

The Search for a Cracking Catalyst: Aluminum- and Surfactant-Modified ZSM-5 Zeolites

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Summary: In the present study, modified ZSM-5 catalysts were synthesized, characterized, and tested for their cracking activity and selectivity toward desired cracked products. The ZSM-5 zeolite was modified by aluminum impregnation to increase the acidic strength as well as by non-ionic Pluronic F127 surfactant to induce the mesoporosity in the zeolitic structure. The catalysts were characterized and their catalytic performance was evaluated in a high-pressure Parr autoclave reactor through *n*-hexadecane cracking. The experiments were performed at a fixed residence time of 60 min, a feed-to-catalyst ratio of 20:1 by weight, different cracking temperatures between 325°C and 400°C, and an initial cold pressure of 1 bar. The reaction products (both gas and liquid) were quantitatively analyzed by a GC-FID system. The results of the cracking experiments showed that at 350°C, the 2.5 wt% aluminum-impregnated ZSM-5 catalyst offered significantly high conversion (79.1%) and selectivity toward gasoline-ranged hydrocarbons compared to the other aluminum-modified catalysts. The modification with F127 considerably reduced the crystallinity of ZSM-5 and resulted in relatively higher conversions but lower liquid yields.

Keywords: ZSM-5; mesoporosity; aluminum impregnation; catalytic cracking; *n*-hexadecane; Pluronic F127.

Introduction

Catalytic cracking is an important industrial process applied for the upgrading of heavy oils, heavy stocks recovered from refinery processes, waste plastics, and biomass. The desire to increase the gasoline production—the most valuable product of the fluid catalytic cracking units—and the yield of olefins used in important petrochemical products is a major incentive for catalytic cracking [1]. Catalytic cracking of heavy hydrocarbons increases the gasoline yield and saves several billion dollars per year. Without the use of catalysts in the catalytic cracking process, the global cost of petroleum refining would increase by at least 10 billion dollars annually [2, 3]. Among the various cracking catalysts, zeolites provide well-defined unique pore structures, specific shape selectivity, and tunable acidity that offer advantages over traditional solid acid catalysts [4, 5].

In today's modernized world where energy needs are progressively growing there is a globally increased demand for cracking catalysts. Zeolite Y and ZSM-5 are two of the most widely used zeolite catalysts in the cracking application. These catalysts enhance the octane number of cracked gasoline and simultaneously increase the yields of propylene, a valuable chemical raw material [6–9]. In particular, ZSM-5 has been found to be highly effective in

cracking heavy oil fractions into lighter hydrocarbons. However, the performance of ZSM-5 catalyst is highly dependent on its structure and composition. As a result, researchers have extensively investigated the structure of ZSM-5 catalysts and their silica-to-alumina ratio. The silica-to-alumina ratio plays highly crucial role in determining activity and selectivity of a zeolitic catalyst [10, 11]. Generally, a higher Si/Al ratio in ZSM-5 favors the formation of unsaturated hydrocarbons and accelerates catalyst deactivation, whereas catalysts with a lower Si/Al ratio tend to promote side reactions, leading to the formation of undesired products and reduced selectivity. This highlights the importance of carefully controlling the silica-to-alumina ratio in ZSM-5 catalysts during the synthesis process to achieve optimal performance in the catalytic cracking reactions [12, 13].

The Si/Al ratio along with acid density are the key factors that determine the performance of a cracking catalyst [14]. In addition to the Si/Al ratio, the pore size also plays an important role in the cracking performance of a zeolite catalyst. The small pore size in the microporous structure of ZSM-5 catalyst limits its effectiveness in catalyzing large molecules, resulting in the production of more gaseous product than gasoline-range product, as observed in

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the cracking of *n*-hexadecane [15]. To address this issue, researchers suggest optimizing zeolite catalysts by developing mesoporous structures and loading suitable amounts of external species to control the pore size and acidity.

Mesoporous zeolites can be synthesized through the use of organic structure-directing agents such as Pluronic F127, P123, and CTAB [16–19], which can be eliminated during a high-temperature calcination process. This results in a porous structure that offers greater accessible surface area and larger pore size than the parent microporous catalyst thereby reducing the diffusion path. These mesoporous catalysts are suitable for reactions involving large molecules [20–23] and are capable of producing lower gas yields while providing relatively bigger size gasoline and diesel range products.

Many studies have used *n*-hexadecane as an investigation molecule to observe the cracking performance of the synthesized catalysts. *n*-hexadecane is chosen as a model compound due to its high molecular weight which closely resembles that of heavy feedstocks and plastics. Additionally, it has well-defined properties, excellent stability, reduced safety hazards, and ease of handling being liquid at room temperature. Rongsheng *et al.* [24] employed four modified ZSM-5 catalysts using SiCl_4 , BCl_3 , NH_4F , and LaCl_3 and found LaCl_3 to be the preferred modification agent. The cracking experiments were conducted at 350°C and in a micropulse reactor. With LaCl_3 -modified ZSM-5 catalysts, the maximum conversion of 87.3% was obtained with the highest gasoline yield of 55.4%. Kustova *et al.* [25] used mesoporous ZSM-11 and compared it with conventional ZSM-11 for catalytic cracking of *n*-hexadecane. The mesoporosity was introduced by using a carbon template. The cracking reactions were carried out at 280°C for 18 h with HC/catalyst ratio of 27.8 and 94.0% conversion was reported. Zahara *et al.* [17] studied *n*-hexadecane cracking over two mesoporous HZSM-5 catalysts synthesized using two different structure directing agents and dimethyl diallyl ammonium chloride acrylamide copolymer as template for mesoporosity. The feed to catalyst ratio was set at 2.7 and experiments were performed at 500°C. The maximum conversion obtained was only 37.2%. Masoudinejad and Mahdavi [26] utilized a catalyst that was a combination of HY-zeolite, Al-hexagonal mesoporous molecular sieves (Al-HMS), and montmorillonite K10. The experiments were conducted at 500°C in a plug flow reactor with 1 g catalyst and 4.7 mL/h *n*-hexadecane flowrate. The catalyst containing SiO_2 - Al_2O_3 ratio of 5 in Al-HMS

was found to be the best with regard to conversion (62.8%) and gasoline yield (65.78%).

The development of cracking catalysts is an ongoing area of research. The effects of different catalytic materials and different methods of preparations on the catalytic ability of the catalysts have been widely studied. The performance of this cracking catalyst is tested using a probe molecule, or in some cases, the actual cracking feedstock. The present study investigates the cracking performance of mesoporous ZSM-5 catalysts modified with a Pluronic F-127 template as well as aluminum-impregnated catalysts. *n*-Hexadecane was used as model compound to compare the cracking activity and selectivity of the synthesized catalysts. The comparison was carried out in terms of conversion and carbon range of the cracked products. The objective was to identify the most effective catalyst that could achieve the maximum conversion with desirable product quality. To our knowledge, no similar study has been reported in the literature.

Experimental

Material

Sodium hydroxide (98% purity, Samchun), ammonium acetate (95% purity, Samchun), aluminum nitrate nonahydrate ($\geq 98\%$, Sigma-Aldrich), tetraethyl orthosilicate (TEOS, 98% purity, Aldrich), sodium silicate (Uni-Chem), Pluronic F-127 (Sigma-Aldrich), *n*-hexadecane (95% purity, molekula), ammonium fluoride ($\geq 98.0\%$ purity, Sigma-Aldrich), nitric acid (67% purity, Sigma-Aldrich), hydrochloric acid (37% purity, Sigma-Aldrich), sodium aluminate (extra pure, Daejung), commercial zeolite ZSM-5 catalysts (NKF-5-300ZY, $\text{SiO}_2/\text{Al}_2\text{O}_3 = 300$ mol/mol; and Thermoscientific, $\text{SiO}_2/\text{Al}_2\text{O}_3 = 50$ mol/mol), and de-ionized water were procured. All the chemicals were used as received without further treatment.

Catalyst preparation

Aluminum impregnated catalysts

The wet impregnation method was employed to improve the acidic behavior of the commercial ZSM-5 catalyst (NKF-5-300ZY, named Z-5N) by impregnating aluminum on its surface. Calculated amounts of aluminum nitrate nonahydrate, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and the catalyst were mixed in water. The mixture was vigorously stirred for 1 h at a temperature of $55 \pm 2^\circ\text{C}$ and allowed to equilibrate at room temperature for 24 h. Afterwards, it was filtered and rinsed 5 to 6 times with distilled water. The solids

(catalyst) obtained were then dried in an oven at 100°C for 24 h to completely remove any residual moisture. Finally, the catalyst was calcined in a muffle furnace at 600°C for 5 h under an air atmosphere. This procedure was carried out in accordance with the literature [27], ensuring reliability and reproducibility of the synthesis. Three catalysts containing 1.0wt%, 2.5wt%, and 5.0wt% aluminum were prepared and, respectively designated as 1AlZ-5N, 2.5AlZ-5N, and 5AlZ-5N.

Surfactant-modified ZSM-5 catalysts

The surfactant Pluronic F-127 was employed to induce the mesoporosity in the ZSM-5 catalyst (Thermoscientific, named Z-5T) following hydrothermal treatment. For this purpose, the ZSM-5 catalyst available in its ammonium form was first calcined at 600°C for 5 h in a muffle furnace to obtain the proton form. 10 g of the calcined catalyst was dissolved in 1.5 M NaOH and stirred at 45°C using magnetic stirring. After 30 min, 12 g of tetraethylorthosilicate (TEOS) were added to the solution and stirred for 4 h at the same temperature. Simultaneously, in a separate vessel, 4 g of Pluronic F-127 were dissolved in 1 M HCl and stirred until completely dissolved. Following that, 0.1 g of NH_4F was added and stirred for 30 min. The second solution was carefully added to the first solution, and the resulting mixture was stirred at 45°C for 24 h. The final solution was transferred into a Teflon-lined autoclave reactor after adjusting the pH to 1 with 1 M HCl. The obtained material was then crystallized at 110°C for 24 h. Afterwards, the product was recovered by centrifugation and washed with deionized water until a clear filtrate was obtained. The catalyst was then dried at 100°C for 24 h and subsequently calcined at 600°C for 5 h in a muffle furnace. The resulting catalyst was in its sodium form and was ion-exchanged with 2 M ammonium acetate solution under vigorous stirring at 65°C for 5 h. The resulting catalyst was filtered, washed several times with deionized water, and then dried in an oven at 100°C for 24 h. Finally, the catalyst was calcined in a muffle furnace at 600°C for 5 h. The procedure followed for the synthesis of mesoporous catalyst was adopted from the literature [28]. The catalyst was named mZ-5T.

Catalyst characterization

X-ray diffraction was conducted to analysis the crystal structure of the calcined catalyst using an Equinox 2000 diffractometer (Thermo Scientific, USA) equipped with a curved position-sensitive detector. The diffraction data was obtained in real-time over a 2θ range of 6.5 to 80° using $\text{CuK}\alpha_1$

radiation (wavelength of 0.15406 nm) generated by a germanium monochromator. The scanning electron microscopy (SEM) micrographs were obtained through Mira 3 TESCAN Field Emission Scanning Electron Microscope. The V-Sorb 2800P surface area and porosimetry analyzer was employed to measure the N_2 -BET surface area, pore size distribution, and nitrogen adsorption-desorption isotherm at 77.3 K. Before the analysis, the catalyst samples were degassed under vacuum at 200°C for 2 h.

Activity tests

The catalytic reactions of *n*-hexadecane were done in a 500 mL high-pressure stirred autoclave reactor from Parr Instrument Co. To begin with the experiments, 12 g of *n*-hexadecane and 0.6 g of a catalyst were loaded into the autoclave reactor at room temperature. The reactor was tightly sealed, and the heater was switched on to achieve the desired temperature. The reaction was then allowed to proceed for 1 hour, during which the reactor was continuously agitated. After completion of the reaction, the reactor was cooled to room temperature, and the gas product was collected in aluminum bags of known volume, while the liquid product was collected in a separate collection vessel. The liquid product was then filtered through a filter paper, followed by passing through a syringe filter to remove the solid impurities. The catalytic conversion of *n*-hexadecane was determined by analyzing the liquid product using a Shimadzu GC-2014 attached to an FID detector. The column used for the analysis was an Agilent DB-1MS, a non-polar dimethylpolysiloxane capillary column that was 30 m in length with an inner diameter of 0.25 mm. An Agilent Carry 630 FTIR spectrometer was utilized to measure the infrared (IR) spectra of the cracked liquid product, with the analysis performed in the range of $650\text{--}4000\text{ cm}^{-1}$. Experiments were performed at different reaction temperatures between 325°C and 400°C, and the maximum temperature achieved in any experiment was 11.03 bar.

Results and discussion

Catalyst characterization

The XRD results of all catalysts are exhibited in Fig. 1. It is apparent that the parent zeolite catalysts exhibit characteristic diffraction peaks in the 2θ range of $8\text{--}9^\circ$ and $23\text{--}24^\circ$ [29-31]. The diffraction patterns of all modified catalysts were identical to those of the respective commercial catalysts, indicating that the zeolite ZSM-5 structure remained unchanged after modification. However, a reduction in the intensity of the mZ-5T catalyst (Fig. 1b) is observed, suggesting a

decrease in the crystallinity of the catalyst. This reduction in crystallinity is attributed to the addition of the surfactant (F-127) during catalyst synthesis, resulting in the formation of an amorphous structure [32]. This decreased crystallinity is also apparent from the SEM images of the mZ-5T catalyst (Fig. 2), which reveals a relatively aggregated (cauliflower like) morphology, unlike the distinct crystals of ZSM-5. The decreased crystallinity may have consequences on quantity as well as strength of acid sites, which may

negatively affect the cracking behavior. However, the induced mesoporosity may give increased access for reactant to reach distant active sites. Additionally, a reduction in well-defined pore dimensions may change product selectivity, leading to increased gaseous products and potentially excessive coke formation due to the development of new types of active sites.

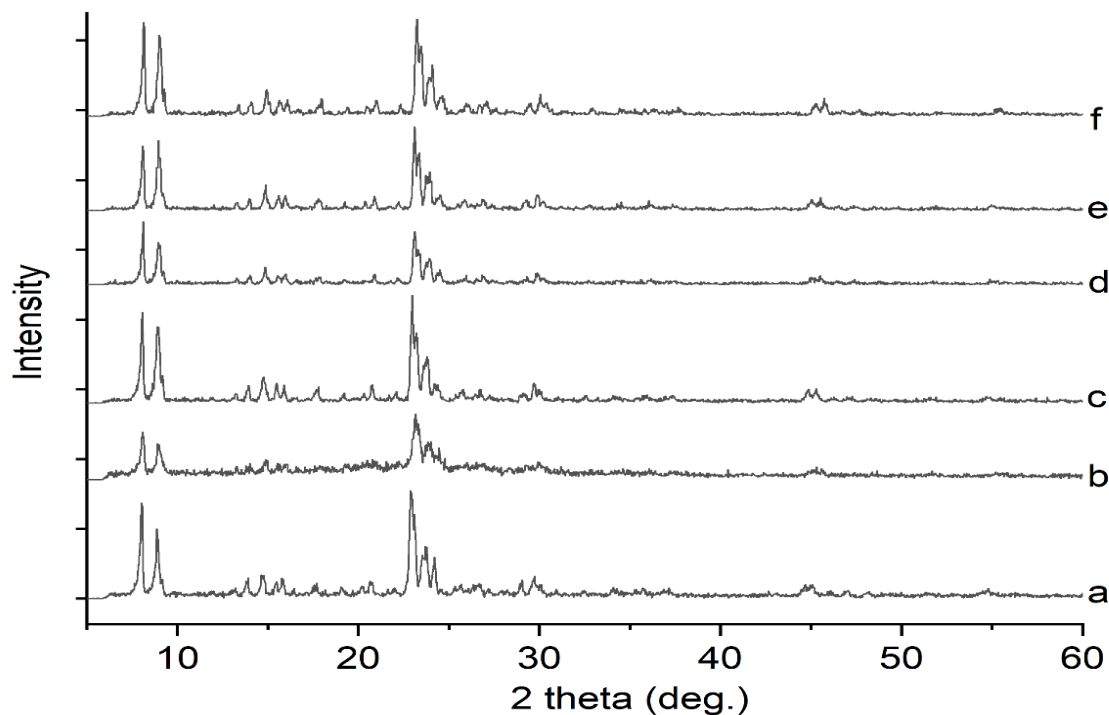


Fig. 1: XRD diffraction pattern of aluminum impregnated and template modified ZSM-5 catalysts: (a) Z-5T (b) mZ-5T (c) Z-5N (d) 1AlZ-5N (e) 2.5AlZ-5N (f) 5AlZ-5N.

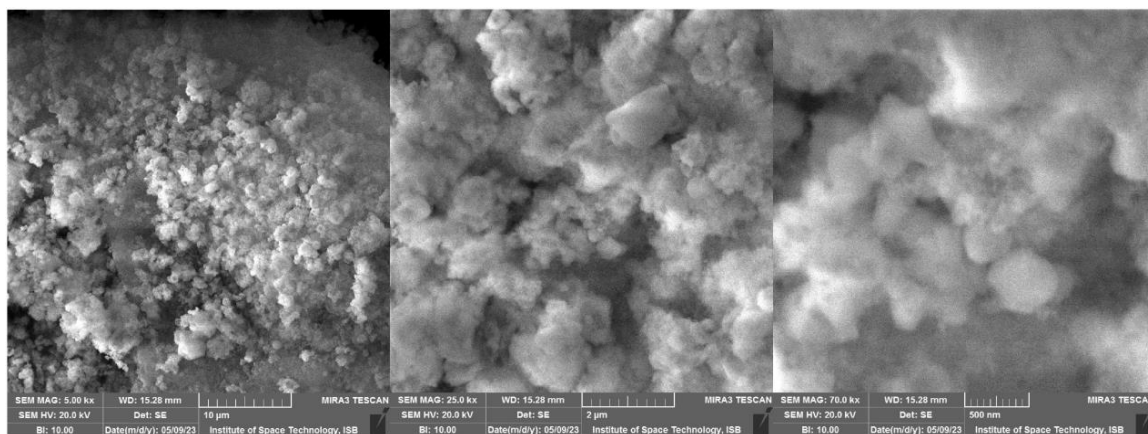


Fig. 2: SEM images of the mZ-5T catalyst at various magnifications.

The structural properties of all catalysts are shown in Table-1. The surface area of the aluminum-impregnated catalysts is found to be lower than that of the commercial Z-5N catalyst, except for the 1AlZ-5N catalyst, which exhibited a larger surface area and pore diameter. Similarly, the mZ-5T catalyst shows a larger surface area and pore diameter compared to the commercial Z-5T catalyst. Fig. 3 shows the N_2 adsorption-desorption isotherms for both commercial and modified catalysts. All catalysts exhibit type I isotherms except for mZ-5T. At low relative pressures, a sudden kink in the curve represents monolayer adsorption, indicating the filling of the microporous surface area of the catalysts primarily occurring on the external surface or nonporous regions of the catalyst. Furthermore, there is no significant change in the adsorption curve with increasing pressure, which is consistent with the characteristic behavior of microporous materials. Conversely, the mZ-5T catalyst exhibited type IV isotherm, which suggests the presence of both mesopores and micropores. The monolayer adsorption and the kink in the curve for this catalyst material indicate its microporous structure. Additionally, the noticeable increase in gas volume in the multilayer region, coupled with hysteresis at relative pressures (P/P_0 between 0.4 and 1.0), indicates capillary condensation in the catalyst material, confirming the presence of a mesoporous pore structure.

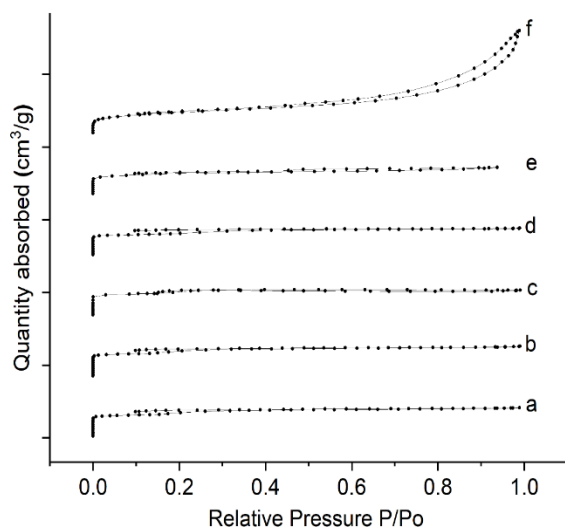


Fig. 3: Pore size distribution of commercial and synthesized catalysts: a) Z-5N; b) 1AlZ-5N; c) 2.5AlZ-5N; d) 5AlZ-5N; e) Z-5T; f) mZ-5T

Table-1: Structural properties of the catalysts.

Catalyst	S_g (m^2/g)	BJH S_g (m^2/g)	BJH v_p (cm^3/g)	BJH d_p (nm)
Z-5N	352.0	69.91	0.0573	26.22
1AlZ-5N	370.4	57.87	0.0505	33.94
2.5AlZ-5N	349.1	82.12	0.0471	30.56
5AlZ-5N	312.1	88.75	0.0666	33.51
Z-5T	308.9	42.72	0.0554	9.57
mZ-5T	326.6	192.5	1.0998	32.91

Catalyst activity

Fig. 4 shows the results of catalytic experiments for *n*-hexadecane cracking at four different temperatures. All catalysts outperformed the thermal cracking of *n*-hexadecane, as thermal cracking resulted in very low conversions. For example, at 350°C, the *n*-hexadecane conversion is only 10.3% under thermal conditions, compared to a minimum conversion of 66.0% over the commercial catalyst Z-5T. It is observed that all modified catalysts performed better than their corresponding parent ZSM-5 zeolite. Moreover, at 350°C, the 1AlZ-5N and 2.5AlZ-5N catalysts offered the highest conversions of 78.3% and 79.1%, respectively. Notably, the 1AlZ-5N catalyst not only provided higher conversion rates but also enhanced selectivity by yielding the maximum liquid product. On the other hand, at 375°C, the mZ-5T catalyst offered the highest conversion rate of 89.0% followed by the 2.5AlZ-5N catalyst. The 2.5AlZ-5N catalyst, however, yielded the highest liquid product of 40% which is nearly double the yield obtained with the mZ-5T catalyst. It is important to note that the parent zeolite catalyst for 2.5AlZ-5N differs in Si/Al ratio from that of the parent zeolite of the mZ-5T catalyst. Again, at 375°C, the thermal run proved highly inefficient, and the *n*-hexadecane conversion could not surpass 16.9% at this temperature. Two additional experiments at 325°C and 400°C were carried out in the absence of a catalyst, along with one experiment using mZ-5T at 325°C, as shown in Fig. 5. At 325°C, the conversion in the thermal run increased from 4.0% to 51.0% in the presence of mZ-5T. Under thermal conditions, the conversion was limited to 27.7% even at the maximum temperature of 400°C investigated in the present study. Generally, the 5AlZ-5N catalyst with 5.0wt% Al loading was found inferior to both the 2.5AlZ-5N and 1AlZ-5N catalysts with 2.5wt% Al and 1.0wt% Al loading, respectively. This suggests that very high Al loading is not desirable and that an optimum Al loading is required to achieve increased activity as well as selectivity for the Al-loaded ZSM-5 catalyst. It is also important to mention that due to the batch nature of the experiments, the pressure also increased during the course of the reaction. For example, at 350°C over the 2.5AlZ-5N catalyst, the pressure reached 10 bar. The maximum pressure in the present study reached to 11.03 bar at 375°C for the mZ-5T catalyst.

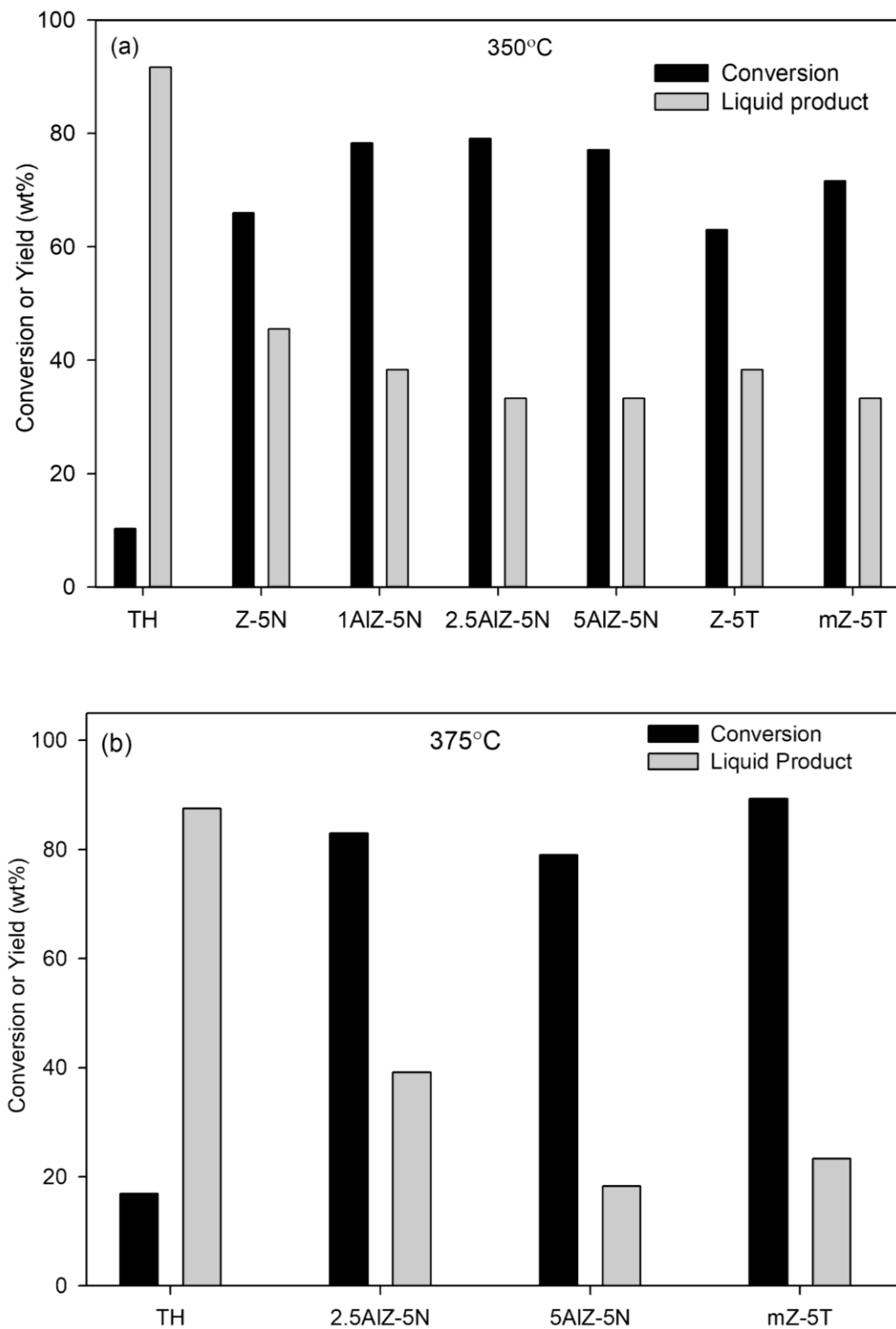


Fig. 4: Results of the catalytic reactions of *n*-hexadecane at different temperatures over different zeolite catalysts: a) 350°C and b) 375°C. 500 ml high pressure autoclave reactor, 1 bar initial cold pressure, 60 min residence time, and 12 g to 0.6 g feed to catalyst ratio. TH stands for thermal run.

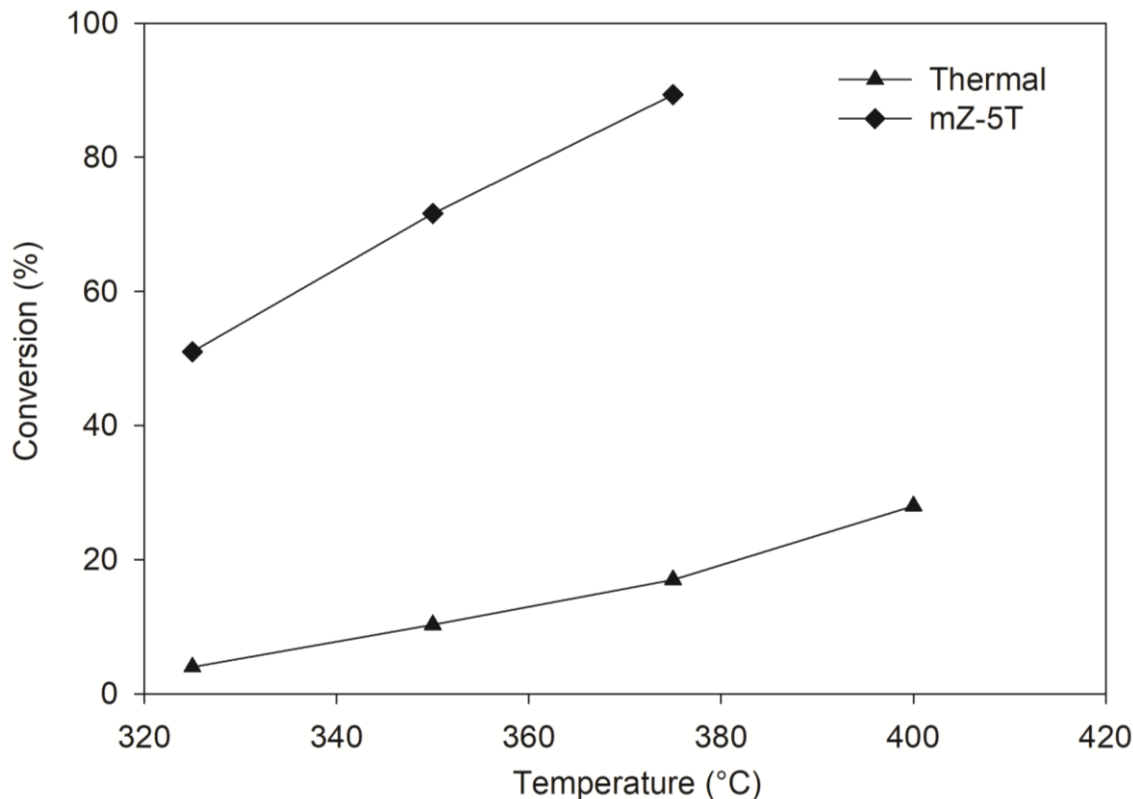


Fig. 5: Effect of temperature on *n*-hexadecane conversion by thermal cracking and catalytic cracking with mZ-5T catalyst. 500 ml high pressure autoclave reactor, 1 bar initial cold pressure, 60 min residence time, and 12 g to 0.6 g feed to catalyst ratio.

Gas chromatography results of the cracked *n*-hexadecane liquid products are shown in Fig. 6. With thermal cracking, at both 350°C and 375°C temperatures, very high yields of C11–C16 range products (>90%) are obtained. This emphasizes that cracking reactions under these conditions primarily resulted in the formation of higher carbon chain hydrocarbons and were unable to effectively crack larger hydrocarbons. The inclusion of catalysts drastically changed the product distribution, and the concentration of C11–C16 is significantly reduced, leading to the production of lower hydrocarbon liquids and gases. At 350°C, both the 1AlZ-5N and 2.5AlZ-5N catalysts exhibited relatively higher selectivity toward C8–C10 products and yielded decreased amounts of <C7 hydrocarbons. At 375°C, as expected, higher hydrocarbons were further cracked, resulting in an increased yield of lower hydrocarbons.

The quality of liquid products was assessed by FTIR analysis of the liquid samples. The FTIR spectra of the cracked liquid products obtained over different catalysts are shown in Fig. 7. The results show that the quality of each product is virtually similar as all liquid samples produced over different catalysts exhibited similar peak ranges. The infrared peaks are observed at 2853.7, 1458.3, 1378.2, and 720.8 cm^{-1} , which are similar to those observed for the liquid products of thermal cracking (not shown). The peaks shown in the region between 2840 and 3000 cm^{-1} correspond to C–H stretching vibrations of alkane. The region at 665–730 cm^{-1} indicates the presence of C=C bending vibrations typically associated with alkenes. The other peaks also displayed C–H stretching, indicating the presence of alkane components in the cracked product.

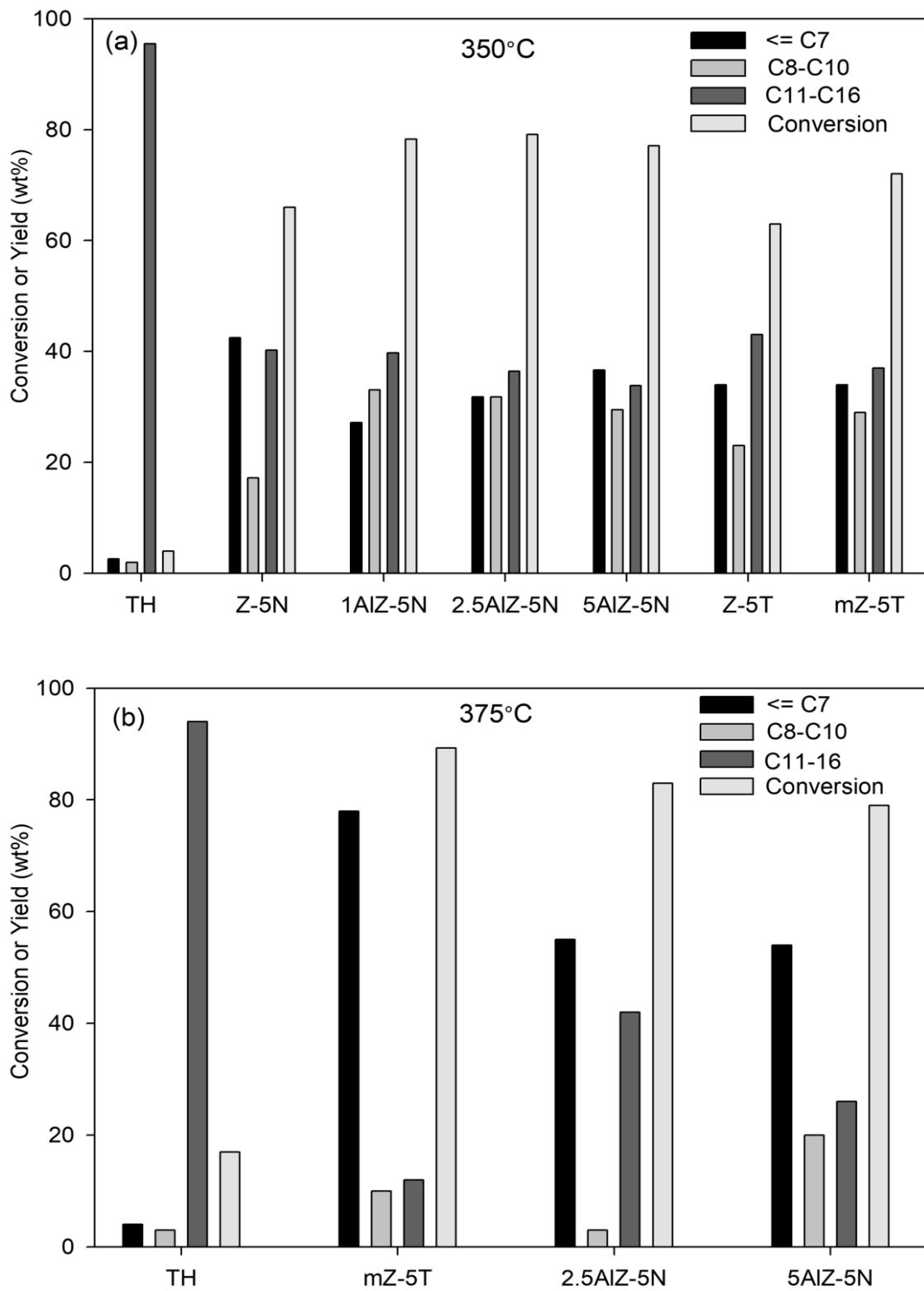


Fig. 6: Results of the GC analysis of the cracked liquid product obtained by the cracking of *n*-hexadecane over different zeolite catalysts: a) 350°C, b) 375°C. 500 ml autoclave reactor, 1 bar initial atmospheric pressure, 60 min residence time, and 12 g to 0.6 g feed to catalyst ratio. TH stands for thermal run.

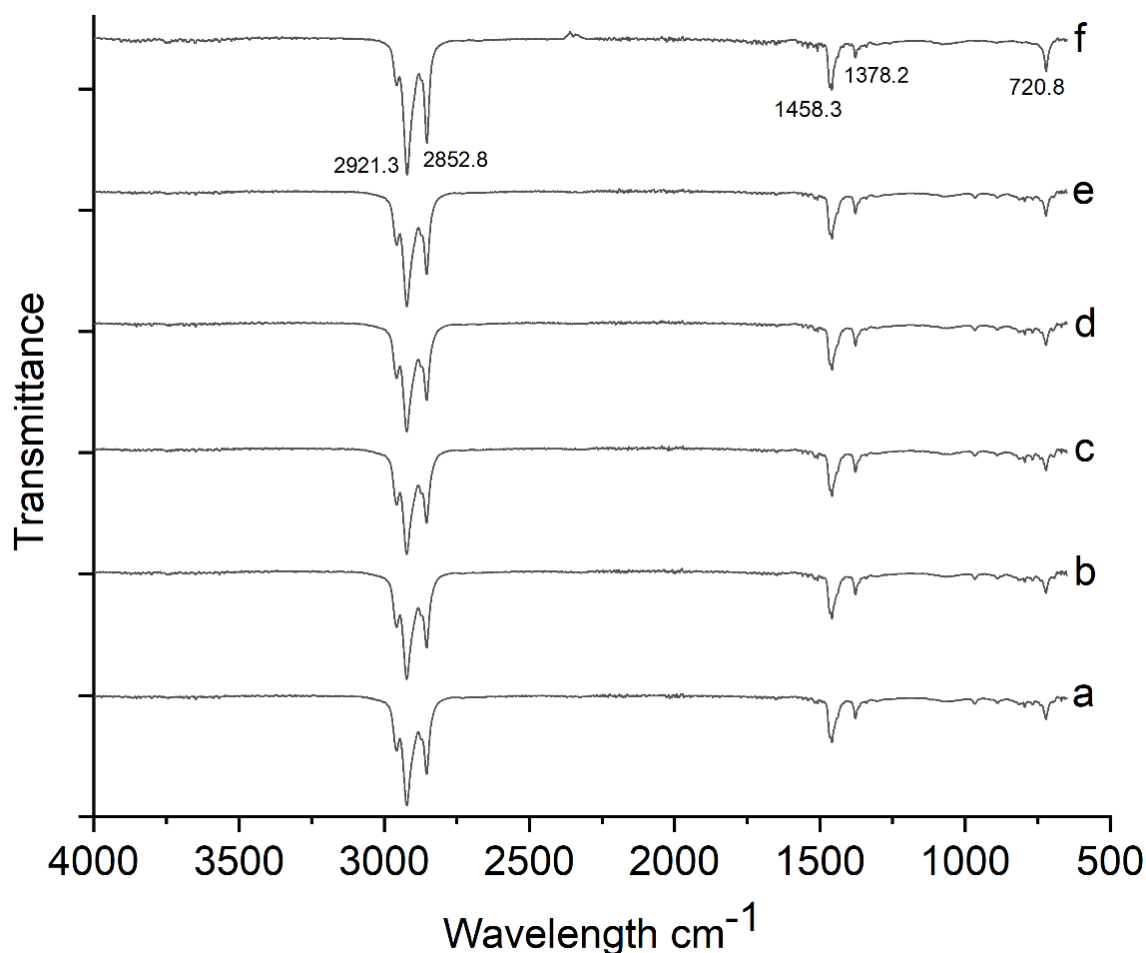


Fig. 7: FTIR characterization of cracked *n*-hexadecane liquid product at 350°C over various catalysts: a) Z-5T; b) mZ-5T; c) Z-5N (d) 1AlZ-5N; e) 2.5AlZ-5N; f) 5AlZ-5N. 500 ml autoclave reactor, 1 bar initial cold pressure, 60 min residence time, and 12 g to 0.6 g feed to catalyst ratio.

Conclusion

ZSM-5 catalysts were modified by aluminum impregnation and by the addition of Pluronic F127 surfactant. Catalyst characterization confirmed that all catalysts retained their zeolitic structure. However, the addition of the F127 template reduced the crystallinity of the parent ZSM-5 catalyst. The results of *n*-hexadecane cracking showed that the thermal cracking is not effective even at 400°C where the conversion reached only 27.7%. At a moderate temperature of 350°C, the aluminum-modified catalysts with 1.0wt% and 2.5wt% Al loading offered high conversion (~80%) and high selectivity toward liquid products compared to 5.0wt% Al loading of the catalyst. A very high Al loading is thus not suitable, instead, an optimum Al loading is desired for increased activity and better selectivity of Al-loaded ZSM-5 catalysts. At a higher temperature of 375°C, the 2.5wt% Al-loaded catalyst

maintained high liquid selectivity, but the liquid product with lower hydrocarbons was resulted. The mesoporous mZ-5T catalyst showed better performance at higher temperatures, delivering 89.0% conversion of *n*-hexadecane, although it provided a relatively decreased liquid yield.

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