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HIGH TEMPERATURE TRANSFORMATIONS OF NH_4A ZEOLITE

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ABSTRACT

Transformations of various forms of $NaNH_4A$ zeolite were investigated in the paper. It was determined that the degree of ion exchange considerably influences the stability of the A framework and the formation of crystalline phases in the high temperature region. The sillimanite phase forms from NH_4A zeolite, while in the case of mixed forms the carnegite phase is found only for small degrees of ion exchange

INTRODUCTION

The positions and mobility of cations in zeolite type structures determine many properties of these systems including the thermal ones. By the thermal transformation of various ion exchanged forms of A zeolite a series of new phases forms[1], with most commonly the appearance of several exothermal DTA peaks Because of the priority of various positions during ion exchange, systems with mixed cations are very interesting. In NaLiA systems, regardless of the ratio, typical sodium, i.e lithium phases were simultaneously formed[2], so there was a reason for also investigating $NaNH_4A$ systems The structure of NaA zeolite is such that the Na^+ ions occupy three[3], and the NH_4^+ ions in NH_4A four different positions[4] The exact position of the cations is unknown in mixed forms, however, it is known that the Na^+ ions from six-membered rings are exchanged first NH_4 forms with the loss of ammonia transform to H^+ forms, with increase of the H^+/Na^+ ratio decreasing the stability of the A fremework[5] It is not known which crystalline phases form by high temperature transformations of these systems and it is not clear what is the type of the influence of the Na^+/H^+ ratio

EXPERIMENTAL

The samples were prepared by standard procedures of ion exchange from 4A zeolite manufactured by Union Carbide The thermal analysis of samples was performed on a Mettler instrument at a heating rate of 10^o/min in the flow of dry nitrogen X-ray investigations were performed on a Phylips powder diffractometer PW-1051. CuK_α radiation and a graphite monochromator were applied. The IR spectra were performed on a Perkin Elmer 397 spectrophotometer

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RESULTS AND DISCUSSION

The results of thermal analysis of typical $NaNH_4A$ zeolites are given in Figure 1. In all cases there is one endothermal peak (DTA) with simultaneous mass loss (TG). The intensity and shape of the peak depend on the degree of ion exchange Na^+/NH_4^+. It is known that in the case of ammonium zeolite forms, beside dehydration, deamonation also occurs. IR spectral results presented in Figures 2, 3 and 4 show that after heating at 700°C in the systems NH_4A and $Na_{4.4}(NH_4)_{7.6}$ A the bands at 1650, 1460 and 1400 cm^{-1} disappear, which means that both these processes are finished. At the same time changes also occur in the structural part of the spectrum. It was determined by X-ray analysis that after this thermal treatment the A framework collapses in the case of NH_4 and partially in the case of $Na_{4.4}(NH_4)_{7.6}$ A while it is still stable for $Na_{11}(NH_4)_1$ A. At a heating rate of 10^0/min the dehydration and dealumination processes are parallel. It is probable that under those conditions part of the aluminum from the framework (tetrahedral coordination) transforms to the cation position, Al^{3+}, [5], which may be important in the crystallization of other phases.

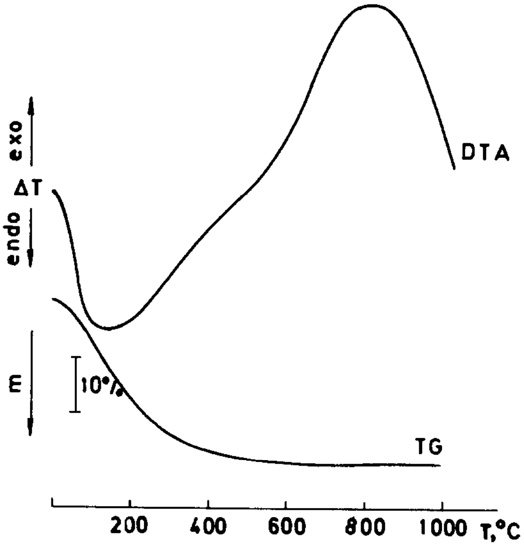

Figure 1. Thermal analysis of $Na_{4.4}(NH_4)_{7.6}$ A

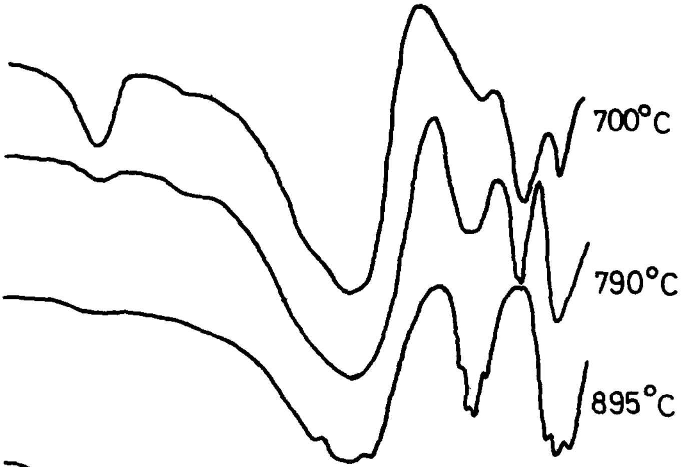

Figure 2.
IR spectra of
$Na_{11}(NH_4)_1$ A

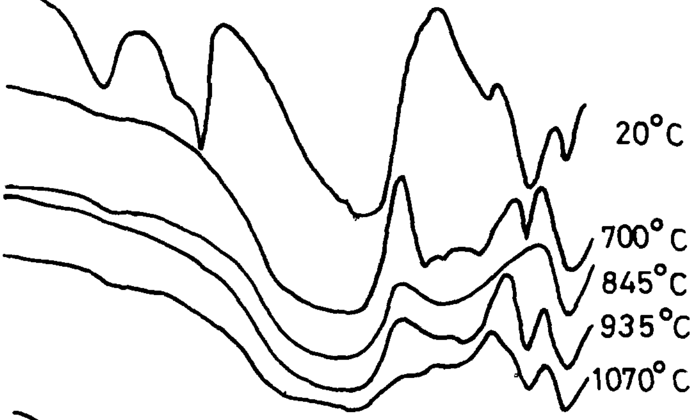

Figure 3.
IR spectra of
$Na_{4.4}(NH_4)_{7.6}$ A

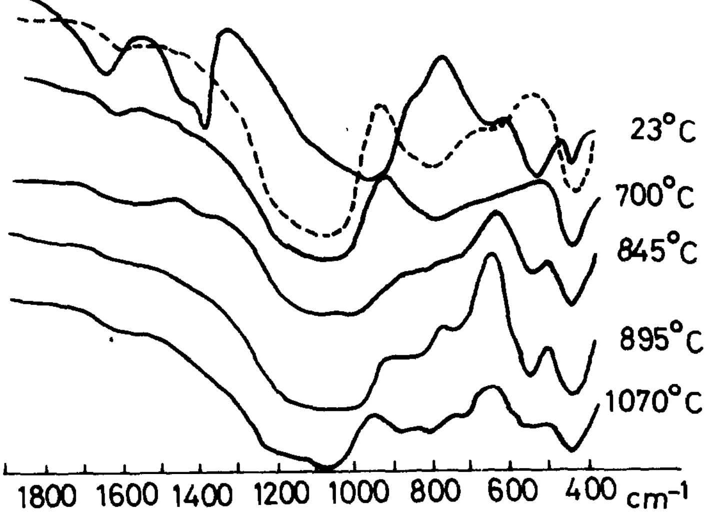

Figure 4. IR spectra
of NH_4 A

All systems in which the number of NH_4^+ ions per elementary cell is equal to or greater than eight, have only one relatively broad exothermal peak in the rerion of higher temperatures, whcih is followed by a mass change of less than 1%. Since one exothermal peak may be the consequence of one slow transformation, but also of a set of several reactions (with different enthalpies), the samples were heated by a program to certain temperatures and then analysed. At higher temperatures the amorphous phase formed from NH_4A zeolite is arranged into sillimanite The process of sillimanite crystallization was very slow In was determined bv X-ray analysis that crystallization starts between 700-800°C, at 800°C the reflexion intensities are already considerable. The framework was completely formed at 890°C. The small fraction of the amorphous phase at that temperature may be ascribed to the difference in Si/Al stoichiometric rations in zeolite A and sillimanite. Already at 1100°C collapse of the crystalline framework begins which indicates that sillimanite formed in such conditions is not thermally stable

In the case of mixed systems with more than four Na^+ ions per elementary cell again only sillimanite crystallized. The temperature at which the framework forms is also 890°C.

A system with a very low degree of exchange, one Na^+ ion per elementary cell behaves like a pure sodium form. Varnegite forms from the amorphous phase at about 790°C which at a still higher temperature recrystalizes into nepheline.

In these systems the number of Al^{3+} ions increases with the decrease of Na^+ ions per elementary cell, the fraction of tetrahedrally coordinated aluminum consequently leads to sillimanite crystallization, when the Na^+/NH_4^+ ration surpasses 0.5.

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