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Experimental Study on Catalytic Reduction of SO₂ 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 SO₂ with CO to elemental sulfur is considered to be the best technology for the removal of SO₂ from flue gas. Adding rare earth oxide CeO₂ with variable valences to La₂O₃ forms a mixture of rare earth oxides. By means of dipping CeO₂, La₂O₃ and their mixture, whose carriers are all γ -Al₂O₃, are used as the catalyst for the reduction of SO₂ 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 SO₂ 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 SO₂ 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 SO₂ 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 SO₂ 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 O₂, the catalytic reduction reaction is inhibited. In this paper, the rare earth compound CeO₂-La₂O₃/ γ -Al₂O₃ is used as a catalyst to study the catalytic process of catalytic reduction of SO₂ in the presence of oxygen.

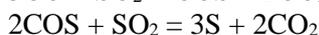
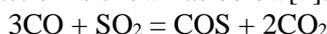
2. Basic mechanism

The current research on the reduction of SO₂ with CO suggests that there are two main mechanisms.

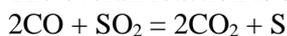
2.1. Intermediate product mechanism



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].

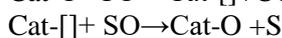
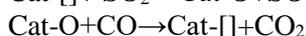
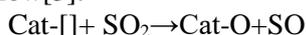


The overall reaction is shown as below.



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.

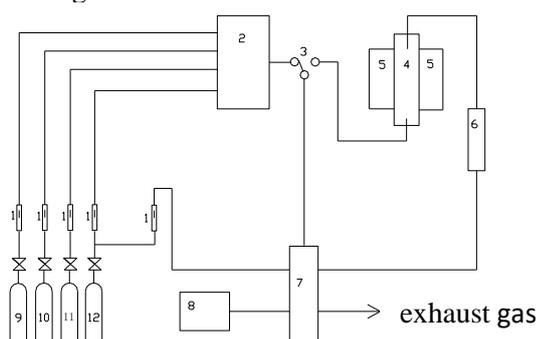
Table 1. Catalyst composition

Group	1	2	3	4	5	6	7
Catalyst composition	12% La_2O_3	8% CeO_2	6% CeO_2 - 10% La_2O_3	6% CeO_2 - 12% La_2O_3	8% CeO_2 - 10% La_2O_3	8% CeO_2 - 12% La_2O_3	10% CeO_2 - 15% La_2O_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- O_2 cylinder, 10- SO_2 cylinder, 11- CO cylinder, 12- 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 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, O_2 was gradually added with an increasing amount of 0.01% (volume ratio) until the conversion rate of SO_2 reached 0. Then stop adding O_2 until the conversion rate of 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.

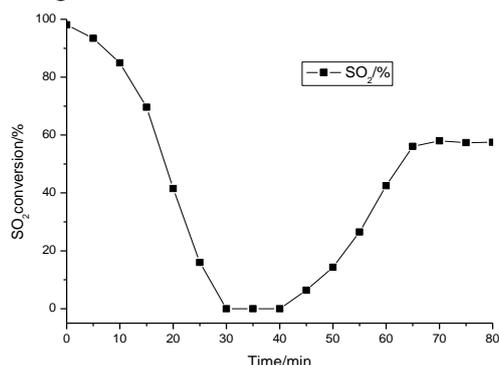


Figure 2. Oxygen resistance curve of $\text{La}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$

0.01% O_2 is added during 0-40min, and then stopped. It can be seen that the addition of 0.01% O_2 reduced the SO_2 conversion rate to 0 at 30min, and the SO_2 conversion rate increases to 57.5% after oxygen is stopped. This indicates that O_2 could seriously poison the catalyst, but the catalyst partially recovers its activity after stopping adding 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.

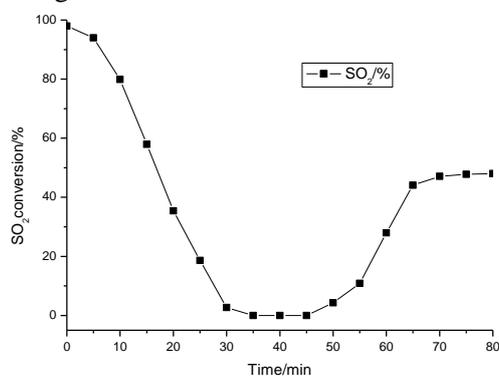


Figure 3. Oxygen resistance curve of $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$

0.01% O_2 is added during 0-40min, and then stopped. It can be seen that the addition of 0.01% O_2 reduced the SO_2 conversion rate to 0 at 35min, and the SO_2 conversion rate increases to 48.1% after oxygen is stopped. This indicates that O_2 could seriously poison the catalyst, but the catalyst partially recovers its activity after stopping adding O_2 .

5.3. Oxygen resistance curve of 6% CeO_2 - 10% $\text{La}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$

Experimental result is shown in Figure 4.

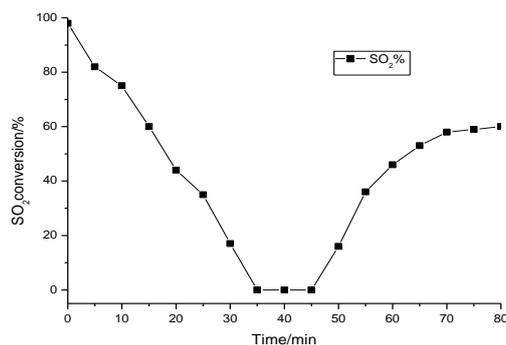


Figure 4. Oxygen resistance curve of 6%CeO₂- 10%La₂O₃/γ-Al₂O₃

0.01% O₂ is added during 0-45min, and then stopped. It can be seen that the addition of 0.01% O₂ reduced the SO₂ conversion rate to 0 at 35min, and the SO₂ conversion rate increases to 60.0% after oxygen is stopped. This indicates that O₂ could seriously poison the catalyst, but the catalyst partially recovers its activity after stopping adding O₂.

5.4. Oxygen resistance curve of 6%CeO₂- 12%La₂O₃/γ-Al₂O₃

Experimental result is shown in Figure 5.

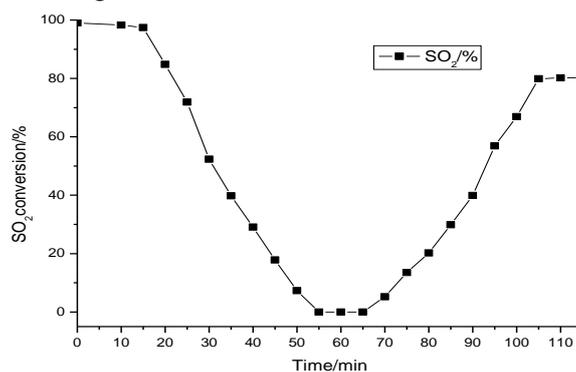


Figure 5. Oxygen resistance curve of 6%CeO₂- 12%La₂O₃/γ-Al₂O₃

0.01% O₂ is added during 0-65min, and then stopped. It can be seen that the addition of 0.01% O₂ reduced the SO₂ conversion rate to 0 at 55min, and the SO₂ conversion rate increases to 80.0% after oxygen is stopped. This indicates that O₂ could seriously poison the catalyst, but the catalyst partially recovers its activity after stopping adding O₂.

5.5. Oxygen resistance curve of 8%CeO₂- 10%La₂O₃/γ-Al₂O₃

Experimental result is shown in Figure 6.

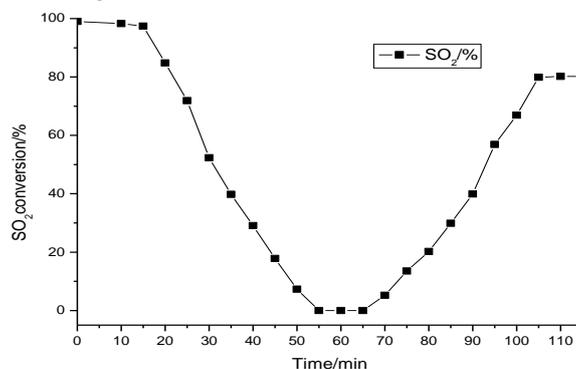


Figure 6. Oxygen resistance curve of 8%CeO₂- 10%La₂O₃/γ-Al₂O₃

0.01% O₂ is added during 0-65min, and then stopped. It can be seen that the addition of 0.01% O₂ reduced the SO₂ conversion rate to 0 at 55min, and the SO₂ conversion rate increases to 80.0% after oxygen is stopped. This indicates that O₂ could seriously poison the catalyst, but the catalyst partially recovers its activity after stopping adding O₂.

5.6. Oxygen resistance curve of 8%CeO₂- 12%La₂O₃/γ-Al₂O₃

Experimental result is shown in Figure 7.

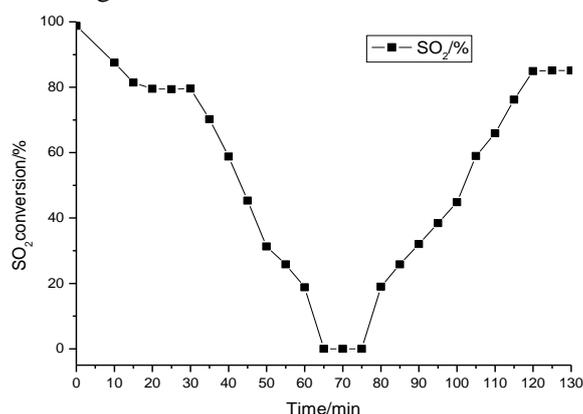


Figure 7. Oxygen resistance curve of 8%CeO₂- 12%La₂O₃/γ-Al₂O₃

0.01% O₂ is added during 0-30min, 0.02% O₂ is added during 35-65min, and then stopped. It can be seen that the SO₂ conversion rate decreases to 80% after the addition of 0.01% O₂ at 20min, and then decreases to 0% after the addition of 0.02% O₂ oxygen at 65min. This indicates that O₂ could seriously poison the catalyst, but the catalyst partially recovers its activity after stopping adding O₂.

5.7. Oxygen resistance curve of 10%CeO₂- 15%La₂O₃/γ-Al₂O₃

Experimental result is shown in Figure 8.

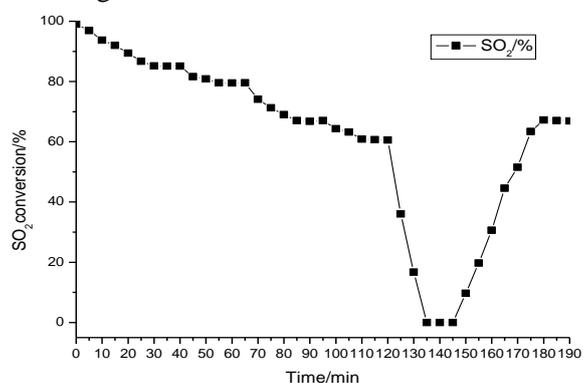


Figure 8. Oxygen resistance curve of 10%CeO₂- 15%La₂O₃/γ-Al₂O₃

0.01% O₂ is added during 0-40min, 0.02% O₂ is added during 45-65min, 0.03% O₂ is added during 70-95min, 0.04% O₂ is added during 100-120min, 0.05% O₂ is added during 125-145min, and then O₂ was stopped. This indicates that O₂ could seriously poison the catalyst, but the catalyst partially recovers its activity after stopping adding O₂. It can be seen that the catalyst can withstand up to 0.04% O₂, and 0.05% O₂ will completely poison the catalyst. The SO₂ conversion rate can be restored to 67.0% after stopping adding O₂. This indicates that O₂ could seriously poison the catalyst, but the catalyst partially recovers its activity after stopping adding O₂.

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 O₂, 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 O₂, catalyst activity recovered within a certain time, but the activity after the recovery was lower than that before the poisoning. This indicates that O₂ 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% CeO₂-12% La₂O₃/γ-Al₂O₃ and 10% CeO₂-15% La₂O₃/γ-Al₂O₃ catalysts have relatively good oxygen resistance, and 10% CeO₂-15% La₂O₃/γ-Al₂O₃ can withstand 0.04% O₂. The oxygen resistance of the catalyst has a tendency to increase with the increase of CeO₂ and La₂O₃ content.

• The catalytic reduction performance of 7 kinds of catalysts will be restored to a certain extent after stopping adding O₂. The SO₂ conversion rate after restoration ranks from high to low as follows: 8% CeO₂-10% La₂O₃/γ-Al₂O₃ > 8% CeO₂-12% La₂O₃/γ-Al₂O₃ > 6% CeO₂-12% La₂O₃/γ-Al₂O₃ > 10% CeO₂-15% La₂O₃/γ-Al₂O₃ > 6% CeO₂-10% La₂O₃/γ-Al₂O₃ > La₂O₃/γ-Al₂O₃ > CeO₂/γ-Al₂O₃. It can be seen that the mixed catalyst of CeO₂ and La₂O₃ has a better recovery capacity than the single component catalyst.

Acknowledgments

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References

- [1] Wang, J., Zhang, H.M. (2004) The present situation and development trend of flue gas desulfurization in China's power industry. *Techniques and Equipment for Environmental Pollution Control*, 5(6): 12-16.
- [2] Hu, H., Li, S.L. (2004) Study on Mechanism of Catalytic Reduction of SO₂ by CeO₂-La₂O₃/γ-Al₂O₃. *Chinese Journal of Catalysis*, 25(2): 115-119.
- [3] Liu, W., Sarofim, A.F. (1994) Reduction of SO₂ by CO to Elemental Sulfur over Composite Oxide Catalysts. *Applied Catalysis B: Environmental*, 4: 167-186.
- [4] Wang, S.Z. (1999) Study on catalytic reduction of SO₂ by rare earth oxides such as PrO/γAl₂O₃. *Acta Scientiae Circumstantiae*, 19(6):652-656.
- [5] Jia, L.S., Qin, Y.N. (2004) XPS study on the vulcanization process of perovskite LaCoO₃ in the presence of oxygen. *Chinese Journal of Catalysis*, 25 (1): 19-22.