Research progress on catalytic denitrification technology in chemical industry

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Abstract. In recent years, due to the rising emission of NOx annually, attention has been aroused widely by people on more and more severe environmental problems. This paper first discusses applying NOx removal and control technologies and relating chemical principles. Of many technologies, selective reduction reaction (SCR) is the most widely used. Catalysts, the concentration of NOx at the entrance of SCR catalytic reactor, reaction temperature, NH3/NOx mole ratio and NH3 slip rate analyzed later contributes to the removal efficiency of NOx. Finally, the processing and configuration of SCR de-NOx system are briefly introduced.

1. Introduction
Nitrogen oxides which refer to the mixture of more than 90% of NO and NO2 have become severe air pollutants. They are produced from the combustion of coal, oil, natural gases and contribute to the destruction of ozone, environmental problems and threat of human health [1].

Governments over the world deliver emission cutting regulations and standards in response to the protection of environment and reduction of NOx emission. Nowadays, three ways are generally used to control the generation of NOx named pre-combustion denitrification, combustion denitrification and post-combustion denitrification respectively. Among a variety of technologies, the selective catalytic reduction is widely applied in commercial in the control of NOx because of its outstanding ability in no formation of by-product and secondary pollution, convenient system and process, easy maintenance and high NOx removal efficiency. Therefore, SCR is the most common technology used around the world. [1-3]

2. NOx Control Technology
For the protection of environment, countries around the world make efforts to develop advanced technology for the purpose of lowering NOx emission. NOx reduction technology can be categorized into three types in terms of combustion life cycle: pre-combustion denitrification, combustion denitrification and post-combustion denitrification respectively.

Low nitrogen fuel is employed in pre-combustion NOx reduction technology. Its industrial application is relatively rare due to the high cost.

In-combustion NOx reduction uses low NOx combustion technology. Although this strategy is well-developed as well as requires relatively low investment and construction cycle, de-NOx efficient is usually lower than 40%. In countries that strictly control the emission of NOx such as Japan and German, low NOx combustor is applied first to half the NOx content followed by post-combustion NOx reduction technology for further fuel gas treatment [4,5].
Post-combustion de-NOx technology refers to fuel gas de-NOx technology, mainly including SCR, SNCR, SNCR/SCR hybrid fuel gas de-NOx technology, which has high de-NOx efficiency and is relatively common in Japan, United States and German. In SNCR technology, ammonia aqueous solution or urea as a reductant is injected into furnace and rapidly decomposed into NH3. Afterwards, NOx is reduced by NH3 to form N2 and H2O at temperature around 1000°C. 25%~50% NOx removal efficiency can be obtained in this case. SCR of NOx is an effective means of de-NOx. The addition of catalysts lowers the activation energy of reaction, resulting in up to 95% NOx removal efficiency. The operating temperature of SCR system is around 400°C. SNCR/SCR hybrid of NOx technology in the fuel gas utilizes SNCR and SCR technologies in combination by first injecting reductant into furnace for the reduction of NOx. Then catalytic reduction occurs in the presence of ammonia slip and NOx for further removal of NOx. NOx removal efficient can be up to 40~80% in this case. [6,7]

3. The Chemistry of De-NOx Technology

In principle, De-NOx technology is chemical reactions involving oxidation and reduction processes. Wet de-NOx take places when NOx is oxidized to oxides with higher oxidation states. In reduction methods, NOx with higher oxidization states gains electrons from CH4, NH3 and CO using as reducing agents and is reduced to N2 with lower oxidization states.

4. SCR Technology

SCR process has become the predominant technology in achieving the NOx emission standard because of its low operating temperature, high NOx removal efficiency, and no formation of secondary pollution.

4.1 The mechanism of SCR technology

The reduction of NOx by NH3 selectively forms N2 and H2O on the catalyst at temperature around 250-450°C. Three types of catalyst can be used in the reaction, noble metals, metal oxides and zeolites. Noble metals which are primarily applicable for low temperature and natural gas have the ability to effectively reduce NOx, yet cause the undesired oxidation of NH3 [8]. Metal oxides such as V2O5/TiO2, V2O5-WO3/TiO2 operate well at high temperature window. V2O5 is an active component on the reduction of NO and oxidation of SO2, while TiO2-anatase as a support has an excellent sulfur tolerance. This is because sulfates on TiO2 surface are less stable than on other oxides, and the sulfitation of TiO2 yielding insoluble products in the presence of SO2 and O2 is reversible and even improve NOx removal activity. In addition, increasing V loading will increase the activity of catalyst, and the addition of WO3/MoO3 enhances the acidity, activity, thermostability of catalyst as well as reduce the oxidation of SO2[9]. In presence of As in the exhausted gas, MoO3 prevents the deactivation of catalysts. Zeolites is developed to operate at high temperature where metal oxides are thermally unstable.

The reaction equations are listed as follows:

\[
\begin{align*}
4NH_3 + 4NO_2 + O_2 & \rightarrow 4N_2 + 6H_2O \quad (1-1) \\
4NH_3 + 6NO & \rightarrow 5N_2 + 6H_2O \quad (1-2) \\
4NH_3 + 2NO + 2NO_2 & \rightarrow 4N_2 + 6H_2O \quad (1-3) \\
4NH_3 + 2NO_2 + O_2 & \rightarrow 3N_2 + 6H_2O \quad (1-4) \\
8NH_3 + 6NO_2 & \rightarrow 7N_2 + 12H_2O \quad (1-5)
\end{align*}
\]

The reaction of (1-1) is the standard SCR reaction; When there is no O2 present, reaction (1-2) occurs per (1-2), reaction rate is relatively low. When mole ratio of NH3/NOX=1, (1-3) occurs, and reaction rate is higher than standard SCR reaction; When mole ratio of NH3/NOX>1, reactions follow (1-4), (1-5), reaction rate is lower than (1-1).

4.2 SCR processing parameters

4.2.1 The NOx removal efficiency of SCR
SCR NOX removal efficiency indicates SCR NOX removal effects, influenced by various factors. In engineering application, short-term and long-term NOX removal efficiency are determined. $\eta$ is defined as NOX removal efficiency.

$$
\eta = \left( \frac{C_{in} - C_{out}}{C_{in}} \right) \times 100\% 
$$

(2-1)

Where, $C_{in}$、$C_{out}$ are the concentrations of NOx before and after reactions.

4.2.2 The concentration of NOx at the entrance of SCR catalytic reactor

Because of the complicated combustion process of boiler and the large difference in composition of coal, NOX concentration is fluctuating and irregular at the entrance of de-NOX reactor.

4.2.3 Reaction temperature

Optimal temperature is responsible for the activity of catalysts, which further contributes to the reaction rate. The catalyst of vanadia supported on titania has been most widely used, which is cu

![Figure 1. The relationship of NO conversion ratio with the molar ratio [9]](image)

4.2.4 The slip rate of NH3

NH3 slip rate refers to the volume faction of unreacted NH3 going through the ammonia outlet system in fuel gas. High NH3 slip rate not only increase the operating cost but also cause the secondary pollution. Additionally, slipping NH3 can react with SO3 oxidized in the fuel gas to form viscous ammonium salts like NH4HSO4 and (NH4)2SO4 which then corrode equipment downstream and lower its lifespan. Usually, less than 3% of NH3 slip rate is allowed.

5. The Configuration of SCR De-NOX System

A typical SCR reactor consists of inlet, NH3 storing and injection grids, multi-layers of catalyst and outlet, as shown in Fig. 2.
The mixture of vaporized NH3 and diluted air are injected into flue gas stream through a distribution grid. The use of positioning guide vanes and distribution layer is effective in enabling flowing velocity of fuel gas uniform. Catalysts elements are assembled in steel frame modules and placed in the reactor in the form of catalyst layers [6]. There are usually three layers. VO5-TiO2 catalysts in the form of honeycomb monolith are used most widely now.

High dust configuration is applied mostly in coal-fired plant and NOx conversion of 80-85% can be achieved. Catalytic reactor is located between economizer and the air pre-heater (APH). Fuel gas stream through SCR reactor is at temperature between 300-400˚C, which is optimum for catalyst activity. Cold electrostatic precipitators (ESP) located after preheater ensure the removal of particle. Whereas fuel gas flowing through catalyst layers with 100% dust content has the potential to reduce the lifespan of catalyst. To prevent its erosion and passage block by particles, the fuel gas flows vertically downward, and catalysts with larger channel openings and wall thickness are employed to decrease its surface areas. Besides, NH3 slip rate and SO2 oxidation should be low enough to eliminate the deposition of (NH4)HSO4 onto the APH. [8]

Low dust configuration is often used when coal has low sulfur content. SCR reactor is installed after ESP and upstream of APH. No dust is present in the fuel gas when passing through catalytic reactor, extending the operation time of catalyst. However, fuel gas temperature of this time is usually below 90˚C. As stated before, low temperature will cause side reactions occur potentially and increase the resistivity of dust. Therefore, minimizing catalyst fuel gas passage opening and enlarging surface area of catalyst and installing a reheater before catalytic reactor is necessary for enhancing NOx removal efficiency.

In a tail end configuration, fuel gas undergoes dust removal and desulfurization before flowing through the SCR reactor. Catalyst layers has smaller openings and wall thickness to obtain larger surface areas and higher vanadia content. In this case, the amount of catalysts used can be minimized and deterioration rate is lowered.

To control the concentration of NOx at outlet below 5ppm or lower during the combustion of natural gas, dry and low concentration of NO or water stream injection system is provided [8].

### 6. The Catalyst in SCR System

Honeycomb monolith and plate type catalysts are adopted predominately. Honeycomb monolith catalysts are introduced here. Such catalysts make use of ceramic honeycomb or metal plates as carrier backbone, TiO2-coated cermet or metal as catalytic carrier and V2O5, Wo3 as active components. Honeycomb SCR reactor provides larger surface area, enhancing the utilization of active element. Also,
such form of catalyst has strong mechanical properties and high wear resistance that reduce the C and dust deposition. Composite catalysts are developed based on honeycomb monolith catalysts.

Honeycomb monolith V2O5/AC not only benefits from its geometry but takes advantages of AC as well as such catalysts are prepared from the loading of V2O5 on honeycomb of activated carbon base. Larger area offered by this geometry takes full advantage of active element V2O and provide larger space for reaction happening.

Since honeycomb monolith V2O5/AC has an excellent catalytic activity, lifetime of catalyst can be extended by locating SCR reactor after ESP to eliminate the effect of particles in the fuel gas [10,11].

7. Conclusion
With the development of our society, the demand for electricity is increasing, accompanying with more and more serious environmental pollution. As a result, countries publish rigorous standards to confine the NOx emission in coal-fired plant. SCR de-NOx technology has stepped into the period of public promotion. Urgent action should be taken to optimize the structures of equipment, explore feasible proposals after optimization, dig out inherent rules as well as ameliorate installation used now. Studies including SCR processing parameters, system arrangement and catalyst are described above. More research for amelioration and making the most of SCR technology is worthy of detailed investigation in the future.

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