La$_2$O$_2$S Catalyst for Catalytic Reduction of SO$_2$ with CO in the Presence of O$_2$

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Catalytic reduction of SO$_2$ to sulphur by CO was investigated over La$_2$O$_2$S catalyst. It exhibited outstanding activity in the oxygen-free atmosphere and was inactivated in the presence of oxygen. The life decreased as the oxygen concentration increased, but increased as the reaction temperature increased. The increasing reaction temperature could prolong the life in a certain degree. The catalyst was characterized by XRD, TEM, XPS and BET, the phase structure of La$_2$O$_2$S is very stable; S^{2-} species on the catalyst surface is an active species for SO$_2$ reduction. The inactivation of La$_2$O$_2$S is probably caused by the sulfation of catalyst surface, not by the phase structure changes.

Key Words: Catalytic reduction, Sulphur dioxide, Carbon monoxide, TPR.

INTRODUCTION

SO$_2$ is one of the major components of acid rain and other forms of atmospheric pollution. Recent environmental concern enforces tighter regulations for the emission of SO$_2$, the treatment of SO$_2$ has become a significant problem, various commercial processes for flue gas desulphurization (FGD) have been developed[1]. Currently operating desulphurization, based on the SO$_2$ scribing with lime or limestone, is a costly process requiring large spaces, complicated facilities and disposal of the used sorbents. It is necessary to develop a way with low cost, light equipment, high efficiency method to solve the SO$_2$ pollution problem, the best choice probably is direct catalytic reduction of SO$_2$ to elemental sulphur, which is easier to treat, handle and transport[2,3]. The catalytic reduction of SO$_2$ by CO has received much attention, because this dry desulphurization method conveniently uses one of the exhaust constituents as reducing agent, yields a product of commercial value in the form of almost pure sulphur and generates no secondary pollution[4]. The researchers have developed several types of catalysts including Al$_2$O$_3$-supported transition metals[5], mixed oxides[6,7], metal sulfides[8,9] and perovskite type oxides, using CO as reducing agent. All these catalysts show excellent performance in the absence of oxygen conditions. However, the flue gas contains a certain amount of oxygen, it is essential to consider the influence of oxygen. There were seldom reports about this point, Ma *et al.*[10] had point out that oxygen mainly play a competitive role in the desulphurization process, it only consumed a certain amount reducing agent. Our recent work indicates that oxygen is a poisonous chemical for the desulphurization reaction; most catalyst, such as transition metals, mixed oxides and perovskite type oxides, could be easily oxidized to sulfate by oxygen and led to complete loss of catalytic activity.

In this work, we synthesized a highly stable catalyst La$_2$O$_2$S and used it as the catalyst for the reduction of SO$_2$. Activity tests were carried out to reveal the effect of oxygen, the catalyst properties were determined by X-ray diffraction (XRD), X-ray photoelectron spectra (XPS), SEM, BET.

EXPERIMENTAL

Catalyst preparation: The La$_2$O$_2$S sample was prepared from La$_2$O$_3$ powder (Tianjin Guangfu Fine Chemical Research Institute, China). The fresh La$_2$O$_3$ powder was calcined in air at 700 ℃ for 4 h to remove the impurities from the material and then exposed the samples to air saturated in water vapour for one week to transform the oxide to La(OH)$_3$, the hydrated lanthanum oxide was sulphidized in a gas mixture composed of 1 % mol SO$_2$ and 2 % mol CO in nitrogen at 600 ℃ for 2 h, the XRD analysis revealed that the La$_2$O$_3$ was transformed to La$_2$O$_2$S.

Catalyst characterization: The crystal structures of the catalysts were determined by a powder X-ray diffractometer (D/MAX-2038), using CuK$_\alpha$ (λ = 0.1542 nm) radiation combined with Nickel filter operating at 30 kV and 30 mA. The diffractometer data were recorded for 2θ values between 20 and 90º at a scanning rate of 4º (2θ)/min^{-1}. The patterns were compared with JCPDS reference data for phase identification[11].

The XPS spectra were obtained at room temperature with a PHI-1600 ESCA spectrometer using MgK$_\alpha$ radiation and the background pressure in the analysis chamber was kept below 1×10^{-7} Pa during data acquisition. The binding energy was calibrated with respect to the C1s peak (284.6 eV) of a contaminant carbon.

The BET specific surface area of catalysts was measured by N$_2$ desorption at liquid-nitrogen temperature, using a surface area analyzer (QUDRASORB SI), the particle sizes were measured with scanning electron microscopy (SEM PHILIPS XL-30).

Catalytic activity measurement: The catalytic activities of the prepared samples were evaluated with a packed-bed reactor, an amount of 0.25 g catalyst powder (100-150 mesh) was put into the reactor, reactant gases contain 3 vol. % CO/ 1 vol. % O$_2$/1 vol. % SO$_2$, 5 vol. % CO/ 2 vol. % O$_2$/1 vol. % SO$_2$, 7 vol. % CO/3 vol. % O$_2$/1vol. % SO$_2$, each feed was balanced with N$_2$. Comparison experiment (without O$_2$) was also carried out to investigate the influence of O$_2$ to the title reaction. The outlet gas was analyzed *via* two on-line gas chromatographs (BeiFen SP3420), equipped with thermal conductivity detector (TCD) and two stainless steel columns in series, respectively. The first column was packed with GDX301 for separating N$_2$, CO$_2$, COS and SO$_2$. Another was packed with TDX01 for N$_2$, O$_2$ and CO.

From the activity measurements, the following parameters were derived in order to evaluate the catalytic performance; the per cent conversion of SO$_2$ (X), the selectivity (Ys) and per cent yield of elemental sulphur (Y). X could be calculated by ([SO$_2$]$_{in}$-[SO$_2$]$_{out}$)/[SO$_2$]$_{in}$, where [SO$_2$]$_{in}$ and [SO$_2$]$_{out}$ were concentrations of SO$_2$ in the inlet gas and effluent gas. Ys = ([SO$_2$]$_{in}$-[SO$_2$]$_{out}$-[COS]$_{out}$)/([SO$_2$]$_{in}$-[SO$_2$]$_{out}$), Y = X × Ys.

RESULTS AND DISCUSSION

Activities in the absence of oxygen: Fig. 1 shows the results of SO$_2$-CO reaction over La$_2$O$_2$S catalyst. In this activity test process, a gas mixture with molar ratio of CO/SO$_2$ (2:1, CO 2 %, SO$_2$ 1 %) was fed into the reactor, the weight-hourly-space velocity was fixed at 24000 mL/g-cat/h. It can be seen that La$_2$O$_2$S shows quite high catalytic performance in the absence of oxygen. The conversion rate of SO$_2$ is up to 90 % at 450 ℃, a stoichiometrically complete conversion of SO$_2$ and CO toward to S and CO$_2$ seems to be achieved at 500 ℃, a higher SO$_2$ conversion rate is associated with a higher yield of elemental sulphur, the catalyst could maintain its high activity after a long operation at 500 ℃.

Effect of the inlet O$_2$ concentration on SO$_2$ reduction: Knowing that flue gas containing a certain amount of oxygen, the oxygen concentration may affect the efficiency of SO$_2$ reduction, it is essentially to investigate the effect of oxygen to the desulphurization process. Four different feed concentrations (2 % CO/1 % SO$_2$, 3 % CO/1 % O$_2$/1 % SO$_2$, 5 % CO/ 2 % O$_2$/1 % SO$_2$, 7 % CO/3 % O$_2$/1 % SO$_2$) were tested to assess their influence. Experimental results shown in Fig. 2 reveal that when the reactant gas containing a certain amount of O$_2$, the catalyst is easily to lose its catalytic activity. The life of La$_2$O$_2$S decreased as the oxygen concentration increased. Meanwhile, the catalyst will maintain high activity when the
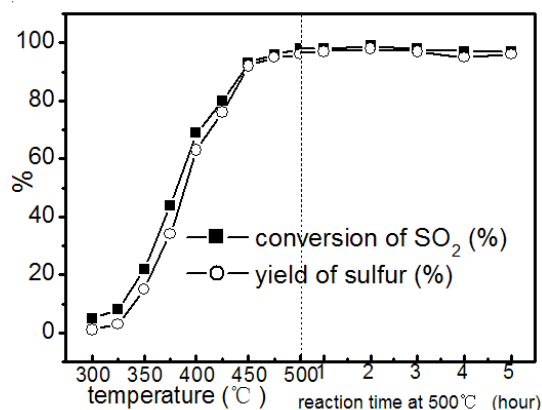

Fig. 1. Activities of La$_2$O$_2$S in SO$_2$-CO reaction, feed gas: 2 % CO, 1 % SO$_2$. WHSV = 24000 mL/g-cat/h
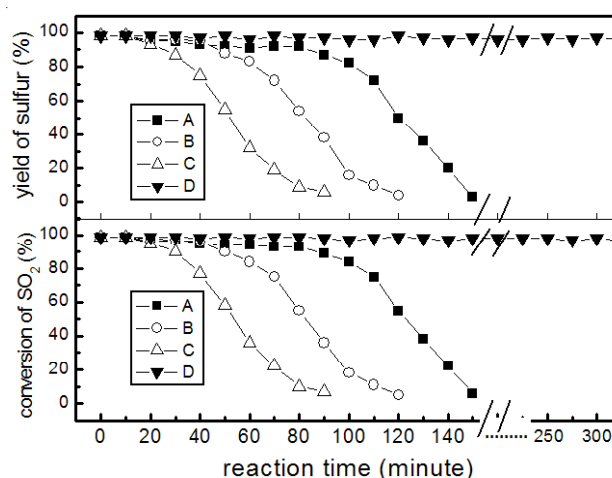

Fig. 2. Effect of the inlet O$_2$ concentrations on desulphurization process (A: 3 % CO/1 % O$_2$/1 % SO$_2$, B: 5 % CO/2 % O$_2$/1 % SO$_2$, C: 7 % CO/3 % O$_2$/1 % SO$_2$, D: 2 % CO/1 % SO$_2$), reaction temperature 500 ℃, WHSV = 24000 mL/g-cat/h

reactant gas doesn't contain oxygen and there is no sign of inactivation after 300 min test.

Effect of temperature on SO$_2$ reduction: To obtain the effect of reaction temperature, three different reaction conditions (500, 550 and 600 ℃) were performed to assess their influence. Fig. 3 shows the relation between reaction time and conversion of SO$_2$ over La$_2$O$_2$S, the life of La$_2$O$_2$S increased as the reaction temperature increased. The activity life is only 2 h when the reaction performed at 500 ℃, the life increased to 250 min as the reaction temperature increased to 600 ℃, it indicates that increasing the reaction temperature could prolong the service life of the catalyst. Similar results, showing a higher reaction temperature could prevent desulphurization catalyst poisoning, were observed in the studies of Ma *et al.*[10].

Characterization of La$_2$O$_2$S by XRD, TEM and BET surface area: Three kinds of La$_2$O$_2$S XRD patterns are shown in Fig. 4: the fresh La$_2$O$_2$S species, the deactivated La$_2$O$_2$S species and the regenerated La$_2$O$_2$S species. The deactivated La$_2$O$_2$S catalyst could be regenerated by the presulfidization method. Briefly, the deactivated catalyst was heated in a mixture gases (8 % CO, 4 % SO$_2$, 88 % N$_2$) from room temperature to 600 ℃ at 10 ℃/min and then maintained at 600 ℃ for 3 h, the flow rate is 50 mL/min and then cooled down to room
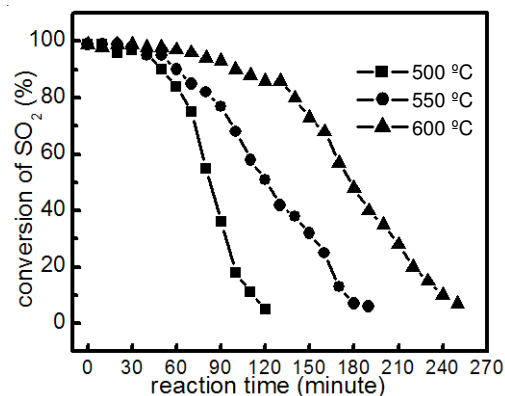
Fig. 3. Effect of different temperature on desulphurization process, 5 % CO/ 2 % O_2/1 % SO_2, WHSV = 24000 mL/g-cat/h
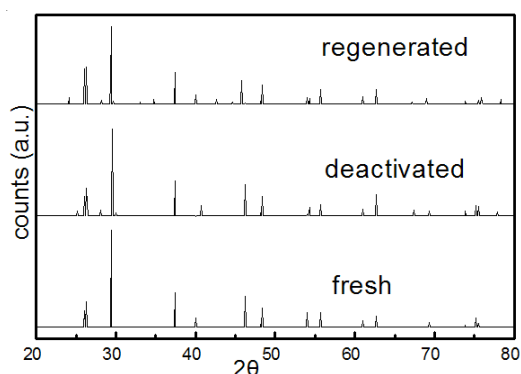

Fig. 4. XRD patterns of different La_2O_2S species

TABLE-1
CHARACTERIZATION OF La_2O_2S CATALYST

Catalyst	Specific surface area (m^2/g)	XRD phase structure
Fresh La_2O_2S	12.3	La_2O_2S
Deactivated La_2O_2S	11.6	La_2O_2S
Regenerated La_2O_2S	11.2	La_2O_2S
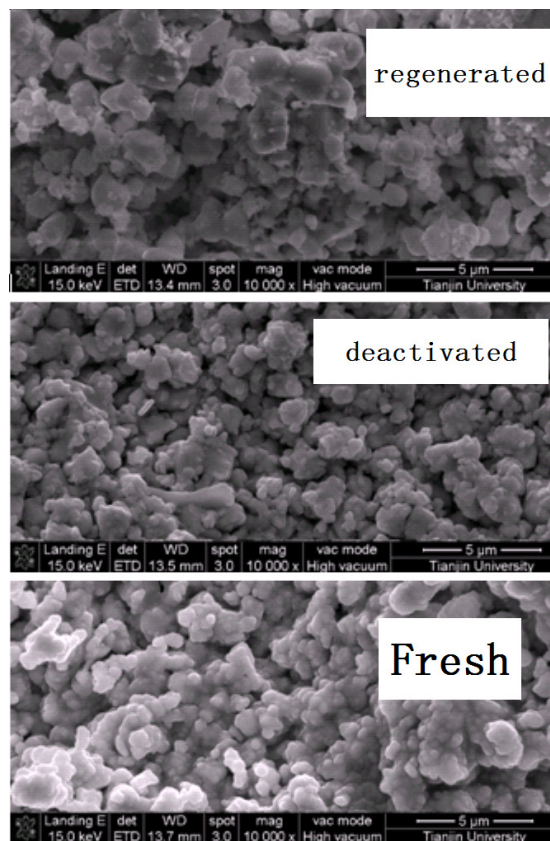
Fig. 5. SEM patterns of different La_2O_2S species

temperature, the catalytic activity could be recovered in a certain degree. According to the JCPDS reference data, the mainly sharp peaks of La_2O_2S structure should be at 2θ = 26.3, 29.4, 46, 48.4, 62.6 and 71.2°. Comparing with these characters on Fig. 4, these three samples have the same XRD patterns; they all show the La_2O_2S structure, no other phases can be found within the XRD allowable error. Fig. 5 reveals that the different La_2O_2S particle size measured with SEM is very similar with each other. Table-1 also shows the BET surface areas and the XRD phase structure of these three kinds of La_2O_2S catalyst. For the fresh La_2O_2S catalyst, the deactivated La_2O_2S catalyst and the regenerated La_2O_2S catalyst, their specific surface area and crystallize size are very similar and also show the same phase structure. It seems that the structure of La_2O_2S is very stable. The catalyst deactivation may be not caused by the structure changes, it possibly due to that the surface active site consumed or inhibited by the oxygen. Therefore, it is necessary to analysis the surface composition of the catalyst.

XPS results: The bending energies of O1s, S2p core levels of these three kind La_2O_2S samples are summarized in Table-2, the O1s profile is shown in Fig. 6. There are three components observed from the fitting. These peaks are located at: (a) ca.

528.5 eV; (b) ca. 531.5 eV; (c) ca. 532.5 eV. The peak at the lower BE (a) can be associated to lattice oxygen. Types (b) and (c) are attributed to adsorbed and SO_4^{2-} oxygen species, separately. It can be observed that there is only a little amount of sulphate oxygen species on fresh La_2O_2S catalyst (5 %), however, its content increased to 83 % after deactivation. It seems that the sulfation of surface may be the possible reason for catalyst deactivation.

From Fig. 7, there exist two kinds of sulphur species on the surface of La_2O_2S catalysts: ca. 162 eV S^{2-}; ca. 169 eV SO_4^{2-}. For the fresh La_2O_2S sample, it shows good catalytic performance, its S^{2-} content is 63 %; after deactivation, the catalyst lose its catalytic activity, meanwhile, the S^{2-} content decreased to 5 %; after the regenerate process, catalytic activity recovery was achieved in a certain degree, meanwhile, the S^{2-}

TABLE-2
BONDING ENERGIES OF O1s, S2p CORE LEVELS OF La_2O_2S CATALYSTS
(FIGURES IN PARENTHESIS INDICATE INTENSITY PERCENTAGE OF ELEMENTS)

Catalyst	O1s			S2p	
	Lattice	Adsorbed	SO_4^{2-}	S^{2-}	SO_4^{2-}
Fresh La_2O_2S	528.5 (21)	531.3 (74)	532.9 (5)	162 (63)	169 (37)
Deactivated La_2O_2S	528.4 (17)		532.7 (83)	162.2 (5)	169.1 (95)
Regenerated La_2O_2S	528.7 (15)	531.5 (13)	532.7 (72)	162.2 (32)	169.2 (68)
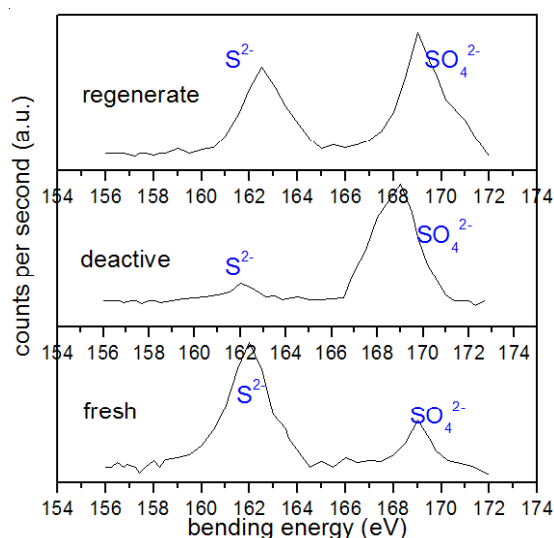
Fig. 6. O1s XPS spectra of La$_2$O$_2$S catalysts
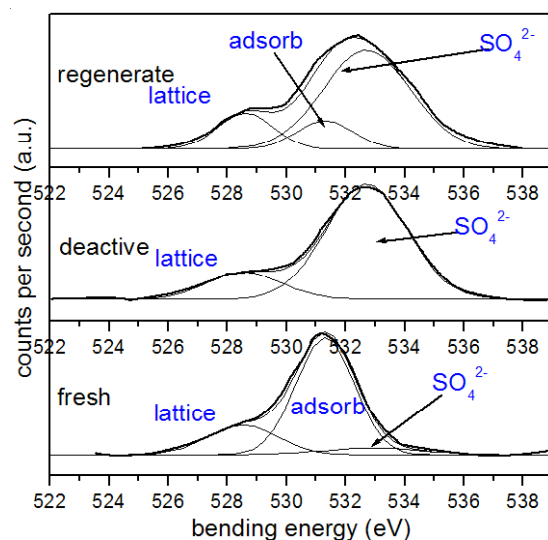
Fig. 7. S2p XPS spectra of La$_2$O$_2$S catalysts

species content also has an improvement. It seems that the catalytic activity was closely related to S^{2-} species content.

Since XRD analysis revealed that the phase structure of La$_2$O$_2$S after reaction did not change, we suppose that the overall reaction follows the COS intermediate mechanism by the following equations:

$$CO + MS \rightarrow COS + M - []$$

$$2COS + SO_2 \rightarrow 2CO_2 + 3S_2$$

$$M - [] + S \rightarrow MS$$
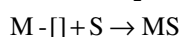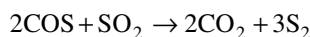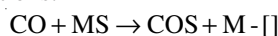
where [] is the lattice sulphur vacancy. According to the investigation by Ma *et al.*[12], the adsorbed CO species would react with La$_2$O$_2$S to produce COS, La$_2$O$_2$S is functional in the reduction of SO$_2$ by COS to element sulphur. The consumed lattice sulphur could be replenished by element sulphur formed by the reduction between SO$_2$ and COS. Therefore, the structure of La$_2$O$_2$S remains stable throughout.

The La$_2$O$_2$S catalyst shows high activity as long as lattice sulphur exists and would lose its activity in the presence of oxygen. From Fig. 2, the life decreased as the oxygen concen-

tration increased, oxygen is very harmful for the SO$_2$ reduction. This probably due to two factors: first, oxygen could be adsorbed to the sulphur vacancy, get activation at high temperature and then react with CO to produce CO$_2$, this decrease the chance for CO react with lattice sulphur to produce the intermediate COS species, result in the inhibition of SO$_2$ reduction. Second, the surface active sulphur species could be oxidized by the adsorbed oxygen, result in the sulfation of catalyst surface and lead to a complete inactivation. From Fig. 3, the life increased as the reaction temperature increased, that is to say the higher temperature could improve the catalytic performance and life of the catalyst, we speculate that increasing the reaction temperature could promote combustion reaction for CO and O$_2$ in the gas phase, decrease the adsorption amount of oxygen on the catalyst surface and depressing the influence of adsorbed oxygen. On the other hand, under the effect of high temperature and reducing agent CO, the poisoned catalyst could get activation in a certain degree. Therefore, higher temperature is beneficial for the SO$_2$ reduction in the presence of oxygen.

Conclusion

This work examines the catalytic reduction of SO$_2$ with CO over La$_2$O$_2$S catalyst in the presence of oxygen, the influence of oxygen concentrations, reaction temperature and reaction time and also analyses the inactivation mechanism. On the basis of the results presented herein, it is concluded the followings: La$_2$O$_2$S is proved to be effective catalyst for SO$_2$ reduction in the oxygen-free atmosphere, it is easier to lose activity in the presence of oxygen; the life decreased as the oxygen concentration increased, the life increased as the reaction temperature increased, increasing reaction temperature could only prolong the life in a certain degree, but can not prevent inactivation. The phase structure of La$_2$O$_2$S is very stable, it also keep the original phase by XRD patterns after deactivation, through the XPS results, S^{2-} species on the catalyst surface is an active species for SO$_2$ reduction, the sulfation of surface may be the possible reason for catalyst deactivation, retard the oxidation of La$_2$O$_2$S is very important for SO$_2$ reduction in the presence of oxygen, further investigation should focus on this aspect.

REFERENCES

1. S.S. Su, B.G. Li, S.Y. Cui and S. Tao, *Environ. Sci. Technol.*, **45**, 8403 (2011).
2. M. Magnusson, E. Fredell and H. Ingelsten, *Appl. Catal. B,* **111-112**, 20 (2012).
3. Y. Mok and H. Lee, *Fuel Process. Technol.*, **87**, 591 (2006).
4. G. Han, N. Park, S. Yoon and T. Lee, *Chemosphere*, **72**, 1744 (2008).
5. C. Chen, C. Wang and H. Weng, *Chemosphere*, **56**, 425 (2004).
6. C. Chen and H. Weng, *Appl. Catal. B*, **55**, 115 (2005).
7. C.-H. Wang, S.-S. Lin, W.-U. Hwang and H.-S. Weng, *Ind. Eng. Chem. Res.*, **41**, 666 (2002).
8. S. Zhuang, H. Magara and M. Yamazaki, *Appl. Catal. B*, **24**, 89 (2000).
9. S. Zhuang, M. Yamazaki, K. Omata, Y Takahashi and M Yamada, *Appl. Catal. B*, **31**, 133 (2001).
10. J. Ma, M. Fang and N. Lau, *Appl. Catal. A*, **150**, 253 (1997).
11. Z. Ma, X. Gao, X.L. Yuan, L. Zhang, Y.F. Zhu and Z.J. Li, *Catal. Commun.*, **12**, 817 (2011).
12. N. Lau, M. Fang and C. Chan, *J. Mol. Catal. A*, **203**, 221 (2003).