The effect of chemical modification on surface properties of natural zeolite

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Introduction

Synthetic zeolites are widely used in catalytic and adsorption processes (water treatment, extraction of heavy metals, etc.) due to their channel structure with elements of a strictly defined size, high degree of crystallinity, catalytic, ion exchange, adsorption properties. However, processes of zeolite synthesis require the use of appropriate equipment, high-quality raw materials and energy, which leads to a higher cost of synthetic zeolites compared to natural ones.

Therefore, it is advisable to study the possibilities of using natural clinoptilolite zeolite at the same level as synthetic zeolites, especially considering the high forecast reserves of zeolitized clinoptilolite-type tuffs of the Sokyrnytsia deposit of Ukraine.

Objectives

The usage of natural zeolites, which are characterized by a polycation composition, as effective sorbents and catalysts, requires their modification in order to obtain monocation-substituted forms. This process includes the stage of formation of the hydrogen form (H-form).

Thus, the purpose of this study was to obtain the H-form of clinoptilolite of the Sokyrnytsia deposit (Ukraine) by chemical modification of natural zeolite (Kl-nat) and to study the surface properties of the obtained samples.

Methods and Materials

Zeolite materials of the clinoptilolite type from the Sokyrnytsia deposit (Ukraine) were used in this work. Their elemental composition determined by X-ray spectral microanalysis is (in mass %): O – 64.60, Na – 0.37, Mg – 0.17, Al – 7.13, Si – 18.35, K – 0.79, Ca – 0.60, Ti – 1.43, Fe – 6.23, Cu – 0.33.

The Kl-H-NH_3 form of clinoptilolite was obtained by the ion exchange method with a 3M NH_4Cl solution at t = 96 °C for 6 h and subsequent thermal desorption of NH_3 at t = 410 °C for 6 h.

The Kl-H form of zeolite was obtained by the method of ion exchange with 1M HCl at t = 96 °C for 6 hours.

The methods of scanning electron microscopy, X-ray phase analysis and IR spectroscopy were used to study the nature of the surface and the ratio of frame-forming elements (Si/Al) of natural and chemically modified clinoptilolite.

Results

The results of the study of the original (Kl-nat) and modified samples ((Kl-H-NH_3 and Kl-H) by the method of raster electron microscopy are presented in Fig. 1. The sample Kl-H-NH_3 has the highest degree of crystallinity; the partial destruction of the crystal structure of the sample Kl-H is observed. This occurs as a result of the dealumination process, the mechanism of which is given below.

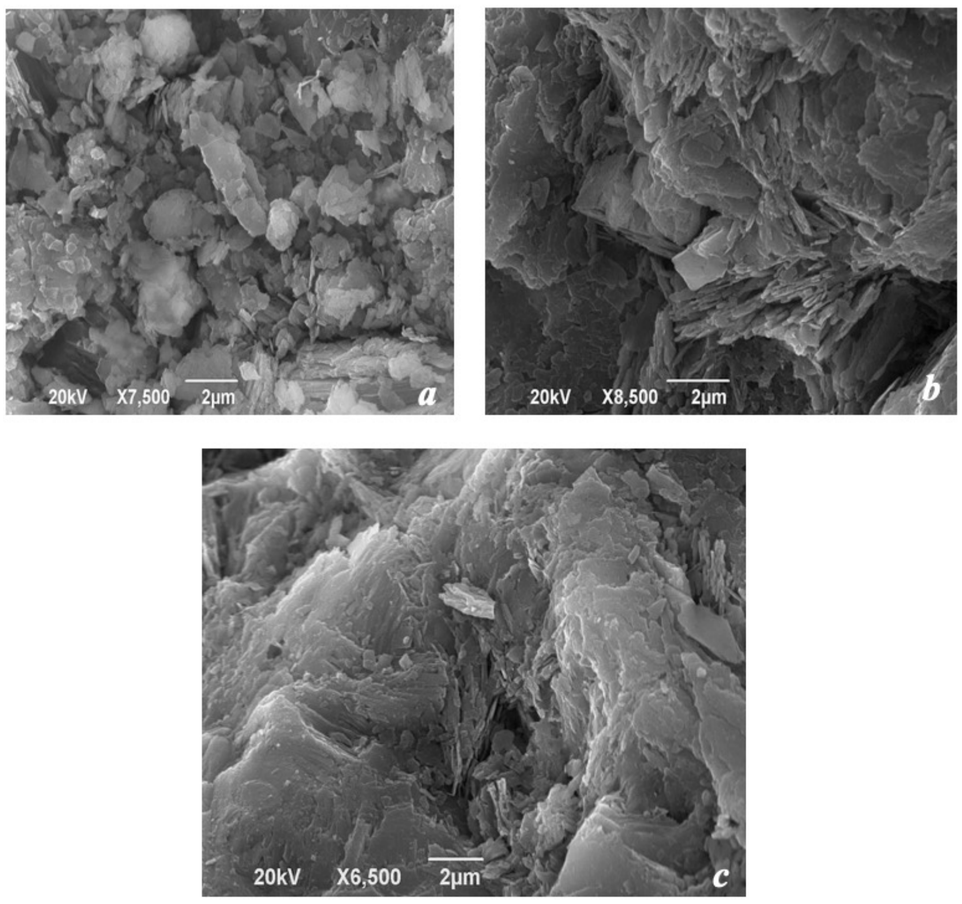
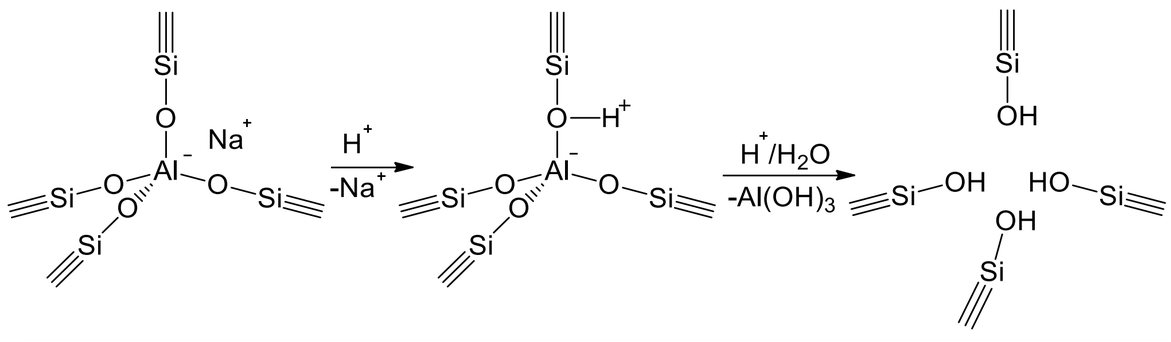


Figure 1. Surface morphology of clinoptilolite:
a – natural clinoptilolite; b – Kl-H-NH_3-sample; c – Kl-H-sample



Acid treatment of clinoptilolite first leads to the formation of Brønsted acid centers, and then silanol groups ≡Si–OH are formed. The dealuminated structure becomes more hydrophobic, its stability decreases due to the repulsion between hydrogen atoms in silanol groups and interaction between silanol groups and intraframework water molecules.

The dealumination process is confirmed by the results of X-ray spectral microanalysis, according to which the ratio of Si/Al in the series Kl-nat, Kl-H-NH_3 and Kl-H changes as follows: 2.5; 4.6; 9.0.

The results of IR spectroscopy of the studied samples indicate the presence of ammonium cations in the sample Kl-H-NH_3, which is undesirable and requires the adjustment of the conditions of the thermodesorption process.

Conclusions

It is shown the possibility of a purposeful change in the nature of the surface of the natural clinoptilolite of the Sokyrnytsia deposit.

The effect of acid treatment on the degree of dealumination of natural zeolite was studied.

It is advisable to carry out thermal desorption for a longer time, which will lead to the complete extraction of NH3 and the preservation of the channel structure of clinoptilolite.

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