



Effect of ZSM-5 on the aromatization performance in cracking catalyst

Conghua Liu^{a,b,*}, Youquan Deng^a, Yuanqing Pan^b, Yusheng Gu^b,
Botao Qiao^a, Xionghou Gao^b

^a Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, PR China

^b Petrochemical Research Institute, Lanzhou Petrochemical Company, PetroChina, Lanzhou 730060, PR China

Received 19 May 2003; received in revised form 30 January 2004; accepted 1 February 2004

Abstract

Cracking of FCC naphtha has been investigated on the model catalysts containing ZSM-5 (Si/Al₂ = 50, 500), Zn-ZSM-5 (Si/Al₂ = 50) and USY. The presence of ZSM-5 and USY causes a tremendous decrease in olefins of gasoline fraction, leading to an enrichment of the aromatics in liquid product. It is evidently that aromatics are generated from lower olefins. The property of lower silica-to-alumina ratio of ZSM-5 and Zn modification enhance the aromatization process for higher cracking reactivity and dehydrogenation. The result of evaluation in confined fluid bed apparatus (CFBA) with the mixture of VGO and VTB as feed further confirms the aromatics generation in cracking reaction stimulated by ZSM-5 additive over base catalysts with different hydrogen transfer activity. Based on these results, relations between scission and aromatization in FCC catalyst containing ZSM-5 zeolite could be proposed. The suggested reaction path could better explain the reasons that effectiveness of ZSM-5 additive to lighter olefins is more profound in base catalyst of low hydrogen transfer activity and why so many researchers had not observed the aromatics generation motivated by ZSM-5 additive in catalytic cracking reaction.

© 2004 Elsevier B.V. All rights reserved.

Keywords: ZSM-5; Aromatics generation; Hydrogen transfer activity; Lighter olefins; FCC catalyst

1. Introduction

The high demand for gasoline pool of lower olefins is directing many refineries towards reducing olefins from their FCC naphtha stream. Obviously, olefins are the potential component for enhancing octane of a gasoline and reduction of olefins is undoubtedly to bring sacrifice to gasoline's octane rating. However, one of the most effective means is to use ZSM-5 as an additive to FCC catalyst to improve FCC naphtha octane. It is generally accepted that the presence of low amounts of ZSM-5 increases the octane number primarily by favoring the catalytic cracking and isomerization of the low-octane compound to more lighter and more branched products [1,2]. The analysis of the cracked naphtha shows that the concentration of aromatics is higher than over cracking catalysts free of ZSM-5 and this constitutes an

additional reason for the increase of the octane rating. There have been appeared two alternative points all the time on the origin of the aromatics. A great many researchers [1,3–6] suggested that the increment of aromatics observed in the cracked naphtha involving ZSM-5 is merely due to concentration effect, as a result of the selective cracking of various hydrocarbons and the absolute quantities of aromatics remained essentially unchanged. However, other researchers [7] held that aromatics could be built up in the presence of ZSM-5 from the lower olefin and lower paraffin generated from the bulky hydrocarbon molecules. Recently, some researchers [8] have paid great attention to the effect of hydrogen transfer characteristics of the base cracking catalyst on the performance of ZSM-5 additive. The effectiveness of ZSM-5 additive to enhance lighter olefins was evidently decreased by hydrogen transfer activity increment of the base cracking catalyst.

The quantity of aromatics in FCC naphtha is one of the most important factors, which influences the octane rating. The aim of the present study is to examine the possible aromatics generation and the aromatization mechanism stimulated by ZSM-5 additive in catalytic cracking reaction over

* Corresponding author. Present address: Department of Petroleum Processing, Petrochemical Research Institute, Lanzhou Petrochemical Company, PetroChina, Lanzhou 730060, PR China. Tel.: +86-931-7935420; fax: +86-931-7361506.

E-mail address: lch4138@163.com (C. Liu).

base FCC catalysts with different hydrogen transfer characteristics.

2. Experimental

Zeolite samples used in the experiment were as follows: ZSM-5 (Si/Al₂ = 50); Zn-ZSM-5 (Si/Al₂ = 50); ZSM-5 (Si/Al₂ = 500); USY (Si/Al₂ = 6.5); the selected base FCC catalysts were LCAT (RE₂O₃, 1.2 wt.%) and HCAT (RE₂O₃, 3.8 wt.%), which were all provided from Catalyst Plant of Lanzhou Petrochemical Company.

The acidity properties of samples were determined using pyridine-FT-IR method. The sample was initially evacuated to 10⁻³ Pa at 350 °C for 4 h and then was cooled to 200 °C to be saturated with pyridine for 5 min. After removed of the physical-adsorbed pyridine, the sample was examined in Nicolet510p Fourier transform IR spectrometer in the range 1350–1800 cm⁻¹. The concentration of Bronsted-acidic sites and Lewis-acidic sites of samples was measured on the bands at 1540 and 1450 cm⁻¹, respectively [9]. The acid amounts could be expressed as absorbance in the indicated bands per weight of sample.

Model catalysts were prepared by the following procedure: a slurry containing zeolite sample; kaolin; Al₂O₃ binder was mixed thoroughly. The mixture was dried at 100 °C for 20 h, followed by a process of smashing and sieving to get the model catalyst having a particle size 0.4–0.8 mm. The model catalyst was examined by micro-activity (MAT) experiment in accordance with ASTM test procedure D-3907 with FCC naphtha (as shown in Table 2) as feed. The catalyst was initially deactivated for 2 h at 800 °C in the presence of 100% steam before testing. The quantity of catalyst was 5 g, and the catalyst/oil ratio was 3.2.

Microspheroidal ZSM-5 additive (ZA) was prepared as follows: a slurry containing 25% Zn-ZSM-5; 65% kaolin; 10% Al₂O₃ binder was homogenized and subsequently was sprayed drying at an inlet temperature of 500–600 °C, obtaining microspheres which have an average particle size 50–70 μm. The microspheroidal sample was washed, filtrated and dried. The base catalyst containing ZSM-5 additive was evaluated in a confined fluidized bed apparatus (CFBA) at 500 °C with the mixture of Xinjiang vacuum gas oil (VGO) and vacuum tower bottom (VTB) as the feed (as shown in Table 1). The catalyst was initially deactivated for 10 h at 800 °C with 100% steam before testing. The inventory of catalyst was 180 g, and the catalyst/oil ratio was 4.0.

The products obtained in MAT and CFBA were analyzed as follows: hydrocarbon composition and octane number of naphtha were analyzed by Varian CP-3380 and the components were identified in a PIONA-library and classified as paraffins, *i*-paraffins, olefins, naphthenes and aromatics. The gas product was determined by HP6890. The gasoline yield contained the gasoline in the liquid product and the C₅⁺ in the gas product. The coke content of catalyst was handled

Table 1
Main properties of Xinjiang feedstock

Items	Xinjiang VTB	Xinjiang VGO	Mixture (VTB/VGO = 3/7)
Density, ρ ₂₀ (kg m ⁻³)	944.2	883.8	901.8
Residual coke (wt.%)	9.87	0.07	3.10
Average molecule (wt.%)	828	319	390
Simulated distillation (°C)			
IBP	420	286	306
10%	435	347	339
30%	465	392	372
50%	–	453	416
70%	–	500	460
90%	–	–	502

in situ combustion, using a CO₂ IR carbon detector and measured by DF190 instrument. Hydrogen transfer characteristics can be expressed as hydrogen transfer index (HTI), defined as $(iC_4^0 + nC_4^0) / \sum C_4^-$ in cracking gas product.

3. Results and discussion

3.1. MAT evaluation with FCC naphtha as the feed

From Table 2, it can be seen that except for matrix, the aromatics in liquid product after MAT reaction all increase remarkably and the absolute aromatics (on the basis of feed) also rise obviously. Firstly, under the cracking conditions ZSM-5 type zeolite is very active for the cracking of all the components in the gasoline range, except for aromatics. Therefore, the high concentrations of aromatics are retained in the liquid product. Compared with paraffins, the olefins are easily cracked, which can be found in Table 2 that the olefins decrease violently and the amount of paraffins almost do not change. Secondly, on ZSM-5 zeolites aromatics are built up from lower olefins. The phenomenon was also observed in the conversion of propene on a HZSM-5 type zeolite at 500 °C [10,11]. It could be proposed that a hydrogen transfer reaction takes place on the Bronsted sites of the zeolite and the lighter olefins undergo cyclization and dehydrogenation to form aromatics. The possible aromatization essentially leads to the increment of aromatics. Compared with the ZSM-5 zeolite with low silica (Si/Al₂ = 50), the ZSM-5 zeolite with high silica (Si/Al₂ = 500) reduces the cracking rate of olefins, resulting in more *i*-paraffins and less aromatics. This can be explained by the fact that in Table 3 both the amounts of Lewis sites and Bronsted sites of the latter are much smaller than those of the former, indicating that the higher silica-to-alumina ratio reduces the cracking reactivity of the ZSM-5 model catalyst [12]. After the Zn modification (Zn-ZMS-5) the density of Bronsted sites drops and the amount of Lewis sites increases obviously. Therefore, the Zn modification decreases the crackability of ZSM-5 and enhances its dehydrogenation, leading to higher concentration of aromatics in liquid product. It can

Table 2
MAT evaluation with FCC naphtha as the feed

	Model catalysts					
	FCC naphtha (the feed)	ZSM-5 (Si/Al ₂ = 50)	Zn-ZSM-5 (Si/Al ₂ = 50)	ZSM-5 (Si/Al ₂ = 500)	USY	Matrix (kaolin + Al ₂ O ₃ binder)
Liquid product (wt.%)	100	55.3	57.7	65.8	81.8	92.7
Coke yield (wt.%)	–	0.5	0.7	0.3	1.3	0.2
PIONA (vol.%)						
<i>n</i> -Paraffins	5.4	3.8	4.0	4.8	8.3	6.9
<i>i</i> -Paraffins	23.1	19.2	18.6	25.5	33.3	24.0
Olefins	41.8	12.3	10.9	24.9	16.0	39.4
Naphthenes	5.7	7.1	7.2	7.5	7.6	5.9
Aromatics	24.0	57.6	59.3	37.3	34.8	23.8
MON	79.8	81.1	81.8	82.0	80.4	80.2
RON	91.1	91.5	91.4	91.3	91.4	90.5
Aromatics (on the basis of feed)	24.0	31.9	34.2	24.5	28.5	22.1

Table 3
Bronsted site and Lewis site amounts of ZSM-5 zeolites obtained from pyridine-adsorbed FT-IR spectra

Samples	Acid amounts (a.u./g)	
	Bronsted site	Lewis site
ZSM-5 (Si/Al ₂ = 50)	15.4	4.8
Zn-ZSM-5 (Si/Al ₂ = 50)	3.8	7.8
ZSM-5 (Si/Al ₂ = 500)	1.2	1.0

be verified that the Zn modification promotes the aromatization process in the MAT experiment as observed by many researchers [11,13,14]. Compared with ZSM-5 zeolite, the USY zeolite also exhibits some capability of aromatization. As to the USY zeolite, because of the absence of the shape selectivity, the degree of aromatization is not limited and easily leads to the formation of coke. This can explain the higher coke yield obtained in USY sample in Fig. 2. Furthermore, the almost unchangeable content of hydrocarbons in matrix sample clearly results from its too low reaction activity.

From Fig. 1, it can be found that with increment of the content of ZSM-5 in the model catalyst, the decrease

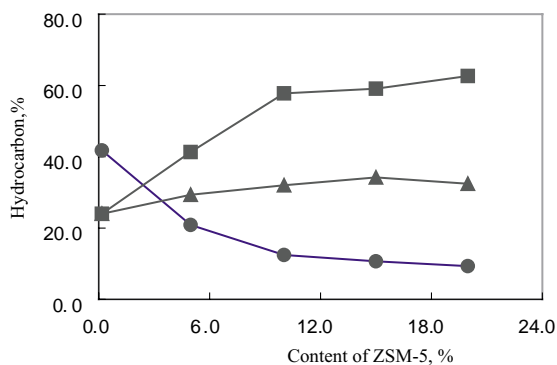


Fig. 1. Relationship of aromatics and olefins with the content of ZSM-5 in model catalyst: (■) aromatics in liquid product; (●) olefins in liquid product; (▲) aromatics on the basis of feed.

in olefins in liquid product is accompanied by roughly equal increase in aromatics concentration with the absolute amount of aromatics rising essentially. When the content of ZSM-5 is more than 15%, the augment of aromatics appears to be falling. It can be suggested that ZSM-5 zeolite raises the cracking/hydrogen transfer ratio excessively with its continuous increment [5]. This can further confirm that the aromatics generation will be enhanced by ZSM-5 zeolite in desirable amount in MAT experiment.

3.2. CFBA evaluation with the mixture of Xinjiang VGO and VTB as the feed

ZSM-5 zeolites can be introduced into FCC catalyst either through incorporating into the colloid mixture before spray drying or through additive as an independent particle. In this experiment, we adopted the latter means to investigate the impact of ZSM-5 zeolite on the performance of base FCC catalysts with remarkably different HTI, as illustrated in Table 4. It can be seen that after adding ZA (ZSM-5 zeolite additive) into base FCC catalyst, LPG increases and naphtha drops with the LCO yield remaining essentially constant. This indicates that the ZSM-5 additive enhances the selective crackability of components in gasoline. Compared with those over LCAT with low HTI, LPG yield and naphtha yield obtained in HCAT base catalyst with ZSM-5 additive change slightly.

However, as shown in Table 5, the naphtha components difference over the two base catalysts with ZSM-5 additive

Table 4
Product distribution of FCC catalysts having different HTI with ZSM-5 additive in CFBA

Catalysts	LPG (%)	Naphtha (%)	LCO (%)	Coke (%)	HTI
LCAT	14.89	51.06	19.02	7.97	1.51
LCAT 90% + ZA 10%	16.75	48.89	18.97	7.92	1.76
HCAT	13.98	52.12	19.10	8.08	2.03
HCAT 90% + ZA 10%	15.01	50.82	19.36	7.89	2.45

Table 5
PIONA analyses of cracked naphtha with ZSM-5 additive in CFBA

Catalysts	<i>i</i> -Paraffin (%)	<i>n</i> -Paraffin (%)	Olefin (%)	Naphthene (%)	Aromatic (%)	RON	MON	Aromatic (on the basis of feed), %
LCAT	33.6	4.4	22.5	9.2	30.3	91.6	80.9	15.5
LCAT 90% + ZA 10%	30.8	4.0	23.4	9.8	32.0	92.8	81.6	15.6
HCAAT	36.0	5.6	17.6	8.8	32.0	92.0	80.9	16.7
HCAAT 90% + ZA 10%	34.7	5.1	14.4	10.1	35.7	92.8	81.4	18.1

is distinctive. As to the LCAT, the olefins raise by 0.9% and the paraffins drop by 3.2% and aromatics concentration lifts by 1.7% with the absolute aromatics (on the basis of feed) remaining almost constant after incorporation of ZSM-5 additive. Comparatively, olefins obtained in HCAAT decrease by 3.2% and aromatics concentration increases by 3.7% with the absolute aromatics (on the basis of feed) lifting obviously. In addition, the RON and MON ratings are all enhanced after addition of ZSM-5 zeolite. The phenomenon of aromatics generation after ZSM-5 addition can also be found in Fig. 2. The obvious different effect of ZSM-5 additive on the performance of base catalyst with different HTI is surely much interesting.

3.3. Reaction pathways over ZSM-5 in catalytic cracking reaction

Many previous researchers [2–6,12] have especially paid attention to the cracking reaction mechanism involved with ZSM-5 and its effectiveness to increase lighter olefins yield and had suggested that the increment of aromatics observed in the cracked naphtha involving ZSM-5 is merely due to concentration effect. Zhao and Harding [8] have studied the impact of hydrogen transfer characteristics of the base cracking catalyst and feedstock on the performance of ZSM-5 additives and find that the relative rate of olefin cracking reactions versus hydrogen transfer reactions determines the effectiveness of ZSM-5 additive in FCC process and pro-

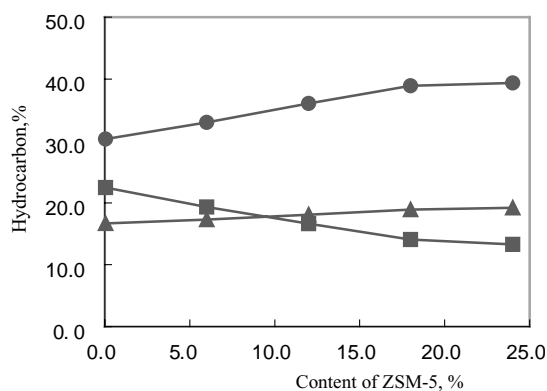


Fig. 2. Relationship of aromatics and olefins with the content of ZSM-5 additive in HCAAT base cracking catalyst with high HTI: (●) aromatics in gasoline; (■) olefins in gasoline; (▲) aromatics on the basis of feed.

pose that maximizing light olefins by using ZSM-5 was more effective in systems with lower hydrogen transfer activity. The significant decrease in naphtha paraffin content occurs, at least in part, due to cracking olefins to LPG, which would have otherwise undergone hydrogen transfer to produce paraffins. It has been suggested the reasons paraffins yields can decline in the presence of ZSM-5 is due to the fact that ZSM-5 prevents or reduces secondary bimolecular reactions such as chain transfer reactions involving a carbonium ion and hydrogen transfer reaction involving an olefin. This can well explain the results of LCAT with low HTI after ZSM-5 addition. As to HCAAT with high HTI, the rate of cracking gasoline component by ZSM-5 is remarkably suppressed by the high hydrogen transfer activity. The reaction path after ZSM-5 addition can be diagramed in Fig. 3. In practice, on the Bronsted sites of ZSM-5, the carbenium ions are easily isomerized or cyclized to form naphthenes especially in the form of cyclohexenes because of its shape-selectivity, and in the meantime the carbeniums can also undergo β -scission to obtain light olefins. In the pseudo-equilibrium between carbenium ions and naphthenes, the naphthenes can continue to be dehydrogenated to generate aromatics or can undergo protonation to return to be carbenium ions. If the base catalyst has higher hydrogen transfer activity, that means strong capacity for hydride ions, it can quickly accommodate the hydride ions that are released by the dehydrogenation of naphthenes, resulting finally in formation of aromatics and paraffins. This means that the synergistic interaction of ZSM-5 and base cracking catalyst can really enhance the build-up of aromatics. On the other hand, if the base catalyst has lower hydrogen transfer activity, it cannot easily catch hold of the hydride ions set free by the dehydrogenation of naphthenes, resulting in β -scission of carbeniums to the formation of lighter olefins.

The proposed reaction path in cracking process after ZSM-5 addition is capable of accounting for the reason that effectiveness of ZSM-5 additive to lighter olefins is more profound in base catalyst of low hydrogen transfer activity and why so many researchers [3–6] cannot observe the generation of aromatics after incorporation of ZSM-5 additive in cracking reaction. In the case of base catalyst with low HTI, the cracking rate of carbonium ion is much faster than its aromatization rate, urging more components in gasoline to crack to be lighter olefins and the rate of aromatics generation stimulated by ZSM-5 zeolite is too slow to be scrutinized. The assumption of aromatics on ZSM-5

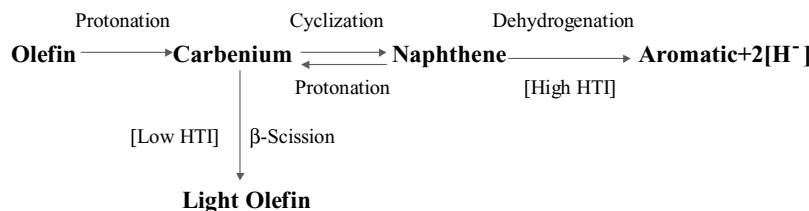


Fig. 3. Reaction pathways over ZSM-5 zeolite contained FCC catalyst.

zeolite from olefins could explain the higher HTI frequently observed in the gaseous hydrocarbons after incorporation of ZSM-5 additive in cracking reaction (Table 4).

4. Conclusions

The model catalysts containing ZSM-5 or USY in cracking of FCC naphtha causes a tremendous decrease in olefins of gasoline fraction, leading to an enrichment of the aromatics in liquid product. Compared with ZSM-5, aromatization occurring on the active sites of USY is apt to form coke for the absence of shape selectivity. The result of evaluation in CFBA with the mixture of VGO and VTB as feed further confirms the aromatics generation in cracking reaction stimulated by ZSM-5 additive over commercial base catalysts with different hydrogen transfer activity.

Based on these results, relations between scission and aromatization in catalytic cracking reaction over base FCC catalyst containing ZSM-5 zeolite could be proposed. More or less, there is the pseudo-equilibrium between a cyclization of carbenium ions and a protonation of naphthenes on the Bronsted sites of ZSM-5, and in the meantime the carbeniums can also undergo β -scission to obtain light olefins. If the base catalyst has higher hydrogen transfer activity, it can quickly seize the hydride ions that are released by the

dehydrogenation of naphthenes, resulting finally in formation of aromatics and paraffins. On the other hand, if the HTI of the base catalyst is very low, it cannot easily capture the hydride ions, resulting in β -scission of carbeniums to the formation of lighter olefins. The suggested reaction path could better explain why effectiveness of ZSM-5 additive to lighter olefins is more profound over base FCC catalyst of low hydrogen transfer activity.

References

- [1] R.J. Madon, *J. Catal.* 129 (1991) 275.
- [2] J.S. Buchanan, J.G. Santiesteban, W.O. Haag, *J. Catal.* 158 (1996) 279.
- [3] J. Biswas, I.E. Maxwell, *Appl. Catal.* 58 (1990) 1.
- [4] J.S. Buchanan, *Appl. Catal.* 74 (1991) 83.
- [5] Z. Zainuddin, F.N. Guerzoni, J. Abbot, *J. Catal.* 140 (1993) 150.
- [6] Y.G. Adewuyi, *Appl. Catal. A: Gen.* 163 (1997) 15.
- [7] G. Anders, L. Buckhardt, V. Illgen, et al., *Appl. Catal.* 62 (1990) 271.
- [8] X. Zhao, R.H. Harding, *ACS Pet. Chem. Div. Prepr.* 44 (1999) 500.
- [9] E.P. Parry, *J. Catal.* 2 (1963) 371.
- [10] Y. Ono, H. Kitagawa, Y. Sendoka, *J. Chem. Soc., Faraday Trans. 1* 83 (1987) 2913.
- [11] T. Mole, J.R. Anderson, G. Creer, *Appl. Catal.* 17 (1985) 141.
- [12] J.S. Buchanan, *Appl. Catal. A: Gen.* 171 (1998) 57.
- [13] H. Berndt, G. Lietz, B. Lücke, et al., *Appl. Catal. A: Gen.* 146 (1996) 351.
- [14] J.A. Biscardi, G.D. Meitzner, E. Iglesia, *J. Catal.* 179 (1998) 192.