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THERMOCHEMICAL PROPERTIES OF CHEMICALLY MODIFIED ZEOLITE

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Abstract

Zeolites chemically modified with 1, 4 or 6 M aqueous solutions of NaOH were studied by DTA, TG and ETA (emanation thermal analysis) in the temperature range 20–1200°C. The structural changes in the modified zeolites at room temperature and in the modified zeolites annealed at 1000°C were studied by XRD analysis. Thermal analysis demonstrated dehydration, dehydroxylation, structural changes and a glass transition. A gradual loss in crystallinity of the chemically modified zeolites was also observed. XRD analysis revealed structural changes caused by chemical treatment and also by annealing.

Keywords: chemically modified zeolite thermochemical properties, DTA, emanation thermal analysis, TG, zeolite

Introduction

Zeolites provide excellent model systems in which it is possible to study ion exchange and physical, chemical, thermochemical, etc. properties under readily accessible experimental conditions. Among the naturally occurring species, the most abundant are of the clinoptilolite type. They are found in specific rocks and constitute large deposits in certain areas of the world. Large deposits of zeolite occur near the village of Nižny Hrabovec in Slovakia. The content of clinoptilolite is up to 70% [1]. The standard method used to modify the sorption ability of zeolites (crystalline aluminosilicate) is ion exchange with cations. Cations can be introduced into those solids by using aqueous solutions of the corresponding salts. The monosodium form was obtained by chemical treatment of the natural zeolite with 1, 4 or 6 M aqueous solutions of NaOH. It exhibits an excellent sorption uptake of a caesium [2] and a good uptake of cobalt [3]. This chemical treatment can also cause dealumination, amorphization and changes in the structure and other properties of the zeolite.

From a general survey, the thermal properties of modified zeolites have been related to structural characteristic such as IR frequency and unit cell dimensions [4].

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Such correlations help in the prediction of changes which occur as concerns dehydration/dehydroxylation and phase transformation [5].

This paper reports on the influence of temperature on the structural stability of natural zeolite and zeolite modified with 1, 4 or 6 M aqueous solutions of NaOH.

Experimental

All experiments were performed on zeolite from the deposit at Nižny Hrabovec, which contains up to 70% of clinoptilolite; its granularity was in the range 1–2.5 mm. Samples of the zeolite were modified with 1, 4 or 6 M aqueous solutions of NaOH for 4 h at 80°C [6]. The natural and chemically modified zeolites were observed by DTA, TG, ETA (emanation thermal analysis) and XRD analysis.

DTA and TG curves were recorded simultaneously on an automatic Derivatograph Q1500D in a static air atmosphere; the heating rate was 10°C min^{-1} up to 1200°C.

The ETA consisted in the measurement of radon release from previously labelled samples by an impregnation technique. The concentrations of ^{228}Th and ^{224}Rn in the leachate were determined by gamma-spectrometry after storage for 3 days in a sealed vessel [7]. The radon diffusion probe affords a possibility of detecting even very fine changes caused in the zeolite by chemical treatment.

Results and discussion

The DTA, TG and ETA results were compared for each type of zeolite. Figure 1 presents DTA, TG (part A) and ETA (part B) records on the natural, chemically not treated zeolite, while Figs 2, 3 and 4 depict DTA, TG (part A) and ETA (part B) results on the zeolite chemically modified with 1, 4 and 6 M aqueous solutions of NaOH. The DTA curves exhibit simple dehydration peaks for all the zeolite samples, at T_{endo}=180°C. At the same temperature in the ETA curves of all the zeolites, there are peaks which correspond to the emanation of radon caused by the dehydration process. The dehydration depends on features such as the grain size, the concentration of structural defects, the crystalline composition, the water content of the sam-

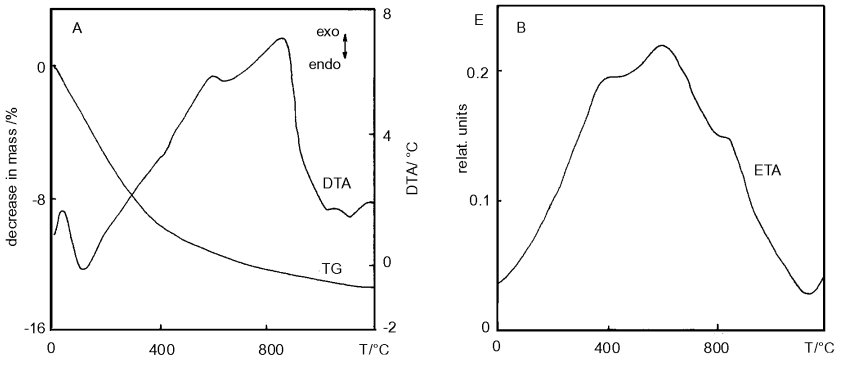

Fig. 1 Thermal analysis records of natural zeolite. A – DTA and TG records, B – ETA record

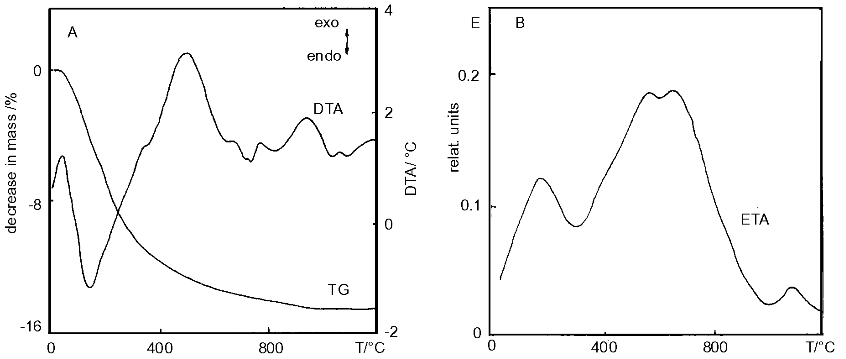

Fig. 2 Thermal analysis records of zeolite modified with a 1 M aqueous solution of NaOH. A – DTA and TG records, B – ETA record

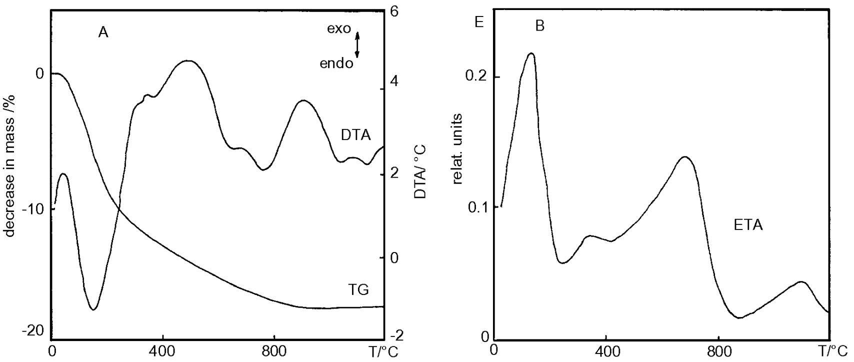

Fig. 3 Thermal analysis records of zeolite modified with a 4 M aqueous solution of NaOH. A – DTA and TG records, B – ETA record

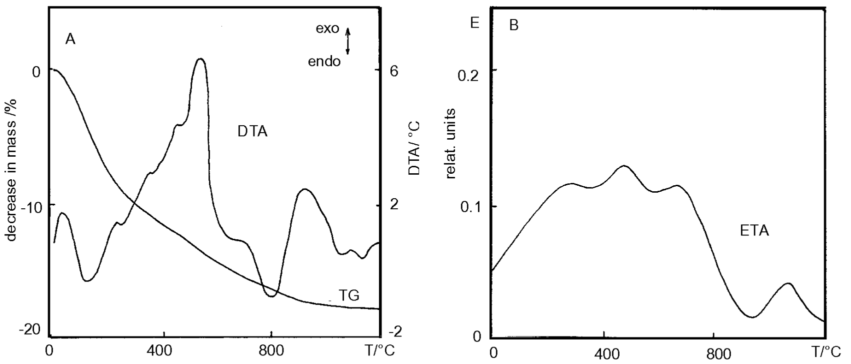

Fig. 4 Thermal analysis records of zeolite modified with a 6 M aqueous solution of NaOH. A – DTA and TG records, B – ETA record

ples, the humidity of the air and also the type of exchangeable ions. It was earlier shown that, if the exchangeable sites are occupied by monovalent cations, the endothermic peak is simple [8].

A weak endothermic peak at about T_{endo}=70°C for all the zeolite samples is due to dehydration/dehydroxylation. These two processes can be distinguished only in the case of exchangeable cations with low energies of hydration, e.g. Rb. In other cases, the two processes overlap [9].

About 1000°C, DTA reveals a small endothermic peak for all the modified zeolites; this is caused by collapse of the zeolite structure and the formation of an amorphous phase.

At 1100°C, there is an ETA peak associated with a glass transition. This is supported experimentally: at this temperature, the zeolite begins to melt.

The TG curves of all the zeolites indicate a major loss in mass of from 12 to 15% in the temperature range from 100 to 450°C, generally due to dehydration. The mass losses above 500°C may be caused by dehydroxylation. In general, the dehydroxylation of the zeolites is slow and occurs in this case in the range 600–800°C. It may be accompained by a distinct mass loss of up to 1–1.5% in this range, as is seen in Figs 1–4.

From about 400 to 900°C, the DTA curves exhibit several exothermic peaks which correspond to successive structural changes in the zeolite. The ETA records too contain very similar peaks, supporting the view that these peaks reflect only structural changes in the zeolite.

The presumption that the peaks in the range from 400 to 900°C correspond to structural changes in supported by the XRD records in Fig. 5. Figure 5a depicts

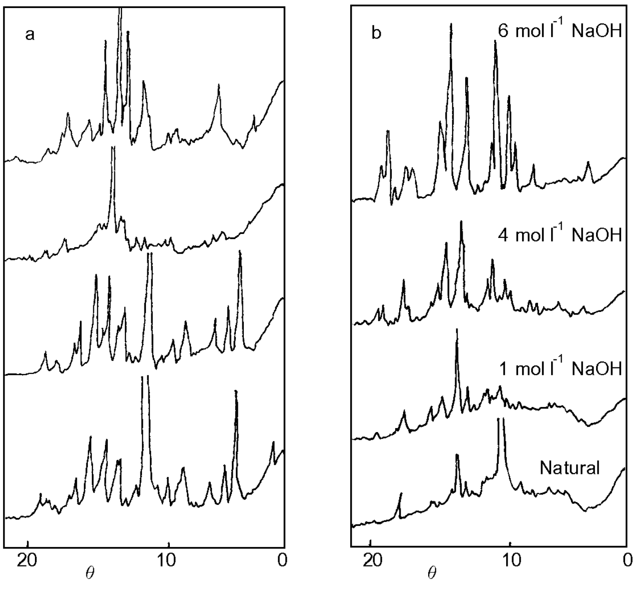

Fig. 5 Records of XRD analysis of natural and chemically modified zeolites. a – at room temperature, b – annealed at 1000°C

XRD records of the natural zeolite and the zeolites modified with 1, 2 or 4 M aqueous solutions of NaOH at room temperature. The curves indicate the structural changes caused in the zeolites modified by the chemical treatment. Figure 5b presents XRD records on the natural zeolite and the zeolite by 1, 2 or 4 M aqueous solutions of NaOH and annealed at 1000°C. Comparison of these two Figures reveals that annealing at 1000°C caused structural changes in all the zeolites.

Conclusions

Analysis of the DTA, TG and ETA records proves a useful tool for estimation of the changes caused in the thermal properties and zeolite lattice as a consequence of cation exchange. The overall results allowed a characterization of the structural and morphological changes in the natural and chemically modified zeolites. These results will be very useful as concerns optimization of the conditions for thermal treatment of natural and chemically modified zeolites in order to immobilize the radionuclides sorbed from waste water.

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