



- **RESEARCH ARTICLE** -

## Comparison of Hydrothermal Method and Ultrasonic Method in Zeolite Synthesis and Investigation of Catalytic Activities of Synthesized Zeolites

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### Abstract

In this study, ZSM-5 and beta zeolites, which constitutes the most industrially important artificial zeolite species., were synthesized and the effects of synthesized zeolite in catalytic cracking were investigated. ZSM-5 and beta zeolite were synthesized by varying synthesis time, synthesis method and calcination temperatures. The composition of the synthesis was kept constant and than compared with ultrasonic method and hydrothermal method.

ZSM-5 and beta zeolite derivatives were synthesized with changing the synthesis method. Beta zeolite is obtained as a result of the synthesis with low temperature in 20 minutes with using of ultrasonic method. On the other hand, ZSM-5 zeolite is achieved at the end of the synthesis with high temperature in 72 hours with using of hidrothermal method.

The X-Ray Powder Diffraction (XRD) patterns and Scanning Electron Microscopy (SEM) images of ZSM-5 zeolites showed that the crystal structure and phase purity of ZSM-5 increased with increase in synthesis time and not affected by the calcination temperature. Otherwise, the crystal structure and phase purity of beta zeolite increased with increase in calcination temperature.

To determine the catalytic performances of the products, the catalytic cracking processes were performed. First of all, thermal cracking was realized without catalyst for comparison with the others. Then, catalytic cracking was carried out with CaO, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, natural zeolite, ZSM-5 and beta zeolite.

Compairing the results, the catalytic efficiency of the synthesized products were higher than the others. Yield of over 70 % was obtained with synthesized ZSM-5 and zeolite beta.

### Keywords:

Synthesis of zeolite, ZSM-5, zeolite Beta, catalytic cracking, the catalyst

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**Introduction**

In today's world, a large amount of total energy sources are formed from fossil-derived fuels, which is called primary energy sources, and majority of these fuels are based on oil. Oil, which is the leading primary energy source, has a significant role among world countries both in terms of politically and economically (Sevil, 2003). Researchers are concentrated on renewable energy sources because of ever-increasing world population and energy consumption, which is also increasing parallel to industrialization, inadequate to meet existing reserves (Kumar et al., 2011). Catalytic cracking as a renewable energy process is the fuel production of short-chain hydrocarbons from long-chain hydrocarbons (Castro et al., 2014). Catalyst is the most important material in catalytic cracking processes. Zeolites take the first place among the catalysts used in catalytic cracking processes (Huang et al., 2010; Mastral et al., 2006; Seo et al., 2003; Rahimi and Karimzadeh, 2011). More than 150 types of zeolites have been synthesized which are not only utilized in petrochemical industry but also in many other areas. Zeolites are generally defined as aqueous aluminum silicates containing alkali and alkaline earth elements. In addition; since zeolites have the following properties, ability of ion exchange, adsorption and molecular sieve structure, uniform crystal structure, silica content, low density and pore structure, they are utilized in many industrial sectors such as energy, agriculture and stockbreeding, mining and metallurgy, construction, detergent, paper industry and nuclear industry (Zhang et al., 2013; Coelho et al., 2012; Kim et al., 2012). Zeolites are divided in two as natural and synthetic. Natural zeolites are easier to find and process than other mines. Despite this, synthetic zeolites are preferred since natural zeolites are not within the desired purity and pore diameters. ZSM and its derivatives, which are synthesized according to area of utilization, also used in petroleum industry as catalyst for hydrocarbon conversion reactions. ZSM and its derivatives are materials with hydrophobic and organophilic structure with high silica content (Tissler et al., 1989; Zhang et al., 2012).

Zeng et al. (2017), synthesized Al-ITQ-13 zeolites with different Si / Al atomic ratios. In their study, they reported that crystallization is occurred in a short time (16 hours total synthesis time) in the continuous flow stainless steel reactor. Khoshbin and Karimzadeh (2017), in their study, synthesized a series of ZSM-5 zeolites with ultrasonic energy and examined their catalytic cracking efficiencies. They reported that effect of ultrasound force (100, 200 and 300 W) on physico-chemical properties of synthesized zeolites was investigated. They reported that the sample synthesized with 200 W ultrasound power exhibited the highest catalytic activity.

In this study, tetra-propyl-ammonium-bromide (TPABr) doped ZSM was synthesized and characterized by ultrasonic method and hydrothermal (conventional) method. Thus, these two methods are compared. Characterization of ZSMs are determined by; X-Ray Powder Diffraction Device (XRD) and Scanning Electron Microscope (SEM).

Results indicate that ZSMs obtained by ultrasonic method exhibits similar XRD and SEM results in the literature. Literature reviews shows that the lowest mixing time is 5h, for the

hydrothermal method general mixing time is 72h. In our study with ultrasonic method, mixing time is reduced to 20 minutes.

### **Material**

In this study, conventional hydrothermal method and ultrasonic method are compared. The effect of calcination temperatures on synthesis is investigated by changing calcination temperatures both in hydrothermal and ultrasonic method. The individual catalyst efficiencies of the CaO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> compounds were measured one by one to compare the catalyst efficiency of the synthesized product.

### **Reactor Design**

Reactor is designed in order to use in product synthesis with hydrothermal method. In this reactor; A sample chamber made of chrome-nickel stainless steel with high-pressure resistance, an AC Servo motor which produces stable speed and torque control under 1 rpm speed range and chrome-nickel stainless steel mixing apparatus is utilized. Rotation speed, temperature and pressure are controlled by digital screens. The mouth of the sample chamber is designed to be well sealed. Due to a security concerns, the automatic on and off buttons are put into two different places and are activated with the same press. In order to transfer the generated steam out of the chamber, a transfer pipe with a manual open-close switch is mounted to the chamber. Designed reactor is shown in Figure 1.



Figure 1. Reactor

### **Ultrasonic Laboratory Device**

General application areas of ultrasonic homogenizer are followed as; Sample preparation, cell disruption, homogenization, dispersion and separation, particle size reduction and chemical reactions. In the experimental study, the Hielscher model table-type UP200S Ultrasonic

Laboratory instrument with adjustable sound waves amplitude (%) and adjustable rotation speed is used.

### Chemicals

Chemicals during ZSM derivative zeolite synthesis are as followed ; powdered silica (Sigma, 99.8 %) as silica source, aluminum hydroxide (Merck, pure powder) as alumina source, sodium hydroxide (Sigma, >98.4 %), tetra-propylammonium bromide (TPABr) (Fluka, >98 %) as the organic ligand, ammonium chloride (Sigma, 99.998 %) to dispose of sodium ions. Calcium oxide (Aldrich, 99.995%) and silicon dioxide (Aldrich, 99.5%) are used as catalyst in catalytic cracking.

### Method

#### Synthesis of ZSM Derivative Zeolites

In this study; 12.84 Na<sub>2</sub>O: Al<sub>2</sub>O<sub>3</sub>: 76.73 SiO<sub>2</sub>: 6.4 TPBr: 3962.6 H<sub>2</sub>O compositions, which is proposed by Demirkan (2002), is taken as reference [15]. Synthesis of ZSM-derived zeolites was carried out by preparing three different mixtures (mixtures A, B and C). For mixture A; 20.10 g of silica were added to 162.50 ml of deionized water. For mixture B; 4.48 g of NaOH and 0.68 g of Al(OH)<sub>3</sub> were dissolved in 18.75 ml of deionized water. The prepared B mixture was added onto A mixture and stirred for 15 minutes. After then, 7.43 g of TPABr was dissolved in 75 ml of water to prepare mixture C. Mixture C is added onto A and B mixture followed by 110 ml deionized water addition. The final mixture was stirred for 15 minutes and the synthesis gel is obtained. The synthesis gel is homogenized by ultrasonic method for 20 minutes. After 20 minutes, sample is filtrated and washed several times with deionized water. Washed sample is dried and exposed to high temperature. Then, synthesized sample is reacted with 1M 250 ml NH<sub>4</sub>Cl solution in order to dispose of sodium ions. The sample is again washed, dried and exposed to high temperature respectively. Different aging methods and different calcination temperatures have been tried during synthesis. In the hydrothermal method, the samples were kept in the reactor for 72 hours. Methods and calcination temperatures are given in Table 1.

Table 1. Codes and Changed Parameters of Synthesized Samples

Sample Code	Aging Method	Aging Time	Calcination Temperature	Calcination Time
SNT-1	Ultrasonic Method	20 minutes	540 °C	2 hours
SNT-2	Ultrasonic Method	20 minutes	800 °C	2 hours
SNT-3	Ultrasonic Method	20 minutes	1100 °C	2 hours
SNT-4	Ultrasonic Method	1 hours	540 °C	2 hours
SNT-5	Ultrasonic Method	30 minutes	540 °C	2 hours
SNT-6	Ultrasonic Method	30 minutes	800 °C	2 hours
SNT-7	Ultrasonic Method	30 minutes	900 °C	2 hours
SNT-8	Ultrasonic Method	30 minutes	1100 °C	2 hours
SNT-9	Hydrothermal Method	72 hours	540 °C	2 hours
SNT-10	Hydrothermal Method	72 hours	800 °C	2 hours
SNT-11	Hydrothermal Method	72 hours	900 °C	2 hours

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SNT-12	Hydrothermal Method	72 hours	1100 °C	2 hours
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### ***Characterization Methods***

The crystal structure analysis of each synthesized sample was determined by X-Ray Powder Diffraction Device (XRD), while the particle sizes and morphologies of synthesized products were determined by Scanning Electron Microscope (SEM).

### ***Experiments of Catalytic Cracking***

Catalytic cracking experiments were carried out with the catalysts in the literature in order to compare and examine the catalytic efficiencies of synthesized samples with fixed data. CaO, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, natural zeolite, synthesized beta zeolite and synthesized ZSM-5 are used as catalysts to obtain light hydrocarbon products from heavy hydrocarbons with distillation. Machine oil with heavy hydrocarbon content, collected from industrial wastes, is selected as raw material. For the experiment, a total of 90 ml of oil was filtered off and the solid impurities in the filtrate were removed. The catalytic cracking experiment was completed in 3 hours with gradual temperature increase. The amount of product coming in every 10 minutes was recorded following the sample temperature and vapor temperature in the reactor.

## **Results**

### ***Characterization of Synthesized Zeolites***

#### ***Results of X-Ray Diffraction Pattern Analysis***

X-ray diffraction patterns are taken to determine crystal structures of ZSM-derivative zeolites synthesized during different synthesis methods, calcination temperatures and synthesis times. The zeolites obtained from homogenization with the Ultrasonic Method were found to be a characteristic peak for the peak beta zeolite in XRD patterns at  $2\theta \approx 22.4^\circ$ . XRD results are shown in Figure 2 and 3. The magnitude of the peak intensity indicates that the crystals formed in beta zeolite synthesis are homogeneous and in a uniform structure. It was found that the peak size formed at  $2\theta \approx 22.4^\circ$  increased with increasing calcination temperature (Gür, 2006). Hydrothermal Method requires a long homogenization time. Apart from that, it was observed in the XRD patterns that there is no effect of calcination temperature change on the zeolite crystallinity obtained by Hydrothermal Method. The XRD patterns of the samples obtained by the Hydrothermal Method show that the peaks at  $2\theta \approx 23^\circ$  are characteristic peaks of ZSM-5 zeolites which are shown in Figures 4 and 5 [15]. As a result; SNT-3, SNT-8 and SNT-12 samples obtained at high calcination temperature have the most uniform peaks. In addition, it is observed that the low temperature SNT-9 sample in the Hydrothermal Method also has uniform peaks.

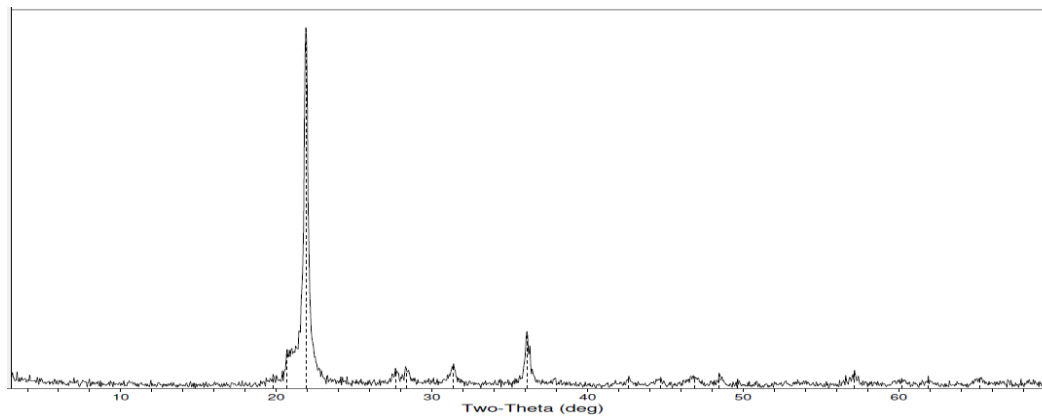


Figure 2. XRD Pattern of SNT-3 Coded ZSM Derivative Zeolite Example

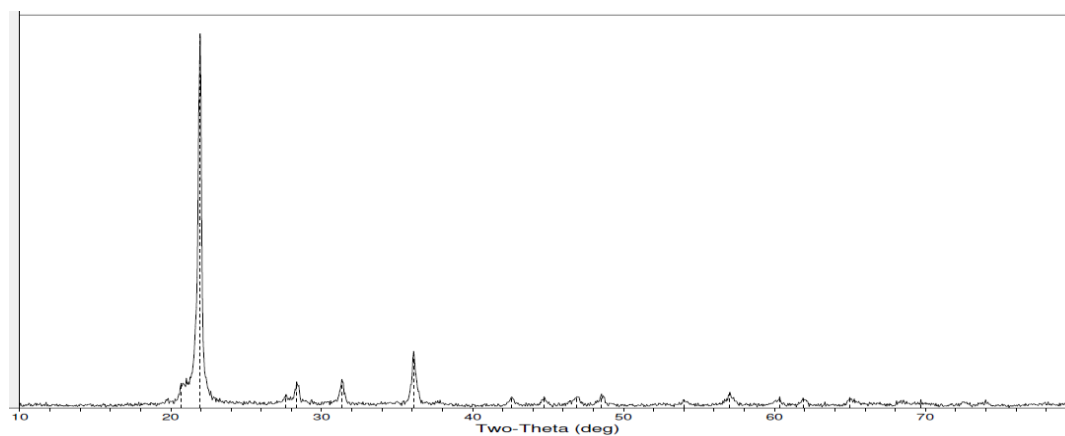


Figure 3. XRD Pattern of SNT-8 Coded ZSM Derivative Zeolite Example

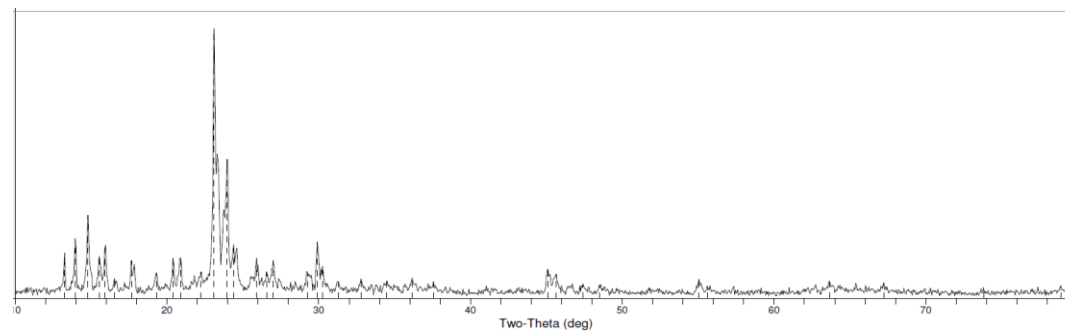


Figure 4. XRD Pattern of SNT-9 Coded ZSM Derivative Zeolite Example

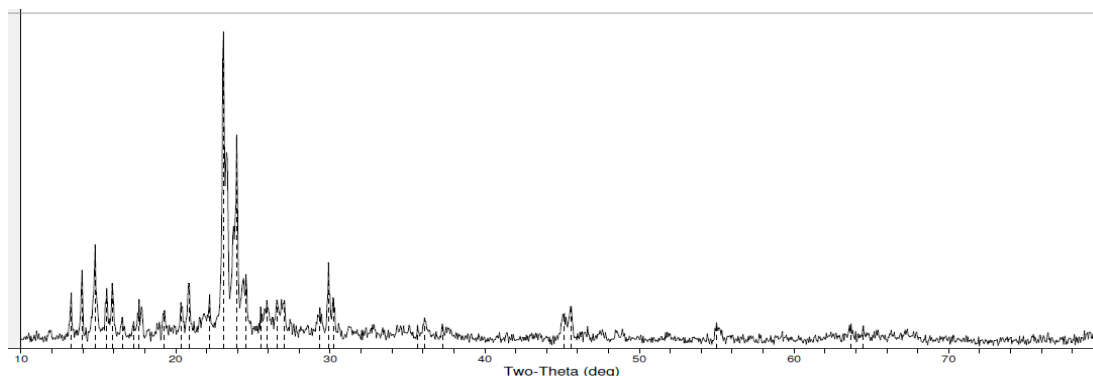


Figure 5. XRD Pattern of SNT-12 Coded ZSM Derivative Zeolite Example

### ***Scanning Electron Microscope (SEM) Analysis Results***

SEM images of SNT-3, SNT-8 obtained with Ultrasonic Method and SNT-9, SNT-12 coded ZSM derived zeolite samples obtained with Hydrothermal Method are shown in Fig.6 When SEM images are examined; It was found that the crystal sizes of the zeolites obtained by Ultrasonic Method are smaller than those of the zeolites obtained by the conventional Hydrothermal Method. It was determined that the crystal dimensions of samples obtained by ultrasonic method have homogeneity while the crystal dimensions of samples obtained by hydrothermal method do not exhibit homogeneous distribution In our study, SEM images of the samples obtained by ultrasonic method are similar to Askari et.al's (2013) studies.

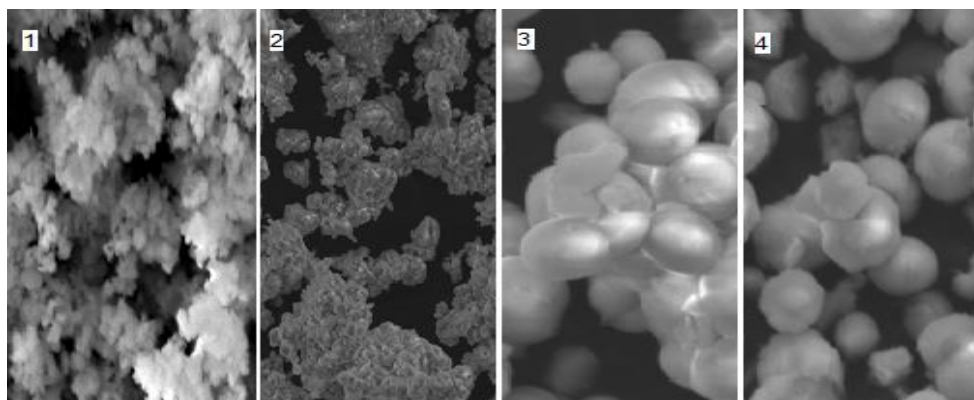


Figure 6. 1) SNT-3, 2) SNT-8, 3) SNT-9, 4) SNT-12; Coded ZSM Derivative Zeolite Samples SEM Analysis Results

### ***Data Obtained from Catalytic Cracking***

Catalytic cracking experiments are carried out with waste oils each 90 ml in the presence of  $\text{SiO}_2$ ,  $\text{CaO}$  and  $\text{Al}_2\text{O}_3$ , natural zeolite, synthesized ZSM-5 and synthesized beta zeolite catalysts and in the absence of any catalyst. The efficiency increases of the synthesized samples are higher compared to natural zeolite and oxidized compounds. According to calculations performed, last one hour is the range which efficiency increase is highest within 3 hours test period. Product

efficiency according to temperature is given in Figure 7. As shown in Figure 7, under the same reaction conditions, ZSM-5 and beta zeolite have the highest product yields compared to the other catalysts. The synthesized zsm-5 and beta zeolite catalysts have productivity increase of respectively 14.3% and 11% compared to the result of catalytic cracking obtained with natural zeolite catalyst the nearest to them. When the increase in efficiency between ZSM-5 catalyst and other catalysts is evaluated; have been detected that, respectively, 60% for without catalyst, 50% for SiO<sub>2</sub>, 44.1% for Al<sub>2</sub>O<sub>3</sub> and 33.3% for CaO. Also for Beta zeolite, it was determined that this state was, respectively, 55.4% according to without catalyst, 45.8% according to SiO<sub>2</sub>, 40% according to Al<sub>2</sub>O<sub>3</sub> and 29.5% according to CaO.

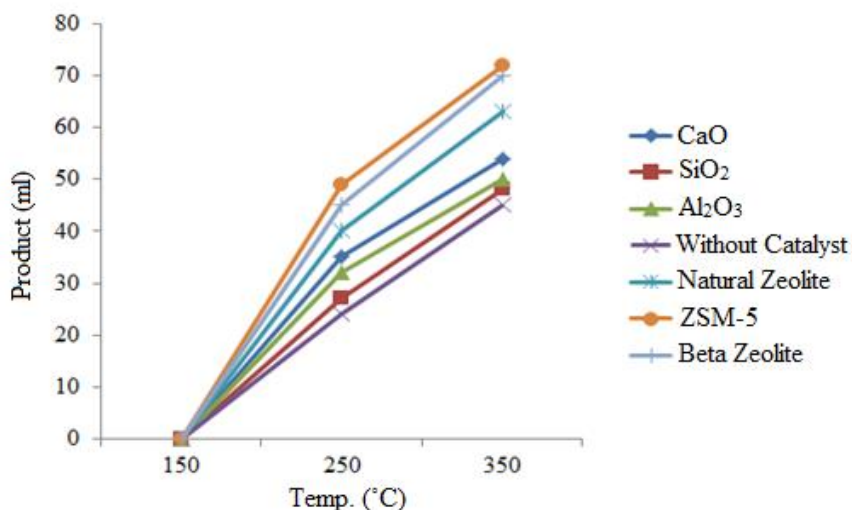


Figure 7. Product Yield vs Temperature

Comparisons of product quantities obtained by catalytic cracking are given in Table 2.

Table 2. Product Quantities and Yields% Obtained by Catalytic Cracking

Catalyst	60.Minutes	120.Minutes	180.Minutes	Total	Yield %
No Catalyst	6 ml	18 ml	21 ml	45 ml	50.0 %
SiO <sub>2</sub>	7 ml	20 ml	21 ml	48 ml	53.3 %
Al <sub>2</sub> O <sub>3</sub>	11 ml	21 ml	18 ml	50 ml	55.5 %
CaO	15 ml	20 ml	19 ml	54 ml	60.0 %
Natural Zeolite	15 ml	25 ml	23 ml	63 ml	70.0 %
Beta Zeolite	16 ml	29 ml	25 ml	70 ml	77.7 %
ZSM-5	16 ml	33 ml	23 ml	72 ml	80.0 %



## Discussion

In this study, where ZSM-type zeolites are synthesized, different homogenization methods were tested. During the aging methods, the effects of calcination temperature differences and the duration of the synthesis on the crystal structure were investigated. Ultrasonic Method and Hydrothermal method are compared while synthesis composition kept constant during experiments. Despite the composition is constant, it is observed that synthesized sample differs depending on the homogenization method. Zeolite beta formation by ultrasonic method was determined by analysis of XRD peaks and SEM images. On the other hand, it was found that ZSM-5 type zeolite is obtained with the same composition by 72 hours homogenization process with hydrothermal method.

Crystal formations and crystal morphologies of the samples obtained by ultrasonic method varied with different calcination temperatures. It is found that net crystal structures are obtained in samples which exposed to high calcination temperatures. In addition, it is determined with SEM images that crystal dimensions are stable with high calcination temperatures.

In hydrothermal method, crystal formations and crystal structures are not affected by the calcination temperature changes.

In the Ultrasonic Method, much shorter homogenization time is sufficient compared to Hydrothermal Method. ZSM-derived zeolite is synthesized with Hydrothermal Method in 72 hours while this time was reduced to 20 minutes with Ultrasonic Method.

Type ZSM-5; 10-ring MFI-type zeolites with cross-sectional channel structure, having a pore size of  $5.1 \times 5.5 \text{ \AA}$ . Beta type is; 12-ring BETA type zeolites with cross-sectional channel structure, with a pore size of  $7.6 \times 6.4 \text{ \AA}$ . They both have the same chemical composition with no significant structural difference. Also, utilization areas are generally common.

When ultrasonic method and hydrothermal method compared, in addition to positive contributions of the ultrasonic method such as not to heat the sample for synthesis and reduction in synthesis time, it is found that equipment and electricity costs are lower than other method.

As shown in Table 2, a total product yield of over 75% was obtained in catalytic cracking process with ZSM-5 and beta zeolite catalysts.

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