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Simultaneous removal of NO_X and SO_2 from coal-fired flue gas by catalytic oxidation-removal process with H_2O_2

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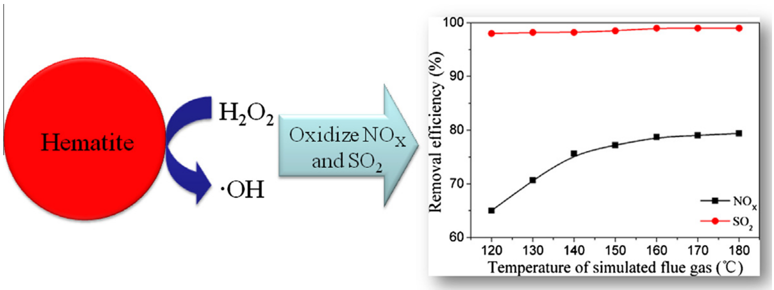
HIGHLIGHTS

- A novel catalytic oxidation-removal technology is proposed to simultaneously removal of SO_2 and NO_X.
- The oxidation removal of ·OH radicals is the main reaction.
- The NO_X removal efficiency reaches the maximum value of 80%, and the SO_2 is about 99% with this process.
- Material balances indicate that no other byproducts except NO_3^-, SO_3^{2-} and SO_4^{2-} were produced in this process.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel oxidation-removal process capable of removing NO_X and SO_2 simultaneously was proposed, which utilized the injection of ·OH radicals from H_2O_2 catalytic decomposition over hematite and assisted with a glass made ammonia-based washing tower. Oxidation experiments were conducted in a quartz reactor within an oil bath. Effects of H_2O_2 flow, temperature of simulated flue gas, volume ratio and preheated temperature on NO_X and SO_2 removal efficiencies were investigated. Results indicated that SO_2 was cleaned up quite efficiently and the removal efficiency was nearly 100% under all conditions. The NO_X removal efficiency depended primarily on H_2O_2 flow and volume ratio between purged gas and total gas, but temperature of simulated flue gas and preheated temperature had slighter influence on the NO_X removal efficiency; The H_2O_2 flow had a significant interaction with the volume ratio. The ion products in solution were analyzed with ion chromatography (IC), and the material balances for NO_X and SO_2 were calculated. It showed NO_X was removed in the oxidation formation of NO_3^-, but SO_2 was mainly in the formation of SO_3^{2-}. Results of material balances indicated that the main products of this oxidation-removal process were NO_3^-, SO_3^{2-} and SO_4^{2-}. The reaction pathways of removal of NO_X and SO_2 with this oxidation-removal process were preliminarily discussed. Meanwhile, compared with air discharge flue gas treatments, the present method had lower initial investment and operating costs.

1. Introduction

NO_X (nitric oxide and its group of compounds) and SO_2 released from coal-fired power plants result in serious environmental pollution and threaten industrial production and human life. Hence, great efforts have been made to develop technologies for flue gas purification. The mainstream technique is treatment for individual gas emission. For NO_X removal, advanced flue gas treatment technologies are adopted, including dry and wet techniques. The dry techniques are classified as selective catalytic reduction (SCR) by NH_3 at 300–500 °C [1], selective noncatalytic reduction (SNCR) [2], adsorption [3] and electron beam irradiation [4]. The wet techniques use scrubber columns in which NO_X is absorbed by absorbent. Similarly, for SO_2, wet flue gas desulfurization (WFGD) using alkaline solutions (of sodium, calcium and magnesium

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compounds) as absorbents are the most effective and widely used process [5]. Among those denitrification techniques, SCR is considered as the most effective one for NO_X removal. However, the high concentration of ash in the flue gas and high temperature reduces the performance and longevity of SCR catalysts [6,7]. To solve this problem, one attractive option is to place the SCR unit downstream of the electrostatic precipitators where ash has been removed and the temperature is about 120–180 °C. Series of magnesium-based catalysts were prepared to apply in the low-temperature SCR [3,6,8]. However, most of magnesium-based catalysts are not resistant to SO_2 [9,10], which limits its wide utilization. Therefore, many technologies have been developed for simultaneous desulfurization and denitrification at low temperature. Khan and Adewuyi [11] investigated the oxidant oxidation removal of NO by aqueous solution of sodium persulfate in a bubble column reactor. The operating cost is uncontrollable due to the difficult recycle use of absorbent. Wang et al. [12] utilized oxidation absorption with the injection of ozone and a glass made alkaline washing tower. Higher operating cost is invested comparing with the conventional process because of the continuous injection of O_3. The electron beam irradiation can also satisfy with the low-temperature removal of NO_X and SO_2, but its high operating cost limits the industrial application [13,14]. Therefore, it is desirable to develop a low-cost and high-efficiency technology for desulfurization and denitrification.

Some transition metal oxides such as iron oxides (FeO_X) or zirconium oxides (ZrO_X) have been reported to catalytically decompose H_2O_2 into strong oxidizing substances including ·OH radicals [15,16]. ·OH radicals nonselectively oxidize NO_X and SO_2 immediately even at low temperature. The oxidation products are likely to be absorbed in the glass made ammonia-based washing tower. The products of dentrification and desulfurization are important agriculture fertilizer and industrial raw materials. Meanwhile, both transition metal oxides and H_2O_2 are of low cost and readily available. In recent years, the catalytic decomposition of H_2O_2 has been widely used in the water-treatment. Therefore, there have been strong interests to develop a technology of catalytic decomposition of H_2O_2 for the flue gas treatment.

In this paper, a new technology was developed to purify the flue gas. ·OH radicals from catalytic decomposition of H_2O_2 over hematite were injected into the oxidation reactor to oxidize NO_X and SO_2. Finally, these oxidation products and remaining SO_2 were removed in the glass made ammonia-based washing tower.

2. Experimental sections

2.1. Experimental apparatus

The experimental apparatus for simultaneous desulfurization and denitrification in the oxidation reactor is shown in Fig. 1. The experimental gases are supplied by compressed gas cylinders filled with NO, SO_2 and N_2. ·OH radicals from catalytic decomposition of H_2O_2 (30 wt% H_2O_2, Sinopharm Chemical Reagent Co., Ltd.) over hematite are injected into the oxidation reactor. The oxidation reactions of simultaneous desulfurization and denitrification proceed to completion between the area where ·OH radicals are injected and the position of the glass made washing tower. The oxidation reactions involve O_2 oxidation of NO to NO_2, and SO_2 to SO_3, ·OH radical oxidation of NO or NO_2 to HNO_3 mist, and SO_2 or SO_3 to H_2SO_4 mist. The mists, remaining SO_2 and NO_X then passed through a glass made ammonia-based washing tower and were converted to NH_4NO_3, $(NH_4)_2SO_4$, $(NH_4)_2SO_3$ or NH_4HSO_3. The washing tower is a glass-made cylinder with 70 mm inner diameter and 300 mm in length. Total volume of the washing tower is about 1269 mL and running temperature is about 293 K. The absorbent is 1 wt% ammonia solutions and 2 L is used in one test. The H_2O_2 flow is ranging from 0.3 to 0.5 mL min^{-1}. The volume ratio between total gas and purged gas, which is utilized to inject ·OH radicals into oxidation reactor, is ranged from 0 to 10, and the total flow is 240 mL min^{-1}. NO_X content is 550 ppm, and SO_2 content is 17,000 ppm. The catalyst in the fix-bed is 0.8 g.

2.2. Preparation of catalyst

The catalyst was prepared by iron nitrite ($Fe(NO_3)_3{\cdot}9H_2O$, AR) produced by Sinopharm Chemical Reagent Co., Ltd. 10 g $Fe(NO_3)_3{\cdot}9H_2O$ was mixed in the 100 mL deionized water under agitating with magnetic stirrer at the temperature of 80 °C until the solution was dried. The obtained compounds were firstly dried at 120 °C for 4 h followed by calcinations at 550 °C in air for 5 h.

2.3. Data process

NO_X and SO_2 removal efficiencies at different conditions were obtained after 1 h at steady state. Removal efficiencies were obtained by using the equation:

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

C_{in} and C_{out} is the NO_X or SO_2 concentrations of inlet and outlet, respectively. η is the removal efficiency.

2.4. Characterization

Ion products in the sample solutions were analyzed with ion chromatography (Dionex, China). Chromatographic conditions: Anion dual 2 anion column, eluent (0.01 mol L^{-1} Na_2CO_3), flowrate (1 mL min^{-1}), injection volume (15 μL), column temperature (303 K). The qualitative results of ion products in solution were obtained according to the retention time and the peak area, respectively.

3. Results and discussions

3.1. NO_X and SO_2 removal efficiency in different systems

NO_X and SO_2 removal efficiencies in different reaction systems are shown in Fig. 2. Blank tests were conducted using H_2O_2 solution without hematite catalyst added. These tests showed less than 12% removal of NO_X, and more than 98% removal of SO_2. Oxidation-removal tests were conducted with H_2O_2 as oxidant and hematite as catalyst. H_2O_2/hematite system showed significant NO_X and SO_2 removal at nearly 80% and 100% respectively. It indicates that there is a significant cooperative effect between hematite and H_2O_2. The cooperative mechanism can be described by the following reaction [16,17]:

$$\equiv\mathrm{Fe(III)} + \mathrm{H_2O_2} \rightarrow \equiv\mathrm{Fe(III)} + \mathrm{HO_2^{\cdot}}(\mathrm{O_2^{\cdot-}}) + \mathrm{H^+}(2\mathrm{H^+}) \quad (2)$$

$$\equiv\mathrm{Fe(II)} + \mathrm{H_2O_2} \rightarrow \equiv\mathrm{Fe(III)} + {}^{\cdot}\mathrm{OH} + \mathrm{OH^-} \quad (3)$$

$$\mathrm{HO_2^{\cdot}} \rightleftharpoons \mathrm{H^+} + \mathrm{O_2^{\cdot-}} \quad (4)$$

$$\equiv\mathrm{Fe(III)} + \mathrm{HO_2^{\cdot-}} \rightarrow \equiv\mathrm{Fe(II)} + \mathrm{O_2}(+\mathrm{H^+}) \quad (5)$$

Free radicals, mainly ·OH radicals, have an extremely strong oxidation ability for removal of NO_X and SO_2 [18,19], leading to a sharp increase in removal efficiencies (·OH radicals have been detected in the supporting information in the 6th and 7th part). In order to study the roles of H_2O_2 and catalyst in removal of NO_X and SO_2 by wet scrubbing with the catalytic oxidation-removal process