

Reactive Adsorption Desulfurization Coupling Olefin Conversion in Fluid Catalytic Cracking Gasoline Upgrading Process

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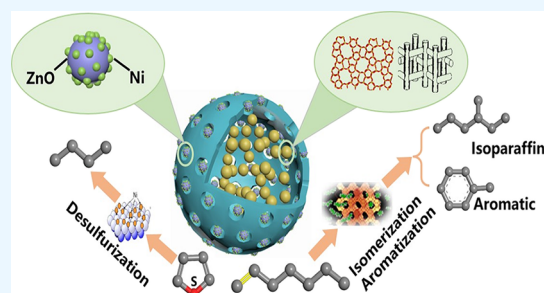
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ABSTRACT: Reactive adsorption desulfurization experiments were carried out on fluid catalytic cracking gasoline over a Ni/ZnO adsorbent in a fixed bed reactor. Results demonstrated that desulfurization is accompanied by hydrogen transfer, while isomerization and aromatization reactions are rare. Reactive adsorption desulfurization coupling olefin conversion was attempted by mixing a catalyst consisting Zn-ZSM-5 with an adsorbent at a certain proportion. The process reduced the loss of octane number and sustained ultradeep desulfurization ability simultaneously. An Fe-modified Ni/ZnO adsorbent was developed, which possessed better olefin retention ability than the Ni/ZnO adsorbent. The Ni–Fe/ZnO adsorbent mixed catalyst exhibited better olefin conversion performance and lower octane number loss than that of the Ni/ZnO adsorbent mixed catalyst because more olefins were retained for isomerization and aromatization reaction on the catalyst. The proportion of the catalyst added and the operating conditions of the process were optimized, ultralow sulfur gasoline was produced, and loss of octane number was low under optimal operating conditions. The amount of octane number lost was reduced by 85% compared with conventional reactive adsorption desulfurization. In addition, the process exhibited excellent desulfurization and olefin conversion performance in multiple regeneration cycles, demonstrating the feasibility of continuous processing.



1. INTRODUCTION

New environmental legislations require ultralow sulfur concentration in gasoline because trace amounts of sulfur not only causes the formation of acid rain by discharging sulfur oxide but also increases the emission of hazardous substances by deactivating catalysts in vehicle exhaust converters.¹ In China, more than 70% of the gasoline pool consists of fluid catalytic cracking (FCC) gasoline, which contains a large number of sulfur-containing compounds and olefins that contribute to a high octane number.² Therefore, the effective desulfurization of FCC gasoline has attracted considerable interest.³

Traditional hydro-desulfurization is the most widely used desulfurization process.⁴ However, the saturation of a large quantity of olefins during the process leads to great loss of octane number.⁵ Reactive adsorption desulfurization is considered the most promising alternative due to ultradeep desulfurization, low hydrogen consumption, and low octane number loss.⁶ A representative process of reactive adsorption desulfurization is S-Zorb, which was proposed by Conoco Phillips Company⁷ and developed by SINOPEC.

The conventional adsorbent used in the S-Zorb process consists of Ni, ZnO, Al₂O₃, and SiO₂.⁸ The active metal Ni can adsorb sulfur compounds, and ZnO not only acts as the acceptor of sulfur but also promotes the continuously regeneration of sulfide nickel species.⁹ The sulfur atoms of

sulfur-containing molecules are captured by the active metals of adsorbents, and then C–S bonds are broken. The sulfur atoms are stored by ZnO, and the hydrocarbon portions of the molecule are released back to the product stream.¹⁰

Reactive adsorption desulfurization has a much lower octane number loss than conventional hydro-desulfurization because of moderate operating conditions.¹¹ However, the adsorbent contains active metals that can capture olefins via π complexation¹² in the presence of hydrogen, which inevitably causes the loss of octane number.

Considerable effort has been focused on the study of factors affecting reaction performance and on solving the problem of octane number loss in reactive adsorption desulfurization. Some researchers¹³ optimized the operation conditions of reactive adsorption desulfurization but generally found that octane number loss would not be less than one unit even under optimal operating conditions.

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Some researchers have attempted to solve this problem by optimizing the composition of adsorbents. Ullah et al.¹⁴ investigated the effect of Ni content and preparation conditions of adsorbents on desulfurization activity and stability. Wang et al.¹⁵ reported that Cu can act as an active metal for reactive adsorption desulfurization according to density function theory. Liu et al.⁵ reported a Cu/ZnO adsorbent that allowed ultradeep desulfurization and high selectivity with low olefin saturation. Zhang et al.¹⁶ showed that Pb modifiers in the adsorbents of reactive adsorption desulfurization can weaken olefin adsorption on the surface and suppress olefin saturation effectively. These methods reduce the olefin saturation reaction to a certain extent but cannot fundamentally achieve deep desulfurization and solve the problem of octane number loss simultaneously.

Many desulfurization technologies have been combined with the octane number recovery process.¹⁷ However, most of these technologies consist of two separated units, and their complicated processes substantially increase equipment and operation costs. For this reason, some attempts¹⁸ have been made to combine desulfurization and olefin conversion in one reactor by synthesizing Ni-HZSM-5 catalysts with desulfurization and aromatization activities in the hydro-desulfurization process. In fact, reactive adsorption desulfurization is more suitable for the isomerization and aromatization of olefins due to its moderate operating conditions than hydro-desulfurization. Therefore, introducing the olefin conversion reactions into reactive adsorption desulfurization to resolve the problem of octane number loss is feasible.

For many years, we have devoted considerable effort to designing and developing adsorbents for reactive adsorption desulfurization and gradually found that an adsorbent modified by Fe exhibits excellent desulfurization performance and olefin retention ability. In this work, we aim to achieve deep desulfurization and maintain the octane number simultaneously by coupling reactive adsorption desulfurization and olefin conversion. HZSM-5 is an ideal material for olefin isomerization and aromatization due to its unique micropore channels, large specific surface area, and stable structural characteristics.^{19–21} An Fe-modified adsorbent was mixed with an olefin conversion catalyst consisting of Zn-ZSM-5, in which olefins can be retained during desulfurization and converted on the catalyst. The addition ratio of catalyst and operation conditions of the reactive adsorption desulfurization coupling olefin conversion process were studied experimentally. The regeneration performance of the adsorbent mixed with the olefin conversion catalyst was investigated, and the properties of the product gasoline were analyzed.

2. EXPERIMENTAL SECTION

2.1. Feedstock Properties and Adsorbents Preparation. In this study, the typical FCC gasoline with high olefin and sulfur content was used as feedstock for desulfurization experiments. Its detailed properties are presented in Table 1.

The S-Zorb industrial catalyst support containing ZnO, Al₂O₃, and SiO₂ was obtained from CNPC Huabei Petrochemical Company. The Ni/ZnO–Al₂O₃–SiO₂ adsorbent was synthesized by the incipient impregnation method. Quantitative Ni(NO₃)₂·6H₂O was dissolved in deionized water in a beaker, and then the solution was added to the support and stirred for 2 h. After 24 h of impregnation at room temperature, the mixture was dried at 120 °C for 12 h and then calcinated at 550 °C for 3 h. The Ni–Fe/ZnO–Al₂O₃–SiO₂

Table 1. Properties of the FCC Gasoline

properties	values
density (g/cm ³)	0.73
total sulfur (mg/kg)	486.23
RON	92.60
hydrocarbon group composition (wt %)	
<i>n</i> -paraffin	5.00
<i>i</i> -paraffin	32.28
olefin	34.13
naphthene	7.13
aromatic	21.46

adsorbent was synthesized through the incipient impregnation method by impregnating Fe(NO₃)₃ on Ni/ZnO–Al₂O₃–SiO₂. The impregnation method was the same as the impregnation of Ni(NO₃)₂·6H₂O on ZnO–Al₂O₃–SiO₂.

The HZSM-5 molecular sieve with a SiO₂/Al₂O₃ ratio of 50 was purchased from Shandong Zibo Catalyst Plant and calcined at 550 °C before use. To reduce cracking activity and improve isomerization and aromatization selectivity, we performed hydrothermal treatment on the molecular sieve at 500 °C for 2 h and then loaded zinc nitrate by equal volume impregnation.

2.2. Experimental Apparatus and Procedure. Desulfurization experiments were performed at a fixed bed reactor with an internal diameter of 15 mm and constant temperature zone of about 10 cm. The schematic diagram of the experimental system is shown in Figure 1. It mainly consisted of the oil and gas feed system, reaction zone, product separation and collection system, and temperature and pressure control system. For each experiment, approximately 12 g of adsorbent was loaded in the constant temperature area of the reactor, and quartz sand was embedded in the remaining zone. Nitrogen was injected into the reactor to purge the process section for 30 min. Subsequently, the fresh adsorbent was reduced in situ by pure hydrogen with a flow rate of 230 mL/min at 420 °C and 2 MPa total pressure for 2 h. The feedstock was then injected into the system and mixed with hydrogen in a preheater, where the mixture was heated to about 300 °C. The preheated mixture entered the reaction zone from the bottom of the reactor. The experiment was carried out under a stable condition (total pressure of 2 MPa, reaction temperature of 420 °C, molar ratio of H₂ to oil of 0.3, and weight hourly space velocity (WHSV) of 3 h^{−1}). Eventually, the effluent was cooled and separated into a gasoline product and incondensable gas. The gasoline product was collected for analysis every 2 h.

The breakthrough time was defined as the time when the sulfur content of product reaches 10 mg/kg. The breakthrough sulfur capacity, which is the amount of adsorbed sulfur per gram of adsorbent, was calculated based on the breakthrough time. The calculation formula is shown in eq 1.

$$q_{\text{breakthrough}} = \frac{m}{12 \times 1000} \int_0^t (C_0 - C_t) dt \quad (1)$$

where $q_{\text{breakthrough}}$ is the breakthrough sulfur capacity of the adsorbent (mg/g), m is the total quality of the feedstock involved in the reaction, 12 is the the total mass of adsorbent and catalyst added in the reactor, t is the breakthrough time, C_0 is the initial sulfur content of the feedstock, and C_t is the sulfur content of the product.

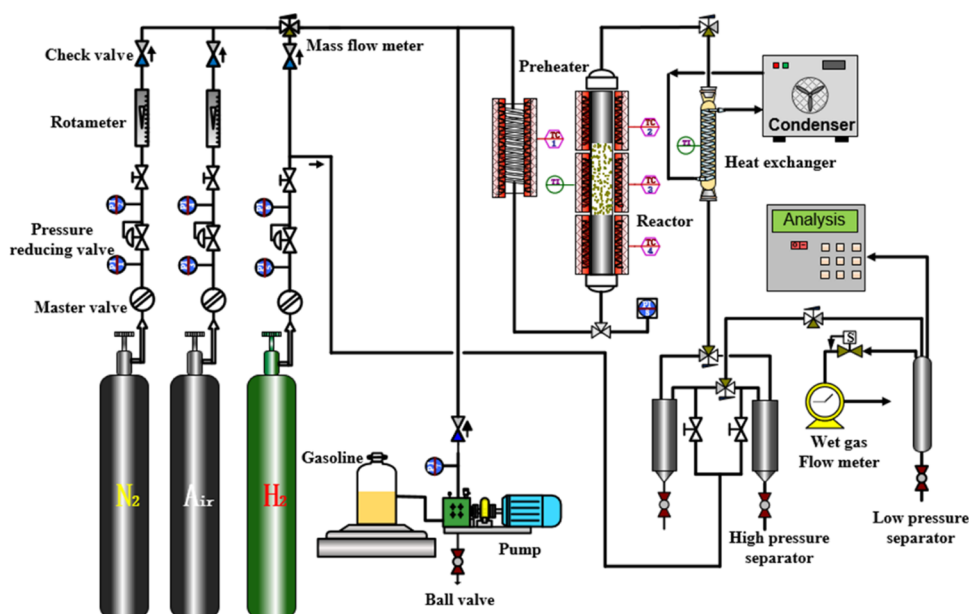


Figure 1. Schematic diagram of the fixed-fluidized bed reactor.

Table 2. Changes of Hydrocarbon Group Composition after RADS Reaction (wt %)

	carbon number	nP	iP	O	N	A	total	
feedstock	3	0.19	0.00	0.03	0.00	0.00	0.22	
	4	0.72	0.44	1.73	0.00	0.00	2.89	
	5	1.23	9.52	11.76	0.14	0.00	22.65	
	6	0.98	8.09	7.90	1.89	0.58	19.44	
	7	0.69	4.08	5.83	2.61	2.99	16.20	
	8	0.37	3.47	3.17	1.49	6.04	14.54	
	9	0.25	2.20	2.13	0.65	7.00	12.23	
	10	0.27	1.77	1.23	0.26	3.97	7.50	
	11	0.27	2.13	0.35	0.09	0.88	3.72	
	12	0.03	0.58	0.00	0.00	0.00	0.61	
	total	5.00	32.28	34.13	7.13	21.46	100.00	
	product	3	0.26	0.00	0.01	0.00	0.00	0.27
		4	1.46	0.47	1.04	0.00	0.00	2.97
5		3.36	11.23	7.91	0.52	0.00	23.02	
6		1.94	9.31	5.40	2.53	0.68	19.86	
7		1.03	4.20	4.86	2.94	3.32	16.35	
8		0.53	3.61	2.75	1.40	6.66	14.95	
9		0.35	2.40	1.76	0.68	6.81	12.00	
10		0.28	1.84	1.08	0.12	3.36	6.68	
11		0.23	1.99	0.10	0.06	0.79	3.17	
12		0.05	0.68	0.00	0.00	0.00	0.73	
total		9.49	35.73	24.91	8.25	21.62	100.00	

2.3. Product Analysis. Quantitative analysis of the total sulfur concentration was determined with an RPP-2000S sulfur trace analyzer, which was produced by Taizhou Zhonghuan Analysis Instrument Company. The samples were burned at 900 °C, and the sulfur-containing compound generated SO₂, which showed an excited state (SO₂^{*}) under irradiation with ultraviolet light. The amount of photons emitted from SO₂^{*} to SO₂ was measured with a photomultiplier tube and used in analyzing sulfur content in samples.

The hydrocarbon group composition of feedstock, and its desulfurization products were determined by an Agilent 6890 gas chromatograph equipped with an FID detector and a PONA capillary column (50 m × 0.2 mm × 0.5 μm), using a multidimensional analysis method for classifying hydrocarbons

as normal paraffin (nP), isoparaffin (iP), olefin (O), naphthene (N), and aromatic (A). The research octane number (RON) of the gasoline was calculated based on the PONA analysis results.

3. RESULTS AND DISCUSSION

3.1. Variation in Hydrocarbon Group Composition in FCC Gasoline after RADS Reaction. The hydrocarbon group composition distributions of the feedstock and the desulfurization product collected at the 10th hour in reactive adsorption desulfurization are listed in Table 2. The adsorbent used for the reaction was Ni/ZnO.

Table 3. Changes in Hydrocarbon Group Composition after RADS Reaction in Detail (wt %)

carbon number	nP	iP	N	n-O	i-O	Cyc-O	total
3	+0.07	+0.00	+0.00	-0.02	-0.00	+0.00	+0.05
4	+0.74	+0.03	+0.00	-0.67	-0.02	+0.00	+0.08
5	+2.13	+1.71	+0.38	-2.09	-1.42	-0.34	+0.37
6	+0.96	+1.22	+0.64	-0.64	-1.33	-0.53	+0.32
7	+0.34	+0.12	+0.33	-0.58	-0.12	-0.27	-0.18
8	+0.16	+0.14	-0.09	-0.19	-0.19	-0.04	-0.21
9	+0.10	+0.20	+0.03	-0.09	-0.20	-0.08	-0.04
10	+0.01	+0.07	-0.14	-0.07	-0.08	+0.00	-0.21
11	-0.04	-0.14	-0.03	-0.00	-0.25	+0.00	-0.46
12	+0.02	+0.10	+0.00	-0.00	-0.00	+0.00	+0.12
total	+4.49	+3.45	+1.12	-4.35	-3.61	-1.26	-0.16

As shown in Table 2, the olefin content of the product decreases by 9.22 wt %. The alkane and cycloalkane content increases relative to that in the feedstock, indicating that the hydrogenation reaction coexists with desulfurization. The content of aromatics remains unchanged overall, indicating that aromatic hydrocarbons are stable during reactive adsorption desulfurization. To clarify the reason for the change in hydrocarbon group composition, we compared variation in the hydrocarbon group composition of the products collected at the 10th hour with the feedstock. The comparison is presented in Table 3.

As indicated by Table 3, the detailed variation in *iso*-paraffins is basically similar to the absolute values of change in *iso*-olefins; the increase in normal paraffins is basically equal to the decrease in normal olefins. This result shows that change in hydrocarbon composition is caused by the saturation of olefins, and little isomerization and aromatization reactions occur in reactive adsorption desulfurization.

In addition, the sum of the content of low-carbon-number hydrocarbon increases slightly, whereas the content of high-carbon-number hydrocarbon decreases slightly, indicating that a small amount of cracking reactions occur during the process. The octane number of the product gasoline decreases from 92.6 of the feedstock to 88.6 of the product gasoline due to the saturation reaction of the olefins.

3.2. Coupling Performance of Adsorbent and Olefin Conversion Catalyst. The above analysis shows serious octane number loss due to olefin saturation in the traditional reactive adsorption desulfurization. To reduce the loss of octane number, an Fe-modified Ni/ZnO adsorbent was prepared and mixed with an olefin conversion catalyst. In order to determine the benefits of the Fe-modified adsorbent mixed with an olefin conversion catalyst, different loading methods with different catalyst composition were used (Figure 2). The proportion of catalyst added was 10 wt %.

The hydrocarbon group composition, RON, and desulfurization performance of gasoline products obtained through different catalyst loading methods are illustrated in Table 4.

The results show that the adsorbent modified with Fe maintains excellent desulfurization performance, and its olefin retention ability obviously increases. The purpose of ultradeep desulfurization can still be achieved after adding the olefin conversion catalyst, but the breakthrough time is slightly shortened due to the reduced content of the desulfurization active substances. Olefin content decreases, whereas the content of *iso*-paraffins and aromatics increases in the process using Ni/ZnO adsorbent mixed catalyst. These effects are attributed to the isomerization and aromatization reactions on

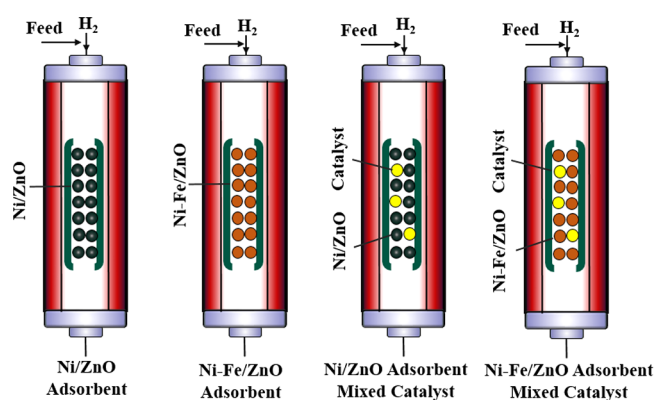


Figure 2. Different types of reactive adsorption desulfurization coupling olefin conversion catalyst systems.

the catalyst. The content of aromatic hydrocarbons in gasoline produced using the Ni-Fe/ZnO adsorbent mixed catalyst is significantly higher than that in gasoline produced using the Ni/ZnO adsorbent mixed catalyst.

This result can be attributed to the excellent olefin retention ability of the Ni-Fe/ZnO adsorbent, which retains more unreacted olefins to undergo isomerization and aromatization reactions on the catalyst. Octane number loss is reduced by 2.9 units in the Ni-Fe/ZnO adsorbent mixed catalyst process compared with the conventional reaction adsorption desulfurization process on the Ni/ZnO adsorbent, demonstrating the superiority of reactive adsorption desulfurization coupling olefin conversion.

3.3. Effect of the Proportion of Olefin Conversion Catalyst to Adsorbent. The above analysis shows that the addition of olefin conversion catalysts can reduce the loss of product gasoline octane number through isomerization and aromatization reactions in the catalysts. However, this method has adverse effect on breakthrough time, and the yield of product gasoline shows certain loss due to the cracking reaction on the catalysts. The olefin conversion results should be optimized during ultradeep desulfurization, and thus experimental investigation on the mixing ratio of olefin conversion catalyst is necessary.

The desulfurization test was performed under 420 °C reaction temperature, 2 MPa total pressure, 3 h⁻¹ WHSV, and 0.3 H₂-to-oil molar ratio. Changes in the hydrocarbon group composition of the reaction products containing different proportions of olefin conversion catalysts are shown in Figure 3a. Figure 3b shows the influence of the olefin conversion

Table 4. Effect of Loading Method on the Desulfurization Performance

loading method	Ni/ZnO	Ni-Fe/ZnO	Ni/ZnOmixed catalyst	Ni-Fe/ZnOmixed catalyst
hydrocarbon composition (wt %)				
<i>n</i> -paraffin	9.49	7.95	9.15	7.16
<i>i</i> -paraffin	35.73	33.93	37.92	36.58
olefin	24.91	28.72	21.53	24.05
naphthene	8.25	7.28	8.45	7.89
aromatic	21.62	22.12	22.95	24.32
breakthrough time (h)	22.83	24.81	20.30	22.46
sulfur capacity (wt %)	3.26	3.54	2.90	3.21
RON of product	88.6	90.3	90.4	91.5
liquid yield (wt %)	99.47	99.55	97.83	98.46

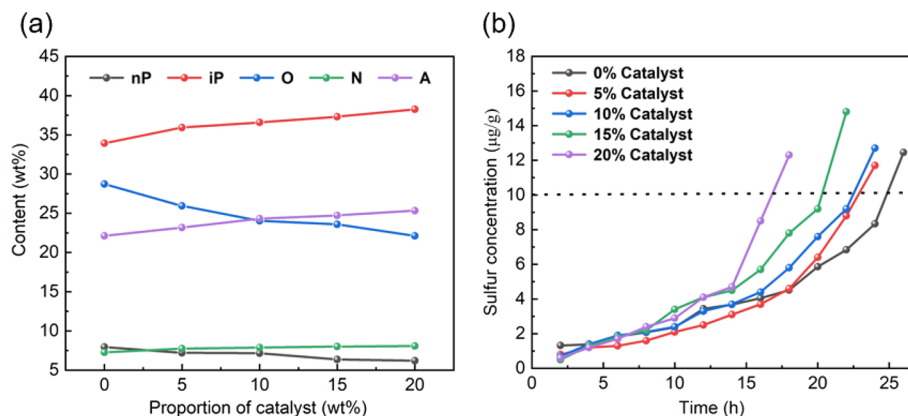


Figure 3. Effect of the addition ratio of upgrading catalyst on hydrocarbon group composition (a) and desulfurization performance (b).

catalyst addition ratio on the desulfurization curve in reactive adsorption desulfurization coupling olefin conversion.

As shown in Figure 3a, the content of olefins and normal alkanes in the product gasoline gradually decreases with increasing proportion of catalysts, whereas the content of *iso*-paraffins and aromatics increases significantly, and the content of cycloalkanes increases slightly.

The reason for these changes is that reactions involving olefins mainly occur on the active metal center through π complexation in traditional reactive adsorption desulfurization. Olefin conversion catalysts have rich pore structures and dense acid centers and can thus adsorb more olefins at the same proportions as adsorbents. The saturation reaction of olefins decreases, resulting in decreased content of normal paraffins and *iso*-paraffins. However, as the content of conversion catalysts increases, more olefins can undergo isomerization and aromatization reactions, which increase the content of *iso*-paraffins and aromatics.

As indicated in Figure 3b, the ultradeep desulfurization of gasoline can still be achieved in reactive adsorption desulfurization coupling olefin conversion, indicating that the addition of the olefin conversion catalyst has no effect on the desulfurization depth of the reaction adsorption desulfurization process. However, with the increase of catalyst proportion, the breakthrough time shows a downward trend. This is because the increase in catalyst proportion will reduce the content of adsorbent, which acts as the active center of desulfurization.

Table 5 shows the breakthrough sulfur capacities of the adsorbent, RON, and liquid yields of the product gasoline as the proportion of olefin conversion catalyst increases. Increased proportion of olefin conversion catalysts improves the octane number of the product gasoline, but the

Table 5. Effect of the Addition Ratio of Upgrading Catalyst on Desulfurization Performance

proportion of catalyst (wt %)	5	10	15	20
breakthrough time (h)	22.83	22.42	20.29	16.79
sulfur capacity (wt %)	3.28	3.22	2.91	2.41
RON of product	90.7	91.5	91.8	92.2
liquid yield (wt %)	98.82	98.46	97.52	96.54

breakthrough sulfur capacity is shortened, and the product yield is reduced. In view of the breakthrough sulfur capacity, octane number, and the yield of product gasoline, the catalyst addition ratio was selected as 10 wt %.

3.4. Effect of Operating Conditions. In reactive adsorption desulfurization coupling olefin conversion, the operation conditions are an important factor affecting desulfurization and hydrocarbon conversion performance. Therefore, the influences of reaction temperature, total pressure, WHSV, and molar ratio of hydrogen to oil on desulfurization performance and hydrocarbon group composition should be explored.

3.4.1. Effect of Reaction Temperature. The effects of reaction temperature on desulfurization performance and hydrocarbon group composition were explored at 2 MPa, 3 h⁻¹, and 0.3 H₂-to-oil molar ratio. The effect of reaction temperature on the hydrocarbon group composition of the product is shown in Figure 4a. The dependence of desulfurization curve on reaction temperature is presented in Figure 4b.

As reaction temperature increases, the content of olefins decreases and then increases, and content of *iso*-paraffins and normal paraffins increases and then decrease, whereas the content of aromatics increases monotonously. These results are

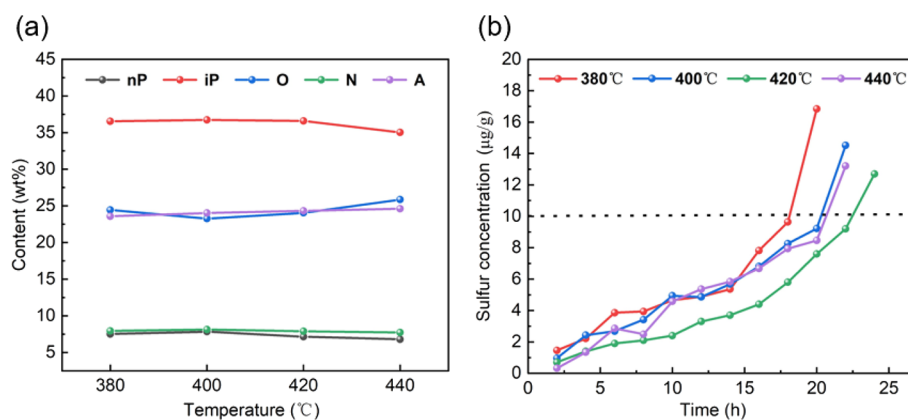


Figure 4. Effect of reaction temperature on the hydrocarbon group composition (a) and desulfurization performance (b).

attributed to the accelerated reactions of olefin saturation at increasing temperature. The saturation and isomerization of olefins are exothermic reactions, and thus further increase in temperature inhibits the saturation and isomerization on catalysts. By contrast, the aromatization reaction is endothermic, and the increase in temperature not only accelerates the aromatization rate but also promotes the aromatization reaction.

As shown in Figure 4b, the breakthrough time is significantly prolonged when the reaction temperature rises significantly from 380 to 420 °C. However, the breakthrough time shortens slightly when the reaction temperature continues to increase. The increase in reaction temperature is beneficial to the contact probability between sulfur compounds and metal active centers in adsorbents. Also, a high temperature is conducive to the cleavage of C–S bond in sulfur compounds. However, the desulfurization reaction is exothermic and high reaction temperature is not favorable in thermodynamics. In addition, high temperature is disadvantageous to the adsorption balance between sulfur compounds and active metals. Therefore, the breakthrough time decrease when the reaction temperature continues to rise from 420 to 440 °C. On the other hand, extremely high temperature also leads to cracking reactions and reduces the liquid yield of the product gasoline.

Breakthrough times, breakthrough sulfur capacities, RON, and liquid yields are listed in Table 6. In view of the breakthrough sulfur capacity, octane number, and the yield of product gasoline, 420 °C of reaction temperature was selected.

Table 6. Effect of Reaction Temperature on Desulfurization Performance

temperature (°C)	380	400	420	440
breakthrough time (h)	18.11	20.29	22.42	20.65
sulfur capacity (wt %)	2.60	2.91	3.22	2.97
RON of product	91.1	91.2	91.5	92.0
liquid yield (wt %)	98.91	98.72	98.46	96.28

3.4.2. Effect of Total Pressure. The effect of total pressure on desulfurization performance and hydrocarbon group composition were explored through experiments carried out at 420 °C, 3 h⁻¹, and 0.3 H₂-to-oil molar ratio. The effect of total pressure on the hydrocarbon group composition of the products is shown in Figure 5a. The dependence of

desulfurization curve on total pressure is presented in Figure 5b.

The content of olefins and aromatics decreases significantly with increasing total reaction pressure, whereas the content of *iso*-paraffins and normal paraffins increases significantly. High pressure improves the contact probability between olefins and hydrogen, which aggravates the olefin saturation reaction. The aromatization function of olefins on the conversion catalysts is inhibited by the increase in pressure, which lowers the content of aromatics.

As shown in Figure 5b, the breakthrough time is significantly prolonged when the total pressure increases from 1.6 to 2.0 MPa. However, the growth rate of breakthrough time slows down when the total pressure continues to increase. The increase in reaction pressure is mainly beneficial to the adsorption of sulfur compounds on the active metals of adsorbents. The adsorption concentration of sulfur compounds on adsorbent surfaces is close to saturation at 2 MPa. Thus, a small change in breakthrough time was observed as reaction pressure further increases.

Table 7 shows the breakthrough times, breakthrough sulfur capacities, RON, and liquid yields. Sulfur capacity basically saturates at reaction pressure of 2 MPa, which was selected as the appropriate reaction pressure.

3.4.3. Effect of the Molar Ratio of H/Oil. The effects of H₂-to-oil molar ratio on desulfurization performance and hydrocarbon group composition were explored through experiments carried out at 420 °C, 2 MPa, and 3 h⁻¹. The effect of H₂-to-oil molar ratio on the hydrocarbon group composition of reaction products is shown in Figure 6a. The dependence of desulfurization curve on the H₂-to-oil molar ratio is presented in Figure 6b.

As shown in Figure 6a, as the molar ratio of hydrogen to oil in the reaction increases, the olefin content of the product gradually decreases, whereas the content of *iso*-paraffins increases significantly, the content of normal paraffins and cycloalkanes increases slightly, and the content of aromatics shows a slow decreasing trend.

A high molar ratio of hydrogen to oil increases hydrogen partial pressure, which accelerates the regeneration rates of active metals. Adsorbed alkenes on the active metal center increase in quantity and undergo saturation reactions, which increase the content of alkanes. The molar ratio of hydrogen to oil is mainly adjusted by the increase in the hydrogen flow rate. As the molar ratio of hydrogen to oil increases, the contact time of olefins with catalysts is shortened. This effect is

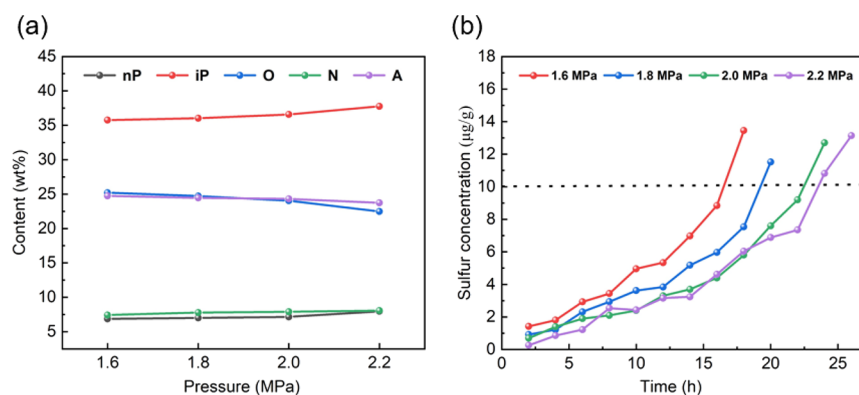


Figure 5. Effect of reaction pressure on the hydrocarbon group composition (a) and desulfurization performance (b).

Table 7. Effect of Reaction Pressure on Desulfurization Performance

pressure (MPa)	1.6	1.8	2.0	2.2
breakthrough time (h)	16.50	19.24	22.42	23.29
sulfur capacity (wt %)	2.37	2.76	3.22	3.34
RON of product	91.9	91.7	91.5	91.2
liquid yield (wt %)	96.71	97.98	98.46	98.57

Table 8. Effect of Molar Ratio of H/Oil on Desulfurization Performance

molar ratio of H/oil	0.2	0.3	0.4	0.5
breakthrough time (h)	19.54	22.46	24.12	24.61
sulfur capacity (wt %)	2.79	3.21	3.45	3.52
RON of product	91.7	91.5	91.3	91.2
liquid yield (wt %)	97.79	98.46	98.49	98.55

unfavorable to olefin isomerization and aromatization reactions on catalysts. The content of iP generally shows an upward trend because more *iso*-alkenes undergo the saturation reaction with the increase of the hydrogen-to-oil ratio.

As shown in Figure 6b, as the molar ratio of hydrogen to oil increases, the breakthrough time increases monotonously because high hydrogen partial pressure can provide more quantities of active hydrogen for the decomposition of sulfur compounds and is thus beneficial to the regeneration of active metals and to the desulfurization reaction.

The breakthrough times, breakthrough sulfur capacities, RON of the product, and liquid yields are listed in Table 8. The 0.3 molar ratio of hydrogen to oil was selected because of the relatively high breakthrough sulfur capacity and octane number of the product.

3.4.4. Effect of the WHSV. Experiments exploring the effect of WHSV on desulfurization performance and hydrocarbon group composition were carried out at 420 °C, 2 MPa, and 0.3 H₂-to-oil molar ratio. The effect of WHSV on the hydrocarbon group composition of reaction products is shown in Figure 7a. The dependence of desulfurization curve on WHSV is presented in Figure 7b.

As shown in Figure 7a, as WHSV increases in the reaction, the olefin content of the reaction products gradually increases, and the content of *iso*-paraffins, normal paraffins, cycloalkanes, and aromatics decrease slightly. These results are caused by the shortened contact time between olefins with adsorbents and catalysts. The shortened contact time not only reduces the saturation reaction of olefins but also is not conducive to the isomerization and aromatization reactions of olefins on catalysts.

As shown in Figure 7b, as WHSV increases, the breakthrough time decreases monotonously because the accumulation rate of sulfur atoms on the adsorbent gradually increases with the increase of WHSV, and this effect makes the adsorbent reach the saturation sulfur capacity quickly. The contact time between sulfur compounds and adsorbent is shortened as WHSV increases, and thus desulfurization performance decreases. Table 9 lists the breakthrough times, breakthrough sulfur capacities, RON, and liquid yields. A WHSV of 5 h⁻¹ was selected due to its nearly saturated sulfur capacity and relatively high octane number.

3.5. Regeneration Performance of Adsorbent Coupling Olefins Conversion Catalyst Process. The regener-

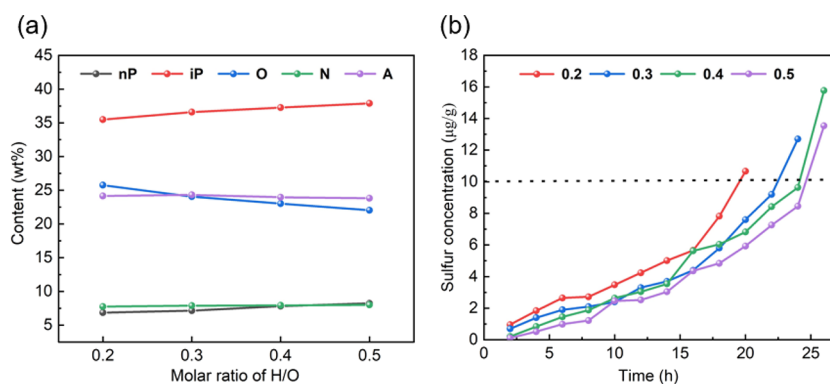


Figure 6. Effect of the molar ratio of H/Oil on hydrocarbon group composition (a) and desulfurization performance (b).

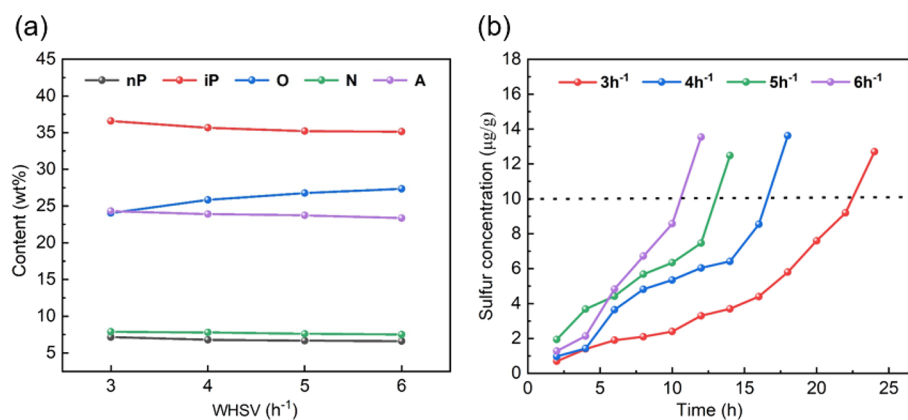


Figure 7. Effect of WHSV on hydrocarbon group composition (a) and desulfurization performance (b).

Table 9. Effect of WHSV on Desulfurization Performance

WHSV (h ⁻¹)	3	4	5	6
breakthrough time (h)	22.42	16.57	13.01	10.57
sulfur capacity (wt %)	3.22	3.17	3.11	3.04
RON of product	91.5	91.8	92.0	91.8
liquid yield (wt %)	98.46	98.63	98.87	99.07

ation property in reactive adsorption desulfurization coupling olefin conversion is an important criterion because adsorbents need to be periodically regenerated in the process. The regeneration experiments were carried out at 505 °C and air flow rate of 300 mL/min for 2 h. The desulfurization test for multiple regeneration cycles was performed under 420 °C reaction temperature, 2 MPa total pressure, 5 h⁻¹ WHSV, and 0.3 H₂-to-oil molar ratio.

The hydrocarbon group composition of the products for multiple regeneration cycles in reactive adsorption desulfurization coupling olefin conversion is shown in Figure 8a. The desulfurization curve for multiple regeneration cycles in reactive adsorption desulfurization coupling olefin conversion is shown in Figure 8b.

As shown in Figure 8a, the hydrocarbon composition of the products shows little change as regeneration cycles increases, indicating the good regeneration performance of catalysts to maintain isomerization and aromatization functions. The content of normal alkanes and *iso*-alkanes in the product slightly decreases, and the content of olefins slightly increases. These effects may be attributed to a small amount of uneliminated sulfur and carbon deposition covering the active

metal center as regeneration cycles increase. In addition, the breakthrough time does not decrease significantly with the increase of regeneration times, proving the excellent regeneration performance of adsorbent mixed with the catalyst. Detailed breakthrough times, breakthrough sulfur capacities, RON, and liquid yields are listed in Table 10.

Table 10. Desulfurization Performance for Multiple Regeneration Cycles

cycles	1st	2nd	3rd	4th
breakthrough time (h)	13.01	12.66	12.12	12.43
sulfur capacity (wt %)	3.11	3.03	2.91	2.97
RON of product	92.0	91.9	92.0	92.1
liquid yield (wt %)	98.46	97.53	98.37	98.51

3.6. Product Properties of the Adsorbent Coupling Olefin Conversion Catalyst Process. Table 11 lists the boiling ranges and density data of the feed and the gasoline produced from the conventional reactive adsorption desulfurization process and reactive adsorption desulfurization mixed olefin conversion catalyst process.

The initial distillation and front boiling points of the product gasoline after the conventional reactive adsorption desulfurization process slightly move forward, possibly because a small amount of cracking reactions occurs. In general, the distillation range does not change much compared with the feed. Different from the conventional reactive adsorption desulfurization process, the front boiling range of the gasoline produced by the reactive adsorption desulfurization coupling olefin

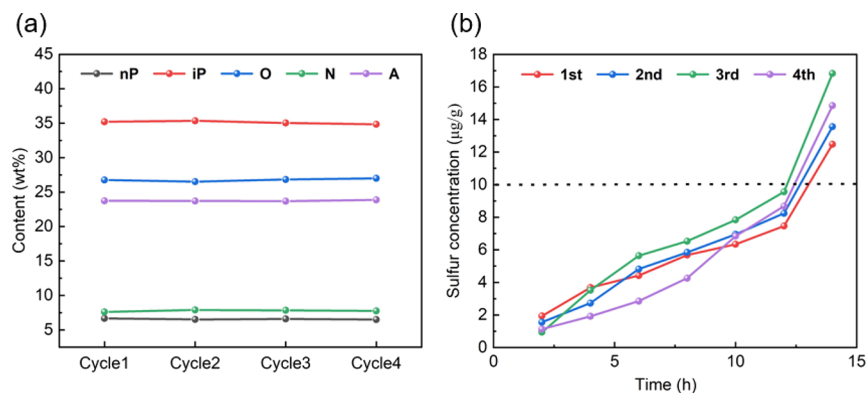


Figure 8. Hydrocarbon group composition (a) and desulfurization performance (b) for multiple regeneration cycles.

Table 11. Boiling Range Data of Products over Different Processes

item	feed	Ni–Fe/ZnO	Ni–Fe/ZnO mixed catalyst
boiling range (°C)			
IBP	42.9	41.6	38.6
10%	63.5	62.3	57.7
30%	81.0	80.2	73.7
50%	103.0	101.5	99.8
70%	131.6	131.2	142.7
90%	166.1	167.9	175.3
FBP	194.9	195.3	199.4
density (g/cm ³)	0.732	0.732	0.731

conversion catalyst process decreases dramatically, which can be attributed to the cracking reactions on the olefin conversion catalyst.

However, the end boiling range increases compared with the feed. This change can be interpreted as an increase in the content of aromatics because of the aromatization reactions on the olefin conversion catalyst. In addition, the density of the gasoline product by the conventional reactive adsorption desulfurization and reactive adsorption desulfurization coupling olefin conversion catalyst process does not change considerably.

4. CONCLUSIONS

The desulfurization reaction, olefin saturation reaction, and a small degree of cracking reaction simultaneously occur in the traditional reactive adsorption desulfurization process.

The adsorbent modified by Fe can reduce the saturation reaction of olefins while ensuring the desulfurization performance, which can retain more olefins for conversion on catalysts. The results show that the reactive adsorption desulfurization coupling olefin conversion process can achieve deep desulfurization, and the content of aromatics and *iso*-paraffins in the product increases significantly, which makes up the loss of octane number caused by the hydrogenation saturation of olefins. The octane number loss is reduced by 2.9 units in the Ni–Fe/ZnO adsorbent mixed catalyst process compared with the conventional reaction adsorption desulfurization process on the Ni/ZnO adsorbent.

The mixing ratio of the olefin conversion catalyst was investigated, and the appropriate addition ratio was selected as 10 wt % by considering the breakthrough sulfur capacity, octane number, and the yield of product gasoline. The effect of operation conditions on reaction performance was studied. Moderate temperature, high pressure, high molar ratio of hydrogen to oil, and low WHSV improve desulfurization ability, and low pressure, low molar ratio of hydrogen to oil, and low WHSV improve the olefin conversion ability. The optimal operation conditions are as follows: the reaction temperature is 420 °C, total pressure is 2 MPa, molar ratio of hydrogen to oil is 0.3, and WHSV is 5 h⁻¹. The octane number loss of this process is reduced by 85% compared with conventional reactive adsorption desulfurization under the optimal operating conditions. Multicycle regeneration experiments show that the reactive adsorption desulfurization coupling olefin conversion process exhibits excellent regeneration performance, which is suitable for producing qualified gasoline with ultralow sulfur and a high octane number.

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Notes

The authors declare no competing financial interest.

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