Simultaneous removal of SO2 and NO from flue gas using CeO2 promoted CuO/γ-Al2O3 catalysts

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Abstract. The simultaneous desulfurization and denitrification performance of the Cu8Ce3 and Cu8Ce3S catalysts were studied in a fixed-bed reactor. The test results show that the presence of SO2 has a poisoning effect on the denitrification performance of Cu8Ce3 when the flue gas temperature is below 350°C, but this kind of toxic effect is reversible. The root cause is that the sulfate species such as CuSO4 and Ce2(SO4)2 formed on the surface of Cu8Ce3S have a lower denitration activity below 350°C than CuO and CeO2. However, Changes in catalyst pore structure after desulfurization could not affect the amount of NH3 adsorbed significantly. The formation of SO4²⁻ on the Cu8Ce3S catalyst surface increased the number of Lewis acid sites on the catalyst surface, which improved the catalyst's strength ability to react with NH3 to ensure that Cu8Ce3S has a faster reaction rate than that of Cu8Ce3 above 350°C. The catalytic selectivity of Cu8Ce3S for NH3 is better than that of Cu8Ce3 at 350-500°C, which is the fundamental reason for the improvement of denitration efficiency at high temperatures.

1. Introduction
Numerous researchers have conducted extensive research on CuO/γ-Al2O3 desulfurization and denitrification using various reactor systems such as moving and fixed beds under laboratory conditions[1-3]. However, it has not yet been used on a large scale. The effects of test parameters such as flue gas temperature, SO2, NH3 adsorption amount, and oxidation rate on simultaneous desulfurization and denitrification performance need to be further studied. In the absence of SO2, over-oxidation of NH3 is the main reason for the decline in denitrification activity at high temperatures. However, the denitrification behavior in the presence of SO2 is more complicated, and there is no clear and in-depth study so far. Studies in the literature[4-5] are also limited to the influence of the catalyst on the adsorption performance of NH3.

In this paper, the performance of simultaneous desulfurization and denitrification of fresh catalysts at different reaction temperatures was studied in a fixed-bed reactor. The comprehensive influence reveals the effect mechanism of SO2 on the simultaneous desulfurization and denitrification performance at different temperatures, with a view to providing a theory and basis for the industrial application of CuO/γ-Al2O3 catalyst.

2. Experimental

2.1. Catalyst preparation
The CuO-CeO$_2$/γ-Al$_2$O$_3$ series catalysts were prepared by wet impregnation with pure γ-Al$_2$O$_3$ pellets (30-40 mesh, BET surface area of 185 m$^2$/g, Fushun Petrochemical Co.) and an aqueous solution of Cu(NO$_3$)$_2$.5H$_2$O and Ce(NO$_3$)$_3$.6H$_2$O (analytical pure, 40-60 mesh, BET surface area of 218 m$^2$/g, Tianjin Zhonghai Oil Chemical Research Institute). Fresh γ-Al$_2$O$_3$ was being kept in Cu(NO$_3$)$_2$ and Ce(NO$_3$)$_3$ aqueous solutions for 4h at room temperature followed by evaporation at 90℃ with stirring. After dried in oven for 20h and subsequently calcined under N$_2$ air for 6h at 500℃ in muffle furnace, Finally, CuO-CeO$_2$/γ-Al$_2$O$_3$ were obtained. The catalyst is termed as Cu8Ce3 in the text which contains 8.0 wt% of CuO and 3.0 wt% of CeO$_2$.

At 400℃, The fixed-bed reactor (as described in 2.2) containing fresh Cu8Ce3 was fed with 2000 ppm of SO$_2$ and 5% O$_2$ simulated flue gas, the sulfurization test is completed, When the SO$_2$ concentration detected at the outlet was less than 400 mg/m$^3$ (the desulfurization efficiency was less than 20%, the time of which is defined as adsorption saturation time) and Cu8Ce3S is obtained.

2.2. Experimental device and experimental method
The denitration test was carried out in the fixed bed reactor (20mm in diameter and 1.25m in length). A monolithic catalyst sample (50 mesh) was fitted in the reactor and heated to the setting temperature at steady state. A gas mixture containing 750 ppm NO, 900 ppm NH$_3$, 2000 ppm SO$_2$, 5% O$_2$ and balance N$_2$ are introduced into the reactor. In all the runs, the total flow rate was controlled at 0.4 L/min.

The concentration of NO, SO$_2$ and NH$_3$ in the feed gas and tail gas is detected by FT-IR DX4000 gas analyzer, whose NO measurement range is 0-2000 ppm, NH$_3$ measurement range is 0-2000 ppm, and measurement accuracy is ±3%. O$_2$ concentration is tested by the ecom-J2KN flue gas analyzer with a measuring range of 21% and the measurement accuracy of 0.2%.

3. Experimental results and discussion
3.1. Simultaneous desulfurization and denitration performance of fresh catalysts at different temperatures
The test was performed using a transient method. Simulated flue gas consisting of 750 ppm NO, 900 ppm NH$_3$, and N$_2$ was passed into a fixed-bed reactor carrying fresh catalyst for denitration reaction. SO$_2$ of 2000 ppm was then introduced into the simulated flue gas for simultaneous desulfurization and denitration reactions after the denitration efficiency became stable for 1 hour (the timing is started). Observe the trend of desulfurization and denitration efficiency, and stop desulfurization when the denitration efficiency is stable again (about 2.5h) Trends.

At 350℃-500℃, SO$_2$ did not poison the denitration efficiency. At 350℃, the denitration efficiency of Cu8Ce3 was stabilized at 70% and 85% before, after, and after stopping the introduction of SO$_2$. No significant change occurred. Especially at 400℃-450℃, the denitration efficiency has improved
significantly when SO\textsubscript{2} ceases to pass in, which is significantly higher than the level before SO\textsubscript{2} introduction, rising from 65\% to 90\% at 400\textdegree°C, and from 50\% to 80\% at 450\textdegree°C, especially at 500\textdegree°C, the denitration efficiency increased twice, the first increase from 21\% to 43\% (45 minutes after accessing SO\textsubscript{2}), and the second increase from 43\% to 70\% (165 minutes after accessing SO\textsubscript{2}), which indicates that the presence of SO\textsubscript{2} at this temperature is beneficial to improve the denitration performance of the catalyst.

People have carried out in-depth research on supported metal oxide catalysts [6,7,8], and it is generally believed that the inhibitory effect of SO\textsubscript{2} on SCR activity comes from the change of the physical properties of the catalyst surface and(or)the change of the active phase of the catalyst. Nam[9]'s research on V\textsubscript{2}O\textsubscript{5}/Al\textsubscript{2}O\textsubscript{3} catalysts found that aluminum sulfate generated in the flue gas due to the presence of SO2 significantly reduced the surface area of the catalyst, leading to a serious decrease in the activity of the SCR catalyst, and the surface of the catalyst poisoned by SO\textsubscript{2} was found to have a large amount of ammonium sulfate deposited and blocked the catalyst channels. Xie Guoyong[10]believes that the formation of copper sulfate and ammonium sulfate at 200-300\textdegree°C reduces the specific surface area and pore volume of the catalyst, which is the reason for the decrease in denitration efficiency at low temperatures. The test tested the specific surface area and pore structure of Cu8Ce3 and Cu8Ce3S. Table 1 shows that the specific surface area, pore volume, and pore size of the catalyst after sulfidation all decreased to varying degrees, and the pore structure became worse. The characteristics are not conducive to the diffusion of gas on the catalyst surface [11,12], which seems further verifies the previous conclusions.
Fig 2. Effect of temperature on simultaneous desulfurization and denitrification efficiency of CuCe3

Xie Guoyong [10] found that the quantity of adsorbed NH3 on the catalyst surface and the NH3 oxidation activation determine the denitrification activity of the catalyst. In order to further verify the improvement effect of SO2 on denitrification performance at high temperature 400-500℃, the effect of sulfurization on the adsorption and oxidation activity of NH3 was studied at temperature 0-550℃. Figure 4 shows that the NH3 desorption quantity of Cu8Ce3S after desulfurization does not decrease significantly comparing with Cu8Ce3, but the desorption peak of NH3 shifts to a high temperature direction. The NH3 desorption peak of Cu8Ce3 occurred at about 200℃, while the desorption peak of Cu8Ce3S moved to about 300℃, indicating that the adsorption strength of NH3 on Cu8Ce3S surface is stronger than that of Cu8Ce3. This difference is origin from the acidity change caused by SO42- on the surface of Cu8Ce3S catalyst[13]. It has been agreed that the acidity of the surface of the catalyst plays an important role in the adsorption of NH3 and the SCR reaction [13,14,15]. There are both Br-Ønsted and Lewis acid sites on the surface of CuO/γ-Al2O3 catalyst.
However, only the NH$_3$ in the Lewis acidic position has denitration activity, indicating that SO$_4^{2-}$ increases the number of Lewis acidic sites on the catalyst surface, which improves the adsorption strength for NH$_3$, and the higher NH$_3$ adsorption quantity at high temperature ensures that Cu8Ce3S has a high denitration efficiency.

The pore structure of the Cu8Ce3S catalyst was further investigated. From Table 1, it can be found that the specific surface area, pore volume, and pore diameter of the catalyst after sulfurization showed different degrees of reduction. However, due to the increase of Lewis acidic sites, the amount of NH$_3$ adsorption did not change significantly.

![Fig 3. NH$_3$ desorption performance of catalyst before and after desulfurization](image)

**Fig 3.** NH$_3$ desorption performance of catalyst before and after desulfurization

| Sample    | BET surface area $A$ (m$^2$/g) | Pore volume (cm$^3$/g) | Average Diameter (nm) |
|-----------|---------------------------------|------------------------|-----------------------|
| Cu8Ce3    | 201.4769                        | 0.418285               | 5.7514                |
| Cu8Ce3S   | 192.3416                        | 0.398967               | 5.5669                |

![Fig 4. NH$_3$ oxidation performance of catalyst before and after desulfurization](image)

**Fig 4.** NH$_3$ oxidation performance of catalyst before and after desulfurization

Fig. 4 shows that the NH$_3$ oxidation and NO formation rate of Cu8Ce3S are lower than that of Cu8Ce3 at 150-500°C. The NH$_3$ oxidation rate of Cu8Ce3 at 300°C is 54%, which is much higher than 24% of Cu8Ce3S, which can be considered as the reason for the difference in the denitration efficiency of Cu8Ce3 and Cu8Ce3S at this temperature. After the introduction of SO$_2$, the active components CuO and CeO$_2$ on the surface of the fresh catalyst quickly react with SO$_2$ to form CuSO$_4$ and Ce$_2$(SO$_4$)$_3$[8], whose catalytic activity were lower than that of CuO and CeO$_2$. This is the reason why the catalytic activity of Cu8Ce3 decreases at low temperature. At 350-500°C, the NH$_3$ oxidation rate of Cu8Ce3 is 80-90%, Cu8Ce3S is 40% -80%, and the NO oxidation formation rate of Cu8Ce3S
is lower than that of Cu8Ce3, indicating that most of NH3 is oxidized to N2 and that the presence of CuSO4 and Ce2(SO4)2 improved the selectivity of the catalyst for NH3.

4. Conclusion
When the flue gas temperature is lower than 350°C, the presence of SO2 has a poisoning effect on the catalyst's denitrification performance, but this poisoning effect is reversible. When the flue gas temperature is higher than 350°C, the presence of SO2 can improve the denitrification performance of the catalyst.

CuSO4 and Ce2(SO4)2 sulfate species formed on the catalyst surface have a denitration activity below 350°C that is lower than CuO and CeO2, which is the root cause of the decrease in denitrification efficiency at low temperatures. The catalytic selectivity of sulfate species to NH3 is higher than that of CuO and CeO2 at 350-500°C, which is the fundamental reason for the improvement of denitrification efficiency at high temperatures.

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