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THERMAL ANALYSIS OF NaMgA ZEOLITES

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ABSTRACT

Water desorption from NaMgA zeolites was investigated as a function of magnesium ion content with the help of thermal analytical methods such as combined TG–DTG–DTA, TMA and X-ray heating technique. At least five partly overlapping desorption effects of water were observed from DTA and DTG features. The amount of water corresponding to individual desorption peaks was determined by experimental methods of separation. An assignment of the desorption effects to the related adsorbed forms of water is suggested.

INTRODUCTION

The improvement in instrumentation for thermal analysis resulting in better resolution of the desorption effects leads to the further application of these methods to the investigation of the water–zeolite system. Thermal analytical studies on synthetic zeolites of type A have shown that desorption of water is a complex process, depending on experimental conditions, zeolite structure and cation content. For zeolites of type A containing monovalent ions, three more or less overlapping desorption effects were obtained by differential thermal analysis (DTA) and thermogravimetry (TG) as well as differential scanning calorimetry (DSC) [1,3,5]. Substitution of monovalent by bivalent cations leads to the appearance of additional peaks in the DTA and DSC curves. Assignment of desorption effects to certain adsorption structures of water needs the separation of these peaks. Vucelic and co-workers [3] carried out combined DSC–EGA (evolved gas analysis) experiments and separated the effects by a mathematical method. On the basis of these results, they determined the desorption energy for different bound waters in A zeolites exchanged by monovalent and bivalent cations to comparable extents. The dependence of water desorption on cation content was examined by Dyer et al. [1,4] for Sr-, Co- and Ni-containing zeolites by

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combined DTA–TG measurements. They determined the desorbed amount of water related to the DTA peaks and suggested a detailed location of cations and water molecules.

Some previous studies showed that characteristic DTA traces were produced in a low temperature range when sodium ions were partially exchanged by magnesium ions [6,7]. These observations initiated a more detailed combined TG–DTG–DTA investigation, completed by an X-ray heating technique (Guinier–Lenne) and TMA (thermomechanical analysis) experiments, the results of which are reported in this paper.

EXPERIMENTAL

Thermal analytical measurements were made using a microthermoanalyzer (Setaram, Lyon, France) consisting of a combination between a microbalance MTB 10-8, a symmetrical oven and a DTA attachment. This apparatus allowed combined TG–DTG–DTA investigations. Experiments were carried out by heating approximately 10 mg of zeolite powder (< 0.1 mm) for TG and DTA, respectively, in a nitrogen or argon flow of 50 ml min^{-1} at heating rates from 1.67 to 10 K min^{-1}. The gas stream was dried by passing it through a bed of activated zeolite 4A pellets.

Determination of the amount of water associated with the individual desorption effects was carried out using slow heating rates (1.67 and 3.33 K min^{-1}) with separation of the TG curve into temperature intervals corresponding to the observed DTA and DTG peaks. Heating was continued stepwise up to peak maximum temperature and was finally held at this temperature. A further set of experiments involved partial readsorption whereby zeolite samples were first activated by heating to 770 K in the thermoanalyzer, followed by cooling during which nitrogen (undried or saturated with water vapour) was passed over the samples for a fixed time. The exact amount readsorbed could be determined by the microbalance and, when a defined degree of coverage had been reached, the zeolite was reheated and the desorption effects recorded. X-Ray heating experiments were performed with a Guinier–Lenne camera. Other details and experimental procedures were as previously described [8]. TMA was carried out in a static atmosphere using a DuPont 941 instrument. The samples were carefully tamped into a small glass straight-sided cup into which a flat-bottomed silica TMA probe was a smooth fit. Heteroionic forms of zeolite A were prepared by ion exchange of Zeosorb 4A (VEB Chemiekombinat, Bitterfield, G.D.R.) with 0.2 M solutions at ambient temperature.

The degree of exchange was checked by complexometric titration and flame photometry of the solution after ion exchange, as well as by dissolution of the solid. Samples were stored over saturated sodium chloride solution for a minimum of 2 weeks prior to measurement.

RESULTS

This paper is concerned with thermal analytical investigations on A zeolites containing up to about 5 magnesium ions p.u.c. The term p.u.c. (per unit cell) is used for convenience and refers to the psuedo unit cell which is one eighth of the true unit cell.

Thermal and sorptive properties of A zeolites almost completely exchanged by Mg^{2+} ions will be reported later. Zeolite composition and total weight losses observed to 770 and 1270 K are shown in Table 1. X-Ray powder diffraction patterns show that no appreciable breakdown in the crystal structure ensued from magnesium exchange.

Thermal analysis of sodium A zeolite shows that desorption of water starts at room temperature. The first DTA effect arises as a flat shoulder in the low temperature range with the main endothermal peak maximizing about 435 K. On further heating, a broad endothermal effect of lower intensity is observed with a maximum temperature of 640 K. The obtained DTA traces are in good agreement with DSC curves reported by Vucelic et al. [2].

Exchange of sodium by magnesium ions in zeolite A leads to significant alterations in the thermal desorption behaviour of water. Even the introduction of small amounts of magnesium ions causes the development of a sharp peak maximizing about 375 K on the broad shoulder observed in sodium A zeolite. The intensity of this effect grows with increasing content of Mg^{2+} ions, whilst the shoulder forming the background diminishes in intensity.

The main endothermal effect at 435 K essentially does not change in peak area up to medium degrees of exchange.

A new thermal effect is observed, as an increasing shoulder, at about 490–510 K for zeolites with Mg^{2+} contents of 33% and more. The desorption effect at about 640 K decreases in intensity with growing magnesium ion content, whilst the peak maximum moves to lower temperatures.

TABLE 1

Thermogravimetric and chemical analyses of NaMgA samples

Sample	No. of Mg ions p.u.c.	No. of Na ions p.u.c.	No. of H_2O p.u.c.	Molecules of water lost	
				Room temp.–770 K	770–1270 K
NaA	0	12	27.1	26.7	0.4
NaMg16.7A	1	10	30.6	30.1	0.5
NaMg33.8A	2	8	32.6	31.4	1.2
NaMg47.2A	2.8	6.4	33.5	32.1	1.4
NaMg65.0A	3.9	4.2	34.5	32.8	1.7
NaMg70.0A	4.2	3.6	35.4	33.4	2.0

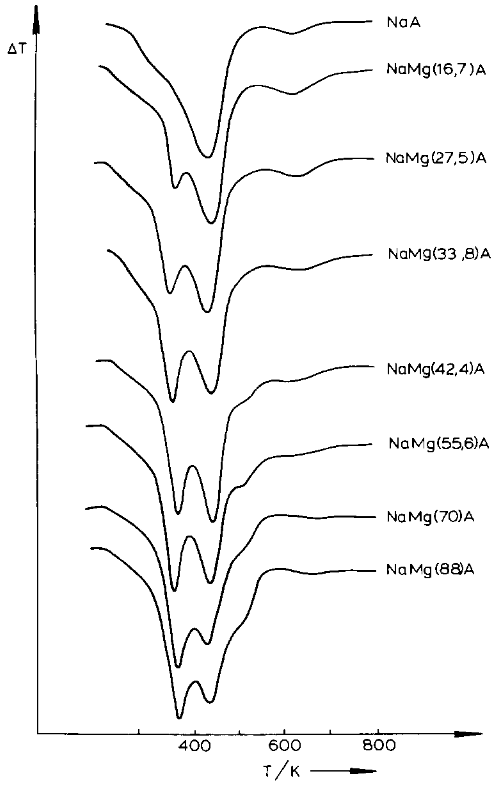

Fig. 1. DTA curves for NaMgA samples. Heating rate 10 K $\min^{-1}$.

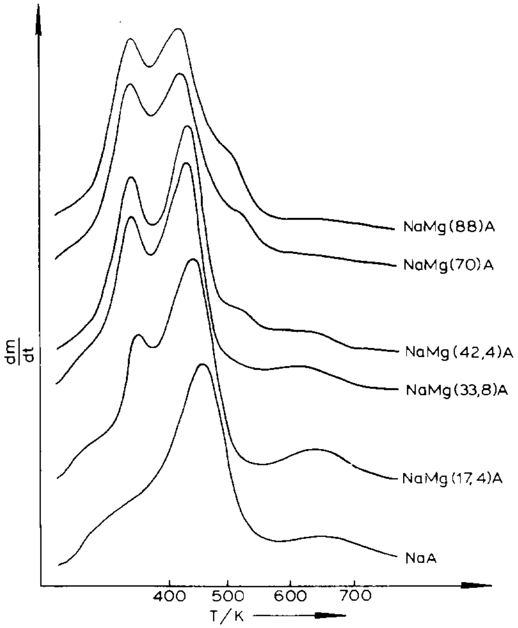

Fig. 2. DTG curves for NaMgA samples. Heating rate 10 K $\min^{-1}$.

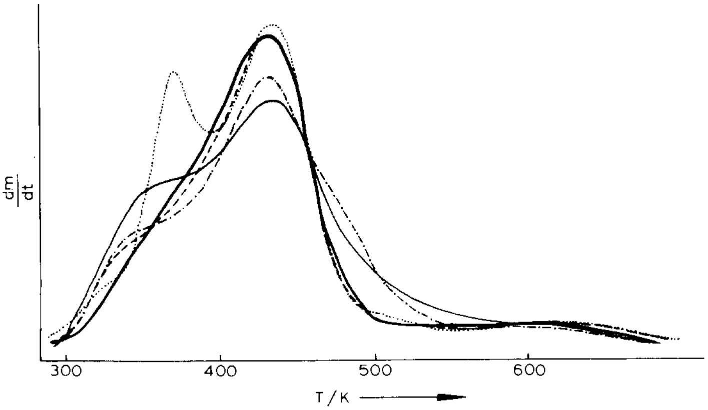

Fig. 3. DTG curves for alkaline earth-exchanged A zeolites. Heating rate 5 K min^{-1}. ———, NaBe(18.0)A; ———, NaSr(47)A; —·—, NaCa(46.8)A; — — —, NaLi(32)A; ..... NaMg(32)A.

Comparison of the DTA (Fig. 1) and DTG curves (Fig. 2) shows a qualitative agreement. All thermal effects are related to the degree of water desorption.

The influence of ion strength and coordination ability on water desorption of A zeolites were investigated by the exchange of other alkaline earth ions. DTG curves are presented in Fig. 3. Comparison of the features noted demonstrates that only zeolites containing magnesium ions show an intensive thermal effect at about 375 K.

The assignment of the individual desorption effects to certain adsorption forms of water require the prior determination of those water molecules associated with an individual desorption event.

DISCUSSION

The thermogravimetrically determined weight loss in NaA zeolite agrees very well with the theoretical value of 27–28 H_2O p.u.c. [7,10]. Detailed suggestions concerning the location of ions and water molecules in NaA zeolite from thermal analytical experiments, with the X-ray evidence of Gramlich and Meier [9], was published recently by Dyer and Wilson [1]. The water amounts for the individual desorption effects determined in this work are similar to the early reported values, except that the water content corresponding to the low temperature shoulder is somewhat smaller. It may well be that the lower heating rate used in this study is responsible for the smaller amount of desorbed water observed in the low temperature region.

It can be seen from Table 1 that increasing exchange of sodium by magnesium ions leads to increasing water content and the total amounts of

TABLE 2

Water lost in the separate desorption effects

Sample	Water molecules p.u.c. corresponding to the peaks I–V					
	I	II	III	IV	V	Total
NaA	3.0	4.5	14.8	0	3.9	26.2
NaMg16.7A	3.2	6.9	14.8	1.1	4.1	30.1
NaMg33.8A	3.0	7.8	15.1	2.1	3.8	31.4
NaMg47.2A	2.3	10.9	15.0	2.5	2.9	32.1
NaMg55.6A	2.0	10.7	14.0	3.3	2.7	32.7
NaMg65.0A	1.8	11.8	13.3	3.7	2.2	32.8
NaMg70.0A	1.6	11.8	13.7	3.8	2.5	33.4

water heating to 770 K are in good agreement with published values for zeolites with certain degrees of exchange [7,10].

Magnesium-containing samples have higher water contents than alkali metal- [7,11] and Ca-, Sr- and Ba-exchanged A zeolites [1,12]. This is due to the higher available volumes in the cages caused by exchange of alkali metal ions for magnesium ions in conjunction with the higher coordination ability of magnesium ions compared with other mono- and bivalent ions.

Desorption of water from zeolites containing magnesium is a complex process. From the results obtained for the amount of water responsible for the separate desorption effects and the DTA features, it is apparent that four or five energetically different forms of water are observed, depending upon the degree of exchange. The first desorption effect (peak I) arises as a shoulder in both DTA and DTG traces at temperatures below 360 K and diminishes in intensity with the progressive exchange of sodium by magnesium ions. With increasing Mg^{2+} content, peak I becomes more overlapped by peak II. The low desorption temperature indicates that the water responsible for peak I is a loosely bound form in that it interacts only with other water molecules. Such an easily removable form of water is reported for other synthetic and natural zeolites [13].

This form of water probably is located in the eight O rings in a bridged form as suggested for NaA [1,9].

With increasing degree of exchange, these water molecules are more strongly influenced by the magnesium ions and Table 2 lists the number of water molecules for peak I which are desorbed in flowing dry inert gas at room temperature up to the disappearance of the low temperature shoulder.

Water bound in the manner described above in the eight O rings on the external surface of zeolite crystallites should cause adhesion between small particles by formation of hydrogen bonding between them. This should be observed in samples of low magnesium content (< 3–4 Mg^{2+}), and those samples of low Mg content are noticeably less free-running powders than those of high Mg content.

Unfortunately, X-ray data on cation siting for magnesium ions in A zeolite is not yet available, either in the dehydrated or the hydrated state. Ion exchange, sorption kinetic measurements, and theoretical calculations of lattice–cation interactions suggest that the distribution of magnesium is similar to that of calcium. This is valid, particularly, for the dehydrated zeolites [14]. The first Mg^{2+} (per α-cage) exchanges one Na (3) and one Na (1), the next replaces Na (2) and Na (1), and the last two Mg ions should exchange two Na (1).

Characteristic of the presence of magnesium ions in zeolite A is the formation of the sharp and intensive desorption effect, maximizing about 375 K. Because of the unambiguous connection between the presence of Mg^{2+} ions and the intensity of this endothermal effect, it seems most likely that the water corresponding to peak II is that coordinated solely to magnesium. The incoming magnesium ions should be present initially as fully hydrated species in the α-cage in octahedral coordination. Octahedral coordination of cations such as Co^{2+}, Ni^{2+} and Ca^{2+} in hydrated A zeolites has been observed by spectroscopic and X-ray methods [15–17]. Mg^{2+} is more hydrated than other mono- and bivalent ions and, whereas the bare ion has a small Pauling radius, the hydrated ion is the largest of the alkaline earths [18]. Because of their high charge/size ratio, Mg^{2+} ions fulfil their coordination sphere with the mobile water molecules in the zeolite cages. Indeed, they move in the A zeolite framework with their hydration sphere intact as they do in aqueous solution, unlike Ca^{2+} which loses water to enter the A supercage [25–27]. Magnesium ions coordinate the water molecules stronger than other bivalent ions and therefore the desorption of water takes place at higher temperatures. For Ni^{2+} and Co^{2+} in A zeolites, the initial loss of 3 or 2 coordinatively bound water molecules was suggested in the

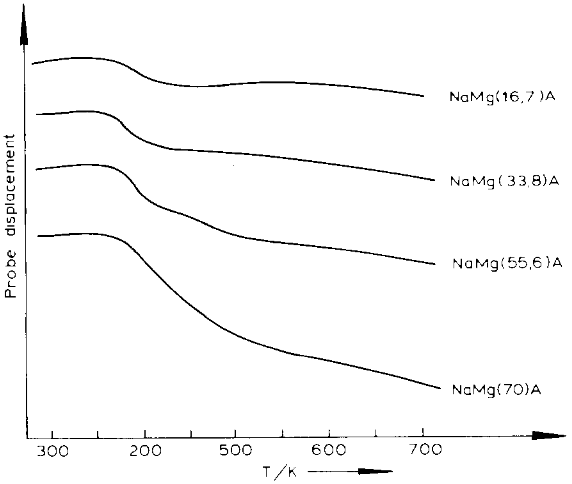

Fig. 4. Thermomechanical analysis curves for NaMgA samples. Sample height 5 mm, without loading; heating rate 5 K min^{-1}.

temperature range between room temperature and about 345 K from variation of the coordination sphere from octahedral to tetrahedral symmetry and the incorporation of oxygens of the zeolite framework as ligands [4]. In a similar way, the amount of water desorbed corresponding to peak II (see Table 2) can be explained satisfactorily by assuming a loss of 3 water molecules, which is equivalent to the conversion $Mg(H_2O)_6 \rightarrow Mg(H_2O)_3$ with 1 water molecule from each Na^+ ion remaining in the S2 position after introduction of one magnesium ion. The loss of coordinated water from the magnesium ions and sodium ions in the S2 position is accompanied by a marked unit cell shrinkage illustrated by both the TMA plots (Fig. 4) and the Guinier-Lenne-patterns (Fig. 5). It is suggested that these features represent the exchange or loss of ligands. Instead of water, at least one oxygen of the framework is now coordinated to magnesium ions occupying fixed lattice positions. The divalent ions should adopt site S2 coordinated to 3 H_2O. Statements concerning the exact symmetry of this state are not possible from the results of the present experiments. The more intense interaction of ions in fixed positions with the framework results in decreasing repulsion forces and leads to smaller lattice dimensions.

The peak maximum of desorption effect III arises at about 500 K as observed for all other ion exchanged forms of A zeolite and does not change significantly with Mg^{2+} content. Some authors assign it to water bound only to the zeolite framework via hydrogen bonding between water and oxygen atoms of the zeolite [3,7]. This effect is relatively broad and should contain some energetically similar adsorption forms of water. In the same temperature range, water coordinated by Na^+ ions in the S1 position is desorbed, as observed in NaA, with the loss of 2 H_2O from the $Mg(H_2O)_3$ species located in the S2 position. This second process is associated with an ion resiting whereby the magnesium ions adopt their preferred site S1 occupancy. In this position, the Mg^{2+} are expected to be tetrahedrally coordinated with three oxygens of the framework and one water molecule. Similar arrangements were found for Co^{2+} and Ca^{2+} in A zeolite after initial water has been lost [19,20]. In the readsorption of water on zeolites containing Co^{2+}, Wichterlova et al. [20] observed the conversion of tetrahedrally to octahedrally coordinated species after addition of at least 15 H_2O p.u.c. Water present as a clathrate-like structure not coordinated by cations, has been suggested for A zeolites containing Na and Ca based upon X-ray measurements [9,17]. The amount of water lost in the temperature range corresponding to peak III does not change markedly in NaA and the samples containing up to about 3 Mg. Only at higher contents ($Mg > 3$) does the intensity of this effect diminish, probably due to the decrease in the desorbed amount of water linked to Na^+ ions in localized positions in the six O ring (S1). Each of the sodium ions in site S1 is coordinated by one H_2O as envisaged from X-ray measurements on hydrated NaA [9]. Desorption effect IV appears in magnesium exchanged samples as a well-developed

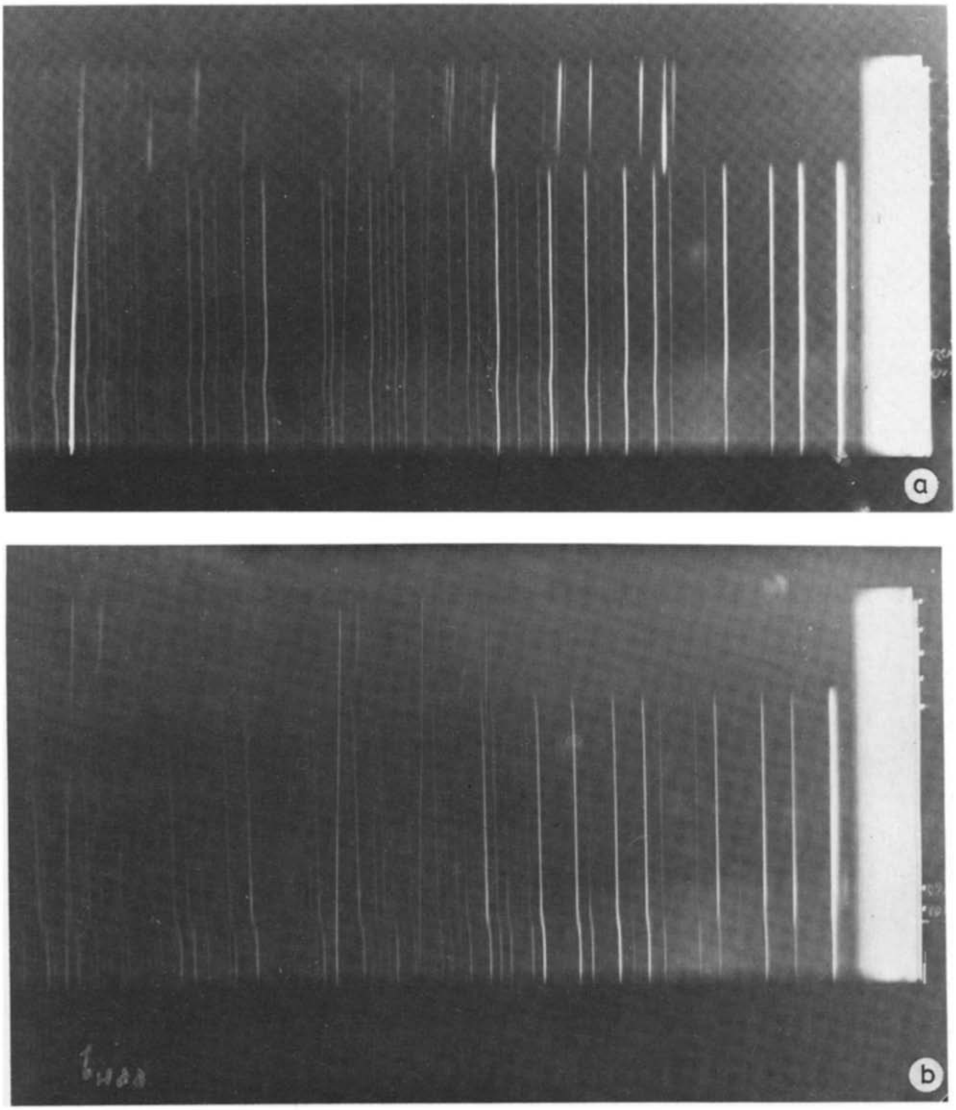

Fig. 5. Guinier–Lenne pattern of (a) NaMgA8.5A and (b) NaMgA88A. Heating rate 0.5 K min^{-1}.

shoulder at about 500 K and is characteristic of the presence of multivalent ions. Water loss in this temperature range is proportional to increasing magnesium content and corresponds to about 1 H_2O per Mg^{2+} ion (see Table 2). This effect can be allocated to the desorption of the last water coordinated to magnesium in the S1 or S1′ positions. The bivalent cations can occupy the S1 or S1′ positions in the dehydrated zeolite (site S1′ is slightly displaced from the centre of the hexagonal openings into the β-cages) as, from X-ray investigations of dehydrated CaA zeolite, Thoni [17] suggested a distribution of three Ca in the S1 and the other three in the S1′ positions and the site occupancy of magnesium would be similar. The observed expansion (Figs. 4 and 5) in unit cell dimensions for samples of low magnesium content ($Mg < 2$) is associated with the peak II desorptions, which create repulsion forces between ions in fixed positions, particularly Na in S1. Magnesium ions have a high polarizing ability and are able to realize strong interactions with the aluminosilicate framework, hence magnesium ions are screened by the O atoms of the framework [21] and may not develop strong repulsions to the other cations. This leads to smaller expansions in this temperature range with increasing magnesium content.

Desorption effect V has a maximum temperature at about 640 K and is due to the removal of a strongly bound form of water as observed for mono- and bivalent ions in zeolite A. On readsorption of small amounts of water, followed by repeated desorption, a peak of comparable intensity is seen in DTA and DTG traces in the same temperature range (see Fig. 6). There are some discrepancies concerning the interpretation of this form of adsorbed water in the literature. Results of thermal analytical- [3,4], NMR spectroscopic [22] and sorption experiments [3] lead to the conclusion that this water is adsorbed inside the β-cages as molecular water or as OH groups, whereas results of calorimetric [23] and dielectric relaxation [24] measurements suggest that these water molecules are adsorbed on so-called delocalized cations (in the S2 position), which should be able to form stronger bonds to water. The small dependence of the shape and position of peak V in both DTA and DSC traces on the nature of the cations as well as the higher desorption energy of this water points to its source being water from the β-cages.

It can be seen from Table 2 that, with increasing magnesium content, the desorbed amount of water of peak V decreases from 3.9 H_2O for NaA

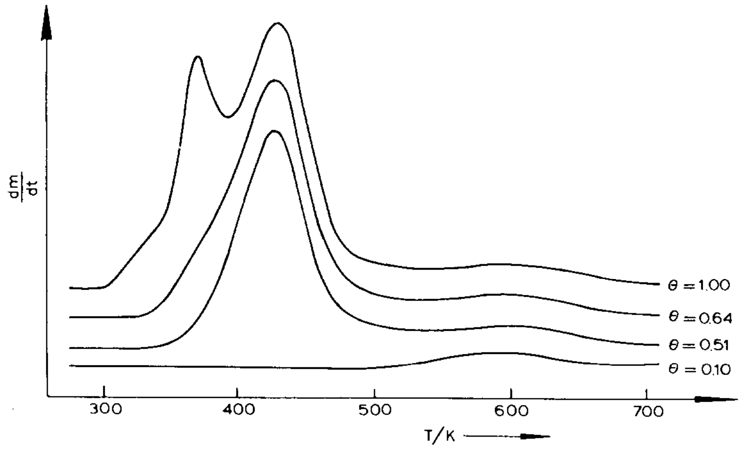

Fig. 6. DTG curves of water desorption from NaMg32A. Dependence on coverage.

(which is nearly the total sorption capacity of sodalite units for water) to about 2.5 H_2O for sample NaMg70A. This decrease is probably due to the presence of magnesium ions in the β-cages and this has support from observations that some bivalent ions (Zn^{2+}, Co^{2+}, Ni^{2+}, Ca^{2+}) have been assigned to sites in the β-cages by X-ray crystallographic studies [16,17].

A continuous desorption of water is observed on further heating of the samples and the final temperature of this process (and the desorbed amount) depends upon the magnesium content. For NaA the desorption is complete at about 800 K and corresponds to the decomposition of about 0.5 OH group p.u.c., assuming that desorbed water molecules are formed by the condensation of structural OH groups. The sample with the highest magnesium content shows water loss up to the collapse of the framework and about 2 OH groups p.u.c. are desorbed. These OH groups are thought to be introduced during ion exchange as structural OH groups, as those created by interaction of Mg^{2+} with water to form hydroxocations $Mg(OH)^+$ have no appreciable thermal stability.

The water losses corresponding to the separate desorption effects are listed in Table 2. The values determined by the several methods agree well to an uncertainty of ± 1 H_2O p.u.c. for the large effects and ± 0.5 H_2O p.u.c. for the small desorption peaks. Adsorption of water after heating (up to 770 K)–cooling cycles is reversible with respect to the total adsorbed amount, Figure 6 demonstrates that adsorbed water is not freely distributed between all available sites but the sites are occupied successively in the sequence of decreasing strength of bonds formed. Therefore, the experimental methods herein described for separation of the desorption effects are justifiable.

TMA (Fig. 4) and X-ray heating results (Fig. 5) demonstrate the same behaviour with respect to the changes in unit cell dimension with increased temperature. At low Mg contents, the initial decrease is followed by a small expansion at temperatures above 450 K, like that for NaA. With an increasing degree of exchange (> 1 Mg), a continuous shrinkage of the framework is observed.

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