

Study of the performance of modified nano-scale ZSM-5 zeolite on olefins reduction in FCC gasoline

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Abstract

Nanoscale HZSM-5 zeolite (20–50 nm) was hydrothermally treated with steam containing 0.8 wt.% NH₃ at 773 K firstly and then was modified with mixed rare earth oxides and Ga₂O₃. Both the parent nanoscale HZSM-5 and the modified nanoscale HZSM-5 zeolites catalysts were characterized by TEM, XRD, IR, NH₃-TPD, and XRF techniques. IR and NH₃-TPD results showed that the total amount of acids sites in the parent nanoscale HZSM-5 zeolite decreased after the hydrothermal treatment, especially for the strong acid sites. The following modification using the mixed rare earth oxides had little effect on the acid properties of the hydrothermally treated nanoscale HZSM-5 catalyst; however, the further modification using Ga₂O₃ increased the total acid sites of nanoscale HZSM-5 catalyst, especially for the Lewis acid sites. On the other hand, the amount of total acid sites in Ga₂O₃ modified catalyst was still less than that in the parent HZSM-5 catalyst. The performance of the modified nanoscale HZSM-5 zeolite catalyst on olefins reduction in fluidized catalytic cracking (FCC) gasoline was investigated and it was found that the activity and stability of the modified catalyst was satisfactory, but the initial activity slightly decreased. After 300 h on stream, the olefins content in the FCC gasoline decreases from 49.6 to 15.1 vol.%. Further work showed that the ability of nanoscale HZSM-5 zeolite catalyst for aromatization reduced while its isomerization ability increased. The ratio of *iso*-paraffins to *n*-paraffins in FCC upgraded gasoline reached 8.2. The yield of upgraded gasoline reached 96 wt.%, while the research octane number (RON) was increased from 89.4 to 90.0. The components of the upgraded gasoline met the requirement of European III gasoline standard.

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1. Introduction

The rapid development of automotive industry brings about the great increase in fuel consumption, and, as a sequence, the air pollution caused by exhaust gas becomes more and more serious [1,2]. In order to reduce the emission of harmful exhausted gas and tiny particles from vehicles, more stringent regulation for transportation fuel come into effect in many countries and areas to restrict the sulfur and olefin contents in gasoline. In China, one of the most serious problems of gasoline quality is excessive olefin and sulfur contents. Currently about 80% of the gasoline pool as a whole to supply the Chinese market directly originates from FCC units and sulfur and olefin in gasoline are mainly from FCC gasoline, so the quality of FCC gasoline will

directly affect the performance of finished product. At present, it is difficult to change the gasoline pool composition remarkably, due to the lack of the catalytic reforming, alkylation, isomerization and oxygenous compounds producing units. Therefore, it is crucial to decrease the olefins and sulfur contents in FCC gasoline. So far, several methods have been adopted for decreasing the olefins content, such as the optimization of the FCC process, and the application of new FCC catalysts (GOR, TOM, FRG) [3–5]. However, the olefins content in gasoline is only reduced by a value of 6–18 vol.%. The olefins content in the present commercial gasoline pool still cannot meet the new Chinese national standard at all. Therefore, it is urgent to put forward a novel technique to reduce the olefins content in gasoline greatly with the research octane number (RON) of gasoline preserved.

In recent years, there has been a growing interest in the synthesis and application of nanoscale zeolites [6,7]. Zeolites with a crystal size smaller than 100 nm are the potential replacement for existing zeolite catalysts and can be used in novel environ-

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mentally benign catalytic processes. It is well known that the crystal size of zeolites has a great effect on the catalytic activity and selectivity. It has been reported that when the crystal size of HZSM-5 zeolite is reduced to the nanoscale, super catalytic properties such as higher activity, lower coke content and better stability can be obtained in various reactions such as the conversion of methanol to hydrocarbons [8] and the oligomerization of ethylene [9].

In the previous study, we had found that the parent nanoscale HZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio equal to 25.5) zeolite catalyst had higher ability and better stability for olefins reduction in FCC gasoline than microscale ones ($\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio equal to 23.5) [10]. We also had investigated the effect of different modification procedures on performance of the nanoscale HZSM-5, such as hydrothermal treatment and the modification combining hydrothermal treatment and loading La_2O_3 and NiO. The results indicated that these modification procedures were effective for adjusting the acid property of the nanoscale HZSM-5 catalyst and improving its stability in reducing the olefins content of FCC gasoline. The components of FCC gasoline upgraded by the modified nanoscale HZSM-5 catalysts could meet the requirement of the new Chinese National Standard [11–14]. However, regulatory changes being enacted over the next 10 years will require dramatic changes of fuel compositions. The less and less sulfur and olefin contents in gasoline are required, so it is an inexorable trend for refineries to produce low sulfur and olefin gasoline for environment protection. In this circumstance, it is necessary to develop technology and catalyst more effective in reducing sulfur and olefin contents in FCC gasoline, so as to meet the requirement of the higher and stricter standard.

Hydrothermal treatment is usually employed to adjust the acidity of HZSM-5 zeolite and improve its stability [15–18]. Lago et al. [19] reported that the mild steaming favored the generation of catalytic sites with specific efficiency. Rare earth ion-exchanged faujasites was also employed in the process of FCC due to their superior catalytic properties [20,21]. It is generally accepted that the major role of the elements gallium or zinc is to accelerate the combination of surface hydrogen, formed via the dehydrogenation and dehydrocyclization process involved as key steps in the conversion of alkanes to aromatics via alkenic intermediates [22,23]. The modification effects on microscale HZSM-5 have been studied widely in relation to their catalytic performance, while they are rarely reported for nanoscale HZSM-5 and the report of the modified nanoscale ZSM-5 catalyst applied to upgrading FCC gasoline is also scarce. In this paper, we combined hydrothermal treatment and mixed rare earth oxides and gallium oxide loading procedures to modify the parent nanoscale HZSM-5 and then investigated its catalytic performance on the olefins reduction in FCC gasoline.

2. Experimental

2.1. Materials

The compositions of FCC gasoline were as follows: olefins, 49.6 vol.%; aromatics, 11.4 vol.%; paraffins, 39.0 vol.%; sulfur, 200 ppmw; RON 89.4. Gallium nitrate was analytical grade. The

mixed rare earth carbonate was industrial grade and the useful content of mixed rare earth oxide was 42 wt.%. Microscale HZSM-5 (4–6 μm) was synthesized by the Department of Catalysis Chemistry and Engineering of Dalian University of Technology, and the molar ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ was 23.5. To ensure the continuity from the previous works, the nanoscale ZSM-5 with $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio equal to 25.5 was synthesized following the procedure described in literature [24] and selected as the only parent catalyst in this study.

2.2. Catalyst preparations

In a typical process, the strip nanoscale NaZSM-5 catalyst was obtained (\emptyset 1 mm \times 2 mm) by extruding the mixture of 80 wt.% nanoscale NaZSM-5 and 20 wt.% alumina, then it was dried at 393 K for 12 h and calcined at 813 K for 3 h. Na^+ ions in NaZSM-5 were replaced with NH_4^+ by allowing the NaZSM-5 to contact a solution of 0.4 mol/L NH_4NO_3 at 298 K for 2 h. Solids were separated from the solution by filtration. The exchange procedure was repeated three times using fresh NH_4NO_3 solutions to ensure complete exchange of Na^+ ions. The residual Na content was less than 0.07 wt.% analyzed by atomic absorption. Catalyst samples were then dried in flowing air at 393 K for 12 h and calcined at 813 K for 3 h to decompose NH_4^+ to H^+ , thus the acidic form of the zeolite, denoted by HZ, formed. The sample HZ was hydrothermally treated in the steam containing 0.8 wt.% NH_3 at 773 K for 3 h and this sample was denoted by HZ1. Then the sample HZ1 was loaded with 3.0 wt.% mixed rare earth oxide by impregnating HZ1 with the same volume of the solution containing mixed rare earth carbonate, dried at 393 K for 12 h and calcined at 813 K for 3 h, thus the sample HZ2 is prepared. The sample HZ2 was impregnated with the equi-volume solution of gallium nitrate, dried at 393 K overnight and calcined at 813 K for 3 h, finally the sample HZ3 is obtained. To compare the effect of the amount of Ga_2O_3 on the performance of catalyst in reducing the olefins content of FCC gasoline, HZ3 samples with different loadings (0.5, 0.9 and 2.0 wt.%) of Ga_2O_3 were prepared, and these samples were denoted by HZ3-Ga(0.5), HZ3-Ga(0.9) and HZ3-Ga(2.0), respectively.

2.3. Catalyst characterizations

The crystal size and morphology of nanoscale ZSM-5 were determined on a JEM-1200CEX transmission electron microscope (TEM). Elemental analyses (XRF) of both the parent and the modified nanoscale HZSM-5 zeolites were performed on a Bruker SRS 3400 \times spectrometer. Pore volume and surface area were obtained on a Quantachrome Autosorb-1 using the BET method. Adsorption capacities for normal hexane and cyclohexane were also measured by the flow adsorption method. The adsorption capacity for 2,2,3-trimethylbutane (2,2,3-TMB) was used to characterize the secondary pores contained in the polycrystalline grains of nanoscale ZSM-5 zeolites. X-ray diffraction (XRD) patterns were recorded on a D/max-2400 diffractometer using the $\text{Cu K}\alpha$ radiation at 40 kV and 30 mA with a scanning rate of $2^\circ/\text{min}$. The acid properties of the parent

nanoscale HZSM-5 and the modified nanoscale ZSM-5 catalyst were obtained on a Quantachrome Chembet 3000 using the ammonia temperature programmed desorption (NH₃-TPD) method. Acid sites and acid type distribution were determined by infrared spectroscopy (IR) of chemisorbed pyridine. All spectra were recorded on a Nicolet-740 Fourier transform infrared spectrometer at a resolution of 4 cm⁻¹. The catalyst samples used for IR were finely grounded and pressed into a self-supporting wafer (8–10 mg/cm², diameter = 15 mm), then were placed into an infrared cell with KBr windows. The evacuation at 773 K (ca. 10⁻⁴ Torr) for 4 h was carried out prior to adsorption of pyridine. IR spectra were recorded after subsequent evacuation at increasing temperatures from 423 to 973 K (1 h at each temperature).

2.4. Catalytic tests

The reaction on these catalysts was conducted on a continuous flow fixed-bed reactor (diameter 10 mm). Reaction conditions were as follows: temperature, 643 K; hydrogen pressure, 3.0 MPa; H₂/gasoline (volume ratios), 600; weight hourly space velocity (WHSV) of FCC gasoline, 3 h⁻¹; the loading of the catalyst was 2 g. The composition of liquid and gas products was analyzed on an SRI 8610 gas chromatograph using a flame ionization detector and a capillary column (50.0 m × 0.32 mm) containing OV-101, and the RON was calculated as described in the literature [25] or measured according to ASTM D2699 standard. The total sulfur in gasoline was determined by microcoulometric titration using ASTM D method 3120.

3. Results and discussions

3.1. Characterizations of nanoscale ZSM-5

Fig. 1 shows the TEM image of ZSM-5, demonstrating that the mean crystal size of ZSM-5 is about 20–50 nm.

Table 1 lists the pore volume, surface area and adsorption capacity of both the nanoscale and microscale HZSM-5. As shown in Table 1, there are significant differences in the physicochemical properties between these two kinds of crystals. Compared with the microscale HZSM-5, the nanoscale HZSM-5 has much larger pore volume, higher cyclohexane adsorption capacity and larger surface area. The nanocrystal ZSM-5 with morphology of polycrystalline grains generates the secondary pores from inter-crystal gap of nanoscale ZSM-5. Its outstanding adsorption capacities for 2,2,3-TMB exhibits the existence of secondary pores whose openings are wide enough to allow free entering of relatively large molecules such as 2,2,3-TMB molecules. The micrometer crystal shows no adsorption for the

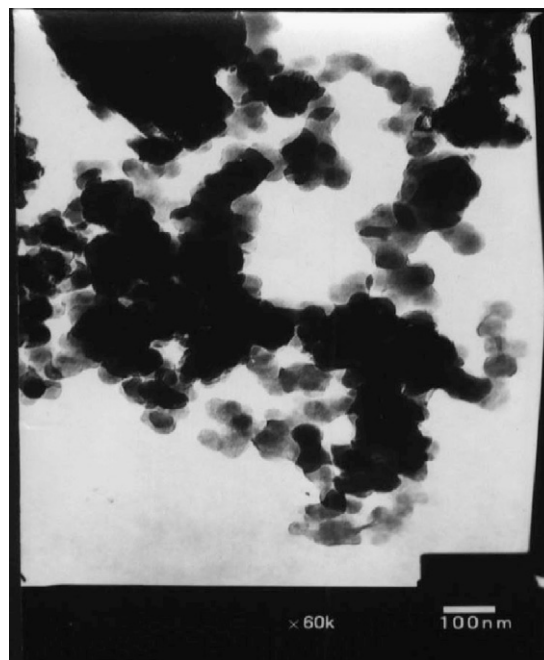


Fig. 1. TEM image of the nanoscale ZSM-5.

large molecules 2,2,3-TMB, indicating the lack of secondary pores in its structure.

Table 2 presents the results of the olefin reduction and the physicochemical properties of the spent nanoscale HZSM-5 and microscale HZSM-5 catalysts using the FCC light fraction ($\leq 70^\circ\text{C}$) as feedstock. It can be readily seen that the activity and stability of the nanoscale HZSM-5 catalyst are much better than those of the microscale HZSM-5 catalyst. Although the amount of deposited cokes (time on stream of 10 h) caused by olefin reduction reaction on the nanoscale HZSM-5 catalyst is the nearly same as that on the microscale HZSM-5 catalyst, the performance on olefin reduction of the nanoscale HZSM-5 catalyst is satisfactory. The nanoscale HZSM-5 zeolite demonstrates high ability to resist coking and has large capacity for coke. Shorter path and more mouths for diffusion cause a delay in blocking the channel system by coke. Coke deposits mainly in the secondary pores among nanocrystal zeolite aggregates. Higher C₆ adsorption capacity and larger surface area are also observed for the spent nanoscale HZSM-5 catalyst. However, surface areas decrease in the spent microscale HZSM-5 catalyst is very large in comparison with that of the spent nanoscale one. The mainly reason is that the pores are blocked by coke deposited on the microscale HZSM-5 catalyst. As reported in the literature [26], the pore blockage is an important cause for surface areas reduction and deactivation of the microscale HZSM-5 cat-

Table 1
Physicochemical features of nanoscale and microscale HZSM-5 zeolites

Catalyst samples	Pore volume (cm ³ /g)	Surface area (m ² /g)	Adsorption capacity (wt.%)		
			Hexane	Cyclohexane	2,2,3-TMB
Nano-HZSM-5 (20–50 nm)	0.728	309.6	9.80	8.45	65.2
Micro-HZSM-5 (4–6 μm)	0.650	286.4	8.86	2.90	1.80

Table 2
Results of the olefin reduction and physicochemical properties of spent catalysts

Catalyst samples	Olefin content of product (vol.%)		Coke (wt.%)	Adsorption capacity (wt.%)			Surface area (m ² /g)
	2 h ^a	10 h ^a		Hexane	Cyclohexane	2,2,3-TMB	
Nano-HZSM-5 (20–50 nm)	13.0	22.0	9.98	7.63	6.52	18.6	284.3
Micro-HZSM-5 (4–6 μm)	11.6	36.8	10.7	3.72	1.36	0	142.6

Reaction conditions: $p = 3.0$ MPa, $\theta = 643$ K, $WHSV = 3$ h⁻¹, H_2/oil (v/v) = 600.

^a 2 and 10 h represent the reaction time.

alyst. Comparison of the results in Tables 1 and 2 indicates the significant decrease in the adsorption capacity of the nanoscale HZSM-5 catalyst for 2,2,3-TMB, confirming that the coke formation mainly occurs in the secondary pores, which accounts for its improved stability. In this way, the nanoscale ZSM-5 zeolite is superior in performance to the microscale one.

Fig. 2 is the XRD patterns of the HZ and HZ3-Ga(0.9) catalysts. The X-ray diffraction pattern of the HZ3-Ga(0.9) catalyst closely matches with that of the HZ catalyst shown in Fig. 2, which indicates that the combined-modification procedure has no obvious effect on crystal structures and that the mixed rare earth oxide and gallium oxide are well dispersed. However, the combined-modification procedure decreases crystallinity of the HZ by 15%.

Fig. 3 illustrates the NH₃-TPD curves of the HZ, HZ1, HZ2 and HZ3-Ga(0.9) catalysts. It can be seen that both the weak and strong acid sites of the HZ1 catalyst are small in number compared with those of the HZ catalyst, especially for the strong acid sites. Comparison of the HZ1 and HZ2 catalysts reveals that both the weak and strong acid sites of the two catalysts are not appreciably different. Therefore, the modification by loading the mixed rare earth oxides has only a marginal effect on the acid sites of the hydrothermally treated nanoscale HZSM-5 catalyst. The third step modification by the loading of Ga₂O₃ increases the total acid sites of nanoscale HZSM-5 catalyst loaded by the mixed rare earth oxides; the HZ3-Ga(0.9) catalyst has more total

acid sites than the HZ2 catalyst, while the HZ3-Ga(0.9) catalyst has still fewer total acid sites than the HZ catalyst. The strong acid sites, which are active sites for hydrogen transfer reactions, can accelerate the formation of aromatics as well as that of coke. Thus the strong acid sites decrease could prevent the modified nanoscale HZSM-5 catalyst from coke deposition to improve its stability.

The acid strength distribution based on pyridine desorption temperature of different samples are listed in Table 3. The point of 450 °C in this work is considered to be the border between the strong and weak acid sites; that is, the weak and medium strength sites are those desorbed below or equal 450 °C, while the strong acid sites are those desorbed above 450 °C. Table 3 demonstrates that the hydrothermal treatment and loading mixed rare earth produces a decrease in the total acid content of the nanoscale HZSM-5. The proportion of weak and medium strength acid sites increases from 85.2 to 87.2%, while that of strong acid sites decreases obviously. However, the total amount of acid increased after loading gallium oxide. From Table 3, we can also see that the ratio of Lewis to Brønsted acid sites can be regulated by the combined-modification procedure; that is, the weak and medium-strength Lewis acid sites increase obviously, whereas, the weak and medium-strength Brønsted acid sites decrease slightly. With the increase in the loading of gallium oxide, the Lewis/Brønsted acid sites ratio of the catalysts increases obviously. When the loading of gallium oxide is about 1.0 wt.%, the

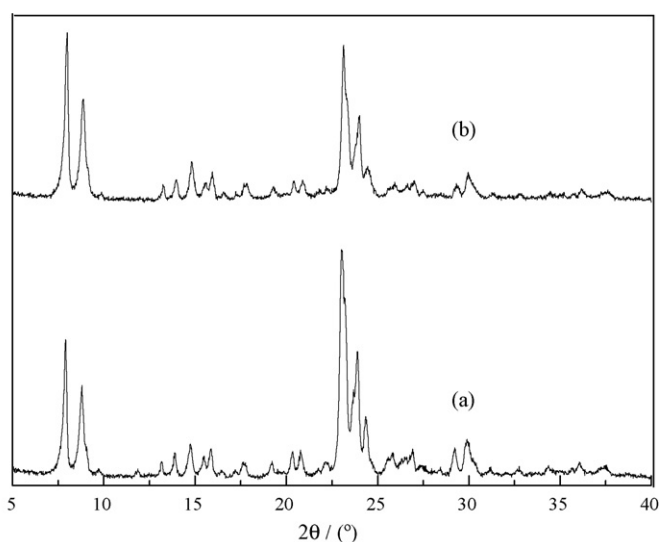


Fig. 2. XRD patterns of HZ and HZ3-Ga(0.9) catalysts. (a) HZ and (b) HZ3-Ga(0.9).

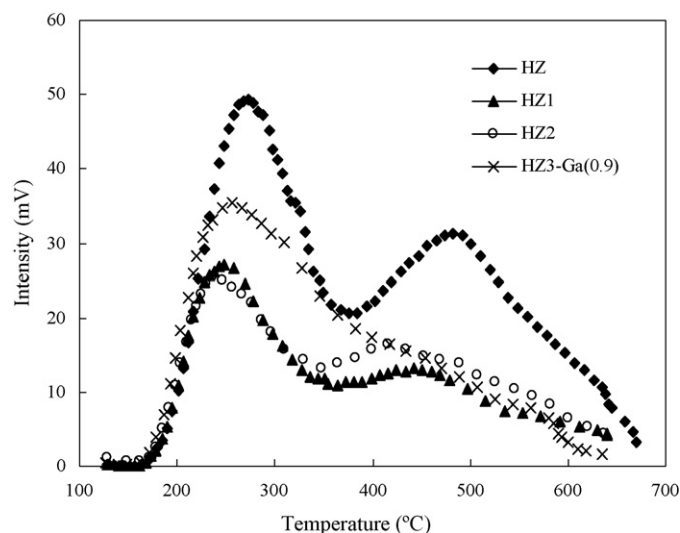


Fig. 3. Ammonia TPD curves of the different catalysts.

Table 3

Total acid and acid type distribution of the parent nano-HZSM-5 and the modified nano-HZSM-5 catalysts

Catalyst samples	Total acid (mmol/g)	B acid (mmol/g)	L acid (mmol/g)	L/B	Total acid distribution (%)		B acid distribution (%)		L acid distribution (%)	
					≤450 °C	>450 °C	≤450 °C	>450 °C	≤450 °C	>450 °C
					HZ	1.802	0.775	1.027	1.33	85.2
HZ1	1.028	0.534	0.494	0.93	87.2	12.8	45.6	6.30	42.5	5.60
HZ2	1.006	0.486	0.520	1.07	90.5	9.50	44.1	4.20	46.3	5.40
HZ3-Ga(0.5)	1.285	0.523	0.762	1.46	91.6	8.40	39.3	3.50	53.1	4.10
HZ3-Ga(0.9)	1.347	0.514	0.833	1.62	91.8	8.20	35.1	3.20	56.7	5.00
HZ3-Ga(2.0)	1.353	0.457	0.895	1.96	91.2	8.80	32.9	3.20	58.5	5.40

Lewis/Brønsted acid sites ratio is close to 1.6. The results are consistent with those reported in literature [27,28].

3.2. Performance of the parent nanoscale HZSM-5 catalyst and the modified nanoscale HZSM-5 catalysts by different procedures for the olefins reduction in FCC gasoline

The performance of the different catalyst samples on reducing olefins in FCC gasoline is shown in Figs. 4 and 5 and Table 4. Fig. 4 illustrates the change of the olefins content of product

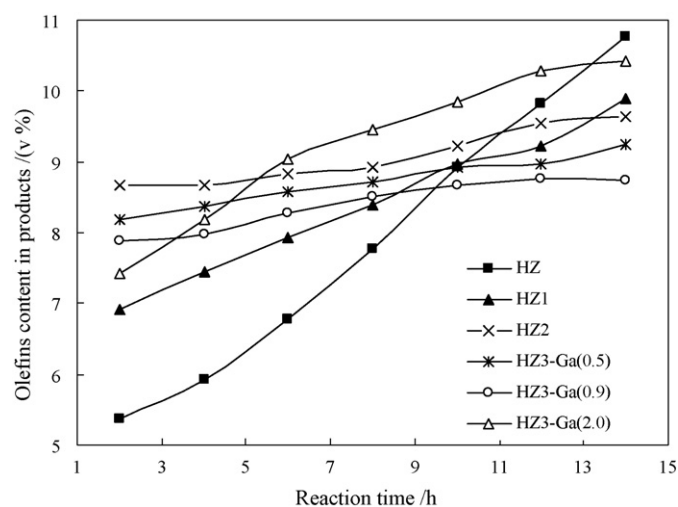


Fig. 4. Change of olefins content in gasoline with reaction time over different catalysts.

Table 4

Changes of *iso*-*n*-paraffins ratio with reaction time over different catalysts

Catalyst samples	<i>Iso</i> - <i>n</i> -paraffins ratio ^a						
	2 h ^b	4 h ^b	6 h ^b	8 h ^b	10 h ^b	12 h ^b	14 h ^b
HZ	5.0	5.6	6.4	6.3	6.8	6.6	6.4
HZ1	7.9	8.1	8.0	8.1	8.2	8.0	8.1
HZ2	8.1	8.0	8.2	8.3	8.1	8.2	8.0
HZ3-Ga(0.5)	7.8	8.0	7.8	8.0	8.0	7.9	7.9
HZ3-Ga(0.9)	7.8	8.2	8.2	8.0	8.2	8.1	8.2
HZ3-Ga(2.0)	6.8	7.2	7.0	7.1	7.0	6.6	6.4

Reaction conditions: $p = 3.0$ MPa, $\theta = 643$ K, $WHSV = 3$ h⁻¹, H_2/oil (v/v) = 600.

^a C₄–C₆.

^b 2, 4, 6, 8, 10, 12, and 14 h represent reaction time.

gasoline with reaction time. It can be clearly seen that the stability of the modified nanoscale HZSM-5 catalysts is superior to that of the parent nanoscale HZSM-5. The catalysts obtained by the different modification procedures still exhibit stronger capability in reducing olefins of FCC gasoline, while the initial activity slightly decreases. The gallium oxide loading has a noticeable effect on activity and stability of catalysts; suitable amount of gallium oxide loading (0.5–0.9 wt.%) can enhance the activity for olefins reduction and improves stability of the catalysts, whereas, excessive gallium oxide loading (2.0 wt.%) deteriorates the activity and stability of the catalysts. Fig. 5 illustrates the change of aromatics content of product gasoline with reaction time. The results indicate that the aromatization activity of the HZ1 and HZ2 catalysts decreases obviously compared to that of the HZ catalyst, but the stability of aromatization is satisfactory. By loading suitable amount of Ga₂O₃ to the HZ2 catalyst, the olefins conversion activity and aromatics selectivity could be further increased in comparison with that of the HZ2 catalyst. It is interesting to note that when gallium oxide loading is about 1.0 wt.%, the HZ3-Ga(0.9) catalyst exhibits the stronger activity and the better stability of aromatization. This might be accounted for from two ways; on one hand, the nanoscale HZSM-5, because of its small size, has more acidic centers at porthole and extra-surface, and its shorter channel

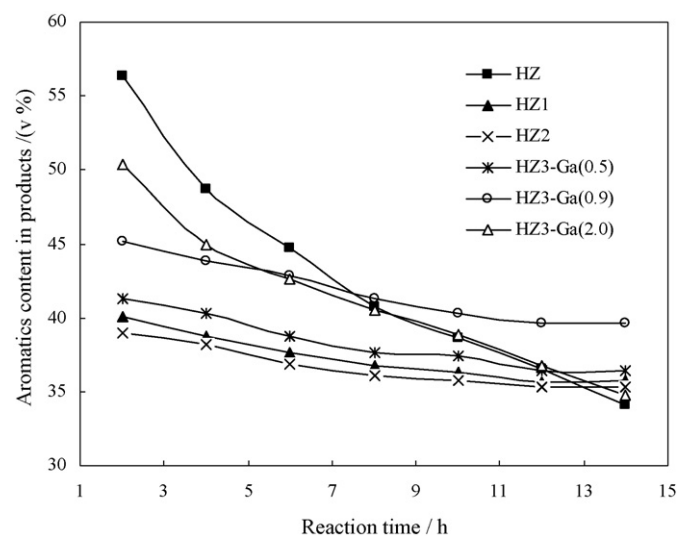


Fig. 5. Change of aromatics content in gasoline with reaction time over different catalysts.

length increases the diffusion rate of molecules and shortens the residence time of molecules in channels of nanocrystal, resulting in less coke formation in channels. The coke formation mainly occurs in the secondary pores. The significant decrease of 2,2,3-TMB adsorption in the spent catalyst confirms this hypothesis (see Table 2) [10]. On the other hand, as far as the acidity characterization and the reaction results are concerned, this modified nanoscale HZSM-5 catalyst has suitable acid property. The NH₃-TPD and IR results show that the acid strength of the HZ is weakened and the strong acid sites is decreased obviously, and that the Lewis/Brønsted acid sites ratio is adjusted to about 1.6 by the combined-modification procedure. As reported in literature [29], the catalyst with adequate Lewis acid sites and suitable Lewis/Brønsted acid sites ratio has the satisfactory activity and stability in the aromatization and isomerization processes of hydrocarbons. These aromatization and isomerization processes can be regarded as results of synergistic function by Brønsted acid sites with Lewis acid sites. When gallium oxide loading is increased to 2.0 wt.%, the HZ3-Ga(2.0) catalyst has the highest aromatization activity at reaction initial stage; however, the stability is dissatisfactory probably because the excessive gallium oxide in the HZ3-Ga(2.0) brings about an obvious increase in Lewis acid sites that enhance hydrogen transfer reaction. Simultaneously, the synergistic function of the excessive gallium oxide and the acid sites in external surfaces of zeolite results in acceleration of coking. The pores of catalyst would be blocked by coke created in outer surface of zeolite, which deactivates the catalyst.

Table 4 indicates that the isomerization activity of the HZ1 and HZ2 catalysts is obviously higher than that of the HZ catalyst. The ratio of *iso*-paraffins to *n*-paraffins increases from about 6.4 to 8.2. The effect of the gallium oxide loading on isomerization activity of the catalysts is inconspicuous, but the modified catalysts (HZ3-Ga(0.5) and HZ3-Ga(0.9)) exhibit the stronger activity and the better stability in the isomerization. However, the activity and stability of the modified catalyst (HZ3-Ga(2.0)) with excessive gallium oxide in the isomerization are deteriorative. This is possibly due to the coke formation in the channels and external surfaces of catalyst.

3.3. Long-term durability performance of the combined-modification nanoscale HZSM-5 zeolite catalyst (HZ3-Ga(0.9)) for the olefins reduction in FCC gasoline

Table 5 illustrates the evaluation results of the HZ3-Ga(0.9) catalyst in the olefins reduction of FCC gasoline. It can be seen that the HZ3-Ga(0.9) catalyst not only has stronger olefins reduction ability and better stability but also has stronger capability to simultaneously reduce the sulfur and benzene contents in FCC gasoline. The olefins content in the FCC gasoline decreases from 49.6 to 15.1 vol.% on the HZ3-Ga(0.9) catalyst. Meanwhile, the ability of olefins reduction does not change much within 300 h on-stream. The aromatics content increases from 11.4 to 33.5 vol.%, and the paraffins content increases from 39.0 to 51.4 vol.%. Meanwhile, the benzene content in FCC upgraded gasoline decreases from 2.84 to 0.66 vol.%. Furthermore, the aromatization and isomerization activity of the HZ3-Ga(0.9) catalyst are found to be stable. The RON of FCC upgraded gasoline increased while the olefins content reduced greatly. Table 5 also shows that the HZ3-Ga(0.9) catalyst has strong ability to reduce the sulfur contents of gasoline. The sulfur content in FCC gasoline upgraded is decreased from 200 to 100 ppmw. The nanoscale HZSM-5 zeolite has high activity to decompose thiophene into H₂S and small molecule fragments and shows high ability to resist sulfide poisoning. The previous investigation [30] of removal of thiophene from coke-oven benzene (thiophene content 1000 ppmw) indicated that nanoscale HZSM-5 catalysts exhibit the stronger ability and the better stability than the microscale HZSM-5 catalysts. Within time on stream of 98 h, the content of thiophene was reduced to 320 ppmw over the nanoscale HZSM-5 catalyst, whereas, it was only reduced to 580 ppmw over the microscale HZSM-5 catalyst during time on stream of 4 h. Because of the larger surface area, more acid sites and especially the more complex effects of electric field on nanoscale HZSM-5, cleavage of the C–S bond occurs leading to the formation of –SH groups. These surface species undergo subsequent reaction. This result was consistent with the production of large amount of H₂S in gaseous products. The modification using gallium oxide increases the amount of total

Table 5
Composition of FCC gasoline before and after treatment by HZ3-Ga(0.9) catalyst

Time onstream (h)	Composition of product gasoline					RON
	Aromatics (vol.%)	Olefins (vol.%)	Paraffins (vol.%)	Benzene (vol.%)	Sulfur (ppmw)	
24	36.4	12.8	50.8	0.85	–	93.3
72	35.5	12.6	51.9	0.59	–	92.6
120	33.8	14.1	52.1	0.62	–	92.5
168	32.8	15.7	51.5	0.61	–	92.1
216	32.4	16.4	51.2	0.63	–	91.7
264	33.2	16.8	50.0	0.63	–	92.5
300	32.1	16.6	51.3	0.66	–	92.4
Average value ^a	33.5	15.1	51.4	0.66	100	92.5 (90.0 ^b)
FCC feedstock	11.4	49.6	39.0	2.84	200	89.4 ^b

Reaction conditions: H₂/oil (v/v) = 600, WHSV = 3 h⁻¹, *p* = 3.0 MPa, *θ* = 643 K, *t* = 300 h.

^a Calculated on the basis of the data during the reaction for 300 h.

^b RON measured according to ASTM D2699 standard.

Table 6
The changes of components of FCC gasoline on HZ3-Ga(0.9) catalyst

Component (vol.%)	Feedstock	Product (average)
Olefins	49.6	15.1
Paraffins	39.0	51.4
<i>Iso</i> - <i>n</i> -C ₄	1.06/0.59	4.45/0.75
<i>Iso</i> - <i>n</i> -C ₅	7.88/2.34	13.9/1.24
<i>Iso</i> - <i>n</i> -C ₆	8.47/2.35	13.0/1.23
<i>Iso</i> - <i>n</i> -C ₇	7.09/1.93	5.18/0.89
<i>Iso</i> - <i>n</i> -C ₈	3.02/1.07	2.30/0.66
<i>Iso</i> - <i>n</i> -paraffins	3.3	8.2
Naphthenes	3.20	7.80
Aromatics	11.4	33.5
Benzene	2.84	0.66
Toluene	1.86	10.5
Xylene	2.81	12.6
C ₉ aromatics	2.64	8.10
C ₉ ⁺ aromatics	1.25	1.64
Research octane number	89.4	90
Boiling range (°C)		
10% distills	60	65
50% distills	78	76
90% distills	180	185
Dry point	199	202
Density (g/cm ³)	0.722	0.735
The yield of gasoline range product (wt.%)		96

acid sites and Lewis acid sites in the nanoscale HZSM-5 catalyst, enhancing the activity of hydrogen transfer to increase the cracking-desulfurization ability of the nanoscale HZSM-5 catalyst. Consequently, the HZ3-Ga(0.9) catalyst exhibits strong ability to remove thiophene from FCC gasoline.

Table 6 presents the composition changes of FCC gasoline before and after olefins reduction on the HZ3-Ga(0.9) catalyst. We can see that components of FCC gasoline change remarkably after the olefins reduction reaction. The C₄–C₆ *iso*-paraffins content and the C₇–C₉ aromatics content increases obviously, both of which are the products of gasoline range with the high RON. It can be also seen from Table 6 that the environmentally harmful benzene content decreases obviously, that the C₉⁺ aromatics content increases to a small extent, and that the dry point and density of FCC gasoline increase slightly. During the reaction, the yield of gasoline range product is maintained above 96 wt.%, and about 4 wt.% of FCC gasoline is cracked into C₁–C₃ hydrocarbons, such as ethane, ethylene, propane and propylene. From the above results, we can see that the olefins in gasoline are transformed largely into *iso*-paraffins (C₄–C₆ *iso*-paraffins mainly) and *alkyl*-aromatics (C₇–C₉ aromatics mainly) by isomerization, aromatization, alkylation and hydrogen transfer reactions.

The reason for the gasoline RON increased could be given if Tables 5 and 6 are considered together. Namely, the C₄–C₆ *iso*-paraffins and the C₇–C₉ aromatics contents increase greatly, the naphthenes content increase to some extents, and the ratio of *iso*-paraffins content to *n*-paraffins content changes from 3.3 to 8.2.

At present, the olefins reduction of FCC gasoline is carried out in the presence of expensive hydrogen, so hydrogen consumption determines the applicability of the new method. The analytic results of the gas products of the olefins reduction catalytic process in our work are as following: hydrogen, 97.2 vol.%; ethane, 0.37 vol.%; ethylene, 0.31 vol.%; propane, 0.75 vol.%; propylene, 1.37 vol.%. The calculation shows that the hydrogen consumption in the reaction process is about 0.43 wt.%, that is, 4.3-kg hydrogen per 1000-kg feedstock gasoline. If these gas products can be reused reasonably, the hydrogen consumption could be very low.

4. Conclusions

The simple catalytic process, the low cost of catalyst, the satisfactory yield of gasoline range product, the low hydrogen consumption confirm us that the newly developed modified nanoscale HZSM-5 zeolite is a promising catalyst for the olefins reduction in FCC gasoline. The most outstanding characteristic of this zeolite catalyst is that the olefins content is greatly reduced while avoiding the loss of the RON of FCC gasoline. Meanwhile, the newly developed modified nanoscale HZSM-5 zeolite catalyst has comprehensive performance on reducing the olefin, benzene and sulfur contents in the process for upgrading FCC gasoline. Through this catalytic process, the guidelines of gasoline composition can meet the requirement of the European Union III standard.

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