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Characterization of modified nanoscale ZSM-5 zeolite and its application in the olefins reduction in FCC gasoline

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Nanoscale HZSM-5 zeolite was hydrothermally treated with steam containing 0.8 wt% NH_3 at 773 K and then loaded with La_2O_3 and NiO. Both the parent nanoscale HZSM-5 and the modified nanoscale HZSM-5 zeolites catalysts were characterized by TEM, XRD, IR, NH_3-TPD and XRF, and then the performance of olefins reduction in fluidized catalytic cracking (FCC) gasoline over the modified nanoscale HZSM-5 zeolite catalyst was investigated. The IR and NH_3-TPD results showed that the amount of acids of the parent nanoscale HZSM-5 zeolite decreased after the combined modification, so did the strong acid sites deactivating catalysts. The stability of the catalyst was still satisfactory, though the initial activity decreased a little after the combined modification. The modification reduced the ability of aromatization of nanoscale HZSM-5 zeolite catalyst and increased its isomerization ability. After 300 h onstream, the average olefins content in the gasoline was reduced from 56.3 vol% to about 20 vol%, the aromatics (C_7–C_9 aromatics mainly) and paraffins contents in the product were increased from 11.6 vol% and 32.1 vol% to about 20 vol% and 60 vol% respectively. The ratio of *i*-paraffins/*n*-paraffins also increased from 3.2 to 6.6. The yield of gasoline was obtained at 97 wt%, while the Research Octane Number (RON) remained about 90.

KEY WORDS: Nanoscale HZSM-5 zeolite; hydrothermal treatment; ammonia; modification; fluidized catalytic cracking gasoline; olefins reduction; lanthanum; nickel.

1. Introduction

The rapid development of automotive industry brings about the great increase of fuel consumption, and, as a consequence, the air pollution caused by exhaust gas becomes more and more serious [1,2]. For this reason, the governments all over the world have been tightening regulations on the compositions of gasoline, such as aromatics and olefins content and sulfur-containing compounds content, etc. In China, one of the most serious problems of gasoline quality is excessive olefin content because of the high proportion of fluidized catalytic cracking (FCC) gasoline. It is the high olefin content of gasoline that causes the terrible automobile emissions. At present, however, it is difficult to change the gasoline pool composition remarkably because of the lack of the catalytic reforming, alkylation, isomerization and oxygenous compounds producing units. To meet the government regulations, therefore, it is a critical way to decrease the olefins content in FCC gasoline. So far, although several measurements have been taken to decrease the olefins content, such as the optimization of FCC process, the application of new FCC catalysts (GOR, TOM, FRG) and so on [3–5], the olefins content in gasoline is reduced only by 6–18 vol%. The olefin content in the present commercial gasoline pool cannot meet the national standard, to say nothing of the developed country standard. Therefore, it is urgent for a novel technique to greatly reduce the olefins content in gasoline, while preserving the research octane number of gasoline (RON).

As we well know, the crystal size of zeolites has a great effect on catalytic activity and selectivity. When the crystal size of HZSM-5 zeolite is reduced to the nanoscale, it exhibits higher activity, lower coke content and better stability as a catalyst in the conversion of methanol to hydrocarbons [6] in the oligomerization of ethylene etc. [7]. Recently, there has been a growing interest in the synthesis and application of nanoscale zeolites [8,9]. Zeolites with a crystal size less than 100 nm are the potential replacement for existing zeolite catalysts and for some novel environmentally benign catalytic processes.

In a previous study, we found that the parent nanoscale HZSM-5 zeolite catalyst had stronger ability and better stability for olefins reduction than the microscale ones [10,11], and found that olefins were greatly transformed into aromatics (from 2 to 64 vol%) with a high RON using the FCC light fraction as feedstock (≤70 °C). However, regulatory changes being enacted over the next 10 years will require dramatic

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changes in fuel compositions. The hydrocarbon composition of the gasoline will shift away from aromatics and olefins to those that can be burnt cleanly e.g., naphthenes, paraffins and particularly isoparaffins. In this circumstance, the parent nanoscale HZSM-5 should be modified to weaken its aromatization activity, enhance its isomerization activity and obviously improve the stability.

Hydrothermal treatment is usually employed to adjust the acidity of HZSM-5 zeolite and improve its stability [12–15]. Lago *et al.* [16] reported that mild steaming favored the generation of catalytic sites with specific efficiency. Rare earth ion-exchanged faujasites also enjoyed the position of considerable technological importance due to their superior catalytic properties. Rare earth elements could prevent aluminum loss from Y-zeolite structure and could enhance the structural resistance to the severe hydrothermal conditions in the process of FCC [17,18]. Rare earth-modified bifunctional Ni/HY improved the nickel dispersion and the ratio of metallic to acid function, thus improving its high catalytic activity and isomerization selectivity [19]. The modification effects on microscale HZSM-5 have been studied widely in relation to their catalytic performances, while it is seldom reported for nanoscale HZSM-5. In this paper, we first combined hydrothermal treatment and metal-oxide loading measurements to modify the nanoscale HZSM-5, and investigated its catalytic performances in the olefins reduction in FCC gasoline.

2. Experimental

2.1. Materials

The compositions of FCC gasoline were shown as follows: olefins 56.3 vol%, aromatics 11.6 vol%, paraffins 32.1 vol% and RON 90.8.

2.2. Catalyst preparation

The synthesis of nanoscale ZSM-5 followed the procedure described in a previous publication [20]. The ratio of SiO_2/Al_2O_3 was 25.5. By extruding the mixture of 80 wt% nanoscale NaZSM-5 with 20 wt% alumina, the strip nanoscale NaZSM-5 catalyst was obtained ($\varnothing 1\,mm \times 2\,mm$). After it had been dried at 393 K for 12 h, then calcined at 813 K for 3 h, ion exchange (three times) was carried out with 0.4 mol/L NH_4NO_3 solution, and then calcined at 813 K for 3 h. Then the hydrothermal treatment (steam containing 0.8 wt% NH_3, 773 K, 3 h, WHSV 1 h^{-1}) and "dry" impregnation (the volume of the solution containing lanthanum nitrate does not exceed the pore volume of the support) were performed on the obtained HZSM-5 zeolite, dried at 393 K for 12 h and calcined at 813 K for 3 h. The obtained lanthanum-modified zeolite was impregnated in the equivolumatic solution of nickel nitrate, dried at 393 K overnight and calcined at 813 K for 3 h; the very catalyst of olefins reduction in gasoline was finally prepared. The catalyst contained 3.0 wt% of lanthanum and 1.5 wt% of nickel oxides.

2.3. Catalyst characterization

The crystal size and habit of nanoscale HZSM-5 were determined on a Japan JEM-1200CEX Transmission Electron Microscope (TEM). Silicon and aluminum content of zeolite were obtained on a Bruker SRS 3400× spectrometer. Pore volume and surface area were obtained on a Quantachrome AUTOSORB-1 using the BET method. Adsorption capacity for normal hexane (n-C_6) and cyclohexane (c-C_6) were also measured by flow adsorption method. The adsorption capacity to 2,2,3-trimethylbutane (2,2,3-TMB) was used to characterize the secondary pores contained in the polycrystalline grains of ZSM-5 zeolites as given in the literature [21]. X-ray diffraction patterns were recorded on a D/max-2400 diffractometer using the Cu Kα radiation at 40 kV and 30 mA with a scanning rate of 2°/min. The acid properties of the parent nanoscale HZSM-5 and the right catalyst were obtained on a Quantachrome CHEMBET 3000 using the Temperature Programmed Desorption (TPD) of ammonia 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 ground and pressed into a self-supporting wafer (8–10 mg/cm^2, diameter = 15 mm), these were then 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 the adsorption of pyridine. IR spectra were recorded after subsequent evacuation at increasing temperatures from 423 to 723 K (1 h at each temperature).

2.4. Catalytic tests

The reaction on this catalyst was conducted on a continuous flow fixed-bed reactor (diameter 10 mm). Reaction conditions were listed as follows: temperature 643 K, hydrogen pressure 3.0 MPa, H_2/gasoline (volume ratios) 600, weight space velocity of FCC gasoline 3 h^{-1}, the loading of catalyst 2 g. The composition of liquid and gas product was analyzed on a SRI 8610 gas chromatograph using a flame ionization detector and a capillary column (50.0 m × 0.32 mm) containing OV-101, the RON was calculated as described in the literature [22] or measured according to ASTMD2699 standard.

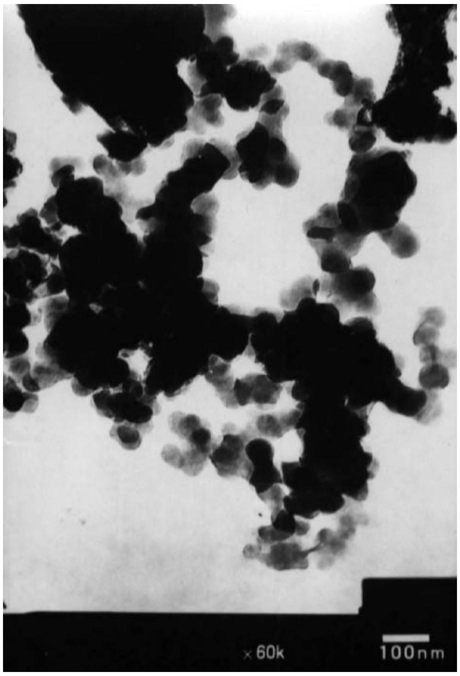

Figure 1. TEM picture of nanoscale ZSM-5.

3. Results and discussion

3.1. Characterization of nanoscale ZSM-5

Figure 1 is the TEM picture of ZSM-5, which shows that the crystal size of ZSM-5 is about 20–50 nm.

Table 1 lists the results of pore volume, surface area and adsorption capacity of both 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 to the microscale HZSM-5, the nanoscale HZSM-5 has much larger pore volume, higher c-C_6 adsorption capacity and larger surface area. Moreover, its outstanding adsorption capacity to 2,2,3-trimethylbutane exhibits the existence of secondary pores whose openings are wide enough to allow free entry of relatively large molecules such as 2,2,3-trimethylbutane molecules.

Table 2 presents the results of benzene alkylation reaction with ethene and the physicochemical properties of the spent catalysts. It can readily be seen that the activity of nanoscale HZSM-5 decreases slightly, and the reaction conversion is still satisfactory in spite of the large amount of deposited cokes caused by benzene alkylation. Higher C_6 adsorption capacity and larger surface area are also observed for spent nanoscale HZSM-5 catalysts. The significant decrease of its adsorption capacity to 2,2,3-trimethylbutane confirms that the coke formation mainly occurs in the secondary pores, which account for its better stability. In this way, the nanoscale ZSM-5 zeolite is superior in performance to the microscale one [23].

Figure 2 is the XRD spectra of both the parent and the modified nanoscale HZSM-5. The X-ray diffraction pattern of the modified nanoscale HZSM-5 is completely matched with that of the parent nanoscale HZSM-5 catalyst shown in figure 2, which indicates that the combined-modification measurement has no obvious effect on crystal structures. However, the combined-modification measurement decreases the crystallinity of the parent nanoscale HZSM-5 by 20%.

Figure 3 lists the NH_3-TPD of both the parent and the modified nanoscale HZSM-5. It can be seen that both weak and strong acid sites decrease drastically after the combined-modification measurement, especially for the strong acid sites, which could prevent it from coke deposition and improve its stability.

The effect of the combined-modification measurement on the total acid content and the acid type

Table 1
Physicochemical features of nanoscale and microscale HZSM-5 zeolites [23]

Particle size	Pore volume (cm^3/g)	Surface area (m^2/g)	Adsorption capacity (wt%)		
			n-C6	*c*-C6	2,2,3-TMB
20–50 nm	0.728	436	12.70	7.70	64
10 μm	0.610	366	11.80	6.05	0

Table 2
Results of alkylation of benzene with ethene and physicochemical properties of spent catalysts [23]

Particle size	Conversion of ethene (%)	Selection of ethene (%)	Reaction time (h)	Coke (%)	Adsorption capacity (wt%)			Surface area (m^2/g)
					n-C6	*c*-C6	2,2,3-TMB	
20–50 nm	90	92.02	46	4.24	7.03	6.21	17.4	263
10 μm	80	78.88	28	0.42	3.42	1.05	0	131

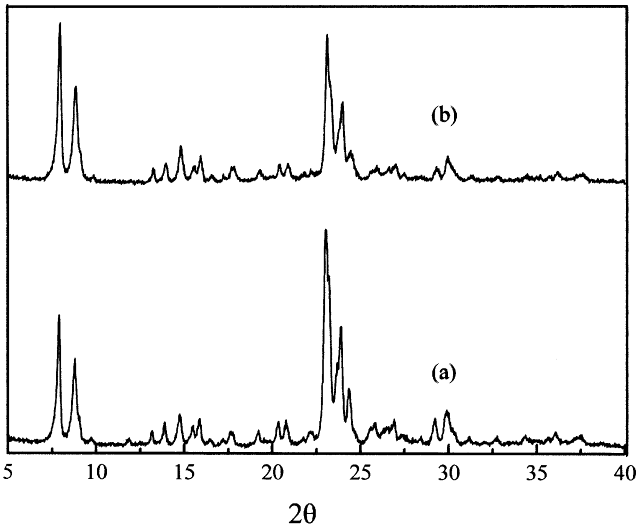

Figure 2. XRD spectra of parent nanoscale HZSM-5 and modified nanoscale HZSM-5 catalysts (a) unmodified (b) modified.

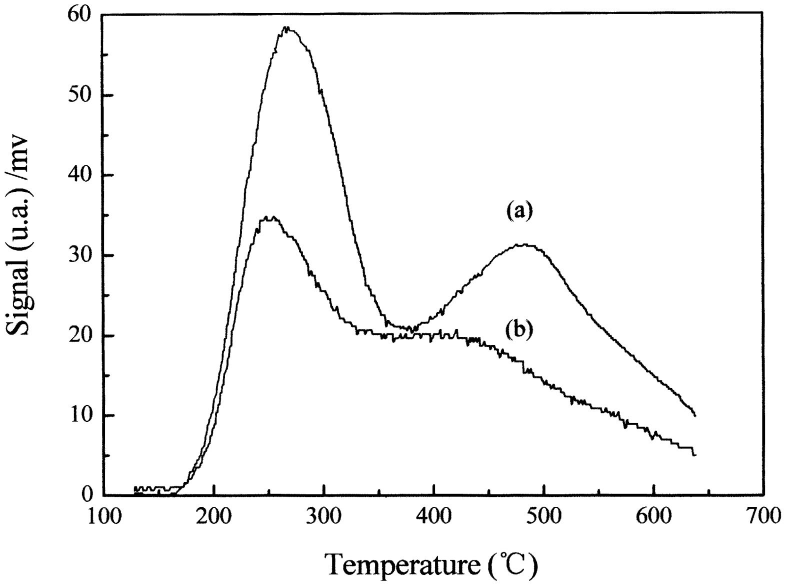

Figure 3. TPDA curves of the parent nanoscale HZSM-5 and the modified nanoscale HZSM-5 catalysts (a) unmodified (b) modified.

distribution of nanoscale HZSM-5 can be seen in table 3.

Table 3 tells us that the combined-modification measurement produces a decrease in the total acid content of the nanoscale HZSM-5. The proportions of weak and medium-strength acid sites (pyridine desorption temperature $\leq 350\,^{\circ}\mathrm{C}$) increase, while that of strong acid sites (pyridine desorption temperature $>350\,^{\circ}\mathrm{C}$) decreases obviously.

From table 3, we can also see that the ratio of Brønsted/Lewis acid sites could be adjusted by the combined-modification measurement, that is, the weak and medium-strength Brønsted acid sites increase, whereas the weak and medium-strength Lewis acid sites

Table 3
Total acid and acid type distribution of nano-HZSM-5 before and after the combined modification

Samples	Total acid (m mol/g)	B acid (m mol/g)	L acid (m mol/g)	Total acid distribution (%)		B acid distribution (%)		L acid distribution (%)	
				≤350 °C	>350 °C	≤350 °C	>350 °C	≤350 °C	>350 °C
(a)	1.802	0.775	1.027	85.2	14.8	36.1	6.9	49.1	7.9
(b)	1.235	0.568	0.667	90.7	9.30	44.0	4.9	47.0	4.1

Table 4
Composition of FCC gasoline before and after treatment by modified nanoscale HZSM-5 zeolite catalyst

Time onstream (h)	Composition (vol%)				RON
	Aromatics	Olefins	Paraffins	Benzene	
14	19.9	19.8	60.3	1.53	91.8
50	19.2	19.8	61.0	0.70	90.4
86	20.9	19.1	60.0	0.82	90.1
122	20.8	20.2	59.0	0.82	90.3
158	19.9	21.8	58.3	0.81	90.2
194	18.7	22.5	58.8	0.85	90.0
230	18.0	22.7	59.3	0.84	90.4
266	17.6	23.5	58.9	0.91	90.3
302	17.9	23.7	59.3	0.91	90.3
Average value[a]	19.2	21.5	59.3	0.91	90.4
FCC feedstock	11.6	56.3	32.1	2.64	90.8

Note: Reaction conditions: V(H2)/V(Oil) $= 600$, WHSV $= 3\,\mathrm{h}^{-1}$, $p = 3.0\,\mathrm{MPa}$, $\theta = 643\,\mathrm{K}$, $t = 300\,\mathrm{h}$.

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

decrease slightly. The Brønsted/Lewis acid sites ratio is close to unity or slightly lower than unity.

3.2. Performance of the combined-modification nanoscale HZSM-5 zeolite catalyst for the olefins reduction in FCC gasoline

Table 4 illustrates the evaluation results of the combined-modification nanoscale HZSM-5 zeolite catalyst in the olefins reduction of FCC gasoline. It can be seen that by this measurement the nanoscale HZSM-5 zeolite catalyst not only has stronger olefins reduction ability but also has better stability in olefins reduction in FCC gasoline. The olefins content in the FCC gasoline decreases from 56.3 to 21.5 vol% on this modified nanoscale HZSM-5 catalyst. Meanwhile, the ability of olefins reduction does not change much within 300 h onstream. The aromatics content increase from 11.6 to 19.2 vol%, the paraffins content increases from 32.1 to 59.3 vol%, while the benzene content is lower than 1.0 vol%. Also, its aromatization and isomerization activity are found to be stable. Its RON is preserved while the olefins content is reduced greatly. As far as the acidity characterization and the reaction results are concerned, this modified nanoscale HZSM-5 catalyst has suitable acidity. The NH_3-TPD and IR results show

Table 5
The changes of component of FCC gasoline on modified nanoscale HZSM-5 zeolite catalyst

Component (vol%)	Feedstock	Product (average)
Olefins	56.3	21.5
Paraffins	32.1	59.3
i/n-C_4	1.06/0.59	5.45/0.75
i/n-C_5	5.48/1.90	14.6/3.24
i/n-C_6	5.07/0.94	15.4/1.20
i/n-C_7	6.09/1.92	6.19/0.88
i/n-C_8	3.02/1.07	3.31/0.65
iso-/n-paraffins	3.2	6.6
Naphthenes	3.00	7.50
Aromatics	11.6	19.2
Benzene	2.64	0.91
Toluene	1.88	4.85
Xylene	2.91	6.73
C_9 aromatics	3.14	5.24
C_9^+ aromatics	1.03	1.56
Research octane number	90.8	90.4
Boiling range (°C)		
10% distills	60	64
50% distills	78	81
90% distills	176	183
Dry point	199	203
Density (g/cm^3)	0.717	0.731
The yield of gasoline range product (wt%)		97

that the acid strength of the parent nanoscale HZSM-5 is weakened and the strong acid sites is decreased obviously, and the Brønsted/Lewis acid sites ratio is close to unity by the combined-modification measurement. As reported in the literature [24], the catalyst with the Brønsted/Lewis acid sites ratio close to unity (or slightly lower than unity) is of the satisfactory stability.

Table 5 presents the composition changes of FCC gasoline before and after olefins reduction on the modified nanoscale HZSM-5 zeolite catalyst. We can see that components of FCC gasoline change remarkably after the olefins reduction reaction. The C_4–C_6 isoparaffins content increases obviously and the C_7–C_9 aromatics content increases to some extent, both of which are the products of the gasoline range with a high RON. It can also be seen from table 5 that the environmentally harmful benzene content decreases obviously, the C_9^+ aromatics content increases to a small extent and the dry point and density of FCC gasoline increase slightly. During the reaction, the yield of gasoline range product is maintained above 97 wt%, and about 3 wt% of FCC gasoline is cracked into C_1–C_3 hydrocarbon, such as ethane, ethylene, propane and propylene. From the above results, we can see that the olefins in gasoline are transformed largely into isoparaffins and partly to aromatics by isomerization, aromatization, alkylation and hydrogen-transfer reactions.

The reason that the RON of the gasoline remains unchanged could be obtained if table 4 and table 5 are considered together, that is, the C_4–C_6 *i*-paraffins content increases greatly, the naphthenes and the C_7–C_9 aromatics content increase to some extent and the ratio of *i*-paraffins content to *n*-paraffins content changes from 3.2 to 6.6.

At present, the olefins reduction of FCC gasoline is catalyzed in the presence of expensive hydrogen; so hydrogen consumption determines the applicability of new measurements. The analytic results of the gas products of the olefins reduction catalytic process in our work are listed as follows: hydrogen 96.9 vol%, ethane 0.47 vol%, ethylene 0.30 vol%, propane 0.97 vol% and propylene 1.35 vol%. The material calculation shows that the hydrogen consumption in reaction process is about 0.46 wt%, that is, 4.6-kg hydrogen per 1000-kg feedstock gasoline. If those gas products can be reused reasonably, the hydrogen consumption could be very low.

4. Conclusions

The simple catalytic process, the satisfactory yield of gasoline range product and the low hydrogen consumption confirm 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 olefins content is greatly reduced avoiding the loss of the RON of FCC gasoline. Through this catalytic process, the guidelines of gasoline composition can meet the requirement of the Europe Union II standard.

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