

The XRF Value and Surface Area Changes of the Activated and Calsined Clinoptilolite Mineral

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Abstract

Within the scope of this work, the XRF values and surface area changes of clinoptilolite subjected to different time and temperature was investigated. Clinoptilolite (Ca, K₂, Na₂, Mg)₄, Al₈Si₄₀, O₉₆. 24 H₂O) mineral from Gördes-Manisa region in Turkey, with 1-3 and 3-5 mesh size, was used in the experimental studies for the determination of the XRF values and surface area changes. In this study, natural clinoptilolites were characterized before and after acid treatment followed by thermal treatment at 120oC for 0,00, 12 and 24 hours and then respectively calcined at 200oC, 400oC, and 600oC for 5 hours. The measurements in respect to XRF values were made by using X-ray fluorescence spectrometry and the measurements in respect to the surface area changes of clinoptilolite samples (m²/g) were carried out with nitrogen gas adsorption technique in the liquid nitrogen atmosphere at -98oC. The surface area changes were obtained at the maximum level for 24 hours activation and calcination at 200°C.

Key words: Clinoptilolite, activation, calcination, XRF values, surface area changes

1. Introduction

Zeolite is the name of a group of minerals. They are formed by the change of volcanic ashes in water. Over the last 200 years, 50 types of natural zeolites and more than 200 types of synthetic zeolites have been defined and it has been seen that 9 types of zeolite are found in the nature in large quantities and as highly pure deposits. These are analcime, clinoptilolite, chabazite, erionite, ferriyonit, heulandite, lomandit, mordenite and philipsite. Clinoptilolite is one of the most abundant ones in the world with the best technological features. It can adsorb water, gases, minerals, and mineral ions at various rates and does not contain any hazardous elements. It is a natural mineral which is resistant to the temperatures up to 800oC and to acids and bases from 1,5 pH to 11 pH [1].

Zeolites have an unusual crystalline structure and a unique ability to change ions. A very large number of small channel are present in its structure. These channels have typical diameters of 0.5 to 0.7 nm, only slightly larger than the diameter of a water molecule. As seen in Table 1, zeolite has a chemical composition of 3-dimensional hydrated silicic mineral of aluminium containing

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alkali and earth-alkali cations, such as Na, K, Ca and Mn [2, 3, 4]. Main characteristics of zeolite are high cation exchange capacity, balanced water retention/release, nutrition via ion exchange, arranging acidity and air porosity without any structural change [5, 6].

Table 1. Chemical Structure of Clinoptilolite Mineral

	Anonymous, 2008	Rota Mining, 2012
Chemical content*	%	%
SiO ₂	65-72	65-72
CaO	2.5-3.7	2,4-3,7
Fe ₂ O ₃	0.8-1.9	0,7-1,9
Al ₂ O ₃	10-12	10-12
K ₂ O	2.3-3.5	2,5-3,8
MgO	0.9-1.2	0,9-1,2
Na ₂ O	0.3-0.65	0,1-0,5
TiO ₂	0-0.10	-
MnO	0-0.08	0-0,08
LOI**	9-12	9-14
SiO ₂ /Al ₃ O ₂	5.4-6.0	5,4-7,2
Cr ₂ O ₃	-	0-0,01

*Analyzed by XRF Spectrophotometer

**LOI: Loss On Ignition

Zeolites tend to give off structural zeolitic water when heated, and tend to regain it when cooled. Up to 700-800 °C, no significant change is observed in the crystal structure of clinoptilolites [7]. Zeolites have a wide area of usage. They are used in producing Portland cement and light constructional materials in addition to paper and feed industry [8, 9]. They are also utilized in fertilization [10] and in reducing the amount of heavy metal contents in waste water and soil [11, 12] besides in regulating soil [13]. The possibility of using the synthetic zeolites as adsorbent in water purification has been investigated in a number of studies [14, 15], but developing a more appropriate type for real industrial application has not been achieved yet.

2. Materials and Method

Sample Collection and Preparation

The raw material, belonging to the family of natural Zeolites, called clinoptilolite and having a chemical formula of $(Ca, K_2, Na_2, Mg)_4, Al_8Si_{40}, O_{96} \cdot 24 H_2O$, was supplied from Rota Mining Inc. The chemical content of this material seen in Table 1, analyzed with XRF spectrophotometer by the company mentioned above is made up of 90-95% clinoptilolite, 0-5% cristobalite and 0-5% tridymite. 1-3 and 3-5 mm in size two 25-pound clinoptilolite bags were supplied by ROTA Mining Inc. in Istanbul.

In order to modify and develop clinoptilolite, firstly it was washed by distilled water and passed through a sieve. Secondly, it was activated by 1 M HCL solutions at 110 °C for 12 hours, and washed with distilled water until becoming clear, dried at room temperature, respectively. The Activation Process was carried out with Experimental Setup given at Figure 1.



Figure 1. The Activation Process for Experimental Setup

Both sizes of clinoptilolite (1-3 mm and 3-5 mm) were subjected to heat treatment in Asch Oven (Carbolite, 0-1100 °C) at different temperature such as 200 °C, 400 °C and 600 °C, for five hours, after than they are naturally cooled.

Analytical Methodology

The measurements in respect to XRF values were made by using X-ray fluorescence spectrometry in the Instrumental Analysis Laboratory of Gizem Frit Ceramic Industry in Sakarya. The samples which were respectively activated for 12 and 24 hours and calcinated at 200°C, 400°C and 600°C analyzed in respect to surface area change by the Center for Application of Technology and Research in Afyon Kocatepe University. The measurements in respect to the surface area of clinoptilolite samples (m²/g) were carried out with nitrogen gas adsorption technique in the liquid nitrogen atmosphere at -98°C by Micromeritics Gemini 2360. Test procedure conducted is shown schematically in Figure 2.

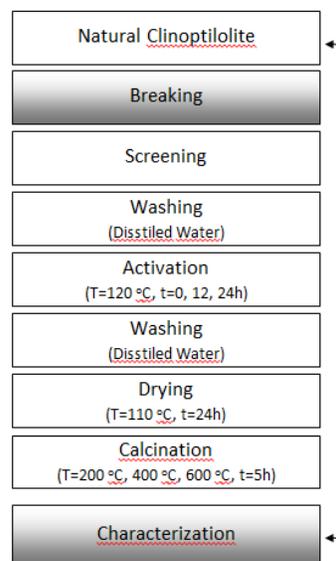


Figure 2. Experimental Flow Diagram

The most important results obtained from Table 2 explained below:

- a) L.O.I and SrO values were changed after activation (in 1M HCL for 12 hours) and calcination (at 200 °C for 5 hours).
- b) SiO₂ and CaO values were decreased as activated in 1M HCL for 24 hours and calcinated at 600 °C for 5 hours. This decline is thought to be the cause of formation of calcium silicate.
- c) Al₂O₃ value increased in calcinated at 600 °C for 5 hours but not activated sample.
- d) Na₂O (activated in 1m HCl for 12 hours and calcinated at 600 °C for 5 hours) with an alkaline K₂O can be transformed into another substance

B) Surface Area Changes (SAC) m²/g

The results were given at table 3 and evaluated in respect to data as follows:

1. Sifted, Washed in Distilled Water, Dried, Grinded but not Activated and non-calcinated.
2. Activated in 1M HCL for 12 hours and Calcinated at 200 oC for 5 hours.
3. Activated in 1M HCL for 24 hours and Calcinated at 200 oC for 5 hours.
4. Activated in 1M HCL for 12 hours and Calcinated at 400 oC for 5 hours.
5. Activated in 1M HCL for 24 hours and Calcinated at 400 oC for 5 hours.
6. Activated in 1M HCL for 12 hours and Calcinated at 600 °C for 5 hours.
7. Activated in 1M HCL for 24 hours and Calcinated at 600 °C for 5 hours.

Table 3. Surface Area Changes (SAC) m²/g

Surface Area Changes m ² /g							
Sample No:	1	2	3	4	5	6	7
Single Point SAC	36.5105	51.2583	57.3687	53.1541	53.4002	41.6919	37.1533
BET SAC	37.9912	52.7838	58.9697	54.7000	54.9934	43.1248	38.5196
Langmuir SAC	41.1403	59.6909	66.6495	61.8486	62.1914	48.8385	43.6581

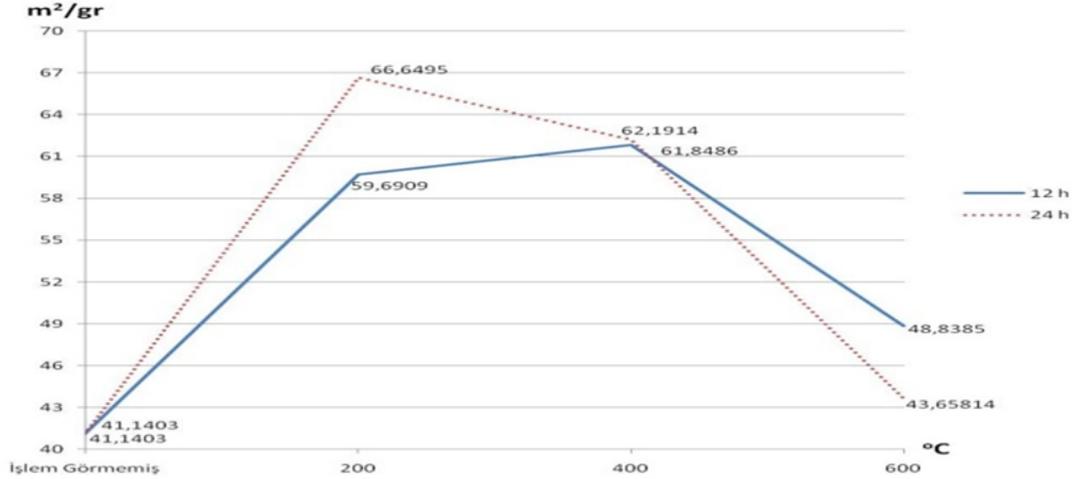
In Table 4, percentage of surface area changes depending on calcination temperature together with activation time, and in Table 5, surface area changes (m²/g) in respect to calcination and activation of samples given in Table 3 can be seen easily. Accordingly, the surface area changes were maximum for 24 hours activation time and at 200°C calcination level. Langmuir Surface Area Changes are given in figure 3.

Table 4. % Surface Area Changes

Langmuir % Surface Area Changes	200 °C		400 °C		600 °C	
	12h	24h	12h	24h	12h	24h
	45.091	62.005	50.335	51.169	18.699	6.120

Table 5. Surface Area (SA) Changes m^2/g

Surface Area Changes m^2/g							
Sample No:	1	2	3	4	5	6	7
Langmuir SA	41.1403	59.6909	66.6495	61.8486	62.1914	48.8385	43.6581

**Figure 3.** Langmuir Surface Area Changes

Conclusions

The maximum changes at the levels of SiO₂, CaO, Al₂O₃ and Na₂O was obtained after activation (12- 24 hour) and calcination (600 oC) processes. The maximum surface area changes were determined in the clinoptilolite samples activated for 24 hours and calcinated at 200°C.

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