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THE ANALYSES OF THE EFFECT OF HEAT TREATMENT ON THE STRUCTURAL PROPERTIES OF ZEOLITES FROM TURKEY USING FT-IR, MAS NMR AND XRD METHODS

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ABSTRACT

Upon the heat exposure, natural zeolites show structural alterations which leads to a possibility to be used for different purposes in science and industry including building stones, concrete bricks and ceramic foam etc. The effect of heat treatment at 800°C with different treatment times of 30, 60, 150 min of clinoptilolite rich zeolites from Gördes region of Turkey were investigated by Fourier Transform IR (FT-IR), solid state magic angle spinning nuclear magnetic resonance (MAS NMR), and X-ray diffraction (XRD) spectroscopic methods. The obtained spectroscopic results indicated that rather than a total collapse, severe structural distortions occur for the investigated samples.

Keywords: Zeolite, FT-IR, MAS NMR, XRD

1. INTRODUCTION

Zeolites, hydrated crystalline aliminosilicates having large voids and channels in the order of 3-10Å and a high SiO_2/Al_2O_3 ratio have been widely used in the field of industry, agriculture, biomedical and environmental protection purposes [1-6]. Clinoptilolites structurally having HEU type zeolites show common HEU framework topology. They have high thermal stability and their Si/Al ratio is bigger than 4 [7-12]. Knowledge of the thermal stability and structural changes of natural zeolites after heating allows obtaining useful information for possible applications in different fields e.g. civil engineering, catalysis and ceramic industry. It is possible to find many studies in the literature about the properties and possible applications of heat treated zeolites [13-18].

In order to follow the structural evolution of the synthetic or natural zeolites for various purposes, MAS NMR, FT-IR and XRD spectroscopic techniques are widely employed and they provide valuable information [19-21]. It was previously reported by Çağlar Duvarcı et al. that the structure of clinoptilolite from Gordes region was collapsed at 800°C [13]. In this work, it is aimed to investigate the structural behavior of the zeolite samples from the same region when the samples immediately exposed to 800°C with 30, 60 and 150 min periods of time. In comparison with the untreated zeolite sample, the structural changes were monitored with ^{29}Si, ^{27}Al, ^{1}H MAS NMR, FT-IR and XRD spectroscopic techniques. Hereby, all the results obtained were discussed and explained in detail.

2. EXPERIMENTAL

2.1. Materials and Methods

Natural zeolite samples were obtained from Gördes region of Turkey. The samples were dry sieved using Retsch sieving equipment and ground to pass 63µ sieve. They were labelled as UZ (untreated zeolite), Z30 (treated 30 min at 800°C), Z60 (treated 60 min at 800°C) and Z150 (treated 150 min at 800°C). The temperature of the oven was set to 800°C before the samples were put in it. Therefore, the structural behaviors of the samples after the sudden exposure to a high temperature (800°C) were examined.

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2.2. Instrumentation

Infrared spectra of the zeolite samples were recorded (4000–400 cm^{-1}) with Bruker Tensor 27 spectrometer at a resolution of 4 cm^{-1} using KBr pellet technique. Solid state magic angle spinning (MAS) NMR spectra were recorded at 11.75 T. All MAS NMR spectra were acquired on a JEOL ECZ 500R spectrometer. Resonance frequencies of ^{1}H, ^{27}Al, and ^{29}Si were adjusted 500.15 MHz, 130.32 MHz and 99.36 MHz, respectively. All of the NMR spectra were acquired with π/2 single pulse and a relaxation delay time of 5s. Spectra observed with very short pulses which pulse width adjusted to 1µs. Number of scan for ^{1}H, ^{27}Al and ^{29}Si were adjusted as 256, 3000 and 5000, respectively. 3.2 mm zirconium oxide rotors were used and they were spun at 10 kHz. Chemical shifts were quoted in ppm from external standard. Adamantane, aluminium nitrate and TMS were used as external standard for ^{1}H, ^{27}Al and ^{29}Si, respectively. The XRD diffractograms were obtained with a Bruker instrument, using CuKα radiation (λ=1.54 Å) at 40 kV and 20 mA, in the range 5-40 °2θ. The samples were scanned with a step of 0.02° 2θ.

3. RESULTS AND DISCUSSIONS

3.1. IR Studies

FT-IR spectra of the natural and heat treated samples are given in Figure 1. The band appeared at 3633 cm^{-1} is related to isolated or bridging O-H stretching vibrations [13, 22] and vibrations at 3459 and 1640 cm^{-1} refer to stretching and bending vibrations of water molecules [22]. The 1049 cm^{-1} band is due to antisymmetric stretching vibrations of internal T-O bonds in TO_4 tetrahedral structure where T stands for any atom in tetrahedral such as Si and Al [23, 24].The band at 793 cm^{-1} could be attributed to symmetric O-T-O vibrations [22, 23, 25, 26]. The bands observed at 734 and 672 cm^{-1} refer to symmetric stretching vibrations of the free tetrahedral group TO_4 [22, 26].The vibrational band at 607 cm^{-1} can be assigned as O-T-O bending vibrations [22, 26]. The bands at 521 and 468 cm^{-1} are due to “pore opening” vibrations and bending vibrations of TO_4 [22, 23, 25].

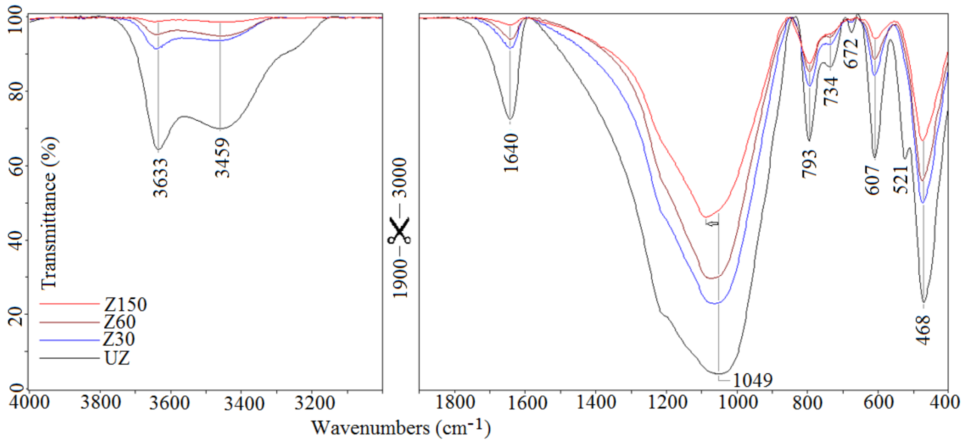

Figure 1. FT-IR spectra of treated (30, 60, 150 min) and untreated (UZ) zeolite samples

3.2. ^{29}Si, ^{27}Al and ^{1}H MAS NMR Studies

^{29}Si and ^{27}Al MAS NMR spectra of the untreated and heat treated clinoptilolite samples were given in Figure 2 and Figure 3. In previously reported works with different origins of clinoptilolite samples, observed ^{29}Si peaks were assigned as -92.30, -95 ppm (Si(0Al)), -101.3499, -100 ppm (Si(1Al)), -106.8226, -106 ppm (Si(2Al)) and -117.347, -111 ppm (Si(3Al)), respectively where the numbers (0, 1, 2 and 3) beside the Al indicate the number of aluminum atoms in the second coordination sphere [27-29]. In this work, the mentioned values, since the peaks were broad enough, were found approximately as -93, -99, -105 and -111 ppm, respectively. Since, Loewenstein’s rule avoids the formation of Al-O-Al bondings only possibility is the existence of Al(4Si) units in the framework [30]. Therefore, ^{27}Al

MAS NMR spectrum yielded a resonance peak at around 62 ppm due to tetrahedrally coordinated aluminum as in agreement with the previously published works [19, 31]. In addition to that, the very small broad peak at around 0 ppm is due to octahedrally coordinated AlO_6 units (Figure 3) [32]. ^1H MAS NMR spectra are given in Figure 4. Untreated sample shows an intense broad peak around 5 ppm due to water molecules. Spinning side bands are marked with asterisks. Peaks from bridging OH groups become visible as comparatively sharp peaks following the heat treatment as seen in Figure 4.

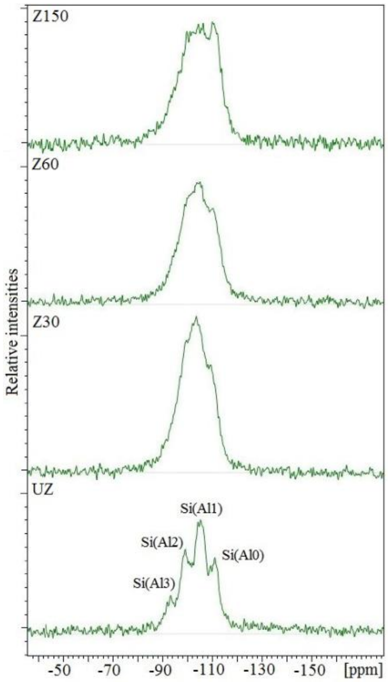

Figure 2. ^{29}Si MAS NMR spectra of treated (30, 60, 150 min) and untreated (UZ) zeolite samples.

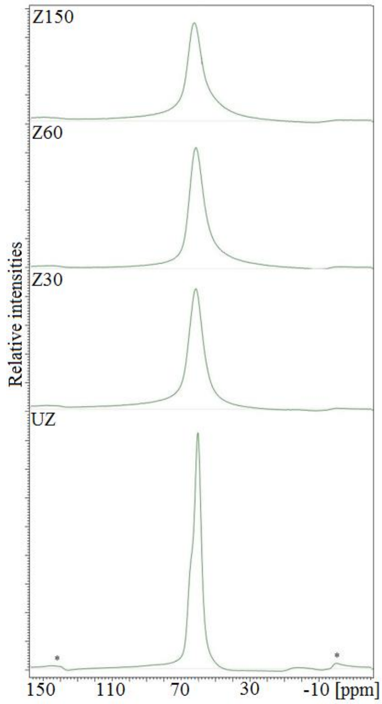

Figure 3. ^{27}Al MAS NMR spectra of treated (30, 60, 150 min) and untreated (UZ) zeolite samples

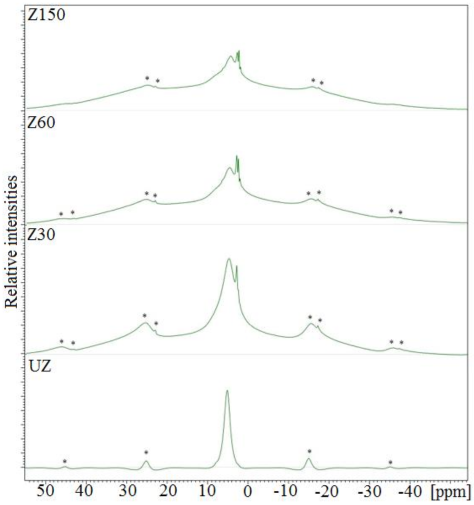

Figure 4. ^{1}H MAS NMR spectra of treated (30, 60, 150 min) and untreated (UZ) zeolite samples.

3.3. XRD Studies

The X-ray diffraction patterns of clinoptilolite samples before and after thermal treatment at 800 °C for 30, 60 and 150 minutes are shown in Figure 5. Untreated clinoptilolite sample (UZ) exhibits good crystallinity and gives sharp peaks. X-ray diffraction analysis of the samples showed the positions of many characteristic peaks corresponding to the well crystallized clinoptilolite as indicated by the characteristic narrow and intense diffraction peaks at 2θ = 9.83°, 22.36°, 26.00° and 31.94° [7, 24, 33-34]. The other peaks in same pattern belong to the some impurities in the clinoptilolite. The quantitative XRD analysis showed that the main mineral component of the UZ is clinoptilolite (80–85%), together with minor amounts of Opal A (5–10%) Opal-CT (5–6%), smectite, mica-illite feldspar (1–3%). The method given by Esenli and Sirkecioğlu [35] was used to determine the content of clinoptilolite sample. As the thermal treatment time increased for Z30 and Z60 samples (Figure 5), the intensities of the clinoptilolite peaks are decreased gradually. After heating of the clinoptilolite at 800 °C for 150 minutes, clinoptilolite peaks still appeared in the XRD pattern but their intensities decreased significantly indicating the considerable collapse of the crystal lattice. In addition, an appearance of increase of the background and increase in the broadness of peaks in the interval 20° and 30° 2θ (especially for Z150 sample) are due to the formation of amorphous structure. Similar changes after thermal treatment of clinoptilolite were reported by other researchers [13, 36-38].

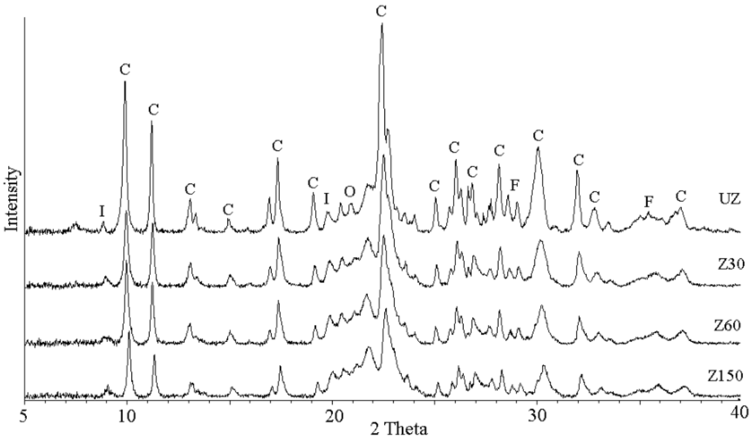

Figure 5. X-Ray diffraction pattern of untreated (UZ) and thermally treated (Z30, Z60 and Z150) clinoptilolite type zeolite samples (C, clinoptilolite; I, illite; O, opal-A; F, feldspar).

4. CONCLUSIONS

In brief, following conclusions can be summed up:

i. Bridging stretching OH vibrations (3633 cm^{-1}) and stretching and bending vibrations of water molecules (3459 and 1640 cm^{-1}) reduced in intensity severely but still trace amount of them can be seen in the infrared spectrum after treatment at 800°C for 150 min (Figure 1). This fact was also verified by ^{1}H MAS NMR (Figure 4)

ii. The broad peak around 0 ppm (Figure 3) due to six-coordinate aluminum occurred by the expulsion of A1 from the framework sites, disappeared just after the following heat exposure of 800°C for 30 min indicating the full destruction of this structure. The pore opening vibrational bands at 521 cm^{-1} disappeared as well indicating a distortion in the simultaneity of the pore dynamics (Figure 1).

iii. By analyzing ^{27}Al MAS NMR spectra (Figure 3), it was seen that the intensity of the band at around 60 ppm belonging to tetrahedrally coordinated aluminum was reduced nearly to its half when compared to untreated clinoptilolite sample addressing the partial destruction of this structure but it is not still fully collapsed even after the heat treatment at 800 °C for 150 min. This fact was also supported by the findings of XRD data (Figure 5).

iv. Si-O stretching vibrations appeared as the most shifted bands at around 36 cm^{-1} in the infrared spectrum (Figure 1) and ^{29}Si MAS NMR spectrum imply an agreement with this showing a severe broadening and distortion in the silicium resonance bands (Figure 2).

v. Finally, based on the spectroscopic results employed in this work, it can be concluded that a severe distortion was seen in the clinoptilolite structure of the investigated zeolite sample at 800°C with 150 min treatment time but full decomposition was not observed. Depending on the purpose, the examined zeolite samples can still be functional at 800°C for a period of 150 minutes.

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