

THERMAL ANALYSIS OF SYNTHETIC ZEOLITES OF THE A SERIES. (Part I)

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ABSTRACT

Samples of powdered zeolite A (sodium form) were examined by thermogravimetric (TG), thermomechanical (TMA) and differential thermal analyses (DTA). The features observed were rationalized by consideration of the recent structural evidence¹ as to the positioning of water molecules and cations within the unit cell.

The effect of successively replacing the monovalent (Na) ions by divalent (Sr) ions was considered by similar procedures. Explanations are offered for the observed analyses.

INTRODUCTION

Most of the previous applications of thermal analysis to zeolite chemistry have been directed to the use of thermogravimetry, to determine water content² or ammonia loss,³ or the differential thermal analysis of structural transformations at elevated temperatures.⁴ Whilst investigating the loss of thermal stability caused by introducing barium into the A lattice it was noticed⁵ that this substitution caused new features to appear on DTA curves. Similar preliminary studies⁶ on samples of NaA which had been partially exchanged by Sr showed complex features in the range ca. 100–250°C.

Recent detailed X-ray crystallographic determination¹ of the position of water molecules and sodium cations within the A framework has enabled various thermal analyses to be explained with more satisfaction and this paper recounts the studies on parent NaA (4A) and various heteroionic forms in which Na has been replaced by Sr.

EXPERIMENTAL

Thermal analyses were carried out on a Dupont 900 differential thermal analyser with the 950 (thermogravimetric) and 941 (thermomechanical) attachments.

Ion exchange was used to prepare heteroionic forms of powdered Linde Molecular Sieve (4A) as supplied by BDF, Ltd. The degree of exchange was checked by isotope dilution analysis (using 22-Na) and by flame photometry.

The sieve was sedimented to obtain a uniform size range prior to exchange and all thermal analyses were carried out on samples which had been equilibrated for one week over saturated sodium chloride solution.

X-ray Guinier powder photographs were used to assess the crystallinity of exchanged samples.

RESULTS

The samples prepared had the compositions shown in Table I. (N.B. the term p.u.c. is used for convenience and strictly refers to the pseudo-cell which is one eighth of the true unit cell.)

TABLE I

PSEUDO UNIT CELL COMPOSITION OF Na-Sr A ZEOLITES

<i>Sample No.</i>	<i>Number of Na</i>	<i>Number of Sr</i>	<i>Number of H₂O</i>
1	11.6	0.2	27.3
2	11.0	0.5	27.4
3	10.6	0.7	27.5
4	7.1	2.4	28.4
5	5.4	3.3	30.3
6	3.8	4.1	31.6
7	3.1	4.4	30.9
8	2.4	4.8	31.2

Representative thermal analyses are in Figs. 1-3. X-ray analysis showed that no appreciable breakdown in structure had occurred on ion-exchange with the exception of the sample with the highest strontium content which showed a slight loss of crystallinity.

DISCUSSION

Hydrated NaA

The first paper describing the structure of zeolite A was that of Reed and Breck⁷, the co-originators of the synthetic zeolite A. This publication established the aluminosilicate structure and some cation positions in the anhydrous material and more recent work has been directed to locating cation and water positions in the hydrated zeolite. Latterly Gramlich and Meier¹ have allocated detailed cation and water positions to NaA which, although not finally established, are accepted as reasonable postulates. A summary of their sitings is in Table 2.

On the basis of the information in Table 2 the analyses of hydrated NaA can be rationalized as follows:

(i) DTA has an endothermic water loss maximizing about 120°C. This corresponds to a change in slope on the TG and is equivalent to about 10 molecules of

water lost. This loosely bound water can be presumed to be $1\text{H}_2\text{O}_\alpha$, $3\text{H}_2\text{O}_{\text{II}}$ and $6\text{H}_2\text{O}_\beta$. This leaves $4\text{H}_2\text{O}_\beta$, $8\text{H}_2\text{O}_\text{I}$ and $6\text{H}_2\text{O}$ which presumably locate 4 to the Na_{II} and 2 filling the empty site II. This is the total of 18/19 structured water noted by Morris⁸ from dielectric relaxation methods.

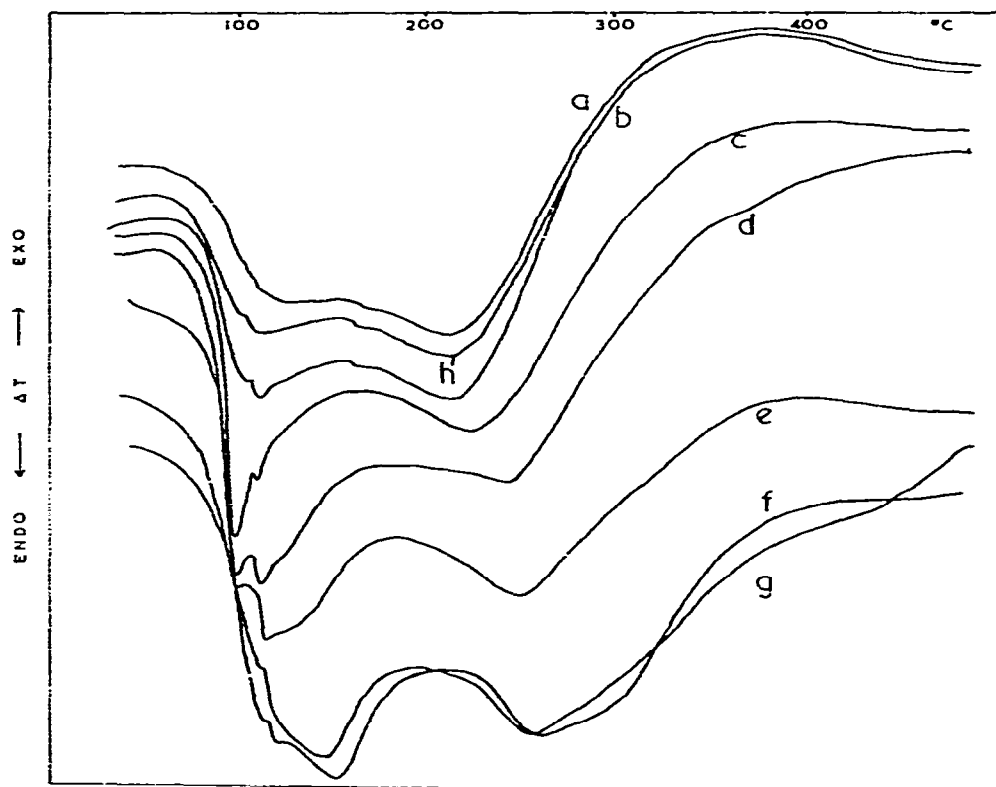


Fig. 1. Differential thermal analysis curves. a = NaA; b-g = samples 3-8; and h = sample 1 and 2.

TABLE 2

SUGGESTED LOCATION OF IONS AND WATER MOLECULES IN PSEUDO UNIT CELL OF NaA

All numbers are idealized.

Location	Number of H_2O	Designation	Number of Na	Designation
In sodalite unit (β -cage)	4	H_2O_β	—	—
Site I (near to '6' ring)	8	$\text{H}_2\text{O}_\text{I}$	8	Na_I
Bridge across '8' ring near to site II	6×2	$\text{H}_2\text{O}_\alpha$	—	—
Site II (near to '8' ring)	3	$\text{H}_2\text{O}_{\text{II}}$	3	Na_{II}
In central cavity (α -cage)	1	$\text{H}_2\text{O}_\alpha$	1	Na_α
Total	28		12	

^a These 20 water molecules form in a shape close to the pentagon dodecahedral which is well-known in clathrate hydrates.

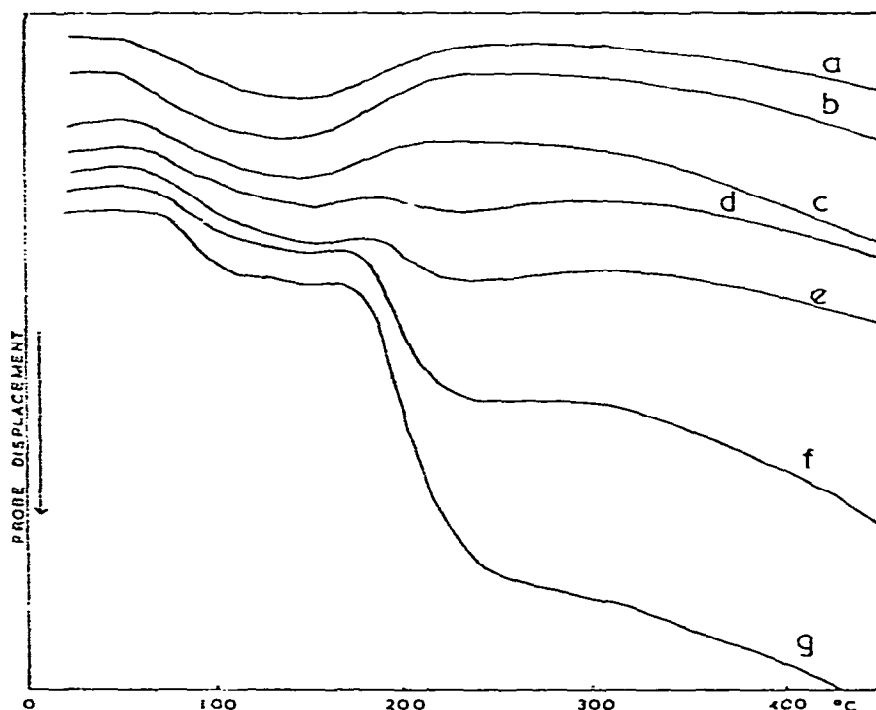


Fig. 2. Thermomechanical analysis curves. a = NaA and sample 1; b = sample 2 and 3; c-g are samples 4-8.

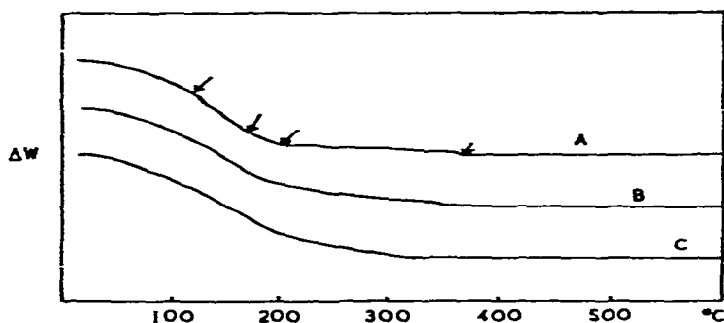


Fig. 3. Thermogravimetric analysis curves. A = NaA and samples 1-3; B = sample 4 and C = samples 5-8. The arrows on curve A give indication of the changes in slope referred to in the text.

(ii) At roughly 165°C a distinctive small endotherm appears (see Fig. 1). This coincides with a further change in TG curve slope and with the marked expansion in cell volume illustrated by the TMA plot. It is suggested that these features represent the final removal of the elements of the pentagon dodecahedral arrangement of water molecules envisaged by Gramlich and Meier¹ (see Table 2) and presages the resiting of Na into the sites they are known to occupy in the anhydrous unit cell⁷ (i.e., in "sentinel" positions in site II). Evidence for this assumption is also provided by the

observation that the endotherm occurs at a temperature equivalent to a further loss of $8\text{H}_2\text{O}_I$ (i.e. equivalent to one from each Na_I).

(iii) A logical consequence of (ii) is that the remaining $6\text{H}_2\text{O}$ in the supercage are distributed one to each pair of Na_{II} as they approach their final sentinel position. The loss of these 6 water molecules occurs in the range ca. $170\text{--}350^\circ\text{C}$ in a two-stage water loss (from the slope of the TG) and is represented by the second large DTA feature.

(iv) The final water loss is that of $4\text{H}_2\text{O}_\beta$ over a long temperature range (see DTA, TMA and TG) and is accompanied by further unit cell shrinkage (TMA).

Na-Sr A samples

A review of the DTA traces reveals that the introduction of Sr into the unit cell causes the first water loss to occur in two stages, the first up to about 100°C and the second to ca. 120°C . Whilst the number of Sr p.u.c. is ≤ 4 these two stages correspond to roughly a 7:3 water molecule distribution between the two stages but the distribution is nearer to 9:1 when the number of Sr ions > 4 . It may well be that the second water loss represents H_2O bound to Sr in the α cage which will be expected to decrease when the total number of ions present is less than 8 (i.e. 4Na , 4Sr p.u.c.). A corollary to this is that when $\text{Sr} \leq 4$ the same amount of water is so bound, implying that whilst the first Sr to enter the unit cell replaces Na_2 and one Na_{II} subsequent Sr replace Na_I . Further evidence for this given by the disappearance of the feature at 165°C from the DTA when $\text{Sr} > 1$, restated this assumption is that an exchange of more than 4Na p.u.c. causes the disruption of sodium (and water) from site I. As a consequence it would be expected that when the initial water loss is over (at $\sim 120^\circ\text{C}$) some form of ion resiting should occur to allow the divalent ions to adopt their preferred site I occupancy and the monovalent ions their preferred site II occupancy (viz., their sitings in the anhydrous zeolite⁹). Hence the new feature in the region $120\text{--}140^\circ\text{C}$ (see curve 'd') may be due to this resiting, confirmation of this is the new expansion observed in the TMA (curved) for the sample with $\text{Sr} > 2$ p.u.c.

It can also be seen from Table 3 that when the strontium content is ≥ 3 ions p.u.c. the total water content increases and the extra water is lost in the region $170\text{--}225^\circ\text{C}$. The implication from this is that the exchange of $2\text{Na}_I \rightarrow \text{Sr}$ creates empty site I's which "fill" with water to "preserve" the structure. It may well be that a distribution of site I $3(\text{Na}-\text{H}_2\text{O})_I$, $(2\text{Sr}-\text{H}_2\text{O})_I$ and $3\text{H}_2\text{O}_I$ accounts for the eight water molecules lost by sample number 5 in the temperature range $170\text{--}225^\circ\text{C}$, and this would mean that the eight water molecules lost between $120\text{--}170^\circ\text{C}$ could logically be distributed $3(\text{Na}-\text{H}_2\text{O})_{II}$, $1(\text{Sr}-\text{H}_2\text{O})_{II}$ and $2(\text{H}_2\text{O}-\text{H}_2\text{O})_{II}$ which would give all site II's occupied by two moieties. Similar distribution can be envisaged for the other samples with higher strontium contents.

The TMA shows that, as the total number of ions in the unit cell decrease, removal of water in the region $170\text{--}225^\circ\text{C}$ causes large contractions in crystal dimensions, this is consistent with the views outlined above in that the number of empty site I must increase as the number of ions decrease. It may well be that these contrac-

TABLE 3

WEIGHT LOSSES FROM TGA OF Na-Sr A SAMPLES

Figures are number of molecules of water lost to nearest whole number.

Sample No.	Approximate temperature range (°C)					Total (compare with last column in Table 1)
	0-100	100-120	120-165	165-240	240-700	
1	7	3	9	5	3	27
2	6	3	10	5	3	27
3	7	4	8	5	3	27
4	7	3	8	6	4	28
5	7	4	8	8	3	30
6	7	3	9	9	3	31
7	8	1	8	9	4	31
8	9	1	8	10	4	32

tions are marking the onset of lattice breakdown and certainly samples containing ~4 Sr p.u.c. which have been heated to 300°C have a weaker X-ray powder pattern than samples with < 4 Sr p.u.c. A further pointer is an apparent new endotherm at roughly 300°C in the DTA of sample 8.

CONCLUSION

Accurate knowledge of the crystallographic sitings of ions and water molecules within the A framework has enabled explanations to be made of the thermal analyses of NaA and Na-SrA. The results reinforce the views that ion-exchange mechanisms in zeolite A are not simple and can involve quite complex rearrangements. Further papers are in the course of preparation and will report similar interpretations of thermal analyses on zeolite A containing Co(II), Ni(II) and other transition metal ions.

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