Brief Communications

Influence of exchangeable cations on the character of dehydration of phillipsite

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Various ion-exchange forms of phillipsite (Phi) were prepared. Anomalous dependences of the extent of rehydration and heats of immersion Q_i on the temperature of thermovacuum treatment were revealed for the initial Na,K- and K-forms made by ion exchange. The curves pass through a minimum between 100 and 180 °C, indicating structural changes accompanied by considerable contraction of the zeolite framework. No structural changes were observed when the ammonium form of phillipsite was evacuated at elevated temperatures; the curve $Q_i = F(T)$ passes through a maximum at 250 °C. It was calculated that NH_4-Phi is thermally much less stable than Na,K-Phi or K-Phi.

Key words: zeolites, phillipsite, K-phillipsite, NH_4-phillipsite, ion exchange, water adsorption, heat of immersion, phase transition.

The patterns of dehydration and thermal stability are among the most important issues associated with the application of zeolite sorbents and catalysts. The character of dehydration of zeolites and its reversibility are determined not only by the type of framework structure, but also by the nature of exchangeable cations.

In the previous work,[1] we studied the dehydration of natural natrolite, whose cations (Na^+) cannot exchange with NH_4^+ in aqueous solutions. It was of interest to extend the study to another natural zeolite, phillipsite (Phi).

Experimental

Ion exchange was carried out both under mild conditions in aqueous solutions and by the vapor-phase procedure.[2] To prepare NH_4-Phi by the vapor-phase procedure, crystals of natural Phi selected under a microscope (~1 mm) were mixed with NH_4Cl and placed in a thick-walled glass ampule. The outgassed mixture was sealed in the ampule and heated for 160 h at a temperature of vigorous sublimation of NH_4Cl (200 °C, 700 Torr). After cation exchange, zeolite was thoroughly washed out with hot distilled water until no Cl^- ions were found in the solution. The K-form of phillipsite (K-Phi) was prepared in an aqueous solution of KCl under mild conditions of ion exchange.

Heats of immersion were determined on a DAK-1-1 differential calorimeter. The procedure described previously[3] was used in the investigations involving adsorption microcalorimetry. The curves describing dehydration and rehydration of zeolite as a function of the temperature of evacuation (4 h) were recorded with a gravimetric adsorption unit with a spring balance.

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Table 1. Chemical composition (wt.%) of zeolites

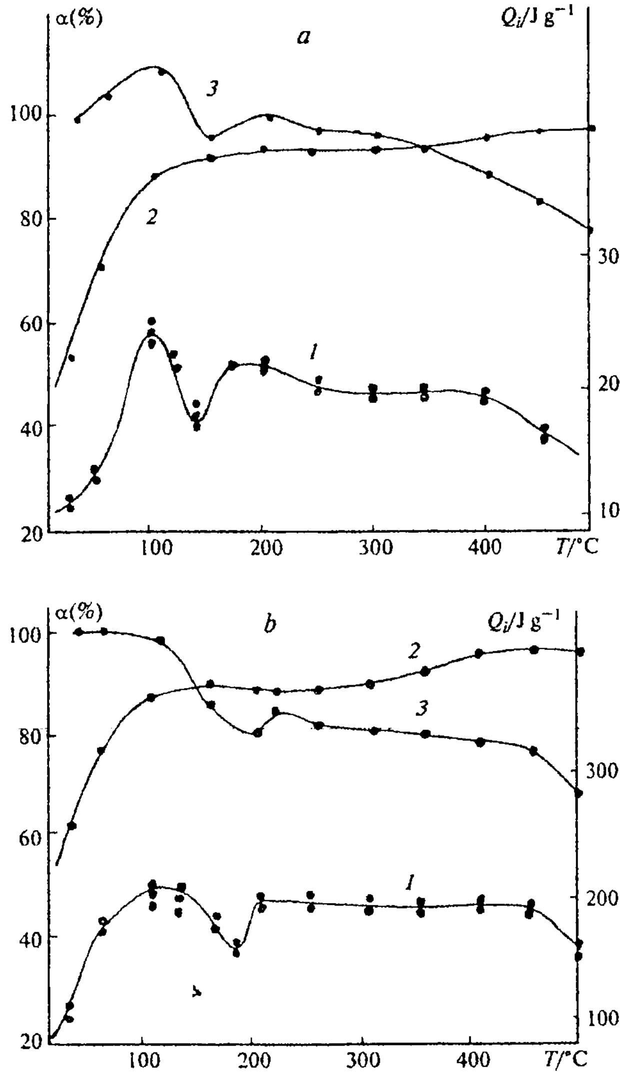
Zeolite	SiO_2	Al_2O_3	Na_2O	K_2O	CaO	MgO	H_2O
Na,K-Phi	55.63	18.04	3.20	9.75	0.18	0.05	13.20
K-Phi	55.60	18.07	0.02	12.84	0.10	0.02	13.21
NH_4-Phi	54.61	18.41	0.16	0.71	0.15	0.48	23.90

Chemical compositions of samples of initial phillipsite (Na,K-Phi) and synthetic K-Phi and NH_4-Phi are presented in Table 1.

Results and Discussion

After evacuation at room temperature, zeolites Na,K-Phi and K-Phi lose 55 and 65% of the adsorbed water, respectively, and the heats of rehydration (immersion) (Q_i) for these samples were 100 and 110 J g^{-1} (Fig. 1, *a* and *b*). An increase in the temperature of evacuation to 50 °C results in a noticeable increase in the loss of water in these zeolites (70 and 80%). Almost 90% water in Na,K-Phi and K-Phi can be removed after evacuation at 100 °C, and the heats of immersion Q_i reach the maximum values of 235 and 200 J g^{-1}.

Unlike thermal profiles of other zeolites of the analcime group, the curve of rehydration for the initial Na,K-Phi indicates an anomalous (~10%) increase in the adsorption volume at 100 °C. This effect is not observed for K-Phi. Similar effects are observed for zeolites of the natrolite group,[4] for which an increase in the adsorption volume also coincides with the liberation of the highest heats of rehydration at 200 °C. An increase in temperature from 100 to 140 °C is not accompanied by a noticeable loss of the adsorbed water, although a sharp decrease in the rehydration capacity and a decrease in the heats of immersion of Na,K-Phi are observed exactly in this narrow temperature range. At temperatures between 140 and 200 °C, the amount of rehydration water again increases to 100%, and the heats of immersion increase to a value of 215 J g^{-1}. It is most likely that structural changes in Na,K-Phi, which have previously been reported,[5,6] occur in the 100—140 °C temperature region. These changes can also be followed



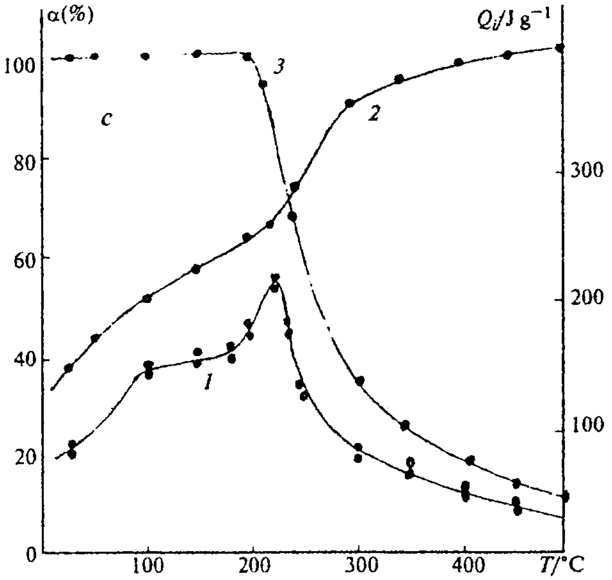


Fig. 1. Heat of immersion (Q_i) in water (at 25 °C) for zeolites Na,K-Phi (*a*), K-Phi (*b*), and NH_4-Phi (*c*): *1*, as a function of the temperature of evacuation (4 h); *2*, relative values of dehydration (α in % of the overall weight loss); and *3*, relative values of rehydration at $p/p_s = 0.5$ and $T = 25$ °C (α in % of the total water content in the initial sample).

in K-Phi, but at higher temperatures, from 130 to 180 °C (see Fig. 1, *b*). It is noteworthy that a negligible weight loss can be detected on the curve of K-Phi dehydration at these temperatures. Thus, the appearance of minima on the curves describing rehydration and heats of immersion in the absence of water loss on the dehydration curves indicate the formation of deformed structures of zeolites Na,K-Phi and K-Phi within the 100—200 °C temperature range. As mentioned previously,[7] these changes occur due to the shrinkage of the zeolite framework.

When Na,K-Phi is heated at temperatures ranging from 200 to 550 °C, only 5% water is additionally removed, but the zeolite structure is destroyed over this temperature range. Over the 200—500 °C temperature range, zeolites Na,K-Phi and K-Phi show similar patterns (profiles) of dehydration, rehydration, and heats of immersion. The data obtained do not agree with the notion[5] that Phi cannot completely be rehydrated after the treatment at 250 °C. Only in the 250—400 °C temperature region, does the rehydration capacity of the initial samples of Na,K-Phi and K-Phi decrease by 10 and 5%, respectively. The heats of rehydration in this temperature range remain nearly unaltered for both zeolites. However, the lack of variation in the heats does not necessarily imply the same or similar physicochemical properties of these zeolites. In this case, the enhanced heats of rehydration shown by zeolite with a reduced sorption capacity are compensated by the energy loss associated with a high temperature dehydration involving release of water molecules tightly held in the first coordination sphere of exchange cations.[8] Evacuation at 500 °C decreases the adsorption capacity of the Na,K-Phi and K-Phi samples by 20—30% only, whereas after evacuation at 600 °C, a 35% decrease was detected.

The curves describing the heats of rehydration and the extents of dehydration and adsorption (rehydration) of NH_4-Phi differ substantially in character from the corresponding curves obtained for Na,K-Phi and K-Phi. As seen in Fig. 1, *c*, NH_4-Phi loses ~40% of the adsorbed water following evacuation at room temperature, and that is 15 and 20% less than the water loss for Na,K-Phi and K-Phi. The heat of rehydration of NH_4-Phi is 90 J g^{-1}, which is also somewhat lower than the heat measured for alkali-cation forms of Phi. As the temperature of evacuation increases to 100 °C, the weight loss of volatiles increases to 50%, and the heats of rehydration of NH_4-Phi increase by 60 J g^{-1}. Within the 100—225 °C temperature range, the weight loss of volatiles for NH_4-Phi is 65%, rehydration occurs almost reversibly, and the heat of rehydration achieves the highest value (215 J g^{-1}). As the temperature increases to 300 °C, the weight loss of volatile components increases sharply and reaches 90%. In this narrow temperature range, the degree of rehydration decreases: from nearly complete at 225 °C to 35% at 300 °C. Correspondingly, the heat of rehydration of NH_4-Phi decreases to 80 J g^{-1}. With the further increase in temperature from 300 to 500 °C, the loss of volatile components increases by 10%, and the heats of rehydration and adsorption decrease accordingly.

The process of dehydration for NH_4-Phi can be divided into the following steps: reversible dehydration and rehydration, *i.e.*, desorption and adsorption of water, occur at the first step (25—225 °C), and the heats of immersion increase when the extent of desorption increases. These observations are also confirmed by the IR spectra of NH_4-Phi, which indicate that the intensity of absorption bands of the NH_4 ion remains unchanged at temperatures below 225 °C, but a decrease in intensity of the absorption bands of water molecules is readily seen. At the second step (225—300 °C), all three measured parameters change sharply, implying irreversible structural changes caused by the decomposition of ammonium ions. The zeolite transforms into a metastable state retaining its rehydration capacity. However, a strong decrease in intensity of the absorption bands of ammonium ions and the appearance of absorption bands assigned to structural OH groups are observed. Dehydroxylation accompanied by a strong decrease in the heats of rehydration and immersion occurs at the last stage (>300 °C).

Thus, insertion of ammonium ions into the Na,K-Phi structure substantially changes the pattern of dehydration, rehydration, and heats of immersion as a function of the temperature of evacuation. No low-temperature deformation, which is common to Na,K-Phi and K-Phi, is observed for NH_4-Phi. The loss of the rehydration capacity of NH_4-Phi initiated at a lower temperature compared to alkali-cationic forms of phillipsite and it is accompanied by a more considerable decrease in the adsorption capacity.

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