

Kinetics of proton transfer in the zeolitic tuff

Research Article

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Abstract: The kinetics of a proton transfer into dilute acid solutions containing natural zeolitic tuff was studied by following the pH evolution of the liquid phase. Four different solutions with tuff contents of 9, 3, 1 and 0.5 (% wt) and three different particle size fractions ($\leq 2000 \mu\text{m}$) were studied. The proton concentration of the solution was decreased by increasing the zeolite amount and decreasing the particle size fraction. The proton transfer reaction was analyzed with chemical reactions and diffusion model equations. Analysis shows that the adsorption and/or ion exchange are possible mechanisms and are expressed by a second order reaction model.

Keywords: Zeolite tuff • Clinoptilolite • Particle size • Proton diffusion

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1. Introduction

Clinoptilolite rich zeolitic tuff has been widely studied in aqueous solutions as an ion exchanger in an effort to find applications in industries such as waste water treatment, agriculture application, animal feed, and construction materials [1]. Besides the low cost, the ease of exchange of the cation in their microporous structure makes zeolites profitable as an ion exchanger. The variety, amount and location of the cations (Na^+ , Ca^{2+} , K^+ , Fe^{2+} , Mg^{2+} etc.) present in the zeolite pores are important for industrial applications. In addition to the zeolitic mineral, the tuff also contains non-zeolitic phases such as quartz and calcite. In an aqueous solution some physicochemical phenomena such as hydrolysis, degradation, dissolution and phase transformations can be observed depending on the purity and the chemical composition of the tuff. The chemical behavior of the tuff rich in clinoptilolite mineral in different aqueous media, such as KCl, CuCl_2 [2], HCl and NaOH [3-5] has been studied demonstrated their importance in technology. Most of the previous studies have concentrated on the equilibrium and the neutralization capacity of the clinoptilolite rich tuff [2-5]. The different cation content of the tuff depends on the purity and results in different equilibrium pH in these studies.

Based on these concepts the purpose of this study is to kinetically analyze the proton transfer of the natural zeolitic tuff in dilute HCl solutions by evaluating the effect of the parameters such as amount and particle size of the zeolite.

2. Experimental Procedures

The chemical composition of the tuff used in this study is from the Gördes (Manisa), Fındıcak deposit and was found to contain 14.1% Al_2O_3 , 64.5% SiO_2 , 1.9% MgO , 1.7% Na_2O , 5.3% K_2O , 1.1% CaO , 2.0% Fe_2O_3 and 9.4% H_2O . A Philips X-Pert Pro diffractometer was employed, using $\text{CuK}\alpha$ within the $5-40^\circ 2\theta$ range and 0.02 sec^{-1} step size. The Si/Al ratio was 4.04 and the monovalent to bivalent cation ratio ($(\text{Na}^+ + \text{K}^+)/(\text{Ca}^{2+} + \text{Mg}^{2+})$) was 2.93. The zeolite used in this study was typical clinoptilolite, based on the XRD diagram and the chemical analysis [6]. The tuff includes some impurities such as feldspar ($(\text{Na}, \text{K}, \text{Ca}) \text{AlSi}_3\text{O}_8$) and quartz (SiO_2) as shown in Fig. 1. This natural zeolitic tuff (thereafter Z) was crushed to 2 mm, and then sieved in order to classify the particles into three size ranges: 2000 - 850 μm , 500 - 250 μm and below 150 μm . All particle ranges were further ground to a particle size of less than 100 μm for the XRD experiments.

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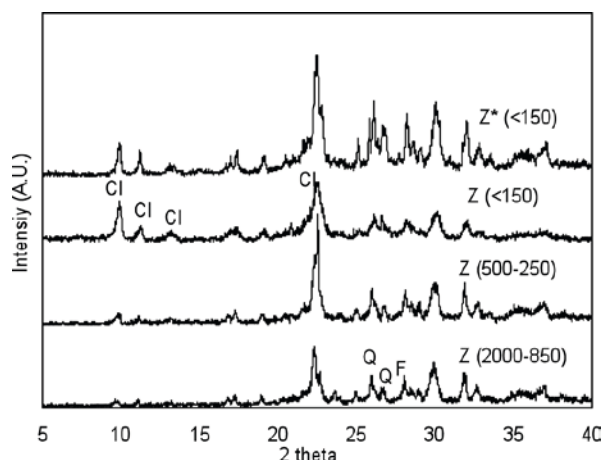


Figure 1. The XRD patterns of the zeolites before acid treatment Cl: clinoptilolite, F: feldspar, Q: quartz, and after acid treatment for a particle size of $<150\ \mu\text{m}$.

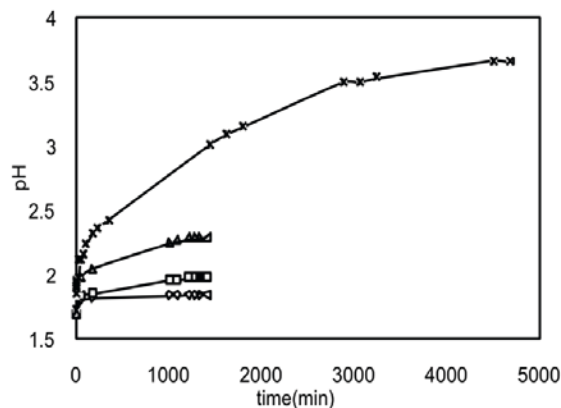
50 mL of 0.02 M HCl solution was added to the different amounts of zeolites, 0.25 g, 0.5 g, 1.5 g, 4.5 g and then shaken at a rotation of 100 rpm in a thermostated shaker (GFL-1092). The pH of the solution was measured against time at room temperature (21°C) using a pH meter (744 Metrohm).

3. Results and Discussion

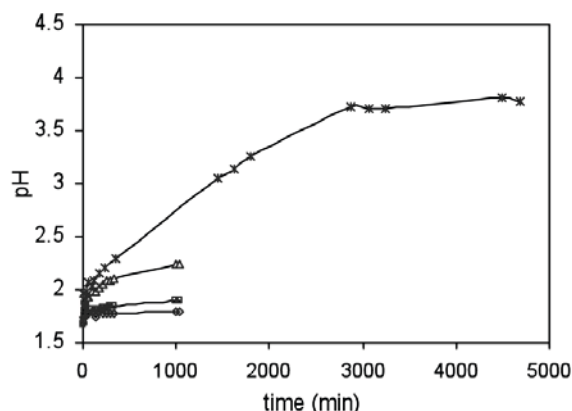
The powder XRD patterns of the zeolites before (Z) and after acid treatment (Z^*) are shown in Fig. 1. A decrease in the characteristic peaks of clinoptilolite around $2\theta = 9.83^\circ$, 11.29° , and 13.15° are seen with increasing particle size and this is likely due to the presence of the non-zeolitic impurities, like quartz (SiO_2) in the big fraction of the tuff. After acid treatment (Z^*), as expected, a considerable decrease in the characteristic peaks of clinoptilolite for the particle size fraction of $<150\ \mu\text{m}$ were not observed. This supports the idea that the crystal structure of zeolitic tuff is still stable after acid treatment.

Fig. 2 shows the change in the pH of the dilute acidic solutions with time depending on the amount of zeolite for different particle size fractions. It is clear from Fig. 2 that the time to reach equilibrium decreases with decreasing amount and particle size of the zeolite. The impurities mentioned before result in delaying the tuff reaching equilibrium by delaying the diffusion of proton to the pores in the crystal.

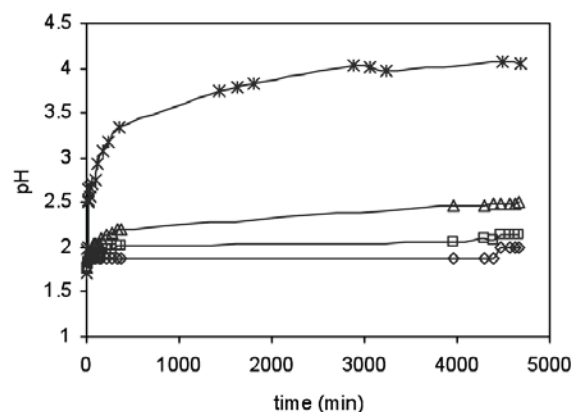
As seen from Table 1, the pH of the aqueous solutions at equilibrium, pH_e increases when a high amount of zeolite with a small particle size was used. Due to the availability of the cations (M) to be exchanged, broken bands occurred when crushing the zeolite.



(a)



(b)



(c)

Figure 2. Change in the pH of the dilute acid solutions with time for the Z in particle size ranges of (a) 2000 - 850 μm ; (b) 500 - 250 μm ; (c) $<150\ \mu\text{m}$, zeolite percent: 0.5% ($\diamond$), 1% ($\square$), 3% (Δ), 9% ($\times$).

Table 1. The kinetic parameters for the adsorption of a proton [H⁺] onto a zeolite particle.

Particle size (μm)	Zeolite concentration % (w/v)	Pseudo-second order							Intra-particle diffusion			
		pH _e	q _e ^(cal) (mg g ⁻¹)	q _e ^(exp) (mg g ⁻¹)	k ₂ (g mg ⁻¹ min)	h* (mg g ⁻¹ min)	Error	R ²	k _{id} (mg g ⁻¹ min ^{0.5})	C (mg g ⁻¹)	Error	R ²
2000-850	0.5	1.85	1.1680	1.1930	0.0338	0.0461	0.0008	0.9935	0.0221	0.3989	0.0367	0.7137
	1	1.98	0.9973	0.9940	0.0147	0.0146	0.0032	0.9671	0.0215	0.2103	0.0101	0.8949
	3	2.29	0.5143	0.5090	0.0455	0.0120	0.0003	0.9899	0.0104	0.1414	0.0045	0.8198
	9	3.65	0.2073	0.2140	0.1500	0.0064	0.0002	0.9667	0.0023	0.0901	0.0010	0.7309
500-250	0.5	1.81	0.8712	0.9860	0.0640	0.0486	0.0113	0.8242	0.0135	0.4771	0.0341	0.4708
	1	1.94	0.8626	0.9410	0.0156	0.0117	0.0047	0.9186	0.0158	0.2997	0.0109	0.7927
	3	2.35	0.4363	0.4460	0.0372	0.0071	0.0006	0.9617	0.0075	0.1694	0.0040	0.7018
	9	3.77	0.2159	0.2150	0.1004	0.0047	0.0130	0.9053	0.0022	0.0926	0.0009	0.8079
<150	0.5	1.88	0.7073	1.3190	0.1584	0.0792	0.0797	0.4791	0.0090	0.4667	0.0507	0.5503
	1	2.17	0.7982	0.9350	0.0200	0.0128	0.0071	0.9205	0.0085	0.3415	0.0151	0.7849
	3	2.50	0.4205	0.4480	0.0406	0.0072	0.0009	0.9496	0.0039	0.1905	0.0036	0.7691
	9	4.06	0.2161	0.2160	0.8383	0.0392	0.0001	0.9610	0.0011	0.1576	0.0019	0.2750

* = $k_2 \times q_e^2$ (The initial rate of chemical reaction when $t \rightarrow 0$)

3.1 Proton transfer kinetics

Two kinetic models: pseudo-second-order chemical reaction and intraparticle diffusion were used to analyze the kinetics of the proton transfer process. The chemical reaction model equation [7] is in the form:

$$q = \frac{tk_2q_e^2}{1 + tk_2q_e}$$

where q and q_e (mg proton/g zeolite) are the proton amount adsorbed by zeolite at time t and equilibrium, respectively, and k_2 (g mg⁻¹ min) is the chemical reaction rate constant.

The intraparticle diffusion model is given by the following equation [8].

$$q = k_{id}t^{1/2} + C$$

Where k_{id} is the intraparticle diffusion rate constant and C (mg g⁻¹) is a constant that gives an idea about the thickness of the boundary layer [9]. These two models are fitted to the experimental data by minimizing the error.

$$\text{Error} = [\sum(q^{(exp.)} - q^{(cal.)})^2]/n$$

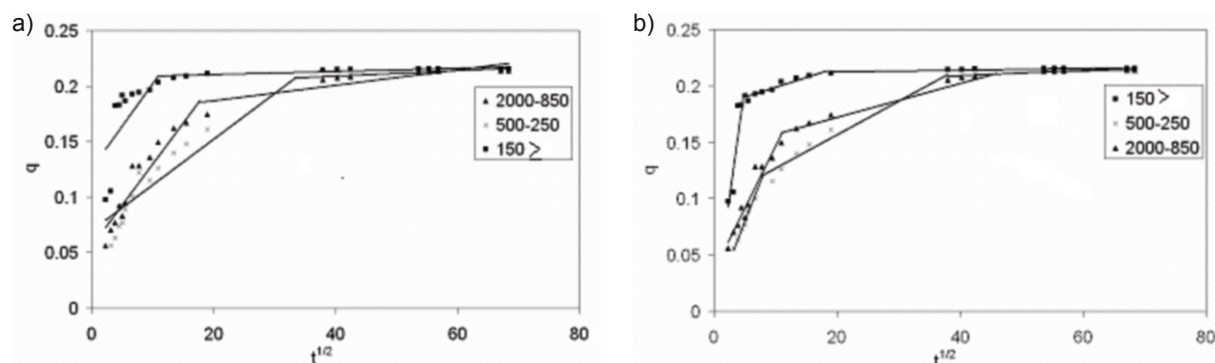
Where the superscripts (exp.) and (cal.) indicate the experimental and calculated values respectively, and

n is the number of the observation. The corresponding model parameters are presented in Table 1. The initial rate of the chemical reaction, h , increases with a decrease in the zeolite amount. The same behavior was observed for the parameter C in the intraparticle diffusion model. The parameter C also increased with a decrease in the particle size. This increase in the amount causes the transfer that is controlled by the chemical reaction and the intraparticle diffusion thereby eliminating the boundary effect and the external diffusion reaction. The proton transfer can be fit by the second-order kinetic model rather than the one stage intraparticle diffusion model for all of particle sizes and the amounts.

The intraparticle diffusion model showing lower representation of the data was used to represent the multi-linear plots of q vs. $t^{1/2}$ curve (Figs. 3a and 3b). The parameters of the two and three-stage intraparticle diffusion models are presented on Table 2. The correlation coefficient is increased when the model is fitted with increasing stages of the intraparticle diffusion model. The transfer rate, $k_{id,i}$ is decreased in the latter stages showing that the transfer process is controlled by these stages in the heterogeneous porous structure of the zeolite. The correlation coefficients are still lower than found in the second order rate model.

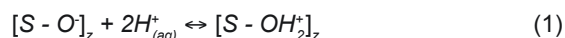
Table 2. The kinetic parameters for a multistage intra-particle diffusion model with a 9 % (w/v) zeolite concentration.

Particle size (μm)	One stage		Two stages				Three stages					
	$k_{id,1}$ ($\text{mg g}^{-1} \text{min}^{0.5}$)	R^2	$k_{id,1}$ ($\text{mg g}^{-1} \text{min}^{0.5}$)	R^2	$k_{id,2}$ ($\text{mg g}^{-1} \text{min}^{0.5}$)	R^2	$k_{id,1}$ ($\text{mg g}^{-1} \text{min}^{0.5}$)	R^2	$k_{id,2}$ ($\text{mg g}^{-1} \text{min}^{0.5}$)	R^2	$k_{id,3}$ ($\text{mg g}^{-1} \text{min}^{0.5}$)	R^2
2000-850	0.0023	0.7309	0.0074	0.8925	0.0007	0.7380	0.0110	0.9347	0.0015	0.9414	0.0001	0.9820
500-250	0.0022	0.8079	0.0041	0.8449	0.0003	0.7983	0.0141	0.9849	0.0030	0.9637	0.0003	0.7983
<150	0.0011	0.2750	0.0076	0.4949	0.0001	0.7923	0.0392	0.8468	0.0018	0.9219	0.0001	0.7684

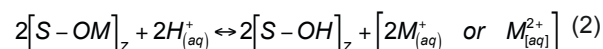
**Figure 3.** The intra-particle diffusion plots with (a) two stage and (b) three stage proton diffusion in the particle size ranges of 2000 - 850 μm , 500 - 250 μm and <150 μm with a 9% zeolite amount (w/v).

4. Conclusions

An analysis of the proton transfer to natural zeolitic tuff was examined kinetically. It was well fitted by a second order chemical reaction model. The possible mechanisms for this process are adsorption on the negatively charged zeolite surface (Reaction 1)



and/or exchange of the cation (M) with the H^+ in the dilute solution phase (Reaction 2).



where S is the surface central metal (Si,Al). The effect of the particle size and the amount of the tuff on the

kinetics of proton transfer in the solution was followed. An application of the intraparticle diffusion model demonstrated that the external film diffusion resistance can be eliminated by increasing the particle size and the amount of zeolite. The multi-stage intraparticle diffusion model concluded that the proton transfer is fast in the early stages, but slow for all of the particle size ranges in the latter stages of the diffusion.

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