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ZSM-5 zeolites with different SiO₂/Al₂O₃ ratios as fluid catalytic cracking catalyst additives for residue cracking

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ABSTRACT

Three proton-type ZSM-5 zeolites with different SiO₂/Al₂O₃ ratios (SARs) of 33, 266, and 487 were characterized and examined as fluid catalytic cracking catalyst additives for residue oil cracking. The catalytic performance of the ZSM-5 additives was evaluated using an ultra-stable Y-zeolite (USY)-based fluid catalytic cracking catalyst in a fixed fluid bed unit. As observed, the cracking of primary olefins over the hybrid catalysts consisting of USY-based catalyst and ZSM-5 additive was considerably inhibited by increasing the SAR of the ZSM-5 zeolite, thus avoiding substantial loss of gasoline paraffins. The introduction of ZSM-5 additives led to higher liquid petroleum gas yields as well as higher isobutane and isopentane yields. The improved yields were attributed to the combined effects of the ZSM-5 additives and USY-based catalyst. The variations of gasoline paraffins and aromatics both accounted for the enhancement in the octane number values. The use of ZSM-5 with higher SARs (266 and 487) led to an enhancement in the octane number with minimal loss of gasoline. This enhancement was mainly attributed to the moderate aromatization and isomerization reactivity of the ZSM-5 additives that mainly originated from their relatively small pores and suitable acidic properties with higher SARs.

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1. Introduction

Fluid catalytic cracking (FCC) is a key oil-conversion process in refineries, whereby the heavy oil is converted into valuable gasoline (C₅–C₁₂), light olefins (C₃–C₄), and other products in the presence of zeolitic catalysts. Primary cracking of heavy oil produces large quantities of olefins (primary olefins), and most of the generated olefins, usually C₅⁺ olefins, undergo secondary cracking owing to their high reactivity when adsorbed onto acidic catalysts at elevated temperatures. To improve the quality of gasoline, i.e., by achieving high octane numbers, or en-

hance the yield of light olefins, ZSM-5 zeolites have been widely used as FCC catalyst additives since the 1980s [1–4].

By changing the crystal size, the SiO₂/Al₂O₃ ratio (SAR), and the dosage of ZSM-5 zeolite, a high degree of flexibility to meet the requirements of refineries can be achieved toward the FCC process [5,6]. For instance, Kuehler [7] studied the cracking performance of additives containing ZSM-5 with different SARs. The results showed that using ZSM-5 with a SAR of 40 afforded a higher octane number, but simultaneously led to a substantial loss in gasoline. In contrast, high gasoline yields were maintained when ZSM-5 with higher SARs (550 and 850) were used.

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Buchanan et al. [5] investigated the effects of SAR on the selectivity of hexene/octene cracking. The authors proposed that the effects on reaction selectivity were mainly related to diffusional blockage especially by non-framework alumina, and that the density of acid sites was not important in determining the selectivity of the catalysts. Arandes et al. [8] demonstrated that using ZSM-5 zeolite as an FCC catalyst additive for residue cracking was effective toward increasing the contents of C₃- and C₄-olefins in the liquid petroleum gas (LPG) and C₅- and C₆-olefins in gasoline because of the predominant occurrence of cracking reactions by β -scission over hydrogen transfer reactions. Gao et al. [6] investigated the influence of ZSM-5 zeolite particle size on the yield of propylene. The authors found that a higher amount of propylene and a higher quality of gasoline could be obtained when small ZSM-5 particles were used as additives. Reddy et al. [9] examined the cracking of heptane over ZSM-5 featuring different morphologies and particle sizes. ZSM-5 nanosheets showed slightly lower catalytic activities than particulate ZSM-5, and the distribution of the hydrocarbon products was independent of the morphology of the ZSM-5 zeolites.

Despite this significant progress, a definite conclusion on the influence of SAR of ZSM-5 zeolites on the gasoline quality (i.e., octane number) in the cracking of residue oil has yet to be reached. Furthermore, using suitable ZSM-5 additives to improve the octane number of gasoline without incurring significant losses of gasoline or minimizing the production of LPG is essential, and is particularly important for FCC-operated refineries with limited gas handling capacity.

In this work, three proton-type ZSM-5 zeolites with different SARs were selected as catalyst additives for residue cracking under FCC conditions. The acidity of the zeolites was characterized by pyridine adsorption-based infrared (IR) spectroscopy (Py-IR) and ammonia temperature-programmed desorption (NH₃-TPD). The cracking of residue oil over the hybrid catalysts consisting of USY-based catalysts and ZSM-5 additives was performed in a fixed fluid bed reactor. The effects of SAR on the product distribution and the octane number of gasoline were investigated in detail.

2. Experimental

2.1. Preparation of catalysts

Three proton-type ZSM-5 zeolites with different SARs were purchased from Nankai Catalyst Plant, and directly used without any treatments. The SARs of the three types of zeolites, determined by inductively coupled plasma optical emission spectrometry (ICP-OES; Perkin Elmer, Optima 5300DV), are 33, 266, and 487, respectively, and are denoted as ZSM-5-l,

ZSM-5-m, and ZSM-5-h in the SAR order from low to high. The ZSM-5 additives were prepared as follows. The slurry comprising ZSM-5 (25 wt%), kaolin matrix (65 wt%), and alumina binder (10 wt%) with a liquid-to-solid mass ratio of 5 was thoroughly mixed and spray-dried to form microspheres with a typical particle size of 70 μ m. The additives were identified as Z-l, Z-m, and Z-h, correspondingly. Commercial USY-based FCC catalyst LEO-1000 (denoted as USY), supplied by PetroChina Ltd., was employed as the base catalyst to evaluate the effect of SAR on the catalytic cracking performance. The hybrid catalysts, containing 2.5 wt% ZSM-5 zeolite, were obtained by physical mixing of the USY-based catalyst and respective ZSM-5 additive, and are denoted as USY/Z-l, USY/Z-m, and USY/Z-h, respectively.

2.2. Sample characterization

X-ray diffraction (XRD) data were collected at ambient temperature in the 2θ range of 5°–80° with a step of 0.02° on a Rigaku D/max diffractometer with Cu K α radiation and equipped with a graphite monochromator. The crystal morphology was studied by scanning electron microscopy (SEM; Hitachi S4800). IR spectra of the zeolites following adsorption of pyridine (Py-IR) were recorded on a Bruker TENSOR27. NH₃-TPD was performed on a Micromeritics AUTOCHEM II 2920.

2.3. Catalytic cracking tests

The cracking of residue oil was performed at 500 °C for 60 s on a laboratory-designed fixed fluid bed unit. The hybrid catalysts were deactivated at 800 °C for 10 h in the presence of steam prior to the test. The catalyst loading and feedstock input were 200 and 50 g, respectively. The gaseous and liquid effluents were determined by gas chromatography (HP 6890). The paraffins (P), olefins (O), naphthenes (N), and aromatics (A) contents (PONA analysis) of cracked gasoline were analyzed by gas chromatography (Varian CP-3380). The amount of coke deposited on the catalyst was assessed by burning the sample in a carbon analyzer (DF 190). The properties of the residue oil are listed in Table 1.

3. Results and discussion

3.1. Zeolite characterization

Figure 1 shows the XRD patterns of the ZSM-5 zeolites with SARs of 33, 266, and 487 (ZSM-5-l, ZSM-5-m, and ZSM-5-h, respectively). All patterns were in good agreement with the orthorhombic phase of ZSM-5 zeolite. The relative crystallinity

Table 1
Properties of residue oil.

Item	MCR ^a (wt%)	Mr ^b (g/mol)	Viscosity ^c (mm ² /s)	Metal (μ g/g)								Saturate (wt%)	Aromatic (wt%)	Resin (wt%)	C (wt%)	H (wt%)	N (wt%)
				Ca	Cu	Pb	Ni	V	Fe	Na							
Value	4.17	473	17.27	6.94	0.27	0.03	6.52	9.59	5.16	200		63.0	33.6	3.4	84.97	12.64	0.11

^a Microcarbon residue; ^b Molecular weight; ^c Viscosity at 100 °C.

Fig. 1. XRD patterns of the ZSM-5 zeolites with SARs of 33 (ZSM-5-l), 266 (ZSM-5-m), and 487 (ZSM-5-h).

values of ZSM-5-l, ZSM-5-m, and ZSM-5-h were 91, 88, and 90 wt%, respectively, relative to the standard zeolite ZSM-5 reference.

Figure 2 shows the SEM images of the three ZSM-5 samples at different magnifications. The morphology of ZSM-5-m differed considerably from that of ZSM-5-l and ZSM-5-h. In contrast to the spherical features of the ZSM-5-m crystals, ZSM-5-h zeolite crystals, with a regular morphology, were primarily oriented along the *b*-axis [10–12]. Though the size of the crystals in ZSM-5-l varied, the morphology of the ZSM-5-l crystals was comparable with that of ZSM-5-h crystals.

Figure 3 displays the Py-IR spectra of the ZSM-5 zeolites. The peaks at 1452 and 1542 cm^{-1} were ascribed to pyridine attached to Lewis and Brönsted acid sites, respectively [13,14]. With increasing SARs, the density of both the Brönsted acid sites and Lewis acid sites declined markedly as observed in Fig. 3 and Table 2. ZSM-5-l, which featured a low SAR, displayed a higher content of Brönsted acid sites when compared with the other zeolite samples. Accordingly, it is expected that reactions, such as olefin cracking, that are catalyzed by Brönsted acid sites will occur predominantly.

Fig. 3. Py-IR spectra of the ZSM-5 zeolites with different SARs.

Table 2

Acidity of the ZSM-5 zeolites determined by Py-IR spectroscopy at 200 °C.

Zeolite	Brönsted sites ($\mu\text{mol/g}$)	Lewis sites ($\mu\text{mol/g}$)	Brönsted/Lewis
ZSM-5-l	535.4	42.1	12.7
ZSM-5-m	193.6	25.5	7.6
ZSM-5-h	28.3	5.5	5.2

Figure 4 shows the NH_3 -TPD profiles of the ZSM-5 zeolites with varying SARs. The ZSM-5 zeolites displayed two prominent desorption peaks at 232 and 442 °C, which were assigned to weak acid sites and strong acid sites, respectively [15]. An increase in SAR resulted in a marked decrease in the density of both acid sites, consistent with the Py-IR analysis of the zeolites.

3.2. Catalytic cracking tests

The fixed fluid bed data for residue cracking are given in Table 3. Under the given conditions, the USY-based catalyst achieved a gasoline yield of 49.60% and a LPG (sum of $\text{C}_{3\text{s}}$ and $\text{C}_{4\text{s}}$) yield of 16.52%. Hybrid catalyst USY/Z-l achieved a significantly higher LPG yield (up to 22.44%) and a considerably

Fig. 2. SEM images of the ZSM-5 zeolites at different magnifications. (a), (a'), ZSM-5-l; (b), (b') ZSM-5-m; (c), (c') ZSM-5-h.

Fig. 4. NH_3 -TPD profiles of the ZSM-5 zeolites with different SARs.

Table 3

Fixed fluid bed data for residue cracking over USY and hybrid catalysts.

Item	USY/Z-l	USY/Z-m	USY/Z-h	USY
Dry gas (wt%)	2.78	2.80	2.57	2.58
H_2	0.09	0.12	0.10	0.09
H_2S	0.15	0.16	0.16	0.16
CH_4	1.05	1.14	1.06	1.06
C_2H_6	0.53	0.55	0.53	0.56
C_2H_4	0.96	0.83	0.72	0.71
LPG ^a (wt%)	22.44	19.98	19.10	16.52
C_3H_8	2.26	2.11	1.80	1.55
C_3H_6	6.80	5.65	5.53	4.42
$n\text{-C}_4\text{H}_{10}$	1.29	1.35	1.24	1.20
$i\text{-C}_4\text{H}_{10}$	8.00	7.16	6.68	5.91
C_4H_8	4.09	3.71	3.85	3.44
C_5^+ Gasoline ^b (wt%)	42.76	44.10	46.40	49.60
LCO ^c (wt%)	16.56	17.25	16.59	16.81
HCO ^d (wt%)	6.56	6.84	6.57	5.92
Coke (wt%)	8.12	8.27	8.00	7.79
Total (wt%)	99.22	99.24	99.23	99.22
Conversion (wt%)	76.11	75.14	76.07	76.50

^a Liquid petroleum gas, combined total C_3 and C_4 ;

^b Cracked gasoline with the cut point (C_5 -200 °C);

^c Light cycle oil with the cut point (200–340 °C);

^d Heavy cycle oil above 340 °C.

lower C_5^+ gasoline yield of 42.76%. With increasing SARs, LPG yields decreased gradually (19.98% for USY/Z-m and 19.10% for USY/Z-h), and the loss of gasoline was considerably inhibited, achieving 44.10% and 46.40% yields for USY/Z-m and USY/Z-h, respectively.

Furthermore, the introduction of ZSM-5 additives attenuated the conversion level of feedstock because the pores of ZSM-5 were only 5–6 Å wide, insufficiently large for big molecules to enter. Compared with the USY-based catalyst, a slight decrease in the conversion degree of residue oil was detected in the presence of the hybrid catalysts. Moreover, the introduction of ZSM-5 additives had little influence on the formation of dry gas and coke, although relatively high gas and coke selectivity were observed over hybrid catalyst USY/Z-l.

It is widely recognized that the olefins in gasoline have a much higher reactivity when compared with the paraffins generated over acidic ZSM-5 catalysts [16,17]. Upon adsorption onto the acid sites of ZSM-5, especially on Brönsted acid sites,

the olefins initially interact with the acid sites to form the intermediate products, carbenium ions. These intermediate products react subsequently to yield smaller olefin molecules, including propylene and butenes, via a β -scission mechanism [17]. Consequently, the cracking of gasoline olefins declines with decreasing densities of Brönsted acid sites (increase in SAR), and more gasoline olefins are saturated by hydrogen atoms via intermolecular hydrogen transfer reactions. Hence, we may deduce that the significant changes in the catalytic properties of the three hybrid catalysts are mainly related to the change in the acidity of the ZSM-5 additives due to the change in the SAR.

Other factors, such as the particle size and morphology of ZSM-5 zeolite, may also influence the selectivity of the catalysts. It was previously reported that compared with the FCC catalyst containing typical ZSM-5 zeolite (average particle size of 5.48 μm), the catalyst containing small particles (average particle size of 1.99 μm) could lead to increases in the LPG and propylene yields by 0.41% and 0.08%, respectively [6]. By studying the effects of the morphology and the particle size of ZSM-5 on the catalytic performance for heptane, Baba and co-workers found that ZSM-5 nanosheets showed a slightly lower catalytic activity than particulate ZSM-5 (17.6% vs. 17.8%), and the distribution of the hydrocarbon products was independent of the morphology of ZSM-5 [9]. According to these literature results, we can conclude that differences in the particle size and morphology of ZSM-5 zeolites can also influence the selectivity of the catalysts to a certain extent, however, such differences would not entirely account for the significant changes in the catalytic performance of the hybrid catalysts.

To further understand the effect of SAR of the ZSM-5 zeolites on the selectivity of the hybrid catalysts, the SAR dependency of $\Delta\text{C}_{ns}/\text{C}_{ns}(\text{USY})$ ($n = 3, 4$) of the hybrid catalysts is shown in Fig. 5. The high $\Delta\text{C}_{3s}/\text{C}_{3s}(\text{USY})$ values suggested that ZSM-5 zeolite had a higher C_{3s} selectivity relative to C_{4s} , and the highest $\Delta\text{C}_{3s}/\text{C}_{3s}(\text{USY})$ value of 50% was attained over the hybrid catalyst USY/Z-l. The $\Delta\text{C}_{ns}/\text{C}_{ns}(\text{USY})$ values decreased with increasing SARs. The cracking of gasoline occurring in the pores of ZSM-5 zeolite was acid-catalyzed, accordingly, the decline in $\Delta\text{C}_{ns}/\text{C}_{ns}(\text{USY})$ was mainly due to a decrease in the acid density

Fig. 5. SAR dependence of $\Delta\text{C}_{ns}/\text{C}_{ns}(\text{USY})$ ($n = 3, 4$) of the ZSM-5 zeolites. (C_{3s} , combined propane and propylene, wt%; C_{4s} , combined n -butane, i -butane and all butenes, wt%).

of the ZSM-5 zeolites. The sharper decline in $\Delta C_{3s}/C_{3s}(\text{USY})$ with increasing SARs, relative to $\Delta C_{4s}/C_{4s}(\text{USY})$, may result from a decrease in the extent of cracking of C_6 olefins that is believed to have a higher C_{3s} selectivity over C_{4s} , and declines more drastically when compared with gasoline olefins with higher carbon numbers [16–18]. Additionally, other factors, such as the difference in the morphology of ZSM-5 crystals, may contribute to the change in $\Delta C_{ns}/C_{ns}(\text{USY})$ because the morphology of ZSM-5 crystals has been reported to influence product selectivity [19,20].

Previously, Madon proposed that ZSM-5 zeolites could catalyze both normal and branched olefin cracking to give propylene, butenes, 2-methyl 1-butene, and 2-methyl 2-butene [21]. In the present work, the following interesting phenomenon was noted: besides these light olefins, the yields of isobutane and isopentane increased markedly in the presence of ZSM-5 zeolite catalysts. The highest yields of isobutane and isopentane were obtained in the presence of hybrid catalyst USY/Z-1 as shown in Table 3 and Fig. 6. According to the related literature reports [16–18], the cracking of normal octene over Brönsted acid sites mainly involves the intermediate formation of carbenium C_8^+ . As shown in Scheme 1, carbenium C_8^+ can undergo β -scission (cleavage of C–C bond at the β -position to the positively charged atom) to form smaller olefins and a smaller carbenium (not shown in Scheme 1), or react with other paraffin molecules via intermolecular hydrogen transfer. The smaller carbenium may further release a hydrogen cation to form another olefin, or react with paraffin in close proximity. Because of the narrow pore and low acid density of ZSM-5 zeolites, the carbenium C_8^+ reacts to predominantly form smaller olefins, including propylene, butenes, and pentylenes. As the shift of the double bond in the olefins occurs easily at elevated temperatures, large amounts of isobutene and isopentene are obtained during the cracking reactions. When these olefins are subsequently adsorbed onto the USY-based catalyst with a high density of acid sites, they are saturated by hydrogen atoms through intermolecular hydrogen transfer to form isobutane and isopentane.

The results of the PONA analysis and the octane number of cracked gasoline are shown in Table 4. The presence of ZSM-5 additives had pronounced effects on the gasoline composition, especially paraffins and aromatics. The reduction of paraffins

Fig. 6. SAR dependence of isobutane and isopentane yields of the ZSM-5 zeolites.

Scheme 1. Possible cracking routes of normal octene molecules over ZSM-5 zeolites.

appears to be inconsistent with the fact that the reactivity of olefins over ZSM-5 zeolites is much higher than that of paraffins [17]. To rationalize this finding, it is necessary to understand the interaction mechanism between the USY-based catalyst and ZSM-5 additives. Primary cracking of the feeds produces large quantities of gasoline olefins, which would be saturated via intermolecular hydrogen transfer over the USY-based catalyst. Upon introduction of ZSM-5 additives with low SAR (i.e., 33), the gasoline olefins with a high reactivity could be easily converted into light olefins, thus consequently leading to reduced yields of gasoline paraffins. With increasing SARs, the cracking of gasoline olefins over ZSM-5 additives declines, and more olefins are preserved and then saturated by hydrogen atoms over the USY-based catalyst. Furthermore, the extent of cracking of gasoline aromatics over the hybrid catalysts is relatively low, which could lead to increased concentrations of aromatics. The aromatization of hydrocarbon molecules over the hybrid catalysts may also contribute to the increase in the aromatics concentration. As a result, the motor octane number (MON) values of gasoline, which are mainly determined by the aromatics concentration, increased upon introduction of the ZSM-5 additives. These values decreased gradually with increasing SARs (Table 4).

Notably, the research octane number (RON), which is one of the most important indexes of gasoline, could be improved upon introduction of the ZSM-5 additives (Table 4). The use of ZSM-5 additives increased the RON value of gasoline from 88.6 (over the USY-based catalyst) to 91.1 (USY/Z-1), 91.7

Table 4
PONA analysis and octane number of cracked gasoline.

Item	USY/Z-1	USY/Z-m	USY/Z-h	USY
<i>n</i> -Paraffins (%)	2.82	2.88	3.09	3.45
Isoparaffins (%)	34.86	37.68	40.05	43.14
Cyclo-olefins (%)	2.02	1.88	1.78	1.52
Iso-olefins (%)	7.02	7.02	7.74	7.22
<i>n</i> -olefins (%)	3.12	2.98	3.59	3.38
Naphthenes (%)	10.89	10.03	10.11	10.00
Aromatics (%)	39.26	37.53	33.65	31.29
RON ^a	91.1	91.7	90.2	88.6
MON ^b	84.2	83.9	83.2	81.4

^a Research octane number; ^b Motor octane number.

Graphical Abstract

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ZSM-5 zeolites with different SiO₂/Al₂O₃ ratios as fluid catalytic cracking catalyst additives for residue crackingPusheng Liu, Zhongdong Zhang, Mingjun Jia, Xionghou Gao*, Jihong Yu*
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Higher SARs led to reduced cracking of primary olefins over ZSM-5 additives. Using ZSM-5 with SARs of 266 and 487 efficiently enhanced the octane number of gasoline with minimal loss of gasoline.

(USY/Z-m), and 90.2 (USY/Z-h). However, as mentioned before, a substantial loss in gasoline was observed in the presence of hybrid catalyst USY/Z-l. In contrast, the loss of gasoline was considerably inhibited by increasing the SAR to 266 or 487. These results suggest that changing the SAR of ZSM-5 zeolites enables the formation of efficient hybrid FCC catalysts, which can improve the octane number of gasoline without substantial loss of gasoline. In our study, the enhancement in the RON value of gasoline was mainly attributed to the moderate aromatization and isomerization reactivity of the ZSM-5 additives that are mainly attributed to the relatively small pores and suitable acidic properties of the ZSM-5 zeolites with higher SARs.

4. Conclusions

The cracking of residue oil was investigated over hybrid catalysts comprising USY-based catalysts and ZSM-5 additives. The product distributions over the hybrid catalysts were rationalized in terms of the acid properties and olefin cracking reactions involved. The cracking of primary olefins over the hybrid catalysts was considerably inhibited by increasing the SAR of the ZSM-5 zeolite that inhibited substantial loss of gasoline paraffins. The introduction of ZSM-5 additives led to increased yields of olefinic gases as well as higher yields of isobutane and isopentane, which may be attributed to the combined effects of ZSM-5 additives and USY-based catalysts. MON values, which are mainly influenced by the concentration of gasoline aromatics, increased with increasing densities of acid sites on ZSM-5 zeolites. The variations of the gasoline paraffins and aromatics both accounted for the enhancement of the RON values. Using ZSM-5 zeolites with higher SARs of 266 and 487 resulted in octane enhancement with minimal loss of gasoline. The current findings provide insight into the development of more efficient FCC catalyst additives for octane enhancement with minimal loss of gasoline.

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不同硅铝比ZSM-5分子筛作为助催化剂在渣油裂化中的应用

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摘要: 采用不同方法表征了硅铝比($\text{SiO}_2/\text{Al}_2\text{O}_3$)为33、266和487的质子型ZSM-5分子筛, 并研究了ZSM-5分子筛作为助催化剂在渣油裂解中的应用. 与USY分子筛基催化剂混合后, 在固定流化床上, 评价了ZSM-5分子筛助催化剂的催化裂化性能. 研究发现, 提高ZSM-5分子筛硅铝比, 可以有效抑制混合催化剂对汽油烯烃的裂解, 从而避免了汽油烷烃的大量损失. 加入ZSM-5助催化剂后, 伴随着液化气(LPG)产率的增加, 异丁烷和异戊烷产率增加, 这可能是由USY基催化剂和ZSM-5助催化剂的综合效应引起的. 汽油烷烃和芳烃含量的变化, 引起了汽油辛烷值的增加. 高硅铝比ZSM-5分子筛(硅铝比为266和487)不仅可以显著改善汽油的辛烷值, 而且有效避免了汽油的大量损失. 催化汽油辛烷值的改善主要是由于高硅铝比ZSM-5分子筛具有适宜的芳构化和异构化活性, 这些变化主要源于高硅铝比ZSM-5分子筛小的孔道直径和适宜的酸性.

关键词: 催化裂化; ZSM-5分子筛; 渣油; 辛烷值

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