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ZEOLITE SYNTHESIS BY ALKALI FUSION METHOD USING TWO DIFFERENT FLY ASHES DERIVED FROM TURKISH THERMAL POWER PLANTS

TÜRK TERMİK SANTRALLERİNDEN İKİ FARKLI UÇUCU KÜL KULLANARAK ALKALİ YAKMA METODUYLA ZEOLİT SENTEZİ

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Synthesis.

ABSTRACT

In this study, Faujasite (Na-LSX) $(3.5(Ca_{0.3})3.5(Na_{0.6})3.5(Mg_{0.1})Al_7Si_{17}O_{48}\cdot 32(H_2O))$ type zeolites and Ca-Filipsite $(CaK_{0.6}Na_{0.4}Si_{5.2}Al_{2.8}O_{16}\cdot 6(H_2O))$ type zeolites were produced from Sugözü Thermal Power Plant and Çatalağzı Thermal Power Plant fly ashes by alkali fusion method followed by water leaching, respectively. In these methods, fly ashes and sodium hydroxide (NaOH) were mixed in certain proportions and sintered at 600 °C in ash furnace. Then, zeolites were obtained from the ground materials after water leaching and solid/liquid separation, respectively. Cation Exchange Capacity (CEC), X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Fourier-Transform Infrared Spectroscopy (FTIR), X-Ray Fluorescence (XRF) and Atomic Absorption Spectrometer (AAS) analyses were used to characterize the synthesized zeolites. The zeolites synthesized with Sugözü fly ashes in a ratio of 1:2 had 136.93 meq/100 g CEC, whereas the CEC of synthesized zeolite from Çatalağzı fly ashes was found to be 247.88 meq/100 g. As a result, zeolites, which can be used as wastewater treatment agent, energy storage material, catalyst and separator, were synthesized by using 2 different Class F fly ash.

Anahtar Sözcükler:
Zeolit,
Fojasit,
Na-LSX,
Filipsit,
Sentez.

ÖZ

Bu çalışmada, Sugözü termik santrali uçucu küllerinden sonrasında su liçi ile desteklenen bazik füzyon tekniği kullanılarak fojasit (Na-LSX) $(3.5(Ca_{0.3})3.5(Na_{0.6})3.5(Mg_{0.1})Al_7Si_{17}O_{48}\cdot 32(H_2O))$ türü, Çatalağzı uçucu küllerinden ise aynı tekniği kullanarak Ca-Filipsit $(CaK_{0.6}Na_{0.4}Si_{5.2}Al_{2.8}O_{16}\cdot 6(H_2O))$ türü zeolitler sentezlenmiştir. Bu yöntemlerde öncelikle yüksek sıcaklıkta kül fırınında uçucu küller ve sodyum hidroksit (NaOH) belirli oranlarda karıştırılarak 600 °C'de sinterlenmiş sonrasında öğütülen malzemelerden saf suda liç işlemi ile zeolitler elde edilmiştir. Katyon Değiştirme Kapasitesi (KDK), X-Işını Kırınımı (XRD), Taramalı Elektron Mikroskobu (SEM), Fourier Dönüşümlü Kızılötesi Spektroskopisi (FTIR), X-Işını Fluoresans (XRF) ve Atomik Adsorpsiyon Spektrometresi (AAS) analizleri ile sentezlenen zeolitler karakterize edilmiştir. Sugözü uçucu külleri ile (1:2 oranda) sentezlenen zeolitler 136,93 meq/100 g KDK'ne sahipken aynı oranda Çatalağzı uçucu külleri ile sentezlenen zeolitlerin 247,88 meq/100 g KDK'ne sahip oldukları belirlenmiştir. Sonuç olarak F sınıfı 2 ayrı uçucu kül kullanarak atıksu arıtıcı, enerji depolayıcı, katalist ve separator olarak kullanılabilecek zeolitler sentezlenmiştir.

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INTRODUCTION

Zeolites are crystalline, microporous and aqueous alumina silicate minerals formed on the three dimensional TO_4 tetrahedral complex containing oxygen atoms in their corners. The term zeolite was first mentioned by the mineralogist Cronstedt, who observed this process when the stone was heated and then moved in the 18th century. Cronstedt has defined this mineral with the word "zeolite" which means "boiling stone" in Greek. During the 19th century, microporous structures of natural zeolites and their functions in ion exchange and adsorption processes were examined in detail. When natural zeolites could not meet the demands of industry, the necessity of synthetic zeolites emerged. In the 1940s, zeolites were produced by imitating the production conditions of natural zeolites. Compared to natural zeolites, synthetic zeolites have superior advantages such as uniform pore sizes, high ion exchange capacity and high purity (Xu et al., 2007; Cardoso et al., 2015; Lee et al., 2017).

Zeolite minerals have an aluminasilicate building consisting of an infinite extensible three-dimensional network of tetrahedral AlO_4 and SiO_4 structures connected to each other by sharing oxygen atoms (Wdowin et al., 2014; Vandermeersch et al., 2016; Zhang and Ostraat, 2016). The smallest unit of structure of a zeolite crystal is SiO_4 or AlO_4 tetrahedrals. These structures combine to form the zeolite crystal (Figure 1).

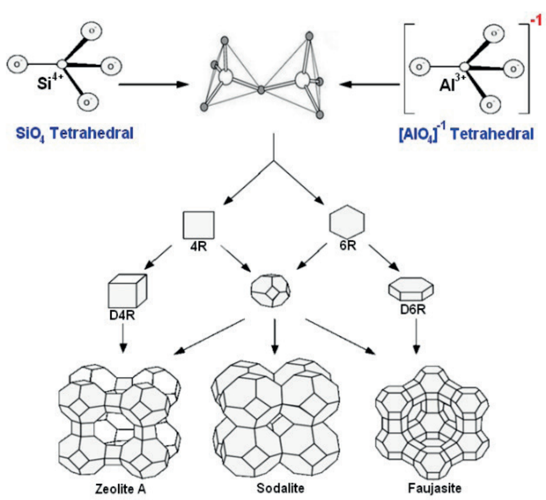


Figure 1. Zeolite formation from the tetrahedrals

The silicon ion is of +4 valence. The aluminum ion has +3 and the oxygen ion has -2 valence. A silicon ion meets only -4 values of the four oxygen ions surrounding it. Thus, each oxygen ion has a value of -1 and can be combined with another silicon ion. In case the Si atom is replaced by the Al atom in the structure, the skeleton structure has -1 valence ($[AlO_4]^-$). Additional cations are needed to make the electrical charge of the current structure neutral. These are alkali and alkaline earth metal ions present in the medium during formation or synthesis. This unified convergence of different geometries form a crystalline structure that contains channels and pores similar to honeycomb in zeolite structure. In other words, the negative nature of zeolites is provided by Al atoms. The negative and porous nature of zeolites allows zeolites to be named as artificial sieves. Simple formula of zeolites can be given as following equation:

$$M_xD_y[Al_{x+2y}Si_{n-(x+2y)}O_{2n}].mH_2O \quad (1)$$

Where M is Na, K or other monovalent cations, D is Mg, Ca, Sr, Ba or other divalent cations (Gottardi, 1978; Xu et al., 2007).

There are basically two zeolite synthesis methods including hydrothermal and alkali fusion techniques. In the hydrothermal synthesis method, alumina silicates are leached in alkali solutions at high temperatures. In alkali fusion technique, alkali chemicals and alumina silicates are sintered at high temperatures after mixing. Furthermore, in most processes, alkali fusion technique is followed by hydrothermal method. Both of the methods require high temperatures, time and pressures. The main sources for zeolite synthesis are commercial chemicals, which are very rich in aluminasilicate, mineral resources in the earth's crust and industrial by-products. Fly ash is a by-product produced during the generation of electricity in thermal power plants using pulverized coals. Zeolites are used in energy storage, pollution control and purification, catalyst, animal feed, filling material, construction and many other industrial sectors (Bukhari et al., 2015; Jha and Singh, 2016; Grela et al., 2016).

Approximately 15 million tonnes of fly ash are produced per year in thermal power plants located in Turkey. Evaluation of industrial plant tailings, reduction of residual quantities and transformation of these materials into useful products are the most important problems of industrialization. The processing of these resources has gained importance since the end of 20th century and developed in parallel with technology. Compared to the rest of the world, there are few studies to obtain nano-sized end-products from fly ashes in Turkey (Top et al., 2018).

In this study, zeolite synthesis from fly ashes by alkali fusion method followed by leaching was investigated. Two different power plant fly ashes in Turkey were used for zeolite synthesis. Synthesized zeolites were characterized by XRD, XRF, CEC, SEM, AAS, and FTIR analyses.

1. EXPERIMENTAL

1.1. Materials

The fly ashes of Çatalağzı (in Zonguldak province) and Sugözü (in Adana province) Thermal Power Plants were used as raw materials. The mineralogical properties of these materials were determined using a Rigaku Minflex XRD device equipped with PDXL software with current database. The samples basically consist of quartz (SiO_2), mullite ($Al_{4.8}Si_{1.2}O_{9.6}$), hematite (Fe_2O_3) and CaO phases (Figure 2).

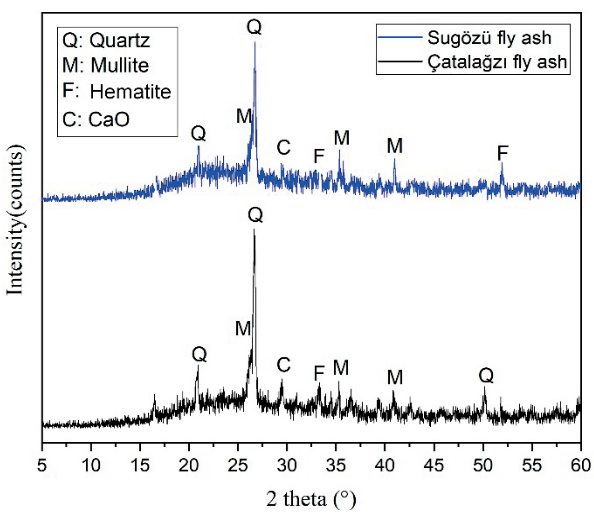


Figure 2. XRD patterns of the fly ashes

The chemical composition of fly ashes were determined using a Minipal 4 Panalytical XRF device (Table 1). Minor contents (< 10%) in the XRF analyses were confirmed by AAS analyses after the materials were dissolved in aqua regia. Total sulfur content was determined by Eltra Cs 580 Carbon Sulphur Determinator device. SiO_2 + Al_2O_3 + Fe_2O_3 contents of the ashes were above 70%. In addition, CaO contents were below 10% for both of ashes. The major mineral phase distributions confirmed that they were F-class fly ashes according to ASTM C 618.

Table 1. XRF analysis results for fly ashes

Contents (%)	Sugözü fly ash	Çatalağzı fly ash
SiO_2	55.20	45.90
Al_2O_3	24.10	24.20
CaO	5.50	9.87
Fe_2O_3	8.11	10.66
K_2O	1.62	4.21
SrO	0.27	0.13
BaO	0.26	ND*
MnO	ND*	0.12
ZrO_2	0.19	ND*
TiO_2	1.44	1.36
SO_3	0.72	1.07
LOI*	2.34	2.48

*LOI: Loss on ignition, ND: Not determined

Particle size analysis were determined by Malvern Mastersizer. d_{100} and d_{50} values were 80 µm and 16 µm for Sugözü fly ashes, 500 µm and 40 µm for Çatalağzı fly ashes, respectively. Quanta 650 Field Emission SEM was used for the morfological structure analysis. Spheral structures confirmed characteristic feature of the fly ashes were observed (Figure 3). The densities of Sugözü fly ashes and Çatalağzı fly ashes were found to be 2.33 and 1.86 g/cm^3, respectively.

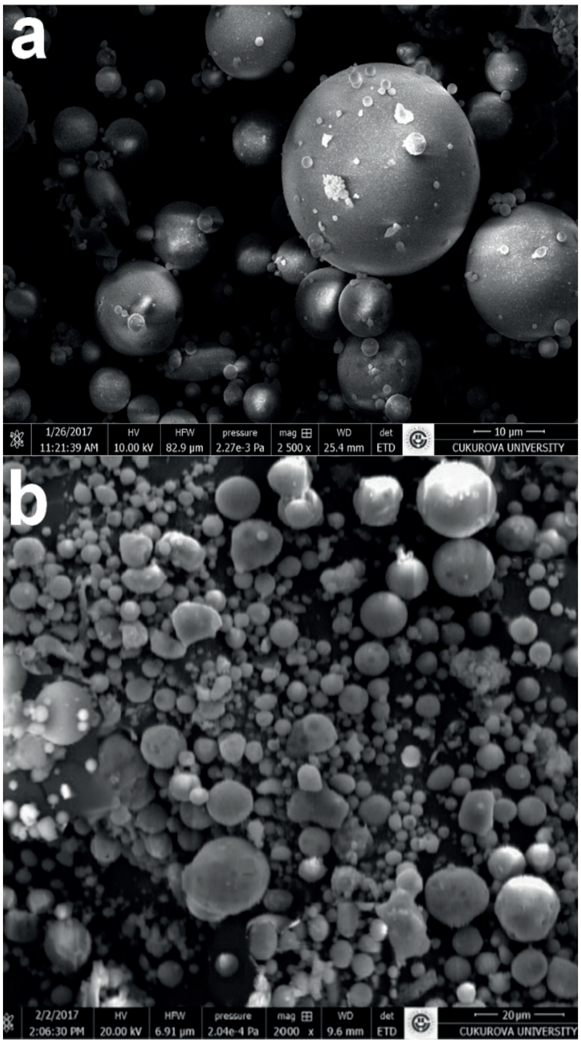


Figure 3. SEM micrographs of the fly ashes (a: Sugözü fly ash, b: Çatalağzı fly ash)

The materials were kept in the oven until a constant weighing and then used in the experiments.

Reagent grade (98%) NaOH pellets (-3 mm sized) purchased from TEKKIM Chemical Company was used for the fusing stages. The other reagent grade chemicals used for the analyses were obtained from Merck and Sigma Aldrich.

1.2. Methods

In the tests for the production of zeolites, fly ashes were separately mixed with NaOH pellets (< 3 mm) in a certain ratio and this solid mixture was burned in Protherm (PLF model) ash oven for 3 hours. Then the mixture was milled with Retsch RM 100 grinder and leached in pure water at a certain temperature with 20% solid rate. The characterization tests for zeolites were conducted after the solid/liquid separation (Figure 4).

Fly ash + NaOH (1:1 and 1:2 ratios by weight)

↓

Fusing at 600 °C and 3 hours

↓

Grinding

↓

Leaching with pure water at 80-90 °C

↓

Solid/liquid separation → Liquid phase

↓

Drying at 60-70 °C

↓

Characterization tests for zeolites

Figure 4. Flowsheet of the present study

The CEC values of fly ash and synthesized zeolites were calculated by K^+ adsorption method (Top et al., 2018). Firstly, a certain amount of samples were added in 10% potassium chloride (KCl) solution for 15 minutes at a stirring rate of 300 rpm. After K^+ loading, solid/liquid separation was performed. The solid filtrate was finally washed with ethyl alcohol. Then, the solid residue was added into 1 M ammonium acetate (CH_3COONH_4) solution and K^+ ions were replaced by NH_4^+ ions. The solution was stirred at 300 rpm. The amount of K^+ in the filtered liquid after solid/liquid separation was measured by an AAS (Perkin Elmer PineAacle 900H). The measured K^+ values were calculated for the 100 g material according to the following Equation 2. The CEC unit is meq/100 g.

$$CEC = \left[\frac{\frac{Measured\ content\ (mg)}{Sample\ weight\ (g)}}{39.09} \right] * 100 \qquad (2)$$

Nicolet 6700 FTIR with ATR (Attenuated Total Reflection) apparatus was used for characterization of some zeolite species. All the tests were duplicated.

2. RESULTS AND DISCUSSIONS

2.1. Experiments with Sugözü Fly Ashes

The chemical composition of the synthesized zeolites obtained from Sugözü fly ashes were given in Table 2. Na doping was obvious and the water contents derived from chemical formula of zeolites caused high LOI values.

Table 2. XRF analysis of synthesized zeolites using Sugözü fly ashes

Contents (%)	1:1 Fly ash/ NaOH	1:2 Fly ash/ NaOH
SiO_2	33.63	26.83
Al_2O_3	17.40	15.80
Na_2O	14.34	19.10
CaO	5.72	4.90
Fe_2O_3	6.02	5.16
K_2O	0.90	0.43
SrO	0.23	0.29
CuO	0.03	0.05
MnO	0.06	0.05
TiO_2	1.25	1.24
LOI*	19.90	25.97

*LOI: Loss on ignition

After the experimental procedure, mullite peak disappeared and faujasitic peaks was found to be dominant (Figure 5). The quartz peak intensity was significantly reduced by 1:2 ratio. This shows the success of faujasite transformation.

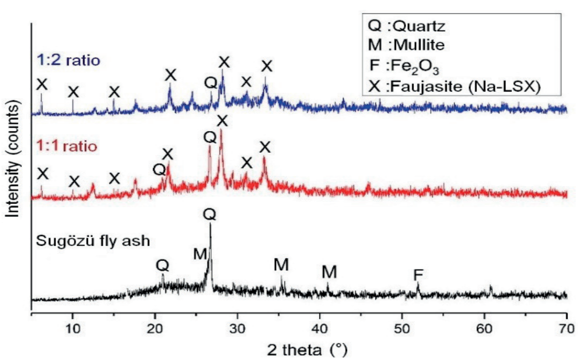


Figure 5. XRD diagrams of the fly ash and products

The CEC values of the synthesized zeolites had an increasing trend (Table 3).

Table 3. CEC values of the fly ash and products

Samples	Sugözü Fly ash	1:1 Fly ash/NaOH	1:2 Fly ash/ NaOH
CEC (meq/100 g)	22.33	121.53	136.93

The SEM images of the materials are shown in Figure 6 and 7. For zeolites obtained by using 1:1 fly ash/NaOH mixing, crystallization was not materialized as desired (Figure 6). However, the structure of the crystals in zeolites synthesized with 1:2 ratio defined the faujasitic structure. Small and polyhedral crystals assembled around a point was clearly visible (Figure 7). XRD peaks and SEM images of zeolites obtained by using 1:2 material were found to be compatible with faujasite (Na-LSX) materials in the literature (Chumee, 2013; Ikeda et al., 2014; Ma et al., 2016).

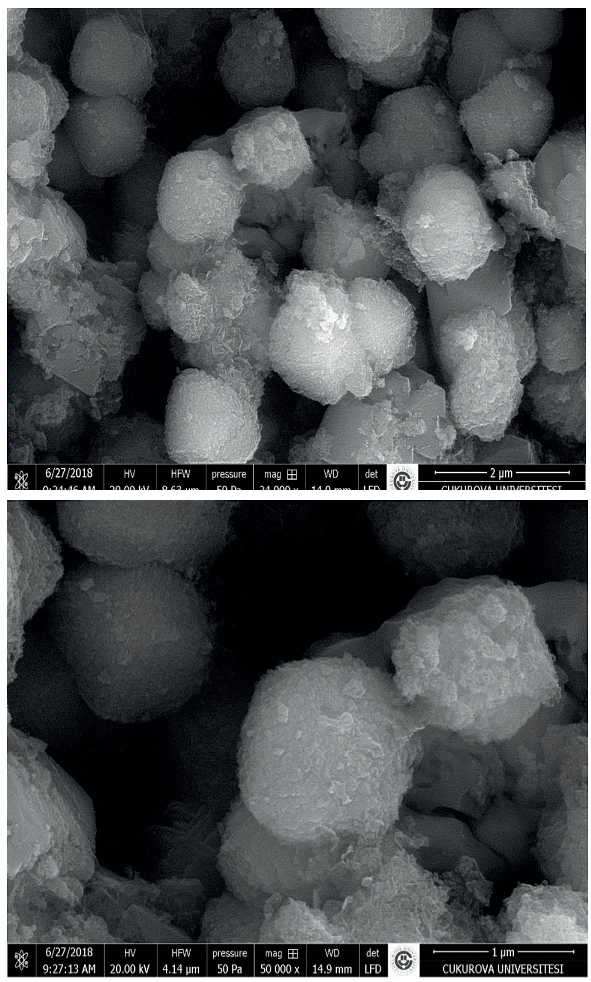


Figure 6. SEM micrographs of the zeolites synthesized at 1:1 Sugözü fly ash/NaOH ratio

Figure 8 shows the FTIR analysis of Sugözü fly ash and the products synthesized. The band at 3487 cm^{-1} shows the -OH bonds in the materials and the peak at 1630 cm^{-1} shows the adsorbed water molecules. In addition, the strong peak at 950 cm^{-1} shows the Al-O and Si-O bonds in the tetrahedral structures which are characteristic of zeolites. The peaks in the area less than 700 cm^{-1} indicate the footprints of the materials. The peaks in this region were similar to faujasite type zeolites. The FTIR analyses of synthesized Na-LSXs were similar to the studies by Khemthong et al. (2007) and Chumee (2013).

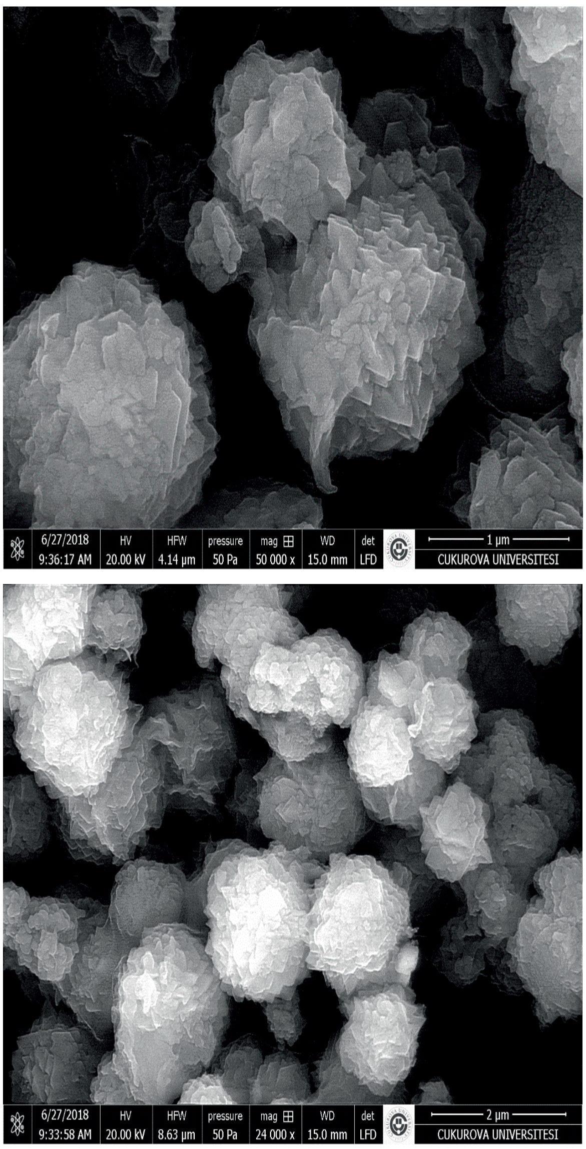


Figure 7. SEM micrographs of the zeolites synthesized at 1:2 Sugözü fly ash/NaOH ratio

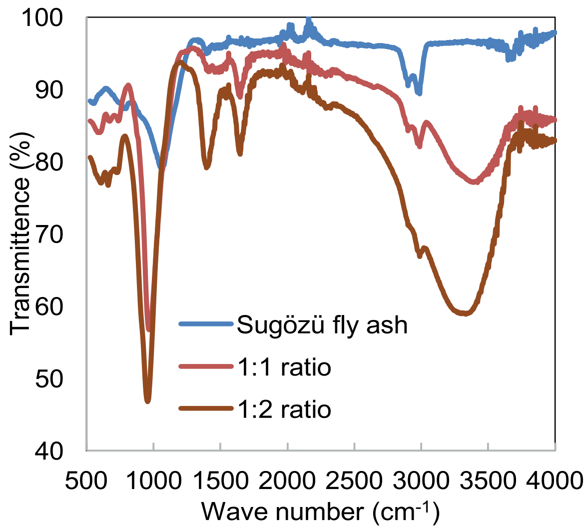


Figure 8. FTIR analysis results of Sugözü fly ash and the products

2.2. Experiments with Çatalağzı Fly Ashes

The same fusion technique procedure followed by water leaching was applied to the Çatalağzı fly ashes to produce zeolites. The chemical analysis results showing the composition of the materials obtained from experiments performed with the addition of fly ash/NaOH at a ratio of 1:1 and 1:2 were listed in Table 4. When the contents of the obtained materials were examined, it was seen that Na loadings were low.

Table 4. XRF analysis of synthesized zeolites from Çatalağzı fly ashes

Contents (%)	1:1 Fly ash/ NaOH	1:2 Fly ash/ NaOH
SiO_2	37.40	37.71
Al_2O_3	20.24	18.93
Na_2O	0.22	0.27
CaO	11.88	11.82
Fe_2O_3	13.38	13.16
K_2O	2.55	0.98
SrO	0.12	0.10
MnO	0.11	0.10
TiO_2	1.98	1.78
LOI*	11.99	15.04

*LOI: Loss on ignition

It was determined that Ca-Phillipsite type zeolites were synthesized when 1:2 ratio of Çatalağzı fly ash/NaOH mixture was fused and leached (Figure 9).

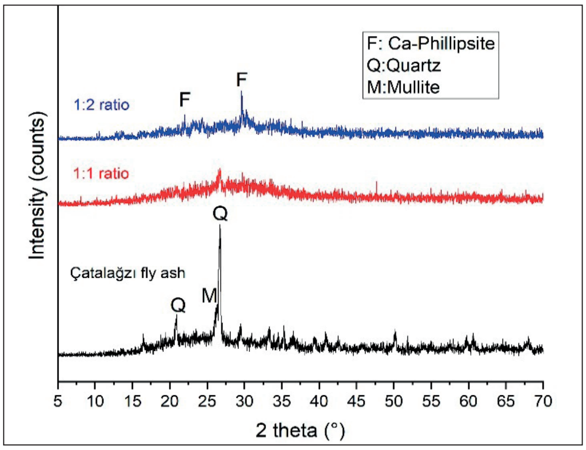


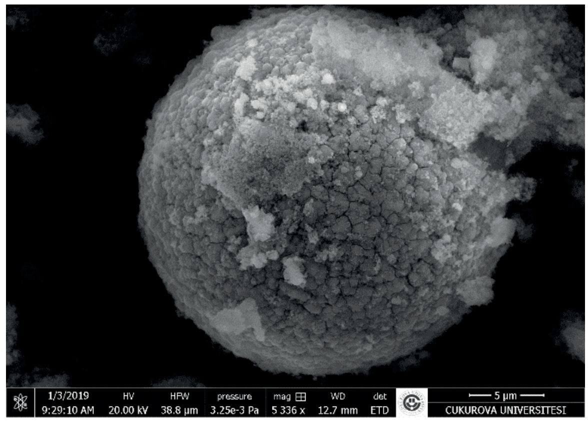
Figure 9. XRD diagrams of Çatalağzı fly ash and the synthesized products

However, the materials synthesized at 1:1 ratio had amorphous structure, mostly. A camber between 10° and 45° at the XRD peaks confirmed amorphous silica characteristic. Besides, the high rate of noise in the peaks was a sign of impurities.

The CEC values of the zeolites obtained from Çatalağzı fly ash were higher than those synthesized from Sugözü fly ashes (Table 5). Figure 9 and 10 show SEM images of the material synthesized with 1:1 and 1:2 mixing ratio, respectively. 1:1 mixing ratio resulted in the formation of zeolite crystals which did not develop well on fly ash surfaces (Figure 10). However, tetragonal structures, which are characteristic of Ca-Filipsite type zeolites, were seen at 1:2 mixing ratio. In addition, crystal twinnings, which was formed by using the common surface of the crystals, was also another characteristics of phillipsite type zeolites, were observed (Figure 11).

Table 5. CEC values of the fly ash and products

Samples	Çatalağzı Fly ash	1:1 Fly ash/NaOH	1:2 Fly ash/NaOH
CEC (meq/100 g)	12.23	156.42	247.88



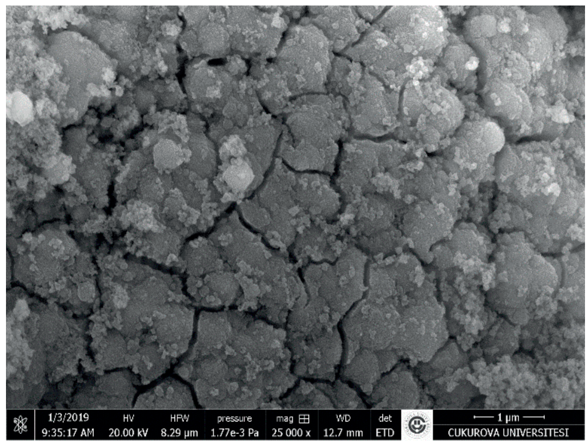


Figure 10. SEM micrographs of the zeolites synthesized at 1:1 Çatalağzı fly ash/NaOH ratio

CONCLUSIONS

Sugözü and Çatalağzı fly ashes were converted into faujasite (Na-LSX) and Ca-phillipsite type zeolites by alkali fusion method followed by water leaching, respectively.

Ca-Phillipsite type zeolites have abundant usage areas from wastewater treatment to energy storage. In addition, faujasite type zeolites can be used as catalyst and can also be used in the separation of gases such as oxygen and nitrogen from air. Characterizations of these useful synthesized materials were revealed by using XRD, XRF, CEC, SEM, AAS, and FTIR analysis techniques.

The zeolites synthesized with Sugözü fly ashes in a ratio of 1: 2 had 136.93 meq/100 g CEC, whereas the zeolites synthesized with Çatalağzı fly ashes had 247.88 meq/100 g CEC.

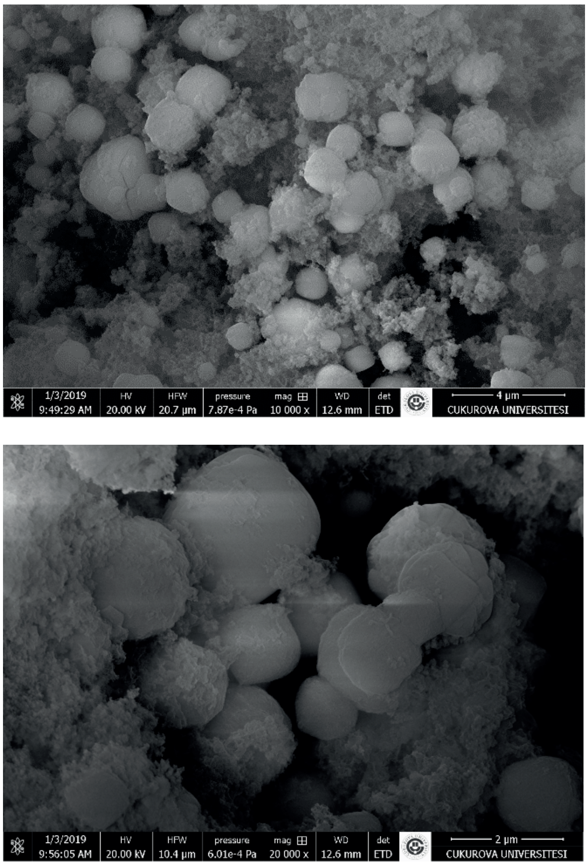


Figure 11. SEM micrographs of the zeolites synthesized at 1:2 Çatalağzı fly ash/NaOH ratio

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