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THERMAL ANALYSIS OF WATER AT X- AND A-TYPE ZEOLITES

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ABSTRACT

The nature of the sorbed water has been examined by differential scanning calorimetry and effluent gas analysis at the zeolites of the types X and A, with univalent and bivalent cations.

The desorption heats depending on the coverage and the cation form of zeolite have been determined. All these experiments point to the existence of only one general desorption mechanism independent of the ion-exchanging cation. The nature of the sorbed water is discussed.

INTRODUCTION

In the preceding work[1] the qualitative differential scanning calorimetric (DSC) analysis of sorbed water at synthetic zeolites of A type has been recorded. Two desorption processes at 430 and 600 K have been found with all zeolites, regardless of the cation present. This fact cannot be brought into agreement with the hypothesis that water is bound to the zeolite cation by the lone pair of electrons of oxygen[2–6]. Under the light of these experiments, the model of hydrogen-bound water to the oxygen atoms of an aluminosilicate framework seems much more probable. However the results of calorimetric and DTA analyses of some authors[2, 3, 6] show, that the heat of desorption decreases in the order:

$$Li^+ > Na^+ > K^+ > Rb^+$$

$$Mg^{2+} > Ca^{2+} > Ni^{2+} > Co^{2+} > Cu^{2+} > Cd^{2+} > Zn^{2+}$$

This order shows a very good correlation with the decrease of the heats of hydration with increasing ionic radius—one of the main proofs in favour of the cation hypothesis. On the other hand the dependence of the heats of sorption on the coverage of zeolite by water is not conclusive evidence of the cation hypothesis, for the order of the heats of desorption takes no account of the coverage.

In this paper, besides DSC and effluent gas analysis of the water at the X-type zeolites, desorption heats have been determined as a function of the coverage.

EXPERIMENTAL

4 A and 13 X Carbon Air Company powder zeolites were used. Other zeolites were made by cation exchange as described earlier[1]. The degree of the cation exchange of X zeolite was about 90%, Table 1, column 2. The cation composition of the A zeolite was given in previous paper[1], and the degree of exchange was about 90%.

TABLE 1

Cation of X zeolite	*Degree of cation exchange*	*Coverage, θ*	*Peak position by DSC analysis (K)*	*Peak position by effluent gas analysis*
Li^+	92	0.96	432	432
Na^+	100	0.96	434.8	434.8
K^+	98	0.95	426	426
Rb^+	88	0.95	430	430
Ag^+	97	0.92	410	410
Mg^{2+}	97	0.96	432	432
Ba^{2+}	82	0.99	428	428
Ca^{2+}	96	0.97	438	438
Cd^{2+}	92	0.96	432	432
I Zn^{2+}	93	0.96	426	426
II Zn^{2+}	64	0.96	420	420
III Zn^{2+}	36	0.96	428	428

Thermal analysis samples were prepared by pressing zeolites into an aluminium sample pan. The samples with different quantities of sorbed water were obtained at increasing temperature, by the partial desorption of the sample with a maximum quantity of water in the DSC calorimeter itself. Later on, after cooling in the absence of external air, the DSC analysis was performed in the usual way. The quantity of the remaining sorbed water was determined by effluent gas analysis, and the thermal changes by DSC. For $\theta = 1$ by BET and NMR methods[11], the value for A zeolite of 153 mg H_2O on 1 g of zeolite was used, and 180 mg H_2O on 1 g zeolite for X zeolite.

A Perkin-Elmer DSC-1B analyser was used for thermal analysis with an attachment for effluent gas analysis and automatic interpolation of the base-line described earlier[12].

RESULTS

Qualitative analysis

The thermograms of the sorbed water at 13 X zeolites exhibit much similarity for all the cation forms. In Fig. 1 the results of DSC and simultaneous effluent gas analysis at NaX zeolite are presented. There is only one well-expressed maximum at 430±7 K for all the zeolite cation forms. Towards higher temperatures the peak becomes asymmetric, but an especially high temperature peak, as in case of A zeolite, could not be noticed. In Fig. 1, due to the flow of dry nitrogen, there is no desorption

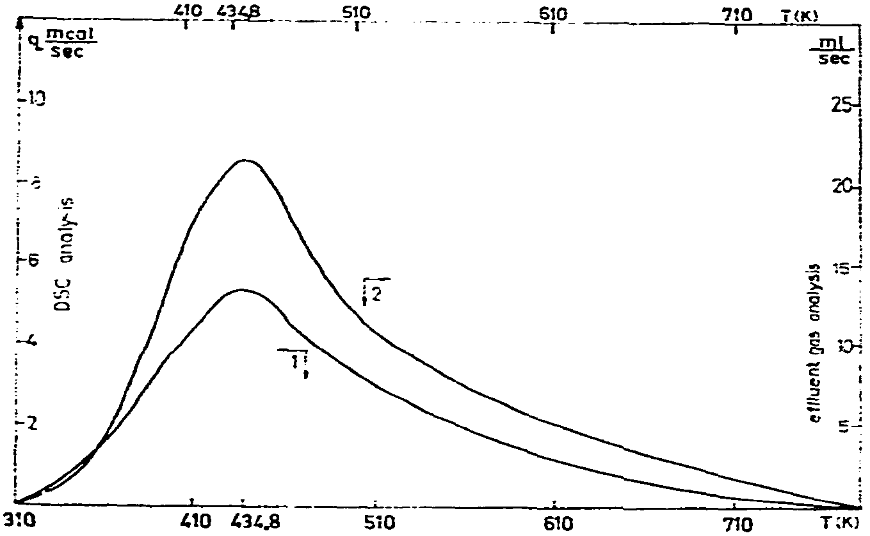

Fig. 1. Qualitative DSC (curve 1) and effluent gas (curve 2) analysis of water at X zeolite.

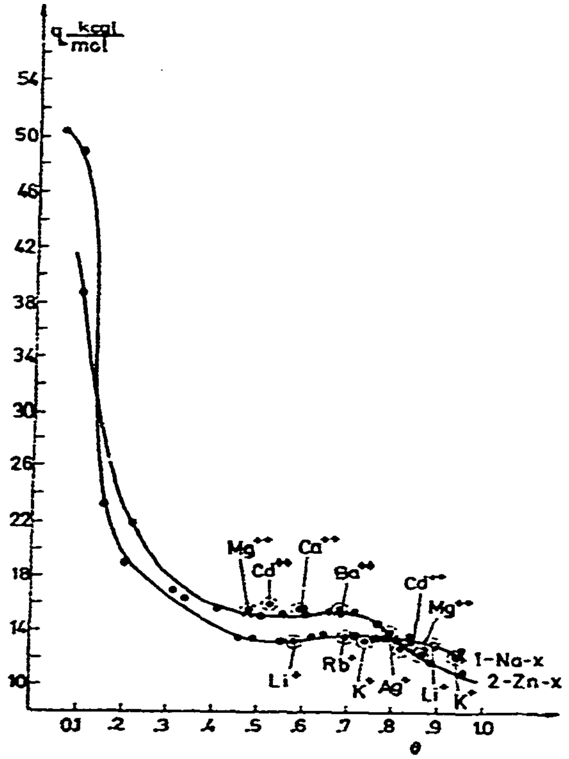

Fig. 2. Quantitative analysis of heats of desorption of water from X zeolite. Curve 1, NaX zeolite, full circles; curve 2, ZnX zeolite, full circles. Open circles denote the corresponding values for exchanged zeolites.

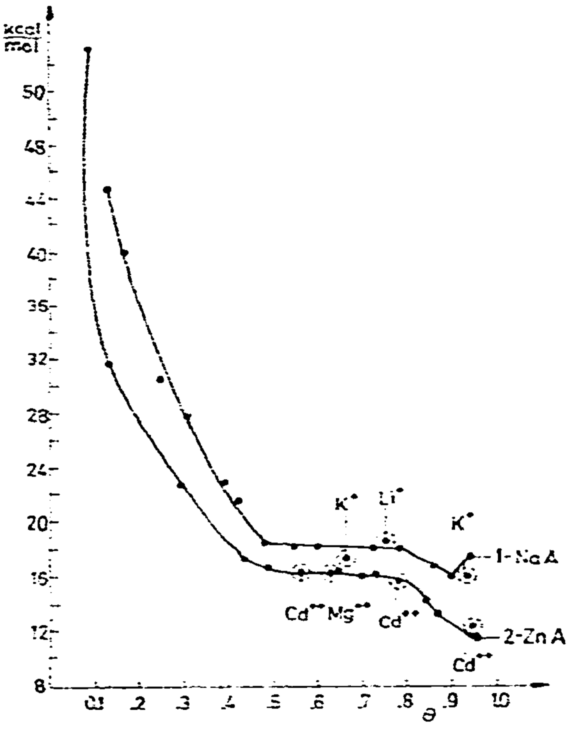

Fig. 3. Quantitative analysis of heats of desorption of water from A zeolite. Curve 1, NaA zeolite, full circles; curve 2, ZnA zeolite, full circles. Open circles denote the corresponding values for exchanged zeolites.

peak of water from the poly layer which appears in other cases as well as with the A zeolites, and also with X zeolites at temperatures around 310 K. The results for different counterions are presented in Table 1. The characteristic desorption temperature of 430 K for A zeolites[1] is also found for all X zeolites, regardless of the change in crystal structure.

During desorption the partially substituted zeolites of the types Ba Na zeolite, ZnX zeolite, BaX zeolite and CdX zeolite did not lead to any new results, in contrast to Dayer et al.[13] who observed two peaks.

Quantitative analysis

One series of measurements was devoted to examining the dependence of the desorption heats on the nature of the counterions and the coverage by water, both at X and A zeolites. The characteristic curves $\underset{\sim}{Q} = f(\theta)$ were obtained, and are shown in Figs. 2 and 3.

For small coverage, approximatively up to $\theta = 0.15$ very high desorption heats were found, sharply falling with increasing coverage. Unfortunately the experimental error of measurements in this interval is rather high (15–20%), so that there is the possibility that these values may be considerably lower. In the region from $\theta = 0.15$ to 0.4 the heats of desorption decrease considerably slower, and lie in the limits characterized by physisorption. The experimental error from $\theta = 0.15$ on does not exceed 5%. From $\theta = 0.4$ on all the curves have the same plateau. In the plateau region, the values for the heats of desorption mostly agree with the integral sorption heats, determined calorimetrically[7] earlier. At the end of the monolayer, from $\theta > 0.8$ a decrease of the desorption heats begins. In Fig. 2 the typical curves for NaX (curve 1) and ZnX zeolite (curve 2) are shown. As can be seen, the sorption heat for bivalent Zn is hardly higher than the error limit (6%) with respect to NaX zeolite in the plateau region. However the desorption heats for any coverage and any cation lie precisely on the curve for NaX, or ZnX zeolite.

For A zeolite (Fig. 3) there is also the difference between univalent and bivalent cation zeolites (ca. 1 kcal). However, the curve for NaA lies higher than that for ZnA zeolite. As also for X zeolites, all the univalent and bivalent counterions for the given coverage lie on the corresponding curves.

DISCUSSION AND CONCLUSIONS

The qualitative results for desorption of water from the zeolite 13 X are in complete agreement with previous qualitative DSC results for A zeolites, published earlier[1]. There is just one well-defined desorption peak, appearing at 430 K regardless of the nature of counterions in zeolite. It is possible that a high temperature peak exists also with 13 X zeolite, which is not so well expressed as with A zeolite. This result agrees well with the hypothesis presented in our preceding paper[1], where we hypothesize that the water is bound through hydrogen atoms to the oxygen ions of the aluminosilicate framework in α and β cages. The difference in the bonding energies in α and θ cages of A zeolite is sufficiently high and two desorption peaks are recorded. The desorption peaks of 13 X zeolite occur at the same temperature, independent of the nature of counterions (evidence of the same mechanism of bonding of water as with A-type zeolites). It is also obvious, that due to the open structure of X zeolite, the difference in energies of hydrogen bonding in the cages of X zeolite is considerably smaller than in A zeolite, so that the two peaks are not separated.

As expected, the results of quantitative analysis show a strong dependence of the desorption heat on the coverage. Accordingly, for comparison of the heats of desorption of water from different cation exchanged zeolites of both X and A type the coverage must be the same. The most convenient way is to compare in the region of the coverages at the plateau (around $\theta = 0.6$) where the sorption heat is almost constant. This eliminates the difficulties with preparing different samples with almost equal coverages. All our experimental results indicate that the desorption heats of all cations of the same valency have the same value. Small differences between univalent and bivalent cationic forms of zeolite exist. Nevertheless, the dependence is not a simple one. For A-type zeolites, the desorption heats for the bivalent cationic forms are a bit lower than for the univalent ones, while for X zeolites it is the other way about.

So we could not find any correlation between the hydration heats of cations and the desorption heats of the corresponding cationic zeolites, as was published earlier. In this respect considerable attention is drawn to the results showing that there is no significant difference between the desorption heats for univalent and bivalent cationic forms of zeolites, as would have been expected, had any sorption mechanism, similar to hydration, taken place. Thus the results of DSC analysis do not disprove the hypothesis of hydrogen bonding of water to the oxygen atoms of the aluminosilicate framework.

The influence of cations on the sorption of water, if geometrically-steric effects are neglected, is minor. The change of cation, as well as the change of crystal structure, or the magnitude of the cavities in zeolite, influence the topographical change of the density of electromagnetic field in the cavities of zeolite.

So it comes to minor differences in the polarisation of molecules of water, showing a change in the energies of interaction between water and the aluminosilicate oxygens. As shown by our results, these differences can be noticed only between univalent and bivalent cationic forms. Inside one series, univalent or bivalent, they could not be noticed. Cations can influence significantly only sorption characteristics strongly depending on the sterical effects: the quantity of the sorbed molecules, isotherms and sorption kinetics.

Such a mechanism is similar to that postulated by Barrer and Bratt[7]. However, the generally accepted proposal[7,13] that the zeolites are similar to concentrated solutions of salts, does not assume this mechanism, and cannot be completely accepted. Namely, three seoption regions can be assumed, as schematically given in Figs. 2 and 3.

The region II represents the region of moderate coverage, where the main quantity of water is sorbed. In this region we have the mechanism of hydrogen bonding of water molecules to the oxygens of the aluminosilicate framework. The influence of the cations on the sorption of water is very weak, and it is mostly expressed in the change of topography of electromagnetic field in the crystal cavity. Due to weak interactions the influence of the sorbed water at the field in the cage is rather mild. Results of NMR and electrical conductivity confirm this model. The spin–spin relaxation time of Li^+ ion in LiX zeolite up to a $\theta = 1$ covering by water is slightly prolonged, and remains characteristic of the solid state. The electrical conductivity slowly increases, but activation energy remains constant around ~ 11 kcal $gmol^{-1}$ (all the way to $\theta \sim 1$), which is close to the activation energy of completely dry zeolite of X type (13.6 kcal $gmol^{-1}$ for NaX, 14.7 kcal $gmol^{-1}$ for KX zeolite and 17 kcal $gmol^{-1}$ for LiX). It is clear from these results, that the zeolite in region II is far from similar to the concentrated solutions of salts.

From $\theta > 1$ by a slow process cations become more and more mobile. The sorption heat approaches the condensation heat of water (9.7 kcal mol^{-1}). The electrical conductivity steeply increases with the decrease of the activation energy to the value of $\sim$1–2 kcal $gion^{-1}$. Zeolites in region III are very similar to concentrated solutions of salts.

The most problematic region is region I, at very small coverage, where it is difficult to obtain reliable experimental data. However this region is very interesting because the molecule is exposed to the strongest influence of the crystal field. It is evident, that the sorbtion heats are very high. The relaxation times of both sorbed molecules and cations are characteristic of the solid phase. One possible mechanism is chemisorption, leading to the dissociation of water by formation of surface hydroxyl groups. The impossibility of removing small quantities of water up to destruction of the structure at ~ 800°C would point out at this possibility. There are also other possibilities. Very attractive seems the hypothesis of a specific "sorption in a strong electromagnetic field" of the zeolite cage. The greatest part of the dipole–field interaction goes right to the first molecules, where by further sorption this energy is more uniformly distributed.

The molecular electronic shape is maximally deformed depending on the configuration of the zeolite field. The water molecule by this means is not specially connected to either skeleton or cation. It is clear that the answer to this question cannot be given without reliable experiments.

Also at this moment some other questions remain open, concerning the specificity of some types of zeolite e.g. Ba zeolites, Sn zeolites and CaA zeolite. It seems that by dehydration of the two former the crystal structure is partly destroyed, and with CaA zeolite there exist two completely equal peaks. While dehydration of Ba and Sr zeolites can be understood from these considerations, the special characteristics of the CaA zeolite demand supplementary experiments.

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