Cation Exchange in Zeolites, Structure Modification by Using a Microwave

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By

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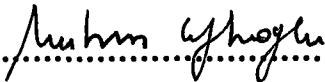
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ABSTRACT

In this research, characterization and modification of clinoptilolite minerals from different deposits have been studied to determine its utility for different applications.

Clinoptilolite minerals obtained from the source located in Western Anatolian were characterized by using Fourier Transform Infrared Spectroscopy (FTIR) to determine the structural properties. The FTIR spectra of the samples showed the characteristic vibrations of the clinoptilolite framework. Thermal properties were determined using Differential Thermal Analyzer (DTA), Thermal Gravimetric Analyzer (TGA), and Differential Scanning Calorimetry (DSC). The analysis showed that the structure of the samples were stable up to 650 ^{0}C and due to the Fe_2O_3 present in the tuff, phase inversion was observed. Accelerated Surface Area and Porosimeter (ASAP 2010) used to determine the adsorption-related properties using N_2 and Ar adsorption isotherms. The samples showed different adsorption behaviour toward each gas. The pore size distribution of clinoptilolite samples showed that they have mesaporous structure.

The clinoptilolite was modified by ion exchange using 1N NaCl salt solution in waterbath, and in microwave maintained at 80 ^{0}C for 10 min, 60 min and 120 min. The efficiency of each method on ion exchange was compared. The Na^+ amount in the zeolite was found to be 2.25 and 3.24 % by weight after 2 hours of exchange in waterbath and microwave, respectively. The results showed that microwave method used for modification was more efficient.

ÖZ

Bu araştırmada değişik yataklardan alınmış klinoptilolit minerali, çeşitli uygulama alanlarında kullanılabilmesinin belirlenmesi için karakterize ve modifiye edildi.

Batı Anadolu'daki yataklardan alınan klinoptilolit mineralinin yapısal özelliklerinin FTIR Spectrometresi kullanılarak belirlendi.FTIR Spectralarından alınan sonuçlara göre bütün klinoptilolit örnekler karakteristik klinoptilolit adsorpsiyon bandlarını gösterdi. Klinoptilolit mineralinin ısısal özellikleri ısısal analiz sistemleri kullanılarak belirlendi. Analizler çalışılan örneklerin 650 ^{0}C'ye kadar yapılarında bir değişiklik olmadığı, yatakta mevcut olan Fe_2O_3 'ten kaynaklanan faz değişimi olduğu gözlenmiştir. Yüzey alan ve gözenek tayin cihazı ile klinoptilolitin adsorpsiyona bağlı özellikleri N_2 ve Ar adsorpsiyonu ile belirlendi. Örnekler kullanılan gazlara göre fakli adsorpsiyon davranışı göstermiştir. Klinoptilolit örneklerinin mesaporous (ortaboy gözenek) oldukları bulunmuştur.

Daha sonra Bigadiç minerali iyon değişim yöntemi ile modifiye edildi. İyon değişimi, 1N NaCl cözeltisi ile sıcaklığı 80 ^{0}C ye sabitlenmiş su banyosu ve mikrodalgada 10, 60 ve 120 dak. yapıldı. Mikrodalga ve subanyosu ile iyon değişiminin modifikasyona etkileri yapılan analizler sonucunda karşılaştırıldı. İki saat sonunda mikrodalga ve subayosunda yapılan katyon değişimi sonunda zeolit içindeki Na^+ yüzdesi sırası ile 3.24%, 2.25 % olarak bulunmuştur. Bu sonuçlar mikrodalganın daha etkin olduğu göstermiştir.

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Chapter 1

INTRODUCTION

Zeolites are crystalline aluminosilicates of group IA and IIA elements such as sodium, potassium, barium, magnesium and calcium. The physical structure is porous with interconnected cavities in which metal cations and water molecules are present. The fundamental building unit of the zeolite is a tetrahedron of four oxygen atoms surrounding a relatively small silicon or aluminium atom. They have been known since the eighteenth century but they remained as a curiosity for scientists and collector until their unique physical and chemical properties determined by many researches. These minerals are recognised as some of the most important silicates in volcanic rocks. These are mostly formed by reaction of pore-waters with volcanic glass and also by alteration of pre-existing feldspars, feldspathoids, poorly crystalline clays and biogenic silica. Because of their ion-exchange, adsorption and molecular sieve properties, as well as large deposits existing in different parts of the world many researches have focused on different applications of zeolites among which wastewater treatment, stack-gas clean-up, natural gas purification, petroleum production, agricultural and aquaculture are just few examples.

Ion exchange property of zeolite has been studied for many years, it is mostly used to modify the zeolite properties in order to prepare new types of conductors, semi-conductors, visual display units, dielectric gas sensor and catalyst. Both the synthetic and natural zeolites widely used as ion exchanger for these purposes but often limited to countries having their own deposits.

Clinoptilolite is the widespread natural zeolite mineral found in nature with high purity. Schaller considered this kind of zeolite a new mineral in 1923. In 1934, Hey and Bannister showed that clinoptilolite considered to rich silicon heulandite. This mineral has high thermal resistance. Heating up to 750 °C does not modify its original structure. This feature, according to Mumpton, is due to the high silicon concentration. Mason and

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Sand state that the thermal resistance is due to its main exchangeable cations. (Alietti, 1972) Clinotilolite belongs a structural group 7 and has a monoclinic symmetry and a Si/Al ratio between 4.25 and 5.25. Its structure is presented by a series of interconnected channels.

The purpose of this research is to examine the clinoptilolite from different deposits in Western Anatolian that is available as many sedimentary deposits. The present work consists of two parts; the first part includes the characterization of the clinotptiloite using different methods, the second part includes it structure modification by ion exchange using microwave and waterbath.

In chapter two of the present work, general information about zeolites including its structure, types and uses are discussed. The methods and the instruments that are used to characterize the clinoptilolite are given in the following chapter. In chapter four the modification method are described. Finally, the experimental work and the results of characterization and modification are examined.

Chapter 2

ZEOLITES

2.1 History of Zeolites

Zeolites form a family of minerals, which have been known since the 18th century but they remained a curiosity for scientist until their unique physico-chemical properties attracted the attention of many researches. The history of zeolites begins in 1756 with the discovery of first zeolite mineral stilbite, by the Swedish mineralogist Cronsdent. He recognised zeolites as a new class of mineral consisting of hydrated aluminosilicate of the alkali and alkaline earths. 1777 Fontana described the phenomenon of adsorption on charcoal. In 1840 Damour observed the crystal of zeolites could be reversibility dehydrated with no apparent change in their transparency or morphology. The history followed by the discovery of some important properties of zeolite. Way and Thompson in 1850 clarified the nature of ion exchange in soil [5]. In 1857 Damour demonstrated the hydration-dehydration properties [32]. In 1858 Eichorn demonstrated that the zeolite minerals chabazite and natrolite were capable of exchanging Na^+ and Ca^{++} cations from dilute solutions. In the intervening years, extensive studies both on synthetic zeolites have been demonstrated [42].

Grandjean in 1909 observed that dehydrated chabazite adsorbs ammonia, air, hydrogen and other molecules. In 1925 Wiegel and Steihoff reported the first molecular sieve effect. The Leonard described the first use of X-Ray diffraction for identification in mineral synthesis. The first structures of zeolites were determined in 1930 by Taylor & Pauling. In 1932 Mc.Bain established the term 'Molecular Sieve' to define porous solid materials that act as sieves on a molecular scale and still this term is used. By the mid-1930s the ion exchange, adsorption, molecular sieve and structural properties of zeolite minerals as well as a number of reported synthesis of zeolite was described in literature [5]. Barree's work in 1938, Samanish's in 1929, Samanishi and Hemmi's in 1934 on the zeolite adsorption and molecular sieve phenomena were carried out on crystals from basalt vugs. Soon zeolite included developing processes based on the

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natural materials. In the late 1940s Linde Division of Union Carbide Corporation in Tonawanda, instituted a program of zeolite synthesis under the direction of M. Milton and D. Breck to produce chabazite for air separation and other adsorption and molecular sieve application [32].

Although, zeolites have attractive properties they did not find significant use commercially until the late 1960s. The first industrial production of the zeolites dates back to 1954 when Union Carbide Cooperation first commercialised the Linde molecular sieve a new class of industrial materials for separation and purification proceess. In 1959 a zeolite Y-based catalyst was marketed by Carbide as an isomerization catalyst. The use of zeolites as catalyst was followed by the introduction of zeolite X as a cracking catalyst in 1962 by Mobil Oil Company. In 1969 Grace described the modification chemistry based on steaming zeolite Y to form an 'ultra-stable' zeolite Y. In 1967 and 1969 Mobil oil reported the synthesis of the high silica zeolites beta and ZSM5. In 1974 Henkel introduced zeolite A in detergents as a replacement for the environmental suspect phosphates. In 1977 Union Carbide introduced zeolites for ion-exchange separations. In the 1980s there has been extensive work carried out on the synthesis and applications of ZSM5 and a growing number of other members of the high silica zeolite family. The 80's saw major developments in secondary synthesis and modification chemistry of zeolites [5].

At present time, there are number of other new applications of zeolite in various stages of developments. The growing knowledge of their properties together with the growing needs for many industrial applications the zeolite promise an exciting future in the developing industry.

2.2 Structure and Fundamental Structural Units of Zeolites

Zeolites are porous crystalline, hydrated alumina silicates of group I and II elements, in particular with sodium, potassium, and barium. Structurally the zeolite framework consists of an assemblage of SiO_4 and AlO_4 tetrahedra, joined together in various regular arrangements through shared oxygen atoms, to form an open crystal lattice containing pores of molecular dimensions into which quest molecules can penetrate. The zeolite framework is open, contain channels and interconnected voids filled with exchangeable cations and the water molecule [5].

The structural formula of a zeolite is best expressed for the crystallographic unit cell as:

$$M_{(xn)} \cdot ((AlO_2)_x (SiO_2)y) \cdot wH2O$$
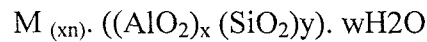
M is the cation valance n, w is the number of water molecules and the ratio y/x (that is Si/Al) usually has the values of 1-5 depending upon the structure. The sum (x+y) is the total number of tetrahedra in the unit cell. The portion within the parenthesis represents the framework composition [8]. The fundamental building unit of zeolite is given in Figure1.
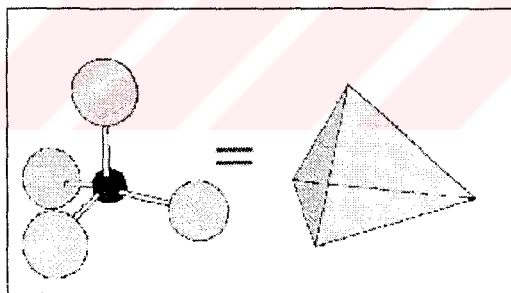
Figure 1: Representation of SiO_4^{-4} or AlO_4^{-5} tetrahedra

As stated earlier all zeolites have framework three-dimensional structures constructed by joining SiO_4^{4-} or AlO_4^{5-} coordination polyhedra. By definition these tetrahedra are assembled together such that the oxygen at each tetrahedra corner is shared within that identical tetrahedra (Si or Al) [10]. These tetrahedra come together to form the 3D structure as shown in Figure 2. Since the positive charge of an silicon atom

is higher than an aluminium atom the net charge on the each site of an aluminium tetrahedron is negative and it is balanced by one of the exchangeable cations present in the framework [4].
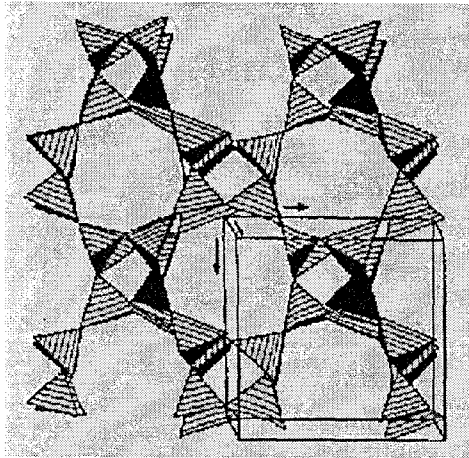
Figure 2: Tetrahedra linked together to create a three- dimensional structure

The variety of natural zeolite types results from differences in the way in which the tetrahedra may link in space in one, two or three dimensions; and from the type of other ions that substitute within the interstices. The tetrahedra of oxygen atoms are arranged in four, five, six, and eight member rings commonly called secondary building unit (SBU), which are combined to form the channels and cavities of the various zeolites given in Figure 3 [5]. The nature of the void spaces and interconnecting channels in dehydrated zeolite is important in determining the physical and chemical properties. The channels in natural zeolites contain water that make up the 10-25 % of their weight. The adsorbed water may be driven-off by heating under vacuum at several hundred °C. The percentage of water may be removed from a zeolite by this procedure is a good measure of its adsorption capacity, since the void left by the water molecules will be available for the adsorption of other molecules.
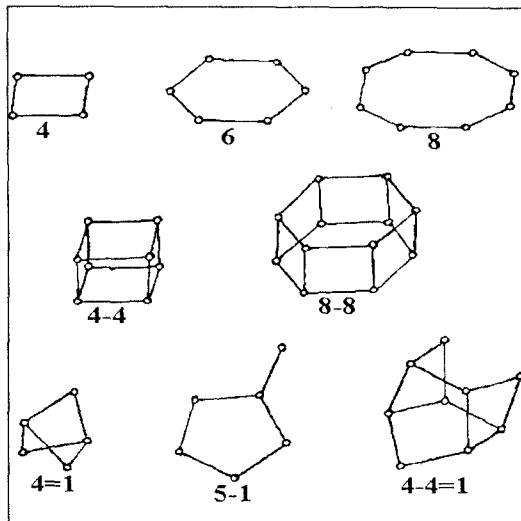
Figure 3: The secondary building units in zeolite framework

Single four ring, single six ring, single eight ring, and double four ring,

double eight ring, complex 5-1 complex 4-4-1

2.3 Properties of Zeolites

The following are some of the important properties of zeolites that make them an important material compared to other crystalline inorganic oxide materials. [5]

i. Zeolites have microporous character with uniform pore dimensions.

ii. Zeolites have molecular sieve property.

iii. Zeolites have ion-exchange property.

iv. Zeolites are used as catalysts.

v. Zeolites have high thermal stability

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Table 1: Zeolite Types in Commercial Application

Zeolite Minerals	Synthetic Zeolites
Clinoptiloite	A & X (Na, K, Ca forms)0
Mordenite	Y(Na, Ca, NH_4, rare earth forms)
Chabazite	L (K, NH_4 forms)
Eroinite	Omega & Zeolon, Mordenite
	(Na, H forms)
Phillipsite	ZSM-5 (Various forms) and etc...

2.4 Natural Zeolites

Zeolite minerals are recognised as some of the most important authigenic silicates in altered pyroclastic and volcaniclastic rocks. These are mostly formed by reaction of porewaters with volcanic glass and also by alteration of pre-exisitng feldspors, feldpathoids, poorly crystalline clays, and biogenic silica [37].

A natural zeolite is framework of alumina-silicate whose structure contains channels filled with water and exchangeable cations where ion exchange is possible at most 100 °C.

The general formula for the natural zeolite is:

(Li,Na,K)a (Mg,Ca,Sr,Ba)$_d$ [Al (a+2d) Si (n-(a+2d) O (2n)] mH_2O
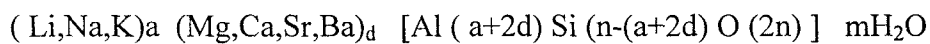
There are many natural zeolite sources available in Turkey and most of the encountered types are clinoptilolite, analism as indicated in Table 2 [36].

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Table 2: Natural Zeolite Sources Available in Turkey

Balikesir, Bigadic	Clinoptilolite
Emet, Yukari Yoncaağaç	Clinoptilolite
Izmir Urla	Clinoptilolite
Kapodokya Yöresi (Tuzköy-Karain)	Clinoptilolite
Gördes	Clinoptilolite
Bahçecik,, Gülpazari, Göynük	Analsim
Polatli, Mülk, Oglakçi, Ayas	Analsim
Nalihan, Çayirhan, Sabanözü	Analsim
Kalecik, Çandar, Sabanözu,Hasayar	Analsim

2.5 Clinoptilolite

Clinoptilolite, silica rich zeolite, is a member of a heulandite group of natural zeolite. It is iso-structural with the zeolite heulandite, which it differs in having higher Si/Al and monovalent/divalent cation ratios. The higher thermal stability of clinoptilolite compared with heulandite was obtained in terms of an elevated Si/Al ratio. The Si/Al ratio is between 4.25-5.25 for clinoptilolite and 2.7-4 for heulandite. Heulandite transforms into other phase at about 230 °C and becomes noncrystalline at about 350 °C. Clinoptilolite survives its crystal structure up to about 700 °C. [15]

Clinoptiloilte mineral is colourless. Some may be colored as brick red, white due to the presence of finely oxides of iron or similar impurities. It has glassy lustre or silky luster. The density of clinoptilolite range between 1.7 and 2.3 g/cc [8]. It has uniform and regular pore size. The composition, purity and property change among the deposits.

According to literature the structure of clinoptilolite consists of a two dimensional system of the three types of channels; two parallel channels, channel A (10 member ring), channel B(8 member ring) and they are perpendicularly intersected by channel C (8 member ring) with sizes 4.4*7.2 $A°$, 4.1*4.7 $A°$ and 4.0*5.4 $A°$, respectively. The c-axis projection of the clinoptilolite structure is given in Figure 4 [46].
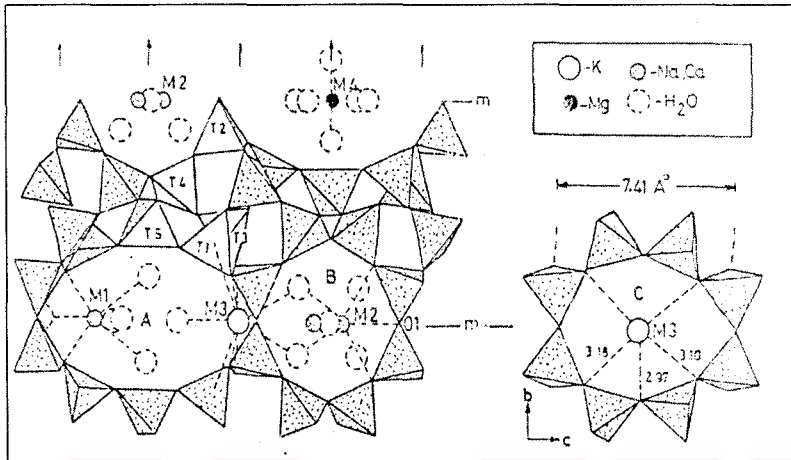
Figure 4: The main cation positions in clinoptilolite

M(1), located in channel A, coordinated with two framework oxygen atoms and five water molecules. One of these molecules may not be directly associated to M(1), giving pseudo-octahedral system. Ca+2 and preferably Na^+ occupy this site.

M(2), is situated in channel B, coordinated with three framework oxygen atoms and five water molecules. M(2) is occupied by Na^+ and preferably by Ca^{+2}.

M(3), in channel C, coordinated by six framework oxygen atoms and three water molecules. This site is occupied by K^+ and preferably by Ba^{+2}. Because this position is very close to M(1) a simultaneous occupancy of both sites is not possible.

M(4), which is located in channel A like M(1), but a center of inversion. Six water molecules achieve its octahedral coordination and occupied by Mg^{+2} [3].

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2.6 Application Areas of Zeolites

Since their introduction as a new class of commercial adsorbent and mineral in 1954, molecular sieve zeolites have grown into industry and have lead to the creation of a new branch of chemical technology. Both the natural and synthetic form zeolites are used as adsorbent and desiccant in drying and gas purification systems. They have greatly commercialised in the hydrocarbon-processing field and used as catalysts in synfuel production, petroleum refining and petrochemical industries. Besides their general common uses recently few other practical uses of zeolites as ion exchangers are emerged. But it is commonly known that not all zeolites can do all things. For example clinoptilolite will react differently in systems depending on its exact elemental composition, purity, porosity, hardness and other extensive properties of the rock. Similarly, even though a given zeolite possess attractive properties for a given application, it may not be the best economic choice for the application, compared with some other natural or synthetic zeolites [29].

The most important recent uses of zeolites as ion exchangers:
- .Water/Waste water treatment
  - Ammonia & Heavy metal Removal from Wastewater.
  - Treatment of Radioactive Wastes.
- Detergent Industry
- Soil conditioning & related uses.
- Animal feed supplements

S.K. Ouki et al. studied the potential use of natural zeolite in Pollution Control and recovery of metal. What they conclude is the usefulness of natural zeolites for pollution control applications depends primarily on their ion exchange capabilities and their porous, 3D framework structure [21].

Zeolites are widely used as ion exchangers in wastewater treatment for the removal of ammonium ions, heavy metals and radioactive wastes. Mercer et al. found that clinoptilolite was the most promising ion-exchanger for the ammonium removal from wastewater. In many regions of the world where clinoptilolite, mordenite, phillipsite & chabazite are available as a cheap mineral, they have been much used for the processes in wastewater treatment. Among theses clinoptilolite is the most often used natural zeolite mineral for this purpose [2,30]. Hazard of lead in drinking water and soils is obvious and it should be removed before it is taken in by humans and animals. Studies confirm the ability of synthetic zeolite A to take up this element from water and soil. In Russia zeolite is being used in gold-processing plant as cation exchange filter to remove gold from wash and wastewater [10].

When spent nuclear fuel elements are removed from a nuclear reactor they are stored under water in ponds. Fission products (especially radioisotopes Cs & Sr) build-up in pond water during this storage period. This contaminated pond water is the main source of medium-level radioactive waste and must be decontaminated. Zeolites have been used for this and related purposes by the nuclear industry for many years [10]. The earliest recorded use of clinoptilolite for this purpose was in 1960 by Ames. He used minerals from Hector deposit to selectively remove Cs and Sr from low-level radioactive wastewater created by nuclear reactors [32]. Additionally incorporation of clinoptilolite into diet of sheep grazing on grass contaminated by Chernobyl accident has reduced the level of Cs uptake into the sheep [10].

Growing awareness of the environmental damage created by the use of polyphosphates in detergent industry caused a search of less hazardous replacements in the recent years. The function of the polyphosphate was as to build up the cleaning efficiency of detergents primarily by removing Ca^{+2} and Mg^{+2} ions from washing water to prevent their precipitation by surfactant molecules. The use of zeolites as builders was suggested in the 1970s and since then it has been demonstrated that they can effectively carry out the water softening exercise needed for successful laundering [10].

Clinoptilolite and mordenite is used to control soil p^H, moisture content and manure malodour. The control of p^H is related to the ability of the zeolite to function as a slow release agent to improve nitrogen retention in the soil. Generally 5-10% by weight of clinoptilolite is being used in horticultural applications. Most of the studies have promising results that; plants grow larger and have more extensive root systems and need only the addition of water for months [8].

Since 1970s, after the idea of producing bigger meat animals, clinoptilolite about 3-5% is normally added to the diets of chickens, pigs, cattle, sheep and rabbits. For example studies in the USA, Australia, Cuba and etc has confirmed generally that pigs taking in clinoptilolite show beneficial weight gains and are less subject to diseases than pigs fed by normal diets [8].

Additionally, zeolites are being used in odour control such as; in medical treatment rooms, truck cabs, ashtrays and toilets [32].

Chapter 3

CHARACTERIZATION OF ZEOLITE

Before a zeolite can be used for a certain application it's necessary to characterize the zeolite, to see if it has the desired properties for that applications. If not, another synthesis method should be used or the zeolite must be modified, to meet the specifications. Zeolite synthesis, modification, characterisation and application are strongly related to each other [5].

In the determination of some important characteristic properties of zeolites such as; structural, thermal and adsorption related properties various characterisation techniques are available. In determination of structural, thermal and adsorption-related properties, XRD and Fourier transform Infra-red (FTIR), thermal analysis (TGA, DTA, DSC) and gravimetric or volumetric adsorption systems can be used, respectively.

3.1 Structural Properties

The X-Ray Powder Diffraction analysis is the main method of investigation of zeolite containing rocks and is used to identify the crystalline phase of zeolite. Method is based on the fact that every crystalline material has its own characteristic X-Ray diffraction pattern. The intensity of the diffraction peaks can be used to determine the crystallinity of the sample. For that purpose the intensity of the particular peak (or peaks) is compared with the intensity of the same peak of a standard sample [5].

Ülkü S., (1984) had studied the possible utilization of natural Turkish zeolite in water treatment. The zeolites tested were taken from Bigadiç-Balikesir. The X-Ray Powder Diffraction method was applied to identify the crystalline phase and the chemical analysis of the same zeolite was performed [47].

IR spectroscopy has been widely used for studying the structure and properties of materials. IR spectrum gives information about the presence of the impurities, organic and inorganic materials in the zeolite structure. The fundamental vibrations of the framework of a zeolite have been studied in literature.

According to Breck, IR spectra can be divided into two classes. The first class of vibrations arises due to internal vibrations of the TO_4 tetrahedron, which is the primary unit of structure, and is not sensitive to other structural units. The second class of vibrations is related to the linkages between tetrahedra. The intense and adsorption characteristics of clinoptilolite are given in Table 3 [8].

Table 3 : Clinoptilolite IR Assignments (Breck.1974)

CLASS	VIBRATION	
Internal Tetrahedra	• Asymmetry Stretch [O-Si(Al)-O stretching]	$1250 \ cm^{-1}$-950 cm^{-1}
	• Symmetry Stretch	$750 \ cm^{-1}$- 650 cm^{-1}
	• T-O Double Ring	$500 \ cm^{-1}$- 420 cm^{-1}
External Linkages	• T-O Double Ring	$650 \ cm^{-1}$- 500 cm^{-1}
	• Pore Opening	$420 \ cm^{-1}$- 300 cm^{-1}
	• Symmetry Stretch	$750 \ cm^{-1}$- 820 cm^{-1}
	• Asymmetry Stretch	$1150 \ cm^{-1}$-1050 cm^{-1}
Additional	• H bonded H_2O, H-O stretching	$3400 \ cm^{-1}$
	• Isolated OH Stretching	$3700 \ cm^{-1}$

Valentina N. et al., (1995) studied the quantitative determination of the heulandite and clinoptilolite content of zeolitic tuffs by IR spectroscopy. All zeolites appear to exhibit a typical IR pattern, and are given in Figure 5 [14].
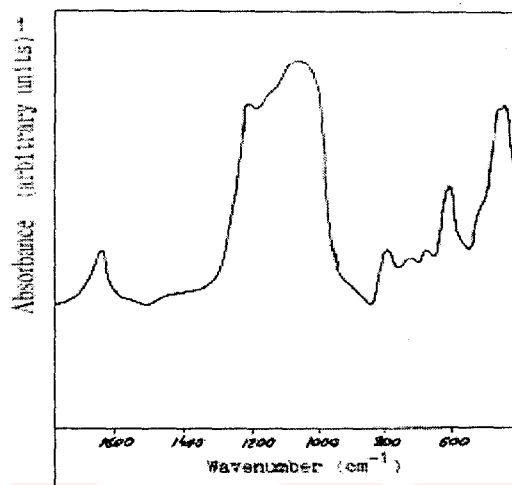
Figure 5: IR Spectrum of Clinoptilolite (Valentina, 1995)

3.2 Adsorption Related Properties (Surface Area, Pore Volume, Micropore Surface Area and Pore Size Distribution)

Physical adsorption measurements are widely used to determine the adsorption characteristics such as; surface area, pore volume and pore size distribution.

The first step in the presentation of the adsorption isotherm is the identification of the isotherm type and hence the natures of the adsorption process. In this way it is possible to obtain information about the type or pore structure of the adsorbent and this is the most commonly used computational procedure for quantitative evaluation of the isotherm. The pysisorption isotherms are generally in six forms and presented in Figure 6 [48].

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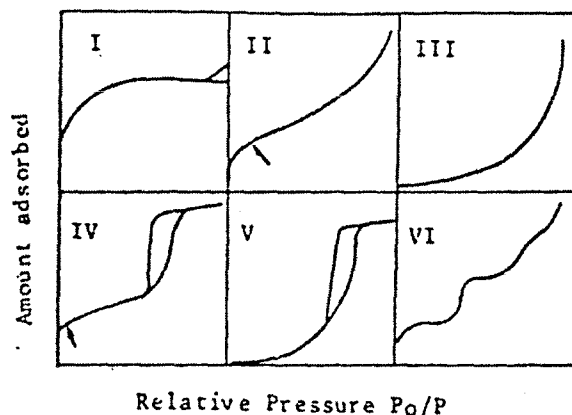
Figure 6: Types Isotherms

Type I is characteristic of adsorbent having extremely small pores and external surfaces. (e.g. activated carbons, molecular sieve alumina and certain porous oxides) Type II isotherm is inductive of either non-porous or macroporous adsorbent. It represents the unrestricted monolayer - multilayer adsorption. The inflection point on the isotherm often taken to indicate the stage at which monolayer coverage is complete and multilayer adsorption about to begin. Type III isotherm represents an uncommon case where adsorbate-adsorbent interactions play an important role. Type IV isotherm is the characteristic features of the hysteresis loop. This type of isotherm attributed to monolayer-multilayer adsorption since it follows the same path as the corresponding part of a type II isotherm. Type V isotherm is related to the type III isotherm where adsorbent-adsorbate interaction is weak, but it is obtained with certain porous adsorbents. Type VI isotherm, represents stepwise multilayer adsorption with non-porous solid. [38,47]

As mentioned above, adsorption related properties of the zeolite samples were derived from N_2 and Ar adsorption carried out at a cryogenic temperature either LN_2 or LAr at their boiling temperatures of 77 K and 87 K, respectively. A contraction, of the channels by chilling to low temperatures damps vibrations of the atoms, shrinks the effective diameter of the apertures and cuts down the kinetic energy of gas molecules. Therefore, for specific gases a sharp drop of the

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diffusion rate occurs at distinct critical temperatures. Such specific effects on adsorption are illustrated in Figure 7 for Na-Zeolite A to show the behaviour of nitrogen.
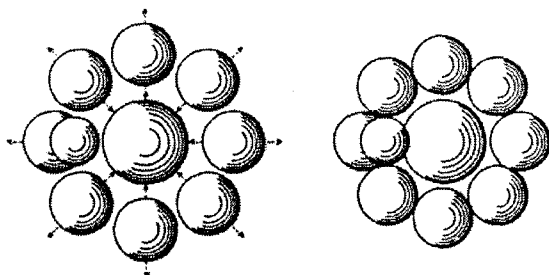
Figure 7: Effect of temperature on Na-Zeolite A for adsorption of nitrogen.

The large nitrogen atom is in the centre of the oxygen cage. The arrows indicate thermal vibration, which is greatly damped at very low temperatures. The smaller sphere indicates sodium ion near the cavity. The vibrations of the atoms at low temperatures explains the characteristic temperature functions of gas adsorption as shown in Figure 8 below $-100\ ^0$C and $-150\ ^0$C for nitrogen and argon, respectively. The gases are trapped below the critical temperatures [50].
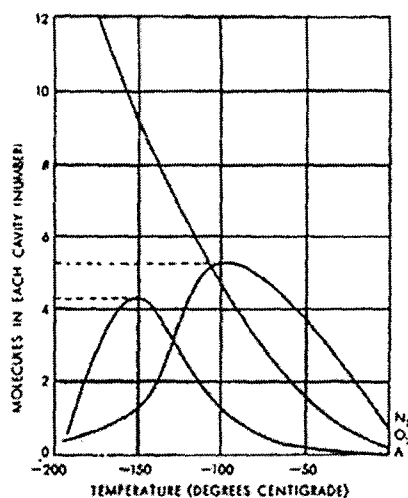
Figure 8: Gas adsorption by Zeolite A molecular sieve at low temperatures.

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3.2.1 Surface Area

The Langmuir and B.E.T adsorption methods are still the most widely used procedures for the determination of the surface area of finely divided and porous materials.

3.2.1.1 Langmuir Model

The simplest theoretical model for monolayer adsorption is due to Langmuir model. The Langmuir model was originally developed to represent chemisorption on a set on a distinct localized adsorption sites. The basic assumptions on which the model is based on are as follows;

1. Molecules are adsorbed at a fixed number of well-defined localized sites.
2. Each site can hold one adsorbate molecule
3. All sites are energetically equal.
4. There is no interaction between molecules adsorbed on neighbouring sites [38].

$$\frac{P}{V} = \frac{1}{bVm} + \frac{P}{Vm} \qquad \text{...[1]}$$

Where;

P is the pressure

Po is the saturation pressure

Va is the quantity of gas adsorbed at pressure P

Vm is the quantity of gas adsorbed at monolayer

b is the empirical constant

3.2.1.2 B.E.T Model

The B.E.T model has been used to interpret Type II isotherm and named from the surnames of its originators, Branauer, Emmett, and Teller. It is the most widely used procedure for the determination of surface area of finely divided and porous material. The B.E.T model is based on assumption that each molecule in the first adsorbed layer is considered to provide one site for the second and subsequent layers. The molecules in the second and subsequent layers, which are in contact with other sorbate molecules rather than with the surface of the adsorbent, are considered to behave essentially as the saturated liquid. In this manner the equilibrium constant for the first layer molecules in contact with the surface of the adsorbent is different [38].

$$P/[Va(Po-P)] = 1/(Vm*C) + [(C-1)/(Vm*C)] (P/Po) \ldots\ldots\ldots\ldots[2]$$

According to the theory, C is a constant, which is related exponentially to the heat of adsorption of the first layer. In practice, the value of C can be used to define the measure of heat of adsorption. A high value of C ($\cong$ 100) is associated with a sharp knee in the isotherm. If C value is low (<20) the sharp knee cannot be identified as a single point in the isotherm [16].

3.2.2 Characterization of Micropores : Pore Size Distribution

MP, Dubinin-Radushkevich, Dubinin-Astakhov and Horvath-Kawazoe methods are the evaluated mathematical models for pore size distribution.

3.2.2.1 MP Method

Mikhail et al. proposed a method for constructing pore size distribution from the t-plot. The t-plot is a plot of t, the statistical thickness, versus the relative pressure, P/Po. The t-plot employs a composite t-curve obtained from the data on number of nonporous adsorbents with BET C constants similar to

those of the microporous sample being tested. The standard t-curve is expressed by the empirical de Boer equation [43].

$$t(A^{\circ}) = 13.99/[\log(P/Po) + 0.034] \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots [3]$$

MP method consists of determining the slope at each point on the t-plot, which presumably gives the surface area accessible to N_2 molecules at that particular temperature (or pressure). The decrease in surface area between successive points, then, gives the volume of pores filled for presumed pore shape. For slit-shaped pores the volume filled is;

$$V = (At_1 - At_2) [(t_1 + t_2)/2] \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots [4]$$

At_1 and At_2 are surface areas, t_1 and t_2 thickness of two successive points on the t-plot, the mean slit pore group is $W = (t_1 + t_2)/2$. Thus, a cumulative pore-volume curve may be constructed, from which the differential PSD may be obtained [7].

3.2.2.2 Dubinin-Raduskevich and Dubinin-Astackhov Methods

The second means of determining PSDs of microporous materials from gas adsorption measurements is based on the theory of volume filling of micropores. The theory of filling of micropores (TVFM) is applied most widely for describing the physical adsorption of gases and vapours in micropores. This theory is based on the assumption that the characterization adsorption equation is expressing the distribution of the degree of filling of the adsorption space. This theory incorporates earlier work by Polanyi in regard to the adsorption potential A which is defined as [48];

$$A = RT \, Ln \, (P_o/P) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots [5]$$

TVFM equation represented as;

$$\theta = W/W_0 \quad \dots \dots [6]$$

D-A equation $\quad \theta = \mathrm{Exp}\left[-\left(\dfrac{A}{\phi Eo}\right)^{n}\right] \quad \dots \dots [7]$

in case where n=2 , corresponds to well known D-R equation;

D-R equation $\quad \theta = \mathrm{Exp}\left[\dfrac{RT}{\phi Eo}\right]^{2}\left[Ln^{2}\,\dfrac{Po}{P}\right] \quad \dots \dots [8]$

Where; θ degree of filling of adsorption volume

E_0 characteristic energy of the adsorption

ϕ is the affinity coefficient

3.2.2.3 HK Method

G. Horvath and K.Kawazoe developed a method of calculating the effective micropore size distribution of slit-shaped pores in molecular sieves from adsorption isotherm. Satio and Foley extended the HK approach to cylindrical pores in order to give a better description of adsorption in zeolitic materials [48].

$$RTLn\left[\dfrac{P}{Po}\right] = K\left[\dfrac{\left(N_a A_a + N_A A_A\right)}{\sigma(l-d)}\right] * \left[\dfrac{\sigma^4}{3\left(l-\dfrac{d}{2}\right)^3} - \dfrac{\sigma^{10}}{9\left(l-\dfrac{d}{2}\right)^9} - \dfrac{\sigma^4}{3\left(\dfrac{d}{2}\right)^3} + \dfrac{\sigma^{10}}{9\left(\dfrac{d}{2}\right)^9}\right] \quad \dots [9]$$

22

where;

N_a the number of atoms per unit area of adsorbent

N_A the number of the molecules per unit area of adsorbate

A_a & A_A are constants in Lennard-Jones potential for adsorbent &   adsorbate

σ is the distance between a gas atom and the nuclei of the surface at zero interaction energy.

3.2.3 Characterization of Macro-Mesopores

The Kelvin equation, BJH adsorption and desorption method are used in the characterization of the mesoporous and macroporous materials.

3.2.3.1 Kelvin Equation

In porous adsorbent there is continuous progression from multilayer adsorption to capillary condensation in which the smaller pores become completely filled with liquid sorbate. This occurs because the saturation vapor pressure in a small pore is reduced by the effect of surface tension [38].

The mesopore size is usually calculated with the aid of the Kelvin equation in the form.

$$Ln\frac{P^*}{Po} = -\left[\frac{2\gamma * vCos\theta}{RTr_m}\right] \quad\text{..[10]}$$

where;

P^* is the critical condensation pressure

γ is the liquid surface tension

θ is the contact angle between the solid and the condensed phase

r_m the mean radius of the curvature of temperature liquid meniscus

3.2.3.2 BJH Method

BJH method uses the Kelvin Equation for calculating the pore size distribution. This method involves an imaginary emptying of condensed adsorptive in the pores in a stepwise manner as relative pressure is likewise decreased.   The mathematics of the technique is equally applicable whether following the adsorption branch of the isotherm from high to low pressure or the desorption branch. Barrett, Joyner and Halenda, hence called BJH, described this method [48].

3.3 Thermal Properties

The dehydration properties of zeolites are important in case where they are used in adsorption and related applications. The crystal structures of some zeolites do not change after the application of thermal process and can easily adsorb water again. However, in some zeolites the irreversible change in structure occurs as a result of dehydration. Differential Scanning Analysis, Thermoravimetric Analysis and Differential Thermal Analysis give information about the dehydration properties of zeolites.

3.3.1 TGA Method

The continuos and uninterrupted thermogravimetric analysis curve states that there is no change in its structure, if curve exists as steps then it means its structure has been changed. Mumpton (1960) have been investigated the thermal behaviour of clinoptilolite and reported that clinoptilolite showed no noticeable breaks in the weight loss curve [25].

Alietti et al. (1975) and Reenwijk (1974) have been investigated the dehydration behaviour and water content of clinoptilolite. They found that there are three types of water exists in the natural zeolite structure having different volatility; 'external', 'loosely bound zeolite' and 'tightly bound zeolite' water. Based on their study 'external' water released up to 85 ^{0}C, 'loosely bound' water

is lost rapidly up to 185 ^{0}C, and then more gradually to 185 ^{0}C. After 285 ^{0}C the clinoptilolite started to loose its 'tightly bound 'water. After 700 ^{0}C there is no noticeable weight loss takes place in the structure [25].

Figure 9: TGA curve of different clinoptilolites a) 88% zeolite content Gördes b) 90% Zeolite content Gördes c) 90% Zeolite content Bigadiç d) %95 zeolite content Bigadiç (Esenli and Kumbasar, 1994)

3.3.2 DTA Method

Differential thermal analysis determines the temperature at which thermal reaction takes place within the sample. The degree and nature of the reactions that is whether endothermic or exothermic changes are involved is obtained from this analysis curve. The low temperature endotherm represents the loss of water while the high temperature endotherm represents conversion of the zeolite to another amorphous or crystalline phase. The high temperature exotherm represents the loss of structure [8].

Aliberti et al. (1975) investigated the thermal behaviour of clinoptilolite by means of DTA and derivative thermogravimetry (DTG). He reported that the clinoptilolite exhibited strong dehydration effect centred on 130 ^{0}C and weaker dehydration effect about 400 ^{0}C [25].

25

Bish (1995) studied the thermal behaviour of zeolites. He reported that in the determination of thermal stability of zeolites amount and type of extra framework cations, Al/Si ratio, presence or absence of water, time, temperature and heating rate are the important effects [17].

Mumpton (1960) have investigated the dehydration behaviour of clinoptilolite using differential thermal analysis. He reported that aside from a broad endothermic peak between 0 ^{0}C and 400 ^{0}C, clinoptilolite exhibited no thermal reactions up to about 1000 ^{0}C [25].

Esenli and Kumbasar (1994) had studied the thermal behaviour of clinoptilolite samples from Bigadic, Gördes and Kemalpaşa regions of Turkey. The DTA curves of some samples show endotherm at 120 °C and 750 °C , while the rest show three endotherms at 120 °C, 230 °C and 730 °C. The DTA curves of the studied samples are given in Figure 10 [11].
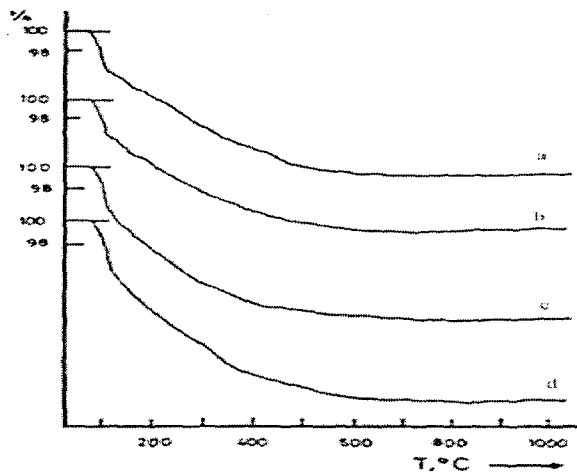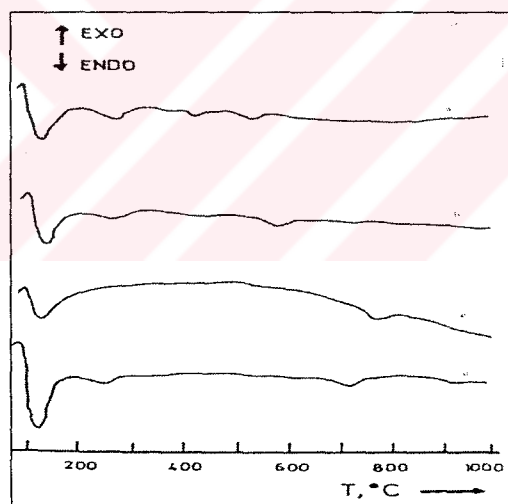

Figure 10: DTA curve of different samples a) 88% Zeolite content Gördes b) 90% Zeolite content Gördes c) 90% Zeolite content Bigadiç d) Zeolite content %95 Bigadiç (Esenli and Kumbasar, 1994)

3.3.3 DSC Method

Differential Scanning Calorimetry is another thermal analysis technique can be used in the determination of thermal and dehydration behaviour of clinoptilolite. Knowlton et al (1975) reported that desorption of three types of water observed by TGA should yield three endothermic DSC peaks. However; the broadness of the peaks for the 'external' and ' loosely bound zeolite ' water, along with small amount 'tightly bound zeolite' water make three types of water endotherms less visible.

Bish (1995) have studied the effects of composition on the dehydration behaviour of clinoptilolite. He reported that the amount of water given off at particular temperature varied with composition. The derivative TGA curves resembles the DSC curves of the identical sample. He studied TGA and DSC curves of different cationic forms of clinoptilolite samples and in Figure 11 and Figure 12 the DSC curves Na and Ca formed clinoptilolite studied are given, respectively. The Ca-clinoptilolite gives endotherm at lower temperature than the Na-clinoptilolite [6].
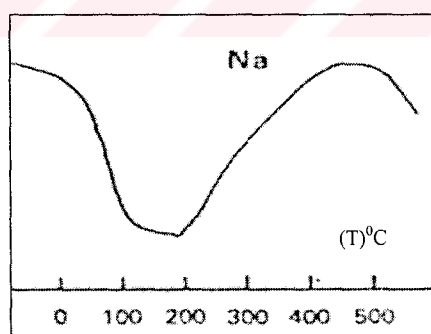
Figure 11: DSC curve of Na-clinoptilolite (Bish, 1978)
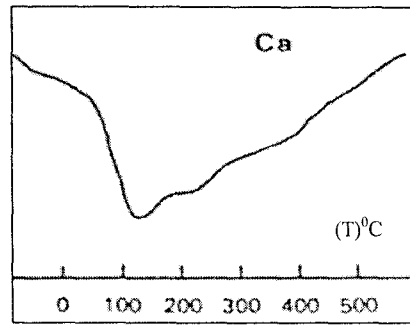
Figure 12: DSC curve of Ca-clinoptilolite (Bish,1978)

Chapter 4

MODIFICATION OF ZEOLITES

Modification of a zeolite encompasses a variety of techniques to further control the acid activity and/or the shape selectivity of a specific zeolite structure. After modification, numbers of characterization techniques have been applied in order to identify the changes brought about within the material upon treatment. The modification of zeolite structure is done by several different methods and the most commonly used ones are ion exchange and acid leaching. In the recent years, microwave heating is being used both in industry and by researches.

4.1 Acid Leaching

It was early recognized that zeolite minerals are decomposed by acid, many of them with the subsequent formulation of gels. A detailed classification of silicate minerals that is related to the internal structure was purposed. Silicates which are decomposed by treatment with strong acids may be classified into one of two groups a)those that separate insoluble silica without the formation of a gel b)those that gelatinise upon the acid treatment. The rule generally fallowed is that those zeolites that have a framework structure silicon/aluminium ratio greater than 1.5 generally decompose and form participate hydrous silica.

It is further observed that in acid leaching process, the first step of transformation is the hydration of the aluminium tetrahedra with a change in coordination to octahedral. In the synthesis of layer type minerals the formation of these short chains is the structure determining step rather than the 'grafting' of aluminium octahedra onto already performed silica sheet.

The acid leaching mechanism is carried out as follows; (N.Y. Chen 1976)

$$
\begin{array}{ccc}
\text{O} & \text{HCl} & \text{Si} \\
| & & | \\
\text{-Si-O-Al-O-Si} & \longrightarrow & \text{Si-OH} \quad \text{—OH} \quad \text{—OH-Si-} \\
| & & | \\
\text{O} & \text{+3 H}_2\text{O} & \text{OH} \\
& & \text{Si}
\end{array}
$$
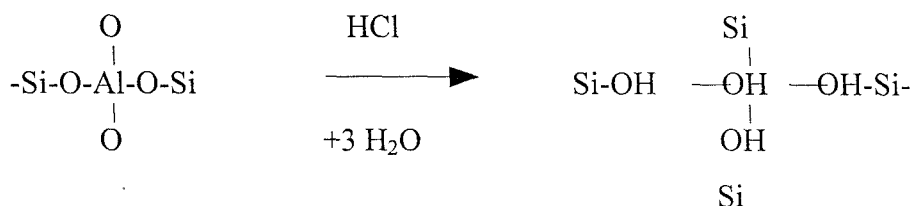
Delalumination depends on many parameters. Besides the type of the zeolite and the nature of the reactant (the size of which might play an important role because of sieving effects) the temperature periods of dealumination determines the degree of dealumination. Also known that; the alumination dissolution is increased by increasing in acid concentration.

In general, corroborated with a large number of similar dealuminating to take place the reactant molecule must be chemisorbed as a positive ion, in thermal and electrostatic interaction, this eliminate O(-2) from the framework and shares the constituent of higher electronegativity with the structural Al(+3) ion. As a result; an empty nest (actually a framework vacancy) is created which under special circumstances may undergo same stabilization.

4.2 Ion Exchange

One of the most important properties of zeolites is their ability to exchange cations. The type and distribution of cations influence the adsorption behaviour of zeolites; thus by ion exchange, sorbent with different molecular sieve and adsorption properties can be prepared [46].

Clay minerals because of their two-dimensional framework structure may undergo swelling or shrinking with ion exchange process. Zeolites and felspathoids do not undergo any appreciable dimensional change with ion exchange since they have three-dimensional structure.

30

The cation exchange behaviour of the zeolite mineral depends upon:

1.The nature of the cation species, the cation size both anhydrous and hydrated and the cation valance.

2.The temperature

3.The concentration of the cation species in solution

4.The anion species associated with the cation in the solution

5.The solvent

6.The structural characteristics of the particular zeolite [16].

As mentioned above, ion exchange depends as much on the properties of the exchanger as on the properties of the ions undergoing exchange. The affinity of an ion towards a given ion exchanger for example the ion exchangeability depends primarily on the charge of the ion, the ionic radius and the degree of hydration. The larger the charge on the ion the greater is the force which it is attracted by the functional groups of opposite charge on the ion exchanger. In the case of equivalent ions the magnitude of their radii is decisive for their ion exchange capacity. The greater the volume of the ion , the weaker is its electric field in the solution and thus the smaller is its degree of hydration. The so-called hydrodynamic radii of ions decrease with increasing atomic weight and hence their exchange energy (energy which the ion is transported from the solution to the ion exchanger).

The ion exchange process may be presented as follows,

$$z_B\, A^{Z_A} + \overline{z_B\, B^{Z_B}} \rightleftharpoons z_B\, \overline{A^{Z_B}} + z_A\, B^{Z_B}$$
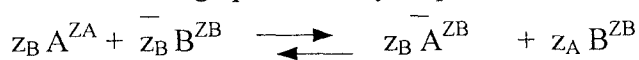
In the equation above, z_A & z_B are the valances of the ions, A^{Z_A} initially in the solution, B^{Z_B} initially in the zeolite, characters with a bar related to a cation inside the zeolite crystal.

Simple examples are:

$$\overline{Na^+} + K^+ \rightleftharpoons Na^+ + \overline{K^+} \quad \text{for uni-univalent exchange}$$

$$2\,\overline{Na^+} + Ca^{+2} \rightleftharpoons 2\,Na^+ + \overline{Ca^{+2}} \quad \text{for uni-divalent exchange}$$

31.
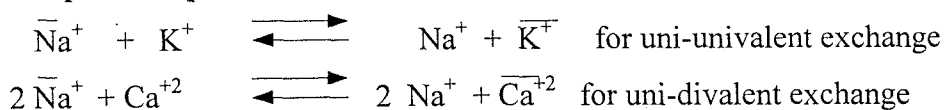
4.3 Microwave Heating

The heating and processing of materials with microwave is becoming increasingly popular for industrial applications, such as curing, sintering, joining and drying. In microwaves, a form of radiowaves (neither nuclear nor ionizing radiation) passes through the material instead of direct heating. (Figure 13)
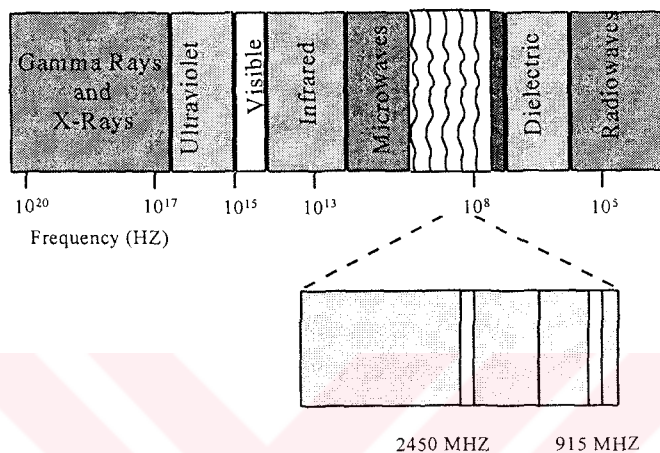
Figure 13: Microwave Radiation

The molecules in the material then act like miniature magnets attempting to align themselves with the electric field. Under the influence of this high frequency alternating electrical field, the particles oscillate about their axes intermolecular friction, which presents itself as heat.

Since the mid-1980s uses of in chemical analysis have been widely investigated. Many organic and inorganic reactions could proceed under microwave condition with much higher rate than the conventional methods. Besides the rapid reaction rate, microwave heating has some other advantages. In the conventional heating the heat source causes the molecules react from the surface toward the center but microwaves produce a volume heating effect that molecules are set in action at he same time. It also prevents temperature gradients.

As far as the synthesis of zeolite is concerned, microwave heating is commonly applied to obtain pure and/or perfect crystals of uniform size or with different Si/Al ratios, than obtained using conventional heating methods [18,49].

Han et al. [18] had studied the synthesization of zeolites using microwave heating. The study showed that, zeolite A membranes have been successfully synthesized in microwave in much shorter time than the conventional methods and the zeolite crystals obtained in this way are small and uniform in size. The researches concluded that microwave heating could be considered as rapid, simple and valid method in synthesis of zeolite membranes.

Chapter 5

EXPERIMENTAL

5.1 Materials and Methods

Clinoptilolite mineral used in this study was obtained from two different zeolatic formations, Bigadiç and Gördes, Western Anatolia. Experiments were performed in two parts. In the first part, the samples were characterized using different instrumental techniques. In the second part, clinoptilolite samples were modified by ion exchange and the modified zeolites were characterized to examine the changes in their structure.

Clinoptilolite minerals from Bigadiç and Gördes deposits were first crushed into small pieces using hammer and sieved into different size ranges. The final Bigadiç grain size fraction was between 2-4.75 mm and used in ion exchange experiments for modification of the clinoptilolite structure. Some of the crushed samples were washed with bidistilled water at 100 °C to remove soluble impurities. This procedure was repeated for several times until effluent water was clear. Then the washed zeolite particles were dried at 160 °C under vacuum for 4 hours. The washed and unwashed samples were then ground and sieved using stainless steel sieves. The final powder was in 45-75μ size ranges and used to carry out the characterization experiments.

The parent material contains calcium, magnesium, barium, sodium and etc as exchangeable cations. The clinoptiloite samples were analysed by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP 96, Varian) to determine the chemical composition of the cations in the structure is given in Table 14. The samples were dissolved as follows. The certain amount ($\cong$0.1 gr) of clinoptilolite powder was put into 6.4 ml HF solution and heated on hot plate in self-sealing crucible until all the liquid was evaporated. This procedure.

was repeated with addition of 2 ml HF and then sample was dried in oven at 400 °C for 1 hour. The calcined sample was dissolved in 6 ml HNO_3 and 3 ml HCl. The solution was then diluted to concentration ranges available for measurements.

5.2 Material Characterization

The original clinoptilolite minerals from various origins of the sedimentary deposits were characterised using different instrumental techniques.

The infra-red spectra of all original, washed and humidified clinoptilolite samples were taken by Fourier Transform Infrared Spectrophotometer (FTIR-8201, Shimadzu) using KBr pellet techniques. Typical pellet contains 1-2 %wt sample in KBr and was prepared by mixing 0.004 mgr zeolite powder with 0.2 mgr of KBr. The amount of the zeolite in the KBr pellet was chosen so to provide the linear dependence of optical density of characteristic IR. bands vs zeolite content. The original clinoptilolite minerals were kept in desiccator for several weeks and then IR spectrums were taken. In order to provide constant relative humidity saturated NH_4Cl solution was placed in desiccator which provides 75% relative humid air at 25 °C were then analysed by FTIR.

The adsorption related properties of the zeolite samples were derived from N_2 and Ar adsorption data collected from volumetric adsorption system. (Micromeritics ASAP 2010) The powdered samples (<45 µ) were dried in vacuum oven at 160 °C at least 4 hours prior to the adsorption measurements the samples. Then they were degassed at either 350 °C or 450 °C for 24 hours. In each run the effect of degassing condition was determined. The volumetric adsorption systems measure the quantity of gas n (of standard volume Va, or general quantity q) taken up or released at a constant temperature (T) by an initially clean solid surface as a function of gas pressure P. The quantity of gas adsorbed is expressed as its volume at standard conditions of T, P while the pressure is expressed as a relative pressure which is the actual gas pressure P is

divided by the vapour pressure (Po) of the adsorbing gas (P/ Po). The analysis was carried out at a cryogenic temperature either LN_2 or LAr at their boiling temperatures of 77 K and 87 K, respectively [35].

Thermal behaviour of original and modified clinoptilolite samples from different sedimentary deposits were established by Differential Scanning Calorimeter (DSC 50, Shimadzu), Differential Thermal Analyser (DTA50, Shimadzu), Thermogravimetric Analyser (TGA-51/51H, Shimadzu). The powdered form of the zeolite samples was heated in a dry N_2 stream up to 1000 ^{0}C at a heating rate of 10 ^{0} C/min.

5.3 Modification by Ion-Exchange

The exchange experiments were carried out both in constant waterbath and microwave maintained at 80 °C. In the experiment carried out in water-bath, 100 gr. of clinoptilolite sample was put into 1600 cm^3 1N NaCl solution for 2 weeks. The Na-exchanged samples were washed with distilled water until all Cl^- is removed, dried in oven and kept in desiccator.

The exchange was also carried out in microwave with frequency and maximum power of the microwave radiation of 2.450 GHz 1.2 KW, respectively. Approximately 0.5 gr. of clinoptilolite samples and 10 ml of 1 N· NaCl solution were placed in a specially made Teflon-lined polyamid vessel through which microwave radiation can transmit. The temperature and pressure inside the vessels were controlled automatically by control vessel. The safety pressure, temperature and power of the microwave were set 120 psia, 80 °C, and 300 watts, respectively. The temperature reached to set value within 3 minutes and samples were held at that temperature for 10 minutes, 1 hour and 2 hours. Then left to cool down. The Na-exchanged samples were then washed with distilled water until all Cl^- is removed, dried in oven and kept in desiccator.

Chapter 6

RESULTS AND DISCUSSION

6.1 FTIR Analysis

The IR spectrums of original clinoptliolite samples from different origins are given in Figure 14.
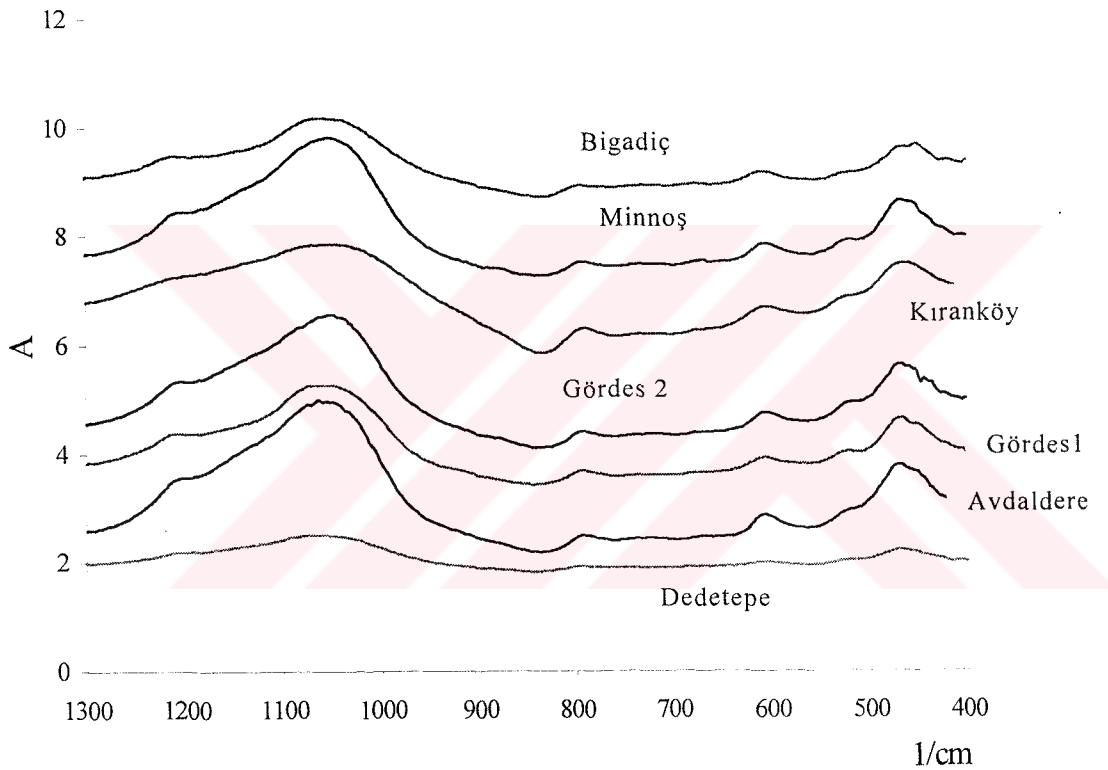
Figure 14: The IR Spectrums of different clinoptilolite minerals from different origins.

The range between 1200 cm^{-1} and 400 cm^{-1} wavenumber was examined because in the IR spectrums of zeolites this range has been used to determine the structural properties. All of the samples showed the same structural properties and following adsorption bands were observed. The samples exhibited asymmetric stretch vibration around 1200 cm^{-1}. The 850-750 cm^{-1}

band observed in the spectrum refers to the symmetry stretch due to external linkages between tetrahedra. The bands at 1050 cm^{-1} and 450 cm^{-1} are assigned to asymmetry stretch and T-O bending mode, respectively which are related to internal tetrahedron vibrations. The 609 cm^{-1} band in the spectrums is related to T-O double ring vibration of free tetrahedral group.

The original and moist forms of clinoptilolite samples from different sedimentary deposits were examined by normalizing their absorbance values at 3400 cm^{-1}- 3700 cm^{-1}, 1600 cm^{-1} and 609 cm^{-1} wavenumbers. The normalized absorbance values of 3400 cm^{-1}-3700 cm^{-1}, 1600 cm^{-1} and 609 cm^{-1} peaks are given in Figure 15, Figure 16 and Figure 17, respectively.

Figure 15: Normalized absorbance values of different clinoptilolite samples ranged at 3400-3700 cm^{-1} wavenumbers

Figure 16: Normalized absorbance values of different clinoptilolite samples at 1600 cm^{-1} wavenumber
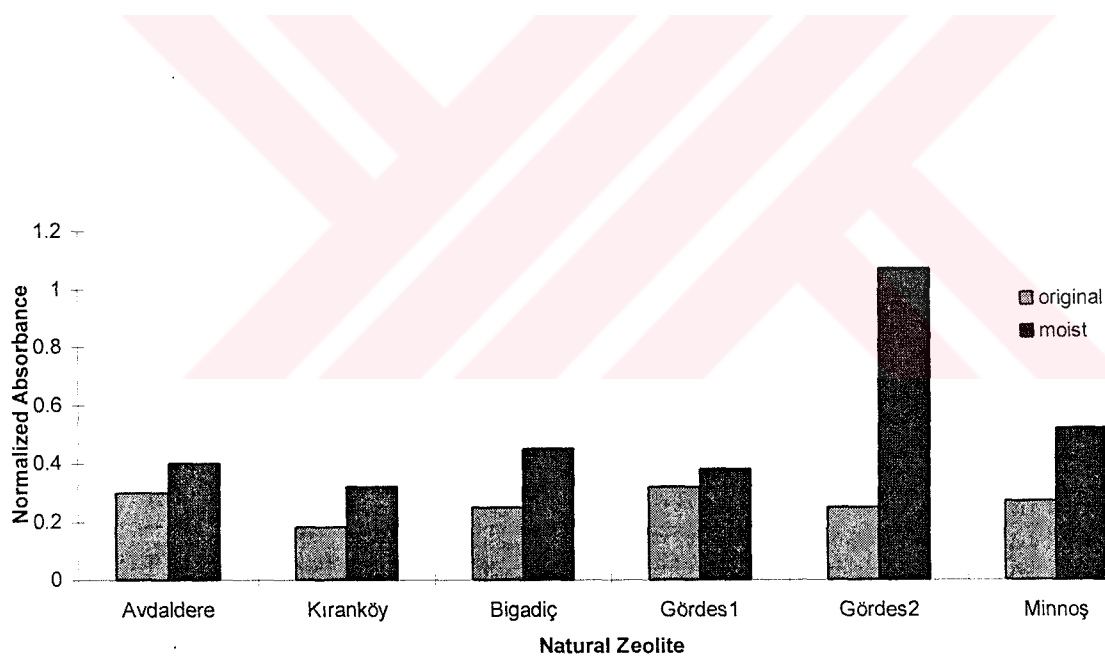
Figure 17: Normalized absorbance values of different clinoptilolite samples at 609 cm^{-1} wavenumber

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In all moist clinoptilolite samples the absorbance values at three wavenumbers were increased and gave higher peaks. The increase in the normalized absorbance values at 3400-3700 cm^{-1}, 1600 cm^{-1} was expected because all of the clinoptilolite samples were kept in desiccator at constant relative humidity maintained by saturated NH_4Cl solution and absorb water. This situation was also supported by TGA analysis of the moist Gördes 1st and 2nd mine samples.
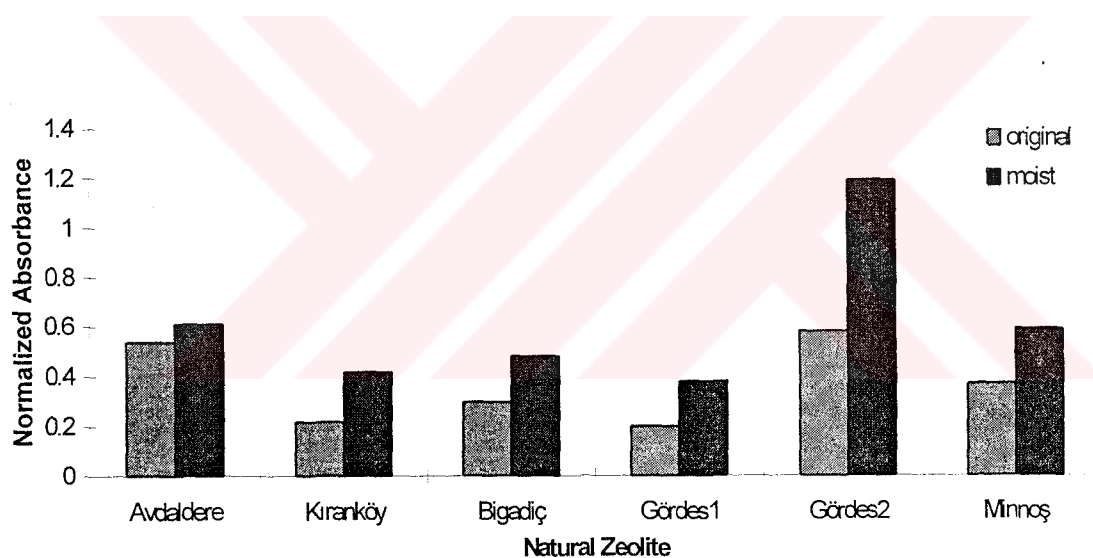
The normalized absorbance values of the samples were increased at 609 cm^{-1} wavenumber. This may result from the movement of the water molecules that are located in sites or between the tetrahedral rings. The exchangeable cations in the zeolite structure are bound to the pore walls with water molecules and in the presence of humidity the length of these cation-water bound increases. As a result the amplitude of the intensity at 609 cm^{-1} wavenumber may became larger. Thus, using 609 cm^{-1} band as criteria for clinoptilolite content should be made with care. The samples should be in the state of the same moisture content for a healthy comparison.

The original and moist FTIR spectra of different clinoptilolite minerals were given in Figure 18, Figure 19, Figure 20, Figure 21, Figure 22 and Figure 23. The IR spectrums all samples showed one or more adsorption bands near 1600 cm^{-1} caused by deformation of water molecules and in the stretching region (3400-3700 cm^{-1}) the spectra contains adsorption bands caused by the isolated H_2O molecules [8].
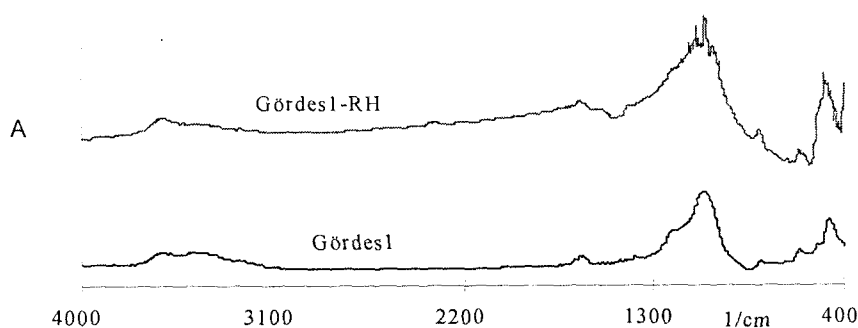
Figure 18: FTIR Spectrum of original and moist Gördes 1st mine.
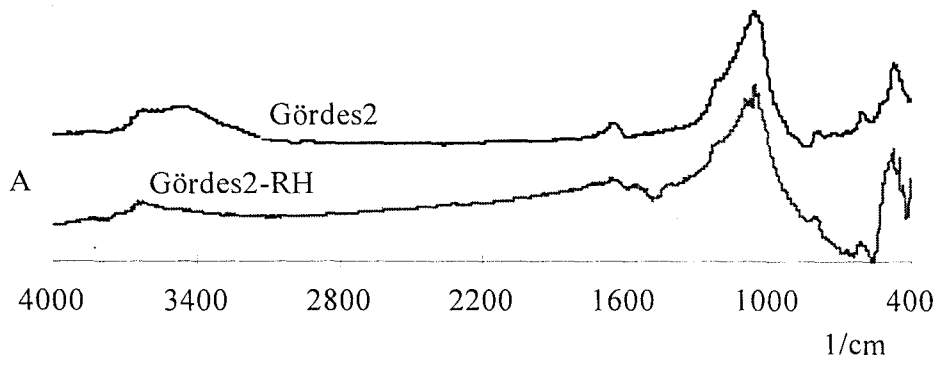
Figure 19: FTIR Spectrum of original and moist Gördes 2nd mine
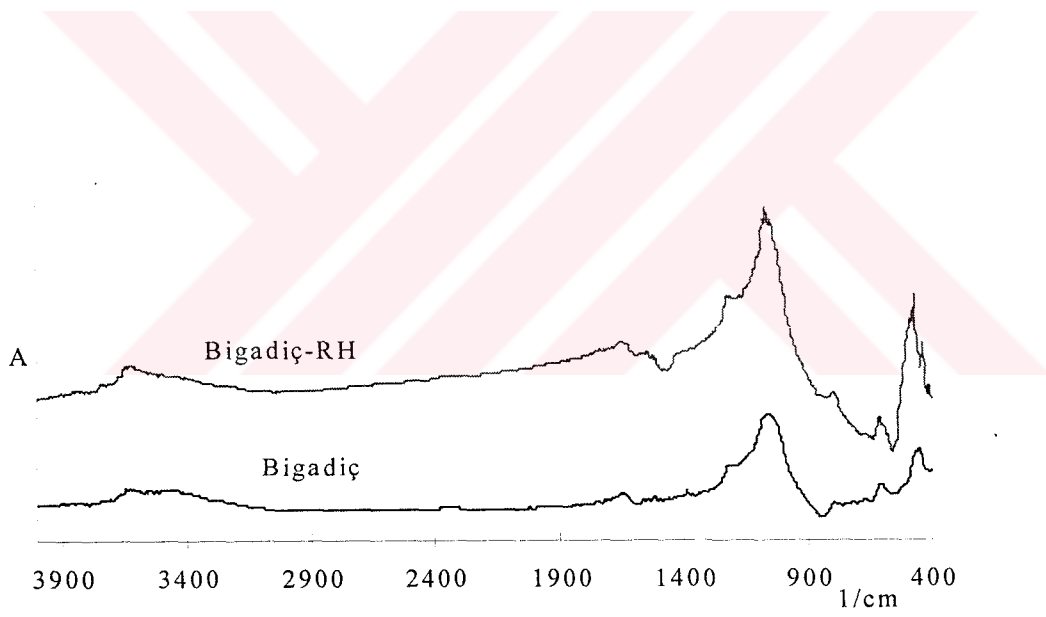
Figure 20: FTIR Spectrum of original and moist Bigadiç
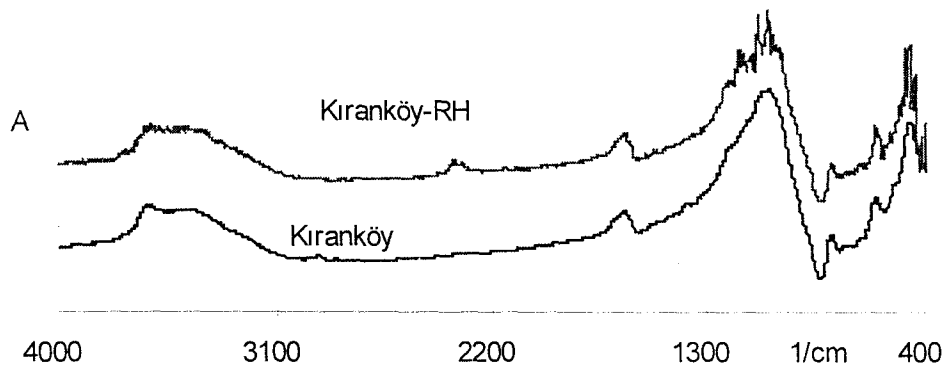
Figure 21: FTIR Spectrum of original and moist Kiranköy
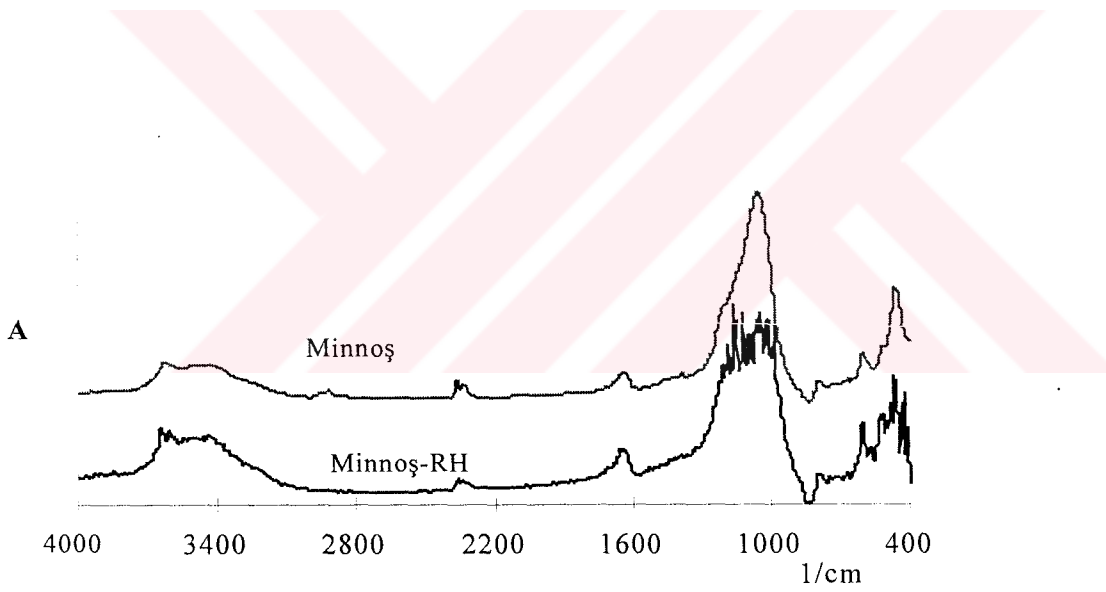
Figure 22: FT IR Spectrum of original and moist Minnos
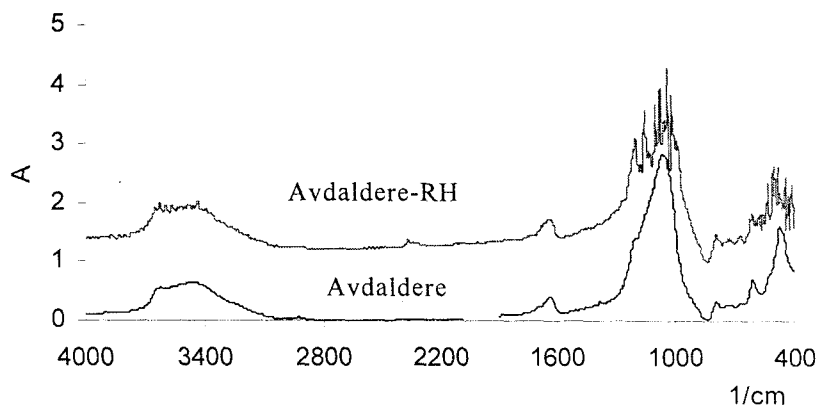
Figure 23: The IR Spectrum of original and moist Avdaldere

The influence of washing on the clinoptilolite content of zeolites from different sedimentary deposits was examined by investigating the 609 cm^{-1} and 450 cm^{1} bands. The absorbance values of these peaks were normalized and given in Figure 24 and Figure 25.
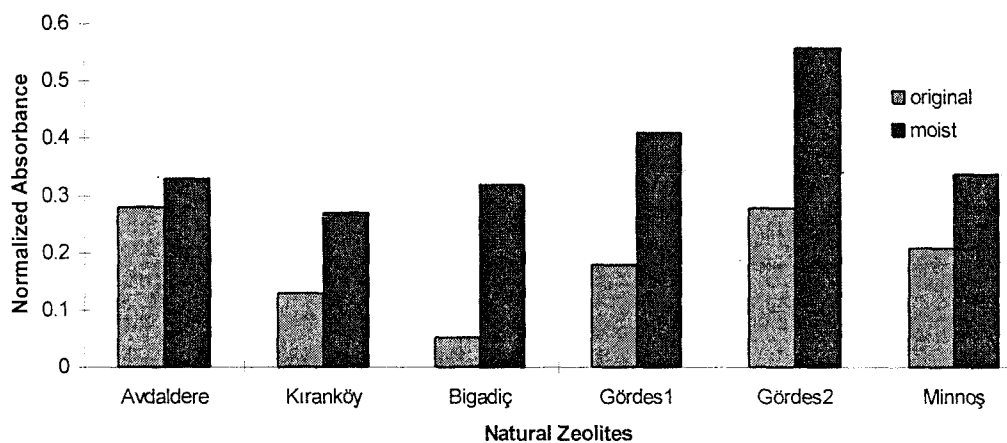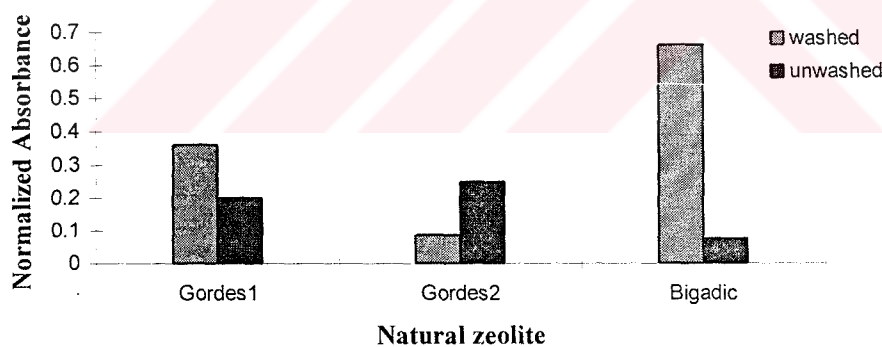

Figure 24: Normalized Absorbance values of different clinoptilolite samples at 609 cm^{-1} wavemumber
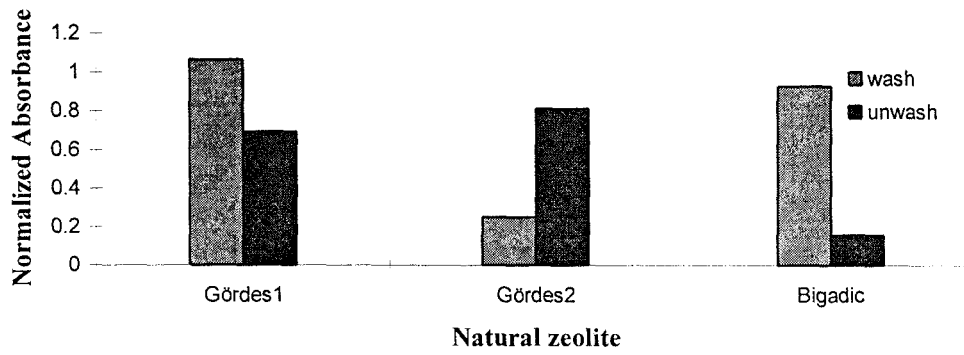
Figure 25: Normalized Absorbance values of different clinoptilolite samples
at 450 cm^{-1} wavenumber

The 609 cm^{-1} and 450 cm^{-1} peaks are the typical clinoptilolite bands which represents the amount of pure clinoptilolite amount in the rock. The absorbance values of 609 cm^{-1} peak of Gördes 1st mine and Bigadiç samples were increased when they were washed. It shows that the washing improved the clinoptilolite content because, soluble impurities on the external surface of the mineral were removed by washing. However, it was just the opposite for Gördes 2nd mine natural zeolite sample. When the sample was washed the clinoptilolite in the mineral maybe thrown away with the effluent water and caused decrease in the absorbance value at 609 cm^{-1}.

The IR spectra of original and washed clinoptilolite samples from different origins are given in Figure 26, Figure 27 and Figure 28.
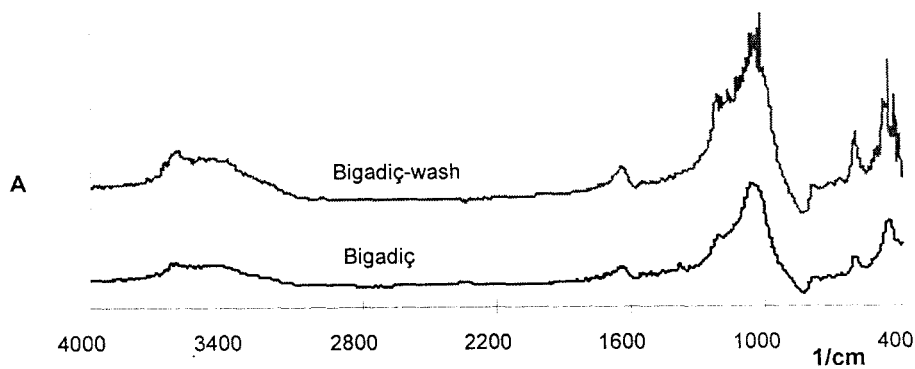
Figure 26: FTIR Spectrum of original and washed Bigadiç

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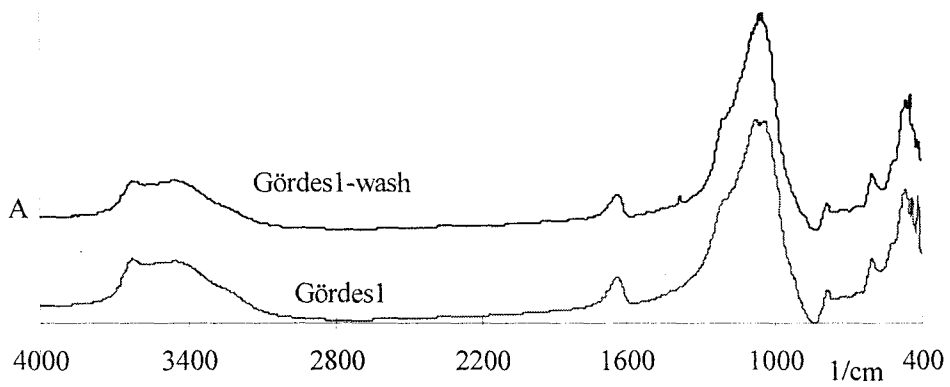
Figure 27: FTIR Spectrum of original and washed Gördes1st mine
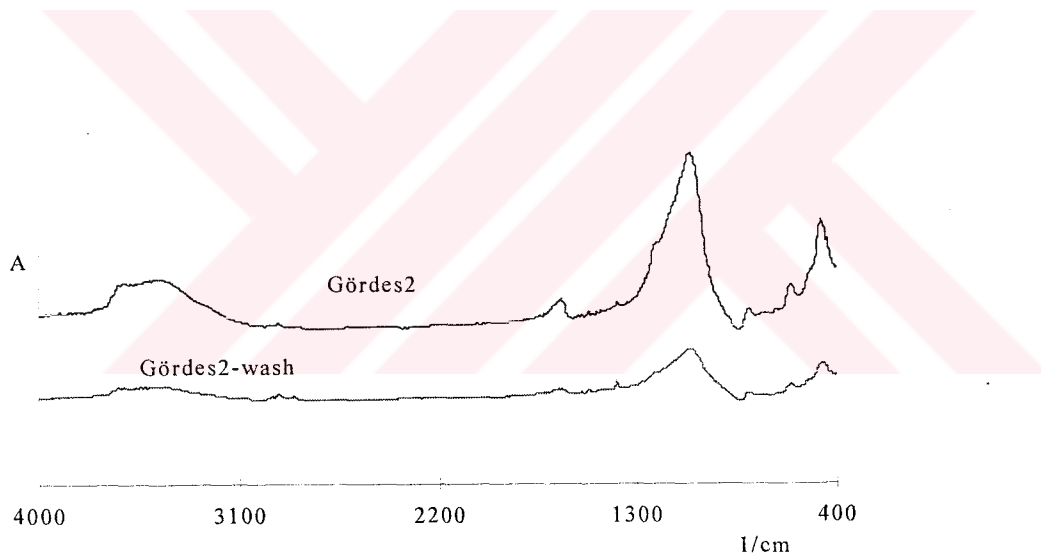
Figure 28: FTIR Spectrum of original and washed Gördes2nd mine

6.2 Thermal Analysis

TGA curves of the clinoptilolite samples from different origins are given in Figure 29.
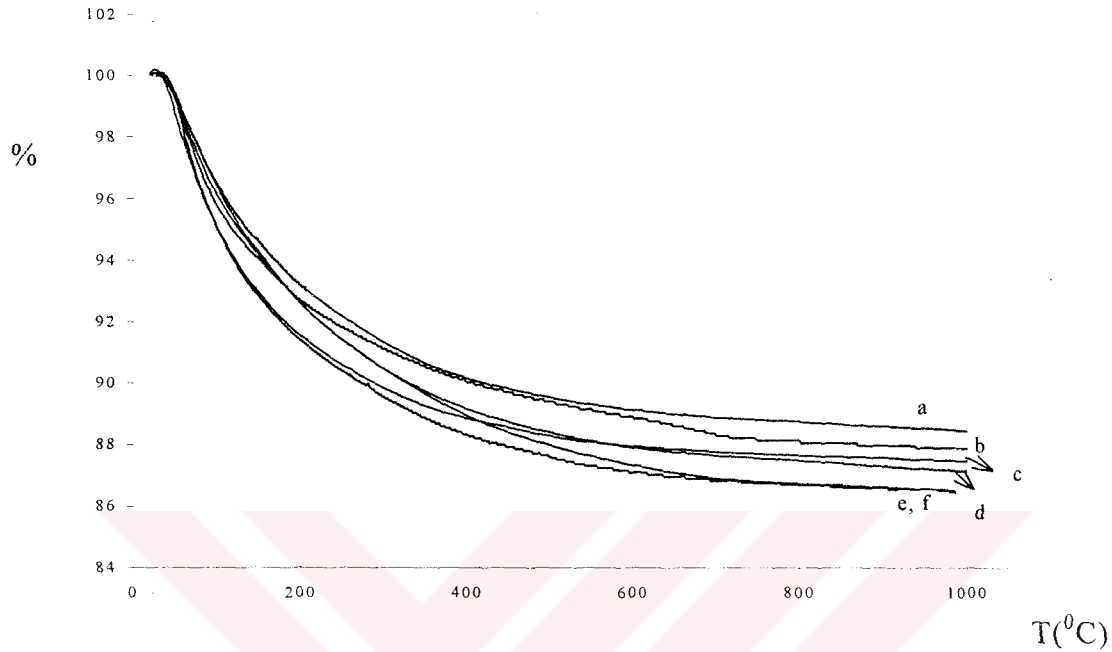
Figure 29: TGA curves of clinoptilolite minerals from different origins a)Dedetepe b)Gördes 1st mine c)Avdaldere d)Kıranköy e)Gördes 2nd mine f)Bigadiç

Clinoptilolite samples from different origins were examined by TGA using the procedure outlined Knowlton and White (1976). The smooth and continuos exhibited TGA curves show that no structural deformation occurred when they were heated up to 1000 ^{0}C only water content of the samples were changed. The percent lost of 'external' water, 'loosely and tightly bound zeolite' water is given in Table 4. The samples showed the same dehydration behaviour. External water, loosely bound and tightly bound water content in all samples were about 3.5%, 5.5% and 2.0%, respectively. After 500 ^{0}C there weight loss was observed as indicated in Table 4 which may be due to the CaCO$_3$ present in the samples.

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Table 4: % Weight losses of original clinoptilolite minerals kept in ambient air.

NATURAL ZEOLITE	$< 85\,^0C$ external water	85^0-285^0C loosely bound water	285-500^0C tightly bound water	$>500\,^0C$	Total
Avdaldere	4.35	5.84	1.70	0.78	12.70
Gördes 1st mine	3.66	5.17	2.27	1.09	12.19
Gördes 2nd mine	4.27	6.07	1.72	1.50	13.50
Bigadiç	3.28	6.07	2.68	1.46	13.51
Kıranköy	3.05	6.32	2.25	1.23	12.85
Dedetepe	3.04	5.45	1.93	1.05	11.59

In order to examine the thermal behaviour and water content changes in moist forms of the samples they were kept in ambient and 75 % relative humid air and then their TGA analysis were done and compared.

Table 5: % Weight losses of original clinoptilolite minerals kept in 75% RH air at 25 ^{0}C.

NATURAL ZEOLITE	< 85 ^{0}C external water	85^0-285^{0}C loosely bound water	>285^{0}C tightly bound water	Total
Gördes 1st mine	3.62	5.63	3.28	12.51
Gördes 2nd mine	5.11	5.58	3.29	13.90

Because all of them were kept in constant relative humid desiccator supplied by saturated NH_4Cl solution the moist forms of the clinoptilolite minerals have higher % H_2O as expected, as given in Table 5. During the storage in desiccator the samples were absorbed water, also supported by FTIR analyses.

The derivative TGA (DTG) curves for the original samples are given in Figure 30 that are useful in pinpointing the breaks in TGA curves.
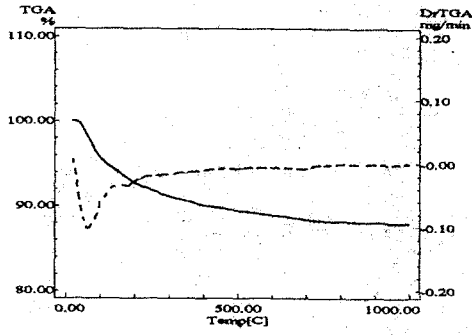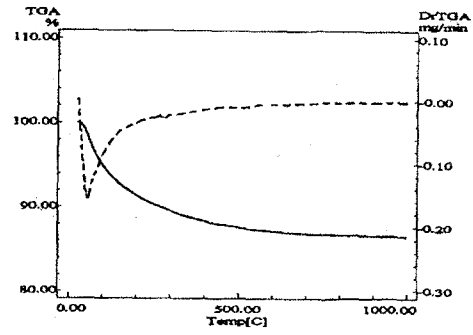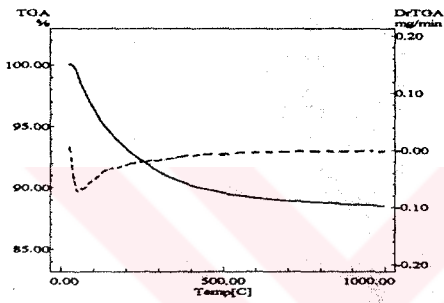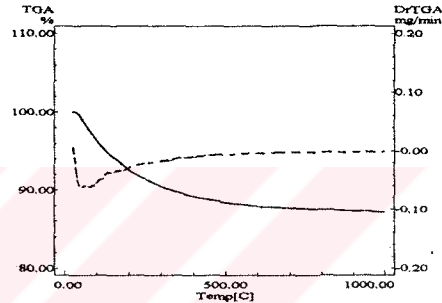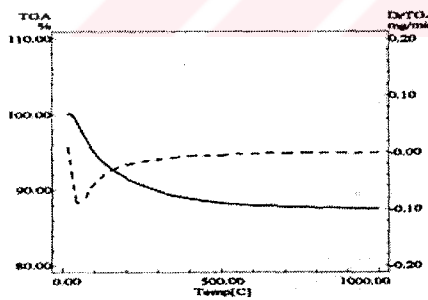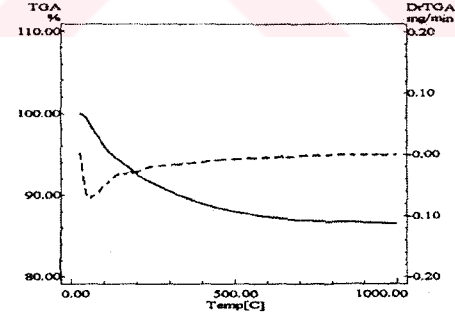
Figure 30: TGA and DTG of different clinoptilolite minerals from different origins a)Gordes 1st mine b) Gordes 2nd mine c) Avdaldere d) Kıranköy e)Bigadiç f) Dedetepe

Table 6 : Peak minimum temperatures of clinoptilolite minerals in DTG curves

Natural Zeolite	Peak minimum (^{0}C)
Gördes 1st mine	52.03
Gördes 2nd mine	50.01
Avdaldere	51.23
Kıranköy	51.35
Bigadiç	51.41
Dedetepe	51.87

The DSC curves for clinoptilolite samples from different origins is given in Figure 31.
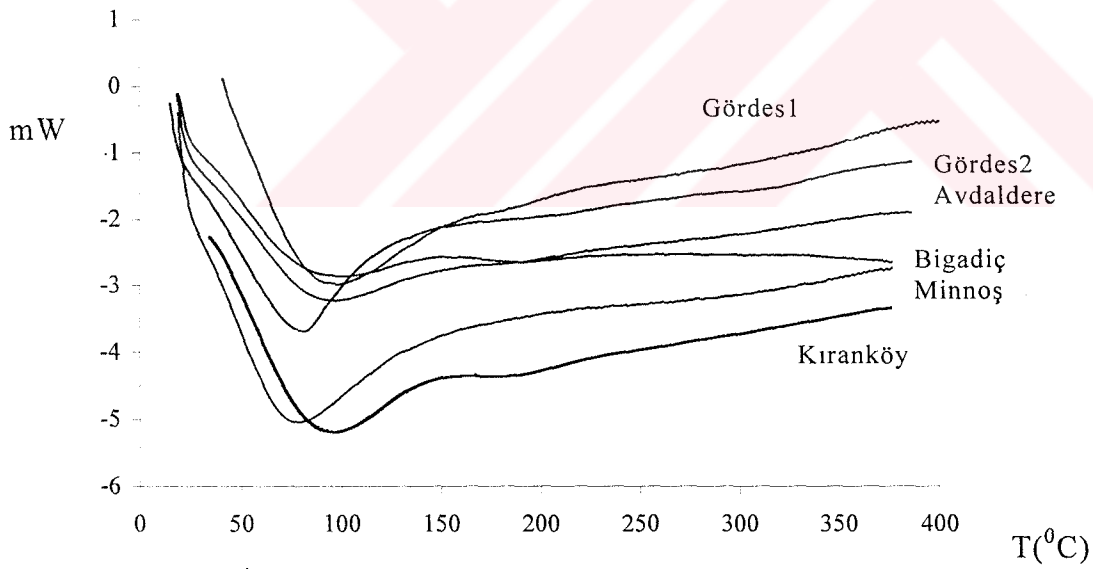
Figure 31: DSC curves of clinoptilolite minerals from different origins

Table 7: Dehydration behaviour of different clinoptilolites minerals (DSC)

NATURAL ZEOLITES	Endotherm (^0C)	$\Delta H_{dehydration}$/g H_2O (J/gr)	
Kıranköy	95.48	(35-396 ^0C)	1716
Gördes 1st mine	97.50	(41-396 ^0C)	2026
Gördes 2nd mine	83.46	(17-442 ^0C)	2702
Bigadiç	88.92	(21-396 ^0C)	2918
Avdaldere	95.48	(20-396 ^0C)	3335

The shape of DSC curves closely resembles the shape of DTG curves. The peak minimum temperatures determined from the DSC curves are significantly different than those found in DTG curves, reflecting the difference in water vapour pressure between two experiments. The dehydration behaviour of different natural zeolites is given in Table 7. Avdaldere. Kıranköy and Gördes 1st mine samples exhibit a large, broad main endotherms at about 95 ^0C, Bigadiç and Gördes 2nd mine samples exhibited a large, broad endotherms at lower temperatures as shown in Table 7, corresponding to 'loosely bound zeolite' water. At higher temperatures second endotherm exhibits but it was not certain as the first endotherm. The chemical analysis of original Bigadiç sample was given in Table 14. In the DSC curve of the Bigadiç sample broad endotherm was observed at 88 ^0C. This thermal behaviour is related to chemical compositions as it was mentioned in chapter 3.

The dehydration heat for Gördes 2nd mine, Bigadiç and Avdaldere are quite high that shows they can be use in energy applications.

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Differential thermal analysis curves of clinoptilolite samples from different sedimentary deposits are given in Figure 32 and are useful in characterizing the zeolites.
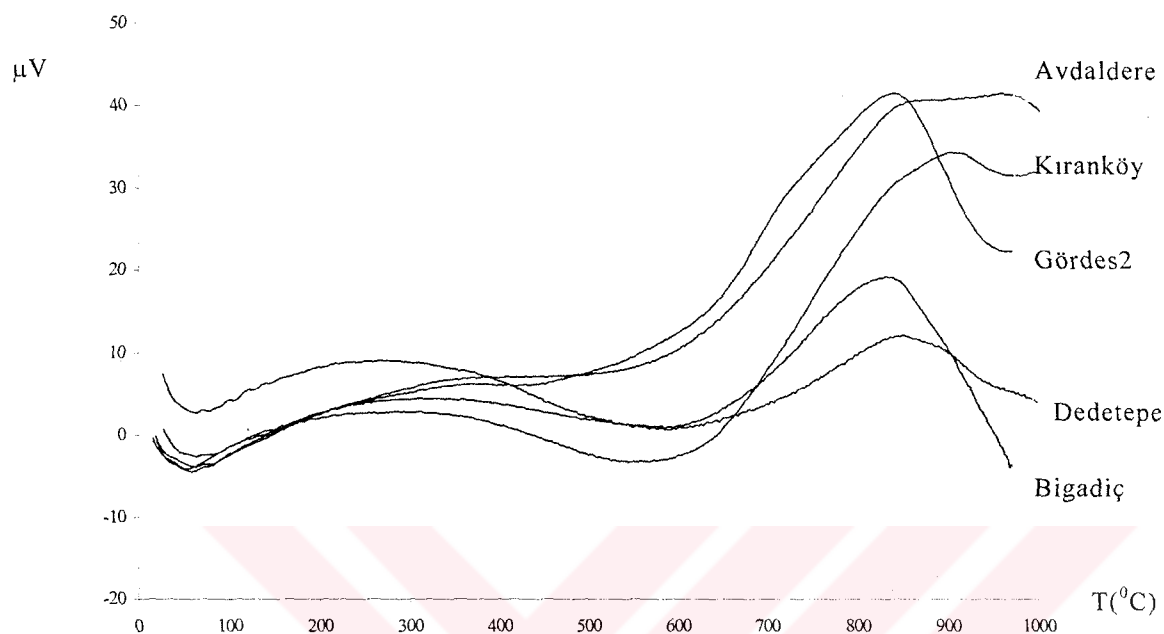
Figure 32: DTA curves of clinoptilolite minerals from different origins

The DTA patterns of the samples indicated that clinoptilolite was stable toward dehydration. The samples have broad endotherms at lower temperatures, which is the characteristic of natural zeolites. At higher temperatures second endotherm exhibits but it was not certain as the main endotherm indicates the conversion of zeolite to another amorphous or crystalline phase. On the DTA curves it was understood that no thermal reaction took place within the samples to higher temperatures at about 650 ^0C. The dehydration behaviour of the clinoptilolte samples was given in Table 8.

Table 8: Dehydration behaviour of different clinoptilolite minerals (DTA)

NATURAL ZEOLITE	Endotherm at (^{0}C)	Peak maximum at (^{0}C)
Bigadiç	62.4	833
Avdaldere	65.2	850
Kıranköy	54	903
Gördes 2nd mine	60.8	837
Dedetepe	62	847

In DTA patterns of all samples the characteristic broad endotherms were observed at low temperature ranges. Bigadiç, Kıranköy, Dedetepe and Avdaldere clinoptilolites gave first endotherm nearly at same temperatures while Gördes 2nd mine sample has rather lower first endotherm temperature corresponding to presence of water in the structure. The high temperature second broad endotherms for all clinoptilolite samples were centred at 550 ^{0}C. It may be the starting temperature of the conversion of clinoptilolite to another amorphous or crystalline phase or conversion of the Fe_2O_3 present in the tuff to another phase.

All samples have peak maxima nearly at the same temperature around 835 ^{0}C except Kıranköy showing the inversion to another phase. Kıranköy has peak maximum at 903 ^{0}C and it is more stable toward phase inversion compared to other samples. This phase inversion is maybe due to Fe_2O_3.

6.3 Adsorption Analysis

The adsorption isotherm of Bigadiç clinoptilolite for N_2 adsorption is given in Figure 33 and Figure 34.
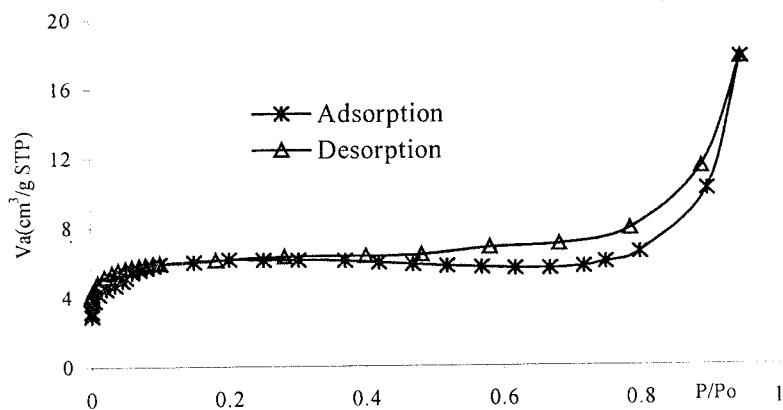
Figure 33: N_2 Adsorption isotherm of Bigadiç clinoptilolite
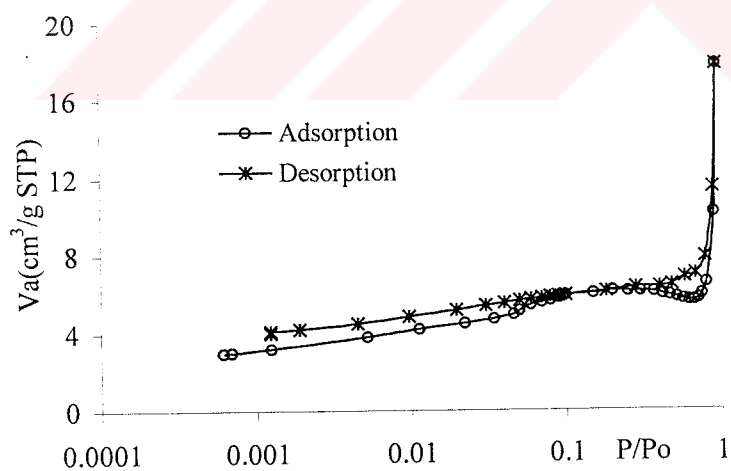
Figure 34: N_2 Adsorption isotherm of Bigadiç clinoptilolite (log scale)

The adsorption isotherms of different clinoptilolite samples were determined either by N_2 or Ar gases at 77 K and 87 K are given in Figure 35 and Figure 36, respectively. The adsorption behaviour of clinoptilolite samples toward each gas, surface areas determined from B.E.T and Langmuir models were examined.

The N_2 and Ar adsorption amounts (V_a) of the clinoptilolite samples were low as indicated in Figure 35 and Figure 36, respectively. Because contraction of the zeolite channels occurs at lower temperatures [50]. Also the number of Ar and N_2 molecules in each zeolite cavity drops below -150 ^0C for argon and -120 ^0C for nitrogen given in Figure 8 [50].

The cryogenic temperatures at which the experiments were carried out also effects the surface area results. The adsorbed amount N_2 and Ar gases of hence the surface area of adsorbent will decrease with the decreasing temperature. Additionally, at lower temperatures sharp drop of the diffusion rates occurs and takes more time to reach equilibrium. The adsorbed amount of N_2 and Ar gases will increase with the increasing equilibrium time.

Since the equilibrium time interval was set 45 sec for Ar and 90 sec for N_2 adsorption in this study, calculated surface areas using B.E.T and Langmuir models for Ar adsorption was lower compared to N_2. Özkan, F. (1996) was studied the N_2 adsorption of Bigadiç sample in her Ph.D thesis. Since Özkan used 120 sec equilibrium time interval, Langmuir and B.E.T surface areas she has found from both models were 96.75 m^2/gr, 50.15 m^2/gr, respectively and higher than those we found in this study given in Table 9 and 10.
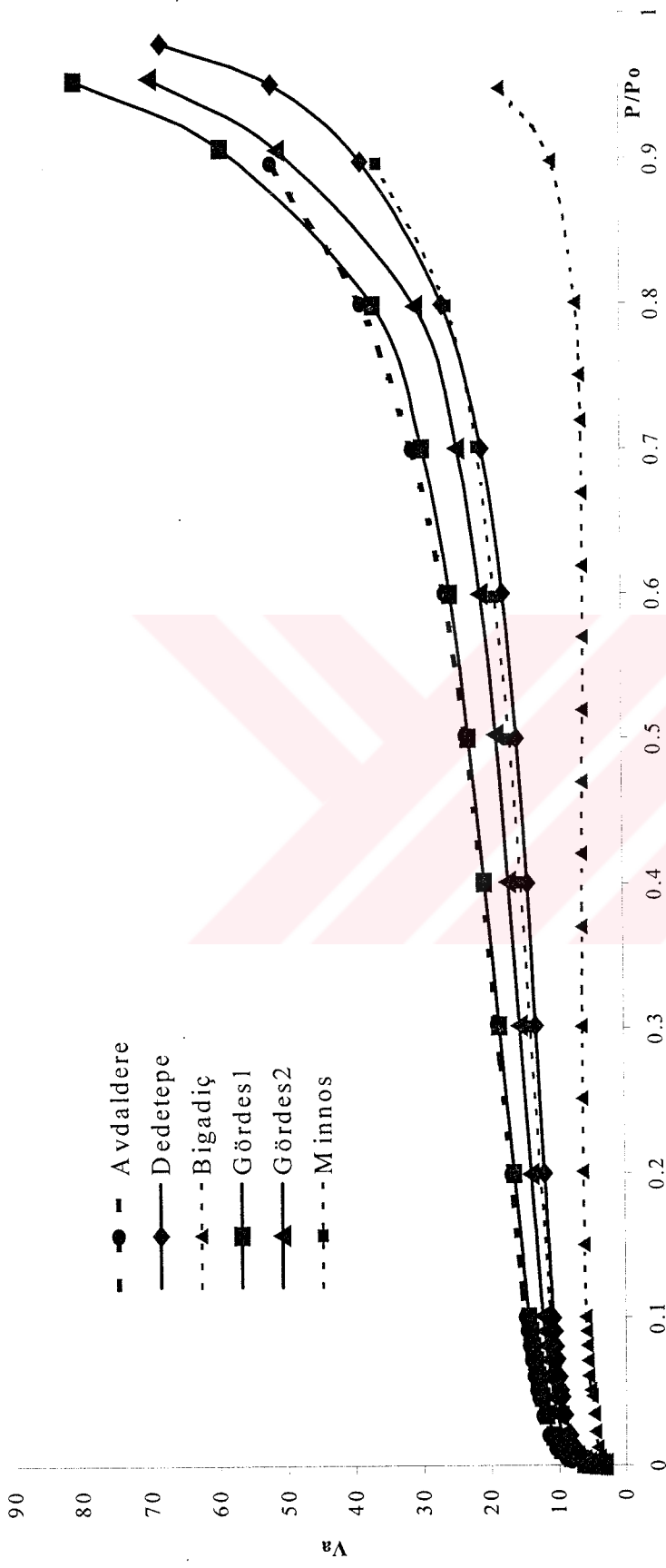
Figure 35: N₂ Adsorption Isotherms of original clinoptilolite samples
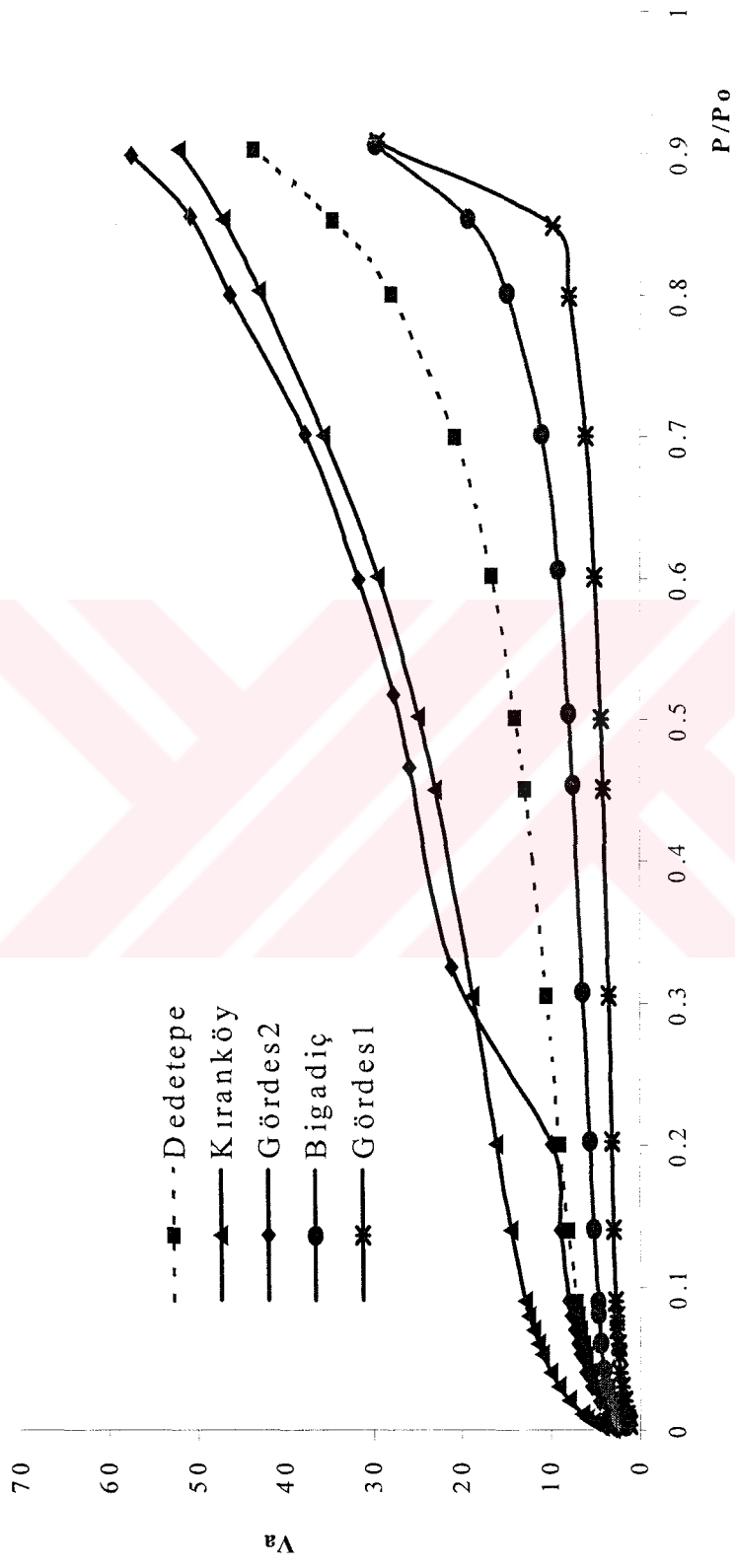
Figure 36: Ar Adsorption Isotherm of original clinoptilolite minerals

Table 9: The results of N$_2$ Adsorption Experiments of clinoptilolite minerals

NATURAL ZEOLITE	BET THEORY			LANGMUIR THEORY		
	Surface Area (m^2/gm)	C-Value	VM (cc/gm)	Surface Area (m^2/gm)	b-Value	VM (cc/gm)
Bigadiç	22.65	1440	5.20	27.96	0.01	6.42
Gördes I	56.99	299.84	13.09	81.15	0.03	18.64
Gördes II	47.29	3630.37	10.87	67.52	0.03	15.51
Avdaldere	57.9390	1117.47	13.31	81.21	0.02	18.65
Dedetepe	41.95	710.89	9.64	56.79	0.02	13.05
Kiranköy	17.88	717.53	4.11	24.24	0.02	5.57
Minnos	42.71	2516.19	9.81	60.60	0.023	13.92

Bet method; the range of relative pressure (P/Po) was adjusted in order to supply 99.95% correlation factor.

Langmuir method; the range of relative pressure (P/Po) was adjusted in order to supply 99.95% correlation factor.

Table 10: Results of Ar Adsorption experiments of clinoptilolite minerals

NATURAL ZEOLITE	BET THEORY			LANGMUIR THEORY		
	Surface Area (m²/gm)	C-Value	VM (cc/gm)	Surface Area (m²/gm)	b-Value	VM (cc/gm)
Bigadiç	17.25	205.78	4.52	22.45	0.02	5.88
Gördes I	9.50	782.69	2.49	13.56	0.03	3.55
Gördes II	32.38	55.51	8.49	45.24	0.04	11.86
Kiranköy	53.15	56.14	13.93	76.28	0.05	19.99
Dedetepe	29.04	55.71	7.61	41.54	0.05	10.89

Bet method; the range of relative pressure (P/Po) was adjusted in order to supply 99.95% correlation factor.

Langmuir method; the range of relative pressure (P/Po) was adjusted in order to supply 99.95% correlation factor.

The sample weight, degas time and temperature are the important factors in the determination of adsorption isotherms. The effect of degas temperature was investigated for Ar adsorption. There is only 1% weight difference between 350 ^{0}C or 450 ^{0}C heated samples obtained from TGA analysis showed that degassing the sample either at 350 ^{0}C or 450 ^{0}C did not change the results much.

Table 11: The effect of degas temperature on Ar Adsorption results of Bigadiç clinoptilolite

METHOD		DEGAS TEMPERATURE	
		350 ^{0}C	450 ^{0}C
BET	Surface Area (m^2/gm)	17.70	16.60
	C	69.03	87.43
	Vm (cc/gm)	4.64	4.35
LANGMUIR	Surface Area (m^2/gm)	23.65	23.48
	B	0.04	0.04
	Vm (cc/gm)	6.20	6.15

B.E.T method; the range of relative pressure (P/Po) was adjusted in order to supply 99.95% correlation factor.

Langmuir method: the range of relative pressure (P/Po) was adjusted in order to supply 99.95% correlation factor.

The helium gas is used in the free-space measurement in the pre-treatment step of the analysis. But the helium might not be released from the sample pores before analysis and effects surface area results. The analysis was carried out either by entering or measuring the free-space and the results were given in Table 12. The result was not effected in both cases showing that helium was released from the pores.

Table 12: The effect of Free-Space analysis type on Ar Adsorption results of Bigadiç clinoptilolite **(Degas at 350 ^{0}C)**

METHOD		Free-Space Entered	Free-Space Measured
BET	Surface Area (m^2/gm)	17.70	17.25
	C	69.03	205.78
	Vm (cc/gm)	4.64	4.52
LANGMUIR	Surface Area (m^2/gm)	23.65	22.45
	B	0.04	0.02
	Vm (cc/gm)	6.20	5.88

B.E.T method; the range of relative pressure (P/Po) was adjusted in order to supply 99.95 correlation factor.

Langmuir method; the range of relative pressure (P/Po) was adjusted in order to supply 99.95 correlation factor.

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The pore size distribution curves for different clinoptilolite samples were determined using desorption data in the relative pressure range of 0.95<P/Po<0.4 is given in Figure 37. The limiting pore widths (r^p) corresponding to the relative pressure (P/Po) of each sample was taken from Sing and Gregg (1981) given in Table 13. The amount desorbed at each P/Po is obtained from the experiment. The difference between the successive values of Va gives the ΔV values. Finally, dividing the ΔV by the limiting pore width Δr gives the pore size distribution.

In Figure 37 Gördes 1st mine, Gördes 2nd mine and Avdaldere samples there exist two maxima at 18 Å and 32 Å. The maximum occurs at 25 Å for Dedetepe, 18 Å for Minnoş, Bigadiç and Kıranköy, showing that all the clinoptilolite samples have mesaporous structure.

Table 13: The values of r^p at different P/Po values for nitrogen at 77.4 K. (Sing and Gregg, 1981)

P/Po	r^p(Å)	P/Po	r^p(Å)
0.40	15.60	0.75	40.5
0.45	17.40	0.80	50.7
0.50	19.45	0.85	67.5
0.55	21.85	0.90	101.9
0.60	24.9	0.95	199
0.65	28.7		
0.70	33.7		
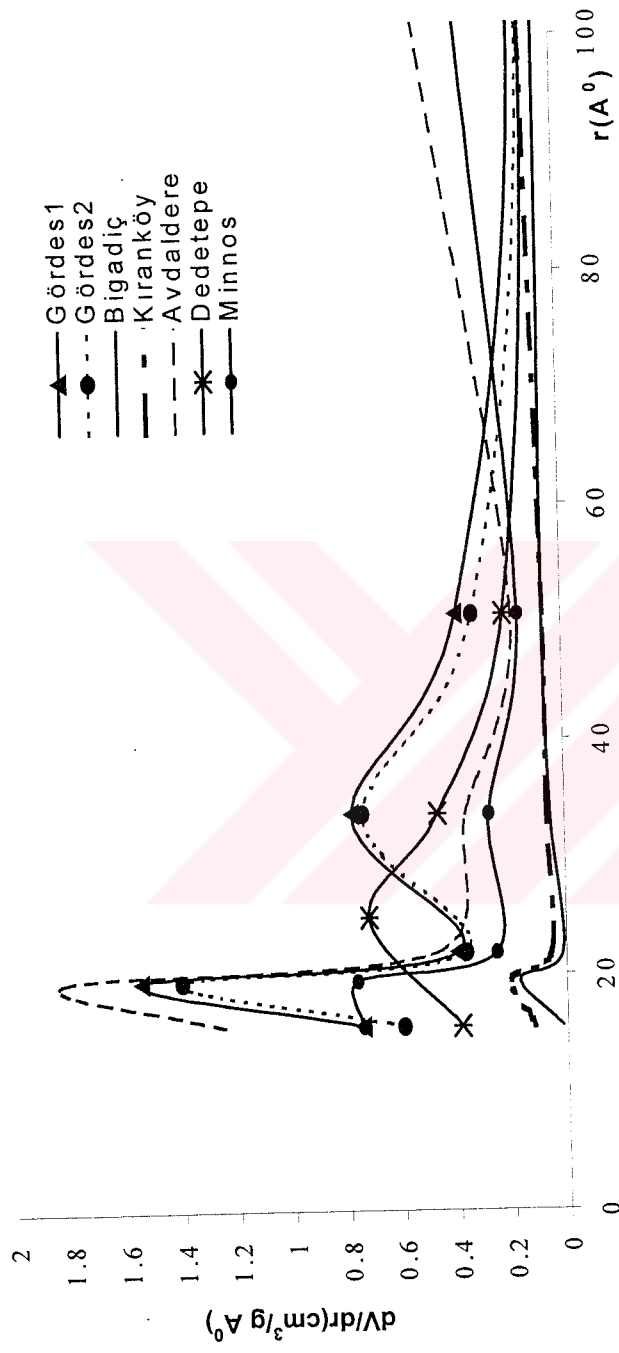
Figure 37: Pore size distribution of different clinoptilolite samples determined by BJH method for N₂ adsorption.

6.4 Ion Exchange Studies

There are several methods are available in order to determine the chemical compositions of the materials. In this study three dissolution was used and chemical composition of original Bigadiç mineral is given in Table 14.

Table 14: Chemical composition of Bigadiç clinoptilolite

	%w/w*
Al_2O_3	10.75
BaO	0.24
CaO	3.37
Co_3O_4	0.003
Cr_2O_3	0.005
Cu_2O	0.002
Fe_2O_3	1.10
K_2O	2.33
Li_2O	0.018
MgO	1.35
MnO	0.012
Na_2O	0.62
NiO	0.007
PbO	0.008
Si_2O	67.48
ZnO	0.0008
H_2O	12.62
Total	**99.86**

*Three Dissolution Method

Özkan, F. (1996) was used the wet chemistry atomic adsorption method in her PhD studies. As mentioned before in this study three dissolution was used. The chemical composition of the sample determined from each method is compared in Table 15 as shown. Three methods gave different results caused by the different techniques of analysis.

Table 15: Chemical analysis of original Bigadiç clinoptilolite by different methods.

	%w/w*	%w/w**
Al_2O_3	10.75	10.91
SiO_2	67.47	71.75
Fe_2O_3	1.10	0.54
MgO	1.35	1.08
CaO	3.37	2.30
Na_2O	0.62	1.19
K_2O	2.33	4.3
MnO	0.01	0.008
H_2O	12.62	7.77
Total	**99.62**	**99.85**

*   Three Dissolution Method

** Wet Chemistry Atomic Adsorption Method (Özkan, F.,1996)

The exchange was carried out both in waterbath and microwave. The change cation amounts in the zeolite are given in Figure 38 and Figure 39 for waterbath and microwave exchange, respectively. In both cases, Fe^{+3}, Zn^{+2}, Pb^{+2}, Li^+, Cu^{+2} and Co^{+3} amounts in the zeolite were very small did not alter much as shown in the Figure 38 and Figure 39. The noticeable changes of Ba^{+2}, Mg^{+2} and K^+ amounts in the zeolite were detected. But the major change in zeolite was observed in Ca^{+2} amount. It shows that most of the Na^{+2} cations in the solution were exchanged with Ca^{+2} cations in the zeolite. This is related to the dimensions of unhydrated radius of the exchanging cation. (Table 16) If the hydrated ions are approximately the same size as the channel dimensions, the exchange becomes difficult. The Na^+ in the solution probably go to site positions in which Ca^{+2} ions are located. The Ca^{+2} ions were coordinated with 3 framework oxygen atoms and five water molecules for that reason Ca^{+2} ions are more easily removed from clinoptilolite structure.

Table 16: Properties of Cations (Semmens, M., Seyfarth, M. 1975)

Cation	Ionic Radius (Å)	Hydrated Radius (Å)
Na^+	0.98	3.58
Mg^{+2}	-	4.28
K^+	1.30	3.31
Ca^{+2}	0.99	4.12
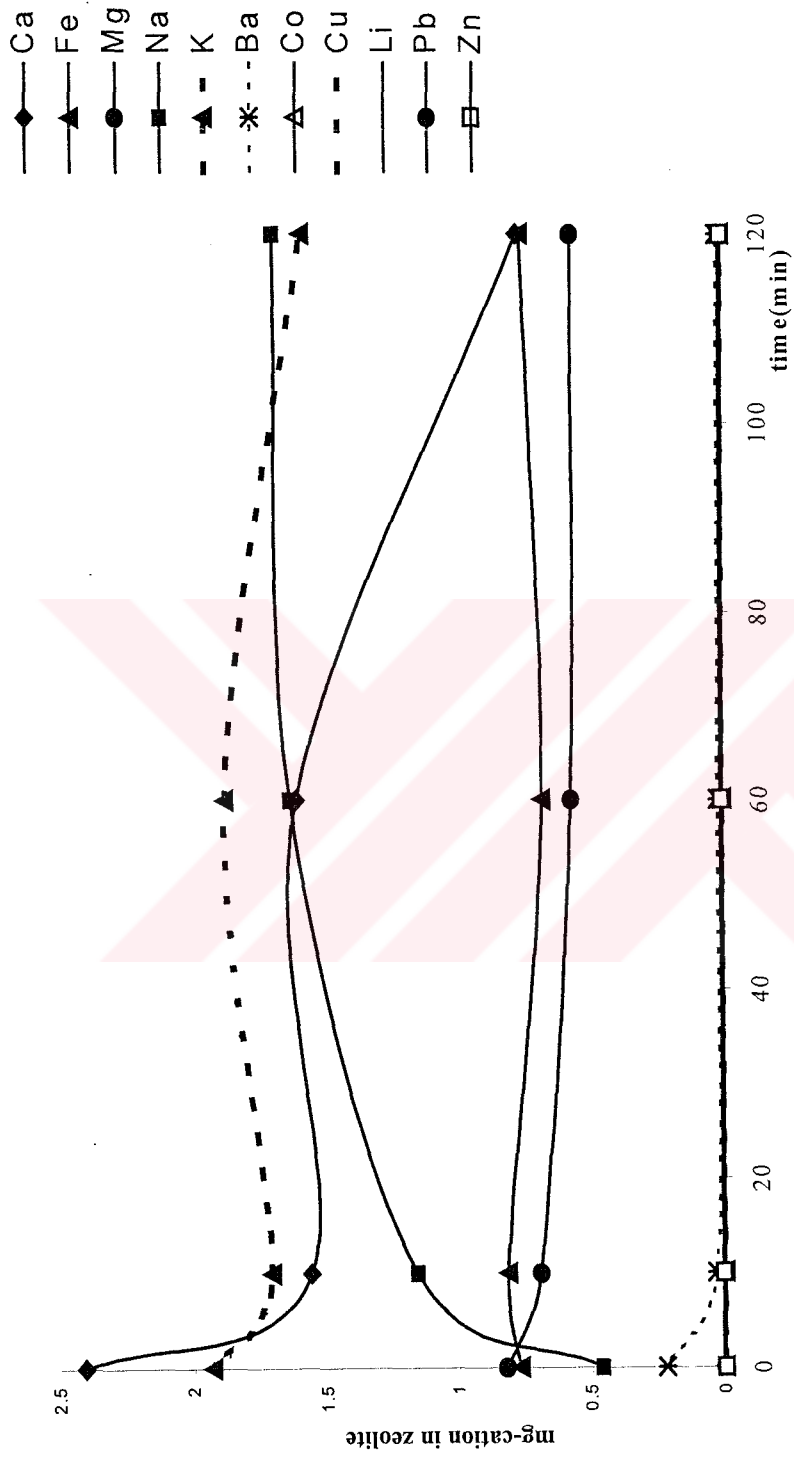
Figure 38: The changes in cation amounts of Bigadiç clinoptilolite in waterbath

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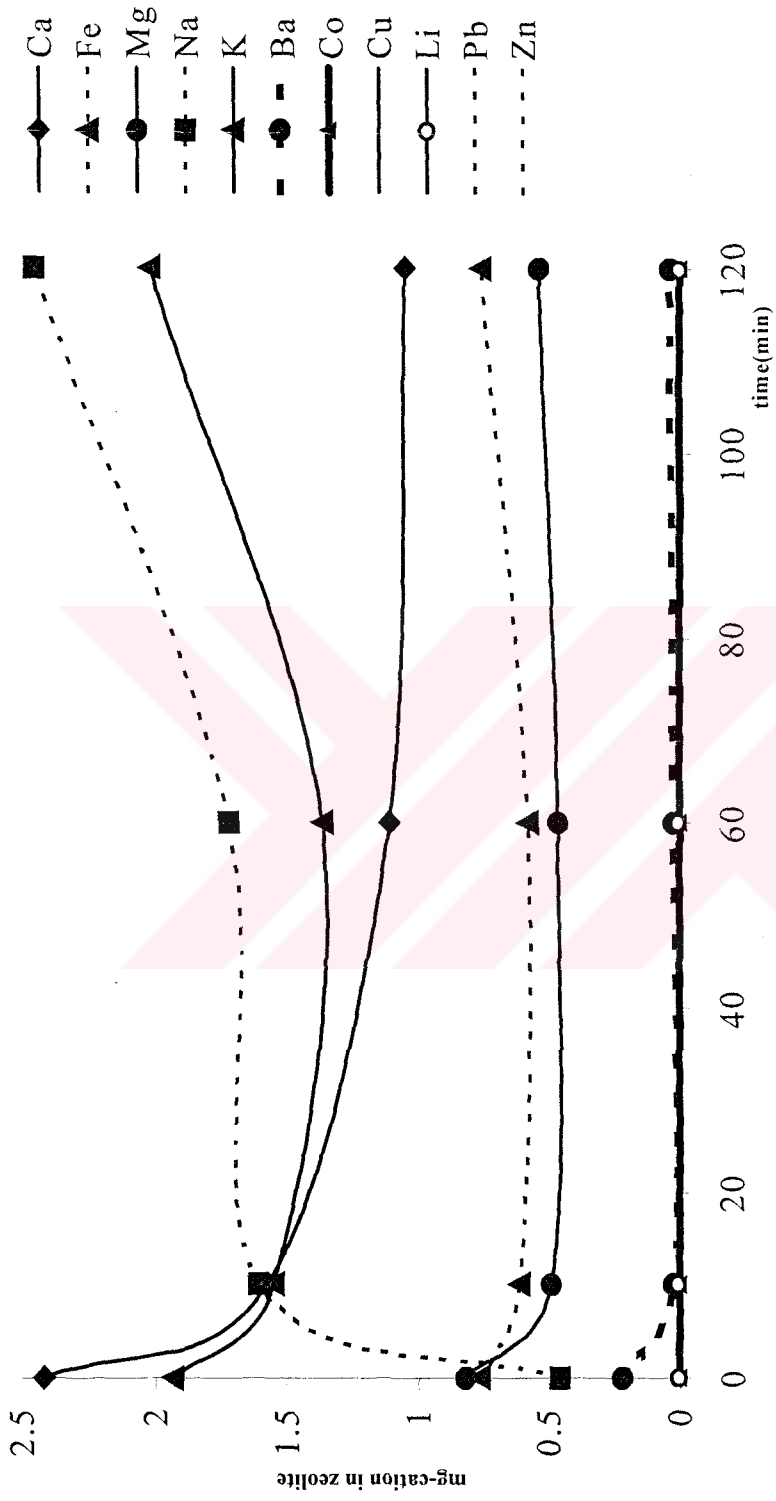
Figure 39: The changes in cation amounts of Bigadiç clinoptilolite in microwave

Legend: Ca, Fe, Mg, Na, K, Ba, Co, Cu, Li, Pb, Zn

Y-axis: mg-cation in zeolite

X-axis: time(min)

The Na^{+2} amounts in zeolite were 1.158 mgr, 1.63 mgr, 1.69 mgr and 2.41 mgr after 10 min, 60 min, 120 min and 2 weeks of waterbath exchange, respectively. The Na$^+$ amounts in the zeolite were 1.51 mgr, 1.72 mgr and 2.46 mgr after 10 min, 60 min and 120 min of microwave exchange, respectively.

The weight % of Na$^+$ and other exchangeable cations are given in Table 17. At the end of 2 weeks of waterbath exchange Na$^+$ amount was still lower than Na$^+$ amount in microwave.

The Na amount in terms of mmol Na$^+$/gr zeolite was calculated for Na-Bigadiç at different exchange times and is given in Figure 40. In microwave at each exchange interval the Na$^+$ amount in the zeolite was high compared to waterbath. This shows that microwave method is more effective and rapid as discussed in chapter 4.
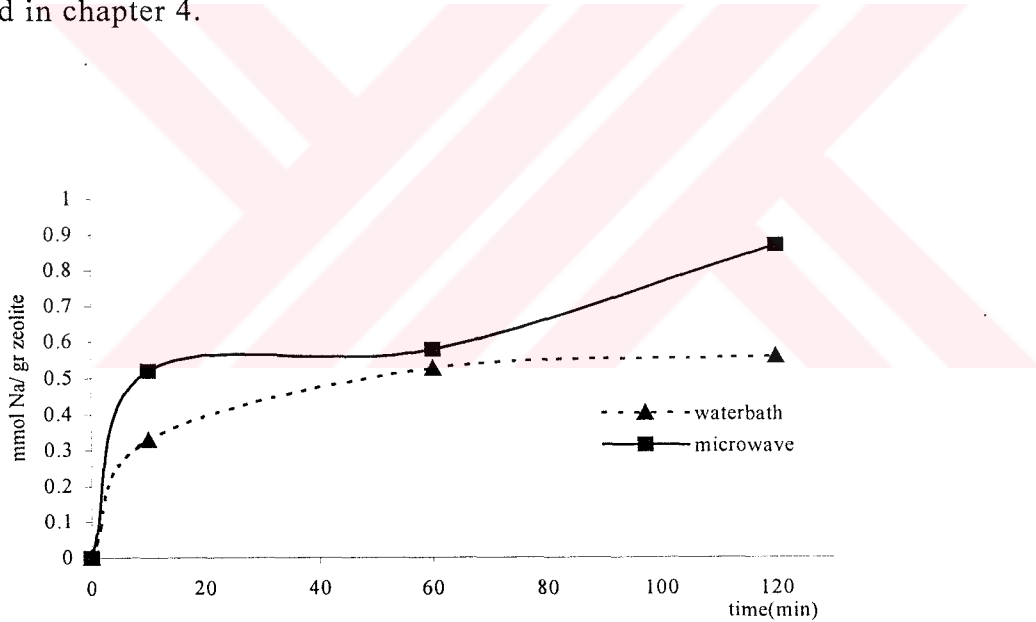
Figure 40: The Na amount in Na-Bigadiç in waterbath and microwave

Table 17: The Weight % of cations in Bigadiç clinoptilolte at different times

	Bigadiç	WATERBATH				MICROWAVE		
		10'	1h	2h	2week	10'	1h	2h
Al$_2$O$_3$	10.20	10.12	10.17	9.64	9.60	9.49	9.44	10.42
BaO	0.05	0.04	0.02	0.019	0.035	0.024	0.028	0.046
CaO	2.86	2.16	2.21	1.06	0.61	1.42	1.55	1.44
Co$_3$O$_4$	0.003	0.002	0.001	0.001	0.002	0.001	0.001	0.003
Cr$_2$O$_3$	0.001	0.04	0.13	0.008	0.003	0.009	0.459	0.001
Cu$_2$O	0.002	0.002	0.004	0.002	0.002	0.002	0.001	0.002
Fe$_2$O$_3$	1.018	1.15	0.95	1.07	0.88	1.04	0.83	1.07
K2O	2.23	2.04	2.22	1.89	1.93	1.66	1.64	2.39
LiO	0.017	0.02	0.02	0.016	0.017	0.017	0.015	0.015
MgO	1.185	1.13	0.92	0.919	0.436	0.917	0.773	0.882
MnO	0.001	0.03	0.01	0.012	0.007	0.006	0.009	0.003
Na$_2$O	0.524	1.54	2.16	2.25	3.22	2.03	2.31	3.24
NiO	0.007	0.05	0.14	0.05	0.05	0.02	0.39	0.01
PbO	0.010	0.01	0.01	0.006	0.011	0.009	0.005	0.004
SiO$_2$	1.476	3.75	4.29	3.747	3.150	3.399	0.136	0.395
ZnO	0.007	0.01	0.01	0.005	0.006	0.009	0.005	0.014

The maximum exchangeable amount of Na^+ was calculated by adding up the meq Na^+ amounts of all the cations in the zeolite and the exchanged amount of Na^+ was calculated from final Na^+ amount in the zeolite at time, t. The maximum exchangeable amount and exchanged amount of Na^+ versus time is given in Figure 41 and Figure 42 for waterbath and microwave exchange, respectively.
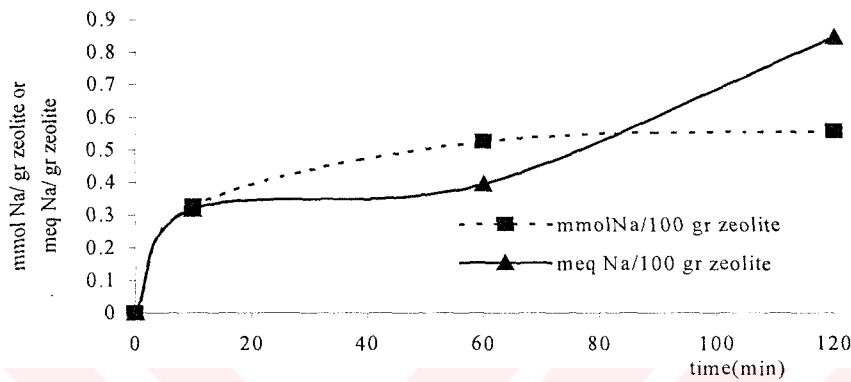
Figure 41: The maximum exchangeable and exchanged amount of Na^+ in Na-Bigadiç in waterbath.
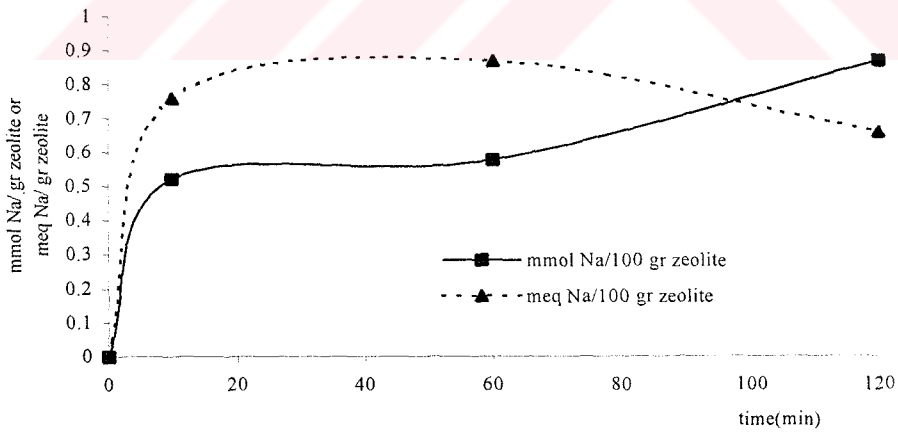
Figure 42: The maximum exchangeable and exchanged amount of Na^+ in Na-Bigadiç in microwave.

6.5 Thermal Studies of Ion Exchanged Bigadiç Clinoptilolite

The TGA curve of Bigadiç clinoptilolite cation exchanged with 1 N NaCl in waterbath was given in Figure 43.
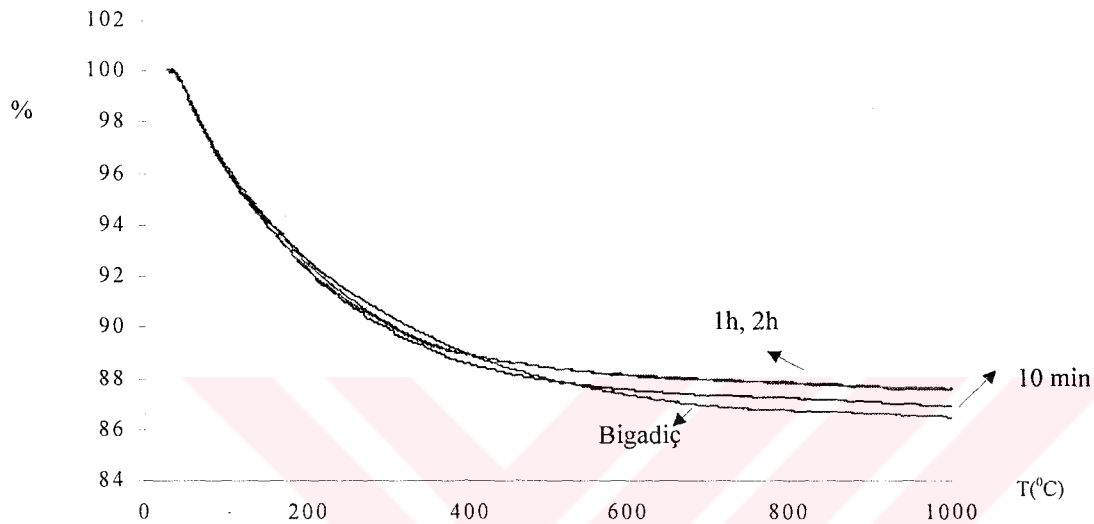
Figure 42: TGA curve of cation exchanged Bigadiç clinoptilolite in waterbath

All cation exchanged Bigadiç samples with 1N NaCl in waterbath at different times gave smooth and continuos TGA curves that shows they only loose their water and no structural deformation occurred as they were heated up to 1000 ^{0}C.

The TGA curve of Bigadiç clinoptilolite cation exchanged with 1 N NaCl in microwave was given in Figure 44.
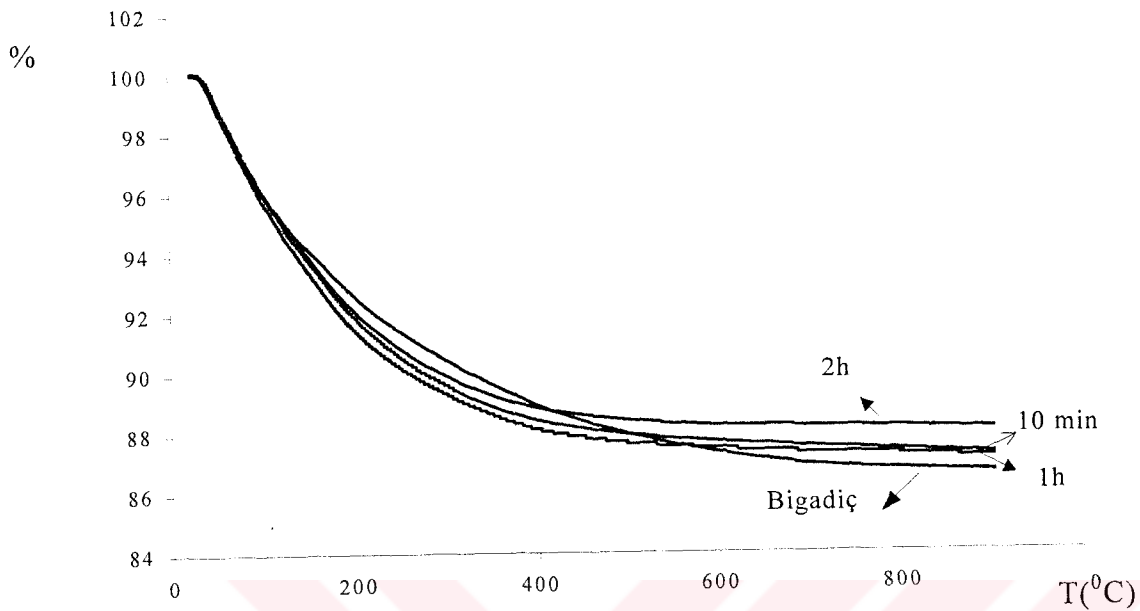
Figure 44: TGA curve of cation exchanged Bigadiç clinoptilolite in microwave

All cation exchanged Bigadiç samples with 1N NaCl in microwave at different times gave smooth and continuos TGA curves that shows they only loose their water and no structural deformation occurred as they were heated up to 1000 ^{0}C.

The percent loss of external water, loosely bound and tightly bound water of Na-exchanged Bigadiç samples treated in microwave at different times was given in Table 18. The total percent loss of water of original Bigadiç sample was %13.51 as given in Table 4. The total water lost percent in all microwave treated samples were lower compared to the original sample. In microwave heating the zeolites were dried at shorter times and losses their water easily as discussed in chapter 4. Also the samples were washed with bidistilled water and dried in vacuum oven at 160 ^{0}C at least for 4 hours. Then they were stored in closed bottles and none were in contact with the atmosphere before use. This also causes the decrease in total water amount of

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the samples. Because the samples were also dried in vacuum oven and kept under same conditions as microwave treated samples. The same situation is observed in Na-Bigadiç samples treated in waterbath as seen in Table 19.

Table 18: % Weight losses of cation exchanged Bigadiç clinoptilolite in microwave

Exchange Time	$< 85\ ^0C$ external water	85^0-285^0C loosely bound water	$>285^0C$ tightly bound water	Total
10min.	3.27	6.98	2.66	12.94
1 hour	3.57	6.96	2.48	13.12
2 hours	3.28	6.54	2.06	12.01

Table 19: % Weight losses of cation exchanged Bigadiç clinoptilolite in waterbath

Exchange Time	$< 85\ ^0C$ external water	85^0-285^0C loosely bound water	$>285^0C$ tightly bound water	Total
10min.	3.26	6.72	3.10	13.14
1 hour	3.27	6.40	2.81	12.52
2 hours	3.28	6.39	2.63	12.29
2 weeks	3.49	6.74	2.35	12.64

Differential thermal analysis curves of original and cation exchanged Bigadiç with 1 N NaCl in microwave is given in Figure 45.

Figure 45: DTA curve of cation exchanged Bigadiç clinoptilolite in microwave

The shape of the first endotherms for all samples was the same. The second endotherm of Na-exchaged samples in microwave are not certain as the second endotherm of the original sample. This is related to the type and the amount of the cations in the structure as discussed in Chapter 3.

Table 20: Dehydration behaviour of cation exchanged Bigadiç clinoptilolite in microwave (DTA)

	Endotherm at (^{0}C)	Peak maximum at (^{0}C)
Original Bigadiç	43.24 ±5	834 ±5
10 min	65.52 ±5	833 ±5
1 hour	62.40 ±5	833 ±5
2 hours	65.52 ±5	836 ±5

The dehydration behaviour of original and Na exchanged Bigadiç clinoptilolite in microwave is given in Table 20. The fist endotherm temperature of original Bigadiç sample was 43.25 ^{0}C. The first endotherm temperatures of Na exchanged Bigadiç sample in microwave in different times were nearly the same and they shifted to higher temperatures compared to the original one. These first endotherm temperatures correspond to presence of zeolite water in the structure. The second endotherms were disappeared as the samples exchanged with Na$^+$. The replacement of the Na$^+$ in the clinoptilolite structure as the exchange proceeds caused the different shapes of second endotherm on DTA curves. The original Bigadiç sample has exotherm starting at 650 ^{0}C and peak maximum around 835 ^{0}C which indicates that all samples keep their original crystal structure up to 650 ^{0}C.

Differential thermal analysis curves of original and cation exchanged Bigadiç with 1 N NaCl in waterbath is given in Figure 46.

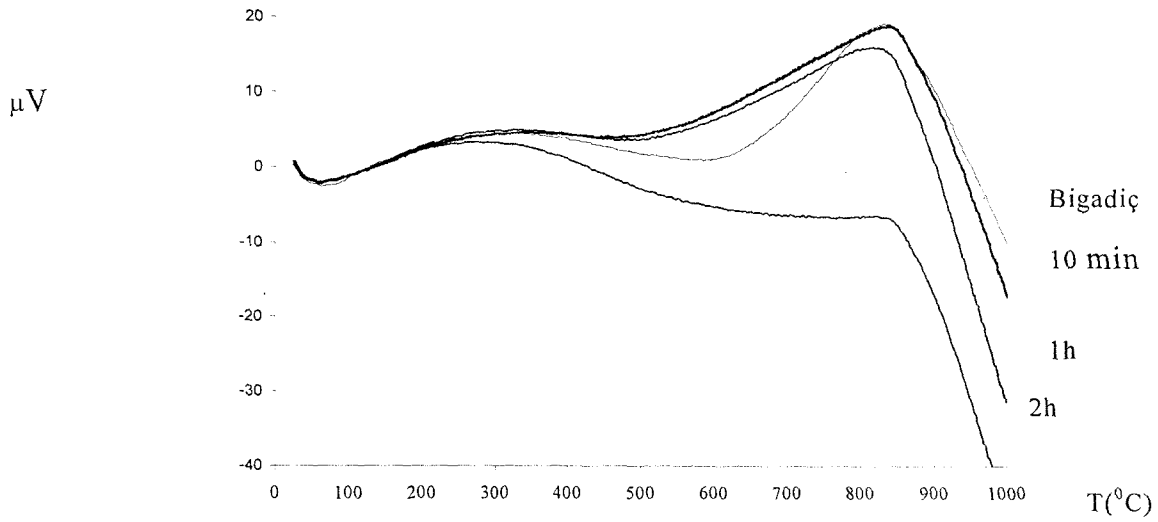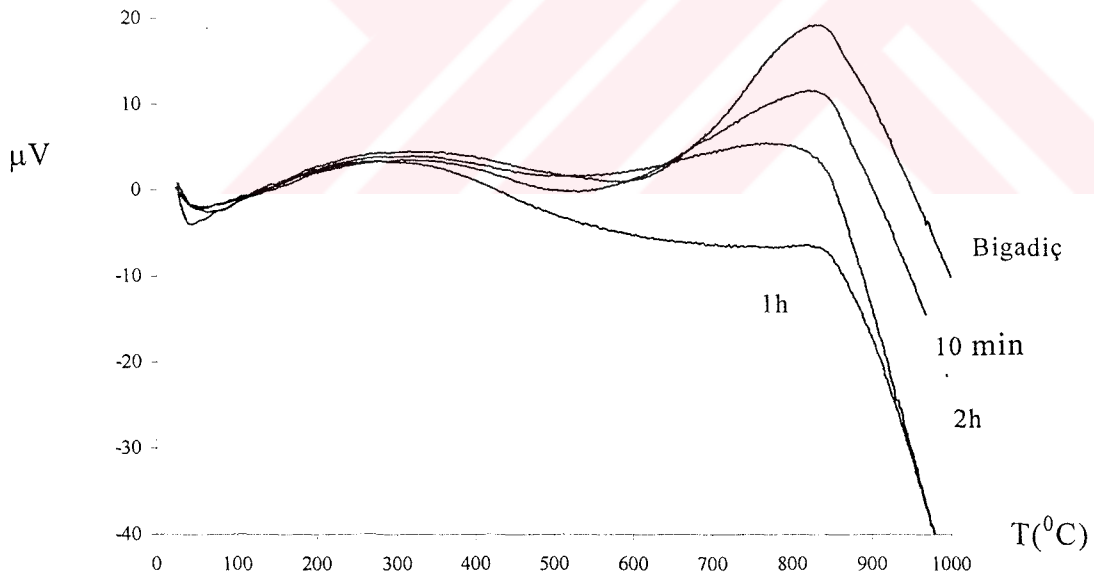Figure 46: DTA curve of cation exchanged Bigadiç clinoptilolite in waterbath

Table 21: Dehydration behaviour of cation exchanged Bigadiç clinoptilolite in waterbath (DTA)

	Endotherm at (^{0}C)	Peak maximum at (^{0}C)
Original Bigadiç	43.24 ±5	834 ±5
10 min	40.56 ±5	826 ±5
1 hour	40.56 ±5	815 ±5
2 hours	40.56 ±5	814 ±5
2 weeks	40.56 ±5	815 ±5

The dehydration behaviour of original and Na exchanged Bigadiç clinoptilolite in waterbath is given in Table 21. The first endotherm temperatures for original and Na exchanged Bigadiç sample in waterbath in different times were nearly the same but are lower than the first endotherm temperatures of the microwave samples. The second endotherms are more visible in case waterbath exchange compared to microwave exchange. Because at each exchange more Na^+ cations were replaced and the exchange degree of Na^+ is higher in microwave case as indicated in Figure 39. As mentioned in chapter 3 the amount of cations directly influences the thermal behaviour of samples and as a result of cation content difference microwave treated samples gave different shape of DTA curve compared to waterbath treated samples.

The original Bigadiç sample has peak maximum at 835 ^{0}C. All of the Na exchanged samples in waterbath in different times have peak maximums around 820 ^{0}C which is lower than the peak maximum temperatures of the samples treated in microwave. This indicates that microwave treated samples were thermally more stable compared to waterbath treated samples.

Chapter 7

CONCLUSIONS

The characterization of clinoptilolite minerals from different zeolatic formations and the modification of the clinoptilolite with ion exchange were studied in this study. The thermal, structural and adsorption related properties of zeolites were determined by different characterization techniques.

The infra-red spectroscopy has been used to determine the structural properties. The FTIR spectrums of the original samples were examined and the results showed that the samples have characteristic vibrations of the clinoptilolite framework. The influence of washing on the clinoptilolite content was also examined. The clinoptilolite content of Gördes 1st mine and Bigadiç samples were increased while the clinoptilolite content of Gördes 2nd sample decreased after washing. The moist forms of the original samples were also examined in infra-red spectroscopy. The increase in water and clinoptilolite content was observed in the FTIR spectrums of the moist samples and samples should have the same moisture content in order to compare their clinoptilolite content by 609 cm^{-1} peak.

The TGA, DTA and DSC instruments were used to determine thermal properties of clinoptilolite samples. The TGA curves of the all samples were smooth and continuos showing that no structural deformation occurred as they were heated up to 1000 ^{0}C, only loose water. The derivative TGA curves closely resembles the DSC curves of the clinoptilolites. Broad endotherm exhibits in all DSC curves that is centred at 90 ^{0}C showing the presence of water in the structure. The DTA curves were also examined. The exotherm at 830 ^{0}C in all clinoptilolite samples shows no structural change occurs up to 650 ^{0}C which is the starting temperature of this peak.

The adsorption related properties were determined by volumetric adsorption system. The Accelerated Surface Area and Porsimeter (ASAP 2010) was used to carry out the adsorption analysis. The adsorption isotherms were determined from the adsorption and desorption data obtained during the analysis. But in the adsorption

isotherms, the desorption line lies below the adsorption line for some clinoptilolite samples. This situation was not expected and there might be problem with the operation of the instrument. The analysis should be repeated for those conditions and results should be checked. The cryogenic temperature (LN_2 and LAr at their boiling temperatures) at which the experiments were carried out and the equilibrium time interval are effective parameters on the adsorption and related results.

The Bigadiç clinoptilolite was modified by ion exchange method. The ion exchange process was carried out both in microwave and waterbath. The exchanged amount results showed that microwave is more rapid and efficient method. The TGA and DTA analysis of the exchanged samples both in microwave and waterbath was also performed. The DTA curves showed that microwave treated samples were more stable toward dehydration as they have higher peak maximum temperatures compared to waterbath.

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APPENDIX

THE RESULTS OF ICP ANALYSES

The Concentration of elements in the clinoptilolite mineral

The Original Clinoptilolite Sample:

Element	Concentration (ppm)
Al	54.113
Ba	0.4146
Ca	20.457
Co	0.0215
Cr	0.009
Cu	0.0161
Fe	7.1318
K	18.578
Li	0.0813
Mg	7.163
Mn	0.011
Na	3.8936
Ni	0.0552
Pb	0.087
Si	6.9153
Zn	0.0571

W_o= 101.2 mg H_2O (TGA analysis)= 12.92 %

W_{lost}= 78.5 mg SiO_2 = 64.64 %

W_{left}= 22.7 mg

W_{water}= 13.08 mg

W_{SiO2}= 65.42 mg

The 10 min Waterbath exchanged sample

Element	Concentration (ppm)
Al	54.208
Ba	0.34526
Ca	15.613
Co	0.012759
Cr	0.32371
Cu	0.019849
Fe	8.1569
K	17.099
Li	0.079804
Mg	6.9095
Mn	0.2257
Na	11.58
Ni	0.40645
Pb	0.09779
Si	17.72
Zn	0.06464

W_o= 100.4 mg H_2O (TGA analysis)= 12.623%

W_{lost}= 78.9 mg SiO_2 = 65.97 %

W_{left}= 21.5 mg

W_{water}= 12.67 mg

W_{SiO2}= 66.23 mg

The 1 hour Waterbath exchanged sample

Element	Concentration (ppm)
Al	54.844
Ba	0.21061
Ca	16.08
Co	0.008016
Cr	1.1377
Cu	0.038386
Fe	6.7601
K	18.785
Li	0.072409
Mg	5.653
Mn	0.084962
Na	16.308
Ni	1.109
Pb	0.051102
Si	20.417
Zn	0.050123

W_o= 101.9 mg H_2O (TGA analysis)= 12.24 %

W_{lost}= 77.8 mg SiO_2 = 64.11 %

W_{left}= 24.1 mg

W_{water}= 12.47 mg

W_{SiO2}= 65.33 mg

The 2 hours Waterbath exchanged sample

Element	Concentration (ppm)
Al	51.547
Ba	0.17039
Ca	7.6496
Co	0.006909
Cr	0.069087
Cu	0.02214
Fe	7.5262
K	15.835
Li	0.077382
Mg	5.5983
Mn	0.091548
Na	16.877
Ni	0.36223
Pb	0.056104
Si	17.689
Zn	0.036624

W_o= 101.0 mg H_2O (TGA analysis)= 12.02 %

W_{lost}= 79.0 mg SiO_2 = 66.02 %

W_{left}= 22.0 mg

W_{water}= 12.322 mg

W_{SiO2}= 66.678 mg

The 2 weeks Waterbath exchanged sample

Element	Concentration (ppm)
Al	54.208
Ba	0.34526
Ca	15.613
Co	0.012759
Cr	0.32371
Cu	0.019849
Fe	8.1569
K	17.099
Li	0.079804
Mg	6.9095
Mn	0.2257
Na	11.58
Ni	0.40645
Pb	0.09779
Si	17.72
Zn	0.06464

W_o= 100.4 mg H_2O (TGA analysis)= 12.62 %

W_{lost}= 78.9 mg SiO_2 = 65.97 %

W_{left}= 21.5 mg

W_{water}= 12.67 mg

W_{SiO2}= 66.23 mg

The 10 min microwave exchanged sample

Element	Concentration (ppm)
Al	50.403
Ba	0.21216
Ca	10.175
Co	0.007426
Cr	0.076434
Cu	0.017925
Fe	7.2831
K	13.835
Li	0.079447
Mg	5.5497
Mn	0.044254
Na	15.104
Ni	0.14053
Pb	0.079117
Si	15.951
Zn	0.074563

W_o= 100.4 mg H_2O (TGA analysis)= 12.94 %

W_{lost}= 78.9 mg SiO_2 = 65.75 %

W_{left}= 21.50 mg

W_{water}= 12.89 mg

W_{SiO2}= 66.01 mg

The 1hour microwave exchanged sample

Element	Concentration (ppm)
Al	50.068
Ba	0.25154
Ca	11.112
Co	0.006968
Cr	4.0263
Cu	0.005159
Fe	5.8263
K	13.662
Li	0.071442
Mg	4.6732
Mn	0.070166
Na	17.192
Ni	3.0472
Pb	0.043426
Si	0.63696
Zn	0.036617

W_o= 100.2 mg H_2O (TGA analysis)= 13.02 %

W_{lost}= 81.80 mg SiO_2 = 68.64 %

W_{left}= 18.40 mg

W_{water}= 13.02 mg

W_{SiO2}= 68.78 mg

The 2 hours microwave exchanged sample

Element	Concentration (ppm)
Al	56.352
Ba	0.41667
Ca	10.54
Co	0.026084
Cr	0.01335
Cu	0.021391
Fe	7.657
K	20.247
Li	0.073421
Mg	5.437
Mn	0.026539
Na	24.558
Ni	0.08842
Pb	0.034796
Si	1.886
Zn	0.11187

W_o= 100.3 mg H_2O (TGA analysis)= 11.84 %

W_{lost}= 77.40 mg SiO_2 = 65.40 %

W_{left}= 22.90 mg

W_{water}= 11.80 mg

W_{SiO2}= 65.60 mg

Calculation of Normalized Absorbance Value in FTIR Spectra:

The absorbance values at each peak in FTIR spectra of zeolites were normalized to the same absorbance scale by dividing the peak height (mm) to the height of maximum peak (mm) then multiplying the result with the absorbance value of the maximum peak.
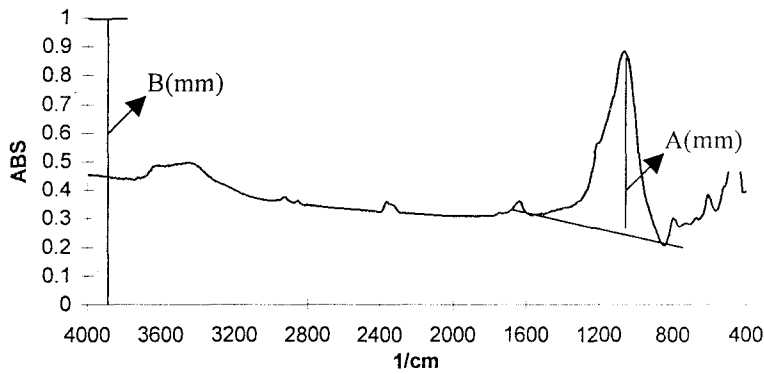
Maximum absorbance value = 1

Height of maximum absorbance value= B(mm)

Height of 1150 cm^{-1} peak= A(mm)

Normalized Absorbance value of 1150 cm^{-1} peak;

N.A.= (A/B)* 1