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Selective oxidation of H₂S over V₂O₅ supported on CeO₂-intercalated Laponite clay catalysts

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A series of V_2O_5 supported on CeO₂-intercalated clay catalysts (named V_2O_5 /Ce-Lap catalysts) with mesoporous structure and high specific surface area were prepared. The structural characteristics and physicochemical properties were studied in detail. These catalysts were evaluated for the H₂S selective oxidation. It was revealed that all V_2O_5 /Ce-Lap catalysts showed high catalytic activities in the temperature range of 120–220 °C due to the redox reaction of highly dispersed V⁵⁺ species, and the catalytic mechanism obeyed a redox process, *i.e.* a stepwise mechanism. Additionally, the chemically absorbed oxygen also played an important role in H₂S selective oxidation. Among them, the 5% V₂O₅/Ce-Lap catalyst presented the best catalytic activity and excellent regenerability at 180 °C. Finally, the catalyst deactivation mechanism was explored.

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1. Introduction

Nowadays, a large amount of toxic H_2S is released by combustion of fossil fuels owing to energy demand.¹ Thus, the conversion of H_2S to elemental sulfur is desired to reduce its impact on the environment. The most popular currently utilized technology for the production of elemental sulfur from H_2S -containing gas is the Claus process.² However, because of the thermodynamic limitations, it is difficult to remove H_2S completely and 1% H_2S is still left in Claus tail gas.³ In order to remove the residual H_2S , various processes of additional purification are applied. Among them, the most well-known is H_2S selective catalytic oxidation technology; in this process, H_2S is directly oxidized to elemental sulfur by oxygen over a suitable catalyst. The irreversible reaction equations are as follows (eqn (1) is the main reaction, and eqn (2) and (3) are side reactions):⁴

$$(1/n)S_n + H_2O \rightarrow H_2S + 1/2O_2$$
 (1)

$$1/nS_n + O_2 \to SO_2 \tag{2}$$

$$H_2S + 3/2O_2 \rightarrow SO_2 + H_2O$$
 (3)

It is noted that SO_2 can be formed *via* the deep oxidation of H_2S or the further oxidation of elemental sulfur, causing a decrease in sulfur yield. Therefore, the conversion efficiency strongly depends on the catalyst activity. Pillared interlayered clays (PILCs) supported vanadium species catalysts, such as Ti, Zr, Fe PILC supported V_2O_5 catalysts,^{1,3,5,6} have been of great research interest in the past few decades because PILCs can be tailored to particular applications by varying the size and separation of the pillars as well as their composition. Unfortunately, their microporous and moderate porosity structure limits their further application (a pore volume of 0.15–0.40 cm³ g⁻¹).⁷ This means that when PILCs are used as catalyst supports, the loaded active component will block interlayer pores, as a result, the active component becomes inaccessible to most reactants. On the other hand, for vanadium based catalysts, the catalyst deactivation should be seriously considered owing to their possible application in practical industries. Thus, it is desirable to design, explore and develop suitable catalysts with high catalytic performances.

Recently, a new approach was developed to synthesize aluminaintercalated Laponite clay composites with mesoporous structure and high specific surface area in the presence of surfactants.⁸ In this process, the surfactants were first intercalated into the galleries and form micelles, acting as templates, then, alumina nanoparticles were embedded surrounding the micelles. Finally, the composites were obtained after removal of the surfactants by heating. Using this method, CeO₂-intercalated clay composites were synthesized successfully.⁹ As expected the good redox property and the high mobility of the capping oxygen of CeO₂¹⁰⁻¹² make CeO₂-intercalated clay composites suitable and attractive catalyst supports to load and modify vanadium species.

In this study, a series of CeO_2 -intercalated clay composites supported V_2O_5 catalysts with mesoporous structure and high

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specific surface area were prepared and investigated for H_2S selective oxidation. It is desirable that the catalytic performances could be enhanced. Moreover, the physicochemical properties of catalysts were characterized by using various techniques. Besides, the catalytic mechanism and catalyst deactivation were explored.

2. Experimental

2.1 Catalyst 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 CeO₂intercalated Laponite clay composites were synthesized according to the procedures described by Li *et al.*⁹ The prepared CeO₂intercalated Laponite clay composites were denoted as Ce-Lap. The V₂O₅ loaded Ce-Lap catalysts containing 3, 5 and 8% V₂O₅ were prepared by the wetness impregnation method using NH₄VO₃ as the active component precursor. The impregnated materials were dried at 100 °C overnight, and then were calcined at 400 °C for 4 h. The samples were denoted as *n*% V₂O₅/Ce-Lap, where *n*% refers to the V₂O₅ loading content (weight percentage) on the support.

2.2 Catalyst characterization

X-ray diffraction (XRD) patterns were recorded on a PANalytical X'Pert PRO powder diffraction system using Cu K α radiation ($\lambda = 0.15418$ nm) in the 2 θ range of 10–80° (at a scanning rate of 0.5° min⁻¹).

UV-vis diffuse reflectance spectra (UV-vis DRS) were recorded in the air against $BaSO_4$ in the region of 12 500–24 000 cm⁻¹ on a Hitachi UV-3000 spectrometer.

The chemical composition of samples was determined by X-ray fluorescence (XRF) using an XRF1800 spectrometer, and an Rh tube as the excitation source.

Thermal stability was investigated by thermogravimetry (TG-DSC, Seteram Labsys). Typically, around 30 mg of the sample was heated in an Al_2O_3 crucible at a constant heating rate of 10 °C min⁻¹ from 25 to 1000 °C, with air purging at a flow rate of 30 mL min⁻¹.

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

BET surface areas and textural properties of catalysts were determined by nitrogen adsorption–desorption isotherms using a gas sorption analyzer NOVA1200. Prior to N₂ adsorption measurements, the samples were degassed at 300 $^{\circ}$ C for 3 h.

FTIR spectra of these V_2O_5 /Ce-Lap catalysts were collected on the Bruker Tensor 27 spectrometer with 256 scans at a resolution of 4 cm⁻¹.

 H_2 temperature-programmed reduction (H_2 -TPR) experiments were conducted using a Micromeritics Chemisorb 2720 apparatus. TPR profiles were obtained by passing a 5% H_2 /He flow (50 mL min⁻¹) through the pretreated catalyst (100 mg).

Reduction temperature was increased from room temperature to 900 °C at a rate of 10 °C min⁻¹. Hydrogen concentration in the effluent was continuously monitored using a thermoconductivity detector. Prior to each TPR run, the catalyst was pre-heated in He flow from room temperature to 300 °C and held for 30 min.

 O_2 temperature-programmed desorption (O_2 -TPD) was carried out using the same apparatus as in H₂-TPR experiments (Micromeritics Chemisorb 2720). The sample was heated from room temperature to 900 °C at a rate of 10 °C min⁻¹ in pure He. Before each TPD test, 100 mg of the sample was pre-heated in He flow from room temperature to 300 °C and held for 30 min. After cooling to room temperature, 2% O_2/N_2 was fed into the reactor at 50 mL min⁻¹ for 30 min, then, pure He was fed into the reactor at 50 mL min⁻¹ for 30 min to purge away any residual O_2 .

2.3 Catalytic performance evaluation

All catalytic performance evaluations were performed in a continuous flow fixed-bed quartz reactor at atmospheric pressure. A catalyst (0.6 g, 20–40 mesh) was placed in the central section of the reactor. The mixture gas containing 5000 ppm H₂S, 2500 ppm O₂ and balance gas (N₂) was fed into the reactor at 200 mL min⁻¹ of the total gas flow rate (GHSV = 7000 h⁻¹) and reacted in the temperature range of 120–220 °C. The effluent stream was detected using 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:

$$\begin{split} H_2 S \, \text{conversion} &= \frac{(H_2 S)_{\text{in}} - (H_2 S)_{\text{out}}}{(H_2 S)_{\text{in}}} \\ \text{Sulfur selectivity} &= \frac{(H_2 S)_{\text{in}} - (H_2 S)_{\text{out}} - (SO_2)_{\text{out}}}{(H_2 S)_{\text{in}} - (H_2 S)_{\text{out}}} \end{split}$$

Sulfur yield = $(H_2S \text{ conversion}) \times (Sulfur \text{ selectivity})$

3. Results and discussion

3.1. Structural and textural properties of V_2O_5 /Ce-Lap catalysts

Nitrogen adsorption–desorption isotherms and the BJH pore size distribution calculated from the desorption branch (insert) of all catalysts and supports are shown in Fig. 1, and the textural properties are listed in Table 1. It is significant to observe that the specific surface area and total volume of host clay are $322 \text{ m}^2 \text{ g}^{-1}$ and $0.24 \text{ cm}^3 \text{ g}^{-1}$, respectively. After the CeO₂ modification, they increase to $580 \text{ m}^2 \text{ g}^{-1}$ and $1.12 \text{ cm}^3 \text{ g}^{-1}$. On the other hand, all catalysts possess type IV isotherms, a typical characteristic of mesoporous materials.¹³ Therefore, for the larger specific surface area, typical isotherms associated with the BJH pore size distribution indicate that Ce-Lap composites with mesoporous structure were successfully obtained, and the mesoporous structure remained after the V₂O₅ addition.



Fig. 1 Nitrogen adsorption–desorption isotherms and pore size distribution calculated from the desorption branch (insert) of V₂O₅/Ce-Lap catalysts: (a) Laponite, (b) 8% V₂O₅/Ce-Lap, (c) 5% V₂O₅/Ce-Lap, (d) 3% V₂O₅/Ce-Lap and (e) Ce-Lap.

Table 1 Textural properties of V₂O₅/Ce-Lap catalysts

Catalyst	$S_{\mathrm{BET}}^{a} \left(\mathrm{m}^{2} \mathrm{g}^{-1}\right)$	$V_{\rm p}^{\ b} ({\rm cm}^3 {\rm g}^{-1})$	$D_{\rm p}^{\ c} ({\rm nm})$	
Lap	322	0.24	2.9	
Ce-Lap	580	1.12	7.7	
3%V ₂ O ₅ /Ce-Lap	378	0.48	5.0	
5%V ₂ O ₅ /Ce-Lap	367	0.36	3.9	
8%V ₂ O ₅ /Ce-Lap	284	0.32	4.7	

 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.

Additionally, the high specific surface area and mesoporous structure are favorable for H_2S selective oxidation reaction, as they allow V_2O_5 to be well dispersed on the support. However, the nitrogen adsorption capacity decreases slightly with the rise of V_2O_5 loading, attributed to the pore blockage by the loaded V_2O_5 . Meanwhile, the steps of hysteresis loops shift towards lower relative pressure, indicating that relatively small sized pores are formed,¹³ which is confirmed by the pore size data in Table 1.

XRD was employed to further investigate the structure of V_2O_5 /Ce-Lap catalysts. As shown in Fig. 2, for Ce-Lap, it can be noticed that the characteristic diffraction peaks of host clay are maintained. Meanwhile, new peaks corresponding to CeO₂ appear at 28.2°, 47.7° and 56.4°. This demonstrated that CeO_2 was successfully intercalated into the galleries. This is in accordance with the results of nitrogen adsorption-desorption isotherms. Meanwhile, for all catalysts, no peak for V2O5 was observed, implying that V₂O₅ is highly dispersed on Ce-Lap. However, CeO2 is better crystallized with the rise of V2O5 loading, which is perhaps due to the interaction of vanadium species with cerium species. However, compared with host clay, the structure of V₂O₅/Ce-Lap is seriously damaged. This can be explained by the fact that the acid properties of the precursor (metal salt) solutions cause the leaching and damage of the clay layer.⁷ Such an argument is supported by the XRF analysis. As shown in Table 2, the MgO content in all catalysts is smaller



Fig. 2 XRD patterns of V₂O₅/Ce-Lap catalysts: (a) Laponite, (b) Ce-Lap, (c) 3% V₂O₅/Ce-Lap, (d) 5% V₂O₅/Ce-Lap and (e) 8% V₂O₅/Ce-Lap.

Table 2 Chemical composition (wt%) of the samples investigated

Catalyst	SiO ₂	MgO	V_2O_5	CeO ₂
$3\%V_2O_5/Ce-Lap$	59.9 58.02	23.24	3.37	12.4
8%V ₂ O ₅ /Ce-Lap 8%V ₂ O ₅ /Ce-Lap	59.47	17.69	8.32	13.28

than that in host $clay^7$ and the content decreases with the rise of V_2O_5 loading. As is known, the Laponite consists of an octahedral MO_6 layer sandwiched between two tetrahedral SiO_4 layers. Magnesium atoms are at the center of the MO_6 octahedra. When the magnesium is leached out in the acidic environment, the Si residue is more likely in the form of amorphous silicate particles. Thus, the loss of magnesium implies the damage of clay layers. As a result, more amorphous silicate particles are formed with the rise of V_2O_5 loading.

Fig. 3 exhibits the FTIR spectra of all catalysts; the spectra reveal intense bands at around 1200 cm^{-1} , which correspond to the Si–O vibration of SiO₄ tetrahedra. Apparently, the intensities of the bands weakened with the rise of V₂O₅ loading due to



Fig. 3 FTIR spectra of V_2O_5/Ce-Lap catalysts: (a) Laponite, (b) Ce-Lap, (c) 3% V_2O_5/Ce-Lap, (d) 5% V_2O_5/Ce-Lap and (e) 8% V_2O_5/Ce-Lap.



Fig. 4 TG patterns of V₂O₅/Ce-Lap catalysts: (a) Laponite, (a) Ce-Lap, (b) 3% V₂O₅/Ce-Lap, (c) 5% V₂O₅/Ce-Lap and (d) 8% V₂O₅/Ce-Lap.

the content of SiO₄ tetrahedra decreasing with the rise of V₂O₅ loading. This was confirmed by XRF analysis. Meanwhile, the bands appearing at around 1660 cm⁻¹ are attributed to the bending vibration of adsorbed water and the broad bands at 3200 cm⁻¹–3600 cm⁻¹ are generally assigned to the vibration of –OH groups. In addition, the bands located at 3678 cm⁻¹ and 3742 cm⁻¹ correspond to the vibration of –OH groups and silanol groups, respectively. Moreover, a band at 818 cm⁻¹ was clearly observed, which is supposed to be related to the deformation of V–O–V bridges arising from V₂O₅.¹⁴ Thus, it confirms the formation of V₂O₅.

Fig. 4 provides the thermogravimetric (TG) analysis patterns of all samples. In the case of Ce-Lap, the curve shows two distinct weight losses; the first one can be assigned to the removal of adsorbed and hydration water molecules on the surface of clay layers, at temperatures below 150 °C.9 While the second weight loss observed in the temperature range of 600-900 °C corresponds to the dehydroxylation of clay structure.^{1,15} In this process, an inflection point is found at around 800 °C due to the collapse of clay structure.¹⁶ Additionally, the slight weight loss that occurred at 150-600 °C is attributed to the removal of interlayer water. For the V2O5/Ce-Lap catalysts, it is noticed that a new weight loss appears at around 200 °C, which can be attributed to the dehydroxylation of V₂O₅.¹ The weight loss amount of the two steps increases with the rise of V₂O₅ loading. This can be attributed to the desorption of adsorbed water on the CeO₂ surface¹⁷ as well as the easier and larger amount removal of structural -OH due to the damage of layer structure. Meanwhile, the second weight loss shifts towards the lower temperature range. Likewise, the inflection point is found at around 450 °C, indicating that the thermal stability of the catalysts is reduced because the layer structure is damaged.

3.2 Surface species analysis

UV-vis DRS was employed to characterize the chemical status of the loaded vanadium species. As shown in Fig. 5, the neat spectra reveal the presence of two bands at 260 nm and 350 nm as the main features of the catalysts. As reported, the band at



Fig. 5 UV-vis DRS spectra of V_2O_5 /Ce-Lap catalysts: (a) 3% V_2O_5 /Ce-Lap, (b) 5% V_2O_5 /Ce-Lap and (c) 8% V_2O_5 /Ce-Lap.

260 nm is related to the isolated V⁵⁺ in a 4-fold coordination state. While the band at 350 nm corresponds to the polymeric V_2O_5 chains, which are formed by the isolated V⁵⁺ species with the formation of a V–O–V bridge,^{1,5,18,19} which is in good correlation with the FTIR result. Furthermore, it is worth mentioning that no bands appear in the range of 600–800 nm, which relate to the crystalline V_2O_5 species. Therefore, the UV-vis DRS analysis suggests that vanadium species are mainly present in a highly dispersed state of isolated V⁵⁺ and polymeric V₂O₅.

Fig. 6 presents the V 2p XPS spectra of a represented catalyst (5% V₂O₅/Ce-Lap). For the fresh catalyst, the spectrum is predominated by a single peak that appeared at 517.8 eV, which is the typical characteristic of V⁵⁺. Thus, the XPS analysis confirms the unique existence of V⁵⁺.²⁰ In order to further explore the reaction mechanism, the XPS spectra of Ce 3d for 5% V₂O₅/Ce-Lap are displayed in Fig. 7. For the fresh catalyst, the peaks labeled m and n refer to $3d_{2/5}$ and $3d_{2/3}$ spin–orbit states, respectively. Moreover, the bands labeled m^I and n^I correspond



Fig. 6 $\,$ V 2p XPS spectra of (a) the fresh 5% V_2O_5/Ce-Lap catalyst and (b) the used 5% V_2O_5/Ce-Lap catalyst.



Fig. 7 Ce 3d XPS spectra of (a) the fresh 5% $V_2O_5/Ce\-Lap$ catalyst and (b) the used 5% $V_2O_5/Ce\-Lap$ catalyst.

to the presence of Ce^{3+} . While the peaks labeled m, m^{II}, m^{III}, n, n^{II} and n^{III} are related to the existence of Ce^{4+} .^{20,21} XPS analysis reveals the partial existence of Ce^{3+} (area percentage is 22%). As is known Ce^{3+} can result in a charge imbalance, and the vacancies and the unsaturated chemical bonds on the catalyst surface are favorable for the formation of chemisorbed oxygen,^{22–24} which is the most active oxygen and plays an important role in oxidation reactions.^{22,25}

3.3 Reductive properties of catalysts

The reducibility of all catalysts was investigated by H₂-TPR experiments. Their H₂-TPR profiles are shown in Fig. 8. It is clearly observed that only one main peak appears at 300 °C for host clay, corresponding to the slight reduction of Laponite. Apparently, after the CeO₂ modification, a poor resolved peak appears at 460 °C, which acts as a shoulder and overlapped with a broad peak with maximum at 570 °C. The two peaks can be attributed to the removal of surface oxygen from CeO₂ and formation of non-stoichiometric cerium oxides, CeO_x from CeO₂, respectively. Meanwhile, the peak that appeared at 820 °C is



Fig. 8 H_2 -TPR profiles of V₂O₅/Ce-Lap catalysts: (a) Laponite, (b) Ce-Lap, (c) 3% V₂O₅/Ce-Lap, (d) 5% V₂O₅/Ce-Lap, (e) 8% V₂O₅/Ce-Lap and (f) 5% V₂O₅/Lap.

probably associated with the reduction of bulk CeO₂ to Ce₂O₃.²⁶ However, because of the low content of Ce³⁺, there are no peaks for Ce³⁺ species in XRD and H₂-TPR patterns. Nevertheless, for V_2O_5 /Ce-Lap catalysts, the two peaks at 440 °C and 570 °C are replaced by a new single peak that appeared in the range of 570–600 °C, which can be assigned to the reduction of V^{5+} to $V^{4+,3,5}$ Moreover, the reduction temperature of V_2O_5 /Ce-Lap is lower than that of V₂O₅/Lap at around 630 °C. The reduction can be attributed to the weakening of the vanadyl group, which is caused by the significant interaction of vanadium species with cerium species.²⁷ Meanwhile, the new peak shifts towards higher temperature with the rise of V₂O₅ loading. This can be explained by the fact that with the rise of V_2O_5 loading, more surface vanadium atoms interact with the internal vanadium layer and increase the bond strength of the vanadyl group. Moreover, the lower reduction temperature reveals that vanadium species is highly dispersed on Ce-Lap.²⁸⁻³⁰ This is in agreement with the UV-vis DRS analysis.

3.4 O2-TPD analysis of catalysts

The ability to capture and release oxygen of all samples was clarified by O2-TPD measurements. As shown in Fig. 9, there exist three oxygen desorption peaks for Ce-Lap, the one that appeared at 120 °C corresponds to the removal of ordinarily chemically adsorbed oxygen. While the one located at 800 °C is ascribed to the removal of lattice oxygen. Finally, the one located at between these two temperatures (450 °C) can be attributed to the desorption of oxygen chemically adsorbed on the oxygen vacancies.^{31,32} However, after the addition of V₂O₅ into the Ce-Lap, a distinctive feature is observed: the curves are dominated by two peaks located at 370 °C and 470 °C, respectively. Both of them correspond to the desorption of oxygen chemically adsorbed on the oxygen vacancies. Meanwhile, the peak that appeared at higher temperature becomes obscured and could be ignored. Among all the catalysts studied, the 5% V₂O₅/Ce-Lap catalyst exhibits the strongest peak intensity, indicating that it possesses the largest amount of oxygen vacancies.



Fig. 9 O_2 -TPD profiles of V_2O_5 /Ce-Lap catalysts: (a) Ce-Lap, (b) 3% V_2O_5 /Ce-Lap, (c) 8% V_2O_5 /Ce-Lap and (d) 5% V_2O_5 /Ce-Lap.

4. Catalytic performances

4.1 Effect of reaction temperature

Fig. 10 shows the effect of temperature on the catalytic activities of V₂O₅/Ce-Lap catalysts for the oxidation of H₂S. It can be seen from Fig. 10(A) that the H₂S conversion initially increases with the rise of reaction temperature up to 180 °C, but slightly falls upon further increasing the temperature to 220 °C. Besides, an increase in H₂S conversion is found when V₂O₅ loading raised from 3% to 5%. Nevertheless, H₂S conversion decreases with the rise of V_2O_5 loading up to 8%. The maximum H₂S conservation (98%) is obtained at 180 °C for the 5% V₂O₅/Ce-Lap catalyst. Fig. 10(B) shows the relationship between sulfur yield and reaction temperature for these catalysts. Similar trends are observed for sulfur yield, because of the high and constant sulfur selectivity (almost 99%). Likewise, the maximum sulfur yield (98%) is obtained at 180 °C for the 5% V₂O₅/Ce-Lap catalyst. As reported, ^{1,3,5,6,33} the reaction temperature for H₂S selective oxidation over pillared clay supported metal oxide catalysts is higher than 200 °C and the maximum sulfur yield is about 95%. Thus, the V₂O₅/Ce-Lap catalysts can not only reduce the reaction temperature but also improve the catalytic activities significantly.

The catalytic activity of Ce-Lap is investigated to determine the influences of vanadium species on H_2S selective oxidation.



Fig. 10 Effect of temperature on (A) conversion of H_2S and (B) sulfur yield for $V_2O_5/Ce\mbox{-Lap}$ catalysts.

As is shown the Ce-Lap exhibits the maximum sulfur yield (60%) at 200 °C. Thus, it can be deduced that the highly dispersed V^{5+} species and the enhanced physicochemical properties play important roles in H₂S selective oxidation. Furthermore, the slight decrease of catalytic activity for the 8% V₂O₅/Ce-Lap catalyst is mainly due to the decrease of specific surface area.

4.2 Catalytic mechanism

The V 2p and Ce 3d XPS spectra of the used 5% V₂O₅/Ce-Lap catalyst are presented in Fig. 6 and 7 respectively. For V 2p, a new peak that appeared at 516.8 eV corresponds to the V^{4+} state^{18,20,34} (the area percentage is about 40%). Meanwhile, no new peak can be detected for Ce 3d. Nevertheless, the proportion of Ce³⁺ increases from 22% to 35%. Thus, it indicates that both V⁵⁺ and Ce⁴⁺ participate in the oxidation reaction and the catalytic mechanism obeys the Mars-van Krevelen or redox process,¹² *i.e.* the stepwise mechanism. Based on this, the catalytic oxidation process can be tentatively proposed as follows: H₂S firstly was oxidized to elemental sulfur by V⁵⁺ and Ce⁴⁺, and then the V⁴⁺ and Ce³⁺ were re-oxidized by the gas phase oxygen in a separate step. Moreover, the high catalytic activities of $V_2O_5/$ Ce-Lap catalysts are mainly due to the redox reaction of V⁵⁺. And the redox reaction of cerium species is responsible for the poor catalytic activity of Ce-Lap.

In order to further explore the catalytic mechanism, the O 1s XPS spectra of 5% V₂O₅/Ce-Lap are provided in Fig. 12. For the fresh catalyst, the spectrum is dominated by the peak that appeared at 532 eV, which is related to the oxygen chemically adsorbed on the oxygen vacancies. While a small shoulder peak that appears at around 530 eV should be attributed to the lattice oxygen.²¹ The two peaks remain after reaction. However, the intensity of the peak at 532 eV decreases obviously. Moreover, it is particularly important to observe that the variation trend of H₂S conversion and sulfur yield is extraordinarily consistent with that of the chemically absorbed oxygen on oxygen vacancies (Fig. 9), when V_2O_5 loading increases from 3% to 8%. Thus, it can be concluded that the large amount of chemically absorbed oxygen on oxygen vacancies, which is caused by the interaction of vanadium species with cerium species, plays an important role in H₂S selective oxidation.

The S 2p XPS spectrum of used 5% V₂O₅/Ce-Lap is presented to study the catalyst deactivation mechanism. As shown in Fig. 13, two peaks at around 164 eV and 169 eV are detected, which can be assigned to the presence of SO_4^{2-} and S_n respectively.³⁵ Moreover, the area percentage of SO_4^{2-} and S_n is 65% and 35%, respectively. This demonstrates that the surface sulfur species mainly exist in the form of sulfate species and perhaps are VOSO₄, Ce(SO₄)₂ and Ce₂(SO₄)₃.³⁶ As is known, the sulfate species associated with elemental sulfur deposited on the surface can cause the deactivation of the catalyst. However, the actual content of each sulfur species is unknown. According to the stepwise mechanism, the slower oxidation rate of the catalyst active phases by oxygen as compared to the reduction rate by H₂S also leads to catalyst deactivation.¹⁰ Therefore, the detailed reason for catalyst deactivation is not very clear.

100

90

4.3 Regeneration experiments

In order to further explain the deactivation mechanism and investigate the regenerability of V_2O_5 /Ce-Lap catalysts, a set of successive deactivation-regeneration experiments were carried out on the 5% V_2O_5 /Ce-Lap catalyst at 180 °C. In the experiment, after each deactivation step (reaction for 7 h, the sulfur yield reduces to 85%), prior to regeneration, the catalyst was purged in an N₂ atmosphere at 300 °C for 30 minutes, then 2% O_2 was fed for 90 minutes. The profiles of regeneration experiments are shown in Fig. 11. It can be seen that the H₂S conservation decreases with reaction time, but it is still higher than 96%. Nevertheless, the sulfur selectivity remains constant at 99%. Thus, similar trends are observed for H₂S conversion and sulfur yield, even the cycle is repeated three times. This suggests that the catalytic activities are highly reproducible and the catalysts possess good regenerability.

As is known to all both vanadium sulfate and cerium sulfate are hardly oxidized because VOSO₄ is less active^{4,18} and Ce(SO₄)₂ and Ce₂(SO₄)₃ can disrupt the redox reaction between Ce⁴⁺ and Ce³⁺due to their high thermal stability.³⁷ Thus, the good regenerability reveals that the slower oxidation rate of the catalyst by oxygen as compared to the reduction rate by H₂S



Fig. 11 Conversion of H₂S (A) and sulfur selectivity (B) obtained with 5% V₂O₅/Ce-Lap at 180 °C in 3 cycles with successive regenerations (reactant composition in vol%: H₂S/O₂/N₂ = 5/2.5/92.5 at 7000 h⁻¹ of GHSV).



Fig. 12 O 1s XPS spectra of (a) the fresh 5% V_2O_5 /Ce-Lap catalyst and (b) the used 5% V_2O_5 /Ce-Lap catalyst.



Fig. 13 The S 2p XPS spectrum of the used 5% V₂O₅/Ce-Lap catalyst.

is the main reason for catalyst deactivation. However, the increase of Ce^{3+} content can create more oxygen vacancies, which is favorable for the oxidation reaction. The durability behavior of the 5% V₂O₅/Lap catalyst is established to determine the influence of Ce^{3+} . As shown in Fig. 11(A), for the 5% V₂O₅/Lap catalyst, the H₂S conversion decreases sharply with reaction time. After reaction for 5 h, the sulfur selectivity remains at 100%. However, the H₂S conversion drops to 90%, which is much lower than that of the 5% V₂O₅/Ce-Lap catalyst, indicating that the 5% V₂O₅/Lap catalyst. Thus, the existence of Ce^{3+} can provide resistance to the catalyst deactivation obviously.

5. Conclusions

A series of V_2O_5 /Ce-Lap catalysts with mesoporous structure and high specific surface area were prepared. The structure of V_2O_5 /Ce-Lap catalysts was partially damaged due to the collapse of the clay layer. However, the surface oxygen property was enhanced and favorable for H_2S selective oxidation. Moreover, vanadium species are mainly presented in a highly dispersed state of isolated V⁵⁺ and polymeric V₂O₅, while Ce⁴⁺ and Ce³⁺ coexisted in the catalyst. The catalysts exhibited high catalytic activities and sulfur selectivity in the temperature range of 120–220 °C due to the redox reaction of highly dispersed V⁵⁺ species. And the catalytic mechanism obeyed a redox process, *i.e.* a stepwise mechanism. Furthermore, the chemically absorbed oxygen also plays an important role in H₂S selective oxidation. Among them, the 5% V₂O₅/Ce-Lap catalyst presented the best catalytic activity and excellent regenerability at 180 °C. It is worth mentioning that Ce⁴⁺ also participated in the oxidation reaction. The catalyst deactivation was mainly due to the slower oxidation rate of the catalyst active phases by oxygen as compared to the reduction rate by H₂S. The existence of Ce³⁺ could provide resistance to the catalyst deactivation obviously.

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