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Skeletal isomerization of light FCC naphtha

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Abstract

The factors affecting the age of olefin skeletal isomerization catalyst are investigated. Molecular sieves with different acid strength and distribution show different activity and stability. Weak and moderate acid centers are responsible for the skeletal isomerization of olefin (SIO) and strong acid sites catalyze dimerization and cracking reaction under the test conditions. The pore structure of molecular sieve influences the products distribution significantly in the skeletal isomerization of 1-hexene. Choosing suitable modification methods to diminish external surface acid center could reduce the influence of external surface coke on molecular sieve activity. Under the same olefin saturation level, the octane loss of light FCC naphtha decreases remarkably by SIO comparing with direct hydrogenation.

Keywords: FCC naphtha; Hexene; Skeletal isomerization; Modification; External surface; Beta; ZSM-5

1. Introduction

To provide clean fuels is the main target of refineries in the next 15 years. Experimental data show that reducing sulfur and olefin content in gasoline may be one of the best ways to improve automobile emissions. The sulfur and olefin content in gasoline will be limited to less than 200 ppm and 20 vol.%, respectively, in China from 2003. More restrictive standards in 2006 less than 30 ppm of sulfur and 10 vol.% of olefin will be required for Chinese gasoline.

The components of the gasoline pool in a refinery vary from case by case. FCC naphtha in gasoline pool contributes about 75–80% in China comparing with 40% in the United States. On the other hand, approximately 90–98% of the sulfur and nearly all the olefin in the pool are from FCC naphtha. The olefin content in most of FCC naphtha is higher than 40 vol.%. Considering the capital investment and other factors, post-treating process becomes desirable schedule for achieving sulfur and olefin reduction in the pool. But the olefin saturation will lead to octane loss. So it is necessary to find effective ways to make up the octane loss for olefin reduction. Promoting olefin transferring into other high octane number compound, e.g. isomerizing liner olefin to branched olefin, especially multisubstituted olefin, then hydrogenation into isoparaffin, will minimize the octane loss.

There are a lot of research reports on the skeletal isomerization of olefin (SIO), especially for butene-1 to isobutene [1–5]. Considerable interest has been shown in this reaction because isobutene is the alkene precursor in the synthesis of methyl tertbutyl ether (MTBE) and ethyl tert-butyl ether (ETBE). But the study of C_5^+ olefin skeletal isomerization has been done a little. In this paper, the skeletal isomerization of 1-hexene and light FCC naphtha will be introduced.

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2. Experiment

2.1. Catalyst

Molecular sieves SAPO-11, *Y*, Beta, ZSM-5-*x* applied here are all in the acidic form, where *x* represents the Si/Al atomic ratio. Beta-Si-*x* is prepared by chemical liquid deposition (CLD) using $Si(OC_2H_5)_4$, where *x* represents the amount of deposition agent added (ml) per gram of Beta. Beta-EDTA-*x* is prepared by extraction aluminum using EDTA, where *x* represents the amount of EDTA added (g) per gram of Beta.

2.2. Catalytic reaction

The catalytic reactions were conducted in a fully automated fixed bed reactor with an on-line analytical system (G.C. Trace 2000) equipped with a 50 m OV-101 capillary column. The isomerization catalyst and hydrogenation catalyst are loaded in series. The reactant 1-hexene contacts first with isomerization catalyst and the effluent then come into the hydrogenation zone packing a commercial hydrogenation catalyst. The experiment conditions used in this work were $4.0\,h^{-1}$ WHSV, H_2/hydrocarbon ratio of 16 mol/mol, $14\,kg/cm^2$ total pressure, and reaction temperatures ranging from 523 to 643 K. In light FCC naphtha isomerization reaction, a 50 ml pilot plant was used. The isomerization catalyst and hydrogenation catalyst were also loaded in series. The isomerizaiton catalyst was Beta-Si-0.2 and the hydrogenation catalyst was a commercial NiW catalyst. The experiment conditions were $2.0\,h^{-1}$ WHSV, H_2/hydrocarbon ratio of 300 vol./vol., $14\,kg/cm^2$ total pressure, and reaction temperatures 563 K.

The conversion of 1-hexene, Conv. is calculated as follows:

$$\text{Conv.} = 100 - \left(\frac{A_{\text{hexane}}}{\sum A_{\text{all compounds in product}}}\right) \times 100$$

The yield of C_6^-, *iso*-C_6 and C_6^+, $Y_{C_6^-}$, $Y_{i\text{-}C_6}$, $Y_{C_6^+}$ are calculated as follows:

$$Y_{C_6^-} = \frac{\sum A_{C_6^-}}{\sum A_{\text{all compounds in product}}} \times 100, \quad Y_{i\text{-}C_6} = \frac{\sum (A_{\text{2-methylpentane}} + A_{\text{3-methylpentane}} + A_{\text{dimethylbutane}})}{\sum A_{\text{all compounds in product}}} \times 100,$$

$$Y_{C_6^+} = \frac{\sum A_{C_6^+}}{\sum A_{\text{all compounds in product}}} \times 100$$

Table 1
Thermodynamics equilibrium distribution (mol%) of hexene isomers at 600 K

Isomer	Distribution	Hydrogenated isomers	Distribution
1-Hexene	1.3		
Cis-2-hexene	2.9		
Trans-2-hexene	5.3		
Cis-3-hexene	1.4		
Trans-3-hexene	2.8	Hexane	13.7
2-Methylpentene	11.6		
4-Methylpentene	1.2		
2-Methyl-2-pentene	13.3		
Cis-4-methyl-2-pentene	3.2		
Trans-4-methyl-2-pentene	4.2	2-Methylpentane	33.5
3-Methylpentene	1.2		
Cis-3-methyl-2-pentene	19.4		
Trans-3-methyl-2-pentene	16.4		
2-Ethyl-butene	3.7	3-Methylpentane	40.7
2,3-Dimethyl-1-butene	5.3		
2,3-Dimethyl-2-butene	6.7		
3,3-Dimethyl-1-butene	0.3	Dimethylbutane	12.3

The selectivity of *iso*-C_6, $S_{iso\text{-}C_6}$ is obtained from

$$S_{iso\text{-}C_6} = \frac{\sum (A_{2\text{-methylpentane}} + A_{3\text{-methylpentane}} + A_{\text{dimethylbutane}})}{\sum A_{\text{all } C_6}} \times 100$$

The selectivity of dimethylbutane, S_{DMC_4} is obtained from

$$S_{DMC_4} = \frac{\sum A_{\text{dimethylbutane}}}{\sum A_{\text{all } C_6}} \times 100$$

2.3. *Equilibrium distribution*

Hexene isomers are composed of more than 17 components. The thermodynamic equilibrium distribution at 600 K is shown in Table 1 [6]. In GC analysis, the retention time of isomers is so close that they are very difficult to be separated. The products from hydrogenation zone are composing of only five compounds: 2,2-dimethylbutane, 2,3-dimethylbutane, 2-methylpentane, 3-methylpentane and hexane. The concentration of each is shown in Table 1. Experiments show that the hydrogenation catalyst (commercial RS-1 catalyst) has no skeletal isomerization activity.

3. Results and discussion

3.1. *Molecular sieves with different structure*

The acid amounts and strengths of different molecular sieves were determined by TPD of ammonia. The ammonia desorption peak temperature was used to characterize acid strength. From Table 2 we can see that the weak acid (NH_3-TPD desorption peak temperature less than 200 °C) and moderate acid (NH_3-TPD desorption peak temperature between 200 and 250 °C) strength is similar for different molecular sieves. But the amount of acid center and strength of strong acid (NH_3-TPD desorption peak temperature more than 250 °C) center are quite different.

Table 3
Product distribution of different molecular sieves

Molecular sieves	SAPO-11	*Y*	Beta	ZSM-5-90
Conv. (%)	84.8	34.1	81.9	85.2
$Y_{C_6^-}$ (%)	7.3	2.41	13.9	20.4
$Y_{i\text{-}C_6}$ (%)	76.5	31.7	65.3	57.7
$Y_{C_6^+}$ (%)	1.1	0.0	2.8	7.1
S_{DMC_4} (%)	5.0	0.0	9.1	2.7

The order of total acid amounts was ZSM-5-90 < SAPO-11 < Beta < *Y*; the order of weak and moderate acid amount was Beta < ZSM-5-90 ≈ SAPO-11 < *Y* and the order of strong acid strength was SAPO-11 ≪ ZSM-5-90 ≈ Beta ≈ *Y*.

Table 3 shows the yield of products and selectivity of dimethylbutane (DMC_4) in the reaction of 1-hexene over different molecular sieves. Among the catalysts tested, SAPO-11, Beta and ZSM-5-90 showed higher conversions (Conv.) for 1-hexene than *Y*. Among these three molecular sieves, SAPO-11 gave the highest *iso*-C_6 yield ($Y_{i\text{-}C_6}$) and Beta the highest DMC_4 selectivity (S_{DMC_4}), and ZSM-5-90 the highest cracking yield ($Y_{C_6^-}$).

The products from 1-hexene contained C_3, C_4, C_5, C_6 and C_6^+ compounds, without methane and ethane. The formation of C_4, C_5 and C_6^+ indicates that dimerization and the sequential cracking reaction took place during the reaction. There are two necessary factors for dimerization and cracking reaction, the first is that

Table 2
Acid distribution and acid strength of different molecular sieves

	Amount of acid center (acid strength) (mmol/g (°C))				
	Total acid	Weak acid	Moderate acid	Strong acid	Weak + moderate acid
Y	1.443	0.468 (178)	0.519 (226)	0.455 (364)	0.987
Beta	0.869	0.146 (173)	0.117 (221)	0.607 (349)	0.263
SAPO-11	0.533	0.228 (174)	0.064 (225)	0.241 (297)	0.292
ZSM-5-90	0.474	0.098 (172)	0.191 (224)	0.185 (361)	0.289

the space in the sieve should be large enough for reaction, the second is that the catalyst should have enough acid strength. The molecular sieves used in the present study could be classified into two types, 12-member ring (MR) and 10-MR, based on its channel window opening. Beta is in 12-MR form, which fit the first prerequisite. Large pore zeolite Beta without any products limitation has highest DMC_4 selectivity. ZSM-5-90 is in 10-MR form, but has intersecting channels with 9 Å diameter. Since the dimer molecules are too bulky to come out from the pore of ZSM-5, these must be converted to smaller molecule. At the same time, both Beta and ZSM-5-90 have strong acid center, which satisfy the second prerequisite of dimerization and cracking reaction.

The cracking product yield and C_6^+ products yield may be controlled by acid strength of acid center and pore structure together, which is similar with Xu' [7] opinion.

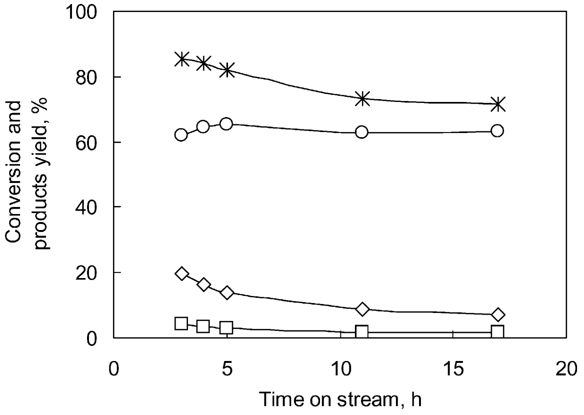
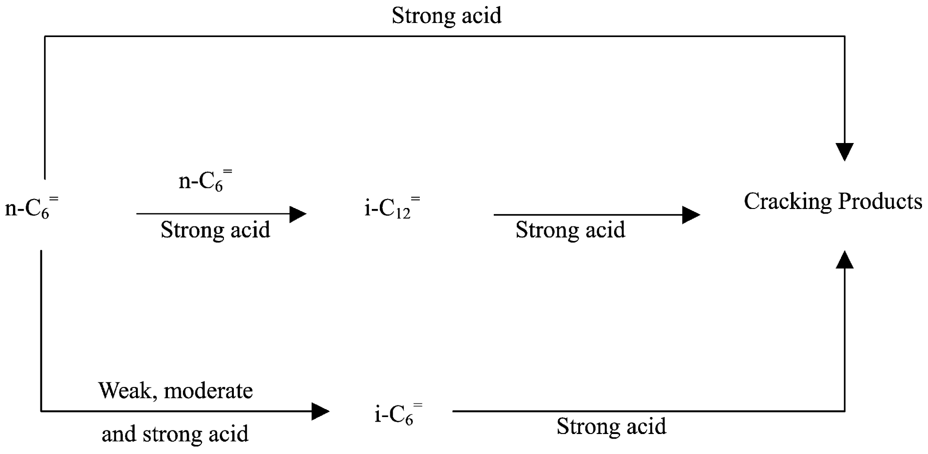


Fig. 1. The activity and products distribution of Beta vs. time on stream. (✳) Conv.; (◇) $Y_{C_6^-}$; (○) $Y_{i\text{-}C_6}$; (□) $Y_{C_6^+}$. Conditions: 4.0 h^{-1} WHSV, H_2/hydrocarbon ratio of 16 mol/mol, 14 kg/cm^2 total pressure, reaction temperature: 563 K.

SAPO-11 presents a unidimension system with 10-MR opening. The amount of acid center is close to ZSM-5-90, but the strength is much lower. So the dimerization cracking reaction is blocked. The 1-hexene conversion and *iso*-C_6 yield of SAPO-11 was quite close to Beta and ZSM-5-90, which was correlated to the amount of weak and moderate acid centers. For the case of Beta zeolite using in the reaction, the conversion of 1-hexene decreased from 85 to 70% after 11 h, then reached to steady state (see Fig. 1). Although the conversion change was remarkable, the *iso*-C_6 yield did not change much. As we know the strong acid centers are unstable because of coke deposition. The acid distribution of used zeolite had been examined, it was found that only weak and moderate acid centers survive. So it can be concluded that 1-hexene skeletal isomerization only needs weak or moderate acid centers. The relationships between product distributions and acid strength have been explained in Scheme 1.

Although *Y* is also a 12-MR zeolite like Beta, its activity is the lowest in sieves examined. The quick deactivation of *Y* is due to its large supercage which favoring the accumulation of coking precursor. The



Scheme 1.

Table 4
Acid amount and distribution of ZSM-5 with different Si/Al

	ZSM-5-10		ZSM-5-90	
	Temperature[a] (°C)	Acid amount (mmol/g)	Temperature[a] (°C)	Acid amount (mmol/g)
Weak acid	178	0.261	172	0.117
Moderate acid	235	0.132	230	0.175
Strong acid	349	0.321	360	0.182

[a] NH_3-TPD desorption peak temperature.

data shown in Table 3 were collected in 5 h on stream. It suggests that coke might be one of the most important factors influencing the product distribution and catalytic activity. The products yield are determined not only by molecular sieve pore structure but also by its coke resistance ability.

3.2. Influence of Si/Al

The effect of the Si/Al ratio of ZSM-5 on the catalytic activity and stability was studied. The acid amount and distribution of ZSM-5-10 and ZSM-5-90 are listed in Table 4. The amount of strong acid centers decreased with the increase of Si/Al ratio (ZSM-5-20 has a similar tendency). The acid strength of ZSM-5-90 was stronger than ZSM-5-10.

The catalytic activities and stabilities of ZSM-5-10, ZSM-5-20 and ZSM-5-90 are shown in Figs. 2, 3 and 4, respectively. ZSM-5-10 lost almost 50% activity in about 26 h on stream due to the deactivation of acid

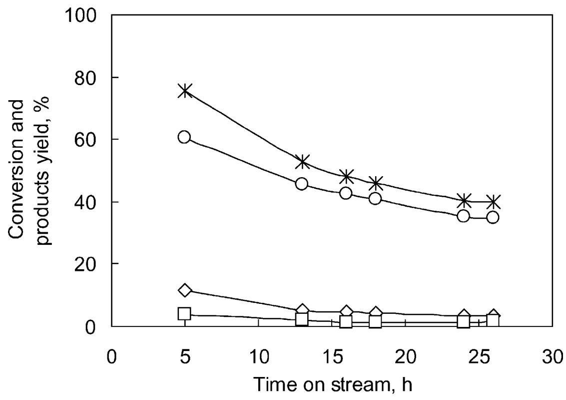


Fig. 2. The activity and products distribution of ZSM-5-10 vs. time on stream. (✱) Conv.; (◇) $Y_{C_6^-}$; (○) $Y_{i\text{-}C_6}$; (□) $Y_{C_6^+}$ Conditions: 4.0 h^{-1} WHSV, H_2/hydrocarbon ratio of 16 mol/mol, 14 kg/cm^2 total pressure, reaction temperature: 563 K.

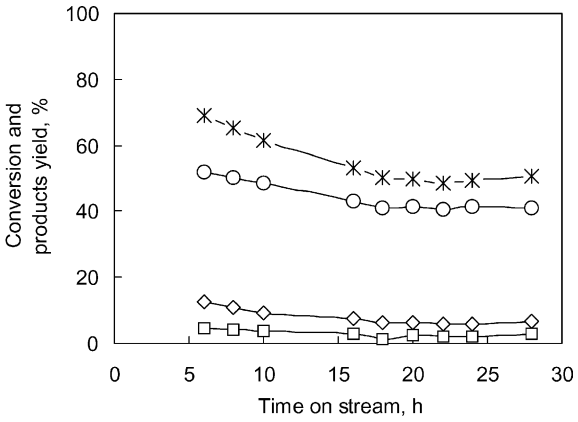


Fig. 3. The activity and products distribution of ZSM-5-20 vs. time on stream. (✱) Conv.; (◇) $Y_{C_6^-}$; (○) $Y_{i\text{-}C_6}$; (□) $Y_{C_6^+}$ Conditions: 4.0 h^{-1}WHSV, H_2/hydrocarbon ratio of 16 mol/mol, 14 kg/cm^2 total pressure, reaction temperature: 563 K.

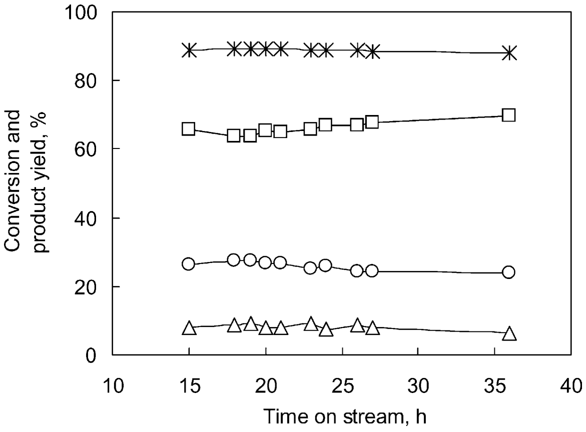


Fig. 4. The activity and products distribution of ZSM-5-90 vs. time on stream. (✱) Conv.; (◇) $Y_{C_6^-}$; (○) $Y_{i\text{-}C_6}$; (□) $Y_{C_6^+}$ Conditions: 4.0 h^{-1} WHSV, H_2/hydrocarbon ratio of 16 mol/mol, 14 kg/cm^2 total pressure, reaction temperature: 563 K.

sites resulting from carbonaceous deposit, especially for strong acid sites. The yield of isomers and cracked products also changed significantly. ZSM-5-20 lost almost 30% activity in about 28 h. The tendency of change is quite similar with ZSM-5-10. It is remarkable to note that ZSM-5-90 lost little its initial activity over 36 h. The isomer yield of ZSM-5-90 increased while the cracking yield decreased. High Si/Al ratio leads to high and stable *i*-C_6 yield versus time on stream, which means that zeolite with less acid center has good stability.

From the above discussion, we had concluded that olefin skeletal isomerization only needs weak and moderate acid centers. If the above discussion was correct, the ZSM-5-10 might have the highest conversion ability. Because ZSM-5 with low Si/Al ratio has much more weak and moderate acid centers. But the result is contrary to expectation. Studying the difference of ZSM-5 with different Si/Al, it is found that ZSM-5-10 and ZSM-5-20 are all hydrothermal synthesized, ZSM-5-90 is prepared by $(NH_4)_2SiF_6$ treatment using hydrothermal synthesized ZSM-5 as precursor. This may be the largest difference of ZSM-5 except SiAl ratio. The description of acid distribution (determined by Lutidine and NH3-IR) is as follow:

- Outer surface:
  The amount of acid center is ZSM-5-10 $>$ ZSM-5-20 $\gg$ ZSM-5-90.
- Inner surface:
  The amount of acid center is ZSM-5-10 $>$ ZSM-5-20 $>$ ZSM-5-90.

So we can see that the main difference of ZSM-5-10 and ZSM-5-90 is the amount of acid center on zeolite outer surface. Almost all the outer surface acid centers of ZSM-5-90 are eliminated.

Coke could be produced on outer and inner surface, but beginning from outer surface, the coking speed is much higher on outer surface than on inner surface. On the same position, strong acid center forms coke much easier than weak center. So the strong acid center on outer surface were poisoned by coke first, then moderate acid centers on outer surface, then the strong acid centers on inner surface, the last poisoned center is weak and moderate acid centers located on inner surface.

Even so, the activity of ZSM-5-10 should be higher than that of ZSM-5-90, because even all of the outer surface acid center on ZSM-5-10 lost, the inner acid amount is still higher than ZSM-5-90. We have to take the influence of outer surface coke into consideration. Because the channel of ZSM-5 is only 5.3 Å × 5.6 Å opening, the coke may narrow the pore size of ZSM-5. At the same time, more outer surface acid center lead to high coking tendency.

3.3. Influence of surface modification

Based on the above results, it is supposed that outer acid center may be the crucial factor leading to catalyst deactivation. To prove the hypothesis, $Si(OC_2H_5)_4$ (molecular diameter is about 0.92 nm) is used as modification agent to remove the outer acid centers of Beta, the treated zeolite named Beta-Si-0.2. Because most of surface of zeolite is in inner surface, contribution of outer surface to whole surface is little, after modification, the amount of acid center changes little. The catalytic activity and stability are shown in Fig. 5. During the reaction, *i*-C_6 selectivity of Beta-Si-0.2 was kept to be constant, and only a little bit lower than thermodynamics equilibrium. EDTA modification has the same effect on acid distribution comparing with Si modification. If increasing the amount of $Si(OC_2H_5)_4$, not only the outer surface acid would be overlaid, but also the pore diameter would be lessened. Since the shape of channel in Beta is bottle-like, the linear olefin would diffuse into the channel, but the *iso*-products could not diffuse out easily, which results in high coking

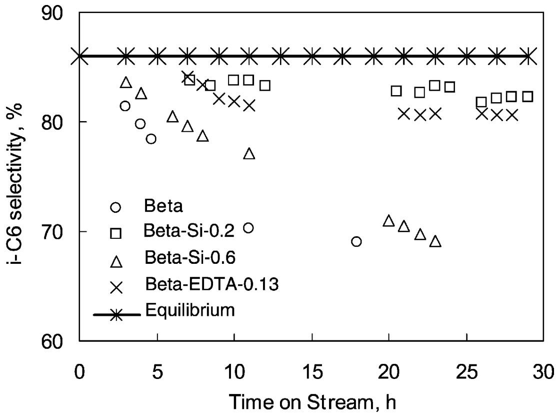
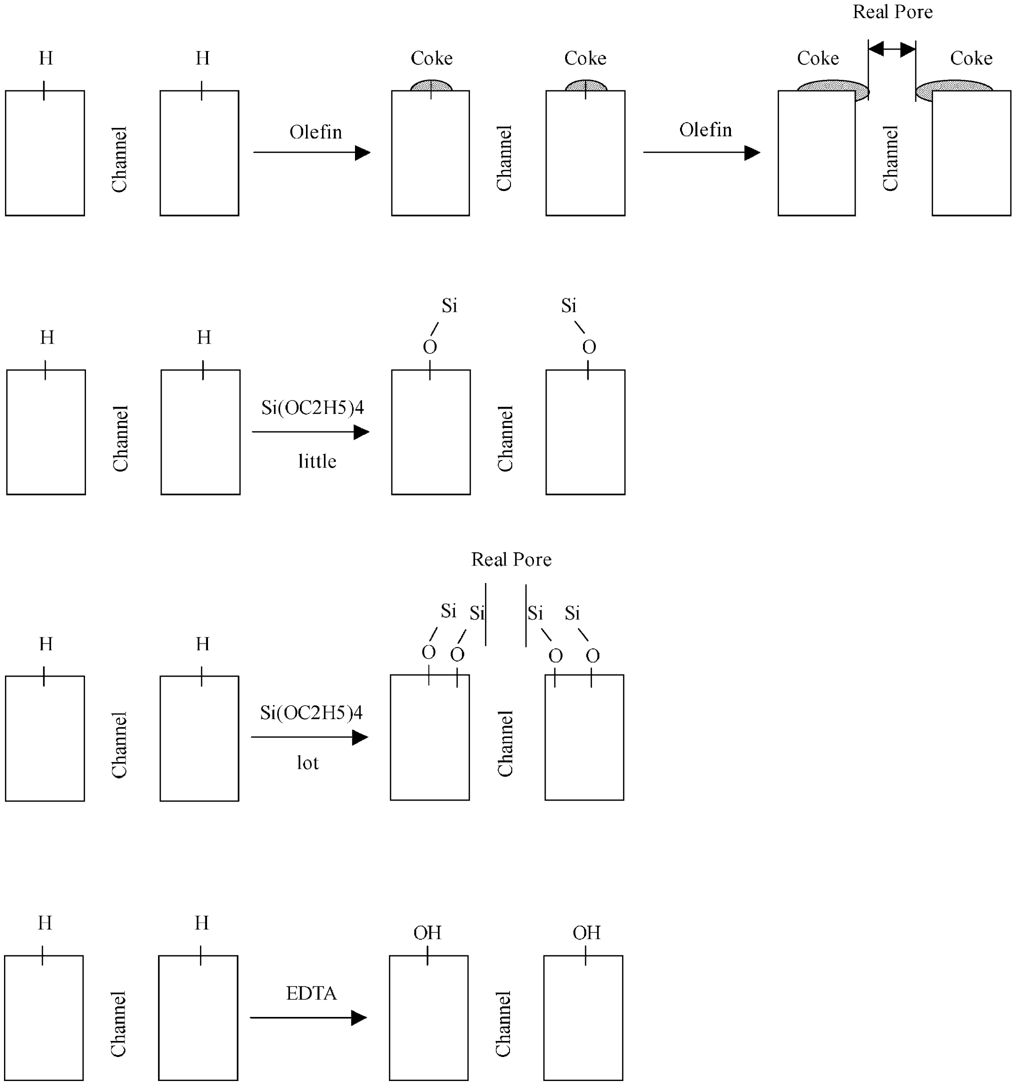


Fig. 5. $S_{iso\text{-}C_6}$ vs. time on stream over Beta with different modification method. Conditions: 4.0 h^{-1} WHSV, H_2/hydrocarbon ratio of 16 mol/mol, 14 kg/cm^2 total pressure, reaction temperature: 563 K.



Scheme 2.

possibility (see Beta-Si-0.6). The relationship among acid center, coke and real pore size of molecular sieves has been explained in Scheme 2, where H represents acid center, OH represents non-acid center.

3.4. The isomerization of FCC naphtha

The olefin distribution in typical RFCC naphtha was shown in Table 5. From this table, we can see that most of the olefin is light olefin, olefin with five carbon contribute about 15% to full range FCC naphtha, and olefin with 4, 5 and 6 carbon contribute about 60% to all olefin content.

The type of olefin in FCC naphtha is shown in Table 6. Most of the olefin is in linear or mono-substituted type. If they were saturated by hydrogenation, the products will be linear or mono-substituted paraffin with very low octane number. So it is necessary to convert linear olefin into branched olefins.

Because most of the olefin is concentrated on light distillation of FCC naphtha, the hydrogenation and isomerization following hydrogenation of light FCC

Table 5
Olefin distributions in FCC naphtha

	Olefin content in RFCC naphtha (wt.%)	Individual olefin distribution (wt.%)	Cumulative olefin distribution (wt.%)
C_4	3.5	6.6	6.6
C_5	15.0	27.9	34.5
C_6	13.1	24.5	59.0
C_7	8.9	16.5	75.5
C_8	5.9	11.0	86.5
C_9	4.3	8.1	94.6
C_{10}	2.3	4.3	98.9
C_{11}	0.6	1.1	100.0
Total	53.6	100.0	

Table 6
Olefin types in FCC naphtha

	Linear	Mono	Multi	Cyclo	Total
C_4	3.4				3.4
C_5	7.0	7.2		0.7	14.9
C_6	4.6	6.1	0.3	1.8	12.7
C_7	3.4	3.4	0.6	2.1	9.6
C_8	2.6	1.7		1.0	5.2
C_9	2.1	2.4		0.1	4.5
Total	23.1	20.8	0.9	5.7	50.4

naphtha is studied. The result is shown in Table 7. It is found that the light FCC naphtha after hydrogenation, the olefin content decreased significantly, paraffin is the main product, and the ratio of *iso*/*n*-paraffin is about 1.80. If the feed first was isomerized then hydrotreated, the *iso*/*n*-paraffin ratio was up to 3.27.

Analyzing the *iso*/*n*-paraffin ratio of different carbon number paraffin, it was found that after isomerization and the following hydrogenation, the *iso*/*n*-paraffin ratio in product is very close to equilibrium, and much higher than that of direct hydrogenation treatment (see Table 8). The C_6 selectivity in *iso*-hydrotreated FCC naphtha is also close to equilibrium (see Table 9).

Table 7
Product distributions of hydrotreated light FCC naphtha

PIONA	Feed	Direct-hydrotreated	*Iso*-hydrotreated
n-Paraffin (%)	5.1	32.3	21.5
i-Paraffin (%)	21.9	57.9	70.2
Olefin (%)	71.9	5.6	4.7
Naphthene (%)	0.8	3.9	3.4
Aromatics (%)	0.3	0.3	0.2
Iso/*n*-paraffin	4.3	1.8	3.3

Table 8
Iso/*n*-paraffin ratio in light FCC naphtha

	Feed	Direct-hydrotreated	*Iso*-hydrotreated	Equilibrium
i-C_5/n-C_5	4.0	1.1	3.9	4.0
i-C_6/n-C_6	4.5	1.9	5.7	6.3

Table 9
C^6 selectivity in *iso*-hydrotreated FCC naphtha

	Real result	Equilibrium
DMC_4 (%)	11	12
$2MC_5 + 3MC_5$ (%)	74	75
n-C_6 (%)	15	14

Table 10
Full range FCC naphtha properties

	Feed	Direct-hydrotreated	*Iso*-hydrotreated
RON	92.9	84.1	88.2
MON	80.3	75.7	77.6
RON loss		8.8	4.7
$(R + M)/2$ loss		6.7	3.7
Olefin (%)	53.63	27.4	28.0
Olefin saturation (%)		48.9	47.8

The advantage of isomerization in octane reservation was listed in Table 10. It is the result for the mixture of *iso*-hydrotreated light FCC naphtha and untreated heavy FCC naphtha. It was found the road octane $(R + M)/2$ loss is 3 units less comparing with direct hydrogenation. The RON loss decreases 4.1 units under the same olefin saturation level.

4. Conclusions

1. The olefin skeletal isomerization activity and stability will be good if the catalyst has only weak and less acid center. Dimerization and cracking reaction are catalyzed by strong acid center. The pore structure of molecular sieve affects the catalytic results significantly. All the knowledge relates to how to control the deactivation of catalyst.

2. The influence of external surface coke on molecular sieve activity could be reduced by choosing suitable means to diminish external surface acid center or by choosing molecular sieve with weak or moderate acidity.
3. The olefin isomerization of real FCC naphtha decreases the octane loss comparing with direct hydrogenation. It is an effective way to remove olefin from FCC naphtha for minimal loss in octane number.

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