Effect of Combustible Gas Components on SNCR Reaction with Reducing Agent in Ceramic Kiln

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Abstract. Selective non-catalytic reduction (SNCR) is a denitrification method used in NOx process-control of ceramic kiln. In this study, the effect of combustion gas components (CO, H₂, CH₄) on NOx removal in the SNCR process was investigated, using ammonia and urea as reducing agent in a lab-scale experimental platform. The results showed that the addition of CO slightly promoted the NOx removal efficiency when ammonia was used as reducing agent, while when urea was used as reducing agent, the addition of CO inhibited the denitrification. The increase of H₂ and CH₄ addition ratio in the simulated flue gas reduced the de-NOx efficiency. With the same addition ratio, the effect of CH₄ on the reduction of denitration efficiency was much more obvious than that of H₂. When ammonia was used as reducing agent, the ammonia escape was much greater than that of urea.

1. Introduction
Ceramic industry is one of the traditional advantageous industries in China, which counts for considerable amount of NOx emission of industrial sources. At present, the technology of dust removal and desulfurization has been widely used in ceramic flue gas treatment, but the research and application of NOx control is still lagging behind. NOx control technologies can be broadly divided into three categories: “pre-combustion”, “combustion modification” and “post-combustion”, in which the third one refers to flue gas treatment after the combustion process [1]. Two major post-combustion de-NOx technologies are the selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR), which are widely used in various industries. For ceramic industry, there are mainly two flue gas discharge ports, one is the combustion furnace of the spray drying tower, the other is the ceramic kiln after combustion [2]. The temperature of flue gas discharged from ceramic kiln is around 150 °C, which only low temperature SCR denitration technology is suitable. SNCR is a useful method for the control of NOx emission by injecting reducing agent into the flue gas at the relatively higher temperature range of 850 - 1100 °C [3]. Meanwhile, the temperature of burning area of ceramic kiln is at the same temperature window. Therefore, using SNCR technology in ceramic kiln for NOx control draws more and more attention. The performance of the SNCR process is affected by several parameters. Since the laboratory research of Lyon [4], many investigations on the flue components were conducted, but only focused on the oxygen content [5] and NO initial concentration [6], few studies have reported the effect of other gas component. In this study, the effect of combustible gas composition...
(CO, H₂ and CH₄) on the removal efficiency in the SNCR process was investigated, using an injection of ammonia and urea in a lab-scale experimental platform.

2. Materials and method

2.1. Experimental platform and steps

In this study, the experiment was carried out on a denitrification experimental platform, which consists of four parts: gas distribution and temperature control system, reaction furnace, denitrification agent injection system and tail gas treatment system. The main experimental steps were as follows: first, raising the high-temperature reactor to the experimental temperature in advance. Second, introducing the simulated flue gas into the reactor through the gas distribution system. After 10 min of stabilization, the initial concentration of NO and NO₂ were measured. Then reducing agent was injected into the reaction furnace from the injection system. 10 min latter, the concentrations of NO and NO₂ after reaction were measured, and part of the flue gas was collected by absorbing flask for latter NH₃ escape test.

The basic experimental conditions were as follow: NSR 1.0, total gas flow 10 L/min, reaction temperature 850-900 °C, oxygen content 10%(v/v), CO₂ concentration 10%(v/v), NO initial concentration 400-450 ppm, which simulated the flue gas atmosphere of burning area of ceramic kiln.

2.2. Analytical methods

The concentration of NOx (NOx=NO + NO₂) before and after de-NOx process were detected by flue gas analyzer (Testo 350, Germany). NOx removal efficiency is defined as follow:

\[
\text{NOx Removal} = \frac{(\text{NOx}_{\text{in}} - \text{NOx}_{\text{out}})}{\text{NOx}_{\text{in}}} \times 100\% \quad (1)
\]

The concentration of NH₃ was detected by Ion chromatography (IC, Thermol ICS1100, America) after collected by air sampler (Laoying 2020, China) at a flow rate of 0.5 L/min for 20 min. The concentration of NH₃ after denitration process is defined as follow:

\[
\text{NH}_3 (\text{mg/m}^3) = \frac{\text{NH}_3 (\text{mg/L}) \times V_0}{V_{\text{nd}}} \quad (2)
\]

Which, NH₃(mg/L) - the concentration of NH₃ detected by IC; V₀ - the volume of absorption liquid ml; V_nd - flue gas sampling volume in standard state (101.325kPa, 273K), L.

3. Results and discussion

The effect of CO, H₂ and CH₄ on denitration efficiency with the addition ratio increasing from 0% (m/m, combustible gas / NO) to 100% were shown in figure 1-3.

![Figure 1](image1.png)

(a) reducing agent: ammonia
(b) reducing agent: urea

Figure 1. Effect of CO on SNCR reaction with denitrification reductant

It can be seen in figure 1 that the addition of CO can slightly promote the NOx removal when aqueous ammonia was used as denitration reducing agent. When the addition ratio of CO was 0, the NOx
removal efficiency was 60.86%. As the addition ratio increased as equal as NO, which was 400 ppm, the NOx removal rose to 70.48%. Kiplinen et al [7] believes that the presence of NH3 inhibits the oxidation of CO, and CO would promote the reaction of NH3 and O2 to generate NO, leading to the reduction of denitration effect. On the other hand, when the concentration of CO increases, more OH groups can be generated by reaction (3) - (5), which can increase the reaction rate of reaction (6), so the removal efficiency of NOx in this stage rises. However, when the urea was used as de-NOx agent, the results were just the opposite. With the increase of the CO addition ratio, the NOx removal efficiency decreased. When the CO addition ratio was 400 ppm, the NOx removal efficiency dropped to 34.38%. Comparing the ammonia escape when ammonia and urea used as NOx reducing agent, it can be found that the ammonia escape decreased with the increasing CO addition ratio, and exceeded relative standard when the CO addition ratio was less than 70%. As the CO addition ratio rose to 100%, the ammonia escape was 5.63 mg/m³. And when urea used as NOx reducing agent, the ammonia escape met the standard requirement, as the urea addition ratio rose from 0% to 100%.

\[
\begin{align*}
\text{CO} + \text{OH} & \rightarrow \text{CO}_2 + \text{H} \quad (3) \\
\text{H} + \text{O}_2 & \rightarrow \text{OH} + \text{O} \quad (4) \\
\text{O} + \text{H}_2\text{O} & \rightarrow 2\text{OH} \quad (5) \\
\text{NH}_2 + \text{NO} & \rightarrow \text{N}_2 + \text{H}_2\text{O} \quad (6)
\end{align*}
\]

![Figure 2](image_url)

(a) reducing agent: ammonia

(b) reducing agent: urea

Figure 2. Effect of H2 on SNCR reaction with denitration reductant

The effect of H2 on SNCR reaction with reducing agent was shown in figure 2. It can be seen in figure 2 that the increase of H2 addition ratio in the simulated flue gas reduced the denitration efficiency. When the H2 addition ratio was 100%, which was 400 ppm, the NOx removal efficiency dropped to 11.94%. The NOx control effect decreased as urea used as NOx reducing agent as well, while the decrease scope was not as great as ammonia used. It can be inferred that H2 played an inhibitory role in NOx removal, as reaction (7) and (8), consuming OH and O in the system. Thus, the reaction (6), (9) and (10) were inhibited, and the denitration efficiency was reduced. The ammonia escape was a lot less when H2 was introduced into the system, and slightly decreased with the increasing addition ratio. The ammonia escape remained quite small, and all met the standard requirement when urea was used as de-NOx agent.

\[
\begin{align*}
\text{H}_2 + \text{O} & \rightarrow \text{H}_2\text{O} \quad (7) \\
\text{H}_2 + 2\text{OH} & \rightarrow 2\text{H}_2\text{O} \quad (8) \\
\text{NH}_3 + \text{OH} & \rightarrow \text{NH}_2 + \text{H}_2\text{O} \quad (9) \\
\text{NH}_3 + \text{O} & \rightarrow \text{NH}_2 + \text{OH} \quad (10)
\end{align*}
\]
The effect of CH₄ on SNCR reaction with denitrification reductant was shown in figure 3. When the aqueous ammonia and urea were used as de-NOx agent, the NOx removal efficiency decreased as the addition ratio raised. The reason was similar to that of H₂. With the same addition ratio, the effect of CH₄ on the reduction of denitrification efficiency was much more obvious than that of H₂. It can be concluded that the presence of CH₄ consumes OH and O in the system while the concentration of CO generated is low (reaction (11) and (12)), which eventually leads to the reduction of denitrification efficiency. When the addition ratio of CH₄ was 100%, which was 400 ppm, the NOx removal was 18.20% when aqueous ammonia was used and 37.30% as urea used. The ammonia escape was all above 8 mg/m³ with the CH₄ addition ratio rose from 0 to 100% when the ammonia was used as de-NOx agent, which exceeded standard value and much greater than that of urea used as NOx reducing agent.

\[
\text{CH}_4 + 6\text{OH} \rightarrow \text{CO} + 5\text{H}_2\text{O} \quad (11)
\]

\[
\text{CH}_4 + 3\text{O} \rightarrow \text{CO} + 2\text{H}_2\text{O} \quad (12)
\]

Figure 3. Effect of CH₄ on SNCR reaction with denitrification reductant

4. Conclusion

In this study, the effect of combustible gas composition on SNCR reaction with reducing agent in cement kiln was studied, the main conclusions are shown as follows:

1. The addition of CO slightly promoted the NOx removal when the aqueous ammonia was used as de-NOx reducing agent, while when urea was used as reducing agent, the addition of CO inhibited the denitification.

2. The increase of H₂ and CH₄ addition ratio in the simulated flue gas reduced the denitrification efficiency. With the same addition ratio, the effect of CH₄ on the reduction of denitrification efficiency was much more obvious than that of H₂.

3. The ammonia escape was much greater when aqueous ammonia used as de-NOx agent, and barely met relative standard requirement.

Acknowledgments

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