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 zeolitite 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 parametres.

EXPERIMENTAL

The starting materials for investigated was a sample of clinoptilolite tuffs of deposit Novakovic (Republic of Bosniaand Herzegovina). For analysis were used the purified samples with the grain size is of -63 + 0 μm. 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 $2\Theta = 4-35^o$ 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 whit disorder distribution of Si/Al, determined by the authors Ambruster and Yang [2].This structure model have 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 Figure1.

Table1. Data collection and refinement parameters obtained by Rietveld's method of acid-treated zeolite.

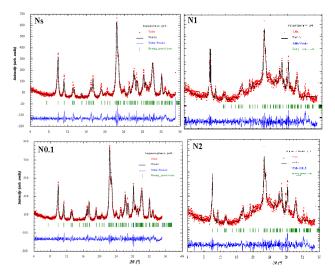| sample	N_S	$N_{0.1}$	N_1	N_2
prof.function	TCH – pV	TCH – pV	TCH – pV	TCH – pV
space group	$C\,2/m$ (12)	$C\,2/m$ (12)	$C\,2/m$ (12)	$C\,2/m$(12)
a (Å)	17.661 (4)	17.675 (2)	17.603 (3)	17.634 (3)
b (Å)	17.871 (3)	17.892	17.832 (3)	17.853 (3)
c (Å)	7.3963 (3)	7.4088 (2)	7.377 (3)	7.3991 (3)
β	116.267	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 is solving the structure of dealuminated zeolite is the appearance the phenomena of order-disorder distribution of Al−Si and extrafarmework Al. Based the investigation of Wust et al. [2], dissolved Al^{3+} from the framework surface are incorporated into the channel. The Al/Si tetrahedral distribution is highly disorder indicated by T − O distances (tetrahedar and oxygen). In the structure of clinoptilolite has established the existence of five tetrahedar positions. The length of the T–O bond, indicates the presence of aluminum (Al^{3+}) in one of these tetrahedar positions, the highest probability of finding Al^{3+} is in the T2 position.With a increase 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
$\langle T_1 - O \rangle$	1.635	1.637	1.578	1.60
$\langle T_2 - O \rangle$	1.648	1.649	1.604	1.62
$\langle T_3 - O \rangle$	1.632	1.633	1.610	1.60
$\langle T_4 - O \rangle$	1.617	1.619	1.599	1.57
$\langle T_5 - O \rangle$	1.637	1.645	1.603	1.6
$\langle T - O \rangle$	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 extrafarmework [2]. Nightingal [7] calculated that the hydration radius of Al^{3+} (4.75 Å), that is the approximate value of the hydration radii of the cation Mg^{2+} (4.28 Å) and Ca^{2+} (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.
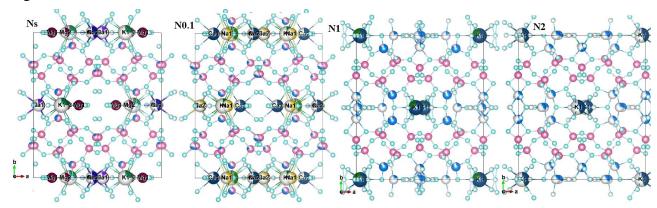

Figure 2. The refined structures of observed starting and acid teatred zeolitic tuff of Novaković deposit.

CONCLUSION

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

1. The crystal structures of samples Ns and N 0.1 were refined in space group *C*2/*m*, structural model whis is used was Takeuchi [6].

2. The structure of dealuminated zeolite N1 and N2 were refined in space group C2/m whit disorder distribution of Si/Al, determined by the authors Ambruster and Yang [2].

Based on the presented parameter 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 go 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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