Denitration performance of CuO/γ-Al₂O₃ catalysts modified by CeO₂

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Abstract. CuO-CeO₂/γ-Al₂O₃ catalysts with different CeO₂ loadings were synthesized by wet impregnation method. Selective catalytic reduction (SCR) of NO over the two kinds of catalysts was carried out in a fixed bed reactor. CuO-CeO₂/γ-Al₂O₃ catalysts reached NO conversion efficiency 65% at 150°C and maintained over 80% at 200-400°C. The maximum efficiency is stably reached at 300°C. CuO-CeO₂/γ-Al₂O₃ catalysts showed wider temperature range than that of the CuO/γ-Al₂O₃. NH₃-TPD tests were carried out to study the adsorption and oxidation behavior of NH₃ over CuO-CeO₂/γ-Al₂O₃ catalysts with different CeO₂ loadings in the presence of oxygen. The NH₃ adsorption and activation performance were modified attributing to the modification of the Surface acidity of the CuO-CeO₂/γ-Al₂O₃ catalysts. The mass transfer was improved due to the promotion of the pore numbers in 8-50, 50-200μm which was another NO conversion promotion factor. Surface acidity and the pore volume decreased obviously as CeO₂ overloaded in CuO-CeO₂/γ-Al₂O₃, with a negative influence of NH₃ adsorption and oxidation performance. It is considered to be the main factor of the NO conversion efficiency decreased. Introduction

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 V₂O₅-WO₃(MoO₃)/TiO₂ [1-2], but it has the problems of high NO removing temperature and narrow temperature window (300-400°C) [3-5]. Therefore, it is necessary to develop a new SCR catalyst with a higher temperature and a wide temperature window.

It is found that the low temperature catalytic activity sequence of metal oxides at low temperature (120°C) is Mn>Cu≥Co>Fe>V>Ni[6-7], in which copper oxides show better middle low temperature catalytic activity[8], and CeO₂ is often added as an auxiliary agent in the catalyst to improve the oxygen storage capacity of the catalyst and to improve its activity[9-11]; in addition, CeO₂ can also act as a dispersion to enhance the thermal stability and anti-sintering ability of catalyst[12] and to enhance the adsorption capacity of the catalyst for NH₃ and to improve the low-temperature catalytic activity of the catalyst[13]. Therefore, the modification of copper-based catalysts with CeO₂ is expected to obtain more excellent low-temperature denitrification performance and a wider denitrification temperature window.
This paper aimed at investigating the denitration performance of the copper-based catalysts modified by CeO$_2$ at different temperatures. The techniques employed were XRD, BET, NH$_3$-TPD. The effects of CeO$_2$ loading, NH$_3$ adsorption and oxidation activity on the catalysts, and pore structure on the denitration activity were detailed investigated, revealing the intrinsic mechanism of the influence.

2. Methodologies

2.1. Catalyst preparation

The CuO/γ-Al$_2$O$_3$ and CuO-CeO$_2$/γ-Al$_2$O$_3$ series catalysts were prepared by wet impregnation with pure γ-Al$_2$O$_3$ pellets(30-40mesh, BET surface area of 185m$^2$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 218m$^2$g$^{-1}$, Tianjin Zhonghai Oil Chemical Research Institute). Fresh γ-Al$_2$O$_3$ was being kept in different concentrations of Cu(NO$_3$)$_2$ and Ce(NO$_3$)$_3$ aqueous solutions for 4h at room temperature followed by evaporation at 90$^\circ$C with stirring. After dried in oven for 20h and subsequently calcined under N$_2$ air for 6h at 500$^\circ$C in muffle furnace, Finally, five catalysts of Cu8, Cu8Ce2, Cu8Ce3, Cu8Ce5 and Cu8Ce8 were obtained. The catalyst is termed as Cu8Cex in the text which contains 8.0 wt% of CuO and x wt% of CeO$_2$.

2.2. Experimental device and experimental method

The catalyst activity test was carried out in the fixed bed reactor (20mm in diameter and 1.25m in length) shown in Figure 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$_3$, 5%O$_2$,and balance N$_2$ is introduced into the reactor. In all the runs, the total flow rate was controlled at 0.4 L/min.

The adsorption and desorption experiment of NH$_3$ were carried out with temperature programmed desorption (TPD) method. In the research process, the catalyst was first dried at 600$^\circ$C for 1h, and was then transferred into a fixed bed of quartz tube, in which NH$_3$ (900ppm) and N$_2$ are absorbed in the catalyst for 2h, and then the surface adsorption was purged with N$_2$. The NH$_3$ was finally introduced into N$_2$ (0.4L/min) and programmed to 550$^\circ$C, at the heating rate of 8$^\circ$C/min, In which process the concentration of NH$_3$ (NO) at the outlet was detected synchronously.

The oxidation experiment of NH$_3$ with O$_2$ was carried out under NH$_3$(900ppm), O$_2$(5%) and N$_2$(as equilibrium gas, space velocity:10900h$^{-1}$) atmospheres to investigate the conversion of NH$_3$ at different temperatures.

The pore structure characteristics of the catalyst 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.

![Figure 1. System diagram.](image-url)
3. Experimental results and discussion

3.1. Denitration characteristics of the catalyst

The denitration performance of the catalyst under different CeO2 loadings at different temperatures are shown in Figure 2.

![Figure 2](image-url)

**Figure 2.** Effect of temperature on denitration performance of catalysts with different CeO2 content.

Figure 2 shows that the temperature has a significant effect on the denitration performance of the catalyst. The NO removing efficiency is gradually increased in the range of 150-300°C and is gradually decreasing in the range of 300-500°C, indicating that the NO removing efficiency of sample 2-sample 4 is significantly improved in the whole temperature range with the addition of CeO2. The NO removing efficiency of sample 2 to 4 can maintain more than 80% in the temperature range of 200°C-350°C, and that of sample 5 is the lowest in the same temperature range, indicating that there is an optimal load of CeO2, too high or too low load is not conducive to improve the NO removing efficiency.

3.2. Adsorption and oxidation characteristics of NH3 on catalyst surface

Since the denitration activity of the copper-based catalyst is related to the NH3 adsorption amount on the catalyst surface and the NH3 oxidation activity at different temperatures, the adsorption amount of NH3 on the catalyst surface is related to the acidity and temperature of the catalyst surface[14-15], and the surface acidity of the catalyst determines the denitration activity in the high temperature [16], the oxidation activity of the catalyst surface determines its denitration activity at low temperatures. Therefore, in order to reveal the inherent mechanism of denitration performance and temperature window change of the copper-based catalyst modified by CeO2, the adsorption and oxidation characteristics of NH3 on the catalyst surface were studied.

3.2.1. Adsorption characteristics of NH3 on catalyst surface. The process of NH3 adsorption and desorption properties as a function of temperature are shown in Figure 3. NH3 is seen to desorbed from the catalyst in the temperature range of 50-500°C and the NH3 desorption area of sample 2-5 is significantly higher than that of unmodified sample 1, attributing to the addition of CeO2. NH3 adsorption amount reaches the maximum when CeO2 loading is 5%, however, excessive CeO2 loading is unbeneficial, such as sample 5, the NH3 desorption amount is smaller than sample 4. The NH3 desorption temperature and desorption peak gradually shifted toward the high temperature as the CeO2 loadings increased indicating that thermal stability of NH3 is improved with the addition of CeO2.
It can also be seen from the Figure 3 that two major NH₃ desorption peaks (peak A and peak B) are observed for sample1-3 in the temperature ranges of 50-300 ℃ and 300–400 ℃, compared with sample4-5, which are only one desorption peak(peak A). This is characteristic of the presence of two adsorbed NH₃ species differing in thermal stability. This desorption peak intensity is corresponded to intensity of the acid adsorption site on the surface of the catalyst as previously mentioned[17-19]. The intensity of the acid adsorption site is enhanced with CeO₂ loading. It is reported in previous papers [19-23] that there are two kinds of acid sites on the surface of CuO/γ-Al₂O₃: Br Ønsted acid site and Lewis acid site. However, only NH₃ absorbed in Lewis acid site has denitration activity, and NH₃ absorbed in Br Ønsted Acid site does not participate in SCR reaction. The amount of NH₃ adsorbed at Lewis acid is the decisive factor of NO removing efficiency. It can be seen from the Figure 3 that the NO removing efficiency is directly proportional to the intensity of the desorption peak B, Sample 3 has the highest denitration efficiency, indicating that the NH₃ adsorbed on L acid site of sample 3 is the most, although the total amount of NH₃ adsorbed on sample 3 is lower than that on sample 4, and sample 2 and sample 5 have the same trend. Although the amount of NH₃ adsorbed on sample 3 is the same, the denitration efficiency of sample 2 is higher than that on sample 5, based on the results mentioned above, we can infer that there are one strong Lewis acid site at desorption peak B and one weak Lewis acid and Br Ønsted acid at desorption peak A.

**Figure 3.** NH₃ desorption characteristics as a function of the operating temperature.

**Figure 4.** NH₃ oxidization characteristics as a function of the operating temperature.
3.2.2. Oxidation characteristics of NH$_3$ on catalyst surface. The oxidation activity of the catalyst surface is related to its denitration activity at low temperatures. The oxidation performance of CeO$_2$ modified catalyst for NH$_3$ is shown in Figure 4.

Figure 4 shows that as the temperature increases, NH$_3$ is gradually oxidized, and the catalyst modified by CeO$_2$ has a significantly higher oxidation capacity for NH$_3$ than the unmodified catalyst. From the temperature point of view, the oxidation rate of NH$_3$ is gradually increased with the increase of CeO$_2$ loading in the range of 150$^\circ$C-200$^\circ$C, but the oxidation rate of NH$_3$ in the sample with the highest CeO$_2$ loading is the lowest in the modified catalyst. Corresponding to the order of denitration efficiency of the catalyst in this temperature range, this aspect shows that with the increase of CeO$_2$ loading, the oxidation activity of NH$_3$ is improved, and the low-temperature denitration performance of the catalyst is improved, and the CeO$_2$ loading is too high. The amount promotes the oxidation activity of the catalyst to move toward a high temperature direction, which is disadvantageous to the low temperature catalytic performance of the catalyst.

As the temperature continues to increase, the oxidation rate of NH$_3$ is further improved. At 350$^\circ$C, the NH$_3$ oxidation rate of all the samples has reached more than 80%, of which sample 5 reaches 95%, but the denitration efficiency at this temperature is mainly affected by the surface strongly acidic adsorption site of the catalyst, therefore, the denitration efficiency of sample 5 is still relatively low, although the oxidation rate of NH$_3$ is higher in this temperature.

3.3. XRD and BET characterization

The XRD analysis of each catalyst sample is shown in Figure 5. The diffraction peaks are 28°, 37°, 47° and 67°, respectively, of which 37°, 47° and 67° are distinct γ-Al$_2$O$_3$ phases, and 28° is the phase of CeO$_2$, the crystal phase of CuO is CuAl$_2$O$_4$, which diffraction peak is 38.8°, however, the addition of CeO$_2$ weakened the diffraction peak of CuAl$_2$O$_4$, indicating that the addition of CeO$_2$ reduced the CuO grain size and promoted the dispersion of CuO on the surface of the carrier[24]. With the increase of CeO$_2$ loading, the obvious CeO$_2$ diffraction peak appeared from sample 4. It indicated that the excessive CeO$_2$ in the sample formed multi-layer coverage on γ-Al$_2$O$_3$, resulting in the formation of larger grains on the surface of the active component.

![Figure 5. XRD analysis of the catalysts.](image-url)

Results in Table 1 imply that the specific surface area and pore volume of the catalyst decrease continuously, and the average pore diameter increases continuously as the CeO$_2$ loading increases. However, it can be seen from the pore size distribution curve of Figure 6 that the number of pores of the catalysts in the 8-50nm and 50-200nm, reaching a maximum in sample 3 and sharply reducing in sample 5, are gradually increased with more CeO$_2$ loading.
The analysis suggests that the mass transfer rate and reaction rate of the gas in the pore are related to the diffusion coefficient of gas in the pores of the catalyst surface. The diffusion of gas in the porous medium belongs to Knudsen diffusion, and its diffusion coefficient $D_e$ is

$$D_e = \frac{D_e \varepsilon_p}{\tau} \quad (1)$$

Where $D_e$ is the comprehensive diffusion coefficient; $\varepsilon_p$ is the surface porosity of the catalyst, and $\tau$ is the bending factor.

Increasing the number of pores from 50nm to 200nm is beneficial to increase the overall diffusion coefficient $D_e$, thereby increasing the mass transfer rate of the gas in the pores of the catalyst, further increasing the catalytic efficiency of the catalyst[26].

### Table 1. Pore structure parameter of the catalysts.

| Sample | BET surface area $A \,(m^2/g)$ | Pore volume $(cm^3/g)$ | Average Diameter $(nm)$ |
|--------|--------------------------------|------------------------|-------------------------|
| 1      | 201.4871                       | 0.416385               | 5.7514                  |
| 2      | 193.2814                       | 0.419685               | 5.5974                  |
| 3      | 190.8290                       | 0.407840               | 5.7186                  |
| 4      | 187.0714                       | 0.387058               | 6.5263                  |
| 5      | 158.0065                       | 0.364095               | 7.8524                  |

**Figure 6.** Pore size distribution of samples 1 to 5.

Therefore, although the specific surface area of samples 2 and 3 modified by CeO$_2$ is slightly decreased, the number of pores in the surface of the sample is greatly improved in the range of 50-200 nm, which contributes to the improvement of the NH$_3$ in the adsorbed state and the NO in the gaseous state, another reason for the improvement of the denitration efficiency. However, due to the overloading of CeO$_2$, the specific surface area pore, volume and the number of pores in the range of 50 to 200nm of sample 5 decreased dramatically, which was due to the fact that the active components on the catalyst surface are agglomerated due to the excessive CeO$_2$ loading, blocking the surface gap of the catalyst[27]. which was not conducive to the formation of such pore structure. The mass transfer rate of surface chemical reaction was inhibited, which was also the main reason for the significant decrease in catalytic activity.
4. Conclusions
The addition of CeO<sub>2</sub> can increases the temperature range of 200-400°C significantly, NO removing efficiency can be maintained above 80% in this temperature range and can reach 90% at 250°C, showing better NO removing efficiency at low temperature. The NO removing efficiency show best when CeO<sub>2</sub> is at 3% loading. However, excessive CeO<sub>2</sub> addition is unbeneficial for NO removing efficiency.

The addition of CeO<sub>2</sub> improves the surface acidity of the catalyst, which improves the adsorption capacity of the catalyst for NH<sub>3</sub>, that improving the denitration performance of the catalyst at high temperature, and the oxidation performance of NH<sub>3</sub>, which improves the low-temperature denitration performance of the catalyst, thereby improving the overall efficiency. The denitration performance and temperature window of the modified catalyst are improved as a whole.

The addition of CeO<sub>2</sub> increases the number of pores in the catalyst within 50 to 200um, increasing the mass transfer rate of the chemical reaction in the pores of the catalyst, and thus improving the denitration efficiency. Excessive CeO<sub>2</sub> loading reduces the specific surface area and pore volume of the catalysts, and the number of pores in the range of 50 to 200nm is also drastically reduced, resulting in a decrease in denitration performance.

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