Numerical evaluation of the effectiveness of NO₂ and N₂O₅ generation during the NO ozonation process

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ABSTRACT
Wet scrubbing combined with ozone oxidation has become a promising technology for simultaneous removal of SO₂ and NOₓ in exhaust gas. In this paper, a new 20-species, 76-step detailed kinetic mechanism was proposed between O₃ and NOₓ. The concentration of N₂O₅ was measured using an in-situ IR spectrometer. The numerical evaluation results kept good pace with both the public experiment results and our experiment results. Key reaction parameters for the generation of NO₂ and N₂O₅ during the NO ozonation process were investigated by a numerical simulation method. The effect of temperature on producing NO₂ was found to be negligible. To produce NO₂, the optimal residence time was 1.25 sec and the molar ratio of O₃/NO about 1. For the generation of N₂O₅, the residence time should be about 8 sec while the temperature of the exhaust gas should be strictly controlled and the molar ratio of O₃/NO about 1.75. This study provided detailed investigations on the reaction parameters of ozonation of NOₓ by a numerical simulation method, and the results obtained should be helpful for the design and optimization of ozone oxidation combined with the wet flue gas desulfurization methods (WFGD) method for the removal of NOₓ.

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Introduction
The most abundant gaseous pollutants emitted from power plants and industrial boilers are sulfur dioxide (SO₂) and nitrogen oxides (NOₓ), which make a dramatic contribution to acid rain and smog formation (Price et al., 1997). For the recent severe hazy weather that invaded most areas of China more than once (Hou et al., 2011; Jiang et al., 2014; Liu et al., 2014), China has established more rigorous legislation to control the emission of SO₂ and NOₓ from stationary sources (Huang et al., 2014). Generally, SO₂ is controlled effectively by wet flue gas desulfurization methods (WFGD), and low NOₓ burners (Nishimura et al., 1997), selective catalytic reduction (SCR) (Topsøe, 1994) and selective non-catalytic reduction (SNCR) (Tayyeb Javed et al., 2007) are typically used for the removal of NOₓ. Since exhaust gas from power plants and industrial boilers contains multiple pollutants, combined technologies such as WFGD + SCR or WFGD + SNCR are commonly applied. However, these combined technologies require expensive investments and operating costs, resulting in an increasing amount of attention paid to simultaneous removal technologies with high efficiency, low investment and reasonable operating cost.

Up to now, numerous simultaneous removal technologies have been reported, such as activated carbon adsorption technology (Sumathi et al., 2010), the dielectric barrier discharge (DBD) plasma flue gas treatment (Obradović et al., 2011), and various types of wet scrubbing (Hu et al., 2010; Liu and Zhang, 2011; Raju et al., 2008; Wang et al., 2012; Zhao et al., 2011). For wet scrubbing...
technology, ozone has been a typical oxidant used for the oxidation of NO.

In 1997, Nelo et al. (1997) already began to study the use of ozone for the oxidation of nitrogen oxides. Mok and Lee (2006) reported a two-step process which combined rapid oxidation by ozone and aqueous absorption by sodium sulfide. The process achieved high removal efficiencies for both SO2 and NOx. Wang et al. (2007) also studied a similar two-step process that could remove NOx, SO2 and Hg effectively. As the higher oxidation states of NO (N2O3, N2O5) are much more soluble in water (500.0 g/dm3) than NO (0.032 g/dm3) and NO2 (213.0 g/dm3) (Dora et al., 2009), the wet-scrubbing removal efficiency of NOx relies highly on the resultant composition of NOx during the NO-oxidation process; whereas, the oxidation products of NO ozonation vary as the reaction environment and running parameters change. Compared with NOx, N2O5 is easier to remove in scrubbing systems, but needs more O3 for its generation. Hence, detailed investigations on the reaction environment and running parameters for ozonation of NOx are required for the design and optimization of this ozone oxidation combined with WFGD method for the removal of NO.

For this complex reaction system, numerical simulation is needed because it can provide more detailed information about the reaction system. CHEMKIN is one of the most widely used and validated kinetic software programs (Zajemska et al., 2014). It is accurate for industrial burners, gas turbines, chemical processing and so on (Abbás et al., 2011; Gui et al., 2014; Li et al., 2010; Yang et al., 2013). Therefore, CHEMKIN is suitable to study the effectiveness of NO2 and N2O5 generation during the NO ozonation process. Wang et al. (2006) studied an ozone-NO reaction co-flow jet by direct numerical simulation. However, in that research, only the reactions between O3 and NOx in the turbulence time scale were observed. Because of the low reaction rate of O3–NO reactions, NO2 was the main product, with minor amounts of NO3 and N2O5. Furthermore, the concentration of N2O5 of the simulation was not verified by laboratory testing due to the difficulty of measuring of N2O5.

Recently, Skalska et al. (2011) have investigated the kinetic model of NOx ozonation and determined the rate constants of NO3 (NO2, NOx) and N2O5 based on Fourier transform infrared (FT-IR) spectroscopy, although only at 25°C. Also, we studied the O3 oxidation processes of NO and SO2 on a qualitative scale, as well as their coexistence, with the help of an in-situ IR spectrometer (Sun et al., 2014). These studies suggested that in-situ FT-IR spectroscopy should be a suitable technology for the measurement of N2O5. However, these reported studies did not focus on the effect of running parameters, especially the residence time, on the production of NO2 or N2O5 for industrial application. Moreover, as far as we know, quantitative studies on the production of N2O5 have rarely been reported.

This article focused on simulating the reactions between O3 and NO under different reaction conditions and running parameters using a numerical simulation method. Meanwhile, the simulated concentration of N2O5 was verified by experimental studies with the help of in-situ FT-IR spectroscopy. More importantly, the suitable running parameters for the generation of NO2 and N2O5 including reaction temperature, residence time, and the molar ratio of O3/NO, were studied.

1. Experimental set-up

Fig. 1 illustrates the schematic diagram of the experimental system for NO oxidation by O3, consisting of a gas supply system, gas-phase mixer, reactor and flue gas analyzing system. The details of each apparatus and the experimental gas conditions were described in our previous research (Sun et al., 2014).

In Fig. 2, different IR spectra are shown. The bands at 743, 1246 and 1720 cm\(^{-1}\) were assigned to N2O5 (Wängberg, 1993). The concentration of N2O5 was calculated according to the formula:

\[ c = \frac{A_{1000}}{b_{\text{NO}N_A}} \]  

where c (mol/dm\(^3\)) is the concentration, A is the absorbance, N\(_A\) (mol\(^{-1}\)) is the Avogadro constant, b (cm) is the path length, and \(\alpha\) (cm\(^2\)/mol) is the absorption cross section. The absorption cross section could be calculated by the equation given by Wängberg (1993).

2. Kinetic mechanism of the reactions between O3 and NOx

The reactions between O3 and NOx are complicated, which include not only the decomposition of ozone and N2O5 but also numerous intermediate transient reactions. Mok and Lee (2006) came to the conclusion that 12 reactions were involved in the mechanism. However, several important species such as OH in the reactions between O3 and NOx were not considered. Wang et al. (2006) provided a more detailed kinetic mechanism. However, reactions related to NOx were missed. NO3 is unstable due to its strong oxidizing properties, but it is one of the higher oxidation states of NOx and should not be neglected in the mechanism. The reactions between NO3 and other species are R66–R76 shown in Table 1, where a new 20-species, 76-step detailed kinetic mechanism was proposed and listed (R1–R76). The rate constants for all the reactions listed in Table 1 were acquired from the National Institute for Standards and Technology (NIST) (Database).

3. Modeling

Computations of the NO ozonation process were all made using the CHEMKIN 4.1 software package (Reaction Design Co., Ltd, San Diego, USA) (Kee et al., 2006). The cylindrical shear-flow reactor model was used in the computations. The model took radial diffusion into account, neglecting axial diffusion. Moreover, the model only included gas chemistry. The reaction mechanism of the NO ozonation process has been described above. NO concentration in the inlet ranged from 200 to 400 ppm. NO2 concentration in the inlet was from 0 to 20 ppm. The ozone concentration in the inlet depended on both NO concentration and O3/NO molar ratio. The other component of the inlet atmosphere was N2.
4. Results and discussion

4.1. Verification of the model

In Fig. 3 the simulation results and Mok's experiment results at 443 K and 2.94 sec, with 280 ppm NO and 20 ppm NO₂, are compared (Mok and Lee, 2006). As shown in Fig. 3, the production of NO₂ was determined by the total amount of added ozone, and the calculation results fitted quite well with those in Mok's experiment.

Both the results of the simulation and Mok's experiment showed that NO mainly reacted to form NO₂ with the added O₃ under this reaction condition. The mechanism indicated that reactions like R1 (Table 1), R29, R31, R32, R33, R64 and R69 took part in the conversion of NO. However, reaction R1 is the predominant step because of the high conversion rate of R1.

Fig. 4 shows the comparison between the results of simulation and the results of our experiments at 298–318 K. Experiments were conducted with 300 ± 10 ppm NO. Because the molar ratio of O₃/NO was so large, the subsequent transformation of NO₂ should be considered. Many reactions occurred in the process of NO oxidation. However, reactions R1, R2 and R3 dominated at first due to their high reaction rates. Reactions R2 and R3 indicated the deep transformation of NO₂ into NO₃ or N₂O₅. Therefore, the concentration of N₂O₅ could not be ignored when the molar ratio O₃/NO was >1. Based on the comparison of the reaction rate of R2 and R3 (Table 1), the existence of NO₃ was neglected because of the lower reaction rate of R2.

From Fig. 4, the results of the simulation agreed well with the results of the experiments. The above comparisons of Mok's and our experiments demonstrated that the mechanism was suitable and accurate for the O₃–NOₓ reactions.

4.2. Reaction parameter studies for the generation of NO₂

As we discussed above, the generation of NO₂ could be easily achieved when the molar ratio of O₃/NO was below 1. Under these molar ratios of O₃/NO, the major oxidation product was NO₂. However, the exhaust gas conditions of the power plants and industrial boilers vary due to the complicated operating conditions. Typically, as Saidur et al. (2010) reported, the temperature of the exhaust gas leaving industrial boilers ranges from 423 to 523 K. Due to the various types of industrial boilers, working conditions of boilers and other reasons, the NOₓ concentration of industrial boilers could range from 72 to 455 ppm (Costa and Azevedo, 2007; Costa et al., 2003; Yamamoto et al., 2010). Thus, the effect of flue gas conditions on the generation of NO₂ should be considered and the experimental results are shown in Fig. 5.

4.2.1. Effect of temperature on the production of NO₂

Fig. 5a shows the effect of temperature on the production of NO₂. The simulation was carried out by keeping the residence time at 5 sec and the molar ratio of O₃/NO at 1. In Fig. 5, the concentration of NO₂ was 294.65 ppm at 333 K when the initial NO concentration was 300 ppm. It could be concluded that the NO was almost completely converted to NO₂. Comparing the concentrations of NO₂ at 333 and 423 K, it was indicated that the higher temperature was beneficial to the generation of NO₂, but the effect was not remarkable. Due to
the kinetic reaction mechanism, the increase of temperature was beneficial to the reaction between NO and O₃. However the reaction rate of R1 was very high, and the effect of reaction temperature could be neglected.

4.2.2. Effect of the residence time on the production of NO₂

The effect of the residence time on the production of NO₂ is presented in Fig. 5b. The simulation was conducted at 373 K, when the molar ratio of O₂/NO was 1. In Fig. 5b, when the initial NO concentration was 300 ppm and the residence time was 0.417 sec, the concentration of NO₂ was 220.68 ppm, which meant that the production rate of NO₂ was only 73.56%. When the residence time was extended to 1.25 and 2.08 sec, the concentration of NO₂ was 286.83 and 294.76 ppm, respectively. Hence, the production rate of NO₂ only gained 3% increment, when the residence time changed from 1.25 to 2.08 sec. For industrial application, 95.61% oxidation percentage in 1.25 sec would be sufficient. Moreover, the oxidation rates of NO for two other initial NO concentrations were also
high when the residence time was 1.25 sec. Thus the optimal residence time can be set as 1.25 sec in order to decrease the volume of the reactor.

4.2.3. Effect of the molar ratio of O$_3$/NO on producing NO$_2$

Fig. 5c displays the effect of the molar ratio of O$_3$/NO on the production of NO$_2$. The simulation was executed at 373 K and 5 sec. With the increase of the molar ratio of O$_3$/NO, the concentration of NO$_2$ increased until the molar ratio of O$_3$/NO reached 1.0 for all three initial NO concentrations. The reaction of R1 was very fast, thus R1 was the dominant reaction step when the molar ratio of O$_3$/NO was less than 1. We also observed the same phenomenon in our previous research (Sun et al., 2014). We found that the concentration of NO decreased and the generation of NO$_2$ increased in proportion to the increase of the injected ozone concentration. We also discovered that when the molar ratio of O$_3$/NO was less than 1, NO was gradually oxidized to NO$_2$ and no higher NO$_x$ chemical state products were formed. When the molar ratio of O$_3$/NO was more than 1, N$_2$O$_5$ was produced. The generation of N$_2$O$_5$ was mainly ascribed to reactions such as R2 and R3. In order to obtain NO$_2$, the molar ratio of O$_3$/NO can simply be selected as 1.

4.3. Reaction parameters studies for the generation of N$_2$O$_5$

As analyzed above, N$_2$O$_5$ is the easiest to absorb among all oxidation states of nitrogen oxides. However, the generation conditions of N$_2$O$_5$ are relatively strict. In order to get the optimal conditions for the generation of N$_2$O$_5$ to reduce the operating cost, research on the reaction parameters for producing N$_2$O$_5$ is needed, and the experimental results are shown in Fig. 6.

4.3.1. Effect of temperature on the production of N$_2$O$_5$

Fig. 6a shows the effect of temperature on the production of N$_2$O$_5$. The investigated temperature range in this study varied from 333 to 423 K. The simulation was carried out at 5 sec with the molar ratio of O$_3$/NO at 1.75. As shown in Fig. 6a, with the increase of the temperature of the exhaust gas, the concentration of N$_2$O$_5$ increased until the temperature of the exhaust gas reached 383 K for all three initial NO concentrations. When the temperature of gas was higher than 383 K, the concentration of the produced N$_2$O$_5$ decreased very rapidly. The decrease of N$_2$O$_5$ at this temperature should be ascribed...
to the decomposition of O₃, NO₃ and N₂O₅. High reaction temperature accelerated the reaction rate of the reverse reactions such as R3 and R9, and the forward reactions such as R61 and R69. We also observed a similar phenomenon in our previous study (Sun et al., 2014). We found that the N₂O₅ decreased with the increasing reaction temperature in the high temperature region (373–453 K). Even at 453 K, we found that N₂O₅ and O₃ disappeared. Therefore, the temperature of the exhaust should be controlled strictly for the production of N₂O₅. If the temperature of the exhaust is higher than 373 K, facilities such as a sprinkling system should be used in the system.

4.3.2. Effect of the residence time on the production of N₂O₅

Fig. 6b presents the effect of the residence time on the production of N₂O₅. The simulation was conducted at 353 K with the molar ratio of O₃/NO at 1.75. As shown in Fig. 6b, when the initial NO concentration was 300 ppm and the residence time was 7, 8 and 9 sec, the concentration of 2N₂O₅ was 222.25, 231.05 and 239.15 ppm, respectively. This meant that the production of N₂O₅ varied from 74.08% to 79.71% when the residence time was changed from 7 to 9 sec. Clearly, the concentration of N₂O₅ increased with increasing residence time. These results indicated that longer residence time was favorable for the formation of N₂O₅, so that less NO₂ was left in the reaction zone. Dora et al. (2009) also observed that residence time lower than 8 sec reduced the effectiveness of NO ozonation when the applied molar ratio of O₃/NO was equal to 1.14. Thus, the residence time should be chosen at about 8 sec.

4.3.3. Effect of the molar ratio of O₃/NO on the production of N₂O₅

Fig. 6c shows the effect of the molar ratio of O₃/NO on the production of N₂O₅. The simulation was executed at 353 K and the residence time was selected as 5 sec. With the increase of molar ratio of O₃/NO, the concentration of N₂O₅ increased. When the initial NO concentration was 300 ppm and the molar ratio of O₃/NO varied from 1.45 to 2, the concentration of N₂O₅ increased from 187.16 to 275.78 ppm. This showed that the production rate of N₂O₅ grew from 62.38% to 91.93% when the O₃/NO molar ratio varied from 1.45 to 2. If the reaction rates of R1, R2 and R3 are high enough, the molar ratio O₃/NO should be selected as 1.5 to ensure N₂O₅ as the main product. However, the reaction rates of R3 and especially R2 were not very high. Thus, N₂O₅ was not easy to generate. In order to produce more N₂O₅, more O₃ is needed. We also found that the amount of NO₂ was small when the molar ratio of O₃/NO was 2 (Sun et al., 2014). Considering the usage of O₃ and the production rate of N₂O₅, the molar ratio O₃/NO can be chosen as about 1.75.

5. Conclusions

In this study, suitable process conditions of NO₂ and N₂O₅ were investigated by numerical simulation. A new 20-species, 76-step detailed kinetic mechanism was proposed between O₃ and NOₓ. The concentration of N₂O₅ was measured by an IR spectrometer. The calculation results showed good agreement with both the published experimental results and our experimental results. Due to the high oxidation rate of NO by ozone, the effect of temperature on the generation of NO₂ can be neglected. The production rate of NO₂ for 300 ppm NO varied from 95.61% to 98.28% when the residence time changed from 1.25 to 2.08 sec. The optimal residence time can be set as 1.25 sec in order to decrease the volume of the reactor. With the increase of the molar ratio of O₃/NO, the concentration of NO₂ increased until the molar ratio of O₃/NO was 2 (Sun et al., 2014). Considering the usage of O₃ and the production rate of N₂O₅, the molar ratio O₃/NO can be chosen as 1.75.
obtain sufficient NO₂, the molar ratio of O₃/NO can be selected as 1.0 to reduce the usage of O₃.

N₂O₅ is the easiest to absorb among all the states of nitrogen oxides, but the reaction conditions for the generation of N₂O₅ are rigorous. With the increase of the temperature, the concentration of N₂O₅ increased until the reaction temperature reached 383 K. The temperature of the exhaust gas should be controlled strictly for a high production rate of N₂O₅. The production rate of N₂O₅ for 300 ppm NO varied from 74.08% to 79.71% when the residence time was changed from 7 to 9 sec. The residence time can be chosen as 8 sec in order to produce enough N₂O₅. The production rate of N₂O₅ for 300 ppm NO concentration varied from 62.38% to 91.93% when the molar ratio of O₃/NO was from 1.45 to 2. Considering both the usage of O₃ and the production rate of N₂O₅, the molar ratio O₃/NO can be selected as about 1.75.

Overall, the study provided suitable reaction parameters for the generation of NO₂ or N₂O₅, depending on specific emission requirements and the changing exhaust conditions. Meanwhile, the model is a powerful tool to develop an effective and economical reactor for the ozonation of NO.

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