Thermochimica Acta, 11 (1975) 55–64

THERMAL ANALYSIS OF SYNTHETIC ZEOLITES OF THE A SERIES

PART II. ZEOLITES CONTAINING NICKEL AND COBALT IONS

A. DYER AND M. JUDANNE WILSON
Department of Chemistry and Applied Chemistry, University of Salford,
Salford M5 4WT, Lancs. (England)

(Received 12 August 1974)

ABSTRACT

A previous publication[1] has rationalized the thermal analyses of zeolite A samples, containing sodium and strontium ions, on the basis of X-ray structural evidence[2]. This paper examines the thermogravimetric (TG), thermomechanical (TMA) and differential thermal analyses (DTA) of zeolite A containing sodium, cobalt and nickel ions. The results are linked to the structural analyses of Amaro et al.[3] and, in the case of nickel, to the spectroscopic studies of Klier and Ralek[4].

INTRODUCTION

The incorporation of transition metal ions into zeolite matrices, to promote catalytic activity, has generated a plethora of investigations using a wide range of instrumental techniques. The use of thermal analysis has been somewhat neglected except in relationship to high temperature studies under something approaching catalytic conditions[5]. Some preliminary investigations[6] showed that quite complex DTA traces were produced when sodium ions were partially replaced from A by Ni. These features occur at moderate temperatures and are evident in more recent work[7,8].

This work is a careful thermal investigation of hetero-ionic forms of zeolite A to determine the origin of the thermal events occurring, particularly in the region 70–160 °C, when the original sodium ions in the zeolite have been partially replaced by nickel or cobalt.

EXPERIMENTAL

The preparation of samples, thermal and chemical analyses were carried out as previously described[1]. X-ray Guinier powder photographs again were used to assess crystallinity.

Some experiments were made to back-exchange the transition metal ion for sodium as an additional check for structural breakdown[8].

RESULTS

The samples prepared had the compositions shown in Tables 1 and 2.

X-ray results and back-exchange experiments showed that loss of zeolite structure during ion exchange had occurred only in the two samples (Ni-9, Co-9) containing the highest amount of transition metal ion. Thermal analyses are shown in Figs. 1–6.

TABLE 1

THERMOGRAVIMETRIC AND CHEMICAL ANALYSES OF NaNiA SAMPLES

Sample	*No. of Na ions p.u.c.**	*No. of Ni ions p.u.c.*	*No. of H_2O p.u.c.*	*Molecules of water lost per temperature range (°C)* RT–X	X	X–125	125–180	180–320	320–600
Ni-1	11.6	0.2	27.3	7	110	3	10	4	3
Ni-2	11.2	0.4	27.3	7	110	3	10	4	3
Ni-3	10.8	0.6	28.9	8	110	3	13	2	3
Ni-4	8.8	1.6	31.0	6.5	100	6.5	13	5	
Ni-5	7.0	2.5	31.1	6.5	90	6.5	14	3	1.3
Ni-6	6.6	2.7	33.8	9	90	17		5	3
Ni-7	6.2	2.9	33.9	9	90	17		5	3
Ni-8	5.2	3.4	39.1	9	75	4**	18***	6	2.6
Ni-9	2.2	4.9	39.8	9	75	6	11	7	7

* p.u.c. (per unit cell) is used for convenience and strictly refers to the pseudo cell which is one eighth of the true unit cell.

** Range 75–115 °C.

*** Range 115–180 °C.

TABLE 2

THERMOGRAVIMETRIC AND CHEMICAL ANALYSES OF NaCoA SAMPLES

Sample	*No. of Na ions p.u.c.*	*No. of Co ions p.u.c.*	*No. of H_2O p.u.c.*	*Molecules of water lost per temperature range (°C)* RT–100	100–130	130–165	165–270	270–600
Co-1	11.6	0.2	27.3	7.5	13.0	4.0	3.0	
CO-2	11.2	0.4	28.2	8.5	13.0	4.0	3.0	
Co-3	10.8	0.6	28.2	11.0	13.0	1.0	3.0	
Co-4	8.8	1.6	33.5	8.5	4.5	13.5	4.5	2.5
Co-5	6.6	2.7	32.5	9.0	5.2	9.1	6.6	2.6
Co-6	5.4	3.3	33.8	10.4	6.3	7.9	5.3	3.9
Co-7	5.0	3.5	34.6	10.7	6.8	7.0	5.2	4.9
Co-8	4.4	3.8	34.6	11.0	7.3	5.1	5.1	6.1
Co-9	1.2	5.4	45.7	22.0	11.2		6.0	6.5

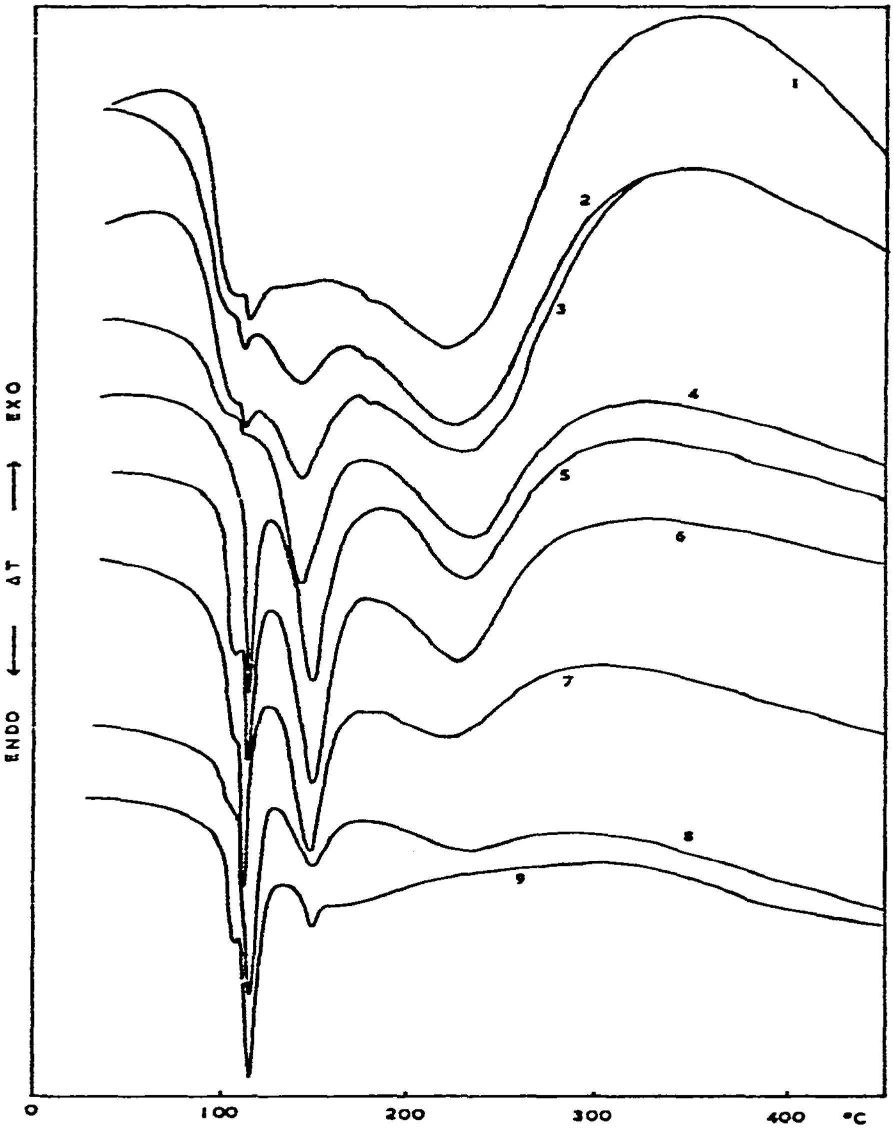

Fig. 1. DTA curves for NiNaA samples. Reference, alumina; heating rate, 20 °C min^{-1}, atmosphere static air; ΔT scale 1 to 3 = 0.2 °C in.$^{-1}$; 4 to 7 = 0.5 °C in.$^{-1}$, 8 and 9 = 1 °C in.$^{-1}$.

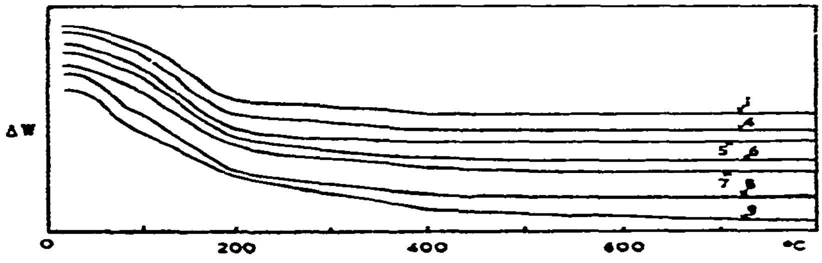

Fig. 2. TG curves for NiNaA samples. Heating rate, 20 °C min^{-1}; atmosphere, static air.

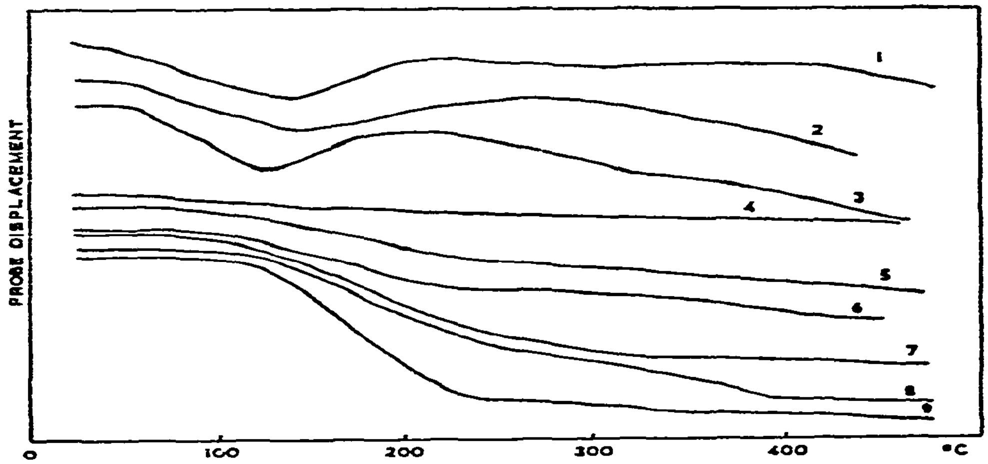

Fig. 3. Thermomechanical analysis curves for NiNaA samples. Sample height, 5 mm; tray loading, 100 mg; heating rate from 50 to 250°C = 2.5°C min^{-1}, above 250°C = 5.0°C min^{-1}; Y axis scale 1 to 3 = 0.02 mV $in.^{-1}$, 4 to 9 = 0.2 mV $in.^{-1}$.

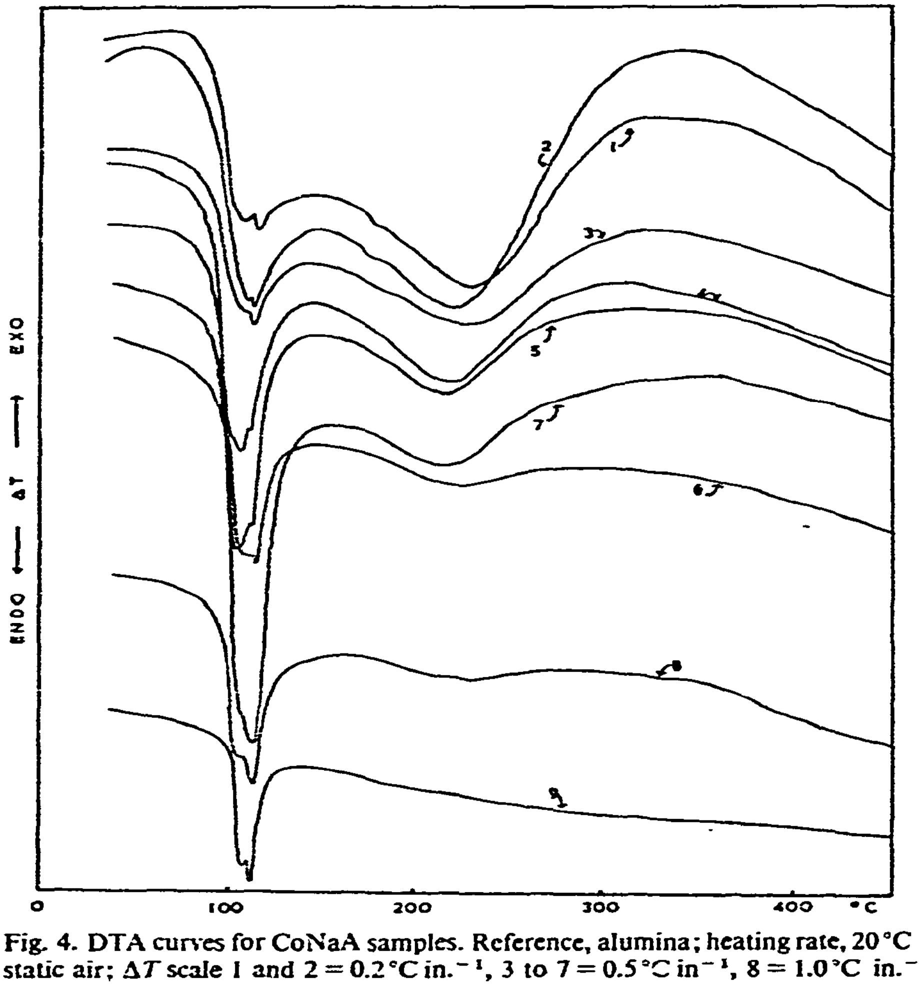

Fig. 4. DTA curves for CoNaA samples. Reference, alumina; heating rate, 20°C min^{-1}; atmosphere, static air; ΔT scale 1 and 2 = 0.2°C $in.^{-1}$, 3 to 7 = 0.5°C in^{-1}, 8 = 1.0°C $in.^{-1}$, 9 = 2.0°C $in.^{-1}$

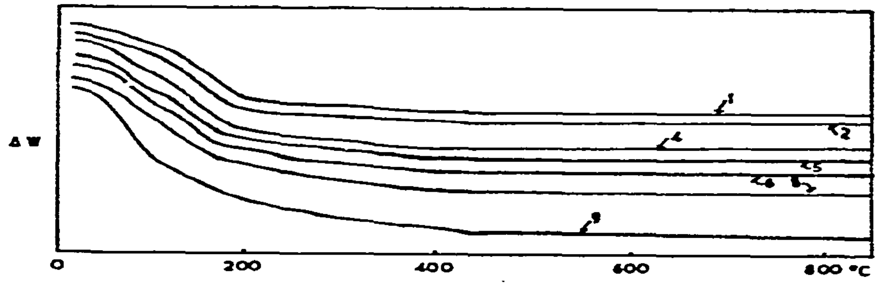

Fig. 5. TG curves for CoNaA samples. Heating rate, 20 °C min^{-1}; atmosphere, static air.

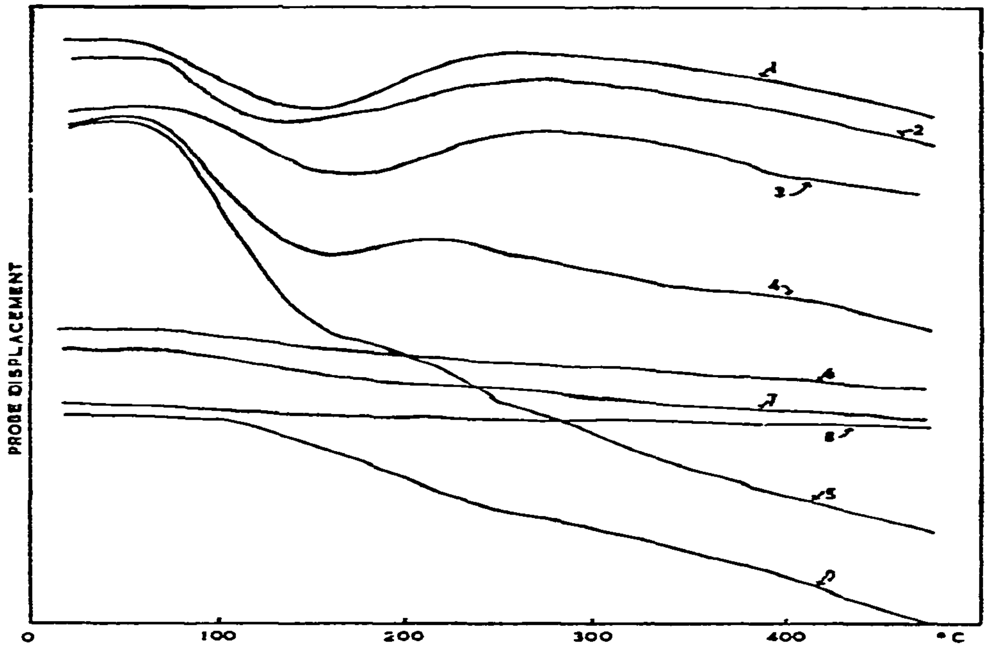

Fig. 6. Thermomechanical analysis curves for CoNaA samples. Sample height, 5 mm; tray loading, 100 mg; heating rate from 50 to 250 °C = 2.5 °C min^{-1}, above 250 °C = 5.0 °C min^{-1}; Y axis scale 1 to 5 = 0.02 mV in.$^{-1}$, 6 to 9 = 0.2 mV in.$^{-1}$.

DISCUSSION

(I) *Sodium/nickel zeolites*

(a) Samples Ni-1, Ni-2 are similar in respect of thermal analyses to NaA, but undergo colour changes when heated. The evidence of Klier and Ralek[4] is that the initial light-green colouration of samples is that typified by hydrated nickel salts and indicates the presence of the hexaaquonickel(II) ion in the zeolite α cage. On heating the samples assume a pink colouration persisting to about 70 °C which Klier and Ralek[4] ascribe to Ni associated with 3 water molecules linked to oxygen in the aluminosilicate framework. Further heating gives a change to yellow but with pinkish tinges persisting to about 150°C. Klier and Ralek[4] suggest this is a Ni, associated with framework oxygen and 1 water molecule, becoming Ni linked directly to 0 in the β cage. The X-ray evidence of Amaro et al.[3] is consistent with this tenet.

Thus the DTA evidence can be summarised from:

	A	*B*	*C*	*D*
	$\{Ni(H_2O)_6\}^{2+} \rightarrow$	$\{-Ni(H_2O)_3\}^{2+} \rightarrow$	$\{-Ni-H_2O\} \rightarrow$	$Ni-O^-$
Temperature (°C)	RT	RT→70	70→115	115→140
Colour	pale green	pink	pink-yellow	yellow
Location	α cage	Site II	Site I	β cage

where A → B occurrence of shoulder on DTA;
B → C endotherm at 115°C;
C → D endotherm at 140°C.

It should be noted that (i) both endotherms increase with increasing Ni content; (ii) the second endotherm moves to a higher temperature when the number of Ni p.u.c. > 1, which may be the result of species such as Ni–O–Ni forming in the sodalite (β) cage[3]. This may be why the water loss at higher temperatures is less than expected for samples of high Ni content.

(b) Sample Ni-3 differs from Ni-1 and Ni-2 only in respect of an additional molecule of water lost up to 110°C, which logically is the extra water taken into the large cavity during the exchange. $Na_z^+ \rightleftharpoons \frac{1}{2}Ni_z^{2+}$, and an increase of 3 molecules of water lost between 110 and 180°C. The reason for this latter difference is not clear.

(c) Sample Ni-4 has >1 Ni p.u.c. and 1 Ni fully hydrated in the sodalite unit, the remainder being hydrated in the α cage[3]. Table 3 shows only 6 Na in position I (i.e., the 6 O rings) assuming that 2 Na have moved from Site I to Site II to allow a Ni ion to enter the sodalite cage. The first water loss coincides with $\{Ni_\alpha(H_2O)_6\} \rightarrow \{Ni_{II}(H_2O)_3\}$ and is therefore 3.2 H_2O_{II} + 3.6 H_2O_α (observed 6.5 H_2O). The next water loss is roughly 20 H_2O (12 H_2O_B + 8 H_2O_I) leaving only H_2O_β to be lost beyond about 180°C.

(d) Sample Ni-5 has >2 Ni p.u.c. and, by X-ray evidence[3], the introduction of a third Ni disrupts the pentagon dodecahedron of H_2O molecules indigenous to the parent NaA.

Suggested sitings (Table 3) can be made on the rationale that Site II has an occupancy of 2 moieties whilst the large cavity contains discrete $\{Ni(H_2O)_6\}^{2+}$ ions (Na aq.)[3].

Now the first water loss is the facile removal of 4.5 H_2O_2 from 1.5 Ni aq. to give 1.5 $Ni(H_2O)_3$ *plus* 1.5 H_2O to allow 1.5 $Ni(H_2O)_3$ in or near to Site II. (N.B. the early slope of the TG for Ni-5 is >Ni-4.)

There is now a residual 20 H_2O in the large cavity of which 3 H_2O are lost

TABLE 3

POSSIBLE SITE OCCUPANCIES IN NaNiA SAMPLES (AT RT)

Sample	*Sodalite unit (β cage)*		*Site I*		*Site II*		*Bridge*	*Large cavity (α cage)*			*Total H_2O content (see Table I)*
	H_2O_β	Ni_β	Na_I	H_2O_I	Na_{II}	H_2O_{II}	H_2O_B	Na_α	Ni_α	H_2O_α	
Ni-1	4		8	8	3	3	12	0.4	0.3	1	28
Ni-2	4		8	8	3	3	12	0.2	0.4	1	28
Ni-3	4		8	8	2.8	3.2	12		0.6	1.7	28.9
Ni-4	3.7	1	6	8	2.8	3.2	12		0.6	3.6	30.5
Ni-5	3.7	1	6	8	1	11			1.5	9	31.7
Ni-6	3.7	1	6	8	0.6	11.4			1.7	10.2	33.3
Ni-7	3.7	1	6	8	0.2	11.8			1.9	11.4	34.9
Ni-8	3.7	1	5	8		12			2.5	15	38.7
Ni-9	3.7	1	2.2	8		12			3.9	23.4	47.1

(ca. 125 °C) as $1.5\ Ni_{II}(H_2O)_3 \rightarrow 1.5\ Ni_I H_2O$ *plus* a further $3.5\ H_2O_{II}$ from empty windows. The next loss is $14\ H_2O$ ($8\ H_2O_I + 6\ H_2O_{II}$?) removed up to 180 °C and finally water is taken from the β cages, possibly in two stages due to $1.5\ H_2O$ trapped by Ni ions or perhaps from the $\{Ni_2OH_2\}^{6+}$ proposed by Amaro et al.[3].

(e) Sample Ni-6 resembles Ni-5 except that the first loss is $9\ H_2O$ (1.7 Ni aq. $\rightarrow 1.7\ Ni(H_2O)_3 = 5.1\ H_2O$ *plus* 3.7 from windows not occupied by cations). The subsequent loss of $17\ H_2O$ could then be $5.1\ H_2O_{II}$ from Ni ions, $8\ H_2O_I$ and $3.7\ H_2O_{II}$. The first loss is as for Ni-5.

(f) Samples Ni-7 and Ni-8 differ only from Ni-6 in a marked change in the TG profile for Ni-8 consistent with a very rapid initial water loss from Site II's denuded of cations and the second slower loss of $4\ H_2O$ which perhaps distinguishes the $2.5\ Ni(H_2O)_3 \rightarrow 2.5\ Ni-H_2O$.

(g) Sample Ni-9 has undergone some loss of crystallinity and by the argument above should contain $47.1\ H_2O$. A similar sample prepared by ion exchange at RT contained $44.7\ H_2O$[7] and showed no evidence of breakdown. It could be that steric restrictions enforce the Ni aq. to share coordination with water in Site I or II or with each other. Hexaaquonickel(II) ions sharing one edge would give a water content of 43.2.

(h) TMA results. Samples Ni-1, 2, 3 resemble NaA but the extra feature in Ni-4 in the temperature range 50 to 125 °C could result from the ion movements outlined in part (a) of this section. Samples Ni-5, 6, 7, 8 show increasing shrinkage as the temperature rises in accord with the decreasing ionic occupancy in Site II. The steeper slope for Ni-9 probably indicates breakdown above 140 °C and certainly samples heated to above 140 °C have weakened X-ray powder patterns and assume a grey colouration consistent with NiO formation. However, Ni-7 (viz., Ni p.u.c. <3) when slowly heated and cooled in an open dish underwent reversible colour changes (green$\rightleftharpoons$pink$\rightleftharpoons$yellow) and showed no evidence of a grey colouration even after several cycles.

(2) Sodium/cobalt zeolites

(a) Samples Co-1, 2, 3 have thermal analyses very similar to those of Ni except that the amount of water lost at temperatures $<100\,^{\circ}C$ increases with Co content. As even gentle heating produces the well-known pink→blue colour change associated with $\{Co^{II}(H_2O)_6\} \rightarrow \{Co^{II}(H_2O)_4\}$ it seems that this first water loss is just that of "bulk" NaA plus water from changes in the coordination sphere of the colbalt ion.

(b) Samples Co-4, 5, 6, 7, 8. The TG profile changes markedly, as does the DTA, and changes in thermal analyses can be explained by the following steps:

The first water loss is from "empty" 8 oxygen windows (i.e., Site II not occupied by a cation) plus that water freed by $\{Co(H_2O)_6 \rightarrow Co(H_2O)_4\}$.

The second loss arises from $Co(H_2O)_4 \rightarrow Co_I$ rejecting the appropriate number

TABLE 4

WATER LOSS FROM HIGH Co CONTENT SAMPLES

Approx. range (°C)	*Source of water lost*	*Co-4*	*Co-5*	*Co-6*	*Co-7*	*Co-8*
RT–100	Site II (empty windows)	5.2	6	6	6	6
	$\{Co(H_2O)_6\}_x \rightarrow \{Co(H_2O_4\}_x$ (No. of Co p.u.c. × 2)	3.2	3.4	4.6	5	5.6
	Total calculated	8.4	9.4	10.6	11	11.6
	Total observed	8.5	9.0	10.4	10.7	11.0
100–130	No. of $Co(H_2O)_4\}_x \rightarrow Co_I$	1.6	1.7	2.3	2.5	2.8
	No. of $Na_I \rightarrow Na_{II}$	3.2	3.4	4.6	5.0	4.4
	Total calculated	4.8	5.1	6.9	7.5	7.2
	Total observed	4.5	5.2	6.3	6.8	7.3
130–165	Estimated residue in α cage not associated with a cation (see Table 5)	12.8	8.6	7.4	7.0	7.6
	Observed	13.5	9.1	7.9	7.0	5.1
165–270	Removal of H_2O_I (see Table 5)	4.8	6.3	5.7	5.5	5.2
	Observed	4.5	6.6	5.3	5.2	5.1
270→	Water in β cage, calc.	2.5	2.5	2.5	2.5	2.5
	Water in β cage, observed	2.5	2.6	3.9	4.9	6.1
	Total calculated	33.3	31.8	33.1	33.5	34.1
	Total observed	33.5	32.5	33.8	34.6	34.6

TABLE 5

SUGGESTED OCCUPANCY OF LARGE CAVITY AFTER 2nd WATER LOSS (NaCoA)

Sample	*Site I*		*Site II*	
	Co/Na$_I$	*H$_2$O$_I$**	*Na$_{II}$*	*H$_2$O$_{II}$*
Co-4**	1.6 Co		4.0	12.8
	4.8 Na	4.8		
Co-5	1.7 Co		3.4	3.4
	3.2 Na	6.3		5.2***
Co-6	2.3 Co		4.6	4.6
	0.8 Na	5.7		2.8***
Co-7	2.5 Co	5.5	5.0	5.0
				2.0***
Co-8	2.8 Co	5.2	4.4	4.4
				3.2***

* Number of H_2O_I = number of Site I − number of Co_I.

** This sample is anomalous but shows resemblance to both Co-3 and Co-5.

*** Number of H_2O = number of empty Site II × 2.

of Na_I ions and H_2O_I molecules to positions in Site II whereupon the waters are lost.

The third loss is water from the α cage which is not in Site I.

The fourth loss is water in Site I.

The final loss is from the β cages.

The experimental justification for the above statements is summarized in Tables 4 and 5, and supported by the evidence from Amaro et al.[3] that when water is removed from an aquated cobalt ion in A zeolite, the ion adopts a position of trigonal symmetry with 3 oxygens in Site I and is not associated with a water molecule in this position. This movement results in a gross distortion in the framework which is

TABLE 6

POSSIBLE SITE OCCUPANCIES IN NaCoA SAMPLES (AT RT)

Sample	*Sodalite unit (β-cage)*		*Site I*		*Site II*		*Bridge*	*Large cavity (α-cage)*			*Total H$_2$O content (see Table I)*
	H$_2$O$_β$	*Co$_β$*	*Na$_I$*	*H$_2$O$_I$*	*Na$_{II}$*	*H$_2$O$_{II}$*	*H$_2$O$_B$*	*Na$_α$*	*Co$_α$*	*H$_2$O$_α$*	
Co-1	3		8	8	3	3	12	0.4	0.2	1.2	27.2
Co-2	3		8	8	3	3	12	0.2	0.4	2.4	28.4
Co-3	3		8	8	2.8	3.2	12		0.6	3.6	29.8
Co-4	3		8	8	0.8	12			1.6	9.6	32.6
Co-5	2.5	1	6	8	0.6	12			1.7	10.2	32.5
Co-6	2.5	1	5.4	8		8			2.3	13.8	32.3
Co-7	2.5	1	5.0	8		8			2.5	15.0	33.5
Co-8	2.5	1	4.3	8		8			2.8	16.8	35.3
Co-9	2.5	1	1.2	8		8			4.4	26.4	44.9

consistent with the observed increase in water lost above 270°C with increasing cobalt content. Presumably water is trapped by lattice distortion as the structure collapses and this is also in agreement with the results of Amaro et al.[3].

The inferred sitings at RT are in Table 6 and there is a general similarity to the nickel samples except that when there are no Na_{II} present the number of H_2O_{II} is 8 rather than 12 (Table 1). An explanation of this might be based upon, edge sharing between hexaaquocobalt(II) ions, or edges of these complex ions satisfying the rationale that Site II contains two species.

The TMA results resemble those of Ni 1-9 and again show signs of thermal instability at high transition metal content.

ACKNOWLEDGEMENTS

One of us (M.J.W.) wishes to express a sincere appreciation to the Community of the Sisters of Notre Dame for the opportunity to pursue these studies. Mr. J. G. Brown (Dept. of Physics and Applied Physics) is thanked for his help with X-ray powder photography.

REFERENCES

1 A. Dyer and M. J. Wilson, *Thermochim. Acta*, 10 (1974) 299.
2 V. Gramlich and W. M. Meier, *Z. Kristallogr.*, 133 (1971) 134.
3 A. A. Amaro, C. L. Kovaciny, K. B. Kunz, P. F. Riley, T. B. Vance, Jr., R. Y. Yanagida and K. Seff, in J. B. Uytterhoeven (Ed.), *Proc. 3rd Int. Conf. Molecular Sieves, Zürich 1973*, Leuven University Press, 1973, p. 113.
4 K. Klier and M. Ralek, *J. Phys. Chem. Solids*, 29 (1968) 951.
5 V. Penchev, H. Minchev, V. Kanazirevo and I. Tsolovski, *Adv. Chem. Ser.*, 102 (1971) 434.
6 A. Dyer and W. Z. Celler, unpublished work.
7 I. J. Gal, O. Jankovic, S. Malcic, P. Radovanov and M. Todorovic, *Trans. Faraday Soc.*, 67 (1971) 999.
8 A. Dyer, W. Z. Celler and M. Shute, *Adv. Chem. Ser.*, 101 (1971) 436.