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Inverse Gas Chromatographic Determination of the Surface Properties of ZSM-5 Zeolite ¹

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Abstract

Zeolites are microporous members of the smectite group and are widely used in industrial applications. The surface, morphological mineralogical and physico-chemical properties of zeolites are studied by different instrumental analysis techniques. The surface functional groups were determined by Fourier transform infrared (FTIR) spectra. The morphology and surface functional groups of the materials have been analyzed with the aid of scanning electron microscopy (SEM) images and X-ray diffraction (XRD). The pore properties including the Brunauer-Emmett-Teller (BET) surface area, pore volume, pore size distribution and average pore diameter of the zeolite was determined by physical adsorption of N₂ at -196 °C. Inverse gas chromatography (IGC) was applied to characterize the surface of zeolite.

Keywords: ZSM-5 zeolite; surface properties, morphological properties, physico-chemical properties.

ZSM-5 Zeolitinin Yüzey Özelliklerinin Ters Gaz Kromatografisiyle Belirlenmesi

Öz

Zeolitler, simektit grubunun mikro gözenekli üyeleridir ve endüstriyel uygulamalarda geniş kullanım alanı bulurlar. Zeolitlerin yüzey, morfolojik, mineralojik ve fizikokimyasal özellikleri farklı aletli analiz teknikleri ile incelenmiştir. Yüzey fonksiyonel grupları Fourier dönüşümlü kızılötesi (FTIR) spektrumları ile belirlenmiştir. Malzemelerin morfolojisi ve yüzey fonksiyonel grupları taramalı elektron mikroskobu (SEM) görüntüleri ve X ışını kırınım desenleri yardımıyla analiz edilmiştir. Zeolit, Brunauer-Emmett-Teller (BET) yüzey alanı, gözenek hacmi, gözenek büyüklüğü dağılımı ve ortalama gözenek çapı da dâhil gözenek özellikleri, -196 °C de N₂ atmosferinde fiziksel adsorpsiyon ile belirlenmiştir. Zeolit yüzeyini karakterize etmek için ters gaz kromatografisi (TGK) uygulanmıştır.

Anahtar Kelimeler: ZSM-5 zeoliti, Yüzey özellikleri, Morfolojik özellikler, Fizikokimyasal özellikler

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1. Introduction

Zeolites are a group of minerals of great scientific and industrial importance. The first zeolite mineral was discovered in the middle of the 18th century by the Swedish mineralogist A. Cronstedt. Zeolites are crystalline, hydrated aluminosilicates consisting of a three-dimensional network of $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$ tetrahedra. The tetrahedra are linked by sharing oxygen atoms. More than 150 different zeolite and zeolite-like frameworks are known today, both natural and synthetic [1].

A general formula for zeolite structures can be written as: $\text{M}_x/n[(\text{AlO}_2)_x(\text{SiO}_2)_y] \cdot w\text{H}_2\text{O}$

where n is the valence of cation M , w is the number of water molecules per unit cell, x and y are the total number of tetrahedral atoms per unit cell. The y/x ratio (Si/Al ratio) usually ranges from 1 to 5 or 10 to 100 for high silica zeolites. The framework structure contains channels or interconnected voids that are occupied by the cations and water molecules. The cations are mobile and ordinarily undergo ion exchange. The water may be removed reversibly, generally by application of heat [2]. The special structures of zeolite materials contribute to their unique properties and applications. For example, the microporous nature of zeolites with uniform pores of molecular dimensions allows certain hydrocarbon molecules to enter the crystals while other molecules are rejected based on the molecular size. This makes the phenomenon of shape selectivity possible in catalytic reactions [3]. The ion exchange properties of zeolite materials result from the exchangeable cations and lead to many different applications, such as water softening. The high surface area and high thermal stability of zeolites make them desirable materials for a wide range of applications including adsorbents, detergents and catalysts [4].

Some of the important analyses used broadly in the literature are Infra-red (IR) spectroscopy, and BET using for determination of specific surface area and pore size distribution analysis. Usually, a combination of several instrumental analyses is used to identify the characteristics of the zeolites for specific applications. Transmission spectroscopy like FTIR spectroscopy is the most commonly used method in studying zeolites. It is a useful method to find out the structure, bonding, and chemical properties of zeolites minerals and it has an analytically successful history [5 – 7]. The BET gas adsorption theory is the foundation for the measurement of surface area in high specific surface materials [8] and it is remarkable that the BET method give a higher specific surface area for the finely grained sample than that of the coarse sample. By BET method, the external surface can only be measured because of the limitation in N_2 adsorption [9]. Pore size and pore size distributions are necessary if the material is to be fully characterized. The Density Functional Theory (DFT) was used to determine the distribution of mesoporous. This method uses the N_2 desorption branch of the isotherm and relates the amount of adsorbate desorbed to the average size of pores affected by this desorption. After evaporation of the condensed liquid adsorbate (core), a layer is calculated from the thickness equation. The thickness of this layer decreases with each successive decrease in pressure. The measured quantity of gas desorbed in each step is composed of a quantity equivalent to the liquid core evaporated in that step plus the quantity absorbed from the walls of pores whose cores were evaporated in that step and previous ones [10].

This study aims at investigating surface, morphological, mineralogical and physico-chemical properties of ZSM-5 zeolite in general through a combination of instrumental tests including FTIR, XRD, SEM, BET and IGC analysis. For this reason zeolite ZSM-5 (CBV 28014) was purchased from Zeolyst International Inc. Characterization and surface properties of zeolites were investigated with FTIR, XRD, SEM, BET and IGC analysis. The structural properties of ZSM-5 zeolite were analyzed, N_2 -sorption, SEM and FTIR techniques.

2. Materials and Methods

ZSM-5 zeolite (CBV28014, $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio=280) was directly supplied in the ammonium form by Zeolyst International. For the IGC analysis, the polar probes used were *n*-hexane *n*-heptane, *n*-octane, *n*-nonane.

Properties were taken from literature of the probes [11]. These probes are commonly used for solid surface characterizations by IGC method. The chromatographic experiments were performed with Agilent 7890 gas chromatography equipped with a flame ionization detector (FID). A vacuum pump was used for packing the solids into the columns. High purity nitrogen was used as the carrier gas with a flow rate of about 40 mL/min. The flow rate of carrier gas was corrected for pressure drop and temperature change in the column using James-Martin gas compressibility factor. A stainless steel column (2.00 m long, 5.35 mm I.D.) previously washed with methanol and acetone was packed with zeolite powders. The two ends of the column were plugged with silane-treated glass wool. Measurements were carried out in the temperature range of 290-320 °C. The column was stabilized overnight in stream of nitrogen at 350 °C. The dead volumes of the columns were determined by injecting methane. At least three replicate determinations were used in averaging the net retention volume (V_N).

Surface area, pore volume and pore size distribution was determined using an automatic adsorption instrument at 77 K (Quantachrome, Autosorb 1C). The FTIR spectra of zeolite were recorded on a Perkin Elmer 100 FTIR spectrometer in the 4000 to 400 cm^{-1} wave number range using DRIFT (Diffuse Reflectance Infrared Fourier Transform) technique. A spectrum of the zeolite was obtained using KBr dilution and finely powdered KBr as reference. Scanning electron microscopy (SEM) observation of the ZSM-5 was done by a Jeol JSM-5600 LV (Tokyo, Japan). Prior to SEM observation, all samples were coated with a thin layer of gold using a Polaron SC7620 (Quorum Technologies Ltd., East Sussex, UK). The XRD patterns were recorded X-Ray Diffraction Pan analytical Empyrean technique using $\text{CuK}\alpha$ wavelength $\lambda = 1.541 \text{ \AA}$ with angle range $2\theta = 5\text{-}60^\circ$.

3. Results and Discussion

FTIR-spectroscopy enables to obtain necessary information about individual minerals, non-crystalline admixtures and, simultaneously, to detect presence of organic matter. Absorption of infrared radiation by zeolites depends critically on atomic mass, and the length, strength and force constants of inter-atomic bonds in the structures of these minerals. It is also controlled by constraints of the overall symmetry of the unit cell, and the local site symmetry of each atom within the unit cell [5]. Absorption of infrared radiation is also strongly influenced by a degree of crystalline order [12] and by size and shape of the mineral particles [13].

Figure 1 shows the FTIR spectrum of the zeolite sample. The hydroxyl vibrations can be observed in the 4000-3000 cm^{-1} spectral region, and the crystal structure in the 1500-400 cm^{-1} region. The near -IR region (4000-3000 cm^{-1}) gives valuable information on the nature or origin of different types of OH groups. The spectra of ZSM-5 exhibit a band at 1398 cm^{-1} which is typical of ammonium ions. The bands that appear at 1225, 1102, 795 and 447 cm^{-1} and the characteristic strong doublet at 550-560 cm^{-1} confirms the symmetric and asymmetric Si-O-Si or Si-O-Al bonds. The strong absorption band in the region 1000-1200 cm^{-1} has been assigned to the internal vibration of SiO_4 , AlO_4 tetrahedra for ZSM-5, and also for silica and quartz. The band around 1084 cm^{-1} is attributed to the internal asymmetric stretching vibration of Si-O-T linkage and is observed to shift towards higher wavenumbers with increasing Si/Al ratio of the zeolite. This shift is due to the slightly lower mass of aluminum as compared to that of silicon [14]. The band near 795 cm^{-1} is assigned to the symmetric stretching of the external linkages, and the strong band near 550 cm^{-1} is attributed to the double five-ring lattice vibration of the external linkages. The absorbance at around 450 cm^{-1} is due to the T-O bending vibrations of the SiO_4 and AlO_4 internal tetrahedral. The absorption bands around 550 and 450 cm^{-1} are characteristic of the ZSM-5 crystalline structure. Bands at 3552, 3582, 3600 and 3662 cm^{-1} were assigned to the silanol groups (Si-OH-Al) situated in different crystallographic positions. Bands at 3728 and 3773 cm^{-1} were assigned to Al-OH and Si-OH groups' presents in the aluminosilicate structure [15,16].

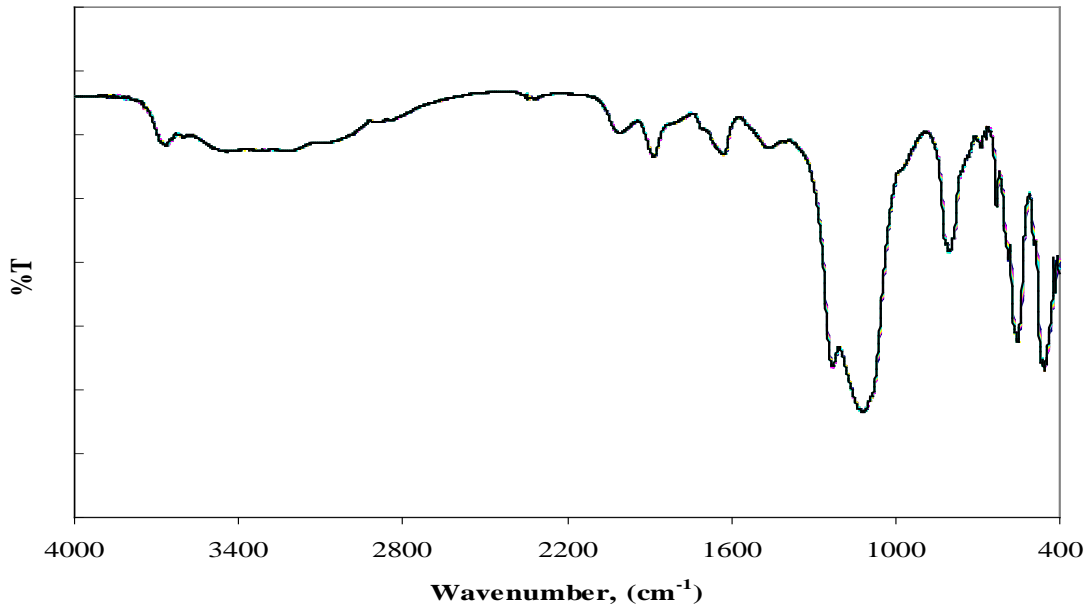


Figure 1. FTIR spectrum of the ZSM-5 zeolite

Figure 2A shows adsorption-desorption isotherms of N_2 at 77 K. According to the International Union of Pure and Applied Chemistry (IUPAC) classification the type of isotherms has a tendency towards a composite of types I and IV, which indicates that zeolite is containing micropores and mesoporous. Type I isotherms with an almost horizontal plateau at higher relative pressures, indicating highly microporous materials with a narrow pore size distribution. The desorption branch of the isotherm show small hysteresis loop which reveal a low development of meso- and macroporosity).

Figure 2B shows the pore size distribution (PSD) of the zeolite obtained using the Density Functional Theory (DFT) method. Zeolite exhibit two peaks around 7-20 \AA and 20-65 \AA . It appears that zeolite include micropores and mesoporous. Specific surface area has been obtained from the Brunauer-Emmett-Teller (BET) equation in the relative pressure range from 0.01 to 0.15. Mesoporous area and mesoporous volume have been obtained from the t-plot analysis.

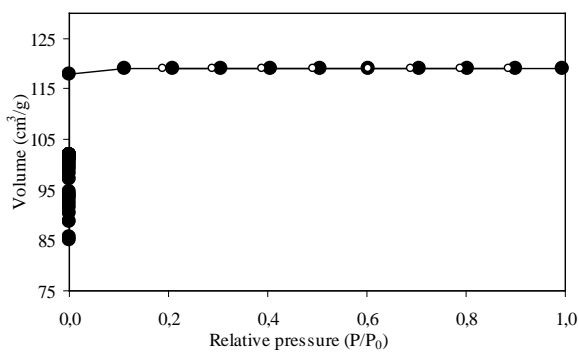


Figure 2A. N_2 adsorption-desorption isotherms at 77 K for the zeolite

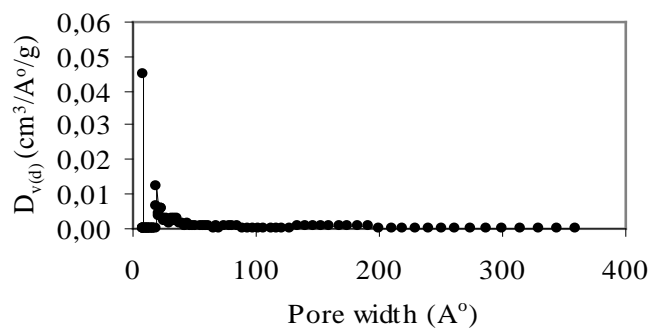


Figure 2B. The corresponding pore size distribution for the zeolite

XRD analysis is an effective technology to identify the crystalline structures of the zeolites. XRD patterns values for ZSM-5 (MFI structure) is given in Figure 3, which agrees well with those reported in the literature. A strong diffraction peak near $2\theta=5-10^\circ$ and $21-25^\circ$, corresponding to the crystalline of zeolite. [17-19]. The peaks at $2\theta = 7.9^\circ$, 8.9° , 23.3° , 24.5° , and 26.8° which correspond to the planes (101), (200), (301), (501), (303), and (503), respectively, were associated with the ZSM-5 (MFI) framework [20]. The two small peaks determining aluminum content in the zeolite framework were also detected at 2θ of $42.0-45.0^\circ$.

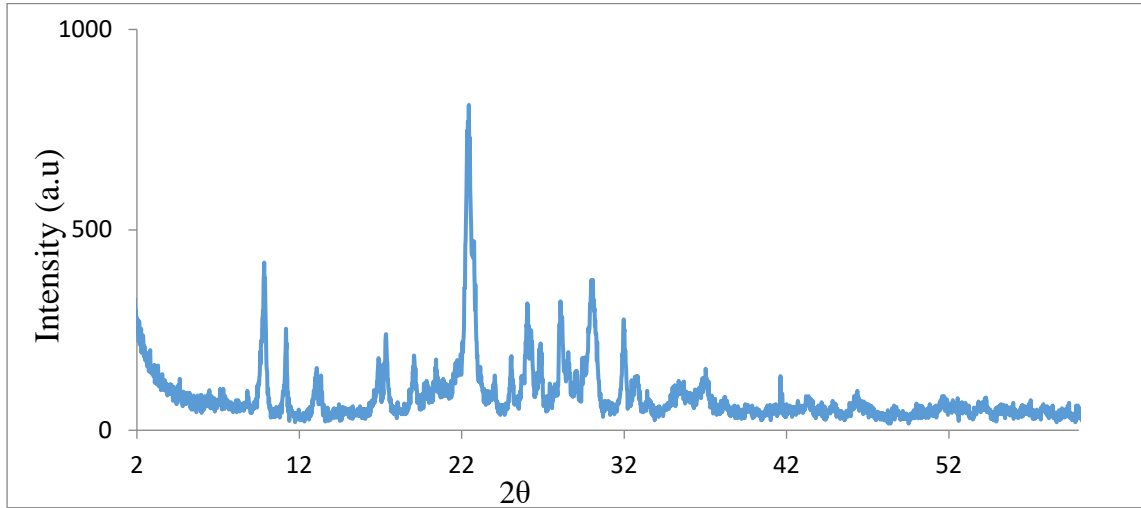


Figure 3. X-Ray Diffraction of Zeolite ZSM-5

To investigate the surface morphology at the micron level, SEM observations were carried out in the ZSM-5 (Fig. 4). The electron micrographs show convincingly that the size and morphology of the crystals depend on the Si/Al molar ratio.

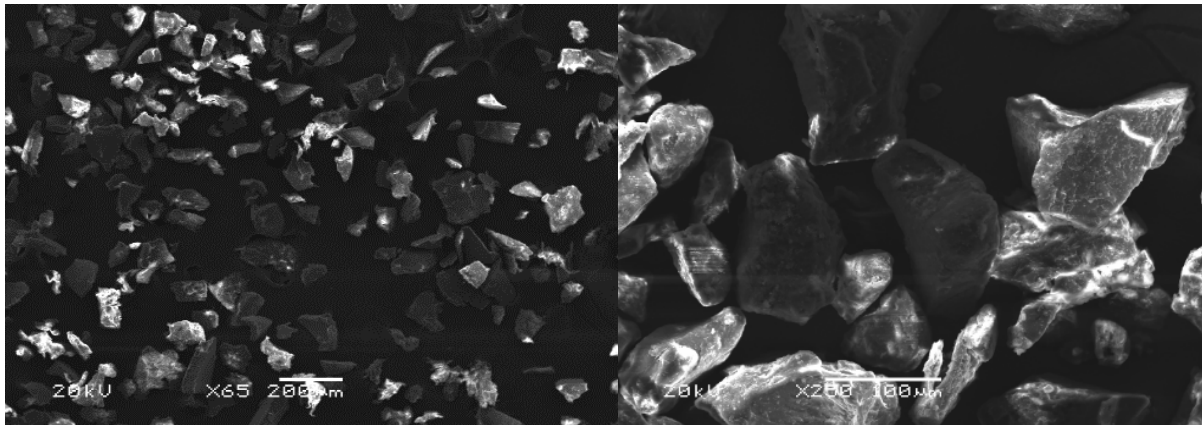


Figure 4. SEM image of ZSM-5 zeolite

The dispersive component of the surface free energy, γ_S^d , was determined by injection of a homologous series of n-alkanes having between 6 and 9 carbon atoms. One of the most commonly measured parameters for the description of the energy situation on the surface of a solid is the surface energy. The surface energy can affect, e.g. catalytic activity or the strength of particle-particle interaction. The dispersive components of zeolite at experimental temperatures were calculated. The obtained γ_S^d values for zeolite were ranged from 45.8 $\text{mJ}\cdot\text{m}^{-2}$ at 290°C, 38 $\text{mJ}\cdot\text{m}^{-2}$ at 300°C, 31.4 $\text{mJ}\cdot\text{m}^{-2}$ at 310°C, and 32.6 $\text{mJ}\cdot\text{m}^{-2}$ at 320°C. The variation of γ_S^d calculated as a function of temperature. It was observed that γ_S^d values decrease with temperature.

Polar probes were used for the investigation of acid-base nature of the surfaces. The free energy of the acid-base interactions of polar probes with the samples, ΔG^{SP} , was calculated. Table 1 shows the free energy of the specific interactions between the sample and polar probes at different temperatures. It was observed that; the ΔG^{SP} value decreases the temperature increases. The lowest ΔG^{SP} was observed with the acidic DCM solvent. It can be observed

that for zeolite, probes with large DN number (such as THF and acetone) show higher ΔG^{SP} values, which suggest that the surface of ZSM-5 is acidic. Since DN and AN^* are expressed in the same units, the high $-\Delta G^{SP}$ value for the probe high DN/AN^* indicates that the adsorption sites are partly acidic. Benzene does not conform to this sequence, as commonly seen in the literature [21]. This is probably because of the fact that benzene is a very weak base and, therefore, its interaction with protons is weak as compared to the interaction of π -electrons of benzene ring with Na^+ ions. Very low values can be observed for TCM, implying that although the adsorption mechanism of this molecule is considered as a combined mechanism, the porosity is much more important than the chemical surface groups because the specific contribution. The values of the specific enthalpy of adsorption, ΔH^{SP} and the specific entropy of adsorption, ΔS^{SP} computed by varying $\Delta G^{SP}/T$ against $1/T$ are presented in Table 1. By plotting $-\Delta H^{SP}/AN^*$ versus DN/AN^* , K_A and K_D can be obtained from the slope and the intercept, respectively (Figure 2). The values of K_A and K_D for zeolite are found to be 1.45 and 0.24. According to the values obtained from $K_D/K_A = 0.16$ is reflected the surface of zeolite is acidic.

Table 1. The variation of ΔG^{SP} with temperature, and ΔH^{SP} and ΔS^{SP} values of polar probes on zeolite.

T(°C)	$-\Delta G^{SP}$ (kJ/mol)				$-\Delta H^{SP}$	$-\Delta S^{SP}10^3$
	290°C	300°C	310°C	320°C	(kJ/mol)	(kJ/mol.K)
Benzene	-0,94	-0,90	-1,01	-1,44	18,29	33,40
Acetone	6,52	5,59	5,67	5,47	45,50	68,90
DCM	3,65	3,42	3,52	3,08	24,78	36,80
TCM	-1,89	-1,69	-2,07	-2,49	54,62	97,80
THF	10,15	6,63	6,12	6,60	114,10	183,60

4. Conclusion

In order to be able to better identify the nature of the zeolite surface, analysis techniques, such as FTIR, BET, XRD SEM and IGC were also applied. Overall, the results showed that IGC is an effective method to characterize the zeolite surface properties especially when combined with additional techniques such as BET, FTIR, XRD and SEM analysis. Surface properties of the ZSM-5 zeolite are highly important in their application for catalysis in industry. The BET specific surface area of the ZSM-5 zeolite is high because of has higher Si/Al molar ratio (SiO_2/Al_2O_3 mole ratio=280). FTIR spectra also show that the active zeolite catalyst contain some extra-framework octahedral aluminium in addition to the normal tetrahedral framework aluminium. This is in support of the 3660 cm^{-1} broad band observed in the FTIR spectra assigned to hydroxyl groups associated with extra-lattice aluminium.

The characterization of the surface properties for zeolite were investigated by IGC. Showed that IGC is a powerful analytical technique very useful for studying the surface properties of ZSM-5 zeolite and for monitoring adsorption processes. Surface information on adsorption was obtained from the temperature variation of the partition coefficients for probes at zero coverage. The dispersive component of free energy of adsorption probably was related to

structural heterogeneities on the lateral surfaces, as well as to the channels and pores present at 290–320 °C. The experimental results indicate that γ_S^d values of studied material gradually decreased with increasing column temperature which is consistent with the fundamental concept of Gibbs free energy. The values of K_A and K_D indicated that zeolite surface is acidic.

5. Acknowledgements

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6. References

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Uzun Özet

Giriş

Zeolitler, büyük bilimsel ve endüstriyel öneme sahip bir grup minerallerdir. İlk zeolit minerali 18. yüzyılım ortalarında İsveçli mineralog A. Cronstedt tarafından keşfedildi. Zeolitler, tetrahedral $[\text{SiO}_4]^{4-}$ ve $[\text{AlO}_4]^{5-}$ üç boyutlu ağından oluşan kristalimsi, hidratlanmış alüminosilikat yapıdadır. Bugün hem doğal hem de sentetik olarak 150'den fazla farklı zeolit ve zeolit benzeri yapı bilinmektedir. Kimyasal kompozisyonları çok benzer olmasına rağmen her bir zeolit türü kendi özel kristal yapısına sahiptir. Çoğu yapılar basit geometrik şekilde birleşmiş SiO_4 , AlO_4 tetrahedralleri olarak görülür. Katyonların kanal içinde yer değiştirebilmeleri zeolitlere ‘moleküler elek’ özelliği kazandırır. Bu kanallar tetrahedrallerin birleşmesinden oluşan çok yüzeylilerin (polihedron) üç yönlü bağlanması şeklindedir. Zeolitlerin gözenek boyutları kristal yapılarına ve bir dereceye kadar da içerdikleri katyonlara bağlıdır. Çoğu zeolit de kristal yapı Si-O-Al atomlarının meydana getirdiği halkalarla bağlanmış gözeneklerden oluşur. Bu halkaların oluşturduğu geçit pencere olarak adlandırılır ve pencere boyutu halkalardaki atom sayısı ile orantılıdır.

Zeolitin genel formülü: $\text{M}_x/\text{n}[(\text{AlO}_2)_x(\text{SiO}_2)_y] \cdot \text{wH}_2\text{O}$ olarak ifade edilir.

burada n, M katyonunun değeridir, w, birim hücre başına su molekülü sayısıdır, x ve y, birim hücre başına toplam tetrahedral atom sayısıdır. y/x oranı (Si/Al oranı) genellikle 1 ila 5 veya yüksek silika zeolitleri için 10 ila 100 arasındadır.

Çatı yapısı, katyonlar ve su molekülleri tarafından işgal edilen, kanalları ve ara boşlukları içerir. Bu katyonlar hareketlidir ve düzenli biçimde iyon değişimini gerçekleştirirler. Yüzey suyu, hacimce %50'lere varan bir oranda, çatı içinde bulunmasına rağmen, ısıtılarak, çatıya zarar vermeden yapıdan uzaklaştırılabilir ve tersinir olarak yapıya alınabilir. Gözenekli yapı ve geniş yüzey alanına sahip üç boyutlu bu kafes yapısı zeolit minerallerine teknolojik ve ticari önem kazandıran özelliklerin başında gelmektedir.

Bu çalışmada ZSM-5 zeolitinin yüzey, morfolojik, mineralojik ve fizikokimyasal özelliklerini, çeşitli enstrümantal analiz tekniklerini (FTIR, XRD, SEM, BET ve TGK) kullanarak incelemeyi amaçlamaktadır. Bu amaçla, zeolit ZSM-5 (CBV 28014), Amerikan Zeolyst firmasından satın alınmıştır. Zeolitlerin karakterizasyonu ve yüzey özellikleri FTIR, XRD, SEM, BET ve TGK analizleri ile incelendi. ZSM-5 zeolitinin yapısal özellikleri N_2 sorpsiyonu, SEM ve FTIR teknikleri ile analiz edildi.

Metod

ZSM-5 zeoliti (CBV28014, $\text{SiO}_2/\text{Al}_2\text{O}_3$ mol oranı=280) sentetik olarak Amerikan Zeolyst firmasından NH_4 türünde temin edilmiştir. TGK'de polar çözücüler olarak n-hekzan n-heptan, n-oktan, n-nonan kullanıldı. Bu çözücüler TGK yöntemiyle katı yüzey karakterizasyonların da genellikle kullanılmaktadır. Deneysel Agilent 7890 model alev iyonlaşma dedektörlü (FID) TGK cihazında yapıldı. Yüzey alanı, gözenek hacmi ve gözenek büyüklüğü dağılımı, 77 K'de (Quantachrome, Autosorb 1C) otomatik azot adsorpsiyonu yüzey karakterizasyon cihazı kullanılarak belirlendi. Zeolitin FTIR spektrumları, DRIFT (difüze yansıma) tekniği kullanılarak 4000 ila 400 cm^{-1} dalga sayısı aralığında bir Perkin Elmer 100 FTIR spektrometresinde kaydedildi. ZSM-5'in mikro yapısı Jeol JSM-5600 LV (Tokyo, Japonya) taramalı elektron mikroskobu (SEM) kullanılarak incelendi. Zeolitin kristal yapısını belirlemek amacıyla X-ışını difraktometresi (X-Ray Diffraction Pan analytical Empyrean) kullanıldı. $\text{CuK}\alpha$ radyasyon kullanılarak her birinin $2\theta = 5-60^\circ$ aralığındaki kristal yapısı incelendi.

Sonuçlar ve Tartışma

Zeolit yüzeyinin yapısını daha iyi tanımlayabilmek için; FTIR, BET, XRD, SEM ve TGK gibi analiz teknikleri uygulanmıştır. Genel olarak sonuçlar TGK'nin, özellikle BET, FTIR, XRD ve SEM analizi gibi ek tekniklerle birleştirildiğinde zeolit yüzey özelliklerini karakterize etmek için etkili bir yöntem olduğunu göstermiştir. ZSM-5 zeolitinin yüzey özellikleri, endüstrideki kataliz uygulamalarında oldukça önemlidir. ZSM-5 zeolitinin BET spesifik yüzey alanı, yüksek Si / Al molar oranına ($\text{SiO}_2/\text{Al}_2\text{O}_3$ mol oranı=280) sahip olması nedeniyle yüksektir. Zeolitlerin kristal yapısında kuvvetli aktif asidik merkezlerin oluşturulması için birinci yol iyon değişimidir. Zeolitlerde iyon değişimi; kararlılık seçicilik, adsorpsiyon, katalitik aktiflik ve zeolitin iyon değişim kapasitesine bağlı olarak değişir.

Zeolitin yüzey özelliklerinin karakterizasyonu TGK ile incelenmiştir. TGK, ZSM-5 zeolitinin yüzey özelliklerini incelemek ve adsorpsiyon proseslerini izlemek için çok faydalı olan güçlü, analitik bir tekniktir. Adsorpsiyonla ilgili yüzey bilgileri, sıfır yüzey kaplanmasında çözücüler için dağılım katsayılarının sıcaklık ile değişimlerinden elde edildi. Serbest yüzey enerjisinin dağılım bileşeni, 290–320 $^\circ\text{C}$ 'de bulunan kanal ve gözeneklerin yanı sıra, muhtemelen yanal yüzeylerdeki yapısal heterojenlikler ile ilgilidir. Deneysel sonuçlar, incelenen materyalin γ_s^d değerlerinin artan kolon sıcaklığı ile giderek azaldığını göstermektedir. K_A ve K_D değerleri, zeolit yüzeyinin asidik olduğunu göstermiştir.