



# Reduction of SO<sub>2</sub> by CO and COS over La<sub>2</sub>O<sub>2</sub>S—a mechanistic study

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## Abstract

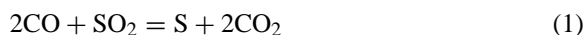
The mechanism of the catalytic reduction of SO<sub>2</sub> by CO and COS over lanthanum oxysulfide was studied using a combination of temperature-programmed reaction coupled with mass spectrometry (TPR/MS) and feed-perturbation step-analysis techniques. The results showed that COS interacts more readily with lanthanum oxysulfide than CO does. The interaction of COS with the lanthanum catalyst was different from that of CO. In addition, COS preferentially reacted with SO<sub>2</sub> to form CO<sub>2</sub> and sulfur instead of following the disproportionation (to form CO<sub>2</sub> and COS) and decomposition (to form CO and sulfur) reactions. The redox mechanism is not the main reaction route for the reduction of SO<sub>2</sub> by CO and COS over lanthanum oxysulfide. SO<sub>2</sub> was strongly adsorbed by the oxysulfide and was retained in the oxysulfide even when heated in an inert gas stream, while COS was very reactive and did not remain long in the oxysulfide. These results suggest that COS has access to certain specific active sites in the oxysulfide and the catalytic reduction of SO<sub>2</sub> by COS possibly proceeds via adsorbed COS reacting with pools of SO<sub>2</sub> adspecies to form CO<sub>2</sub> and sulfur.

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**Keywords:** Lanthanum oxysulfide; Sulfur dioxide; Carbonyl sulfide; Carbon monoxide; Reduction mechanism

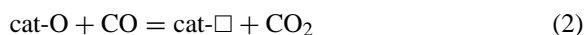
## 1. Introduction

The catalytic reduction of SO<sub>2</sub> by CO (Eq. (1)) has been extensively studied using various catalyst systems such as lanthanum oxysulfide [1], lanthanum oxysulfide–cobalt disulfide [2,3], titanium dioxide [4], titanium dioxide–cobalt disulfide [4], ceria [5] and others [4].



Two generic types of reduction mechanisms, namely, the redox mechanism, shown in Eqs. (2)–(4),

and the COS-intermediate mechanism, shown in Eqs. (5)–(7), have been proposed for the reaction. The redox mechanism in which oxygen vacancies are created by reducing the oxide catalysts seems to describe the oxide catalysts such as ceria and titania well. The oxygen anion vacancies are the active sites for the reduction of SO<sub>2</sub> and they extract the oxygen atoms from the sulfur dioxide molecules.



where  $\square$  denotes the oxygen anion vacancy. COS has been observed to reduce SO<sub>2</sub> faster than CO does and it

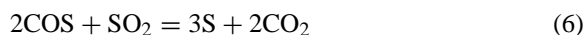
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has been argued that COS is a stronger reducing agent than CO to produce the active vacancy in Eq. (2) [4]. This redox mechanism suggests that a pre-reduced catalyst can and will more promptly reduce SO<sub>2</sub> at the anion vacancies created. In other words, if a pre-reduced catalyst does not reduce the SO<sub>2</sub> which the catalyst comes into contact immediately after the catalyst treatment, the SO<sub>2</sub> reduction reaction will not follow the redox route.

For catalysts containing lanthanum oxysulfide and/or cobalt disulfide, the COS mechanism seems to describe the process better since the intermediate COS is readily produced by the reaction between CO and cobalt disulfide.



COS is produced by Eq. (5) and by lanthanum oxysulfide and CO [6]. Once formed, COS is more reactive than CO in reducing SO<sub>2</sub> and the reaction is catalyzed by lanthanum oxysulfide [1,2]. Thus, the COS reduction of SO<sub>2</sub> (Eq. (6)) is favored once COS is formed.

However, in the reported COS-intermediate mechanism studies involving lanthanum oxysulfide, only the formation of COS via the reaction of CO with cobalt disulfide and lanthanum oxysulfide has been elucidated in detail [2,3,6]. The reaction between COS and SO<sub>2</sub> (Eq. (6)) has not received much attention and the mechanism involved is still not clear. It is possible that the COS reduction of SO<sub>2</sub> can proceed via an accelerated COS-redox mechanism over the catalyst. Other possible reaction routes such as the surface reaction between co-adsorbed COS and SO<sub>2</sub> molecules cannot be ruled out. This paper focuses on the reaction of COS with SO<sub>2</sub> over lanthanum oxysulfide and determines if the reduction of SO<sub>2</sub> over lanthanum oxysulfide follows the redox mechanism. The role of COS as a reaction intermediate in the reduction of SO<sub>2</sub> by CO will also be examined.

## 2. Experimental

### 2.1. Interaction of COS and CO with La<sub>2</sub>O<sub>2</sub>S

The temperature-programmed reaction technique coupled with mass spectrometry (TPR/MS) was used

in this study. The TPR system contains an electrical furnace with a programmable temperature controller and a quartz micro-reactor. It has been described elsewhere [6]. The lanthanum oxysulfide catalyst used in this study was prepared by the sulfidization method described in [7]. Briefly, 0.1 g lanthanum oxysulfide was heated in a feed of 98 ml min<sup>-1</sup> from room temperature (~20 °C) to 600 °C at 10 °C min<sup>-1</sup>. The feed stream for the COS study comprised 820 ppmv COS in He while that for the CO study contained 820 ppmv CO in He. The oxysulfide sample was purged with the feed until the effluent composition was steady before the heating started. A split stream of the effluent from the reactor was sent to a high-speed process mass spectrometer (MS-250, ABB EXTREL) for composition measurement.

### 2.2. Catalyst pre-treatment effect

This experiment was designed to determine the role of the redox mechanism in the reduction of SO<sub>2</sub> over lanthanum oxysulfide and to demonstrate the importance of the simultaneous presence of COS and SO<sub>2</sub> to make the reduction reaction occur. Two 0.1 g catalyst samples were used.

The first lanthanum oxysulfide sample was maintained at 600 °C in a 90 ml min<sup>-1</sup> He carrier stream for 1 h before a reaction stream containing 820 ppmv CO and 410 ppmv SO<sub>2</sub> in He was fed to the reactor at 98 ml min<sup>-1</sup>. The reactor was kept at 600 °C until the reduction of SO<sub>2</sub> started again. The catalyst sample was then reduced by a reduction stream containing 820 ppmv CO in He at 98 ml min<sup>-1</sup> at 600 °C for 2 h before switching back to the reaction stream. The reduced catalyst was then kept at 600 °C for 2 h.

The second lanthanum oxysulfide sample was heated in the reduction stream at 600 °C for 2 h. It was then cooled to room temperature in the He carrier stream before the COS reaction stream containing 820 ppmv COS and 410 ppmv SO<sub>2</sub> in He at 98 ml min<sup>-1</sup> was switched into the reactor. The sample was finally heated to 600 °C at 10 °C min<sup>-1</sup> after the composition of the effluent became steady.

### 2.3. Step changes in feed composition

About 0.05 g lanthanum oxysulfide was heated in the reactor to the reaction temperatures with Ar flow.

Three temperature steps at 335 °C, 400 °C and 600 °C were used to give low, moderate and almost complete conversion of COS for the reduction of SO<sub>2</sub>. Three feed streams at a flow rate of 100 ml min<sup>-1</sup> with the following compositions were used:

1. 2200 ppmv SO<sub>2</sub>, 3600 ppmv COS and 4.6% He in Ar;
2. 3500 ppmv SO<sub>2</sub> and 6.7% He in Ar; and
3. 5000 ppmv COS and 4.4% He in Ar.

The feed sequence was (1)→(2)→(3)→(2)→(1)→(3)→(1). This sequence was chosen to examine the effect of the SO<sub>2</sub> and COS streams on each other. Sufficient time was allowed for the composition of the effluent to reach a steady state after the feed switch. The oxysulfide sample was then purged with Ar until the SO<sub>2</sub> and COS in the effluent was zeroed out before a new feed gas stream was switched to the reactor.

### 3. Results and discussion

#### 3.1. Interaction of COS and CO with lanthanum oxysulfide

##### 3.1.1. Carbon monoxide

The TPR results for the CO reduction of lanthanum oxysulfide from room temperature to 600 °C are shown in Fig. 1. There were no significant changes in the relative concentrations of CO, CO<sub>2</sub>, COS and CS<sub>2</sub> at temperatures below 300 °C. CO<sub>2</sub> began to appear in the effluent at just above 300 °C, well before the CO was consumed. This was probably due to the desorption of the CO<sub>2</sub> adspecies formed by the reaction of the pre-adsorbed CO on the lanthanum oxysulfide [6]. The desorption of the CO<sub>2</sub> adspecies made room for the further adsorption of CO, which could in turn react to form more CO<sub>2</sub>. COS was produced later at higher temperatures. The consumption of CO and the production of CO<sub>2</sub> peaked at about 370 °C and rose abruptly at temperatures above 500 °C. On the other hand, the production of COS peaked at 380 °C and then fell back to a lower level. The mechanism of the production of COS has been discussed in detail elsewhere [6] and can be summarized in the following two reaction steps:

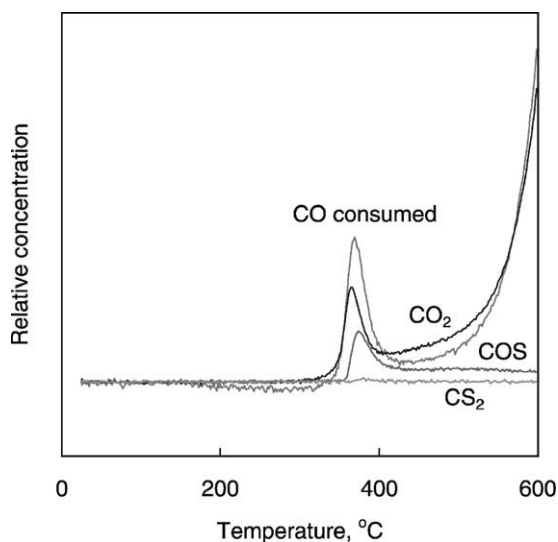


Fig. 1. TPR of lanthanum oxysulfide using CO as the reducing agent. The relative concentration curves were obtained by adjusting the raw MS intensity data for zero, the fragmentation effect and instrument sensitivity. Note that the CO curve is a consumption curve, which was computed from the difference of the CO in the feed and the effluent. All the other curves are production curves.

where \*S is a lattice sulfide ion and \* is an anion vacancy with two negative charges created in lanthanum oxysulfide. Two types of CO oxidation processes are thought to be associated with the CO<sub>2</sub> formation [6]. They include a low-temperature oxidation attributable to the loosely bound oxygen species in the surface of the oxysulfide, and a high-temperature oxidation associated with the more tightly bound lattice oxygen, which becomes available when the temperatures are high enough.

##### 3.1.2. Carbonyl sulfide

The TPR results for the reaction between COS and lanthanum oxysulfide are shown in Fig. 2. The reaction started at about 220 °C with a moderate production of CO<sub>2</sub> from the oxidation of COS. The reaction became more vigorous at temperatures above 400 °C and produced significantly more CO<sub>2</sub>, COS and CO. The disproportionation of COS to CO<sub>2</sub> and CS<sub>2</sub> shown in Eq. (10) occurred at temperatures around 400 °C and the production of CS<sub>2</sub> peaked at around 550 °C. The decomposition of COS to CO and sulfur shown in Eq. (11) became increasingly important as the

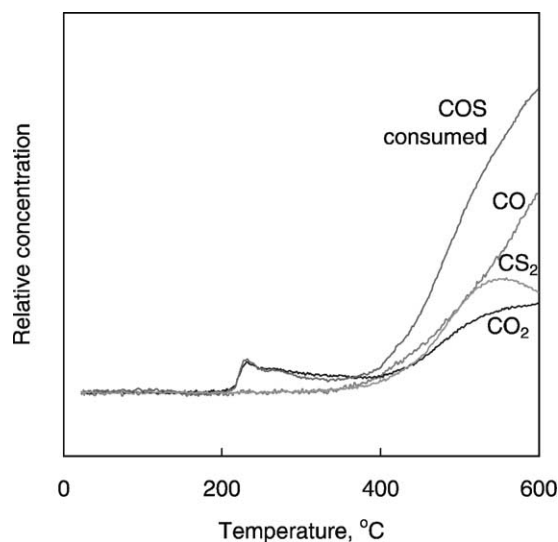


Fig. 2. TPR of lanthanum oxysulfide using COS as the reducing agent. The relative concentration curves were obtained by adjusting the raw MS intensity data for zero, the fragmentation effect and instrument sensitivity. Note that the COS curve is a consumption curve, which was computed from the difference of the COS in the feed and the effluent. All the other curves are production curves.

temperature rose.

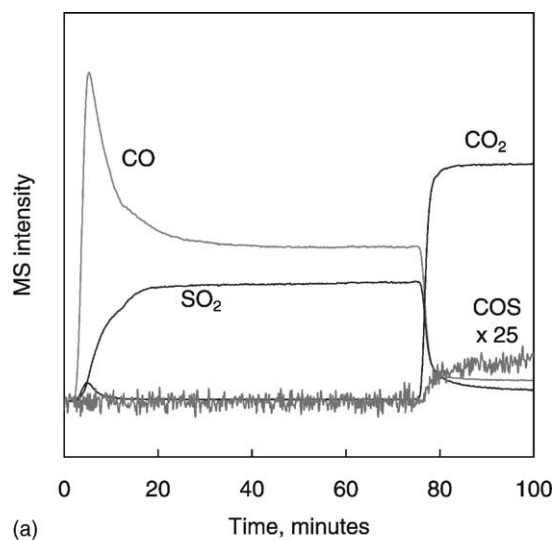


The oxidation of COS to form  $\text{CO}_2$  at temperatures below  $300^\circ\text{C}$  was probably due to the oxidation of the loosely bound oxygen species in the surface of the oxysulfide catalyst.

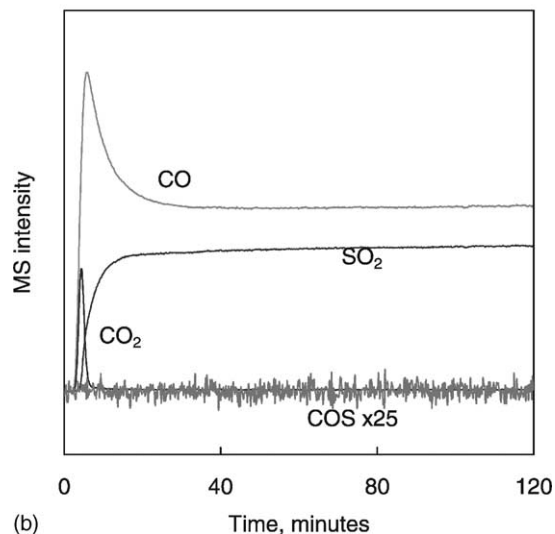
A comparison between Figs. 1 and 2 indicates clearly that both CO and COS reduced lanthanum oxysulfide but COS interacted more readily with lanthanum oxysulfide and in a way different from CO. A possible reason for the latter is that COS may have access to certain active sites in lanthanum oxysulfide that are not available to CO. These active sites could be the key to unlocking the mechanism of the reduction of  $\text{SO}_2$  over lanthanum oxysulfide and thus the role of the COS intermediate in this reaction.

### 3.2. Catalyst pre-treatment

Fig. 3 shows the reactivation of the oxysulfide catalyst in the reduction of  $\text{SO}_2$  by CO after (a) being



(a)



(b)

Fig. 3. Recovery of  $\text{SO}_2$  reduction reaction by CO over lanthanum oxysulfide at  $600^\circ\text{C}$  after the oxysulfide was heated in a stream of (a) He and (b) CO. COS curves are scaled up by 25 times. All these intensity curves have been adjusted for zero but not for the fragmentation effect and instrument sensitivity.

heated in He and (b) being reduced by CO. When the  $\text{SO}_2$  and CO reaction stream was first introduced to the oxysulfide catalyst, no immediate catalytic reaction took place. Instead,  $\text{SO}_2$  was preferentially adsorbed by the catalyst and displaced both CO and  $\text{CO}_2$  from the catalyst. It took more than 1 h for the He-heated catalyst sample to achieve a significant level of

reaction between  $\text{SO}_2$  and CO to produce  $\text{CO}_2$  and COS (Fig. 3a). The effect of heat-treating the catalyst in inert gas has been discussed elsewhere [6]. This treatment could drive off most of the loosely bound and reactive sulfur from the catalyst causing difficulty in the production of the reaction intermediate COS, thus prohibiting the reduction of  $\text{SO}_2$ . Although heating alone can deactivate the oxysulfide for the  $\text{SO}_2$  reduction reaction, this deactivation is temporary and the reaction can resume eventually. Analogous to the formation of oxygen anion vacancies on lanthanum oxide [8], Lau and Fang [6] proposed the formation of anion vacancies on lanthanum oxysulfide upon heating. Should this reaction follow the redox mechanism, these vacancies would reduce the  $\text{SO}_2$  molecules when they came into contact and thus would reactivate the oxysulfide catalyst immediately. This immediate reactivation, however, was not observed.

This phenomenon was even more pronounced for the sample pre-reduced by CO (Fig. 3b). The sample could not be reactivated in 2 h. On the other hand, the as synthesized  $\text{La}_2\text{O}_2\text{S}$  catalyzed the reduction of  $\text{SO}_2$  by CO immediately once the  $\text{SO}_2/\text{CO}$  mixture was fed to the material at the same reaction temperature ( $\sim 600^\circ\text{C}$ ). Thus, the He-treatment and pre-reduction processes deactivate the catalytic material. This strongly supports the argument that the CO-redox mechanism described by Eqs. (1)–(3) is not the main reaction path for the reduction of  $\text{SO}_2$  by CO over lanthanum oxysulfide. Otherwise, the redox mechanism would lead to the reactivation of the catalyst as soon as the reaction stream was introduced. It should also be pointed out that since the interaction between CO and lanthanum oxysulfide produces COS, the CO-reduced oxysulfide should have been reduced by COS. Thus, the COS-redox mechanism could not be a reaction route for the reduction of  $\text{SO}_2$ . Furthermore, there was no COS produced in the 2 h after the  $\text{SO}_2$  and CO feed was introduced to the CO-reduced sample. This observation together with the simultaneous production of COS during the reactivation of the heat-treated oxysulfide sample, shows that the catalytic reduction of  $\text{SO}_2$  over the oxysulfide catalyst was strongly associated with COS and the simultaneous presence of COS and  $\text{SO}_2$  was vital to the reaction. This argument is further supported by the rapid reduction of  $\text{SO}_2$  by COS over the CO-reduced catalyst (see Fig. 4).

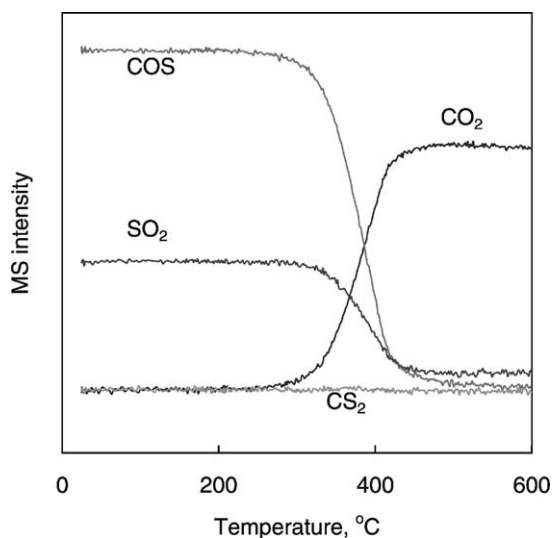


Fig. 4. Recovery of  $\text{SO}_2$  reaction by COS in TPR after the oxysulfide was heated in carbon monoxide. All the intensity curves have been adjusted for zero but not for the fragmentation effect and instrument sensitivity.

The COS– $\text{SO}_2$  reaction started at temperatures as low as  $300^\circ\text{C}$ . A large amount of  $\text{SO}_2$  and COS was consumed when the temperature was greater than  $400^\circ\text{C}$ . This suggests that COS was more reactive than CO for the reduction of  $\text{SO}_2$  over lanthanum oxysulfide because the ignition temperature of the CO– $\text{SO}_2$  reaction was greater than  $360^\circ\text{C}$  [1]. These results suggest that the active sites for the COS– $\text{SO}_2$  reduction reaction were readily present on the CO-reduced catalyst at temperatures as low as  $300^\circ\text{C}$ . In addition, it is critical for COS and  $\text{SO}_2$  to be simultaneously present over the oxysulfide catalyst for the reduction of  $\text{SO}_2$  to occur. The reaction mechanism for the COS and  $\text{SO}_2$  reaction could involve the direct interaction of these two species over the oxysulfide catalyst.

In the COS reduction of  $\text{SO}_2$ , there was no detectable  $\text{CS}_2$  and the  $\text{CO}_2$  peak at  $\sim 200^\circ\text{C}$ , which was observed in the COS-TPR of lanthanum oxysulfide, was absent. This suggests that COS was preferentially scavenged by  $\text{SO}_2$  before disproportionation could occur, and the oxidation of COS below  $300^\circ\text{C}$  (Fig. 2) was suppressed in the presence of  $\text{SO}_2$ . Since  $\text{SO}_2$  was preferentially adsorbed onto the oxygen ions of the catalyst [6], the adsorption could have stabilized the



loosely bound oxygen as adsorbed sulfite and sulfate and made the oxygen unavailable to oxidize COS.

### 3.3. Step changes in feed concentration

In Stream 1, the COS to SO<sub>2</sub> ratio was less than stoichiometric and a portion of SO<sub>2</sub> always remained while COS was completely consumed at 600 °C. The conversion increased with temperature from 335 °C to 600 °C as illustrated in Figs. 5 and 6a. The steady-state conversion of COS was only about 10% at 335 °C and 70% at 400 °C. The responses to the perturbation sequence in the feed were the same at all three temperatures and in the following discussion we focus on the results for 400 °C (Fig. 6).

In general, as soon as the COS and SO<sub>2</sub> stream (Stream 1) was introduced to the oxysulfide catalyst, COS reacted immediately with the SO<sub>2</sub> to produce an equivalent amount of CO<sub>2</sub>. Only a negligible amount of COS, if any, was adsorbed to the oxysulfide catalyst. There was no ratable amount of CS<sub>2</sub> found in the effluent gas. COS is very reactive over the oxysulfide catalyst and tends to react with SO<sub>2</sub> rather than staying adsorbed on the catalyst or disproportionating to CS<sub>2</sub>.

When SO<sub>2</sub> (Stream 2) was fed to the catalyst, a significant amount of SO<sub>2</sub> was consumed at the beginning with no COS, CO, CO<sub>2</sub> and CS<sub>2</sub> found in the effluent gas suggesting that the SO<sub>2</sub> was adsorbed onto the catalyst. If there were any COS adspecies left on the catalyst from the previous experiment, CO<sub>2</sub> would have been found in the effluent. Thus, it can be deduced that the COS adspecies was too reactive to remain on the oxysulfide at 400 °C.

When COS (Stream 3) was sequenced into the reactor, COS was rapidly consumed and a surge in CO<sub>2</sub> was observed. This surge was probably due to the reaction of COS with the SO<sub>2</sub> adspecies left behind from the previous SO<sub>2</sub> containing feed streams. CS<sub>2</sub> was produced at a later stage, as a result of the disproportionation of COS when the COS–SO<sub>2</sub> reaction slowed down due to the depletion of the SO<sub>2</sub> adspecies. No SO<sub>2</sub> was detected throughout this step. The SO<sub>2</sub> adspecies, if present, would be strongly adsorbed by the oxysulfide.

The feed-perturbation experiment was carried out in the following order (a) COS + SO<sub>2</sub>, (b) SO<sub>2</sub>, (c) COS, (d) SO<sub>2</sub>, (e) COS + SO<sub>2</sub>, (f) COS and (g) COS + SO<sub>2</sub>. The effects of COS and SO<sub>2</sub> pre-treatments on

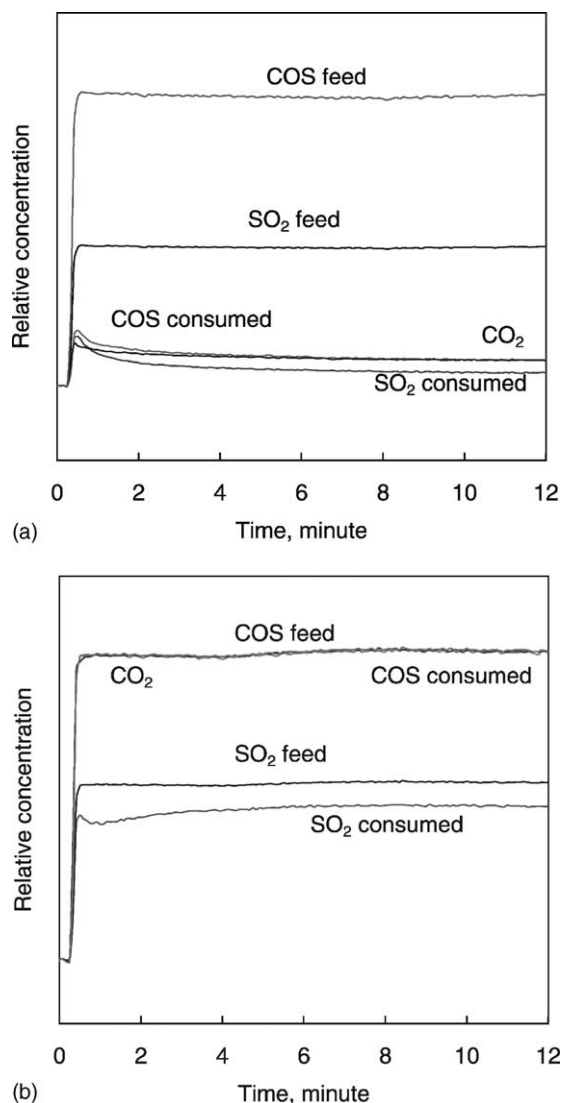


Fig. 5. Step perturbation with COS + SO<sub>2</sub> at (a) 335 °C and (b) 600 °C. The relative concentration curves were obtained by adjusting the raw MS intensity data for zero, the fragmentation effect and instrument sensitivity. The COS feed, COS consumption and CO<sub>2</sub> curves are nearly coincident indicating almost complete conversion of COS in the SO<sub>2</sub> reduction reaction.

the subsequent reaction over the lanthanum oxysulfide catalyst are summarized in Table 1. It is apparent that pre-treating the oxysulfide catalyst with COS increased the subsequent adsorption of SO<sub>2</sub> but SO<sub>2</sub> pre-treatment showed no apparent effect on the subsequent reaction with COS. However, the adsorption

Table 1  
Effects of COS and SO<sub>2</sub> pre-treatment on the subsequent reaction catalyzed by lanthanum oxysulfide

Pretreatment	Subsequent reaction	Effects
COS	SO <sub>2</sub>	SO <sub>2</sub> adsorption was increased
COS	SO <sub>2</sub> + COS	SO <sub>2</sub> adsorption was increased
SO <sub>2</sub>	COS	No significant effect
SO <sub>2</sub>	SO <sub>2</sub> + COS	SO <sub>2</sub> adsorption was reduced

of SO<sub>2</sub> was reduced by the SO<sub>2</sub> pre-treatment. A possible explanation is that SO<sub>2</sub> is strongly adsorbed to the oxysulfide. The SO<sub>2</sub> adspecies is so stable that the adsorption sites are only freed for further adsorption when the adspecies reacts with COS to form sulfur and CO<sub>2</sub>. Thus, SO<sub>2</sub> pre-treatment does not alter the population of the SO<sub>2</sub> adspecies to affect the subsequent COS reaction.

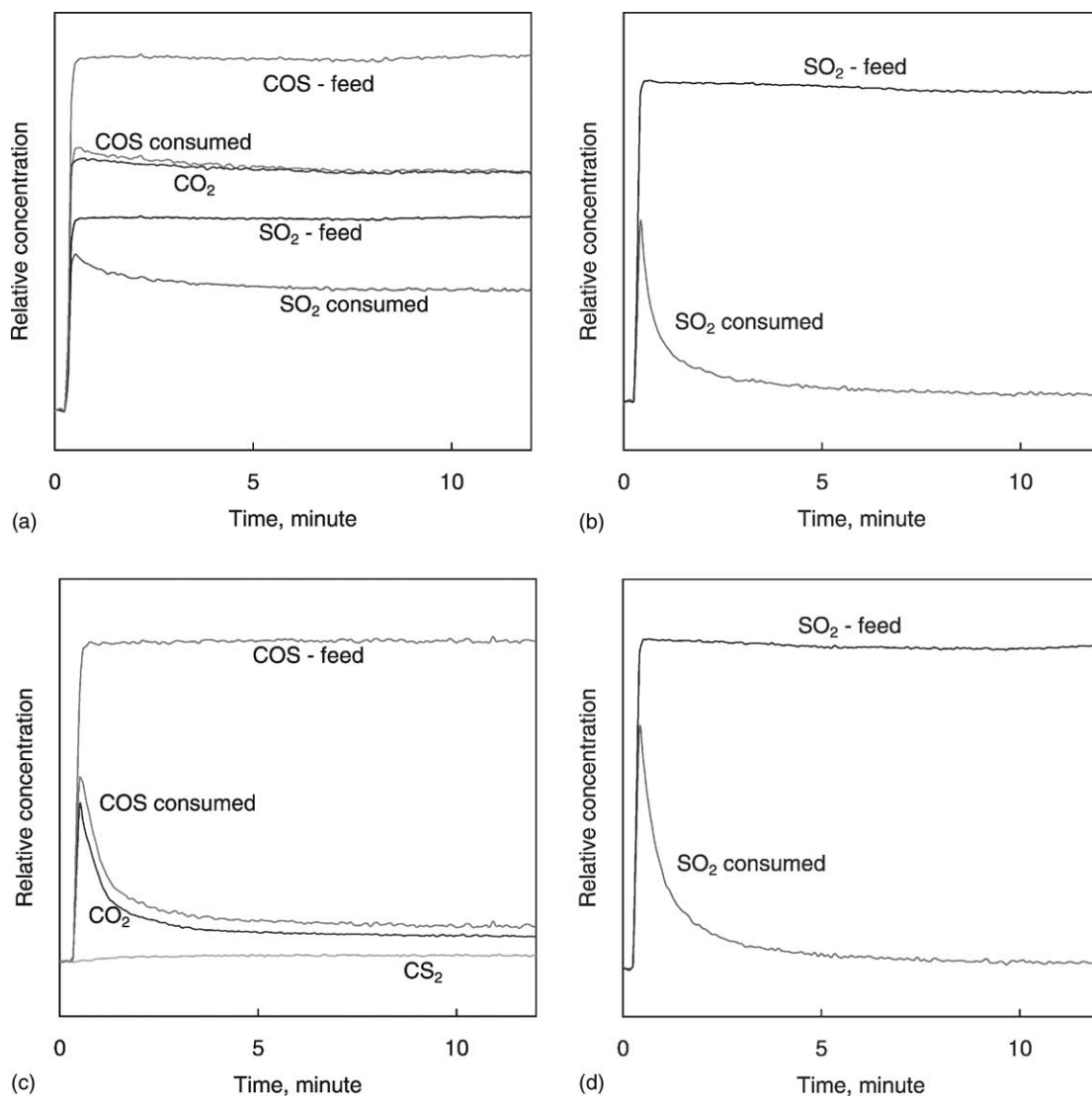


Fig. 6. Step change experiment at 400 °C: (a) COS + SO<sub>2</sub>, (b) SO<sub>2</sub>, (c) COS, (d) SO<sub>2</sub>, (e) COS + SO<sub>2</sub>, (f) COS, and (g) COS + SO<sub>2</sub>. The relative concentration curves were obtained by adjusting the raw MS intensity data for zero, the fragmentation effect and instrument sensitivity.

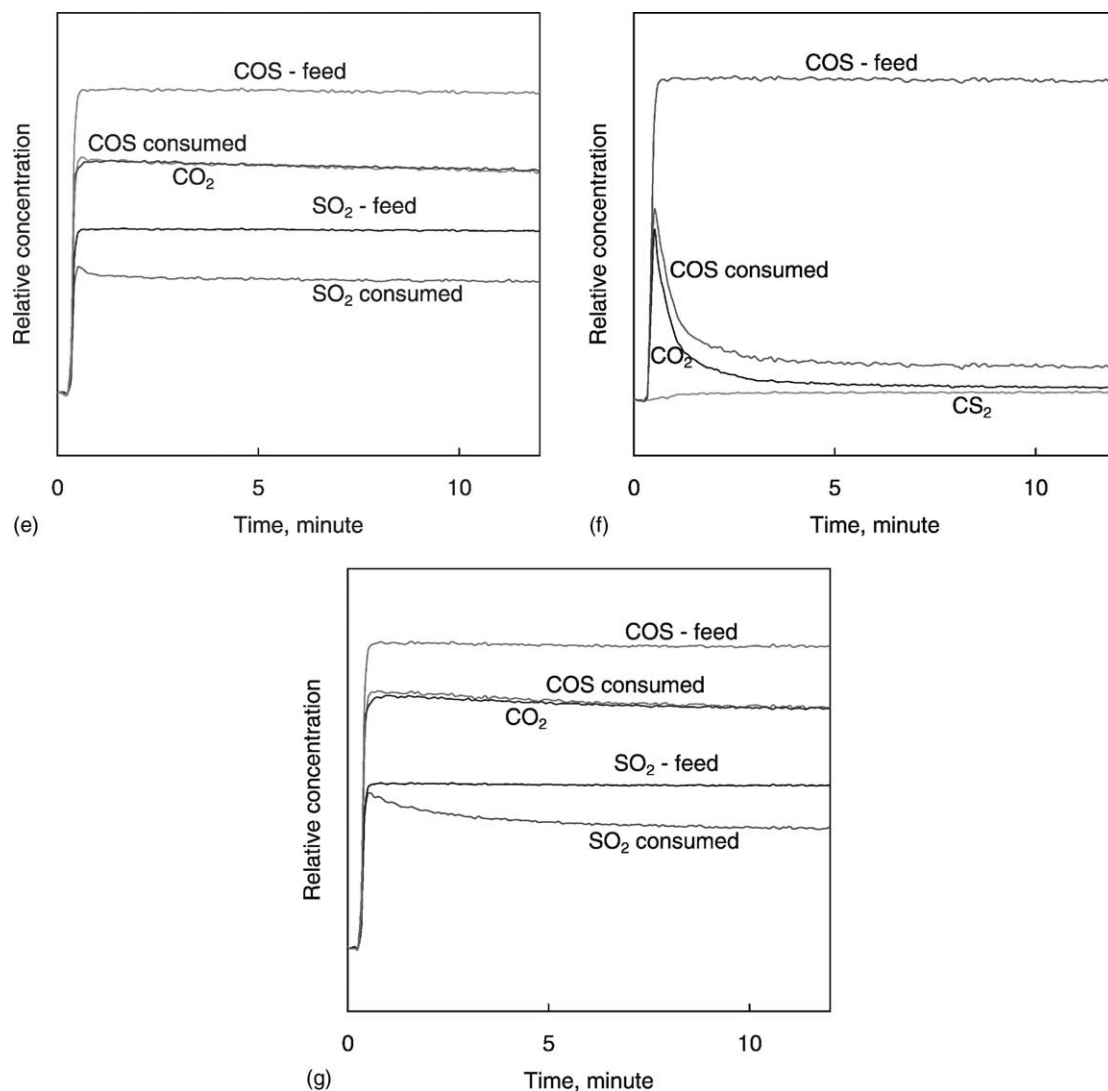


Fig. 6. (Continued).

In the COS (Stream 3) experiment, the amount of CO<sub>2</sub> produced at steady state was larger than CS<sub>2</sub>, suggesting that in addition to the disproportionation of COS, the oxysulfide catalyst was also reduced by COS. Furthermore, more COS was consumed than the total CO<sub>2</sub> and CS<sub>2</sub> produced. This indicates the presence of at least another reaction, i.e. the decomposition of COS. It is also possible that COS was adsorbed to the oxysulfide, probably at the adsorption sites opened up by COS reduction, even though the COS adspecies

may not be stable long enough to survive the feed change and the Ar purge.

#### 4. Conclusions

In summary, we can conclude that the redox mechanism route is not the main reaction path for the reduction of SO<sub>2</sub> by CO and COS over lanthanum oxysulfide. The reduction probably proceeds through a



surface reaction path involving both the SO<sub>2</sub> and COS adspecies. Undoubtedly SO<sub>2</sub> is readily and more favorably adsorbed on the lanthanum oxysulfide and adheres to the oxygen ions with the existence of other adsorption sites for SO<sub>2</sub>. Nonetheless, we can imagine that there are always pools of SO<sub>2</sub> molecules adsorbed on the oxysulfide when SO<sub>2</sub> is present in the feed gas.

On the other hand, COS is very reactive and may have access to certain active sites in the lanthanum oxysulfide, which are not available to other species such as CO. The reduction of the oxysulfide by COS possibly produces more adsorption sites for the reactants. Analogous to lanthanum oxide and other rare earth oxides [8,9], oxygen vacancies are expected to form in the oxysulfide, and the COS reduction to the oxysulfide is expected to promote this vacancy formation process through the scavenging of the loose oxygen species and possibly via other more direct routes. That is,



where \*O is a lattice oxide ion and \* is an anion vacancy.

But the COS adspecies is very unstable in the oxysulfide and tends to react immediately with the SO<sub>2</sub> coming into contact, to disproportionate to CS<sub>2</sub> and CO<sub>2</sub>, or to decompose to CO. Thus, the catalytic reduction of SO<sub>2</sub> by COS probably takes place when newly adsorbed COS comes into contact with pools of adsorbed SO<sub>2</sub> to react to form carbon dioxide and

sulfur. The reduction of SO<sub>2</sub> by CO follows the same route but with a step to form the COS intermediate. Although some of the present results suggest that the reduction reaction is associated with the anion vacancies, understanding how the reduction reaction is related to these vacancies and how the reactants are accommodated in these sites needs more research.

### Acknowledgements

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