Study on Denitration Performance of CeO$_2$ Modified CuO/γ-Al$_2$O$_3$ Catalyst Under Different Flue Gas Components

Qi-Long ZHANG $^{1,*}$, Yong DONG$^2$, Lin CUI$^2$

1 Shandong Branch of Huadian Electric Power Research Institute, No.14508, Jingshi Road, Jinan 250014, Shandong Province, China
2 National Engineering Laboratory For Coal-fired Pollutants Emission Reduction, Shandong University, Jinan 250061, China
*Email:1353206004@qq.com

Abstract: The effects of different flue gas components such as n(NH$_3$)/n(NO) ratio, SO$_2$ and H$_2$O on the NO removing efficiency of Cu8Ce3 catalyst were studied in a fixed bed reactor. The experimental results show that the diffusion pressure and diffusion rate of NH$_3$ in the catalyst microporous are the main factors affecting the NO removing efficiency, when n(NH$_3$)/n(NO) ratio < 1.05. The n(NH$_3$)/n(NO) ratio no longer plays a decisive role in the denitration efficiency, when n(NH$_3$)/n(NO) ratio > 1.05. The effect of water vapor and SO$_2$ on the denitration efficiency is different at 350°C and 400°C. The water vapor and NH$_3$ have a competitive adsorption relationship on the catalyst surface, which reduces the adsorption of NH$_3$ on the catalyst surface. This is the reason why the efficiency is suppressed at 350°C; the addition of water vapor can improve the surface acidity of the catalyst at 400°C, which is why the denitration efficiency is improved at this temperature. At 400°C, the adsorption rate of SO$_2$ on the surface of Cu8Ce3 catalyst is higher than that at 350°C. As the temperature of flue gas increases, the adsorption amount of NH$_3$ on the catalyst surface is reduced. This is why the denitration efficiency is depressed under the SO$_2$ intervention. The adsorption and oxidation efficiency of NH$_3$ in the sulfided catalyst at 400°C is improved, which is the main reason for the improvement of denitration efficiency at this temperature.

1. Introduction

Selective catalytic reduction (SCR) is the most effective process for removing nitrogen oxides from coal-fired flue gas from power plants. Until now, the most widely used catalyst in industrial applications is V$_2$O$_5$-WO$_3$(MoO$_3$)/TiO$_2$[1-2], but it has the problems of high NO removing temperature and narrow temperature window (300-400°C)[3-5], In the low-load phase of start-up and shutdown of the unit, it is easy to cause NOx exceeding the emission standard. Among the developed SCR catalysts, the CeO$_2$ modified CuO/γ-Al$_2$O$_3$ catalyst has been widely concerned because of its high medium and low temperature denitration efficiency[3, 5, 6]. Therefore, the modification of copper-based catalysts with CeO$_2$ as an auxiliary agent is expected to obtain better low-temperature denitration performance and a wider denitration temperature window. However, the denitration performance of CuO-CeO$_2$/γ-Al$_2$O$_3$ catalysts in industrial applications needs further verification.

In this paper, the denitration performance of CuO/γ-Al$_2$O$_3$ absorbent modified by CeO$_2$ was studied in different reaction atmosphere in a fixed bed reactor. The effects of different simulated flue gas components on the denitration efficiency of the catalyst were studied in depth, and the internal mechanism of the influence was revealed.
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$^{-1}$, 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$^{-1}$, Tianjin Zhonghai Oil Chemical Research Institute). Fresh γ-Al$_2$O$_3$ was kept in Cu(NO$_3$)$_2$ and Ce(NO$_3$)$_3$ aqueous solutions for 4h at room temperature followed by evaporation at 90°C with stirring. After dried in oven for 20h and subsequently calcined under N$_2$ air for 6h at 500°C 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$_2$.

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) shown in fig 1. A monolithic catalyst sample (50mesh) was fitted in the reactor and heated to the setting temperature at steady state, A gas mixture containing 750ppm NO, 900ppm NH$_3$, 2000ppm 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 0-2000ppm, NH$_3$ measurement range is 0-2000ppm, 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%.

![Diagram](image)

1. Gas cylinder; 2. Pressure reducing valve; 3. mass flowmeter; 4. Steam generator; 5. Gas mixer; 6. Constant temperature water bath; 7. Fixed bed reactor; 8. heating furnace; 9. FTIR analyzer

Fig 1. system diagram

3. Experimental results and discussion

3.1 Effect of n(NH$_3$)/n(NO) ratio on denitration efficiency

Fig 2 shows that the NO removing efficiency increases as the n(NH$_3$/n(NO) ratio increases when n(NH$_3$)/n(NO)<1.05 and almost unchanged with the increase of the n(NH$_3$)/n(NO) ratio when n(NH$_3$)/n(NO)>1.05. The optimum n(NH$_3$)/n(NO) ratio of the catalyst in denitration process used in this experiment is 1.05. S. Albonetti et al$^{[7]}$ believes that the denitrification reaction is controlled by internal diffusion and out diffusion of ammonia in the catalyst pores at higher reaction temperature. while the higher n(NH$_3$)/n(NO) ratio, A higher ammonia diffusion pressure can be formed in the catalyst pores and the gas diffusion rate of NH$_3$ is increased and the denitration efficiency of the catalyst is improved. It can be inferred that when the n(NH$_3$)/n(NO) ratio exceeds 1.05, the diffusion of ammonia gas in the catalyst pores, which plays a major role in the denitrification reaction in the case of lean NH$_3$, no longer plays a major role in the denitrification reaction. Centi et al$^{[8]}$ has reported
that NO conversion over 4.8wt % CuO/γ-Al₂O₃ passes through a maximum value at NH₃/NO=1. Zhao Qingsen⁹ has reported that NH₃ oxidation performance is increased with the addition of CeO₂ in the catalyst. It can be inferred that the CuO-CeO₂/γ-Al₂O₃ catalyst used in this test oxidizes more NH₃ during the denitration process compared to the CuO/γ-Al₂O₃ catalyst [⁸]. This is why the catalyst used in this test requires a higher n(NH₃)/n(NO) ratio during the denitration process.

![Fig 2. Effect of n(NH₃)/n(NO) ratio on denitration efficiency](image)

3.2 Effect of water vapor content on denitration efficiency

The coal-fired flue gas contains a certain amount of water vapor. In order to better investigate the commercial application prospect of CuO-CeO₂/γ-Al₂O₃. In this experiment, water vapor was added to the simulated flue gas at 350°C and 400°C respectively to investigate the effect of water vapor on the denitration performance of the catalyst. Fig 3 shows that the denitration efficiency under both temperature conditions has a decreasing trend with the increase of water vapor content in the simulated flue gas, indicating that the increase of water vapor content is not conducive to the denitration reaction, which is due to the competitive adsorption between water vapor and NH₃ [¹⁰]. During the experiment, it was also found that the denitration efficiency gradually returned to the original level as the supply of water vapor decreased, indicating that water vapor does not poison the catalyst. The denitration efficiency of the catalyst at 400°C has been higher than that of 350°C, indicating that the presence of water vapor increases the denitration efficiency of the catalyst at higher temperatures. It is believed that the inhibition of catalyst activity by water vapor is mainly [¹⁰] because water vapor can combine with the acid center of the catalyst surface, affecting the effective adsorption of NH₃ on the active center, thus forming competitive adsorption, thereby reducing the SCR reaction rate. At 400°C, the addition of water vapor can improve the surface acidity of the catalyst and increase the adsorption amount of NH₃ by the catalyst, which is the reason for the denitration efficiency.
3.3 Effect of SO\textsubscript{2} on denitrification efficiency

Under the simulated flue gas composed of 788ppm NH\textsubscript{3}, 750ppm NO and 5%O\textsubscript{2}, The denitrification efficiency of the catalysts were investigated before and after the addition of SO\textsubscript{2} at 350°C and 400°C, respectively. This experiment adopts the transient method. 2000 ppm of SO\textsubscript{2} was added to the simulated flue gas for denitrification efficiency test, when the denitrification efficiency was stable for one hour and the SO\textsubscript{2} was cut off in the simulated flue gas to observe the change of denitrification efficiency after the denitrification efficiency was stabilized for another 1h. As shown in Fig 4, the denitrification efficiency of Cu8Ce3 is stable at about 98% at 350°C, when there is no SO\textsubscript{2} in the flue gas and decreases sharply to 70% at 75 min, when SO\textsubscript{2} is introduced at 350 °C, then the denitrification efficiency remains stable as the reaction proceeds. The denitrification efficiency of the Cu8Ce3 catalyst quickly recovered to about 90%, when SO\textsubscript{2} was removed at 190min , which was lower than that before, indicating that SO\textsubscript{2} poisoned the catalyst at 350°C. A similar experimental phenomenon appeared after the intervention of SO\textsubscript{2} at 400 °C, the denitrification efficiency decreases sharply to about 64%, when the SO\textsubscript{2} is removed and is restored to the level before the SO\textsubscript{2} is introduced, indicating that the SO\textsubscript{2} catalyst is poisoned in denitrification process as SO\textsubscript{2} intervening at 400 °C.

3.4 Sulfur capacity of the Cu8Ce3 absorbent

In order to further examine the competitive adsorption relationship between SO\textsubscript{2} and NH\textsubscript{3} on the catalyst surface, The effect of temperature on the sulfur capacity of Cu8Ce3 in the temperature 350 and 400°C was studied experimentally. The calculated typical gas composition was 2000ppm SO\textsubscript{2},
5%O₂, and N₂ as the balance and the total flow rate was controlled at 0.4L/min. The test is stopped when the SO₂ detected by the outlet stream exceeds 360 ppm (desulfurization efficiency ≥ 80%), and the time (t₀) consumed is defined as the adsorption saturation time, which is recorded by the computer. Fig 5 shows the SO₂ adsorption saturation time (t₀) of Cu8Ce3 is 56min at 350°C, 88min at 400°C, increasing significantly with the increase of temperature.

The adsorption capacity and adsorption rate of SO₂ for Cu8Ce3 catalyst at 400°C is significantly higher than that of 350°C. It is speculated that the competitive adsorption strength of SO₂ and NH₃ on the catalyst surface is higher than that of 350°C, indicating that the adsorption of NH₃ on the catalyst surface is reducing resulting in low-denitration efficiency, which explains why the denitration efficiency of Cu8Ce3 catalyst at 400°C is lower than that of 350°C during SO₂ intervention. The denitration efficiency of Cu8Ce3 at 400°C is significantly higher than that of 350°C. When SO₂ is removed from the flue gas, indicating that the desulfurization moves the denitration temperature window of the catalyst to the high temperature direction. Xie Guoyong’s research [11,12] shows that the denitrification activity of the CuO/γ-Al₂O₃ catalyst depends on the NH₃ adsorption amount and oxidation activation which were improved under desulfurization at 400°C, correspondingly, the denitrification activity is also gradually increased.

4. Conclusion
N(NH₃)/N(NO) ratio is the determinant of denitration efficiency by increasing the diffusion pressure and diffusion rate in the NH₃ catalyst channel when n(NH₃)/n(NO)<1.05, however, it will no longer plays a major role in denitration efficiency when n(NH₃)/n(NO)>1.05, The optimum n(NH₃)/n(NO) ratio of the denitration catalyst used in this test was 1.05. With the introduction of H₂O, water vapor can combine with the acid center of the catalyst surface, affecting the effective adsorption of NH₃ on the active center, by forming competitive adsorption with NH₃ on the catalyst surface, which is the reason why the denitration efficiency is suppressed at 350°C. The addition of water vapor can improve the surface acidity of the catalyst and increase the adsorption capacity of the catalyst for NH₃ at 400°C, which is the reason for the denitration efficiency improved.

The adsorption rate of SO₂ on the surface of Cu8Ce3 catalyst under 400°C is higher than that of 350°C, which leads to the adsorption of NH₃ on the catalyst surface at 400°C less than that of 350°C, which is the important cause of the inhibition of denitration efficiency under SO₂ intervention. The oxidized efficiency of NH₃ on the catalyst surface is improved after desulfurized, which is the main reason for the denitration efficiency being improved at 400°C.

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