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# Study of $SO_2$ effect on selective catalytic reduction of $NO_x$ with $NH_3$ over Fe/CNTs: The change of reaction route

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## ABSTRACT

Fe/CNTs catalyst exhibits perfect performance when it is used in selective catalytic reduction of $NO_x$ with $NH_3$ ($NH_3$-SCR), meeting the requirements of low-temperature conversion and no vanadium use, which is thought to be a potential candidate for traditional $V_2O_5$–$WO_3$ ($MoO_3$)/$TiO_2$ catalysts. However, small amount of $SO_2$ remained after the desulfurization process severely impacts the activity of Fe/CNTs. TGA, XPS and TPD tests were used to investigate the properties of $SO_x$-species formed on the catalysts; TPSR tests were proceeded to reveal the difference of reaction pathway between normal SCR reaction and that in presence of $SO_2$. The results showed that ferric sulfate was the major sulfate species accumulated on Fe/CNTs, which enhanced the adsorption of $NH_3$ species while constrained the adsorption of $NO_x$ species. Reaction pathway study suggested the adsorption and activation of $NO_x$ species over Fe/CNTs were conductive to the formation of intermediates which was the key to its excellent low-temperature performance. While this effective reaction pathway was inhibited with $SO_2$ in the feed gas and led to the low-temperature activity loss (< 275 °C). Instead, ferric sulfates formed on Fe/CNTs promoted the reaction between adsorbed $NH_3$ species and gaseous NO through which SCR performance at higher reaction temperature was promoted and this became the dominating reaction pathway. The transform of dominating reaction route was the reason for the change of de-$NO_x$ performance over Fe/CNTs in presence of $SO_2$.

## 1. Introduction

As a kind of atmospheric pollutants, nitrogen oxides ($NO_x$) can cause environmental problems and induce respiratory disease. To high-efficiently control the emission of $NO_x$ produced by fossil combustion in power plants, the technique of selective catalytic reduction of $NO_x$ with ammonia ($NH_3$-SCR) has been widely used. High concentrated $SO_2$ and ash (*e.g.*, $K_2O$, CaO and $As_2O_3$) in the fuel gases have heavily inhibited the performance of catalysts, so placing the SCR unit downstream of the desulfurizer and electrostatic precipitators is an optional way to solve this problem [1,2]. The temperature of fuel gases is lower than 300 °C after desulfurization, implying that the $V_2O_5$-$WO_3$ (or $MoO_3$)/$TiO_2$ catalysts, a kind of traditional SCR catalysts well-performed at high temperature (350 °C–400 °C), do not meet the low temperature requirements anymore. New types of Mn- [3–5], Fe- [6–9], Ce- [10–12], Cu- [13,14] based catalysts were developed by means of the modification of surface structure and the enhancement of redox properties to achieve low-temperature $NO_x$ conversion and meet environment-friendly demand for no vanadium as well. Recently, the application of carbon nanotubes (CNTs) as catalyst carrier or composite carrier [15–18] helps the preparation of low-temperature catalysts by using its unique electronic and structural properties [19], especially taking iron oxide as the active sites [6,8]. We also developed a new kind of highly dispersed $Fe_2O_3$/CNTs catalysts and it showed good low temperature SCR performance with more than 85% NO conversion from 175 °C to 275 °C [7].

The fuel gas after the process of desulfurization still contains small accounts of $SO_2$ which can deactivate the catalysts because of its high chemical binding strength and oxidative condition of the feed gas [20]. Some researchers [21–23] have suggested that the rapid formation of ammonium sulfates ($NH_4HSO_4$ and $(NH_4)_2SO_4$) caused the blockage on the catalyst surface and its decomposition behavior with the change of reaction temperature were the key deactivation reason. *Zhu* et al. [24] further proved that $NH_4HSO_4$ on V/AC catalysts could react with NO with the help of AC. Other opinions [21,25] believed that $SO_2$ could combine with active sites to form metal sulfate which may cut off the redox circle of active phases and lead to the catalytic deactivation. *Zhang* et al. [21] reported that cerium in Ce-Ti composite oxide could

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aggravate the oxidation of $SO_2$ to form bulk-like cerium sulfates on the surface of catalyst this process could block the active sites of Ce-O-Ti and cause the decline of $NO_x$ conversion. *Wang* et al. [25] found that the acidic $SO_2$ could easily adsorbed on the isolated $Cu^{2+}$ on Cu/SAPO-34 to form cupric sulfates and resulted in the ability losing of active $Cu^{2+}$on $NO_x$ conversion. For iron-based catalysts, such like natural olivine [26], Mn-Fe spinel [27], Fe-W/Zr [28], the presence of $SO_2$ severely disturbed the $NO_x$ conversion below 300 °C. *Jiang* et al. [29] illustrated that the competitive adsorption between $SO_2$ and NO was the factor of deactivation on the Fe-Mn/$TiO_2$ at 150 °C. *Liu* et al. [30] believed that the combination between $SO_2$ and iron oxide could not only influence the adsorption behavior but also cut the desirable reaction pathway off below 250 °C. Therefore, it is necessary to investigate the sulfated effect over $Fe_2O_3$/CNTs to provide the guidance for its application.

In this work, the impact of $SO_2$ in $NH_3$-SCR process over Fe/CNTs was systematically investigated. The properties of new sulfate species will be confirmed by thermo gravimetric analysis (TGA), X-ray photoelectron spectrometer (XPS) and temperature programed desorption (TPD) tests. Temperature programed surface reaction (TPSR) tests will be carried out to explore the adsorption behavior of reactant and reaction pathway of $NH_3$-SCR with or without $SO_2$ on Fe/CNTs catalyst.

## 2. Experimental

### 2.1. Catalysts preparation

Raw multi-walled carbon nanotubes (Chengdu Organic Chemicals Co., LTD) were first suspended in mixed solution of nitric acid (68 wt. %.) and sulfuric acid (1:1,v/v) and refluxed at 110 °C for 5 h for purification and introduce oxygenated surface groups on the wall of CNTs. Then the CNTs was washed with deionized water till pH 6–7, and dried at 80 °C for 12 h.

Fe/CNTs catalyst was conducted by wet impregnating method [7]. Simply, the pre-treated CNTs was dispersed in ethanol solution with a certain amount of $Fe(NO_3)_3{\cdot}9H_2O$ solution added in, and the mixture was stirred and dried at room temperature. Afterwards, the catalysts were calcined at 350 °C for 3 h, which was denominated as fresh-Fe/CNTs. The catalysts were dominated as $SO_2$-Fe/CNTs (225 °C, 250 °C, 275 °C or 300 °C) after their SCR reaction with $SO_2$ at different temperatures.

### 2.2. Activity test

The SCR activity tests were carried out in a fixed-bed quartz tube reactor (inner diameter = 8 mm). The reactant gases were fed to the reactor by using a mass flow controller, and its condition were as follows: 1000 ppm NO, 1000 ppm $NH_3$, 3 vol.% $O_2$, Ar balance, and 200 ppm $SO_2$ (when used). The total flow rate of the reaction mixture was 300 mL/min, corresponding to GHSV of 30000 $h^{-1}$. The outlet concentration of reaction gas, including NO and $NO_2$, were monitored by a NO-$NO_2$-$NO_x$ analyzer (Thermo Scientific 42i-HL) and the outlet $N_2$ was analyzed by gas chromatograph (GC-7890II). $NO_x$ conversion was calculated based on the following equations:

$$NO_x \text{ conversion} = \frac{c\ NOx(\text{in}) - c\ NOx(\text{out})}{c\ NOx(\text{in})} \times 100\%$$

### 2.3. Reaction kinetics testing

The reaction kinetics of the catalysts in and off $SO_2$ ambient were also measured on a fixed-bed flow reactor. To get the reaction rate and activation energy, reactions were carried out by varying the weight of catalysts ranging from 50 to 150 mg to make sure the $NO_x$ conversion < 15% at different temperatures and small amount of silica granules were used to guarantee the same GHSV as mentioned above. The rate was determined by the equation as followed:

$$\text{Rate} = \frac{F^*x}{W^*S}$$

F is the flow of gaseous molecules (mol/s); W is the weight of the catalysts (g); $x$ is the fractional conversion; S is the surface area ($m^2$/g). Active energy (Ea) of SCR reaction is calculated following Arrhenius equation by which ln R *vs* 1000/T ($K^{-1}$) plot is given to confirm the slope and then is used to calculate the active energy.

### 2.4. Catalysts characterization

BET surface areas of the samples were determined from adsorption-desorption isotherms of $N_2$ at −196 °C on a Quantachrome SI instrument. The morphology features and elementary composition of the catalysts was analyzed by transmission electron microscope (TEM) and an energy dispersive X-ray spectrometer (EDS). Thermo gravimetric analysis (TGA) was performed on SII EXSTRA TG/DTA-6300 under dry $N_2$ flow (100 mL/min) with the heating rate of 10 °C/min from 30 °C to 900 °C to realize the thermal decomposition of the catalysts. X-ray photoelectron spectrometer (PHI-5300) was used for X-ray photoelectron spectroscopy (XPS) measurements with a monochromatic X-ray source of Mg Kα, and the binding energies of Fe 2p, O 1s, S 2p and N 1s were calibrated internally by the carbon deposit C 1s binding energy (BE) at 284.6 eV.

Temperature programed desorption (TPD) and temperature programed surface reaction (TPSR) experiments were both performed on a fixed-bed flow reactor and detected with a computer-interfaced quadruple mass spectrometer (Omnistar, Pfeiffer Vacuum GmbH) to record the signal of $NH_3$ ($m/z$ = 16), $NO_x$ ($m/z$ = 30), $N_2O$ or $CO_2$ ($m/z$ = 44), $N_2$ ($m/z$ = 28), and $SO_2$ ($m/z$ = 64). Before each experiment, 100 mg sample was pretreated in He at 200 °C for 60 min to remove the adsorbed $H_2O$ and other gases. For TPD experiments ($NH_3$-TPD, $NO_x$-TPD), samples were first exposed to the corresponding adsorption gas (1% $NH_3$/He; 1% NO/He and 3 vol.% $O_2$) at room temperature until reaching an adsorption equilibrium. After purging in He for 60 min to remove physically adsorbed gas, desorption process was carried out by the temperature ramped from room temperature to 600 °C at a heating rate of 10 °C/min under He. For series TPSR experiments, subsequent to $NH_3$ or $NO_x$ adsorption and purging steps, He gas was switched to NO/He or $NH_3$/He to detect the reaction pathway on catalysts surface and the heating process still carried out as mentioned above. Without any adsorption process, temperature programed decomposition (TPDC) was also carried out on the fixed-bed flow reactor with 10 °C/min ramp under He and the out gases were also monitored with the mass spectrometer.

## 3. Results and discussion

### 3.1. SCR reaction performance

#### 3.1.1. SCR activity

The SCR activities over the fresh-Fe/CNTs exhibited a good low-temperature SCR activity with over 85% $NO_x$ conversion from 200 °C to 275 °C, which was attributed to the fine dispersion of α-$Fe_2O_3$ and its interaction with CNTs [7]. To investigate the continuous change of SCR performance on fresh-Fe/CNTs at different reaction temperature, $SO_2$ was added into the fixed-bed quartz tube reactor when the SCR reaction gets stable in 60 min. As shown in Fig. 1A, with the addition of $SO_2$, $NO_x$ conversion over fresh-Fe/CNTs displayed a continuous decline by about 55% and 30% at 225 °C and 250 °C, respectively. However it went to the opposite over 275 °C, and a slight enhancement at 275 °C and 25% increment at 300 °C were observed. These results proved the effect caused by the addition of $SO_2$ was related to the reaction temperature, which was also consistent with results obtained in previous studies [31]. After the fluctuation of $NO_x$ conversion with the addition