Pilot scale study on medium/low temperature SCR denitration technology for industrial flue gas

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Abstract: Based on laboratory research, the titanium-based honeycomb molding catalysts with MnO\textsubscript{x}/CeO\textsubscript{2}/V\textsubscript{2}O\textsubscript{5} as the main active material were prepared, and a pilot scale study on medium/low temperature SCR denitration technology for ceramic kiln flue gas was carried out on a 5000 m\textsuperscript{3}/h pilot scale equipment. The influences of flue gas flow, ammonia-nitrogen molar ratio and ammonia concentration on denitration efficiency were investigated. The result showed that the medium-low temperature SCR denitration technology had an excellent NO\textsubscript{x} removal efficiency. Under the conditions of the flue gas flow was 3000 m\textsuperscript{3}/h, the ammonia-nitrogen molar ratio was 1.2:1, and the ammonia concentration was 25%, the NO\textsubscript{x} removal efficiency could reach 86%, and NO\textsubscript{x} emission concentration and ammonia escape amount were less than 40 mg/m\textsuperscript{3} and 1 mg/m\textsuperscript{3} in the flue gas, respectively. The technology can achieve deep reduction of NO\textsubscript{x} in ceramic kiln flue gas, and has a good application prospect.

1. Introduction
Nitrogen oxides (NO\textsubscript{x}) emitted from the combustion of fossil fuels are one of the main atmospheric pollutants, which have given rise to damage the ecological environment and eventually endanger human health in a direct or indirect way\textsuperscript{[1,2]}. In the existing flue gas denitration technology, the high temperature (300-400 °C) selective catalytic reduction (SCR) technology has been relatively mature. The catalyst bed is placed after the economizer and before desulfurization and dedusting system. However, the catalysts are easily poisoned in a high sulfur and high dust environment, which seriously affect its activity and service life. Therefore, vigorous development of medium/low temperature SCR catalysts are promising because the denitration reactor can be located downstream of the particulate control device and desulfurization system, where the temperature is about 120–250 °C\textsuperscript{[3,4]}. In recent years, the research on medium/low temperature SCR catalysts has been greatly developed\textsuperscript{[5-7]}, and honeycomb catalysts have uniform distribution of active components, and can maintain strong activity even if the surface of catalysts are worn. Therefore, honeycomb catalysts are most widely used in the SCR denitration project\textsuperscript{[8,9]}. In this study, the titanium-based honeycomb molding catalysts with MnO\textsubscript{x}/CeO\textsubscript{2}/V\textsubscript{2}O\textsubscript{5} as the main active material were prepared, and a pilot scale study on medium/low temperature SCR denitration technology for ceramic kiln flue gas was carried out on a 5000 m\textsuperscript{3}/h pilot equipment. Meanwhile, the influences of flue gas flow, ammonia-nitrogen molar ratio and ammonia concentration on the denitration efficiency were also systematically investigated. The research results can provide technical support for the ceramic kiln flue gas denitration.
2. Experimental section

2.1 Characteristics of ceramic kiln flue gas

The ceramic factory is located in Guangdong province, China. The emission concentrations of particulate matter, \( \text{SO}_2 \), and \( \text{NO}_x \) from ceramic kiln flue gas are 32-58 mg/m\(^3\), 512-565 mg/m\(^3\) and 113-209 mg/m\(^3\), respectively. While the current emission limits for \( \text{SO}_2 \) and \( \text{NO}_x \) are 50 and 100 mg/m\(^3\), respectively. So that the emission concentrations of \( \text{SO}_2 \) and \( \text{NO}_x \) from ceramic kiln flue gas are exceeding the current emission standards. Therefore, efficient pollution control technologies must be developed to reduce pollutant emissions. The pollutant emission characteristics of ceramic kiln flue gas are shown in Table 1.

| Ceramic kiln flue gas pollutants | Temperature (°C) | particulate matter (mg/m\(^3\)) | \( \text{SO}_2 \) (mg/m\(^3\)) | \( \text{NO}_x \) (mg/m\(^3\)) |
|-------------------------------|-----------------|---------------------|-------------------|------------------|
| Emission concentrations       | 180-250         | 32-58               | 512-565           | 113-209          |
| Average emission concentrations| 220             | 40.7                | 522               | 145              |

2.2 Molding of honeycomb catalyst.

The prepared titanium-based catalyst powder was mixed with binder, pore former, lubricant, and then titanium-based honeycomb molding catalyst for final industrial application was obtained through the process contain kneading, extrusion molding and drying. The size of the prepared monolith catalyst is 0.15×0.15×0.9 m. The appearance of the honeycomb catalyst is shown in Fig.1.

![Fig.1 The appearance of honeycomb molding catalyst](image)

2.3 Design of the medium/low temperature SCR denitration pilot scale equipment

The pilot equipment with the size of 0.8×0.8×4.0 m was designed for a maximum gas flow of 5000 m\(^3\)/h. A total of 2 layers of catalysts were filled in the equipment, the interval between each layer of catalysts was 1m. In addition, each layer contain 25 pieces of prepared honeycomb catalyst, thus the amount of catalysts installed in the entire denitration pilot plant were 50 monoliths, and the total packed volume of the catalysts were 1 m\(^3\).

3. Results and discussion

The denitration pilot scale equipment was located in the ceramic factory of Guangdong province, China. The basic operating conditions for denitration experiments: the flue gas flow was 3000 m\(^3\)/h, the ammonia-nitrogen molar ratio was 1.2:1 and the ammonia concentration was 25%.
3.1 The effect of flue gas flow
Under the premise of basic experimental conditions, the influence of flue gas flow on the NO\textsubscript{x} removal efficiency was investigated, the result is shown in Fig.2. It can be seen that with the increasing of flue gas flow, the NO\textsubscript{x} removal shows a significant downward trend. When the flue gas flow increased from 2000 to 5000 m\textsuperscript{3}/h, the NO\textsubscript{x} removal rapidly decreased from 86.6% to 78.7%; This phenomenon may be attributed to the fact that the molecular weight of NH\textsubscript{3} contacted by the unit gas is relatively decreased when the flue gas flow increases, and the contact time between NO\textsubscript{x} and NH\textsubscript{3} in the flue gas is insufficient, thereby reducing the reduction effect of NH\textsubscript{3} on NO\textsubscript{x}. When the flue gas flow range is 2000-3000 m\textsuperscript{3}/h, the NO\textsubscript{x} removal efficiency can be maintained over 85%.

![Fig.2 Influence of flue gas flow](image)

3.2 The effect of ammonia-nitrogen molar ratio
Under the premise of basic experimental conditions, the amount of NH\textsubscript{3} entering the SCR equipment was adjusted. The designed ammonia-nitrogen molar ratios were 0.7:1, 0.8:1, 1:1, and 1.2:1, respectively. The effect of ammonia-nitrogen molar ratio on the NO\textsubscript{x} removal is shown in Fig.3. It can be seen that the NO\textsubscript{x} removal shows a significant upward trend with the increasing of ammonia-nitrogen molar ratio. When the ammonia-nitrogen moral ratio increases to 0.8:1, the NO\textsubscript{x} removal efficiency is more than 75%; In general, with the increase of ammonia-nitrogen moral ratio, the molecular weight of NH\textsubscript{3} in unit gas is relatively increased, and the reaction contact area is more sufficient, resulting in the reduction effect of NH\textsubscript{3} on NO\textsubscript{x} is enhanced.

![Fig.3 Influence of ammonia-nitrogen moral ratio](image)

3.3 The effect of ammonia concentration
The H\textsubscript{2}O in flue gas can induce the deactivation of catalysts. Therefore, under the premise of basic experimental conditions, the influence of ammonia concentration on the NO\textsubscript{x} removal was also investigated, the result is shown in Fig.4. It can be seen that the NO\textsubscript{x} removal shows a significant
downward trend with the increasing of H₂O. The result indicates that the decrease in activity brought about by H₂O increased might be caused by its competitive adsorption with the reactant on the active sites over the catalyst surface. When the ammonia concentration range is 15-25%, the NOₓ removal efficiency can be maintained over 75%. It shows that the catalysts have excellent water resistance.

3.4 The long running test
The denitration system stability test was verified by continuous running experiments. The stability under the best experimental conditions is shown in Fig.5. The NOₓ removal efficiency reached a stable level of about 86% during the 16 hours test, indicating that the medium/low temperature SCR denitration technology presented high SCR activity and stability.

4. Conclusions
In summary, the titanium-based honeycomb molding catalysts with MnOₓ/CeO₂/V₂O₅ as the main active material were prepared, and a medium/low temperature SCR denitration pilot scale equipment with a maximum gas flow of 5000 m³/h was manufactured to control the ceramic kiln flue gas pollutants. Meanwhile, the influences of flue gas flow, ammonia-nitrogen molar ratio and ammonia concentration on the NOₓ removal were also systematically investigated. The result of the pilot study confirmed that the medium/low temperature SCR denitration technology exhibited high activity and stability for NOₓ reduction with a removal efficiency of about 86% under the best experimental conditions. Besides, when the flue gas flow range was less than 5000 m³/h, the ammonia-nitrogen ratio range was 0.8-1:1, and the ammonia concentration range was 15-25%, the denitration efficiency can exceed 75%, and the ammonia escape amount can be less than 1 mg/m³.
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