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A novel method for enhancing on-stream stability of fluid catalytic cracking (FCC) gasoline hydro-upgrading catalyst: Post-treatment of HZSM-5 zeolite by combined steaming and citric acid leaching

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Abstract

This article describes a novel modification method consisting of steaming and subsequent citric acid leaching to finely tune acidity and pore structure of HZSM-5 zeolite and thereby to enhance the on-stream stability of the zeolite derived fluid catalytic cracking (FCC) gasoline hydro-upgrading catalyst. A series of dealuminated HZSM-5 zeolites and their derived catalysts were prepared and characterized by X-ray diffraction (XRD), X-ray fluorescence spectroscopy (XRF), ^{27}Al MAS NMR, nitrogen adsorption, temperature programmed desorption of ammonium (NH_3-TPD) and infrared (IR) spectroscopy of chemisorbed pyridine. The results showed that the citric acid leaching could preferentially remove the extra-framework Al (EFAl) species formed by steaming treatment and thus reopen the EFAl-blocked pore channels of the steamed zeolite. The steaming treatment at a suitable temperature and subsequent citric acid leaching not only decreased the strength of acid sites to a desirable degree but also increased the ratio of medium and strong Lewis acidity to medium and strong Brönsted acidity, both of which conferred the resulting catalyst with superior selectivity to aromatics, good hydroisomerization activity and gasoline research octane number (RON) preservability, as well as enhanced on-stream stability. The results fully demonstrated that the treatments by steaming and followed citric acid leaching can serve as an important method for adjusting the physicochemical properties of HZSM-5 zeolite.

Keywords: Fluid catalytic cracking (FCC) gasoline hydro-upgrading catalyst; On-stream stability; HZSM-5 zeolite; Steaming; Citric acid leaching

1. Introduction

In Asia countries, especially in China, one of the most urgent challenges encountered in producing clean vehicle fuels is the high olefin content in fluid catalytic cracking (FCC) gasoline that takes a share of 40–60% in commercial gasoline pool. To reduce the olefin content in FCC gasoline, many methods (such as optimization of the FCC process, use of novel olefin reduction FCC catalysts, and application of selective hydrogenation) have been attempted, but the resulting poorer process performance either in gasoline research octane number (RON) or in gasoline yield is still challenging refineries in Asia countries [1].

In the previous study [2], we developed a novel FCC gasoline hydro-upgrading catalyst system that used HZSM-5 zeolite and γ-Al_2O_3 as support and Ni and Mo as active metals. While having superior olefin reduction ability and excellent RON preservability, this catalyst system suffered from a quick loss in activity due to the coke buildup in long-term operation. It has been widely accepted that the coke deposit in hydrocarbon conversion catalysts can be related to the shape-selective reactions catalyzed by acid sites on the zeolites involved [3] and thus finely tuning zeolite acidity and pore structure is considered to be an effective way to lessen catalyst deactivation by coking and thereby to extend catalyst operational life. For this reason, steaming treatment techniques of zeolites have been developed and are now widely used to remove part of aluminum species in zeolite frameworks with the aim of decreasing the acidity of the resulting

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catalysts [4–6]. However, the extra-framework Al (EFAl) species formed during steaming usually have undesirable effects on the catalytic activity and diffusibility of zeolites [7–9], so subsequent acid leaching is usually employed. Inorganic acids (e.g., HCl) are commonly used as Al leaching reagents, but they unavoidably induce further dealumination of zeolites [6,10]. Therefore, a moderate dealumination method that does not seriously affect framework Al species while preferentially removing EFAl species should be pursued.

Recently, it has been reported that citric acid treatment can be used to optimize the acidity of ultra-stable Y (USY) [11] and β [12] zeolites, but to the best of our knowledge this method has not been applied to the modification of zeolite ZSM-5. Herein, we report a novel modification method consisting of steaming and subsequent citric acid leaching for finely tuning acidity and pore structure of HZSM-5 zeolite and its application in suppressing the deactivation of NiMo/HZSM-5-γ-Al_2O_3 FCC gasoline hydro-upgrading catalysts. In view of the fact that many industrially important processes, such as Cyclar [13], Z-former [14] and Alpha [5], use HZSM-5 zeolite as catalysts, the method introduced here may be also of significance for optimizing the performance of the catalysts involved.

2. Experimental

2.1. HZSM-5 zeolite modification

The parent HZSM-5 zeolite (Sample PHZ, SiO_2/Al_2O_3 molar ratio = 51.2, Shanghai Huaheng Chemical Plant, PR China) was steamed in 100% water vapor flowing at weight hourly space velocity (WHSV) 1 h^{-1} at different temperatures for 4 h to obtain a series of Samples SHZ-T (the letter "T" denotes steaming temperature) and was leached with a 1.2 M citric acid solution (10 mL/g zeolite) at 65 °C for 6 h to obtain Sample AHZ, respectively; then, Samples SHZ-T were further treated with a 1.2 M citric acid solution (10 mL/g zeolite) at 65 °C for 6 h to obtain Samples SAHZ-T. All of them were used as catalyst support.

2.2. Catalyst preparation

Firstly, different preformed extruded sticks (Ø1.5 mm × 2–3 mm) were obtained by extruding the HZSM-5 zeolites obtained above using 30 wt.% pseudoboehmite (usually referred as SB powder, Condea, Germany) as binder; then, the sticks were dried at 110 °C overnight and calcined at 520 °C for 5 h; finally, they were impregnated with aqueous solutions of ammonium molybdate and nickel nitrate successively. After each impregnation step, the solids were dried at 120 °C for 5 h and calcined at 480 °C for 4 h to obtain a series of NiMo/HZSM-5-γ-Al_2O_3 catalysts, which hereafter will be referred as C-x, where "x" indicates the corresponding zeolite used.

2.3. Catalytic performance test

Using FCC gasoline from a refinery in China as feedstock, the catalytic performance of the catalysts was assessed in a 10 mL continuously flowing fixed bed microreactor under the following conditions: 390 °C, 1.8 MPa, H_2/gasoline volumetric ratio 200, gasoline WHSV 2 h^{-1}. The catalysts were presulfurized for 1 h at 150, 230 and 260 °C and for 4 h at 290, 320 and 340 °C, respectively, with a CS_2 (3 wt.%)/ *n*-octane mixture as vulcanizer and hydrogen as carrier gas. The feedstock and the products were analyzed by an Angilent gas chromatograph installed with a 50 m long PONA capillary column.

2.4. Characterizations

X-ray diffraction (XRD) analysis was carried out on a Shimadzu Lab XRD-6000 diffractometer that uses Cu Kα radiation and works at 40 kV, 30 mA, and a scan rate of 4°/min. The compositions of the different samples were obtained by X-ray fluorescence (XRF) analyses conducted on a ZSX-100e 4580 instrument. The ^{27}Al MAS NMR spectra were recorded on a Varian $^{\text{Unity}}$Inova 300 spectrometer. Nitrogen adsorption was used to measure the surface areas and pore volumes of the samples. Acid type distributions were determined by infrared (IR) spectroscopy of chemisorbed pyridine.

Temperature programmed desorption of ammonia (NH_3-TPD) was carried out as follows. The sample (0.10 g) to be tested was first pretreated in flowing He (30 mL/min) at 500 °C for 30 min, then cooled down to 100 °C and saturated with NH_3 to equilibrium state. The He flow was then flushed until the baseline of the integrator was stable. NH_3-TPD was then started from 100 to 600 °C at a heating rate of 15 °C/min. The concentration of ammonia in the exit gas was monitored continuously by a gas chromatogram installed with a thermal conductivity detector.

3. Results and discussion

3.1. Structure characterization

The XRD patterns of the different samples are shown in Fig. 1. The diffraction patterns of the four HZSM-5 samples show almost the same peaks, indicating that the steaming or/ and the followed citric acid leaching did not significantly change the structure of the HZSM-5 zeolite. As shown in Table 1, however, the crystallinity of Sample SHZ-480 decreased to 94% because of the formation of the amorphous phase during the steaming process [10]. It is also interesting to note that the citric acid leaching of the parent zeolite PHZ and steamed Sample SHZ-480 yielded two samples AHZ and SAHZ-480 with increased crystallinity because of the removal of the amorphous phase, which is formed either during the calcination of the as-synthesized zeolite for removing the organic template and the subsequent treatment with dilute HCl solution for producing the H-form zeolite PHZ or during the steaming treatment of Sample PHZ. Moreover, no signals ascribed to NiO and MoO_3 phases are observed in the XRD patterns of all the catalysts prepared, indicating that the metals are well dispersed. The slight decrease in the intensities of the main diffraction peaks in

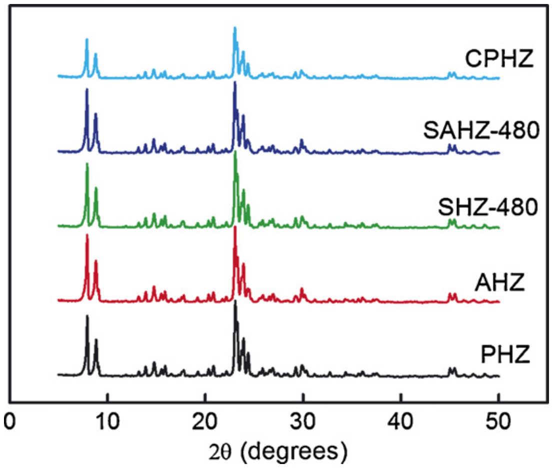

Fig. 1. XRD patterns of the samples.

Fig. 1 results from the dilution effect of the binder SB powder.

The bulk molar SiO_2/Al_2O_3 (including both framework and extra-framework species) ratios of the different samples were analyzed by XRF and the results are given in Table 1. The bulk molar SiO_2/Al_2O_3 ratios of AHZ and SHZ-480 are nearly identical to that of the parent zeolite (Sample PHZ), while that of SAHZ-480 is increased from 51.2 to 53.8. These results can be interpreted from the ^{27}Al MAS NMR spectra of the samples, as shown in Fig. 2. The two distinct peaks with chemical shifts at 0 and 54 ppm assigned to octahedral EFAl and tetrahedral framework Al, respectively [15], are clearly resolved for Sample SHZ-480, implying that steaming leads to the dealumination of the zeolite framework and thereby the formation of EFAl species, but these EFAl species still reside in the zeolite. After the subsequent citric acid leaching, the signal representing EFAl species decreased and that representing framework Al species almost remained unchanged. Here, we can see the significant differences between the citric acid treatment and the HCl treatment or steaming/HCl treatment reported in literatures [6,10] which stated that the peak representing octahedrally coordinated EFAl at 0 ppm appeared after the parent zeolite was treated by HCl or still apparently existed after the steamed zeolite was further treated by HCl, while both accompanied with the decreased intensity of the peak at 54 ppm.

The variations of the BET surface areas and the pore volumes of the different samples further prove the above statement, as shown in Table 2. After steaming, the BET surface area and pore volumes (both micropore volume and total pore volume) of the zeolite, especially that of micropores, decreased due to the pore channel blockage by the EFAl species formed; the BET surface area and pore volumes of the sample obtained by leaching the steamed sample with citric acid were recovered to or even higher than those of the parent zeolite. The increases in the BET surface area and pore volumes of Sample SAHZ-480 may be ascribed to the removal of the EFAl species originally residing in the parent zeolite as well as those formed during steaming, consistent with the XRD and ^{27}Al MAS NMR analysis results. The reopened pore channels of the zeolite after the removal of EFAl species by citric acid leaching may play an important role in catalytic reactions from the point of view of shape selectivity and mass transfer in the zeolite channels, which will be further discussed in the later part of this article.

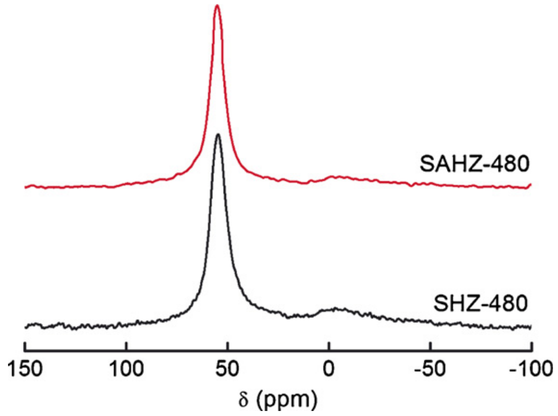

Fig. 2. ^{27}Al MAS NMR spectra of the zeolites.

Table 2
Specific surface areas and pore volumes of the parent HZSM-5 zeolite and those treated by steaming and by steaming and citric acid leaching

Zeolites	Surface area (m^2/g)			Pore volume (cm^3/g)	
	BET	Micropore	External	Micropore	Total
PHZ	354.8	228.9	125.9	0.140	0.235
SHZ-480	343.6	217.0	126.6	0.135	0.230
SAHZ-480	354.1	237.1	117.0	0.142	0.244

3.2. Acidity characterization

The effects of the steaming or/and citric acid leaching on the acid quantity and strength distribution of the resulting catalysts were studied by the NH_3-TPD technique and the results are

Table 1
The different treatment methods and the characteristics of the resulting zeolites

Zeolites	Treatment methods	Relative crystallinity (%)	Composition		
			Al_2O_3 (wt.%)	SiO_2 (wt.%)	SiO_2/Al_2O_3 (mol/mol)
PHZ	Parent	98[a]	3.20	96.6	51.2
AHZ	Acid leaching	102	3.17	96.6	51.7
SHZ-480	Steamed	94	3.20	96.6	51.2
SAHZ-480	Steamed/acid	97	3.05	96.7	53.8

[a] This value was provided by the manufacturer Shanghai Huaheng Chemical Plant, PR China.

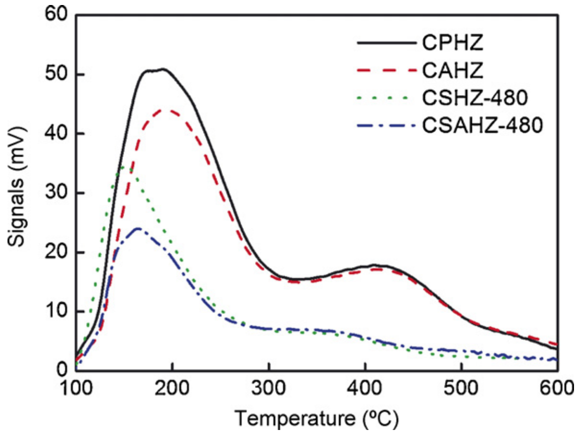

Fig. 3. NH_3-TPD curves of the catalysts.

shown in Fig. 3. It can be seen that each curve in the figure has two desorption peaks appearing at high temperature and low temperature, respectively, with the former assigned to strong acid sites and the later to weak acid sites. The single citric acid leaching (Sample CAHZ) leads to the decrease in weak acid sites, but does not obviously change strong acid sites of the catalyst. The treatment by steaming (Sample CSHZ-480) causes the significant decreases in both weak and strong acid sites due to the dealumination of the zeolite framework; the followed citric acid leaching after steaming brings about a further decrease in weak acid sites, but a minor increase in strong acid sites. The different changes in the strong acid sites of the parent and steamed zeolites arisen from the citric acid treatment can be attributed to the fact that the citric acid treatment has the following three co-occurring effects:

(1) the slight dealumination of the zeolite framework that results in the decrease in the acidity;
(2) the removal of the EFAl species that increases the acidity through eliminating the blockage/coverage of acid sites by EFAl species;
(3) the realumination of HZSM-5 zeolites that increases the acidity [12].

The first effect is dominant when the parent sample is treated with single citric acid, while the later two effects become manifested when the subsequent citric acid leaching is followed after steaming, consistent with the facts the decrease in strong acid sites of Sample CAHZ and the minor increase in strong acid sites of Sample CSAHZ-480 compared with Samples CPHZ and CSHZ-480, respectively. Furthermore, the peak positions in Fig. 3 shift towards to lower temperatures in the order of CPHZ, CAHZ > CSHZ-480, CSAHZ-480, indicating the decrease in the strength of acid sites.

To distinguish the changes in Brönsted (B) and Lewis (L) acid sites on the catalysts caused by the different treatments, the FTIR spectrum analyses of pyridine adsorbed on the different samples were made and the results are summarized in Table 3. It is well known that the adsorption bands at 1545 and 1450 cm^{-1} can be unanimously assigned to pyridine coordinated to B and L acid sites, respectively, and the total and the medium and strong acidities can be calculated after pyridine desorption at 200 and 350 °C, respectively. As seen in Table 3, the single citric acid treatment (Sample CAHZ) leads to the decreases in both B and L acid sites of different strengths due to its slight dealumination effect on the zeolite framework; the single steaming treatment (Sample CSHZ-480) gives rise to the significant decrease in B acid sites, but the increase in weak L acid sites. So, it is reasonable to suggest that some EFAl species produced behave as weak L acid sites, as reflected by the significant decrease in weak L acid sites of the zeolite further treated by citric acid leaching (Sample CSAHZ-480). However, there is no knowledge on the effect of the steaming and/or citric acid leaching on the single strong acidity because medium acidity and strong acidity cannot be distinguished by the pyridine-adsorbed FTIR measurements.

Table 3
Acid type distributions of the different catalysts derived from the zeolites treated by the different methods

Catalysts	Acidity (μmol/g)							
	Weak		Medium and strong			Total		
	L	B	L	B	L/B	L	B	L + B
CPHZ	83.2	42.0	46.3	189.0	0.25	129.5	231.0	360.5
CAHZ	67.8	27.8	42.7	181.0	0.24	110.5	208.8	319.3
CSHZ-480	92.0	17.3	40.0	79.3	0.50	132.0	96.6	228.6
CSAHZ-480	53.3	19.7	38.5	75.9	0.51	91.8	95.6	187.4

3.3. Catalytic performance

The catalytic performance of the above catalysts for FCC gasoline hydro-upgrading was assessed and the typical results after they were run for 24 h are presented in Table 4. Compared with catalyst CPHZ prepared from the parent zeolite HZSM-5, catalyst CAHZ prepared from the zeolite treated only by citric acid leaching is featured by its slightly improved activity for olefin reduction via hydroisomerization and aromatization and inappreciably reduced coke deposition because of the tiny change in its acidity; catalyst CSHZ-480 prepared from the zeolite treated only by steaming has weaker acidity and higher ratio of medium and strong L acidity to medium and strong B acidity that is favourable for aromatization, but shows the lowest olefin reduction and aromatization activities and moderate coke deposition, which can be ascribed to the EFAl species formed during steaming that not only cause the pore channel blockage but also suppress the excellent aromatization activity of the HZSM-5 zeolite conferred by its original pore structure [16]; catalyst CSAHZ-480 prepared from the zeolite treated by the combined steaming and citric acid leaching shows distinctly increased activity for olefin reduction, remarkably decreased coke deposition, and good RON preservability, which is attributed not only to its weaker acidity and higher ratio of medium and strong L acidity to medium and strong B acidity that are favourable for aromatization, but also to the removal of the EFAl species by citric acid leaching that greatly reopens the pore channels of the zeolite and thus confers the catalyst with improved activity and better stability.

Table 4
FCC gasoline hydro-upgrading results of the different catalysts (24 h TOS)

Catalysts	Feedstock	CPHZ	CAHZ	CSHZ-480	CSAHZ-480
Composition of the liquid product (vol.%)					
Isoparaffin	32.26	38.74	39.22	41.64	40.11
Olefin	39.13	20.45	19.10	20.98	14.91
Aromatics	17.24	19.31	19.38	18.03	23.54
RON	91.4	90.2	90.1	89.8	90.9
Coke (wt.%)	–	4.78	4.51	3.84	2.03

Table 5
Acid type distribution of the catalysts

Catalysts	Acidity (μmol/g)							
	Weak		Medium and strong			Total		
	L	B	L	B	L/B	L	B	L + B
CSAHZ-450	57.0	21.8	40.5	111.4	0.36	97.5	133.2	230.7
CSAHZ-480	53.3	19.7	38.5	75.9	0.51	91.8	95.6	187.4
CSAHZ-520	36.1	9.6	30.0	46.8	0.64	66.1	56.4	122.5
CSAHZ-560	10.8	8.3	16.8	17.6	0.95	27.6	25.9	53.6

3.4. Acidity versus reaction performance

The results presented above seem to suggest the idea that if the pore channels of the zeolite used are open, increasing the ratio of medium and strong L acidity to medium and strong B acidity and decreasing the total acidity of the catalyst should substantially improve the catalytic performance of the corresponding catalyst for FCC gasoline hydro-upgrading. Is this idea true or not, especially for this complicated FCC gasoline hydro-upgrading system that involves many possible reactions, such as hydroisomerization, aromatization, hydrocracking, hydrogen transfer, and so on?

3.4.1. Acidity

To answer the question above, a series of catalysts were prepared by using the HZSM-5 zeolites treated by combined steaming at different temperatures and citric acid leaching and their acidities were characterized by the NH_3-TPD and pyridine-adsorbed FTIR techniques, as shown in Fig. 4 and Table 5, respectively. The NH_3-TPD curves in Fig. 4 indicate that both weak and strong acid sites of the catalysts decrease with the increasing steaming temperature. When the steaming condition is too severe, i.e., the steaming temperature is high, almost all the strong acid sites disappear, with only part of weak acid sites remaining (e.g., Sample CSAHZ-560). Table 5 shows that the B and L acidities of different strengths also decrease with the increasing steaming temperature, with the concentration of B acid sites decreasing more rapidly than that of L acid sites, resulting in an increasing trend of the ratios of medium and strong L acidity to medium and strong B acidity, similar to the results obtained for zeolites H-BEA [17] and SAPO-11 [18].

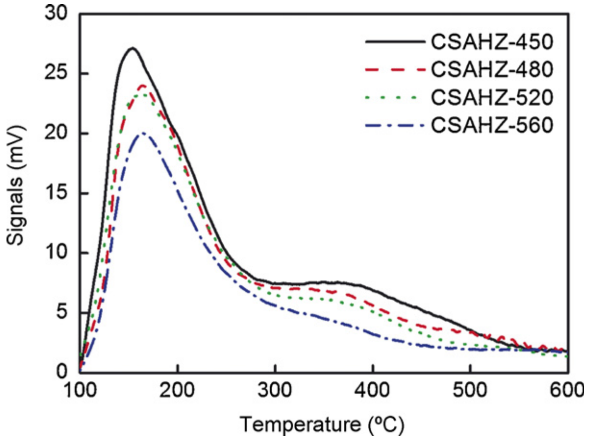

Fig. 4. NH_3-TPD curves of the catalysts.

3.4.2. Reaction performance

The performances of the NiMo/HZSM-5-γ-Al_2O_3 catalysts made from the different zeolites listed in Table 5 for FCC gasoline hydro-upgrading as function of time on stream (TOS) and as function of steaming temperature are shown in Figs. 5 and 6, respectively. Though all the catalysts suffer from decaying in their activities with the increasing TOS, as indicated by the gradually increased olefin and isoparaffin contents and slowly decreased aromatics contents in the products, they differ from each other in their initial activities and deactivation rates, illustrating the significant influence of acidity on the catalytic performances of the catalysts.

3.4.2.1. Acidity versus initial activity. As shown in Fig. 5, during the period of the first 3 h TOS, with the zeolite steaming temperatures at 450, 480, 520 and 560 °C, the contents of

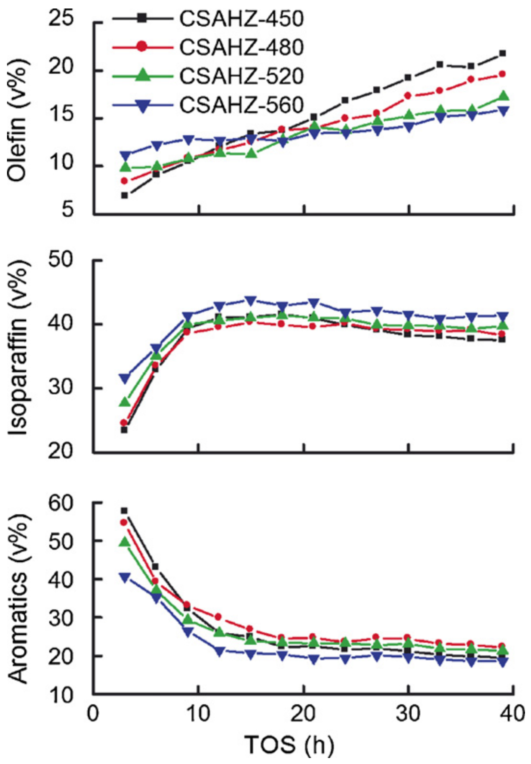

Fig. 5. Varying trends of typical compositions in the liquid products obtained on the catalysts with TOS.

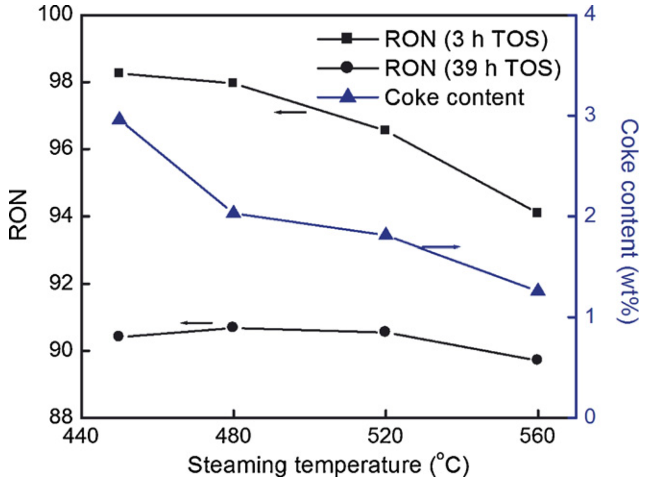

Fig. 6. RON and coke content as functions of steaming temperature of the HZSM-5 zeolite.

aromatics in the liquid products obtained on the resulting catalysts are increased from 17.24 vol.% of the feedstock to 57.63, 54.49, 49.49 and 40.70 vol.%, respectively, i.e., the increment of aromatics content decreases with the increasing steaming temperature. In other words, the initial aromatization activity is in good accordance with the acidity of the resulting catalysts, as shown in Fig. 4 and Table 5. This can be fairly explained by the results of de Lucas et al. [4] and Song et al. [19]. de Lucas et al. [4] found that on zeolite ZSM-5 the dehydrocyclization reactions of lower hydrocarbons leading the formation of aromatics require strong acid sites. Song et al. [19] further stated that among all the steps involved in olefin aromatization, the formation of dienes or cycloolefins from mono-olefins through hydrogen transfer is the key step and these reactions can be catalyzed by strong acid sites; so, the stronger acidity a catalyst has, the higher initial aromatization activity it exhibits. Here, it is noted that during the initial period the contents of isoparaffins in the products are lower than that in the feedstock (32.26 vol.%) because the isoparaffins that are originally contained in the feedstock and formed by the hydrogenation of isoolefin are transformed into aromatics on strong acid sites. Moreover, by analyzing the composition and RON data given in Figs. 5 and 6 at 3 h TOS, it is obvious that aromatization is the foremost factor in preserving gasoline RON when the olefin content is reduced.

3.4.2.2. Acidity versus stability. With the reactions going on, as shown in Fig. 5, the varying trends of isoparaffin and aromatics contents in the products obtained on the corresponding catalysts in the first 39 h TOS are different from each other: in the first 18 h TOS, the contents of isoparaffins and aromatics rapidly increase and decrease, respectively; then, they reach at relatively steady states. It is well known that coking occurs preferentially on the strong acid sites [4,20,21], so the numbers of strong acid sites on the catalysts decrease with the increasing TOS due to coke deposition, leading to the drastically decreased aromatization activity during the initial 18 h TOS. The increasing tendency of the isoparaffin contents in the liquid products indicates that the hydroisomerization of olefins can occur on weak acid sites, and then gradually dominates in the parallel and mutually competitive reactions of hydroisomerization and aromatization due to the decreasing strong acid sites. During the operating period from 18 to 39 h TOS, the hydroisomerization and aromatization activities keep at relatively constant values. The results described here can be explained by the fact that the rate of coke formation is depressed because of the dramatically decreased strong acid sites due to the rapid coke buildup during the initial stage. During the whole 39 h TOS, the olefin contents in the products gradually increase with time, indicating the loss in the hydrogenation activity of the catalysts. Moreover, the RON values of the products collected after 39 h TOS given in Fig. 6 do not show obvious decline compared with that of the feedstock, reflecting the important role of aromatization in preserving gasoline RON when the olefin content is reduced.

Furthermore, we find that the different initial activities and deactivation tendencies of the different catalysts shown in Figs. 5 and 6 can be also related to the ratios of medium and strong L acidity to medium and strong B acidity of the catalysts as well as acid strength distributions. The results given in Fig. 5 demonstrate the on-stream stability (defined as the declining trend of the activity of olefin reduction via hydroisomerization and aromatization) of the different catalysts follows the order CSAHZ-450 < CSAHZ-480 < CSAHZ-520 < CSAHZ-560, in good agreement with the increasing order of the ratio of medium and strong L acidity to medium and strong B acidity shown in Table 5. So, it is reasonable to conclude that the increasing ratio of medium and strong L acidity to medium and strong B acidity can enhance the on-stream stability of the NiMo/HZSM-5-γ-Al_2O_3 FCC gasoline hydro-upgrading catalyst, in good accordance with the literatures [22,23] which showed that both hydroisomerization and aromatization relied on the synergism between L and B acid sites. However, when the strong acid sites almost disappear (e.g., Sample CSAHZ-560), the catalyst has lower aromatization activity and thus show the inability in preserving gasoline RON (Fig. 6).

3.5. Lifetime test

Among all the catalysts discussed above, catalyst CSAHZ-480 has the superior performance for FCC gasoline hydro-upgrading, so it is chosen for a 400 h lifetime test. In order to depress the pore mouth blockage by external coke deposition, the pre-sulfurized catalyst was pre-coked with *n*-octane under 390 °C for 24 h to decrease its surface acidity [24]. During the 400 h running, the reaction products collected within a given time interval (6 h) were analyzed to give the changing trend of the lumped compositions with TOS (Fig. 7), and all the products collected were finally mixed together to obtain the average composition during the whole testing time (Table 6). As shown in Fig. 7, the catalyst has high initial olefin reduction and aromatization activities, then suffers a very quick deactivation in the first 18 h TOS, remains almost at constant olefin reduction and aromatization activities in the following 130 h TOS, and finally shows a slowly decreasing tendency in olefin reduction activity and a nearly constant aromatization activity.

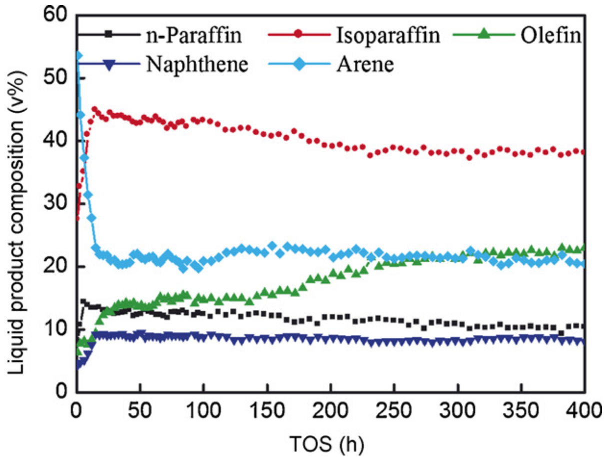

Fig. 7. Varying trends of the lumped compositions of the product obtained on catalyst SCAHZ-480 during 400 h lifetime test.

Table 6
Stability testing result of the catalyst CSAHZ-480

Items	Lumped composition (vol.%)	
	Feedstock	Product
n-Paraffin	5.32	11.35
Isoparaffin	32.26	39.57
Olefin	39.13	18.54
Naphthene	6.06	8.43
Arene	17.24	22.11
Benzene (vol.%)	0.61	0.49
RON	91.4	90.8
S (ppm)	76	<10

From Table 6, it can be seen that the composition of the product gasoline meets the specifications of Category II Unleaded Gasoline as regulated by the World-Wide Fuel Charter and the product yield is as high as 98.0 wt.%, while the product RON decreases by only 0.6 compared with that of the feedstock, demonstrating the effectiveness of the combined steaming and citric acid leaching treatment of HZSM-5 zeolite for enhancing the on-stream stability of the resulting FCC gasoline hydro-upgrading catalyst.

4. Conclusions

This article demonstrates that the treatment of HZSM-5 zeolite with steaming and subsequent citric acid leaching can serve as an important method for enhancing the on-stream stability of the resulting NiMo/HZSM-5-γ-Al_2O_3 FCC gasoline hydro-upgrading catalyst.

The characterization and catalytic performance testing results show that both the acidity adjustment and pore channel opening of the HZSM-5 zeolite have important influences on the catalytic performance of the resulting catalyst. The catalyst based on the parent HZSM-5 zeolite provides high initial activities, but suffers from a rapid deactivation by coking due to its excessive strong acid sites. The citric acid treatment of the parent HZSM-5 zeolite has no significant effect on the catalytic performance of the resulting catalyst due to the slight change in the acidity. While effectively decreasing the acidity of the corresponding catalyst, the steaming treatment of the parent zeolite produces EFAl species, giving rise to the blockage to the micropores of the zeolite and leading to the decrease in the aromatization selectivity of the corresponding catalysts. The citric acid leaching after steaming can preferentially remove the EFAl species formed during steaming and thus reopen the EFAl-blocked pore channels of the zeolite, so the resulting catalyst exhibits the superior selectivity to aromatics, good hydroisomerization activity and good RON preservability as well as superior tolerance to carbonaceous deposits.

The results also show that the combined treatments consisting of steaming at a suitable temperature and citric acid leaching of HZSM-5 zeolite can finely adjust the strength of acid sites and increase the ratio of medium and strong L acidity to medium and strong B acidity, which can greatly enhance the on-stream stability of the resulting catalyst by inhibiting the formation of coke while maintaining the good aromatization selectivity.

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