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# Experimental Study on Catalytic Reduction of SO<sub>2</sub> by Rare Earth Compound in the Presence of Oxygen

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**Abstract.** Compared with a great deal of traditional desulphurization crafts, the catalytic reduction of SO<sub>2</sub> with CO to elemental sulfur is considered to be the best technology for the removal of SO<sub>2</sub> from flue gas. Adding rare earth oxide CeO<sub>2</sub> with variable valences to La<sub>2</sub>O<sub>3</sub> forms a mixture of rare earth oxides. By means of dipping CeO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub> and their mixture, whose carriers are  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, are used as the catalyst for the reduction of SO<sub>2</sub> by CO. Under the condition of oxygen, all kinds of catalyst will be poisoned to some extent. However, the oxygen resistance of the catalyst can be improved by changing the composition of the catalyst. It is found through experiments that this poisoning effect is partially reversible. The structure of the catalyst is not completely destroyed. There is still a great distance from the actual application.

## 1. Introduction

The mainstream technology and effective measure to control SO<sub>2</sub> pollution in coal-fired power plants are still flue gas desulfurization technology. At present, more than 200 kinds of desulfurization technologies have been commercialized at home and abroad[1]. Exhaust gas desulfurization is currently the most effective and widely used technology for controlling SO<sub>2</sub> emission from coal-fired power plants.

With the development of science and technology, some new technologies for desulfurization have emerged. Among many new technologies, the catalytic reduction desulfurization method is particularly attractive. The flue gas direct catalytic reduction desulfurization technology is to reduce SO<sub>2</sub> to elemental sulfur recovery with a reducing agent in the presence of a catalyst. In particular, the use of CO in flue gas to reduce SO<sub>2</sub> to elemental sulfur has a distinct advantage as a cost-effective desulfurization process. This method has no solid waste and will not cause secondary pollution. The recovered sulfur is an important industrial raw material, which can compensate the high cost of desulfurization to a certain extent. However, in the presence of O<sub>2</sub>, the catalytic reduction reaction is inhibited. In this paper, the rare earth compound CeO<sub>2</sub>-La<sub>2</sub>O<sub>3</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is used as a catalyst to study the catalytic process of catalytic reduction of SO<sub>2</sub> in the presence of oxygen.

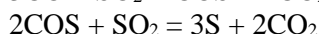
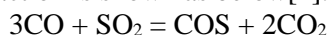
## 2. Basic mechanism

The current research on the reduction of SO<sub>2</sub> with CO suggests that there are two main mechanisms.

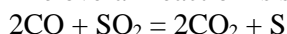
### 2.1. Intermediate product mechanism



This mechanism considers that the whole reaction consists of two parts, with COS as the intermediate product. Many researchers have reported the discovery of COS to support this mechanism. The reaction is shown as below[2].

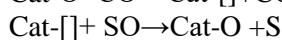
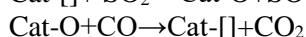
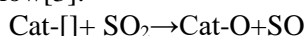


The overall reaction is shown as below.



## 2.2. Redox mechanism

Another mechanism considers this process as an oxidation-reduction process. The reaction is shown as below[3].



## 3. Catalysts preparation

In this study, catalyst is prepared by impregnation method[4]. The catalytic agent of  $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$ ,  $\text{La}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$  and  $\text{CeO}_2\text{-La}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$  are prepared by impregnating  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  in certain stoichiometric ratio. Then, these catalysts are dried and calcined before hydrated under a certain temperature.  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  were analytical reagent. The surface area of  $\gamma\text{-Al}_2\text{O}_3$  is  $280 \text{ m}^2 \cdot \text{g}^{-1}$ . The specific composition of catalyst is prepared in the following table.

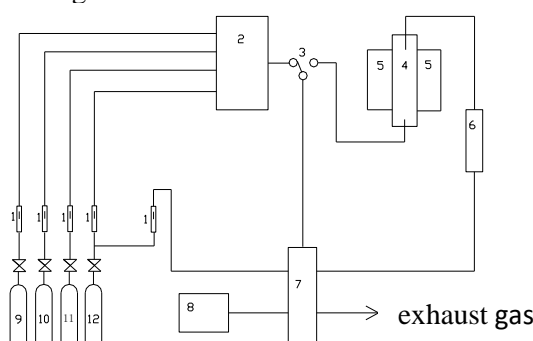
Table 1. Catalyst composition

Group	1	2	3	4	5	6	7
Catalyst composition	12% $\text{La}_2\text{O}_3$	8% $\text{CeO}_2$	6% $\text{CeO}_2$ - 10% $\text{La}_2\text{O}_3$	6% $\text{CeO}_2$ - 12% $\text{La}_2\text{O}_3$	8% $\text{CeO}_2$ - 10% $\text{La}_2\text{O}_3$	8% $\text{CeO}_2$ - 12% $\text{La}_2\text{O}_3$	10% $\text{CeO}_2$ - 15% $\text{La}_2\text{O}_3$

## 4. Experimental apparatus and experimental method

### 4.1. Experimental apparatus

Experimental apparatus is shown in Figure 1.



(1- flowmeter, 2- gas mixing box, 3- switch, 4- reactor, 5- heater, 6- condenser, 7- gas analysis box, 8- gas analyzer, 9-  $\text{O}_2$  cylinder, 10-  $\text{SO}_2$  cylinder, 11-  $\text{CO}$  cylinder, 12-  $\text{N}_2$  cylinder)

Figure 1. Schematic diagram of experimental apparatus

### 4.2. Experimental method

A fixed bed flow reactor made of quartz (diameter 25mm, height 800 mm) is used. 15g catalyst is put in the middle of reactor. The reactor is laid in a tube experimental electrical furnace whose temperature is controlled automatically and temperature difference of the catalyst bed is controlled within  $\pm 1^\circ\text{C}$ . The proportions of the reaction gas was  $\text{SO}_2:\text{CO}=1:3$ . The loading gas was  $\text{N}_2$ . The gas

mixture entered from the bottom of the reactor at a constant flow rate ( $1\text{L}\cdot\text{min}^{-1}$ ). After full activation,  $\text{O}_2$  was gradually added with an increasing amount of 0.01% (volume ratio) until the conversion rate of  $\text{SO}_2$  reached 0. Then stop adding  $\text{O}_2$  until the conversion rate of  $\text{SO}_2$  is stable.

## 5. Experimental results and analysis

### 5.1. Oxygen resistance curve of $\text{La}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$

Experimental result is shown in Figure 2.

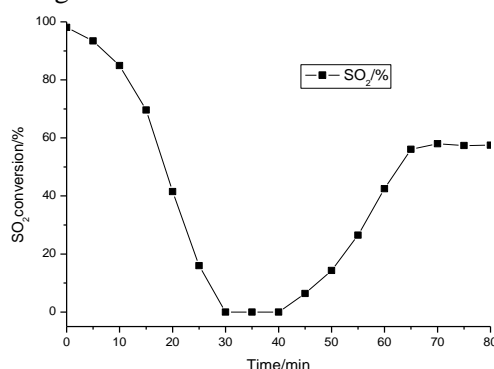


Figure 2. Oxygen resistance curve of  $\text{La}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$

0.01%  $\text{O}_2$  is added during 0-40min, and then stopped. It can be seen that the addition of 0.01%  $\text{O}_2$  reduced the  $\text{SO}_2$  conversion rate to 0 at 30min, and the  $\text{SO}_2$  conversion rate increases to 57.5% after oxygen is stopped. This indicates that  $\text{O}_2$  could seriously poison the catalyst, but the catalyst partially recovers its activity after stopping adding  $\text{O}_2$ .

### 5.2. Oxygen resistance curve of $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$

Experimental result is shown in Figure 3.

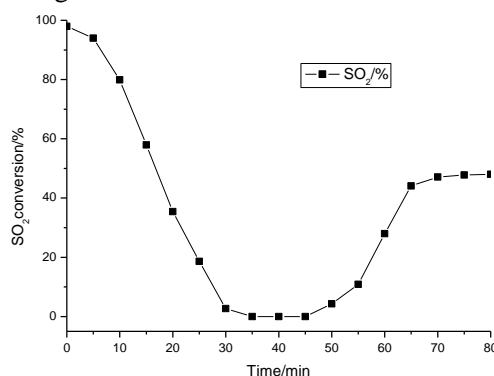


Figure 3. Oxygen resistance curve of  $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$

0.01%  $\text{O}_2$  is added during 0-40min, and then stopped. It can be seen that the addition of 0.01%  $\text{O}_2$  reduced the  $\text{SO}_2$  conversion rate to 0 at 35min, and the  $\text{SO}_2$  conversion rate increases to 48.1% after oxygen is stopped. This indicates that  $\text{O}_2$  could seriously poison the catalyst, but the catalyst partially recovers its activity after stopping adding  $\text{O}_2$ .

### 5.3. Oxygen resistance curve of 6% $\text{CeO}_2$ - 10% $\text{La}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$

Experimental result is shown in Figure 4.

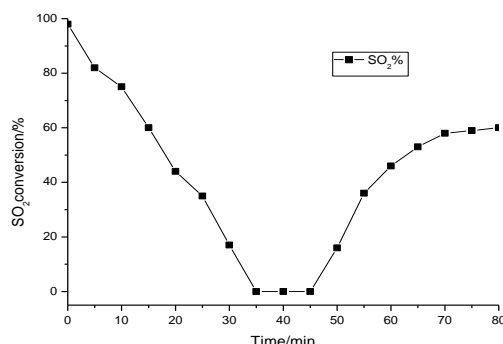


Figure 4. Oxygen resistance curve of 6%CeO<sub>2</sub>- 10%La<sub>2</sub>O<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub>

0.01% O<sub>2</sub> is added during 0-45min, and then stopped. It can be seen that the addition of 0.01% O<sub>2</sub> reduced the SO<sub>2</sub> conversion rate to 0 at 35min, and the SO<sub>2</sub> conversion rate increases to 60.0% after oxygen is stopped. This indicates that O<sub>2</sub> could seriously poison the catalyst, but the catalyst partially recovers its activity after stopping adding O<sub>2</sub>.

#### 5.4. Oxygen resistance curve of 6%CeO<sub>2</sub>- 12%La<sub>2</sub>O<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub>

Experimental result is shown in Figure 5.

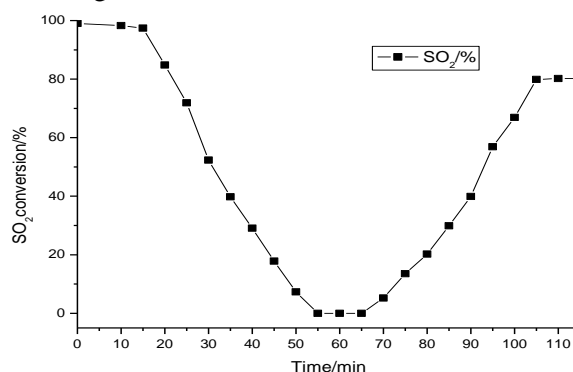


Figure 5. Oxygen resistance curve of 6%CeO<sub>2</sub>- 12%La<sub>2</sub>O<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub>

0.01% O<sub>2</sub> is added during 0-65min, and then stopped. It can be seen that the addition of 0.01% O<sub>2</sub> reduced the SO<sub>2</sub> conversion rate to 0 at 55min, and the SO<sub>2</sub> conversion rate increases to 80.0% after oxygen is stopped. This indicates that O<sub>2</sub> could seriously poison the catalyst, but the catalyst partially recovers its activity after stopping adding O<sub>2</sub>.

#### 5.5. Oxygen resistance curve of 8%CeO<sub>2</sub>- 10%La<sub>2</sub>O<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub>

Experimental result is shown in Figure 6.

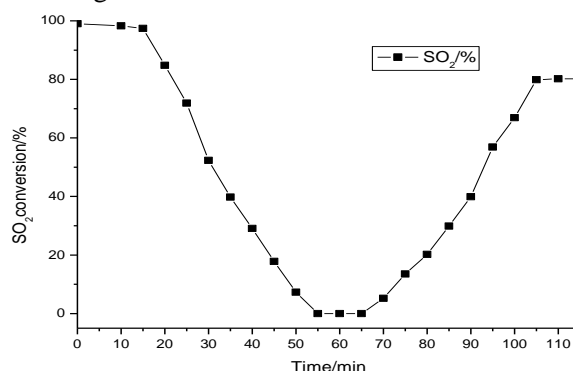


Figure 6. Oxygen resistance curve of 8%CeO<sub>2</sub>- 10%La<sub>2</sub>O<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub>

0.01% O<sub>2</sub> is added during 0-65min, and then stopped. It can be seen that the addition of 0.01% O<sub>2</sub> reduced the SO<sub>2</sub> conversion rate to 0 at 55min, and the SO<sub>2</sub> conversion rate increases to 80.0% after oxygen is stopped. This indicates that O<sub>2</sub> could seriously poison the catalyst, but the catalyst partially recovers its activity after stopping adding O<sub>2</sub>.

#### 5.6. Oxygen resistance curve of 8%CeO<sub>2</sub>- 12%La<sub>2</sub>O<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub>

Experimental result is shown in Figure 7.

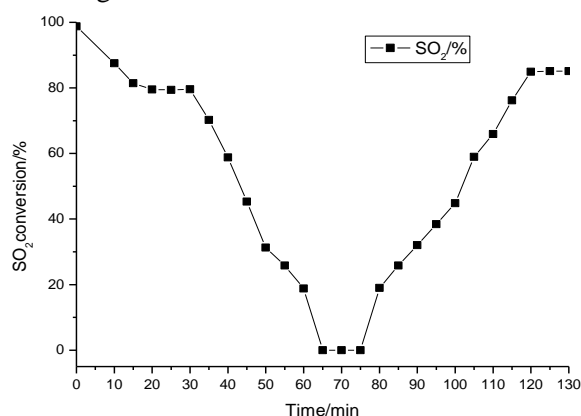


Figure 7. Oxygen resistance curve of 8%CeO<sub>2</sub>- 12%La<sub>2</sub>O<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub>

0.01% O<sub>2</sub> is added during 0-30min, 0.02% O<sub>2</sub> is added during 35-65min, and then stopped. It can be seen that the SO<sub>2</sub> conversion rate decreases to 80% after the addition of 0.01% O<sub>2</sub> at 20min, and then decreases to 0% after the addition of 0.02% O<sub>2</sub> oxygen at 65min. This indicates that O<sub>2</sub> could seriously poison the catalyst, but the catalyst partially recovers its activity after stopping adding O<sub>2</sub>.

#### 5.7. Oxygen resistance curve of 10%CeO<sub>2</sub>- 15%La<sub>2</sub>O<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub>

Experimental result is shown in Figure 8.

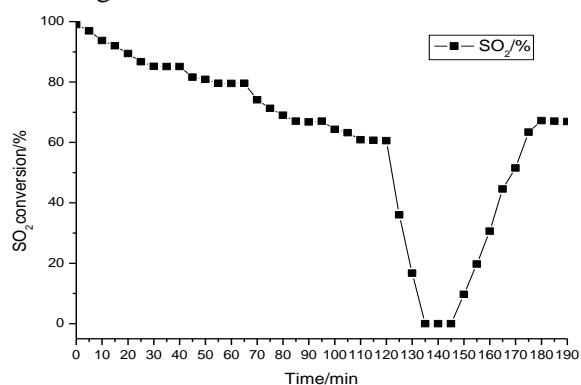


Figure 8. Oxygen resistance curve of 10%CeO<sub>2</sub>- 15%La<sub>2</sub>O<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub>

0.01% O<sub>2</sub> is added during 0-40min, 0.02% O<sub>2</sub> is added during 45-65min, 0.03% O<sub>2</sub> is added during 70-95min, 0.04% O<sub>2</sub> is added during 100-120min, 0.05% O<sub>2</sub> is added during 125-145min, and then O<sub>2</sub> was stopped. This indicates that O<sub>2</sub> could seriously poison the catalyst, but the catalyst partially recovers its activity after stopping adding O<sub>2</sub>. It can be seen that the catalyst can withstand up to 0.04% O<sub>2</sub>, and 0.05% O<sub>2</sub> will completely poison the catalyst. The SO<sub>2</sub> conversion rate can be restored to 67.0% after stopping adding O<sub>2</sub>. This indicates that O<sub>2</sub> could seriously poison the catalyst, but the catalyst partially recovers its activity after stopping adding O<sub>2</sub>.

## 6. Conclusion

The following conclusions can be drawn from the experiment:

• In general, the trend of the oxygen resistance curves of seven catalysts is roughly similar. With the addition of O<sub>2</sub>, desulfurization efficiency of all the 7 catalysts decreased significantly, and the lowest point was almost 0, that is, catalyst poisoning occurred. After the suspension of O<sub>2</sub>, catalyst activity recovered within a certain time, but the activity after the recovery was lower than that before the poisoning. This indicates that O<sub>2</sub> has a very obvious poisoning effect on this type of catalyst, but the effect is partially reversible and the structure of the catalyst is not completely destroyed[5].

• The oxygen resistance of seven catalysts is not very good, and there is still a great distance from the actual application. Among them, 8% CeO<sub>2</sub>-12% La<sub>2</sub>O<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub> and 10% CeO<sub>2</sub>-15% La<sub>2</sub>O<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalysts have relatively good oxygen resistance, and 10% CeO<sub>2</sub>-15% La<sub>2</sub>O<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub> can withstand 0.04% O<sub>2</sub>. The oxygen resistance of the catalyst has a tendency to increase with the increase of CeO<sub>2</sub> and La<sub>2</sub>O<sub>3</sub> content.

• The catalytic reduction performance of 7 kinds of catalysts will be restored to a certain extent after stopping adding O<sub>2</sub>. The SO<sub>2</sub> conversion rate after restoration ranks from high to low as follows: 8%CeO<sub>2</sub>-10%La<sub>2</sub>O<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub>>8%CeO<sub>2</sub>-12%La<sub>2</sub>O<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub>>6%CeO<sub>2</sub>-12%La<sub>2</sub>O<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub>>10%CeO<sub>2</sub>-15%La<sub>2</sub>O<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub>>6%CeO<sub>2</sub>-10%La<sub>2</sub>O<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub>>La<sub>2</sub>O<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub>>CeO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub>. It can be seen that the mixed catalyst of CeO<sub>2</sub> and La<sub>2</sub>O<sub>3</sub> has a better recovery capacity than the single component catalyst.

### Acknowledgments

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