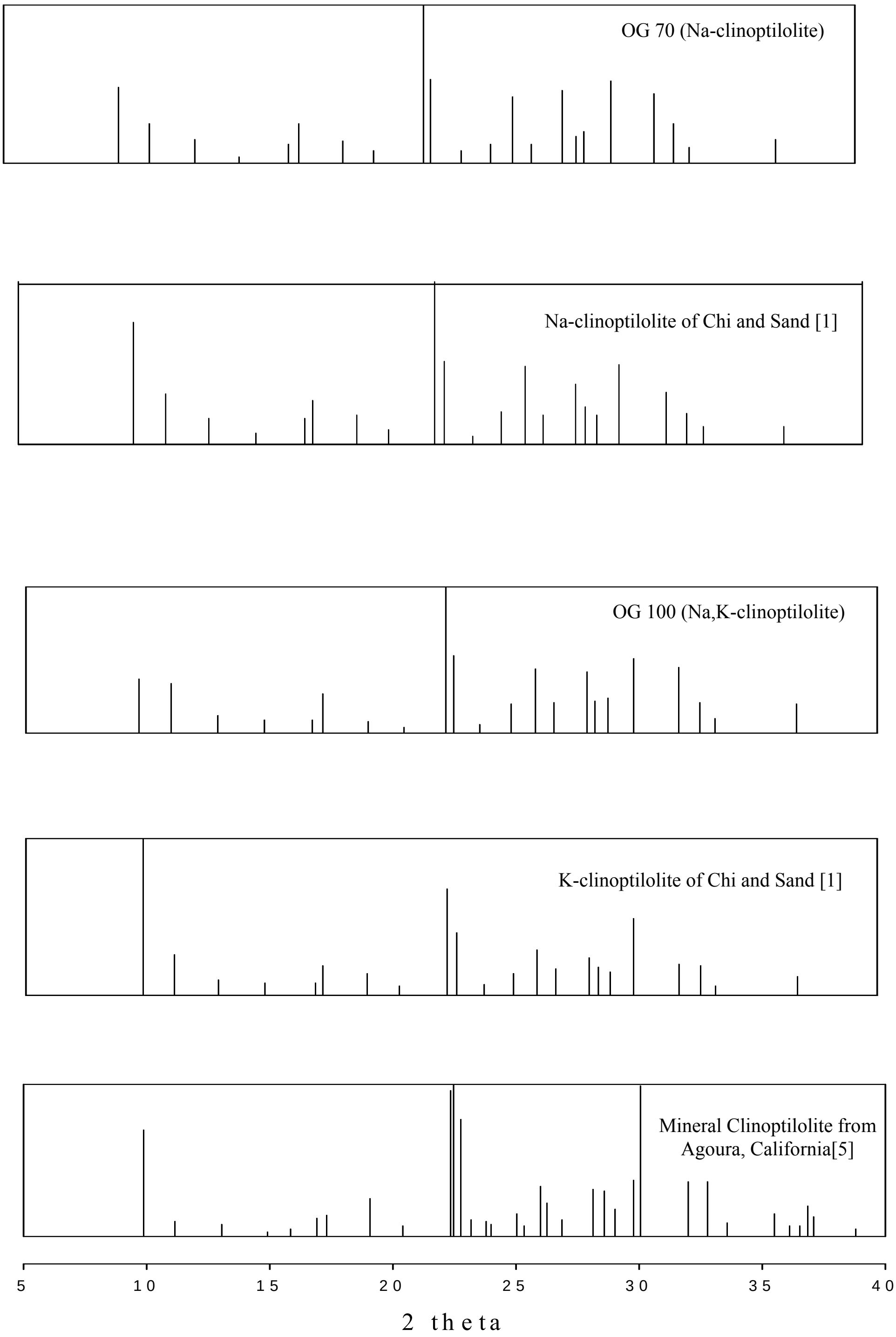
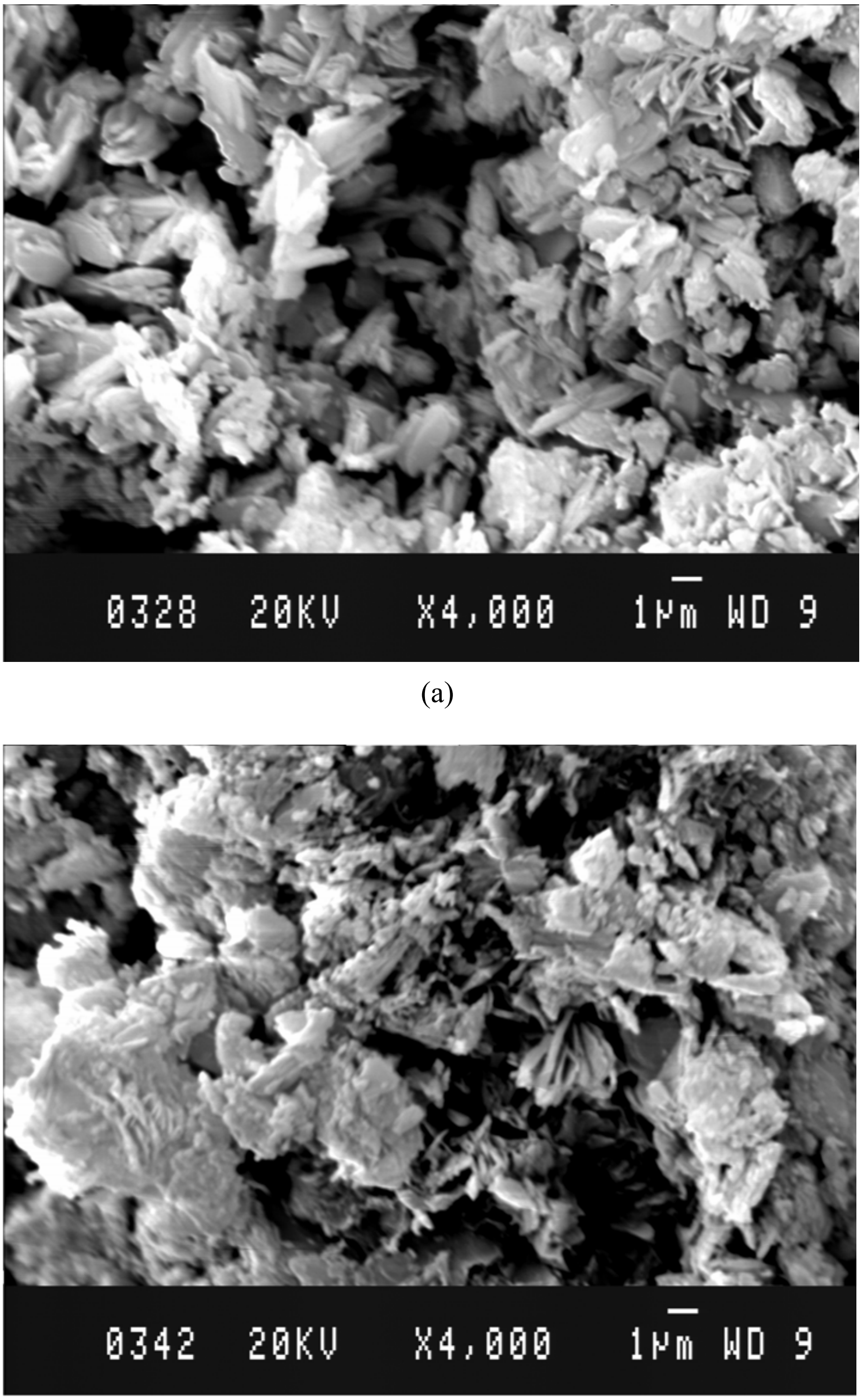


Figure 4.15 X-ray diffraction data in the form of bar charts for OG 70 (Na clinoptilolite) and OG 100 ((Na,K) clinoptilolite), in comparison with the data of Chi and Sand [1] for synthetic Na and K clinoptilolite and data of Wise, Nokleberg and Kokinos [5] for natural clinoptilolite from Agoura, California



(a)

(b)

Figure 4.16 SEM photomicrograph of (a) product OG 69 (Batch Code 2-1, part 3) (b) product OG 74 (Batch Code 5-1, part 3) synthesized at 140^{o}C with the addition of 10 wt% of seed crystals for 70 h

As can be seen from the Figure 4.16 (a) and (b) clinoptilolite crystals are in the form of plates and sheaves of plates. Since SEM images of products were obtained in the form of pellets then some of the crystals seem to be broken because of pressing. It is clear that platy-like crystals are all over the structure. Also considering OG 69 and OG 74 and other similar SEM results given in Appendix D2 which are synthesized from different molar batch compositions, it can be concluded that synthetic clinoptilolite crystals are in the form of plates independent of molar batch composition. Similar results were reported on morphology of synthetic clinoptilolites by many researchers [1, 4, 20]. Natural clinoptilolite can also be in the form of laths beside plates [21], but such a lath like morphology was not observed for synthetic clinoptilolites in our study or in none of the previous studies.

4.11 Chemical Analysis Results

Chemical composition of OG 100 and OG 69 was determined by XRF. OG 100 is a Na,K clinoptilolite synthesized from molar batch composition of 1.05 Na_2O: 1.05 K_2O : 10 SiO_2 : Al_2O_3: 110.1H_2O:0.7 CO_2 (See Table 4.11) and OG 69 is a Na clinoptilolite synthesized from molar batch composition of 2.1Na_2O: 10 SiO_2 : Al_2O_3: 110.1H_2O (See Table 4.2) at 140°C both with the addition of 10 wt% of seed crystals.

Table 4.22 and Table 4.23 shows Na_2O, K_2O, SiO_2, Al_2O_3 content of OG 69 and OG 100 determined by XRF analyses respectively. H_2O contents were determined by TGA considering samples were dried at 105°C for XRF analyses. Also Si/Al ratio, Al/Na+K and K/Na+K ratio for these products are given in these tables.

Since Si/Al ratio is a distinctive property for clinoptilolite and heulandite such that for clinoptilolite this ratio is greater than 4. According to Table 4.22 and 4.23 for both products this ratio is greater than 4 then products are clinoptilolite not heulandite.

Table 4.22 Chemical analysis results of OG 69, a Na-clinoptilolite synthesized from molar batch composition of 2.1Na_2O: 10 SiO_2 : Al_2O_3: 110.1H_2O at 140°C with the addition of 10 wt% of seed crystals (Sample dried at 105°C)

	wt%	mole/1 mole Al_2O_3
SiO_2	68.8	9.33
Al_2O_3	12.5	1.00
Na_2O	7.8	1.03
K_2O	0.4	0.03
H_2O	8.4	5.61
Total	98.6	
Si/Al	4.66	
Al/Na+K	0.94	
K/Na+K	0.03	

Table 4.23 Chemical analysis results of OG 100, a Na;K-clinoptilolite synthesized from molar batch composition of 1.05Na_2O:1.05K_2O:10 SiO_2:Al_2O_3:110.1H_2O:0.7 CO_2 at 140°C with the addition of 10 wt% of seed crystals for 188 h (Sample dried at 105°C)

	wt%	mole/1 mole Al_2O_3
SiO_2	71.2	11.19
Al_2O_3	10.8	1.00
Na_2O	1.6	0.24
K_2O	8.9	0.89
H_2O	5.8	5.14
Total	98.3	
Si/Al	5.59	
Al/Na+K	0.88	
K/Na+K	0.78	

For OG 100, seed added molar batch composition was calculated as 0.93 Na_2O: 0.95 K_2O: 0.06 CaO: 0.03 MgO: Al_2O_3: 9.81 SiO_2: 96.06 H_2O and K/Na+K ratio was calculated as 0.51 for the reactant gel. However as can be seen on Table 4.23 this ratio is 0.78 for the product. Then this shows product is potassium rich although sodium and potassium are equally abundant in the reactant mixture. This is a result of K selectivity of clinoptilolite. Similar results showing potassium selectivity of clinoptilolite were also reported previously by Hawkins et al. (14] and Satokawa and Itabashi (16].

Despite reactant gel for Na-clinoptilolite (OG 69) does not include any K_2O, product was found to include K_2O. This can be originated from seed crystals added to the synthesis gel initially. Considering seed added mixture, molar batch composition was calculated as 1.86 Na_2O: 0.03 K_2O: 0.06 CaO: 0.03 MgO: Al_2O_3: 9.83 SiO_2 : 97.14 H_2O. According to this batch composition K/Na+K is 0.02 just similar to chemical analyses results given in Table 4.22. Although seed crystals may not dissolved completely, cation exchange between reactant gel and seed crystals is probable, for this reason product includes K_2O in it. Beside seed crystals effect, precision of XRF analyses should be considered since for both products summation of weight percentages of components are slightly lower than 100%.

Consequently evidence was obtained from chemical analyses to define these two products as clinoptilolite not heulandite. Also it was found that clinoptilolite structure is more selective to K ion as compared to Na ion.

4.12 Thermal Analysis Results

4.12.1 Thermal Stability Tests

Thermal stability tests were applied in order to observe structural breakdown for synthetic clinoptilolites in comparison with natural clinoptilolite. These were also employed as evidence to define the product as clinoptilolite or heulandite.

Structure breakdown was observed at 450°C for clinoptilolite, heulandite distinction according to the definition of Mumpton (6] who stated that overnight heating at 450°C could not collapse crystal structure of clinoptilolite while collapse heulandite structure completely. For this purpose selected samples were heated to 450°C and 800°C for 2 h. Results were compared with thermal decomposition results of natural Gördes clinoptilolite.

Effect of cation type on thermal stability of clinoptilolite was also investigated. For this purpose thermally treated samples were selected such that they were synthesized from Na and Na,K including systems. Moreover K-exchanged form of a Na clinoptilolite (OG 45) was prepared to see this effect.

Figure 4.17 shows XRD patterns of original samples with thermally treated samples at 450°C and 800°C of (a) Natural Gördes clinoptilolite (CLIG2-1), (b) OG 69 synthesized from Na including system (See Table 4.2), (c) OG 100 synthesized from Na,K including system (See Table 4.11), at 140°C with the addition of 10 wt% of seed crystals. On this figure decomposition of OG 69 is higher than OG 100 and CLIG2-1. However for both OG 69 and OG 100 structure do not collapse completely. Similarly at 800°C while crystal structure of Na clinoptilolite was totally collapsed, crystallinity of Na,K clinoptilolite and Gördes clinoptilolite are comparable.

Figure 4.18 shows XRD patterns of original OG 45 (See Table 4.1), thermal decomposition products of OG 45 at 450°C and 800°C and thermal decomposition product of potassium exchanged form of OG 45 (OG 45-K) at 450°C. On Figure 4.18 it is clear that decomposition degree of K-exchanged form is less than original form of OG 45 at 450 °C. At 800° crystal structure was totally collapsed for OG 45 similar to OG 69.

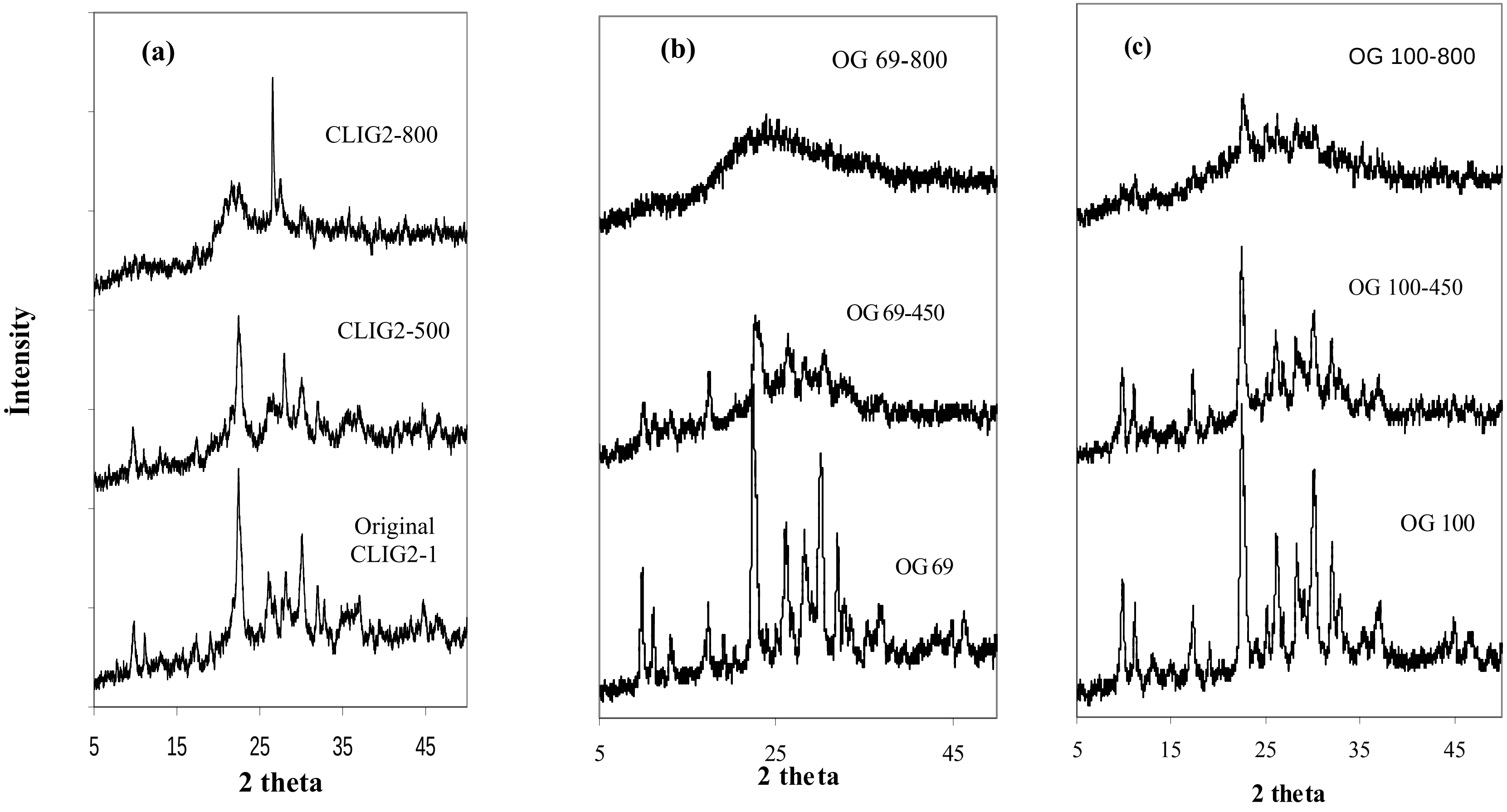


Figure 4.17 XRD patterns of thermally treated (a) Gördes Clinoptilolite (CLIG2-1) at 500°C and 800°C (b) OG 69, a Na clinoptilolite and (c) OG 100 a Na;K clinoptilolite

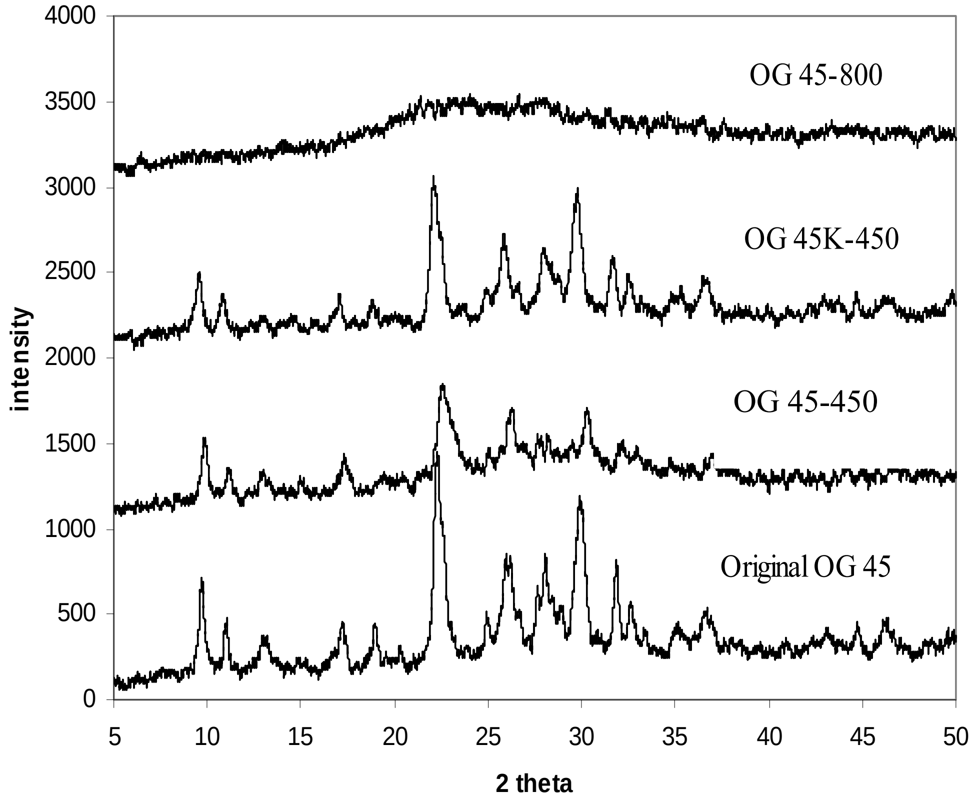


Figure 4.18 XRD patterns of original Na-clinoptilolite OG 45, thermally treated OG 45 at 450°C (OG 45-450) and 800°C (OG 45-800) and thermally treated potassium exchanged OG 45 (OG 45K-450) at 450°C

Products OG 69 and OG 100 are clinoptilolite according to Mumpton's definition. Even at 800°C crystalline structure of OG 100 is comparable with CLIG2-1. Also chemical analyses results mentioned in part 4.11 support this finding such that for both OG 100 and OG 69 Si/Al ratio is greater than 4 which is an indicator of being clinoptilolite

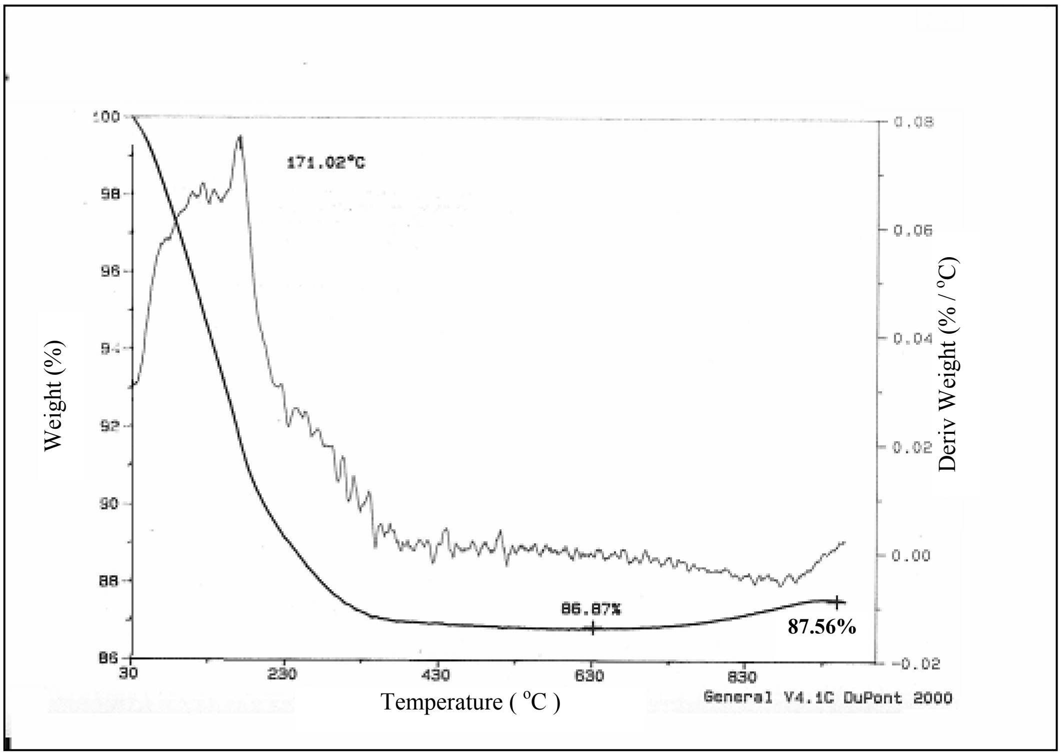
Potassium ion increases the thermal stability of clinoptilolite. (Na,K)-clinoptilolite (OG 100, CLIG2-1) and K exchanged Na clinoptilolite (OG 45-K) are thermally more stable than Na clinoptilolite (OG 69, OG 45). Similar results were reported previously for natural clinoptilolite [23]. To increase thermal stability of clinoptilolite, K ion can be supplied to the structure by ion exchange as well as addition to the reactant mixture before synthesis.

Consequently thermal stability tests showed that thermal behavior of synthetic clinoptilolites is comparable with natural mineral then synthesized products are clinoptilolite not heulandite. Moreover it was observed that thermal stability is related with cation type in the structure.

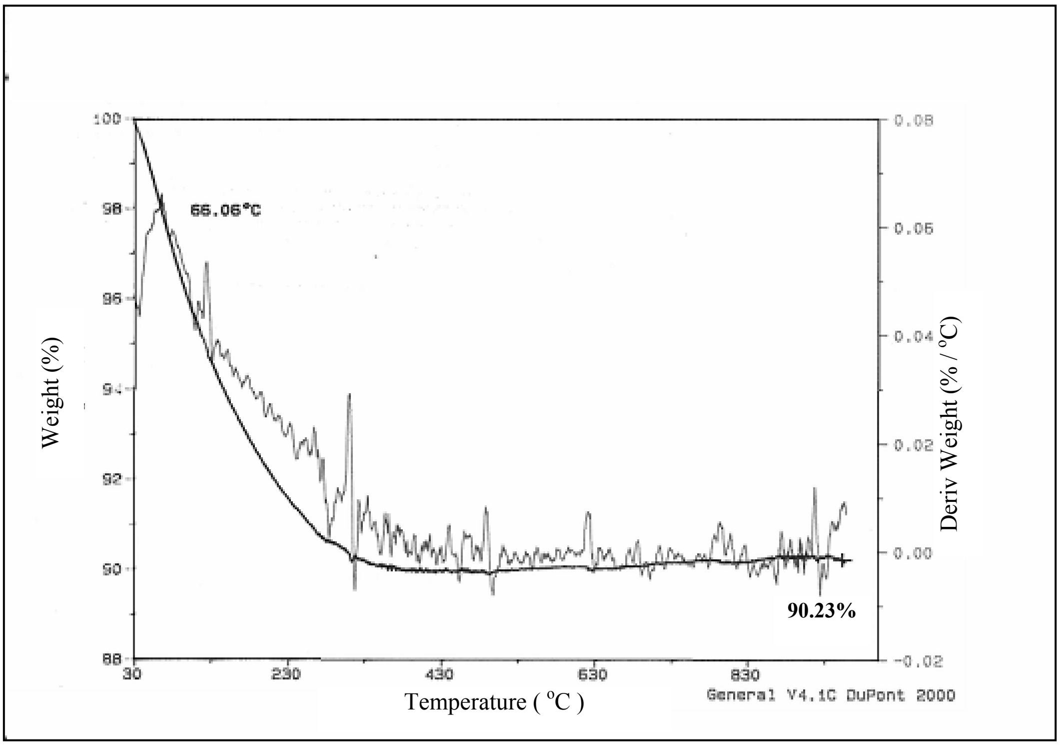
4.12.2 Characterization with TGA

In this study two products were characterized with TGA in order to observe the desorbed water amount and change of weight in the zeolite by heating. The experiments were carried out under nitrogen flow in the temperature range of 30-900 °C with heating rate of 10°C/min.

TGA results of products OG 69 (See Table 4.2) synthesized from Na including system and OG 100 (See Table 4.11) synthesized from Na,K including system were given in Figure 4.19 (a) and 4.19 (b) respectively.



(a)



(b)

Figure 4.19 TGA Scan of products (a) OG 69 (Batch coded 2-1) synthesized from Na including system (b) and OG 100 (Batch coded 7-1) synthesized from Na,K including system at 140°C with the addition of 10wt% of seed crystals

As it is seen in Figure 4.19 (a) and (b), 12.44 % weight loss in the structure of OG 69 and 9.77 % weight loss in the structure of OG 100 was observed up to 900^{o}C due to dehydration. These results were in agreement with mineral clinoptilolite considering 11.26 % weight loss for Gördes clinoptilolite in the study of Tufan [24].

CHAPTER 5

CONCLUSIONS

1. Single phase and highly crystalline clinoptilolite was synthesized from molar batch composition $2.1Na_2O$: $10SiO_2$: Al_2O_3: $110.1H_2O$ at 140°C with the addition of 10 % or 28 % of seed crystals at autogenous pressure for 70 h. By performing this synthesis Chi and Sand's [1] work which was reported to be non-reproducible [2] was re-examined successfully

2. Cation type affects both purity and crystallization rate of clinoptilolite. Single phase clinoptilolite was synthesized for Na and Na,K including systems whereas clinoptilolite was impure for K including systems. Crystallization of K-clinoptilolite is approximately three times slower than the crystallization of Na-clinoptilolite while there is not a significant difference between Na and Na,K clinoptilolite in terms of crystallization rate.

3. Single phase and highly crystalline clinoptilolite was synthesized by using carbonates or chlorides besides hydroxyls as anion source Their addition increased the nucleation period and decresed the crystallization rate of clinoptilolite.

4. Clinoptilolite was synthesized as a single phase by decreasing alkali content of our benchmark composition by 20%, from a molar batch composition of 0.84 Na_2O: 0.84 K_2O: Al_2O_3: $10SiO_2$: 110.1 H_2O. Nucleation period was increased by the decrease of alkali content. On the other hand alkalinity increase of reactant mixture results formation of sanidine.

5. At temperatures 100°C, 120°C, 140°C and 160°C clinoptilolite was crystallized as a single phase. Crystallization rate of clinoptilolite increased by increasing temperature. At 175°C mordenite was crystallized for the same batch composition and conditions.

6. Clinoptilolite was crystallized as a single phase when SiO_2/Al_2O_3 ratio is in between 10 and 12. At lower SiO_2/Al_2O_3 ratios, phases other than clinoptilolite started to appear as a minor or single phase.

7. Starting materials used for the clinoptilolite synthesis should be highly reactive. Clinoptilolite was not synthesized by using thermal decomposition products of mineral clinoptilolite as starting materials for the same batch composition and conditions.

8. Synthetic clinoptilolite crystals were in the form of plates and sheaves of plates independent of synthesis composition and conditions.

9. Chemical analyses of two selected products showed that, products are clinoptilolite not heulandite since their Si/Al ratio is greater than 4. Thermal stability tests for the same products further support this finding such that their crystalline structure did not collapse completely at 450°C.

5.1 Recommendations

1. Further investigations on clinoptilolite synthesis may be focused on unseeded synthesis. For this purpose synthesis composition and conditions yielding pure clinoptilolite for seeded systems can be used as starting point and can be extended by changing mainly composition and temperature.

2. Investigations may be concentrated on the finding of appropriate template molecule to be used for single phase clinoptilolite synthesis especially for unseeded systems.

3. Ion exchange, adsorptive or catalytic properties of synthetic clinoptilolite obtained in this study may be further investigated in comparison with their natural counterparts.

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Appendix A

A.1 Calculation of Reactant Amounts for the Synthesis Performed with Standard Chemical Reagents

A sample calculation is given for the determination of required reactant amounts for the preparation of 100 g synthesis mixture with a composition of BC 5-1= 1.05 Na_2O: 1.05 K_2O: 10 SiO_2 : Al_2O_3: 110.1H_2O.

Reactants used for the preparation of reactant mixture are;

NaOH pellets (98% NaOH, 1.98%H_2O)

KOH pellets (84% KOH, 13.97% H_2O)

$Al(OH)_3$ powder (99.66% $Al(OH)_3$)

Ludox AS-30 (30% SiO_2, 70% H_2O)

Demineralized water

1- NaOH pellet amount determination;

$$\begin{pmatrix}\text{NaOH pellet}\\ \text{amount}\end{pmatrix} = 1.05\ \text{mol Na}_2\text{O} \text{x} \frac{2\ \text{mol NaOH}}{1\ \text{mol Na}_2\text{O}} \text{x} \frac{39.995\ \text{g}}{1\ \text{mol NaOH}} \text{x} \frac{100\ \text{g pellet}}{97\ \text{g NaOH}}$$

= 86. 587 g NaOH pellet

Since 1.98 wt % of NaOH pellets is H_2O, some H_2O will be originated from NaOH pellets and its amount can be calculated as;

$$(H_2O)_{\text{from NaOH pellets}} = 86.587\ \text{g NaOH pellet x} \frac{1.98\ \text{g H}_2\text{O}}{100\ \text{g NaOH pellet}}$$

= 1.714 g H_2O

2- KOH pellet amount determination;

$$\begin{pmatrix}\text{KOH pellet}\\ \text{amount}\end{pmatrix} = 1.05\ \text{mol K}_2\text{O} \text{x} \frac{2\ \text{mol KOH}}{1\ \text{mol K}_2\text{O}} \text{x} \frac{56.11\ \text{g}}{1\ \text{mol KOH}} \text{x} \frac{100\ \text{g pellet}}{84\ \text{g KOH}}$$

= 140.275 g KOH pellet

Since 13.97 wt % of KOH pellets is H_2O, some H_2O will be originated from KOH pellets and its amount can be calculated as;

$$(H_2O)_{\text{from NaOH pellets}} = 140.275\text{ g KOH pellet x }\frac{13.97\text{ g }H_2O}{100\text{ g KOH pellet}}$$

= 19.603 g H_2O

3- $Al(OH)_3$ powder amount determination;

$$\begin{pmatrix}Al(OH)_3\text{powder}\\ \text{amount}\end{pmatrix} = 1\text{ mol }Al_2O_3\text{ x }\frac{2\text{ mol }Al(OH)_3}{1\text{ mol }Al_2O_3}\text{ x }\frac{78.001\text{ g}}{1\text{ mol }Al(OH)_3}\text{ x }\frac{100\text{ g powder}}{99.66\text{ g }Al(OH)_3}$$

= 156.534 g $Al(OH)_3$ powder

4- Ludox AS-30 amount determination;

$$\begin{pmatrix}\text{Ludox AS-30}\\ \text{amount}\end{pmatrix} = 10\text{ mol }SiO_2\text{ x }\frac{60.088\text{ g}}{1\text{ mol }SiO_2}\text{ x }\frac{100\text{ g Ludox AS-30}}{70\text{ g }H_2O}$$

= 2002.933 g Ludox AS-30

$$(H_2O)_{\text{from Ludox AS-30}} = 2002.933\text{ g Ludox AS-30 x }\frac{70\text{ g }H_2O}{100\text{ g Ludox AS}-30}$$

= 1402.053 g H_2O

5- H_2O amount determination;

$$\begin{pmatrix} H_2O \\ \text{required} \end{pmatrix} = 110.1 \text{ mol } H_2O \text{ x } \frac{18.016 \text{ g}}{1 \text{ mol } H_2O}$$

= 1983.56 g H_2O

For the preparation of batch composition BC 5-1, 1983.56 g of water is required however some water was originated from NaOH, KOH and Ludox AS-30. Then extra water to adjust the composition is;

$$\begin{pmatrix} H_2O \\ \text{added} \end{pmatrix} = (m_{H2O})_{\text{required}} - (m_{H2O})_{\text{from NaOH}} - (m_{H2O})_{\text{from KOH}} - (m_{H2O})_{\text{from Ludox AS-30}}$$

= 1983.56 – 1.71 – 19.603 – 1402.053

= 560.194 g H_2O

Amounts of all reactants were calculated as;

NaOH pellet	= 86.587 g
KOH pellet	= 140.275 g
$Al(OH)_3$ powder	= 156.534 g
Ludox AS-30	= 2002.933 g
H_2O	= 560.194 g

Then total weight (W_t) is;

W_t = 86.587 + 140.275 + 156.534 + 2002.933 + 560.194

= 2946. 532 g

For 100 g of batch;

$$1\text{-} \begin{pmatrix} \text{NaOH pellet} \\ \text{amount} \end{pmatrix} = 100 \text{ g batch x } \frac{86.587 \text{ g NaOH pellet}}{2946.532 \text{ g batch}}$$

= 2.94 g NaOH pellet

$$2\text{-} \begin{pmatrix} \text{KOH pellet} \\ \text{amount} \end{pmatrix} = 100 \text{ g batch x } \frac{140.275 \text{ g NaOH pellet}}{2946.532 \text{ g batch}}$$

= 4.76 g KOH pellet

3- $\begin{pmatrix}\text{Al(OH)}_3\text{ powder}\\ \text{amount}\end{pmatrix} = 100\text{ g batch x}\dfrac{156.534\text{ g Al(OH)}_3\text{ powder}}{2946.532\text{ g batch}}$

= 5.31 g $Al(OH)_3$ powder

4- $\begin{pmatrix}\text{Ludox AS-30}\\ \text{amount}\end{pmatrix} = 100\text{ g batch x}\dfrac{2002.933\text{ g Ludox AS-30}}{2946.532\text{ g batch}}$

= 67.98 g Ludox AS-30

5- $\begin{pmatrix}\text{H}_2\text{O}\\ \text{amount}\end{pmatrix} = 100\text{ g batch x}\dfrac{560.194\text{ g H}_2\text{O}}{2946.532\text{ g batch}}$

= 19.01 g H_2O

Consequently for 100 g reactant gel preparation with a composition of BC 5-1: 1.05 Na_2O: 1.05 K_2O: 10 SiO_2 : Al_2O_3: 110.1H_2O required amount of reactants are ;

NaOH pellet = 2.94 g
KOH pellet = 4.76 g
$Al(OH)_3$ powder = 5.31 g
Ludox AS-30 = 67.98 g
H_2O = 19.01 g

= 100 g

Table A.1 Reactant amounts used for 100 g batch preparation

Batch Code	Weight of Sodium Aluminate (g)	Weight of $Al(OH)_3$ (g)	Weight of LUDOX AS-30 (g)	Weight of LUDOX HS-40 (g)	Weight of NaOH (g)	Weight of KOH (g)	Weight of Na_2CO_3 (g)	Weight of K_2CO_3 (g)	Weight of NaCl (g)	Weight of H_2O (g)
BC 1	6.77	---	---	54.89	2.36	---	---	---	---	35.98
BC 2	6.58	---	---	53.30	2.29	---	---	---	---	37.83
BC 2-1	6.58	---	71.07	---	2.29	---	---	---	---	20.06
BC 3	---	5.40	---	51.98	---	9.71	---	---	---	32.91
BC 4	7.14	---	---	57.83	2.48	---	---	---	---	32.55
BC 5-1	---	5.31	67.98	---	2.94	4.76	---	---	---	19.01
BC 6-1	6.51	---	70.30	---	0.24	---	2.61	---	---	20.34
BC 7-1	---	5.26	67.58	---	1.95	3.16	1.25	1.66	---	19.14
BC 8-1	6.68	---	72.18	---	0.25	---	----	---	---	20.89
BC 9-1	6.49	---	70.12	---	0.24	---	---	---	2.86	20.29
BC 12-1	6.69	---	65.05	---	2.33	---	---	---	---	25.93
BC 13-1	6.41	---	76.20	---	2.24	---	---	---	---	15.15

Table A.1 Reactant amounts used for 100 g batch preparation (cont'd)

Batch Code	Weight of Sodium Aluminate (g)	Weight of $Al(OH)_3$ (g)	Weight of LUDOX AS-30 (g)	Weight of LUDOX HS-40 (g)	Weight of NaOH (g)	Weight of KOH (g)	Weight of Na_2CO_3 (g)	Weight of K_2CO_3 (g)	Weight of NaCl (g)	Weight of H_2O (g)
BC 14-1	6.84	---	59.10	---	2.38	---	---	---	---	31.68
BC 15-1	7.16	---	46.38	---	2.49	---	---	---	---	43.97
BC 16-1	7.50	---	32.42	---	2.62	---	---	---	---	57.46
BC 17-1	6.28	---	81.43	---	2.19	---	---	---	---	10.10
BC 18	5.92	---	---	71.95	2.06	---	---	---	---	20.07
BC 19-1	---	5.22	67.05	---	3.48	5.63	---	---	---	18.62
BC 20-1	---	5.37	68.95	---	2.38	3.86	---	---	---	19.44
BC 21-1	---	5.25	67.37	---	3.19	5.17	---	---	---	19.02
BC 22-1	---	5.33	68.49	---	2.65	4.29	---	---	---	19.24

A.2 Calculation of Reactant Amounts for the Synthesis Performed with Decomposed Products

According to the chemical analysis results of Gördes clinoptilolite obtained from Tufan’s MS-thesis and tabulated in Table E.1 in Appendix E1. Analyses results were corrected with respect to 100 g clinoptilolite as;

Component	Wt%
SiO_2	67.71
Al_2O_3	11.38
Fe_2O_3	0.88
MgO	0.12
CaO	0.08
Na_2O	1.22
K_2O	4.25
MnO	0.01
TiO_2	0.04
H_2O	14.31
Total	100.00

For the following calculations it was assumed that;

1- MgO, MnO, TiO_2, Fe_2O_3, CaO are inert materials throughout the crystallization. We’ll name them as others.

2- After decomposition of clinoptilolite water content of the sample will be zero.

3- Decomposed product is a mixture of SiO_2, Al_2O_3, Na_2O, K_2O and others(MgO, MnO, TiO_2, Fe_2O_3, CaO).

For the following calculations decomposed product will be showed with the abbreviation DCP

According to these assumptions if 100 g of clinoptilolite was decomposed, constituents other than water will remain unchanged than 85.69 g of decomposed product can be obtained.

% SiO_2, %Al_2O_3, % Na_2O and %K_2O in decomposed product obtained from100 g of clinoptilolite can be calculated as follows;

$$\%SiO_2 = \frac{67.71\,g\,SiO_2}{85.69\,g\,DCP} \times 100\,g\,DCP$$

$$=79.02\ \%\ SiO_2$$

$$\%\ Al_2O_3 = \frac{11.38\,g\,Al_2O_3}{85.69\,g\,DCP} \times 100\,g\,DCP$$

$$= 13.27\ \%\ Al_2O_3$$

$$\%Na_2O = \frac{1.22\,g\,Na_2O}{85.69\,g\,DCP} \times 100\,g\,DCP$$

$$= 1.42\ \%\ Na_2O$$

$$\%\ K_2O = \frac{4.25\,g\,K_2O}{85.69\,g\,DCP} \times 100\,g\,DCP$$

$$= 1.42\ \%\ K_2O$$

For the preparation of BC 5-1: 1.05Na_2O: 1.05K_2O: Al_2O_3: 10 SiO_2:110.1 H_2O

Raw materials are;

Decomposed Product: 79.02 wt% SiO_2

13.27 wt% Al_2O_3

1.42 wt% Na_2O

4.97 wt% K_2O

NaOH:= 97 wt% NaOH

1.98 wt% H_2O

NaOH:= 84 wt% KOH

13.94 wt% H_2O

1- 1 mole Al_2O_3

$$M_{\text{decomposed product}} = 1 \text{ mole } Al_2O_3 \text{ x } \frac{101.957 \text{ g } Al_2O_3}{1 \text{ mole } Al_2O_3} \text{ x } \frac{100 \text{ g DCP}}{13.07 \text{ g } Al_2O_3}$$

= 768.33 g Decomposed product

2- 10 mole SiO_2

$$(m_{SiO2})_{\text{required}} = 10 \text{ moles x } \frac{60.088 \text{ g } Al_2O_3}{1 \text{ mole } SiO_2}$$

= 600.88 g SiO_2

$$(m_{SiO2})_{\text{from DCP}} = 768.33 \text{ g DCP x } \frac{79.02 \text{ g } SiO_2}{100 \text{ g DCP}}$$

= 607.13 g SiO_2

3- 1.05 moles Na_2O

$$(m_{Na2O})_{\text{required}} = 1.05 \text{ moles x } \frac{61.979 \text{ g } Na_2O}{1 \text{ mole } Na_2O}$$

= 65.0779 g Na_2O

$$(m_{Na2O})_{\text{from DCP}} = 768.33 \text{ g DCP x } \frac{1.42 \text{ g } Na_2O}{100 \text{ g DCP}}$$

= 10.9102 g Na_2O from DCP

To adjust the desired BC 5-1 extra Na_2O should be added

$$(m_{\text{NaOH pellet}})_{\text{added}} = 54.1677 \text{ g } Na_2O \text{ x } \frac{1 \text{ mole } Na_2O}{61.979 \text{ g}} \text{ x } \frac{2 \text{ mole NaOH}}{1 \text{ mole } Na_2O}$$

$$\text{x}\ \frac{39.995\ \text{g}}{1\ \text{mole NaOH}}\ \text{x}\ \frac{100\ \text{g pellet}}{97\ \text{g NaOH}}$$

$$= 72.071\ \text{g NaOH pellet}$$

$$(m_{H2O})_{\text{from NaOH pellet}} = 72.071\ \text{g x}\ \frac{1.98\ \text{g}\ H_2O}{1\,00\ \text{g NaOH pellet}}$$

$$= 1.427\ \text{g}\ H_2O$$

4- 1.05 moles K_2O

$$(m_{K2O})_{\text{required}} = 1.05\ \text{moles x}\ \frac{94.1956\ \text{g}}{1\ \text{mole}\ K_2O}$$

$$= 98.9054\ \text{g}\ K_2O$$

$$(m_{K2O})_{\text{from DCP}} = 768.33\ \text{g DCP x}\ \frac{4.97\ \text{g}\ K_2O}{1\,00\ \text{g DCP}}$$

$$= 38.186\ \text{g}\ K_2O\ \text{from DCP}$$

To adjust the desired BC 5-1 extra K_2O should be added

$$(m_{\text{KOH pellet}})_{\text{added}} = 60.7194\ \text{g}\ K_2O\ \text{x}\ \frac{1\ \text{mole}\ K_2O}{94.1956\ \text{g}\ K_2O}\ \text{x}\ \frac{2\ \text{mole KOH}}{1\ \text{mole}\ K_2O}$$

$$\text{x}\ \frac{100\ \text{g KOH pellet}}{84\ \text{g KOH}}$$

$$= 86.1168\ \text{g KOH pellet}$$

$$(m_{H2O})_{\text{from KOH pellet}} = 86.1168 \text{ g x } \frac{13.94 \text{ g } H_2O}{100 \text{ g NaOH pellet}}$$

$$= 12.0047 \text{ g } H_2O$$

5- 110.1 moles H_2O

$$M_{\text{required H2O}} = 110.1 \text{ moles } H_2O \text{ x } \frac{18.016 \text{ g } H_2O}{1 \text{ mole } H_2O}$$

$$= 1983.5616 \text{ g}$$

Some extra H_2O should be added to adjust the desired BC 5-1

$$M_{\text{extra H2O}} = 1983.5616 - 12.0047 - 1.4270$$

$$= 1970.1299 \text{ g } H_2O \text{ is required}$$

Reactant amounts required for the batch preparation can be summarized as follows;

DCP	768.33
NaOH	72.071
KOH	86.117
H_2O	1970.130
Total	2896.648

100 g batch preparation reactant amounts required are as follows;

DCP	26.53
NaOH	2.49
KOH	2.97
H_2O	68.01
Total	100.00

Appendix B

B.1 Precision Determination of XRD Analyses

XRD analyses for some products were performed more than one at the same conditions for precision determination of clinoptilolite fraction (x_c). In Table B.1 intensity summation of the three selected peaks (ΣI), clinoptilolite fraction (x_c), average of these fractions $<x_c>$ and deviation of each (x_c) from this average value($<x_c>$) was given for products OG 45, OG 69, OG 70, OG 100, and OG 106. Additional 'a', 'b', 'c' in the ID of products shows second, third and forth XRD analysis for the same product. As can be seen on this table, precision of clinoptilolite fractions determined by XRD is ±0.02.

B.2 Finding Clinoptilolite Fraction in CLI-11 Comparing with a Highly Crystalline Product OG 70

Clinoptilolite fraction (x_c) in CLI-11 was found by comparing intensity summation (ΣI) of the three selected characteristic peaks (2θ=22.34, 30.05, 31.99 of CLI-11 with intensity summation of the highly crystalline product (OG 70) (ΣI_o) synthesized in this study.

Intensity summation of 3 selected peaks for CLI-11= $\Sigma I = 2070$
Intensity summation of 3 selected peaks for OG 70 = $\Sigma I_o = 2860$
Clinoptilolite fraction (x_c) in CLI-11 was calculated by the formula;

$$x_c = \frac{\sum I}{\sum I_o} = 0.72$$

Table B.1 XRD analysis results of some selected products obtained at different times

ID	Σ I	x_c	$\langle x_c \rangle$	Deviation of x_c from $\langle x_c \rangle$
OG 70	2900	1.01	1.00	0.01
OG 70-a	2800	0.98		
OG 70-b	2880	1.01		
OG 69	2320	0.81	0.89	0.08
OG69-a	2800	0.98		
OG 100	2460	0.86	0.86	0.01
OG 100-a	2488	0.87		
OG 45	2470	0.86	0.89	0.03
OG 45-a	2640	0.92		
OG 106	2650	0.96	0.98	0.02
OG106-a	2870	1.00		
CLIG2-1	1760	0.62	0.58	0.01
CLIG2-1-a	1640	0.57		
CLIG2-1-b	1650	0.58		
CLIG2-1-c	1630	0.57		
CLI 11	2070	0.72	0.73	0.01
CLI 11-a	2160	0.76		
CLI 11-b	2070	0.72		
OG 43	1200	0.42	0.42	0.01
OG 43-a	1170	0.41		

B.3 Determination of XRD Data of Synthetic Clinoptilolites

Peak listing of synthetic clinoptilolites OG 70 (Na-clinoptilolite) and OG 100 (Na,K clinoptilolite) were obtained by using JADE. d-spacing and 2Θ values were evaluated such that average of them was calculated if they are very close to each other. Also intensity corresponding to these d-spacings was averaged. In Table B2, d-spacings, 2Θ, intensity and their averages were given for OG 100.

Table B.2 2Θ, d-spacing , intensity data obtained from JADE and their averages for OG 100 (Na,K clinoptilolite)

2Θ	d spacing	I/Io	Average 2Θ	Average d spacing	Average I/Io
9.63	9.176	36	9.65	9.16	37
9.67	9.139	37			
10.97	8.059	34	10.97	8.06	34
12.90	6.857	12	12.90	6.86	12
14.80	5.981	9	14.80	5.98	9
16.77	5.282	9	16.77	5.28	9
17.19	5.154	27	17.19	5.15	27
19.08	4.648	8	19.08	4.65	8
20.35	4.32	4	20.23	4.32	4
22.28	3.987	100	22.28	3.99	100
22.59	3.933	53	22.59	3.93	53
23.66	3.757	6	23.66	3.757	6
24.93	3.567	20	24.95	3.565	20
24.97	3.563	19			
25.91	3.436	45	25.94	3.431	44
25.98	3.563	44			
26.71	3.335	21	26.71	3.335	21
28.07	3.176	42	28.07	3.176	42
28.40	3.140	22	28.40	3.14	22
28.85	3.092	25	28.92	3.084	24
28.99	3.077	22			
29.90	2.986	57	29.98	2.977	51
30.07	2.969	46			
31.84	2.808	45	31.84	2.808	45
32.61	2.744	26	32.72	2.735	21
32.83	2.726	17			
33.33	2.686	10	33.33	2.686	10
36.61	2.453	21	36.67	2.448	20
36.74	2.444	19			

Appendix C

C.1 Percent Yield of Product and Percent Maximum Yield Percent Yield, Percent Conversion Calculations for Seed Free Batch

A sample calculation for weight of clinoptilolite in the product, percent maximum yield, percent yield and percent conversion will be given for a product OG 69 synthesized from batch composition BC 2-1: 2.1 Na_2O: Al_2O_3: 10 SiO_2: 110.1 H_2O at 140°C with seeding. The amount of seed added is 10wt% of dry material in batch.

% yield of product was calculated by using weight of product (W_p) and weight of batch (W_b) of OG 69.

Weight of batch (Wb) = 37.89

Weight of product (W_p) = 11.10

$$\%\ \text{yield} = \frac{Wp}{Wb} x100$$

$$= 29.3\ \%$$

To calculate weight of clinoptilolite in the solid product clinoptilolite fraction (x_c) in product OG 69 and weight of product were used. X_c was determined by the calibration plot shown in Figure 3.1.

For the product OG 69

Clinoptilolite fraction (x_c) in the product = 0.89

Weight of clinoptilolite in the solid product (W_c) can be calculated according to Equation 3.1;

$$W_c\,(g) = W_p\,(g) \quad x \quad (x_c)$$

$$= 11.10 \text{ x } 0.89$$

= 9.88 g

To calculate percent maximum yield for seed free batch (%maximum yield)$_{sfb}$, seed free molar batch composition was considered. Seed free batch composition used for the synthesis of OG 69 is BC 2-1 : 2.1 Na_2O: Al_2O_3: 10 SiO_2: 110.1 H_2O

Molecular weights of components are;

Na_2O = 61.979

Al_2O_3 = 101.957

SiO_2 = 60.088

H_2O = 18.016

Formula Weight of seed free BC 2-1;

$(FW)_{sfb}$= (2.1x 61.979) + (1x101.957) + (10x 60.088) + (110.1x 18.016) = 2800.34

A formula for clinoptilolite was selected from literature (5];

Formula for clinoptilolite: $(Na_2O)(Al_2O_3)(SiO_2)_{10}(H_2O)_8$

Formula weight of clinoptilolite $(FW)_c$ was calculated as;

$(FW)_c$ = (61.979 x 1) + (101.957 x 1) + (10x 60.088) + (8x 18.016) = 908.982 g

Percent maximum yield for seed free batch was calculated according to Equation 3.2 as;

$$(\%\text{Maximum Yield})_{sfb} = \frac{(FW)_c}{(FW)_{sfb}} \text{x}100$$

$$= \frac{908.902\text{ g}}{2800.34\text{ g}} \text{x}100$$

$$= 32.46\ \%$$

To calculate % yield for seed free batch($(\%\text{Yield})_{sfb}$) weight of batch (W_b), weight of seed(W_s) weight of clinoptilolite in the product (W_c) and clinoptilolite fraction in CLIG2-1seeds ($x_{c,s}$) were used;

Weight of batch (W_b) = 37.89

Weight of seed (W_s) = 1.21

Weight of clinoptilolite in the product (W_c) = 9.88

Fraction of clinoptilolite in seed crystals ($x_{c,s}$) = 0.58

$$(\%\text{Yield})_{sfb} = \frac{[W_c - W_s(x_{c,s})]}{[W_b - W_s(x_{c,s})]} \text{ x } 100$$

$$= \frac{[9.88 - (1.21\text{x}0.58)]}{[37.89 - (1.21\text{x}0.58)]} \text{ x } 100$$

$$= 24.7\ \%$$

Conversion of limiting reactant for seed free batch $(\%\text{ conversion})_{sfb}$, was calculated by using $(\%\text{Yield})_{sfb}$ and $(\%\text{Maximum Yield})_{sfb}$.

$$(\%\text{ Conversion})_{sfb} = \frac{(\%\text{ Yield})_{sfb}}{(\%\text{ Maximum Yield})_{sfb}} \text{ x } 100$$

$$= \frac{24.7}{32.46} \text{ x } 100$$

$$= 76\ \%$$

D.1 XRD Results of Products

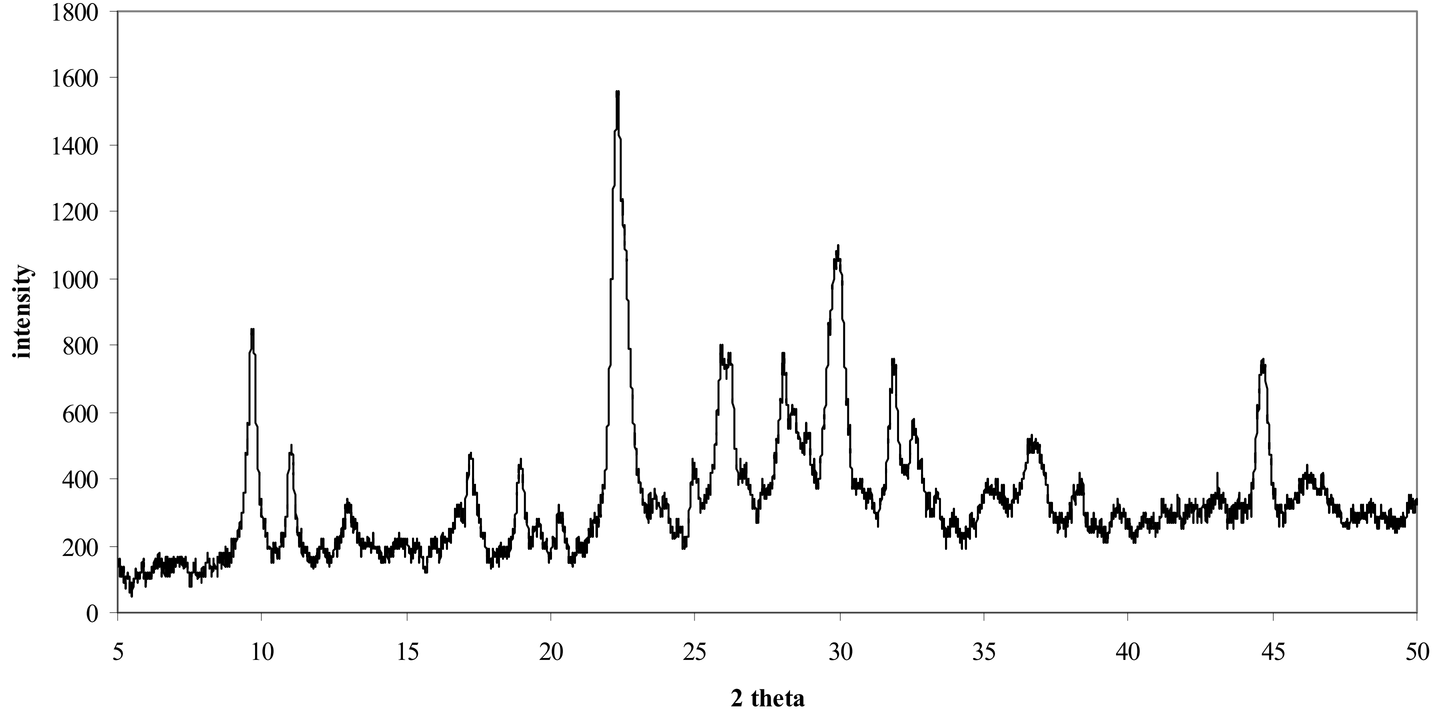

Figure D.1 XRD Pattern of clinoptilolite (OG 106) synthesized from a molar batch composition of 2.1Na_2O: 10 $SiO_2Al_2O_3$: 110.1H_2O: 0.7Cl_2 at 140°C for 474 h with 10 wt% of seed crystals

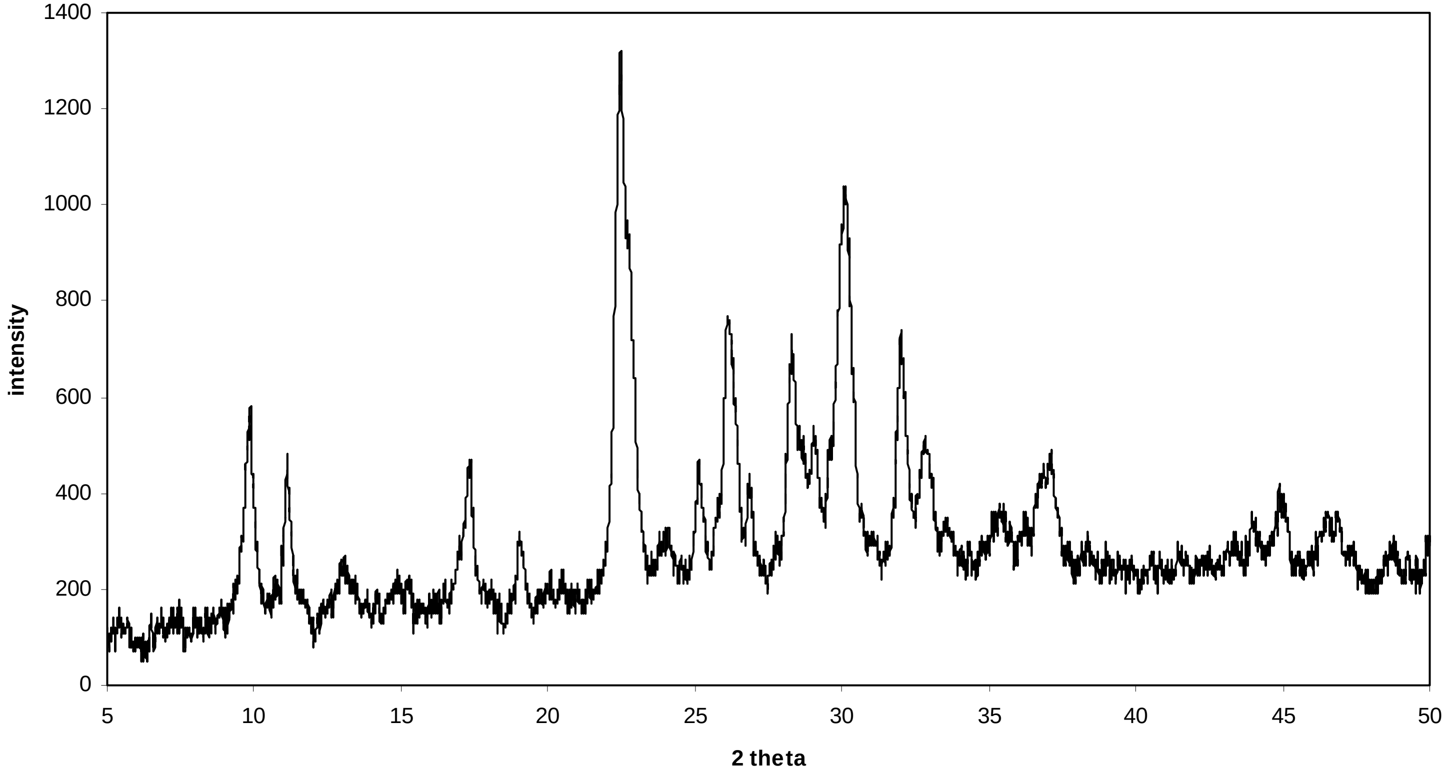

Figure D.2 XRD Pattern of clinoptilolite (OG 100) synthesized from a molar batch composition of $1.05Na_2O$:$1.05K_2O$:$10SiO_2$: Al_2O_3: $110.1H_2O$:$0.7CO_2$ at 140°C for 188 h with 10 wt% of seed crystals

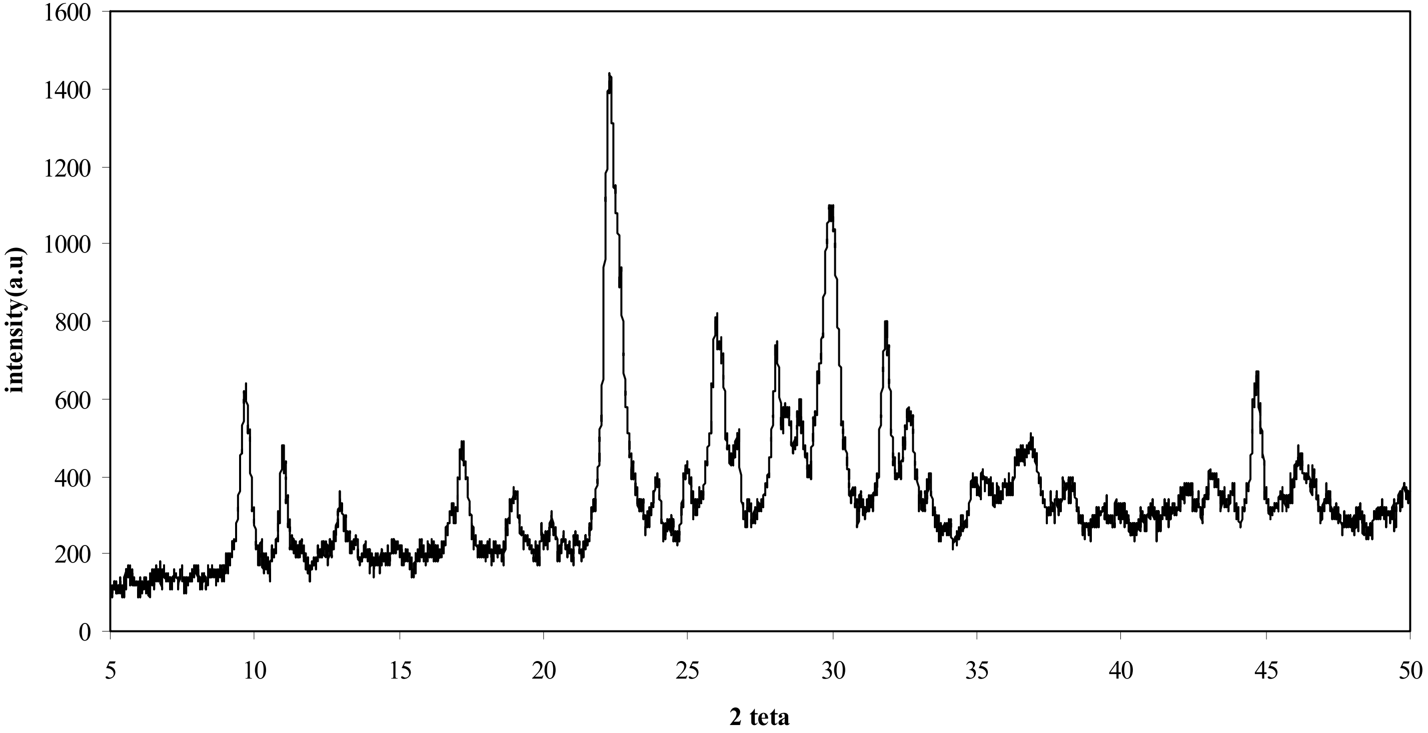

Figure D.3 XRD Pattern of clinoptilolite (OG 40) synthesized from a molar batch composition of 2.1Na_2O: 10 SiO_2: Al_2O_3: 104.9 H_2Oat 100^oC for 1918 h with 28 wt% of seed crystals of dry material

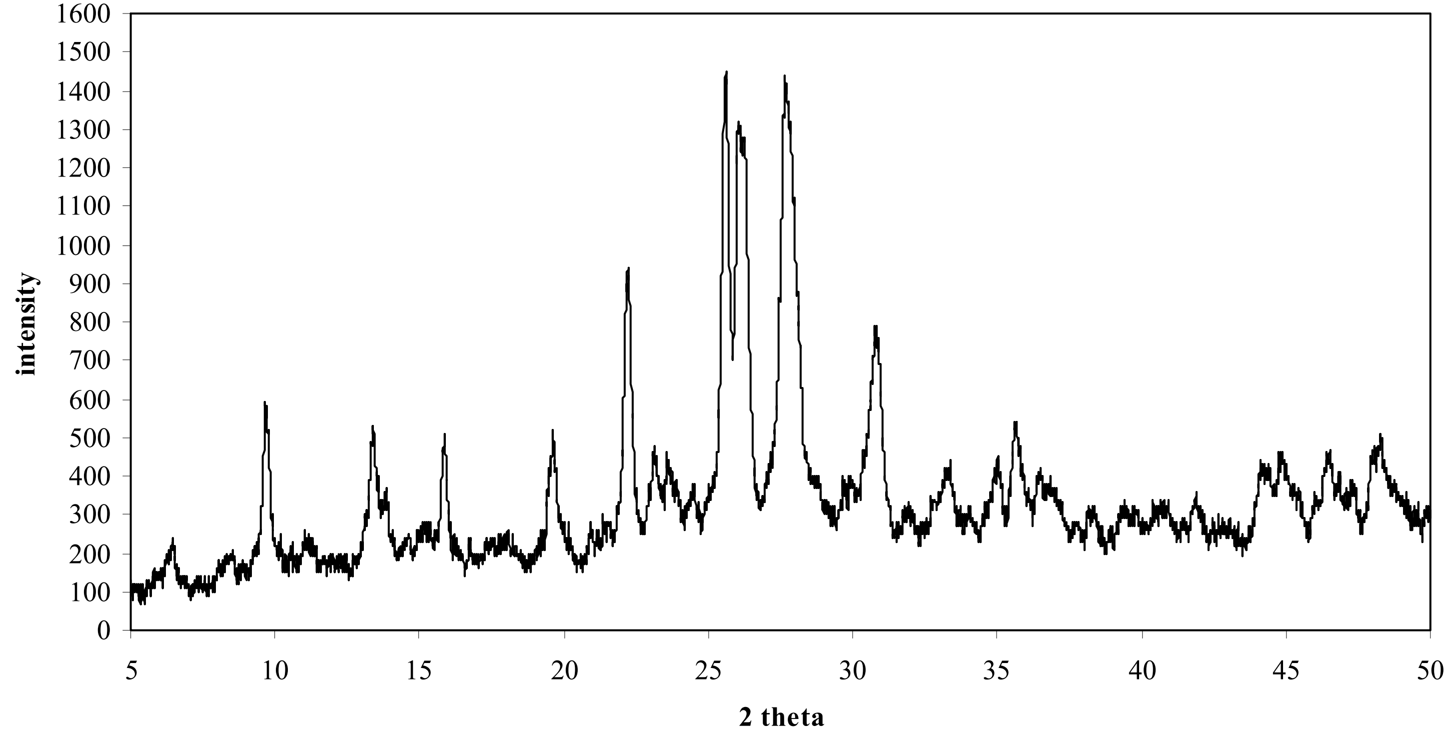

Figure D.4 XRD pattern of OG 112 synthesized from a molar batch composition of $2.1Na_2O$: $10SiO_2$: Al_2O_3: 104.8 H_2O with the addition of 28 wt % of seed crystals at 175°C

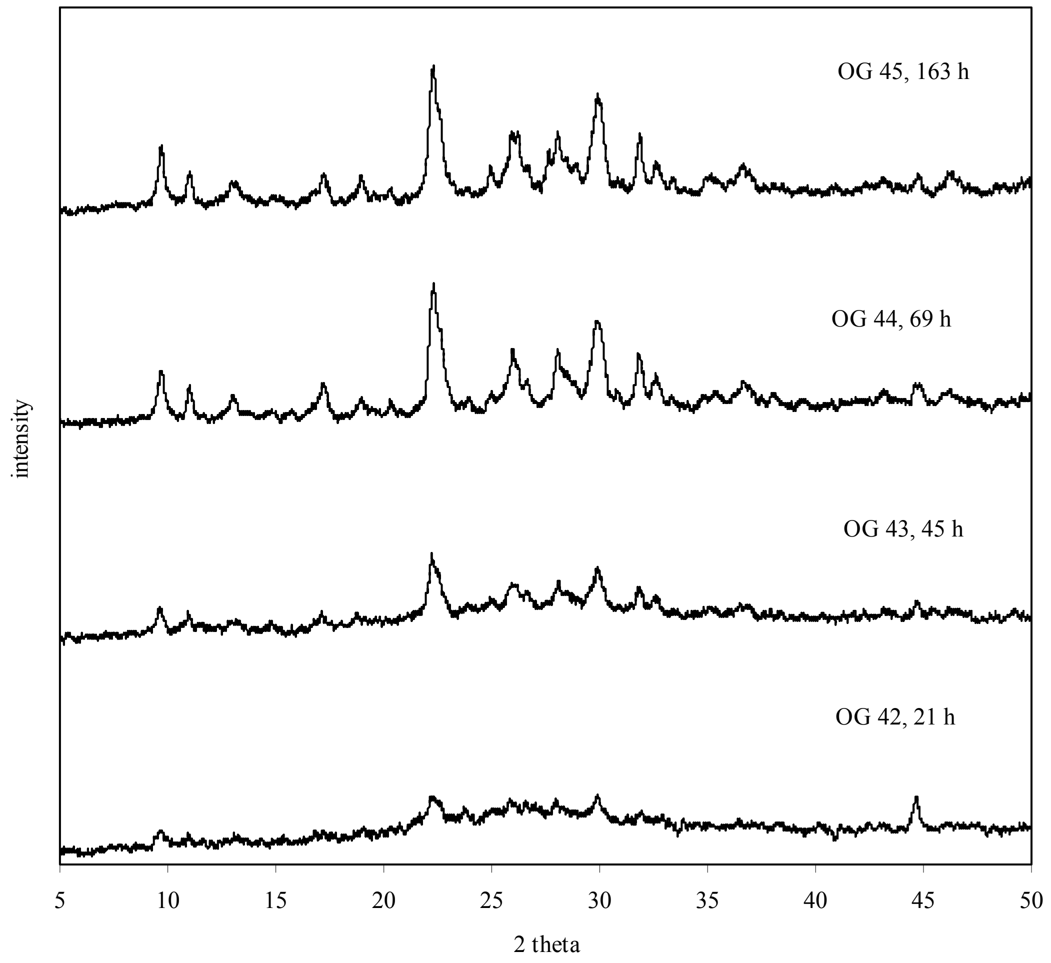

Figure D.5 XRD patterns of products OG 42, OG 43,OG 44,OG 45 synthesized from a molar batch composition 2.1 Na_2O 10 SiO_2: Al_2O_3: 110.1H_2O at 140°C with the addition of 28 wt% of seed crystals at different times.

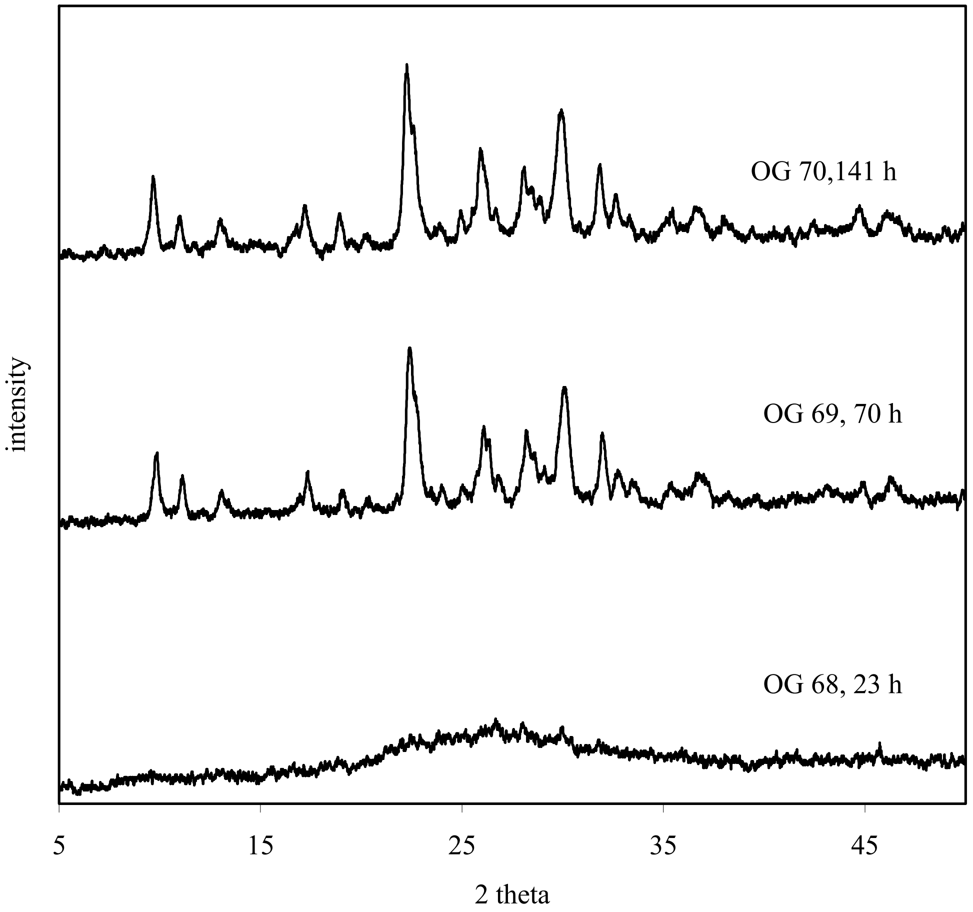

Figure D.6 XRD patterns of products OG 68, OG 69,OG 70 synthesized from a molar batch composition 2.1 Na_2O 10 SiO_2: Al_2O_3: 110.1H_2O at 140°C with the addition of 10 wt% of seed crystals of dry material at different times.

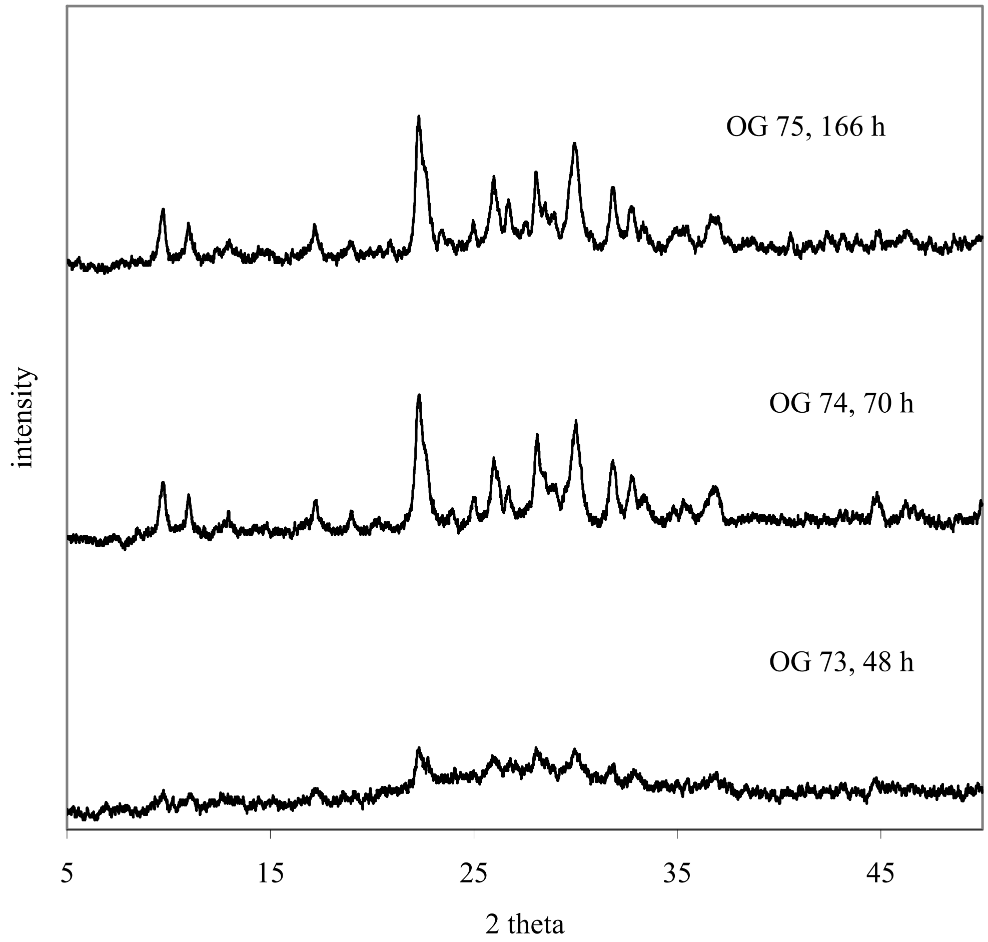

Figure D.7 XRD patterns of products OG 73, OG 74,OG 75 synthesized from a molar batch composition 1.05 Na_2O: 1.05 K_2O:10 SiO_2: Al_2O_3: 110.1H_2O at 140°C with the addition of 10 wt% of seed crystals at different times.

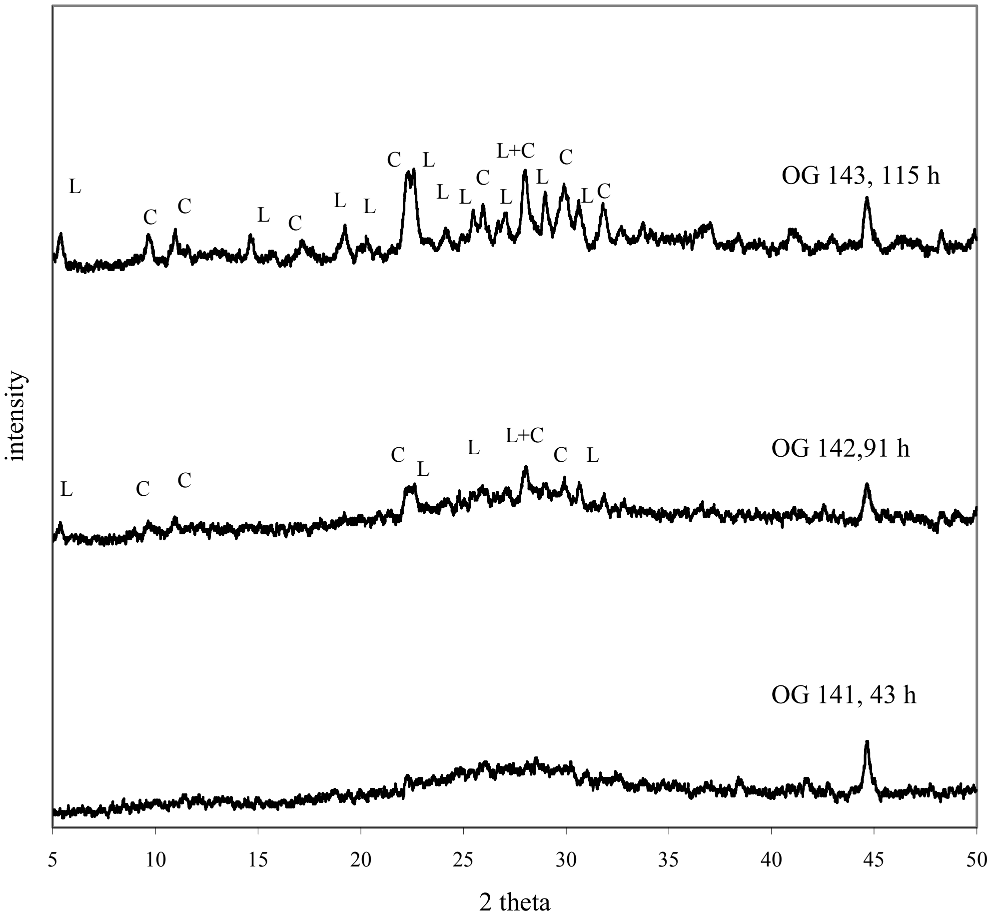

Figure D.8 XRD patterns of products OG 141, OG 142,OG 143 synthesized from a molar batch composition 2.1 K_2O:10 SiO_2: Al_2O_3: 110.1H_2O at 140°C with the addition of 10 wt% of seed crystals at different times.(L:Linde L, C:Clinoptilolite)

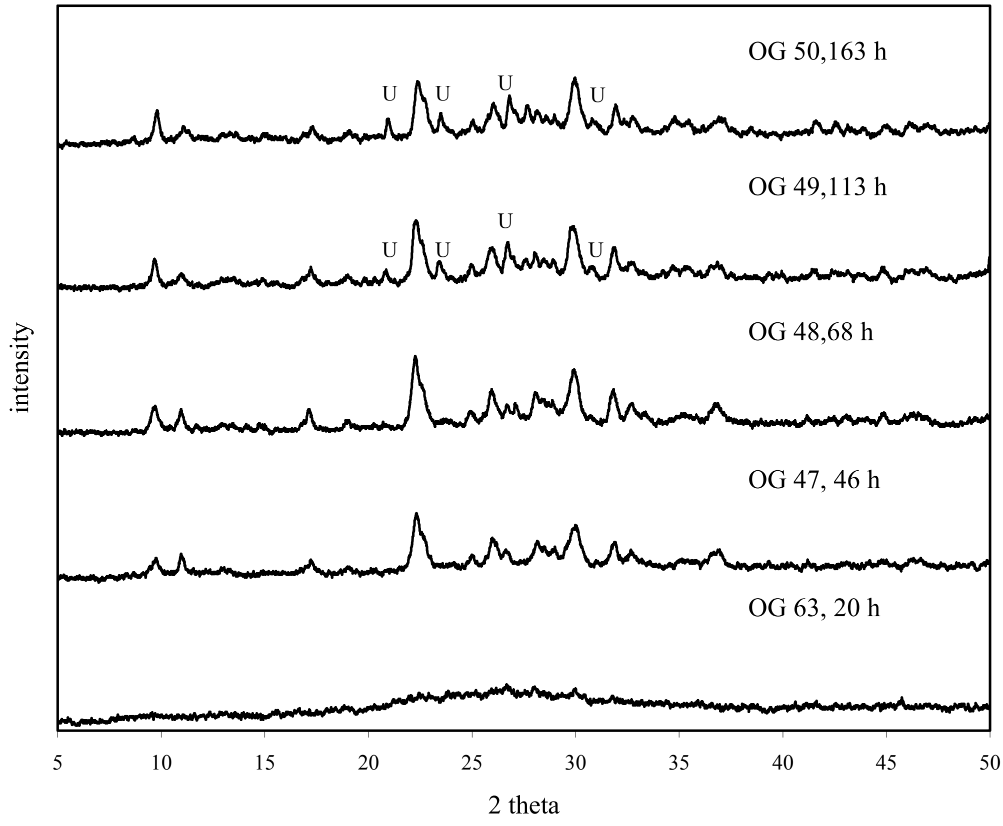

Figure D.9 XRD patterns of products OG 63, OG 47,OG 48, OG 49, OG 50 synthesized from a molar batch composition 1.05 Na_2O:1.05 K_2O:10 SiO_2: Al_2O_3: 110.1H_2O at 140°C with the addition of 28 wt% of seed crystals at different times.(U: Unidentified phase)

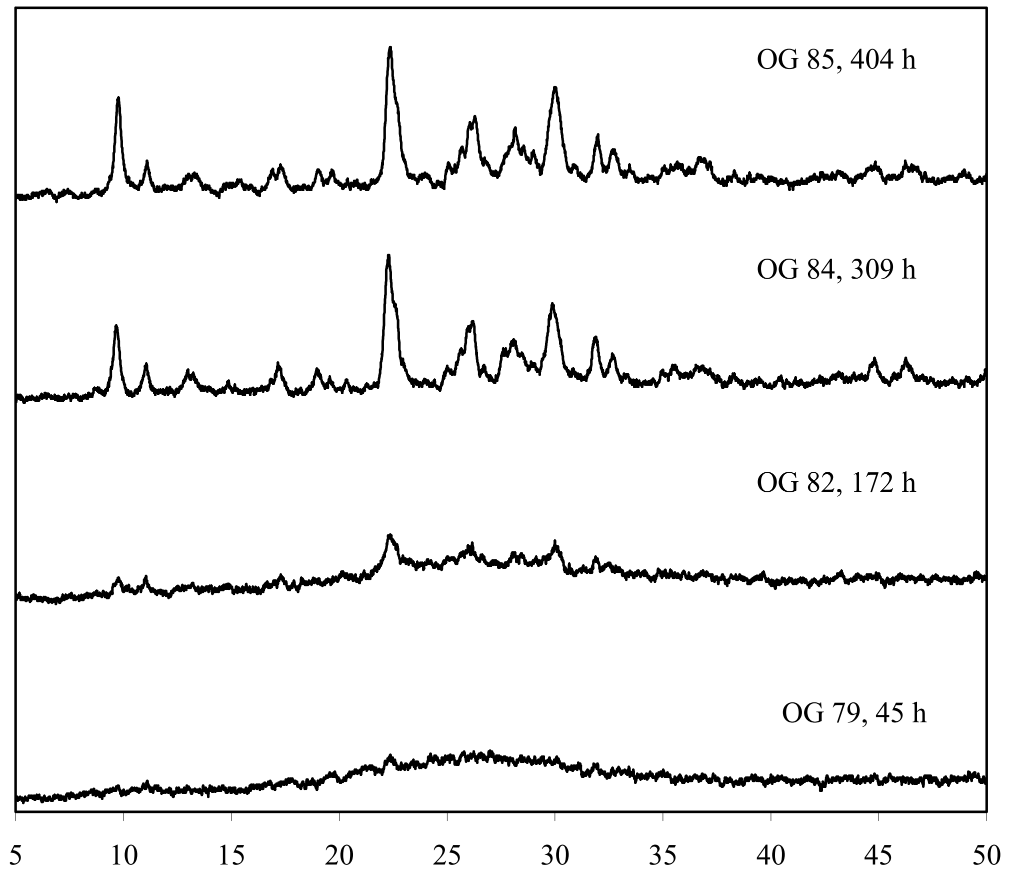

Figure D.10 XRD patterns of products OG 79, OG 82,OG 84, OG 85 synthesized from a molar batch composition 2.1 Na_2O:10 SiO_2: Al_2O_3: 110.1H_2O:0.7CO_2 at 140°C with the addition of 10 wt% of seed crystals at different times.

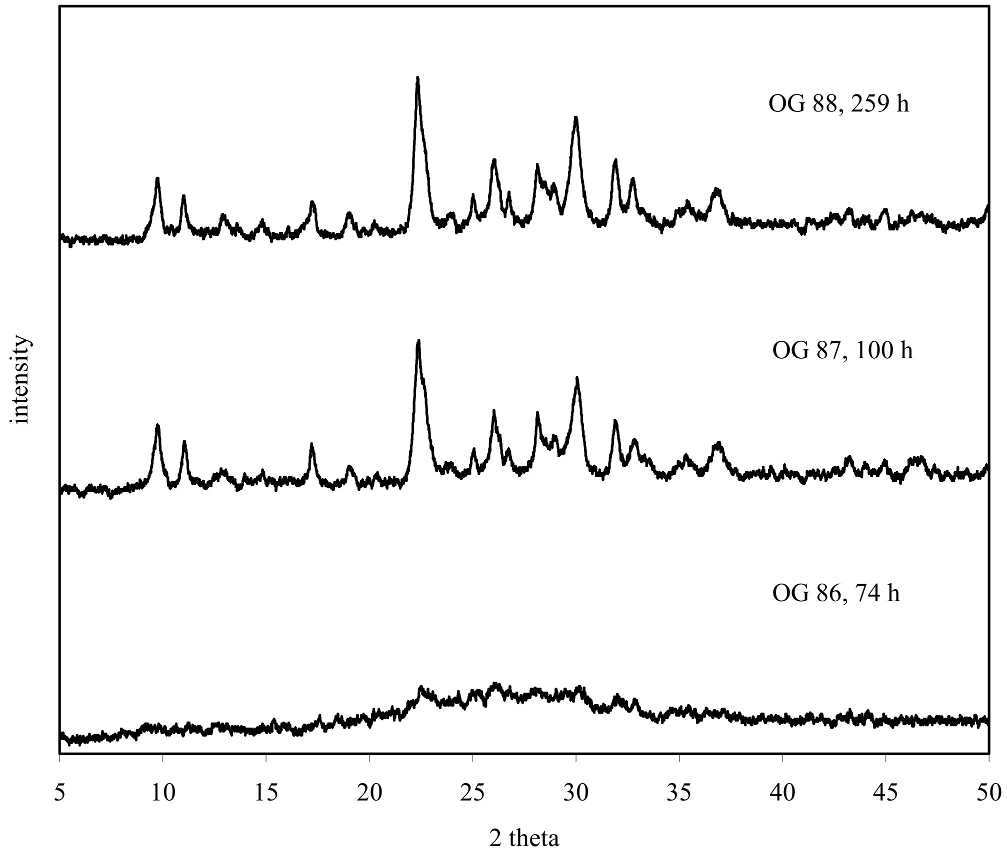

Figure D.11 XRD patterns of products OG 86, OG 87,OG 88 synthesized from a molar batch composition $1.05Na_2O:1.05K_2O:10SiO_2:Al_2O_3:110.1H_2O:0.7CO_2$ at 140°C with the addition of 10 wt% of seed crystals of dry material at different times.

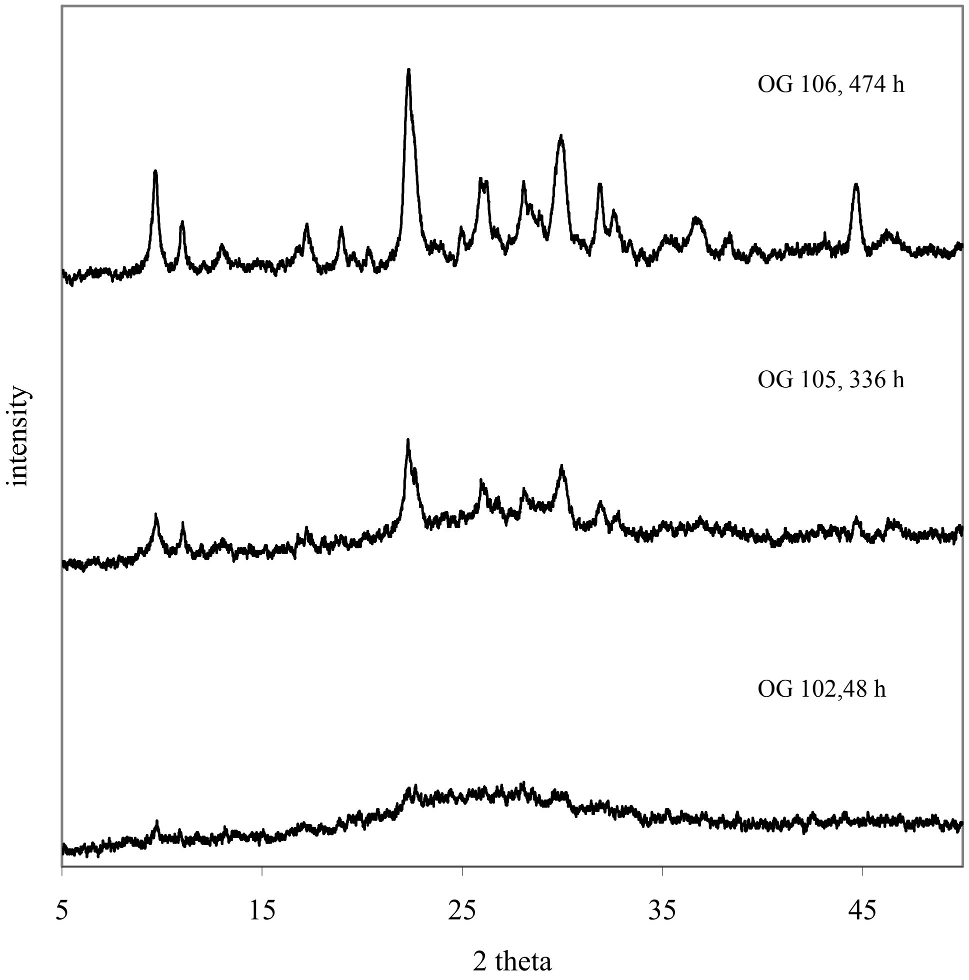

Figure D.12 XRD patterns of products OG 102, OG 105,OG 106 synthesized from a molar batch composition 2.1 Na_2O: 10 SiO_2 : Al_2O_3: $110.1H_2O$: 0.7 Cl_2 at 140^oC with the addition of 10 wt% of seed crystals at different times.

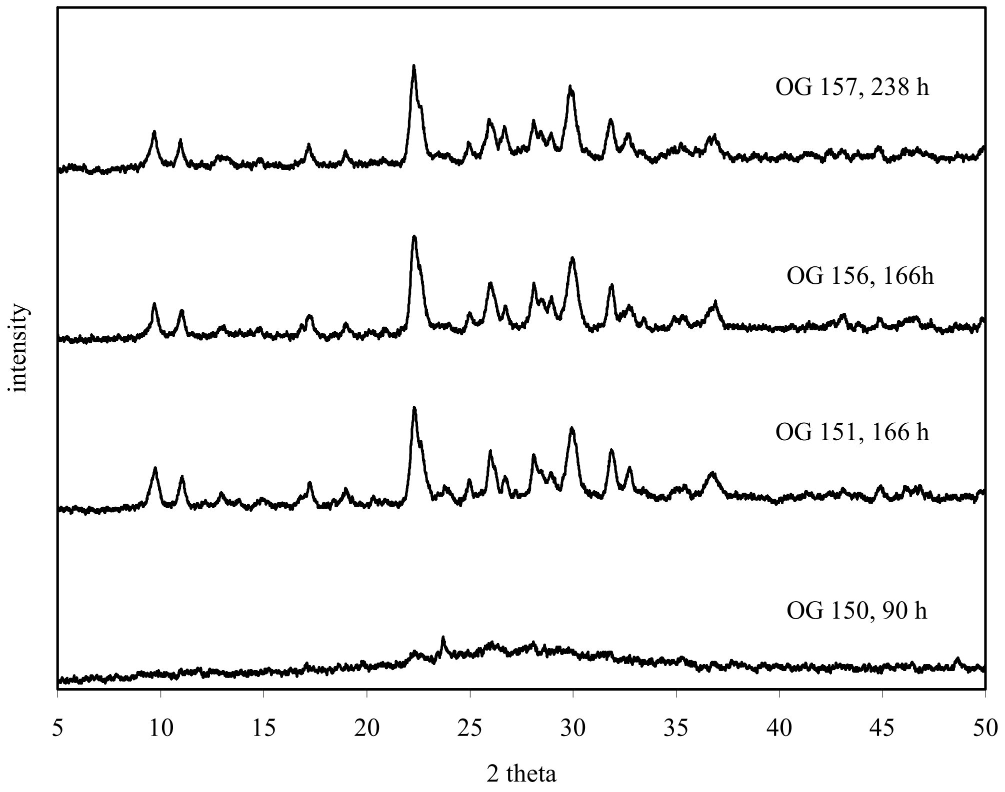

Figure D.13 XRD patterns of products OG 150, OG 151,OG 156, OG 157 synthesized from a molar batch composition 0.84 Na_2O: 0.84 K_2O:10 SiO_2: Al_2O_3: 110.1H_2O at 140°C with the addition of 10 wt% of seed crystals at different times.

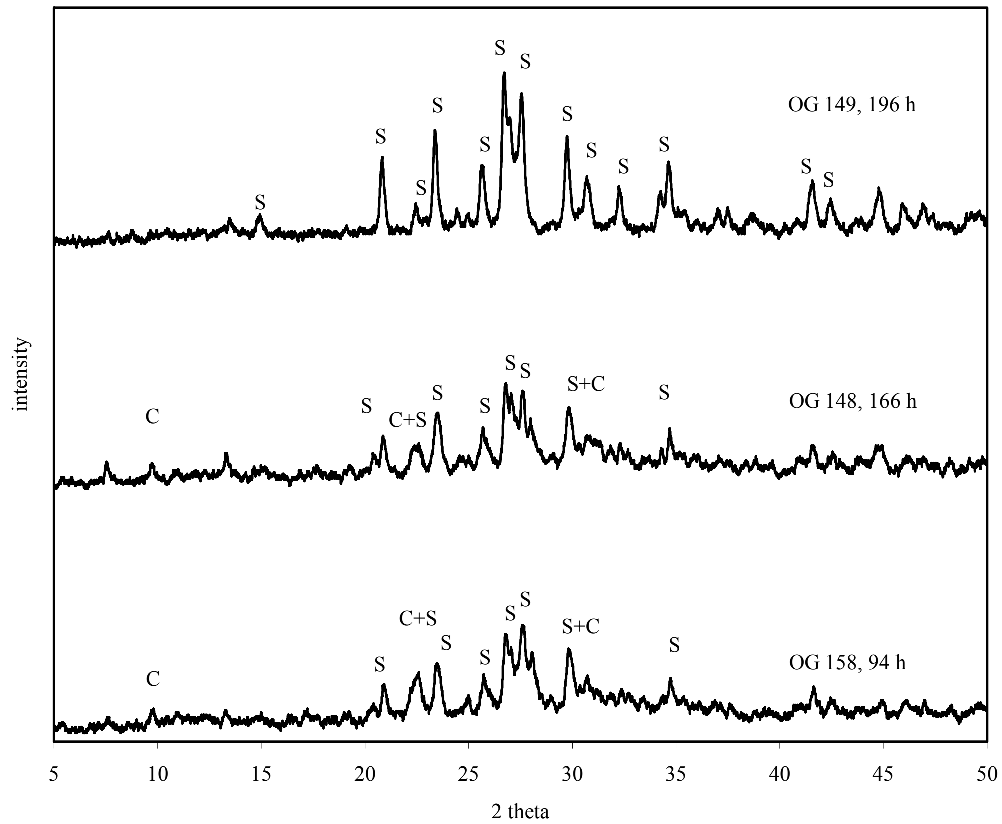

Figure D.14 XRD patterns of products OG 158, OG 148,OG 149 synthesized from a molar batch composition 1.26 Na_2O: 1.26 K_2O:10 SiO_2: Al_2O_3: 110.1H_2O at 140°C with the addition of 10 wt% of seed crystals of dry material at different times. (S:Sanidine, C:Clinoptilolite)

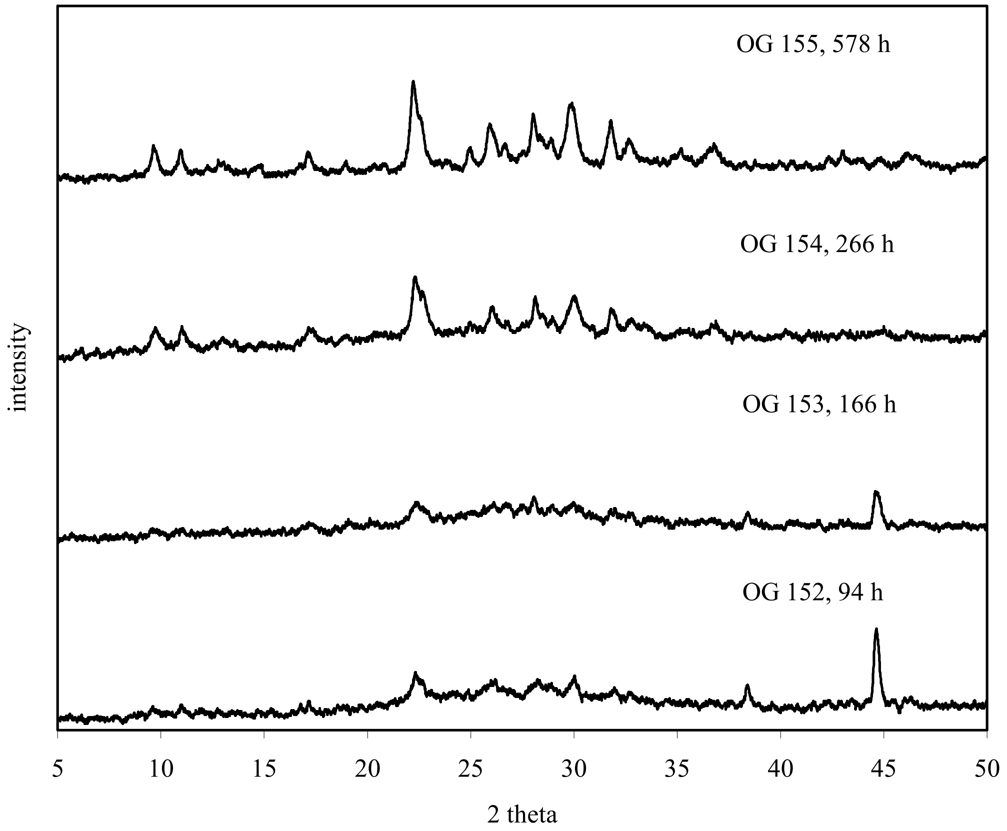

Figure D.15 XRD patterns of products OG 152, OG 153,OG 154, OG 155 synthesized from a molar batch composition 1.05 Na_2O: 1.05 K_2O:10 SiO_2: Al_2O_3: 110.1H_2O at 120°C with the addition of 10 wt% of seed crystals at different times.

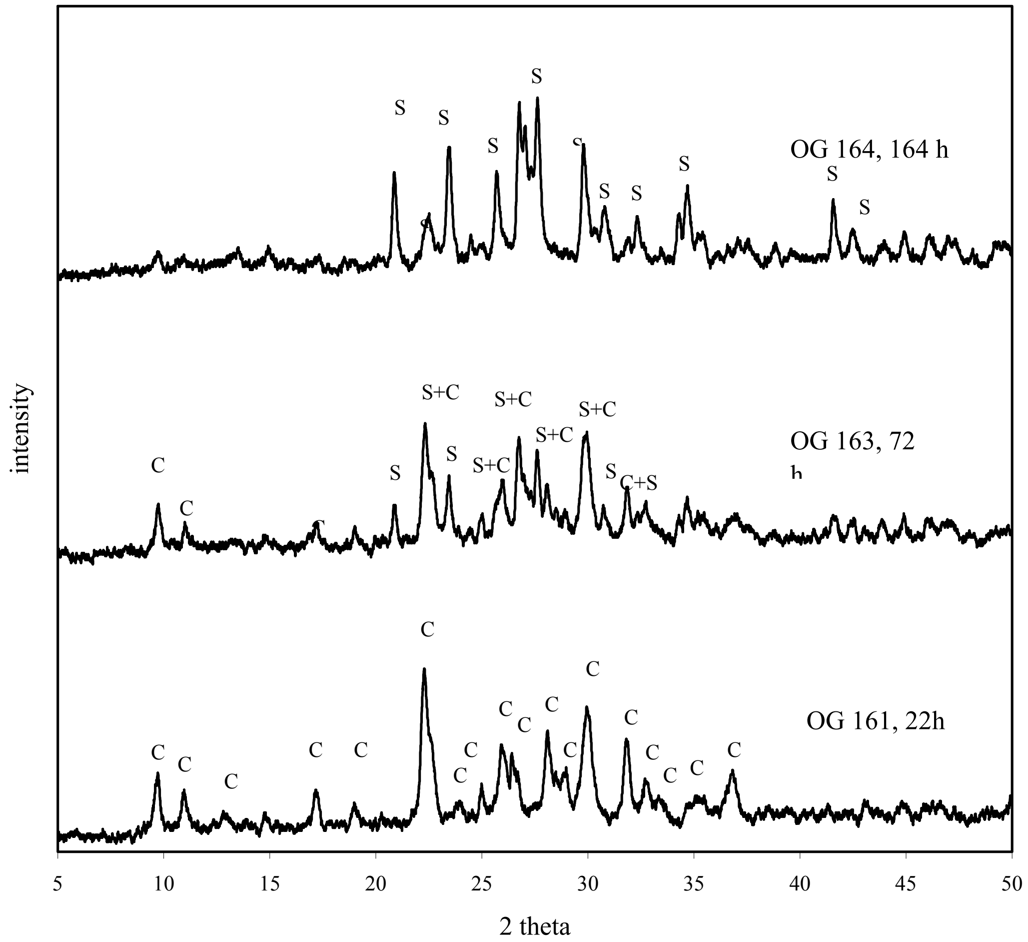

Figure D.16 XRD patterns of products OG 161, OG 162,OG 163,OG 164 synthesized from a molar batch composition 1.05 Na_2O: 1.05 K_2O : 10 SiO_2: Al_2O_3: 110.1H_2O at 160°C with the addition of 10 wt% of seed crystals at different times.(C: Clinoptilolite, S: Sanidine)

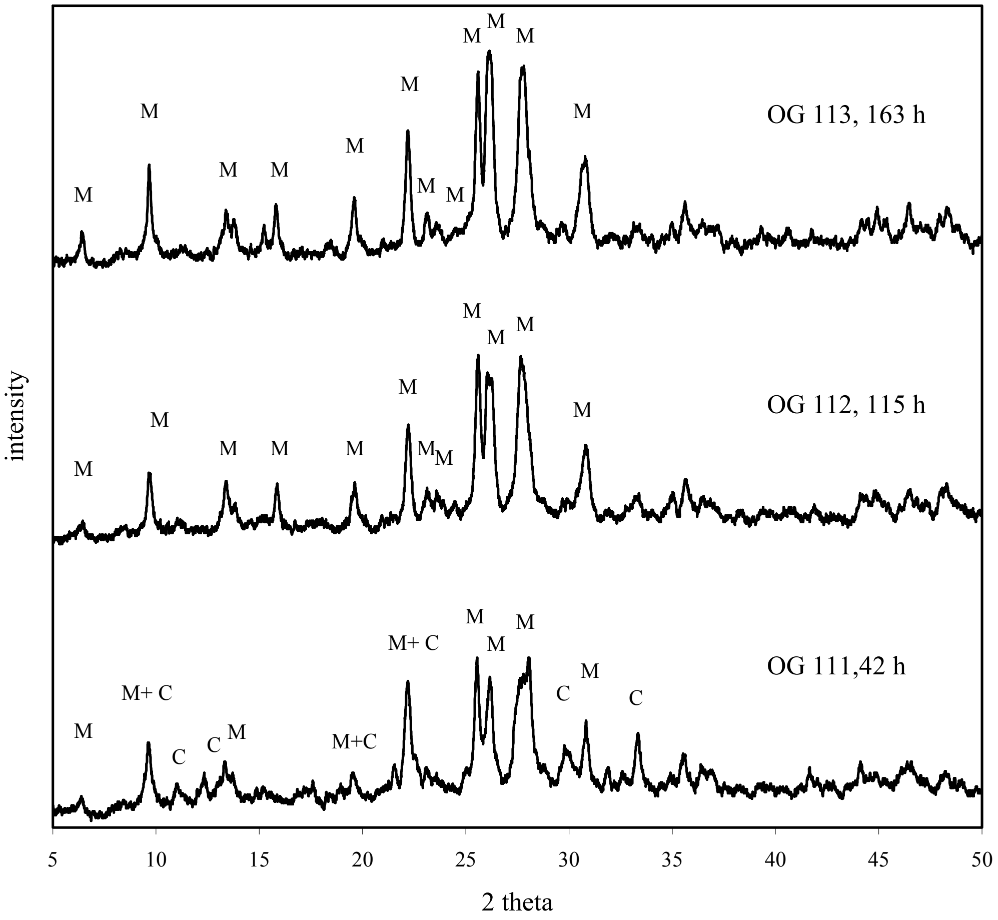

Figure D.17 XRD patterns of products OG 111, OG 112,OG 113 synthesized from a molar batch composition 2.1 Na_2O 10 SiO_2: Al_2O_3: 110.1H_2O at 175°C with the addition of 10 wt% of seed crystals at different times.(M:Mordenite, C:Clinoptilolite)

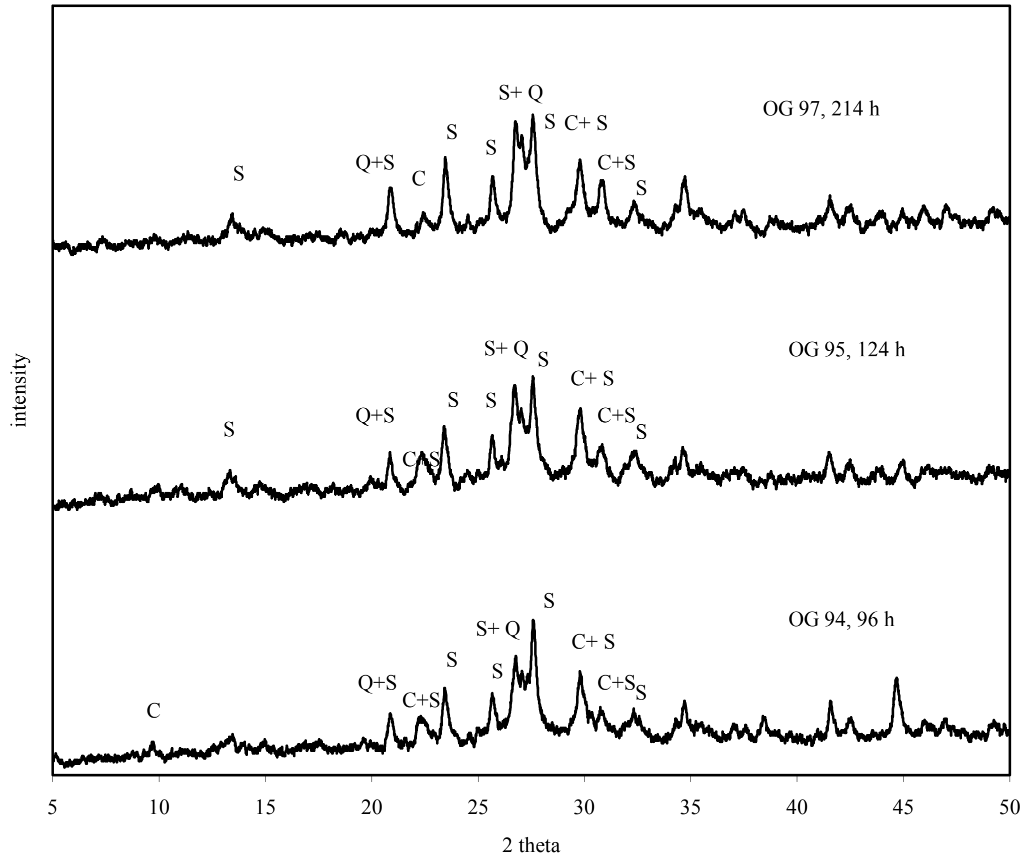

Figure D.18 XRD patterns of products OG 94, OG 95,OG 97 synthesized from a molar batch composition 1.05 Na_2O: 1.05 K_2O:10 SiO_2: Al_2O_3: 110.1H_2O at 140°C by using completely decomposed products of clinoptilolite with the addition of 10 wt% of seed crystals at different times.(S:Sanidine, Q:Quartz, C: Clinoptilolite)

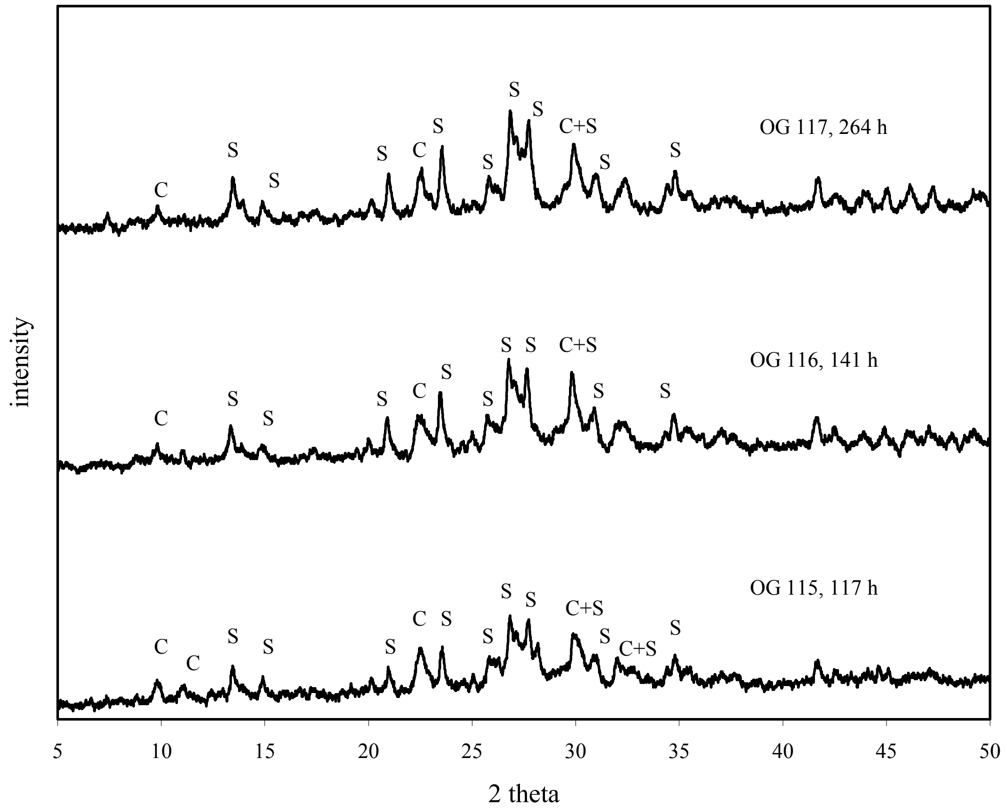

Figure D.19 XRD patterns of products OG 114, OG 116,OG 117 synthesized from a molar batch composition 1.05 Na_2O: 1.05 K_2O:10 SiO_2: Al_2O_3: 110.1H_2O at 140°C by using partly decomposed products of clinoptilolite with the addition of 10 wt% of seed crystals at different times.(S:Sanidine, C:Clinoptilolite)

D.2 SEM Results of Products

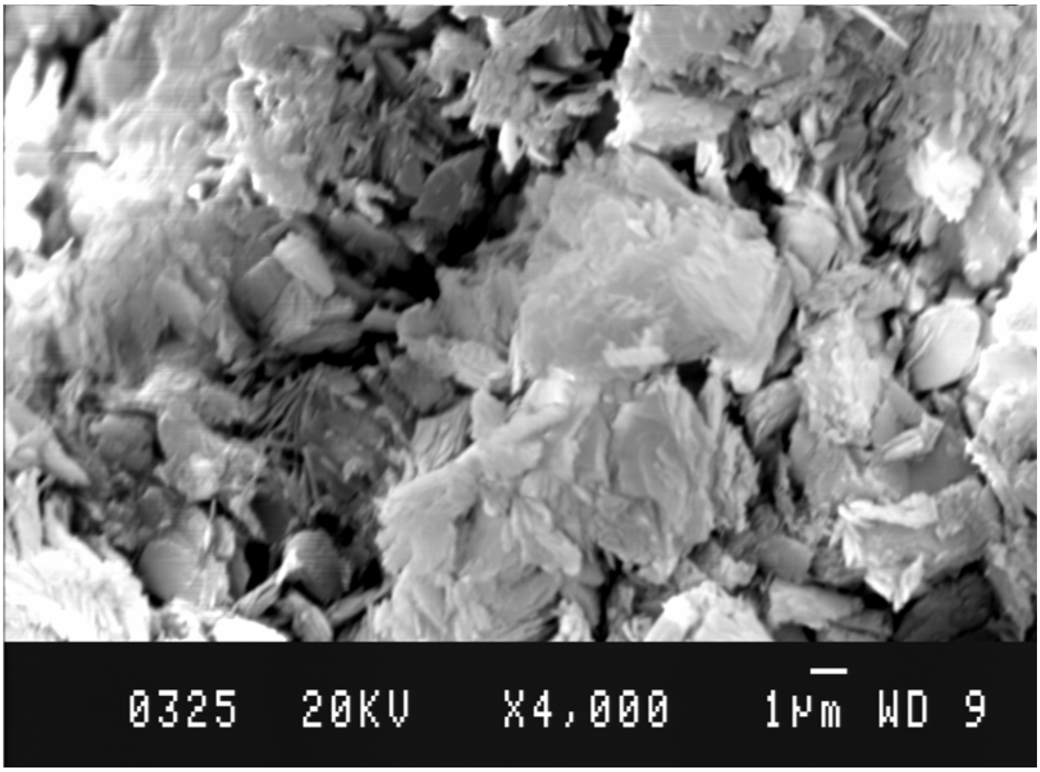

Figure D.20 SEM image of OG 88 synthesized from molar batch composition of 1.05 Na_2O: 1.05 K_2O : 10 SiO_2 : Al_2O_3: 110.1H_2O:0.7 CO_2 at 140°C for 259 h with the addition of 10 wt% seed crystals

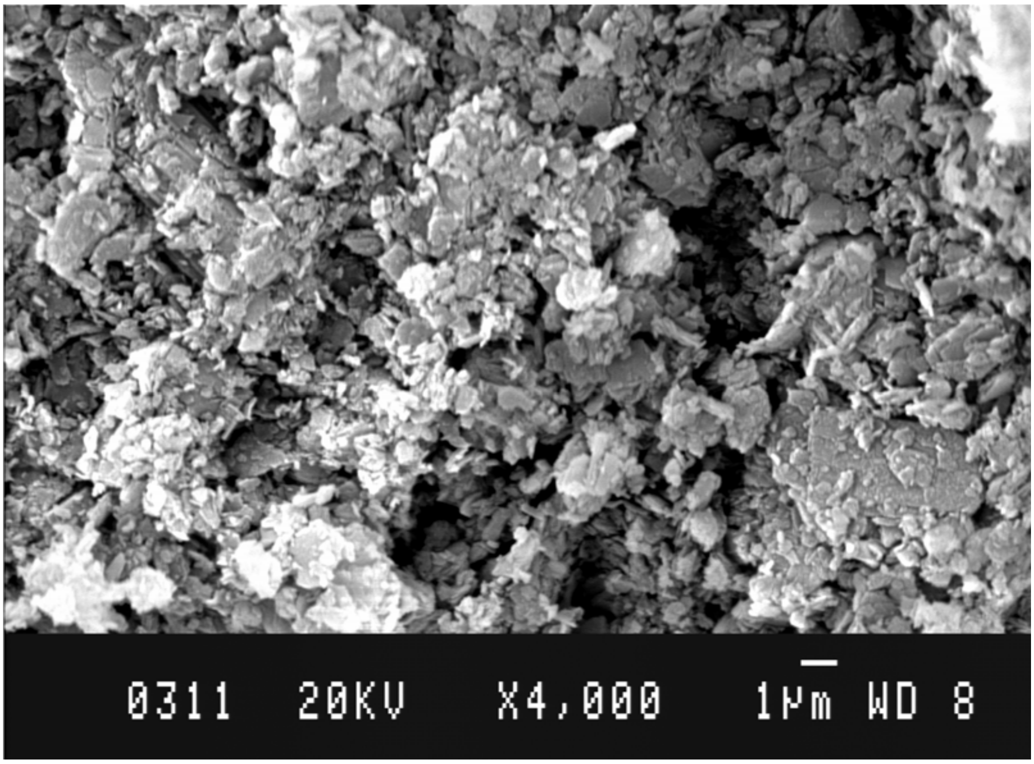

Figure D.21 SEM image of OG 45 synthesized from molar batch composition of 2.1 Na_2O: 10 SiO_2 : Al_2O_3: 110.1H_2O at 140°C for 163 h with the addition of 28 wt% seed crystals

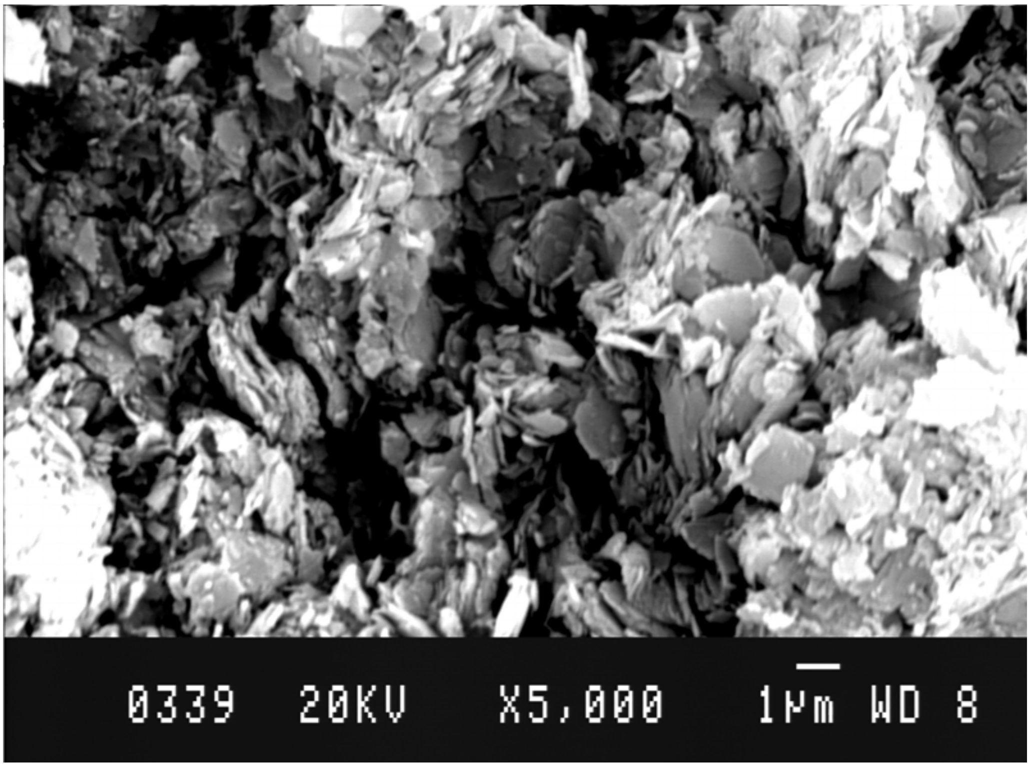

Figure D.22 SEM image of OG 106 synthesized from molar batch composition of 2.1 Na_2O: 10 SiO_2 : Al_2O_3: 110.1H_2O: 0.7 Cl^- at 140^oC for 474 h with the addition of 10 wt% seed crystals of dry material

Appendix E

E.1 SEM Image, XRD Pattern and Chemical Analyses Results for CLIG2-1(Gördes Clinoptilolite)

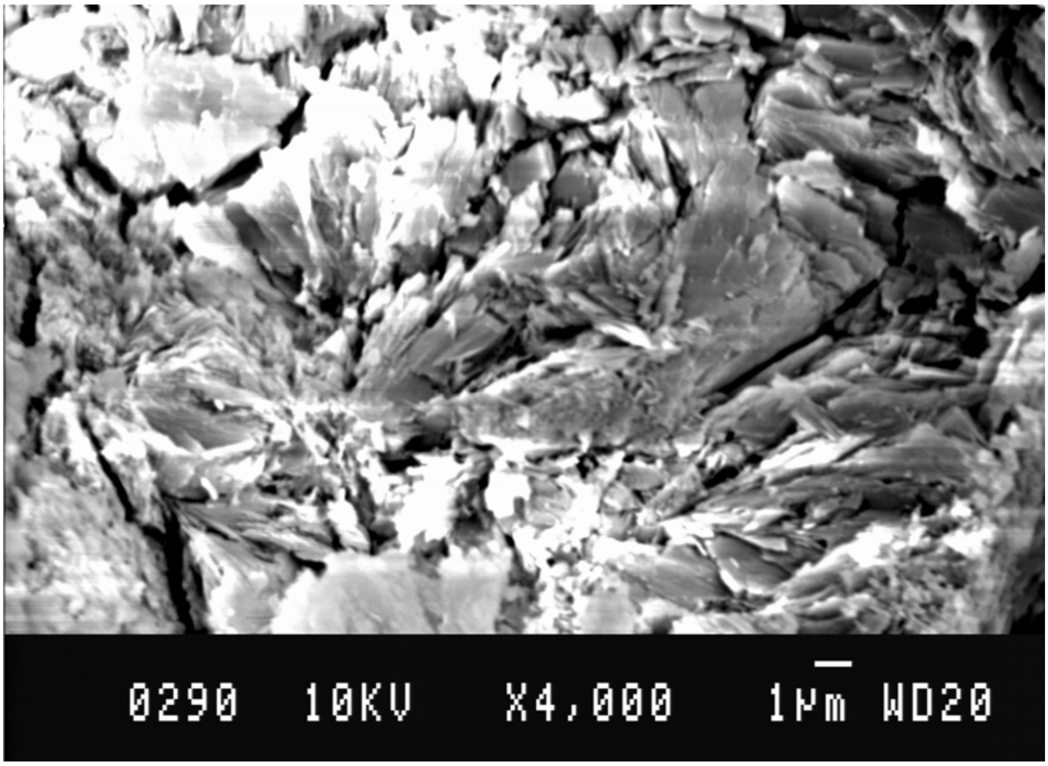

Figure E.1 SEM image of Gördes clinoptilolite (CLIG2-1) which was used as seed crystals and for the preparation of thermally decomposed products

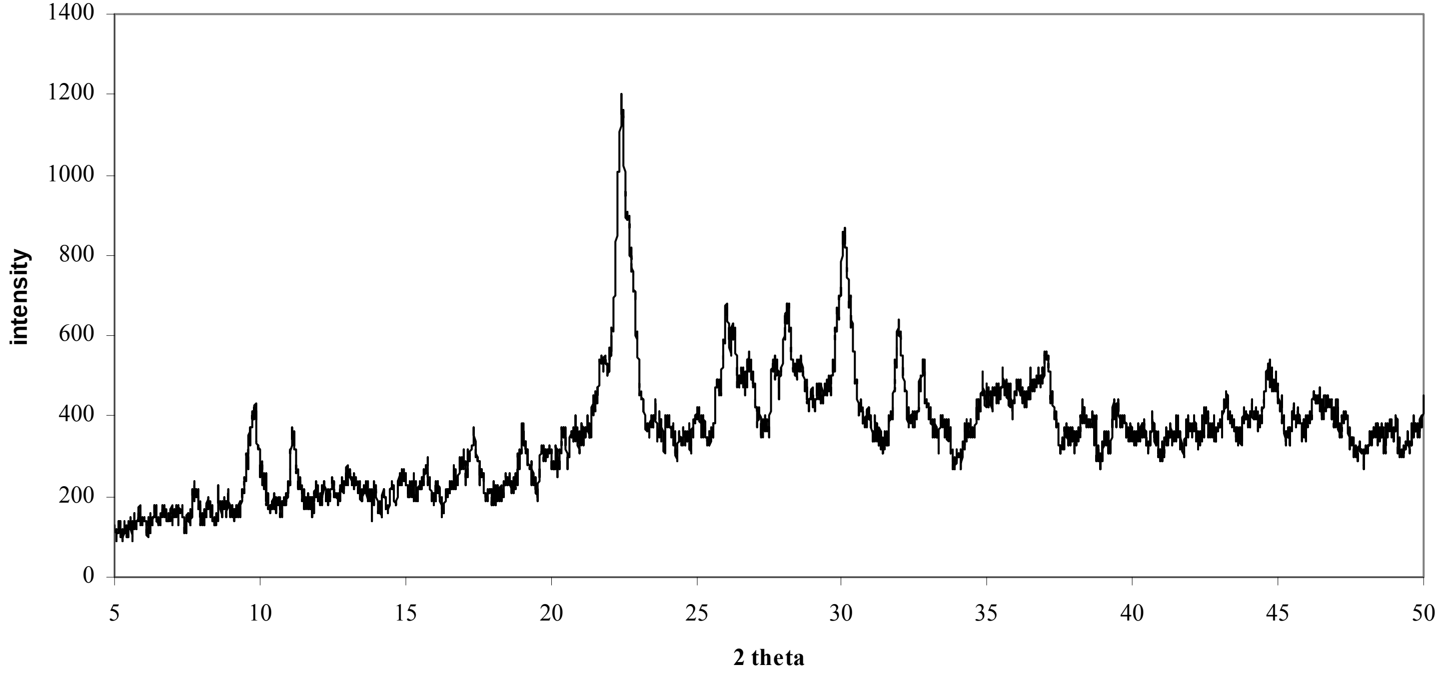

Figure E.2 XRD pattern of CLIG2-1 (Gördes clinoptilolite) which was used as seed crystals and for the preparation of thermally decomposed product

Table E.1 Chemical analysis results of Gördes clinoptilolite from Tufan's thesis (24]

	Wt%	Moles/1 mole Al_2O_3
SiO_2	64.90	10.09
Al_2O_3	10.91	1.00
Fe_2O_3	0.84	0.05
MgO	0.12	0.03
CaO	0.08	0.01
Na_2O	1.17	0.18
K_2O	4.08	0.40
MnO	0.01	0.00
TiO_2	0.03	0.04
H_2O^*	13.71	7.03
Total	95.85	

* This data was obtained by loss on ignition

Table E.2 XRF results of Gördes clinoptilolite (Sample is dried at 105°C)

	Wt%	Moles/1 mole Al_2O_3
SiO_2	72.5	11.18
Al_2O_3	11.0	1.00
Fe_2O_3	1.5	0.08
MgO	1.1	0.25
CaO	2.3	0.38
Na_2O	0.5	0.07
K_2O	3.8	0.37
H_2O^{**}	7.3	7.04
Total	100.0	

** This data is the water content of Gördes clinoptilolite at 105°C. It was obtained from its TGA analysis (24] considering samples were dried at 105°C.

E.2 Chemical Analysis Result and XRD Pattern for CLI-11(Bigadiç Clinoptilolite)

Table E.3 Chemical Analysis Results of CLI 11

	Wt%	Moles/1 mole Al_2O_3
SiO_2	63.98	8.45
Al_2O_3	12.84	1.00
Fe_2O_3	0.62	0.03
MgO	1.17	0.23
CaO	3.46	0.49
Na_2O	0.45	0.06
K_2O	2.90	0.25
MnO	0.00	0.00
TiO_2	0.03	0.03
H_2O	15.38	6.75
Total	100.83	

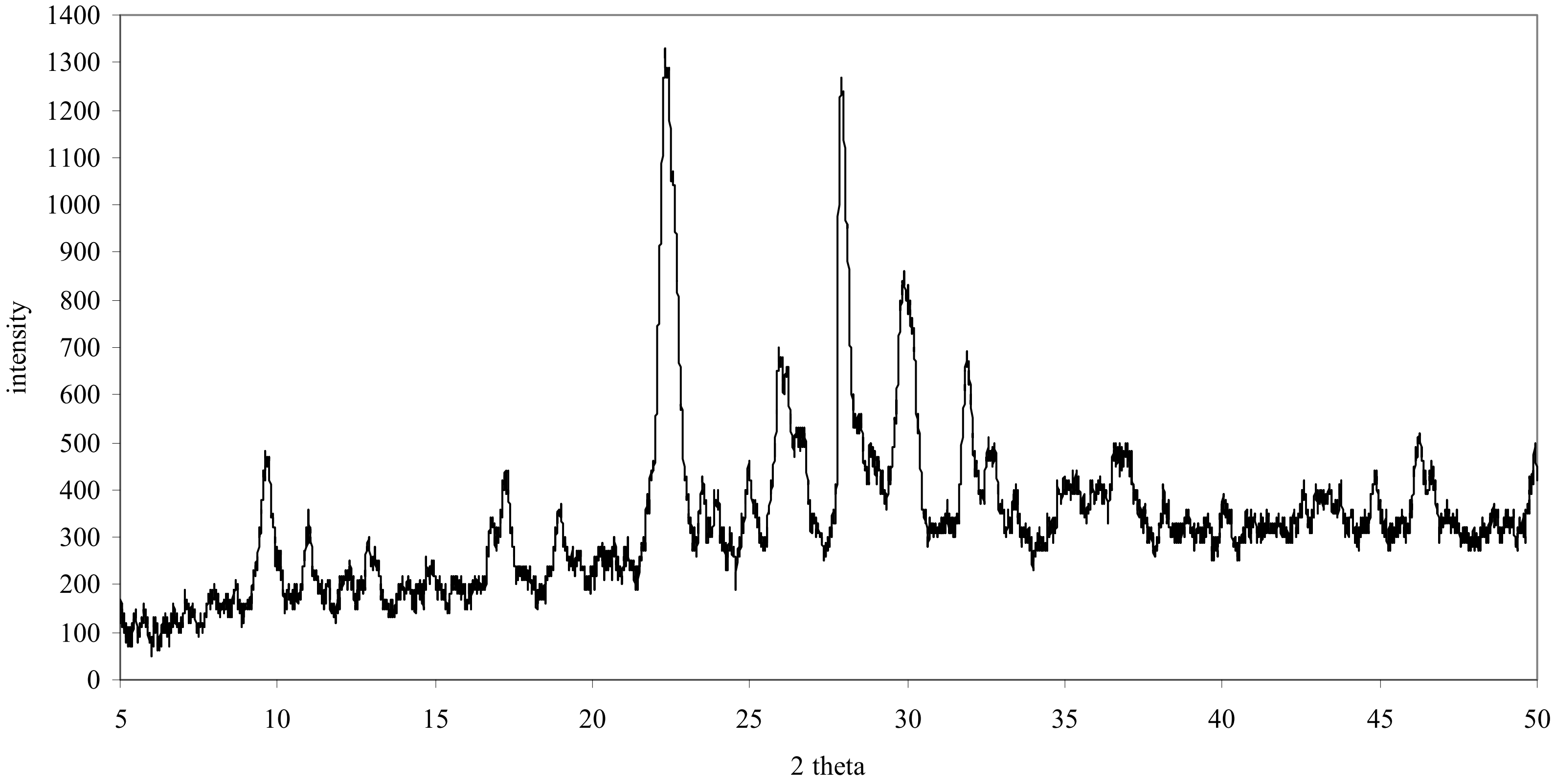

Figure E.3 XRD pattern of CLI-11 (Bigadiç clinoptilolite) which was used for the amorphous clinoptilolite calibration

Appendix F

F.1 XRD Data for Clinoptilolite Mineral from Various References

Table F.1 Peak Listing of Natural Clinoptilolite from Hector, California(2]

Peak No	d-Spacing	Bragg Angle (2θ)	I/I_o
1	9.00	9.82	10
2	7.94	11.13	4
3	6.77	13.07	3
	6.64	13.32	2
	5.91	14.98	1
	5.24	16.91	3
4	5.11	17.34	1
	4.49	19.76	2
	4.48	19.80	2
	4.34	20.45	2
7	3.96	22.43	10
8	3.90	22.78	8
	3.83	23.20	1
	3.73	23.83	1
20	3.55	25.06	2
	3.46	25.73	2
9	3.42	26.03	6
12	3.12	28.59	3
13	3.07	29.06	2
	3.04	29.35	2
14	2.94	30.38	5
	2.87	31.14	1
	2.82	31.70	3
15	2.80	31.93	1
16	2.73	32.78	1
	2.72	32.90	1
	2.68	33.41	1
17	2.44	36.80	1
18	2.42	37.12	1
	2.38	37.77	1

Table F.2 Peak Listing of Natural Clinoptilolite from Szostak's 'Handbook of Molecular Sieves'[8]

Peak no	**d spacing**	**Bragg angle (2θ)**	**I/I_o**	**Peak no**	**d spacing**	**Bragg angle (2θ)**	**I/I_o**
1	8.95	9.87	100	16	2.73	32.78	16
2	7.93	11.15	13		2.67	33.57	4
3	6.78	13.05	9	21	2.52	35.52	6
	5.94	14.90	3		2.48	36.11	3
	5.59	15.84	5		2.46	36.52	3
	5.54	15.98	10	17	2.43	36.85	8
4	5.12	17.30	12	18	2.42	37.09	5
5	4.65	19.07	19		2.32	38.80	2
	4.35	20.40	5		2.09	43.27	3
6	3.98	22.34	61		2.06	44.00	2
7	3.95	22.46	63		2.02	44.92	2
8	3.90	22.75	48	19	1.97	45.93	4
	3.83	23.17	7				
	3.74	23.78	6				
	3.71	23.98	5				
20	3.55	25.03	9				
	3.51	25.33	4				
9	3.42	26.00	18				
	3.39	26.25	12				
10	3.32	26.86	6				
11	3.17	28.13	16				
12	3.12	28.59	15				
13	3.07	29.02	9				
	3.00	29.77	18				
14	2.97	30.05	47				
15	2.79	31.99	16				

Table F.3 Peak Listing of Natural Clinoptilolite from Bigadiç[7]

Peak No	**d-Spacing**	**Bragg Angle (2θ)**	**I/I_o**
1	8.93	9.90	35
2	7.89	11.20	19
3	6.75	13.10	16
	6.65	13.30	10
	5.21	17.00	16
4	5.12	17.30	20
5	4.64	19.11	16
	4.31	20.59	9
7	3.95	22.49	100
8	3.9	22.78	50
	3.83	23.20	15
	3.75	23.71	12
20	3.53	25.21	15
	3.46	25.73	21
9	3.41	26.11	34
	3.15	28.31	30
14	2.96	30.17	45
15	2.78	32.17	28
16	2.73	32.78	14
	2.67	33.53	9
21	2.53	35.45	14

F.2 X-Ray Diffraction Data of Co-existing Phases with Clinoptilolite in the Products

Table F.4 Peak Listing of Natural Mordenite from Aros, Scotland (PDF 06-0239)

d-spacing	Bragg angle	I/Io
13.70	6.45	11
9.10	9.71	31
6.61	13.38	43
6.38	13.87	20
6.10	14.51	26
5.79	15.29	27
5.03	17.62	6
4.87	18.20	13
4.53	19.58	56
4.14	21.45	23
4.00	22.21	72
3.84	23.14	50
3.76	23.64	17
3.62	24.57	9
3.56	24.99	9
3.48	25.58	92
3.39	26.27	85
3.31	26.91	9
3.22	27.68	100
3.10	28.78	20
2.95	30.31	21
2.90	30.85	66
2.74	32.62	11
2.70	33.15	35
2.64	33.94	12
2.56	35.02	50
2.52	35.57	63
2.46	36.42	26
2.44	36.85	26
2.34	38.39	27
2.30	39.15	14
2.75	39.58	14
2.23	40.45	28
2.16	41.74	29
2.12	42.55	15
2.05	44.21	63
2.02	44.86	63
1.99	45.35	64
1.95	46.46	66
1.94	46.89	16
1.92	47.38	33
1.88	48.29	68
1.86	48.79	17
1.85	49.21	17

Table F.5 Peak Listing of Natural Phillipsite from Casal Brunori, Rome (PDF 39-1375)

d-Spacing	**Bragg Angle (2θ)**	**I/I_o**
7.18	12.32	28
7.16	12.35	29
6.42	13.78	8
5.38	16.46	11
5.07	17.48	14
4.94	17.94	17
4.31	20.59	6
4.29	20.69	7
4.13	21.50	28
4.12	21.55	32
4.06	21.87	14
3.27	27.19	36
3.21	27.80	100
3.14	28.44	35
3.13	28.50	34
3.09	28.87	6
2.93	30.49	16
2.76	32.36	23
2.75	32.50	42
2.71	33.00	23
2.70	33.13	42
2.68	33.37	25
2.66	33.69	12

Table F. 6 Peak Listing of Natural Analcime from Knockagh, Country Antrim (PDF 42-1378)

d-Spacing	**Bragg Angle (2θ)**	**I/I_o**
5.85	15.13	18
3.52	25.28	100
2.99	29.86	47
2.92	30.59	12
2.85	31.36	6
2.74	32.65	21
2.55	35.16	16
2.47	36.34	8
2.35	38.27	33
2.25	40.04	7
2.21	40.80	6
2.03	44.60	59
5.85	51.13	18

Table F. 7 Peak Listing of Synthetic Quartz (PDF 33-1161)

d-Spacing	**Bragg Angle (2θ)**	**I/I$_o$**
4.257	20.85	22
3.342	26.65	100
2.457	36.54	8
2.282	39.46	8
2.237	40.28	4
2.127	2.46	6
1.979	45.81	4
1.818	50.14	14
1.802	50.61	1

Table F. 8 Peak Listing of Natural Sanidine (PDF 10-0357)

d-Spacing	**Bragg Angle (2θ)**	**I/I_o**
6.48	13.654	20
5.81	15.248	4
4.118	21.562	25
3.88	22.9	12
3.75	23.7	35
3.6	24.7	4
3.45	25.8	12
3.24	27.5	100
3.21	27.8	40
2.96	30.2	12
2.9	30.8	10
2.76	32.5	6
2.55	35.2	16
2.5	35.9	4
2.41	37.3	4
2.33	38.5	4
2.161	41.8	20

Table F. 9 Peak Listing of Linde L [8]

d-Spacing	Bragg Angle (2θ)	I/I_o
15.8	5.59	100
7.89	11.20	14
7.49	11.81	15
5.98	14.80	25
5.75	15.40	11
4.57	19.41	32
4.39	20.21	13
4.33	20.49	13
3.91	22.72	30
3.78	23.51	13
3.66	24.30	19
3.48	25.58	23
3.26	27.33	14
3.17	28.13	34
3.07	29.06	22
3.02	29.55	15
2.91	30.70	23
2.65	33.79	19
2.62	34.19	8
2.53	35.45	8
2.45	36.65	9
2.42	37.12	11
2.19	41.18	11

Appendix G

G 1 List of Products Synthesized in This Study

ID	Batch code	Seed (wt% of dry material)	T (^{o}C)	t (h)	XRD Results	Clino. Fraction in the solid product(x_c)
OG 1	BC 1	28	~120	~96	amorphous clinoptilolite	0.27
OG 2				~240	clinoptilolite phillipsite	---
OG 3				~528	clinoptilolite phillipsite	---
OG 4	BC 1	28	130	~96	phillipsite clinoptilolite	---
OG 5				~240	phillipsite clinoptilolite	---
OG 6	BC 1	0	130	~240	phillipsite	---
OG 7				~528	phillipsite unidentified phase	---
OG 8	BC 2	28	140	45	phillipsite clinoptilolite	---
OG 9				69	clinoptilolite phillipsite	---
OG 10	BC 2	0	140	66	amorphous phillipsite	---
OG 11				94	amorphous	---
OG 12				41	amorphous phillipsite	---
OG 13				124	amorphous phillipsite	---
OG 14	BC 2	10	140	70	clinoptilolite phillipsite	---
OG 15	BC 3	1	175	19	$Al(OH)_3$	---

ID	Batch code	Seed (wt% of dry material)	T (^{o}C)	t (h)	XRD Results	Clino. Fraction in the solid product(x_c)
OG 16	BC 3	1	175	93	$Al(OH)_3$ clinoptilolite unidentified phase	---
OG 17	BC 3	1	195	135	$Al(OH)_3$ unidentified phase	---
OG 18		10	195	17	amorphous clinoptilolite $Al(OH)_3$	---
OG 19		26	195	39	Gismondine unidentified phase	---
OG 20				92	Gismondine Linde type L unidentified phase	---
OG 21				141	Gismondine Linde type L unidentified phase	---
OG 22	BC 3	3	175	14	amorphous Linde type L	---
OG 23				63	Linde type L Gismondine	---
OG 24				95	Linde type L Gismondine	---
OG 25				141	Linde type L Gismondine	---
OG 26	BC 2	9	140	68	clinoptilolite phillipsite amorphous	---
OG 27		28			clinoptilolite phillipsite amorphous	---
OG 28		80			clinoptilolite amorphous phillipsite	---

ID	Batch code	Seed (wt% of dry material)	T (^oC)	t (h)	XRD Results	Clino. Fraction in the solid product(x_c)
OG 29[1]	BC 2	28	140	68	clinoptilolite	0.86
OG 30[1]	BC 2	28	140	118	clinoptilolite	0.86
OG 31	BC 2-1	28	140	68	clinoptilolite	0.86
OG 32	BC 2-1	28	140	118	clinoptilolite	0.91
OG 33	BC 4	28	140	68	clinoptilolite	0.82
OG 34	BC 4	28	140	118	clinoptilolite	0.88
OG 35	BC 1	0	100	167	Amorphous	---
OG 36	BC 1	28	100	167	Amorphous Clinoptilolite	0.18
OG 37		28	100	336	Amorphous Clinoptilolite	0.18
OG 38		28	100	432	Amorphous Clinoptilolite	0.19
OG 39	BC 1	0	100	432	Amorphous	0
OG 40	BC 1	28	100	1918	Clinoptilolite	0.92
OG 41	BC 1	0	100	1918	Amorphous Phillipsite	---
OG 42	BC 2-1	28	140	21	Amorphous Clinoptilolite	0.17
OG 43		28	140	45	Amorphous Clinoptilolite	0.42
OG 44		28	140	69	Clinoptilolite	0.87
OG 45		28	140	163	Clinoptilolite	0.89
OG 46	BC 5-1	27	140	22	Amorphous Clinoptilolite	0.18

ID	Batch code	Seed (wt% of dry material)	T (^oC)	t (h)	XRD Results	Clino. Fraction in the solid product(x_c)
OG 47	BC 5-1	27	140	46	Clinoptilolite Amorphous	0.58
OG 48		27	140	68	Clinoptilolite	0.75
OG 49		27	140	113	Clinoptilolite Unidentified Phase	0.65
OG 50	BC 5-1	27	140	163	Clinoptilolite Unidentified Phase	0.65
OG 51	BC 3-1	26	140	23	Amorphous Clinoptilolite	0.35
OG 52		26	140	46	Amorphous Clinoptilolite	0.18
OG 53	BC 3-1	26	140	70	Amorphous Clinoptilolite	0.19
OG 54		26	140	118	Clinoptilolite Unidentified phase	0.60
OG 55	BC 2-1	0	140	20	Amorphous	0
OG 56		0	140	45	Amorphous	0
OG 57		0	140	68	Amorphous	0
OG 58		0	140	116	Amorphous	0
OG 59		0	140	163	Amorphous	0
OG 60	BC 1	28	100	648	Clinoptilolite Amorphous	0.59
OG 61		0	100	792	Amorphous	0
OG 62		28	100	1152	Leakage	
OG 63	BC 5-1	27	140	20	Amorphous Clinoptilolite	0.18
OG 64		27	140	38	Amorphous Clinoptilolite	0.32

ID	Batch code	Seed (wt% of dry material)	T (°C)	t (h)	XRD Results	Clino. Fraction in the solid product(x_c)
OG 65	BC 5-1	27	140	49	Clinoptilolite Amorphous	0.77
OG 66		27	140	212	Clinoptilolite Amorphous unidentified phase	0.70
OG 67	BC 5-1	27	140	284	Clinoptilolite Amorphous unidentified phase	0.65
OG 68	BC 2-1	10	140	23	Amorphous Clinoptilolite	0.08
OG 69		10	140	70	Clinoptilolite	0.89
OG 70		10	140	141	Clinoptilolite	1.00
OG 71	BC 1	28	100	1414	Amorphous Clinoptilolite	0.60
OG 72	BC 5-1	10	140	24	Amorphous Clinoptilolite	0.05
OG 73		10	140	48	Amorphous Clinoptilolite	0.18
OG 74		10	140	70	Clinoptilolite	0.78
OG 75		10	140	166	Clinoptilolite	0.79
OG 76	BC 5-1	0	140	42	Phillipsite Unidentified Phase	---
OG 77		0	140	140	Phillipsite Unidentified Phase	---
OG 78		0	140	238	Phillipsite Unidentified Phase	---
OG 79	BC 6-1	10	140	45	Amorphous Clinoptilolite	0.06
OG 80		10	140	75	Amorphous Clinoptilolite	0.10
OG 81		10	140	139	Amorphous Clinoptilolite	0.18
OG 82		10	140	165	Clinoptilolite	0.23

ID	Batch code	Seed (wt% of dry material)	T (^oC)	t (h)	XRD Results	Clino. Fraction in the solid product(x_c)
OG 83	BC 6-1	10	140	262	Clinoptilolite	0.99
OG 84		10	140	309	Clinoptilolite	0.91
OG 85	BC 6-1	10	140	404	Clinoptilolite	0.99
OG 86	BC 7-1	10	140	74	Amorphous Clinoptilolite	0.10
OG 87	BC 7-1	10	140	187	Clinoptilolite	0.80
OG 88		10	140	259	Clinoptilolite	0.93
OG 89	BC 8-1	10	140	25	Amorphous Clinoptilolite	0.09
OG 90		10	140	46	Amorphous Clinoptilolite	0.08
OG 91		10	140	93	Amorphous Clinoptilolite	0.10
OG 92		10	140	261	Amorphous Clinoptilolite	0.19
OG 93		10	140	334	Amorphous Clinoptilolite	0.12
OG 94[2]	BC 5-1	10	140	96	Sanidine Clinoptilolite Quartz	---
OG 95[2]		10	140	124	Sanidine Clinoptilolite Quartz	---
OG 96[2]		10	140	188	Sanidine Clinoptilolite Quartz	---
OG 97[2]		10	140	214	Sanidine Clinoptilolite Quartz	---
OG 98[2]		10	140	239	Sanidine Clinoptilolite Quartz	---
OG 99	BC 7-1	10	140	100	Amorphous Clinoptilolite	0.10

ID	Batch code	Seed (wt% of dry material)	T (^oC)	t (h)	XRD Results	Clino. Fraction in the solid product(x_c)
OG 100	BC 7-1	10	140	188	Clinoptilolite	0.86
OG 101		10	140	264	Clinoptilolite	0.85
OG 102	BC 9-1	10	140	48	Amorphous Clinoptilolite	0.04
OG 103		10	140	70	Amorphous Clinoptilolite	0.07
OG 104	BC 9-1	10	140	140	Amorphous Clinoptilolite	0.04
OG 105		10	140	336	Clinoptilolite Amorphous	0.47
OG 106		10	140	474	Clinoptilolite	0.98
OG 107[7]	BC 5-1	10	140	24	Amorphous Sanidine	---
OG 108[7]		10	140	66	Amorphous Sanidine	---
OG 109[7]		10	140	138	Sanidine	---
OG 110[7]		10	140	234	Sanidine	---
OG 111	BC 2-1	10	175	42	Mordenite Amorphous Clinoptilolite	---
OG 112		10	175	115	Mordenite	---
OG 113		10	175	163	Mordenite	---
OG 114[3]	BC 2-1	No extra seed addition (Decomposed product includes 14% clinoptilolite)	140	45	Amorphous Sanidine Clinoptilolite	---
OG 115[3]			140	117	Amorphous Sanidine Clinoptilolite	---
OG 116[3]			140	141	Sanidine Clinoptilolite	---
OG 117[3]			140	264	Sanidine Clinoptilolite	---

ID	Batch code	Seed (wt% of dry material)	T (°C)	t (h)	XRD Results	Clino. Fraction in the solid product(x_c)
OG 118	BC 6-1	10	175	45	Mordenite Amorphous Clinoptilolite	---
OG 119		10	175	117	Mordenite Amorphous	---
OG 120	BC 6-1	10	175	165	Mordenite	---
OG 121	BC 10-1	10	140	20	Amorphous Clinoptilolite	0.09
OG 122	BC 10-1	10	140	90	Amorphous Clinoptilolite	0.14
OG 123		10	140	139	Amorphous Clinoptilolite	0.08
OG 124		10	140	235	Amorphous Mazzite Clinoptilolite	---
OG 125[8]	BC 5-1	10	140	118	Phillipsite Clinoptilolite	---
OG 126		10	140	118	Phillipsite Clinoptilolite	---
OG 127[8]		10	140	118	Phillipsite Clinoptilolite	---
OG 128[4]	BC 2-1	10	140	119	Mordenite Clinoptilolite	---
OG 129[5]	BC 2-1	10	140	119	Clinoptilolite	0.94
OG 130[6]	BC 2-1	10	140	119	Clinoptilolite	1.03
OG 131	BC 12-1	10	140	144	Clinoptilolite Phillipsite	---
OG 132	BC 13-1	10	140	144	Clinoptilolite	1.00
OG 133	BC 14-1	10	140	144	Leakage	
OG 134	BC 15-1	10	140	144	Phillipsite	---

ID	Batch code	Seed (wt% of dry material)	T (^oC)	t (h)	XRD Results	Clino. Fraction in the solid product(x_c)
OG 135	BC 16-1	10	140	144	Analcime	---
OG 136	BC 17-1	10	140	144	Clinoptilolite	0.98
OG 137	BC 15-1	10	140	Leakage		
OG 138	BC 5-1	10	175	22	Amorphous Mordenite Clinoptilolite	---
OG 139	BC 5-1	10	175	49	Mordenite	---
OG 140	BC 5-1	10	175	165	Mordenite	---
OG 141	BC 3-1	10	140	43	Amorphous	0
OG 142		10	140	91	Amorphous Clinoptilolite Linde L	16
OG 143		10	140	115	Linde L Clinoptilolite Amorphous	5
OG 144		10	140	Leakage		
OG 145		10	140	Leakage		
OG 146	BC 18-1	10	140	Leakage		
OG 148	BC 19-1	10	140	166	Sanidine Clinoptilolite Unidentified Phase	---
OG 149		10	140	196	Sanidine Clinoptilolite	---
OG 150	BC 20-1	10	140	90	Amorphous	0

ID	Batch code	Seed (wt% of dry material)	T (^{o}C)	t (h)	XRD Results	
OG 151	BC 20-1	10	140	166	Clinoptilolite	0.88
OG 152	BC 5-1	10	120	94	Amorphous Clinoptilolite	0.25
OG 153		10	120	166	Amorphous Clinoptilolite	0.20
OG 154		10	120	266	Amorphous Clinoptilolite	0.44
OG 155		10	120	578	Clinoptilolite Amorphous	0.62
OG 156	BC 20-1	10	140	166	Clinoptilolite	0.87
OG 157		10	140	238	Clinoptilolite	0.87
OG 158	BC 19-1	10	140	94	Sanidine Clinoptilolite	---
OG 159		10	140	166	Sanidine Clinoptilolite	---
OG 161	BC 5-1	10	160	22	Clinoptilolite	0.87
OG 162		10	160	46	Clinoptilolite	0.89
OG 163		10	160	72	Sanidine Clinoptilolite	---
OG 164		10	160	164	Sanidine Clinoptilolite	---

1- Synthesis mixture was stirred for 22 h before transferred into autoclaves
2- Completely decomposed clinoptilolite was used as raw material
3- Partly decomposed clinoptilolite was used as raw material
4- Al chips were used as Al source.
5- Al powder dissolved in NaOH solution was used as Al source.
6- Al chips dissolved in NaOH solution was used as Al source.
7- Completely decomposed product was used but synthesis mixture was stirred for 24 h before hydrothermal synthesis
8- Alkali fusion products of clinoptilolite was used as raw material