

A ZSM-5-based Catalyst for Efficient Production of Light Olefins and Aromatics from Fluidized-bed Naphtha Catalytic Cracking

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Abstract A ZSM-5-based catalyst was prepared by spray-dry method for fluidized-bed naphtha catalytic cracking. Multi-techniques, such as X-ray diffraction, scanning electron microscope, ^{27}Al MAS NMR, and NH_3 -TPD, were employed for the investigation of ZSM-5 framework stability, framework dealumination, and catalyst acidity variation in hydrothermal treatment. Catalytic performances of fluidized-bed naphtha catalytic cracking at 630–680 °C indicated that light olefins and other value-added products could be more efficiently produced compared with the commercial process of thermal steam cracking. Long-term catalytic evaluation implied that naphtha catalytic cracking over the catalyst prepared with spray-dry method and hydrothermal treatment can be carried out at a variable reaction condition with a relatively high and stable light olefins yield.

Keywords Naphtha catalytic cracking · Fluidized-bed · ZSM-5 · Hydrothermal treatment · Light olefins · Aromatics

1 Introduction

Light olefins, ethylene and propylene, have the backbone status in petrochemical industry and are mostly used to produce plastics, fibers, and other chemicals. The main

commercial technique for light olefins production is steam cracking of naphtha which requires high reaction temperature (800–880 °C). Energy cost of pyrolysis sector counts for ~70% of production cost in typical naphtha-based olefins plants [1]. Though some innovative technology has been developed in term of energy efficiency, it is still the first energy-consuming process in petrochemical industry. Under the typical steam-cracking condition (820 °C, $\text{H}_2\text{O}/\text{naphtha} = 0.7$), about 30% of ethylene and 15% of propylene can be obtained. To improve the yield of light olefins and optimize the economical efficiency, the application of catalytic cracking process could be an option. Strong and increasing demand for propylene and the non-selectivity character of steam cracking has also driven the development of catalytic olefins technology.

Several types of catalysts for naphtha cracking have been used in naphtha steam cracking and an enhanced olefin yield was obtained [2–5], but still no commercial application has been reported until now. Some of the reported catalysts worked at the temperature range of 750–780 °C, lower than the commercial process by about 50–100 °C. The most successful one is KVO_3 with a boric acid promoter on a low surface area alumina, which has been developed for the so-called Vnijos process [2]. With this catalyst, at the temperature of 780 °C, at a steam to feed ratio of 1:1 and a residence time of 0.15 s, the yield of ethylene from the pyrolysis of gasoline, is 40 wt.%. This value was ~5–10 wt.% higher than the yield in conventional cracking of naphtha. Some other processes of thermal catalytic cracking have been also developed based on various kinds of metal oxides and the presence of these catalysts could increase the yield of ethylene and propylene by 7% or reduce the temperature for a required conversion by ~50 °C [3–5].

Besides the work listed above, naphtha cracking over acidic catalysts has been also reported. Wakui et al. [6]

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studied catalytic cracking or oxidative cracking of n-butane at the temperature range of 600–650 °C over MFI zeolite. Ethylene and propylene yield of 58% was obtained at 650 °C. Aiming at more light olefins production, dehydrogenation-cracking double stage reaction of n-butane was also investigated by them. Yashimura et al. [7] reported light naphtha catalytic cracking with the feed of steam and N₂-diluted light naphtha, which is rich of n-paraffins and iso-paraffins. Ethylene and propylene yield of 61% over La/HZSM-5 and 57% over P-La/HZSM-5 were reported in their work. In our previous study, over an improved modified ZSM-5, naphtha can be converted to light olefins at a moderate temperature with high activity and long-term stability. Considering the high naphthene content of the naphtha feed, a flexible product strategy was proposed [8].

Acidic catalytic cracking using zeolite catalyst, which can be realized in fixed-bed reactor at a lowered temperature with an improved light olefins production, is a very attractive cracking technique, while its application is still facing the difficulty of developing long life-span and hydrothermally stable catalysts. Catalyst deactivation from coke deposition cannot be avoided in the atmosphere of active olefins products and dealumination of zeolite catalysts in steam cracking is also a challenge to long-term performance stability. To overcome these difficulties, in the present work, we try to develop a new fluidized-bed ZSM-5-based catalyst for naphtha cracking process. Cycling reaction–regeneration technique is expected to ensure the reaction activity of zeolite catalyst for naphtha cracking.

Fluidized-bed catalysts are constantly exposed to harsh chemical and physical condition both during reaction and regeneration. To make the molecular sieve for use as a practical catalyst in fluidized bed reaction system, an inorganic oxide matrix is needed in the catalyst formulation to provide physical strength and better heat transfer among the desired properties. In this study, a fluidized-bed catalyst, combining a microporous zeolite, HZSM-5 and complex oxides, SiO₂–Al₂O₃ was prepared and steam-treated at high temperature before the catalytic test. Multi-techniques, such as X-ray diffraction (XRD), scanning electron microscope (SEM), ²⁷Al MAS NMR, and NH₃–TPD, were used to study the influence of hydrothermal treatment. Catalytic performance of the ZSM-5-based catalyst in naphtha catalytic cracking was tested in a micro-scale fluidized-bed reactor.

2 Experimental

2.1 Naphtha Specification

The naphtha feedstock was supplied by CNPC Fushun Petrochemical. Its specification is given in Table 1.

Table 1 Specification of naphtha feedstock (all components are in wt.%)

Carbon no.	Paraffins	Naphthenes	Olefins	Aromatics
C ₄	1.4	–	–	–
C ₅	4.7	–	–	–
C ₆	9.1	6.7	–	–
C ₇	8.0	6.1	1.6	–
C ₈	12.8	6.9	–	0.9
C ₉	9.7	6.1	–	1.9
C ₁₀	7.9	1.7	0.3	1.3
C ₁₁	6.5	1.2	–	0.4
C ₁₂₊	3.7	1.1	–	–
Total	63.8	29.8	1.9	4.5

2.2 Catalyst Preparation and Characterization

The fluidized-bed catalyst used in this study was prepared by spray-dry method. A slurry containing 25 wt.% solid, 35 wt.% being ZSM-5 zeolite (SiO₂/Al₂O₃ = 25) that has been completely dried and calcined, 20 wt.% Al₂O₃ as binder, and 45 wt.% clay as the matrix material, was prepared, colloid milled twice and spray dried in a spray drier. The spray dried powder was divided into two portions. One portion was calcined in air at 650 °C for 3 h and identified for further test as Cat-unst. The other portion was calcined in an atmosphere of 100% steam for 10 h at 800 °C and identified as Cat-st.

The two samples were characterized by powder XRD (RIGAKU D/max-rb powder diffractometer), SEM (KYKY-1000 instrument), and nitrogen physical adsorption (NOVA 4000 analyzer) to determine their crystallinity, morphology, and textural properties, respectively. NH₃–TPD measurement was performed on a chemical adsorption analyzer (Micromeritics Autochem 2910). ²⁷Al MAS NMR spectra were recorded on Varian Infinityplus-400 spectrometer at 104.2 MHz using a 4-mm MAS NMR probe with a spinning rate of 10 kHz.

2.3 Catalytic Test

Naphtha catalytic cracking was performed in a steel micro-scale fluidized-bed reactor over the catalyst after hydrothermal treatment. The scheme of the experimental setup is shown in Fig. 1. Before test, the catalyst was activated at reaction temperature in air flow (30 mL/min) for 30 min and then the atmosphere was replaced by helium. By switching the 4-way valve, naphtha and water, which had been preheated and vaporized at ~350 °C, entered the reactor and contacted the catalyst. The reaction condition

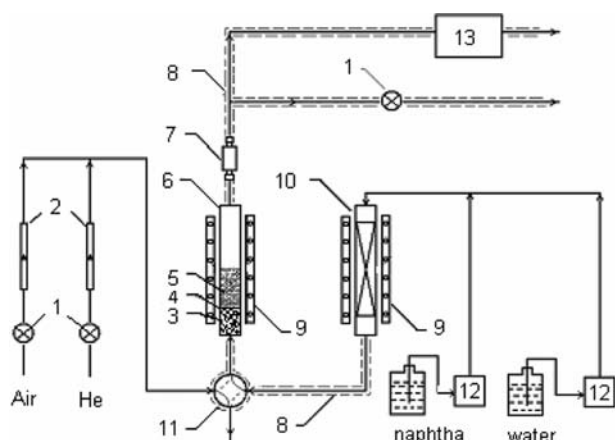


Fig. 1 Schematic experimental setup of fluidized-bed naphtha catalytic cracking. 1, controlling valve; 2, flow meters; 3, quartz sand; 4, distributor; 5, catalyst; 6, reactor; 7, filter; 8, heating line; 9, furnace; 10, vaporizer; 11, four-way valve; 12, pumps; 13, GC

Table 2 Operating condition of catalytic steam cracking of naphtha

Condition	Value
Catalyst loading (g)	10
Naphtha flow rate (g/h)	15
Steam to naphtha ratio (g/g)	0.35
Reaction temperature (°C)	630–680
Time on stream (min)	2–60

was detailed in Table 2. All the effluents from the reactor were kept warm at about 200 °C and analyzed online by Varian gas chromatograph with a capillary column of PONA and a FID detector. The product yield was calculated by the normalization of GC analysis results.

3 Results and Discussion

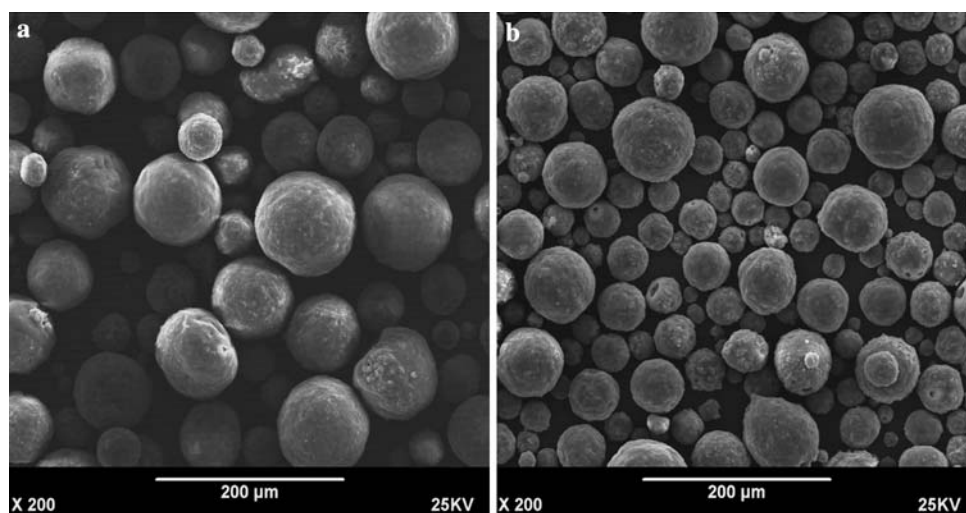
3.1 Catalyst Characterization

3.1.1 Morphology, Crystalline, and Porosity

The catalysts prepared by spray-dry method are sphere-like particles in the SEM photos (Fig. 2). Hydrothermal treatment at 800 °C results in a slight decrease in the particle size. The particle diameter is in the range of 20–80 μm for the parent catalyst (Cat-unst) and 20–60 μm for the catalyst after steam treatment (Cat-st). The X-ray diffraction pattern of the steam-treated catalyst (Cat-st) in Fig. 3, which is identical to the XRD patterns of ZSM-5 zeolite [9], is very close in position and intensity to that of the parent catalyst without treatment, implying that the MFI-structure of ZSM-5 is well-preserved. The nitrogen physical adsorption measurements also prove the framework stability of ZSM-5 in hydrothermal treatment at high temperature. In Table 3, no significant difference is observed in total surface area and volume of the two tested samples. The appearance of a very slight loss in microporous surface area after steam treatment, with the value of 92 m²/g for Cat-unst and 87 m²/g for Cat-st, possibly stems from the partial blockage of MFI channel caused by a slight dealumination of ZSM-5 zeolite. Besides microporous structure, mesoporous structure from the inorganic oxide matrix, SiO₂–Al₂O₃, which provides physical strength and heat or mass transfer was also observed in nitrogen physical adsorption measurement.

Hydrothermal treatment has been widely used in industry [10–12]. Steaming at high temperature usually leads to dealumination of zeolite with the formation of dislodged aluminum which remains in the zeolite channel. Dealumination results in the reduction in crystallinity, surface area, and acid site number [13, 14]. Previous study showed that hydrothermal treatment has predominant

Fig. 2 SEM photos of Cat-unst (a) and Cat-st (b)



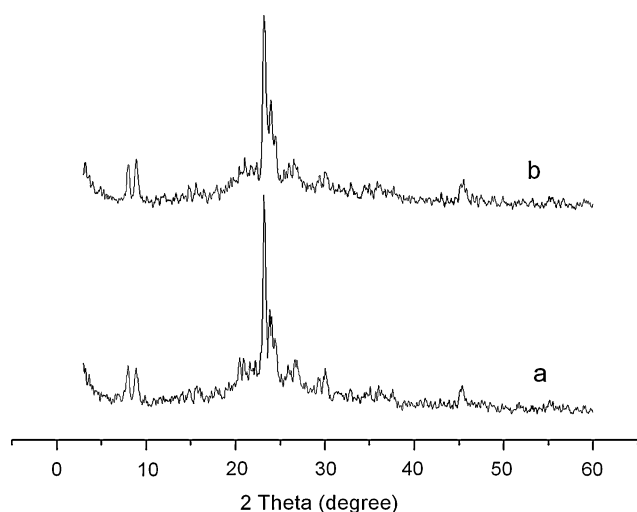


Fig. 3 XRD patterns of Cat-unst (a) and Cat-st (b)

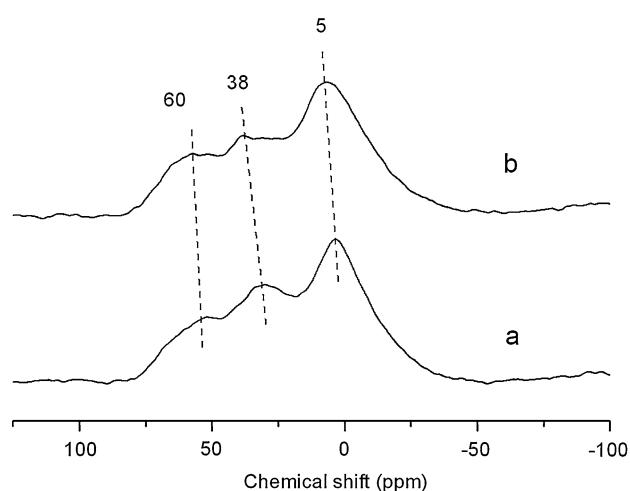


Fig. 4 ^{27}Al MAS NMR spectra of Cat-unst (a) and Cat-st (b)

Table 3 Textural properties of the prepared catalysts

Sample	S_{BET} (m^2/g)	S_{micro} (m^2/g)	V_{total} (cm^3/g)	V_{micro} (cm^3/g)
Cat-unst	112	92	0.091	0.046
Cat-st	111	87	0.105	0.043

effect on the crystallinity of zeolite Y, BETA, and MOR with relatively large pore size and low Si/Al ratio, but ZSM-5 presents its thermal and hydrothermal stability during the treatment [15, 16]. The extremely high hydrothermal stability is closely related to the high Si/Al ratio of ZSM-5 zeolite. The low Al content in ZSM-5 framework limits the extent of aluminum extraction from the framework structure and reduces the occurrence of framework collapse during steam treatment [13].

3.1.2 Dealumination Evidenced by ^{27}Al MAS NMR

The ^{27}Al MAS NMR spectra in Fig. 4 for both the parent catalyst and steam-treated catalyst present three resonance peaks at 60, 38, and 5 ppm. The peak with low intensity at 60 ppm is characteristic of the tetrahedral aluminum species located in the framework of zeolite ZSM-5 [13]. The peak at 38 ppm is attributed to the pentahedral or distorted tetrahedral coordinated aluminum atoms in extra-framework species [17–19]. The strong peak at 5 ppm is assigned to the extra-framework Al with octahedral coordination [20]. The latter two peaks are from the matrix materials which are added to the catalysts for improving the physical strength and heat transfer. A slight chemical shift increase is noted for catalyst after steam treatment. This may stem from the

Table 4 Different Al species (%) determined by ^{27}Al MAS NMR

Sample	$\text{Al}_{\text{tetrahedral}}$ (~60 ppm)	$\text{Al}_{\text{pentahedral}}$ (~38 ppm)	$\text{Al}_{\text{octahedral}}$ (~5 ppm)
Cat-unst	24	25	51
Cat-st	18	24	58

interaction between matrix materials and ZSM-5 zeolite during steam-treating at high temperature. Table 4 details the distribution of aluminum species obtained from deconvolution of the peaks in the ^{27}Al MAS NMR spectra in Fig. 4. The sample without hydrothermal treatment presents 24% tetrahedral coordinated framework Al. After steam treatment, this value is declined to 18%. At the same time, the resonance peak representing octahedral species becomes more intense. This indicates that with hydrothermal treatment, Al species have migrated from framework tetrahedral positions and existed as non-structural Al species in the catalysts. Dealumination occurs during hydrothermal treatment, while the framework and porosity of ZSM-5 are well-kept as discussed in Sect. 3.1.1.

3.1.3 NH_3 -TPD

NH_3 -TPD profiles of the two catalysts, Cat-unst and Cat-st, are given in Fig. 5. The ammonia desorption from both of them occurs in the same temperature ranges, the desorption at low temperature range of 100–310 °C (I) and at high temperature range of 310–550 °C (II), representing the weak and strong acidity. The weaker acidic sites correspond to the terminal silanol group on external surface and the stronger acidic sites correspond to the bridge hydroxyls at the channel

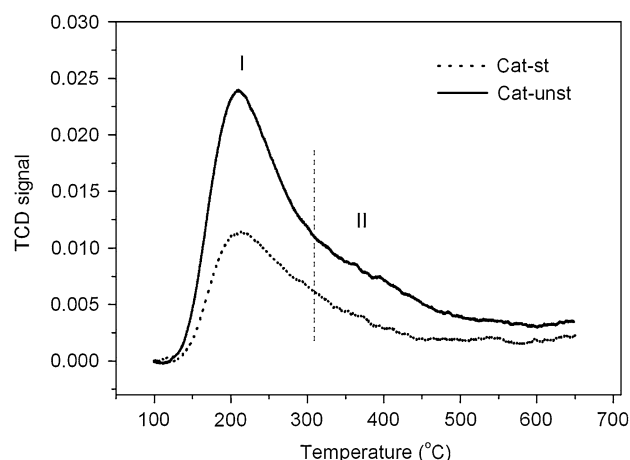


Fig. 5 NH_3 -TPD profiles of Cat-unst and Cat-st

interaction of ZSM-5 [21]. For the steam-treated catalyst (Cat-st), a noticeable intensity decrease is observed compared to the untreated catalysts, implying acid amount reduction after hydrothermal treatment. The active acidic sites, $\text{Si}(\text{OH})\text{Al}$, in concentration is related to the aluminum content of zeolite framework [22]. The acidity difference in this study is generated by the aluminum extraction from the framework structure. During the steam treatment, even no framework collapse, aluminum species dislodgement from framework occurs and results in the loss of the active acidic sites.

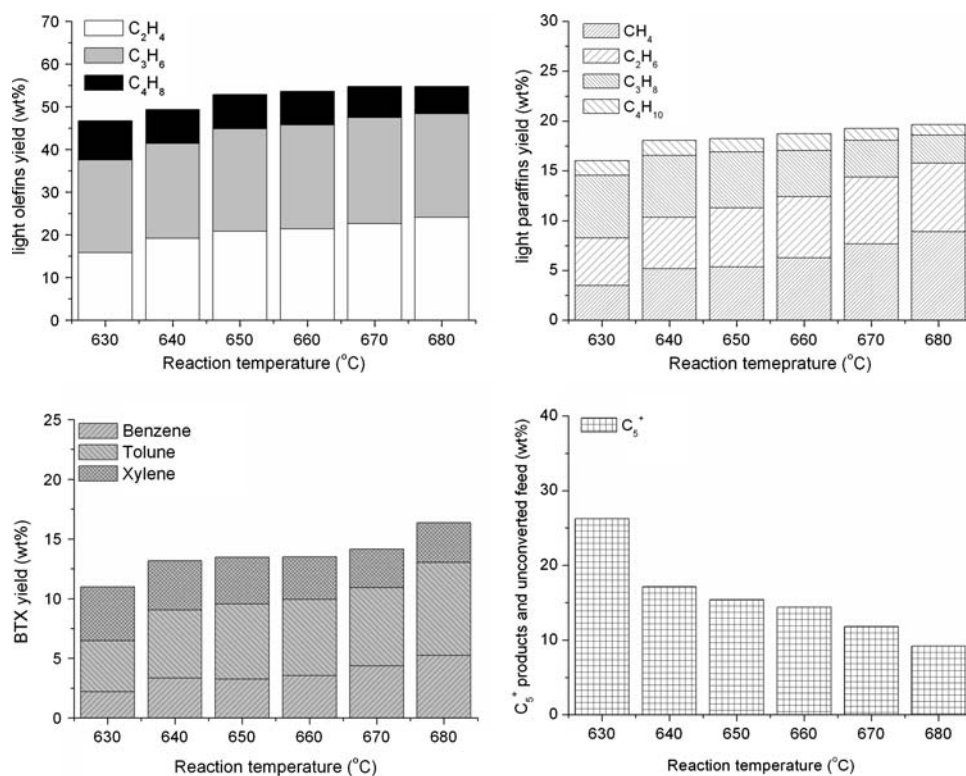
3.2 Catalytic Evaluation

3.2.1 The Evolution of Catalytic Performance with Reaction Temperature

Naphtha catalytic cracking over the steam-treated ZSM-5-based catalyst, Cat-st, was carried out at 630–680 °C in a micro-scale fluidized-bed reactor and the evolution of hydrocarbon yield with reaction temperature is given in Fig. 6. Usually commercial olefins technique of thermal cracking of naphtha at 880 °C can give an ethylene and propylene yield of 45–47 wt.%. In our study, after conversion at 630–680 °C, in the product stream, light olefins (ethylene, propylene, and butenes) are responsible for 47–55 wt.% naphtha conversion and ethylene and propylene yield attains to 48 wt.% at 680 °C.

Commercial ethylene technology is thermal cracking of naphtha at extremely high temperature. Its products are from the thermodynamical reaction and no catalysis performs in this technique. In the present work, naphtha cracking was carried out over an effective ZSM-5-based catalyst. The function of zeolite catalyst is supplying very active reaction centers, bridge hydroxyl groups $\text{Si}(\text{OH})\text{Al}$ on the ZSM-5 surface, to activate the naphtha feed which is rich of stable and saturated hydrocarbons. Previous studies proved reaction over cracking catalyst would occur with decreased reaction activated energy, so cracking process could be

Fig. 6 Products yield of naphtha catalytic cracking over Cat-st at different reaction temperature



carried out at lowered temperature and light olefins could be produced in a more efficient way. Detailed results show that the application of fluidized-bed catalytic cracking reduces the reaction temperature by 200 °C for the required light olefins yield in commercial process, indicating that fluidized-bed catalytic cracking is a very effective and potential way for light olefins production from naphtha catalytic cracking at a lowered reaction temperature.

Among the products of catalytic cracking, light paraffins (C_1 – C_4 alkanes) and BTX also generate. Detailed results in Fig. 6 show that the production of all the three groups of products is favored by the increase of reaction temperature, especially methane and C_2 products. In fact, at relatively low temperature (630–660 °C), propylene yield (22–24 wt.%) is higher than that of ethylene (16–22 wt.%), whereas, at 670 and 680 °C, ethylene and propylene yield are in the same level (22–25 wt.%). Ethylene and propylene are the main products in our work and the light olefins distribution could be varied by the reaction temperature.

It is interesting to observe that under the reaction condition in the present study, besides light olefins can be largely produced, C_6 – C_8 aromatics, benzene, toluene, and xylene, can also generate. This is different from the works of catalytic cracking performed in fixed-bed reactor or fluidized-bed reactor with naphtha feed mainly composed of n-paraffins and iso-paraffins or Fischer–Tropsch-derived hydrocarbon fraction, containing paraffins, olefins, and oxygenates [7, 23]. Light olefins and paraffins were the main products in these two works. The naphtha feedstock in our study is mainly composed of paraffins and naphthenes in boiling range of C_4 – C_{14} (Table 1). The generation of aromatics in our study is associated with the conversion of naphthene as the second main component (~ 30 wt.%) of the naphtha feed over ZSM-5-based catalyst. With this feedstock, production of light olefins and aromatics could be an alternative product strategy of naphtha catalytic cracking.

C_1 – C_4 paraffins appear as by-products, noting that their yield is much lower than thermal cracking, especially methane, which is account for about 15% naphtha conversion in thermal cracking at 880 °C. After naphtha conversion, about 10–25 wt.% C_5^+ products and unconverted hydrocarbons remain in the effluent. For further efficiency improvement of ethylene and propylene production, as suggested by Superflex technique [23], a recycle mode for returning the butenes, C_5^+ products and unconverted hydrocarbons back to reactor would be considered.

3.2.2 The Evolution of Catalytic Performance with Reaction Time

Naphtha conversion over ZSM-5-based catalyst, Cat-st, was performed at 640 °C in the fluidized-bed reactor and the yield of light olefins and aromatics as the function of time on

stream is detailed in Fig. 7. No sharp decrease of yield appears with prolonging the reaction time from 2 to 60 min. The big time difference just causes a slight reduction in ethylene yield, from 18.6 wt.% at 2 min to 15.7 wt.% at 60 min, and a very slight increase in butenes yield, from 8.9 wt.% at 2 min to 9.5 wt.% at 60 min. Propylene yield keeps at 22–23 wt.% during the conversion. A very stable total light olefins yield is preserved during the reaction. This performance stability should be attributed to the catalyst treatment in steam at 800 °C. This treatment in extremely rough condition avoid the further catalyst surface and acidity loss caused by ZSM-5 crystalline collapse and dealumination in the reaction of naphtha cracking, which is performed at relatively high temperature (>600 °C) and accompanied by steam. For comparison, the catalytic cracking was also carried out over Cat-unst under the same condition as over Cat-st, ethylene and propylene yield is higher than the value of Cat-st at the beginning of the reaction (43 wt.%), while this value goes through a sharper decline than Cat-st,

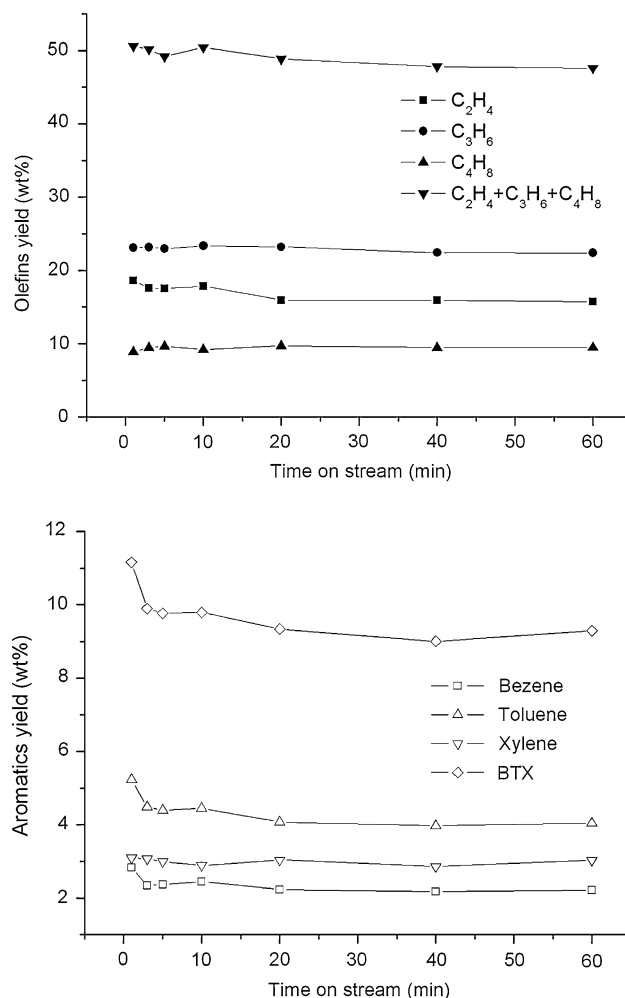


Fig. 7 Olefins and aromatics production in naphtha catalytic cracking over Cat-st at different time on stream (reaction temperature = 640 °C)

implying an unstable catalytic performance caused by poor thermal stability of Cat-unst. Dealumination of ZSM-5 occurs during steam treatment and this treatment will ensure no more acidity and crystalline loss during reaction.

The aromatic products yield over Cat-st with time on stream given in Fig. 7 shows that at the beginning of the reaction, benzene, and toluene are produced with relatively high yield, then the value of BTX yield experiences a decline of 1.9 wt.% in the following 60 min. Aromatics are generated from the secondary reactions of olefins, such as oligomerization, hydrogen transfer, and cyclization, which are very reactive over zeolite catalysts. Hydrogen transfer reaction of olefins products, $(CH_2)_n$, gives rise to alkanes and hydrogen-poor compounds, such as aromatics or even more hydrogen-unsaturated species, coke. In the present study, naphtha can be efficiently transferred to light olefins and aromatics in a long reaction period. This performance with a very weak deactivation during a long reaction time implies the stronger coke resistance of ZSM-5 catalyst, even at relatively high reaction temperature and with light olefins as main products. The higher Si/Al ratio of ZSM-5 and the corresponding lower acid density, compared to other zeolite catalyst, such as Y, Beta, or MOR, account for its high coke resistance. The 10-ring cross channel structure of MFI also prohibits large carbonaceous species formation. These performances in fluidized-bed reaction also imply that catalytic cracking over ZSM-5-based catalyst prepared in this study could be carried out at a long residence time in the cycling fluidized-bed reactor. Residence time is a very important parameter for fluidized-bed reaction. Usually riser employs a very short catalyst residence time to ensure the initial activity of a fresh catalyst [24], while long-term stability of ZSM-5-based catalyst in this study indicates that naphtha conversion could be efficiently transferred to light olefins and other value-added products under a variable reaction condition.

4 Conclusion

A fluidized-bed catalyst, combining ZSM-5 zeolite and $SiO_2-Al_2O_3$ matrix, was prepared with spray-dry method. The catalyst was sphere-like and the particles diameter was in the range of 20–80 μm . Hydrothermal treatment at 800 °C for 10 h caused the dislodgment of partial framework aluminum atoms and corresponding acid sites loss,

while the crystallinity and porosity were well-preserved. The steam-treated ZSM-5-based catalyst was employed in the fluidized-bed catalytic cracking of naphtha and the performance proved its high efficiency in the production of light olefins and aromatics at relatively low temperature. At 680 °C, ethylene and propylene yield is up to 48% and higher than the value in non-catalytically thermal cracking at 880 °C. The very stable catalyst activity in fluidized-bed naphtha cracking at a long reaction period implied that the fluidized-bed catalytic cracking could be performed at a variable and long residence time.

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