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Selective oxidation of H_2S to elemental sulfur over Ce–V mixed oxide and CeO_2 catalysts prepared by the complexation technique

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Abstract

Selective oxidation of H_2S to elemental sulfur was investigated in a fixed bed reactor using Ce–V mixed oxides and cerium oxide (CeO_2) catalytic materials prepared by the complexation technique. The Ce–V mixed oxide with a V/Ce atomic ratio of one and with the $CeVO_4$ crystal structure gave very high sulfur selectivity values (close to one) at almost complete conversion of H_2S, for O_2/H_2S mole ratios close to 0.5. Best operation temperature was found as 250 °C with this catalyst. CeO_2 gave lower selectivities, causing the formation of some SO_2, even at sub-stoichiometric O_2/H_2S feed ratios. It also showed a fast deactivation due to the partial sulfidation of the catalyst surface during the reaction. XPS analysis of the fresh and the used catalysts containing different V/Ce ratios strongly indicated that the selective oxidation of H_2S to elemental sulfur over the Ce–V mixed oxides involved a redox cycle of cerium, rather than a redox cycle of vanadium.

Keywords: H_2S; Selective oxidation; Ceria; $CeVO_4$; Claus process; XPS

1. Introduction

In the first step of conventional Claus process for sulfur recovery from process gases, H_2S is partially converted to SO_2 by thermal oxidation at high temperatures and in the second step, unconverted H_2S is reacted with SO_2 in a catalytic converter to produce elemental sulfur. Efficiency of this process is strongly effected by the equilibrium limitations of the second step (Claus reaction).

$$2H_2S + SO_2 \leftrightarrow (3/n)S_n + 2H_2O \quad (1)$$

However, a single step selective oxidation of H_2S to elemental sulfur is practically irreversible and does not have thermodynamic limitations.

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

Besides the Claus reaction (Eq. (1)), oxidation of the produced sulfur to SO_2 (Eq. (3)) and deep oxidation of H_2S (Eq. (4)) may cause reduction of sulfur selectivity in the one step selective oxidation of H_2S to elemental sulfur.

$$(1/n)S_n + O_2 \rightarrow SO_2 \quad (3)$$

$$2H_2S + 3O_2 \rightarrow 2SO_2 + 2H_2O \quad (4)$$

Development of active and selective catalysts for this selective oxidation process attracted significant attention of the researchers in recent years [1–7]. In earlier studies, titanium based [8], chromium based [9] and iron based [10] oxide catalysts were proposed for this selective oxidation process. Deactivation of titanium based catalysts in the presence of water vapor, toxic nature of chromium containing materials, and the requirement of excess amount of oxygen for the iron based Superclaus catalyst were reported as some of the drawbacks of these catalysts [2,4,5].

Vanadium based mixed oxide catalysts are known to be highly selective in partial oxidation of hydrocarbons [11,12]. These catalysts also attracted the attention of catalysis researchers working on the selective oxidation of H_2S to elemental sulfur [2–5,13,14]. In the work of Shin et al. [4], which was carried out with V_2O_5 and VO_x/SiO_2 catalysts, and also in our recent study [1], which was carried out with Cu–V and Cu–V–Mo mixed oxide catalysts, it was shown that partially reduced catalysts containing V^{4+} were highly selective for the production of elemental sulfur,

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while some amount of SO_2 formation was reported with the oxidized catalysts containing V^{5+}. A redox reaction mechanism involving the surface lattice oxygen is generally accepted for the selective oxidation of H_2S over these vanadium based mixed oxide catalysts. Deactivation of a vanadium oxide catalyst during the selective oxidation of H_2S was claimed to be due to the slower oxidation rate of the catalyst by the gas phase oxygen as compared to the reduction rate by H_2S [4]. Mixed oxides of vanadium with molybdenum [11], with copper and molybdenum [1], antimony [3,12], titanium, bismuth etc. [5] are reported to show high activity and stability in the selective oxidation reactions, probably due to the improvements in the redox ability of these mixed oxide catalysts. Even in the absence of oxygen gas, formation of some sulfur dioxide and elemental sulfur were reported in our earlier studies [15,16] with the Cu–V and Cu–V–Mo mixed oxides, at temperatures lower than 300 °C. This was concluded to be due to the involvement of surface lattice oxygen of vanadium in the selective oxidation of H_2S. Mixed oxides of vanadium with Mn [19] and Cu [1] were also shown to be very efficient adsorbents for high temperature capture of H_2S.

The redox properties and the high mobility of the capping oxygen of ceria lattice [17] makes it an attractive catalyst for the catalytic oxidation reactions. To improve the selectivity and the catalytic performance in selective partial oxidation reactions, ceria may be modified by the addition of other oxides into its structure [18]. Recently, activities of some rare earth ortovanadates in the selective oxidation of hydrogen sulfide were tested [2] and the activity of cerium ortovanadate was reported to be relatively high.

In the present study, Ce–V mixed oxide catalysts having different V/Ce ratios in their structures and a CeO_2 catalyst were prepared by the complexation technique and the catalytic performances of these materials were investigated for the selective oxidation of H_2S to elemental sulfur.

2. Experimental work

2.1. Catalyst preparation and characterization

In this study, three Ce–V mixed oxide catalysts containing different ratios of V/Ce and a cerium oxide catalytic material containing no vanadium was prepared by the complexation method. In this method, cerium nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$) and ammonium monovanadate were used as the cerium and the vanadium sources, and citric acid was used as the complexation agent, respectively. Equimolar amounts of citric acid and the salts of the metals were mixed in the solution. For the Ce–V mixed oxides, V/Ce ratio was adjusted as 1/3, 2/2 and 3/1, in the three different catalytic materials synthesized. The solution was dehydrated at about 67 °C with continuous stirring, until its viscosity had noticably increased. Then, this viscous mixture was dried at 75 °C in a glass dish, for 5–11 days. The solid foam was then calcined at 550 °C, for 8 h. Further details of the complexation technique are available in the literature [16].

The catalytic materials synthesized in this work were characterised by BET (Quantachrome), XRD (Philips PW 1840 employing a Cu Kα radiation source), SEM, mercury porosimeter (Quantachrome), TPR and XPS (SPECS) measurements. As shown in Table 1, these materials have high porosities and reasonably high surface area values. Higher porosity of the CeO_2 catalyst as compared to a Ce–V mixed oxide catalyst containing equimolar quantities of Ce and V (Ce2V2) is also seen in the SEM photographs (Fig. 1).

Table 1
Some physical properties of Ce–V mixed oxide catalysts

Catalyst	V/Ce	BET surface area (m^2/g)	Pore volume (cm^3/g)	Average pore radius (μm)
CeO_2	0	50	0.91	0.31
Ce3V1	3/1	47	0.98	0.31
Ce2V2	1	34	0.78	0.43
Ce1V3	1/3	11	0.17	0.13

2.2. Selective oxidation experiments

H_2S selective oxidation experiments were carried out in a fixed bed quartz reactor packed with 0.2 g of catalyst. An FT-IR Spectrophotometer connected to the exit of the reactor allowed on-line analysis of the reactor exit stream composition.

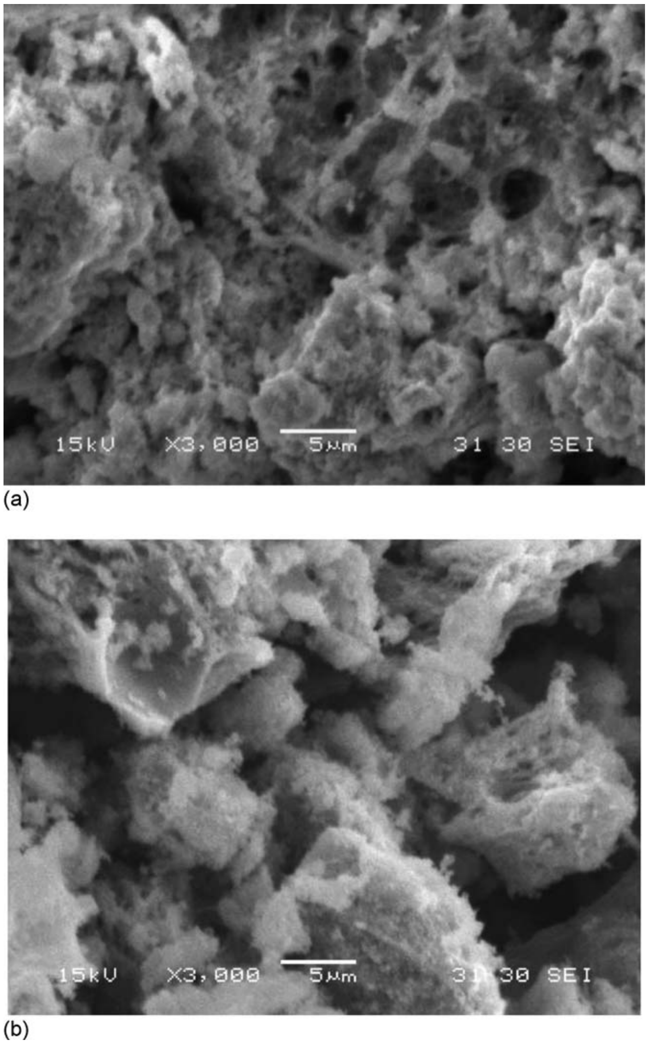

Fig. 1. SEM photographs of (a) CeO_2 and (b) Ce2V2 catalysts.

Concentrations of H_2S, H_2O and SO_2 in the reactor effluent stream were continuously measured. Most of the elemental sulfur was collected in the sulfur condenser placed between the reactor and the FT-IR Spectrophotometer. The temperature of the sulfur condenser was adjusted to 100 °C to allow condensation of the sulfur, while keeping the produced water in the vapor phase. Details of the reaction system and the analysis procedure were reported in our earlier publication [1]. In all these experiments, helium was used as the carrier gas and H_2S concentration was kept as 1%. Total flow rate of the gas mixture was kept constant at 100 cm^3/min (measured at 25 °C). Experiments were carried out with O_2/H_2S feed ratios, ranging between 0 and 2.7, in a temperature range of 200–300 °C.

3. Results and discussions

Hydrogen sulfide selective oxidation experiments carried out with the Ce–V mixed oxide catalyst containing a V/Ce atomic ratio of one (Ce2V2) showed the highest elemental sulfur yields at an O_2/H_2S ratio of 0.5. Formation of some SO_2 was observed for O_2/H_2S ratios higher than 0.5, that is higher than the stochiometric ratio for reaction (2). Some typical results, showing the time dependence of SO_2 and H_2S concentrations measured at the reactor outlet and corresponding to the reactor feed mole fraction ratios of O_2 to H_2S being equal to 0.98 and to zero are given in Fig. 2. This catalyst was found to give highly stable activity in the selective oxidation of H_2S.

Instantaneous fractional conversion of H_2S and the sulfur selectivity were defined as,

$$\text{Fractional conversion} = \frac{(H_2S)_{in} - (H_2S)_{out}}{(H_2S)_{in}}$$

$$S\,\text{selectivity} = \frac{(H_2S)_{in} - (H_2S)_{out} - (SO_2)_{out}}{(H_2S)_{in} - (H_2S)_{out}}$$

The quantitative yields of sulfur were evaluated from the chemical analysis of the reactor exit stream. In our earlier studies, which were conducted for the reaction of H_2S with some mixed metal oxide sorbents in the presence of hydrogen gas [15,16], sulfur balance was also checked by making the chemical analysis of the solid product obtained after the sorption experiments. However, in the present selective oxidation experiments, such a check of sulfur balance could not be made. In these selective oxidation experiments, most of the produced sulfur was collected in the sulfur condenser placed after the reactor. Since the amount of the sulfur produced in our system was too little and the complete collection of the sulfur from the condenser was not possible due to the sticking of some of the sulfur to the walls of the condenser and to the walls of the connecting tubes, precise measurement of the amount of the produced sulfur could not be made. However, the amount of the H_2O produced in our reactor and the amount of the H_2S removed was found to be within the experimental error limits.

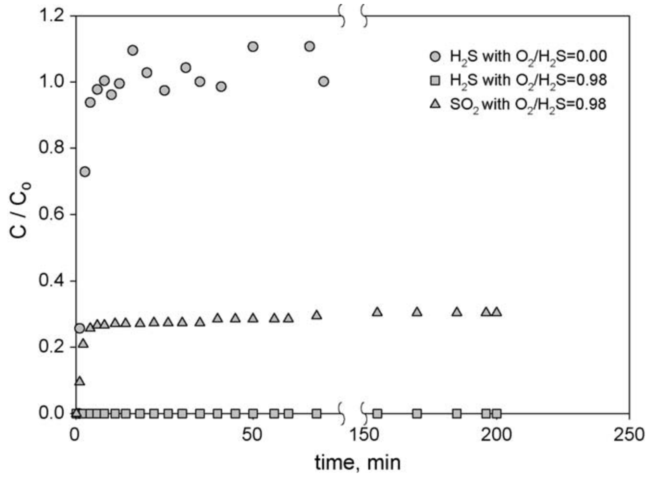

Fig. 2. Fixed bed exit concentrations of H_2S and SO_2 using the Ce2V2 mixed oxide catalyst with O_2/H_2S feed ratios of 0.98 and 0.0, at 250 °C (1% H_2S in the feed stream).

In the experiments carried out at 250 °C, 100% conversion of H_2S was obtained for O_2/H_2S feed ratios equal to or higher than 0.5. Some typical values of the steady state conversion and the sulfur selectivity values obtained at different feed compositions are reported in Table 2. For an O_2/H_2S feed ratio of 0.57, a sulfur selectivity value of 0.96 was obtained. Sulfur selectivity decreased with an inrease in O_2/H_2S ratio over the stoichiometric value, due to the formation of SO_2.

In an experiment carried out in the absence of oxygen gas, very small amount of H_2S conversion was observed only at the very initial times of the reaction, with the Ce2V2 catalyst. After a few minutes of contact of the reacting gas with the catalyst, no further conversion of H_2S was observed (Fig. 2). This result showed that the catalytic selective oxidation mechanism of the Ce–V mixed oxide was different than the Cu–V mixed oxide investigated in our previous study [1]. For the Cu–V mixed oxide, significant conversion of H_2S to elemental sulfur and the formation of some SO_2 were observed, even in the absence of oxygen gas during the first 50 min of the reaction. This observation had been explained by the involvement of lattice oxygen of Cu–V catalyst in the selective oxidation. In that previous study, it was also shown that V^{5+} was reduced to V^{4+} and V^{3+}during this process.

The XRD patterns of the Ce2V2 catalyst prepared in the present study showed that, this catalyst was in the $CeVO_4$ form (Fig. 3a). The XRD patterns of the used catalyst, after the reaction with a stoichiometric feed ratio of O_2/H_2S mixture at 250 °C, indicated no change in the bulk crystal structure (Fig. 3a). However, for the Cu–V mixed oxide catalyst studied in our previous work [1], significant changes were observed in the XRD patterns, after the reaction at similar reaction conditions.

Hydrogen sulfide selective oxidation reactions were repeated at different temperatures in the range between 200

Table 2
Fractional conversion values of H_2S and sulfur selectivities obtained with Ce2V2 catalyst at 250 °C with different O_2/H_2S mole ratios in the feed stream

O_2/H_2S	0	0.57	0.98	2.70
Fractional conversion of H_2S	–	1.0	1.0	1.0
Sulfur selectivity	–	0.96	0.69	0.54

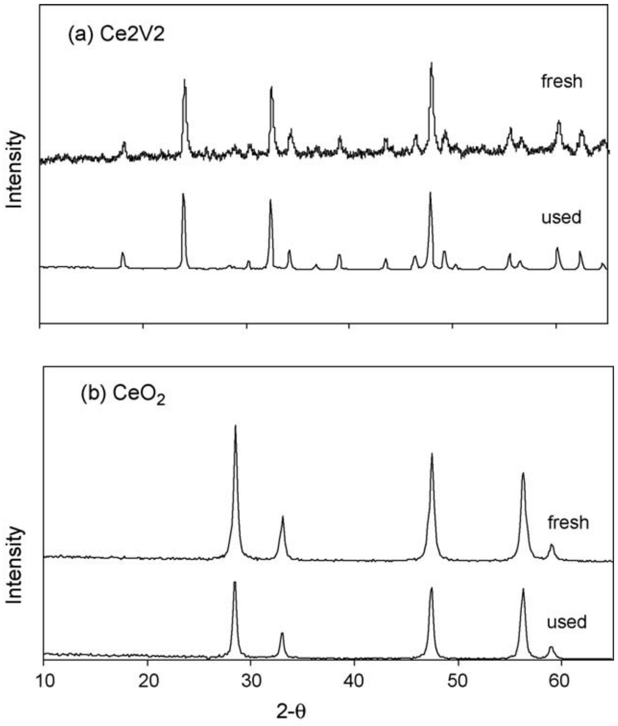

Fig. 3. XRD patterns of the fresh and the used catalysts (after reaction with an O_2/H_2S feed ratio of 0.5 at 250 °C) (a) Ce2V2; (b) CeO_2.

and 300 °C, with the Ce2V2 mixed oxide catalyst using O_2/H_2S feed ratios close to the stoichiometric value of 0.5. As shown in Fig. 4, the highest H_2S conversion was obtained at 250 °C and the catalyst activity was rather stable at this temperature. Steady state sulfur yields obtained with this catalyst, using a feed mixture containing a O_2/H_2S ratio close to 0.5 (Fig. 5), showed a maximum in the sulfur yield approaching to unity, at around 250 °C. With an increase in temperature, the redox ability of this mixed oxide catalyst is expected to increase. This effect caused an increase in the fractional conversion, in the 200–250 °C temperature range. No SO_2 formation was observed with a stoichiometric feed composition of O_2/H_2S, even at temperatures over 250 °C. These results proved the insignificance of reactions (3) and (4) in our system with this Ce–V mixed oxide catalyst, for O_2/H_2S feed ratios close to the stoichiometric value.

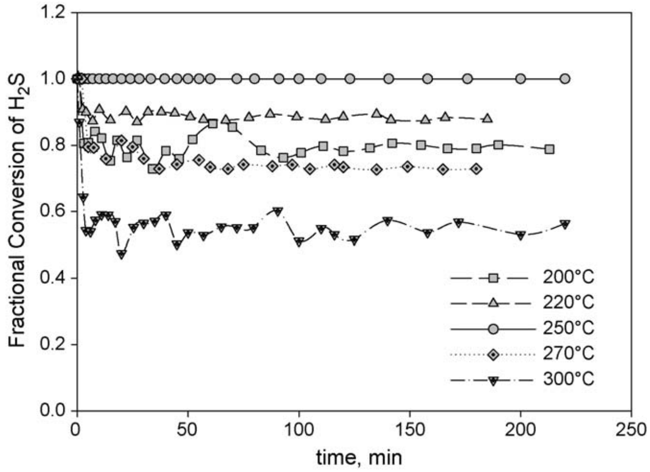

Fig. 4. Fractional conversion of H_2S at different temperatures using the Ce2V2 catalyst at near stoichiometric feed compositions.

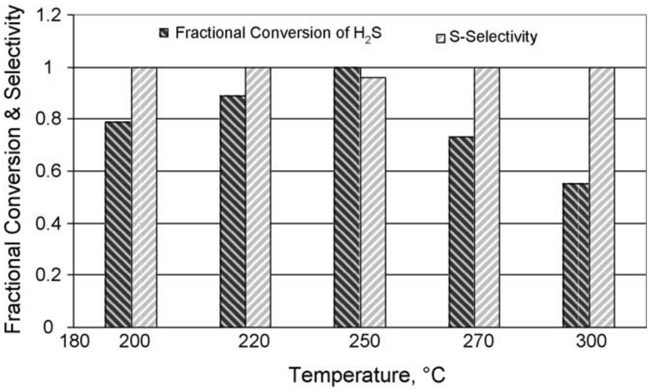

Fig. 5. Variation of the steady state conversion with temperature using the Ce2V2 catalyst with a stoichiometric O_2/H_2S feed composition.

The decrease of the steady state fractional conversion of H_2S, with an increase of temperature over 250 °C, may partly be due to the changes in the surface properties of the Ce2V2 catalyst at high temperatures. At temperatures over 250 °C, a very sharp decrease of H_2S conversion was observed within the first few minutes of the reaction and then the conversion values became stable (Fig. 4). For instance, at 300 °C, H_2S fractional conversion decreased from 1.0 to about 0.55 within the first few minutes of the reaction and then it became stable at this value. This sharp decrease observed during the first few minutes of the reaction indicated a change in the surface properties of the catalyst at temperatures over 250 °C. In fact, the surface area of the used catalyst after the reaction at 300 °C was found as 19 m^2/g, which was about 40% less than the surface area of the fresh catalyst (which was 34 m^2/g). In order to further clarify the decrease of the steady state H_2S conversion with an increase in temperature over 250 °C, another set of experiments were carried out with the Ce2V2 catalyst, which was pre-treated with a gas stream containing stoichiometric amounts of H_2S and O_2 (O_2/H_2S molar ratio being 0.5) at 500 °C. The steady state H_2S fractional conversion values obtained at different temperatures with this pre-sulfided catalyst (Ce2V2–S) are shown in Fig. 6. A maximum was again observed in the H_2S fractional conversion at 250 °C, with this pre-sulfided catalyst. However, this maximum was not as sharp as the corresponding value obtained with the fresh catalyst (Fig. 5). The fractional conversion value obtained at 250 °C with the Ce2V2–S catalyst was about 0.63 and it was much less than the fractional conversion value of 1.0, which was obtained with the fresh catalyst at the same temperature. This difference in conversion values indicated an activity decrease of the catalyst after the pre-treatment step with the H_2S containing gas. However, the fractional conversion values of H_2S obtained at 300 °C with the fresh and the pre-sulfided catalysts were found to be quite close to each other, being around 0.55. The decreasing trend of the steady state conversion values obtained with the pre-sulfided catalyst with an increase in temperature over 250 °C (Fig. 6)

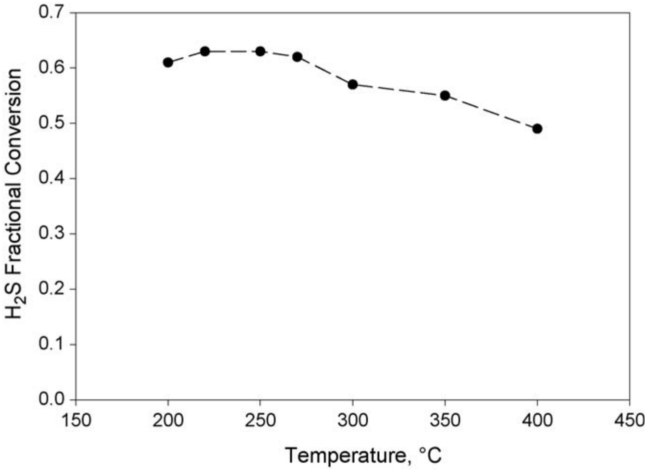

Fig. 6. Temperature dependence of the steady state H_2S conversion using the pre-sulfided catalyst (Ce2V2–S), ($O_2/H_2S = 0.5$ and 1% H_2S in the feed stream).

may be an indication of a shift in the reaction mechanism at higher temperatures.

The Ce/V ratio of the mixed oxide catalyst is another important parameter for the catalytic performance, in selective oxidation of H_2S. The activities of the three mixed oxide catalysts containing Ce/V ratios of 3/1, 2/2 and 1/3 were rather stable throughout the selective oxidation experiments lasting about 4 h. However, a significant decrease of the activity of pure cerium oxide catalyst was observed during the reaction. For the pure CeO_2 catalyst, the decrease of H_2S fractional conversion with reaction time is illustrated in Fig. 7, at 250 and 300 °C reaction temperatures. A rather sharp decrease of the activity of this catalyst was observed, especially after about 100 min of contact. It was interesting to see that the XRD patterns of the fresh and the used cerium oxide catalysts were similar, indicating that the bulk of this catalyst was in cerianite (CeO_2) structure (Fig. 3b), before and after the reaction. Deactivation of the CeO_2 catalyst during the course of the reaction, without a significant change in its bulk structure, is probably due to the faster depletion rate of the capping oxygen layer on the catalyst surface than the reoxidation rate by gaseous oxygen and the resulting changes in the surface structure of the catalyst.

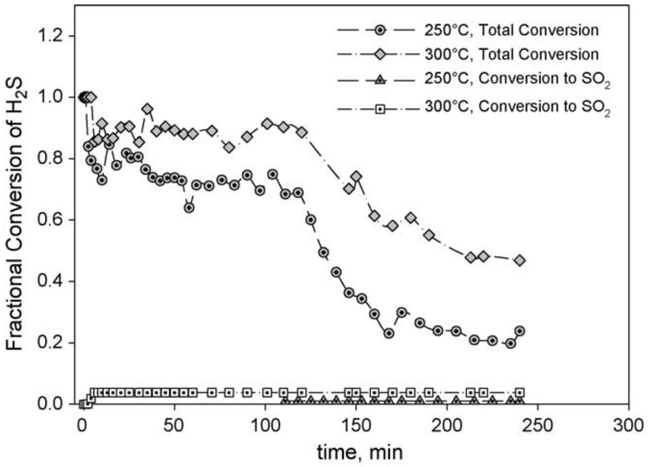

Fig. 7. Activity variation of the CeO_2 catalyst during reaction with an O_2/H_2S feed ratio of 0.5 at different temperatures.

The XPS analysis of the fresh and the used CeO_2 catalysts justified the changes on surface properties of this catalyst (Fig. 8a) after the reaction. The characteristic sulfur signal (S $2p_3$) observed at 166.2 eV clearly showed the formation of a sulfided layer over the CeO_2 catalyst during the selective oxidation reaction of H_2S. Also, the difference in the $3d_{5/2}$ signals of cerium in the fresh and the used CeO_2 catalysts indicated the partial reduction of the oxidation state of surface Ce atoms from +4 to +3, after the sulfidation reaction. The intensity of the characteristic $3d_{5/2}$ signal of Ce^{4+} at 882.2 eV decreased and the intensity of the signal at 885.8 eV increased, after the sulfidation reaction (Fig. 8a). Quantitative analysis of the XPS results indicated a S/Ce atomic ratio of about 0.8, on the surface of the used CeO_2 catalyst. These changes indicated the formation of cerium sulfates on the surface, which was

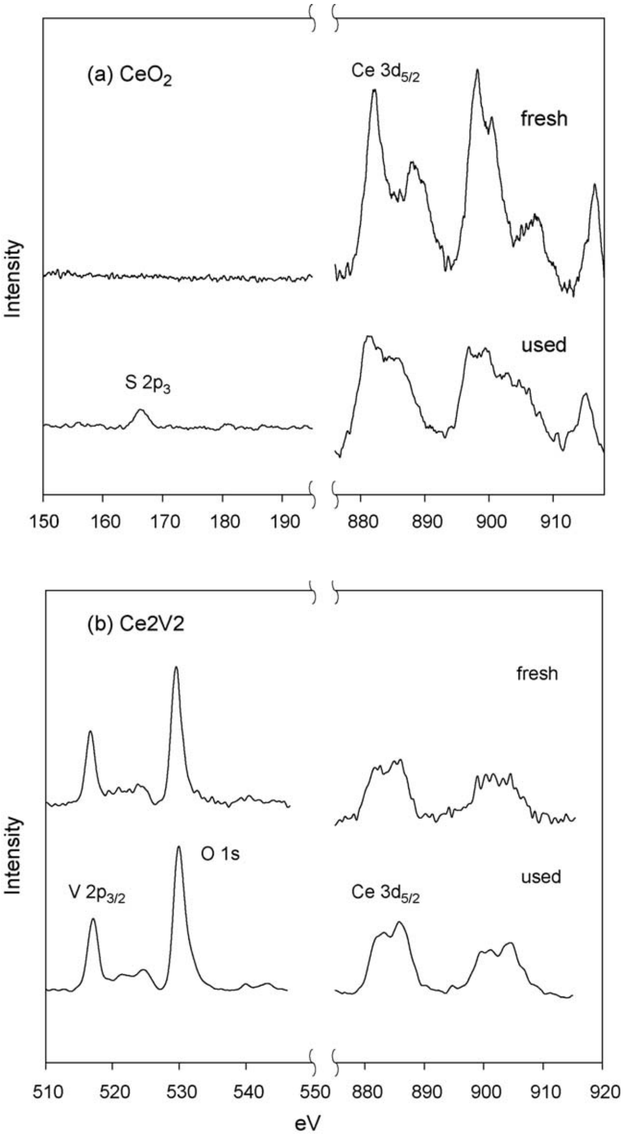

Fig. 8. XPS analysis of the fresh and the used catalysts (a) CeO_2 (b) Ce2V2.

thought to cause the deactivation of this catalyst. In the thermodynamic analysis reported by Ferrizz et al. [22], Ce–O–S phase diagrams, sulfide and sulfate formation under reducing and oxidizing conditions are discussed.

Another interesting observation was that the activity of CeO_2 catalyst was higher at 300 °C than the corresponding values at 250 °C (Fig. 7). However, for the Ce2V2 mixed oxide catalyst the maximum activity was observed at 250 °C. At 250 °C, the fractional conversion of H_2S was about unity with the Ce2V2 catalyst, while the corresponding fractional conversion obtained with the CeO_2 catalyst (at times smaller than 100 min) was less than 0.8. Temperature programmed reduction (TPR) profiles of the CeO_2 and the Ce2V2 catalysts (Fig. 9) suggested some explanation for this observation. TPR profiles of both of these catalysts showed two broad peaks. The maximum of the first TPR peak appeared at about 550 °C and this was considered to be due to the reduction of the surface capping oxygen of ceria. A similar result was reported by Zhu et al. [20] in a study for CO oxidation over a Pd/CeO_2 catalyst. The interesting observation of hydrogen TPR of these two catalysts was that, the reduction of the Ce2V2 catalyst started at about 250 °C, while the reduction of CeO_2 started at a higher temperature (over 350 °C). These results indicated an improvement of the redox ability of the ceria catalyst at lower temperatures by the incorporation of vanadia into the catalyst structure. The second TPR peak observed at 780 °C for the CeO_2 catalyst corresponds to the reduction of the bulk lattice oxygen. For the Ce2V2 catalyst, the second broad peak was observed at 763 °C and it was much bigger than the corresponding TPR peak observed with pure CeO_2. This broad peak obtained at 763 °C corresponds to the removal of oxygen from the bulk of $CeVO_4$, resulting the reduction of V^{+5}.

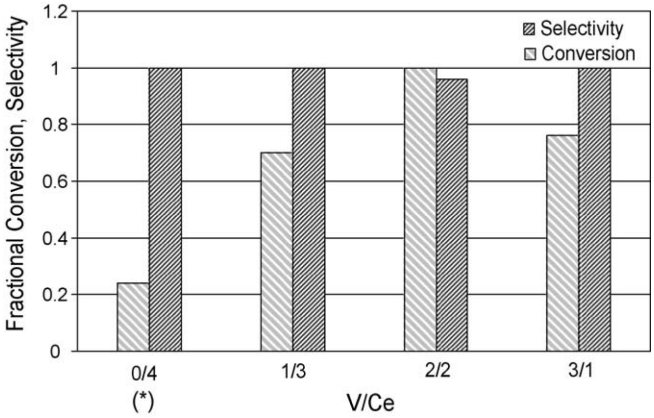

Fig. 10. H_2S fractional conversion and sulfur selectivity values obtained at 250 °C with the catalysts having different V/Ce ratios ($O_2/H_2S = 0.5$). [(*) At a reaction time of 200 min].

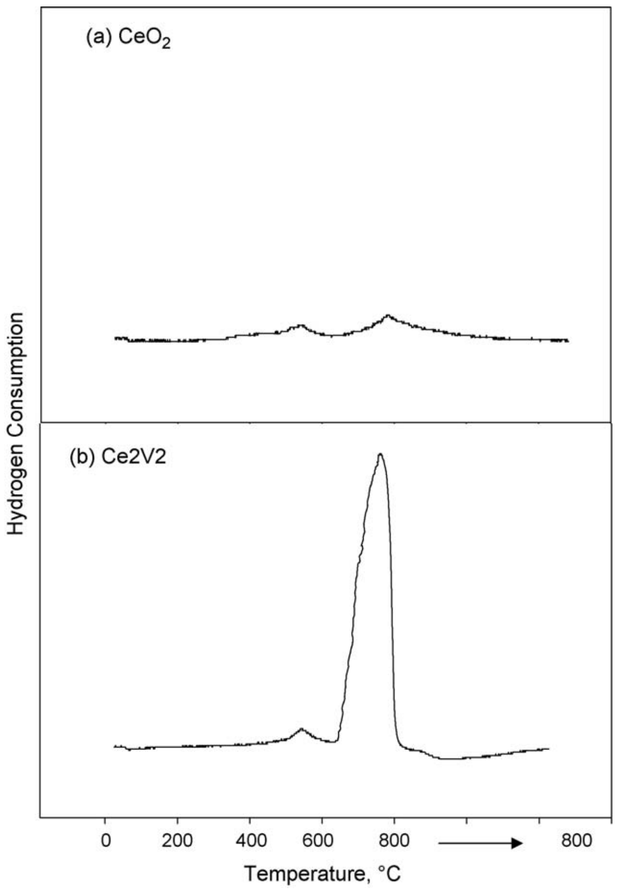

Fig. 9. Hydrogen TPR profiles of CeO_2 and Ce2V2 catalysts.

The steady state conversion and the sulfur selectivity values obtained at 250 °C with the Ce–V mixed oxide catalysts having different Ce/V ratios and using a feed stream containing stoichiometric ratio of O_2/H_2S are shown in Fig. 10. In the same figure, conversion and sulfur selectivity values obtained with the CeO_2 catalyst, at a reaction time of 200 min, are also given. For all these cases, sulfur selectivities were about unity. However, the highest conversion of H_2S was observed with the catalyst containing equal moles of cerium and vanadium (Ce2V2). The BET surface area and the pore volume of the catalyst containing a V/Ce mole ratio of three is much lower than the other catalysts containing lower V/Ce ratios. This is one of the factors causing the lower activity of this catalyst. More importantly, crystal structures and the oxidation states of V and Ce in the Ce–V mixed oxide catalysts determine the activity of these catalysts.

The XRD patterns of all these catalysts are given in Fig. 11. These XRD patterns showed the presence of both $CeVO_4$ and CeO_2 phases in the Ce3V1 catalyst, while the Ce2V2 catalyst contained only $CeVO_4$ phase. The Ce1V3 catalyst was more amorphous and the presence of some $CeVO_4$ phase was also

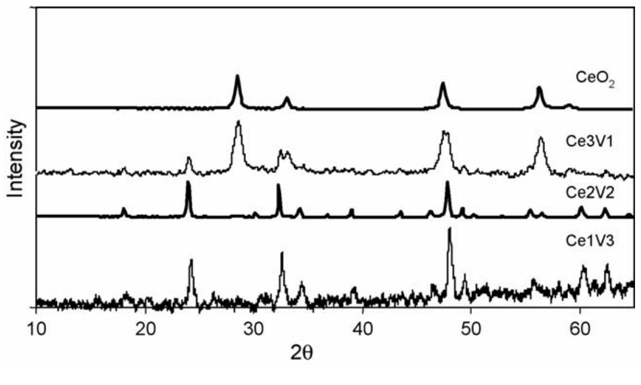

Fig. 11. XRD patterns of the catalysts with different V/Ce ratios.

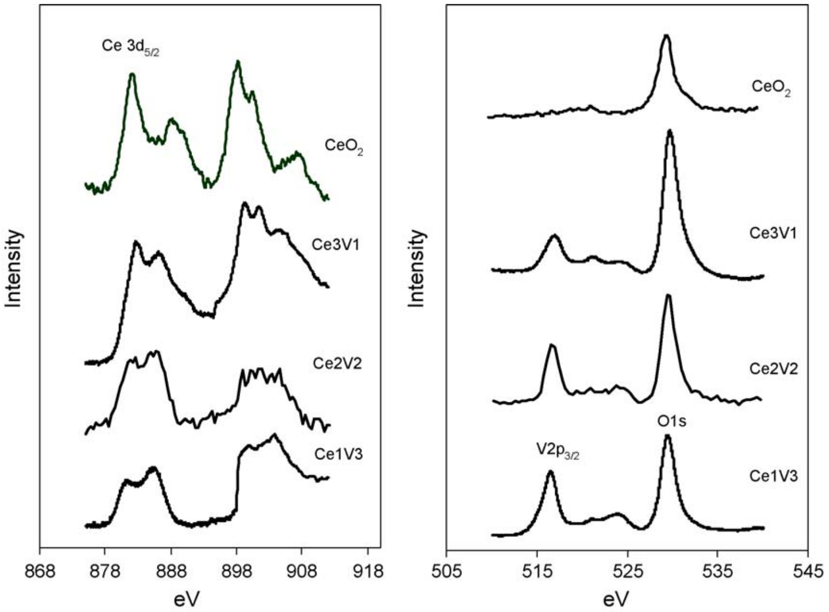

Fig. 12. XPS analysis of the catalysts with different V/Ce ratios.

observed. The XPS analysis of these mixed oxide catalysts showed that vanadium was in the oxidation state of +5, in all of them (Fig. 12 and Table 3). V2p$_{3/2}$ binding energies of all these catalysts were between 517.1 and 517.2 eV and the difference in binding energies between O1s and V2p$_{3/2}$ (Δ_{OV}) were about 12.7–12.6 eV, indicating +5 oxidation state of vanadium. The details of XPS binding energies of different vanadium oxidation states are reported by Silversmit et al. [21]. Comparison of the XPS analysis of the fresh and the used Ce2V2 catalysts also indicated that oxidation state of vanadium did not change after the selective oxidation reaction (Fig. 8b). The V2p$_{3/2}$ signal observed at 517.1 eV in the XPS analysis of the fresh and the used Ce2V2 catalyst justified this. In contrary to the CeO$_2$ catalyst, the XPS analysis of the Ce2V2 catalyst showed that there was no sulfur on the catalyst surface after the sulfidation reaction. No XPS signal was observed at around 166.2 eV for the fresh and the used Ce2V2 catalysts. As reported above, this catalyst was rather stable and showed no deactivation throughout the selective oxidation reaction at 250 °C.

As shown in Fig. 12 and as summarized in Table 3, the binding energy of Ce3d$_{5/2}$ at 882.2 eV indicated that most of the cerium was in +4 oxidation state in the CeO$_2$ catalyst. In the case of mixed oxide catalysts, formation of CeVO$_4$ structure was observed. In this phase, cerium was in +3 oxidation state. The two peaks observed at about 881.8 and 885.8 eV for the Ce3d$_{5/2}$ indicated the presence of +4 and +3 oxidation states of cerium in the mixed oxide catalysts. For the most active mixed oxide catalyst containing equal amounts of cerium and vanadium (Ce2V2), most of the cerium was in +3 oxidation state. For the catalyst containing higher amount of cerium (Ce3V1), most of the cerium was in +4 oxidation state. Results showed that V enhanced the stability of the +3 oxidation state of cerium in the catalyst structure.

Table 3
XPS Analysis of Ce–V oxide catalysts prepared in this work

Sample	O1s (eV)	V2p$_{3/2}$ (eV)	$\Delta_{(O-V)}$ (eV)	Ce3d$_{5/2}$ (eV)
CeO$_2$	529.6	–	–	882.2
Ce3V1	529.8	517.1	12.7	882.5
Ce2V2	529.8	517.1	12.7	885.3–881.8
Ce1V3	529.8	517.2	12.6	885.2–881.6

The XPS results of the fresh and the used mixed oxide catalysts containing equal amounts of V and Ce (Ce2V2) showed some increase in the ratio of signals observed at 885.3 and 881.8 eV, after the sulfidation reaction (Fig. 8b). This increase indicated further reduction of the surface Ce atoms from +4 to +3 state during the sulfidation reaction. However, no change in the oxidation state of V (+5) was observed after the reaction. All these results showed that for the Ce2V2 catalyst containing CeVO$_4$, vanadium and cerium were majorly in V^{5+} and Ce^{3+} oxidation states and the selective oxidation of H$_2$S to elemental sulfur most probably involved a redox cycle of cerium, rather than a redox cycle of vanadium. This conclusion is in agrement with the conclusion of Martinez-Huerta et al. [18] who studied the nature of vanadia-ceria interface in V5+/CeO$_2$ catalysts.

4. Concluding remarks

A Ce–V mixed oxide catalyst containing equimolar quantities of cerium and vanadium gave very high sulfur yields approaching to unity, in the selective oxidation of H$_2$S with a feed stream containing equimolar quantities of oxygen and H$_2$S. Incorporation of vanadium into the ceria structure improved the redox ability of ceria at low temperatures and stabilized its activity in the H$_2$S selective oxidation. However, the activity of pure CeO$_2$ was found to show a decrease during the reaction due to the formation of a partially sulfided layer on the catalyst surface. The active phase of the mixed oxide was found as CeVO$_4$ and this catalyst showed the highest activity at 250 °C.

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