Selective catalytic oxidation of H$_2$S over iron oxide supported on alumina-intercalated Laponite clay catalysts

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HIGHLIGHTS

- Fe/Al-Lap catalysts with mesoporous structure were synthesized.
- Iron oxide mainly exists in form of isolate Fe$^{3+}$ in an oxidative environment.
- Fe/Al-Lap catalysts show high catalytic activities at low temperature.
- The high catalytic activities are ascribed to the interaction between iron oxide and alumina.
- The formed Fe$_2$(SO$_4$)$_3$ and elemental sulfur deposits on surface cause catalyst deactivation.

ABSTRACT

A series of iron oxide supported on alumina-intercalated clay catalysts (named Fe/Al-Lap catalysts) with mesoporous structure and high specific surface area were prepared. The structural and chemical properties were studied by nitrogen sorption isotherms, X-ray diffraction (XRD), UV–vis diffuse reflectance spectra (UV–vis DRS), X-ray photoelectron spectra (XPS), Fourier transform infrared spectroscopy (FTIR), H$_2$ temperature-programmed reduction (H$_2$–TPR) and NH$_3$ temperature-programmed desorption (NH$_3$–TPD) techniques. It was realized that iron oxide mainly existed in the form of isolated Fe$^{3+}$ in an oxidative environment. Fe/Al-Lap catalysts showed high catalytic activities in the temperature range of 120–200 °C without the presence of excessive O$_2$. This can be attributed to the interaction between iron oxide and alumina, which improve the redox property of Fe$^{3+}$ efficiently. In addition, the strong acidity of catalysts and good dispersion of iron oxide were also beneficial to oxidation reaction. Among them, 7% Fe/Al-Lap catalyst presented the best catalytic performance at 180 °C. Finally, the catalytic and deactivation mechanisms were explored.

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1. Introduction

In the past decades, sulfur recovery from H$_2$S, which is generated from crude oil and natural gas refineries industries, has attracted considerable attentions. Because of H$_2$S is a poisonous pollutant and can damage the environment [1]. Until now, the most common used technology is the Claus process. However, because of the
thermodynamic limitations of Claus equilibrium reaction, there is still 4% H2S left in off-gas. In order to remove the residual H2S, the H2S selective catalytic oxidation technique is developed to directly convert H2S to elemental sulfur [1,2]. The reaction equations are as follows: (Eq. (1) as the main reaction, Eqs. (2) and (3) as side reactions) [3–5]:

\[
\text{H}_2\text{S} + \frac{1}{2}\text{O}_2 \rightarrow \frac{1}{2}\text{S}_\text{n} + \text{H}_2\text{O}
\]

(1)

\[
\frac{1}{2}\text{S}_\text{n} + \text{O}_2 \rightarrow \text{SO}_2
\]

(2)

\[
\text{H}_2\text{S} + \frac{3}{2}\text{O}_2 \rightarrow \text{SO}_2 + \text{H}_2\text{O}
\]

(3)

The reaction (Eq. (1)) is irreversible and does not have any equilibrium limitation. However, the sulfur yield mainly depends on the catalyst performance, which can be limited by the oxidation of the produced sulfur and complete oxidation of H2S to SO2 (Eqs. (2) and (3)). Therefore, catalyst with high selectivity and activity is strongly needed [6].

Metal oxide based catalysts such as TiO2, Cr2O3, V2O5, Fe2O3 are considered as the potential catalysts or catalyst supports for H2S selective oxidation. However, each of them has their own disadvantages. TiO2 based catalysts can be poisoned easily in the presence of water [7] and the main drawback of Cr2O3 is its toxic nature [8]. As reported, V2O5 has high activity and selectivity for H2S selective oxidation, but the activity and selectivity mainly depend on the chemical state of vanadium.

Iron oxide, one of the oldest catalysts, has been used as catalyst in the process of H2S selective oxidation. Such as Nguyen et al. and keller et al. have been synthesized SiC-based iron catalysts and used for H2S selective oxidation. Moreover, the catalytic performances, active phase, the optimized reaction conditions and catalytic mechanism were also explored in detail. Furthermore, it was proposed that Fe2O3 transformed into Fe3+ intermediate (Fe2O3-3xSO3(x<2)) in the reaction process, which was considered as the true active phase. [9,10]. However, iron oxide based catalysts have their own disadvantages, such as the low sulfur selectivity as they required an excess amount of oxygen and their fast deactivation caused by sulfidation and sulfur deposition [3]. So, it is essential to modify iron oxide to obtain a catalyst with high selectivity, activity and stability.

Clay is ubiquitous in nature, with nanoscopic size, anisotropic shape, apparently non toxic nature, and low cost. However, the efficient use of clay is restricted by their low porosity and poor thermal stability [11]. Among the various clays, Laponite, with a chemical formula of Sls8[Mg5.5Li0.4H2O24]0.72–0.74 Na0.7, is a type of commercial synthetic hectorite clay. In a unit cell of the Laponite crystal, six octahedral magnesium ions are sandwiched between two layers of four tetrahedral silicon atoms. These groups are balanced by 20 oxygen atoms and four hydroxyl groups [12]. Due to partial magnesium was substituted by lithium, it has exchangeable hydrated sodium ion on its platelets to balance the negative surface charges. Thus, it is considered as a desirable starting material for fabricating nanomaterial.

Herein, a good method was developed to synthesize alumina-intercalated Laponite clay composites with mesoporous structures and high thermal stability in the presence of surfactants [14,15]. In consequence, the composites can be widely used as catalyst supports. Because of the mesoporous structure and large specific surface area allow the well dispersion of catalytic active phase. Moreover, the surface acidity of the composites is improved by the modification of alumina, which is beneficial to the catalytic reaction. Thus, it is expected to enhance the catalytic performance for H2S selective oxidation by the combination of intercalated clay (support) and iron oxide (active phase).

In this work, we prepared a series of iron oxide supported on alumina-intercalated clay catalysts with mesoporous structure and high thermal stability. As expected that the catalytic performance for H2S selective oxidation can be enhanced effectively. Furthermore, the optimized reaction conditions such as time on stream and the O2/H2S ratio were investigated. Besides, the catalysts deactivation mechanism was deeply studied. To the best of our knowledge, it is the first time to report the selective oxidation of H2S over alumina-intercalated clay supported iron oxide catalysts.

2. Experimental

2.1. Catalysts preparation

Laponite clay, was supplied by Fernz Specialty Chemicals, Australia. Nonionic PEO surfactant Tergitol type 15-5-9 was procured from the Sigma Chemical Company. The alumina-intercalated Laponite clay composites were synthesized according to the procedures described by Li et al. [16]. In the process, the surfactants were firstly intercalated into the galleries and forms micelles, acting as templates. Secondly, alumina nanoparticles were introduced into the galleries by enclosing the micelles. Finally, the composites with mesosporous structure were obtained after removal of the surfactants by heating. The prepared alumina-intercalated Laponite clay composites were denoted as Al-Lap. The iron oxide supported on Al-Lap catalysts containing 3, 6, 7 and 8% iron were prepared by wetness impregnation method using Fe(NO3)3 as the active component precursor. The impregnated materials were dried at 100 °C overnight, and then were calcined at 550 °C for 4 h. The samples were denoted as x% Fe/Al-Lap, where x% referred to the iron loading content (weight percentage) on the support.

2.2. Characterizations of the catalysts

The specific surface areas and textual properties of catalysts were determined by nitrogen sorption isotherms using a gas sorption analyzer NOVA1200. Prior to N2 sorption measurement, the samples were degassed at 300 °C for 3 h.

X-ray diffraction (XRD) patterns were recorded on a PANalytical X’Pert PRO powder diffraction system using Cu K radiation (λ=0.15418 nm) in the 2θ range of 10–80° (scanning rate of 0.5°/min). The electron paramagnetic resonance (EPR) spectra were recorded on a JES FA200 spectrometer at –150 °C.

Fourier transform infrared (FT-IR) spectroscopy was measured by the KBr method recorded on a Bruker Tensor 27, scanned from 4000 to 600 cm−1. UV–vis diffuse reflectance spectra (UV–vis–DRS) were recorded in the air against BaSO4 in the region of 12,500–24,000 cm−1 on a Hitachi UV–3000 spectrometer.

The exact iron loading contents were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) on a Perkin Elmer OPTIMA2000.

X-ray photoelectron spectra (XPS) were recorded with a Thermo Electron Escalab250 instrument using Al Ka radiation. The base pressure was 5 × 10−8 Pa. The binding energies were calibrated using C 1s peak of contaminant carbon (BE=285 eV) as standard, and quoted with a precision of ±0.2 eV.

H2 temperature-programmed reduction (H2–TPR) experiments were conducted on a Micromeritics Chemisorb 2720 apparatus. TPR profiles were obtained by passing a 5% H2/He flow (50 ml/min) through the pretreated catalyst (about 100 mg). Temperature was increased from room temperature to 700 °C at a rate of 10 °C/min. Hydrogen concentration in the effluent was continuously
monitored by a thermo conductivity detector. Prior to each TPR run, catalyst was pre-heated in He flow from room temperature to 300 °C and held for 30 min.

NH₃ temperature-programmed desorption (NH₃-TPD) was carried out on the same apparatus as that in H₂-TPR. In the process, the sample was heated from room temperature to 900 °C at a rate of 10 °C/min in pure He. Before each TPD test, 100 mg sample was pre-heated in He flow from room temperature to 300 °C and sustained for 30 min. After cooling to room temperature, 2% NH₃/N₂ was fed to the reactor at 50 ml/min for 30 min, then, pure He was fed to the reactor at 50 ml/min for 30 min to purge away any residual NH₃.

2.3. Catalytic tests

All the tests were performed in a continuous flow fixed-bed quartz reactor at atmospheric pressure. A 0.6 g catalyst (20–40 mesh) was placed in the central section of the reactor. The mixture gas containing 5000 ppm H₂, 2500 ppm O₂ and balance gas (N₂) were fed into the reactor at 200 ml/min (GHSV = 7000 h⁻¹) and reacted in temperature range of 120–200 °C. After the reaction, the effluent stream was detected by a gas chromatograph (GC126) equipped with a FPD and TCD. A condenser was located at the bottom of the reactor to trap the sulfur gas in effluent stream. Instantaneous fractional conversion of H₂S, sulfur selectivity and sulfur yield were defined as follows [6]:

\[
\text{H₂S conversion} = \frac{(\text{H₂S})_{\text{in}} - (\text{H₂S})_{\text{out}}}{(\text{H₂S})_{\text{in}}} \\
\text{Sulfur selectivity} = \frac{(\text{H₂S})_{\text{in}} - (\text{H₂S})_{\text{out}} - (\text{SO₂})_{\text{out}}}{(\text{H₂S})_{\text{in}} - (\text{H₂S})_{\text{out}}} \\
\text{Sulfur yield} = (\text{H₂S conversion}) \times (\text{Sulfur selectivity})
\]

3. Results and discussion

3.1. Textural and structural properties of Fe/Al-Lap catalysts

The nitrogen sorption isotherms of all catalysts are displayed in Fig. 1 and the textual data of all catalysts are listed in Table 1. As shown in Fig. 1, all isotherms are type IV [17], which corresponds to that of mesoporous structure. Moreover, the specific surface area and total pore volume of Al-Lap are 519 m²/g and 0.932 cm³/g, respectively, while the initial clay are 322 m²/g and 0.236 cm³/g. (Table 1). The significantly increase in specific surface area and pore volume associate with the nitrogen sorption isotherms indicate that Al-Lap composites with mesoporous structure were successfully synthesized. The high specific surface area and mesoporous structure of Al-Lap allow iron oxide disperse well on it. However, the amount of adsorbed nitrogen decreases with the rise of iron oxide loading, indicating the decreases in specific surface area and total pore volume (Fig. 1 and Table 1). It can be attributed to the pore blockage by the loaded iron oxide. The exact iron contents in the catalysts determined by ICP are also shown in Table 1.
In order to further investigate the structure of Fe/Al-Lap catalysts, FTIR technology was applied. Fig. 3 shows the FTIR spectra of all catalysts. For all catalysts, the bands appeared at 1200 cm\(^{-1}\) and 1660 cm\(^{-1}\) are corresponding to the bending vibration of Si-O and adsorbed water, respectively. Meanwhile, the broad band at 3200 cm\(^{-1}\)–3600 cm\(^{-1}\) is linked to the vibration of OH groups, which is strengthened after the introduction of alumina. Apparently, 7\% Fe/Al-Lap catalyst has the strongest peak intensity, implying that 7\% Fe/Al-Lap catalyst possesses more OH groups than the other catalysts. Moreover, the new band appeared at 3678 cm\(^{-1}\) for Fe/Al-Lap catalysts should be assigned to the stretching vibration of structure OH groups [19], as known that the structural defect of silicate framework of clay can be formed during the intercalation process, which leads to the form of structure OH group [19,20]. Moreover, both type of OH groups can enhance the acidity of Al-Lap effectively, especially for Lewis acidity. Therefore, it can be expected that 7\% Fe/Al-Lap catalyst possesses the strongest Lewis acidity. Besides, the loaded iron oxide has no obvious influence on the structure of Al-Lap.

3.2. Chemical status analysis of Fe/Al-Lap catalysts

UV-vis DRS is a suitable technique for studying the dispersion and nature of supported iron oxide. Fig. 4 shows the UV-vis DRS spectra of all catalysts. In any case, the adsorption bands can be divided into three charge transfer (CT) bands around 220 nm, 350 nm, 500 nm, respectively. The band under 300 nm corresponds to isolated iron species (Fe\(^{3+}\)) in an oxidic environment, while the band in range of 300–370 nm can be assigned to the existence of oligonuclear Fe\(^{3+}\)O\(_x\) complexes and the band around 500 nm can be ascribed to larger Fe\(_2\)O\(_3\) nanoparticles [21–23]. Moreover, the spectra are dominated by the band around 220 nm, attributed to isolated iron species, indicating that iron oxide are well dispersed on the support. It is beneficial to the oxidation reaction. The percent area of the band around 350 nm (oligonuclear Fe\(^{3+}\)O\(_x\)) almost maintain consistently (39\%) for all catalysts. However, the percent area of band around 500 nm (larger Fe\(_2\)O\(_3\) nanoparticles) is 6.7, 8, 11.5, 19\% for 3, 6, 7, 8\% iron loaded catalysts, respectively, indicating that larger Fe\(_2\)O\(_3\) nanoparticles are more easily formed with the increase of iron loading.

Fig. 5 depicts the Fe 2p XPS spectra of a selected catalyst (7\% Fe/Al-Lap). For the fresh catalyst, it reveals that the spin-orbit splitting of Fe 2p\(_{3/2}\) ground state at 711.9 eV and the Fe 2p\(_{1/2}\) excited state at 725.4 eV, the peak position and energy difference between Fe 2p\(_{3/2}\) and Fe 2p\(_{1/2}\) (13.5 eV) are typical of the Fe\(^{3+}\) state in an oxidic environment [24–27]. Therefore, the XPS analysis confirms the unique presence of Fe\(^{3+}\).

In order to further investigate the nature of iron species, the EPR spectra are presented in Fig. 6. As shown that all spectra are the superposition of the signals from two different types of Fe\(^{3+}\) ions. The signal at g = 4.3 is corresponding to the presence of isolated, oxygen coordinated Fe\(^{3+}\) ions in a distorted tetrahedral environment [9]. While the signal at g = 2.0 can be ascribed to the presence of superparamagnetic iron oxide nanoparticles. Moreover, the spectra are dominated by the signal at g = 4.3, indicating...
that the iron species mainly exist in the form of isolated Fe$^{3+}$ in an oxidic environment. This result is accordance with the XPS and UV-vis DRS analysis.

### 3.3. Reductive properties of catalysts

The redox properties of catalysts are elucidated by H$_2$-TPR measurement. Besides, the dispersion and distribution of the iron oxide can be also provided. Fig. 7 presents the reduction profiles of all catalysts. In the case of Laponite, only a small peak appears at 309°C, which can be attributed to the slight reduction of Laponite. Moreover, for the catalysts, all curves are dominated by one main reduction peak at 440°C, which can be assigned to the reduction of Fe$^{3+}$ to Fe$^{2+}$ [28,29]. And the peak intensity increases with the rise of iron loading.

### 3.4. Acid properties of catalysts

NH$_3$-TPD profiles of all catalysts are exhibited in Fig. 8. The NH$_3$ desorption patterns can be classified into weak acid sites (desorption at 100°C) and strong acid sites (desorption at 850°C). The peak at low temperature is due to ammonia desorption from the weak Bronsted acid sites, while that at high temperature corresponds to the desorbed ammonia from strong Lewis acid sites [30,31]. Compared with the host clay, the intensity of the latter peak is enhanced obviously, and the peak shift towards higher temperature. It indicates that the amount and strength of strong acid sites are improved due to the modification of alumina. It can be attributed to the large amount of −OH groups of Fe/Al-Lap catalysts, which is already confirmed by FTIR analysis. Furthermore, all catalysts are dominated by strong acid sites (Lewis acid sites), as known, H$_2$S can be adsorbed on the Lewis acid sites [32], which is favourable to the oxidation reaction. Therefore, the strong acidity of the catalysts may improve the catalytic performance and play an important role in H$_2$S selective oxidation.

### 4. Catalytic performances

#### 4.1. Effect of reaction temperature

Fig. 9 shows the catalytic performances of all catalysts for the oxidation of H$_2$S at temperature ranging from 120°C to 200°C with the reactant composition of H$_2$S/O$_2$/N$_2$ = 5/2.5/92.5 at 7000 h$^{-1}$ of GHSV. As shown in Fig. 9 (A), for all Fe/Al-Lap catalysts, H$_2$S conversion increases with rise of temperature and complete conversion of H$_2$S can be achieved at 180°C. Besides, an increase in H$_2$S conversion is observed when iron loading increases from 3% to 7%, attributing to the good dispersion of iron oxide on Al-Lap and the strong acidity of the catalysts. Nevertheless, H$_2$S conversion decreases with the iron loading up to 8% because of the formation
is similar to that of H$_2$S conversion previously observed. Among all catalysts, 7% Fe/Al-Lap catalyst presents the best sulfur yield and the maximum sulfur yield is up to 97% at 180 °C. Thus, it is selected to further study the effect of O$_2$/H$_2$S and time on stream for H$_2$S oxidation. Compared with the other metal oxide based catalysts [3,11,33], the synthesized Fe/Al-Lap catalysts have much higher catalytic activities than the other catalysts at low temperature for H$_2$S oxidation.

The catalytic performances of the Al-Lap and Fe/Lap (Laponite supported iron oxide without the modification of alumina) are established to determine the influence of iron oxide and alumina nanoparticles on H$_2$S selective oxidation. For Al-Lap, it shows very low conversion at 120 °C, which increases with temperature and reach a maximum of 60% at 200 °C. It perhaps due to the adsorb H$_2$S on strong acid sites. For Fe/Lap, the conversion almost keeps constant at 30% over the reaction temperature range, suggesting that Fe/Lap possesses poor catalytic activity in the temperature range. Therefore, the above experiments results indicate that the interaction between iron oxide and alumina improves the catalytic performance for H$_2$S oxidation greatly. Moreover, the strong acidity of the catalysts and good dispersion of iron oxide are also beneficial to the oxidation reaction.

### 4.2. Effect of O$_2$/H$_2$S in feed stream

The effect of O$_2$/H$_2$S ratio in feed stream is studied by varying O$_2$ concentration while keeping H$_2$S concentration constant at 5000 ppm. In this study, O$_2$/H$_2$S ratio is kept from 0.5 to 2.5. H$_2$S conversion and sulfur selectivity of 7% Fe/Al-Lap catalyst at 180 °C are shown in Fig. 10. It can be seen that H$_2$S conversion remains constant at 100% and sulfur selectivity decreases from 98% to 88% with increasing of O$_2$/H$_2$S ratio, which is caused by deep oxidation of H$_2$S or/and further oxidation of sulfur via the reaction (2) and (3).

Hence, excessive amount of oxygen is not required for H$_2$S selective oxidation over Fe/Al-Lap catalysts. Moreover, maintaining a stoichiometric O$_2$/H$_2$S ratio can decrease the formation of SO$_2$ effectively.

### 4.3. Durability of Fe/Al-Lap catalysts

Fig. 11 shows the durability behavior of 7% Fe/Al-Lap catalyst at 180 °C with the reactant composition of H$_2$S/O$_2$/N$_2$ = 5/2.5/92.5 at GHSV = 7000 h$^{-1}$. It can be observed clearly that the H$_2$S conversion, sulfur selectivity and sulfur yield are all more than 90% after reaction for 100 h. This result indicates that the 7% Fe/Al-Lap catalysts...
is highly durable under these conditions. It can be seen that, at the initial stage of the reaction, H$_2$S conversion and sulfur yield are 100% and 97% respectively, whereas, it decreases to 94% and 92% as time proceeded. Conversely, sulfur selectivity increases from 94% to 98%. As we known, the FeS$_2$ formation is one of the main reasons for iron oxide based catalysts deactivation [3,6]. Besides, FeS$_2$ is the active site for oxidizing H$_2$S to SO$_2$ [34–36], which is contradict with our results. It indicates that no FeS$_2$ formed in the process of H$_2$S selective oxidation over Fe/Al-Lap catalysts.

4.4. Studies of catalytic and deactivation mechanisms

In order to improve the catalytic performance, it is significant to clarify the catalytic and deactivation mechanisms of Fe/Al-Lap catalysts. The XRD spectra of all used Fe/Al-Lap catalysts are shown in Fig. 12. Compared with the fresh catalysts, no new species are observed. And the structures of catalysts are maintained. The XPS spectra of 7% Fe/Al-Lap catalyst after reaction for 100 h are presented in Fig. 5 and Fig. 13. For Fe 2p XPS spectrum of 7% Fe/Al-Lap catalyst after reaction for 100 h (Fig. 5), the peak position and energy difference are similar with the fresh catalyst, indicating the unique existence of Fe$^{3+}$ and the absence of Fe$^{2+}$. For S 2p$_{3/2}$ XPS spectrum of 7% Fe/Al-Lap catalyst after reaction for 100 h (Fig. 13), two peaks around 164 eV and 169 eV are detected, which can be assigned to the presence of SO$_2$$^-$ and S$^0$ respectively [35]. In addition, the percent area of S$^0$ and SO$_2$$^-$ are 37%, 63% respectively. The total sulfur content is 2.2%wt based on the XPS analysis. All the XRD and XPS results imply the formation of Fe$_2$(SO$_4$)$_3$ and the absence of FeS$_2$, which is already confirmed by durability experiment. Moreover, According to the literature [10], before the Fe$_2$O$_3$/Sic catalyst exhibited stable sulfur selectivity, Fe$_2$O$_3$ needed a short time to transform into Fe$^{3+}$ intermediate (Fe$_2$O$_3$·xSO$_3$ (x<2)), which was considered as the true active phase. However, in our experiment, this step was not observed. The Fe/Al-Lap catalysts exhibited high and stable sulfur selectivity from the beginning of the reaction. Additionally, for S 2p$_{3/2}$ XPS spectrum, there is no peak corresponding to the sulfur in the intermediate. Thus, the above results indicate that the Fe/Al-Lap catalysts present different catalytic mechanism. Based on the report [37], it is tentatively deduced that the catalytic mechanism obey redox reaction mechanism, i.e. the redox of Fe$^{3+}$/Fe$^{2+}$. And the interaction between iron oxide and alumina improves the redox property of Fe$^{3+}$ efficiently at relatively low temperature. On the other hand, due to the relatively low reaction temperature (sulfur dew point), a little elemental sulfur (0.8 wt%) is condensed on the surface and plugs the pore, which causes catalyst deactivation. Moreover, due to the low activity of iron sulfate [10], it can be concluded that the form of Fe$_2$(SO$_4$)$_3$ species (1.4 wt%) may also lead to catalyst deactivation.

5. Conclusions

A series of Fe/Al-Lap catalysts with mesoporous structure and high specific surface area were prepared. The structure, chemical properties and the catalytic behaviors were studied detailed. Iron oxide mainly existed in the form of isolated Fe$^{3+}$ in an oxidic environment. Moreover, Fe/Al-Lap catalysts showed high catalytic activities in temperature range of 120–200 °C due to the interaction between iron oxide and alumina, which improve the redox property of Fe$^{3+}$ efficiently. Moreover, the strong acidity of catalysts and good dispersion of iron oxide were also beneficial to oxidation reaction. Among them, 7% Fe/Al-Lap catalyst present the best catalytic activity and high stability at 180 °C. In addition, excessive amount oxygen was not needed in the selective oxidation reaction. Finally, the catalytic and deactivation mechanisms of the catalysts were studied, the catalytic mechanism obeyed redox mechanism. And the catalyst deactivation was mainly due to the sulfur condensation and formation of Fe$_2$(SO$_4$)$_3$ species.

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