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ELUCIDATING THE DRIVING FACTORS IN SULFUR TRIOXIDE FORMATION UNDER SIMULATED ACTUAL ULTRA-LOW EMISSION PROCESS

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Abstract: Current flue gas pollution control technologies compliant with ultra-low emission standards exhibit limited effectiveness in removing sulfur trioxide (SO_3)—a key condensable particulate matter (CPM) precursor—necessitating high-efficiency, low-consumption control strategies. To address the poorly elucidated formation mechanisms of SO_3 across ultra-low emission systems, particularly within the SCR+WFGD process chain, this study employed experimental simulations where SO_3 was prepared via the contact process and quantified through controlled condensation coupled with sulfate titration. Catalytic oxidation experiments on cesium-doped V_2O_5 in a temperature-controlled fixed-bed reactor under simulated actual flue gas revealed reaction temperature as the governing factor for SO_3 conversion, achieving peak efficiency at 485–505°C. Whereas SO_2 concentration exerted non-dominant effects due to sustained catalytic stability, space velocity proved negligible under high-temperature regimes. These mechanistic insights establish fundamental pathways for developing targeted SO_3 mitigation technologies.

Keywords: Sulfur trioxide (SO_3); Sulfur dioxide (SO_2); Catalytic oxidation; Driving factors; Ultra-low emission

1 INTRODUCTION

During combustion in boilers and passage through selective catalytic reduction (SCR) units, sulfur dioxide (SO_2) in coal-fired flue gas reacts with oxygen (O_2), significantly increasing the concentration of sulfur trioxide (SO_3) [1-2]. SO_3 is highly toxic and corrosive, causing severe irritation to skin, mucous membranes, and other tissues, thereby posing serious risks to ecological systems and human health [3]. Additionally, SO_3 can react with excess ammonia (NH_3) injected into the SCR system, forming ammonium sulfate ($(NH_4)_2SO_4$) and ammonium bisulfate (NH_4HSO_4), which can damage the operational equipment of coal-fired power plants [4]. However, current ultra-low emission control systems recommended for coal-fired flue gas treatment only effectively remove nitrogen oxides (NO_x), SO_2, and particulate matter (PM), lacking efficient methods for SO_3 control. Therefore, it is imperative to develop highly efficient and low-cost SO_3 control technologies to meet the operational safety and environmental emission requirements of coal-fired power plants.

The configuration of simulated polluted flue gas and measurement of pollutant concentrations in clean flue gas are central to laboratory-scale SO_3 control research. The critical step in the former process is SO_3 generation, while in the latter, it is SO_3 sampling. Ozone oxidation and heated sulfuric acid methods are commonly used in laboratories for SO_3 preparation. The ozone oxidation method has advantages in stable SO_3 production but imposes stringent requirements for ozone preparation. The heated sulfuric acid method involves decomposing sulfuric acid by heating to generate SO_3, but this process carries safety risks due to the strong corrosiveness of sulfuric acid [5]. The contact process is commonly utilized for industrial sulfuric acid production, involving vanadium pentoxide (V_2O_5) as a catalyst to oxidize SO_2 to SO_3 under oxygen-rich conditions. This method offers advantages such as high conversion rates, high product purity, and robust adaptability [6-8]. For SO_3 sampling, commonly employed techniques include controlled condensation, alkaline absorption, isopropanol absorption, and salt absorption methods [9]. Among these, the controlled condensation method effectively prevents measurement errors caused by premature SO_3 condensation and reduces the interference from sulfate ions generated by dissolved SO_2. It also exhibits high accuracy under various operational conditions. After collecting SO_3 using controlled condensation, sulfate content in the collected solution can be measured by gravimetric analysis, barium chromate photometry, ion chromatography, turbidity measurement, or titration methods, thereby enabling estimation of SO_3 concentration in the simulated flue gas [10, 11].

In this study, the contact process was employed for SO_3 preparation, and SO_3 was collected and measured using controlled condensation combined with sulfate titration. Experiments on catalytic oxidation of SO_2 to SO_3 were conducted under different operating conditions. The methods for SO_3 preparation and concentration measurement described herein can be utilized in further SO_3 control experiments. The insights obtained regarding SO_3 formation under various conditions will serve as references for the formulation of effective SO_3 control strategies.

2 EXPERIMENTAL METHODS

2.1 Simulation System for SO_3 Generation

In this study, SO_3 was generated via the contact process by conducting catalytic oxidation of SO_2 on an isothermal fixed-bed reactor. The experimental setup was designed to investigate the effects of various operational parameters on the SO_3 conversion rate. A schematic diagram illustrating the principle of the fixed-bed experimental system is shown in **Figure 1**.

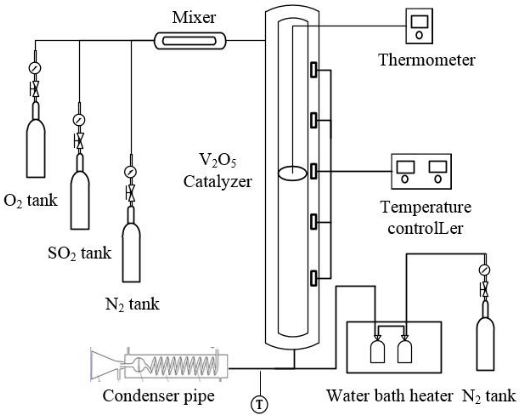

Figure 1 Schematic Diagram of the Fixed-Bed Experimental System

The simulated flue gas was composed of N_2, O_2, SO_2, and water vapor. Compressed gas cylinders containing certified standard gases were connected via pressure regulators and piping to mass flow controllers (MFCs), which provided real-time control of individual gas flow rates. The water vapor content in the simulated flue gas was regulated by adjusting the temperature of a thermostatic water bath and the flow rate of carrier N_2. To ensure the stability of water vapor concentration, a series of gas-washing bottles were placed in tandem within the water bath. To prevent irreversible deactivation of the catalyst by water vapor, the mixing point of water vapor and the rest of the simulated flue gas was positioned downstream of the reactor. The pipeline segment extending from the gas-washing bottle outlet to the SO_3 sampling system inlet was wrapped with an electric heating tape to prevent condensation of SO_3 and water vapor within the line.

The reactor system consisted of a quartz reactor and an external heating unit. The reactor was a cylindrical hollow quartz tube fitted with a quartz sand support plate to hold the catalyst bed. The heating unit, located outside the reactor, was used to maintain the reactor at a target reaction temperature. The catalyst employed in this study was a pelletized cesium-doped V_2O_5 catalyst. A thermocouple was embedded within the catalyst bed to enable accurate monitoring of the catalyst layer temperature, which is referred to as the “reaction temperature” in the following sections [12].

2.2 Measurement of SO_3 Concentration

In this study, SO_3 was collected using the controlled condensation method. The SO_3 sampling system is illustrated in **Figure 2**.

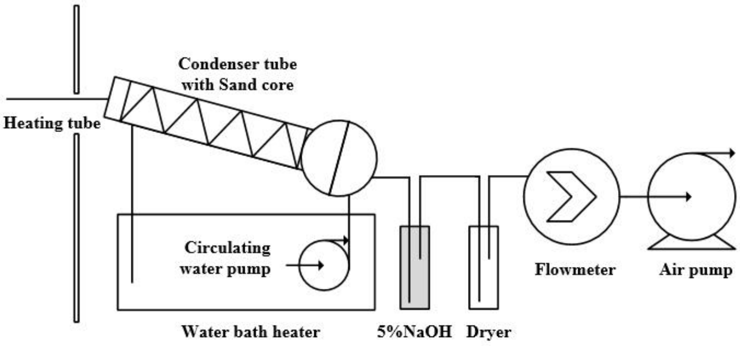

Figure 2 Schematic Diagram of the SO_3 Sampling System

After SO_3 was collected using the controlled condensation method, the condensate within the serpentine condenser was rinsed into a volumetric flask using deionized water, and the solution was subsequently diluted to a fixed volume. The concentration of sulfate ions in the solution was then determined by ion chromatography, enabling efficient and accurate quantification of SO_3 concentration in the experimental gas.

2.3 Calculation of SO_3 Conversion Rate

The SO_3 conversion rate was calculated using the following equation:

$$\alpha = \frac{SO_{3\mathrm{out}}}{SO_{2\mathrm{in}}} \times 100\% \tag{1}$$

where $SO_{3\mathrm{out}}$ represents the calculated outlet concentration of SO_3 in the simulated flue gas, in units of ppm, and $SO_{2\mathrm{in}}$ denotes the inlet concentration of SO_2 as set in the experiment, also in ppm.

Since the catalytic oxidation of SO_2 to SO_3 is a heterogeneous catalytic reaction, its conversion rate is primarily influenced by reaction temperature, reactant concentration, and space velocity. In this study, subsequent experiments were conducted under fixed conditions: the catalyst mass (cesium-doped V_2O_5) was maintained at 10 g, the catalyst bed height at 20 mm, and the total gas flow rate at 2 L/min.

3 RESULT AND DISCUSSION

3.1 Effect of Reaction Temperature on SO_3 Conversion Rate

Catalytic oxidation experiments for SO_2-to-SO_3 conversion were conducted at four different temperatures: 425 °C, 455 °C, 485 °C, and 505 °C, in order to investigate the influence of reaction temperature on SO_3 conversion and to identify the optimal temperature for SO_3 generation. The experimental results are presented in **Figure 3**. As shown in the figure, under various operating conditions with different inlet SO_2 concentrations, the SO_3 conversion rate exhibits a general trend of initially increasing rapidly with temperature, followed by a gradual decline. A peak conversion rate was observed within the 485 °C to 505 °C range, indicating the existence of an optimal reaction temperature for the selected cesium-doped V_2O_5 catalyst.

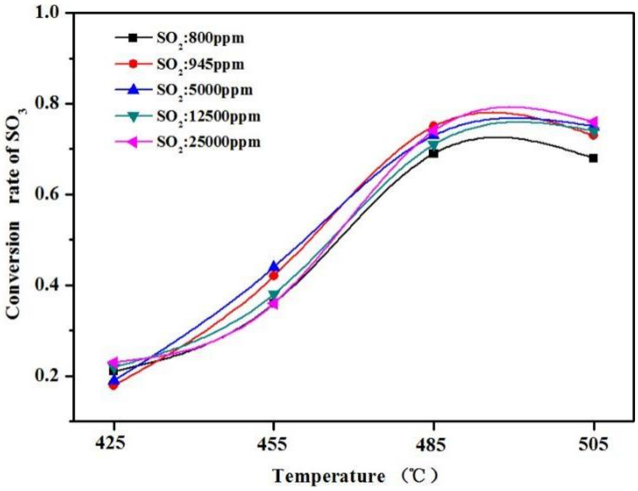

Figure 3 SO_3 Conversion Rate at Different Reaction Temperatures

The observed trend can be explained as follows: at relatively low reaction temperatures, the activation energy required for SO_3 formation remains high, and the catalyst has either not yet reached or has just reached its ignition temperature. Under these conditions, the catalyst's ability to reduce the activation barrier is limited, resulting in a low SO_3 conversion rate. As the reaction temperature increases, the catalyst becomes more active and the activation energy is more effectively overcome, leading to a continuous rise in SO_3 conversion. However, since the oxidation of SO_2 to SO_3 is an exothermic and reversible reaction, excessively high temperatures thermodynamically suppress the forward reaction, thereby limiting further increases in conversion. Additionally, elevated temperatures may promote undesirable interactions between V_2O_5 and the silicon dioxide (SiO_2) support material, accelerating catalyst deactivation and subsequently reducing SO_3 conversion efficiency [13]. In the temperature range of 425–485 °C, the dominant factors are the decreasing activation energy and enhanced catalytic activity, which lead to an increase in SO_3 conversion with rising temperature. In contrast, within the 485–505 °C range, the negative effects—such as thermodynamic suppression of the forward reaction and increased catalyst degradation—become more pronounced. Consequently, the SO_3 conversion rate initially increases and then declines with further temperature elevation in this higher range.

3.2 Effect of SO_2 Concentration on SO_3 Conversion Rate

Catalytic oxidation experiments were carried out under varying SO_2 concentrations of 800 ppm, 945 ppm, 5000 ppm, 12,500 ppm, and 25,000 ppm to investigate the influence of SO_2 concentration on the SO_3 conversion rate. The experimental results are presented in **Figure 4**. As illustrated in the figure, although the trends in SO_3 conversion rate variation with respect to SO_2 concentration differ slightly across different reaction temperatures, the overall magnitude of change remains limited. This indicates that the selected catalyst exhibits strong stability and is capable of sustaining effective SO_3 production across a wide range of SO_2 concentrations.

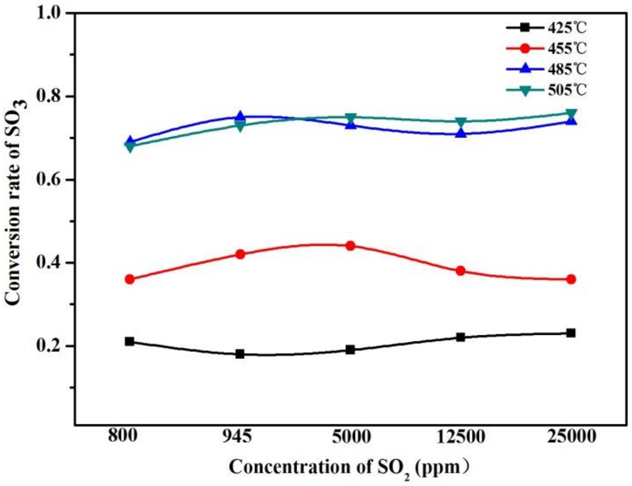

Figure 4 SO_3 Conversion Rate Under Different SO_2 Concentrations

The analysis suggests that within the range of conditions examined in this study, SO_2 concentration is not the dominant factor influencing the reaction. As a result, the SO_3 conversion rate does not exhibit significant fluctuations with varying SO_2 concentrations at different reaction temperatures, demonstrating good overall stability of the catalytic performance.

3.3 Effect of Space Velocity on SO_3 Conversion Rate

Catalytic oxidation experiments were conducted under space velocities of 425 h^{-1}, 850 h^{-1}, and 1275 h^{-1} to investigate the effect of space velocity on the SO_3 conversion rate. The experimental results are shown in Figure 5. As illustrated in the figure, an overall slight downward trend in SO_3 conversion rate was observed with increasing space velocity.

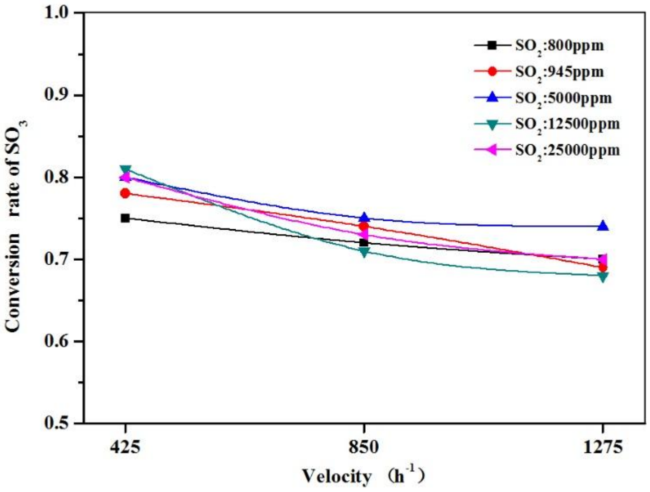

Figure 5 SO_3 Conversion Rate Under Different Space Velocities

The analysis indicates that under constant reactant concentration, a higher space velocity implies a greater quantity of reactants processed per unit time, but with a shorter residence time within the catalyst bed, which can limit the extent of the oxidation reaction. In general, the catalytic conversion rate is governed by two primary factors: the surface reaction rate (which is temperature-dependent) and the residence time of reactants on the catalyst surface (inversely related to space velocity) [14, 15]. At an appropriate reaction temperature, the catalyst exhibits high activity and a rapid reaction rate [16]. Under such conditions, the time required to achieve a target SO_3 conversion (e.g., 70–80%) may be shorter than the actual residence time, thereby reducing the sensitivity of conversion efficiency to changes in space velocity. Due to the interplay of these two factors, the influence of space velocity on SO_3 conversion rate in this study was relatively minor. Even with a substantial increase in space velocity, the variation in SO_3 conversion remained limited.

4 CONCLUSION

In this study, SO_3 was generated via the contact process and subsequently collected using the controlled condensation method. A series of catalytic oxidation experiments were conducted on an isothermal fixed-bed reactor to investigate the performance of a cesium-doped V_2O_5 catalyst for SO_2-to-SO_3 conversion under various operating conditions. The following conclusions were drawn: (1) Reaction temperature is the dominant factor influencing SO_3 conversion. The optimal operating temperature for the selected catalyst lies in the range of 485 °C to 505 °C. (2) SO_2 concentration is not a primary determinant of SO_3 conversion. The catalyst exhibited stable performance across a wide range of SO_2 concentrations. (3) Space velocity has a limited impact on SO_3 conversion at elevated temperatures, suggesting that the catalyst maintains effective activity even under accelerated flow conditions. The work presented in this study provides a solid foundation for future laboratory-scale development of SO_3 control technologies. The proposed methods for simulated flue gas configuration and pollutant concentration measurement are essential steps toward advancing efficient and reliable SO_3 mitigation strategies.

COMPETING INTERESTS

The authors have no relevant financial or non-financial interests to disclose.

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REFERENCES

[1] Luo Hancheng, Pan Weiguo, Ding Honglei, et al. Formation mechanism and control technologies of SO_3 in flue gas from coal-fired boilers. Boiler Technology, 2015, 46(6): 69-72.
[2] Cao Yan, Zhou Hongcang, Jiang Wu, et al. Studies of the fate of sulfur trioxide in coal-fired utility boilers based on modified selected condensation methods. Environmental Science & Technology, 2010, 44(9): 3429. https://doi.org/10.1021/es903661b
[3] Kikuchi R. Environmental management of sulfur trioxide emission: impact of SO_3 on human health. Environmental Management, 2001, 27(6): 837-844. https://doi.org/10.1007/s002670010192
[4] Zhong Lijin, Song Yubao. Causes of air preheater blockage in boiler SCR flue gas denitrification and corresponding solutions. Thermal Power Generation, 2012, 41(8): 45-47.
[5] Chang Jingcai, Dong Yong, Wang Zhiqiang, et al. Simulation experiment on SO_3 conversion and absorption characteristics in coal-fired flue gas. Journal of China Coal Society, 2010(10): 1717-1720
[6] Guo Jingzhi. Progress in sulfuric acid process technology abroad. Chemical Production and Technology, 2003, 10(3).
[7] Han Yinghui, Zhang Junjun, Zhao Yi. Visible-light-induced photocatalytic oxidation of nitric oxide and sulfur dioxide: Discrete kinetic and mechanism. Energy, 2016, 103(15), 725-734
[8] Han Yinghui, Li Xiaolei, Fan Maohong, et al. Abatement of SO_2-NO_x binary gas mixtures using a ferruginous highly active absorbent: Part I. Synergized effects and mechanism, Journal of Environmental Sciences, 2015, 30(1), 55-64.
[9] Ahn J, Okerlund R, Fry A, et al. Sulfur trioxide formation during oxy-coal combustion. International Journal of Greenhouse Gas Control, 2011, 5(12): S127-S135. https://doi.org/10.1016/j.ijggc.2011.05.009
[10] Wang Fangqun, Guo Rong, Sui Jiancai, et al. Detection technologies and applications of SO_3 in flue gas from thermal power plants. Environmental Engineering, 2008, 26(5): 86-87.
[11] Ran Guangfen, Ma Haizhou. Analysis technologies and application status of sulfate. Journal of Salt Lake Research, 2009, 17(4): 58-62.
[12] Boghosian S, Fehrmann R, Bjerrum N J, et al. Formation of crystalline compounds and catalyst deactivation during SO_2 oxidation in V_2O_5 $M_2S_2O_7$ (M = Na, K, Cs) melts. Journal of Catalysis, 1989, 20(51): 121-134.
[13] Gu Keren, Li Hangwei. Application of V_2O_5 catalyst in SO_3 gas production. Hangzhou Chemical Industry, 1997(2): 8-10.
[14] Liu Xin, Zhao Minghui, Liu Dongxu, et al. Boosting catalytic oxidation of H_2S over activated carbon optimized by the synergistic effect of rich defects and nitrogen sites. Surface and Interfaces, 2025, 68, 106672.
[15] Zhao Yi, Han Yinghui, Ma Tianzhong, et al. Desulfurization and Denitrification from Flue Gas by Ferrate (VI), Environmental Science & Technology, 2011, 45(9), 4060-4065.
[16] Wang Xin, Duan Rucheng, Li Zhuocan, et al. The critical role of oxygen vacancies in N_2O decomposition over cobalt-doped CeO2 catalysts. Environmental Science & Technology. 2025, 59, 11, 5839-5847.