Characteristics and Mechanism Study of the CuO/γ-Al₂O₃ Modified by CeO₂ and NaCl

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Abstract. The CuO/γ-Al₂O₃ absorbent was modified by CeO₂ and NaCl, and its desulfurization performance was studied experimentally in a fixed bed reactor. The experimental results show that the adsorption capacity of sulfur dioxide is significantly improved and the adsorption saturation time of sulfur dioxide is significantly extended with CeO₂ and NaCl addition. The sulfur dioxide adsorption saturation time of the absorbent can be extended from 56 minutes to 78 minutes at 400°C, when the CeO₂ loading is 3%, and can be further extended to 104 min, with 2% CeO₂ and 5% NaCl loading. The improvement mechanism of the desulfurization performance of the modified CuO/γ-Al₂O₃ can be attributed to the promotion of the uniform distribution of the active components in the carrier and the optimization of the pore structure of the absorbent.

1. Introduction
At present, the most wildly used treatment of SO₂ from coal combustion is limestone-gypsum wet desulfurization process [1-2], whose desulfurization efficiency is high. However, its investment and operation cost are high, and the high-salt-containing desulfurization wastewater and gypsum are difficult to handle. Dry calcium desulfurization process has a small investment, but has a problem of low desulfurization efficiency. Compared with the process mentioned above, the CuO/γ-Al₂O₃ dry desulfurization process has the advantages of ideal desulfurization efficiency, less absorbent consumption, regenerability, less desulfurization by-products, and simultaneous denitrification under the conditions of ammonia injection [3-6]. The adsorbent in this process uses a porous medium γ-Al₂O₃ as a carrier and CuO as an active material. Under O₂ conditions, CuO can react with SO₂ in flue gas to form CuSO₄ [7]. The adsorbent after saturated adsorption of sulfur dioxide can be recycled after being regenerated with a reducing gas such as NH₃ or CH₄ at a certain temperature [8]. At present, the high cost of absorbent and the low absorption saturation time of SO₂ are the main reasons for the industrialization of CuO/γ-Al₂O₃ desulfurization process [9]. How to further increase the saturation adsorption time of the absorbent is the key to the application of the process. In this paper, the desulfurization performance of CuO/γ-Al₂O₃ absorbent modified by CeO₂ and NaCl was studied in a fixed bed reactor. The related reaction mechanism was discussed by means of XRD and N₂ adsorption characterization methods to provides theory and basis of the industrial application of CuO/γ-Al₂O₃ desulfurization process.
2. Experimental

2.1. Catalyst Preparation

It is considered that the close-packed monolayer capacity is approximately 0.19 g/m$^2$ CuO for Al$_2$O$_3$ [10]. Meanwhile, much research [10-12] show that the optimal loading of CuO on γ-Al$_2$O$_3$ is 8%-14%. In the text, the CuO loading was set to 8%, the CeO$_2$ loading was 2%, 3%, 5%, and 8%, and the NaCl loading was 1%, 3%, 5%, and 7%, respectively. Nine samples were named as Cu8, Cu8Ce2, Cu8Ce3, Cu8Ce5, Cu8Ce8, Cu8Ce2Na1, Cu8Ce2Na3, Cu8Ce2Na5, Cu8Ce2Na7.

The CuO/γ-Al$_2$O$_3$, CuO-CeO$_2$/γ-Al$_2$O$_3$ and CuO-CeO$_2$-NaCl/γ-Al$_2$O$_3$ series adsorbents were prepared by wet impregnation with pure γ-Al$_2$O$_3$ pellets (30-40 mesh, 185 m$^2$g$^{-1}$, Fushun Petrochemical Co.) and an aqueous solution of Cu(NO$_3$)$_2$·5H$_2$O and Ce(NO$_3$)$_3$·6H$_2$O (40-60 mesh, 218 m$^2$g$^{-1}$, Tianjin Zhonghai Oil Chemical Research Institute) and NaCl (30-40 mesh, 198 m$^2$g$^{-1}$, Tianjin Zhonghai Oil Chemical Research Institute). Fresh γ-Al$_2$O$_3$ pellet was impregnated with various concentrations of Cu(NO$_3$)$_2$ and Ce(NO$_3$)$_3$ aqueous solutions for 4 h at room temperature followed by evaporation at 90 °C with stirring. After dried in oven for 20 h and subsequently calcined under N$_2$ air for 6 h at 500 °C in muffle furnace, Finally, these adsorbents were obtained.

2.2. Experimental Device and Experimental Method

The test was performed in the fixed bed reactor (diameter 20 mm and length 1.25 m) shown in figure 1. The test samples were placed in the porous fixed bed reaction zone and then were heated to the set temperature at steady state. The simulated flue gas is composed of 1800 ppm SO$_2$, 5%O$_2$, and N$_2$ as the balance with a flow rate of 0.4 L/min in all the runs. The test stops when the SO$_2$ concentration detected at the experimental device outlet reaches 360 ppm (desulfurization efficiency ≥80%), and the time ($t_0$) consumed is defined as the adsorption saturation time, which is recorded by the computer.

The pore structure characteristics of these sorbents were measured by the specific surface and pore size distribution analyzer (ASAP2020) of Micromeritics, USA, and the specific surface and pore size distribution data were processed by BET method and BJH method, respectively. The crystal phase composition of the catalyst synthesis product was measured by an X-ray diffractometer (XRD, X’Pert PRO) of the Netherlands PANalytical B.V.
3. Experimental Results and Discussion

3.1. Sulfur Capacity of the CuO-CeO$_2$/$\gamma$-Al$_2$O$_3$ Absorbent

For the determination of the optimal sorbent for SO$_2$, the effect of CeO$_2$ loading was tested at 400 °C.

Figure 2 shows that the saturation time of SO$_2$ adsorption increases first and then decreases with CeO$_2$ loading increases. The $t_0$ of Cu8 is 62 min and $t_0$ of Cu8Ce8 is 72 min. The absorbent gets the longest $t_0$ (88 min), when the CeO$_2$ loading is 3%, indicating that the SO$_2$ sulfur capacity of the absorbent is significantly increased with the addition of CeO$_2$. However, it is unbeneficial for sulfur capacity improvement when CeO$_2$ loading is too high or too low.

Furthermore, the effect of temperature on the sulfur capacity of Cu8Ce3 in the temperature range of 300-500 °C was studied experimentally. Figure 3 shows that the SO$_2$ adsorption saturation time of Cu8Ce3 increases continuously with the increase of temperature. The $t_0$ of the absorbent is 56 min at 300 °C, 88 min at 400 °C, 96 min at 450 °C, 100 min at 500 °C. The adsorption saturation time of SO$_2$ increased rapidly at 300-450 °C, However, at 500 °C $t_0$ is not significant compared to 450 °C.

![Figure 2. Effect of CeO$_2$ loading on desulfurization efficiency at 400 °C.](image2)

![Figure 3. Effect of temperature on $t_0$ of Cu8Ce3 absorbent.](image3)

3.2. Sulfur Capacity of the CuO-CeO$_2$-NaCl/$\gamma$-Al$_2$O$_3$ Absorbent

The effect of the loading of NaCl on the SO$_2$ removing efficiency of the CuO-CeO$_2$-NaCl/$\gamma$-Al$_2$O$_3$ series adsorbents were investigated at 400 °C. The experimental results are shown in figure 4. The $t_0$ of five samples were 73 min, 100 min, 144 min, 136 min, and 120 min respectively and was gradually extended with the NaCl loading increased from 0 to 5%. however, $t_0$ decreases to 88min, as NaCl loading increased to 7%, indicating that the NaCl loading has the best value, and the overloaded or low NaCl loading is unbeneicial to the sulfur capacity.
The effect of temperature on the sulfur capacity of Cu8Ce2Na3 in the temperature range of 300-500 °C was studied experimentally. Figure 5 shows the SO2 adsorption saturation time of Cu8Ce2Na3 increases continuously with reaction temperature increasing. The t0 of the absorbent is 92 min at 300 °C, 100min at 350°C, 140min at 400 °C, 144 min at 450 °C, 148 min at 500 °C. The t0 increases rapidly in the range of 300-400 °C, and t increases slowly in the range of 400-500 °C.

In the normal operating conditions of the boiler, the flue temperature of the low-temperature economizer outlet is about 350-400 °C, according to the reaction temperature and the sulfur capacity of CuO-CeO2/γ-Al2O3 and CuO-CeO2-NaCl/γ-Al2O3 series absorbents mentioned above. The influence law can be considered that the Cu8Ce2Na3 absorbent obtained in this study can obtain better desulfurization effect in the temperature range of 350-400 °C.

3.3. Mechanism Analysis

The CuO and CeO2 loading of CuO-CeO2/γ-Al2O3 adsorbent is the most important factor affecting the sulfur capacity, and the specific surface area of the adsorbent determines the loading of CuO and CeO2 [13-14].

It is considered that the copper loading on the adsorbent could obtain the best sulfur capacity near its monolayer dispersion threshold [15] and that the active component oxide will appear in a crystalline state when they were overloaded, this can reduce the desulfurization efficiency [16-17].

Figure 6 shows that The XRD diffraction peaks of CuO-CeO2/γ-Al2O3 adsorbent are 28°, 37°, 47° and 67°, respectively, of which 37°, 47° and 67° are distinct γ-Al2O3 phases, and 28° is the phase of CeO2, the crystal phase of CuO is CuAl2O4, which diffraction peak is 38.8°, however, the addition of CeO2 weakened the diffraction peak of CuAl2O4, indicating the addition of CeO2 reduced the CuO grain size and promoted the dispersion of CuO on the surface of the carrier [13,18], which can also be seen from table 1. With the increase of CeO2 loading, the obvious CeO2 diffraction peak appeared from sample 4. It indicated that the excessive CeO2 in the sample formed multi-layer coverage on γ-Al2O3, resulting in the formation of larger grains on the surface of the active component.

As shown in figure 7 that the 37°, 47°, 67° XRD diffraction peaks of CuO-CeO2-NaCl/γ-Al2O3 are γ-Al2O3 phases, and that 28° is the phase of CeO2(Cu8Ce2), The do not appear. The crystal phase of CeO2 (28°) and two standard diffraction peaks of CuO(35.6° and 38.8°) disappears due to the addition of NaCl. It can be inferred that the addition of NaCl promotes the dispersion of CeO2 on the surface of the adsorbent [19], however, the strong peak of CuAl2O4 diffraction appeared, when the NaCl loading reach 7%, indicating that excessive NaCl loading is not conducive to the dispersion of surfactant components.
Figure 6. XRD analysis of the CuO-CeO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> adsorbent.

Figure 7. XRD analysis of the CuO-CeO<sub>2</sub>-NaCl/γ-Al<sub>2</sub>O<sub>3</sub> adsorbent.

Table 1. Pore structure parameter of the catalysts.

| Sample     | BET surface area \(A(\text{m}^2/\text{g})\) | Pore volume \(\text{(cm}^3/\text{g})\) | Average Diameter (nm) |
|------------|---------------------------------|-------------------------------|-----------------------|
| Cu8        | 190.83                          | 0.41                          | 5.75                  |
| Cu8Ce2     | 193.28                          | 0.42                          | 5.72                  |
| Cu8Ce3     | 201.49                          | 0.44                          | 5.60                  |
| Cu8Ce5     | 187.07                          | 0.39                          | 6.53                  |
| Cu8Ce8     | 158.01                          | 0.36                          | 7.85                  |
| Cu8Ce2Na1  | 202.55                          | 0.44                          | 4.90                  |
| Cu8Ce2Na3  | 224.91                          | 0.47                          | 3.80                  |
| Cu8Ce2Na5  | 199.53                          | 0.43                          | 4.96                  |
| Cu8Ce2Na7  | 141.97                          | 0.37                          | 7.80                  |

It is found that the specific surface area and pore volume of these two kinds of absorbents increase first and decrease continuously with the increase of CeO<sub>2</sub> and NaCl loading, the average pore size of the trend is the opposite trend. The specific surface area and pore volume of the absorbent gradually decrease and the pore diameter gradually increases with the loading of CeO<sub>2</sub> and NaCl exceeds 3%, respectively, which is consistent with the trend of the desulfurization performance of the adsorbent in figures 2 and 4, indicating that the addition of CeO<sub>2</sub> improves the
dispersion of CuO on the surface of γ-Al\textsubscript{2}O\textsubscript{3}, and the addition of NaCl helps the dispersion of CuO and CeO\textsubscript{2} on the surface of γ-Al\textsubscript{2}O\textsubscript{3}, and the specific surface area and pore volume of the adsorbent were increased[18]. It is shown in figures 8 and 9 that the modified catalyst has a richer mesoporous structure and the number of pores is the most abundant especially when the CeO\textsubscript{2} loading is 2% and the NaCl loading is 3%, which is beneficial to the adsorption and oxidation of SO\textsubscript{2} and O\textsubscript{2} on the surface of the absorbent [20], meanwhile, it is also the main reason for the best desulfurization effect of Cu\textsubscript{8}Ce\textsubscript{2}Na\textsubscript{3}. However, overloaded CeO\textsubscript{2} and NaCl can block the voids on the surface, which is not conducive to the progress of the desulfurization reaction.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure8.png}
\caption{Pore size distribution of CuO-CeO\textsubscript{2}/γ-Al\textsubscript{2}O\textsubscript{3} adsorbent.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure9.png}
\caption{Pore size distribution of CuO-CeO\textsubscript{2}-NaCl/γ-Al\textsubscript{2}O\textsubscript{3} adsorbent.}
\end{figure}

4. Conclusion
The proper addition of CeO\textsubscript{2} and NaCl increased the sulfur capacity of the adsorbent at 300-500 °C. Compared with Cu\textsubscript{8}, the SO\textsubscript{2} adsorption saturation time (t\textsubscript{0}) of Cu\textsubscript{8}Ce\textsubscript{2}Na\textsubscript{3} increased from 62 min to 140 min. CuO and CeO\textsubscript{2} were both the SO\textsubscript{2} active adsorption site. On the catalysts surface.

The proper addition of CeO\textsubscript{2} and NaCl increases the specific surface area of the adsorbent, optimizes the pore structure of the adsorbent, and promotes the dispersion of the active components of CuO and CeO\textsubscript{2} on the surface of γ-Al\textsubscript{2}O\textsubscript{3}, but the overloaded additives reduces the specific surface area of the adsorbent and he pore volume. In this test, the optimal loading of CeO\textsubscript{2} is 3%, and the optimum loading of NaCl is 3% when the CeO\textsubscript{2} loading is 2%.
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