**Analysis Results of the Catalysts**

***FTIR Analysis***

Figure 1 shows the FTIR spectra of the clinoptilolite and meerschaum based catalysts upon pre- and post-activation. The wavenumber range of 650-1700 cm-1 was presented in Figure 1 due to that the most of the detected changes were in the fingerprint area after the activation process.

D:\Makaleler\2018 Yayınlar\YL_Tezim_Yayın\Figures\Fig. 3.tif

Figure 1. FTIR spectra of the raw and activated catalysts

In the spectrum of clinoptilolite, three basic groups of bands were originated from the water molecules between 1600-1700 cm-1, Si-O(Si) and Si-O(Al) vibrations in the tetrahedral or alumina and silicon-oxygen bridges in the range of 650-1200 cm-1 and vibrations due to pseudo-lattice structures of structural units between 650-700 cm-1 wavenumber (Mozgawa 2000). After the activation process, the intensity of the peak at around 1600 cm-1, which is associated with the water molecules bound with Na and Ca in the channels and cages of the clinoptilolite, decreased considerably. Another important peak concerning Si-O(Si) and Si-O(Al) asymmetric vibrations was at 1015 cm-1 wavenumber. This peak shifted to a higher wavenumber of 1028 cm-1 due to loss of Al+3 cations by the effect of HCl acid activation process. Finally, the band at 790 cm-1 was originated from stretching vibrations formed by O-Si-O and O-Al-O bonds (Tanaka et al. 2003).

In the spectrum of meerschaum, two bands at 1650 and 1610 cm-1 wavenumber indicated the zeolitic water in the channels and bending vibrations of -OH groups originating from coordinated water molecules with magnesium in the octahedral structure. The broadband at 1450 cm-1 wavenumber was also due to the bending vibrations with regard to the hydroxyl groups of the bound water. Basically, the band and peaks in the range of 650-1300 cm-1 were associated with Si-O bonds in the tetrahedral layer. The band (Si-O coordination band) at 1195 cm-1 was related to the stretching vibrations arising from the Si-O bonds in the Si-O-Si groups of the tetrahedral layer. The double peaks at 966 and 1006 cm-1 wavenumber in the structure of raw meerschaum was due to the vibrations of Si-O-Si planes. These peaks disappeared after activation and shifted to a wavenumber of 1040 cm-1 in a single peak (Alkan et al. 2005).

The changes in the structure following activation process showed that HCl acid attacked and cracked the Mg-O bonds and removed the Mg atoms from the octahedral structure and the tetrahedral layer. The peaks at 780 and 690 cm-1 in the spectrum of raw meerschaum referred to the -OH deformation vibrations and Mg3OH bending vibrations, respectively. The peak concerning Mg-OH was completely disappeared with the effect of activation. The peak around 800 cm-1 wavenumber in the activated meerschaum was the characteristic peak of amorphous silica (SiO2) (free silicate groups) (Sabah and Celik 2002, Wan and Chen 2011).

***XRF Analysis***

Table 1 presents the types and percentages of the compounds determined in the catalysts before and after the activation process according to the XRF analysis.

Table 1. Compounds found in the structure of catalysts before and after the activation process

|  |  |  |  |
| --- | --- | --- | --- |
| Pre-activation | | Post-activation | |
| Compound | wt.% | Compound | wt.% |
| **Clinoptilolite** | | | |
| SiO2 | 73.40 | SiO2 | 90.03 |
| Al2O3 | 13.48 | Al2O3 | 6.47 |
| CaO | 5.14 | Fe2O3 | 1.09 |
| K2O | 3.17 | K2O | 0.85 |
| Fe2O3 | 2.34 | CaO | 0.50 |
| MgO | 1.28 | MgO | 0.47 |
| P2O5 | 0.45 | P2O5 | 0.41 |
| Na2O | 0.21 | TiO2 | 0.13 |
| TiO2 | 0.14 | ZrO2 | 0.01 |
| Trace sum | 0.39 | Trace sum | 0.40 |
| **Meerschaum** | | | |
| SiO2 | 66.63 | SiO2 | 98.75 |
| MgO | 30.84 | MgO | 0.66 |
| CaO | 1.56 | P2O5 | 0.41 |
| P2O5 | 0.44 | CaO | 0.09 |
| NiO | 0.25 | Al2O3 | 0.05 |
| Al2O3 | 0.11 | Fe2O3 | 0.03 |
| Trace sum | 0.17 | Trace sum | 0.01 |

Prior to the activation of clinoptilolite, the presence of several metal oxide compounds was determined with the exception of the SiO2 and Al2O3 compounds, which were predominant in the structure. The majority of these compounds were removed from the structure and the amount of SiO2, which is an important compound in the catalytic activity, has been increased from 73.40% to 90.03% in the acidic centers via activation. On the other hand, the SiO2/Al2O3 ratio, which is another important parameter of catalytic activity for alumina silicate catalysts, was increased from 5.45 to 13.91 improving the catalytic property of clinoptilolite. With exception of the compounds in the table, several metal oxides such as BaO, SrO, MnO, ZrO2, Rb2O were also determined as trace substances. This increase in Si/Al ratio ensured an increase in the acidic sites of the clinoptilolite enhancing the catalytic activity.

Although natural clinoptilolite has a relatively porous structure and large surface area, it cannot effectively catalyse the chemical reactions because of lack of acidic centers in its structure. For this reason, strong active acidic centers should be formed in the crystal structure of it. Alteration of the Si/Al ratio of the mineral does not affect the structure of the catalyst, but it changes the state of the acidic centers which play a very vital role in the catalytic activity. The increase in this ratio also increases the acidity of the catalyst ensuring a development in the quality of the produced oil. Because aluminum-rich clinoptilolites are generally vulnerable to the acid and heat due to the weakness of the aluminum zones found in the flat tetrahedral layers (Beyer 2002, Fan et al. 2006).

The Lewis and Brönsted acid sites of the clinoptilolite catalyst are important factors for determining the activity and product selectivity of it. The vast majority of reaction products are identified by the carbonium ion chemistry (e.g., isomerization, chain/beta-cleavage, H-transfer, oligomerization, alkylation) affected by the strength, distribution, and density of these acid sites. The Lewis acid sites serve to separate the hydride (H-), while the Brönsted acid sites perform the role of proton (H+) addition. These acidic sites are also formed with Al species present in the catalysts containing silica and alumina. For this reason, Al content of each unit cell or Si/Al ratio of the catalyst is highly related to the density of the acidic centers, which also have a vital effect on cracking reactions (Aguado et al. 2006).

The meerschaum catalyst contained a fewer variety of compounds than those of clinoptilolite in its raw form. The most abundant compound in the pre-activated structure was SiO2 with a percentage of 66.63. With the activation process, most of the compounds in the composition were removed and a catalyst with 98.75% SiO2 was obtained. In particular, the MgO compound, which has an important role in forming the fibrous structure of meerschaum, has a very low percentage of 0.66 with a decrease of 97.86% after the activation process. Thus, a catalyst with increased acidity and a higher catalytic activity was obtained.

***SEM-EDX Analysis Results of Catalysts***

Figs. 2 and 3 show the SEM micrographs and EDX spectrum indicating the changes of clinoptilolite and meerschaum before and after activation, respectively. The reason for the appearance of the gold element in the spectra was due to the gold plating process to get better results during analyzes. It was easily understood that the elements with the exception of Si, Al, O, and C were removed owing to the activation process.

In molecular sieve catalysts such as clinoptilolite, the shape selectivity characteristic controls the diffusion and cracking reactions of the vapors formed during pyrolysis into the catalyst. Therefore, it is necessary to increase the catalytic activity by opening the pores of the raw clinoptilolite. As can be seen from the Figure 2, the clinoptilolite lost its intense regions in the rigid structure after the acid and heat activation process and demonstrated a relatively porous structure.

D:\Makaleler\2018 Yayınlar\YL_Tezim_Yayın\Figures\Fig. 4.tif

Figure 2. SEM micrographs and EDX spectra of clinoptilolite before and after activation

D:\Makaleler\2018 Yayınlar\YL_Tezim_Yayın\Figures\Fig. 5.tif

Figure 3. SEM micrographs and EDX spectra of meerschaum before and after activation

According to the spectra, the Si/Al ratio of 4.88 in raw clinoptilolite rose to 14.47 due to removed Al atoms from the structure after the activation process. This result also showed compliance with the XRF results given previously. The increase in Si/Al ratio has resulted in an increase in the acidic sites of the clinoptilolite, thereby increasing the catalytic activity. It was reported that the natural clinoptilolite has a Si/Al ratio of about 5 (Ruiz-Salvador et al. 1998).

In Figure 3, the fibrous structure of the meerschaum was clearly seen from the SEM images before the activation process. After the activation process, the fibrous structure of meerschaum was partially deteriorated due to the removal of water and MgO from the structure, and it became layered and relatively porous. According to the EDX spectrum, the Mg and Ca elements completely disappeared from the structure after the activation process and the Si content increased from 26.97 at.% to 41.26 at.%. Thus, a catalyst with increased acidity and a higher catalytic activity was obtained.

The surface properties and porosity of the mineral as well as several beneficial properties (e.g. absorptive, colloidal and catalytic properties) can be changed by thermal activation or acid activation or both. Silanol (Si-OH) groups in the structure of meerschaum have a certain acidic character and can act as a catalyst or a reaction center. In the chemical structure of meerschaum, there are four different types of water molecules, namely hygroscopic, zeolitic, bounded, and hydroxyl. These water molecules can be removed from the structure via heat treatment leading to changes in the surface area and pore structures of the mineral. The acid treatment of meerschaum also increases the surface area of the mineral by removing the adsorbed cations. This also enhances the crystal structure and pore distribution and limits the distortions that can occur in crystal structure during thermal activation (Inagaki et al. 1990, Rodriguez, Gonzalez, and Munoz 1994).

**References**

Aguado, J., D. P. Serrano, and J. M. Escola. 2006. Catalytic upgrading of plastic wastes. In *Feedstock recycling and pyrolysis of waste plastics: converting waste plastics into diesel and other fuels,* ed. J. Scheirs and W. Kaminsky, 73-110. Chichester: John Wiley & Sons.

Alkan, M., G. Tekin, and H. Namli. 2005. FTIR and zeta potential measurements of sepiolite treated with some organosilanes. *Microporous and Mesoporous Materials* 84(1-3):75-83.

Fan, Y., X. Bao, X. Lin, G. Shi, and H. Liu. 2006. Acidity adjustment of HZSM-5 zeolites by dealumination and realumination with steaming and citric acid treatments. *The Journal of Physical Chemistry B* 110(31):15411-15416.

Inagaki, S., Y. Fukushima, H. Doi, and O. Kamigaito. 1990. Pore size distribution and adsorption selectivity of sepiolite. *Clay Minerals* 25(1):99-105.

Beyer, H. K. 2002. Dealumination techniques for zeolites. In: *Molecular sieves:  science and technology. Postsynthesis modification* *I*, ed. H. G. Karge and J. Weitkamp, 203-255. Berlin: Springer-Verlag.

Mozgawa, W. 2000. The influence of some heavy metals cations on the FTIR spectra of zeolites. *Journal of Molecular Structure*, 555(1-3):299-304.

Rodriguez, M. V., J. D. D. L. Gonzalez, and M. B. Munoz. 1994. Acid activation of a Spanish sepiolite: Physico-chemical characterization, free silica content and surface area of products obtained. *Clay Minerals* 29(3):361-367.

Ruiz-Salvador, A. R., D. W. Lewis, J. Rubayo-Soneira, G. Rodríguez-Fuentes, L. R. Sierra, and C. R. A. Catlow. 1998. Aluminum Distribution in Low Si/Al Zeolites: Dehydrated Na− Clinoptilolite. *The Journal of Physical Chemistry B*, 102(43):8417-8425.

Sabah, E., and M. S. Celik. 2002. Interaction of pyridine derivatives with sepiolite. *Journal of Colloid and Interface Science,* 251(1):33-38.

Tanaka, H., N. Yamasaki, M. Muratani and R. Hino. 2003. Structure and formation process of (K, Na)-clinoptilolite. *Materials Research Bulletin*, 38(4):713-722.

Wan, C., and B. Chen. 2011. Synthesis and characterization of biomimetic hydroxyapatite/sepiolite nanocomposites. *Nanoscale*, 3(2):693-700.