Selective catalytic oxidation of H₂S over iron oxide supported on alumina-intercalated Laponite clay catalysts

Xin Zhang^a, Guangyu Dou^a, Zhuo Wang^a, Li Li^b, Yufei Wang^a, Hailin Wang^a, Zhengping Hao^{a,*}

^a Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, PR China

^b Australian Institute for Bioengineering and Nanotechnology, The University of Queensland, Brisbane, QLD 4072, Australia

HIGHLIGHTS

- Fe/Al-Lap catalysts with mesoporous structure were synthesized.
- Iron oxide mainly exists in form of isolate Fe³⁺ in an oxidic 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 Fe₂(SO₄)₃ and elemental sulfur deposits on surface cause catalyst deactivation.

GRAPHICAL ABSTRACT

The catalytic reaction and deactivation mechanisms for H₂S selective oxidation over Fe/Al-Lap catalysts are shown in the illustration. The catalytic reaction follows Mars–van Krevelen mechanism. Moreover, the interaction between iron oxide and alumina, the strong acidity of the catalysts and the well dispersion of iron oxide improve the catalytic performance efficiently. Meanwhile, the catalyst deactivation is mainly due to the formation of Fe₂(SO₄)₃ and elemental sulfur deposits on the surface.

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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), H₂ temperature-programmed reduction (H₂-TPR) and NH₃ temperature-programmed desorption (NH₃-TPD) techniques. It was realized that iron oxide mainly existed in the form of isolated Fe³⁺ in an oxidic environment. Fe/Al-Lap catalysts showed high catalytic activities in the temperature range of 120–200 °C without the presence of excessive O₂. This can be attributed to the interaction between iron oxide and alumina, which improve the redox property of Fe³⁺ 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 H₂S, which is generated from crude oil and natural gas refineries industries, has attracted considerable attentions. Because of H₂S 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

* Corresponding author. Tel.: +86 10 62923564; fax: +86 10 62923564.

E-mail address: zpinghao@rcees.ac.cn (Z. Hao).

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]:

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-supported 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·xSO₃(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 nontoxic 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 Si₈[Mg_{5.5}Li_{0.4}H₄O₂₄]^{0.7-}Na_{0.7}^{0.7+} [12], 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 [13]. 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-S-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 mesoporous 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 n% Fe/Al-Lap, where n% referred to the iron loading content (weight percentage) on the support.

2.2. Characterizations of the catalysts

The specific surface areas and textural 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 Kα radiation. The base pressure was 5 × 10^{–8} Pa. The binding energies were calibrated using C1 s 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

Table 1
Physicochemical properties of Fe/Al-Lap catalysts.

Sample	S_{BET}^a (m^2/g)	V_p^b (cm^3/g)	D_p^c (nm)	Fe (wt%)
Laponite	322	0.2369	2.9	–
Al-Lap	518	0.9323	7.2	–
3% Fe/Al-Lap	472	0.7266	6.2	2.5%
6% Fe/Al-Lap	413	0.6917	6.7	5.5%
7% Fe/Al-Lap	390	0.6292	6.5	6.7%
8% Fe/Al-Lap	351	0.5057	5.8	7.4%

^a BET specific surface area calculated at $P/P_0 = 0.05–0.25$.

^b Total pore volume estimated at $P/P_0 = 0.99$.

^c BJH pore diameter calculated from the desorption branch.

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.

NH_3 temperature-programmed desorption (NH_3 -TPD) was carried out on the same apparatus as that in H_2 -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% NH_3/N_2 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 NH_3 .

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 H_2S , 2500 ppm O_2 and balance gas (N_2) were fed into the reactor at 200 ml/min ($\text{GHSV} = 7000 \text{ h}^{-1}$) 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 H_2S , sulfur selectivity and sulfur yield were defined as follows [6]:

$$\text{H}_2\text{S conversion} = \frac{(\text{H}_2\text{S})_{\text{in}} - (\text{H}_2\text{S})_{\text{out}}}{(\text{H}_2\text{S})_{\text{in}}}$$

$$\text{Sulfur selectivity} = \frac{(\text{H}_2\text{S})_{\text{in}} - (\text{H}_2\text{S})_{\text{out}} - (\text{SO}_2)_{\text{out}}}{(\text{H}_2\text{S})_{\text{in}} - (\text{H}_2\text{S})_{\text{out}}}$$

$$\text{Sulfur yield} = (\text{H}_2\text{S conversion}) \times (\text{Sulfur selectivity})$$

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 textural data of all catalysts are listed in Table 1. As shown in Fig. 1, all isotherms are type IV [17], which corresponds to trait of mesoporous structure. Moreover, the specific surface area and total pore volume of Al-Lap are 519 m^2/g and 0.932 cm^3/g , respectively, while the initial clay are 322 m^2/g and 0.236 cm^3/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.

Fig. 1. Nitrogen adsorption/desorption isotherms of Fe/Al-Lap catalysts: (a) Laponite, (b) 3% Fe/Al-Lap, (c) 6% Fe/Al-Lap, (d) 7% Fe/Al-Lap, (e) 8% Fe/Al-Lap, and (f) Al-Lap.

The XRD patterns of all samples are presented in Fig. 2. It is significant to note that Al-Lap composites show typical diffraction peaks corresponding to the characteristic of host clay structure, which locate at $2\theta = 20^\circ, 27.7^\circ, 35^\circ, 53^\circ, 61^\circ$, and 72° [18]. But the peak intensity is strengthened, suggesting that Al-Lap composites is better crystallized. However, after iron loaded on Al-Lap, the peak intensity decreases slightly with the increase of iron content up to 7%, which can be attributed to the small delamination of Al-Lap [16]. For 8% Fe/Al-Lap catalysts, the peak at 72° nearly disappears, indicating that the clay structure is damaged. In addition, no alumina and iron oxide peaks are observed for all samples, indicating that alumina and iron oxide are well dispersed on Al-Lap.

Moreover, the intercalated structure of Al-Lap can be examined by the basal spacing of (001) reflection, which appeared at $2\theta = 5^\circ$ [18]. However, in the small angle XRD patterns, no peaks can be observed for the host clay, Al-Lap and all catalysts, which can be attributed to the small platelets of host clay (about 20–30 nm in diameter) and lack of long-range order [14].

Fig. 2. XRD patterns of Fe/Al-Lap catalysts: (a) Laponite, (b) Al-Lap, (c) 3% Fe/Al-Lap, (d) 6% Fe/Al-Lap, (e) 7% Fe/Al-Lap, and (f) 8% Fe/Al-Lap.

Fig. 3. FTIR patterns of Fe/Al-Lap catalysts: (a) Laponite, (b) Al-Lap, (c) 3% Fe/Al-Lap, (d) 6% Fe/Al-Lap, (e) 7% Fe/Al-Lap, and (f) 8% Fe/Al-Lap.

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 $\text{Fe}^{3+}_x\text{O}_y$ complexes and the band around 500 nm can be ascribed to larger Fe_2O_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 $\text{Fe}^{3+}_x\text{O}_y$) almost maintain consistently (39%) for all catalysts. However, the percent area of band around 500 nm (larger Fe_2O_3 nanoparticles) is 6.7, 8, 11.5, 19% for 3, 6, 7, 8% iron loaded catalysts, respectively, indicating that larger Fe_2O_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

Fig. 4. UV-vis DRS spectra of Fe/Al-Lap catalysts: (A) 3% Fe/Al-Lap, (B) 6% Fe/Al-Lap, (C) 7% Fe/Al-Lap, and (D) 8% Fe/Al-Lap.

Fig. 5. Fe 2p XPS spectra of (a) fresh 7%Fe/Al-Lap catalyst (b) used 7%Fe/Al-Lap catalyst.

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

Fig. 6. EPR spectra of Fe/Al-Lap catalysts: (a) 3% Fe/Al-Lap, (b) 6% Fe/Al-Lap, (c) 7% Fe/Al-Lap, and (d) 8% Fe/Al-Lap.

Fig. 7. H_2 -TPR profiles of Fe/Al-Lap catalysts: (a) Laponite (b) 3% Fe/Al-Lap, (c) 6% Fe/Al-Lap, (d) 7% Fe/Al-Lap, and (e) 8% Fe/Al-Lap.

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 $-\text{OH}$ 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_2S 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_2S 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_2S at temperature ranging from 120°C to 200°C with the reactant composition of $\text{H}_2\text{S}/\text{O}_2/\text{N}_2 = 5/2.5/92.5$ at 7000 h^{-1} of GHSV. As shown in Fig. 9 (A), for all Fe/Al-Lap catalysts, H_2S conversion increases with rise of temperature and complete conversion of H_2S can be achieved at 180°C . Besides, an increase in H_2S 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_2S conversion decreases with the iron loading up to 8% because of the formation

Fig. 8. NH_3 -TPD profiles of Fe/Al-Lap catalysts: (a) Laponite (b) Al-Lap, (c) 3% Fe/Al-Lap, (d) 6% Fe/Al-Lap, (e) 7% Fe/Al-Lap, and (f) 8% Fe/Al-Lap.

Fig. 9. Effect of temperature on (A) Conversion of H₂S, (B) Sulfur selectivity, and (C) sulfur yield for Fe/Al-Lap catalysts.

of larger Fe₂O₃ nanoparticles and the decrease of specific surface area [3].

Fig. 9 (B) shows the sulfur selectivity of all catalysts. It is worth observing that the sulfur selectivity is more than 90% for all catalysts, while the H₂S conversion is in a wide range from 60–100%, suggesting that Fe/Al-Lap catalysts possess high and stable sulfur selectivity for H₂S selective oxidation. Compared with the other metal oxide based catalysts [3,11,33], the synthesized Fe/Al-Lap catalysts show higher sulfur selectivity for H₂S oxidation.

Meanwhile, Fe/Al-Lap catalysts have better sulfur yield as shown in Fig. 9 (C). The trend of sulfur yield for Fe/Al-Lap catalysts

Fig. 10. Effect of O₂/H₂S ratio on H₂S conversion and sulfur selectivity for 7% Fe/Al-Lap catalyst at 180 °C.

is similar to that of H₂S 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 O₂/H₂S and time on stream for H₂S 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 H₂S 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 influences of iron oxide and alumina nanoparticles on H₂S 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 H₂S 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 H₂S 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 O₂/H₂S in feed stream

The effect of O₂/H₂S ratio in feed stream is studied by varying O₂ concentration while keeping H₂S concentration constant at 5000 ppm. In this study, O₂/H₂S ratio is kept from 0.5 to 2.5. H₂S conversion and sulfur selectivity of 7% Fe/Al-Lap catalyst at 180 °C are shown in Fig. 10. It can be seen that H₂S conversion remains constant at 100% and sulfur selectivity decreases from 96% to 88% with increasing of O₂/H₂S ratio, which is caused by deep oxidation of H₂S or/and further oxidation of sulfur via the reaction (2) and (3).

Hence, excessive amount of oxygen is not required for H₂S selective oxidation over Fe/Al-Lap catalysts. Moreover, maintaining a stoichiometric O₂/H₂S ratio can decrease the formation of SO₂ 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 H₂S/O₂/N₂ = 5/2.5/92.5 at GHSV = 7000 h⁻¹. It can be observed clearly that the H₂S conversion, sulfur selectivity and sulfur yield are all more than 90% after reaction for 100 h. this results indicates that the 7% Fe/Al-Lap catalysts

Fig. 11. Time on stream behavior of 7% Fe/Al-Lap catalyst for H_2S selective oxidation at 180°C .

is highly durable under these conditions. It can be seen that, at the initial stage of the reaction, H_2S 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_2S to SO_2 [34–36], which is contradict with our results. It indicates that no FeS_2 formed in the process of H_2S 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_4^{2-} and S_n respectively [35]. In addition, the percent area of S_n and SO_4^{2-} are 37%, 63% respectively. The total sulfur content is 2.2%wt based on the XPS analysis. All the XRD

Fig. 12. XRD patterns of used Fe/Al-Lap catalysts: (a) Al-Lap, (b) 3% Fe/Al-Lap, (c) 6% Fe/Al-Lap, (d) 7% Fe/Al-Lap, and (e) 8% Fe/Al-Lap.

Fig. 13. S $2p_{3/2}$ XPS spectrum of used 7% Fe/Al-Lap catalyst.

and XPS results imply the formation of $\text{Fe}_2(\text{SO}_4)_3$ and the absence of FeS_2 , which is already confirmed by durability experiment. Moreover, According to the literature [10], before the $\text{Fe}_2\text{O}_3/\text{SiC}$ catalyst exhibited stable sulfur selectivity, Fe_2O_3 needed a short time to transform into Fe^{3+} intermediate ($\text{Fe}_2\text{O}_3 \cdot x\text{SO}_3$ ($x < 2$)), 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 obeys redox reaction mechanism, i.e. the redox of Fe^{3+} . 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 $\text{Fe}_2(\text{SO}_4)_3$ 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 $120\text{--}200^\circ\text{C}$ 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 $\text{Fe}_2(\text{SO}_4)_3$ species.

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