

Modification of ZSM-5 Catalyst Using Microwave-Assisted and Thermal Methods: Characterizations and n-Heptane Cracking Activity

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In this study, mesoporous zeolite ZSM-5 samples were successfully synthesized using the microwave method, and thermal method to evaluate the efficiency of the n-heptane cracking reaction. The physicochemical properties and characteristics of the catalysts were determined by X-ray diffraction (XRD), N₂ adsorption-desorption at low temperatures, and scanning electron microscopy (SEM). The effects of the n-heptane cracking reaction temperature of the modified zeolite samples between 400 and 600 °C were investigated. As a result, the mesoporous zeolites were successfully prepared, with the external area of modified zeolites increasing 12-13 times for samples with a high Si/Al ratio and increasing 1.4-3 times for materials with a low Si/Al ratio compared with the original zeolites. For zeolite ZSM-5 with a high Si/Al ratio, the microwave approach successfully modified the initial sample in 12 times less time than the hydrothermal method to obtain approximately the same mesopore surface area. The prepared zeolites with a low Si/Al ratio exhibited higher efficiency than the initial sample in the n-heptane cracking procedure, with the conversion efficiency of the former being 4.4-5.2 % higher than that of the latter.

1. Introduction

Light olefins such as ethene and propene are crucial feedstocks in chemical industries to produce various components such as polymers, synthetic fibers, rubbers, and plastic materials. The thermal cracking of naphtha obtained by the distillation of crude oil is still the primary energy-intensive process in the petrochemical industry, which today yields 60 % of the world's propylene and 95 % of the world's ethylene as byproducts of ethylene production in the petrochemical industry (Keyvani and Ostroff, 2015). It requires high reaction temperatures of 800 – 880 °C, which account for 40 % of the total energy consumed annually in the petrochemical industry and produce significant greenhouse emissions (Rahimi and Karimzadeh, 2011). Another drawback of the steam cracking process is the inability to fully control the ratio of propylene to ethylene in the olefins produced, and its direct reliance on the feed type (Liu et al., 2014). This would not be sufficient to meet the global demand for propylene from the petrochemical industry, so new sources of propylene will be required to meet the expected industrial demand in the future. Evidently, processes that are efficient-energy and can control the ratio of light olefins are preferred. One of which gaining attention from researchers to address all of these drawbacks is the catalytic cracking process of hydrocarbons (Park et al., 2010).

To increase the yields of light olefins from the catalytic cracking of hydrocarbons, various types of catalysts such as basic catalysts (Valle et al., 2022), transition metal oxide catalysts (Thangadurai and Tye, 2021), and acidic catalysts (Socci et al., 2019) have been investigated. Solid proton-donor acids, particularly zeolites, are fundamental components used in three vital catalytic reactions in the fields of petroleum refining, petrochemicals, and pollution management, and HZSM-5 is the most active and extensively researched hydrocarbon cracking catalyst as compared to other zeolite types (Rahimi and Karimzadeh, 2011). Specifically, zeolite ZSM-5 is considered a potential catalyst for this process because of its shape selectivity, strong acidity,

and thermal/hydrothermal stability (Li et al., 2017). The micropore size of zeolites restricts diffusion and makes it difficult for bulky structured reactive molecules to interact with the acid sites, resulting in decreased reaction efficiency and catalytic activity (Na and Somorjai, 2015). Apparently, modifying the zeolite with a hierarchical mesoporous structure can enhance the diffusion ability and improve the catalytic cracking activity.

The formation mechanism of the mesoporous structure in zeolite consists of two stages. The framework first experiences partial amorphization or vacancy owing to the chemical expulsion of aluminum from the structure. Then, the Si atoms relocate to the defective parts caused by the expelled aluminum atoms to form new bonds and stabilize the crystal structure. As a result, some vacancies are filled, while others develop into mesopores (van Donk et al., 2003). Mesoporous zeolite modification expands the micropores in the original zeolite crystal into larger pores through chemical treatments, including (i) designing zeolites with intrinsic large pores (Chen et al., 2020) or nanosized particles (Awala et al., 2015); (ii) employing templating methods to endow zeolites with mesoporous characteristics (Khalil et al., 2021); and (iii) hierarchical porous composites (Tran et al., 2021). The final method, which involves dealumination and desilication, is both strong and cost-effective (Verboekend et al., 2016), making it a highly attractive option for practical applications (Zhang et al., 2020). Modern methods of post-synthetic dealumination and desilication include steaming, calcination, and hydrothermal treatment in the presence of acids, bases, or chelating agents such as ethylenediaminetetraacetic acid (EDTA) (Verboekend et al., 2016). Although efficient, these procedures are typically time- and energy-consuming (Chal et al., 2011), limiting the sustainability of hierarchical zeolites.

Microwave (MW) irradiation demonstrates remarkable efficiency in a variety of chemical processes, such as the extraction of metals from soils and plants (Czarnecki and Düring, 2014). In the field of zeolite chemistry, it has been demonstrated that the production of zeolites under MW conditions is more energy- and time-efficient than that under hydrostatic hydrothermal conditions because of advantages such as the absence of a thermal gradient and quick volumetric heating (Meng and Xiao, 2014). The notable advantage of using MW for heating is the faster chemical reaction rate compared to the conventional heating method (up to 1000 times faster) (Rajasekhar et al., 2010). When heated by MW, only the solvent and solute molecules are stimulated, resulting in uniform heating of the solvent. Microwaves not only have a selective heating capability based on the principle that different materials react differently to microwaves but also provides better efficiency and higher product purity with fewer by-products formed, making the filtration step faster and easier. MW also only heat the samples and not the equipment, resulting in lower energy consumption.

Based on these premises, this study aims to utilize microwave-assisted method and thermal method to generate mesopores in the microporous structured zeolite and investigate the activity of mesoporous zeolite ZSM-5 samples in the cracking reaction of n-heptane.

2. Experimental

2.1 Syntheses of prepared materials

This study used two types of zeolite ZSM-5 with different Si/Al ratios, including zeolite ZSM-5 with Si/Al=200 (Z-200) and zeolite ZSM-5 with Si/Al=15 (Z-15) were synthesized according to the previous study (Vu et al., 2018) with some modification. Other chemicals, including n-heptane (Acros Co.), sodium hydroxide (Xilong Co.), and ammonium chloride (Xilong Co.) were purchased and utilized without further purification. The ZSM-5 catalysts were modified by two methods in order to produce mesoporous structure of these microporous materials. In terms of the microwave method, 2.5 g of zeolite ZSM-5 was added to 75 mL of 0.2 M NaOH solution and stirred at room temperature for 5 min. The mixture was then placed in a commercial Electrolux microwave EMM2001 (220 V, 700 W) oven for 10 min, and subsequently quenched in an ice-water bath for 10 min. Finally, the sample was completely filtered and washed with deionized water to pH 7, which was then dried at 80 °C overnight before the characterization. For the thermal method, 75 mL of 0.2 M NaOH solution was heated to 80 °C. 2.5 g of zeolite ZSM-5 was added to the heated NaOH solution and stirred vigorously. After 2 h, the mixture was cooled in an ice-water bath for 10 min. The mixture was then filtered, washed with deionized water to pH 7, and dried overnight at 80 °C.

To convert to the acidic form using an ion-exchange method, 2.0 g of NaZSM-5 was stirred in 100 mL of an NH₄Cl solution (1 M) for 1 h at 80 °C. This procedure was repeated three times with a new NH₄Cl solution. The mixture was then filtered, washed with distilled water, and dried overnight at 80 °C. The final products which were prepared by microwave method were named MZ-15-MW and MZ-200-MW, with the initial materials of Z-15 and Z-200. The modified zeolite products under thermal preparation condition were given the names MZ-15-TH and MZ-200-TH, based on their raw materials of Z-15 and Z-200.

2.2 Catalyst characterization and cracking performance test

Three physicochemical methods, including X-ray Powder Diffraction (XRD), N₂ adsorption-desorption, and scanning electron microscopy (SEM), were used to investigate the characteristics of these produced samples.

Specifically, to identify the crystalline structure and composition of the prepared materials, XRD analysis was carried out on an XRD D2 Phaser Bruker operated at 40 kV and 30 mA ($\text{Cu K}\alpha = 1.5406 \text{ \AA}$) over an angular range of 5° and 50° with a step size of approximately 0.02. The crystalline composition and structure of the prepared catalysts were examined using Brunauer-Emmett-Teller (BET) surface area analysis. Scanning electron microscopy (SEM) characterization was performed using a JSM-IT200 InTouchScope™ Scanning Electron Microscope to analyze the morphologies of the prepared samples.

Catalytic cracking test was conducted in a continuous reactor system. The catalyst was compressed, ground, and sieved to a size of 1-2 mm. The catalyst (0.05 g) was fixed in a quartz reaction tube containing two layers of glass wool. The catalyst was then heated at 450°C for 2 h in a N_2 stream prior to the reaction to convert and activate $\text{NH}_4\text{ZSM-5}$ to HZSM-5. The n-heptane stream was generated by flowing continuously pure N_2 (>99.99 %) over a glass bubbler containing liquid n-heptane, which was put in a water bath at a specific temperature. The flow rate of the stream was adjusted by a needle valve and measured by a flow meter. The products were analyzed with an GC Hewlett Packard 5890 plus device with an FID detector.

3. Results and Discussion

Figure 1 shows the XRD results of the parent zeolite ZSM-5 materials with different Si/Al ratios and the modified zeolites prepared by the microwave and thermal methods. The diffraction results of the prepared zeolites demonstrate that the structure of the synthetic materials was retained after the syntheses, as compared to the original materials. The high-intensity and sharp peaks of modified materials at 2θ of $7-9^\circ$ and $23-25^\circ$ with no other extra peaks corresponded to the parent zeolites ZSM-5; the intensity of the peaks of the modified samples was lower than that of the parent zeolite. On the one hand, figure 1a indicates that the intensities of the typical peaks of samples MZ-200-MW and MZ-200-TH are similar and lower than that of sample Z-200. Notably, the decrease in the peak intensity of the former was much more apparent than that of the latter. On the other hand, figure 1b shows that the characteristic peak intensities of the MZ-15-TH and MZ-15-MW samples were lower than those of the parent MZ-15 materials. This can be explained by the fact that the crystallinity of the zeolites decreased after catalyst synthesis by both microwave and thermal methods. This result may be due to the loss of silicon in the structural framework, leading to structural disorder or partial collapse of the structure at the sites of silicon loss.

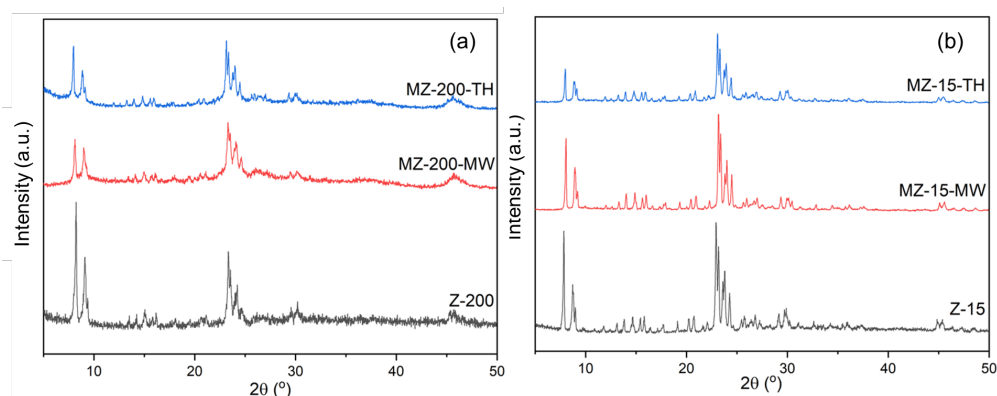


Figure 1: XRD patterns of samples (a) Z-200, MZ-200-MW, MZ-200-TH; (b) Z-15, MZ-15-MW, MZ-15-TH

Table 1: Surface and pore properties of the parent zeolites and the modified zeolite samples

Materials	Specific surface areas (m^2g^{-1})			Specific pore volumes (cm^3g^{-1})		
	$S_{\text{BET}}^{(a)}$	$S_{\text{micro}}^{(b)}$	$S_{\text{meso}}^{(c)}$	$V_{\text{total}}^{(a)}$	$V_{\text{micro}}^{(b)}$	$V_{\text{meso}}^{(c)}$
Z-200	275.9	259.1	16.7	0.202	0.110	0.092
MZ-200-MW	307.3	100.4	206.9	0.357	0.041	0.316
MZ-200-TH	304.1	84.0	220.1	0.391	0.034	0.357
Z-15	330.6	300.4	30.2	0.155	0.122	0.033
MZ-15-MW	338.6	295.4	43.3	0.167	0.120	0.047
MZ-15-TH	363.3	274.8	88.5	0.234	0.101	0.134

S_{BET} : Specific BET surface area; S_{micro} : Micropore surface area; S_{meso} : Mesopore surface area; V_{total} : Total pore volume; V_{micro} : Micropore volume; V_{meso} : Mesopore volume

(a) Total volume adsorbed at $p/p_0 = 0.99$, (b) Based on the t-plot method, (c) = (a) - (b)

Table 1 lists the textural characteristics of these materials. The specific surface area was determined using the Brunauer–Emmett–Teller model. The modified samples had no major change in BET surface area compared to the original samples indicating that the zeolites' structure was not collapsed after the synthesis process. The micro- and mesoporous surface areas of the samples were determined using the t-plot method and shown in Figure 2. In terms of the zeolite with a high ratio of Si/Al, the results show that the mesopore surface area of both synthetic zeolites increased significantly (12-13 times) as compared to the original material Z-200. For the zeolite samples with a low Si/Al ratio, the mesopore surface area of the zeolite synthesized by the microwave approach and hydrothermal method was approximately 1.4 and 3 times higher than that of the original zeolite Z-15. Noticeably, the mesopore surface areas of the MZ-200-MW and MZ-200-TH samples were comparable, proving that the microwave method successfully modified the initial zeolite within a short reaction time which was less than 12 times that of the conventional thermal method. The mesopore surface area results of samples MZ-15-MW and MZ-15-TH are not similar, which indicates that the microwave approach is ineffective for zeolites with a low Si/Al ratio. To sum up, under the same reaction conditions, different Si/Al ratios yielded different mesoporous material efficiencies. This can be explained by the presence of a high Al concentration in the sample with a low Si/Al ratio, which prevented the dissolution of Si, thereby limiting the formation of pores. Table 1 also shows that the specific pore volume increased after the mesoporous modification. The micro- and meso-pore volume results demonstrate the same trend as the surface area results. On the one hand, the mesopore volume of the zeolite samples with a high Si/Al ratio increased three times after the synthesis process using both approaches. On the other hand, the low Si/Al ratio zeolite samples exhibited a slight increase in mesopore volume from 0.033 cm³/g to 0.047 cm³/g when modified by the microwave method and increased by approximately four times when modified by the thermal method.

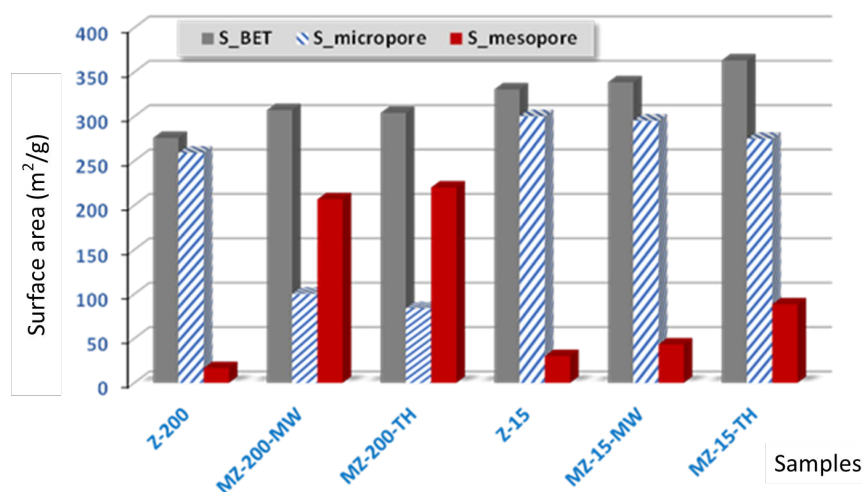


Figure 2: Comparison of micropore and mesopore surface areas of the modified ZSM-5 samples and original ZSM-5 zeolites

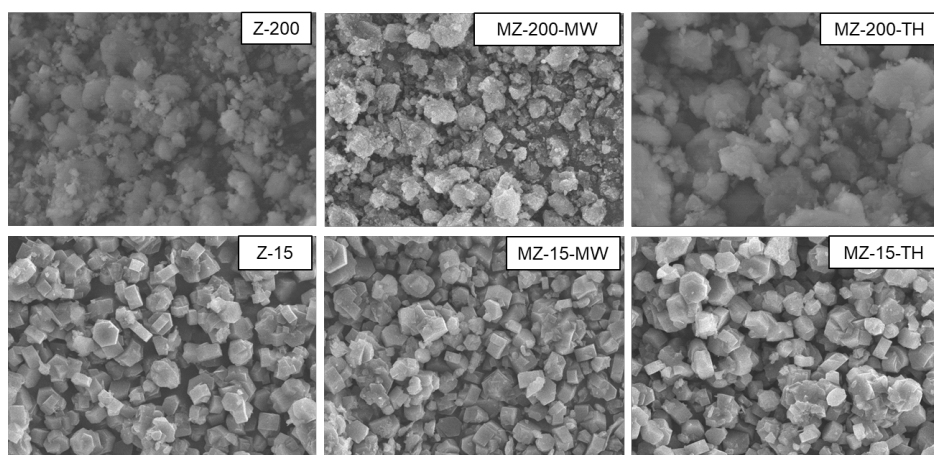


Figure 3: SEM images of modified ZSM-5 samples and original ZSM-5 zeolites

Figure 3 indicates the SEM images of the parent zeolite ZSM-5 with different ratios and the modified materials by microwave and thermal methods. In detail, the modified zeolite samples were not uniform in size after the syntheses. This study used post-synthetic treatments of pristine zeolites to create hierarchical meso-/micro as the top-down method, so silicon loss occurs randomly in the zeolite structure, leading to an uneven particle size. The synthetic samples also contained particles that tended to aggregate into larger particles. This can be explained by the fact that when expanding the pore, the residual surface energy increases suddenly, leading to the particles tending to aggregate to reduce the surface area.

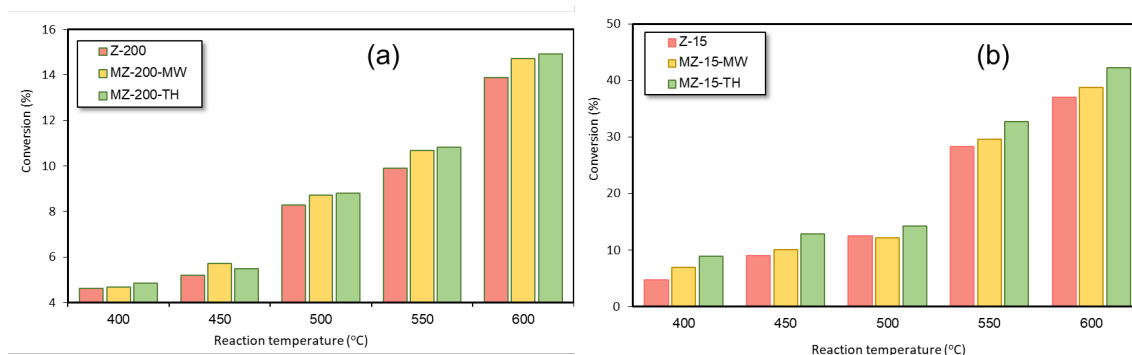


Figure 4: Conversion of n-heptane depending on temperature over (a) Z-200, MZ-200-MW, MZ-200-TH samples; (b) Z-15, MZ-15-MW, MZ-15-TH samples

Figure 4 shows the conversion of n-heptane in the cracking reaction at different temperatures for samples (a) Z-200, MZ-200-MW, MZ-200-TH; (b) Z-15, MZ-15-MW, MZ-15-TH. In general, the conversion of the modified materials by both methods yielded better results than the parent zeolites. On the one hand, as shown in figure 4a, the conversion of n-heptane was generally not high. At 400 °C, the conversion was only approximately 5 %, and at the highest temperature (600 °C), the conversion was only 15 %. This is explained by the high Si/Al ratio of the Z-200, MZ-200-MW, and MZ-200-TH samples, which led to a low number of Bronsted acid sites, affecting the cracking performance. The results showed that the modified samples had a higher conversion rate than the initial material, but the difference was not significant (MZ-200-TH was 1.02 % higher than Z-200 at 600 °C).

On the other hand, the results in figure 4b show that under the same reaction conditions as the high Si/Al ratio zeolite samples, the low Si/Al zeolite samples give higher efficiency; the highest is the sample MZ-15-TH at 600 °C (41.9 %). When the temperature was increased from 500 °C to 550 °C, the conversion increased sharply from approximately 10 % to nearly 30 %. Figure 4b also shows a clear difference in n-heptane conversion between the samples before and after modification. The results show that at high temperatures (550 – 600 °C), the conversion of MZ-15-TH was much higher than that of Z-15 (~ 4.4 % – 5.2 %).

The reactions were carried out continuously at increasing temperatures (30 min at each reaction temperature). After approximately 150 min, the modified materials exhibited higher olefin conversions than the original samples. The efficiency increased gradually with increasing temperature, showing that the activity of the modified samples improved while maintaining the stability of the catalysts. There are two possible reasons for the difference in n-heptane conversion between the modified samples and parent zeolites. On the one hand, desilication reduces the Si/Al ratio, leading to an increase in the number of acid sites in the catalyst. On the other hand, the process of mesopore-supported diffusion makes it easier for olefin molecules to react with the acid sites of the zeolites and allows the products and coke to escape easily, which can increase the catalytic activity. The model of the catalytic cracking of n-heptane over hierarchical ZSM-5 zeolites can be referred to in the study of (Zhang et al., 2017).

4. Conclusions

In conclusion, this study successfully synthesized the mesoporous zeolite ZSM-5 samples using microwave and thermal methods of the initial materials with different Si/Al ratios to evaluate their efficiency in the n-heptane cracking reaction. The external surface area of the prepared mesoporous zeolites increased 12 – 13 times and 1.4 – 3 times to the original zeolites with Si/Al ratios of 200 and 15. For zeolite ZSM-5 with a high Si/Al ratio, the microwave method successfully modified the initial sample in a 12 times shorter time than the hydrothermal way to achieve approximately the same mesopore surface area, proving the effectiveness of the microwave method in mesoporous material synthesis. In the n-heptane cracking reaction, the post-modified zeolite samples exhibited a higher catalytic cracking efficiency but retained the stability of the samples compared to the unmodified materials. Specifically, the conversion of the prepared zeolite samples with a low Si/Al ratio was 4.4 – 5.2 % higher than that of the original material.

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