JOURNAL OF ENVIRONMENTAL SCIENCES 41 (2016) 51–58

Available online at www.sciencedirect.com

ScienceDirect

www.elsevier.com/locate/jes

JOURNAL OF ENVIRONMENTAL SCIENCES

www.jesc.ac.cn

Numerical evaluation of the effectiveness of NO_2 and N_2O_5 generation during the NO ozonation process

Haiqiang Wang*, Zhuokai Zhuang, Chenglang Sun, Nan Zhao, Yue Liu, Zhongbiao Wu*

Department of Environment Engineering, Zhejiang University, Hangzhou 310058, China. E-mail: haiqiangwang@zju.edu.cn
Zhejiang Provincial Engineering Research Center of Industrial Boiler, Furnace Flue Gas Pollution Control, Hangzhou 310058, China

ARTICLE INFO

Article history:
Received 12 February 2015
Revised 15 April 2015
Accepted 4 May 2015
Available online 21 July 2015

Keywords:
Numerical simulation
O_3
NO
N_2O_5
In-situ IR spectra

ABSTRACT

Wet scrubbing combined with ozone oxidation has become a promising technology for simultaneous removal of SO_2 and NO_x in exhaust gas. In this paper, a new 20-species, 76-step detailed kinetic mechanism was proposed between O_3 and NO_x. The concentration of N_2O_5 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 NO_2 and N_2O_5 during the NO ozonation process were investigated by a numerical simulation method. The effect of temperature on producing NO_2 was found to be negligible. To produce NO_2, the optimal residence time was 1.25 sec and the molar ratio of O_3/NO about 1. For the generation of N_2O_5, the residence time should be about 8 sec while the temperature of the exhaust gas should be strictly controlled and the molar ratio of O_3/NO about 1.75. This study provided detailed investigations on the reaction parameters of ozonation of NO_x 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 NO_x.

Introduction

The most abundant gaseous pollutants emitted from power plants and industrial boilers are sulfur dioxide (SO_2) and nitrogen oxides (NO_x), 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 SO_2 and NO_x from stationary sources (Huang et al., 2014). Generally, SO_2 is controlled effectively by wet flue gas desulfurization methods (WFGD), and low NO_x 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 NO_x. 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

---

* *Corresponding authors*. E-mail: zbwu@zju.edu.cn (Zhongbiao Wu).

http://dx.doi.org/10.1016/j.jes.2015.05.015
1001-0742/

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 SO_2 and NO_x. Wang et al. (2007) also studied a similar two-step process that could remove NO_x, SO_2 and Hg effectively. As the higher oxidation states of NO (N_2O_3, N_2O_5) are much more soluble in water (500.0 g/dm^3) than NO (0.032 g/dm^3) and NO_2 (213.0 g/dm^3) (Dora et al., 2009), the wet-scrubbing removal efficiency of NO_x relies highly on the resultant composition of NO_x during the NO oxidation process; whereas, the oxidation products of NO ozonation vary as the reaction environment and running parameters change. Compared with NO_2, N_2O_5 is easier to remove in scrubbing systems, but needs more O_3 for its generation. Hence, detailed investigations on the reaction environment and running parameters for ozonation of NO_x 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 (Abián et al., 2011; Gui et al., 2014; Li et al., 2010; Yang et al., 2013). Therefore, CHEMKIN is suitable to study the effectiveness of NO_2 and N_2O_5 generation during the NO ozonation process. Wang et al. (2006) studied an ozone-NO_x reaction co-flow jet by direct numerical simulation. However, in that research, only the reactions between O_3 and NO_x in the turbulence time scale were observed. Because of the low reaction rate of O_3–NO reactions, NO_2 was the main product, with minor amounts of NO_3 and N_2O_5. Furthermore, the concentration of N_2O_5 of the simulation was not verified by laboratory testing due to the difficulty of measuring of N_2O_5.

Recently, Skalska et al. (2011) have investigated the kinetic model of NO_x ozonation and determined the rate constants of NO_x (NO_2, NO_3, and N_2O_5) based on Fourier transform infrared (FT-IR) spectroscopy, although only at 25°C. Also, we studied the O_3 oxidation processes of NO and SO_2 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 N_2O_5. However, these reported studies did not focus on the effect of running parameters, especially the residence time, on the production of NO_2 or N_2O_5 for industrial application. Moreover, as far as we know, quantitative studies on the production of N_2O_5 have rarely been reported.

This article focused on simulating the reactions between O_3 and NO under different reaction conditions and running parameters using a numerical simulation method. Meanwhile, the simulated concentration of N_2O_5 was verified by experimental studies with the help of *in-situ* FT-IR spectroscopy. More importantly, the suitable running parameters for the generation of NO_2 and N_2O_5 including reaction temperature, residence time, and the molar ratio of O_3/NO, were studied.

1. Experimental set-up

Fig. 1 illustrates the schematic diagram of the experimental system for NO oxidation by O_3, 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 N_2O_5 (Wängberg, 1993). The concentration of N_2O_5 was calculated according to the formula:

$$c = \frac{A1000}{b\sigma N_A} \tag{1}$$

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 σ (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 O_3 and NO_x

The reactions between O_3 and NO_x are complicated, which include not only the decomposition of ozone and N_2O_5 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 O_3 and NO_x were not considered. Wang et al. (2006) provided a more detailed kinetic mechanism. However, reactions related to NO_3 were missed. NO_3 is unstable due to its strong oxidizing properties, but it is one of the higher oxidation states of NO_x and should not be neglected in the mechanism. The reactions between NO_3 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 the all the reactions listed in Table 1 were acquired from the National Institute for Standards and Technology (NIST) (Datebase).

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. NO_2 concentration in the inlet was from 0 to 20 ppm. The ozone concentration in the inlet depended on both NO concentration and O_3/NO molar ratio. The other component of the inlet atmosphere was N_2.