Investigation of clinoptilolite rich natural zeolites from Turkey: a combined XRF, TG/DTG, DTA and DSC study

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Abstract Turkey clinoptilolite-rich tuffs from Gördes and Bigadiç regions of western of Anatolia and their exchanged forms (K^+, Na^+, Mg^{2+} and Ca^{2+}) were characterized by TG/DTG-DTA, DSC and XRF methods and the surface areas were also determined for both tuffs. TG-DTG and DTA curves of all clinoptilolite samples were measured in the temperature range 30–1000 °C. All clinoptilolite samples had major, rapid mass losses between 30 and 200 °C, with slower and less significant mass losses at higher temperatures. The mass loss of the Natural-G is 9.54% while that of the Natural-B sample is 10.50%. Water content increases in the order of K < Na < Ca < Mg for Bigadiç clinoptilolite samples and in the following sequence K < Na < Mg < Ca for Gördes clinoptilolite samples. One mass loss step for all clinoptilolite samples was observed using differential scanning calorimeter (DSC) in the range of 30–550 °C.

Keywords Clinoptilolite · Dehydration ·
Natural zeolites · Thermal analysis · Turkey

Introduction

Zeolites are crystalline hydrated aluminosilicates of the alkali and alkaline earths. They have a framework structure characterized by the presence of interconnected cavities or cages, occupied by the relatively large cations and water molecules [1]. Natural zeolites have voids and channels which are typically in the range of molecular dimensions,

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i.e. 3–10 Å [2]. The exchangeable cations located within the framework play a crucial role in adsorption and thermal properties of the zeolites. The availability and relatively low cost of natural zeolites has stimulated much research on their physicochemical properties [3]. Zeolites have been widely used in various fields such as industry, agriculture and environmental protection.

Clinoptilolite structurally possesses HEU-type zeolites, with common HEU framework topology. Clinoptilolite has a ratio Si/Al >4 with a high thermal stability (600–800 °C). The unit cell is monoclinic C centered and usually characterized on the basis of 72 O atoms and 22 water molecules, with Na^+, K^+, Ca^{2+} and Mg^{2+} as the most common charge-balancing cations [1, 4–6]. Representative cell parameters for clinoptilolite is a = 17.62 Å, b = 17.91 Å, c = 7.39 Å, $\beta = 116°$, 18 [1, 7]. Clinoptilolite consists of a two dimensional system of three types of channels with sizes of 4.4 × 7.2 Å, 4.0 × 5.5 Å and 4.1 × 4.0 Å, respectively [8, 9]. Channels A (10-member rings) and B (8-member rings) are parallel to each other and to the c-axis of the unit cell, while C channels (8-member rings) lie along the a-axis intersecting both A and B channels. In natural zeolites, these channels are predominantly occupied by cations and H_2O [10–12].

A zeolite of the heulandite group with a structure which survives an overnight heating at 450 °C was proposed to be named clinoptilolite by Mumpton [5]. Gottardi and Galli [1] stated that the kind of the thermal behavior of clinoptilolite was strongly dependent on the chemical composition of the original sample. The type of the exchangeable cations, their specific positions within the structure, their coordination to H_2O molecules and their interactions with framework oxygens influence the thermal behavior of the clinoptilolite [8, 12–16]. Four extra-framework cation positions are found in the channels of natural clinoptilolite-heulandite. Calcium

and sodium ions both occupy to sites (M1 and M2) in channels A and B clinoptilolite. In addition, site M3 is occupied by potassium and M4 is occupied by magnesium ions [8, 12, 17–19]. The K cations at M3 site were shown to be thermally stable through high-temperature structural studies [9, 20]. In clinoptilolite, the interchangeable cations are mostly monovalent and their numbers are higher than the divalent ones [21].

Many studies reported on clinoptilolites and those of thermal properties [8, 11, 22–32]. Knowlton et al. [25] used thermogravimetric (TG) and differential scanning calorimetric (DSC) techniques to study the types of water in natural clinoptilolite and attempted to apply their results to clinoptilolite in general. They concluded that the nature of water in clinoptilolite is predominantly dependent on interactions of water molecules with the Si, Al framework. Araya and Dyer [26] examined a variety of cation-exchanged clinoptilolites using TG and DSC in addition to other thermal analysis techniques and they related the temperature and amounts of water loss to the specific cation positions associated with the water molecules.

Turkey has high reserves of zeolite deposits, estimated to be approximately 50 billion tons, mainly consisted of clinoptilolite ores. Large reserves of clinoptilolite can be found in Bigadiç, Balikesir and Gördes, Manisa deposits [33]. According to the General Directorate of Mineral Research and Exploration, Turkey, reserves of clinoptilolite in the Manisa-Gördes region are estimated at 2 billion tones [34]. In Bigadiç, Balikesir deposits, approximately 500 million tons of clinoptilolite reserves have been detected [35, 36].

The Na, K, and Ca content of clinoptilolite-heulandite vary significantly in many deposits; thus thermal and structural properties of the zeolitic tuff should be carefully investigated before using for a certain application (in catalysis, ceramics or lightweight aggregates). The aim of this study is to investigate the mineralogical composition and the thermal behavior of the Gördes and Bigadiç clinoptilolite rich zeolites in order to evaluate them as industrial minerals.

Experimental

Materials and methods

The natural zeolitic tuffs used in this study originated from the deposits in Bigadiç and Gördes, Turkey. Both clinoptilolite samples were crushed and sieved to obtain <63 μm fractions. First, clinoptilolite rich samples boiled in deionized water (100 ml deionized water for 5 g of clinoptilolite) at 60 °C for 2 h in order to remove the soluble salts. Second, these washed zeolites (B-CLN. and G-CLN.)

were activated by washing with 100 ml of 0.2 M HCl solution followed by a washing in de-ionized water. Third, Na^+, K^+, Ca^{2+} and Mg^{2+} ionic forms of two clinoptilolites were prepared by the Batch method, using 1 M solutions at 80 °C for 4 h. Finally, the treated samples were rinsed with de-ionized water and then dried at room temperature. Before the experimental procedure, all samples were dried in an oven at 110 °C for 16 h and stored in a desiccator. Inorganic chemicals such as HCl, KNO_3, $NaNO_3$, $Mg(NO_3)_2$ and $Ca(NO_3)_2$ were supplied by Merck (Darmstadt, Germany) and all solutions were prepared by using de-ionized water.

Instrumentation

The chemical analyses of natural and cation exchanged forms were carried out using a Rigaku ZSX Primus model XRF instrument. BET surface areas were calculated from the first part of the N_2 adsorption isotherm ($0.05 < P/P_o < 0.30$) obtained at liquid nitrogen temperature with N_2 in Autosorb-1C equipment previously degassed at 300 °C for 6 h prior to measurement. High-purity (99.99%) nitrogen was used in adsorption measurements.

Differential thermal (DTA) and thermogravimetric analyses (TG and DTG) were obtained simultaneously with a Setsys Evolution Setaram thermal analyzer at a heating rate of 10 °C min^{-1} in the temperature range 30–1000 °C. Approximately 40 mg of sample was used in each run. Differential Scanning Calorimetric (DSC) analyses of samples were carried out by heating the samples from 30 to 550 °C at 10 °C min^{-1} rate using a Setaram DSC 151 analyser. In DSC experiments, about 15 mg of sample was used.

Results and discussion

Element composition

The samples used in this study originated from the mines near the sites of Bigadiç and Gördes. The chemical compositions of the samples are given in Tables 1 and 2. The presence of elements having smaller concentrations than Al and Si was observed and reported in oxide form. The unit-cell compositions of the clinoptilolite samples, assuming 72 oxygens, are also included in Tables 3 and 4. The Natural G. and Natural B. samples have Si/Al ratios of about 5.3 and 5.5, respectively. Although the elemental composition of the clinoptilolite-rich tuffs from Bigadiç and Gördes are alike, the differences in their cation composition can be observed. Both clinoptilolite samples are characterized by high calcium and potassium and low magnesium and sodium contents. In addition, iron is present. The natural materials contain different cations

Table 1 Chemical composition of the natural and modified clinoptilolites from Gördes region

Component (%)	Natural G	K-G	Na-G	Ca-G	Mg-G
SiO_2	78.293	76.342	77.727	77.941	78.060
Al_2O_3	12.371	12.125	12.327	12.589	12.474
Fe_2O_3	1.205	1.131	1.098	1.175	1.132
MgO	0.446	0.395	0.468	0.486	1.609
CaO	1.763	0.253	0.411	3.854	1.531
Na_2O	0.311	–	4.317	0.161	0.257
K_2O	5.461	9.684	3.611	3.641	4.741
P_2O_5	0.008	0.015	–	–	0.010
Σ	99.858	99.945	99.959	99.847	99.814

Table 2 Chemical composition of the natural and modified clinoptilolites from Bigadiç region

Component (%)	Natural B	K-B	Na-B	Ca-B	Mg-B
SiO_2	78.731	75.645	77.361	77.884	78.309
Al_2O_3	12.001	11.621	12.045	12.119	12.043
Fe_2O_3	1.446	1.312	1.318	1.360	1.353
MgO	0.925	0.574	1.099	1.290	1.813
CaO	3.025	0.217	0.665	3.843	2.694
Na_2O	0.145	–	4.340	0.216	0.153
K_2O	3.493	10.435	3.005	3.052	3.343
P_2O_5	0.016	–	–	0.010	0.013
Σ	99.782	99.804	99.833	99.774	99.721

Table 3 Atom numbers per unit cell and Si/Al ratios of natural and modified clinoptilolites from Gordes

Samples Atoms/unit cell	Natural G	K-G	Na-G	Ca-G	Mg-G
Si	30.280	30.125	30.071	30.044	30.095
Al	5.639	5.638	5.620	5.719	5.667
Fe	0.350	0.335	0.319	0.339	0.327
Mg	0.255	0.232	0.269	0.277	0.924
Ca	0.729	0.107	0.169	1.591	0.632
Na	0.232	–	3.249	0.120	0.189
K	2.691	4.874	1.780	1.788	2.316
P	0.002	0.005	–	–	0.003
Si/Al	5.369	5.342	5.349	5.253	5.309

Table 4 Atom numbers per unit cell and Si/Al ratios of natural and modified clinoptilolites from Bigadiç

| Samples Atoms/unit cell	Natural B	K-B	Na-B	Ca-B	Mg-B
Si	30.263	30.083	29.951	29.998	30.101
Al	5.436	5.446	5.496	5.500	5.455
Fe	0.417	0.391	0.383	0.393	0.391
Mg	0.528	0.339	0.632	0.740	1.037
Ca	1.244	0.090	0.274	1.585	1.108
Na	0.106	–	3.256	0.157	0.110
K	1.709	5.290	1.484	1.499	1.635
P	0.004	–	–	0.002	0.003
Si/Al	5.567	5.523	5.449	5.454	5.517

depending on their geographic source. Ming and Dixon have reported that the main cations are Na^+, K^+ and Ca^{2+} [37]. Iron has been associated with impurities present in zeolitic tuffs such as iron oxides.

N_2 adsorption and surface area (BET)

Nitrogen sorption isotherms the clinoptilolite zeolites are shown in Figs. 1 and 2 (relative pressure P/Po versus adsorbed volume in cc per gram of zeolite). The shape of N_2 adsorption isotherms of the samples correspond to the type II [38] according Gregg and Sing [39]. All samples display type-II isotherms [40]. The isotherms obtained from adsorption measurements give data on the surface area, pore volume and size. The effective pore volumes were estimated from Horvath and Kawazoe model parameters for N_2. Table 5 shows values of some important parameters obtained from the analysis of isotherms. It is found that ion exchange with K^+, Ca^{2+}, Na^+ and Mg^{2+} cations has influence on the effective pore volume and surface area of clinoptilolite. The surface areas determined for the Gördes clinoptilolite rich tuff samples were higher than those from Bigadiç. The areas in the clinoptilolite samples increased slightly after they were treated with nitrate solutions.

Thermal properties

The thermoanalytical techniques TG/DTG, DSC can help us to understand the interactions between adsorbed water-ion as well as the thermal behavior of zeolites. Figures 3, 4 show TG-DTG-DTA curves of natural and cation exchanged forms of Gördes and Bigadiç samples, respectively. Results of thermal analyses are in agreement with literature [5, 14] and the following observations can be drawn:

(1) The DTA curves for natural clinoptilolite samples were essentially similar.

(2) The DTA curves of the Natural B., Natural G., K-B., Na-B., K-G., Na-G., Ca-G., Ca-B. and Mg-G. forms display a single endotherm at temperature ranging from 129 to 170 °C as a result of a single-step dehydration process. Endotherm minima temperatures increase in the sequence K-G. (129 °C) → Natural-B. (139 °C) → Natural-G. (143 °C) → Ca-G. (144 °C)

Fig. 1 The isotherms of the adsorption of nitrogen on the natural and modified Gördes clinoptilolite samples
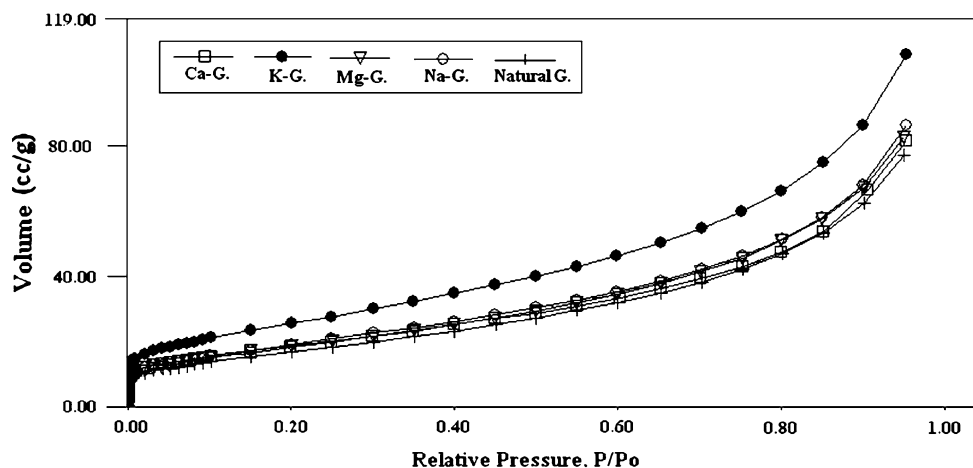
Fig. 2 The isotherms of the adsorption of nitrogen on the natural and modified Bigadiç clinoptilolite samples
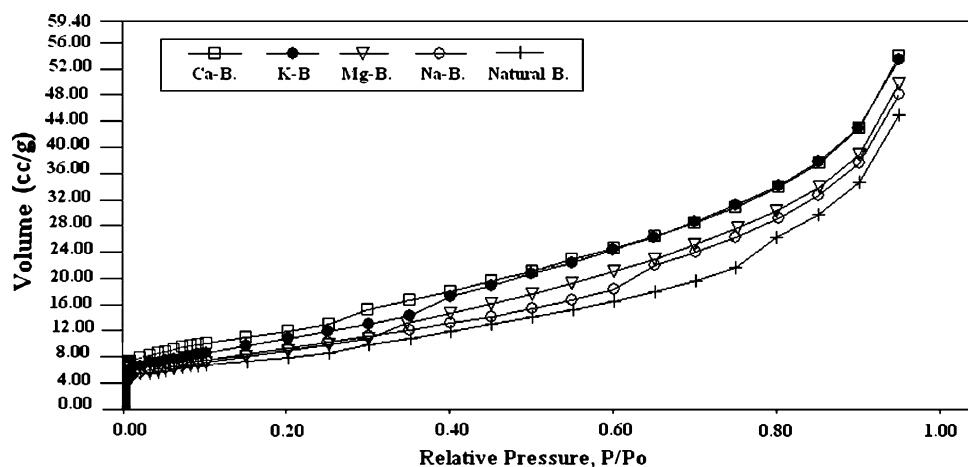

Table 5 N_2 adsorption data of natural and modified clinoptilolite samples

Sample	Specific surface area BET (m²/g)	BET C	Average pore diameter (Å)	Cum. pore volume (cm³/g)
Natural G	63.13	46.60	76.74	0.040
K-G	94.71	61.02	70.94	0.059
Na-G	71.37	45.04	74.99	0.045
Ca-G	67.64	68.20	74.73	0.043
Mg-G	69.08	54.19	74.41	0.043
Natural B	28.40	116.50	98.03	0.020
K-B	40.80	40.90	80.14	0.030
Na-B	35.53	41.70	84.23	0.022
Ca-B	43.39	84.10	77.13	0.031
Mg-B	32.84	47.73	90.61	0.025

→ Ca-G. (146 °C) → Mg-G. (147 °C) → Na-G. (149 °C) → K-B. (155 °C) → Na-B. (170 °C).

(3) The DTA curves of Mg-B. form is characterized by three endotherms related to a three step dehydration process. The endotherms range between 98 and 225 °C. Endotherm minima temperatures increase in the sequence Mg-B. (98 °C) → (164 °C) → (225 °C).

Clinoptilolite belongs to the zeolite group that does not show major structural changes during dehydration processes which exhibit continuous mass-loss curves as a function of temperature. Clinoptilolite structure remains stable up to temperatures between 700 and 800 °C [5, 41]. As can be seen in the Figs. 3 and 4, the main structural changes occur at temperatures below or around 250 °C while the mass loss is constant at temperatures higher than 700 °C.
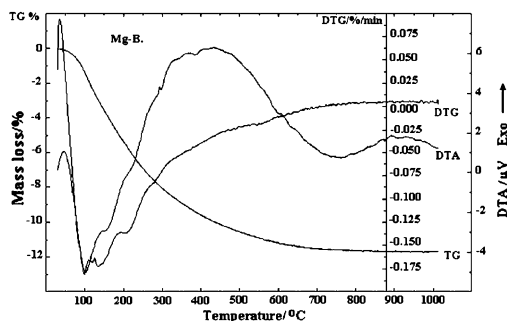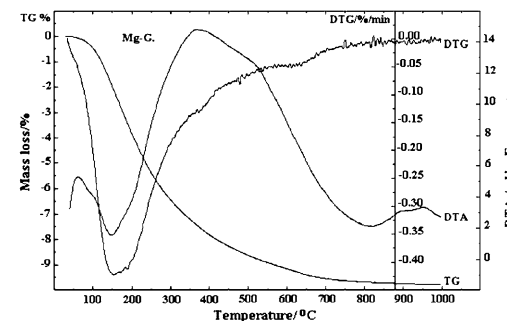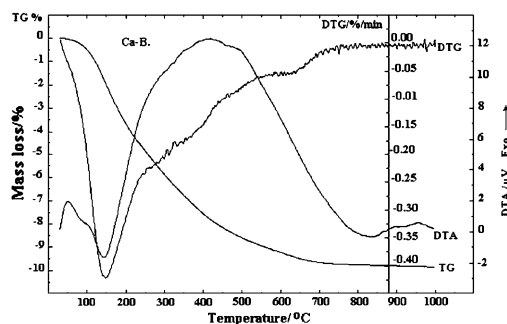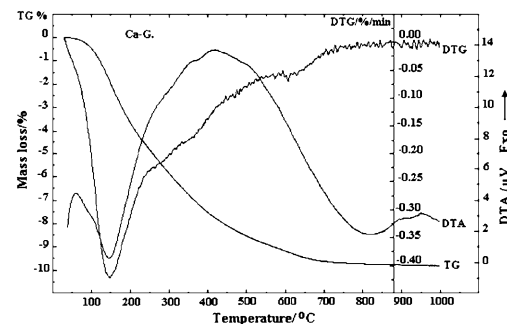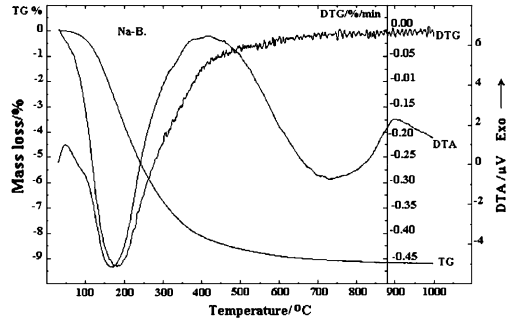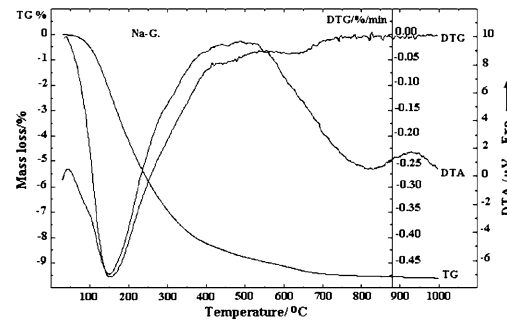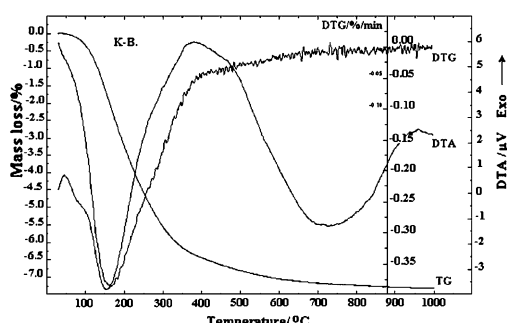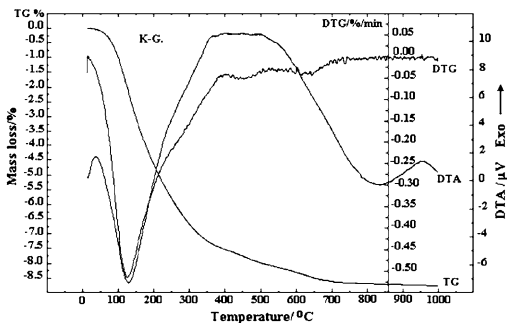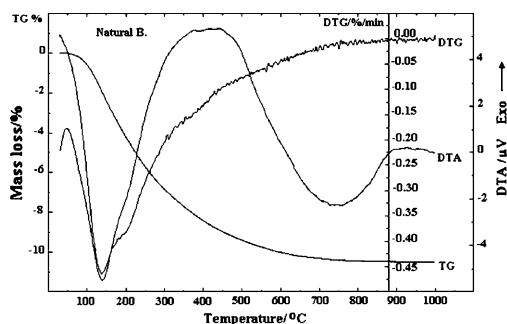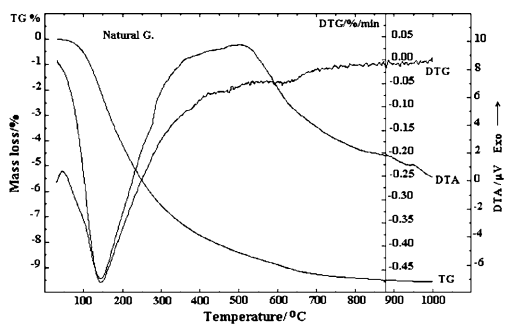
Fig. 3 TG, DTA and DTG curves for the natural and modified Gördes clinoptilolite samples

Fig. 4 TG, DTA and DTG curves for the natural and modified Bigadiç clinoptilolite samples

Table 6 Mass loss (%) of the clinoptilolite samples used at different temperature ranges

| Sample	30–100 °C	100–200 °C	200–300 °C	300–400 °C	400–500 °C	500–600 °C	600–700 °C	700–1000 °C	Total mass loss (%)
Natural G.	0.56	3.63	2.37	1.16	0.66	0.48	0.36	0.28	9.54
K-G.	1.05	3.63	2.00	0.84	0.45	0.32	0.31	0.14	8.76
Na-G.	0.52	3.71	2.71	1.28	0.53	0.34	0.30	0.16	9.59
Ca-G.	0.51	3.35	2.20	1.64	1.01	0.63	0.44	0.20	10.00
Mg-G.	0.48	3.84	2.61	1.36	0.80	0.52	0.38	0.23	9.76
Natural B.	0.61	3.61	2.64	1.56	0.96	0.60	0.30	0.18	10.50
K-B.	0.35	2.91	2.30	0.87	0.36	0.23	0.11	0.13	7.29
Na-B.	0.35	3.39	3.00	1.37	0.48	0.28	0.13	0.15	9.18
Ca-B.	0.50	3.17	2.21	1.67	1.03	0.62	0.42	0.18	9.83
Mg-B.	1.43	3.96	2.67	1.52	0.95	0.62	0.33	0.17	11.68

The mass losses recorded by thermogravimetric analysis (TG) are reported in Table 6. In the temperature range from 100 to 200 °C, the rapid mass loss (2.91–3.96%) is documented by the steep slope of the TG curve as it is attributed to the loss of the water located in the zeolite cavities and bound to the nonframework cations. In the temperature range from 200 to 300 °C, the mass loss is less (2–3%) and it is indicated by the slight slope of the TG curve. In the temperature range from 300 to 400 °C, the rate of loss is even slower (mass loss 0.84–1.67%). In the temperature range from 400 to 500 °C the slope of the TG curve is even lighter indicating a lower mass loss (0.36–1.03%). In the broad interval between 200 and 500 °C more strongly associated water is lost. In the temperature range from 500 to 700 °C, the rest of the water is gradually removed.

The TG curves of all the samples showed a water loss which varied with the variation in the size of non-framework cations. The zeolites exchanged with Na^+ and Mg^{2+} in particular had higher temperature peaks. These cations have smaller ionic radii in the monovalent and bivalent ions. The zeolite water loss was higher in the zeolites exchanged with bivalent cations [42]. Water content increases in the order of K < Na < Ca < Mg for Bigadiç clinoptilolite samples and in the following sequence K < Na < Mg < Ca for Gördes clinoptilolite samples. Because much of the H_2O in structural cavities is associated with extra-framework cations, the nature zeolite dehydration (and the total amount of H_2O) is strongly dependent on the extra framework cations, in particular their hydration energy. Zeolites containing high-hydration-energy cations, such as Ca^{2+} contain significantly more H_2O than those such as K^+ and those with high- hydration energy cations also generally retain their H_2O to higher temperatures [14].

DSC curves for Gördes and Bigadiç samples are shown in Figs. 5, 6, respectively. The DSC curves closely resemble the DTG curves. All clinoptilolite samples from Gördes
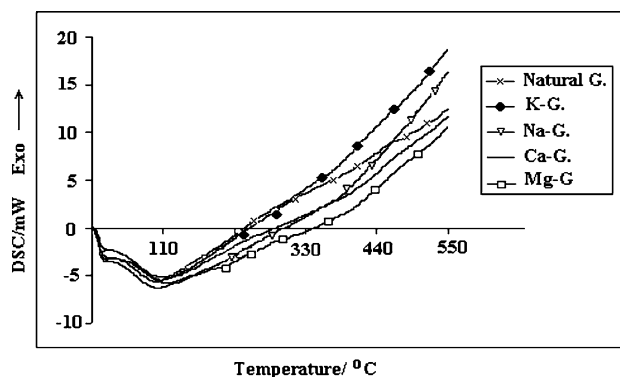
Fig. 5 DSC curves for the natural and modified Gördes clinoptilolite samples
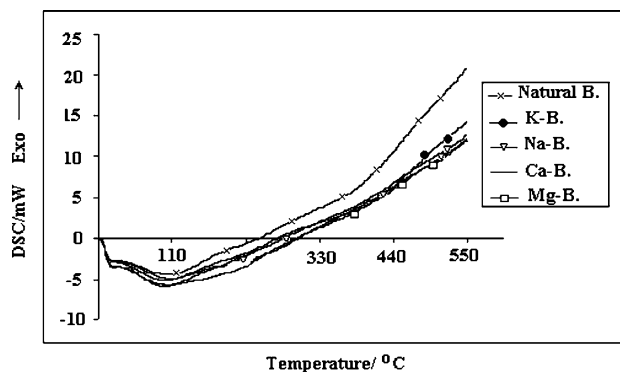
Fig. 6 DSC curves for the natural and modified Bigadiç clinoptilolite samples

have one broad endotherm at temperature ranging from 119 to 134 °C (Table 7). For Gördes clinoptilolite samples, endotherm minima temperatures increase in the sequence:

$$K\text{-}G.(119\,°C) \rightarrow Mg\text{-}G.(120\,°C) \rightarrow Ca\text{-}G.(124\,°C) \\ \rightarrow Na\text{-}G.(134\,°C)$$
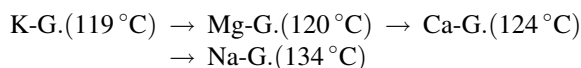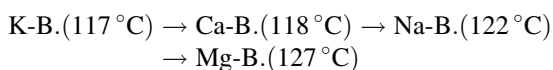
Likewise, DSC curves for natural and cation exchanged samples from Bigadiç show one broad endotherm at temperature ranging from 117 to 127 °C (Table 7).

Table 7 DSC data of the natural and modified clinoptilolites

Sample	Endotherm Temp./°C	$\Delta H/Jg^{-1}$ zeolite
Natural G.	128	56.26
K-G	119	55.06
Na-G.	134	68.80
Ca-G.	124	56.70
Mg-G.	120	79.15
Natural B.	122	57.39
K-B.	117	54.82
Na-B.	122	64.49
Ca-B.	118	57.79
Mg-B.	127	75.60

For Bigadiç clinoptilolite samples, endotherm minima temperatures increase in the sequence:

$$K\text{-}B.(117\,^{\circ}C) \rightarrow Ca\text{-}B.(118\,^{\circ}C) \rightarrow Na\text{-}B.(122\,^{\circ}C)$$
$$\rightarrow Mg\text{-}B.(127\,^{\circ}C)$$

These endotherm temperatures correspond to presence of zeolite water in the structure. Small differences in the peak temperatures observed in the K^+, Ca^{2+}, Na^+ and Mg^{2+} forms of clinoptilolite can be attributed to the dependence of bound strength of water to the composition. In addition, dehydration behavior of the clinoptilolites should be controlled by the exchangeable cation and the sites occupied by cation [14].

The dehydration enthalpy change (ΔH) values of natural and cation exchanged clinoptilolite samples have been measured by differential scanning calorimeter. The enthalpy change (ΔH) values obtained by using peak integration method and tabulated in Table 7. As seen from the Table 7, the dehydration enthalpy change (ΔH) values decreased with the increase in the size of cations. The ionic radii for K^+, Ca^{2+}, Na^+ and Mg^{2+} ions are taken to be 1.33, 1.06, 0.98 and 0.78 Å, respectively [43]. The dehydration enthalpy change (ΔH) decreases in the order $Mg^{2+} > Na^+ > Ca^{2+} > K^+$ for both clinoptilolite samples.

Conclusions

Thermal behavior of the clinoptilolite- rich tuffs was investigated by using TG/DTG, DTA and DSC. The TG/DTG/DTA curves of all the clinoptilolite samples were quite similar. The DTA curves of the Natural B., Natural G., K-B., Na-B., K-G, Na-G., Ca-G., Ca-B. and Mg-G. forms display a single endotherm at temperature ranging from 129 to 170°C as a result of a single-step dehydration process. In comparison with the Mg-form of Gördes clinoptilolite, the Mg-form of Bigadiç clinoptilolite gives three endothermic peaks at 98, 164 and 225 °C as a result of a three-step dehydration process.

Thermogravimetric curves showed no noticeable breaks in the mass-loss curve. All clinoptilolite samples had major, rapid mass losses between 30 and 200 °C, with slower and less significant mass losses at higher temperatures. The TG curves of all the zeolites indicate a major loss in mass of from 9.26 to 10.32% in temperature range 30–500 °C, generally due to dehydration. The mass losses above 500 °C may be caused by dehydroxylation. In general, the dehydroxylation of the zeolites is slow and occurs in this case in the range 600–800 °C. In addition, in the monovalent and bivalent ions, the larger cations had less zeolite water loss, since the greater the size of the nonframework cation, the smaller is the space for the zeolite water. The natural and modified clinoptilolite structure unchanged up to 700 °C hence the zeolitic tuffs can be used for applications at moderate temperatures. The mass loss of the Natural-G is 9.54% while that of the Natural-B sample is 10.50%. In the DSC curves of all clinoptilolite samples, one broad endotherm was observed in the range of 117–134 °C. It was seen that the dehydration enthalpies obtained from DSC curves decreased with increasing cation size.

The thermal properties of clinoptilolite samples depend on the exchangeable cations, as well as the source of the zeolitic rocks. The composition and properties of natural zeolites vary significantly from sample to sample. For these reasons, knowing the thermal stability and thermal transformation properties of zeolitic tuffs is advantageous for some applications in catalysis, ceramics and lightweight aggregates etc. Before using a zeolitic tuff for a certain application its thermal and structural properties should be carefully investigated. Dehydration properties of zeolites are very important for adsorbent applications. It may be concluded that Gördes and Bigadiç clinoptilolites will be useful for wide application in many fields.

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