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Study of the application of structural catalyst in naphtha cracking process for propylene production

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ABSTRACT

Driven by the demand for propylene and environmental gasoline, a fluid catalytic cracking (FCC) naphtha post-treatment process using monolithic catalysts with zeolite washcoat was studied. In this study, the conversion of the olefin in naphtha and the selectivity of propylene in gaseous product have been investigated. The blank results showed that the thermal cracking activity is almost negligible at temperature lower than 770 K with 200 cpsi monoliths since the feed and the catalyst may have short hydrodynamics residence time in the monolithic channels. Therefore the loading of zeolite ZSM-5 could not only enhance the conversion of olefin cracking activity but also the selectivity of propylene via catalytic cracking mechanism. The optimum hydrodynamics residence time for propylene production is 0.5 s in this process. Adding rare earth on ZSM-5 zeolite by ion-exchanging or precipitation method can probably prompt the conversion of olefin in naphtha and increase the selectivity of propylene as well. The results showed that the gaseous products mainly consisted of propylene and C4 olefin which could totally reach 60% and the yield of propylene was about 31% while the olefin content in naphtha could reduce 15%.

1. Introduction

Propylene is one of the most rapidly growing petrochemicals, driven primarily by the high demand of polypropylene. Although steam cracking continues to supply most of the world's propylene, there is an increasing need for propylene from other sources. Propylene production from FCC units is the second important source of worldwide petrochemical propylene supply. As demand has increased, refiners have been able to increase propylene production in FCC's by optimizing catalyst and operating conditions. In particular, the utilization of ZSM-5 additive is increasing as refiners find it profitable to boost FCC propylene production.

However, the potential for production of propylene in existing Refinery FCC units is limited. New on-purpose propylene technologies will be required to provide additional supplies of propylene to meet the growth projections.

Catalytic cracking of olefinic streams to produce primarily propylene along with ethylene and butylenes has been described by several companies in recent years, including Mobil (MOI™), Kellogg Brown & Root (SUPERFLEX™) and Lurgi (PROPYLUR®). These processes are characterized by the use of ZSM-5 catalyst to convert higher molecular weight olefins and paraffin to lighter olefins [1].

But a repeatedly occurred experimental phenomenon was observed. In order to increase the conversion of olefinic streams, the feed weight hourly space velocity should be reduced. However, this would lead to a reduction of the propylene yield. In Li's paper, he noted that propylene was not a chemical stable product, which can be converted to other compounds under the conditions of deep catalytic cracking of heavy oils. The main products comprised alkenes having shorter carbon chain than propylene such as ethylene and aromatics. So the yield of propylene was decreased. This result is not what the researchers expected [2].

So there is a great demand for a new technology which can combine the catalyst with a new reactor that has short hydrodynamics residence time. In general, a monolithic catalyst comprises a honeycomb-like ceramic structure, covered by a thin layer of a porous support material (washcoat) in which a catalytically active component is present. Its straight channels result in extremely low pressure drop and prevent the accumulation of coke. Compared with the normal packed reactor, the monolithic catalyst and reactor can be more easily operated under higher feed weight hourly space velocity [3].

On the basis of previous work, a FCC gasoline catalytic cracked process by a monolithic catalyst with the zeolite washcoat was studied in this paper. During the study, the feed and the catalyst may have short hydrodynamics residence time (HRT) in the monolithic channels. The conversion of the paraffin, olefin,

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naphthene and aromatics in the naphtha, especially the selectivity of propylene were studied.

2. Experimental

2.1. Feed

The gasoline feed used in this work achieved from the FCC unit in Yangzhou Petrochemical Limited Company. The following is the mass fraction of paraffin, olefin, naphthene and aromatic in the feedstock analyzed by gas chromatography (Hewelett-Packard 6890) with a capillary column.

w (paraffin) = 31.74 wt.%; w (olefin) = 36.61 wt.%;
w (naphthene) = 9.81 wt.%; w (aromatic) = 20.28 wt.%.

2.2. Zeolite synthesis

The properties of two commercial ZSM-5 zeolites before and after modification used in this work were listed in Table 1. The rare earth modified zeolites were prepared by impregnation or ion-exchanging method.

Table 1
The physical-chemical properties of zeolites.

Name	SiO_2/Al_2O_3/ (mol/mol)	Crystallization/%	Re_2O_3/wt.%	Micropore volume/$m^3\ g^{-1}$
ZSM-5(1)	50	76.1	–	0.138
ZSM-5(2)	200	90.9	–	0.173
(RE)ZSM-5(1)	50	61.2	1.9	0.137
(RE)ZSM-5(2)	200	50.2	1.4	0.171

2.3. Catalyst preparation

The monolithic supports with cell density of 100, 200, 400 cpsi (cells per square inch) were obtained from JiangSu, China. It was made of cordierite. The diameter of it was 30 mm and the length was 50 mm, containing about 2 g ± 0.3 g washcoated zeolite. Preparation of catalysts, starting from monolithic matrix and their coating can be found elsewhere [4]. The properties of monolithic catalysts with or without washcoat were summarized in Table 2. Before evaluation, the catalysts have been aged at 1073 K for 4 h.

Table 2
The properties of monolith catalysts.

Name	Cell density[a]/cpsi	SiO_2/Al_2O_3/ (mol/mol)	Re_2O_3/wt.%	Zeolite loading/g
A	100	–	–	–
B	200	–	–	–
C	400	–	–	–
D	100	200	–	2.05
E	200	200	–	1.87
F	400	200	–	2.07
G	400	50	–	2.12
H	200	50	1.9	2.29
I	400	50	1.2	1.73
J	200	200	1.4	2.24

[a] cpsi means cells per square inch. The wall thickness of the supports with 100 cpsi, 200 cpsi and 400 cpsi are 0.0177 in., 0.0142 in. and 0.0065 in. while the porosity of the supports are 67.7%, 63.9%, and 75.7%, respectively.

2.4. Experimental procedures

A fixed-bed flow reactor was used for the cracking of naphtha under atmospheric pressure. A piece of monolithic catalyst was put into a stainless reactor. A schematic diagram of experimental apparatus was shown in Fig. 1. The range of parameters utilized in experiments was shown in Table 3.

$$\text{The hydrodynamics residence time (s)} = \frac{50\,\text{mm}}{\text{flow velocity (mm/s)}}$$

Flow velocity refers to the total linear speed of feed and water. The linear speed was calculated by the division of volume speed

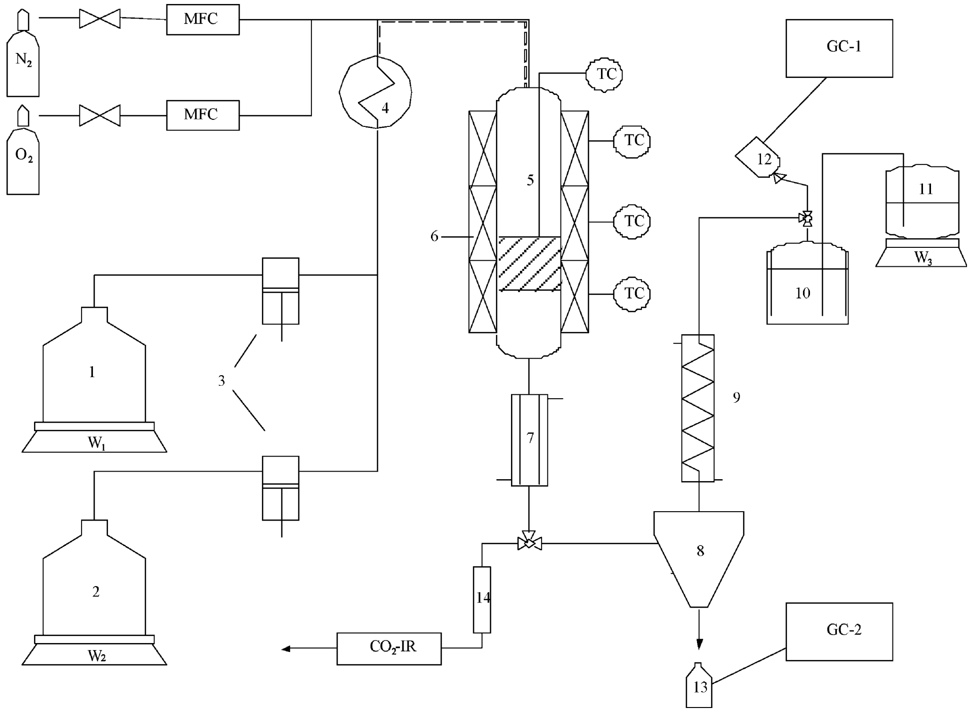

Fig. 1. Schematic of experimental apparatus for the catalytic cracking of a gasoline from FCCU. 1: gasoline Tank; 2: water tank; 3: pumps; 4: evaporation heater; 5: reactor; 6: oven; 7: cooler; 8: oil–water separator; 9: deep cooler; 10: gas holder; 11: water tank; 12: gas product; 13: liquid product; 14: CO–CO_2 converter.

Table 3
Experimental parameters ranges.

Parameter	Range
Reaction temperature	673–973 K
Catalyst loading	See Table 1
Feed mass flow rates	0.3–3.5 g/min
Water mass flow rates	0.1–3 g/min

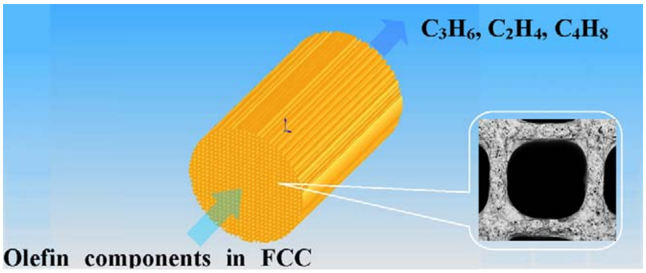

Fig. 2. The illustration of operating regime of the monolithic catalysts.

and the sectional area of monolith catalyst multiplied its porosity. The volume speed was calculated by the Clapeyron Equation considering the reaction temperature. This calculation assumed that the gaseous feedstock in a channel belongs to plug flow.

The illustration of the monolithic catalysts and the catalytic cracking reactions in the monolith channels was shown in Fig. 2.

Gas products were analyzed by gas chromatography (Hewelett-Packard 6890) with an Alumina/KCl PLOT column. Conversion of olefin calculated as transformation of olefins to other hydrocarbons. Selectivity to each product is expressed as wt.% was calculated as amount of formed light olefin to amount of the gas product ($<C_5$).

$$\text{The olefin conversion (wt.\%)}$$
$$= \frac{\text{weight of the olefin in the feed} - \text{weight of the olefin in liquid product}}{\text{weight of olefin in the feed}} \times 100\%$$

$$\text{The selectivity of light olefin in the cracking gaseous (wt.\%)}$$
$$= \frac{\text{weight of light olefin}}{\text{weight of the gas product } (<C_5)} \times 100\%;$$

the light olefin including ethylene, propylene and butylene.

3. Results and discussion

According to the previous papers [1,5], the main catalytic reaction in the FCC gasoline catalytic cracking processing is that the olefin components from C_6 to C_{10} are cracked to the light olefin, such as ethylene, propylene and butylene. By using the monolith catalyst, the hydrodynamics residence time between the gasoline gas and catalyst washcoat film can be controlled from 0.3 s to 1.5 s. It benefits for avoiding the second reactions of propylene.

3.1. The influence of thermal cracking

The reaction temperature and the catalyst are two important factors to this processing of catalytic cracking FCC gasoline. The experiment was designed to use the monolith without catalyst washcoat. There is no catalyst factor in the results. Table 4 is the olefin conversion and the selectivity of ethylene, propylene and butylene during these thermal cracking experiments.

As it shows in Table 4, the thermal cracking at 823 K could enhance the conversion of olefin and the conversion differed by the cell density. The conversions are all beyond 10%. There is the thinnest wall thickness and the largest porosity in the catalyst C. It has the lowest conversion of olefin under 823 K as well. There is the smallest porosity in catalyst B. There are also the lowest selectivity of ethylene and propylene and the highest selectivity of buythlene, comparing with catalysts A and C under 823 K.

Table 4
The results of thermal cracking.

Catalysts	A		B		C	
Temperature/K	773	823	773	823	773	823
Olefin conversion/wt.%	8.4	26.4	3.9	14.2	6.9	10.5
Selectivity/wt.%						
Ethylene	4.6	6.4	4.3	5.8	5.9	13.1
Propylene	8.4	14.2	7.8	11.4	6.7	16.0
Butylene	55.6	40.6	59.4	49.7	44.8	35.7

Under 773 K, the conversion of olefin by catalyst B is less than 5% and was the lowest value. With the porosity from small to large (the monolith in sequence is 200 cpsi, 100 cpsi and 400 cpsi, see Table 2), the selectivity of ethylene is also from small to large. The selectivity of propylene is in the middle and the selectivity of butylene was the largest at the same time. So the influence of thermal cracking cannot be thought about in the experiment with 773 K and 200 cpsi monolith.

3.2. The effect of temperature on the thermal cracking

Catalyst B was evaluated under different temperature. The results in Table 5 show that the conversion of olefin climbed with the elevation of temperature. However the selectivity of ethylene, propylene and butylenes showed obviously different changing trend. The selectivity of ethylene sharply increased whereas the butylenes decreased when the temperature reached above 873 K. In the mean time, the selectivity of propylene increased slowly.

This phenomenon was also demonstrated in Fig. 3.

In this figure it can be seen that the percentage of methane and ethylene in product rose with the reaction temperature and the gasoline conversion increasing. The rising slope of ethylene and methane mass fraction in products is much higher than propylene and butylenes after 873 K, which indicated the mainly reaction mechanism should probably be free radical mechanism under high temperature on monolithic catalyst without washcoat. Since the thermal cracking process follows the free radical mechanism and ethylene is the main product of this mechanism, the increasing of ethylene selectivity was reasonable at elevated temperatures. Besides, the rise of aromatics also implied the polymerization of hydrocarbons led to coking. Therefore in order to increase the selectivity of propylene, the reaction should undergo at lower temperature.

3.3. The effect of hydrodynamics residence time

Using catalyst H, the reaction evaluations were operated at different hydrodynamics residence time by modifying the feed

Table 5
The thermal cracking under the different temperature.

	Temperature/K				
	773	823	873	923	973
Olefin conversion/wt.%	3.9	14.2	23.6	37.0	56.7
Selectivity/wt.%					
Ethylene	4.3	5.8	15.3	17.7	24.0
Propylene	7.8	11.4	19.4	21.2	21.6
Butylene	59.4	49.7	36.6	31.6	21.8

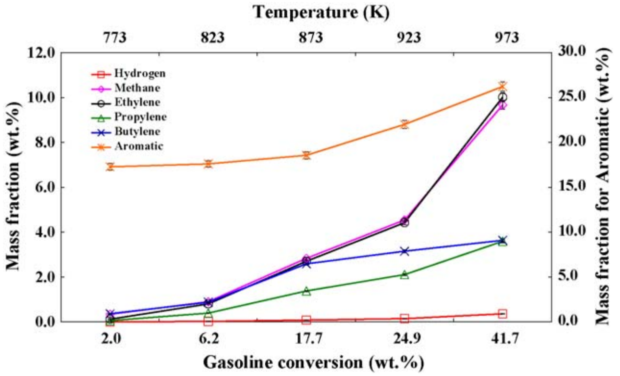

Fig. 3. Thermal cracking of FCC gasoline over catalyst C under different reaction temperature.

Table 6
The effect of hydrodynamics residence time.

HRT/s	Olefin conversion/wt%	Yield of light olefin/wt%	Selectivity/wt%		
			Ethylene	Propylene	Butylene
0.3	47.4	88.5	2.3	31.4	54.8
0.5	46.8	89.1	3.3	34.1	51.6
0.7	45.3	89.0	3.1	32.4	53.5
1.2	49.7	86.2	2.9	29.4	54.0

flow rate under 823 K. The results in Table 6 showed that when the hydrodynamics residence time shorter than 1.0 s the olefin conversion decreased with the hydrodynamics residence time prolong. The maximum yield of light olefin especially the selectivity of propylene occurred as the hydrodynamics residence time was 0.5 s. On the contrast, when the hydrodynamics residence time reached 1.2 s the selectivity of light olefin and propylene sharply dropped.

Fig. 4 demonstrated the conversion of different types of hydrocarbon in feedstock versus hydrodynamics residence time. The results in Fig. 4 showed that with the enhancement of hydrodynamics residence time from 0.3 s to 0.7 s, the total conversion of feedstock increased not derived from the conversion of olefins but from the increasing conversion of paraffin, naphthene and aromatics. This could be the reason for the reduction of olefin conversion while the selectivity of propylene reached the peak around 0.5 s. According to Li's paper [2], even if the hydrodynamics residence time was in 0.75 s, the propylene conversion was still not low. So the olefin conversion is increased, but the selectivity of propylene is decreased. Since the main aimed product of this process is propylene, it can be seen from the results that the optimum hydrodynamics residence time is 0.5 s.

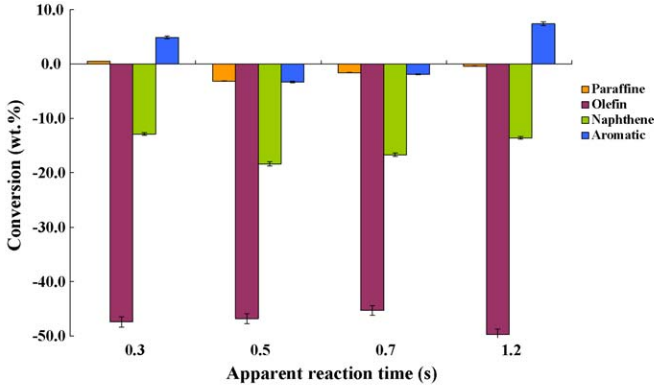

Fig. 4. Conversion of different hydrocarbons versus hydrodynamics residence time.

Table 7
The effect of zeolite catalyst.

Catalysts	Olefin conversion/wt.%	Selectivity/wt.%		
		Ethylene	Propylene	Butylene
A	8.4	4.6	8.4	55.6
D	12.2	5.4	17.8	52.1
B	4.0	4.3	7.8	59.4
E	12.3	3.2	33.0	52.6
C	6.9	5.9	6.7	44.8
F	32.8	1.2	25.7	43.1

3.4. The reaction with catalyst

The catalysts D–F are washcoated the ZSM-5 on the walls of monolith channels. The reaction temperature is 773 K. Table 7 shows the olefin conversion and the light olefin selectivity in these experiments.

Both the olefin conversion and the selectivity of light olefin are increased by using the zeolite. Using the monolith with 400 cpsi, the olefin conversion is better, but the selectivity of propylene is worse than using the monolith with 200 cpsi. On the olefin conversion hand, there are the same results with catalysts D and E; however, the selectivity of propylene shows obviously difference which implied the possibility of mechanism changing under different catalysts. Using the monolith with 200 cpsi, the selectivity of propylene is better.

3.5. The rare earth modification influence

First, the zeolite was modified by the rare earth element. Then a monolith was washcoated with the modified zeolite. The monolithic catalyst I was washcoated with the modified zeolite whose SiO_2/Al_2O_3 ratio was 50. The monolithic catalyst J was washcoated with the modified zeolite whose SiO_2/Al_2O_3 ratio was 200. Table 8 shows the reaction evaluation results from catalyst E (200 cpsi, zeolite without rare earth modification, SiO_2/Al_2O_3 ratio was 200), G (400 cpsi, zeolite without rare earth modification, SiO_2/Al_2O_3 ratio was 50), catalysts I and J.

The results show that the rare earth metal may increase the depth of olefin cracking reaction and also increase the selectivity of aimed products such as ethylene, propylene and butylene. Besides, from Fig. 5 it can be seen that the hydrocarbon reaction selectivity varied from different catalysts.

The results in Fig. 5 showed that after washcoated by zeolite, not only the conversion of FCC gasoline highly increased but also the proportion of olefin converted. On the monolith without washcoat, the main hydrocarbon reactants were naphthene. And the increasing amount of aromatics in liquid products implied one of the main reactions might be naphthene dehydrogenation. Whereas, on the catalysts with zeolite washcoated (E and J), the

Table 8
Reaction evaluation results.

Catalysts	Olefin conversion/wt.%	Selectivity/wt.%		
		Ethylene	Propylene	Butylene
B	4.0	4.3	7.8	59.4
E	12.2	3.2	33.0	52.6
J	20.3	5.0	34.9	46.5
G	43.2	3.3	37.9	45.8
I	60.6	10.7	45.7	34.2

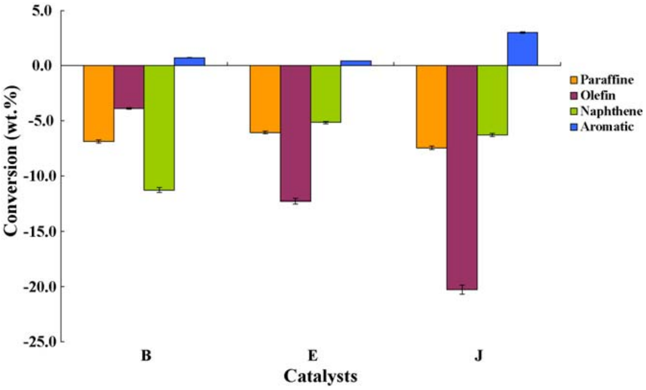

Fig. 5. Conversion of different hydrocarbons on monolithic catalysts. B: without washcoat; E: with ZSM-5(2); J: with (RE)ZSM-5(2).

proportion of olefin conversion among gasoline feedstock obviously raised especially catalyst J. In addition, the conversion of naphthene reduced. This indicated that compared with thermal cracking on blank monolith, the olefins were the most preferable reactants through catalytic cracking catalyzed by zeolite and the rare earth could enhance this preference. And from the rise of aromatics when used (RE)ZSM-5 washcoated catalyst, it indicated that the octane number of naphtha may possibly sustained by this process if used proper catalyst.

3.6. *Effect of SiO_2/Al_2O_3 ratio*

The only difference between catalysts H and J was the silica to alumina ratio of zeolite loaded on 200 cpsi monolith. It can be seen from the results in Table 9 that the catalyst G with lower Si/Al mol ratio showed higher reaction activity and propylene selectivity at various temperature.

4. Conclusions

The monolith matrix can be utilized to investigate the function of zeolite during FCC gasoline catalytic cracking process in short hydrodynamics residence time. The porosity of 200 cpsi monolith is the smallest. The thermal cracking activity is almost negligible at temperature lower than 770 K on 200 cpsi monolith without zeolite washcoat. The optimum hydrodynamics residence time for propylene production is 0.5 s in this process. The loading of ZSM-5 zeolite could enhance the conversion of olefin cracking reaction and the selectivity of propylene. Adding rare earth on ZSM-5 zeolite by ion-exchanging or precipitation method can probably prompt the conversion of olefin in gasoline and increase the selectivity of propylene as well.

Table 9
The effect of SiO_2/Al_2O_3 ratio.

Catalysts	H			J		
Temperature/K	773	758	746	773	758	746
Olefin conversion/wt.%	40.5	36.0	33.8	20.3	15.8	12.5
Selectivity/wt.%						
Ethylene	7.8	6.8	6.9	5.0	4.1	3.2
Propylene	37.5	36.9	37.8	34.9	32.0	32.2
Butylene	45.0	47.0	45.8	46.5	49.5	52.4

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