ELSEVIER

Thermochimica Acta 296 (1997) 59–66

thermochimica
acta

Thermal shrinkage of various cation forms of zeolite A

A. Colantuono, S. Dal Vecchio, G. Mascolo*, M. Pansini[1]

Laboratorio Materiali del Dipartimento d'Ingegneria Industriale, Universitá di Cassino, Via G. Di Biasio 43, 03043 Cassino (Fr), Italy

Received 10 June 1996; accepted 2 January 1997

Abstract

The thermal shrinkage of Li, Na, K, Cs, ammonium, H, and Ca forms of zeolite A has been investigated by dilatometry up to 650°C.

The shrinkages of Li, Na, K, Cs and Ca forms are attributed to the dehydration and partial structural collapse which predominates over the normal thermal expansion and cation migration from one site to another in the zeolitic structure.

The ammonium form shows a noticeable shrinkage and a possible catalytic action of the acid sites produced in the zeolite A in the combustion of ammonia evolved upon heating.

The H form undergoes collapse at temperatures higher than 350–400°C depending on the heating rate. © 1997 Elsevier Science B.V.

Keywords: Thermal; Zeolite A; Dilatometry; Shrinkage

1. Introduction

In a previous paper [1] various cation forms of a natural chabazite were investigated by dilatometry. The marked differences in the dilatometric curves have been interpreted in terms of shrinkage due to dehydration, thermal expansion, cation migration and thermal breakdown of the zeolitic structure.

This paper intends to investigate the dilatometric behaviour of the well-known, synthetic zeolite A, whose use is widespread in important practical applications [2,3]. From the point of view of dilatometry, in fact, no investigation has been reported in the literature. The ability of dilatometry in characterizing the thermal behaviour of chabazite, is still to be tested on different zeolites to assess the general validity of this simple experimental technique. The choice of zeolite A as the zeolitic matrix originated from different types of considerations. A zeolite displaying markedly different features from the natural chabazite of sedimentary origin tested by dilatometry in [1] was required to perform this test properly. In fact synthetic zeolite A has a far lower Si/Al ratio (practically 1) and framework density (1.27 g/cm^3) than sedimentary chabazite (Si/Al $\cong$ 2.5, framework density $=$ 1.45 g/cm^3) [4]. The synthetic origin of zeolite A definitely prevents the occurrence of other phases, which may not be excluded in samples of natural origin, and gives rise to a far smaller average grains dimension than natural zeolites. Zeolite A structure and its thermal behaviour have already been studied [4], which allows a com-

---

*Corresponding author.

[1] Dipartimento d'Ingegneria dei Materiali e della Produzione, Università di Napoli "Federico II", Piazzale Tecchio 80125-Napoli, Italy.

PII S0040-6031(97)00065-8

parison to be made between the data obtained by dilatometry and those reported in the literature (rf).

2. Experimental

Carlo Erba reagent grade zeolite 3A (K form), 4A (Na form) and 5A (Ca form) were used in this investigation.

More or less homoionic Li, Cs, and ammonium forms of zeolite A were obtained by the following procedure: about 10 g of zeolite 4A were left in contact for 1 h, under continuous stirring, with 1 dm^3 of 1.0 M solution of the relevant cation at 80°C. Cation solutions were prepared starting from Carlo Erba reagent grade chloride or nitrate salts. After this exposure the zeolite A was separated from the suspension by filtration, this operation was repeated three times in total.

These powders were washed with distilled water and dried overnight at 80°C. Saturation of the zeolites with water was achieved by showing at least seven days in an environment having higher than 50% relative humidity.

The hydrogen form of zeolite A was obtained by heating a sample of the zeolite A in its ammonium form at 350°C for 2 h. Under these conditions NH_3 was evolved, leaving protons as the charge balancing species.

By pressing the powders at 150 MPa, cylindrical pellets with height = 10 mm and diameter = 10 mm, were prepared. Such pellets, which were characterized by 35% average apparent porosity as measured by the RILEM procedure [5], were tested by dilatometry. A mod. 402 E/7 Netzsch dilatometer was utilized adopting various heating rates: 3, 10 and 30°C/min.

TG analyses were performed using a Netzsch STA 409 apparatus, adopting 80 mg sample with α-Al_2O_3 as a reference and 10 K min^{-1} heating rate.

X-ray diffractometric analyses were performed using a Philips PV 1730 diffractometer.

3. Results and discussion

In the upper part of Figs. 1–5 the dilatometric curves at 3, 10, 30°C/min heating rates of Li, Na, K, Cs and Ca zeolite A are depicted, respectively. These curves report the percent variation in length of the compacts as a function of the temperature. In the lower part of the same figures the corresponding thermogravimetric curves at 10°C/min heating rate are reported.

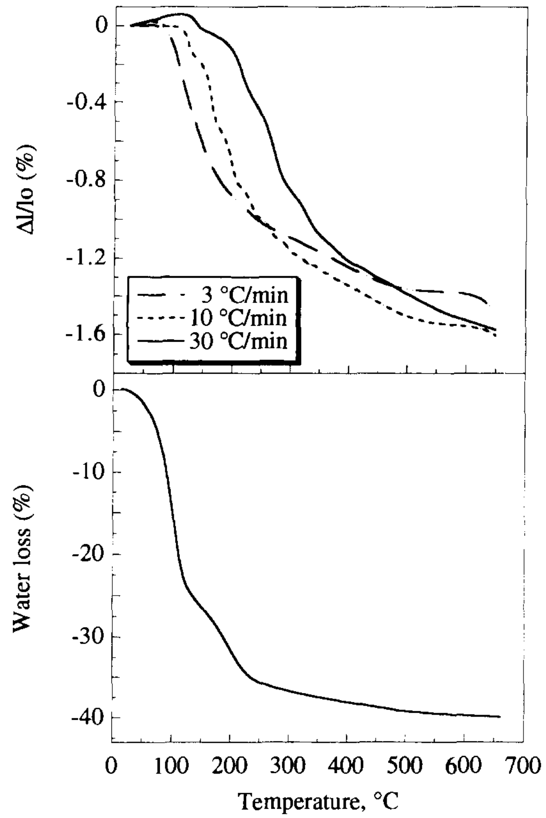

Fig. 1. Dilatometric and thermogravimetric curves of Li form of zeolite A.

Li, K, Cs and Ca zeolite A display a steady shrinkage with increasing temperature, whereas Na zeolite A shows a minimum occurring at increasing temperatures (200, 250 and 350°C) with increasing heating rates (3, 10, 30°C/min).

The interpretation of the dilatometric behaviour of chabazite [1] was made difficult by the simultaneous occurrence of the following phenomena:

1. continuous dehydration with increasing temperature which results in shrinkage of the compacts;
2. the normal thermal expansion upon heating;
3. the thermal collapse of the lower density zeolitic structure which results in a noticeable shrinkage of the compacts;

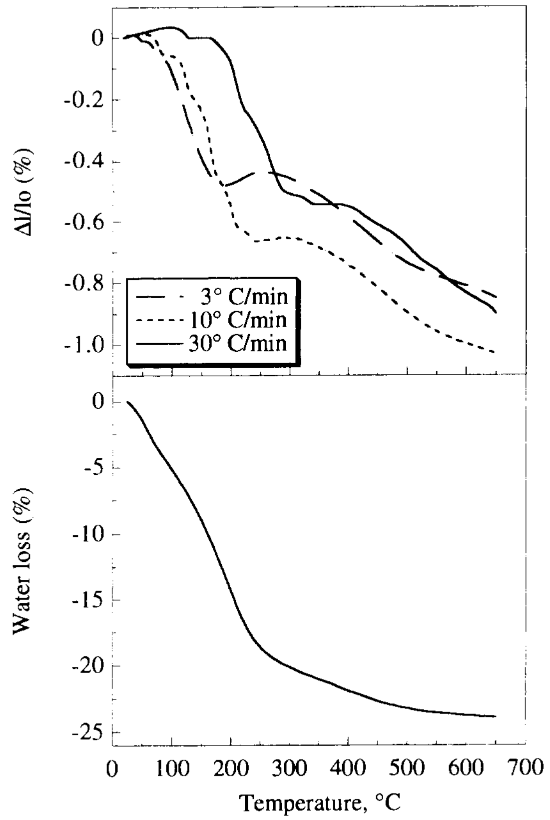

Fig. 2. Dilatometric and thermogravimetric curves of Na form of zeolite A.

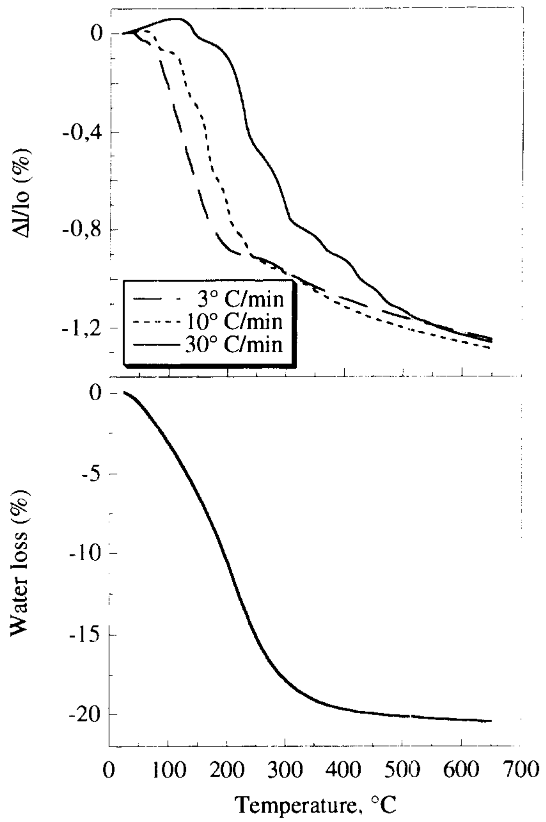

Fig. 3. Dilatometric and thermogravimetric curves of K form of zeolite A.

4. the possible cation migrations from a particular cation site to others which affects the dimensional stability of the compacts.

This same analysis appears to be different in the case of the cation forms of zeolite A reported in Figs. 1–5. In fact, in none of the reported curves the sharp shrinkage of the compacts with increasing temperature, displaying downward concavity, which are typical of a massive thermal collapse of the zeolitic structure, are evident. The values of the shrinkages at 650°C, which range from 0.84 to 1.60%, are typical of continuous dehydration with increasing temperature and do not give any evidence of thermal collapse of the zeolitic structure. Such shrinkage greatly overwhelms the normal thermal expansion. It appears fully justified by the considerable water loss of the various cation forms of zeolite A, which at 650°C range from 17.4 (Cs form) to 39.7 (Li-form)%. The water content of the various alkaline cation forms of zeolite A decrease with the increasing cation size, as one could expect.

It can be said that the occurrence of partial structural damages can be seen by comparing the dilatometric curves of Na and K forms concerning first and second cycle reported in Figs. 6 and 7. The compacts were fully rehydrated after the first heating cycle, they were stored again at a higher than 50% relative humidity. The complete absence of structural damage would require the curves of the first and second cycle to have about the same shape. This does not occur. In fact, shrinkage in the second cycle is far smaller than that in the first cycle. This can be explained only if a portion of the zeolitic structure has undergone thermal collapse during the first cycle. This portion does not rehydrate and, thus may not dehydrate and shrink during the second cycle. In the absence of any shrinkage the more compact phases which arise from the thermal collapse of zeolite A undergo plain thermal

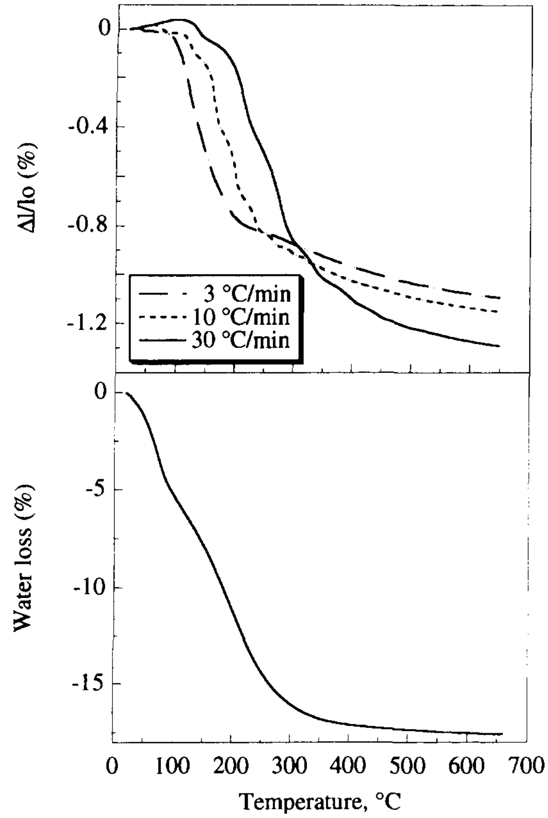

Fig. 4. Dilatometric and thermogravimetric curves of Cs form of zeolite A.

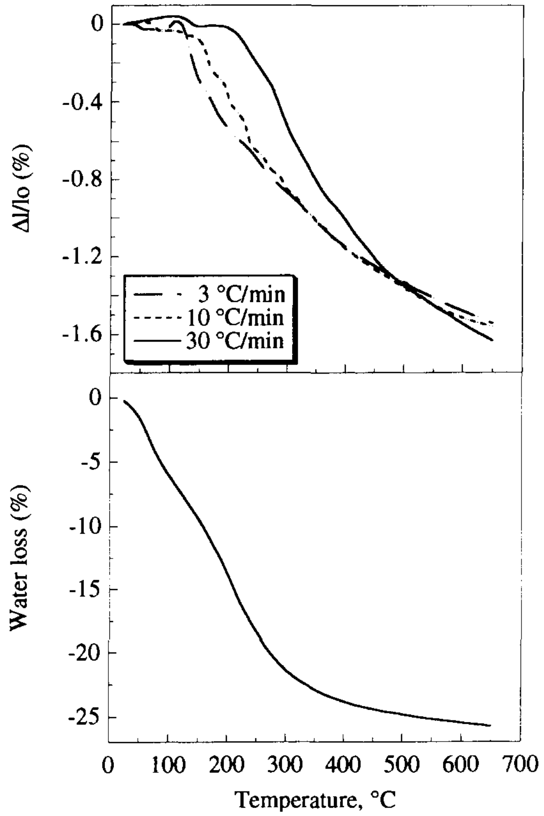

Fig. 5. Dilatometric and thermogravimetric curves of Ca form of zeolite A.

expansion and this will greatly reduce the extent of the final shrinkage of the whole compact in the second cycle.

The increase in heating rate results in a clear increase in the temperature at which a given shrinkage occurs. The structural damage is obviously dependent on the heating rate.

Another point that should be stressed is that in the dilatometric curves of the various cation forms of zeolite A it is not evident that cation migrations from a particular cation site to others affects the dimensional stability of the compacts, as possible in the dilatometric curves of chabazite [1]. It may be explained by the fact that cation movements in chabazite concern the migration of cations from the site II in the large ellipsoidal cage B, which can be entered through six eight-membered rings of 0.3–0.4 nm in diameter, to the site I in the small cage A, which can be entered through a six-membered ring whose free aperture has a radius of about 0.13 nm [6]. Migrations of cations from the cage B to the cage A affect the dimensional stability of chabazite and may be recorded in the dilatometric curves of various cation forms of chabazite. The effect of cation movement in zeolite A are far less dramatic. Zeolite A structure is characterized by a simple cubic cell in which 8 truncated octahedral units (β cages), present at the corners of the cube, are connected by 12 double-4-rings units, present in the middle of the sides, thus enclosing a great cavity having the shape of a truncated cuboctahedron (α cage) [4]. β cages may be entered through 8-membered rings whose free aperture has a diameter of 0.42 nm. Of the 12 sodium ions in the hydrated zeolite 4A, 8 are located near the center of the 6-rings inside the α-cage (site I) and the remaining 4 in the 8-rings (site II). When dehydration occurs. Na^+ ions in site I are displaced 0.04 nm into the α-cage from the center of the 6-ring, 3 of the Na^+

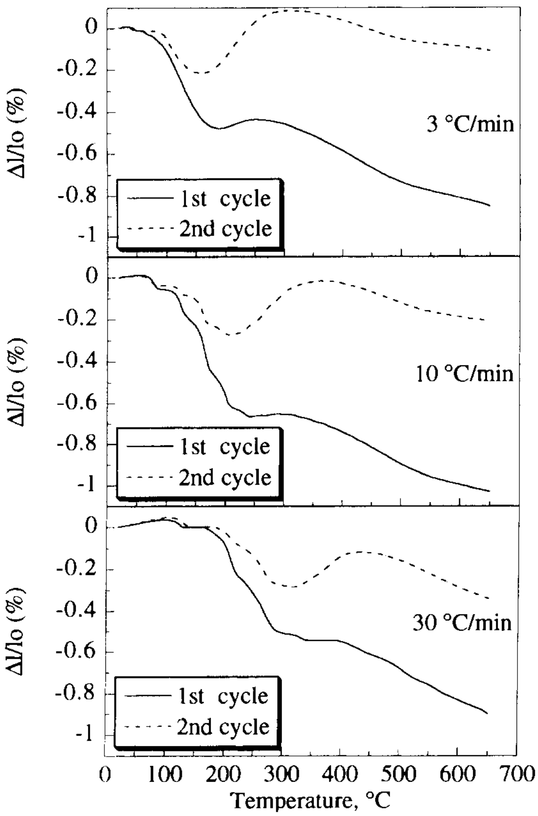

Fig. 6. Dilatometric curves of Na form of zeolite A regarding first and second cycle.

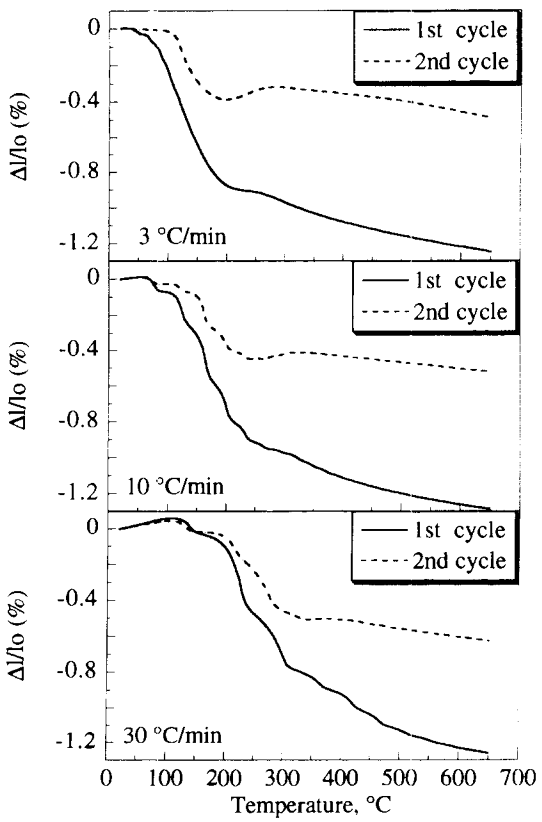

Fig. 7. Dilatometric curves of K form of zeolite A regarding first and second cycle.

ions in site II are located in the 8-ring displaced about 0.12 nm from the center of the ring, and the last Na^+ ions in site II is located opposite the 4-ring. These movements involve only small displacements from the initial position and may be hardly recorded in the dilatometric curves of various cation forms of zeolite A.

In Fig. 8 the dilatometric curves at 10°C/min heating rate of ammonium zeolite A in air and nitrogen (upper part) and the thermogravimetric curve at 10°C/min heating rate (lower part) are depicted. The weight loss at 650°C is 32.8%, which is lower only than that displayed by Li zeolite A alone. It is noteworthy that the final shrinkage of ammonium form of zeolite A is about ten times higher than the one of other cation forms. One should anyway bear in mind that ammonium zeolite A evolves, upon heating, both water and ammonia, thus producing H form of zeolite A.

The dilatometric curve of ammonium zeolite A in air display a sudden increase in temperature, at about 380°C which does not occur in the dilatometric curves of ammonium zeolite A in nitrogen. In order to better understand this phenomenon, the dilatometric behaviour of ammonium form of zeolite A in air at 3, 10 and 30°C/min heating rate is depicted in Fig. 9 by plotting both temperature and percent variation of length of compacts as a function of time. It is evident that the extent of the increase of temperature increases with increasing the heating rate.

This phenomenon could be explained as follows: ammonia evolved upon heating ignites in the temperature range 360–400°C, depending on the heating rate, and burns with the oxygen of air, thus giving rise to a sudden increase in temperature. It should be said that the usual ignition temperature of ammonia is about 600°C, but this value might be noticeably lowered considering that the combustion of ammonia

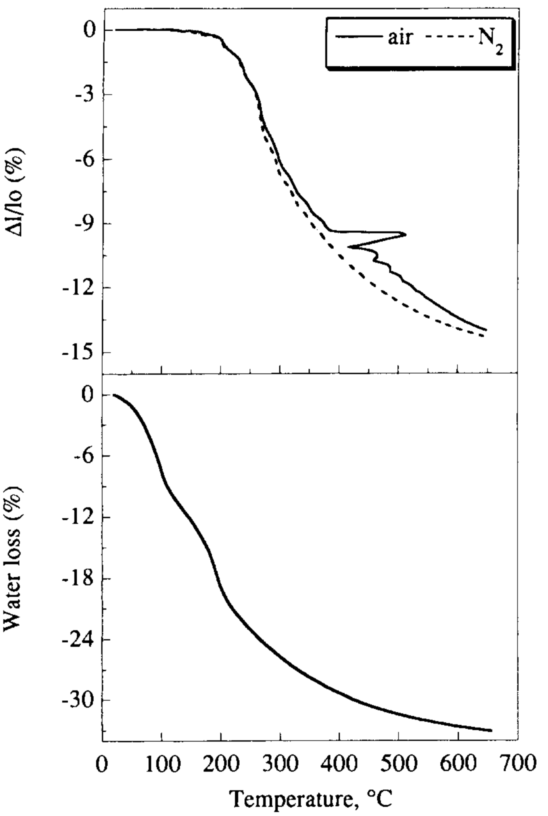

Fig. 8. Dilatometric and thermogravimetric curves of ammonium form of zeolite A at 10°C/min heating rate in air and nitrogen.

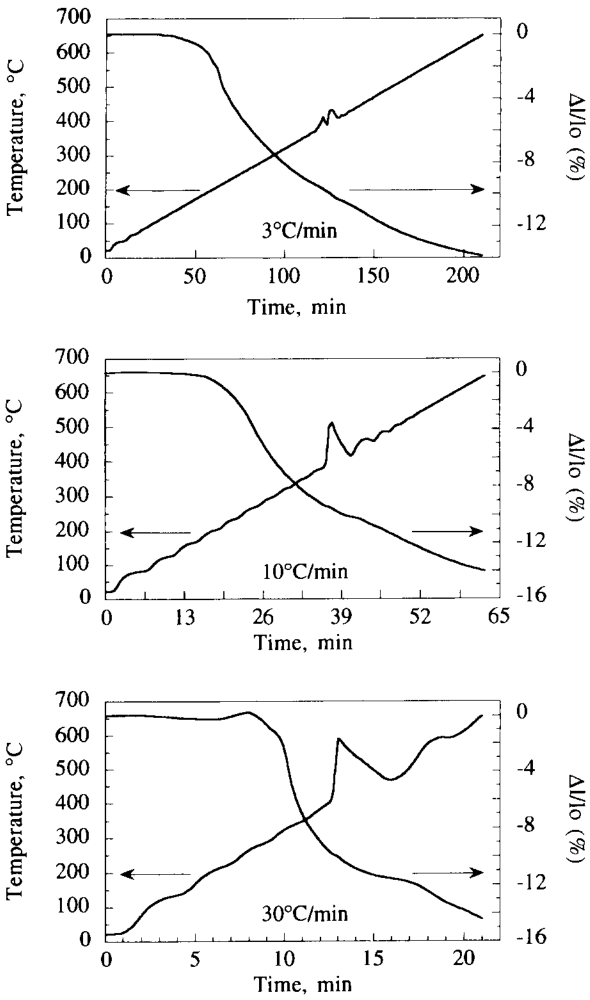

Fig. 9. Temperature and percent variation of length of compacts of ammonium form of zeolite A as a function of time.

is favoured by the acid sites present in the microporous zeolite A structure. In fact the evolution of ammonia has left protons as the charge balancing species which subsequently rearrange to form hydroxyl groups [4]. Such acid sites are known to have strong catalytic properties [4,7] which could be responsible for the lower ammonia ignition temperature. The fact that the extent of the increase of temperature increases with increasing heating rate might be explained considering that even the process of deammoniation of zeolite A has its kinetics. At the lowest heating rate a part of ammonia, after having evolved, has sufficient time for escaping from the surface of the compact and, thus, does not burn. The contrary occurs at the highest heating rate at which the ammonia is still evolving when the ignition temperature is attained. In this case most of the ammonia present on the zeolite surface may burn at the same time, thus giving rise to a far more evident thermal effect. It must be pointed out that no signal have been detected by performing DTA of ammonium form in air. An explanation may be related to the different configuration of furnace chamber of DTA and dilatometer. The horizontal configuration of furnace chamber of dilatometer allows evolved ammonia to remain near the compact, whereas the vertical configuration of furnace chamber of DTA allows a part of evolved ammonia, which is lighter than air, to escape far away from the compact.

Special considerations should be given to the dilatometric and thermogravimetric curves of the hydro-

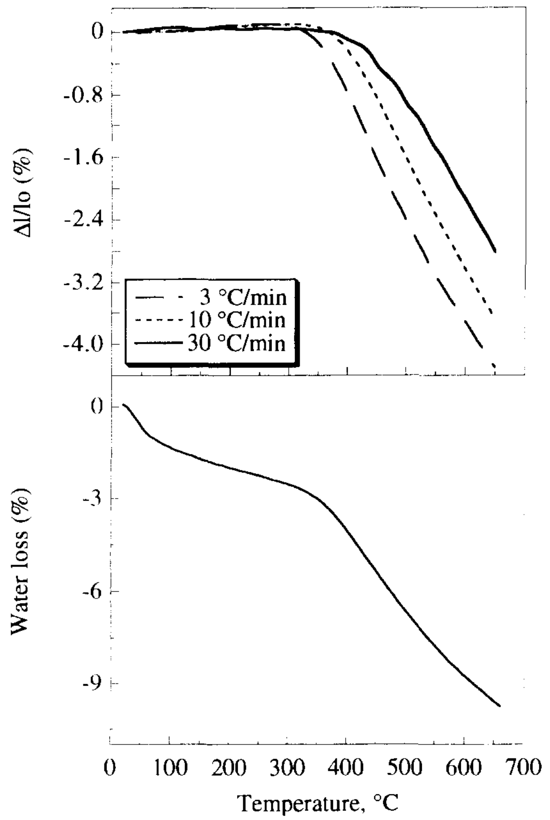

Fig. 10. Dilatometric and thermogravimetric curves of hydrogen form of zeolite A.

gen form of zeolite A reported in Fig. 10. The dimensions of the compacts stay practically constant up to a temperature which ranges from 350 to 400°C depending on the heating rate. At temperatures higher than this value the compact begins to shrink further and attain final values ranging from 3 to 4%. The temperature at which the compact begins to shrink and the magnitude of the shrinkage depend on the heating rate. The water loss of the hydrogen form of zeolite A is far lower than the other cation forms and attain a final value of 9.2% at 650°C. An evident inflection point appears in the thermogravimetric curve at about 370°C, which coincides with the temperature at which the compact begins to shrink. From Fig. 10 it is possible to assess that the water loss at 370°C is about 3.2%, whereas the water loss in the 370–650°C is about 6.0%.

The results of these runs may be explained considering that the final value of the sharp shrinkage beginning at a temperature ranging from 350 to 400°C, as well as the downward concavity of the dilatometric curves are typical of a thermal collapse. Before this temperature is attained the dimensions of the compacts stay constant. This fact suggests that for temperature lower than this value the structure of H form of zeolite A appears thermally stable and that the small shrinkage arising from 3.2% loss of water exactly counterbalances the plain thermal expansion. The remaining 6.0% of water, lost in the range 370–650°C, appears of a different nature from the 3.2% water previously lost. In fact the former water seems to be irreversibly lost as a consequence of the dehydroxylation of H form of zeolite A which destroys zeolite structure. The latter seems water filling up channels and cavities, whose molecules bound to each other mainly by hydrogen bond whose loss is not irreversible.

4. Conclusions

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

1. shrinkage arising from both dehydration and partial thermal collapse of zeolitic structure appears to rule dilatometric behaviour of Li, Na, K, Cs, ammonium, and Ca forms of zeolite A;
2. final shrinkage of ammonium form is about ten times higher than the one of other cation forms;
3. the ignition and combustion of ammonia, evolved upon heating by zeolite A, at a temperature lower than the usual ignition temperature is recorded;
4. thermal collapse of hydrogen form of zeolite A starts in the 350–400°C range.

As in the case of chabazite [11], the study of the dilatometry of zeolite A has proved to be valid in the 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 it is noteworthy that the dilatometric behaviour of various cation forms of zeolite A greatly differs from the dilatometric behaviour of various cations forms of chabazite and that, in spite of it, in both cases dilatometry has attained its goal of supplying useful information on the thermal behaviour of zeolites.

References

[1] A. Colantuono, S. Dal Vecchio, G. Mascolo and M. Pansini, J. Therm. Anal., 47 (1996) 281.

[2] M.J. Schwuger and M. Liphard, Zeolites as Catalysts, Sorbents and Detergent Builders, H.G. Karge and J. Weitkamp Eds., Elsevier Science Publishers B.V., Amsterdam, 1989, 673.

[3] H. Updaek and P. Krings, Zeolites as Catalysts, Sorbents and Detergent Builders, H.G. Karge and J. Weitkamp Eds., Elsevier Science Publishers B.V., Amsterdam, 1989, 701.

[4] D.W. Breck, Zeolite Molecular Sieves: Structure, Chemistry and Use, Wiley, New York, 1974, pp. 771.

[5] RILEM 25 P.E.M., Recommended tests to measure the deterioration of stones and to assess the effectiveness of treatment methods, 13, n° 75, 1980, 177.

[6] E. Passaglia, Natural Zeolites. Occurrence, Properties and Uses, L.B. Sand and F.A. Mumpton Eds., Pergamon Press, Elmsford, 1978, 45.

[7] A. Dyer, An Introduction to Zeolite Molecular Sieves, J. Wiley & Sons, Chichester, 1988, pp. 149.