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A wet process for oxidation-absorption of nitric oxide by persulfate/calcium peroxide

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HIGHLIGHTS

- A novel wet method for NO removal with $Na_2S_2O_8/CaO_2$ as oxidants.
- Free radicals of $O_2^{\cdot -}$, $SO_4^{\cdot -}$ and $\cdot OH$ as the key species were identified by EPR.
- A better understanding of the reaction mechanisms of NO removal with $Na_2S_2O_8/CaO_2$.

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ABSTRACT

This study develops and evaluates a novel wet method for NO removal using a $Na_2S_2O_8/CaO_2$ solution. The effects of these two components both and alone in solution, $Na_2S_2O_8$ concentration, CaO_2 concentration, initial pH, reaction temperature, and the concentrations of NO and O_2 on NO removal efficiency were evaluated using a bubbling reactor. The combination of $Na_2S_2O_8$ and CaO_2 had a synergistic effect on NO removal efficiency. NO removal was effected by CaO_2 concentration, reaction temperature and the initial solution pH, while $Na_2S_2O_8$ concentration and O_2 concentration had little effect. The NO removal efficiency decreased linearly from 94.5 % to 75.1 % when the NO concentration increased from 139 to 559 ppm. The products were characterized using XRD, XPS and IC, and $CaSO_4{\cdot}2H_2O$, NO_3^- and SO_4^{2-} were found to be the main products. The EPR analysis showed that free radicals of $O_2^{\cdot -}$, $SO_4^{\cdot -}$ and $\cdot OH$ were the key species involved in the NO removal process. Finally, the corresponding reaction mechanisms were proposed.

1. Introduction

Nitric oxide (NO) accounts for more than 90 % of NO_x emitted from coal-fired boilers and plays a key role in the formation of photochemical smog and acid rain [1]. Several denitration techniques have been developed to control emissions of NO_x. Recently, selective catalytic reduction (SCR) or selective non-catalytic reduction (SNCR) have been widely used in industrialization [2]. In order to meet the required standards of emission concentrations for SO_2 and NO_x (lower than 35 and 50 mg/m^3, respectively), SCR or SNCR have been used before wet desulfurization in coal-fired boilers. However, this "1 + 1" type of approach to desulfurization and denitration has many disadvantages, including its complex system, large footprint and high operating cost [3,4]. These disadvantages can be addressed by simultaneous removal of NO_x and SO_2 in the same wet scrubber.

Unlike SO_2, NO is an insoluble gas. Therefore, it is much more difficult to remove with conventional wet scrubbing [5]. To convert NO into more easily removable soluble nitrogen oxides, reagents are added that include ozone (O_3) [6], hydrogen peroxide (H_2O_2) [7], chlorine dioxide (ClO_2) [8], potassium permanganate ($KMnO_4$) [9], sodium chlorite ($NaClO_2$) [10], sodium hypochlorite (NaClO) [11], sodium persulfate ($Na_2S_2O_8$) [12], Fe(II)EDTA and $Co(NH_3)_6^{2+}$) [13,14]. There is much interest in hydrogen peroxide (H_2O_2) in particular because it is relatively low cost and does not produce secondary pollution. Cooper et al. [15] studied the injection of H_2O_2 into hot flue gases for NO emission control. At the optimum temperature of 500 °C, hydrogen peroxide can be thermally activated to generate active radicals including hydroxyl radical ($\cdot OH$) and hydroperoxy radical ($HO_2\cdot$). More than 90 % of NO can be effectively converted into soluble nitrogen oxides by these radicals of $\cdot OH$ and $HO_2\cdot$. However, this gas-phase

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oxidation method has so far only been studied in the laboratory due to the limitations imposed by the high temperatures required.

Persulfate can be stimulated by heat [16], UV light [17], ultrasonic [18] or transition metals (Fe^{2+}, Co^{2+}, Cu^{2+}) [19,20] to generate sulfate radical ($SO_4^{\cdot -}$) (Eqs. 1 and 2), which is an oxidant with a similar function to ·OH. Adewuyi et al. [5,12] studied the absorption-oxidation of NO and SO_2 by $Na_2S_2O_8$ aqueous solution in a bubbling reactor. Their results indicated that $Na_2S_2O_8$ can be activated to generate active $SO_4^{\cdot -}$ radical at 50 °C, which then reacts with H_2O to produce ·OH radical. The reaction rate was very slow ($k[H_2O] < 2 \times 10^{-3} s^{-1}$), and so NO and SO_2 were mainly removed by $SO_4^{\cdot -}$ radical in the thermal excitation system of $Na_2S_2O_8$ aqueous solution. Block et al. [21] found that $SO_4^{\cdot -}$ and ·OH radicals coexisted in the dual oxidation ($S_2O_8^{2-}/H_2O_2$) system owing to the significant synergistic relationship between $S_2O_8^{2-}$ and H_2O_2. In our previous studies [22,23], we also showed that the combination of $S_2O_8^{2-}$ and H_2O_2 had a significant synergistic effect on NO removal. In addition, the NO removal efficiency under alkaline conditions was much higher than that under acidic or neutral conditions, reaching 80 % or higher for a long period of time under strongly alkaline conditions adjusted by the addition of sodium hydroxide (NaOH). All these indicated that $S_2O_8^{2-}$ can be activated by strong alkalinity, heat and H_2O_2. This finding was consistent with the conclusions of Zhao et al. [24].

$$S_2O_8^{2-} + \text{heat/UV/ultrasonic} \rightarrow 2SO_4^{\cdot -} \quad (1)$$

$$S_2O_8^{2-} + Me^{n+} \rightarrow SO_4^{\cdot -} + SO_4^{2-} + Me^{(n+1)+} \quad (2)$$

The problems of H_2O_2 instability and extra consumption of NaOH in the dual oxidation ($S_2O_8^{2-}/H_2O_2$) system can be solved by dissolving the solid oxidant CaO_2 in water for producing H_2O_2 and $Ca(OH)_2$ as described in Eq. 3 [25]. As well as a source of H_2O_2 (liberating a maximum of 0.47 g H_2O_2/g CaO_2 [25]), CaO_2 is also a strong alkali oxidant. This means it can activate $S_2O_8^{2-}$ and can therefore be used as an absorbent for the alkaline absorption of NO and SO_2. To the best of our knowledge, no study on wet desulfurization and denitration using the dual component of $S_2O_8^{2-}/CaO_2$ has yet been reported.

$$CaO_2 + H_2O \rightarrow H_2O_2 + Ca(OH)_2 \quad (3)$$

This study was aimed to understand the feasibility of simultaneous absorption of NO using $S_2O_8^{2-}/CaO_2$. Specifically, the effects on NO removal of single and dual component methods, $S_2O_8^{2-}$ concentration, CaO_2 concentration, the initial pH, the reaction temperature, NO concentration, and O_2 concentration were investigated in a bubbling reactor. In addition, the related mechanisms of NO removal by $S_2O_8^{2-}$ and CaO_2 were revealed by free radical detection. The results would contribute to the knowledge of simultaneous removal of NO_x and SO_2 in the same wet scrubber.

2. Experimental

2.1. Materials

Flue gases were simulated by mixing N_2 (99.999 %), O_2 (99.999 %), and NO mixed gas (1 %). All gases were purchased from Air Liquide Tianjin Co., Ltd. Sodium persulfate ($Na_2S_2O_8$, powder, 99 %), sulfuric acid (H_2SO_4, liquid, 98 %), sodium hydroxide (NaOH, pellets, 96 %) and anhydrous calcium chloride ($CaCl_2$, pellets, 96 %) were supplied by Sinopharm Chemical Reagent Beijing Co., Ltd. All reagents used in this experiment were analytically pure. The calcium peroxide (CaO_2) powder (70 %) used was chemically pure and obtained from Shandong Western Chemical Industry Co., Ltd.

2.2. Experimental procedure

Fig. 1 shows the experimental setup used in this study. It consisted of four parts, a simulated flue gas generation system, a bubble column reactor with an inner diameter of 75 mm and a height of 300 mm, a flue gas analysis system and a tail gas absorption system. The NO, O_2 and N_2 (Fig. 1, 1–3) had their flow rates measured by mass flowmeters (Fig. 1, 4) before being mixed in a surge flask (Fig. 1, 5). Concentrations of NO and O_2 were adjusted by diluting with N_2. The flow rate of the simulated flue gas was kept at 2 L/min.

All experiments were conducted at temperatures between 15 and 70 °C. The temperature was controlled by the digital thermostat water bath (Fig. 1, 9) (HWSH, ± 0.1 °C, Shanghai Tian Heng Instrument co., Ltd). For a typical test, the bubble column reactor was first filled with 600 mL of water and heated to the required temperature. Sodium persulfate and calcium peroxide solutions were added into the reactor until the total liquid volume reached 800 mL. The pH of the solution was adjusted by adding 3 mol/L H_2SO_4 or 2 mol/L NaOH solution into the reactor. When the liquid phase was ready, the simulated flue gas was passed through the bubbling reactor, the surge flask (Fig. 1, 10), the drying tube (Fig. 1, 11) containing anhydrous $CaCl_2$ used for the removal of moisture in the simulated flue gas, and finally through another surge flask (Fig. 1, 14) before entering the flue gas analyzer.

The direction of simulated flue gas flow was controlled by a 3-way valve (Fig. 1, 6). The inlet and outlet concentrations of NO_x and O_2 were measured by the ecom-J2KN flue gas analyzer (German RBR Measurement Technology Co., LTD). The pH of the reaction solution was measured before and after each test with a digital pH meter (PHS-3C, E-201F of electrode assembly type, ± 0.01, Shanghai Leici Co., LTD). The tail gas was further cleaned by the exhaust gas absorption unit (Fig. 1, 17) before entering the fume hood (Fig. 1, 18).

2.3. Data analysis

The ions in the spent scrubbing solution were analyzed with a Dionex ICS 1000 ion chromatography system under the following chromatographic conditions: ion pac AS11-HC capillary column (4 × 250 mm), eluent (2 mmol/L NaOH), injection volume (25 μL), column temperature (303 K), flow rate (1.0 mL/min) and automatic regeneration suppression system (60 mmol H_2SO_4 and H_2O). The crystalline structure of fresh and spent solid absorbents was analyzed by X-ray diffraction (XRD, D8 ADVANCE type, BRUKER-AXS in Germany) (60 kV and 50 mA) with a Ni-Filtered Cu Kα, with a scanning 2θ range of 5°–90° and a step size of 0.02. The fresh and spent solids were analyzed by X-ray photoelectron spectroscopy (XPS, PHI Quantera SXM Scanning ESCA Microprobe (Physical Electronics), Ulvac-Phi Inc in Japan) with a hemispherical detector operated at a constant pass energy (PE = 55 eV) using Al Kα radiation (1486.6 eV). All binding energies were referenced to C 1s line at 284.8 eV. Active free radical species were detected with an electron spinresonance (EPR) spectrometer (JES-FA200) using 5,5-dimethyl-1-pyrrolidine N-oxide (DMPO) (99 %, Sigma) as a spin trap agent.

The inlet concentrations of NO_x and O_2 were measured immediately upstream of the gas inlet. The outlet concentrations of NO_x and O_2 from the bubble column reactor were continuously monitored and recorded. Each measurement lasted for 90 min, and the mean concentration within the 90 min was used for the calculation of removal efficiency. When the mixed gas was bubbled through the reactor, NO reacted with the $S_2O_8^{2-}/CaO_2$ solution. The corresponding NO removal efficiency was calculated by:

$$\eta_{NO}(\%) = \frac{NO_{inlet} - NO_{outlet}}{NO_{inlet}} \times 100 \quad (4)$$