Review

Review on the NO removal from flue gas by oxidation methods

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A B S T R A C T

Due to the increasingly strict emission standards of NOx on various industries, many traditional flue gas treatment methods have been gradually improved. Except for selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR) methods to remove NOx from flue gas, the oxidation method is paying more attention to NOx removal now because of the potential to simultaneously remove multiple pollutants from flue gas. This paper summarizes the efficiency, reaction conditions, effect factors, and reaction mechanism of NO oxidation from the aspects of liquid-phase oxidation, gas-phase oxidation, plasma technology, and catalytic oxidation. The effects of free radicals and active components of catalysts on NO oxidation and the combination of various oxidation methods are discussed in detail. The advantages and disadvantages of different oxidation methods are summarized, and the suggestions for future research on NO oxidation are put forward at the end. The review on the NO removal by oxidation methods can provide new ideas for future studies on the NO removal from flue gas.

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I N T R O D U C T I O N

With the development of industry, air pollution caused by the burning of fossil fuel is an unavoidable topic. The pollution mainly comes from the coal combustion in the electric power industry and non-electric coal-burning industry, such as the sintering machine and pellet roasting equipment in the steel industry, all kinds of kilns used in the processing of cement, metallurgy, ceramics, glass, etc., as well as the self-provided coal-fired power boilers, self-provided power plants, and loose coal in various industries. It is also a major cause of haze in China's major industrial cities. The main components in air pollution are NOx, SOx, dust particles, and volatile organic compounds, etc. The Chinese government has imposed strict emission standards for these major combustion pollutants. The ultra-low emission concentrations of dust particles, SOx, and NOx should stabilize below 10 mg/m³, 35 mg/m³, and 50 mg/m³ respectively, from the existing oil-fired boilers, gas-
fired boilers, and coal-fired non-power-generation boilers with the rated capacity above 65 ton/hr (Lin et al., 2020). According to the statistics on the proportion of PM2.5 major components obtained between 2017-2018, nitrates replaced sulfates to become the most important secondary inorganic component of PM2.5 in fine particulate matter in major cities in China (Wang et al., 2017). It highlights the importance and urgency of strengthening NOx emission control.

According to the boiler combustion process and denitrification process layout, the removal technology of NOx in combustion flue gas can be divided into three categories: before combustion, during combustion, and after combustion. The specific removal method is shown in Table 1. Denitrification technology before combustion refers to the fuel treatment before combustion to reduce its nitrogen content, to reduce the source of nitrogen oxide production, thus reducing NOx emissions after combustion. But this technology is expensive and difficult to implement widely. NOx emission reduction technology during combustion focuses on changing the production amount of NOx by adjusting reaction temperature, the ratio of air to fuel, and other reaction conditions in the process of fuel combustion. Use the inhibition conditions on the generation of fuel NOx, which also involves the improvement measures of combustion equipment. Although the low NOx combustion technology has been applied in the actual boilers of power plants, the efficiency of reducing NOx emissions is low, and it is difficult to meet the increasingly strict ultra-low emission standards of flue gas pollutants. Therefore, the technology of denitrification in combustion combined with denitrification of flue gas after combustion has become a popular way to reduce NOx in the coal-burning industry.

At present, selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR) are the most widely used methods with high denitrification efficiency. The development and preparation of commercial SCR catalysts are very mature, mainly V-W-TiO2 with the activity temperature range of 300-400°C (Hong et al., 2017). The denitrification efficiency by NH3-SCR can reach more than 90%, with no secondary pollution and no by-products. However, too high or too low temperature of flue gas will reduce the catalytic activity and thus reduce the efficiency of NOx removal. To maintain the operating temperature of SCR commercial catalysts at 300-400°C, denitrification operation and equipment maintenance costs will be increased. Therefore, the research on SCR catalyst in recent years focuses on the development of low-temperature catalysts (Hu et al., 2017; Xue et al., 2013; Chen et al., 2014; Shan and Song, 2015). Besides, the problems of pipeline corrosion caused by ammonia as a reducing agent and secondary environmental pollution caused by ammonia leakage (<5 ppm) still exist. In the technology of SNCR, ammonia or urea is used as a reducing agent to reduce nitrogen oxides in the flue gas to N2 and H2O. However, the reaction temperature is high (900-1100°C), the denitrification efficiency is low (25%-40%), and the ammonia escape rate is high (5-20 ppm) (Javed et al., 2007, 2009). Whether SCR or SNCR, the presence of NH3 reducing agent will lead to a reaction with SO2 in the flue gas to form (NH3)2SO4 and (NH3)HSO4, resulting in catalyst deactivation, pipeline blockage, and corrosion. However, in the study of wet removal of nitrogen oxides, it was found that other components in the flue gas such as SO2 had a less negative effect on the NO removal efficiency (Park et al., 2015; Guo et al., 2014). On the other hand, SO2 in flue gas adopts the method of wet absorption. So if NOx can be efficiently absorbed, it can not only achieve simultaneous desulfurization and denitrification but also reduce the spaces of flue gas treatment equipment. The nitrogen oxides in the flue gas are mainly NO with very low solubility. The higher the valence of nitrogen, the higher the solubility of NOx (Dora et al., 2009). Therefore, the effect of reaction conditions on the oxidation of NOx improve the NO oxidation efficiency is a new research direction. Also, other components in the flue gas, such as mercury, organic matter, and so on, can be treated by oxidation methods. Lin et al. (2020) summarized the studies on the treatment of nitrogen oxides, organic pollutants and elemental

<table>
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<th>Table 1 – NOx removal technologies.</th>
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<td>Before combustion</td>
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<td>(George et al., 2020)</td>
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<td>During combustion</td>
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<td>(Houshfar et al., 2011; Liu et al., 2017a)</td>
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<td>After combustion</td>
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<td>Coal washing technology</td>
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Dry removal:
- Catalytic decomposition;
- Adsorption method;
- Plasma method;
- Selective catalytic reduction (SCR);
- Selective non-catalytic reduction (SNCR).

Wet removal:
- Alkali absorption method;
- Acid absorption;
- Complexation absorption method;
- Microbiological method;
- Reduction absorption method;
- Oxidation absorption method.

Semi-dry removal:
- Spray drying;
- Powder-particle spouted bed;
- The flue injection.
mercury in flue gas by ozonation, focusing on the deep oxidation of NO and the influence of different absorbents on the absorption efficiency of NO$_2$ and N$_2$O$_5$. The potential of ozonation for the simultaneous removal of multiple pollutants in the flue gas was also evaluated. It is feasible to develop and apply the oxidation method to simultaneously remove various pollutants in the flue gas.

The work content of this article is to summarize the oxidation methods of NO based on liquid oxidants, gas oxidants, and catalysts, including the mechanism, advantages and disadvantages, and applicable conditions of these methods. Suggestions, prospects for the future research contents, and trends of NO oxidation are put forward at the end.

1. NO oxidation by liquid oxidants

1.1. NO oxidation by H$_2$O$_2$

Hydrogen peroxide (H$_2$O$_2$) is a strong oxidant that is easy to obtain, cost-effective, and with no secondary pollutant. The strong oxidizability of H$_2$O$_2$ is due to its potential to generate highly active hydroxyl radicals (•OH). Hydroxyl radicals (•OH) have been used in the treatment of air and water pollution for nearly 20 years (Nora, 2003). More and more researches are devoted to improving the production of hydroxyl radical (•OH) and the utilization rate of H$_2$O$_2$ to improve the oxidation efficiency (Liu et al., 2014a; Zhang et al., 2020; Zhou et al., 2020). Hao et al. (2016) proposed an ultraviolet (UV)-heat/H$_2$O$_2$ system to remove SO$_2$ and NO. SO$_2$ could be completely removed, and the removal efficiency of NO could reach 87.8% when flue gas flow was 4.0 L/min, flue gas residence time was 4.2 sec, H$_2$O$_2$ concentration was 15 wt.%, H$_2$O$_2$ pH of 6, evaporation temperature was 130 °C, UV energy density was 0.064 W/cm$^2$, UV catalysis temperature was 90 °C, NO initial concentration was 500 mg/m$^3$, SO$_2$ initial concentration was 2500 mg/m$^3$. This system inhibited the competition of SO$_2$ for the oxidation of NO, and it was also found that the appropriate amount of SO$_2$ was conducive to the oxidation absorption of NO. Subsequently, Hao et al. (2017) added Na$_2$SO$_3$ in a WFGD absorption solution system, investigating the oxidation removal of NO$_2$ and NO by this system. It was noted that high temperature and Na$_2$SO$_3$ solution with high pH value, as well as, an appropriate amount of SO$_2$ were beneficial to the oxidation absorption of NO and NO$_2$. The high concentration of O$_2$ was also beneficial to the removal of NO, but not to the removal of NO$_2$. The removal rate of NO and NO$_2$ reached 78% and 89%, respectively, when Na$_2$SO$_3$ concentration was 0.05 mol/L, Na$_2$SO$_3$ solution pH was 8, solution volume was 500 mL, reaction temperature was 55 °C, O$_2$ concentration was 6%, flue gas flow was 2.6 L/min, NO initial concentration was 100 mg/m$^3$, and NO$_2$ initial concentration was 300 mg/m$^3$.

Recently, Hao et al. (2019) proposed an UV-heat/H$_2$O$_2$ oxidation integration system, utilizing NH$_2$OH and (NH$_4$)$_2$SO$_3$ as absorbent in dual-area of upper and lower levels to remove SO$_2$ and NO. SO$_2$ was pre-absorbed by NH$_2$OH in the lower absorption zone, and NO was oxidized by vaporized H$_2$O$_2$ in an UV-catalysis reactor, after that, the oxidized NO$_2$ and the residual SO$_2$ were absorbed by (NH$_4$)$_2$SO$_3$ in the upper absorption zone. The optimal reaction conditions for the system were: H$_2$O$_2$ evaporation temperature, H$_2$O$_2$ concentration, O$_2$ concentration, NH$_2$OH concentration, SO$_3$, and (NH$_4$)$_2$SO$_3$ concentration with corresponding values at 110 °C, 15 wt.%, 2%, 2.5 wt.%, and 0.5 wt.%, respectively. The highest removal efficiency of NO and SO$_2$ were 96.3% and 99.3%. The high efficiency attained can be attributed to the residual SO$_2$ improving the oxidation of NO, and O$_2$ promoting the conversion of SO$_3^{2−}$ to SO$_4^{2−}$, and NO$_2$ to NO$_3$−, though higher concentrations of oxygen (6%) inhibits the absorption of NO. The reaction mechanism equations were Eqs. (1)-(14) (Hao et al., 2016, 2017; Guo et al., 2013; Bai et al., 2012; Carole et al., 1995; Jin et al., 2006). Absorbent (NH$_4$)$_2$SO$_3$ in this system can be attained by NH$_2$OH pre-absorbed SO$_2$, to realize the reuse of absorbents reducing the absorbents costs.

\[
\begin{align*}
\text{NO} + \text{•OH} & \rightarrow \text{NO}_2^- + \text{H}^+  \\
2\text{•OH} + \text{NO} & \rightarrow \text{H}_2\text{O} + \text{NO}_2  \\
2\text{NO}_2 + \text{SO}_2^{2−} + 2\text{OH}^- & \rightarrow 2\text{NO}_2^- + \text{SO}_4^{2−} + \text{H}_2\text{O}  \\
\text{NO}_2 + \text{•OH} + \text{H}_2\text{O} & \rightarrow 2\text{NO}_2^- + 2\text{H}^+  \\
\text{SO}_2 + 2\text{NO}_2 + \text{H}_2\text{O} & \rightarrow 2\text{NO}_2^- + \text{SO}_4^{2−} + 4\text{H}^+  \\
\text{H}_2\text{O}_2 + \text{NO}_2^- & \rightarrow \text{H}_2\text{O} + \text{NO}_3^-  \\
2\text{H}_2\text{O} + 2\text{NO}_2^- + 3\text{SO}_2 & \rightarrow \text{N}_2 + 3\text{SO}_4^{2−} + 4\text{H}^+  \\
2\text{•OH} + \text{SO}_2 & \rightarrow 2\text{H}^+ + \text{SO}_4^{2−}  \\
\text{H}_2\text{O}_2 + \text{NO} + \text{NO}_2 & \rightarrow \text{H}_2\text{O} + \text{N}_2  \\
3\text{H}_2\text{O}_2 + 2\text{NO} & \rightarrow 2\text{NO}_3^- + 2\text{H}_2\text{O} + 2\text{H}^+  \\
\text{H}_2\text{O}_2 + \text{SO}_2 & \rightarrow 2\text{H}^+ + \text{SO}_4^{2−}  \\
\text{•OH} + \text{NO} + \text{NO}_2^- & \rightarrow \text{N}_2 + \text{H}^+  \\
\text{H}_2\text{O}_2 + 2\text{NO}_2 & \rightarrow 2\text{H}^+ + 2\text{NO}_3^-  \\
\text{NH}_4^+ + \text{NO}_2^- & \rightarrow \text{N}_2 + 2\text{H}_2\text{O}  
\end{align*}
\]

Fenton reagent prepared from Fe$^{2+}$ and H$_2$O$_2$, producing hydroxyl radical (•OH) and superhydroxide radical (HO$_2$•), has been widely studied and applied in the removal of various pollutants (Zhou et al., 2020; Han et al., 2020; Guo et al., 2020). Zhao et al. (2014) systematically investigated the simultaneous removal of SO$_2$ and NO by Fenton reagent in a bubbling reactor, and the simultaneous removal efficiency of SO$_2$ and NO achieved were 100% and 90%, respectively, when flue gas total flow was 0.02 m$^3$/hr, NO initial concentration was 420 mg/m$^3$, SO$_2$ initial concentration was 2400 mg/m$^3$, Fe$^{2+}$ concentration was 2.8 mmol/L, H$_2$O$_2$ concentration was 11%, solution pH was 3.0, at 55 °C, 0.1 Mpa.

Fig. 1 shows the effects of different factors on NO oxidation by Fenton reagent. An increase in the reaction temperature
increases the oxidation rate. However, according to Henry’s law, increasing temperature will reduce the solubility of the gas, which will to some extent offset the promotion of reaction rate caused by increasing temperature. The increase of Fe$^{2+}$ concentration promotes the generation of hydroxyl radical (•OH) according to Eq. (15) Guo et al., 2011, leading to the increase of oxidation rate of NO as indicated in Eq. (2). However, when the concentration of Fe$^{2+}$ exceeds the demand, the reduction of H$_2$O$_2$ will be significant, resulting in a decrease in •OH formation rate as described in Eqs. (16)-(17) (He et al., 2016), and thereby affecting the oxidation of NO. When the concentration of H$_2$O$_2$ is moderate, the removal efficiency of NO increases with the increase of H$_2$O$_2$ concentration. When H$_2$O$_2$ concentration is in excess, it will accelerate the decomposition of H$_2$O$_2$ as well as the oxidation of Fe$^{2+}$ as described in Eqs. (15)-(17), resulting in the reduction of effective oxidants, which is not conducive for NO oxidation. Therefore, it is crucial to optimize the optimal concentration ratio of Fe$^{2+}$ and H$_2$O$_2$ for NO oxidation in Fenton reagent. The pH value of Fenton reagent directly affects the production amount of •OH. H$_2$O$_2$ can not decompose to •OH under the strong acid, while the complex or precipitation of Fe$^{3+}$ will occur under the high pH value, resulting in the decrease of Fe$^{3+}$ catalytic activity and the decrease of the formation of •OH. The influence conditions aforementioned are generally accepted in the studies of pollutant removal by Fenton reagent (Yuan et al., 2018; Xing et al., 2018).

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \cdotOH + \text{OH}^- \quad (15)
\]

\[
\cdotOH + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2^* \quad (16)
\]

\[
\cdotOH + \text{HO}_2^* \rightarrow \text{H}_2\text{O} + \text{O}_2 \quad (17)
\]

Liu et al. (2019a) adopted Fe$_2$(MoO$_4$)$_3$ catalysts to encourage H$_2$O$_2$ to produce more •OH for simultaneous removal of NOx and SO$_2$. The presence of SO$_2$ reduced Fe$^{3+}$ on the catalyst to Fe$^{2+}$, thus inhibiting the reaction between Fe$^{3+}$ and H$_2$O$_2$ and improving the utilization rate of H$_2$O$_2$ to generate more •OH, and resulted in the improvement of NO oxidation-absorption efficiency. The optimal denitrification rate was 91.4% and the desulfurization rate attained was 100%. Yuan et al. (2018) designed an in situ Fenton system (IF) with a dual ion drop device on a bubbling reactor, that could continuously drip the solution of metal ions and hydrogen peroxide to remove NO by oxidation. Dual ions of Fe$^{2+}$ with M$^{n+}$ (M$^{n+}$ = Ce$^{3+}$, Cu$^{2+}$, Co$^{2+}$, Mn$^{2+}$) were chosen as reagents to compare the removal efficiency of NO. The results of experiments showed that, under the same initial conditions, NO efficiency of dual ions drop was higher than that of single ion drop. Moreover, the NO efficiencies of dropping dual ions containing Fe$^{2+}$ were higher than that of without Fe$^{2+}$. The experimental conditions were total flue gas flow = 600 mL/min, O$_2$ = 5%, NO initial concentration = 500 ppm, the molar ratio of metal ions to H$_2$O$_2$ = 0.05; and in the bubbling reactor, H$_2$O$_2$ initial concentration = 1.0 mol/L, initial pH = 3.0, and solution temperature was 25°C. The promotion of NO oxidation from high to low was Fe$^{2+}$ (20%)/Ce$^{3+}$ (80%) > Fe$^{2+}$ (20%)/Co$^{2+}$ (80%) > Fe$^{2+}$ (50%)/Mn$^{2+}$ (50%) > Fe$^{2+}$ (50%)/Cu$^{2+}$ (50%), and the maximum removal efficiency of NO was 85%. Metal ion solution and H$_2$O$_2$ were continuously added to the bubbling reactor to continuously produce highly active •OH, reacting with liquid NO and its hydrolysates, as described in Eq. (1) and Eqs. (18)-(22) (Liu et al., 2010; Yusuf et al., 2006; Paiva and Kachan, 1998). The oxygen in flue gas could also improve the oxidation of NO under this system, and eventually form NO$_2^-$ and NO$_3^-$, described by Eqs. (23)-(25) (Zhao et al., 2014). In the dual ionic reagents in situ Fenton system (IF), the addition of other metal ions enhanced electron transfer cycle between Fe$^{2+}$/Fe$^{3+}$ and M$^{n+}$/M$^{[n-1]+}$ (M$^{n+}$ = Ce$^{3+}$, Cu$^{2+}$, Co$^{2+}$, Mn$^{2+}$), and enhanced the oxidation of NO by Fenton-like reagent.

\[
\text{NO}_2^- + \cdot\text{OH} \rightarrow \text{NO}_3^- + \cdot\text{H} \quad (18)
\]

\[
\text{NO}_2^- + \text{H}_2\text{O}_2 \rightarrow \text{NO}_3^- + \text{H}_2\text{O} \quad (19)
\]

\[
\text{NO} + \cdot\text{OH} \rightarrow \text{NO}_2^- + \cdot\text{H} \quad (20)
\]

\[
\text{NO}_2^- + \cdot\text{OH} \rightarrow \text{NO}_3^- + \cdot\text{H} \quad (21)
\]

\[
2\text{NO} + 3\text{H}_2\text{O}_2 \rightarrow 2\text{NO}_2^- + 2\cdot\text{H}^+ + 2\text{H}_2\text{O} \quad (22)
\]

\[
\text{NO} + \text{O}_2 \rightarrow \text{NO}_3 \quad (23)
\]

\[
\text{NO} + \text{NO}_2 \rightarrow \text{N}_2\text{O}_4 \quad (24)
\]

\[
\text{N}_2\text{O}_4 + \text{H}_2\text{O} \rightarrow \text{NO}_2^- + \text{NO}_3^- + 2\cdot\text{H}^+ \quad (25)
\]

1.2. NO oxidation by SO$_{2}^{2-}$ and S$_{2}$O$_{8}^{2-}$

Peroxymonosulfates and persulfates activation technology based on SO$_{2}^{2-}$ and S$_{2}$O$_{8}^{2-}$ radicals is an advanced oxidation
technology, which can oxidize and remove a variety of pollutants. Liu et al. (2018b) utilizing a UV-impinging stream reactor with double jacket heat exchanger, (NH₄)₂S₂O₈ reagent as the oxidant, investigated the factors influencing the simultaneous desulfurization and denitration. The highest removal efficiency of NO achieved was 96.1%. Under the single variable condition, the NO oxidation-absorption efficiency increased with the increase of (NH₄)₂S₂O₈ concentration, UV radiation power, activation temperature, and liquid–gas ratio. This may be as a result of the ultraviolet radiation which enhances the decomposition of S₂O₈²⁻ into SO₄⁴⁻, reacts with H₂O to form *OH and both of them have strong oxidation for NO (Antoniou and Andersen, 2015; Xu et al., 2016; Kwon et al., 2015; Liu et al., 2014b). The increase of temperature could strengthen the process (Liu et al., 2014b; Adewuyi et al., 2013), and the increase of liquid–gas ratio increased the contents of the active components of oxidant. Therefore, they were beneficial to improve the oxidation-absorption efficiency of NO. However, the NO oxidation-absorption efficiency decreased with the increase of solution pH, due to the self-consumption among SO₄⁴⁻, *OH, and (NH₄)₂S₂O₈ (Liu et al., 2014b). The increase of flue gas flow resulted in a decrease of the molar ratio of active components to NO, which weakened the oxidation-absorption of NO. The increase of NO initial concentration reduced the molar ratio of active components to NO, and the presence of SO₂ competing with NO consumed as the active components, which resulted in the decrease of NO oxidation-absorption efficiency. The presence of CO₂ and HCl had no significant effect on the oxidation absorption of NO. In the studies on the oxidation of persulfate to remove NO, Liu et al. (Liu and Wang, 2017; Liu and Zhang, 2017) also realized the same results.

Liu et al. (2018c) then carried out a study on simultaneous absorption of SO₂ and NO through the combined thermal activation of (NH₄)₂S₂O₈ by ultrasound (US) and Fe²⁺. Ultrasound can enhance the mass transfer of the gas-liquid phase and produce more free radicals, especially the enhancement of low-frequency and high power density ultrasound was so obvious, to promote the oxidation and absorption of NO (Badday et al., 2012; Wei et al., 2017). In the (NH₄)₂S₂O₈ solution, the addition of Fe²⁺ could produce free radicals, so the appropriate addition of Fe²⁺ promotes the oxidation and absorption of NO in the (NH₄)₂S₂O₈ solution to a certain extent. However, excessive (NH₄)₂S₂O₈ would react with free radicals SO₄⁴⁻ and *OH in self-consumption, resulting in the reduction of NO removal efficiency (Matzek and Carter, 2016; Adewuyi and Sakyi, 2013). In this system, NO and SO₂ entered into (NH₄)₂S₂O₈ solution to form liquid phase NO and H₂SO₃, which could be directly oxidized by (NH₄)₂S₂O₈ solution to HNO₂ and H₂SO₄. However, the most important aspect of the efficiency improvement process was Fe²⁺ that was added to the solution to form a large number of SO₄⁴⁻ and *OH, which enhances the oxidation capacity of the (NH₄)₂S₂O₈ reagent. Fig. 2 illustrates the removal mechanism.

Besides, a vacuum UV-heated reactor was designed by Liu et al. (2018a), to simultaneously remove SO₂ and NO using potassium peroxymonosulfate solution (K₃S₂O₈) as the oxidation absorbent of NO. In this process, not only SO₄⁴⁻ and *OH were produced as key highly active species, which was due to the K₃S₂O₈ solution activated by vacuum UV-heated but also generated O₃, *O, and *OH by the activation of O₃ and H₂O through vacuum UV-heated. The result differs from the previous study (Liu et al., 2018b; Liu et al., 2018c) in that only SO₄⁴⁻ and *OH was produced. The above highly active species could oxidize the NO and the SO₂ after hydrolysis (SO₂²⁻/H₂SO₃⁻) into HNO₂ and H₂SO₄. This pathway is the most critical part of the reaction system, while other reaction pathways, such as the NO and SO₂ direct oxidation by K₂S₂O₇ solution, direct decomposition by vacuum UV, and the side reactions play supplementary roles. UV wavelength of 185 nm showed the best efficiency of NO oxidation removal under all experimental conditions, and the optimal simultaneous removal efficiencies of SO₂ and NO were 100% and 91.3%, respectively.

### 1.3. NO oxidation by ClO⁻ and ClO₂⁻

The unstable ion Cl¹ easily gains electrons to form a stable ion Cl⁻, however, ClO⁻ and ClO₂⁻ have strong oxidation properties. Hypochlorite and chlorate are commonly used in the wet removal of flue gas pollutants. Byoun et al. (2019) used the spray wet scrubber with NaClO of 0.1 L/m³ to conduct the removal experiments of NO, SO₂, and Hg⁰ in flue gas from an industrial combustion device. When the solution pH range was 4.0–6.0, and vaporization temperature was 165°C, the simultaneous removal efficiencies of NO, SO₂, and Hg⁰ were 50%, 80%, and 60%, respectively. Liu et al. (2017b) carried out the oxidation removal of NO in a spray reactor with UV-assisted Ca(ClO)₂ and NaClO aqueous solution. The synergistic action of ultraviolet rays and hypochlorite stimulated the formation of more hydroxyl radicals (*OH) in the solution, which increased the efficiency of oxidation removal of NO to more than 80%. The oxidations of NO by hydroxyl radical were the main
reaction processes, as described in Eqs. (26)-(29), and the direct oxidations by hypochlorite were the auxiliary reactions, as described in Eqs. (30)-(32).

$$\text{HClO} \xrightarrow{UV/\text{light}} \text{OH} + \text{Cl}^* \quad (26)$$
$$\text{NO} + \text{*OH} \rightarrow \text{HNO}_2 \quad (27)$$
$$\text{HNO}_2 + \text{OH} \rightarrow \text{HNO}_3 + \text{HCl} \quad (28)$$
$$\text{NO} + \text{ClO}^- \rightarrow \text{NO}_2 + \text{Cl}^- \quad (29)$$
$$3\text{NO}_2 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3 + \text{NO} \quad (30)$$
$$2\text{NO} + \text{H}_2\text{O} \rightarrow \text{HNO}_3 + \text{HNO}_2 \quad (32)$$

While, Zhao et al. (2019) found that the performances of NO oxidation removal from high to low were NaClO$_2$ > NaClO$_3$ > NaClO in the research of NO removal from diesel engine exhaust by electron beam combined with the wet scrubber. The oxidation removal rate of NO by NaClO$_2$ could reach more than 90% and could adapt to a high concentration of NO and SO$_2$ removal. Wang et al. (2019) added CaO$_2$ to NaClO$_2$ solution for oxidation removal of NO$_x$, and the removal rate reached 95%. Hao et al. (2017) prepared compound oxidant of NaClO$_2$/Na$_2$SO$_3$O$_2$ to investigate the NO oxidation. NO removal efficiency increased with the increase of flow rate, solution pH, and vaporization temperature of compound oxidant, but decreased with the increase of flue gas flow. CO$_2$ had little effect on the oxidation-absorption efficiency of NO. Under the best conditions under which the highest removal efficiency of NO was 82.7% are as follows: NaClO$_2$ concentration was 4 wt.%, Na$_2$SO$_3$O$_2$ concentration was 4 wt.%, the flow rate of NaClO$_2$/Na$_2$SO$_3$O$_2$ was 200 $\mu$L/min, compound oxidant pH was 9, vaporization temperature was 140°C, the residence time of simulated flue gas was 1.5 sec, SO$_2$ initial concentration was 3000 mg/m$^3$, and NO initial concentration was 500 mg/m$^3$. These experimental conditions are suitable for the NO oxidation at the electrostatic dust removal outlet and the subsequent WFGD removal can be carried out together with SO$_2$.

Most recently, Hao et al. (2020) proposed a three-region NO oxidation removal method. NaClO$_2$ (0.9 mmol/L, m, 60°C) was used as the initial absorption solution, deionized water (50°C) as the secondary absorption solution to absorb the ClO$_2$ released by the initial absorption, and Na$_2$SO$_3$ (80 mmol/L m, 50°C) as the final absorption solution to absorb the remnants of NO$_2$ and ClO$_2$. The addition of the deionized water layer, made the dosage of NaClO$_2$ reduce from 3.3 mmol/L m to 0.9 mmol/L m, and the same NO oxidation removal efficiency of 94.5% achieved. The reduction of NaClO$_2$ content was due to the presence of deionized water layer to preserve more ClO$_2$ (Hao et al., 2017; Cosson and Ernst, 1994), thus improving the utilization rate of ClO$_2$ which helps in controlling secondary environmental pollution and reduction in operating costs. In the presence of SO$_2$, the release of ClO$_2$ from NaClO$_2$ solution could be accelerated due to the synergistic effect of SO$_2$ and O$_2$, which promoted the oxidation absorption of NO. Also, ClO$_2$ was found to be highly selective in the oxidation of NO. When removing multiple pollutants from flue gas at the same time, ClO$_2$ was more likely to oxidize NO. These were consistent with the results obtained by Hao et al. (2020) when NO and Hg$^+$ were oxidized by UV/NaClO$_2$, UV/NaClO, UV/Na$_2$SO$_3$O$_2$, UV/KHSO$_3$, and UV/H$_2$O$_2$. The free radicals (ClO$_2$, ClO$^*$, Cl$_2$$^*$) produced by UV/NaClO$_2$ and UV/NaClO had higher activity and selectivity of NO oxidation, compared with that of the others (*OH and SO$_4$$^*$$^*$), and had good tolerance to the high concentration of SO$_2$. Therefore, chlorate has high oxidation efficiency and is easy to obtain, which has good potential for the combined removal of flue gas pollutants.

**1.4. NO oxidation by other liquid oxidants**

Yan et al. (2018) realized that under the same experimental conditions, the efficiency of NO oxidation by KMnO$_4$ was second only to NaClO$_2$ and higher than that of H$_2$O$_2$ and NaClO. However, when KMnO$_4$ was supplemented with other absorbents, its oxidation removal efficiency of NO significantly improved. Pan et al. (2015) carried out the thermodynamic calculation on the process of NH$_3$+H$_2$O-assisted KMnO$_4$ oxidation of NO. The removal efficiency of NO could reach 100% in theory, but it was not so ideal in the actual experiment, just over 50% of NO removal efficiency (Fang et al., 2012; Pan et al., 2013). Ferrate (FeO$_4$$^{2-}$) not only had oxidation property but also could react with alkaline absorption solution to form condensates or precipitations, which were beneficial to the waste solution treatment after pollutant absorption. Therefore, it was considered as a new environment-friendly oxidant. Zhao et al. (2014) used K$_2$FeO$_4$ to oxidize NO in a bubbling reactor. NO removal efficiency was up to 64.8% with K$_2$FeO$_4$ concentration = 0.25 mmol/L, solution pH = 8, flue gas flow = 1 L/min, solution temperature = 47°C. The main oxidizing active substances in the reaction were FeO$_4$$^{2-}$ and HFeO$_4$, which could rapidly oxidize NO to NO$_3$$^-$ (Zhu et al., 2016) carried out the kinetic analysis of NO oxidation by K$_2$FeO$_4$. NO absorption rate increased with the increase of K$_2$FeO$_4$ concentration, NO initial concentration, and solution pH but decreased with the increase of SO$_2$ initial concentration.

The methods and efficiencies of removing NO by liquid phase oxidation are summarized in Table 2. The free radicals that had highly reactive to NO are Cl-radicals, SO$_4$$^*$ and *OH, especially the Cl-radicals, which could attain the high efficiency of NO oxidation removal without too many auxiliary measures. At present, the liquid-phase oxidation of the flue gas through the denitrification technologies mentioned above are still in the laboratory stage, and their industrial application is rarely reported. It is worth noting that the above-mentioned oxidation-absorption methods had a high ability to remove pollutants simultaneously from the flue gas. For liquid-phase oxidation system containing H$_2$O$_2$, the presence of SO$_3$ has a promotion effect on NO oxidation and had good application potential for denitration of flue gas with high sulfur content in small boilers and kilns. The oxidation efficiency was highly dependent on the mass transfer process at the gas-liquid interface. Therefore, liquid-phase oxidation of NO is more suitable for reactors with large gas-liquid contact area. Although, H$_2$O$_2$ is a green oxidant with relatively low price, without secondary pollution, and able to achieve a high denitrification
rate, its shortcomings such as easy to decompose under heat, large consumption of oxidant, and unstable operation of the plant restrict its large-scale industrial application. Other oxidants such as NaClO, NaClO₂, and Na₂SO₃, are expensive and require high corrosion resistance of spray towers, which increase the maintenance cost of the equipment, restricting its application in industry. On the whole, liquid-phase oxidation of NO requires the synergistic effect of other technologies such as photocatalysis, thermal assistance, ultrasound, and others, to improve the utilization of oxidants. It is an important coupling approach for wet denitration technology, but it will increase the cost of operation. Therefore, the coupling mode of liquid oxidizer and other denitration assistance technologies should be selected reasonably.

<table>
<thead>
<tr>
<th>Method</th>
<th>NO removal efficiency</th>
<th>Main active species</th>
<th>Influence factor</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV/heat/H₂O₂</td>
<td>87.8%</td>
<td>•OH</td>
<td>Promotion factor: SO₂</td>
<td>(Hao et al., 2016)</td>
</tr>
<tr>
<td>UV/heat/H₂O₂/Na₂SO₃</td>
<td>78%</td>
<td>•OH</td>
<td>high temperature and pH.</td>
<td>(Hao et al., 2017)</td>
</tr>
<tr>
<td>UV/heat/H₂O₂/Na₂SO₃</td>
<td>96.3%</td>
<td>•OH</td>
<td>Dual influences: O₂.</td>
<td>(Hao et al., 2019)</td>
</tr>
<tr>
<td>H₂O₂/Fe₂(OH)₃</td>
<td>91.4%</td>
<td>•OH</td>
<td>Promotion factor: SO₂.</td>
<td>(Liu et al., 2019a)</td>
</tr>
<tr>
<td>Fenton</td>
<td>90%</td>
<td>•OH</td>
<td>Dual influences: concentration of H₂O₂ and Fe²⁺, high temperature and pH.</td>
<td>(Zhao et al., 2014)</td>
</tr>
<tr>
<td>Denitration methods</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>UV/(NH₄)₂SO₄</td>
<td>96.1%</td>
<td>SO₄²⁻, •OH</td>
<td>Promotion factor: UV light intensity, evaporation temperature. Inhibited factor: SO₂ and high pH.</td>
<td>(Liu et al., 2018b)</td>
</tr>
<tr>
<td>Ultrasound/Fe²⁺/(NH₄)₂SO₃</td>
<td>89.5%</td>
<td>SO₄²⁻, •OH, O₂, •O</td>
<td>Promotion factor: flow rate of oxidant, evaporation temperature, high pH.</td>
<td>(Byou et al., 2019)</td>
</tr>
<tr>
<td>VUV-heat/K₂SO₃</td>
<td>91.3%</td>
<td>ClO₂, ClO*, Cl⁻, Cl₂⁻</td>
<td>Promotion factor: high pH.</td>
<td>(Liu et al., 2017b)</td>
</tr>
<tr>
<td>NaClO</td>
<td>50%</td>
<td>ClO₂, ClO*, Cl⁻, Cl₂⁻</td>
<td></td>
<td>(Zhao et al., 2019)</td>
</tr>
<tr>
<td>UV-NaClO</td>
<td>&gt;80%</td>
<td>ClO₂, ClO*, Cl⁻, Cl₂⁻</td>
<td></td>
<td>(Wang et al., 2019)</td>
</tr>
<tr>
<td>NaClO₂</td>
<td>&gt;90%</td>
<td>ClO₂, ClO*, Cl⁻, Cl₂⁻</td>
<td></td>
<td>(Hao et al., 2017)</td>
</tr>
<tr>
<td>NaClO₂/CaO</td>
<td>95%</td>
<td>ClO₂, ClO*, Cl⁻, Cl₂⁻</td>
<td></td>
<td>(Hao et al., 2020)</td>
</tr>
<tr>
<td>NaClO₂/Na₂SO₃</td>
<td>82.7%</td>
<td>ClO₂, ClO*, Cl⁻, Cl₂⁻</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaClO₂/Deionized water/Na₂SO₃</td>
<td>94.5%</td>
<td>ClO₂, ClO*, Cl⁻, Cl₂⁻</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH₄H₂O-assisted KMnO₄</td>
<td>50%</td>
<td>MnO₄⁻</td>
<td>Promotion factor: high pH.</td>
<td>(Pan et al., 2015)</td>
</tr>
<tr>
<td>K₂FeO₄</td>
<td>64.8%</td>
<td>FeO₄²⁻, HFeO₄⁻</td>
<td>Inhibited factor: SO₂.</td>
<td>(Zhao et al., 2014)</td>
</tr>
</tbody>
</table>

Table 2 - Summarization of removing NO by liquid-phase oxidation.

2. NO oxidation by gas oxidants

2.1. NO oxidation by O₃

2.1.1. Application of NO oxidation by O₃

Ozone with strong oxidation ability can be prepared from the air by industrial discharge technology. DuPont BELCO of the United States combined electro-dynamicventuring washing technology with low-temperature ozone oxidation of NO (LotTox technology) to form a flue gas denitration system (Huang et al., 2017). When the flue gas temperature was lower than 200°C, the denitration rate reached over 90%. This technology is still in the process of continuous innovation. Ma et al. (2016) used O₃ combined with limestone-gypsum washing system for desulphurization and denitrification in industrial carbon black furnace (100,000 ton/year). When the flue gas contained SO₂ = 1000 mg/m³, NOₓ = 900 mg/m³, O₂ = 6%, H₂O = 45 vol.%, the molar ratio of O₂/NOₓ = 2, and the total flue gas flow was 60,000 m³/h, the longest flue-gas residence time was 2.81 sec, and the temperature was 180°C, the liquid-gas ratio of CaCO₃ slurry was 12 L/m³, the maximum desulfurization and denitrification efficiencies were 98% and 95%, respectively. The increase of O₂/NOₓ could improve the removal efficiency of NOₓ, but the effect on the removal efficiency of SO₂ was not significant. The increase in the liquid-gas ratio improved the removal efficiency of SO₂, but it did not affect the removal efficiency of NOₓ. Meng et al. (2019) added (NH₄)₂SO₃ to steel slag slurry to remove NOₓ. The optimal conditions were O₂/NO = 1, (NH₄)₂SO₃ concentration = 0.18 mol/L, steel slag slurry concentration = 5%, reaction temperature = 40°C, slurry pH = 7.5, O₂ concentration = 6%, NO initial concentration = 200 ppm, SO₂ initial concentration = 220 ppm, achieving 78% of NOₓ removal efficiency and 100% of SO₂ removal efficiency. In this removal system, S₂O₃²⁻ promoted the conversion of NO₂ to NO₂⁻, NO₃⁻ inhibited the decomposition of N₂O₃ to NO and NO₂, thereby enhancing the NOₓ removal.

Sun et al. (2011) simultaneously removed NOₓ and SO₂ by ozonation of NO combined with pyrolusite slurry in an agitated bubbling reactor. The extraction rate of manganese, defined as the ratio of the mass of Mn²⁺ in the liquid phase to the total manganese content (in the liquid phase to pyroslu-rite slurry). The removal efficiencies of NOₓ and SO₂ could be achieved 82% and 90%, separately, when O₂ initial concentration = 900 ppm, flue gas temperature = 40°C, total flow rate = 15 L/min, pyrolusite solution concentration = 40 g/L with the temperature at 25°C, O₂ concentration = 5%, agitator speed = 300 r/min, NO initial concentration = 750 ppm, SO₂ initial concentration = 2000 ppm, and the extraction rate of manganese was 85%. The oxidations of SO₂ to SO₄²⁻ and NO to NO₃⁻ need two electrons and one electron, therefore, the molar ratio of O₂/(SO₂ + 0.5NO₂) plays a key role in the efficiency of pollutant removal by oxidation (Sun et al, 2013). It was considered that O₂ oxidized NO to NO₂ according to Eq. (33), when the molar ratio of O₂/(SO₂ + 0.5NO₂) ≤ 18, MnO₂ oxidized SO₂ and NO₂ to MnSO₄ and Mn(NO₃)₂ according to Eqs. (34)-(35); when the molar ratio of O₂/(SO₂ + 0.5NO₂) > 18, O₂ oxidized SO₂ and NO₂ to H₂SO₄ and HNO₃ according to Eqs. (36)-(37),
thus achieve the purpose of removal. The removal efficiency of NO\(_x\) and SO\(_2\) improved with the increase in O\(_3\)/\((SO_2 + 0.5NO_2)\).

\[
\text{NO} + O_3 = NO_2 + O_2 \tag{33}
\]

\[
\text{MnO}_2 + SO_2 = Mn^{2+} + SO_4^{2-} \tag{34}
\]

\[
\text{MnO}_2 + 2NO_2 = Mn^{2+} + 2NO_3^- \tag{35}
\]

\[
SO_2 + 1/2O_2 + H_2O = 2H + SO_4^{2-} \tag{36}
\]

\[
2NO_2 + 1/2O_2 + H_2O = 2H + 2NO_3^- \tag{37}
\]

2.1.2. Effects of molar ratio of O\(_3\)/NO
In the study of ozone oxidation of NO with NaOH as absorbent, the experiments of Jakubiak and Kordylewski (2012) showed that when the chemical equivalent ratio of O\(_3\)/NO = 1, 90% of NO was oxidized to NO\(_2\) but the absorption rate of NaOH solution to NO\(_2\) was only 25%; when O\(_3\)/NO \geq 2.25, the absorption efficiency of NO\(_2\) by NaOH reached 95%. When O\(_3\)/NO \geq 2, the NaOH concentration in the absorption solution and the gas-liquid ratio in the absorber had no effect on the removal efficiency of NO. Presently, the reaction mechanism of ozone homogeneous oxidation of NO is relatively clear. Mok and Lee (2006) and Mok and Yoon (2006) and Wang et al. (2006, 2007) agreed that the chemical equivalent ratio of O\(_3\)/NO\(_2\) was the key to the removal efficiency of NO\(_x\). The key primitive reactions are as follows Eqs. (38)-(40).

\[
O_3 + NO \rightarrow NO_2 + O_2 \tag{38}
\]

\[
O_3 + NO_2 \rightarrow NO_3 + O_2 \tag{39}
\]

\[
NO_2 + NO_3 \rightarrow N_2O_5 \tag{40}
\]

Combined with the experimental analysis of ozone oxidation of NO, the oxidation reaction of ozone with NO conducted according to the chemical equivalent ratio. Below 200°C, when the O\(_3\)/NO \leq 1, the oxidation reaction only generated NO\(_2\) as shown in Eq. (38). When O\(_3\)/NO \geq 1, the reaction occurs under the condition of ozone excess, NO\(_2\) further oxidized to NO\(_3\) and N\(_2\)O\(_5\) as illustrated in Eqs. (39)-(40). Skalska et al. (2011, 2012) believed that when O\(_3\)/NO \geq 1.5, the reaction of Eq. (40) took place, and when O\(_3\)/NO = 2, all the NO was oxidized to N\(_2\)O\(_3\) by O\(_3\). However, when the reaction temperature exceeded 200°C, the ozone would decompose rapidly, and the oxidation efficiency of NO greatly reduced.

2.1.3. Effect of reaction temperature and residence time
Zhang et al. (2014) found that the rate of ozone decomposition increased with the increase of temperature, and the initial concentration of O\(_3\) could not affect this decomposition rule. Therefore, the high temperature would adversely affect the efficiency of NO oxidation by O\(_3\). For the optimization of reaction temperature and residence time of ozone-oxidized NO, Wang et al. (2016) established a 76-step kinetic mechanism to compare the numerical simulation results with the experimental results. Below 440K the temperature had almost no effect on the production of NO\(_2\), but the production of N\(_2\)O\(_5\) increased with the increase of temperature up to a maximum value of 380 K. As the temperature continues to rise, N\(_2\)O\(_5\) rapidly decomposed. The increase in reaction residence time could improve the production amount of NO\(_2\) and N\(_2\)O\(_5\) to some extent. Considering the respective formation rates of NO\(_2\) and N\(_2\)O\(_5\), the reaction residence time was 1.25 sec for NO\(_2\) and 8 sec for N\(_2\)O\(_5\). Lin et al. (2016) verified the effects of reaction temperature and residence time on the formation of N\(_2\)O\(_5\) by experiment and in situ infrared analysis. It was considered that the formation of N\(_2\)O\(_5\) was more sensitive to reaction temperature and residence time than that of NO\(_2\). When O\(_3\)/NO \leq 1, the production of NO\(_2\) was not affected by the residence time of 0-4 s. However, when O\(_3\)/NO = 2, the production of N\(_2\)O\(_5\) could reach saturation in 3-5 sec, and nearly 90% of NO\(_2\) converted to N\(_2\)O\(_5\) at 60-80°C. Moreover, the temperature had a significant effect on the formation of N\(_2\)O\(_5\). N\(_2\)O\(_5\) decreased as the temperature increased, which was nearly undetectable at 130°C.

2.1.4. Effect of absorbents
Yoon et al. (2016) adopted the H\(_2\)O\(_2\) solution provided by an ultrasonic humidifier to absorb NO\(_2\), and the efficiency of NO removal was 88.8%. Besides, the interaction between O\(_3\) and H\(_2\)O\(_2\) could promote the generation of a large number of free radicals, such as *OH, *O\(_2^-\)/HO\(_2^-\) (Zhao et al., 2017). The formation rates of free radicals were higher than the consumption rate of ozone oxidation NO, so the oxidation efficiency of NO was improved (Goldstein and Czapski, 1995; Owusu and Adewuyi, 2006). When combined with NaOH tail gas absorption, the removal efficiency of nitrogen oxides could reach 95% at O\(_3\)/NO = 0.5 (Guo et al., 2018). Sun et al. (2017) experimented on NO\(_x\) removal in a rotating packed bed by ozonation of NO combined with NaOH absorption. The order of efficiency improvement by using different absorbent was KMnO\(_4\) > H\(_2\)O\(_2\) > CO(NH\(_2\))\(_2\) > NaClO. At 25°C, inlet NO\(_x\) concentration = 1200 mg/m\(^3\), NaOH concentration = 0.05 mol/L, KMnO\(_4\) concentration = 0.01 mol/L, O\(_3\)/NO\(_x\) > 0.6, the NO removal efficiency was close to 80%. Interestingly, when O\(_3\)/NO\(_x\) > 0.6, it had little improvement on the removal efficiency of NO\(_x\) by increasing the O\(_3\)/NO\(_x\). When O\(_3\)/NO\(_x\) \leq 0.6, the generation of NO\(_2\) increased with the increase of O\(_3\)/NO\(_x\), facilitating the occurrence of Eqs. (43)-(45). While, when O\(_3\)/NO\(_x\) > 0.6, due to the low reaction rate of hydrolysis reactions of Eqs. (41)-(42) and the short gas-liquid contact time (0.27 sec) in rotating packed bed, NO\(_2\) was not absorbed completely, so the removal efficiency of NO\(_x\) did not increase significantly with the increase of O\(_3\)/NO\(_x\). The results illustrated that the hydrolysis of NO\(_x\) is the decisive factor to increase the absorption rate in the process of ozonation combined with wet removal.
HNO₂(l) + NaOH(l) → NaNO₂(l) + H₂O(l)  \hspace{1cm} (45)  
HNO₃(l) + NaOH(l) → NaNO₃(l) + H₂O(l)  \hspace{1cm} (46)

Sun et al. (2015) pre-oxidized NO to NO₂ or N₂O₃ by O₃ and then absorbed NOₓ and SO₂ by MgO slurry (0.025 mol/L), NaOH (0.05 mol/L), and CaO slurry (0.025 mol/L), respectively. The removal efficiency of NOₓ reached 70%-80%, at O₃/NO = 1, SO₂ = 500 ppm, solution pH around 10, flue gas temperature = 95°C. The removal efficiency of NOₓ using CaO slurry as absorbent was very close to that of NaOH and slightly higher than that of MgO slurry. However, adding triethanolamine (N(CH₂CH₂OH)_₃) to MgO slurry to modify the absorbent, the removal efficiency of NOₓ almost reached 100% at O₃/NO = 1, SO₂ = 500 ppm, solution pH around 11 at 90°C (Wu et al., 2018). These can be attributed to the fact that the alkaline condition was favorable for Eqs. (47)-(48), and triethanolamine (N(CH₂CH₂OH)_₃) could promote the formation of SO₂⁻ according to Eq. (49). Thus, the reaction between NO₂ and SO₂⁻ according to Eqs. (50) was promoted, and thereby improved the removal efficiency of NOₓ according to Eqs. (51)-(53). Conversely, Eq. (54) occurred under acidic condition, and H⁺⁻N(CH₂CH₂OH)_₃ could inhibit the reaction of an oxygen atom with triethanolamine to form O-N(CH₂CH₂OH)₃⁻, and thereby it was not conducive to the removal of NOₓ.

2NO₂ + H₂O → NO₂⁻ + NO₃⁻ + 2H⁺  \hspace{1cm} (47)  
2NO₂ + 2OH⁻ → NO₂⁻ + NO₃⁻ + H₂O  \hspace{1cm} (48)  
SO₃²⁻ + N(CH₂CH₂OH)₃ → SO₂⁻ + N(CH₂CH₂OH)₃⁻  \hspace{1cm} (49)  
NO₂ + SO₃⁻ → NO₂⁻ + SO₃²⁻  \hspace{1cm} (50)  
HNO₂+N(CH₂CH₂OH)₃ → (CH₂CH₂OH)₃⁻−CH₂CH₂ONO+H₂O  \hspace{1cm} (51)  
HNO₃+N(CH₂CH₂OH)₃ → (CH₂CH₂OH)₂⁻CH₂CH₂ONO₂+H₂O  \hspace{1cm} (52)  
2H⁺⁻+NO₂⁻+N(CH₂CH₂OH)₃ → O⁻N(CH₂CH₂OH)₃⁻+NO₂⁻+H₂O  \hspace{1cm} (53)  
N(CH₂CH₂OH)₃ + H⁺ → H⁺⁻N(CH₂CH₂OH)₃ + OH⁻  \hspace{1cm} (54)

2.1.5. Effect of other components in flue gas
The presence of SO₂ in the flue gas had little effect on the efficiency of NO oxidation, which was due to the 10⁻³ of reaction rate constant required for O₃ react with SO₂ than with NO (Lippmann et al., 1980). Sun et al. (2014) analyzed the detailed mechanism of ozonation of NO at 40-180°C and the influence of SO₂ on it by in situ infrared spectrometer, see Eqs. (55)-(60) occurring when the flue gas contained H₂O and SO₂, and small amounts of free radicals (O⁺*, OH⁻, and HO₂*) would produce above 100°C. Limited by reaction activation energy, ozone could hardly oxidize SO₂ (58.17 kJ/mol) at low temperature, therefore, SO₂ would not affect the ozonation of NO (3.176 kJ/mol). However, when ozone was excessive, the formation of NO₃ promoted the occurrence of Eq. (60), thus enhancing the oxidation of SO₂.

H₂O + NO + NO₂ → 2HNO₂  \hspace{1cm} (55)  
H₂O + N₂O₅ → HNO₃  \hspace{1cm} (56)  
HNO₂ + NO → HNO₃ + NO₂  \hspace{1cm} (57)  
HNO₂ + O₃ → HNO₃ + O₂  \hspace{1cm} (58)  
SO₂ + O₃ → SO₃ + O₂  \hspace{1cm} (59)  
SO₂ + NO → SO₃ + NO₂  \hspace{1cm} (60)

Moreover, several experiments of studies (Mok and Lee, 2006; Wang et al., 2007; Wang et al., 2010; Zhang et al., 2015) have shown that Hg⁰ in flue gas also had little effect on the efficiency of ozonation of NO, due to its higher activation energies required by the reaction with ozone. Not only that, compared to other components in flue gas (8000 ppm CO and 20 ppm HCl), ozone was highly selective in the oxidation of NO (NO = 200 ppm, O₃/NO < 2.0, residence time = 2.5 s) (Ji et al., 2018). The presence of CO and HCl had almost no effect on the ozonation of NO to NO₂. The water vapor (10 vol.%) in the flue gas could effectively absorb N₂O₅ below 80°C as indicated in Eq. (56), reducing the decomposition of N₂O₅ (reverse reaction of Eq. (40)), thus promoting the further oxidation of NO₂ to N₂O₅ by excessive ozone Eqs. (39)-(40).

2.2. NO oxidation by ClO₂
ClO₂ as a bleaching agent and oxidant have a mature application in industrial pulp and paper making and water treatment (Tessier and Savoie, 1997; Vincent et al., 1946). Johansson et al. (2018) believed that gaseous ClO₂ had an advantage over liquid ClO₂ in the oxidation rate and could reduce its consumption, thus, proposing a NO-SO₂-ClO₂ flue gas purification system. The efficiency of NO oxidation by ClO₂ increased linearly with the molar ratio of ClO₂ to NO and was completely oxidized when ClO₂/NO > 0.6. This followed the chemical equivalent ratio of the reaction Eqs. (61)-(62). In the range of water content of 0%-25%, H₂O did not affect on the oxidation efficiency of NO, but a small amount of NO₂ would convert to HNO₃. Below 200°C, reaction temperature also had a limited effect on ClO₂ oxidation NO. ClO₂ had almost no oxidation effect on SO₂ at low temperature (< 200°C), thereby the efficiency of ClO₂ oxidation NO was unaffected by SO₂ in the flue gas. Therefore, gas-phase ClO₂ oxidation NO has the advantages of high efficiency and high selectivity, which are beneficial to the application of integrated removal of NO with wet desulfurization while saving oxidant. Straight after that, Johansson et al. (2019) evaluated the effect of scrubber parameters on NOₓ and SO₂ absorption in the system of gas-phase ClO₂ oxidation NO. The mixed solution of Na₂SO₃ (1 g/L) and Na₂CO₃ (10 wt.%) with pH = 7.3, at 25°C, was used as absorbent, and the maximum removal efficiency of NOₓ and SO₂ were 90% and 99%, separately. High pH and Si(IV) were beneficial to the absorption
and removal of NOx. However, there are still few studies on the oxidation of NO by gaseous ClO₂.

\[ \text{NO} + \text{ClO}_2 \rightarrow \text{NO}_2 + \text{ClO} \quad (61) \]
\[ \text{NO} + \text{ClO} \rightarrow \text{NO}_2 + \text{Cl} \quad (62) \]

Through the summary of the above studies on gas-phase oxidation of NO, the homogeneous oxidation of NO has the advantages of fast reaction rate and high oxidation efficiency. Combined with the tail gas wet absorption device, NOx removal efficiency achieved was more than 90%. Also, compared with the liquid phase oxidation technology in the previous section herein, the gas phase oxidation of NO usually does not need the assistance of other oxidation technologies to achieve higher oxidation efficiency. The complex reactions and too much absorption solution of modified additives are not required in the gas phase oxidation of NO. Since the oxidations of other components in flue gas can hardly affect the NO oxidation and other aspects such as SO₂, organic pollutants, can be absorbed by the liquid phase, thus homogeneous oxidation of NO combined with wet absorption method is very suitable for the denitrification of complex flue gas and the simultaneous removal of multiple pollutants in flue gas. Its of great significance to the industrial application of integrated removal of combustion pollutants in the future. In particular, ozone, the decomposition product of which is oxygen, is a strong oxidant without secondary pollution. With the development of discharge technology, the production and application costs of O₃ reduced gradually. At present, NO oxidation by ozone combined with wet absorption has been reported in the industrial denitrification of pulverized coal furnace (Si et al., 2019), industrial kiln (Ma et al., 2016) and glass furnace (Yamamoto et al., 2016). For coal-fired boilers in power plants, the mature application is O₃ oxidation combined with an alkaline absorption solution. For instance, The ozonation technology of Thermalox developed by the International Thermal Energy Company was first applied in 2001 in the denitrification of the boiler of American Electric Power Company’s 375MW coal-fired power plant. The removal rate of NOx was 75%-90%, and the investment cost was only 35% of the SCR, and the cost of removing 1T NOx was only about 25% of SCR method (Shen, 2002). However, the removal efficiency of NO in the gas-phase oxidation is consistent with the chemical equivalent ratio of oxidants. Excessive O₂ and ClO₂ may cause escape, which will increase the operation cost and energy consumption. Therefore, it is more suitable for denitrification of flue gas with a low initial concentration of NO. It can be used to assist low NOx combustion, SCR or SNCR denitration, and combined with liquid-phase oxidation absorption to achieve ultralow emission. Also, the gas-phase oxidants are not tolerant of high temperatures and easy to decompose, which are not conducive to the efficient oxidation of flue gas pollutants at high temperatures. So that only can be applied to the removal of low-temperature flue gas (< 200 °C). These factors are not conducive to the widespread application of gas-phase oxidation technology in flue gas treatment. Therefore, it is a crucial problem for the development of gas-phase oxidation technology to expand the reaction temperature range, which can meet the different temperature range of flue gas treatment require-
ments. Besides, the consumption of oxidants was minimized to decrease the damage caused by energy consumption and leakage.

3. NO oxidation by plasma technology

This section highlights the application of plasma technology for the treatment of flue gas pollutants. The discharge method is used to transfer the electric energy to the electron, generating the free radical through the electron collision, and thus oxidizes the NO in the flue gas (Talebizadeh et al., 2014). Non-thermal plasma technology is generally divided into corona discharge, dielectric barrier discharge, and electron beam irradiation, etc. (Ma et al., 2017). Malik et al. (2011) compared the effect of pulse discharge on NO removal using volumetric plasma (Fig. 3) and surface plasma (Fig. 4) under atmospheric pressure. In this study, the gas components were NO, O₂, and N₂. The production of the active species (Eqs. (63)-(65)) and their reactions with NO are described in Eqs. (66)-(68).

\[ \text{e} + \text{O}_2 \rightarrow \text{e} + 2\text{O} \quad (63) \]
\[ \text{e} + \text{N}_2 \rightarrow \text{e} + 2\text{N} \quad (64) \]
\[ \text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} \quad (65) \]
\[ \text{O} + \text{NO} + \text{M} \rightarrow \text{NO}_2 + \text{M} \quad (66) \]
\[ \text{O}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{O}_2 \quad (67) \]
\[ \text{N} + \text{NO} \rightarrow \text{N}_2 + \text{O} \quad (68) \]

Active components increased with specific input energy (SIE), enhancing the NO removal efficiency. However, the high specific input energy (SIE) led to an increase in the local concentration of active components, promoting the occurrence of Eqs. (69)-(72), so the energy consumed (EC) increased. The
energy consumed decreased with the increase of initial concentration of O₂ and NO. To achieve the same efficiency of NO removal, the volume plasma consumed more energy than surface plasma. In the absence of oxygen, the removal efficiencies of these two plasmas were higher than that of the air. NO removal efficiencies of surface plasma under all experimental conditions were higher than that of volume plasma. The energy efficiency of volume plasma decreased significantly with the increase of energy, but surface plasma was not affected by it. Implying those surface plasmas are more suitable for the reactors with higher energy densities and more compact.

\[ O + O₂ \rightarrow 2O₂ \quad (69) \]
\[ O + O \rightarrow O₂ \quad (70) \]
\[ N + N \rightarrow N₂ \quad (71) \]
\[ N + O \rightarrow NO \quad (72) \]

An et al. (2016) utilized a surface dielectric barrier discharge plasma (SDBD) reactor to explore the oxidation characteristics of NO and Hg⁰. At 110 °C and 301.8 j/L, the oxidation efficiency of NO (200 ppm) and Hg⁰ (100 μg/m³) reached 92.5% and 99.1%, respectively. The oxidation rate of NO was faster, which made it more competitive with Hg⁰ when increased energy input. The increase of initial concentration of NO or Hg⁰ and the coexistence of SO₂ and H₂O could reduce the oxidation efficiency of NO and Hg⁰. In the absence of SO₂, H₂O could promote the oxidation of NO inhibited the oxidation of Hg⁰. Compared with other active components, O₃ contributed the most to oxidation of NO and Hg⁰ in this system, due to the close oxidation efficiency of O₃ to the sum oxidation efficiency of all the active species as shown in Fig. 5. Cui et al. (2018) conducted flue gas desulfurization and denitrification experiments using a dielectric barrier discharge with a wet electrostaticprecipitator system (DBD-WESP). When dielectric barrier discharge (DBD) was used alone and the flue gas contained O₂ and H₂O, the increase of peak voltage Vp-p intensified the self-reaction of the active components Eq. (73) (Edvardsson et al., 2006), when the reaction constant of Eq. (74) (Atkinson et al., 2004) was less than Eq. (73), thus inhibiting the oxidation of NO, and the higher the oxygen content was, the more obvious the inhibition was. Furthermore, in the absence of O₂, the conversion efficiency of NO increased with the increase of Vp-p and decreased with the increase of H₂O. In the DBD-WESP system, when Vp-p = 28 kV, O₂ =3%, H₂O = 0% (in DBD), power supply of WESP = 3.5 W (U = 4.4 kV, I = 0.8 mA) and watersupply was 9.2 L/min, the optimum removal rate of NO and SO₂ were 98.9% and 87.1%, respectively. The improvement in conversion efficiency was due to the easier formation of *OH and *O in the WESP system, which promotes the further oxidation of NO and SO₂.

\[ N^* + OH \rightarrow NO + ^*H \quad c = 4.94 \times 10^{-11} \text{cm}^3/\text{molecule} \cdot \text{s} \quad (73) \]
\[ NO + ^*OH \rightarrow HNO₂ \quad c = 3.3 \times 10^{-11} \text{cm}^3/\text{molecule} \cdot \text{s} \quad (74) \]

Plasma denitrification technology was invented in the 1970s. At present, electron beam discharge combined (EBDC) with wet denitrification is the most widely studied and applied technology. In 1997, Chengdu Thermal Power Plant, in cooperation with the former Japanese EBARA Company, introduced the electron beam denitrification technology and ran it on the boiler of 200 MW unit. The efficiencies of desulfurization and denitrification reached the leading level in China at that time (Yang et al., 2017). After that, the technology was spread to Hangzhou Xielian Thermal Power Co., LTD. At the beginning of 2010, the first set of streamer corona discharge non-thermal plasma desulfurization and denitrification projects in China started in Sinopec Baring Petrochemical Co., LTD (Zhang, 2014). This technology integrates electric dust removal, SCR or SNCR, and low-temperature plasma technology, which avoids the problems of the high initial concentration of NOₓ under low load operation of coal-fired power plant boilers, and low fuel gas temperature at SCR inlet requiring excessive ammonia. In the case of low SCR or SNCR removal efficiency, this technology can still achieve ultra-low emission of flue gas pollutants. Although SO₂, H₂O, and O₂ in flue gas have an effect on plasma oxide of NO comparing with liquid phase and gas-phase oxidation of NO, this technology can efficiently and rapidly simultaneously remove SO₂, NOₓ, VOCs and heavy metals in flue gas (Zhang, 2014). In particular, plasma technol-
ogy is used to purify flue gas with a variety of sulfur content. However, the high price of electron accelerator, the short life of electron gun, the high cost of operation and maintenance, and the high energy consumption all restrict the application and promotion of plasma denitrification technology. Pulse corona induced plasmachemical process (PPCP) is developed on the based on EBDC, which has low electron energy and does not require irradiation shielding, thus improving the safety of the technology. However, there are still problems such as high energy consumption, short pulse power life and high equipment cost (Nasonova et al., 2010). If these bottlenecks can be overcome, plasma technology will be a potential means of denitrification.

4. NO oxidation by catalysts

Compared with O₃, ClO₂, and plasma oxidation, the homogeneous oxidation of NO by O₂ has very low reaction efficiency. For the reaction Eq. (75) high concentration of O₂ is favorable for the positive direction, which is an exothermic reaction. However, the actual about 4-6% of O₂ is in flue gas with high temperature. The stoichiometric ratio required (NO₂/NO > 1) for denitrification cannot be achieved by simply relying on O₂ in flue gas to oxidize NO. Therefore, the study on the heterogeneous catalytic oxidation of NO to change the kinetic characteristics of the reaction has been continuous since the 1970s. Wu et al. (2010) compared MnOx/TeOx catalysts prepared by coprecipitation method and impregnation method. The maximum NO catalytic oxidation efficiency of MnOₓ(0.3)/TeOₓ prepared by coprecipitation method was 89% at 250°C, while that of MnOₓ(0.3)/TeOₓ prepared by impregnation method was 69% at 330°C, with NO initial concentration = 600 ppm, O₂ = 4%, and space velocity (SV) = 25,000 h⁻¹. Park et al. (2012) compared the Mn/TeOx catalysts prepared by dipping manganese acetate and manganese nitrate on nano-scale TeOₓ. NO catalytic oxidation efficiency with manganese acetate as precursor was 88% at 225°C, and was higher than that of manganese nitrate, due to the higher dispersion of manganese species.

\[ 2\text{NO}(g) + \text{O}_2(g) = 2\text{NO}_2 \]  

(75)

4.1. The types of catalysts used for NO catalytic oxidation

4.1.1. Molecular sieve catalysts

The molecular sieve is a kind of silicoaluminate compound with cubic lattice and uniform pore structure and has the characteristics of strong thermal stability, high specific surface area, and strong adsorption (Chen et al., 2018; Cheng et al., 2019; Marta et al., 2019). Some studies on SCR denitrification showed that molecular sieve catalysts had good denitrification performance, hydrothermal resistance and good SO₂ resistance (Wang et al., 2019; Chen et al., 2018; Leistner and Olsson, 2015). Brandin et al. (1989) used H-mordenite for the catalytic oxidation of NO and found that the oxidation activity of NO was related to the content of aluminum in the H-mordenite. Odenbrand et al. (1989) found that NO adsorbed on the H-mordenite catalyst to form NO⁺, and then the adsorption capacity decreased with the decrease of the aluminum content in H-mordenite, which led to the NO oxidation efficiency decrease. The H-mordenite catalyst had good activity at high temperature, and the catalytic oxidation efficiency of NO was the highest at 350°C, which was 50%. Li et al. (2009) found that the catalytic activity of the H-ZSM-5 catalyst to NO oxidation at 10-90°C significantly increased by increasing the ratio of Si to Al, and the maximum oxidation efficiency was 60% at 20°C. Olsson et al. (2009) established the kinetic model of NOx adsorption and oxidation by Cu-ZSM-5 catalysts. It was realized that NO₂ could form nitrates on the surface of Cu-ZSM-5 and blocked the pore of catalyst, thus weakening the catalytic oxidation effect of Cu-ZSM-5 on NO. However, at low temperature, NO could oxidize with nitrates which were weakly adsorbed on the Cu-ZSM-5 surfaces, to alleviate this adverse effect. This phenomenon was found in the study of NO oxidation mechanism of commercial Cu-CHA catalysts, and the activity of Cu-CHA was highest at about 350°C (Ruggeri et al., 2015). At present, the oxidation efficiency of the molecular sieve catalyst for NO oxidation is low (< 60%), and most of them need to be conducted in the high-temperature range of 300-400°C. The research on the application of molecular sieve catalysts for NO oxidation needs to be further improved.

4.1.2. Carbon-based catalysts

Sousa et al. (2012) prepared carbonized gel by sol-gel method using nitrogen-containing polymer precursors as raw materials, melamine and urea as nitrogen sources and investigated the catalytic oxidation of NO by catalysts with different nitrogen contents at room temperature. The NO oxidation efficiency of nitrogen-doped carbon gel was higher than that of undoped carbon gel. When the initial concentration of NO was 1000 ppm, the oxygen content was 20%, the oxidation efficiency of NO was up to 88%. Wang et al. (2011) prepared porous carbon nanofibers (PCNFs) through stable carbonization and activation by water vapor after electrospinning of polyacrylonitrile (PAN) polymer solution in N, N-dimethylformamide (DMF). PCNFs contained high microporous and had catalytic oxidation effect on NO, which could remove the low concentration of NO₂ stably at room temperature. Activated carbon material has the advantages of large specific surface area and low price, and use the abundant pore structure on its surface to adsorb NO and O₂, which can promote the oxidation of NO (Li et al., 2018). Adapa et al. (2006) conducted NO catalytic oxidation experiments on activated carbon fibers (ACFs) prepared with different precursors, indicating that NO oxidation efficiency gradually increased with the increase of oxygen concentration at 30°C. NO catalytic oxidation performance of ACFs prepared by phenolic resin as precursor was better than that of ACFs prepared by asphalt or by viscose as the precursor. Wang et al. (2014) used coprecipitates to load MnO₂ on activated carbon fiber to obtain the MnO₂@AFC catalyst. NO catalytic oxidation efficiency of MnO₂@AFC increased by about 10% comparing with AFC. Hu et al. (2019) compared the catalytic oxidation performance of activated carbon fiber cloth (ACFCs), zeolite, and organic metal skeleton (OMS) for NO at 25°C. NO catalytic activity of the three catalysts was ACFCs > Zeolite > MOFs, but the tolerance of SO₂ was the reverse of this order. Although carbon catalysts have better catalytic oxidation performance for NO at room temperature, they are not suitable for NO oxidation treatment of high-temperature and
4.1.3. Precious metal catalysts

Precious metal catalysts have been studied and applied in catalytic oxidation of formaldehyde, methane, methanol, CO and can show excellent catalytic oxidation performance (Friberg et al., 2019; Qu et al., 2019; Hong et al., 2019). Yang et al. (2019) prepared the Ag/TiO$_2$/AC catalyst supported by activated carbon for photocatalytic oxidation of NO by the sol-gel method. The addition of Ag nanoparticles extended the optical response range of the catalyst to the visible wavelength range, thus improving the photocatalytic activity of the Ag/TiO$_2$/AC on NO. It enabled the oxidation efficiency of NO to be maintained at about 60% after 4 hours under the room temperature, with SV = 1000 h$^{-1}$, O$_2$ concentration = 5%, and NO initial concentration = 350 mg/m$^3$. The TiO$_2$ supported Ru/TiO$_2$ catalyst was prepared by the evaporator impregnation method by Li et al. (2009). Under the conditions of 275°C, SV = 180,000 h$^{-1}$, NO initial concentration = 400 ppm, and O$_2$ = 10%, the catalytic oxidation efficiency of NO could reach 94%.

Kaneeda et al. (2009) using the Pd modified Pt/Al$_2$O$_3$ catalyst to conduct NO catalytic oxidation experiment at 300°C. With the increase of Pd, the catalytic oxidation activity of NO and the resistance to high-temperature sintering of active metal Pt significantly improved. After 60 h of heat treatment at 830°C, Pd-Pt/Al$_2$O$_3$ could still maintain 50% catalytic oxidation efficiency of NO. Desprès et al. (2004) studied the kinetic properties of catalytic oxidation of NO using Pt/SiO$_2$ catalyst with Pt load of 2.5 wt.%. The maximum NO oxidation efficiency reached 88% at 300°C, with H$_2$O = 5% and O$_2$ concentration = 10%. NO oxidation efficiency increased with the increase of oxygen content, but after the oxygen content exceeded 10%, with the continuous improvement of oxygen content no notable increase the oxidation efficiency observed. NO oxidation efficiency decreased with the increase of NO initial concentration. The increase of NO$_2$ initial concentration forming a platinum oxide film on the surface of the catalyst resulted in the deactivation of the catalyst but could be regenerated. Schmitz et al. (2006) adopted a high-throughput method to simulate the kinetic parameters of NO catalytic oxidation using the catalysts prepared by Pt loading on Al$_2$O$_3$andSiO$_2$. The catalytic oxidation activity of Pt loading on SiO$_2$ was higher than that loading on Al$_2$O$_3$. NO catalytic oxidation efficiency could reach 90% at 200°C, with NO initial concentration = 500 ppm, O$_2$ concentration = 8%, and SV = 36,000 h$^{-1}$. The relative importance of the influence factors on NO catalytic oxidation efficiency during the preparation of catalyst was: carrier > pretreatment condition > loading amount > calcination atmosphere > calcination temperature > active metal precursor.

It can be realized that precious metal catalysts have better catalytic performance in the experimental study of NO catalytic oxidation at 200-300°C and high resistance to high-temperature aging. However, due to the high price of raw materials, it is more difficult to apply and popularize them than other non-precious metal catalysts.

4.1.4. Metallic oxide catalysts

Compared with precious metal catalysts, metal oxide catalysts have a wide range of raw materials, low prices, and high activity which is favored by the researchers in the field of catalysis. The application of metal oxide catalyst to catalytic oxidation of NO has become a hot topic. Zhang et al. (2019) synthesized YMn$_2$O$_3$ nanofibers by electrospinning for catalytic oxidation of NO. The maximum conversion rate of NO to NO$_2$ was 81%, at 310°C, with O$_2$ = 10%, NO initial concentration = 500 ppm, and balanced with N$_2$ at weight hourly space velocity (WHSV) was 240,000 ml/gh. When H$_2$O = 5% was used, the NO conversion rate reduced to 66%. YMn$_2$O$_3$ nanofibers had good resistance to hydrothermal aging. Under the action of 10% H$_2$O flow, the morphology remained unchanged after the aging 10 h at 800°C. Tang et al. (2011) explored the reaction pathway of NO oxidation on the surface of MnO$_2$/TiO$_2$. NO first adsorbed on the Mn site to form nitrosyl, which was then rapidly oxidized to nitrate by the lattice oxygen of the manganese oxide. Nitrate decomposed into NO$_2$ at high temperature, and O$_2$ was used to supplement the lattice oxygen vacancy. This reaction mechanism follows the Mars-van Krevelen catalytic mechanism shown in Fig.6. The maximum NO oxidation efficiency was 89% at 250°C, with NO initial concentration = 600 ppm, O$_2$ = 4%, and SV = 25,000 h$^{-1}$. However, when 400 ppm SO$_2$ in flue gas, the catalytic oxidation efficiency of NO decreased rapidly, and only 16% efficiency remained in the end. The hol-
low MnO$_2$-CeO$_2$ catalyst prepared by Shen et al. (2017) with colloidal carbon spheres as templates (CS), had more active sites and oxygen vacancies than that prepared with activated carbon (AC) as templates, thus having higher catalytic oxidation activity of NO. At NO initial concentration = 250 ppm, O$_2$ = 5% SV = 120,000 h$^{-1}$, 220$^\circ$C, the conversion rate of NO could reach 82%. NO oxidation efficiency reduced by about 8% after 5% H$_2$O was introduced, but could be restored after water was turned off. NO oxidation efficiency decreased by about 15% after SO$_2$ was introduced and the efficiency could hardly be restored after SO$_2$ was switched off.

Ce$_{0.2}$Co$_{0.2}$Ti mixed oxide catalyst synthesized by Shang et al. (2015) via the sol-gel method. NO catalytic oxidation efficiency was 76%, under the condition of NO = 400 ppm, O$_2$ = 8%, SV = 30,000 h$^{-1}$, at 300$^\circ$C. The interaction between Ce and Co improved the dispersion of metal oxides and the adsorption capacity of oxygen, which was conducive to the oxidation of NO. Wang et al. (2017) prepared Ce$_{0.2}$Zr$_{0.2}$O$_2$ carrier (CZ) by the surfactant-template method. Then, Cu/CZ catalysts were prepared by the sedition-precipitation method doping different mass of Cu. In the NO catalytic oxidation experiment, Cu(6 wt.%)/CZ calcined at 550$^\circ$C showed the best performance. In the range of 250-370$^\circ$C, the catalytic oxidation efficiency of NO exceeded 50%, with NO initial concentration = 500 ppm, O$_2$ = 5%, SV = 80,000 h$^{-1}$. At 300$^\circ$C, the presence of 5% H$_2$O in the flue gas reduced the catalytic efficiency by about 7%; the presence of 100 ppm SO$_2$ reduced the catalytic efficiency by about 18%, and the presence of 100 ppm SO$_2$ and 5% H$_2$O reduced the catalytic efficiency by about 27%. The interaction between CuO and carrier CZ not only improved the dispersion of CuO particles on the carrier but also caused the formation of more lattice vacancies in the Cu-Ce-Zr solid solution, which was conducive to the adsorption of NO and the activation of O$_2$ by the catalyst, thus promoting the oxidation of NO. Zhang et al. (2013) obtained CrCe/TiO$_2$-PILC nanocomposite catalyst for NO catalytic oxidation by impregnation method with columnar clay TiO$_2$ as a carrier. When the molar ratio of Cr/Ce was lower than 1:0.25, the oxidation efficiency of NO increased with the increase of Ce. Cr$_{1}$Ce$_{0.25}$/TiO$_2$-PILC gained the maximum NO catalytic oxidation efficiency of 69%, under the condition of NO = 400 ppm, O$_2$ = 8%, SV = 35,400 h$^{-1}$, at 350$^\circ$C. The addition of CeO$_2$ strengthened the interaction between the active metal and the carrier increased the content of chemisorbed oxygen on the catalyst surface and the valence of Cr, as well as improved the redox capacity of the catalyst and thus promoted the catalytic oxidation performance of NO. However, when the flue gas contains 4% H$_2$O, the efficiency of NO catalytic oxidation reduced to 45%, and when it contained 200 ppm SO$_2$, the efficiency reduced to 24%. When it contained both 4% H$_2$O and 200 ppm SO$_2$, the efficiency reduced to 21%. The catalytic inactivation caused by water vapor could be recovered after cutting off the water, while the inactivation caused by SO$_2$ could be partially recovered after switching off the SO$_2$.

NO catalytic oxidation efficiency of the above metal oxide catalysts was more than 50% between 200-400$^\circ$C, which can meet the chemical equivalent ratio required for oxidation-absorption denitrification. Also, the multi-metal oxide catalyst can provide more active sites, which is more conducive to the catalytic oxidation of NO. However, its low temperature (< 200$^\circ$C) activity still needs to be further improved to adapt to denitrification application in a higher temperature range. The tolerance to H$_2$O and SO$_2$ still needs to be improved.

4.2. Effect of catalysts on NO oxidation

In the study of Hg$^+$ catalytic oxidation by some commercial selective catalytic reduction catalysts, it was found that V$_2$O$_5$-WO$_3$-TiO$_2$ catalyst could promote the rapid SCR reaction to a certain extent and generated a small amount of NO$_2$, which was conducive to the adsorption and oxidation of mercury (Liu et al., 2015). However, there are few studies on the direct use of commercial catalysts in the oxidation properties of NO. Most studies focus on transition metal oxides. Lu et al. (2009) prepared 15 wt.% transition metal oxide catalysts supported by γ-Al$_2$O$_3$ for NO catalytic oxidation by volume impregnation. Under the condition of NO initial concentration = 540 ppm, O$_2$ = 4%, SV = 3000 h$^{-1}$, each metal oxide catalyst reached the optimal activity at 300$^\circ$C and the order of NO oxidation efficiency was: Mn > Cr > Co > Cu > Fe > Ni > Zn. In the experiment by Tang et al. (2010), the transition metal oxide catalysts prepared by coprecipitation for NO oxidation, its catalytic efficiency ranking was consistent with that of Lu et al. (2000), at 200$^\circ$C, with NO = 500 ppm, O$_2$ = 3%, SV = 51,000 h$^{-1}$. Wang et al. (2016) proved NO catalytic oxidation performance of Co-based catalysts was better than Mn, Fe,Cr, and Ni catalysts. It indicates that Mn, Co, and Cr are relatively effective in catalytic oxidation of NO.

Li et al. (2012) conducted a study on low-temperature (50-250$^\circ$C) catalytic oxidation of NO over Mn−Co−Ce(La)−O$_x$ prepared by coprecipitation method and calcined at 400$^\circ$C. At 100−200$^\circ$C, the maximum NO conversion decreases in order as: Mn−Co−Ce(20 wt.%)-O$_x$ > Mn−Co−La(20 wt.%)-O$_x$ > Mn−Co−O$_x$ > Mn−Co−O$_x$ > Ce−O$_x$ > La−O$_x$. The optimum catalyst conversion rate was about 80%, at 150$^\circ$C with SV = 35,000 h$^{-1}$. For Mn−Co−Ce−O$_x$ catalyst, with the increase of Ce content from 0 wt.% to 20 wt.%, the oxidation efficiency of NO increased significantly but decreased if the content of Ce exceeded 20 wt.%. Oxygen concentration over 3% had little effect on catalytic oxidation efficiency of NO. However, the presence of 15% H$_2$O and 150 ppm SO$_2$ inhibited the activity of the catalyst due to the active sites of the catalyst covered by the formation of sulfates and nitrates. The addition of Ce could help to stabilize the high oxidation state of manganese and improved the redox performance of the MnO$_2$-CeO$_2$ catalyst. Compared with the catalyst of MnO$_2$ or CeO$_2$, the catalytic oxidation efficiency of NO by MnO$_2$-CeO$_2$ at 200$^\circ$C improved by 3-10 times (Qi and Li, 2015). The doping of ZrO$_2$ could reduce the reaction temperature and increase the oxidation efficiency of NO. Even after hydrothermal aging under 10% H$_2$O at 750$^\circ$C for 1 h, the optimum oxidation efficiency of NO by MnO$_2$-CeO$_2$−ZrO$_2$ was 83% at 300$^\circ$C, while that was 72% at 350$^\circ$C by MnO$_x$-CeO$_2$, under the conditions of NO = 200 ppm, O$_2$ = 8%, H$_2$O = 5%, CO$_2$ = 8%, SV = 25,000 h$^{-1}$.

Li et al. (2017) obtained the Co$_x$Mn$_{3-x}$/TiO$_2$ catalyst by Ce modified TiO$_2$ carrier and loaded manganese and cobalt oxide that had a good performance for the catalytic oxidation of NO and Hg$^+$ in the flue gas. Appropriately increasing the content of Co$_x$O$_y$ and CeO$_2$ was helpful to improve the catalytic performance. The addition of Co could increase the content
Fig. 7 – NOx conversion comparison: (a) O3 without catalyst; (b) O3 combined with Al2O3, 0.12 sec; (b) O3 combined with MnO2/Al2O3, 0.08 sec; (b) O3 combined with MnO2/Al2O3, 0.12 sec (Lin et al., 2016).

of Mn2O3, and the addition of Ce could promote the better dispersion of manganese and cobalt oxide. Co12Mn2/Al2O3 exhibited the best performance, which was 88% at 250 °C for Hg0 catalytic oxidation and was 60% at 350 °C for NO catalytic oxidation, under the conditions of Hg0 = 30 μg/m3, NO = 500 ppm, SO2 = 100 ppm, O2 = 6%, H2O = 3%, N2 as balance gas, GHSV = 30,000 h−1. But the low temperature (< 250 °C) oxidation efficiency of NO was less than 40%. The increase of oxygen concentration from 0% to 9% promoted the catalytic oxidation of NO and Hg0. The presence of HgO had little effect on the oxidation of NO, but NO promoted the oxidation of HgO in the presence of high O2 concentration. The presence of SO2 and H2O reduced catalytic oxidation efficiency, especially for NO.

4.3. NO oxidation by O3 combined with catalysts

Ozone has a high oxidation capacity at low temperatures. Some researchers use ozone combined with a catalyst to study NO oxidation and strive to improve the efficiency of NO oxidation and reduce the amount of ozone. Ding et al. (2014) pre-oxidized NO by O3 on the Ce-Ti catalyst and then removed NOx and SO2 by the ammonia-based absorbent. The system of O3/H2O/OCe-Ti encouraged the production of large amounts of *OH free radicals making the removal efficiency of NOx as high as 95% and nearly 100% of SO2 at 120 °C under the conditions of mixed oxidant flow = 100 mL/min, O3 concentration = 8.5 mg/L, H2O flow = 2.4 mL/min, and total gas flow = 400 mL/min. Jogi et al. (2016) reported the NO oxidation by O3 over MnO2/Al2O3 (spherical), below 100 °C. It was suggested that when O3/NO > 1 the catalysts could enhance the deep oxidation of NO2 to N2O3 and reduce the ozone consumption and the reaction time as illustrated in Figs. 7 and 8. However, when O3/NO < 1, catalysts could not promote the oxidation of NO to NO2. With the increase in temperature from 20 °C to 180 °C, the TiO2 catalyst could accelerate the decomposition of ozone that could generate reactive oxygen species for NO oxidation as shown in Fig. 9. After that, Erme and Jogi (2019) compared the application of TiO2, Al2O3, and Fe2O3 to the ozonation of NO, Fe2O3 promoted the oxidation of NO to N2O3 more obviously than TiO2 and Al2O3 at 100 °C. However, it still failed to improve the oxidation efficiency of NO at low ozone concentration (O3/NO < 1).

Guo et al. (2017) synthesized Ce0.85Cu0.07Co0.1O2-δ catalytic by alkaline hydrothermal method, combined with ozone oxidation of NO, and its optimal catalytic activity reached 91.5% at 120 °C, with NOx = 460 ppm, O3 = 2.8 mg/L, O3 flow = 35 mL/min, water flow = 0.10 mL/min, total flow of all reactants = 135 mL/min, and gaseous hourly space velocity (GHSV) = 35,000 h−1. The oxidation efficiency of NOx was correlated with the concentration of *OH which was determined by the activity of the surface bridging-OH. Liu et al. (2019b) used Fe2O3/SAPO-34 to catalyze the reaction between ozone and water (4%) to generate hydroxyl and superoxide radicals on the oxygen vacancy of catalyst, thereby improving the oxidation efficiency of NO under low concentration of ozone (O3/NO = 0.16). The maximum oxidation efficiency of NO in the system was 40.7% at 80 °C, and the oxidation ef-
Fig. 8 – Influence of O₃ concentration on NO₂ production: (a) O₃ without catalyst at 20°C; (b) O₃ without catalyst at 100°C; (c) O₃ combined with TiO₂ at 20°C; (d) O₃ combined with TiO₂ at 100°C (Jõgi et al., 2016).

Fig. 9 – Influence of TiO₂ catalyst on ozone decomposition (Jõgi et al., 2016).

Efficiency of NO remained stable when the water content was less than 8%. Han et al. (2018) prepared black-TiO₂ by sol-gel method and carried out NO catalytic oxidation experiment with a molar ratio of O₃/NO = 0.6 and 6% H₂O, at 60°C. NO catalytic oxidation efficiency of ozone combined with black-TiO₂ was 29.8% higher than that of only using ozone (55%), and was 8.6% higher than that of ozone combined with TiO₂. A large number of surface hydroxyl groups (Vo-OH) were noticed on black-TiO₂ that promoted the generation of OH₂⁺ free radicals due to the synergy between Vo-OH and oxygen vacancy. Compared to O₃/H₂O/TiO₂ system, there was not only abundant *OH in O₃/H₂O/black-TiO₂ system and also numerous OH₂⁺ existed, promoting the conversion of NO to HNO₃. However, excess H₂O could inhibit the activity of the catalyst. Both of these studies improved the oxidation efficiency of NO with the help of free radicals generated by the catalytic reaction between ozone and water. It was noted that the oxygen vacancy on the catalyst was the active site of NO oxidation. As mentioned above, manganese and cobalt oxide have better catalytic oxidation performance of NO (Qiu et al., 2016; Gao et al., 2017), and the interaction between active metals in the multi-metal oxide catalyst promotes the formation of more oxygen vacancies on the catalyst. Using this characteristic, Si et al. (2020) prepared 15%Mn-Co(2:1)/TiO₂ catalysts for NO oxidation under O₃/NO = 0.5 at 50–400°C, with NO initial concentration = 500 ppm, O₂ = 4%, GHSV = 24,000 h⁻¹. Compared with 15%Mn/TiO₂ and 15%Co/TiO₂, the synergistic effect of 15%Mn-Co(2:1)/TiO₂ combined with O₃ was so obvious. NO oxidation efficiency by O₃ combined with 15%Mn-Co(2:1)/TiO₂ was higher than the numerical accumulation efficiency of only using ozone and only using catalyst below 250°C, as shown in Fig. 10. The co-loading of MnOₓ and CoOₓ increased the proportion of Mn²⁺/Mn⁴⁺, which promoted the formation of more oxygen vacancies on the catalyst to maintain electrostatic balance (Jia et al., 2016), this enabled NO to adsorb on the surface of the catalyst to form a large number of monodentate nitrates. As the final step in the decomposition of nitrate species into NO₂, monodentate nitrates is a crucial intermediate product (Tang et al., 2011). Furthermore, the
presence of ozone accelerated the catalytic oxidation process of NO on 15%Mn-Ce(2:1)/TiO\textsubscript{2}. NO oxidation efficiency maintained above 50% under the condition of O\textsubscript{3}/NO = 0.5 at 50-400 °C, which widened the reaction temperature range. N\textsubscript{2}O\textsubscript{5} was not realized under this reaction condition. However, the presence of SO\textsubscript{2} and H\textsubscript{2}O still inhibited the activity of the catalyst.

### 4.4. NO oxidation by catalysts combined with other oxidants

Cui et al. (2019) integrated dielectric barrier discharge combined with MnCe/Ti for NO oxidation to reduce the energy consumption of the DBD system. With the increase of specific energy density, the removal efficiency of NO increased in the range of 30-250 J/L, and the highest removal efficiency was 86.9% when the initial concentration of NO = 200 mg/m\textsuperscript{3}. The dispersion of Mn\textsubscript{3}O\textsubscript{4}-CeO\textsubscript{2} on MnCe/Ti was higher than that of the Mn/Ti-Ce/Ti, the content of Mn\textsuperscript{3+} increased, that was conducive to the catalytic oxidation of NO since weakly adsorbed Mn\textsuperscript{3+}-O bond was more likely to break and release NO\textsubscript{2} (Liu et al., 2017c; An et al., 2014). However, this system is only suitable for a low concentration of NO oxidation. A high concentration of NO and SO\textsubscript{2} will significantly inhibit the efficiency of catalytic oxidation.

Catalyzing H\textsubscript{2}O\textsubscript{2} to decompose free radicals of *OH or HO\textsubscript{2}•/O\textsubscript{2}•− for NO oxidation has high research potential. Meng et al. (2020) used goethite (*FeOOH) as a catalyst, and the electron transfer between Fe\textsuperscript{3+}/Fe\textsuperscript{2+} promoted the decomposition of H\textsubscript{2}O\textsubscript{2} vapor to oxidized NO in coke oven flue gas at 100-350 °C. Different from the H\textsubscript{2}O\textsubscript{2} oxidation system without catalyst, in which the main active species was *OH, the α-FeOOH/ H\textsubscript{2}O\textsubscript{2} system also produced HO\textsubscript{2}•/O\textsubscript{2}•− significantly improving the oxidation efficiency of NO. High oxidation to N\textsubscript{2}O\textsubscript{5} was noticed, under the conditions of H\textsubscript{2}O\textsubscript{2}/NO = 2.0, H\textsubscript{2}O\textsubscript{2} solution feeding rate = 148.9 mL/min, GHSV = 137,747 h\textsuperscript{−1}, NO = 200 ppm, SO\textsubscript{2} = 660 ppm, O\textsubscript{2} = 6%. Between 175-250 °C, the conversion rate of NO was maintained above 90%, and the maximum conversion rate was 98.8% at 225°C, which is very suitable for coke-oven flue gas denitration. α-FeOOH proved to have good NO oxidation selectivity and catalytic stability. Yuan et al. (2020) prepared Fe/ZSM-5 catalyst to catalyze H\textsubscript{2}O\textsubscript{2} and Na\textsubscript{2}S\textsubscript{2}O\textsubscript{4} vapor for NO oxidation and used Ca(OH)\textsubscript{2} solution as absorbent. The optimal experimental conditions were: H\textsubscript{2}O\textsubscript{2} = 10 wt.%, Na\textsubscript{2}S\textsubscript{2}O\textsubscript{4} = 0.5 wt.%, Fe/ZSM-5 = 0.3 g, total flow rate = 1.5 L/min, and reaction temperature = 140 °C. The maximum removal rate of NO was 95.5% when the flue gas contained 500 mg/m\textsuperscript{3} NO, 2000 mg/m\textsuperscript{3} SO\textsubscript{2}, and 30 μg/m\textsuperscript{3} Hg\textsuperscript{0}. With the help of Fe/ZSM-5, H\textsubscript{2}O\textsubscript{2} decomposed to more *OH and Na\textsubscript{2}S\textsubscript{2}O\textsubscript{4} decomposed to more SO\textsubscript{4}2−, which were the major active oxidizing species. The reaction mechanism and influence mechanism were similar to that of liquid-phase oxidation of NO.

Comparison with liquid-phase oxidation and gas-phase oxidation, the catalytic oxidation efficiency of NO depends on the properties of the catalyst, which are affected by the reaction temperature and other components of flue gas. In the existing researches, the catalysts generally applicable temperature
range is 200-400 °C, and the water resistance and sulfur resistance are not good enough, easy to cause the catalyst deactivation. This is a crucial problem in the simultaneous removal of multiple pollutants from flue gas by catalytic oxidation. Despite this, there are still some industrial applications of catalytic oxidation for flue gas treatment. For instance, Meng et al. (2020) used a goethite catalyst combined with H₂O₂ vapor to oxidize coke furnace flue gas and realized high-efficiency denitrification. Tianjin Binhuan Chemical Engineering and Technology Research Institute Co. Ltd. developed a new oxidation catalyst with high catalytic activity at room temperature to 300 °C. In the practical application of air pollution control, desulfurization and denitrification can reach 85%. The advantages of different kinds of catalysts, such as strong adsorption performance of molecular sieve catalysts, the outstanding low-temperature performance of activated carbon catalysts, high chemical adsorption oxygen, and multiple valence state of transition metal oxide catalysts was advisable in preparation of catalysts with higher applicability. The oxidation efficiency of NO can be improved and the reaction temperature range can be widened by the combination of catalysts with various oxidation methods to satisfy the denitrification of different flue gas types. It is a research trend in the future to combine various oxidation methods and make use of their respective advantages to promote the oxidation removal of NO which has a high industrial application prospect.

5. Research prospect of NO oxidation

In this paper, the research status of liquid-phase oxidation, gas-phase oxidation, plasma technology, and gas-solid catalytic oxidation of NO is reviewed. The appropriate removal method should be selected according to different flue gas conditions. For example, the liquid-phase oxidation method can efficiently simultaneously remove multiple contaminants, and the oxidation competition of NO in the gas phase oxidation method is superior to other pollutants. Catalytic oxidation of NO can quickly and efficiently oxidize NO and reduce the consumption of oxidants. However, there are still many problems to be solved in the study of oxidation to remove NO from flue gas.

(1) The study on the deep oxidation of NO is expected. The oxidation products of N₂O₅ has the highest solubility in NO₂. Enhancing NO oxidation to N₂O₅, and reducing the consumption of oxidants as far as possible is still the research purpose of oxidation to remove NO. The use of complex oxidants and the development of catalysts with multiple active sites may promote the deep oxidation of NO.

(2) The study on the enhancement of SO₂ resistance during the catalytic oxidation of NO. In the process of NO oxidation, usually accompanied by a certain amount of SO₂ oxidation. Although SO₂ has little influence on the oxidation efficiency of NO in the gas-phase oxidation process of NO, its effect is more in the liquid-phase oxidation and catalytic oxidation. Especially for catalytic oxidation, the generation of SO₃ will cause a series of problems and lead to poisoning effects on catalysts, thus inhibiting the oxidation of NO. Therefore, the development of catalysts with high selectivity and sulfur resistance to NO oxidation is still a great challenge for NO catalytic oxidation process research. The preparation method of the catalyst and the types of active components can be modified and developed, such as the sol-gel method, co-doping method, and other preparation methods, as well as adding multiple active components to enhance the synergistic effect among active components thus improving the sulfur resistance of the catalyst.

(3) The study on the tolerance of catalysts to water vapor is highlighted. Under the condition of water, N₂O₅ formed after NO deep oxidation will react with water to form nitric acid. Nitric acid is not likely to decompose on the surface of the catalyst at low temperature to deactivate the catalyst. Even if the catalyst has high sulfur resistance, it also faces the problem of catalytic efficiency reduction caused by nitric acid acidification.

(4) The study on the effects of organic pollutants should be investigated. Although there have been many studies on simultaneous desulfurization and denitrification with mercury, the mechanism of the effect of organic pollutants in flue gas on simultaneous removal was incomprehensive. The emission of organic matters is increasing day by day and may become the controlling factor of the emission index in the future. The efficient and stable removal of multiple mixed organics and NOₓ, SO₂, Hg⁰ should be considered, not just the effect of a single organics.

(5) It is hoped that the capture of aerosols can be conducted at the same time. There are some aerosols in the flue gas, especially the oxidation of the gas phase, which may increase the content of the aerosols. The composition, ratio, and flow rate of absorbent and arrangement of absorption devices, as well as the optimization of the tail gas absorption system by combining with the methods of fog removal and dust removal, are also a research direction of the oxidation method for removing nitrogen oxides from flue gas.

(6) How to reduce the running cost is also a problem. The preparation of gas-phase oxidants, heating and evaporating oxidants in liquid phase oxidation, and the production of free radicals enhanced by ultrasound and ultraviolet light, all will have a high running cost. To improve the reaction efficiency and to reduce the cost of oxidation are regarded as a way to reduce the running cost-effectively.

6. Conclusion

In this paper, the oxidation methods, effect factors, and reaction mechanisms of NO removal were reviewed from four aspects: liquid-phase oxidation, gas-phase oxidation, plasma technology, and gas-solid catalytic oxidation. The advantages and disadvantages of different oxidation methods were analyzed. Combined with the idea of removal of a variety of pollutants from flue gas at the same time, the possible research directions of nitrogen oxide oxidation removal in the future are put forward. It inspires the application and popularization of the integrated removal of combustion pollutants in the future.
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