

A thermoanalytical study of the dehydration of NaA, MgNaA, CaNaA and SrNaA zeolites ¹

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Abstract

The activation energies of dehydration and the heat of vaporisation of water in MgNaA, CaNaA and SrNaA zeolites were measured by thermal analysis, and the results were compared with those of NaA zeolite. The thermal stabilities of NaA and MgNaA and SrNaA zeolites, as assessed by the authors, were about 700°C and those of CaNaA and SrNaA zeolites were about 800°C, i.e. below these temperatures most of the water lost by dehydration can be resorbed, but no resorption occurs above these temperatures.

INTRODUCTION

Synthetic zeolite A is well known as a laboratory and industrial desiccant; it has also found use as a catalyst [1]. These uses often involve ion exchanged forms of zeolite A and in this work NaA, MgNaA, CaNaA and SrNaA zeolites were examined for their thermal stabilities. The dehydration and reversibility for the sorption of water by these zeolites were studied thermoanalytically, and the results compared with those determined in DSC studies carried out by Siegel et al. [2], and with earlier DTA results [3,4].

EXPERIMENTAL

Thermal studies were carried out on a Mettler TA 3000 system which included a TG 50 thermobalance, a DSC 30 and a TC 10 data processor. The zeolite samples were stored in a desiccator over saturated NaCl solution. The molecular formulae were $\text{Na}_{12}(\text{AlO}_2)_{12}(\text{SiO}_2)_{12} \cdot 32.2\text{H}_2\text{O}$,

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$\text{Mg}_{2.58}\text{Na}_{6.84}(\text{AlO}_2)_{12}(\text{SiO}_2)_{12} \cdot 29.35\text{H}_2\text{O}$, $\text{Ca}_{3.75}\text{Na}_{4.49}(\text{AlO}_2)_{12}(\text{SiO}_2)_{12} \cdot 21.79\text{H}_2\text{O}$ and $\text{Sr}_{4.84}\text{Na}_{2.32}(\text{AlO}_2)_{12}(\text{SiO}_2)_{12} \cdot 27.0\text{H}_2\text{O}$. The parent NaA zeolite was Batch No. RD 1118/88, supplied by Laporte Inorganics, Widnes, Cheshire, UK.

Kinetics

All DSC tests were carried out in sealed pans containing two holes. The DSC curves showed between two and four endothermal peaks. Using the peak temperatures T_m , and heating rate ϕ , the activation energy E can be calculated by the well-known Kissinger method [5]. The results are listed in Table 1.

The heat of dehydration of MgNaA, CaNaA and SrNaA zeolites

When the above DSC tests were carried out, the heat of dehydration of the samples was obtained using the TC 10 data processor. The following procedure was applied for overlapping peaks, i.e. MgNaA zeolite peaks a and b (Fig. 1). The heats of dehydration (ΔH_a , ΔH_b) for peaks a and b, and for the sum of peaks a and b (ΔH_t) were first calculated independently (TC 10 processor). The ΔH_1 and ΔH_2 values for peaks a and b can then be calculated from

$$\Delta H_1 = \Delta H_t \Delta H_a / (\Delta H_a + \Delta H_b)$$

$$\Delta H_2 = \Delta H_t - \Delta H_1$$

The results are listed in Table 2.

The weight losses during dehydration of MgNaA, CaNaA and SrNaA zeolites

The dehydration of MgNaA, CaNaA and SrNaA zeolites was carried out in the thermobalance. The total weight losses $E_t(25-700^\circ\text{C})$ and the weight losses in various temperature ranges are listed in Table 3.

The heat of vaporisation of water

The heat of vaporisation of water in zeolites can be obtained from the data in Tables 2 and 3; for instance, the ΔH_D of dehydration for MgNaA zeolite (Table 2) is 127.57 J g^{-1} , and the weight lost (Table 3) in the same temperature range, $50-120^\circ\text{C}$, was 8.87%. The heat of vaporisation of water in MgNaA zeolites (ΔH_v) can now be obtained, for that temperature range, as $127.57 \text{ J g}^{-1} \times 8.87\% = 1438.2 \text{ J g}^{-1} \text{ H}_2\text{O}$. The results calculated are listed in Table 4.

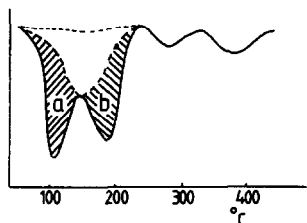


Fig. 1. DSC curve for the dehydration of MgNa zeolite.

Reversibility tests for water adsorption of zeolites

TG tests were performed for NaA, MgNaA, CaNaA and SrNaA zeolites, using a quartz crucible in the temperature range 25–700°C. After maintaining the temperature at 700°C for 20 min, and then cooling to ambient temperature, these samples were equilibrated for 1 h over a saturated solution of NaCl in a desiccator. After resorption, the samples were weighed and the degree of “rehydration” calculated. The samples were then heated in the thermobalance from 25 to 700°C to determine the degree of “rehydration”. TG and DTG curves were compared as shown in Figs. 2 and 3; the results are collated in Table 5. The TG and DTG curves of the rehydrated samples of NaA, MgNaA, CaNaA and SrNaA zeolites are similar to those of the fresh samples. After rehydration for 1 h, more than 80% of the water was resorbed.

Table 6 shows that the water capacities of NaA and MgNaA zeolites when heated at 800°C and held there for 20 min, were 20% less than those of the original samples. Water content changes in CaNaA and SrNaA zeolites were much less; however, when CaNaA and SrNaA zeolites were heated to 900°C and held at that temperature for 20 min, low water regains were noted. The results are listed in Table 7 and shown in Figs. 4 and 5.

From Tables 6 and 7, it can be seen that the NaA and MgNa zeolites are thermally stable to at least 700°C, and that CaNaA and SrNaA zeolites are thermally stable to at least 800°C.

The dehydration of NaA, MgNaA, CaNaA and SrNaA zeolites has been measured by TG and DSC in different temperature ranges. The results are summarised in Table 8, for convenience. From Table 8, the following conclusions can be drawn.

(1) The dehydration activation energies of SrNaA zeolite increase with increasing temperature, unlike those of MgNaA and CaNaA zeolites which are little changed. This probably reflects a steric effect whereby the larger Sr^{2+} ions blocked water removal from sites within the zeolite.

(2) The heat of vaporisation of water in MgNaA, CaNaA and SrNaA zeolites always decreases with increasing temperature. In the lower temperature ranges, it approaches the heat of vaporisation of pure water, 9.770

TABLE 2

The heat of dehydration of MgNaA, CaNaA and SrNaA zeolites

	MgNaA zeolite	CaNaA zeolite		SrNaA zeolite
ΔH_t ($J g^{-1}$ sample) ^a	371.10	179.1		275.11
Temp. range (°C)	50–250	50–150	150–320	50–200
ΔH_D ($J g^{-1}$ sample)	127.57	65.58	237.19	174.65
		11.2		100.46
		9.0		
		220–290		
		300–400		

^a From DSC; heating rate, 5 K min⁻¹.

TABLE 3

The weight losses during dehydration of MgNaA, CaNaA and SrNaA zeolites

	MgNaA zeolite	CaNaA zeolite		SrNaA zeolite
ΔW_t (25–700°C)	30.85%	27.25%		25.40%
Temp. range (°C)	50–20	50–150	150–320	50–200
ΔW (%)	8.87	3.85	17.34	12.1
		2.29		11.4
		1.46		
		220–290		
		300–400		

TABLE 4

The heat of vaporisation of water in MgNaA, CaNaA and SrNaA zeolites

	MgNaA zeolite	CaNaA zeolite		SrNaA zeolite
Temp. range (°C)	50–120	50–150	150–320	50–200
ΔH_V ($J g^{-1} H_2O$)	1438.2	1592.7	1367.9	1443.4
	950.2	498.08		882.9
		548.78		
		220–290		
		300–400		

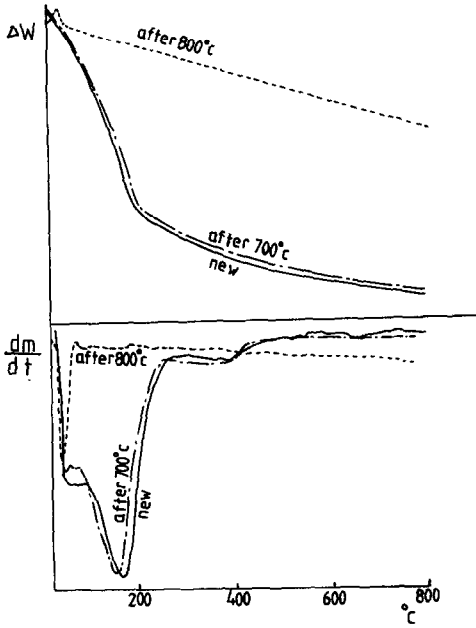


Fig. 2. TG/DTG curves for the dehydration of an initial sample of NaA zeolite and after heating to 700 and 800°C.

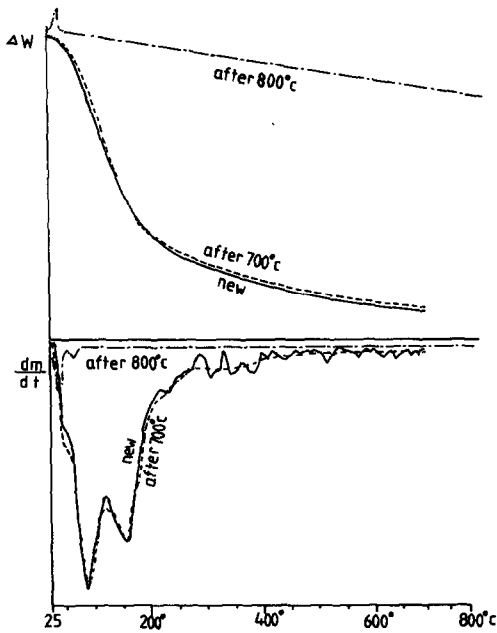


Fig. 3. TG/DTG curves for the dehydration of an initial sample of MgNaA and after heating to 700 and 800°C.

TABLE 5

The rehydration of NaA, MgNaA, CaNaA and SrNaA zeolites after heating to 700°C

	NaA	MgNaA	CaNaA	SrNaA
ΔW_t (25–700°C)	26.25%	30.85%	27.25%	25.40%
Degree of rehydration after 1 h	95.51%	95.58%	98.72%	95.93%
Degree of “rehydration after rehydration” after 1 h	81.37%	86.75%	91.45%	85.28%
Degree of rehydration after 24 h (original sample)	98.59%	96.86%	99.24%	96.04%

TABLE 6

The rehydration of NaA, MgNaA, CaNaA and SrNaA zeolites after heating to 800°C

	NaA	MgNaA	CaNaA	SrNaA
ΔW_t (25–800°C)	26.28%	32.90%	27.86%	24.59%
Degree of rehydration after 1 h	77.82%	72.80%	98.15%	91.52%
Degree of rehydration after 24 h	77.96%	73.10%	98.24%	92.39%
Water capacity after rehydration for 1 h	16.52%	18.62%	95.32%	92.39%
Water capacity after rehydration for 24 h	18.05%	19.56%	96.57%	75.06%

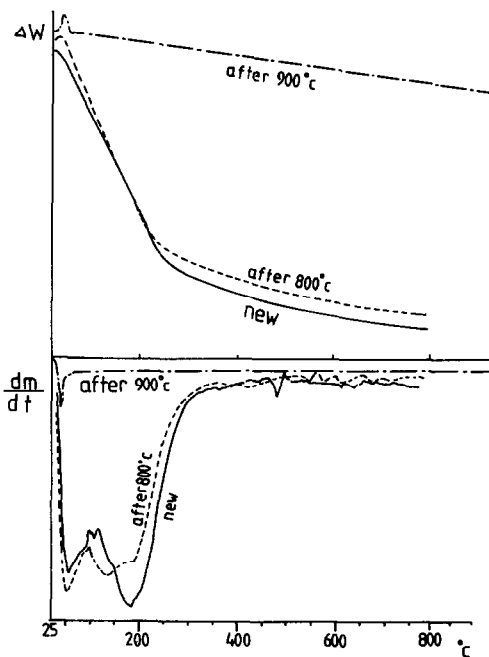


Fig. 4. TG/DTG curves for the dehydration of an initial sample of CaNaA and after heating to 800 and 900°C.

TABLE 7

The rehydration of CaNaA and SrNaA zeolites after heating to 900°C

	CaNa zeolite	SrNaA zeolite
Degree of rehydration after 1 h	77.53%	75.64%
Water capacity after rehydration for 1 h	20.94%	15.35%

kcal mol⁻¹ (226.16 J g⁻¹ H₂O) [6], confirming that this largely represents “free” water being lost from the large central cavity of the zeolite A unit cell. It should be noted that the final weight loss from MgNaA could be a dehydroxylation event.

(3) The limits of thermal stability of NaA and MgNaA zeolites are about 700°C and those of CaNaA and SrNaA zeolites are about 800°C, i.e. at these temperatures most of the dehydrated water was resorbed, but above these temperatures most of the dehydrated water could not be resorbed. The limit for NaA is some 50°C higher than that suggested by Kokotailo and Lawton [7]. X-ray diffraction (XRD) measurements confirmed the loss of structure associated with loss of water capacity.

(4) The ΔH_t values follow the order Mg > Sr > Ca which reflects the cation content. Even though the extent of Mg exchange is lower than that

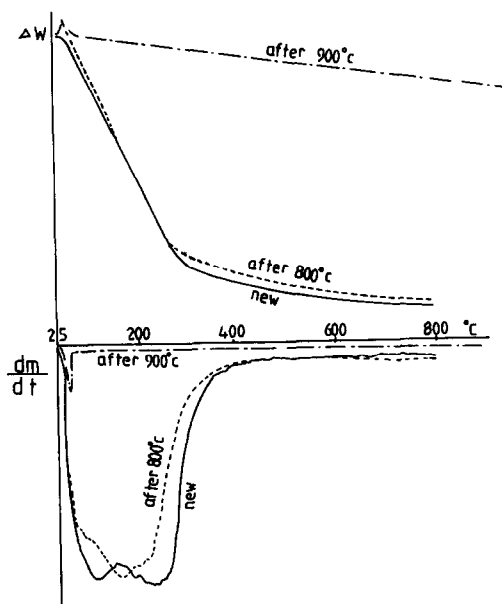


Fig. 5. TG/DTG curves for the dehydration of an initial sample of SrNaA and after heating to 800 and 900°C.

TABLE 8
The parameters of dehydration of MgNaA, CaNaA and SrNaA zeolites

	MgNaA zeolite			CaNaA zeolite			SrNaA zeolite		
	50–120	120–210	220–290	300–400	50–150	150–320	50–200	200–400	
Temp. range (°C)									
E (kJ mol ⁻¹)	93.81	82.55	392.08	117.88	61.58	57.05	74.99	111.95	
ΔH_D (J g ⁻¹ sample)	127.57	121.82	9.0	11.2	65.58	237.19	174.65	100.46	
ΔW (%)	8.87	12.82	1.46	2.29	3.85	17.34	12.1	11.4	
ΔH_V (J g ⁻¹ H ₂ O)	1438.2	950.2	548.78	489.08	1592.7	1367.9	1443.4	882.9	
ΔW_t (25–700°C) (%)	30.85				27.25		25.40		
ΔH_t (J g ⁻¹ sample)	371.10				179.1		275.11		
Thermal stability (°C)	700				800		800		

for both Sr and Ca, the influence of the high hydration energy of the Mg cation is seen.

(5) Tables 5 and 6 show considerable differences in rehydration rates, depending upon the cations present. When this is related to thermal stability, it is clear that CaNaA has the fastest recovery and highest stability. This is in agreement with commercial practice, for instance, in the use of molecular sieve 5A in natural gas treatment. (This is a CaNa exchanged form of zeolite A.)

In some of the data shown it can be speculated that slow water regain relates to ease of access to the smaller β cages in the zeolite A structure [4]. Simplistically, the more cations there are present in the zeolite, e.g. NaA, the more time is needed to recover the water capacity. This effect is most clearly seen in Table 5 where lack of thermal stability was not a factor.

CONCLUSION

From these preliminary studies, it can be shown that simple thermoanalytical techniques can give useful information on the effect of the presence of a divalent ion in zeolite A.

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REFERENCES

- 1 A. Dyer, *Thermochim. Acta*, 110 (1987) 521–526.
- 2 H. Siegel, W. Schmitz, R. Schollner, A. Dyer and H. Enamy, *Thermochim. Acta*, 61 (1983) 329–340.
- 3 A. Dyer and H. Enamy, *Zeolites*, 1 (1981) 7–10.
- 4 A. Dyer and H. Enamy, *Zeolites*, 5 (1985) 66–68.
- 5 H.E. Kissinger, *Anal. Chem.*, 29 (1957) 1702.
- 6 *Handbook of Chemistry and Physics*, 55th edn., CRC Press, Cleveland, OH, USA, 1975, D58.
- 7 G.T. Kokotailo and S.L. Lawton, in J.B. Uytterhoeven (Ed.), *Molecular Sieves*, Proc. 3rd Int. Conf. on Molecular Sieves, Leuven University Press, Leuven, 1973, p. 144 (Recent Progress Reports, paper 112).