

## THERMAL ANALYSIS METHOD AND DIFFERENTIAL SCANNING CALORIMETRY INVESTIGATION OF NATURAL ZEOLITES OF PHILLIPSITE GROUP

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Phillipsite and harmotome form a continuous series of solid solution with common formula  $(K, Na, Ca_{0.5}, Ba_{0.5})_x [Al_x Si_{16-x} O_{32}] 12H_2O$ , where  $x \approx 4-7$  [1]. K, Na, Ca may be the most abundant extra-framework cation, but the name harmotome is retained for the Ba-dominant member of the series.

The dehydration of zeolites processes are important in a variety of applications including pollution abatement, catalysis and gas separation. The thermal stability is connected with the ratio of Si/Al, content of exchanged cations and framework topology.

We studied the samples of natural phillipsite (Khibiny, Russia) and harmotome (Rodopy, Bulgaria). The samples have been examined by X-ray and electron microprobe analyses. The formulae calculated for 32 oxygens were following: phillipsite  $(K_{3.05} Na_{0.53} Ca_{1.26} Sr_{0.04} Ba_{0.03}) [Al_{5.57} Si_{10.26} O_{32}] 11.67H_2O$  and harmotome  $(Ba_{2.03} Na_{0.06} K_{0.07} Ca_{0.12} Sr_{0.02}) [Al_{5.13} Si_{11.02} O_{32}] 12.05H_2O$ . The Si/Al ratio in phillipsite (1.84) and harmotome (2.15) shows they are the zeolites with median silicon content. The water content was determined by weighing the samples before and after heating at  $T=700^\circ C$  with error  $\pm 2 \cdot 10^{-6} g$ .

The zeolites thermal behavior was studied by differential thermal (DTA) and thermogravimetric (TG and DTG) analyses at temperature interval of 20-1300°C with heating rate of 15°C by using derivatograph «Q-1500 D». Harmotome and phillipsite are nonstable at heating and begin to loss water at the room temperatures. Harmotome, with five different water sites in the structure, loses its water in four steps: I – in the interval of 40-80°C, II – 80-230°C ( $T_{max} = 200^\circ C$ ), III – 230-310°C ( $T_{max} = 290^\circ C$ ), IV – 310-440°C ( $T_{max} = 320^\circ C$ ). The total water loss was equal 14.8%. The harmotome structure is destroyed near 440°C and the new phase is formed at  $T=720^\circ C$ , this process is accompanied by exothermal effect. Phillipsite loses its water in five steps: I – in the interval of 50-100°C, II – 100-180°C, III - 180-270°C ( $T_{max} = 205^\circ C$ ), IV – 270-330°C, V – 330-500°C ( $T_{max} = 380^\circ C$ ). The all water (15.6%) is eliminated at temperature 500°C. Our experiments showed that the stable new phases form at heating above 700°C and then the following rehydration doesn't take place. It may be connected with significant constraction of the zeolite structure.

The thermochemical study of the natural phillipsite of the composition  $(Na_{1.08} K_{0.80}) [Al_{1.88} Si_{6.12} O_{16}] 6H_2O$  was performed early by adiabatic calorimetry method in the interval of 15-300 K,

the value of standard entropy at  $T=298.15 K$  was calculated [2]. There are no publications on thermodynamic properties of harmotome.

The thermodynamic characteristics were investigated by differential scanning calorimetry method (DSC «Mettler TA-2000 B»). Details of instrument operation are described in [3].

The enthalpies of total dehydration of zeolites studied were measured by DSC method. The values obtained were following:  $\Delta H_{dehydr}^0 = 1116 kJ/mol$  for harmotome in the temperature interval of 40-440°C and 991 kJ/mol for phillipsite in the interval of 50-500°C. The average bonding strengths of water with zeolite structure relatively to steam  $H_2O$  are 93 kJ (harmotome) and 85 kJ (phillipsite) per one mole of water.

The low-temperature heat capacities of natural zeolites were measured by DSC method in the interval of 110 – 320 K in flowing nitrogen with a scanning rate of 5-10 K/min. The molar enthalpy and melting temperature of indium reference substance (99.9999 % purity) were used to calibrate the DSC. The standard heat capacities of phillipsite-K  $C_p^0(298.15) = 1645.2 J/molK$  and harmotome  $C_p^0(298.15) = 1602.0 J/molK$  were obtained. The specific heat capacities of phillipsite-K studied in this work (1.218 J/gK) and phillipsite-Na investigated by adiabatic calorimetry in [2] (1.223 J/gK) are in a agreement within experimental errors (1-1.5%). The molar values distinct one from another for their composition differences ( $C_p^0(298.15) = 1572.4 J/molK$  for phillipsite-Na [2]). The thermochemical investigation of harmotome was the first.

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