

## Production of light olefins and aromatic hydrocarbons through catalytic cracking of naphtha at lowered temperature

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Naphtha catalytic cracking were carried out at 650°C over modified ZSM-5. Light olefins and BTX could be obtained over the catalysts. The products showed variable distribution with different catalyst modification. Some modification, such as Fe, Cu and La favored the BTX generation and P and Mg modification favored the light olefins production. In N<sub>2</sub> stream cracking catalyzed by LaZSM-5, more than 50% naphtha feed were converted to BTX, while in steam cracking, with an improved modified catalyst, P, La/ZSM-5, naphtha can be converted to light olefins with high activity and long-term stability.

### 1. INTRODUCTION

The low weight olefins, ethylene and propylene, are the most important base chemicals among the petrochemical products. The main commercially technique for light olefins production is steam cracking of naphtha. Though some improvements have been made in this process, it is still the first energy-consuming process in petrochemical industry, which requires high reaction temperature (800-880°C), and accounts for 40 % of the total energy-consuming every year. Under the typical steam-cracking condition (820 °C, H<sub>2</sub>O/naphtha=0.7), about 30% of ethylene and 17% of propylene can be obtained. To improve the yield of light olefins and decrease the cracking temperatures, the application of catalytic cracking process could be an option.

Several types of catalysts for naphtha cracking have been used in steam cracking and the enhanced olefin yield was obtained, while until now still no commercial application has been reported.

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 experimental process that has been developed is the so-called Vniios process, which uses KVO<sub>3</sub> with a boric acid promoter on a low surface area alumina [1]. With this catalyst, at the temperature of 780°C, at a steam to feed ratio of 1:1, and at a residence time of 0.15 s, the yield of ethylene from the pyrolysis of gasoline, is 40 wt%. This value was approximately 5-10 wt % higher than the yield in conventional cracking of naphtha. Kikuchi et al. investigated the calcium aluminate catalysts under various conditions and optimize the condition for producing olefins using this kind of catalysts [2]. Lemonidou tested the catalysts of different phases of calcium aluminate and other complexes of various metal oxides such as Mg, Mn, Ti, In and Zr. In steam cracking of n-hexane, the selectivity of light olefins, ethylene and propylene is 10-18% higher than  $\alpha$ -alumina. The best results were obtained with a calcium aluminate catalyst at the CaO to

$\text{Al}_2\text{O}_3$  molar ratio of 12:7 [3]. Mukhopadhyay et. al reported the steam cracking of naphtha over  $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ . The yield of ethylene and propylene increased by 7 wt% compared to those empty tube under identical conditions. Basu's work over  $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$  in temperature range of 700-850°C also indicated that the presence of catalyst reduced the temperature required for a given conversion by approximately 50°C [4].

Beside the work listed above, naphtha cracking over acidic catalysts was also reported. K. Wakui et al. studied catalytic cracking or oxidative cracking of n-butane at the temperature range of 600-650°C over MFI zeolite. 58 % yield of ethylene and propylene was obtained at 650°C [5]. Aiming at more light olefins production, dehydrogenation-cracking double stage reaction of n-butane was also investigated by them. Yashimura et al. gave the data of light naphtha catalytic cracking with the feed of steam and  $\text{N}_2$ -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 present in the paper [6].

With the same purpose of realizing the catalytic cracking of naphtha at relatively low temperature, a series of catalysts of ZSM-5 were prepared and used in the naphtha cracking. Considering the high naphthene content of the naphtha feed, the modified ZSM-5 catalysts were used in the cracking for a flexible product distribution, such as more light olefins, more BTX or both of them.

## 2. EXPERIMENTAL

### 2.1. Naphtha feedstock

The naphtha used in this study was supplied by Petro-China. This feed was analyzed by Varian gas chromatograph with a capillary column of PONA and data were processed with DHA software. The specification of naphtha is listed in Table 1.

Table 1.  
Specification of naphtha feed (wt %)

Paraffins	30.82
Iso-paraffins	20.63
Naphthenes	33.79
Olefins	8.39
Aromatics	3.61
others	2.76

### 2.2. Catalyst preparation

Two samples of ZSM-5 ( $\text{SiO}_2/\text{Al}_2\text{O}_3=45, 72$ ) were supplied by Fushun subcompany of Petro-China. Protonic form samples were prepared, first by calcining the solid for 3 h in air at 823 K, then by ion-exchanging the calcined solid at 323 K with 1 M solution of ammonium nitrate and finally by calcinations of the ammonium form in air for 3 h at 550 °C. The obtained samples were designated as HZSM-5(45) and HZSM-5(72) respectively.

The catalysts were HZSM-5, or modified ZSM-5, or mix solids of ZSM-5, binder and modification elements. Amorphous  $\text{SiO}_2$  were used as the binder; P, Mg, Ca, Sr, Co, Ni, Cu, Fe, Zn and La were used for modification with ion exchanging method.  $\text{Mg}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ ,  $\text{Ca}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$ ,  $\text{Sr}(\text{NO}_3)_2$ ,  $\text{La}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ ,  $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ ,  $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ ,

$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  and  $\text{H}_3\text{PO}_4$  were used as the precursors of modified elements. The catalyst compositions are listed in the Table 2.

Table 2  
Specification of catalysts

Catalyst	Catalyst composition	
	Zeolite	Modification element (wt %)
Mg-ZSM-5	HZSM-5(45)	Mg(0.62%)
Ca-ZSM-5	HZSM-5(45)	Ca(0.65%)
Sr-ZSM-5	HZSM-5(45)	Sr(0.60%)
La-ZSM-5	HZSM-5(45)	La(1.39%)
Co-ZSM-5	HZSM-5(45)	Co(0.61%)
Zn-ZSM-5	HZSM-5(45)	Zn(0.55%)
Fe-ZSM-5	HZSM-5(45)	Fe(0.75%)
Ni-ZSM-5	HZSM-5(45)	Ni(1.73%)
Cu-ZSM-5	HZSM-5(45)	Cu(2.70%)
P-ZSM-5	HZSM-5(45)	P(1.69%)

### 1.3. Catalytic cracking experiments

The reactions of catalytic cracking of naphtha were performed in a fixed-bed quartz reactor. The scheme of the experimental setup is shown in Fig. 1. Naphtha or naphtha and water was pumped into the reactor and vaporized over quartz particles at the upper part of the bed at approximately 500°C, and then contacted catalysts. The products leaving the reactor were kept warm at about 200°C and analyzed on line by Varian gas chromatograph with capillary column of PONA. The reaction conditions were listed in Table 3.

Table 3  
Operating condition of catalytic steam cracking of naphtha

Condition	Value
Naphtha flow rate (ml/h)	8
Steam to naphtha ratio	0.7-1.4
Residence time (s)	1.8
Reaction temperature (°C)	650
Catalyst volume (ml)	4
Catalyst size, mm	0.4-0.9

## 3. RESULTS AND DISCUSSION

MFI-type zeolite (HZSM-5) has been reported as a catalyst for olefin production from hydrocarbon cracking [5,6]. Some modifications of HZSM-5 will suppress some side-reactions over the acidic catalyst, such as hydrogen-transfer and coke formation. In the present study, in order to investigate the modification effect of the catalysts, the ZSM-5 catalysts with different element modification were tested in the cracking of naphtha. Also to show the difference of the cracking with or without steam, these naphtha catalytic cracking

reactions were carried out in nitrogen atmosphere or in steam and the results are shown in Figs. 2 and 3 respectively.

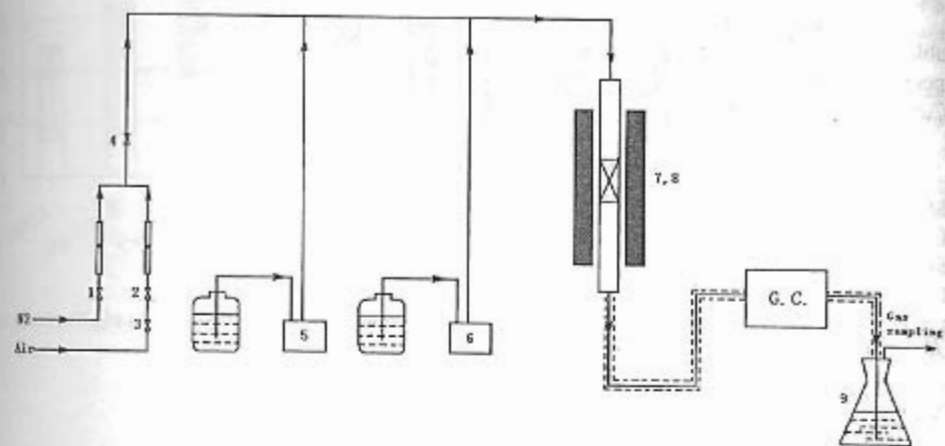


Fig. 1. Schematic experimental setup of naphtha steam cracking  
1, 2, 3, 4-valves; 5, 6-pumps; 7-reactor; 8-furnace; 9-condenser

10 elements, such as P, Mg, Ca, Sr, Co, Ni, Cu, Fe, Zn and La, were used to modify ZSM-5(45) to obtain some special cracking properties. The results in Figs. 2 and 3 give the modification effect on the product distribution in naphtha cracking. When the cracking reactions were carried out in  $N_2$  stream and without steam, the light olefins, i.e. ethylene and propylene, and aromatic products, i.e. BTX take the majority of the products. The distribution between light olefins and BTX varies with the element for modification. Compared to the catalyst of HZSM-5, with ethylene and propylene yield of 30.35% and BTX yield of 48.27%, the incorporation of P, Mg, Ca, La and Cu increases the production of ethylene and propylene, and lowers the BTX production; this is more prominent for the sample of P-ZSM-5 and Mg-ZSM-5 with ethylene and propylene yield of 37.87% and 39.91% and BTX yield of 11.64% and 25.47% respectively; the modification of Co, Ni, Fe and Zn suppresses the BTX generation, and ethylene and propylene yield also decreases to some extent. The modification with P and Mg is thought to decrease Bronsted acidity of zeolite and provide a pathway for reaction to occur with enhanced light olefins production.

For more light olefins production, catalytic cracking was carried out with steam-accompanying. The samples with more light olefins products (P-, Mg-, Ca-, Cu-, La-ZSM-5) in  $N_2$  cracking were used as catalysts for the steam cracking tests and the results with detailed specification are shown in Fig. 3. Under steam condition, compared to the results without steam, more light olefins can be obtained over the sample of P-, Mg-, Ca-, Sr, Cu-ZSM-5, specially for P-ZSM-5, the ethylene and propylene yield of 57% were obtained, and at the same time the BTX yield decreases greatly. This indicates that the steam condition would improve light olefins yield by suppressing the generation of BTX and light paraffins, i.e. methane, ethane and propane, which were thought to be generated from hydrogen transfer Cu-ZSM-5, specially for P-ZSM-5, the ethylene and propylene yield of 57% were obtained, and at the same time the BTX yield decreases greatly. This indicates that the steam condition would improve light olefins yield by suppressing the generation of BTX and light paraffins, i.e. methane, ethane and propane, which were thought to be generated from hydrogen transfer

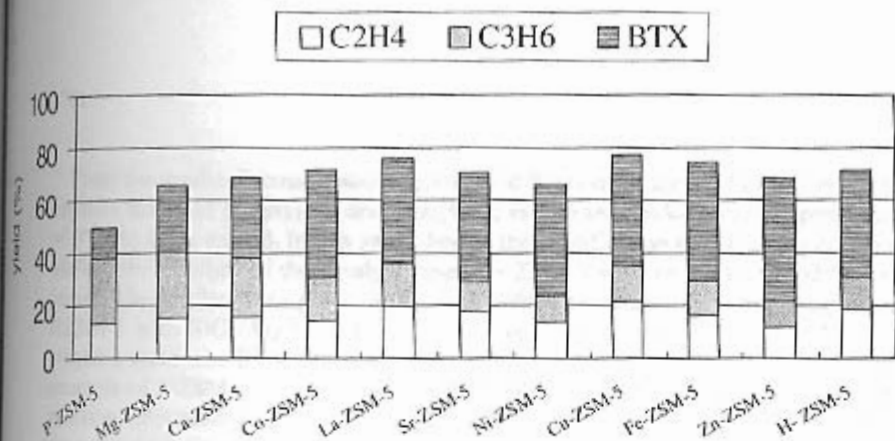


Fig. 2. The yield of light olefins and BTX of naphtha cracking in  $N_2$  over modified ZSM-5

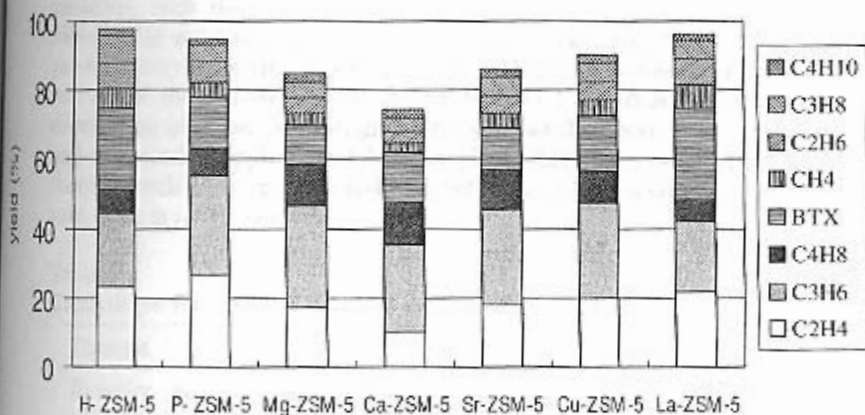


Fig. 3. The product yield of naphtha cracking in steam over modified ZSM-5

above. This may come from the modification of acidity of ZSM-5. For this reason, beside ethylene and propylene, butenes also take a relatively large share in the light olefins products. The cracking over La/ZSM-5 gives some different performance, methane and BTX is relatively high compared to HZSM-5 and other modified ZSM-5, while the yield of light olefins is lower than other catalyst, indicating that hydrogen-transfer is more prominent over La-ZSM-5 than other catalysts.

From the results discussed above, some modification for the acid character of HZSM-5 can improve the yield of ethylene and propylene; and steam cracking can suppress the generation of BTX to some extent. In this study, beside the modification effect on the production of light olefins, the stability of the catalyst based on ZSM-5 with or without modification was also tested. The results were given in Table 4. When the steam cracking was carried out over HZSM-5 with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  of 45 and 72, comparing the data obtained at 1 h and 10 h, the ethylene yield and BTX decreased a lot and propylene or butenes increases with time. For example of HZSM-5(45), ethylene yield of 23.31% can be obtained at the beginning of the reaction, after reaction of 10 h, ethylene yield decreases to 15.55%, and the yield of BTX also decrease with time on stream; at the same time, propylene yield increases from 21.15% to 24.24%, and butenes yield also increases.

This product distribution change, from ethylene as the main cracking products (1 h) to the propylene as the main cracking products (10 h) indicates the activity change of the catalysts, which determined the cracking product distribution over these catalysts. The catalysts in the initial period were active enough to catalyze the naphtha cracking to produce light olefins or paraffins; with the generation of the light hydrocarbons, some other reactions, such as bimolecular reactions and H-transfer reaction may also happen, BTX and more heavier products may generate from this reaction. The coke deposition is thought to be a common reason for the deactivation of the catalysts and this deactivation will varied the product distribution over the catalyst, giving the product distribution with lowered yield of ethylene and enhanced propylene and butanes yield. Keeping a stable product distribution as the thermal cracking in industry and a higher yield of light olefin than the industrial process at a same time is rather difficult.

Table 4  
Catalytic performance of HZSM-5 and modified ZSM-5

Catalyst	HZSM-5(45)		HZSM-5(72)	
	1 h	10 h	1 h	10 h
$\text{C}_2\text{H}_4$	23.31	15.55	24.01	10.58
$\text{C}_3\text{H}_6$	21.15	24.24	23.54	21.07
$\text{C}_4\text{H}_8$	6.49	10.36	5.49	10.36
$\text{CH}_4$	5.63	4.12	4.64	2.77
$\text{C}_2\text{H}_6$	7.55	4.92	6.37	3.1
$\text{C}_3\text{H}_8$	8.03	5.05	5.66	3.44
$\text{C}_4\text{H}_{10}$	1.67	2.11	0.88	1.93
Benzene	6.38	4.61	5.39	3.9
Toluene	10.01	6.22	9.39	3.9
Xylene	6.90	5.35	4.73	4.60

Beside varying the product distribution for more BTX or more light olefins production, some modification with P or Mg or P, La improved the catalytic stability, which made this catalytic cracking a more promising process for industrial application. The result in Fig. 4 indicates that P and La modified ZSM-5, with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  of 45 and 72, is more stable than ZSM-5

without modification. Over the catalyst of P, La/ZSM-5 ( $\text{SiO}_2/\text{Al}_2\text{O}_3=72$ ), ethylene and propylene yield kept higher than 50% for 30 h, and at the beginning 10 h, 55% yield can be obtained.

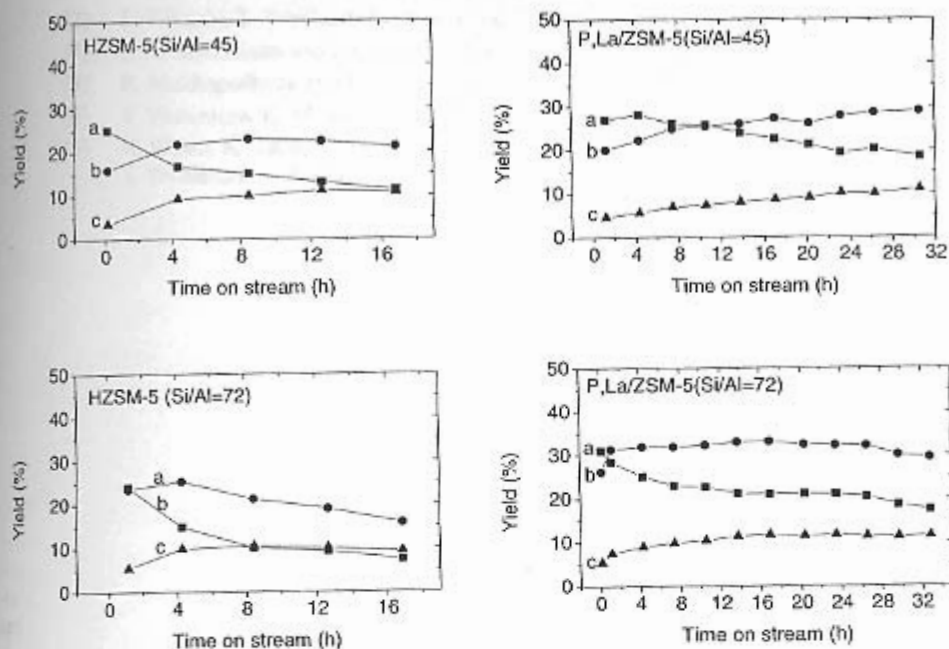


Fig. 4. Yield variations with time on stream in catalytic steam cracking at 650°C (a-C<sub>3</sub>H<sub>4</sub>, b-C<sub>3</sub>H<sub>6</sub>, c-BTX)

#### 4. CONCLUSION

Production of light olefins and BTX from naphtha cracking can be realized over zeolite catalyst at a lowered temperature, such as 650°C. High yield of light olefins indicated that it is promising process and maybe an alternative for the industrial thermal-cracking. Variable product distribution over the modified catalyst made it possible for BTX production at the same time. Some element modification for ZSM-5 and steam cracking condition can increase the light olefin yield and cracking stability and some modification improved the BTX production. With the catalyst of P, La/ZSM-5 ( $\text{SiO}_2/\text{Al}_2\text{O}_3=72$ ), the ethylene and propylene yield higher than 50% kept for more than 30 h; while with LaZSM-5, more than 50% naphtha were transferred to BTX with benzene and toluene as the main. P modification decreased the Bronsted acidity of the modified ZSM-5 catalyst and favored the light olefins production.

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