STRUCTURAL CHARACTERISTICS OF A CLINOPTILOLITE / IRON OXIDE COMPOSITE

Sanja Jevtic[1], *Aleksander Rečnik*[2], *Matjaž Mazaj*[4], *Nevenka Rajić*[1]
[1] Faculty of Technology and Metallurgy, University of Belgrade, Belgrade, Serbia
[2] Institute Jozef Stefan, Ljubljana, Slovenia
[4] National Institute of Chemistry, Ljubljana, Slovenia
E-mail: sanja@tmf.bg.ac.rs

ABSTRACT

A clinoptilolite/iron oxide composite was prepared from a clinoptilolite-rich tuff (Zlatokop deposit, Serbia) by wet impregnation method under acidic conditions. The composite was characterized in detail using a powder X-ray diffraction method (XRPD), thermal analysis (TG/DTG), scanning electron microscopy coupled with X-ray microanalysis (SEM/EDS), transmission electron microscopy (TEM) and by isothermal N_2 sorption measurements at –196 °C.

Keywords: clinoptilolite, wuestite FeO, adsorption, TEM.

INTRODUCTION

Natural clinoptilolite is an efficient adsorbent for heavy metal cations present in water media[1–3]. The adsorption mechanism is mainly based on an ion-exchange reaction between sodium cations from clinoptilolite lattice and heavy metal cations from water solution[4]. In order to prepare clinoptilolite-based adsorbent for anion species, its surface must be modified. The modification can be done by different procedures including treatment with long-chain cationic surfactants that possess a permanent positive charge[5] or by coating of clinoptilolite with different oxides with affinity towards particular anions[6,7]. Thus, it has been reported that Fe-containing clinoptilolite exhibit adsorption ability towards arsenite/arsenate[6], selenite/selenite[8] or chromate/dichromate anions[9]. Since data on Fe-coating onto clinoptilolite surface have been scarce, in this research we performed a detailed characterization of the Fe-modified zeolitic tuff from Zlatokop deposit from Serbia.

EXPERIMENTAL

Zeolitic tuff (NZ) with about 80 wt. % of clinoptilolite, and quartz and albeit as major mineral impurities was used for the composite preparation. NZ was previously converted into Na-rich form (NaNZ) by treating with 2 M NaCl solution at 50 °C and using a solid/liquid ratio of 1:100. NaNZ was then suspended in 0.05 M solution of $Fe_2(SO_4)_3$ in an acetate buffer at pH=3.6 and the suspension was left at a magnetic stirrer overnight. The Fe-modified product (FeNZ) was separated by filtration, washed with deionized water and dried at 90 °C to a constant mass.

RESULTS AND DISCUSSION

A quantitative XRPD analysis of FeNZ gave (wt. %): clinoptilolite – 58(1), quartz – 6(3) and albeit – 9(1) within the bulk sample. The remaining fraction was assigned to an amorphous phase. The Rietveld refinement converged to satisfactory figures of merit Rp = 7.4 and Rwp = 9.9. The final Rietveld plot is shown in Fig. 1.

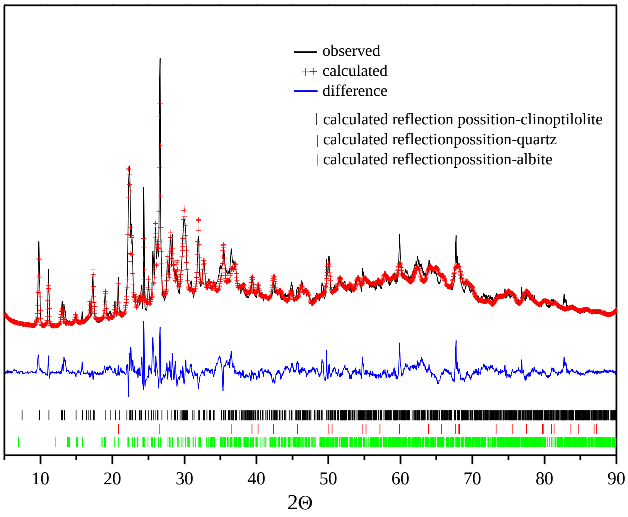

Figure 1. Final Rietveld plot of FeNZ.

Elemental analysis performed by EDS revealed about 6 wt.% of Fe, and showed a decrease of the Na content from 3.2 wt.% (NaNZ) to 2.1 wt.% (FeNZ). Since the decrease of Na in FeNZ is significantly lower than the increase of Fe concentration, it was concluded that the modification involved two phenomena: an ion exchange reaction inside the clinoptilolite lattice and precipitation of Fe-containing species at the surface of NaNZ.

Textural characterization of NaNZ and FeNZ showed that the specific surface area of the FeNZ (117 m^2 g^{-1}) is significantly higher than that of NaNZ (42 m^2 g^{-1}). Also, porosity parameters changed (Fig. 2) indicating that the second porous system was formed during the modification of NaNZ.

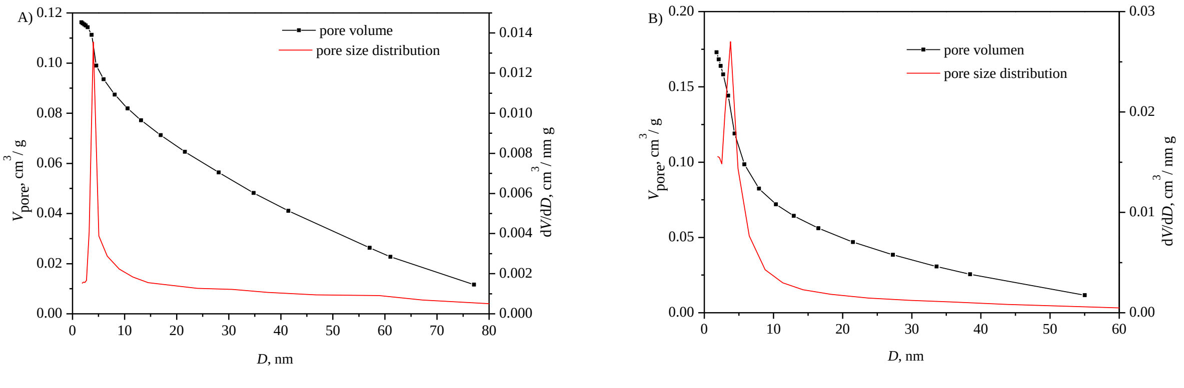

Figure 2. Pore volume and pore size distribution for NaNZ (A) and FeNZ (B).

TG/DTG analysis (Fig. 3) showed that the modification of NaNZ to FeNZ was accompanied with increase of water content from 10 wt.% (NaNZ) to 12 wt.% (FeNZ). This indicated that the Fe-precipitate at the surface of NaNZ contains hydrated species.

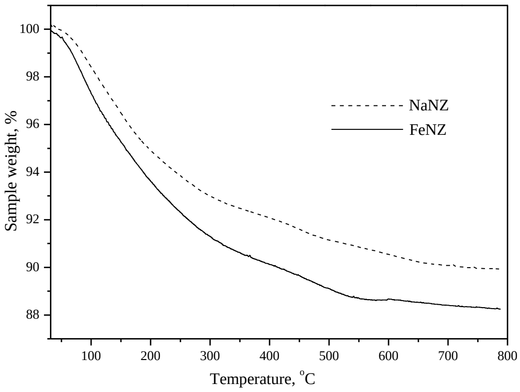

Figure 3. TG curves of NaNZ and FeNZ.

Fig. 4 shows results of TEM analysis. The clinoptilolite phase appears in the form of monoclinic crystalline sheets with well-defined crystal faces. Flaky precipitate at the surface of the clinoptilolite belongs to Fe-precipitate. Particle size of the precipitate varies from 3 to 20 nm exceeding the openings of the clinoptilolite lattice (about 0.4 nm). According to selected area electron diffraction pattern recorded over multiple particles, the precipitate belongs to wuestite FeO. Since the size of wuestite particles are larger than clinoptilolite openings it can be concluded that the crystallization of wuestite occured on the surfaces of the clinoptilolite. However, it should be noticed that a part of the iron coating might also contain amorphous hydroxo Fe(III) species.

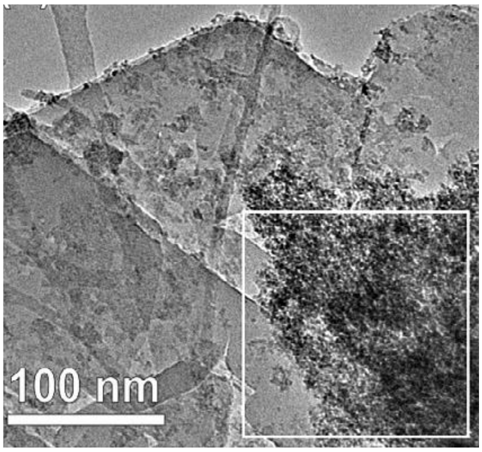

Figure 4. TEM image of FeNZ.

CONCLUSIONS

The surface of natural clinoptilolite was modified by wuestite FeO using a simple wet impregnation method. The wuestite coating increased the specific surface area of the clinoptilolite and changed the textural properties. Crystallinity of clinoptilolite was manily uneffected by the modification. The results indicate that the composite FeO/NZ could be promising adsorbent for use in water treatment.

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