

## THERMAL ANALYTICAL INVESTIGATIONS ON (AgNa)-A ZEOLITES

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### ABSTRACT

During the thermal treatment of silver-exchanged forms of zeolite A, five desorption effects are observed which are assigned to different adsorption forms of water. Dehydration (of water) is accompanied by autoreduction of some of the silver ions. The water adsorption capacity of the (AgNa)-A zeolites depends upon the degree of autoreduction and reduction in hydrogen, respectively. It is possible to suppress the autoreduction by heating in oxygen. With increasing content of silver ions the thermal stability of the samples is decreased. The same was observed after successive reduction in hydrogen.

### INTRODUCTION

Zeolites of type A containing silver ions show some peculiarities under thermal treatment. The desorption of water during the heating of such zeolites to temperatures of 770 K, is accompanied by autoreduction of a part of the silver ions and furthermore the colour of the samples changes from white through yellow and orange to red [1–5]. On the basis of the results of thermodesorption, adsorption and X-ray structural investigations, it can be confirmed that  $\text{Ag}^+ - \text{Ag}^0 - \text{Ag}^+$  clusters are formed during autoreduction [6–8]. The silver ions are arranged in six-membered rings opposite to each other and the silver atoms occupy positions inside the cubooctahedron [3]. The autoreduction of silver ions is connected with oxidation of lattice oxygen ions and the subsequent desorption of the molecular oxygen formed [6]. Jacobs et al. [6] have suggested that the formation of  $[\text{Ag}_3]^{2+}$  clusters was responsible for the changes in colour. The yellow colour and the transition to red were assigned to the presence of one or two such clusters in one sodalite cage, respectively [8]. In contrast, Karge [5] suggested that the coordination states of silver ions or clusters were the reason for these colour changes. He obtained different spectra, dependent on water content, from UV–VIS spectroscopic measurements made during dehydration and rehydration of

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AgA samples. Rehydration of the sample, which was red even after activation in oxygen, led to a transition from orange to yellow without restoration of the initial white of the untreated sample. The three coloured forms of the AgA zeolite were reversible, and fully converted into each other depending only on the state of hydration. Therefore, it was suggested that the degree of autoreduction was not the cause of the differences in colour. The more likely existence of coloured hydrated complexes containing reduced silver was assumed [5]. This was confirmed by hydrogen adsorption measurements on (AgNa)-A zeolites, after preadsorption of water, which showed that two water molecules were adsorbed onto one  $[\text{Ag}_3]^{2+}$  cluster. Studies of CO adsorption of AgA zeolite demonstrated a strong interaction between silver ions and water. Only after extensive dehydration could CO adsorption on  $\text{Ag}^+$  be detected. Thus, it seemed that the initiation of autoreduction needed a certain degree of dehydration to allow the alteration of  $\text{Ag}^+$  to  $\text{Ag}^0$  [5].

There was little information about the possible adsorption state of water in (AgNa)-A zeolites, the process of water desorption, the water adsorption capacity or their dependence upon the degree of exchange. In the present work the processes connected with the thermal treatment of silver A zeolites in different atmospheres were examined with the help of thermal analysis (combined TG-DTG-DTA and microcalorimetric measurements). The aim was to obtain information about the link between dehydration and autoreduction. For this purpose the course of thermal activation of samples with increasing  $\text{Ag}^+$  content in different atmospheres was measured and rehydration experiments were carried out. Furthermore, it was of interest to determine the thermal stability and possible phase transitions in the high-temperature region (800–1300 K).

Activation in  $\text{O}_2$  flow, before reduction of the silver ions in the zeolite by programmed heating in  $\text{H}_2$  flow, was performed to compare the heat effects of the reduction process in the activated and hydrated states.

### *X-ray investigations*

Debye Scherrer and Guinier Lenne techniques were used for the characterisation of new crystalline phases which arose during calcination of (AgNa)-A zeolites to 900 K.

## EXPERIMENTAL

### *Cation exchange*

The (AgNa)-A zeolites were prepared from commercial 4A zeolite (VEB Chemiekombinat Bitterfeld-Wolfen, G.D.R.) by cation exchange with a 0.1 M solution. The amount of silver in the samples was determined by Volhard

titration. The samples were stored in the dark for two weeks over a saturated NaCl solution before being used for measurements.

### *Combined DTA–TG–DTG measurements*

A microthermal analyser (Setaram, Lyon) was used to study the dehydration, dehydroxylation and thermal stability of about 10 mg of zeolite in flowing N<sub>2</sub> and Ar, respectively (50 cm<sup>3</sup> min<sup>-1</sup>). A heating rate of 10 K min<sup>-1</sup> in the temperature range from room temperature to 1400 K was used.

Further investigations of the influence of several pretreatments on the thermal behaviour of the samples were made: i.e., dehydration up to 750 K followed by cooling to room temperature and rehydration over NaCl solution in the dark:

- (i) in O<sub>2</sub> flow;
- (ii) in H<sub>2</sub> flow;
- (iii) in air (one treatment and five treatments).

### *Calorimetric measurements*

The calorimetric investigations on the silver A zeolites were carried out on a heatflow calorimeter (DSC111, Setaram) which allowed the introduction of silica tubes into the measurement and reference cells. In this way it was possible to carry out both pretreatment and subsequent measurement in the flow regime. These investigations used He, O<sub>2</sub> and H<sub>2</sub> flow, respectively (13.3 cm<sup>3</sup> min<sup>-1</sup>) with a heating rate of 5 K min<sup>-1</sup>.

In thermal treatment, O<sub>2</sub> flow was used to try to distinguish the water desorption from the autoreduction observed in inert atmosphere [6].

## RESULTS

The programmed heating of (AgNa)-A zeolites to 770 K showed several partly overlapping endothermal effects in the DTA curves. The TG curves showed that these effects could be matched to corresponding weight losses. (Fig. 1). Desorption started at room temperature. In the initial range of the curves no essential differences in the desorption behaviour were noted which depended upon the silver content. The presence of silver ions caused marked changes in the most intense desorption effect. The temperature of this peak maximum decreased from ~ 430 K, for the sodium form, to ~ 405 K for the most exchanged samples (94% Ag<sup>+</sup>). At the same time the peak became smaller. A small shoulder at ~ 460 K was observed only at Ag<sup>+</sup> contents of more than 50% and was clearer at the higher degrees of exchange. Further heating of the samples at temperatures above 540 K created two effects which characteristically changed with increasing Ag<sup>+</sup> content: (1) the broad

peak, with a maximum at 640 K, decreased in intensity with silver content, and (2) a desorption peak appeared, maximizing at 733 K, which became more intense for samples with high degrees of exchange.

TG weight losses caused by thermal treatment of freshly exchanged and fully hydrated samples are summarized in Table 1. The number of water molecules per pseudo unit cell (PUC) calculated from the weight loss up to 770 K changed little with silver content (26–27 H<sub>2</sub>O/PUC). Samples stored over a longer period became grey and the amounts of water desorbed, after hydration over saturated NaCl solution, were about 1 H<sub>2</sub>O/PUC and 2.5 H<sub>2</sub>O/PUC smaller for low and high degrees of exchange, respectively, in comparison with the freshly prepared zeolites.

From the thermoanalytical curves it can be deduced that water in (AgNa)-A was present in a firmly bound form. To acquire information about the different adsorption states present, the amount of water equivalent to each desorption effect was determined. This was done by sectioning the TG curves at appropriate temperature intervals and by readsorption of amounts of water after activation in an inert atmosphere followed by a new thermal desorption process. Furthermore, the water adsorption capacity after oxidis-

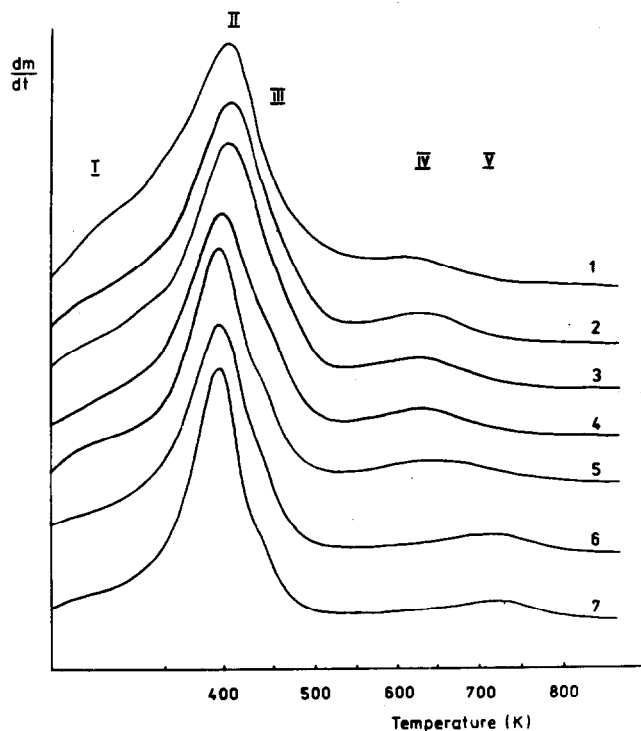


Fig. 1. DTG curves of water desorption from (AgNa)-A zeolites. (1) NaA; (2) (Ag<sub>0.08</sub>Na)-A; (3) (Ag<sub>0.24</sub>Na)-A; (4) (Ag<sub>0.50</sub>Na)-A; (5) (Ag<sub>0.74</sub>Na)-A; (6) (Ag<sub>0.85</sub>Na)-A; (7) (Ag<sub>0.94</sub>Na)-A; (I)–(V) desorption effects of water.

TABLE 1

Thermogravimetric results of desorption from (AgNa)-A zeolites

Zeolite	No. of Ag <sup>+</sup> /PUC	Amount of water desorbed (wt%)	Amount of oxygen desorbed (wt%) <sup>a</sup>	<i>n</i> H <sub>2</sub> O/PUC corresponding to the TG peak areas				
				26.5	2.6	20.4	3.5	–
(Ag <sub>0.17</sub> Na)-A	2.0	20.3	0.05	27.8	4.1	20.3	3.4	–
(Ag <sub>0.24</sub> Na)-A	2.9	20.4	0.07	26.4	3.3	19.4	3.7	–
(Ag <sub>0.50</sub> Na)-A	6.0	17.7	0.14	26.6	3.4	19.9	3.3	–
(Ag <sub>0.739</sub> Na)-A	8.9	16.3	0.19	26.8	3.3	19.7	–	3.8
(Ag <sub>0.922</sub> Na)-A	11.1	15.4	0.22	26.0	2.7	20.0	–	3.3
(Ag <sub>0.939</sub> Na)-A	11.3	14.9	0.23					

<sup>a</sup> The amount of free oxygen formed was deduced from data of Jacobs et al. [6].

ing and reducing pretreatment was measured. The results are presented in Table 2.

The calorimetric measurements provided a method to define the heat effect due to autoreduction. In thermal activation the autoreduction was overlapped by water desorption. Therefore, it was necessary to separate these two processes with the help of experimental methods. For this purpose measurements were carried out in several atmospheres.

Figures 2 and 3 show DSC curves of AgA zeolite obtained by pro-

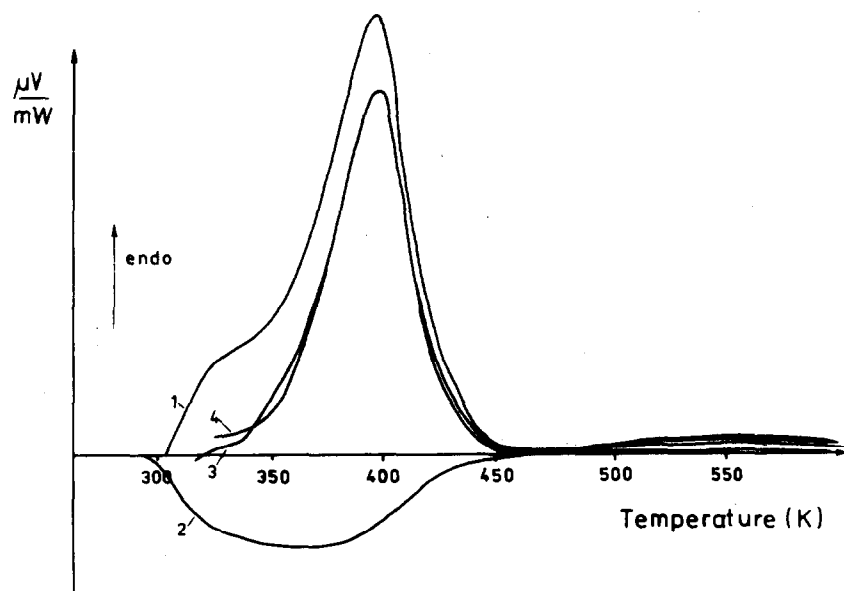


Fig. 2. DSC curves for AgA in oxygen and argon atmospheres. (1) Dehydration in O<sub>2</sub> flow; (2) programmed heating in Ar flow of the preactivated sample in oxygen (see 1); (3) dehydration in Ar flow; (4) summation of curves (1) and (2).

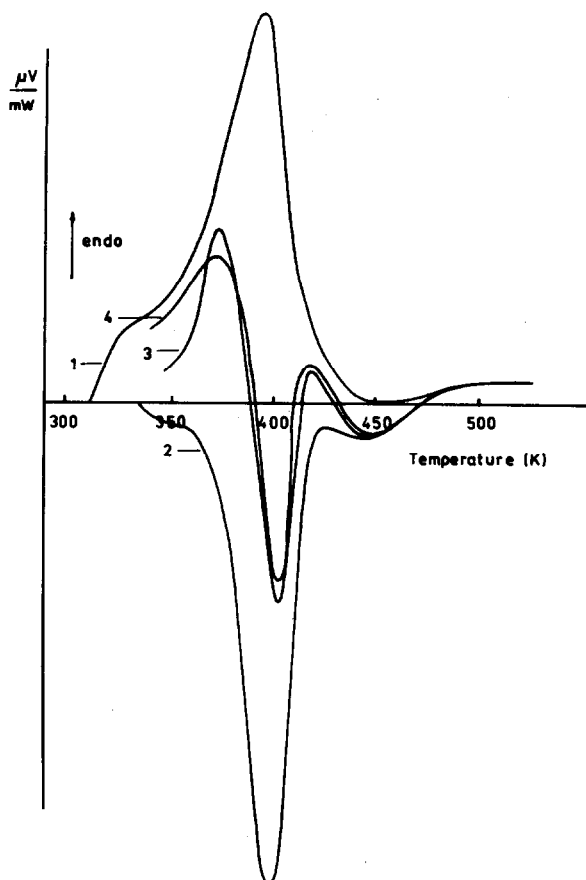


Fig. 3. DSC curves for AgA water desorption and temperature-programmed reduction in hydrogen. (1) Thermal dehydration in oxygen flow; (2) oxygen preactivated sample programmed heated in hydrogen flow; (3) thermal dehydration in hydrogen flow; (4) summation of curves (1) and (2).

TABLE 2

Amount of water readsorbed on (AgNa)-A zeolites after thermal activation in different atmospheres

Pretreatment	Zeolite	$n$ H <sub>2</sub> O/PUC
Untreated samples	(Ag <sub>0.50</sub> Na)-A	27.0
	(Ag <sub>0.939</sub> Na)-A	26.0
In oxygen	(Ag <sub>0.50</sub> Na)-A	27.4
	(Ag <sub>0.939</sub> Na)-A	25.5
In hydrogen	(Ag <sub>0.50</sub> Na)-A	21.0
	(Ag <sub>0.939</sub> Na)-A	0.9
In air, one cycle five cycles	(Ag <sub>0.939</sub> Na)-A	24.5
	(Ag <sub>0.939</sub> Na)-A	23.9
In helium and 20 min in oxygen at 800 K	(Ag <sub>0.939</sub> Na)-A	23.9

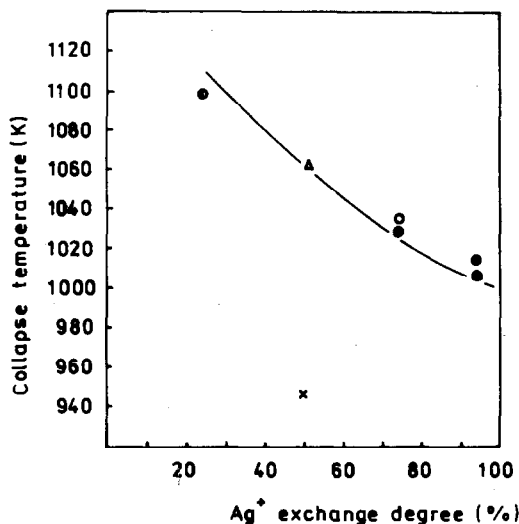


Fig. 4. Thermal stability of (AgNa)-A zeolites. (—) Untreated samples; (Δ) preactivated in air; (○) preactivated five times in air; (×) (Ag<sub>0.50</sub>Na)-A preactivated in H<sub>2</sub>.

grammed heating in an inert atmosphere and under both flowing oxygen and nitrogen.

The sample initially activated in an oxygen flow showed (in curve 2 obtained by programmed heating in argon) a flat exothermic effect in the temperature range 320–470 K. Curve 4 in Fig. 2 is in good agreement with curve 3.

To help the interpretation of this flat exothermic effect (curve 2, Fig. 2) a further experiment was carried out in a hydrogen flow. The sum of curves 1 and 2 under these conditions (see Fig. 2) is again in good agreement with curve 3 which was measured by heating the hydrated sample in a hydrogen flow.

In the temperature range above 900 K the DTA curves for silver zeolites showed several exothermic effects, depending on the extent of ion-exchange, which were assigned by X-ray measurements to the collapse of the zeolitic framework and transitions to new crystalline phases. The temperature of the first exothermic effect due to conversion of the framework into an amorphous phase strongly decreased with increasing silver content. The influences of silver content, and several pretreatment conditions, are illustrated in Fig. 4.

## DISCUSSION

From the results of previous investigations it is known that thermal dehydration of zeolites containing Ag<sup>+</sup> was connected with the autoreduction of a part of the silver ions. In this process [Ag<sub>3</sub>]<sup>2+</sup> clusters are formed

and gaseous oxygen liberated. The results of Jacobs et al. [6], concerning the amount of desorbed oxygen, can be used to calculate the possible influence of oxygen desorption on the TG curves herein. Oxygen was lost from a fully  $\text{Ag}^+$ -exchanged sample between 400 and 650 K in two steps and reached a loss of 0.32 weight% at 650 K. With decreasing silver ion content the amount of desorbed oxygen diminished exponentially. By coupling the thermo-analyzer to a catharometer, via an adsorption tube filled with zeolite 3A, a small amount of oxygen was detected. These results showed that the thermograms were only marginally influenced by oxygen desorption.

The single desorption effects presented in Fig. 1 are marked I to V in sequence of rising temperature. The desorption of the least strongly adsorbed water molecules, which interact solely with other water molecules and which were arranged in the intercrystalline spaces, respectively, led to the formation of a shoulder (I) at about 320 K. The desorbed amounts of water were independent of the silver content. Changes in the peak shape, and the lowering of the maximum temperature of the most intense desorption effect (peak II) with increasing degree of exchange, proved that these effects could be attributed to the desorption of water from different adsorption sites but having only small differences in adsorption energy.

The states of water in the NaA zeolite have been described in detail on the basis of X-ray and thermoanalytical investigations. The main part of water can be imagined to be arranged in a clathrate-like structure, i.e., in a pentagonal dodecahedron containing 20  $\text{H}_2\text{O}/\text{PUC}$ . Joint bonding of the water molecules to cations and to the framework oxygen ions has been suggested [9,10]. A similar arrangement of the water molecules might be present in the (AgNa)-A samples. This was supported by the desorption behaviour in that about 23  $\text{H}_2\text{O}/\text{PUC}$  were desorbed up to 550 K. The reduction in the temperature of the peak maximum with increasing silver content could be explained by the smaller coordination tendency of  $\text{Ag}^+$  for water in comparison to  $\text{Na}^+$  in terms of electropositivity. Because of the higher polarizability of silver ions the interaction with framework oxygen is expected to be stronger and, consequently, that with water may be smaller. Coughlan and Carroll [11] pointed this out with the markedly smaller heat of immersion of water for AgA compared to those of other A-containing monovalent ions.

The shoulder at about 435 K (Fig. 5) was probably caused by desorption of water bound to the remaining sodium ions. This effect was visible only by the decrease in width of the main desorption peak with rising silver ion content. Water desorption in the temperature range 550–760 K (peak IV) was observed up to contents of  $\text{Ag}^+$  of 74% and corresponded to a nearly constant desorption of 3.5  $\text{H}_2\text{O}/\text{PUC}$ . This effect can be assigned to desorption of water from the sodalite cages, because this peak arises in the thermal analytical curves of all alkaline and alkaline earth ion forms of zeolite A at about the same peak maximum temperature. Furthermore, the



amount of water released was that which could be accommodated in the  $\beta$ -cages. Readsorption experiments have shown the reversible formation of these adsorption forms of water.

With increasing  $\text{Ag}^+$  content the major peak was increasingly broadened in the direction of higher temperatures, and the sample with the highest degree of exchange ( $> 90\%$ ) had a peak maximum at 730 K (peak V), whilst in the regions of the preceding effect only a small desorption was found. The formation of peak V was accompanied by desorption of about  $3.5 \text{ H}_2\text{O}/\text{PUC}$  (the same amount as for peak IV). This uptake of water was reversible. Readsorption measurements and NMR investigations have shown that it was present mainly in the molecular state and not bound as OH groups. Because of the higher desorption temperature it can be suggested that these water molecules were coordinated to silver clusters inside the  $\beta$ -cages. Interaction of water with clusters was also conjectured from results of water preadsorption followed by hydrogen sorption and UV-VIS spectroscopic measurements. Jacobs et al. [6] measured the oxygen released by thermal treatment of Ag zeolites and calculated for AgA that at a degree of exchange of 10% the silver ions were overcome by autoreduction. This meant that each sodalite cage accommodated one cluster, which was able to interact with water. The decrease in intensity of the desorption effect with decreasing content of silver ions coincided with the exponential drop of the degree of autoreduction which proceeded simultaneously.

These measurements and the previously reported results have shown that during thermal activation of silver-containing zeolites, dehydration was accompanied by autoreduction of the silver ions. The connection between these processes needed investigation.

The results of the dehydration in oxygen flow and in inert atmosphere

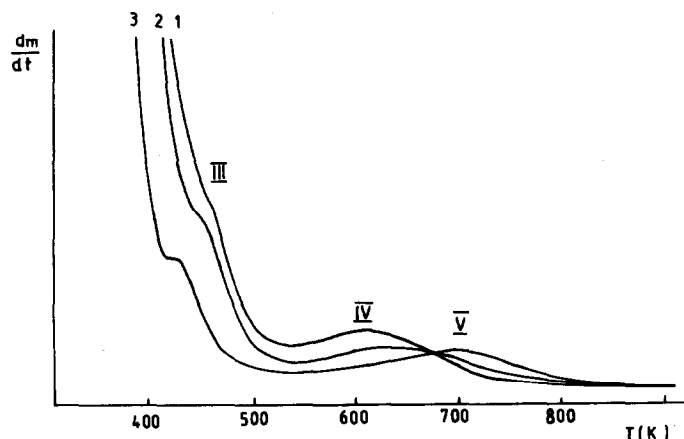


Fig. 5. DTG curves of (AgNa)-A zeolites. Development of the water desorption peaks (III)-(V) as a function of silver content. (1)  $(\text{Ag}_{0.24}\text{Na})\text{-A}$ ; (2)  $(\text{Ag}_{0.74}\text{Na})\text{-A}$ ; (3)  $(\text{Ag}_{0.94}\text{Na})\text{-A}$ .

(Fig. 2) showed that by initially heating in oxygen flow the water desorption can be separated from the autoreduction. The flat exothermic effect (curve 2) can be assigned to this autoreduction process. It is a very complex process which can be connected with the oxidation of framework oxygen, its desorption, and the formation of  $[\text{Ag}_3]^{2+}$  clusters in the sodalite cages.

The autoreduction can be suppressed by heating in an oxygen flow as has been shown by the identity in water contents and desorption maxima observed in the DTA curves of samples preactivated in oxygen flow or untreated.

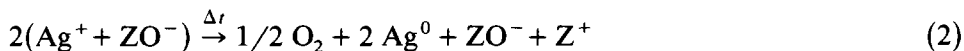
The lower water contents (about 2  $\text{H}_2\text{O}/\text{PUC}$  smaller) of the samples preactivated in He flow, and of the sample preactivated in He flow and treated with oxygen at 800 K for 20 min indicated that, after autoreduction, the number of water adsorption sites was lower. The clusters apparently did not undergo reoxidation under these conditions.

For comparison with autoreduction, the reduction of an AgA sample by temperature-programmed reduction in hydrogen flow was studied. An exothermic effect was noted maximising at 400 K with two shoulders at 360 and 445 K. The first shoulder (Fig. 3, curve 2) occurred at nearly the same temperature and with approximately the same intensity as the "flat" effect assigned to autoreduction. This shoulder could be explained as being due to the low-temperature formation of charged silver clusters as noted by Schollner et al. [12] from temperature-programmed reduction. The intense exothermic effect maximising at about 400 K may be due to the release of heat from hydrogen chemisorption on the cations and from energy originating from the attack of protons on the framework and the rupture of Si-O-Al bridges according to the mechanism



The partial destruction of the sample ( $\text{Ag}_{0.50}\text{Na}$ )-A preactivated in hydrogen flow, showed in the advent of a 115 K reduction in collapse temperature (see Fig. 4).

The strong decrease in this breakdown temperature of the framework with increasing silver content was very apparent: this might be because the formation of one  $\text{Ag}^0$  was linked with the creation of one OH group on the same site according to following mechanism [6]



This reaction occurred at low temperatures even in the presence of water, which was necessary for the formation of OH groups



Pretreatment in oxygen and in helium had no significant influence on the collapse temperature of silver A zeolites. These results showed that the degree of autoreduction must be nearly the same in both atmospheres.

Only treatment in hydrogen flow had a drastic influence on the stability of zeolites including reducible cations due to mechanism (1).

The (Ag<sub>0.34</sub>Na)-A zeolite transformed to carnegieite at about 1150 K. The silver ions probably exist in this crystallographic phase, judged by the absence of silver reflections in the X-ray patterns. In the sample with the highest silver content, i.e., AgA, the formation of a type of spinel was observed, characterized by an intense endothermic DTA effect.

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#### REFERENCES

- 1 M. Ralek, P. Jiru, O. Grubner and H. Beyer, *Collect. Czech. Chem. Commun.*, 26 (1961) 142.
- 2 Y. Kim and K. Seff, *J. Phys. Chem.*, 82 (1978) 921, 925, 1071, 1307.
- 3 L.R. Gellens, W.J. Mortier, R.A. Schoonheydt and J.B. Uytterhoeven, *J. Phys. Chem.*, 85 (1981) 2783.
- 4 H.K. Beyer, P.A. Jacobs and J.B. Uytterhoeven, *J. Chem. Soc., Faraday Trans. 1*, 72 (1976) 674.
- 5 H.G. Karge, in P.A. Jacobs, N.I. Jaeger, P. Jiru and G. Schulz-Ekloff (Eds.), *Metal Microstructures in Zeolites*, Elsevier, Amsterdam, 1982, p. 103.
- 6 P.A. Jacobs, J.B. Uytterhoeven and H. Beyer, *J. Chem. Soc., Faraday Trans. 1*, 75 (1979) 56.
- 7 P.A. Jacobs, L.Ph. Linert, H. Nijs, J.B. Uytterhoeven and H.K. Beyer, *J. Chem. Soc., Faraday Trans. 1*, 73 (1977) 1745.
- 8 L.R. Gellens, W.J. Mortier and J.B. Uytterhoeven, *Zeolites*, 7 (1981) 11.
- 9 A. Dyer and J.M. Wilson, *Thermochim. Acta*, 10 (1974) 299.
- 10 V. Gramlich and W.H. Meier, *Z. Kristallogr.*, 133 (1971) 134.
- 11 B. Coughlan and W.M. Carroll, *J. Chem. Soc., Faraday Trans. 1*, 72 (1976) 2016.
- 12 R. Schollner and H.K. Beyer, *Zeolites*, 4 (1984) 61.