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INVESTIGATION OF NATURAL ANALCIME-RICH ZEOLITE TUFF FROM TURKEY: A COMBINED XRD, XRF, FT-IR AND SEM STUDY

Meryem AKBELEN

Department of Physics, Faculty of Science, Eskişehir Technical University, Eskisehir, Turkey

ABSTRACT

In this study, chemical and structural properties of natural analcime-rich zeolite tuff from Turkey and that of ion-exchanged forms investigated. The microporous structure and the presence of extra-framework cations are of great importance for characterizing the unique properties of zeolites. Ion-exchanged forms (K^+, H^+ and Ca^{2+}) of analcime zeolite were prepared with 1 M KNO_3,1 M $Ca(NO_3)_2$ and 1 M HCl solutions in a shaker for 6 hours at 80 °C. The obtained samples were characterized by X-ray diffraction (XRD), X-ray fluorescence (XRF), Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM) techniques. Quantitative XRD analysis showed that the major component of the natural zeolite was analcime, together with varying amounts of quartz, feldspar and clay mineral.

Keywords: Natural zeolite, Analcime, XRF, XRD, FT-IR

1. INTRODUCTION

Zeolites are naturally occurring hydrated aluminosilicate minerals of the alkali- and alkaline-earth metals. The microporous structure and the presence of extra-framework cations are of great importance for characterizing the unique properties of zeolites. Extra-framework cations are relatively loosely bounded and can be removed or exchanged readily with other metal ions [1, 2]. Analcime (ANA) is a crystalline microporous aluminosilicate mineral with small irregular channels formed by four, six and eight-membered oxygen rings [3]. It has a narrow pore size of 0.26 nm. There are many studies regarding the ion exchange capacity and selectivity of metal ions for analcime zeolites. Tsitsishvili et al. [4] reported that the ion exchange capacity of analcime decreased in the order of $Na^+ > K^+ > Ag^+ > NH_4^+ > Ca^{2+} > Sr^{2+} > Li^+$.

Occurrences of sedimentary analcimes have been discovered in Turkey [5-8]. There are, however limited studies on structural properties of cation exchanged forms of analcime from Turkey. The aim of this study is to investigate the effect of acid- and salt- treatment on chemical and structural properties of the natural analsim zeolite and its ion-exchanged forms (K-A, Ca-A and H-A) using XRD, XRF, FT-IR and SEM analysis.

2. MATERIALS AND METHODS

2.1. Materials and Chemicals

Zeolite sample from Trakya region of Turkey was ground to less than 45 μm. Ion-exchanged forms of analcime zeolite were prepared with 1 M KNO_3,1 M $Ca(NO_3)_2$ and 1 M HCl solutions in a shaker for 6 hours at 80 °C. After this process, solutions were filtered and the sample was washed several times with deionized water at boiling point and then dried at room temperature. Before the experimental processes, all samples were dried for 5 hours in a 120 °C oven and then stored in a desiccator. The resulting ion-

*Corresponding Author: msakizci@eskisehir.edu.tr
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exchanged samples are referred to below as K-A, Ca-A and H-A, respectively, denoting their 1 M KNO_3,1 M $Ca(NO_3)_2$ and 1 M HCl treatments. The organic chemicals like KNO_3, $Ca(NO_3)_2$ and HCl were provided by Merck (Darmstadt, Germany), and all solutions were prepared using deionized water.

2.2. Characterization

The major elemental compositions were obtained on powdered samples fused with lithium tetraborate using X-ray fluorescence analysis (XRF – Rigaku ZSX Primus instrument). X-ray diffraction traces were recorded on powdered analcime samples with a Rigaku, RINT-2200 model diffractometer, using CuKα radiation (λ=1.54 Å), 40 kV and 15 mA power supply over the scan range of 2θ = 3 to 40° with an incremental step size of 0.02°. FT-IR spectra of the analcime samples were recorded using a Perkin Elmer Spectrum 100 model spectrophotometer in wave number range of 400 - 4000 cm^{-1}. The morphology of analcime samples were examined in gold coated samples with ZEISS ULTRAPLUS scanning electron microscope (SEM).

3. RESULTS AND DISCUSSION

3.1. Chemical Analysis

The major elemental compositions of the natural and ion-exchanged analcime samples are given in Table 1, as the mass % of metal oxides. The XRF analysis results exhibited that magnesium (Mg^{2+}), calcium (Ca^{2+}), potassium (K^+) and sodium (Na^+) were the major extra-framework cations in the natural analcime. Acid treatment of analcime samples led to partial dealumination and partial removal of exchangeable cations of the structure. Acid treatment increased SiO_2/Al_2O_3 ratio from 4.44 to 5.56 by removing aluminum from the zeolite structure [5-8].

Table 1. Chemical analyses in oxides (%) for natural and ion-exchanged zeolite samples

Chemical	Nat.-A	K-A	Ca-A	H-A
SiO_2	65.98	67.38	66.45	72.18
Al_2O_3	14.84	15.01	14.71	12.97
CaO	2.54	1.68	2.59	0.72
Fe_2O_3	1.45	1.39	1.40	1.16
MgO	0.86	0.64	0.70	0.73
K_2O	2.20	4.96	2.28	2.25
Na_2O	3.88	2.69	4.15	2.90
TiO_2	0.37	_	0.35	0.34
P_2O_5	0.12	0.15	_	_
CO_2	7.76	5.99	7.37	6.75
MnO	_	0.11	_	_

3.2. X-ray Analysis

The X-ray diffraction patterns of the natural and ion-exchanged analcime zeolites are shown in Figure 1. The analcime in natural sample is the predominant phase with minor amounts of external zeolite components including quartz, feldspar and clay mineral. Characteristic peaks of the analcime sample appear at the following 2θ diffraction angle values: 15.86°, 18.33°, 24.38°, 26,04° and 30,64 24.38° [9]. The quartz peaks occur at 2θ = 20.84°, 26,63° and 36,54°. The intensity of the reflections of Ca-A and K-A remains unchanged. It was observed that after the acid-treatment, analcime sample preserved the crystal structure. After acid-treatment, analcime remained the predominant phase but the intensity of the quartz peak increased [10, 11].

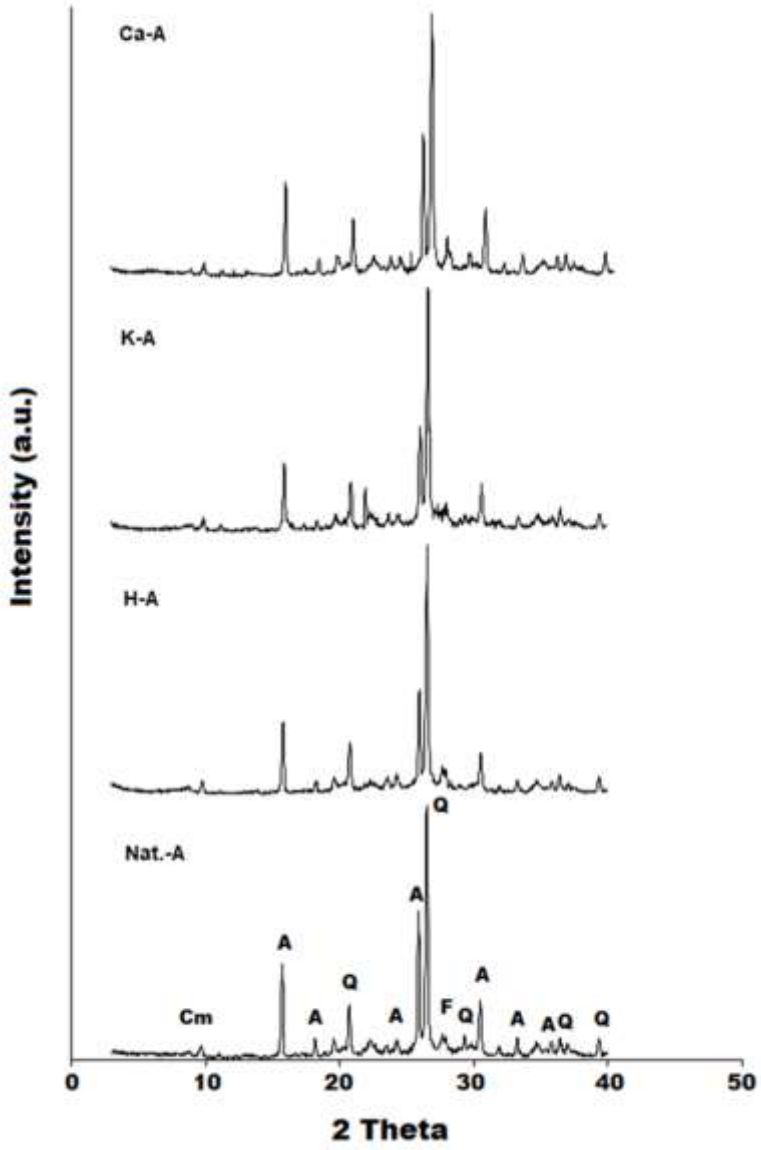


Figure 1. XRD patterns of natural and ion-exchanged analcime samples (Ana analcime, Q quartz, F feldspar, C clay mineral)

3.3. FT-IR Analysis

The FT-IR spectra for natural analcime and Ca-, K- and H-exchanged forms are given in Figure 2. The bands in the region 1600-3700 cm^{-1} can be attributed to the presence of zeolitic water [12-15]. Peaks in the range of 400-1300 cm^{-1} are related to the characteristic bands of zeolite minerals. The sharp absorption band at 1009-1020 cm^{-1} is shifted to a higher wavenumber with loss of Al cations in tetrahedral sites [15, 16]. This result showed the framework dealumination as shown from XRF (Table 1). The band appearing at 775-777 cm^{-1} is related to the symmetric stretching vibration of tetrahedral T-O (T=Si, Al) bonds. The band at 797-799 cm^{-1} can be assigned to vibrations of quartz.

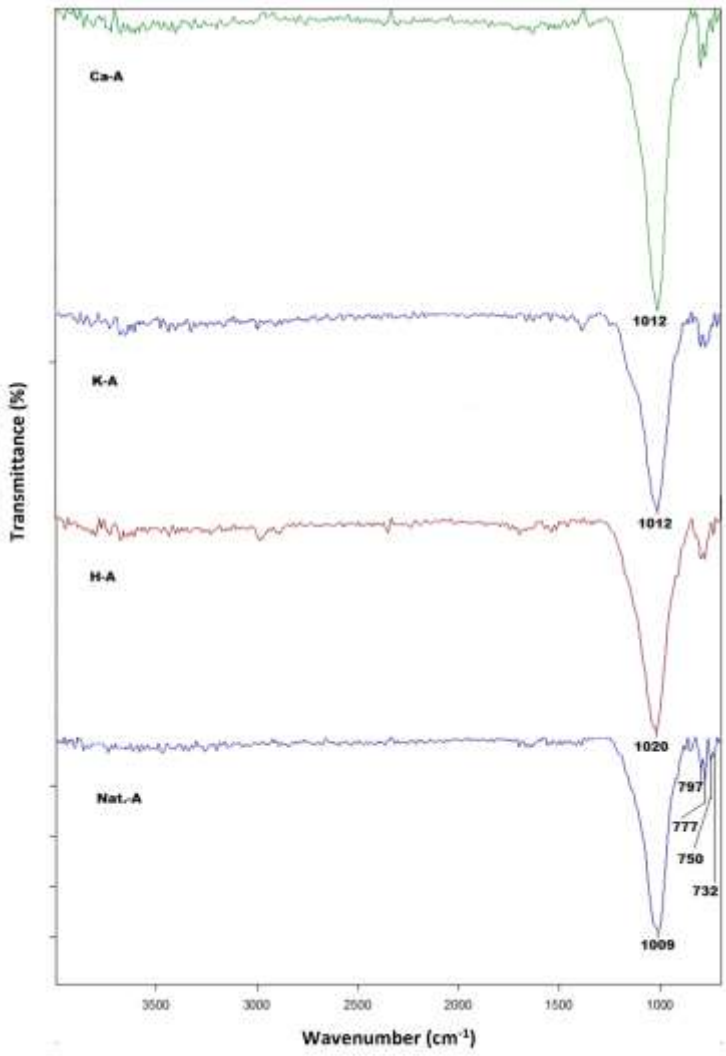


Figure 2. FT-IR spectra of natural and ion-exchanged analcime zeolite samples

3.4. SEM Analysis

Figure 3 showed that the SEM images of natural and ion-exchanged analcime zeolite and the analcime samples exhibited a similar morphology. Analcime sample present as euhedral crystals associated with quartz, feldspar and clay mineral [2]. The association of analcime with potassium feldspar is particularly common.

4. CONCLUSIONS

In the present study, characterization of natural and ion-exchanged analcime samples was performed using XRD, XRF, SEM and FT-IR analyses methods. The XRD patterns showed that the zeolite samples contain analcime and quartz, feldspar and clay mineral as external zeolite component. XRD patterns showed that there are no appreciable changes in the peak reflections after salt solution treatment. Acid treatment of analcime sample led to decationiation and dealumination of the crystal structure. In addition to, the intensity of the diffraction peak corresponding to quartz increased after acid treatment. As a result of the reduction of Al cations, the main band at 1009 cm^{-1} shifted to higher wavelength (1020 cm^{-1}).

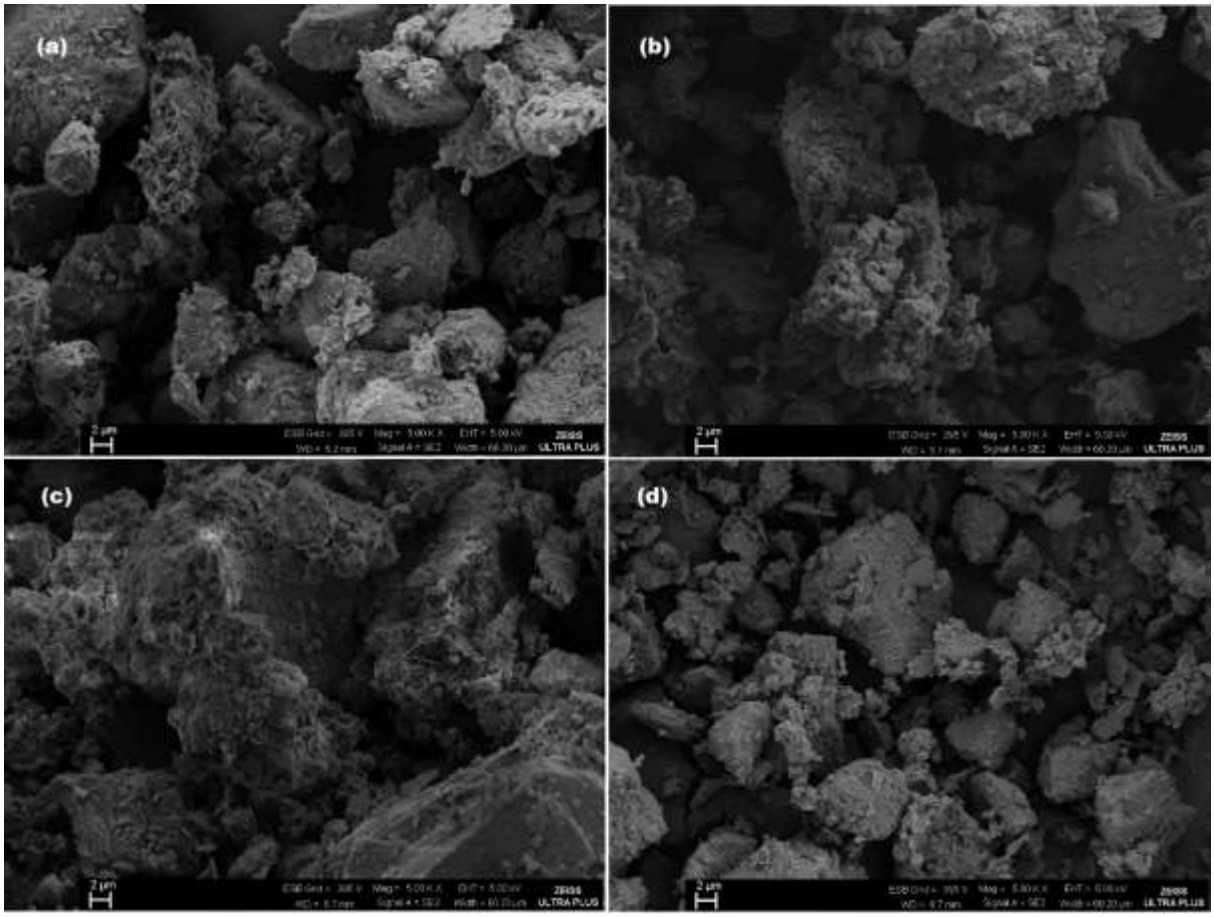


Figure 3. SEM images of (a) natural, (b) Ca-A, (c) K-A and (d) H-A samples

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CONFLICT OF INTEREST

The author stated that there are no conflicts of interest regarding the publication of this article.

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