

8th Serbian-Croatian-Slovenian Symposium on Zeolites



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Editors

Vesna Rakić
Jasna Hrenović
Alenka Ristić

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RIETVELD ANALYSIS OF ZEOLITIC TUFF MODIFIED BY ACID TREATMENT

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ABSTRACT

Acidic zeolites are widely used in the chemical and petroleum industry because of their catalytic activity, remarkable reaction selectivity, and excellent chemical and thermal stability. In this paper, data on the structural properties of the acid treated natural zeolitic tuff are presented.

Keywords: acid treatment, natural zeolite, Rietveld analysis.

INTRODUCTION

The acid treatment of zeolite is very important process for obtaining a new material [1]. Acidic zeolites are widely used in the chemical and petroleum industry because of their catalytic activity, remarkable reaction selectivity, and excellent chemical and thermal stability. During the acid treatment of clinoptilolite, occurs ion exchange of the present cations with hydronium ion. As the acid concentration increases, Al–O bond hydrolysis occurs. Based on the structural analysis (X-ray analysis) it was found gradual conversion of aluminum into hydrated Al, where aluminum is in octahedral coordination [2]. So, not only does H_3O^+ be in a removable position, but also aluminum. The motivations for this work are 1) based of X-ray powder diffraction patterns obtained the structure parameters.

EXPERIMENTAL

The starting materials for investigated was a sample of clinoptilolite tuffs of deposit Novakovic (Republic of Bosnia and Herzegovina). For analysis were used the purified samples with the grain size is of $-63 + 0 \mu m$. Details on experimental work are presented in the literature [3].

Four samples were chosen for structure analysis: Ns – starting sample of zeolitic tuff, N 0.1 – sample treated with 0.1M HCl, N1 – sample treated with 1M HCl and N2 sample treated with 2M.

The X-ray powder diffraction (XRPD) patterns of samples were obtained on a Philips PW-1710 automated diffractometer using a Cu tube operated at 40 kV and 30 mA. The instrument was equipped with diffracted beam curved graphite monochromatic and a Xe-filled proportional counter. The XRPD data were refined to the both structure models with the aid of computer program Fullprof [4]. For a Rietveld profile fitting method the XRPD data were collected by using the step scanning mode in the range of Bragg angle $2\theta = 4-35^\circ$ at each 0.02 step counting for 12.5 s. The divergence and receiving slits were fixed at 1° and 0.1 mm, respectively. All the XRPD patterns measurements were performed *ex situ* at the room temperature in a stationary sample holder [5].

RESULTS AND DISCUSSION

Acid modifications (dealumination) to the zeolite framework can have significant impact on structural properties of zeolites. The process of dealumination are followed by changes in the Si/Al of atomic ratio, and reflect in the corresponding change in the structural parameters. The crystal structures of samples Ns and N 0.1 were refined in space group $C2/m$, structural model whis is used was Takeuchi [6]. Structure model have a disorder distribution of Si/Al in

tetrahedral positions, as well as disorder occupations for cationic positions in zeolite framework. The structure of dealuminated zeolite N1 and N2 were refined in space group C2/m with disorder distribution of Si/Al, determined by the authors Ambruster and Yang [2]. This structure model has a disorder distribution of Si/Al in tetrahedral positions and part of Al atoms is present in octahedral position. The relevant structural and profile parameters factors are given in Table 1. Results of the Rietveld profile refinement of the samples are presented in Figure 1.

Table 1. Data collection and refinement parameters obtained by Rietveld's method of acid-treated zeolite.

sample	N _s	N _{0.1}	N ₁	N ₂
prof.function	TCH – pV	TCH – pV	TCH – pV	TCH – pV
space group	C 2/m (12)	C 2/m (12)	C 2/m (12)	C 2/m(12)
a (Å)	17.661 (4)	17.675 (2)	17.603 (3)	17.634 (3)
b (Å)	17.871 (3)	17.892	17.832 (3)	17.853 (3)
c (Å)	7.3963 (3)	7.4088 (2)	7.377 (3)	7.3991 (3)
β	116.267	116.36	116.52 (3)	116.34 (2)
V (Å ³)	2093.32 (3)	2099.37 (2)	2072.24	2087.681
Chi ²	2.0	2.12	1.22	1.30
R _{wp}	13.8	13.0	10.1	9.69
R _p	10.1	9.43	7.76	7.59
R(F)	9.56	7.32	9.5	7.53
R(B)	9.11	7.29	9.7	9.60

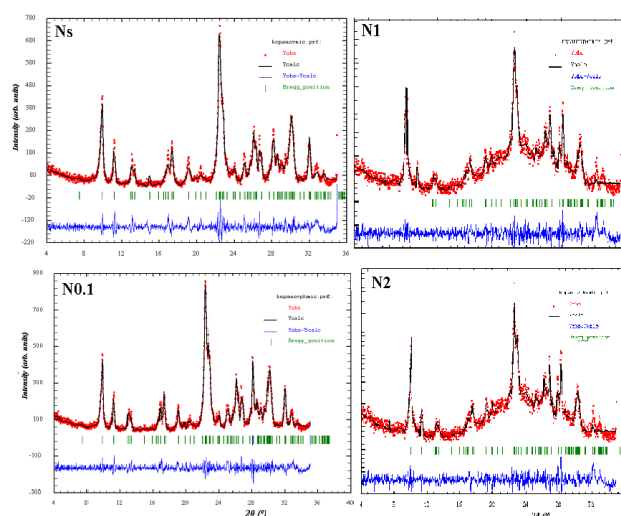


Figure 1. Rietveld refinement patterns for starting and dealuminated zeolite: The dots represent the observed intensities, and the solid line is the calculated one. A difference (obsd-calcd) plot is shown beneath.

The main problem in solving the structure of dealuminated zeolite is the appearance of the phenomena of order-disorder distribution of Al–Si and extraframework Al. Based on the investigation of Wust et al. [2], dissolved Al³⁺ from the framework surface are incorporated into the channel. The Al/Si tetrahedral distribution is highly disordered, indicated by T – O distances (tetrahedral and oxygen). In the structure of clinoptilolite, the existence of five tetrahedral positions is established. The length of the T–O bond indicates the presence of aluminum (Al³⁺) in one of these tetrahedral positions; the highest probability of finding Al³⁺ is in the T2 position. With an increase in the concentration of acids over 0.1 M HCl, there is a breakdown of Al – O – Si bonds and the establishment of new shorter Si – O – Si bonds at the

positions of tetrahedral cavities. The values of bond distances T–O (T= Al/Si) are presented in Table 2. The structure of obtained structure are presented in Figure 2.

Table 2. Average T – O (Å) distances for starting and dealuminated zeolite.

average T – O (Å)	N _s	N _{0.1}	N ₁	N ₂
<T ₁ –O>	1.635	1.637	1.578	1.60
<T ₂ –O>	1.648	1.649	1.604	1.62
<T ₃ –O>	1.632	1.633	1.610	1.60
<T ₄ –O>	1.617	1.619	1.599	1.57
<T ₅ –O>	1.637	1.645	1.603	1.6
<T–O>	1.63	1.64	1.598	1.59

The hydrated cation of aluminium can now occupy the cationic sites in the clinoptilolite channels, achieving octahedral coordination with water molecules or oxygen from the extraframework [2]. Nightingal [7] calculated that the hydration radius of Al³⁺ (4.75 Å), that is the approximate value of the hydration radii of the cation Mg²⁺ (4.28 Å) and Ca²⁺ (4.12 Å). Based on these values, the hydrated aluminum may most likely occupy the cation in positions of M4 in channel A or M2 in channel B. In M4 position it can exist as Al(OH)₃, at other cationic sites, where the electric field is stronger, it is probably in the form of $Al(OH)_2^+$, Figure 2.

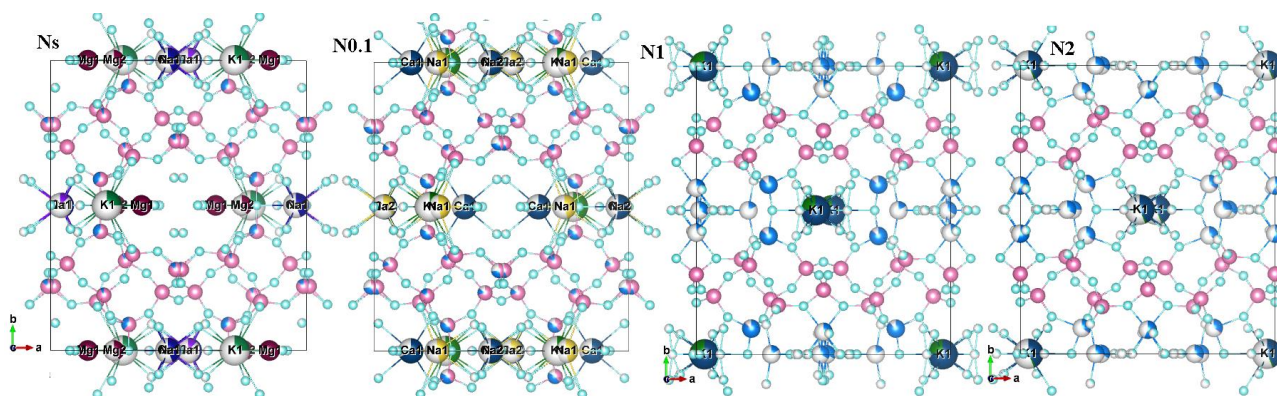


Figure 2. The refined structures of observed starting and acid treated zeolitic tuff of Novaković deposit.

CONCLUSION

The main problem in solving the structure of dealuminated zeolite is the appearance of the phenomena of order-disorder distribution of Al–Si and extraframework Al. The processes of dealumination are followed by changes in the Si/Al atomic ratio, and reflect in the corresponding change in the structural parameters.

1. The crystal structures of samples N_s and N_{0.1} were refined in space group *C2/m*, structural model which is used was Takeuchi [6].
2. The structure of dealuminated zeolite N₁ and N₂ were refined in space group *C2/m* with disorder distribution of Si/Al, determined by the authors Ambruster and Yang [2].

Based on the presented parameters for the structure of dealuminated zeolites, it can be concluded that with increasing acid concentration, cations Na, Mg, and Ca leave their cationic positions. The dealuminated Al from tetrahedral coordination goes to octahedral coordination.

Based on these values, the hydrated aluminum may most likely occupy the cation in positions of M4 in channel A or M2 in channel B.

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