Deep Adsorption Desulfurization of Fluid Catalytic Cracking Light Gasoline on NiO/ZnO-TiO₂ Adsorbents with a High Breakthrough Sulfur Capacity

Guanglin Zhou, Sheng Chen, Weili Jiang,* Qin Li, Hongjun Zhou, Xuecheng Gong, and Xiance Zhang

ABSTRACT: Two kinds of NiO/ZnO-TiO₂ adsorbents were prepared by equal volume impregnation (NiO/ZnO-TiO₂-1) and kneading (NiO/ZnO-TiO₂-2) methods. The adsorbents were characterized by X-ray diffraction, mercury intrusion porosimetry, scanning electron microscopy, energy dispersive X-ray spectroscopy, H₂ temperature-programmed reduction, and H₂ temperature-programmed desorption. It was found that NiO/ZnO-TiO₂-2 had a smaller average pore diameter and a larger specific surface area as well as a more uniform distribution of the nickel element. Additionally, more Ni⁰ active sites together with a stronger interaction between the active component and the support were detected on the surface of NiO/ZnO-TiO₂-2, which was beneficial to the inhibition of olefin saturation during desulfurization. The desulfurization performance of the adsorbents was investigated in a fixed bed reactor with fluid catalytic cracking light gasoline as a feed oil. The evaluation results confirmed NiO/ZnO-TiO₂-2 with a better desulfurization performance with less olefin saturation. It could reduce the total sulfur content from 300 ppmw to less than 5 ppmw, and the breakthrough time and breakthrough sulfur capacity were 91 h and 6.71% (67.1 mg S/g adsorbent), respectively.

1. INTRODUCTION

As the demand for transportation fuel has been increasing in most countries in the past few decades, automobile emissions have become a significant source of air pollution,¹⁻³ and thus more stringent gasoline standards have been put forward around the world.⁴⁻⁵ For example, in China, the United States, and Europe, the sulfur content in gasoline is required to be lower than 10 mg/kg.

The sulfides in gasoline usually include mercaptan, thioether, thiophene, and their derivatives.⁶⁻⁻⁷ Mercaptans and thioethers can be removed through traditional desulfurization technologies such as hydrodesulfurization (HDS)⁹⁻⁻¹¹ and non-hydrodesulfurization.¹²⁻¹³ Thiophene, however, is difficult to remove through traditional hydrodesulfurization because the conjugate structure formed by coplanar carbon and sulfur atoms makes the C–S bond difficult to break.¹¹⁻¹³ Additionally, the traditional desulfurization process is usually accompanied by olefin hydrogenation, which will lead to a reduction in gasoline octane number.¹⁶⁻⁻¹⁸ Thus, new ultradep desulfurization technologies are needed to produce clean gasoline.¹⁹⁻⁻²⁰ An S-Zorb process developed by Conoco Phillips Co. is a widely used technology for producing ultralow-sulfur full-range gasoline.²¹ This process combines the advantages of HDS and adsorption desulfurization, which can effectively remove sulfur compounds through reactive adsorption desulfurization (RADS) using Ni/ZnO-based adsorbents while maintaining the octane number.²²⁻⁻²⁵

Babich and Moulijn investigated the removal mechanism of thiophene on NiO/ZnO.²⁶ Ullah et al.²⁷ studied the possible
RADS mechanism proposing that the key to prepare high-performance adsorbents lied in adsorbents with a high dispersion of metal components and a highly porous structure. Meng et al.28 compared the adsorption desulfurization performance of Ni/ZnO-based adsorbents supported on different supports, finding that the high dispersion of the active components and weak interactions between the active components and the support were beneficial for a better RADS performance. Huang et al.29 prepared Ni/ZnO adsorbents with various Ni/Zn molar ratios and found that the Ni content played a vital role in determining the RADS activity of Ni/ZnO.

It is known that more than three-quarters of commercial gasoline for automobiles in China is FCC (fluid catalytic cracking) light gasoline, where the olefin content is usually over 40%.30 The S-Zorb process is not suitable for FCC light gasoline desulfurization because the olefins are easily hydrogenated to saturate, reducing the octane number of gasolines. So far as we know, little work has been reported on the deep gasoline desulfurization because the olefins are easily hydrogenated to saturate, reducing the octane number of gasolines. Zhou et al.31 discovered that a suitable amount of Ti could improve the dispersion of the active component Ni in the Ni/ZnO adsorbent, increase the number of Ni active sites, and thus enhance the desulfurization performance.

At present, the penetrating sulfur capacity of most adsorbents is about 40 mgS/g. Herein, two kinds of Ni/ZnO-TiO2 adsorbents were prepared by a kneading method and an impregnation method for FCC light gasoline reactive adsorption desulfurization. The adsorbents were characterized by XRD, H2-TPR, H2-TPD, and mercury intrusion. Their effects on desulfurization performances were studied, where it showed that the one prepared by a kneading method had a larger breakthrough sulfur capacity.

## 2. EXPERIMENTAL SECTION

### 2.1. Materials

The FCC light gasoline was obtained from Lanzhou Petrochemical Company. The composition and the basic properties of the gasoline are listed in Table 1. In order to shorten the experimental period, thiophene was added to the feed oil to increase the sulfur content, and the total sulfur content of the feed oil was set to 300 ppmw.

Zinc oxide (industrial grade), a pore-forming agent (carboxymethylcellulose, industrial grade), and titanium dioxide (industrial grade) were purchased from Shandong Zibo Hengyi Chemical Technology Co., Ltd. Nickel nitrate (chemical pure grade) was purchased from Hubei Xinrunde Chemical Co., Ltd., and citric acid (analytical reagent grade) was purchased from Shanghai Dingxu Chemical Co., Ltd. Nitric acid (analytical reagent grade, 65.0–68.0%) was purchased from Sinopharm Chemical Reagent Co., Ltd.

### 2.2. Preparation of Adsorbents

#### 2.2.1. Equal Volume Impregnation Method

Zinc oxide (95.00 g) was mixed with titanium dioxide (5.00 g) and the pore-forming agent (2.00 g). Dilute nitric acid solution (1.8 wt%, 40.00 g) was then added to the mixed powder and stirred. After kneading in a squeezer for 90 min, the template was extruded and dried at room temperature for 12 h. After being dried at 120 °C for 3 h, it was calcined at the air at 500 °C for 3 h to give the ZnO-TiO2 support. Next, a solution was prepared by dissolving 14.68 g of nickel nitrate and 4.60 g of citric acid in deionized water. The ZnO-TiO2 support was impregnated with the above solution through an equal volume impregnation method. After being dried at 120 °C for 3 h, the solid was calcined at 500 °C for 3 h to obtain the Ni/ZnO-TiO2-1 adsorbent with a Ni loading of 4.45 wt%.

#### 2.2.2. Kneading Method

Zinc oxide powder (95.00 g) was mixed with nickel nitrate (14.68 g), citric acid (4.60 g), the pore-forming agent (2.00 g), and titanium dioxide (5.00 g). Dilute nitric acid solution (1.8 wt%, 40.00 g) was then added to the above mixture and mixed well. After kneading in a squeezer for 90 min, the template was extruded and the solid was dried at room temperature for 12 h. The sample was then dried at 120 °C for 3 h before being calcined in the air at 500 °C for 3 h.

### Table 1. Properties of Lanzhou Petrochemical Catalytic Cracking Light Gasoline

| sulfur content (ppmw) | octane number (RON) | hydrogen sulfide (mg/L) | thiosulfide (mg/L) | mercaptan sulfur (mg/L) | thiophene (mg/L) | total sulfur content (mg/L) |
|------------------------|---------------------|------------------------|--------------------|------------------------|-----------------|---------------------------|
| 20                     | 94.9                | 0.08                   | 1.32               | 0.54                   | 17.68           | 19.62                     |
Figure 2. XRD spectra of the two NiO/ZnO-TiO$_2$ adsorbents.

Table 2. Surface and Pore Properties of the Two NiO/ZnO-TiO$_2$ Adsorbents

| adsorbents         | $S_{BET}$ ($m^2g^{-1}$) | pore volume ($mlg^{-1}$) | average aperture (nm) | bulk density ($gcm^{-3}$) | particle strength (N/cm) |
|--------------------|--------------------------|--------------------------|-----------------------|---------------------------|-------------------------|
| NiO/ZnO-TiO$_2$-1  | 30.34                    | 0.24                     | 32.70                 | 1.3                       | 78.4                    |
| NiO/ZnO-TiO$_2$-2  | 31.02                    | 0.23                     | 29.60                 | 1.3                       | 65.7                    |

$^\circ$C for 3 h to form the Ni/ZnO-TiO$_2$-2 adsorbent with a Ni loading of 4.45 wt %.

2.3. Characterization of Adsorbents. XRD patterns were obtained on a D8 Advance type X-ray diffractometer (Cu K$_\alpha$, $\lambda = 1.54051\ \AA$) in a scanning range of 2$\theta = 5$ to 90$\circ$. A mercury intrusion test was carried out on an Autopore IV 9510 automatic mercury injector with a mercury intrusion pressure range of 0.1 to 60000.0 psia. H$_2$-TPR spectra were measured using an AutoChem II 2920 automatic analyzer. The samples were placed in the air at 500 $^\circ$C for 2 h and cooled in an Ar atmosphere. Then, temperature-programmed reduction was carried out in a mixed gas stream of Ar/H$_2$ (90/10 mol/mol, 50 mL/min) at a heating rate of 10 $^\circ$C/min to 700 $^\circ$C. The samples were reduced in a hydrogen atmosphere for 2 h. After cooling to 50 $^\circ$C, hydrogen was adsorbed for 1 h and purged with Ar for 1 h. The temperature-programmed desorption was carried out at a heating rate of 10 $^\circ$C/min to 550 $^\circ$C.

2.4. Desulfurization Experiments. The FCC light gasoline desulfurization reaction was carried out in a 15 mL fixed bed reactor loaded with 15 mL of adsorbent (Figure 1). The experiment was performed at 340 $^\circ$C under a pressure of 0.6 MPa. Prior to the reaction, the adsorbent was reduced by hydrogen at 350 $^\circ$C and 0.5 MPa for 2 h. Then, the gasoline was introduced into the reactor at a weight hourly space velocity (WSHV) of 5 h$^{-1}$ with a H$_2$/oil volume ratio of 25. The outlet product was collected for analysis every 2 h. The sulfur content in the gasoline was detected on an RPP-2000S ultraviolet fluorescence sulfur analyzer. When the sulfur content of the product exceeded 5 ppmw, the adsorbent was considered to be broken through and the reaction would be stopped. The breakthrough sulfur capacity ($S_B$, the amount of sulfur that can be absorbed by a unit volume desulfurizer) was determined as follows:

$$S_B = \frac{Q \times \rho \times (C_{in} - C_{out}) \times t \times 10^{-6}}{m} \times 100$$

In the formula, $Q$ is the gasoline flow rate (mL/h), $\rho$ is the gasoline density (g/mL), $t$ is the breakthrough time (h), $m$ is the mass of the adsorbent (g), and $C_{in}$ and $C_{out}$ are the sulfur contents (ppmw) in the inlet and outlet gasoline.

3. RESULTS AND DISCUSSION

3.1. XRD Analysis. The XRD spectra of the two NiO/ZnO-TiO$_2$ adsorbents are shown in Figure 2. It can be seen that the XRD patterns of the two adsorbents are similar, indicating that they had the same compositions, which were NiO, TiO$_2$, and ZnO. The peaks at 31.77, 34.42, 36.26, 47.54, 56.60, 62.85, 67.95, 69.09, and 72.57$^\circ$ were classified as ZnO (ICDD-PDF No. 65-3411). The diffraction peaks of rutile TiO$_2$ (ICDD-PDF No. 21-1272) were found at 25.28, 37.77, 53.88, and 55.01$^\circ$. The weak diffraction peak that appeared at 43.1$^\circ$ was attributed to the crystalline NiO$_3$, which was generated from the decomposition of the Ni(NO$_3$)$_2$ precursor. The diffraction peaks attributed to NiO of the two adsorbents were extremely weak, suggesting that NiO was highly dispersed on the supports.

3.2. Physical Properties of Adsorbents. The surface and pore properties of the two NiO/ZnO-TiO$_2$ adsorbents are shown in Table 2 and Figure 3. It can be seen from Table 2 that the internal pores of the adsorbents were mainly distributed at 10–50 nm, which was a typical mesoporous structure. The distribution ratio of pores at 25 nm is higher than that of NiO/ZnO-TiO$_2$, while NiO/ZnO-TiO$_2$-I had a higher pore distribution ratio at 25–50 nm. This resulted in the average pore sizes of NiO/ZnO-TiO$_2$-I being larger than those of NiO/ZnO-TiO$_2$-2, which were 32.70 and 29.60 nm, respectively. At the same time, the surface areas of NiO/ZnO-TiO$_2$-1 and NiO/ZnO-TiO$_2$-2 were slightly larger, which was 31.02 $m^2g^{-1}$. The difference in the pore distribution might be explained by the different preparation methods. In the kneading method, the precursor of the active
A component was uniformly mixed with the powder mixture of the prepared support in the form of a solution. The molding adsorbent was obtained by direct extrusion and calcination. The active species was dispersed more uniformly on the support, and at the same time, it participated in the formation of the support pores. As to the impregnation method, the support had been calcined to form a certain pore structure. When the support was impregnated with the active precursor solution, the active species might accumulate and grow inside the pores. This caused damage or blockage to smaller channels, resulting in increased channels. It can also be seen from Table 3 that the particle strength of NiO/ZnO-TiO$_2$-1 was relatively low.

3.3. Morphology and Composition Analysis. The morphology and composition of the two adsorbents were studied through SEM and EDX characterization, listed in Figure 4. Not so much difference could be observed on their SEM pictures, meaning that the two adsorbents have similar surface topography. The EDX results, however, gave more interesting information. First, the composition of the two adsorbents were nearly the same, i.e., with 13–14% Ti, 11–12% Ni, and 74–75% Zn. Nevertheless, one obvious difference was discovered in the distribution of the Ni element. The nickel element in NiO/ZnO-TiO$_2$-1 was very concentrated, while that in NiO/ZnO-TiO$_2$-2 dispersed very well.

3.4. H$_2$-TPR Analysis. The reduction performances of the adsorbents were investigated through H$_2$-TPR experiments, and the results are demonstrated in Figure 5. It is found that the two H$_2$-TPR curves had a similar tendency, with a broad band at 300–550 °C and a weak shoulder band around 330 °C, which belonged to the reduction of NiO species. The lower temperature bands were attributed to the weak

![Figure 3. Pore diameter distribution of the two NiO/ZnO-TiO$_2$ adsorbents.](image)

![Figure 4. SEM and EDX results of (a) NiO/ZnO-TiO$_2$-1 and (b) NiO/ZnO-TiO$_2$-2.](image)

![Figure 5. H$_2$-TPR of the two NiO/ZnO-TiO$_2$ adsorbents.](image)

Table 3. Breakthrough Sulfur Capacities of the Two Ni/ZnO-TiO$_2$ Adsorbents

| sample            | sulfur capacity (%) |
|-------------------|---------------------|
| NiO/ZnO-TiO$_2$-1 | 5.46                |
| NiO/ZnO-TiO$_2$-2 | 6.71                |
interaction between Ni$^{2+}$ species and the ZnO-TiO$_2$ support, while the higher temperature signals were attributed to the strong interaction of Ni$^{2+}$ and the support. The reduction band of NiO/ZnO-TiO$_2$ shifted toward the higher temperature, which implied that there is a stronger interaction between the Ni species and this support than NiO/ZnO-TiO$_2$-1. That is, the NiO species in NiO/ZnO-TiO$_2$-2 was more difficult to reduce. At the same time, the enhancement of metal-support interaction also reduced the amount of free NiO, which was beneficial to the inhibition of the olefin saturation reaction in the desulfurization process. In addition, the reduction peak area of NiO/ZnO-TiO$_2$-2 (19.8) was larger than that of NiO/ZnO-TiO$_2$-1 (12.4), suggesting that the former contained more NiO component that could be reduced, which might be generated in NiO/ZnO-TiO$_2$-2 under suitable reduction conditions.

3.5. H$_2$-TPD Analysis. The adsorbents were further characterized by H$_2$-TPD (Figure 6) in order to study the dispersion state of surface Ni$^0$ species on the adsorbents after reduction. It can be found that both of the adsorbents showed a low-temperature hydrogen desorption peak at 50–140 °C and a high-temperature peak at a range higher than 200 °C. The lower-temperature peak was generally related to the desorption of hydrogen adsorbed on the surface active species Ni$^0$ of the adsorbent support, and the area of the desorption peak was positively correlated with the amount of surface active species Ni$^0$. By calculation, the hydrogen desorption peak area of NiO/ZnO-TiO$_2$-2 (0.142) was larger than that of NiO/ZnO-TiO$_2$-1 (0.063), indicating that more active Ni$^0$ sites were generated on the former after reduction. Together with the EDX results in Figure 4, the possible reason was that for NiO/ZnO-TiO$_2$-1, the active component impregnation was uneven during the impregnation process, which thus caused a large amount of agglomeration of nickel, resulting in fewer active sites. In addition, according to Table 2, NiO/ZnO-TiO$_2$-2 had a smaller average pore diameter and a larger specific surface area, which helped to support more active sites of Ni$^0$.

3.6. Adsorption Desulfurization Performance of the Adsorbents. The adsorption desulfurization performances of the two Ni/ZnO-TiO$_2$ adsorbents were tested with FCC light gasoline, and the results are shown in Figure 7 and Table 3. As revealed, both of the adsorbents had an excellent desulfurization performance, and the sulfur content in the FCC light gasoline could be removed to below 5 ppmw for a long time. The desulfurization performance of NiO/ZnO-TiO$_2$-2 was more superior with a breakthrough time of 91 h and breakthrough sulfur capacity of 6.71% (67.1 mg S/g adsorbent). Compared with 74 h and 5.46% (54.6 mg S/g adsorbent) for NiO/ZnO-TiO$_2$-1, the breakthrough sulfur capacity of NiO/ZnO-TiO$_2$-2 was increased by 23%. Considering the slightly stronger interaction between the support, which would make the NiO species in the adsorbent more difficult to be reduced, together with the more active species Ni$^0$ for NiO/ZnO-TiO$_2$-2, the interaction strength should not have a big impact on the desulfurization performance. The possible reason was that the relatively large specific surface area of NiO/ZnO-TiO$_2$-2 was beneficial to support more active sites on the surface, which was also proven by H$_2$-TPD and EDX. Therefore, for the NiO/ZnO modified by TiO$_2$, it is more favorable to prepare the adsorbent by a kneading method for deep desulfurization.

In addition, it is also known from the H$_2$-TPR results that NiO/ZnO-TiO$_2$-2 contained a lower content of free NiO, which was favorable for suppressing the olefin saturation reaction. The olefin contents of FCC gasoline before and after desulfurization on the two adsorbents are shown in Table 4. As demonstrated, the saturation amount of olefin in the FCC light gasoline after desulfurization on NiO/ZnO-TiO$_2$-2 was smaller.

4. CONCLUSIONS

NiO/ZnO-TiO$_2$ adsorbents for FCC light gasoline desulfurization were prepared by the equal volume impregnation method (NiO/ZnO-TiO$_2$-1) and kneading method (NiO/ZnO-TiO$_2$-2).

Table 4. Olefin Content of FCC Gasoline before and after Desulfurization on the Two Adsorbents

| samples                              | olefin (wt %) | alkane (wt %) | density (g/cm$^3$) |
|--------------------------------------|---------------|---------------|--------------------|
| gasoline before desulfurization      | 42.6          | 55.27         | 0.6879             |
| gasoline after desulfurization on Ni/ZnO-TiO$_2$-1 | 42.0          | 55.99         | 0.6763             |
| gasoline after desulfurization on Ni/ZnO-TiO$_2$-2 | 42.3          | 55.10         | 0.6796             |
2) The NiO/ZnO-TiO2-2 adsorbent had a larger specific surface area and a smaller pore diameter than NiO/ZnO-TiO2-1 because the precursor of the active Ni species was uniformly mixed with the support powder in the NiO/ZnO-TiO2-2 adsorbent. Additionally, the NiO species was more uniformly dispersed and more Ni0 active sites were generated on the adsorbent. The interaction between the active component and the support was proven to be stronger so that the lower content free NiO was reduced, which was beneficial to suppress the olefin saturation in the desulfurization process. The final desulfurization results of the two adsorbents confirmed that the Ni/ZnO-TiO2-2 adsorbent was more excellent in both the desulfurization activity and suppression of olefin saturation.

■ AUTHOR INFORMATION

Corresponding Author
Weili Jiang – College of New Energy and Materials, State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Beijing 102249, China; orcid.org/0000-0002-7602-3343; Email: jiangweilipku@163.com

Authors
Guanglin Zhou – College of New Energy and Materials, State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Beijing 102249, China
Sheng Chen – College of New Energy and Materials, State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Beijing 102249, China
Qin Li – College of New Energy and Materials, State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Beijing 102249, China
Hongjun Zhou – College of New Energy and Materials, State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Beijing 102249, China
Xuecheng Gong – College of New Energy and Materials, State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Beijing 102249, China
Xiance Zhang – College of New Energy and Materials, State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Beijing 102249, China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c06645

Notes
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