The effect of H$_2$O on the reduction of SO$_2$ and NO by CO on La$_2$O$_2$S

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Abstract

The effect of H$_2$O on the catalytic reduction of SO$_2$ and NO on La$_2$O$_2$S was studied using temperature-programmed reaction coupled with fast mass spectrometry, powder X-ray diffraction and X-ray photoelectron spectroscopy. It is found that La$_2$O$_2$S can be completely and irreversibly deactivated in the presence of H$_2$O at 700°C when NO/SO$_2$ is sufficiently high (~1.0). This is caused by the formation of a layer of inactive and stable La$_2$O$_2$SO$_4$ on the oxysulfide. When NO is absent or NO/SO$_2$ is low (~0.4), H$_2$O inhibits the reduction and shifts the selectivity from sulfur to H$_2$S. While the causes of the deactivation can be attributed to the Reverse Claus Reaction between H$_2$O and sulfur in the oxysulfide, the competitive hydrolysis of the COS intermediate and the competitive adsorption of H$_2$O, the shift in selectivity to H$_2$S is attributable to the former two factors.

Keywords: lanthanum oxysulfide, deactivation, selectivity, hydrogen sulfide, hydrolysis

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Introduction

SO₂ and NO are often produced simultaneously in combustion processes. Although there are scrubbing and oxidation treatment processes to remove these acid gases from flue gas, these processes usually produce a huge amount of products that need proper disposal. Catalytic reduction that simultaneously transforms these oxides to their elemental forms is desirable because it is simple and concentrates the pollutants into much smaller packages. A number of catalysts, mainly composite and supported transition metals such as Cu/Al₂O₃ [1], Fe/Al₂O₃ [2], Fe/Cr₂O₃ [3], Co, Mo, CoMo and FeMo supported on Al₂O₃ [4], Co/TiO₂ [5], SnO₂-TiO₂ solid solution [6] and transition metal-La₂O₂S [7] have been studied for the reduction. In particular, lanthanum oxysulfide (La₂O₂S), the active ingredient of the transition metal-La₂O₂S catalysts that are produced from lanthanum perovskite oxides and effective for the reduction of SO₂ [8-9], is the only material known to be highly active for the reduction of SO₂ [10] and the simultaneous reduction of SO₂ and NO [7] on its own without the participation of another material.

On the other hand, H₂O, a common ingredient of flue gas, is known to inhibit the reduction of SO₂ by CO on La₂O₂S and the selectivity is shifted from sulfur to H₂S [10]. The causes of these changes were attributed to the Reverse Claus Reaction between the product sulfur and H₂O, the competitive hydrolysis of the COS intermediate and the water-gas shift reaction. However, the impact of common deactivation factors such as sintering, competitive adsorption of H₂O and change in catalyst composition has not been evaluated. Moreover, the effect of H₂O on the simultaneous reduction of NO and SO₂ on La₂O₂S has also not been studied. This information is important in the development of a viable catalyst for the simultaneous removal of these acid gases.
There are many studies in the literature on the effect of H$_2$O on La$_2$O$_3$, the precursor of La$_2$O$_2$S. La$_2$O$_3$ has a structure close to La$_2$O$_2$S with the sulfide ion replaced by an oxide ion. De Asha, et al. [11] and Paulidou and Nix [12] showed that H$_2$O is dissociatively adsorbed on La$_2$O$_3$ at room temperature. It is likely that La$_2$O$_2$S also adsorbs H$_2$O and the adsorption is dissociative. Toops, et al. [13-14] studied the deactivation of competitive H$_2$O adsorption on La$_2$O$_3$ in the reduction of NO and found that La$_2$O$_3$ was deactivated in the presence of SO$_2$ and La$_2$O$_2$SO$_4$ was formed on the oxide [13].

It has been shown that the reduction of SO$_2$ by CO on La$_2$O$_2$S follows the COS intermediate mechanism [10, 15-16], which can be represented by the following reaction steps:

\[
\begin{align*}
(1) & \quad \text{CO} + \text{S} \rightarrow \text{COS}, \\
(2) & \quad \text{SO}_2 + 2 \text{COS} \rightarrow 3 \text{S} + 2 \text{CO}_2,
\end{align*}
\]

where S is labile sulfur in the oxysulfide. It can be formed by the reduction of SO$_2$ or comes from the lattice when the oxysulfide is heated [15].

\[
(3) \quad *\text{S} \rightarrow \text{S} + *,
\]

where * is an anion vacancy. Reaction (2) is accomplished on La$_2$O$_2$S probably via the surface reaction between COS and pools of SO$_2$ adspecies [16]. Rare earth oxysulfides are highly catalytically active for the hydrolysis of COS to H$_2$S [17].

For the reduction of NO on La$_2$O$_2$S, it has been shown that the reduction probably starts with decomposition of NO to N and O at the anion vacancies [18]. The labile sulfur in the oxysulfide removes O as SO$_2$ to regenerate the vacancies while N desorbs as N$_2$. 
The SO₂ produced is then reduced by CO to sulfur once again on La₂O₂S and this reduction reaction maintains the population of sulfur in the oxysulfide.

It is clear that sulfur plays an essential role in both the reduction of SO₂ and NO. Any interaction between H₂O and the sulfur species would have enormous influences on the reduction reactions. Since the reduction of NO consumes sulfur while the reduction of SO₂ replenishes the oxysulfide with sulfur, the relative amount of NO to SO₂ is expected to be critical to these reduction reactions in the presence of H₂O.

We report here the effect of H₂O on the reduction of SO₂ and the simultaneous reduction of NO and SO₂ by CO on La₂O₂S and, in particular, the impact of H₂O on the surface sulfur species and the COS intermediate, and the influence of the NO/SO₂ ratio on the simultaneous reduction reaction. The changes in the bulk and surface composition of the catalyst due to these reduction reactions in the presence of H₂O are also reported.

Experimental

Catalyst preparation

La₂O₂S was synthesized in-situ in the quartz microreactor from La(OH)₃ powder (Yiaolong, China) using the sulfidization procedure reported by Ma, et al. [19] at 700°C for 3 h. The oxysulfide was then kept in flowing Ar inside the reactor before use. The composition of the synthesized samples was confirmed to be La₂O₂S using powder X-ray diffraction (XRD). The typical XRD diffractogram of these La₂O₂S samples is shown in Figure 1. The specific surface area of these samples was approximately 4 m² g⁻¹, which was comparable to the reported value [19].
TPR/MS

TPR/MS study was performed with the experimental setup shown in Figure 2. A humidifier was used to moisturize the Ar stream at room temperature. About 0.1 g La$_2$O$_2$S was synthesized in-situ in the microreactor. The feed gas at 100 ml min$^{-1}$ at room temperature (~25°C) was obtained by mixing the Ar stream and preblended reaction gases at the gas mixing flask before it was fed to the reactor. The composition of the effluent gas from the reactor was continuously monitored by the mass spectrometer MS250 (EXTREL), which reported the composition every second. The typical composition of the feed gases was:

(C1) 0.4%v SO$_2$ and 0.8%v CO
(C2) 0.16%v NO, 0.4%v SO$_2$, 0.96%v CO (NO/SO$_2$ = 0.4)
(C3) 0.4%v NO, 0.4%v SO$_2$, 0.96%v CO (NO/SO$_2$ = 1.0)
(C4) 0.4%v SO$_2$, 0.8%v CO and 2.9%v H$_2$O
(C5) 0.16%v NO, 0.4%v SO$_2$, 0.96%v CO and 2.9%v H$_2$O (NO/SO$_2$ = 0.4)
(C6) 0.4%v NO, 0.4%v SO$_2$, 0.96%v CO and 2.9%v H$_2$O (NO/SO$_2$ = 1.0)

The TPR temperature program started with purging the La$_2$O$_2$S sample with the feed gas at room temperature until the composition of the effluent gas became steady. Then the sample was heated from room temperature to 700°C at 10°C min$^{-1}$ and kept at 700°C for 2 h or until the composition of the effluent gas became steady again.

Catalyst composition

The changes in the bulk and surface composition of La$_2$O$_2$S due to the reduction reactions in the presence of H$_2$O were monitored with XRD and XPS (X-ray
photoelectron spectroscopy). The as-sulfidized La$_2$O$_2$S was used as the reference. The XRD analysis was performed with the Powder X-ray Diffraction System (Model PW1830, PHILIPS) operated at 2 kW using Cu-anode and graphite monochromator. The samples were spread and pressed onto glass sample holders with no pretreatments.

The XPS analysis was performed with Perkin Elmer Surface Science Analysis System (Model PHI 5600) using monochromatic Al K$_\alpha$ X-ray source according to the procedure described by Lau and Fang [15]. The powder samples were pressed into cup-shaped sample mounts for direct insertion into the instrument. Low energy flooding electrons were used to neutralize the charges built up on the samples and the binding energy (BE) scale was so adjusted to make the adventitious carbon peak at 284.5 eV. Multiplex scans of carbon C1s, nitrogen N1s, oxygen O1s, sulfur S2p and lanthanum La3d were acquired at constant pass energy of 23.5 eV.

Results

Change in catalyst composition

In general, XRD did not find any significant changes in the bulk composition of the catalyst samples after the reactions. The only exception is the sample used in the reduction of NO and SO$_2$ at high NO/SO$_2$ (1.0) in the presence of H$_2$O, a small but significant amount of La$_2$O$_2$SO$_4$ was found (Curve B, Figure 1). On the other hand, XPS revealed changes in the surface composition of the samples when H$_2$O was involved. The XPS O1s and S2p spectra of these samples are showed in Figure 3 alongside with the as-sulfidized La$_2$O$_2$S as reference. The XPS spectra of the as-sulfidized sample are close to those reported by Lau and Fang [15]. Typical C1s, O1s and S2p peaks are listed in Table
1 and the surface concentration of carbon, oxygen and sulfur species, in ratios to La, of the La$_2$O$_2$S samples are listed in Table 2. In general, the O1s spectrum consists two peaks – one at ~529 eV due to oxide and the other at higher BE attributable to the oxygen bonded to sulfur and carbon. The S2p also contains two modes – the sulfide peak, possibly including the adsorbed sulfur, at ~160 eV and a group of S-O (sulfur-oxygen species such as SO$_2$ adspecies, sulfite and sulfate) peaks at 166~169 eV. Lastly, no detectable amount of nitrogen was found in the surface of the catalysts used in the reduction of NO.

Among the various H$_2$O reactions, the hydrolysis of La$_2$O$_2$S most severely depleted the surface sulfur species in the oxysulfide. Reducing SO$_2$ in the presence of H$_2$O gave similar but smaller depletion of sulfur. When COS was present (hydrolysis of COS on La$_2$O$_2$S), a significantly higher concentration of these sulfur species was maintained in the surface possibly due to the constant supply of sulfur from COS. However, in all cases, the concentration of S-O, the sulfur species bonded to oxygen, significantly decreased. This suggests that S-O species such as SO$_2$ adspecies were being displaced by H$_2$O in competitive adsorption.

The reduction of NO at NO/SO$_2$ = 1.0 in the presence of H$_2$O significantly increased the surface concentration of oxygen and sulfur, in which S-O species almost completely dominated the surface sulfur content (see Figure 3b and Table 2). In particular, the sample had La3d$_{5/2}$ peaks at 833.7 eV and 838.0 eV, S2p at 168.6 eV, and O1s at 529.5 eV and 532.4 eV. These peaks are comparable to Aono, et al. [20], who reported La3d$_{5/2}$ at 834.01 eV, S2p at 168.77 eV, and O1s at 528.77 eV for lattice oxygen and 531.75 eV for S-O on lanthanum oxysulfate (La$_2$O$_2$SO$_4$) with the adventitious carbon set
at 284.5 eV. Thus, combining with the XPS and XRD results, it is certain that a layer of La$_2$O$_2$SO$_4$ was formed on the surface of the oxysulfide.

**TPR/MS**

*Deactivation and shift in selectivity*

In the presence of H$_2$O, La$_2$O$_2$S became completely and irreversibly deactivated at 700°C when NO/SO$_2$ was large (~1.0). No H$_2$S was found in the effluent gas. Removing H$_2$O from the feed did not reactivate the sample. When NO was absent or when NO/SO$_2$ was small (~0.4), La$_2$O$_2$S was partially deactivated. Table 3 shows clearly that the conversions of SO$_2$ and NO were lowered significantly in the reduction of SO$_2$ and simultaneous reduction of SO$_2$ and NO, when H$_2$O was present. Besides, the reduction in the conversion of SO$_2$ was more than that of NO.

Figures 4a and 5a are the temporal TPR/MS profiles for the reduction of SO$_2$ and simultaneous reduction of NO and SO$_2$ in the presence of H$_2$O. The respective thermal TPR/MS profiles for these reactions when H$_2$O was removed from the feed are in Figures 4b and 5b. The conversion $C$ is computed with the following equation:

$$ C = \frac{I_o - I}{I_o}, $$

where $I_o$ and $I$ are the intensities of the selected mass fragments of reactant species in the feed and effluent streams respectively. The major mass fragments of H$_2$O, CO, NO, H$_2$S, CO$_2$, COS and SO$_2$ are m/z = 18, 28, 30, 34, 44, 60 and 64 respectively. The formation of N$_2$ (same m/z as CO) from the reduction of NO can interfere with the measurement of CO and thus can apparently lower the conversion. This explains why the conversion of CO is significantly lower than both of NO and SO$_2$ in the reduction of NO and SO$_2$.
(Figure 5). On the other hand, the measurement of H₂O is not affected by the mass
fragments of other reaction species. More detailed discussions on this computation can be
found in our previous publication [18]. It can be seen that the reduction reactions started
sluggishly with higher ignition temperatures and the conversions of NO, SO₂ and CO
were lower than those in the absence of H₂O at the same temperature. In addition, as SO₂
was reduced by CO in the presence of H₂O, a significant amount of H₂S was produced.

*Hydrolysis of La₂O₂S*

Figure 6 shows the thermal TPR/MS profile of the hydrolysis of La₂O₂S. At
>320°C, both H₂S and SO₂ were produced and their profiles were close. The
concentration of the sulfur not bonded to oxygen (S\text{ONLY}/La) in the surface decreased
significantly after hydrolysis (see Table 2). These results suggest the occurrence of the
Reverse Claus Reaction between H₂O and sulfur in the oxysulfide.

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

The H₂S and SO₂ profiles are comparable to the COS formation profile on La₂O₂S
reported by Lau and Fang [15]. The SO₂ and H₂S peaks at ~380°C are due to the reaction
between H₂O and labile sulfur in the surface of La₂O₂S. The formation of SO₂ and H₂S at
higher temperatures are attributed to the reaction between H₂O and lattice sulfur in the
surface of the oxysulfide.

Even though SO₂ was produced in the hydrolysis, the concentration of the surface
S-O (S-O/La) decreased (see Table 2). This suggests that H₂O hindered the adsorption of
SO₂ on La₂O₂S but promoted desorption. The surface oxygen content increased with an
increase in the relative intensity of the O1s peak at ~528.9 eV, indicating that the
concentration of the oxygen that was not bonded to sulfur and carbon such as lattice oxide and the adsorbed oxygen increased. As the sulfide ions in the surface lattice were removed by the hydrolysis, the surface of the oxysulfide was probably ‘oxidized’ to the oxide as the lattice sulfide was replaced by the oxide or hydroxide ions. This is supported by the TPR/MS result in Figure 4b. When CO and SO\textsubscript{2} in stoichiometric ratio (CO/SO\textsubscript{2} = 2) started to react on La\textsubscript{2}O\textsubscript{2}S, more CO than SO\textsubscript{2} stoichiometrically was consumed to remove and convert the oxide/hydroxide to oxysulfide. Additional CO was needed to remove oxygen from the La\textsubscript{2}O\textsubscript{3} lattice in the following transformation:

(6) \[ \text{La}_2\text{O}_3 + 3 \text{CO} + \text{SO}_2 \rightarrow \text{La}_2\text{O}_2\text{S} + 3 \text{CO}_2. \]

*Hydrolysis of COS*

La\textsubscript{2}O\textsubscript{2}S readily catalyzes the hydrolysis of COS to H\textsubscript{2}S (Reaction (7)) with the concomitant formation of CO\textsubscript{2} (see Figure 7). Almost complete conversion of COS was attained at 310°C. This is comparable to that reported by Zhang, et al. [17] on rare earth oxysulfides.

(7) \[ \text{COS} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{S} + \text{CO}_2. \]

The drop in conversion at >310°C can be attributed partly to catalyst sulfation [21], which is a common cause of deactivation for COS hydrolysis catalysts, and partly to the increasing decomposition of COS to CO at higher temperatures.

(8) \[ \text{COS} \rightarrow \text{CO} + \text{S}. \]

*Discussions*

*Causes of deactivation*
Case of the completely deactivated La$_2$O$_2$S

The complete and irreversible deactivation of La$_2$O$_2$S in the reduction of NO by CO at NO/SO$_2$ = 1.0 in the presence of H$_2$O can be attributed to the formation of a La$_2$O$_2$SO$_4$ layer on the surface. La$_2$O$_2$SO$_4$ is inactive for the reduction of NO and SO$_2$ by CO and is stable at typical reduction reaction conditions. This oxysulfate is known to decompose in air to oxide at temperatures $>1000^\circ$C [22]. Removing H$_2$O from feed does not reactivate the catalyst at typical reaction conditions. Toops, et al. [13] reported that the formation of La$_2$O$_2$SO$_4$ was a cause of deactivation for La$_2$O$_3$ in the reduction of NO in the presence of SO$_2$.

Case of the partially deactivated La$_2$O$_2$S

The Reverse Claus Reaction (Reaction (5)) not only competes for labile sulfur with the reduction of SO$_2$ and NO, hinders the formation of the intermediate COS, inhibits the removal of the oxygen left from the decomposition of NO, but also oxidizes the sulfur in the oxysulfide back to SO$_2$, a detriment for the catalytic reduction. All these contribute to the loss of catalyst activity. Furthermore, the ability that H$_2$O oxidizes sulfur in the oxysulfide to SO$_2$ further promotes the formation of sulfur oxides such as SO$_2$ and sulfate, which are already favorably formed by the reactions with NO on La$_2$O$_2$S. In excess NO (NO/SO$_2$ = 1.0) atmosphere, the combined effect of NO and H$_2$O can be responsible for the formation of La$_2$O$_2$SO$_4$, which in turn completely deactivates the catalyst. In addition, H$_2$O can also react with the sulfur in the surface lattice, converting the surface of the oxysulfide to oxide/hydroxide.
In the presence of H₂O, COS is readily hydrolyzed to H₂S. COS is the reaction intermediate for the reduction of SO₂ on La₂O₂S. Although H₂S reacts with SO₂ through the Claus Reaction,

\(2 \text{ H}_2\text{S} + \text{SO}_2 \rightarrow 3 \text{ S} + 2 \text{ H}_2\text{O},\)

this reaction is not so effective to convert SO₂ to sulfur as that between COS and SO₂ (Reaction (2)) at the SO₂ reduction temperature because the Claus Reaction is not favored at such high temperature [21]. The activity of La₂O₂S for the reduction of SO₂ is impaired. At the same time, COS is also an effective reducing agent for converting NO to N₂ on La₂O₂S [7]. The hydrolysis reaction reduces the concentration of COS that is available for the reduction of NO.

As the La₂O₂S catalysts were heated in the moisturized SO₂ reduction stream (Feed C4) and SO₂ and NO reduction stream (Feed C5), negative consumption of H₂O was found when SO₂ (Figure 4a), and NO and SO₂ (Figure 5a) started to be reduced. This suggests that a significant amount of H₂O could be desorbed from the La₂O₂S when the catalyst was heated to the reaction temperature. This also shows that the adsorption of H₂O is significant even in the presence of NO and SO₂. Since H₂O promotes the desorption of SO₂, it inhibits the reduction of SO₂ through competitive adsorption and interferes with the supply of sulfur needed for the NO reduction. Furthermore, the adsorption of H₂O on La₂O₂S possibly involves anion vacancies, which are responsible for the reduction of NO [18], and competes with the reduction for vacancies.

Sintering is a common cause of deactivation for catalysts, but it can be ruled out as a significant cause in this case due to the following reasons. First, sintering is a high temperature process. It is usually slow and occurs in materials with high specific surface
area. Second, the melting point of La$_2$O$_2$S is 1,940°C [23], much higher than the catalyst manufacturing and operation temperature of 700°C and the specific surface area of our samples is only 4 m$^2$ g$^{-1}$. Third, the reaction time for the TPR run at slightly more than 3 h is short.

Shift in selectivity

The shift in selectivity from sulfur to H$_2$S is attributable to, first, the Reverse Claus Reaction between H$_2$O and sulfur in La$_2$O$_2$S and, second, the competitive hydrolysis of COS. Both reactions effectively convert sulfur and COS to H$_2$S while at 700°C, the Claus Reaction becomes ineffective in removing H$_2$S, resulting in a substantial amount of H$_2$S left in the effluent. Hence, the reaction between H$_2$S and NO on La$_2$O$_2$S can play a significant role in the NO reduction reaction when H$_2$O is present. Further investigation on this H$_2$S reaction is warranted.

Conclusions

In this study, the effect of H$_2$O on the catalytic reduction of SO$_2$ and NO on La$_2$O$_2$S has been investigated using TPR/MS, XRD and XPS. It is found that La$_2$O$_2$S can be completely and irreversibly deactivated at 700°C in the presence of H$_2$O when NO/SO$_2$ is sufficiently high (~1.0). The cause of the deactivation is attributable to the formation of a layer of inactive and stable La$_2$O$_2$SO$_4$ on the oxysulfide. When NO is absent or NO/SO$_2$ is low (~0.4), H$_2$O inhibits the reduction reactions on La$_2$O$_2$S and shifts the selectivity from sulfur to H$_2$S. The deactivation can be attributed to the Reverse Claus Reaction between H$_2$O and sulfur in the oxysulfide, the competitive hydrolysis of
the COS intermediate and the competitive adsorption of H₂O. The shift in selectivity to H₂S is caused by the Reverse Claus Reaction and hydrolysis of the COS intermediate. It is critical to keep NO/SO₂ sufficiently low in order to avoid the complete and irreversible deactivation of La₂O₂S in the presence of H₂O.

Acknowledgements

This work was supported by the Research Grant Council of the Hong Kong Special Administration Region, China (Project No. HKUST6001/01P).

References

Figures

Figure 1. XRD diffractogram – (A) La$_2$O$_2$S as synthesized and (B) formation of La$_2$O$_2$SO$_4$ after the reduction of NO and SO$_2$ at NO/SO$_2$ = 1 in the presence of H$_2$O.

Figure 2. Flow schematic of the experimental setup.

Figure 3. XPS spectra (a) O1s and (b) S2p of La$_2$O$_2$S for SO$_2$ reduction – effect of H$_2$O. Curves from bottom to top: (A) as-sulfidized, (B) as-hydrolyzed, (C) after COS + H$_2$O reaction, (D) after SO$_2$ + CO + H$_2$O reaction and (E) NO + SO$_2$ + CO + H$_2$O reaction. All spectra are normalized to the same intensity span.

Figure 4. Reduction of SO$_2$ by CO on La$_2$O$_2$S in the (a) presence and (b) absence of H$_2$O. (a) is plotted on time scale while (b) on temperature scale. (b) shows the reduction of SO$_2$ on La$_2$O$_2$S which has been hydrolyzed in the last TPR run. $C_{\text{H}_2\text{O}}$, $C_{\text{CO}}$ and $C_{\text{SO}_2}$ are conversion curves of H$_2$O, CO and SO$_2$ based on the intensity m/z=18, 28 and 64 respectively (left Y-axis). The remaining curves are the mass intensities for H$_2$S (m/z=34) and CO$_2$ (m/z=44) (right Y-axis). The dashed line in (a) marks the beginning of the 700°C soaking step. The H$_2$S intensity is scaled up by 5 and $C_{\text{H}_2\text{O}}$ by 2.

Figure 5. Reduction of NO and SO$_2$ by CO on La$_2$O$_2$S at NO/SO$_2$ = 0.4 in the (a) presence and (b) absence of H$_2$O. (a) is plotted on time scale while (b) is
plotted on temperature scale. $C_{\text{H}_2\text{O}}$, $C_{\text{NO}}$ and $C_{\text{SO}_2}$ traces are the conversion of $\text{H}_2\text{O}$, $\text{NO}$ and $\text{SO}_2$, and based on the intensity $m/z=18$, 30 and 64 respectively. $C_{\text{CO}}$ ($m/z=28$) is the sum of the consumption of $\text{CO}$ and formation of $\text{N}_2$. The $\text{CO}_2$ ($m/z=44$) intensity curve traces the sum of the formation of $\text{CO}_2$ and $\text{N}_2\text{O}$. Left Y-axis is conversion and right Y-axis is the intensity. The dashed line in (a) marks the beginning of the 700°C soaking step. The $\text{H}_2\text{S}$ ($m/z=34$) intensity is scaled up by 10 and $C_{\text{H}_2\text{O}}$ by 2.

Figure 6. Hydrolysis of La$_2$O$_2$S.

Figure 7. Hydrolysis of COS on La$_2$O$_2$S. $C_{\text{COS}}$ is the conversion curve of COS based on the intensity $m/z=60$ (left Y-axis). The remaining curves are the mass intensities for $\text{CO}$ ($m/z=28$), $\text{H}_2\text{S}$ ($m/z=34$) and $\text{CO}_2$ ($m/z=44$) (right Y-axis). The CO intensity is scaled up by 5.