A Process for Producing Ultraclean Gasoline by Coupling Efficient Hydrodesulfurization and Directional Olefin Conversion

Yu Fan
State Key Laboratory of Heavy Oil Processing, Dept. of Chemical Engineering, China University of Petroleum,
Beijing 102249, P.R. China

The Key Laboratory of Catalysis, China National Petroleum Corporation, Dept. of Chemical Engineering,
China University of Petroleum, Beijing 102249, P.R. China

Gang Shi
The Key Laboratory of Catalysis, China National Petroleum Corporation, Department of Chemical Engineering,
China University of Petroleum, Beijing 102249, P.R. China

Xiaojun Bao
State Key Laboratory of Heavy Oil Processing, Dept. of Chemical Engineering, China University of Petroleum,
Beijing 102249, P.R. China

The Key Laboratory of Catalysis, Dept. of Chemical Engineering, China National Petroleum Corporation,
China University of Petroleum, Beijing 102249, P.R. China

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To solve the contradiction between ultradeep hydrodesulfurization (HDS) and octane recovery in clean gasoline production, this article proposes a novel two-stage fluid catalytic cracking (FCC) gasoline hydro-upgrading process with the selective HDS catalyst in the first reactor and the complemental HDS and octane recovery catalyst in the second reactor. The process achieved the relayed removal of sulfur-containing compounds with different natures, providing itself with excellent HDS performance, and the hydroisomerization and aromatization of olefins in the second stage endowed the process with superior octane recovery ability and high product yield while remarkably reducing the olefin content of FCC gasoline. The process was also featured by low hydrogen consumption due to the low first-stage olefin saturation and the balanced second-stage hydrogenation and dehydrogenation. The two-stage process developed here sheds a light for efficiently producing ultralow sulfur gasoline from the poor-quality FCC gasoline of high olefin and sulfur contents. © 2012 American Institute of Chemical Engineers *AIChE J,* 59: 571–581, 2013

Keywords: FCC gasoline, two-stage process, ultradeep hydrodesulfurization, olefin reduction, octane recovery

Introduction

Increasingly stricter environmental regulations on exhaust emissions of gasoline-powered transportation vehicles are compelling refiners over the world to produce gasoline with low or even ultralow sulfur and olefin contents. This is because sulfur-containing compounds are responsible for SO_x emission that leads to the formation of acid rain and sulfate aerosols, and gasoline-range olefinic hydrocarbons have been demonstrated to contribute to the formation of photochemical smog in susceptible urban areas.[1,2] Therefore, removal of sulfur-containing compounds and olefins in gasoline has become a key and common focus both in the petroleum refining industry and environmental catalysis. It has been widely recognized that hydrotreating is the most important technique for producing clean transportation fuels in industrial pratice.[3,4] Moreover, it is well known that for diesel fuels increasing hydrotreating severity (e.g., by increasing operating pressure or/and temperature) can realize both deep desulfurization and cetane improvement,[5,6] but for gasoline fuels, especially fluid catalytic cracking (FCC) gasoline, this may cause excessive hydrogenation of olefins in gasoline, giving rise to serious octane loss.[7,8]

In most Asian countries, such as China, FCC gasoline with high sulfur and olefin contents usually takes a share of about 75% in commercial gasoline pool. In view of the negligible sulfur and olefin contents in the other gasoline blending components (such as reforming gasoline, alkylation gasoline, and isomerization gasoline) excluding FCC gasoline, more than 90% of sulfur-containing compounds and about 90% of olefins in typical refinery gasoline pools come from FCC gasoline, so the sulfur and olefin reduction of this stream plays an important role in clean gasoline production.[2] Selective hydrodesulfurization (HDS) technology with high

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Correspondence concerning this article should be addressed to Y. Fan at fanyu@cup.edu.cn.

HDS ratio and low olefin saturation is desired to meet the requirement for moderate desulfurization,[9] such as SCANfining[10,11] and Prime-G.[12,13] However, such selective HDS techniques have two drawbacks when applied to ultradeep HDS. On the one hand, application of selective HDS to ultradeep HDS inevitably leads to uncontrollable saturation of olefins and increased octane loss, especially for FCC gasoline with high olefin content (e.g., $\geq$40 vol %); on the other hand, great olefin reduction is also desirable for producing ultraclean gasoline, so only selective HDS with low olefin saturation cannot guarantee the achievement of strict specifications on ultraclean gasoline. In most Asian countries, such as China, FCC gasoline has the olefin content as high as 40–50 vol %, so olefin reduction is as important as sulfur reduction for ultraclean gasoline production. In view of the aforementioned disadvantages of various selective HDS techniques, several combined processes by coupling FCC gasoline hydrofining and octane recovery, such as Oct-Gain[14] and Isal,[15,16] have been developed. In the two processes mentioned, ultradeep HDS that is unavoidably accompanied with complete saturation of high-octane olefins was performed at the first, and then the octane loss due to complete olefin saturation was compensated by partly hydroisomerizing and cracking paraffins formed from olefin saturation, which consequently results in low gasoline yield (about 90%) due to excessive cracking, high hydrogen consumption due to the complete saturation of olefins, and large loss in product research octane number (RON $>$1.5).[17]

The above analyses suggest that the existing techniques can hardly accomplish the objectives of ultradeep HDS and olefin reduction of FCC gasoline with acceptable RON loss. On the basis of our previous works, the following perceptions have been gained for solving this problem: the capability to cleanse FCC gasoline requires a thorough understanding about the characteristics of this largest component in gasoline pool, the relationship between octane loss and hydrocarbon composition, and the wide differences in the desulfurization reactivities of the various sulfur-containing species in FCC gasoline. The combination of these factors requires an integration of suitable technologies, in which each technology is chosen in terms of the unique characteristics of the particular fraction of the FCC gasoline being processed. More specifically, we found that:

(1) To achieve ultradeep HDS of FCC gasoline over a single catalyst loaded in a single reactor seems an impossible task, because the sulfur-containing compounds with different natures require the different catalysts that should be tailor-made and operated under suitable conditions; more importantly, to achieve complete sulfur removal in a single reactor either by increasing catalyst activity or by increasing operation severity is bound to give rise to concomitant olefin saturation and thereby great octane loss. This suggests that a combined catalyst system that realizes relayed sulfur removal is needed.

(2) When olefin reduction is not optional but mandated, for example, for FCC gasoline with high olefin content, octane recovery that makes up the octane loss caused by the remarkable reduction of olefins could not be accomplished via either hydroisomerization or hydroaromatization of hydrocarbons. This is because hydroisomerization alone cannot offset the product octane loss due to excessive olefin saturation, while the only hydroaromatization via transforming olefins into high-octane aromatics in the presence of hydrogen is confronted with the problems of catalyst deactivation and restriction of clean gasoline specifications on aromatics content.[18] Obviously, a trade-off is to develop a catalyst system and the corresponding process with compromised hydroisomerization and hydroaromatization performances.[18,19]

Inspired by the earlier findings, we developed the selective HDS catalyst of K-P modified Co–Mo/Al_2O_3 and the hydroisomerization/aromatization catalyst of Ni–Mo/modified HZSM-5. The former catalyst with more active sites for HDS and less active sites for olefin saturation had a good HDS selectivity,[20] and the latter catalyst showed the compromised hydroisomerization and aromatization performances and the compensating HDS function.[21] However, each of the two catalysts cannot realize the coupling of ultradeep HDS and excellent octane recovery.

On the basis of the above two catalysts, the process with the olefin hydroisomerization and aromatization in the front and the selective HDS in the rear was investigated in our unpublished work and the results showed that the process had the following disadvantages: (1) the front catalyst was apt to be quickly deactivated due to the fast formation of gums from the dienes in FCC gasoline feedstock at high reaction temperature;[22,23] (2) the rear selective HDS catalyst operated at low reaction temperature could produce a number of thiols because of the recombination of H_2S and olefins.[24,25] The two disadvantages led to the addition of two apparatuses for removing dienes and thiols, respectively, increasing the investment cost. Therefore, a process cascaded in the reverse order should become the optimal technique for hydro-upgrading FCC gasoline, as demonstrated in this work. Changing the cascaded order of catalysts in a process can change the HDS mechanism, the product distribution, the olefin reduction, and the octane recovery of the whole process, so the two-stage process developed herein is different from our unpublished work.

Herein, we propose a novel two-stage process with the selective HDS in the front and the olefin hydroisomerization and aromatization in the rear for hydro-upgrading inferior FCC gasoline with high sulfur and olefin contents. This two-stage process is obviously different from the Prime-G and Oct-gain processes. The differences can be clarified by the following explanation: the Prime-G process is a selective HDS technique with high HDS ratio and low olefin saturation to meet the requirement for moderate desulfurization, but the two-stage process has the process of supplementary HDS and olefin hydroisomerization–aromatization in addition to the selective HDS process, endowing the two-stage process with the advantages of ultradeep HDS, excellent octane recovery, and high liquid yield. The Oct-gain process accomplishes the ultradeep HDS and the complete saturation of high-octane olefins into low-octane paraffins in the first reactor via deep hydrogenation reactions rather than via selective HDS, and then the produced low-octane paraffins are hydroisomerized and cracked to recover product octane number at severe reaction conditions in the second reactor; different from the Oct-gain process, the two-stage process accomplishes the selective HDS in the first reactor that enables the first-stage product to have enough high-activity olefins (not low-activity paraffins in the first-stage product of the Oct-gain process), and then the further HDS and the hydroisomerization and aromatization of enough residual olefins are finished at moderate reaction conditions in the second reactor. In summary, the Prime-G and Oct-gain processes accomplish HDS in a single reactor, while this two-stage process developed herein removes different sulfur-containing compounds in different reactors, greatly reducing

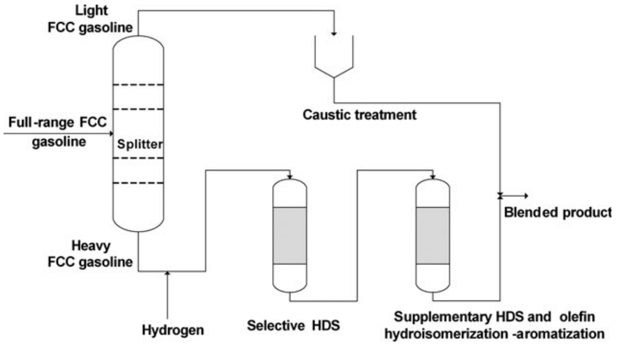

Figure 1. Schematic diagram of the two-stage process.

the HDS severity of each reactor and efficiently coupling ultradeep HDS and octane recovery.

In this article, we first introduce the two-stage process configuration, then describe the optimization of the operating conditions and the stability testing results obtained for a device scale of 200 mL, and finally present the mechanism explanations for the high product yield, the low hydrogen consumption, and the excellent HDS efficiency of the two-stage process.

Configuration of the Two-Stage Process

It is well known that the light fraction of a FCC gasoline contains the high content of high-octane C_5—C_6 olefins and the low sulfur content, whereas the heavy fraction contains more low-octane C_6^+ olefins and the very high sulfur content, so the heavy fraction of FCC gasoline obtained by fractionating the full-range FCC gasoline is generally chose as the feedstock rather than the full-range FCC gasoline to minimize the sulfur content and the octane loss of gasoline product obtained by blending the light fraction and the hydrotreated heavy fraction.[17]

With the aforementioned two kinds of catalysts and the suitable feedstock, the two-stage process configuration is described in Figure 1. First, the full-range FCC gasoline is separated into light and heavy cracked naphtha fractions (LCN and HCN) through distillation at 60°C, in which the LCN contains a large part of high-octane olefins with thiols as major sulfur-containing compounds,[17] and the HCN contains a relatively lower concentration of olefins but most of the sulfur-containing compounds including thiophenes, alkylthiophenes and benzothiophenes. The LCN is processed by the caustic treatment with a 10% NaOH solution to remove the predominant C_2 and C_3 thiols, guaranteeing the minimal sulfur content in the light fraction. Then, the HCN is hydrotreated by the selective HDS with the high desulfurization ratio and the low olefin saturation, enabling the selectively desulfurized gasoline to have enough olefins for the followed octane recovery stage; subsequently, the hydroisomerization and aromatization of residual olefins and the compensating HDS are achieved in the octane recovery stage. Finally, the hydro-upgraded HCN is blended with the caustic-treated LCN, so the ultraclean gasoline product can be obtained.

Experimental

Catalysts

The catalyst CMKP2 for selective HDS is composed of Al_2O_3 support and K–P modified Co–Mo.[20] The catalyst SCZM for olefin hydroisomerization and aromatization is composed of Ni–Mo and HZSM-5 zeolite support modified by the steaming and citric acid treatments.[21] The preparation procedures of these two catalysts had been described elsewhere[20,21] and their properties are presented in Table 1.

Catalytic assessments

The assessment experiments of the two-stage process with the HCN of FCC gasoline as feedstock were performed in a testing device designed for continuous operation. This testing device mainly consists of two identical 200-mL reactors in cascade, a gas-feeding system controlled by a mass flowmeter, and a syringe pump liquid feeding system. The first fixed-bed reactor, with an internal diameter of 25 mm, was loaded with 100 mL of catalyst CMKP2 and the second reactor, also with an internal diameter of 25 mm, was loaded with 200 mL of catalyst SCZM.

First, the two oxidic catalysts were presulfurized at 230, 290, and 360°C for 6 h, by a stream containing 3.0 wt % CS_2 in straight-run naphtha through the two catalyst beds in the presence of pure H_2. Then, the HCN was fed into the reactors at a predetermined flow and the reaction was performed at a total pressure of 1.0–2.5 MPa, a volumetric ratio of H_2 to oil of 200–500, 220–280°C and a FCC gasoline liquid hourly space velocity (LHSV) of 2.0–5.0 h^{-1} in the first reactor, and 320–380°C and a FCC gasoline LHSV of 1.0–2.5 h^{-1} in the second reactor. After a stabilization period of 48 h, the reaction products were collected and analyzed.

The conversion of total sulfur (TSC) and the conversion of olefins (OC) were calculated as follows

$$\mathrm{TSC}(\%) = \frac{S_f - S_p}{S_f} \times 100 \tag{1}$$

$$\mathrm{OC}(\%) = \frac{O_f - O_P}{O_f} \times 100 \tag{2}$$

where, S_f and S_p indicate the mass fraction of total sulfur in the HCN feedstock and products, respectively; O_f and O_p indicate the volume fraction of olefins in the HCN feedstock and products, respectively.

The iso-paraffin (aromatics) increment is defined as

$$\text{iso-Paraffin(aromatics)increment} = \text{iso-Paraffin(aromatics)}_p - \text{iso-Paraffin(aromatics)}_f \tag{3}$$

Table 1. Properties of Catalysts CMKP2 and SCZM

Item	CMKP2	SCZM	
Packing density	0.76	0.71	g/mL
BET surface area	197	326	m^2/g
Micropore surface area	–	224	m^2/g
External surface area	197	102	m^2/g
Total pore volume	0.420	0.239	mL/g
Micropore volume	–	0.106	mL/g
Mesopore volume	0.420	0.133	mL/g
Total acidity	151.0	282.1	μmol/g
Medium and strong Brönsted acidity	–	127.5	μmol/g
Modified HZSM-5 zeolite	–	75.0	wt %
Alumina	81.0	21.0	wt %
NiO	–	1.0	wt %
MoO_3	12.0	3.0	wt %
CoO	3.0	–	wt %
K_2O	2.3	–	wt %
P_2O_5	1.7	–	wt %

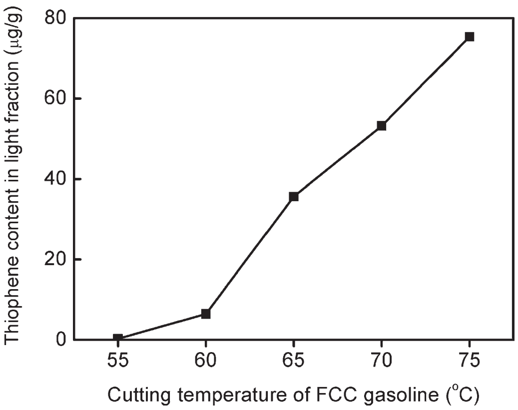

Figure 2. Thiophene content in light fraction at different cutting temperature of full-range FCC gasoline.

where, iso-paraffin(aromatics)$_f$ and iso-paraffin(aromatics)$_p$ indicate the volume fraction of iso-paraffins (aromatics) in the HCN feedstock and products, respectively.

RON loss is defined as

$$\mathrm{RON_{loss}} = \mathrm{RON_f} - \mathrm{RON_p} \tag{4}$$

where RON$_f$ and RON$_p$ are the RON values of the HCN feedstock and products, respectively.

To elucidate the HDS mechanism of the two-stage process, we prepared several model compounds, which are 1.0 wt % thiophene in cyclohexane, 1.0 wt % 2,5-dimethylthiophene in cyclohexane, 1.0 wt % benzothiophene in cyclohexane, 0.5 wt % thiophene and 0.5 wt % 2,5-dimethylthiophene in cyclohexane, and 0.5 wt % thiophene and 0.5 wt % benzothiophene in cyclohexane. The conversion of a model sulfur-containing compound and the HDS ratio of a model sulfur-containing compound were denoted as CMS and HDSMS, respectively. CMS and HDSMS were calculated as follows

$$\mathrm{CMS}(\%) = \frac{\mathrm{MS_f} - \mathrm{MS_p}}{\mathrm{MS_f}} \times 100 \tag{5}$$

$$\mathrm{HDSMS}(\%) = \frac{\mathrm{TS_f} - \mathrm{TS_P}}{\mathrm{TS_f}} \times 100 \tag{6}$$

where, MS$_f$ and MS$_p$ indicate the mass fraction of a model sulfur-containing compound in the feedstock and the product, respectively; TS$_f$ and TS_p indicate the mass fraction of all sulfur-containing compounds in the model feedstock and the product, respectively.

After the presulfurization of the two oxidic catalysts, the above model compounds were assessed over the selective HDS catalyst under the conditions of H_2/model compound volumetric ratio at 300, 1.5 MPa, 240°C, and LHSV at 3.0 h^{-1}, and over the hydroisomerization/aromatization catalyst under the conditions of H_2/model compound volumetric ratio at 300, 1.5 MPa, 360°C, and LHSV at 1.5 h^{-1}.

Product analyses

The hydrocarbon compositions of the feedstock and products were determined using an Agilent 1790 gas chromatograph installed with a flame ionization detector and a HP-PONA capillary column (50 m×0.2 mm). The RONs of the feedstock and products were obtained on the ASTM-CFR octane rating engine (Ethyl Chemical, America). The contents of total sulfur in the feedstock and products were measured by a WK-2C microcoulombmeter (Jiangsu Jiangfen Electroanalytical Instrument, PR China). Sulfur-containing species were analyzed quantitatively using a gas chromatograph (HP 6890) with a pulse-flame photometric detector (O. I., PFPD 5380) and qualitatively using a gas chromatograph (HP 5790) with a mass spectrometer (MS 80).

Results

Determination of cutting temperature of full-range FCC gasoline

FCC gasoline fractionation is increasingly more important as the great reduction of sulfur-containing compounds in FCC gasoline is more and more urgent. The thiophene content in light fraction at different cutting temperature of full-range FCC gasoline is shown in Figure 2. Despite the normal boiling point of thiophene at 83°C, the thiophene content in the light gasoline fraction quickly increases in the case of cutting temperature >60°C due to the azeotropic effect of thiophene and hydrocarbons, in accordance with the literature results.[26] It is well known that thiophene cannot be extracted in a caustic treating process,[17,26] so the sulfur content of the light gasoline fraction with thiophene is relatively high when the cutting temperature is higher than 60°C, leading to the undesirable sulfur content in the blended full-range gasoline product. Herein, the cutting temperature of FCC gasoline was selected at 60°C to minimize the thiophene content with high-octane C_5—C_6 olefins in the light fraction, so the predominant C_2 and C_3 thiols in the light fraction (<60°C) can be removed efficiently by the caustic treatment with a 10% NaOH solution,[27] guaranteeing the minimal sulfur content in the light fraction.

Matching operation conditions of the two kinds of catalysts

On the basis of the two kinds of catalysts developed and the process configuration determined, the reaction conditions of the whole process were optimized using a HCN with boiling point ≥60°C as the feedstock. The properties of the feeding FCC gasoline used are listed in Table 2.

Pressure Optimization. Under the conditions of H_2/oil volumetric ratio at 300, 240°C and LHSV 3.0 h^{-1} for the first reactor, and 360°C and LHSV 1.5 h^{-1} for the second reactor, the reaction performance of the two-stage process vs. the reaction pressure was investigated and the results are shown in Figures 3 and 4. For the selective HDS in the first

Table 2. Properties of the Feeding FCC Gasoline

Item	Full-Range	LCN (<60°C)	HCN (>60°C)
Weight (%)	100	25.9	74.1
Density (g/mL, 20°C)	0.73	0.64	0.77
RON	91.4	93.8	88.7
Total sulfur (μg/g)	1017	54.2 (12.5)*	1354
Thiol (μg/g)	40.1	46.8 (5.4)†	34.2
Group composition (v %)			
n-Paraffin	5.5	6.4	4.8
Iso-paraffin	28.3	42.2	24.1
Olefin	39.6	49.8	35.6
Naphthene	6.9	1.2	7.9
Aromatics	19.7	0.4	27.6

*Total sulfur content in the LCN after the caustic treatment is given in parenthesis.

†Thiol content in the LCN after the caustic treatment is given in parenthesis.

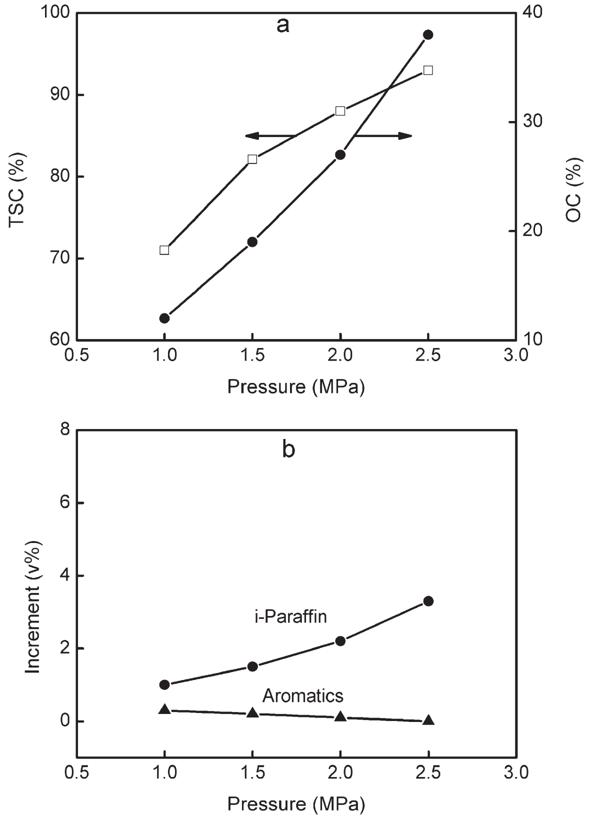

Figure 3. Effects of reaction pressure on TSC and OC (a) and the increments of object hydrocarbons (b) in the first-stage selective HDS.

stage, the TSC, the OC, and the iso-paraffin increment increases with the increasing reaction pressure, indicating the promoting effects of pressure on the removal of sulfur-containing compounds, the reduction of olefins, and the OC into iso-paraffins. It is also noted from Figure 3b that the aromatics increment is close to zero, showing the inability of the catalyst in the first reactor for olefin aromatization.

Comparing Figures 3a and 4a, one can see that through the octane recovery after the selective HDS, the TSC and the OC can be further increased, indicating that the octane recovery process in the second reactor is capable of performing complementary desulfurization and olefin reduction. The results in Figures 3b and 4b show that the catalyst in the second reactor has excellent olefin hydroisomerization and aromatization activity, yielding a product with the remarkably increased contents of iso-paraffins and aromatics whose octane values are equivalent or even higher than those of the corresponding olefins. It can be observed from Figure 4b that with the increasing reaction pressure, the iso-paraffin increment and RON loss increase, while the aromatics increment decreases, indicating the importance of aromatization in octane preservation. Considering that marginal RON loss acceptable to refineries is 1.0, the reaction pressure should be less than 2.0 MPa, as shown in Figure 4b. Moreover, due to the low product yield (93.5 wt %) when the pressure is at 1.0 MPa, 1.5 MPa is considered as a suitable reaction pressure, at which both the RON loss (0.5 unit) and liquid yield (98.4 wt %) are acceptable.

Temperature Optimization. When the first reactor is operated under the conditions of H_2/oil volumetric ratio 300, 1.5 MPa, and LHSV of 3.0 h^{-1}, the selective HDS performance of the first reactor vs. the reaction temperature was studied and the results are shown in Figure 5. With the increasing reaction temperature, the TSC, the OC, and the iso-paraffin increment increase, showing a similar trend with the increasing pressure, as depicted in Figure 3. Our previous work has demonstrated that in the case of OC $\leq$ 20% at the selective HDS stage, the RON loss is less than 1.0 unit.[27] Thus, a suitable reaction temperature for the selective HDS reactor should be at around 240°C at which a satisfactory desulfurization ratio and an acceptable olefin saturation can be achieved, as seen in Figure 5a.

When the first reactor is operated under the conditions of H_2/oil volumetric ratio of 300, 1.5 MPa, 240°C, and LHSV of 3.0 h^{-1} and the second reactor is run under the conditions of H_2/oil volumetric ratio of 300, 1.5 MPa, and LHSV of 1.5 h^{-1}, the reaction performance of the second stage vs. the reaction temperature was studied and the results are shown in Figure 6. After the octane recovery following the selective HDS, the TSC increases while the liquid yield decreases with the increasing reaction temperature, as shown in Figure 6a. This indicates that increasing the reaction temperature promotes both HDS reactions[28] and cracking reactions that lead to the formation of small-molecule hydrocarbons.[29] Figure 6b shows that with the increasing temperature of the second reactor, the aromatics increment increases, while the iso-paraffin increment decreases. It is well known that olefin hydroisomerization is exothermic but olefin aromatization is endothermic,[19] so high temperature benefits the aromatics

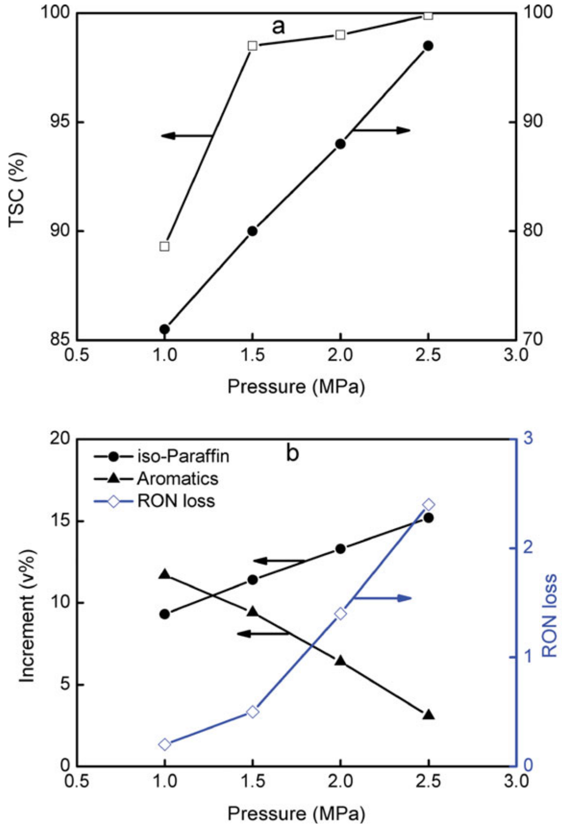

Figure 4. Effects of reaction pressure on TSC and OC (a), and the RON loss and the increments of object hydrocarbons (b) in the octane recovery stage after the selective HDS.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

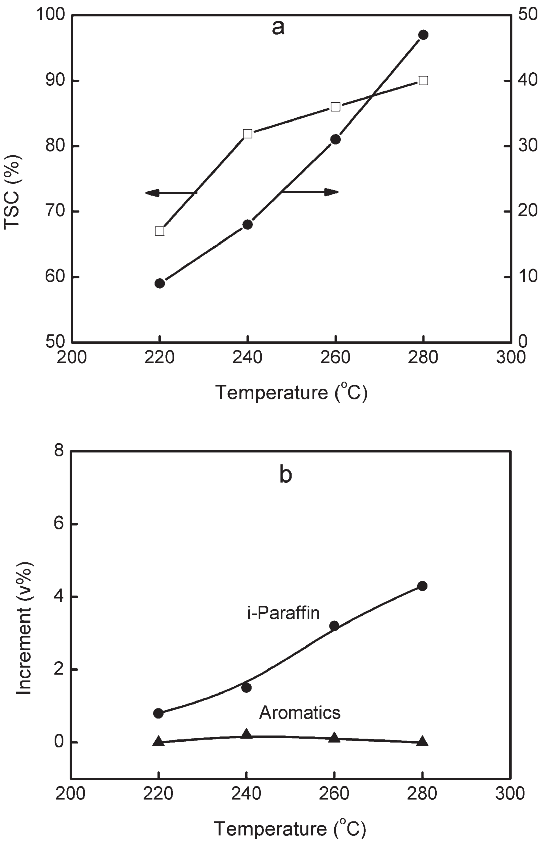

Figure 5. Effects of reaction temperature on TSC and OC (a) and the increments of object hydrocarbons (b) in the first-stage selective HDS.

formation but restrains the iso-paraffin formation. Our previous work has proven that when the aromatics increment is less than 10 vol %,[21] the catalyst SCZM shows outstanding stability, which suggests that an appropriate reaction temperature for the second reactor should be around 360°C at which an acceptable RON loss (0.5 unit) and a high liquid yield (98.4 wt %) can be guaranteed.

Liquid Space Velocity Optimization. Under the conditions of H_2/oil volumetric ratio 300, 1.5 MPa, 240°C for the first reactor, and 360°C for the second reactor, the dependence of the reaction performance of the two-stage process on LHSVs of the two reactors was determined and the results are given in Figure 7. It can be seen from Figure 7a that with the increasing LHSVs, the TSC decreases while the liquid yield increases. This is because high space velocity reduces the residence time of sulfur-containing compounds and hydrocarbons and, thus, limits sulfur conversion and hydrocarbon cracking.[30] The results in Figure 7b reveal that the iso-paraffin and aromatics increments decrease with the increasing LHSVs, suggesting the weakened olefin hydroisomerization and aromatization. Because the hydroisomerization and aromatization of olefins need longer reaction time,[31] the high space velocity is unfavorable for the deep OC into iso-paraffins and aromatics.

As shown in Figure 7, in the case of LHSV $< 3.0\ h^{-1}$ for the first reactor and LHSV $< 1.5\ h^{-1}$ for the second reactor, ultradeep HDS (TSC $\geq$ 98%) can be realized but the liquid yield is relatively low (94.2 wt %) and the aromatics increment is too high (>10 vol %) to guarantee the long-term operation of the catalyst in the second reactor.[29] On the contrary, in the case of LHSV $> 3.0\ h^{-1}$ for the first reactor and LHSV $> 1.5\ h^{-1}$ for the second reactor, ultradeep HDS cannot be finished in spite of the high liquid yield. Hence, the optimal space velocities for the first and the second reactors should be 3.0 and 1.5 h^{-1}, respectively.

H_2/oil Ratio Optimization. Under the conditions of 1.5 MPa, 240°C and LHSV 3.0 h^{-1} for the first reactor, and 360°C and LHSV 1.5 h^{-1} for the second reactor, the reaction performance of the process was correlated with the H_2/oil volumetric ratio in Figure 8. With the increasing H_2/oil ratio, the TSC increases slightly but the OC decreases obviously as shown in Figure 8a, indicating the minor effect of the H_2/oil ratio on HDS. The obvious decrease in the OC results from the fact that the increasing H_2/oil ratio reduces the residence time of olefins over the catalysts and, thus, lowers their conversion, as evidenced by the decreased iso-paraffin and aromatics increments in Figure 8b. It is known that a low H_2/oil volumetric ratio can lead to the deactivation of the catalyst in the second reactor due to the prolonged residence time of olefins and the weakened inhibition effect of hydrogen on coking,[32] so the high H_2/oil ratio seems to be advantageous. However, the high H_2/oil ratio causes the high process cost and the low olefin reduction as above mentioned, so a suitable H_2/oil volumetric ratio should be at around 300.

Stability testing of the combined catalyst system

According to the above discussion, the optimum operating conditions are: H_2/oil volumetric ratio 300, 1.5 MPa, 240°C

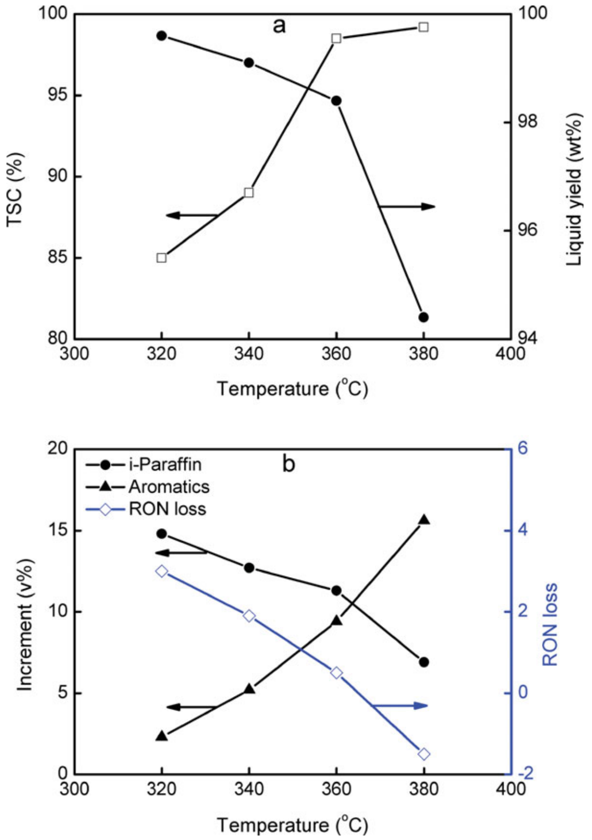

Figure 6. Effects of reaction temperature on TSC and liquid yield (a), and the RON loss and the increments of object hydrocarbons (b) in the octane recovery stage after the selective HDS.

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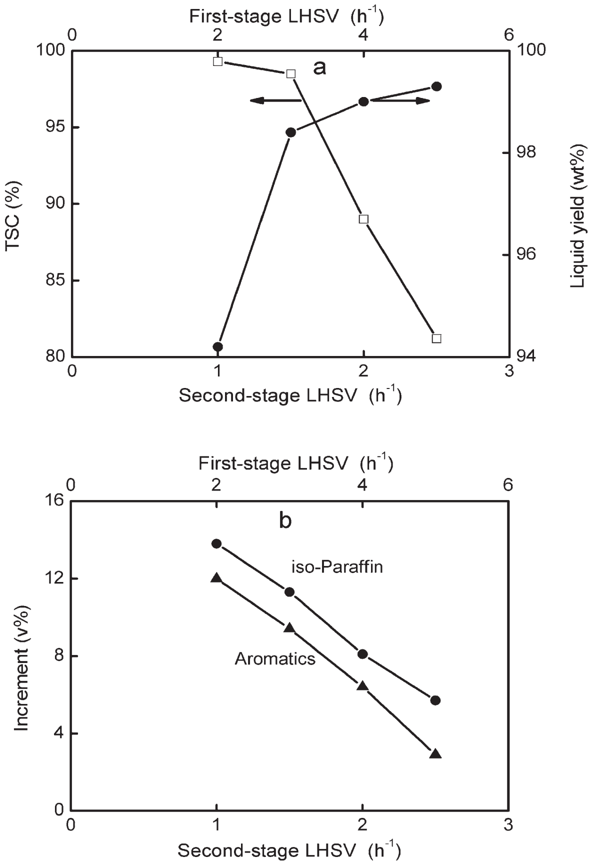

Figure 7. Effects of space velocity on TSC and liquid yield (a), and the increments of object hydrocarbons (b) in the two-stage process.

and LHSV 3.0 h^{-1} for the first reactor, and 360°C and LHSV 1.5 h^{-1} for the second reactor. Under the optimal operating conditions, the stability testing of the combined catalyst system was performed and the results are shown in Figure 9 and Table 3. During the 500-h run, the contents of iso-paraffins, aromatics, olefins, and sulfur in the obtained HCN product remained stable, suggesting the outstanding stability of the combined catalyst system. The comparison of Tables 2 and 3 demonstrates that the two-stage process with the selective HDS in the front and the supplementary HDS and olefin hydroisomerization–aromatization in the rear has the features of ultradeep HDS (98.5% desulfurization ratio for the HCN and 98.3% for the full-range gasoline), excellent olefin reduction (29.1 vol % for the HCN and 22.4 vol % for the full-range gasoline), good RON preservation (0.5 unit RON loss for the HCN and 0.3 unit RON loss for the full-range gasoline), and high liquid yield (98.4 wt % for the HCN and 98.8 wt % for the full-range gasoline).

Discussion

High product yield of the two-stage process

The high product yield of the two-stage process can be attributed to the optimized physicochemical properties of the catalyst in the second reactor in view of the almost 100 wt % liquid yield of the first stage (Table 3) due to the low acidity of the selective HDS catalyst and the relatively lower reaction temperature.[20] As shown in Figure 10, the steaming pretreatment generates the lattice defect sites in HZSM-5 zeolites, providing the space for the insertion of partial extraframework Al (EFAl) generated by the steaming treatment;[33,34] then, the hydroxylation between —OH groups of citric acid and partial Al (OH) $_2^+$ cations (i.e., EFAl) can form Al (OH) $_4^-$ anions; finally, the Al (OH) $_4^-$ anions are reinserted into the framework vacancy of the steamed HZSM-5 zeolites by the realumination effects.[35] The dealumination and followed realumination can finely tune the distributions of acid type and strength over the HZSM-5-based catalyst in the second reactor and, thus, restrain the cracking of hydrocarbons.[21] Moreover, the steaming and citric acid treatments endow the HZSM-5 support of the catalyst in the second reactor with a suitable pore structure

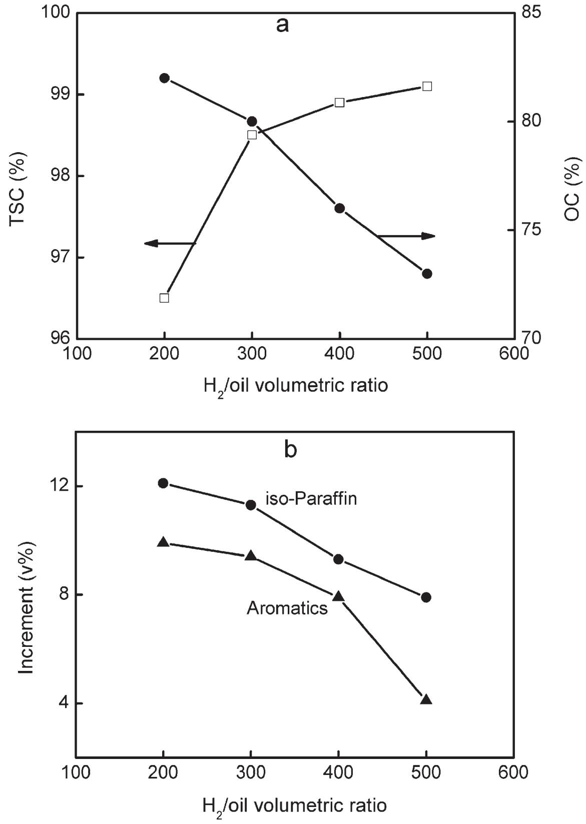

Figure 8. Effects of H_2/oil ratio on TSC and OC (a), and the increments of object hydrocarbons (b) in the two-stage process.

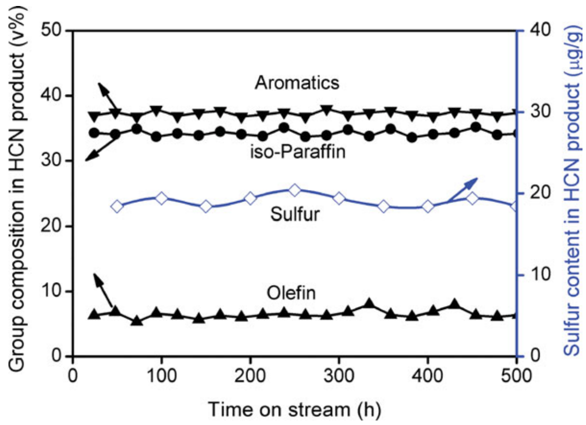

Figure 9. Stability trend of the two-stage process with the HCN gasoline as feedstock.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table 3. Assessment Results of the Two-Stage Process

Item	HCN Intermediate Product After Selective HDS	HCN Terminal Product After Selective HDS and Octane Recovery	Full-Range Product Obtained by Blending the Caustic-Treated LCN and the HCN Terminal Product
Liquid yield (wt %)	99.9	98.4	98.8
RON	87.9	88.2	91.1
Total sulfur (μg/g)	241.2	19.4	17.6
Chemical H_2 consumption (m^3/m^3)		16.0	
Group composition average (vol %) (500 h)			
n-Paraffin	9.8	13.0	11.3
Iso-paraffin	25.6	33.9	36.5
Olefin	29.1	6.5	17.2
Naphthene	7.8	9.4	8.1
Aromatics	27.7	37.2	26.9

composed of mesopores and micropores,[21] promoting the diffusion of object hydrocarbons after effective reactions. Thus, the optimized acidity and pore structure of the modified HZSM-5-based catalyst in the second reactor greatly suppress the cracking side-reactions, guaranteeing the high product yield of the process.

Low chemical H_2 consumption of the two-stage process

The chemical H_2 consumption of the two-stage process developed here (Table 3) is much lower than that (44 m^3/m^3) reported in literatures.[15,16] The reasons are as follows: on the one hand, the high HDS activity and selectivity of the catalyst in the first reactor guarantee the high HDS ratio and low olefin saturation (referring to Tables 2 and 3), effectively reducing the hydrogen consumption for saturating olefins; on the other hand, for the olefin reduction and octane recovery in the second reactor, the remnant olefins in the gasoline after the selective HDS are converted mainly into iso-paraffins and aromatics (Table 3) in a manner without net hydrogen consumption: as shown in Figure 11, one linear olefin molecule (C_nH_{2n}) can be converted into one aromatics molecule (C_nH_{2n-6}) by losing six hydrogen ions or into one paraffin molecule (C_nH_{2n+2}) by receiving two hydrogen ions,[18] that is, the generated hydrogen due to the formation of one aromatics molecule from one linear olefin molecule can make up the consumed hydrogen due to the formation of three paraffin molecules from three linear olefin molecules. Therefore, when the aromatics increment is 9.6 vol % and the paraffin increment is 18.0 vol % after the two-stage process (Tables 2 and 3), the amount of hydrogen generated from olefin aromatization surpasses that consumed by olefin saturation, without the net consumption of the feeding hydrogen.

High-efficient HDS mechanism coupled with directional olefin conversion in the two-stage process

The distributions of sulfur-containing compounds in the HCN feedstock and products of the two-stage process are shown in Table 4. In the HCN feedstock, thiophene, alkyl thiophene, and benzothiophene are in absolute majority among the various sulfur-containing compounds, taking a share of about 97%. After experiencing the selective HDS in the first reactor, 99.7% of benzothiophenes, 98.3% of trimethyl thiophenes, and 94.3% of dimethyl thiophenes are removed, but only about 70.8% of thiophenes and 77.7% of methyl/ethyl thiophenes are removed. Moreover, the thiol content greatly increases because H_2S produced during the selective HDS can easily react with olefins to form thiols.[36] After experiencing the octane recovery in the second reactor, the high-content thiophenes, methyl/ethyl thiophenes, and thiol from the first reactor are effectively removed.

To elucidate the HDS mechanism of the two-stage process, the model compounds were assessed over the selective HDS catalyst and the results are shown in Table 5. The conversions of the three model sulfur-containing compounds are close to their HDS ratios, indicating the high desulfurization ratios of their converted products. The reactivities of different model sulfur-containing compounds decrease in the order of thiophene >2,5-dimethylthiophene >benzothiophene, in accordance with the results in the literature.[37] However, the mixture of thiophene and 2,5-dimethylthiophene and that of thiophene and benzothiophene show distinct reactivities. Clearly, 2,5-dimethylthiophene and benzothiophene restrain the thiophene conversion, but thiophene hardly influence the conversion of the former two.

The selective HDS catalyst of K–P modified Co–Mo/Al_2O_3 in the first reactor with the compromised stacking and dispersion of active Co–Mo–S phases has the sufficient and exposed stackings that effectively promote the adsorption of relatively large sulfur-containing compounds (such as benzothiophene),[27] so the influence of steric hindrance on the adsorption of sulfur-containing compounds over the catalyst can be ignored. In this case, the charge properties of sulfur-containing compounds become a critical factor in affecting their adsorption. Thus, the above phenomenon can be

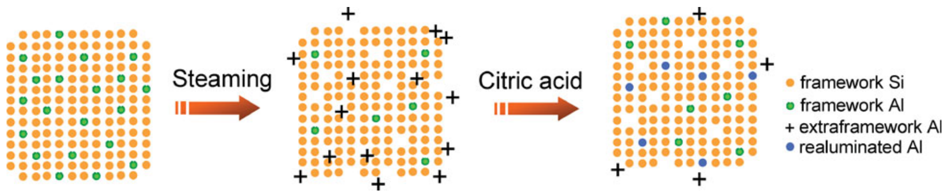

Figure 10. Acidity adjustment schematic diagram of the HZSM-5 support of the second-stage catalyst.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

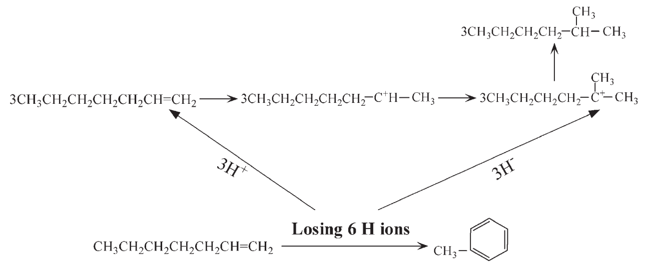

Figure 11. Schematic diagram of the self-generating balance between hydrogenation and dehydrogenation in the second stage.

Table 4. Distributions of Sulfur-Containing Compounds in the HCN Feedstock and Products of the Two-Stage Process

Sulfur-Containing Compounds (μg/g)	HCN Feedstock	HCN Intermediate Product After Selective HDS	HCN Terminal Product After Selective HDS and Octane Recovery
Thioether	4.78	1.28	0.00
Thiol	34.2	56.9	1.14
Thiophene	241.9	70.7	1.62
Methyl/ethyl thiophene	408.5	91.1	7.5
Dimethyl thiophene	338.6	19.2	7.8
Trimethyl thiophene	135.7	2.30	1.71
Benzothiophene	189.8	0.50	0.00

explained as follows: it is known that the hyperconjugation effect between branched-chain alkyl groups and thiophene with π-conjugated structure can be generated, enhancing the density of electron clouds on the ring of thiophene.[38] Moreover, the hyperconjugation effect increases with the increasing number of branched-chain alkyl groups, so 2,5-dimethylthiophene has a higher charge density compared to thiophene and, thus, is easier to be adsorbed onto supported Co–Mo–S active sites with electropositivities.[39] Benzothiophene has π-conjugated structures on the aromatic ring and the thiophene ring, endowing itself with a higher negative charge compared to alkyl thiophene.[40] Thus, the electronegativities of the above sulfur-containing compounds increase in the order of thiophene < 2,5-dimethylthiophene < benzothiophene. As mentioned above, benzothiophene and 2,5-dimethylthiophene have higher electronegativities than thiophene, so they are preferentially adsorbed on the active Co–Mo–S phases without steric hindrance, restraining the efficient adsorption and followed conversion of small thiophene due to the occupation of available adsorption spaces (Figure 12). In view of the larger kinetic diameter of benzothiophene than that of 2,5-dimethylthiophene,[41] benzothiophene presents the stronger restraining effect on the adsorption and conversion of thiophene compared to 2,5-dimethylthiophene (Table 5).

The activity of the catalyst in the second reactor for hydrodesulfurizing the above model compounds was also assessed and the results are shown in Table 6. Over the catalyst, the conversion and the HDS ratio of thiophene are much higher than those of benzothiophene, and the presence of benzothiophene in the thiophene-containing feedstock hardly influences the conversion of the latter, distinctively different from the situation over the catalyst in the first reactor. This is because the high surface area and the low metal content of the Ni–Mo/modified HZSM-5 catalyst guarantee the superior monolayer dispersion of supported metal sulfides on which the small thiophene is easily adsorbed and desulfurized,[42] but the relatively large benzothiophene cannot be adsorbed due to steric hindrance.[27] The desulfurization of a small amount of benzothiophene can be finished by the adsorption and followed C—S cleavage on the medium and strong Brönsted (B) acid sites of the modified HZSM-5 zeolite. In addition, the results in Table 6 show that the presence of benzothiophene scarcely affects the conversion of thiophene, further indicating the different adsorption sites for benzothiophene and thiophene over the second-stage catalyst.

According to the above discussion, the results in Table 4 can be explained rationally as follows: the preferential adsorption of the relatively large sulfur-containing compounds (such as benzothiophene, trimethyl thiophene, and dimethyl thiophene) reduces the number of active adsorption sites for the small sulfur-containing compounds (such as thiophene and methyl/ethyl thiophene), so the conversions of thiophene and methyl/ethyl thiophene are restrained and thereby their contents are relatively high in the product obtained over the selective HDS catalyst.

In the second reactor for octane recovery after the selective HDS, thiol, thiophene, and methyl/ethyl thiophene in the absolute majority of sulfur-containing compounds in the selective HDS product are greatly eliminated, indicating the compensating desulfurization effect of the catalyst in the second reactor. The HDS reaction of thiophene follows two pathways:[43,44] (1) the hydrogenation pathway proceeds via thiophene hydrogenation to 2-hydrothiophene, and further hydrogenation to 2,5-dihydrothiophene and subsequent S—C scission; (2) the direct desulfurization pathway is initiated by thiophene hydrogenation to 2-hydrothiophene and immediately followed by the S—C scission of 2-hydrothiophene. Over the catalyst in the second stage, the active metal sites with high monolayer dispersion facilitate the adsorption and desulfurization of thiophene and methyl/ethyl thiophene. Moreover, the catalyst contains the modified HZSM-5 zeolite with medium and strong B acid sites that favor the S—C scission[45,46] and, therefore, presents high desulfurization ratios for thiophene and methyl/ethyl thiophene (Figure 13). Similarly, the remarkable decrease in the thiol content can be attributed to the efficient adsorption and removal of thiols over the second-stage catalyst (Figure 13).

Excitingly, the two-stage process also presents excellent olefin reduction and minimal octane loss accompanied with

Table 5. Reactivity Results of Model Sulfur-Containing Compounds Over the First-Stage Catalyst

Item	$CMS_{thiophene}$ (%)	$CMS_{2,5\text{-dimethylthiophene}}$ (%)	$CMS_{benzothiophene}$ (%)	HDSMS (%)
Thiophene	95.5			95.5
2,5-Dimethylthiophene		91.1		89.6
Benzothiophene			80.7	78.8
Thiophene and 2,5-dimethylthiophene	86.5	89.9		85.3
Thiophene and benzothiophene	73.1		79.8	75.2

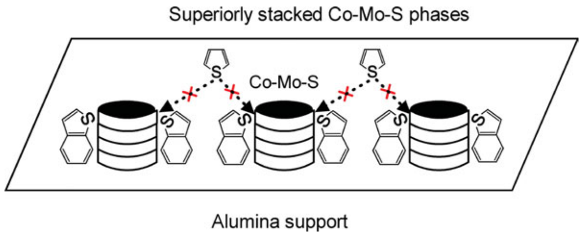

Figure 12. Schematic diagram of the hindrance effect of preferentially adsorbed benzothiophene on the adsorption of thiophene by the occupation of available adsorption spaces over the first-stage catalyst.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the above high-efficient HDS capability, resolving the bottleneck problem in producing ultraclean gasoline. The K–P modified Co–Mo/Al_2O_3 catalyst in the first reactor with the compromised stacking and dispersion of active Co–Mo–S phases can not only effectively remove relatively large sulfur-containing compounds as discussed above but also direct the minimal olefin saturation due to much less exposed olefin hydrogenation sites as discussed in the literatures,[27,47,48] endowing itself with a high desulfurization ratio and an optimal octane loss. The catalyst in the second reactor with the modified HZSM-5 zeolite as support and Ni–Mo as active metals presents not only the superior capability in removing small sulfur-containing compounds as discussed above but also the well-directed balance between olefin hydroisomerization and aromatization due to its finely tuned strength and distribution of Lewis (L) and B acid sites,[21] accomplishing the combination of complemental desulfurization with great olefin reduction and excellent octane recovery.

In summary, coupling the high-efficient removal of the different sulfur-containing compounds at the different stages with the directional olefin conversion endows the two-stage process with the capabilities of ultradeep HDS and minimal octane loss, providing a new and facile technology path for producing ultralow sulfur gasoline with high quality.

Conclusions

A novel two-stage process for producing ultraclean gasoline was developed with the selective HDS as the first stage and the complemental HDS, olefin reduction, and octane recovery as the second stage. The optimization results of reaction conditions for the whole process showed that the desirable reaction performances for HDS, olefin reduction, high product yield, and acceptable RON loss could be obtained under the conditions of H_2/oil volumetric ratio at 300, 1.5 MPa, 240°C and the LHSV of 3.0 h^{-1} for the first stage, and 360°C and the LHSV of 1.5 h^{-1} for the second stage. The two-stage process with the good reaction stability of the combined catalyst system presented not only the capability of ultradeep HDS originating from the relayed HDS effect between the different stages but also the performances of superior olefin reduction and good octane recovery resulting from the highly efficient conversion of olefins into aromatics and iso-paraffins. Moreover, the process had high product yield due to the proper acidity and pore structure of the second-stage catalyst, and low hydrogen consumption because of the low olefin saturation in the first stage and the excellent balance between hydrogenation and dehydrogenation in the second stage. The above advantages endow the two-stage process with a promising perspective for producing ultraclean and high-quality gasoline.

Table 6. Reactivity Results of Model Sulfur-Containing Compounds Over the Second-Stage Catalyst

Item	$CMS_{thiophene}$ (%)	$CMS_{benzothiophene}$ (%)	HDSMS (%)
Thiophene	96.9		96.9
Benzothiophene		38.7	35.4
Thiophene and benzothiophene	96.1	37.5	63.2

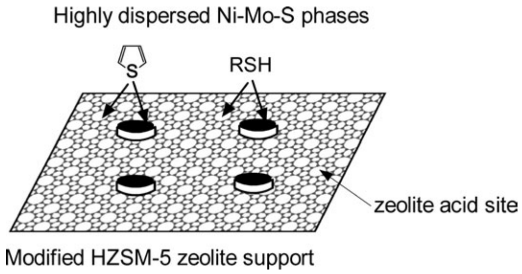

Figure 13. Schematic diagram of the adsorption of thiophene and thiol on the active sites of the second-stage catalyst.

Acknowledgments

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