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EFFECT OF THE ACID TYPE ON THE NATURAL ZEOLITE STRUCTURE

Fehime Çakıcıoğlu-Özkan[1]*, Metin Becer[1]

İzmir Institute of Technology, Chemical Engineering Department, Gülbahçe Köyü, Urla 35430, İzmir-Turkey.

Abstract: In this study, Clinoptilolite-rich zeolitic tuff was treated with acids such as HCl, HNO_3, H_2SO_4, and H_3PO_4. The effect of periods of time (3 hours and 6 hours), concentration (1 M, 2 M, 3 M, 5 M, and 10 M) and the type of acid were taken as parameters. In the characterization of the zeolites, XRD, ICP-AES, and FTIR techniques were used. As the acid concentration and the treatment time were increased, the aluminum and cation removal from the structure was increased. HCl and HNO_3 were more effective acids for the dealumination than H_2SO_4 and H_3PO_4. It was found out that considerable change in the texture of the zeolitic tuff did not take place during the H_3PO_4 treatment. On the other hand, acid treatment resulted in an increase in the micropore surface area and volume of the zeolite. The specific surface area of the zeolitic tuff (19 m^2/g) was increased up to 213 m^2/g, 236 m^2/g, 202 m^2/g, 118 m^2/g with HCl, HNO_3, H_2SO_4, and H_3PO_4 treatments, respectively. In the cases of HCl and HNO_3, an increase in their concentration furthermore than 5 M caused to the collapse of the structure.

Keywords: Acid treatment, texture, clinoptilolite, modification.

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***Corresponding author.** e-mail: fehimeozkan@iyte.edu.tr.

INTRODUCTION

Zeolites are porous, crystalline, hydrated aluminum silicates of alkali and alkaline earth cations that possess a three-dimensional structure. The zeolite framework consists of an assemblage of SiO_4 and AlO_4 tetrahedra joined together in various regular arrangements through shared oxygen atoms to form an open crystal structure containing pores of molecular dimensions into which guest molecules can penetrate. The negative charge created by the substitution of an AlO_4 tetrahedron for a SiO_4 tetrahedron is balanced by exchangeable cations (e.g., Na^+, K^+, Ca^{2+}, Mg^{2+}), which are located in the structural channels and cavities throughout the structure (1).

Clinoptilolite, which is a member of the heulandite group, is the most abundant natural zeolite minerals (2). Compositions and purity vary widely among the deposits throughout the world. There is always the problem of impurities, which block the channel system. The cations, which occupy the considerable space in the micropores of zeolites, are removed with acid treatment. Besides, to the cations, the framework aluminum may be removed. This is called as dealumination and may result with the destruction of the texture of zeolite mineral. Therefore, the advantage of the acid treatment is to remove the impurities and so develop the new pores. The disadvantage, which encountered at high acid concentration, is the dealumination that can cause the partial or total destruction of the zeolite framework. In acid treatment, besides to acid treatment conditions (acid concentration, treatment temperature and time), and the nature of acid the resistant properties of natural zeolite against to acid are all important parameters. Many of these parameters have been extensively studied for Y-zeolite (3), mordenite (4) and faujasite (5), phillipsite (6). For clinoptilolite, HCl is the widely used acid and its effect on the texture was studied by means of N_2 (7, 8), H_2O (9) and CO_2 (10) adsorption.

In this study, it aimed to present the effect of the acid (HCl, HNO_3, H_2SO_4, H_3PO_4) treatment on the textural properties of natural zeolite mineral, clinoptilolite. The treated zeolite can be used as support for photocatalysis application for future study.

MATERIALS AND METHODS

Materials

All chemicals were of analytical grade and were used without further purification. Deionized water was used for preparation of the solutions.

Methods

The zeolitic tuff, obtained from Gördes, (Turkey) was crushed and sieved to the particle size in the range of 850– 2000 μm. Then it was washed with distilled water for 2 hours at 60 °C to remove the soluble salts. The zeolite obtained (NCW) was dried in a vacuum (10^{-3} mbar) oven at 160 °C for 24 hours and stored for acid treatment.

In the acid treatment, five grams of zeolite NCW and 100 mL of acid (HCl, HNO_3, H_2SO_4, H_3PO_4) solutions were mixed in a water bath (GFL 1092) with a mixing rate of 200 min^{-1} at 60 °C for 6 or 3 hours. Then zeolites are washed with double distilled water until no chloride was detected into the solution. The zeolites obtained were stored for characterization. The chemical composition of the zeolites was obtained by measuring the cation content of the solutions by means of Inductively Coupled Plasma Atomic Emission spectroscopy (ICP-AES 96, Varian). The mineralogical and crystallographic determination was made by using X-ray diffraction (X-Pert Pro Diffractometer) using CuKα radiation (λ =1.54051 Å) at 45 kV and 40 mA with a step size of 0.02° 2Θ in the 5-40° 2Θ range. The nitrogen adsorption isotherms of the zeolites were obtained at liquid nitrogen temperature (77 K) by using a volumetric adsorption system (ASAP 2010, Micromeritics). Prior to the determination of the adsorption isotherms, the zeolites were degassed for 4 h at 350 °C. The infrared spectra (FTIR) of the zeolites in the range of 400-4500 cm^{-1} were recorded with a Fourier transformed infrared spectrometer (FTIR-8601-Shimadzu) at room temperature by using KBr (1/50) pellet technique.

In the code of the treated zeolites obtained, the first letter shows the acid used; C for HCl, S for H_2SO_4, N for HNO_3 and P for H_3PO_4. The following number is the acid concentration (M). With HCl, the effect of the treatment time was also studied and coded as 6h or 3h (treatment period for 6 hours or 3 hours respectively). Treatment period with other acids is 6 hours.

RESULTS AND DISCUSSION

The chemical composition of the washed natural zeolite (NCW) was found as (wt. %): 14.1 Al_2O_3, 64.2 SiO_2, 1.8 MgO, 1.7 Na_2O, 5.3 K_2O, 1.0 CaO, 1.8 Fe_2O_3, and 10.3 H_2O. As seen from the XRD pattern of the NCW (Figure 1), the natural zeolite is rich in clinoptilolite (2Θ=9.92°, 22.49°, 30.15°) with the presence of low-cristoballite and quartz (2Θ= 26.64°) as impurities. Considering the chemical composition the natural zeolite used in this study was classified as Ca-clinoptilolite (1).

In the acid treatment studies, both acid concentration and treatment time were effective; the higher the acid concentration and the longer the treatment time, the more cation and aluminum were removed from the zeolite structures, causing the increase in Si/Al ratios (Table 1). This is due to the attack of a proton to cationic [Al-OM]z and / or aluminum sites [Al-OH]z and is represented by the following reactions (11).

$$[\mathrm{Al\text{-}OM}]_z + n\mathrm{H}^+(aq) \rightarrow [\mathrm{Al\text{-}OH}]_n + \mathrm{M}^{n+}{}_{(aq)} \qquad (1)$$

$$[\mathrm{Al\text{-}OH}]_z + n\mathrm{H}^+(aq) \rightarrow [\mathrm{Al\text{-}OH}]_z + \mathrm{M}^{n+}{}_{(aq)} \qquad (2)$$

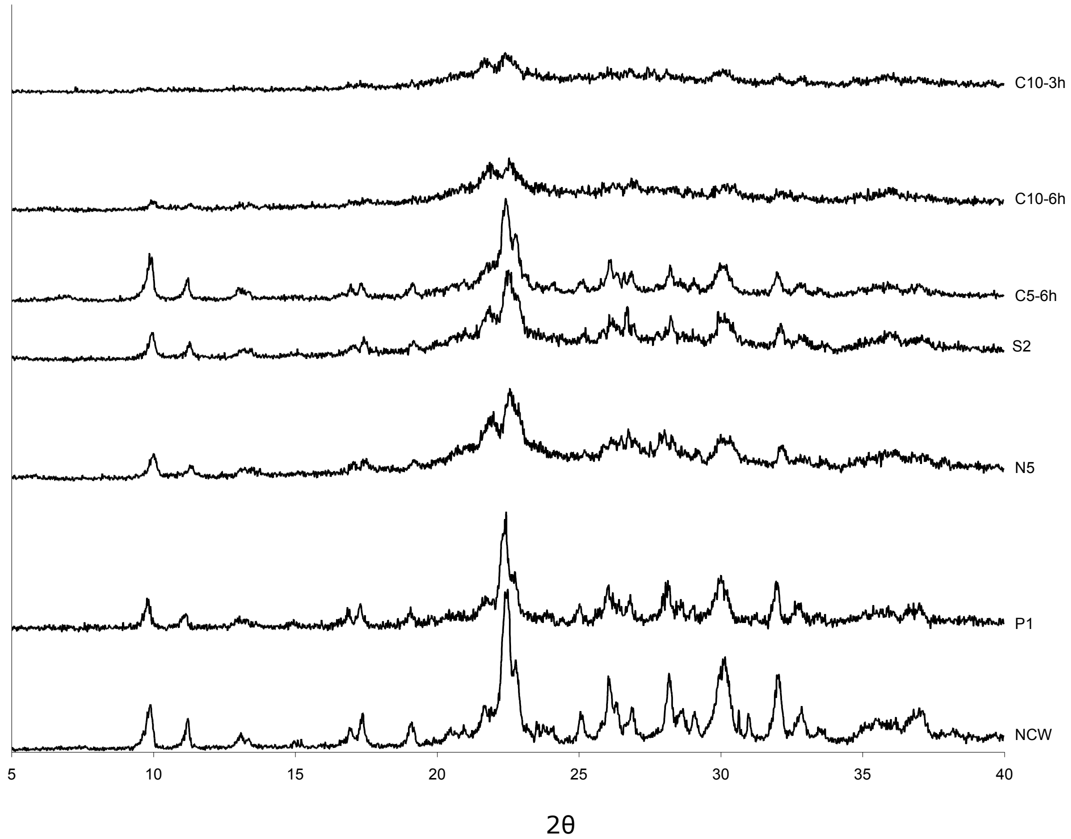

Figure 1. X-ray diffraction patterns of the untreated (NCW) and acid treated zeolites.

Figure 1 displays the representative XRD patterns of the natural and its acid treated forms. It was seen that HCl, HNO_3 and H_2SO_4 treatments are very effective on the crystal structure of the zeolites: the patterns of the HCl treated samples showed that, as the acid concentrations and treatment period increased, intensities of the characteristic peaks decreased, meaning a loss in the crystallinities of the zeolites. From the XRD data of the HCl-treated zeolites for 6 h, it is clear that, with 5 M and 10 M HCl treatments, the characteristic peaks almost disappeared which means that the crystal structures were collapsed and the amorphous phases were generated. XRD results of HCl, H_2SO_4 and HNO_3 treated samples confirmed the Si/Al ratios indicating that more framework aluminum atoms were affected leading to more crystallinity loss. As expected, H_3PO_4 treatment did not affect the crystal structure so much for being the weakest acid of all. Peak intensities decreased slightly and no other extra peaks for any phosphate compounds were detected in the pattern.

Figure 2 displays the FTIR spectra of the representative acid-treated zeolites. The strong band at 1060 cm^{-1} is responsible for framework stretching vibration in T (Si or Al)-O-Si units. As seen from the Figure the position of the band shifted from 1065 cm^{-1} to 1088 cm^{-1} with increasing the Si/Al ratio from 4.04 (for NCW) to 10.8 (for C10-6h). The O-T-O pseudo-lattice vibrations of free TO_4 tetrahedra, O-T-O framework vibrations and the vibrations of hydroxyl in the extra framework of Si-OH and Si-OH-Al groups were estimated by calculating the area under the peaks among the frequencies 570-680 cm^{-1}, 850-1600 cm^{-1} and 3101-3940 cm^{-1}, respectively.

The nitrogen adsorption isotherm data were evaluated to understand the effect of acid type on the textural properties of the zeolites by using the t-plot and Langmuir and Dubinin-Astakhov (D-A) methods and the results were presented in Table 2. From the properties given in the Table, it was understood that the acid treatment caused a noticeable increase in the specific surface area (A_L), total (V_{max}) and micropore volumes (V_{mic}) with respect to the untreated one. However, the nature of the acid used has a different effect on the texture of the zeolite since the ligands cause to form the complexes on the zeolite surface. Surface central atom T (Al or Si) on the zeolite is the center to form an outer-sphere complex on the protonated zeolite surface ($T\text{-}OH^{2+}$) with the ligands (L^{n-}) (12, 13).

Table 1. Cations content of the zeolites, (wt %.).

Cations	**NCW**	**S1**	**S2**	**C1-6h**	**C3- 6h**	**C5-6h**	**C10-6h**	**C3- 3h**	**C10-3h**	**N1**	**N2**	**N5**	**P1**
Al	15. 9	14	13. 8	13. 9	11	9. 4	7. 8	12. 6	9. 4	12. 7	12. 6	11. 9	14
Ca	2. 9	0. 3	0. 1	0. 3	1. 5	0. 02	1. 2	1. 6	1. 1	0. 1	1. 8	0. 05	2.5
Fe	2. 5	0. 6	0. 5	1. 2	2. 7	0. 9	2. 4	2. 9	2. 9	0. 8	1. 8	0. 9	3.1
K	9. 9	8. 8	8. 8	9. 3	1. 8	8. 2	1. 4	1. 9	1. 3	8. 5	2. 8	8. 4	6.0
Mg	1. 4	0. 7	0. 7	0. 8	1. 5	0. 5	1. 5	1. 9	1. 7	0. 7	1. 7	0. 7	2.0
Na	3. 2	2	2. 1	1. 5	1. 4	1. 9	1. 5	1. 7	1. 4	2. 1	1. 4	1. 9	1. 8
Si	64. 2	73. 6	73. 9	73	80	79	84	76. 6	82	75. 1	78. 4	76. 1	70. 2
Si/Al	4. 04	5. 25	5. 35	5. 25	7. 3	8. 4	10. 8	6. 08	8. 7	5. 91	6. 18	6. 39	5. 01

Table 2. Nitrogen adsorption characteristics of original (NCW) and acid treated zeolites

	NCW	**C1-6h**	**C3-6h**	**C5-6h**	**C10-6h**	**C3-3h**	**C10-3h**	**S1**	**S2**	**N1**	**N2**	**N5**	**P1**
Si/Al	4.04	5.25	7.3	8.4	10.8	6.08	8.7	5.25	5.35	5.91	6.18	6.39	5.01
A_L[a]	19	93	203	213	173	182	179	171	202	202	226	180	118
V_{mic}[b]	0. 005	0. 029	0. 064	0. 063	0. 047	0. 056	0 .047	0. 048	0. 055	0. 062	0. 068	0. 049	0. 04
V_{lim}[c]	0. 01	0. 036	0. 072	0. 078	0. 059	0. 064	0. 073	0. 060	0. 079	0. 082	0. 077	0. 072	0. 043
A_{Ext}[b]	3	6	15	29	29	17	33	25	34	20	23	29	7
n[c]	1.00	1.60	1.76	1.61	2.38	2.26	1.02	1.61	1.03	1.12	2.63	1.00	1.88
E[c]	11	19	28	22	22	21	23	29	27	35	25	27	25
V_{max}[d]	0.013	0.04	0.078	0.089	0.073	0.072	0.079	0.073	0.086	0.086	0.09	0.078	0.05

[a] A_L: Langmuir surface area (m^2/g)

[b] V_{mic} and A_{Ext} are micropore volume (cm^3/g) and external surface area (m^2/g) respectively, from t-plot.

[c] V_{lim}, Limiting micropore volume (cm^3/g), n, exponential constant, and E, Characteristic Energy (kJ /mol), from Dubinin – Astakhov (P/Po= 0.0001-0.1).

[d] V_{max}: Maximum amount adsorbed at a relative pressure (P/P_o) of 0.89.

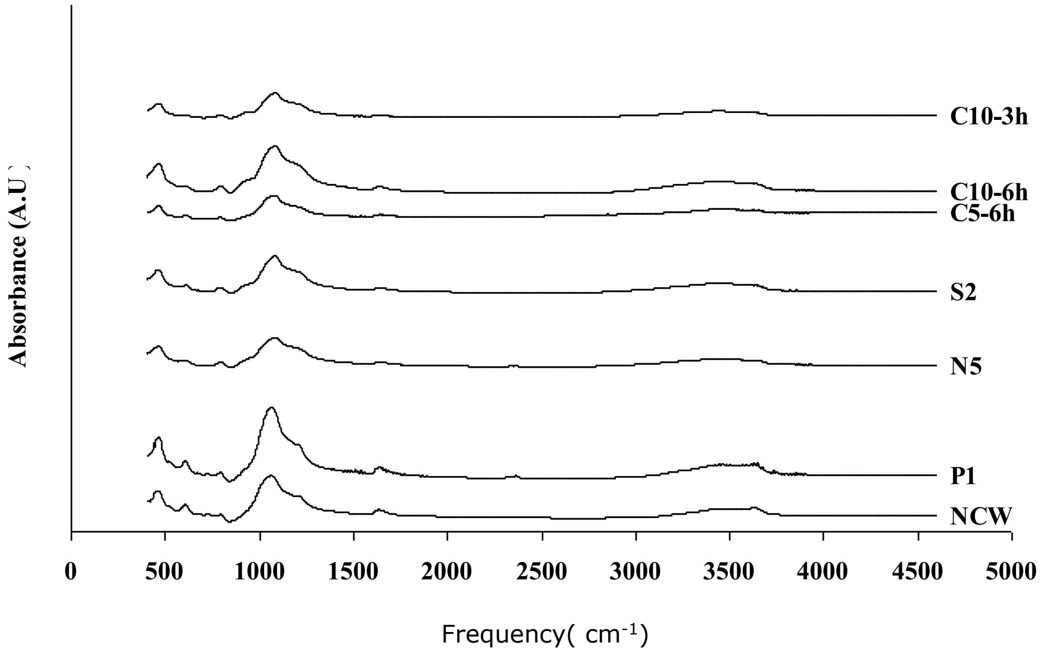

Figure 2. FTIR spectrum of untreated (NCW) and acid treated zeolites.

$[\text{T-OH}]_z$ $+L^{n-}_{(aq)}$ + $H^+_{(aq)}$→ $[\text{T-OH}_2^+]_z$ +
L^{n-} (aq) →$[\text{T-OH}_2^{+--n-}]z$ (3)

HCl and HNO_3 acids can cause surface precipitation by adsorbing on the external surface to form an outer-sphere complex that involves ion exchange reaction (4). The inner-sphere complexes on the protonated sites can also occur

$[\text{T-OH}]_z$ $+L^{n-}$(aq) + $H^+_{(aq)}$→ $[\text{T-OH}_2^+]_z$ +
$L^{n-}_{(aq)}$ →$[\text{T-L}^{(-n+1)}]_z$ (4)

Readsorption of the dissolved cation (M^{n+}) in the solution covalently bonded to the surface to form an inner-sphere complex. However, this kind of complex occurred with the extensive ion-pairing ligand such as SO_4^{2-} with the multivalent cation

$[\text{T-OH}]_z$ $+L^-_{(aq)}$ $+M^{n+}_{(aq)}$→ $[\text{T-L-M}^{n+}]_z$ +
OH^- (5)

$[\text{T-OH}]_z$ $+L^-_{(aq)}$ $+M^{z+}$(aq)→ $[\text{T-OM-L}^{n-2}]_z$ +
H^+ (6)

The zeolites treated with bi- and tri-protic acids such as H_2SO_4 and H_3PO_4 have smaller microporous volumes when compared with the treated with mono-protic acids such as HCl and HNO_3. With acid treatments, the maximum nitrogen adsorption capacity, V_{max} of natural zeolite increases in a way similar to the pore volumes and area. The micropore volumes are obtained from the t-plot method (V_{mic}) and the Dubinin-Astakhov method (V_{lim}). A change in the V_{lim} values has the same trend as in the V_{mic} values but are higher. For the HCl and HNO_3 treated zeolites both micropore volume increases markedly with increase in the Si/Al ratio and then decrease with further increase in the concentration of the acid. The reduction in micropore volume due to structural degradation of the zeolite crystals and the complexes (Eq.4 and Eq.5) formation hardly occurs but does for only HCl and HNO_3 acid treatment. In the case of NCW zeolite, the volume of pores accessible to nitrogen is only 0.005 cm^3/g, thus indicating that most of the pores are blocked by the cations as an impurity. In HCl treatment, as the acid concentrations increased, the micropore volumes of the zeolites increased up to 0.064 cm^3/g for 3 M HCl but decreased with the further increase in the acid concentrations. The external surface areas of the HCl treated zeolites increased gradually with increasing the Si/Al ratio and reached a maximum of 33 m^2/g at 10 M HCl treatment. Similar behavior was observed for other protic acid HNO_3 treated samples. On the other hands, the most effective acid was H_2SO_4 on the developing external surface even the extracted aluminum atoms were not so high as HNO_3 and HCl treatment. This can be explained with the formation of inner-sphere complexes caused to more increase in the external surface areas (Eq.6 and Eq.7). H_3PO_4 treatment increased the Si/Al ratio as well but not so much as other acids. However, it is very effective in developing the micropore structure without destruction of the crystal structure.

The parameter E, adsorption characteristic energy, calculated from the Dubinin-Astakhov equation is very low for original NCW zeolite with respect to acid treated forms. The formation of new pores accessible for nitrogen causes to increase the E values which is closely related to adsorbate-adsorbent interaction (14). According to Suzuki (15), the parameter n in the D-A equation may originally be considered to have integer values of 1, 2 and 3 corresponding to adsorption on the surface, in the micropores and ultra-micropores respectively. In the present study, its value is 1 for untreated natural zeolite, NCW and achieves the value up to about 2 for acid treated zeolites.

HCl, HNO_3, H_2SO_4, and H_3PO_4 acids were used in the acid treatment to improve the textural properties of the natural zeolite. The cations that occupy the considerable space in micropores of zeolites and structural aluminum were removed during the treatment. Nitrogen was able to diffuse more easily and adsorb more densely in the cavities of the acid treated zeolite. H_3PO_4 treatment did not destroy the framework of the zeolite structure and improved the microporosity. In the case of the HCl and HNO_3 treatment, the micropore structure of the zeolites was improved. However, a decrease in microporosity was observed in HCl and HNO_3 concentrations higher than 3M.

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