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Experimental study on reaction characteristics of NO in $(NH_4)_2SO_3$ solution

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ABSTRACT

The effects of various factors on the NO removal activity in the $(NH_4)_2SO_3$ solution were investigated to explore more details and characteristics of the related reactions using full infrared sensor flue gas analyzer (FISFGA). It was found that the conversion yield of NO (9.0%–29.0%) was obviously improved with the increase of gas–liquid contact area, NO residence time and $(NH_4)_2SO_3$ concentration as well as the adding of $CuSO_4$. However, it was mainly limited by gas–liquid mass transfer rate and slightly inhibited by the gas velocity. Moreover, the FISFGA analysis revealed that two nitric oxide (NO) conversion route with different reduction product of N_2O and N_2 existed simultaneously upon the existence form of SO_3^{2-}. It was confirmed by the calculations and the experiments of pH factor that the NO reduction steps were based on the following equation: (1) $NO + HSO_3^- \leftrightharpoons N_2O + SO_4^{2-} + H^+$; (2) $NO + SO_3^{2-} \leftrightharpoons N_2 + SO_4^{2-}$. In this system, Eq. (1) with N_2O product was the major pathway, but the ratio of Eqs. (2) to (1) was intensified in the presence of $CuSO_4$. It is believed that the suitable additives could promote the NO reduction to N_2 furtherly.

Introduction

NO_x and SO_2, from coal-fired flue gas, have caused serious environmental problems, e.g., acid rain and photochemical smog [1–4]. The methods of nitrogen oxides controlling, including selective catalytic reduction (SCR) [5,6], selective catalytic oxidation (SCO) and selective non-catalytic reduction (SNCR), suffer from high cost and low selectivity [7–9]. For the desulfurization process, the wet limestone–gypsum flue gas desulfurization has been widely applied in industry [10]. In the present, more efficient, stable and mature ammonia desulfurization process is rapidly evolved to control sulfur dioxide [11–13]. $(NH_4)_2SO_3$, as the main product of this technology, is easily decomposed and oxidized to hinder its further application [14,15]. Interestingly, according to the feedback data in the actual ammonia desulfurization process, NO could react with $(NH_4)_2SO_3$, to form $(NH_4)_2SO_4$ which can be used as a fertilizer in agriculture [16,17]. However, due to the insolubility of NO, the simultaneous reaction ammonia desulfurization and denitrification process, which can reduce the cost of flue gas desulfurization and improve material utilization, are difficult to be achieved. Therefore, the research on promoting the reaction of NO with $(NH_4)_2SO_3$ is of great value.

In the previous study, the process and mechanism of NO absorption in the sulfite solution were analyzed based on the dynamics and the gas–liquid mass transfer theory [18–20]. Sada et al. [21–24] and Ellchl et al. [25] found that the ferrous complex, as a reducing substance, could promote the absorption of NO in Na_2SO_3 solution. In recent years, more experiments have been reported to comprehensively explore the characteristics and mechanisms of the NO absorption in the mixed solution of sulfite and iron complexes [26–28]. Wang et al. [29] explored the simultaneous absorption of SO_2 and NO in the mixture solution of Fe^{2+}-EDTA and Na_2SO_3, finding that the presence of SO_2 remarkably promoted the NO removal efficiency, and NO was reduced to N_2O. Zhu et al. [30] and Xiang et al. [31] focused on the Fe^{2+}-EDTA regeneration catalyzed by activated carbon or selenium in absorption of NO using mixed the solution of Na_2SO_3 and Fe^{2+}-EDTA. Yan et al. [32,33] discussed the absorption of NO in $(NH_4)_2SO_3$ solution combined with Fe^{2+}-EDTA and Fe^{2+}-Cit. Sun et al. [34] found that the addition of CaSO3 in the bubbling reactor could obviously enhance the absorption efficiency of NO, which reached 75%. Most researches were summarized and simplified in

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Table S1. However, the research on the absorption of NO in the sole $(NH_4)_2SO_3$ solution has not been reported until now. Moreover, the associated mechanism and the impact of the industrial environment are still unclear. Therefore, it is necessary to further explore the absorption characteristics of NO in $(NH_4)_2SO_3$ solution.

In this work, various affecting factors were explored during the reaction of NO with $(NH_4)_2SO_3$. The mechanism involved in NO reaction process was analyzed and verified by discussing the NO removal efficiency and N_2O selectivity.

Experimental section

Experimental agents

The reagents used in the experiments are analytical grade. $(NH_4)_2SO_3{\cdot}H_2O$ (≥92%, Aladdin Industrial Corporation, China), $NaHSO_3$ (58.5%–65.0%, Aladdin Industrial Corporation, China), Na_2SO_3 (≥97%, Aladdin Industrial Corporation, China), K_2SO_3 (≥90%, Aladdin Industrial Corporation, China), C_2H_5OH (≥99.8%, Guangdong Chemical Reagent Engineering-technological Research and Development Center, China), $C_2H_4(OH)_2$ (≥99.5%, Guangdong Chemical Reagent Engineering-technological Research and Development Center, China), CH_3OH (≥99.9%, Guangdong Chemical Reagent Engineering-technological Research and Development Center, China), $MnSO_4{\cdot}H_2O$ (99.%, Guangdong Chemical Reagent Engineering-technological Research and Development Center, China), $MgSO_4{\cdot}7H_2O$ (≥99.5%, Shanghai Shan Pu Chemical Co., Ltd., China), $Al_2(SO_4)_3$ (99.95%, Shanghai Shan Pu Chemical Co., Ltd., China), $FeSO_4{\cdot}7H_2O$ (≥99.0%, Shantou Xilong Chemical Factory Guangxi Guangdong, China), $Fe_2(SO_4)_3$ (99.95%, Shantou Xilong Chemical Factory Guangxi, China), $CuSO_4{\cdot}5H_2O$ (≥98%, Guangdong Chemical Reagent Engineering-technological Research and Development Center, China), $ZnSO_4{\cdot}7H_2O$ (99.5%, Shangdong Xilong Chemical Factory Guangdong, China).

Experimental apparatuses

The experimental apparatus consists of the gas distribution system, absorption system and analysis system shown in Fig. 1. N_2 and NO were supplied by the gas cabinet (Fig. 1, part 1) contained four compressed cylinders (Jiangsu Institute of Metrology, Nanjing), controlled and distributed by the intake system (Fig. 1, part 2) and mixed in the mixed gas cylinder (Fig. 1, part 3). All gases were diluted by N_2 in the mixed gas cylinder and obtained the desired NO concentrations by adjusting the intake system.

NO absorption experiments were carried out in bubbling reaction column (Fig. 1, part 4) (#1: ф 4.5 cm × 30 cm). The bubbling reactor was equipped with a heated tank (Gongyi Yuhua Instrument Co.) to control the reaction temperature. The wash gas cylinder was filled with deionized water to clean the gas from the bubbling reactor. The inlet and outlet concentrations of NO and NO_2 in the mixed gas were dried and detected online by a full infrared sensor flue gas analyzer (FISFGA) (Fig. 1, part 6) (Sensonic D-2 and Sensonic IR-1, EU).

Experimental methods

Before the experiment, the heated tank was turned on to adjust to the reaction temperature (basic temperature: 20 °C). When the temperature turned stable, N_2 was turned on and set the gas flow rate at 200 mL/min to purge the system. Twenty minutes later, the simulated flue gas (basic parameters v: 100 mL/min, NO: 600 ppm) was prepared by operating the intake system. When the desired gas was stable, three-way valve was switched and simulated flue gas via the pipeline into the bubbling reactor. And then, the flue gas analyzer was connected to computer and record real-time data online every two seconds. The solution was prepared by sulfites, sulfates and surfactants (basic concentration: 0.05 M, 0.01 M and 2 M, respectively).

The conversion efficiency of NO is calculated as following Formula (1):

$$\eta = \frac{C_{in} - C_{out}}{C_{in}} \times 100\% \quad (1)$$

where η is the NO conversion efficiency (%); C_{in} is the initial concentration of NO in the mixed gas (ppm); C_{out} is the NO concentration in the exports (ppm).

The N_2O selectivity is calculated according to the Formula (2)

$$\theta = \frac{2 \times c_{N2O}}{c_{in} - c_{out}} \times 100\% \quad (2)$$

Where θ is the N_2O selectivity (%); C_{in} is the initial concentration of NO in the mixed gas (ppm); C_{out} is the NO concentration in the exports; C_{N2O} is the N_2O concentration in the gas after absorption (ppm).

Results and analysis

Effect of NO concentration on NO conversion efficiency

For a clear reflection of the experimental phenomenon, the concentrations of NO were preset to 400 ppm, 600 ppm and 800 ppm, and the effect of NO concentration on NO conversion was studied under the basic parameters (20 °C, pH = 7.5, $C_{((NH4)2SO3)}$ = 0.05 M, the gas flow rate = 100 mL/min), as shown on Fig. 2.

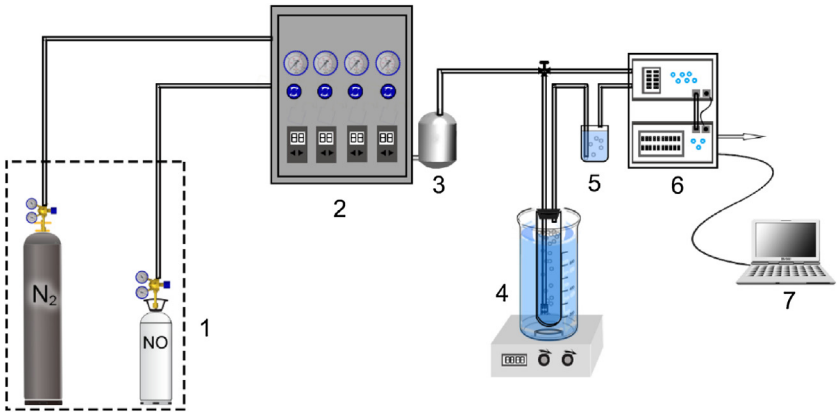

Fig. 1. System flow chart (1) gas cabinet (2) intake system (3) mixed gas (4) bubbling reactor (5) wash gas cylinders (6) flue gas analyzer (7) computer.

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