



Research article

Formation and decomposition of NH_4HSO_4 during selective catalytic reduction of NO with NH_3 over $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalysts



Ya-Juan Shi, Hang Shu, Yu-Hua Zhang, Hong-Mei Fan, Ya-Ping Zhang, Lin-Jun Yang*

Key Laboratory for Energy Thermal Conversion and Control, Ministry of Education, Southeast University, Nanjing 210096, Jiangsu, China

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ABSTRACT

Based on commercial $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalysts, the formations of ammonium bisulfate (ABS) and ammonium sulfate were detected from the reactions among SO_3 , NH_3 and H_2O in the flue gas during the process of selective catalytic reduction (SCR) of NO with NH_3 , leading to the deactivation of the catalyst and the increased number concentration of fine particles. The mechanism of formation and decomposition of ABS during SCR of NO with NH_3 was investigated through the In Situ Diffuse Reflectance Infrared Spectroscopy (DRIFTS) and the Thermo Gravimetric analyzer coupled with Fourier Transform Infrared analyzer (TG-FTIR). The results of the in situ DRIFTS showed that ABS deposited on the surface of the catalysts could be generated from the adsorption activation of NH_3 with SO_2 in presence of O_2 . It also could be produced by the direct reaction between NH_3 and the intermediate metal sulfates on the surface of the catalysts. In addition, it suggested that the reaction between NO and NH_4^+ in ABS promoted ABS decomposition. TG-FTIR demonstrated that the process of ABS decomposition on the catalysts was composed of two steps. Moreover, the temperature window of the complete pyrolysis of ABS was delayed by catalysts.

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1. Introduction

The SCR DeNOx technology has been fully developed and widely used with NH_3 in coal-fired power plants because of its high removal efficiency of NOx in the flue gas. As the critical part of the SCR system, $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalysts are mainly applied to reduce NOx, in which vanadium oxide is the main active component [1].

SCR reactors are installed between the boiler economizer and the air pre-heater where the temperature is suitable for $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalysts to reach high DeNOx efficiency. However, in this case, part of SO_2 , which is high in concentration in the flue gas is converted to SO_3 with H_2O and NH_3 according to the following side reactions [2,3].



One of the products is $(\text{NH}_4)_2\text{SO}_4$ which is drying powdery can be removed by soot blowing so that it has little effect on the catalyst. But

NH_4HSO_4 (ABS) is a kind of sticky and corrosive substance which can cause the formation of fine particles due to nucleation, condensation, and coagulation. Z. Li, et al. [4] ever observed obvious increase of SO_4^{2-} and NH_4^+ emissions in the tailpipe of the SCR system based on the measurement of two coal-fired power plants and the particles were concentrated in sub-micrometer particulate matter (PM_{10}). Meanwhile, the generation of $(\text{NH}_4)_2\text{SO}_4$ or NH_4HSO_4 aerosol was supposed to depend on the molar ratio of NH_4^+ to SO_4^{2-} during the SCR process. A. Stavros [5] suggested that the particles formed in an ammonia SCR system for diesel vehicles could contain sulfate, nitrate, and chloride salts with ammonium. Some fine particles deposit in the micropores of the catalyst surface and were adsorbed on the active acid sites which result in the plugging and deactivation of catalysts [6,7]. Some fine particles condense on the surface of metal within the air pre-heater led to the plugging and corrosion [8]. Most of the fine particles go into the subsequent treatment system as aerosols within the flue gas, contributing to a significantly increased concentration of fine particles in the tailpipe, which finally deteriorates the haze condition [9,10]. Although the formation of ABS has been revealed, more detailed studies are needed to indicate the mechanism of formation and decomposition of ABS during the NH_3 -SCR process, especially over the commercial $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalysts.

Both formation and decomposition of ABS are mainly related to catalysts, temperature, concentrations of reactants and fly ash. It is difficult for ABS to decompose because of strong thermal stability. There have already been many studies on temperature of formation and

* Corresponding author.

E-mail address: yj@seu.edu.cn (L.-J. Yang).

decomposition of ABS on the surface and in the pores of catalyst [11–13]. Z.P. Zhu [12] has concluded that the decomposition of pure ABS began at about 390 °C while ABS was loaded on 5 wt.% V_2O_5/TiO_2 catalyst started at 450 °C, approximately, indicating that the decomposition of ABS was connected with the characteristic of catalysts. It has been generally accepted that the formation temperature of ABS was in the range of 190 °C–240 °C while the decomposition temperature was about 350 °C. In addition, the current studies [12,14] on the decomposition of ABS by TG in hot air are generally widely different from that in the practical SCR process. Moreover, it has been expected that ABS formation in SCR is due to ammonia escape, which is actually a kind of unilateral understanding. Therefore, based on the commercial $V_2O_5-WO_3/TiO_2$ catalyst, we studied the characteristic of fine particles generating during the NH_3 -SCR process by X-ray diffraction (XRD), Scanning Electron Microscope (SEM) and Electrical Low Pressure Impactor (ELPI). Then, the mechanisms of formation and decomposition of ABS, as well as the influences of NO were discussed by in situ DRIFTS and TG-FTIR. Finally, we hope that this work will be helpful to reduce ABS during the SCR process.

2. Experimental

2.1. Catalysts preparation

The monolithic $V_2O_5-WO_3/TiO_2$ catalyst used in the experiment was bought from a thermal power plant and composed of 0.899 wt.% V_2O_5 , 86.81 wt.% TiO_2 and 4.61 wt.% WO_3 . The catalyst was initially pulverized and screened to even fine granule whose diameter were about 0.3–0.45 mm. Ammonium (bi)sulfate (Analytical grade, Sinopharm Chemical Reagent) was loaded on the catalyst by volume impregnation method for the experiment in case of need.

2.2. Catalytic activity test

As Fig. 1 shows, simulated gas of 800 ppm NO, 800 ppm SO_2 , 5 vol.% O_2 and 8 vol.% H_2O with a balance of N_2 were injected into the SCR reactor after mixing and preheating. 800 ppm NH_3 was also added into the SCR reactor before the entrance to avoid the adverse reaction in pipe and mixer. The total flow rate was 1 m³/h. In addition, the flow

deflectors were installed at the entrance to insure homogeneous mixing of NH_3 and flue gas. The vapors were introduced into the reactor by a micro-injection pump connected with a heating pipe. The reactor was a self-made fixed bed and continuous flow reactor with the inner diameter of 50 mm. There was 50 g of catalyst placed on the porous tray of the reactor. The space velocity in the reactor was controlled at 20,000 h⁻¹.

The reactor temperature was controlled by the temperature controllers and detected with a PT100 platinum resistance at upper, middle, and lower position of the reactor. The SO_2 , NO_x and O_2 concentrations were measured with an ECOM-J2KN flue gas analyzer (RBR Ltd., Germany). Exhaust gas sampling was conducted in the tailpipe by a Dekati PM₁₀/PM_{2.5} Sampler. Concentration and size distributions of the fine particles were online tested with a Dekati ELPI (Dekati Ltd., Finland).

2.3. Techniques of characterization

Carl Zeiss Ultra Plus high resolution field emission scanning electron microscope equipped with Oxford X-MAX type spectrometer (Carl Zeiss AG, Germany) was used to analyze the morphology and elemental composition of the catalyst and particulate matter. The catalyst and particle phase composition were tested by a Smart Lab TMX ray diffract meter with Cu target acting as X-ray source (D/max 2500/PC, Rigaku, Japan).

In situ DRIFTS were carried out on FTIR (Nicolet 6700, Thermo Fisher, USA) at a resolution of 4 cm⁻¹ (32 scans) with the spectral range of 4500–400 cm⁻¹. Firstly, the catalyst samples were pre-treated in high-purity N_2 for 1 h at 400 °C with a flow rate of 20 mL/min. Next, during the cooling process, the background values were obtained and deducted from the sample spectra to get final spectra. Afterwards, 10 mg of the catalyst sample was tableted in CaF_2 as the background and the surface of the self-supporting sheet was smooth and intact without cracks. In addition, after the pre-adsorption of the samples by NH_3 or SO_2 , the sample spectra were obtained at a steady state after purging with N_2 for 40 min. Finally, the sample spectra were obtained by the calculation through the method of Kubelka-Munk.

In TG-FTIR experiments, TG and DTG were carried out in a thermal gravimetric and differential thermal analyzer (STA 409C, NETISCH, Germany) with 10 mg samples in a platinum crucible in a high purity

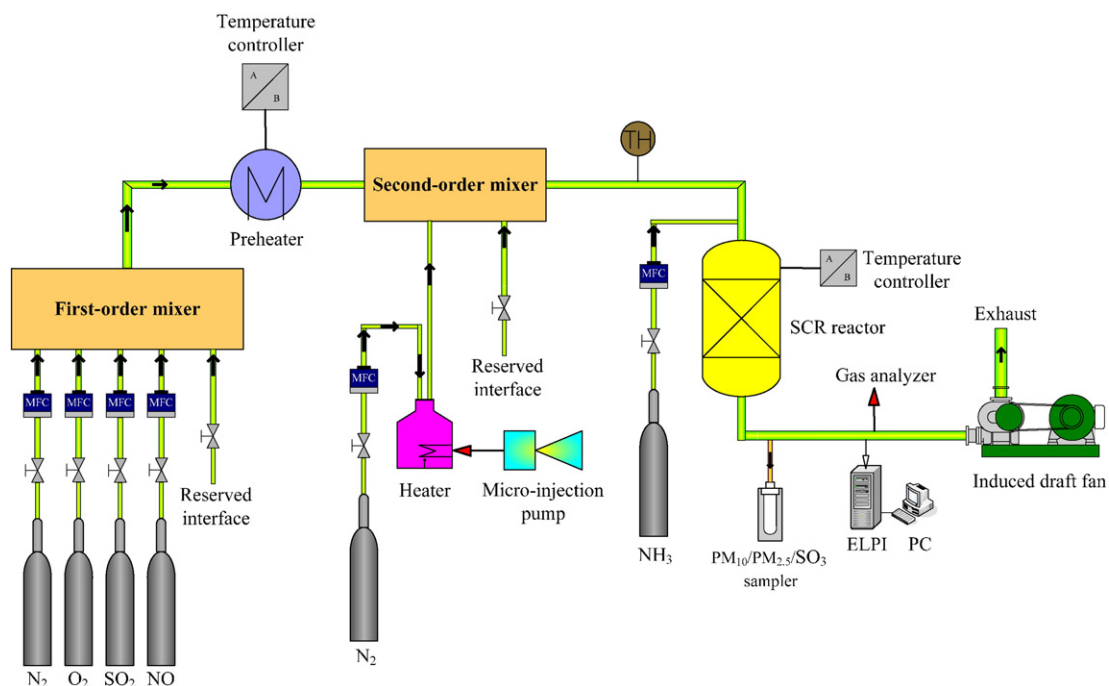


Fig. 1. Schematic diagram of the experimental system.

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