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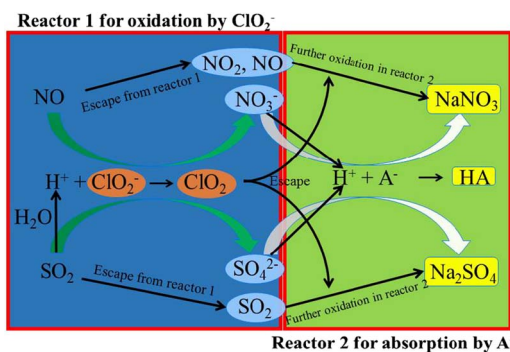
An integrated dual-reactor system for simultaneous removal of SO₂ and NO: Factors assessment, reaction mechanism and application prospect



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GRAPHICAL ABSTRACT



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ABSTRACT

This paper developed an integrated dual-reactor system for simultaneous removal of SO₂ and NO, in which, the first reactor is mainly used to oxidize NO by NaClO₂, and the second reactor is used to deeply removal of SO₂, NO, NO₂ and absorb the acidic ClO₂ released from the first reactor by sodium humate (HA-Na). This novel system exhibits some superiorities, including the reagents dosages very low, the lower emitted concentrations of SO₂ and NO_x than the ultra-low emission standards, the mild applied conditions of pH and temperature in view of practical application. The best concentrations of NaClO₂ and HA-Na were determined as 0.03%wt and 1.0% wt. The appropriate pH ranges were selected as 3–7 for NaClO₂ and 11–12 for HA-Na. The variation of temperatures of the dual reactors exhibited a slight effect on the yield of NO₂. The presence of CO₂ produced a remarkable inhibition on the removal of SO₂ and NO_x. The addition of HCO₃⁻ in NaClO₂ significantly decreased the removal efficiency of NO as well as the yield of NO₂. The existence of HCO₃⁻ in HA-Na accelerated the release of NO₂. The removal products of SO₂ and NO in the dual-reactor system were determined as Na₂SO₄ and NaNO₃ by XRD, XPS and EDS. The reaction mechanism for simultaneous removal of SO₂ and NO was speculated. Finally, the application prospect of this novel system was initially analyzed.

1. Introduction

In 2015, Chinese government had issued the ultra-low emission

standards of SO₂ and NO_x for the coal-fired power plant, the concentrations of SO₂ and NO_x should be controlled below 35 and 50 mg/m³ respectively. The mature conventional systems of Selective Catalytic

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Reduction (SCR) with Wet Flue Gas Desulfurization (WFGD) can hardly meet this standard [1–3]. Hence, it is urgent to develop an advanced approach to realize the deep removal of SO₂ and NO. And it is better to not only meet the ultra-low emission standards but also complete the removal of SO₂ and NO_x in a simplified system.

A lot of works have been conducted to develop an advanced method for simultaneous removal of SO₂ and NO. Raghunath and Mondal [4] used NH₃/NaClO as a complex absorbent to absorb SO₂ and NO. Liu and Wang [5] conducted the simultaneous removal of SO₂ and NO by permonosulphuric (PMS)/Cu²⁺/Fe³⁺, and demonstrated sulfate radicals (SO₄^{•-}) and hydroxyl radicals (HO) were the dominative oxidants. Liu et al. [6] and Chiu et al. [7] respectively prepared a porous activated carbon and the composites of VO_x, MnO_x and CuO_x/SiO₂ to carry out the experiments of multi-pollutants removal, and some meaningful results were obtained. Liu et al. [8] adopted O₃, O and HO generated by vacuum ultraviolet motivating O₂/H₂O/H₂O₂ to simultaneously remove SO₂ and NO. Zhang et al. [9] carried out the simultaneous removal of SO₂ and NO by ammonia-Fe(II)EDTA. Also some other methods, such as the biofilter-Fe(II)EDTA [10], ozone oxidation with alkalinity absorption [11,12], activated carbon adsorption [13] and photocatalytic oxidation [14], had been reported to be used for simultaneous removal of SO₂ and NO.

Dual areas control is one of the developed methods for deep removal of SO₂ [15], in which the bottom area is used to partly remove SO₂ and guarantee a good oxidation of sulfite to sulfate in the pH range of 4.6–5.3, the upper area is used to complete the deep removal of SO₂ in the pH range of 5.8–6.4 [16] and promise the emitted SO₂ concentration lower than 35 mg/m³. In fact, this system could cooperate with our advanced wet method to realize the deep and simultaneous removal of SO₂ and NO. In previous work [17], we experimentally verified the good performance of a complex absorbent NaClO₂/humate (HA-Na) on the removal of SO₂ and NO (99.8% and 98%). But the results indicated that the desirable pH for NaClO₂/HA-Na mixture was 8–9, which was a compromise, because the suitable pH for the HA-Na existence as well as the absorption of acidic gases was alkaline, but the alkaline conditions were unfavorable for activating NaClO₂ (generation of ClO₂) to exhibit the strong oxidizing ability [18,19]. Hence, it is sensible to design an appropriate way to separate NaClO₂ and HA-Na in two areas to conduct the oxidation and absorption for deep removal of SO₂ and NO.

The authors considered that a dual-reactor system was likely to be adopted to coordinate with the complex absorbent of NaClO₂/HA-Na to conduct the deep and simultaneous removal of SO₂ and NO. The specific process is that NaClO₂ and HA-Na are separately in the dual reactor, in which, the first reactor is mainly used to effectively oxidize NO to NO₂ and NO₃⁻, meanwhile some SO₂ would be inevitably oxidized in this process, the second reactor is used to absorb the residual NO/NO₂/SO₂ and the Cl-containing oxidants those escaped from the first reactor. The experimental results indicated that the method showed a perfect performance on the simultaneous removal of SO₂ and NO, with very low amounts of reagents dosages. It had a great potential to be applied in the power plants and industrial boilers and furnaces, as well it could replace the SCR system to simplify the flue gas cleaning system.

2. Experimental section

HA-Na (98% w/w) and NaClO₂ (99%w/w) employed in the experiments are analytical grade (Kermel Company). The anhydrous CaCl₂ was used as a dryer before the flue gas analyzer. 1 mol/L of H₂SO₄ and 1 mol/L of NaOH were used to adjust the pH of the solutions of HA-Na and NaClO₂. The dual-reactor system was substituted by two bubbling reactors (Fig. 1). The experimental setup is composed of simulated flue gas generation, dual-reactor system and flue gas detection. SO₂, NO, O₂, CO₂ and N₂ gases were provided by the compressed cylinders (North special gas company, Baoding) and metered by mass flow controller, the mixed gases were diluted by N₂ to the desired concentrations. The concentrations of NO, SO₂, CO₂ and O₂ in the

simulated flue gas are 100–400 mg/m³, 1000–4000 mg/m³, 0–10% and 0–6% respectively. The experiments of simultaneous removal of SO₂ and NO were carried out in the dual reactors, the first reactor was used to oxidize/absorb 95% NO and 98% SO₂ by NaClO₂, then the residual NO, NO₂, SO₂ and residual ClO₂/ClO₂⁻ were absorbed by HA-Na in the second reactor. The diameters and heights of the bubbling reactors are 70 and 150 mm. The temperatures of bubbling reactor 1 and 2 were controlled by two thermostated water baths, ± 0.1 °C (ZDHW, Zhongxingweiye company, Beijing). The corresponding pH was detected over time by two pH meters, ± 0.01, (PHS-3C, E-201-C-Q9 of electrode assembly type, Leici company, Shanghai). The inlet and outlet concentrations of SO₂, NO₂, NO, CO₂ and O₂ in the simulated flue gas were detected online by a flue gas analyzer (ECOM-J2KN, RBR Company, Germany). The reaction conditions for each experiment were summarized in Table 1. The removal efficiencies of SO₂ and NO were calculated with the following formula:

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

Where, η is the SO₂/NO removal efficiency, C_{in} and C_{out} are the inlet and outlet of SO₂/NO concentrations, mg/m³.

An X-ray diffractometer (XRD, D8 ADVANCE type, BRUKER-AXS in Germany) (40 kV and 20 mA) was used to characterize the compounds in the fresh and spent NaClO₂ and HA-Na, the scanning range was from 10 to 90° with a scanning velocity of 9°/min. The X-ray photoelectron spectroscopy (XPS) of the spent NaClO₂ and HA-Na was carried out on an ESCALAB250 spectrometer with Al K α source (1486.6 eV), the binding energies of O 1s, C 1s, S 2p, Cl 1s and N 1s were determined at a 10 kV voltage with a base pressure of 2×10^{-9} Mbar. An energy dispersive X-ray spectrometer (EDS, Vantage DIS type, Thermo NORAN Company) was used to determine the elements in the fresh and spent NaClO₂ and HA-Na. The XRD, XPS and EDS characteristics were carried out after drying and grinding the solid reactants and products.

3. Results and discussion

3.1. Performances of various concentration ratios of NaClO₂ and HA-Na on the simultaneous removal of SO₂ and NO

Fig. 2 shows the performances of various concentration ratios of NaClO₂ and HA-Na on the simultaneous removal of SO₂ and NO. Table 2 shows the combining forms of NaClO₂ and HA-Na. It can be seen that the removal efficiencies of SO₂ are stable over 99% in all Groups, and the emitted concentrations of SO₂ are lower than 35 mg/m³, which meets the ultra-low emission standard of SO₂. Thus the research will focus on the NO removal.

It can be found that as the concentration ratio of NaClO₂ and HA-Na changes, the removal efficiencies of SO₂ and NO, and the residual NO₂ concentrations are varied. The reasons for these phenomena are complicated. Compared the results of Groups 1 and 2, it can be found that as the concentration of HA-Na decreases, the removal efficiencies of SO₂ and NO are decreased and the residual NO₂ concentration is increased, which indicates that the decreasing HA-Na is unfavorable for the absorption of SO₂ as well as the cooperative absorption of NO and NO₂. Compared the results of Groups 1 and 3, it can be found that the decreasing NaClO₂ decreases the NO removal efficiency, which is a result of the worse oxidation of NO. But it is surprising from the comparison among Groups 2, 3 and 4 that the decreasing NaClO₂ from 1%wt to 0.5%wt results in an increase of NO removal efficiency as well as an increase of NO₂ concentration, meanwhile the duration time of NO removal is shortened. The possible reason for the phenomena was that the decreasing NaClO₂ decreased the solution pH, so the generation rate of ClO₂ from SO₂ + H₂O + ClO₂⁻ was accelerated [17,18], resulting in a promotion on the gaseous oxidation of NO by ClO₂, with producing more NO₂, and then a higher removal efficiency of NO [20]. But the decrease of the molar ratio of NaClO₂/NO would be surely decreased

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