Catalysis Letters Vol. 105, Nos. 1–2, November 2005 (© 2005)
DOI: 10.1007/s10562-005-8007-z

Hβ/HZSM-5 composite carrier supported catalysts for olefins reduction of FCC gasoline via hydroisomerization and aromatization

Yu Fan[a,b], Xiaojun Bao[a,b,*], and Gang Shi[b]

[a] *State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Beijing 102249, P. R. China*
[b] *The Key Laboratory of Catalysis, China National Petroleum Co., China University of Petroleum, Beijing 102249, P. R. China*

Received 26 August 2004; accepted 23 July 2005

In order to develop a novel catalyst system that has excellent olefin reduction ability for FCC gasoline without loss in research octane number (RON), different catalysts supported on single- and binary-zeolite carriers consisting of Hβ or/and HZSM-5 were prepared and their catalytic performances for FCC gasoline upgrading were assessed in the present investigation. Acidity measurements by pyridine-adsorbed Fourier transformed infrared spectroscopy (FTIR) showed that hydroisomerization and aromatization activities were closely related to the density of acid sites and the ratios of medium Lewis acidity and strong Brönsted acidity to total acidity. Compared with the single HZSM-5 supported catalyst, the single Hβ supported catalyst was found to have much better olefin reduction performance, but the product RON still suffered from a loss of 1.6. Compared to the single-zeolite supported catalysts, the binary-zeolite Hβ/HZSM-5 supported catalysts with the mass ratio of Hβ to HZSM-5 at 6.6 offered much more stable activity and selectivity to arene, which played an important role in preserving gasoline RON.

KEY WORDS: FCC gasoline; Hβ and HZSM-5; hydroisomerization; aromatization; acidity; octane number.

1. Introduction

Today, in China approximately 80% of gasoline comes from FCC gasoline in which the olefins content is usually as high as 50–65 vol.%. The high olefins content has caused more and more serious air pollution [1,2], therefore various measures have been taken to control the olefins content of FCC gasoline. It has been found that by means of operation optimization of FCC units and use of novel olefins reduction FCC catalysts the olefins content can be decreased to around 35 vol.%, which is still much higher than the upper value 20 vol.% as regulated by the World-Wide Fuel Charter on Category 2 unleaded gasoline. Several selective hydrogenation routes have been proposed and some of them have been put into pilot-scale operations, but none of them enables satisfactory olefins control with acceptable loss in both gasoline research octane number (RON) and yield. Therefore, it is urgent to develop a novel technique that can preserve the octane value while reducing the olefins content of gasoline. To accomplish this objective, converting olefins (especially C_5–C_7) in FCC gasoline into *i*-paraffins and aromatics will be the best choice. By this way, the loss of gasoline RON due to olefins reduction can be compensated by increasing the content of *i*-paraffins and aromatics that have higher octane number. Obviously, a novel catalyst system with balanced olefin hydrogenation, paraffin isomerization and olefin aromatization abilities needs to be developed.

Nowadays, zeolite β has been widely applied in hydroisomerization of hydrocarbons because of its special pore system and surface acidity [3,4]. It was found that due to the presence of large intersecting pores in the framework of zeolite β, the isomerization activity and selectivity for *n*-hexane transformation of Pt/Hβ catalysts were higher than those of conventional Pt/H-mordenite (HMOR) catalysts [5]. For the hydroisomerization of *n*-heptane, the high acid strength and the 12-membered-ring pores of 0.65 nm of MOR can greatly diminish the diffusion of di- and especially tri branched products out of the pores, giving rise to increased cracking opportunity of hydrocarbons [6]. In comparison to MOR, the 12-membered-ring tri-directional zeolite β is a promising catalyst for the branching isomerization of *n*-heptane due to the faster diffusion rates of reactants and products through the more open structure [7].

As to the aromatization of light paraffins ($\leq C_7$), several processes, such as Cyclar [8–10], Z-Forming [8,11], Aromax [12] and LNA [13], have been developed after the pioneering work due to Mobil Oil Co. that used ZSM-5 as catalyst in 1973 [14]. However, a single ZSM-5 gives low selectivity for the conversion of alkanes to aromatics [15,16], because an effective reaction sequence from alkanes to aromatics requires the presence of both acid sites and dehydrogenation centers. Ono *et al.* [17] showed that the introduction of Ga or Zn species had a positive effect on the rate and selectivity of alkane aromatization. Moreover, the Alpha process [18] for the production of aromatics from olefin-rich hydrocarbons showed that Zn-doped H-ZSM-5 had excellent selectivity for olefin aromatization.

---

* To whom correspondence should be addressed.
E-mail: baoxj@cup.edu.cn.

From the point of view of the olefin reduction and RON preservation of FCC gasoline, it is reasonable to consider that a catalyst system based on composite carriers consisting of both 10- and 12-membered-ring zeolites should provide a balanced isomerization and aromatization performance and thus benefit the upgrading of FCC gasoline. To this goal, in this investigation, a series of catalysts based on 12-membered-ring (Hβ) or/and 10-membered-ring (HZSM-5) zeolites with different compositions were prepared and their catalytic activity and selectivity for FCC gasoline hydroisomerization and aromatization were assessed.

2. Experimental

2.1. Catalyst preparation

The bifunctional catalysts investigated in this work consist of H-zeolite as the acid part, Ni–Mo as the metal part, and a binder (pseudo-boehmite). Zeolites β ($n_{Si}/n_{Al}=21$) and ZSM-5 ($n_{Si}/n_{Al}=32$) were directly supplied in ammonium form by the Catalyst Plant of Nankai University (Tianjin, P. R. China). Pseudo-boehmite was supplied by Tianjin Hengmeilin Chemical Corporation. (P. R. China).

The catalyst preparation procedure consists of three main steps: mixing of zeolites, incorporation of metallic function, and activation of the metal part. Firstly, different kinds of H-zeolites were fully blended by grinding after the ammonium forms of zeolites were calcined at 550 °C for 6 h to obtain the protonic form. Then, the supported catalysts were prepared. by impregnating the mixture of zeolites with $(NH_4)_6Mo_7O_{24}$ and $Ni(NO_3)_2$ (Beijing Chemical Co., P. R. China) using the fractional step method. Finally, the impregnated solids were extruded using pseudo-boehmite as binder and calcined at 500 °C for 4 h. Table 1 lists the nomenclature of the catalysts prepared with different compositions.

Table 1
Catalysts compositions (wt%)

Catalyst	Hβ	HZSM- S	γ-Al_2O_3	NiO	MoO_3
A	76	–	20	1	3
B	71	5	20	1	3
C	66	10	20	1	3
D	56	20	20	1	3
E	38	38	20	1	3
F	20	56	20	1	3
G	–	76	20	1	3

2.2. Characterization

Surface area, pore volume and pore size measurements of the catalysts were conducted with a volumetric adsorption apparatus (ASAP 2405N, Micromeritics Instruments Inc., America) at 78 K using liquid N_2. Before analysis, the catalyst samples were evacuated at 300 °C for 4 h under a vacuum of 1.33×10^{-3} Pa to remove all the adsorbed moisture from the catalyst surface and pores.

The nature of acid sites was determined by pyridine-adsorbed Fourier transformed infrared (Py-FTIR) spectrum experiments on a MAGNA-IR 560 FTIR instrument. Pyridine adsorption experiments were conducted on self supported wafers in an *in situ* IR cell. Samples were dehydrated at 500 °C for 5 h under a vacuum of 1.33×10^{-3} Pa followed by adsorption of purified pyridine vapor at room temperature for 20 min. The system was then evacuated at different temperatures and TR spectra were recorded. Total Lewis acidity and total Brönsted acidity, medium and strong Lewis acidity and medium and strong Brönsted acidity, and strong Lewis acidity and strong Brönsted acidity can be calculated after pyridine desorption at 200, 300 and 400 °C, respectively.

2.3. Catalytic performance tests

The catalytic performance tests were carried out in a flowing-type apparatus designed for continuous operation. This apparatus consisted of a gas feeding system controlled by a mass flowmeter and a liquid feeding system by a syringe pump. The reactor, with an internal diameter of 10 mm, was filled with the catalyst sample (ca. 6 g). There were three heating zones in the reactor, with the top one as the preheater. The temperature of each zone was independently controlled within ± 1 °C by thermostats. The temperature of the catalytic bed was measured by a thermocouple placed inside the reactor. The gas and liquid products were analyzed by an Agilent 1790 gas chromatograph (Agilent Shanghai Co., Ltd., P. R. China) installed with a flame ionization detector and a Hβ-PONA capillary column (50 m × 0.2 mm).

In all runs, the catalysts were brought to identical reaction conditions. The reactant FCC gasoline was fed into the reactor by a syringe pump at LHSV (liquid hourly space velocity) of 2 h^{-1}. At the total pressure of 2.0 MPa, pure hydrogen gas (10 ml/(min·gcat)) was mixed with the liquid feedstock and the reaction was carried out at temperature ranging from 270 to 330°C in steps of 30 °C. The reaction products were collected and analyzed for a time interval of 1 h. The coke deposited on the catalysts after the reaction was quantified by an automatic carbon analyzer (HV-4B, Wuxi Analysis Instruments Inc., P. R, China). The properties of the feeding FCC gasoline are listed in table 2.

3. Results and discussion

3.1. Catalyst Characterization

3.1.1. Pore structure measurements

Surface area, pore volume and pore size of the different catalysts are given in table 3. It can be seen that each parameter of the pore structure decreases with the decreasing Hβ content (or with the increasing HZSM-5 content) in the catalysts, indicating that Hβ has more micropores and capacious channel than HZSM-5, due to the unique topological structure of zeolite [19].

Referring to table 1, it is seen that the surface areas (366–356 m^2/g) and pore volumes (0.285–0.275 ml/g) of the different catalysts do not differ from each other with HZSM-5 addition ranging from 5 to 10 wt% (Catalysts A–C), but they decrease significantly when the HZSM-5 addition increases up to more than 20 wt% (Catalysts D–G), which are ascribed to the great difference between the pore structures of Hβ and HZSM-5. A small amount of HZSM-5 substituting for Hβ can not distinctly change pore properties of the catalysts, but with the increasing HZSM-5 substitution, the effect of HZSM-5 on the pore structure becomes so prominent as to take on an obvious pore characteristics of HZSM-5 in the catalysts.

3.1.2. *Acidity measurements*

To discriminate between Lewis and Brönsted acid sites, typical pyridine adsorption experiments followed by FTIR measurements were carried out. As shown in table 4, it is clear that Hβ has more Lewis acid sites (especially medium Lewis acid), while HZSM-5 has more Brönsted acid sites (especially strong Brönsted acid), though their total acidities are almost identical. It is also observed that the number of Brönsted acid sites gradually increases and that of Lewis acid sites smoothly decreases with the increasing HZSM-5 content in the catalysts, in agreement with the difference of acid properties between these two zeolites.

3.2. *Catalytic reaction performance*

3.2.1. *Acidity properties versus reaction performance*

Acidity properties play an important role in upgrading FCC gasoline via hydroisomerization and aromatization. Thus, establishing the relationship between acidity properties and reaction performance is helpful for optimizing the composition of the catalysts.

(1) The density of acid sites versus reaction performance
Here, the acid density of a catalyst is defined as total acidity divided by total surface area, and the *i*-paraffins (arenes) increment is defined as the difference of *i*-paraffins (arenes) amount between the feedstock and the product. Figure 1 shows the relationship between the acid density of the catalysts and hydroisomerization activity. It can be seen that as a whole, the increase of acid density reduces *i*-paraffins increment, but the trends for the three curves in figure 1 are different from each other. At 270 °C, there are one platform stage in the front of the curve and one slope stage at the tail part of the curve; at 330 °C, the reverse situation is observed; at 300 °C, only one slope stage exists. These phenomena are interpreted as follows: at low temperature, the increase in acid density hardly changes hydroisomerization activity due to the negligible occurrence of hydrogen transfer reactions, so the curve stays at the platform stage; however, these hydrogen transfer reactions can be greatly enhanced with the further increased acid density and thereby decrease the selectivity to i-paraffins. When the reaction temperature is raised to 300 °C, even a slight increase in acid density will lead to the smooth reduction of hydroisomerization activity and this trend holds for the whole curve because of the promoting effect of increasing temperature on hydrogen transfer reactions. Further increase in temperature to 330 °C results in the quick decrease of hydroisomerization activity with the gradual increase of acid density, and after the acid density reaches at 1.6 μmol/m^2, its effect on hydroisomerization activity becomes insignificant, suggesting that the side reactions such as cracking and dehydrogenation attain their maxima at this moment. Moreover, in the case of the same acid density, lower temperature favors hydroisomerization reaction, which is consistent with the exothermal nature of the reaction. In a word, lower reaction temperature and lower acid density are good for hydroisomerization.

Acid density influences not only hydroisomerization activity but also aromatization activity, The effect of acid density on aromatization activity is shown in figure 2. It can be seen that at 270 °C, aromatization activity continually increases with acid density, while there exist maxima on the other two curves with the further increase in reaction temperature. This is because at low temperature the increase of acid density causes stronger interactions between reactants (mainly olefins) and' acid sites, and thus accelerates arene generation. However, with the further increase in reaction temperature, too many acid sites contrarily reduce aromatization reaction (especially at high temperature) due to the massive occurrence of the side reaction (i.e., cracking). Meanwhile, it should be pointed out that the unlimited

Table 2
Properties of the feeding FCC gasoline

Density (20 °C) (g·cm^{-3})	S (ppm)	RON	Lumped composition (vol%)				
			n-paraffins	*i*-paraffins	olefins	napthenes	arenas
0.714	250	91.7	6.3	28.3	41.1	7.0	17.4

Table 3
Pore structure parameters of various catalysts

Catalyst	Surface area (m^2/g)			Pore volume (mlg)			Pore diameter (Å)
	Micropore	Meso- and macro-pore	Total	Micropore	Meso-and macro-pore	Total	
A	273	93	366	0.126	0.159	0.285	31.2
B	270	91	361	0.124	0.155	0.279	30.9
C	267	89	356	0.123	0.152	0.275	30.9
D	261	85	346	0.120	0.145	0.265	30.6
E	250	77	327	0.116	0.133	0.249	30.4
F	239	69	308	0.110	0.120	0.230	29.9
G	227	61	289	0.105	0.106	0.211	29.2

Table 4
Acidity properties of the different catalysts

Catalyst	Acidity (μmol/g)						
	Weak acid		Medium acid		Strong acid		Total
	Lewis	Brönsted	Lewis	Brönsted	Lewis	Brönsted	
A	72.6	81.4	207.6	54.2	48.4	64.4	528.6
B	70.3	81.6	197.9	54.4	46.2	78.0	528.4
C	68.0	81.8	188.3	54.5	43.9	95.9	532.4
D	63.4	82.2	169.1	54.8	39.5	118.9	527.9
E	54.2	83.1	130.7	55.4	30.6	173.4	527.4
F	45.4	83.9	94.3	55.9	22.2	225.1	526.8
G	35.7	84.8	53.8	56.5	12.9	282.5	526.2

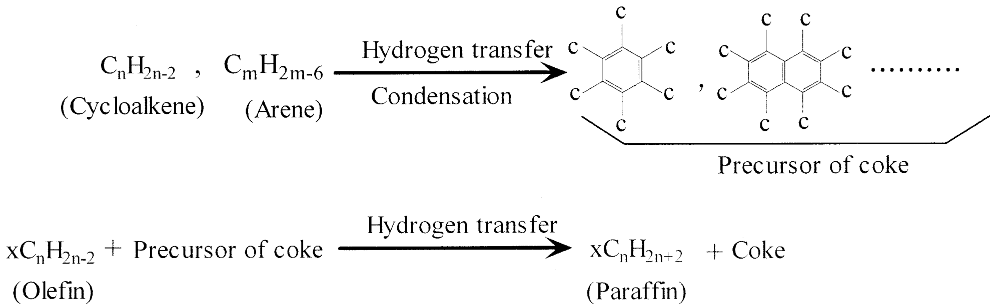
increase of acid density at low temperature is harmful to the stability of the catalysts, despite the fact that the increase of acid density can improve aromatization activity at low temperature.

It is known that hydrogen transfer can be divided into two types according to whether the desorption of arenes occurs [20,21].i.e.:

Type I:

$$3C_nH_{2n}(\text{Olefin}) + C_mH_{2m}(\text{Cycloalkane or Olefin}) \xrightarrow{\text{Hydrogen transfer}} 3C_nH_{2n+2}(\text{Alkane}) + C_mH_{2m-6}\ (\text{Arene})$$

Type II:



$$\underset{(\text{Olefin})}{xC_nH_{2n-2}} + \text{Precursor of coke} \xrightarrow{\text{Hydrogen transfer}} \underset{(\text{Paraffin})}{xC_nH_{2n+2}} + \text{Coke}$$

At low temperature, arenes mainly come from hydrogen transfer due to its exothermal nature. Appropriately increasing acid density promotes Type I hydrogen transfer reactions and restrains Type II hydrogen transfer reactions, but higher acid density will increase the concentration of protonated olefins and thus raise the probability of polymerization between protonated olefins and olefins (or cycloalkane) in gas phase as well as the probability of Type II hydrogen transfer reactions. In addition, higher acid density also enhances the adsorption of olefins and accelerates hydrogen transfer, so the hydrogen-deficient molecules formed via hydrogen transfer are very difficult to desorb from the catalyst surface and will continually evolve hydrogen until they are finally converted into coke. Therefore, suitable acid density is also very necessary even at low temperature. In addition, it is found that in the case of the same acid

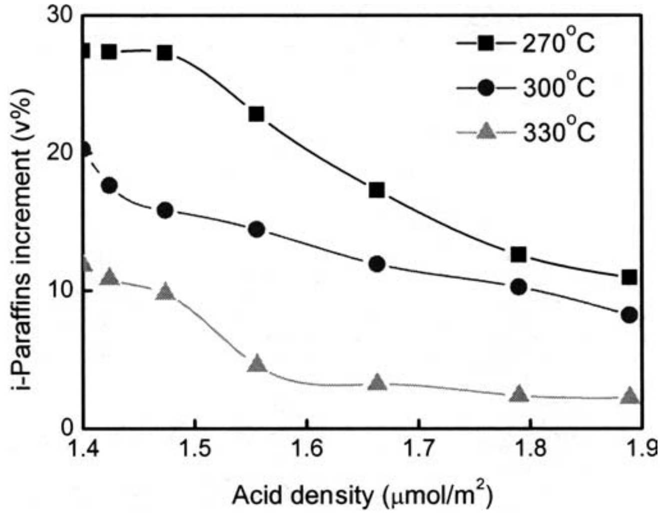


Figure 1. Effect of acid density on *i*-paraffins increment.

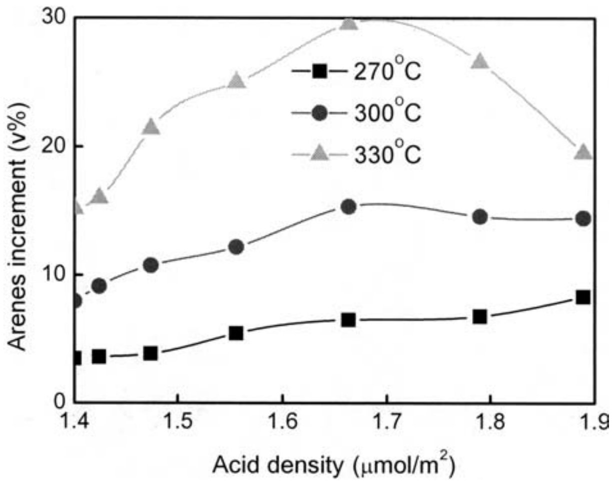


Figure 2. Effect of acid density on arenes increment.

density, higher temperature favors aromatization reaction, which is coincident with the endothermal nature of the reaction.

(2) Acid type and strength versus reaction performance
From table 4 it can be found that except for the two terms medium Lewis acid and strong Brönsted acid, the differences among the others are relatively small, so the discussion on these two terms will be emphasized.

At lower and higher temperatures (figure 3a and b), the more the number of medium Lewis acid sites is, the better the hydroisomerization activity is, just opposite to the effect of strong Brönsted acid. This difference is because strong Brönsted acid can promote hydrogen transfer reactions at low temperature and remarkably enhance cracking reactions at high temperature, which decreases the selectivity for hydroisomerization. Thus, for hydroisomerization medium Lewis acid is preferred. By comparing figure 3a with b, it is also noted that with

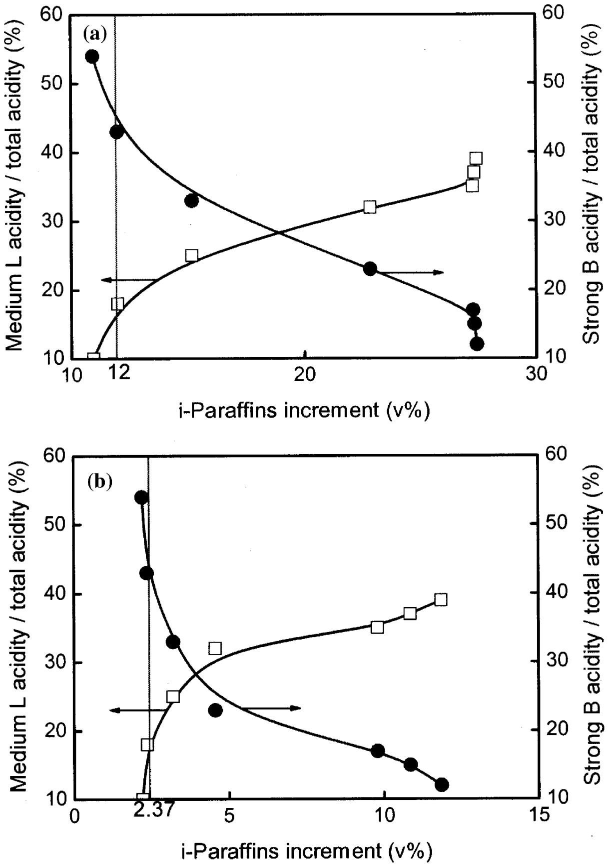


Figure 3. Effect of the ratios of medium Lewis acidity to total acidity and strong Brönsted acidity to total acidity on *i*-paraffins increment at (a) 270 °C and (b) 330 °C.

the same percentage of medium Lewis acid and strong Brönsted acid, the *i*-paraffins increment at low temperature is 12 vol%, much higher than 2.37 vol% obtained at high temperature. The reason for the different *i*-paraffins increment is that *i*-paraffins are prone to splitting into small molecules at high temperature, which lowers the selectivity for hydroisomerization. In summary, low reaction temperature and more medium Lewis acid sites are good for hydroisomerization.

The effect of the ratios of medium Lewis acidity to total acidity and strong Brönsted acidity to total acidity on *i*-paraffins increment at different temperatures is shown in figure 4. It is clear that the varying trends of the curves in figure 4a are completely different from those in figure 4b. At low temperature, Increasing medium Lewis acidity is harmful to improving aromatization activity, while the increase in strong Brönsted acidity is always in favor of augmenting arene content. The reasons for the above difference are as follows; more strong Brönsted acid sites enhance hydrogen transfer, the primary path to producing arenes at low temperature, and more medium Lewis acid sites boost hydroisomerization of olefins and lessen the participation of olefins in hydrogen transfer. At high temperature, there exists a turning point in the curve, suggesting that an appropriate acidity percentage is necessary to reach at the maximum aromatization activity. A suitable increase of medium Lewis acid sites can accelerate dehydrogenation of naphthenes and cyclo-alkenes and hence promote the generation of arenes, but the excessive increase of medium Lewis acid sites will lead to dehydrogenation of arenes to form coke, which decreases arene increment. As for strong Brönsted acid, despite that high temperature suppresses hydrogen transfer reactions from the point of view of thermodynamics, high temperature can significantly accelerate cyclization reactions catalyzed by strong Brönsted acid. The cyclization reactions result in the massive formation of cyclo-hydrocarbons and increase the concentration of reactants, and thus promote hydrogen transfer reactions. The moderate increase in strong Brönsted acid sites makes their promoting effect on hydrogen transfer surpass their impeding effect and thus increases the arenes increment. However, the excessive increase in strong Brönsted acid sites will bring about cracking reactions and decrease the concentration of cyclo-hydrocarbons; thus, their impeding effect predominates and thereby the arenes increment decreases. Moreover, comparing figure 4a with b, it can be seen that with the swine percentage of medium Lewis acid and strong Brönsted acid, the arenes increments at high temperature and at low temperature are 29.55 and 6.51 vol%, respectively, signifying that high temperature is advantageous for promoting aromatization activity. Briefly speaking, the synergism between medium Lewis acid sites and strong Brönsted acid sites provides the possibility to overcome their individual shortcomings to accomplish the best aromatization activity of the catalyst.

3.2.2. *Carrier composition of the catalysts versus reaction performance*

In order to clarify the effect of carrier composition on reaction performance, the catalysts consisting of different ratios of Hβ to HZSM-5 in carriers were prepared and as following:

$$\text{Conversion of olefins}(\%) = \frac{\text{olefins (vol\%) in feedstock} - \text{olefins (vol\%) in product}}{\text{olefins (vol\%) in fed stock}} \times 100$$

$$\text{Selectivity to particular hydrocarbons (\%)} \\ = \frac{\text{particularhydrocorbons (vol\%) in product} - \text{ particular hydrocorbons (vol\%) infeedstock}}{\text{olefins (vol\%) in feedstock} - \text{olefins (vol\%) in product}} \times 100$$

The relationship between the carrier compositions of the catalysts and reaction performance is shown in figure 5. As shown in figure 5a, in the mass, the olefins conversion decreases with the increasing HZSM-5 content or the decreasing Hβ content, and the higher reaction temperature is, the steeper the decreasing slope is. Increasing the HZSM-5 content or decreasing the Hβ content in the carriers leads to the narrowed pore channels of the catalysts (referring to table 3) and thus confines the diffusion of olefins, and results in the increased acid strength of the catalysts (referring to table 4) and hence strengthens the adsorption of olefins. Consequently, the adsorption of olefins on the catalysts is facilitated and the desorption is restrained, resulting in coke formation on acid sites (especially on those with strong acidity) [22] and poor olefins conversion. Obviously, the increasing temperature unavoidably gives rise to more serious dehydrogenation and carbon deposition on the catalysts, both contributing to the descending slope of the curves in figure 5a.

Figures 5b and c also indicates that the increasing HZSM-5 content or the decreasing Hβ content is always unfavorable for the conversion of olefins into *i*-paraffins due to the increased hydrogen transfer at low temperature and cracking at high temperature. Contrarily, the increasing HZSM-5 content or the decreasing Hβ content is good for the conversion of olefins into arenes because of the improved hydrogen transfer at low temperature and the accelerated cyclization and dehydrogenation at high temperature, except for the turning

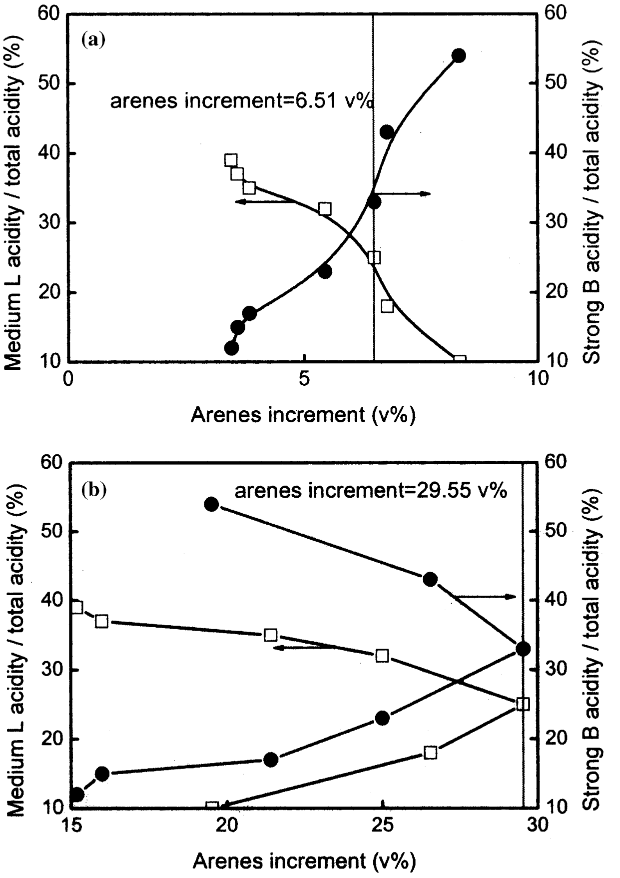


Figure 4. Effect of the ratios of medium Lewis acidity to total acidity and strong Brönsted acidity to total acidity on arenes increment at (a) 270 °C and (b) 330 °C.

point at 330 °C at which the rate of cracking is greater than that of the formation of arenas. Due to their differences in acidity and pore structure, relatively, Hβ has better olefins hydroisomerization ability, while HZSM-5 presents higher olefins aromatization ability. However, it should be noted that this feature of HZSM-5 may be counteracted by its much higher cracking activity compared to Hβ at all temperatures as shown in figure 6, more or less limiting its application to the aromatization upgrading of FCC gasoline because of the expensive processing cost involved. These results elucidate that neither single HZSM-5 nor single Hβ alone based catalysts may present satisfactory performance for the upgrading of FCC gasoline via hydroisomerization and aromatization, but a catalyst based on composite carriers consisting of HZSM-5 and Hβ with a suitable composition may hopefully provide a possible solution to satisfy the clear gasoline regulations.

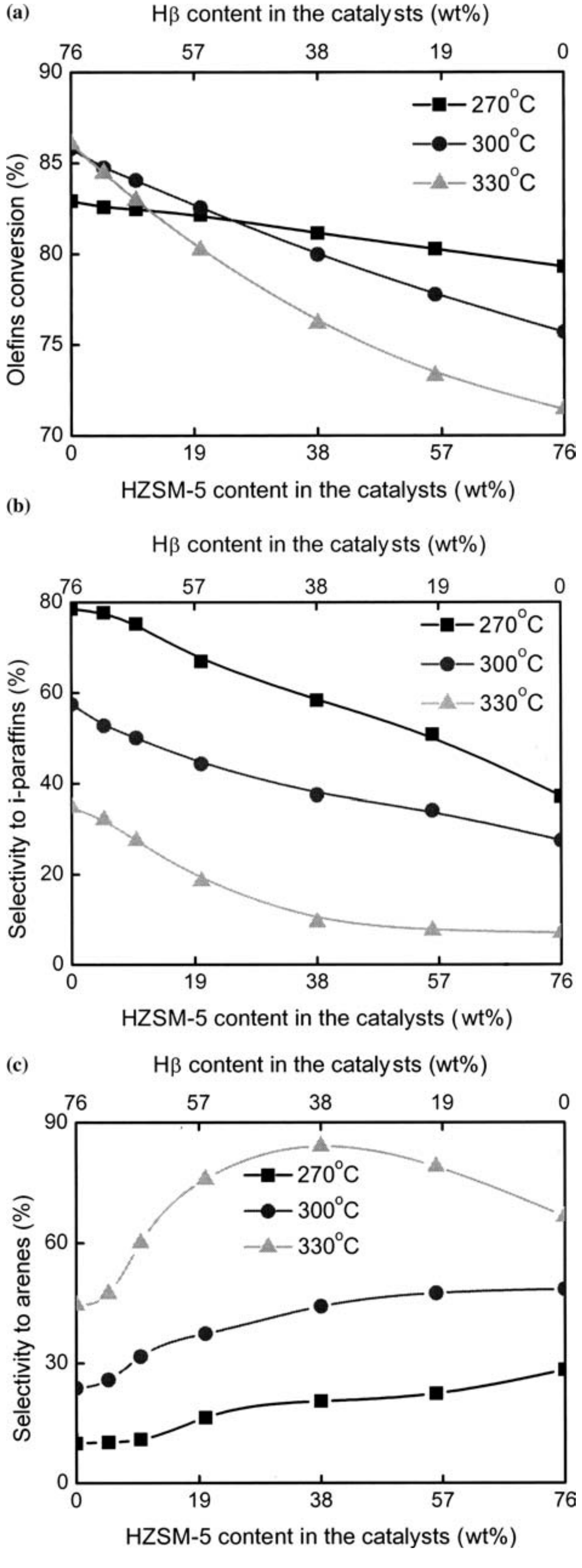


Figure 5. Effect of carrier composition on (a) olefins conversion; (b) selectivity to *i*-paraffins; and (c) selectivity to arenes at different temperatures.

3.2.3. *Comparison of overall reaction performance*

To search for the best ratio of Hβ to HZSM-5- in the composite carrier as described above, a series of cata-

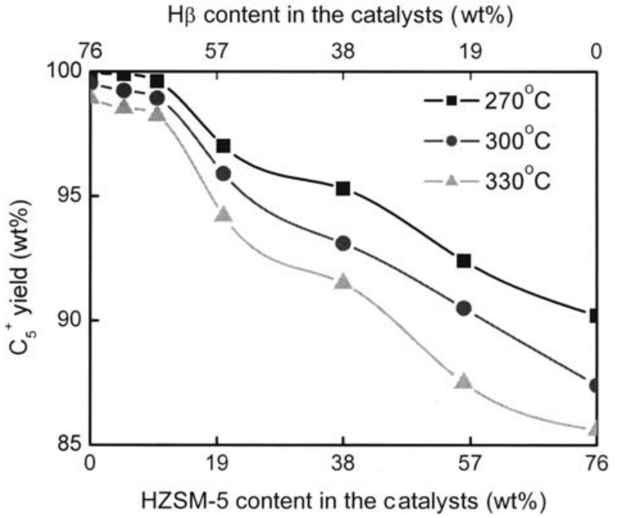


Figure 6. Effect of carrier composition on C_5^+ yield at different temperature.

lysts with different compositions were prepared and their overall reaction performances were compared. The typical results are listed in table 5.

Referring to table 1, it is evident that after run for 8 h, the catalyst base on single HZSM-5 (Catalyst G) becomes inactive in aromatization and gives the lowest *i*-paraffins content and RON among the five catalysts in table 5. The catalyst base on single H*β* (Catalyst A) shows excellent hydroisomerization activity (giving an increment of 16.2 vol% in *i*-paraffins content compared to that of the feedstock), moderate aromatization activity, and the highest liquid yield (99.5 wt%), but the product RON suffers a loss of 1.6, fully demonstrating the inability of hydroisomerization alone in preserving gasoline RON, in accordance with the results reported in the literatures [23,24]. Compared with the two catalysts above, Catalyst C based on the composite carrier with a ratio of H*β* to HZSM-5 at 6.6 displays good hydroisomerization activity and the optimum aromatization activity (giving an increment of 11.9 vol% in arenes content compared to that in the feedstock), and increases the product RON by 0.4, illustrating that the importance of aromatization in preserving gasoline RON. In view of the stringent regulations for the arenes content in gasoline, a combination of hydroisomerization with aromatization becomes the only method for FCC gasoline upgrading. In addition to the above-mentioned advantage, Catalyst C also offers higher liquid yield and lower coke deposition, presenting itself a potential catalyst system for commercial development for which the long-term stability is crucial. Although the product RON over Catalyst D, in which the ratio of H*β* to HZSM-5 in carrier is lower than 6.6, is almost identical to that of feedstock, Catalyst D has much lower liquid yield and much higher olefins content and coke deposition. On the contrary. Catalyst B, in which the ratio of H*β* to HZSM-5 is higher than 6.6, results in the product RON loss of 1.5 in spite of its higher liquid yield and lower coke deposition. All these data clearly reveal that the carrier composition, especially the HZSM-5 content, plays an important role in the hydroupgrading of FCC gasoline.

4. Conclusions

In order to develop a novel catalyst system to reduce the olefins content in FCC gasoline without loss in gasoline RON, different catalysts based on single- and binary-zeolite carriers were prepared and their catalytic performances for the hydroupgrading of FCC gasoline were studied. The results showed that acid properties of the catalysts were closely related to reaction performance. The low density of acid sites favored hydroisomerization of olefins and an appropriate acid density was desirable for improving aromatization activity. At low and high temperature, the conversion of olefins into *i*-paraffins could be promoted by more medium Lewis acid sites and restrained by more strong Brönsted acid sites, respectively; at low temperature, increasing

Table 5
Upgrading results of FCC gasoline over different catalysts*

Catalyst		Specification of Category 2					
		Unleaded Gasoline	A	B	C	D	G
Lumped composition (v%)	*n*-paraffins	–	10.9	10.1	8.8	8.5	8.5
	i-paraffins	–	44.5	44.2	43.1	40.2	36.9
	olefins	<20.0	9.8	10.4	9.9	15.9	27.0
	naphthenes	–	9.6	9.3	8.9	8.8	8.8
	arenes	<40.0	25.2	26.1	29.3	26.5	19.0
RON		–	90.1	90.2	92.1	91.6	87.2
C_5^+ yield (wt/o)		–	99.5	98.9	98.7	95.5	91.2
Coke content (mg/g cat)		–	23.5	23.9	24.6	33.9	49.9

*$P = 2$ MPa, $T = 315$ °C, LHSV $= 2$ h^{-1}, H_2/oil (v/v) $= 200$, $t = 8$ h,
Coke content – defined as m (coke) divided by m (cat.)

medium Lewis acid sites and strong Brönsted acid sites could weaken and strengthen the catalyst aromatization activity, respectively, but a suitable increase in both could greatly improve the aromatization activity at high temperature. The carrier composition played an important role in the hydroupgrading of FCC gasoline. The single HZSM-5 based catalyst provided outstanding initial activity, but poor stability for aromatization, while the single Hβ based catalyst showed good stability for both hydroisomerization and aromatization activities, but suffered from loss in product RON. Compared with single zeolite based catalysts, the Hβ/HZSM-5 composite carrier based catalysts with a suitable composition displayed balanced hydroisomerization and aromatization activity that contributed to the RON preservation when the olefins content in FCC gasoline was reduced, higher liquid yield and good stability, demonstrating that the Hβ/HZSM-5 composite carrier based Ni-Mo catalyst could be taken as a potential catalyst system for the hydroupgrading of FCC gasoline.

Acknowledgements

The authors acknowledge the financial support from Ministry of Science and Technology of China through the National Basic Research Program (No. 2004CB217807).

References

[1] B. Vavra, Nat. Petro. News 92 (2000) 16.
[2] R.A. Sanchez-Delgado, J. Mol. Catal. 86 (1994) 287.
[3] J.K. Lee and H.K. Rhee, Catal. Today 38 (1997) 235.
[4] Z.B. Wang, A. Kamo, T. Youeda, T. Komatsu and T. Yashima, Appl. Catal. A: Gen. 159 (1997) 119.
[5] F. S. Modica, US Patent 5233121(1993).
[6] A. Chica and A. Corma, J. Catal. 187 (1999) 67.
[7] K.J. Chao, H.C. Wu and L.J. Leu, Appl. Catal. A: Gen. 143 (1996) 223.
[8] Y. Adachi and M. Ueda, Petrotech. 15 (1992) 786.
[9] T. Ueda, Aromatics 44 (1992) 288.
[10] G. Giannetto, R. Monque and R. Galiasso, Catal. Rev. Sci. Eng. 36 (1994) 271.
[11] T. Kondoh, S. Inoue, K. Hirabayashi and S. Shibata, Zeolite News Lett. 9 (1992) 20.
[12] T.R. Hughes, W.C. Buss, P.W. Tamm and R.L. Jacobson, in: Proc.7th Int. Zeolite Conf. (Tokyo.1985) p. 725.
[13] K. Kato and S. Fukase, Sekiyu Gakkaishi 37 (1994) 77.
[14] D.E. Gantz and J.W. Hellwege, US Patent 3756942 (1973).
[15] I. Nakamura and K. Fujimoto, Catal. Today 31 (1996) 335.
[16] G.L. Price, V. Kanazirev, K.M. Dooley and V.I. Hart, J. Catal. 173 (1998) 17.
[17] Y. Ono, H. Nakatani, H. Kitagawa and E. Suzuki, Stud. Surf. Sci. Catal. 44 (1989) 279.
[18] Y. Nagamori and M. Kawase, Micropor. Mesopor. Mater. 21 (1998) 439.
[19] M.M.J. Treacy and J.M. Newsam, Nature (London) 332 (1988) 249.
[20] P.B. Venuto, L.A. Hamilton and P.S. Landis, J. Catal. 5 (1966) 484.
[21] P.B. Venuto and P.S. Landis, Adv. Catal. 18 (1968) 303.
[22] S.K. Sahoo, N. Viswanadham, N. Ray, J.K. Gupta and I.D. Singh, Appl. Catal. A: Gen. 205 (2001) 1.
[23] Y. Fan, X.J. Bao, G. Shi, W.S. Wei and J. Xu, Appl. Catal. A: Gen. 275 (2004) 61.
[24] Y. Fan, X.J. Bao, D. Lei, G. Shi, W.S. Wei and J. Xu, Fuel 84 (2005) 435.