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Dilatometry of Na-, K-, Ca- and NH_4-clinoptilolite

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Abstract

The dilatometric behaviour of Na-, K-, NH_4- and Ca-clinoptilolite has been investigated.

Na-, K- and NH_4-clinoptilolite sensibly shrink (from 0.4 to 2.0%) up to about 350°C, while for higher temperatures only very small shrinkages (0.2%) have been detected. These dilatometric behaviours appear to be dominated by dehydration upon heating.

Ca-clinoptilolite moderately shrinks up to 300°C (1.0%) and undergoes a more evident shrinkage (2.1%) at higher temperatures. The former shrinkage has been ascribed to dehydration upon heating, the latter higher one to structural damages.

The different dilatometric behaviours have been interpreted in terms of the thermal properties of zeolites of the clinoptilolite type.

1. Introduction

Several studies concerning the thermodilatometry of zeolites or zeolite-bearing materials are reported in literature [1–11]. In these papers the dilatometric behaviour of various zeolites was interpreted in terms of: (a) shrinkage by dehydration, (b) thermal expansion upon heating, (c) thermal collapse of the zeolitic structure, and (d) possible cation migrations from one site to another. The main conclusion was that the thermodilatometric behaviour of zeolites is strongly affected by their structures and by their chemical composition, in particular by the extraframework cations composition.

The thermodilatometric behaviour of clinoptilolite, a natural zeolite of great technological interest [12] widespread in many countries of the world [13], was partially characterized by Ullrich et al. in [7]. Actually they reported the thermodilatometric curves of different samples of natural clinoptilolite coming from Garsebach (Germany), Itaya (Japan) and Hector (California, USA) in their original composition. This approach appears more appropriate when the thermodilatometric behaviour of a particular zeolite-bearing, naturally occurring material must be performed as it was done in [11]. When the thermodilatometric behaviour of a zeolite is investigated, the cation form in which the zeolite is present, is known to assume a role of crucial importance [2–6,8,9].

Such considerations promoted the investigation on the thermodilatometric behaviour of Na-, K-, and Ca-exchanged samples of a natural clinoptilolite. These cation forms were chosen inasmuch as these cations mostly make up the cation population of naturally occurring, clinoptilolite bearing materials [14].

Together with these cation forms, even the thermodilatometric behaviour of a NH_4-exchanged sample of

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clinoptilolite was investigated in order to confirm the results of a previous paper [10] in which synthetic zeolites A and X and natural chabazite were found to catalyze the combustion of ammonia evolved upon heating their ammonium form, whereas clinoptilolite did not show this ability at all.

2. Experimental

The naturally occurring, clinoptilolite-bearing material used in this investigation comes from Pentalofos (Thrace, northeastern Greece). This material was found to contain a high amount of clinoptilolite (up to 90%) together with smaller contents of feldspars, micas and clays [15]. The Ca cation is present to the greatest extent in clinoptilolite in its original composition [15].

More or less homoionic Na-, K-, Ca-, and NH_4-clinoptilolite were obtained by the following procedure: about 5 g of clinoptilolite were contacted for 1 h, under continuous stirring, with 1 l of 1 M solution of the relevant cation at 80°C. The amount of NH_3 evolved by NH_4-clinoptilolite upon heating was determined by the Kjeldahl method [16]. Cationic solutions were prepared starting from Carlo Erba reagent grade chloride or nitrate salts. After clinoptilolite was separated from the suspension by filtration, this same operation was repeated for a total of three times. The resulting powders were washed with distilled water, dried overnight at 80°C and stored for at least 3 days in an environment having about 50% relative humidity to allow water saturation of clinoptilolite.

Such powders were pressed at 150 MPa to produce cylindrical pellets having height = 10 mm and diameter = 10 mm. Such pellets, which are characterized by 35% apparent porosity measured by the RILEM procedure [17], were tested by dilatometry in air. A mod. 402 E/7 Netzsch dilatometer was utilized at 10°C/min heating rate. Thermodilatometric data were collected under the form of curves which report the percent variation of length of the cylinders ($\Delta L/L_o(\%)$) as a function of temperature.

Thermogravimetric analyses (TGA) were performed in air with a Netzsch thermoanalyzer STA409, a 100 mg sample, α-Al_2O_3 as reference and a 10°C/min heating rate.

X-ray diffractometric analyses (XRD) were performed with a X'Pert of Philips.

3. Results and discussion

In Figs. 1–4 the thermodilatometric curves of Na-, K-, NH_4- and Ca-exchanged clinoptilolite are reported, respectively, together with their thermogravimetric curves.

All the curves have in common that up to 100°C no sensible variation in the length of the specimens is recorded, while a different thermodilatometric behaviours may be observed for each samples at higher temperatures.

As far as Na-clinoptilolite is concerned (Fig. 1), the specimen shrinks almost linearly in the temperature range 100–400°C (6×10^{-3}%/°C slope). Only a very small contraction (0.2%) has been detected in the

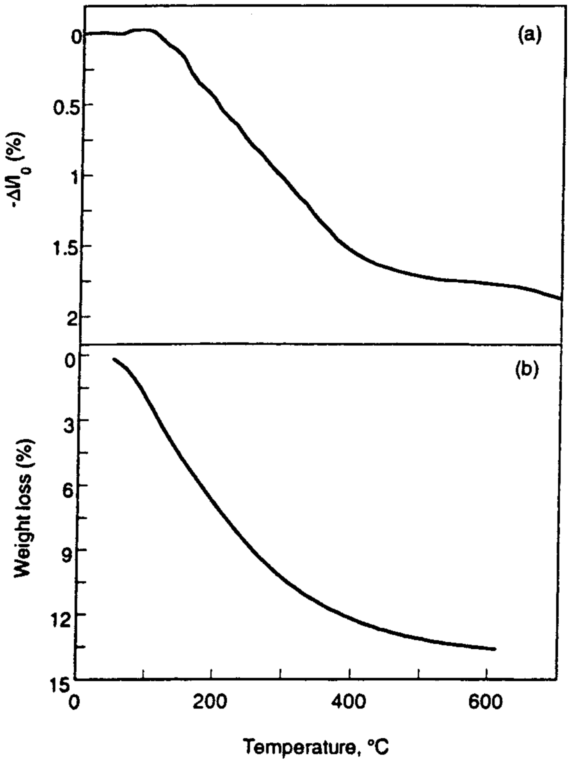

Fig. 1. Dilatometric (a) and thermogravimetric (b) curves of Na-clinoptilolite.

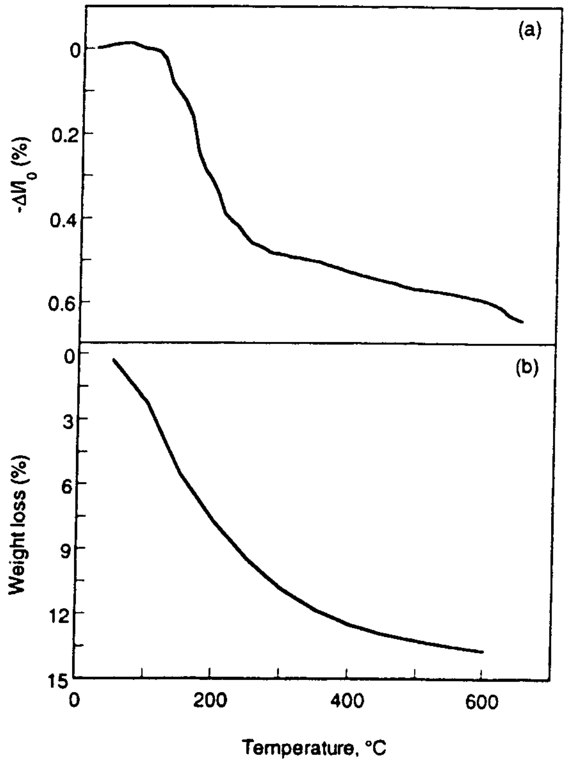

Fig. 2. Dilatometric (a) and thermogravimetric (b) curves of K-clinoptilolite.

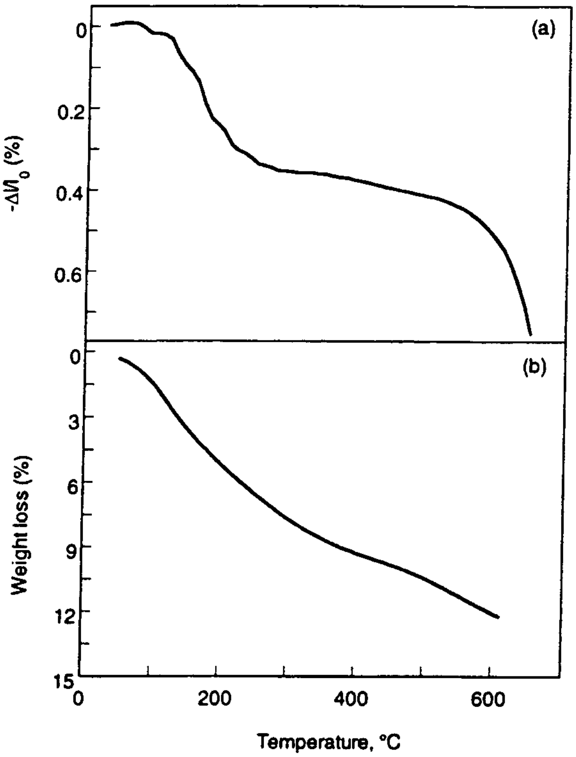

Fig. 3. Dilatometric (a) and thermogravimetric (b) curves of NH_4-clinoptilolite.

temperature range 400–650°C, thus attaining a final value of about 2%.

As far as K-clinoptilolite is concerned, a small shrinkage (0.6%) occurs in the temperature range 100–300°C. At increasing temperatures the length of the specimen does not sensibly change (less than 0.1%) even if a very small negative slope of the thermodilatometric curve may be recorded.

The NH_4-clinoptilolite behaves similarly to K-clinoptilolite, the only differences being a slightly smaller shrinkage (0.4%) in the temperature range 100–300°C and a higher in modulus negative slope in the final temperature range 600–650°C. The final shrinkage attained by both K-clinoptilolite and NH_4-clinoptilolite is about 0.7%.

The thermodilatometric curve of NH_4-clinoptilolite closely resembles to that of NH_4-clinoptilolite coming from La Rioja reported in [10]. Even in this case no exothermal effect arising from ammonia combustion catalyzed by the zeolitic substrate, previously observed in the thermodilatometric curves of ammonium exchanged chabazite, A and X zeolites, may be recorded. The absence of such thermal effect in this case can be attributed to two possible phenomena. The first is the low catalytic activity of H-clinoptilolite, resulting from ammonia evolution upon heating. The second is the relatively low cation exchange capacity of clinoptilolite according to its high Si/Al ratio. Such low cation exchange capacity results in a small amount of ammonia evolved upon heating (1.7 meq/g) which could not result sufficient to the ammonia–air mixture to fall within their flammability limits.

As far as Ca-clinoptilolite is concerned, a first moderate shrinkage (1.0%) takes place in the temperature range 100–300°C, followed by a second, more evident (2.1%), in the temperature range 400–650°C, thus attaining a final value of shrinkage of about 3.1%.

The thermodilatometric curves of Na-, K- and NH_4-clinoptilolite do not reveal any structural damage in

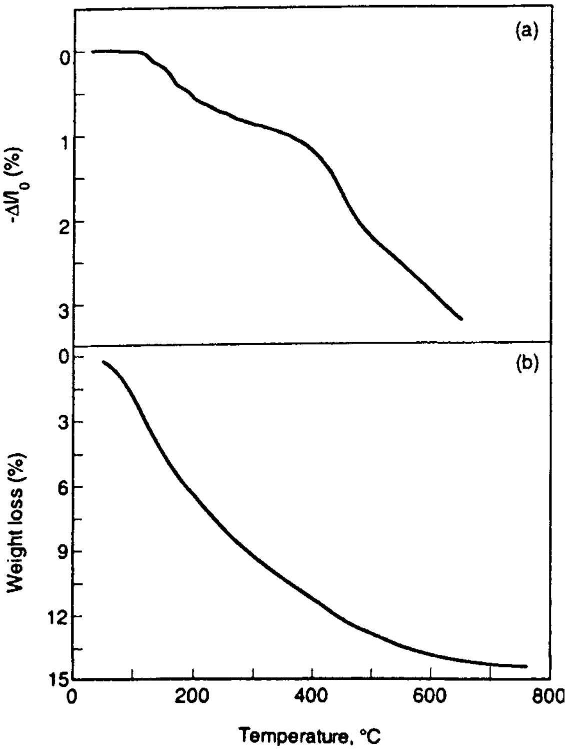

Fig. 4. Dilatometric (a) and thermogravimetric (b) curves of Ca-clinoptilolite.

the examined temperature range. These shrinkages are clearly related to dehydration. The extent of these shrinkages is smaller than those recorded for other, previously investigated zeolites, such as chabazite and zeolite A [8,9]. This finding should be likely ascribed to the relatively small amount of volatile substances evolved upon heating by Na-, K-, and NH_4-exchanged clinoptilolite (ranging between 12.0 and 13.8%). Actually such amounts are far lower than those evolved by similar cation forms of chabazite and zeolite A. On the other hand this result agrees with the higher amount of void space present in chabazite and zeolite A (framework density 1.45 and 1.27 g/cm^3, respectively [13]) than in clinoptilolite (framework density 1.71 g/cm^3, [13]).

In the case of the thermodilatometric curve of Ca-clinoptilolite the first moderate shrinkage (1.0%), recorded in the temperature range 100–300°C, appears related to dehydration on account of reasons exactly analogous to those reported for Na-, K-, and NH_4-exchanged clinoptilolite. It is noteworthy that the second, more evident (2.1%), shrinkage, recorded in the temperature range 400–650°C, appears to be related more likely to structural damages that begins to occur starting from 400°C. This supposition appears confirmed not only by the higher in modulus negative slope of the thermodilatometric curve for temperatures higher than 400°C, but also by X-ray diffraction analysis performed on thermally treated sample which revealed a partial loss of crystallinity.

The thermodilatometric curves of clinoptilolite samples coming from Garsebach (Germany), Itaya (Japan) and Hector (California, USA) in their original composition, reported in [7], closely resemble to those of Na-, K-, and NH_4-clinoptilolite reported in this paper. Anyway the two groups of thermodilatometric curves cannot be directly compared as no indications concerning the chemical composition of investigated samples is reported in [7].

The thermodilatometric behaviour of various cation forms of clinoptilolite should be interpreted in terms of the thermal properties of zeolites of the clinoptilolite type which were carefully investigated by Gottardi and Galli [14]. They reported three types of thermal behaviours for these zeolites:

1. Clinoptilolite undergoes reversible dehydration with small contractions of the framework upon heating up to about 230°C. In the temperature range 230–260°C irreversible structural changes, which hinder the dehydration, occur. Heating at temperatures higher than 450°C results in the thermal collapse of the framework.
2. Clinoptilolite undergoes reversible dehydration with small contractions of the framework upon heating up to about 280°C. In the temperature range 280–400°C irreversible structural changes, which hinder the dehydration, occur. Heating at temperatures higher than 550°C results in the thermal collapse of the framework.
3. Clinoptilolite undergoes continuous reversible dehydration with only a very small lattice contraction and the lattice is not destroyed by heating if not over 750°C.

Gottardi and Galli [14] stated that the kind of the thermal behaviour of clinoptilolite was strongly dependent on the chemical composition of the original

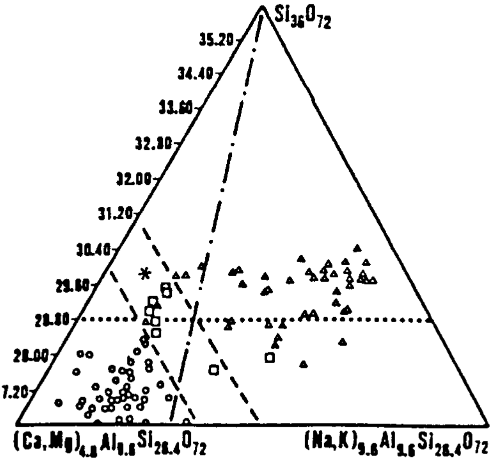

Fig. 5. Mole plot of zeolites of the clinoptilolite type [14]. Circles, squares and triangles denote thermal behaviour of type I, II, and III respectively. The asterisk points the original composition of Pentalofos clinoptilolite sample.

sample and reported the triangular diagram of Fig. 5 where the circles, the squares and the triangles denote samples of clinoptilolite displaying I, II and III type thermal behaviours, respectively. The chemical composition of the Pentalofos sample in its original composition was reported in [15] and turned out $Na_{0.2}K_{0.6}Mg_{0.7}Ca_{2.0}Al_{6.2}Si_{29.8}$ 19.6H_2O. This composition falls in an area of the diagram where clinoptilolite displays either type II or III thermal behaviour.

Our thermodilatometric results appear consistent with those of literature [14]. The thermodilatometric curves of Na-, K-, and NH_4-clinoptilolite, which display only moderate shrinkages which were ascribed to reversible dehydration without the occurrence of any structural damage, appear to perfectly fit into the thermal behaviour of type III. Conversely the thermodilatometric curve of Ca-clinoptilolite, which was interpreted in terms of shrinkage by dehydration up to about 300°C and in terms of partial thermal collapse of the zeolitic structure at higher temperatures, appears to likely fit into the thermal behaviour of type II. In particular Gottardi and Galli [14] emphasized that Ca-clinoptilolite is destroyed at 450 or 500°C, the higher value being that of the high-silica clinoptilolite. This finding is explained by the attraction towards oxygen atoms of dehydrated clinoptilolite framework performed by Ca which results far stronger than the attraction displayed by monovalent cations. Such stronger attraction results in lattice deformations for temperatures lower than 300°C and in thermal collapse for temperatures higher than 400°C.

4. Conclusions

The main conclusions that may be drawn from this investigation are the following:

1. Shrinkage arising only from dehydration appears to dominate the dilatometric behaviour of Na-, K-, and NH_4-clinoptilolite.
2. No exothermal effect arising from the combustion of ammonia evolved upon heating NH_4-clinoptilolite has been detected.
3. Shrinkage arising from dehydration, in a first stage, and from partial thermal collapse of the zeolitic structure, in a second stage, appears to dominate the dilatometric behaviour of Ca-clinoptilolite.
4. The dilatometric behaviour of Na-, K-, and NH_4-clinoptilolite perfectly fits into type III thermal behaviour of clinoptilolite, whereas the dilatometric behaviour of Ca-clinoptilolite appears to likely fit into the thermal behaviour of type II, according to [14].

As in the case of chabazite [8] and zeolite A [9], the study of the dilatometry of various cation exchanged forms of clinoptilolite supplied valid elements of characterization of its thermal behaviour. The general validity of this simple experimental technique in characterizing the thermal behaviour of zeolites seems to be confirmed by the results of this investigation. In fact, although the dilatometric behaviour of various cation forms of chabazite, zeolite A and clinoptilolite greatly differs from each other, dilatometry has attained its goal of supplying useful information on the thermal behaviour of zeolites in all the investigated cases.

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