



## Full Length Article

SO<sub>2</sub> promotion in NH<sub>3</sub>-SCR reaction over V<sub>2</sub>O<sub>5</sub>/SiC catalyst at low temperatureShuli Bai<sup>a,\*</sup>, Zibo Wang<sup>b</sup>, Huanying Li<sup>a</sup>, Xu Xu<sup>b</sup>, Minchao Liu<sup>a</sup><sup>a</sup>School of Chemical and Environment Engineering, Wuyi University, Jiangmen 529020, China<sup>b</sup>School of Environmental Science and Engineering, Yangzhou University, Yangzhou 225127, China

## HIGHLIGHTS

- Silicon carbide supported vanadium catalysts were prepared by pore volume impregnation method.
- SO<sub>2</sub> show a promotion effect on the carbon-based catalyst at low temperature.
- Carbon play an important role on SO<sub>2</sub> promotion effect.

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## ABSTRACT

Silicon carbide (SiC) supported vanadium catalysts were obtained using the wet chemical impregnation method, and their removal of NO<sub>x</sub> with the presence of SO<sub>2</sub> at low temperature was evaluated. The effect of carbon was observed by comparing different carbon-based catalysts. V<sub>2</sub>O<sub>5</sub>/SiC (1 wt.%) catalyst had a NO<sub>x</sub> removal efficiency of 86% in the presence of SO<sub>2</sub> at 250 °C with a GHSV of 180,000 h<sup>-1</sup>. In this study, the temperature-programmed desorption of NH<sub>3</sub> (NH<sub>3</sub>-TPD) and temperature-programmed decomposition (TPDC) of NH<sub>4</sub>HSO<sub>4</sub> deposited on the catalysts and reaction were performed to determine the influence of carbon on the performance of a carbon-based catalyst in the presence of SO<sub>2</sub>. The NO on the carbon support can effectively react with the NH<sub>4</sub>HSO<sub>4</sub> formed on the catalyst surface at low temperatures. Additionally, the adsorption of NH<sub>3</sub> was higher on carbon-based catalysts that were pre-adsorbed with SO<sub>2</sub> + O<sub>2</sub>. Thus, SO<sub>2</sub> promotes the activity of a carbon-based catalyst at low temperatures, and carbon has very important effect on the promotion of that activity.

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## 1. Introduction

Selective catalytic reduction (SCR) of NO<sub>x</sub> with NH<sub>3</sub> is an effective method for removing NO<sub>x</sub> from stationary sources and has a high deNO<sub>x</sub> efficiency [1]. The most widely used catalysts is V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>(MoO<sub>3</sub>)/TiO<sub>2</sub> [2]. However, to avoid generating sulfate from the reaction of SO<sub>2</sub> and NH<sub>3</sub> on the catalyst surface, the required reaction temperature for this catalyst is higher than 350 °C [3]. The SCR reactor is usually located downstream of the particle controller and deSO<sub>x</sub> device, and the temperature of the flue gas is usually lower than 300 °C. As a result, the flue gas must be reheated for deNO<sub>x</sub>, increasing the cost of deNO<sub>x</sub>. A better option would be using a low-temperature, high activity SCR catalyst. In previous studies [4–8], a couple of low-temperature deNO<sub>x</sub> catalysts had high catalytic activity for removing NO<sub>x</sub>, but their

reactions were prone to SO<sub>2</sub> poisoning, making their use impractical. To address this gap, other low-temperature and resistant SO<sub>2</sub> poisoning deNO<sub>x</sub> catalysts are needed. It was recently reported that V<sub>2</sub>O<sub>5</sub>/AC has good catalytic activity for removing NO [9–12], and the catalytic activity and SO<sub>2</sub> promotion effect of the V<sub>2</sub>O<sub>5</sub>/AC catalyst have been extensively studied. The carbon support probably plays an important role in the SO<sub>2</sub> promotion effect. Our group [13,14] also demonstrated that SO<sub>2</sub> promotes the activity of V<sub>2</sub>O<sub>5</sub>/CNTs catalysts when the V<sub>2</sub>O<sub>5</sub> loading weight is below 1 wt.%. Yang et al. verified that the addition of CNTs onto V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalysts improves the oxidation of NO to NO<sub>2</sub>, promoting NO<sub>x</sub> removal [15]. Zhang et al. reported that carbon nanotubes that have been modified with CeO<sub>2</sub> or MnO<sub>x</sub>-CeO<sub>x</sub> can resist to SO<sub>2</sub> poisoning [16,17]. However, it is difficult to assess the nature of SO<sub>2</sub> promotion versus SO<sub>2</sub> poison resistance for all catalyst with carbon-containing elements. It is unclear whether the carbon element in the catalyst influences the efficacy of SO<sub>2</sub>. Thus, it remains challenging to characterize how the carbon element content of a

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catalyst influences the boost from SO<sub>2</sub> as well as the role of carbon in this catalytic process.

Silicon carbide has recently been studied due to its good chemical stability and thermal conductivity [18]. Because of these characteristics, SiC is widely used in catalytic reactions. It has excellent catalytic activity and high selectivity in these reactions [19,20]. Considering the advantages of SiC, the role of carbon in the removal of NO in the presence of SO<sub>2</sub> might be clarified by studies on SiC. In this study, silicon carbon was used for catalyst support, and we investigated the influence of carbon on the SO<sub>2</sub> promotion of NO reduction over V<sub>2</sub>O<sub>5</sub>/SiC catalyst at low temperature. It is helpful to understand the catalytic properties of carbon, which can provide a theoretical basis and technical guidance for the industrial application of carbon-based catalysts.

## 2. Experimental

### 2.1. Catalyst preparation

Raw SiC (Institute of Coal Chemistry, Chinese Academy of Science) samples, carbon nanotube (Chengdu Organic Chemistry Co., Ltd., Chinese Academy of Sciences), and SiO<sub>2</sub> (Shanghai Chemical Reagent Co., Ltd.) were purified using a previously published method [13]. V<sub>2</sub>O<sub>5</sub>/SiC catalysts were obtained by wetness impregnation method of the supports with an aqueous solution of ammonium metavanadate in oxalic acid. The V<sub>2</sub>O<sub>5</sub> precursor used was ammonium metavanadate. The catalysts were dried overnight at 80 °C, and then at 110 °C for 5 h. Then, the catalysts were calcined at 500 °C for 5 h with argon stream, and pre-oxidized at 250 °C for 5 h in air. For comparison, the support of CNTs-SiO<sub>2</sub> was prepared by physical mixture of CNTs and SiO<sub>2</sub> powders and the support of SiO<sub>2</sub>-SiC was obtained by physical mixture of SiO<sub>2</sub> and SiC powders. The details were as follows: 300 mg of CNTs-SiO<sub>2</sub>-50% was obtained by mixing 150 mg of CNTs with 150 mg of SiO<sub>2</sub> powder thoroughly; 300 mg of SiC-SiO<sub>2</sub>-80% was prepared by mixing 240 mg of SiC with 60 mg of SiO<sub>2</sub> powder thoroughly; 300 mg of SiC-SiO<sub>2</sub>-50% was prepared by mixing 150 mg of SiC powder with 150 mg of SiO<sub>2</sub> powder thoroughly; 300 mg of SiC-SiO<sub>2</sub>-20% was obtained by mixing 60 mg of SiC powder with 240 mg of SiO<sub>2</sub> powder thoroughly. The pore size and surface area of the catalysts were presented in Table 1.

### 2.2. Catalyst characterization

The characterizations of the catalysts were analyzed via scanning electron microscopy (SEM HITACHI S-4800) and Powder X-ray diffraction (XRD) patterns of catalyst samples were test on a D8 Advance X-ray diffractometer (Bruker, Germany) operated with a Cu K $\alpha$  radiation (wavelength 1.5406 Å) at 2.2 kW. X-ray photoelectron spectroscopy (XPS) was used on a Kratos Axis Ultra-DLD with Al K $\alpha$  as radiation source and calibrated with the carbon (1s) line at 284.4 eV.

**Table 1**  
BET surface area and pore structure analyses of catalysts.

Catalyst	BET SA (m <sup>2</sup> /g)	Total pore volume (ml/g)	Average pore diameter (Å)
CNTs	229	0.74	12.9
SiC	33.9	0.31	11
SiO <sub>2</sub>	269	0.25	22
CNTs-SiO <sub>2</sub> -50%	245	0.42	14.2
SiC-SiO <sub>2</sub> -80%	86	0.28	11.3
SiC-SiO <sub>2</sub> -50%	146	0.27	13.5
SiC-SiO <sub>2</sub> -20%	198	0.26	16.4

The temperature-programmed desorption of NH<sub>3</sub> (NH<sub>3</sub>-TPD) was test in a fixed-bed quartz reactor. V<sub>2</sub>O<sub>5</sub>/SiC catalyst (1 wt.%) was selected to study the influence of adsorbed SO<sub>2</sub> on NH<sub>3</sub> adsorption by using a previously published method [13].

The temperature-programmed decomposition (TPDC) of NH<sub>4</sub>-HSO<sub>4</sub> deposited on the catalysts and reaction were test in a fixed-bed reactor using a previously published method [13].

### 2.3. Catalytic performance

SCR activity tests were performed in a fixed-bed glass reactor (6 mm inner diameter and 600 mm length). NO in Ar, SO<sub>2</sub> in Ar (when used), pure O<sub>2</sub> and pure Ar, were used to mimic the flue gas, and NH<sub>3</sub> in Ar was used as the reductive gas. All gases were controlled by mass flow controller and test by gas analyzer (ZR-3100TZ) that was equipped with NO, NO<sub>2</sub>, SO<sub>2</sub> and O<sub>2</sub> sensors as well as an analyzer (PGD-100, Austria) equipped with N<sub>2</sub>O. The reaction atmospheres conditions were as follows: 450 ppm NO, 500 ppm NH<sub>3</sub>, 5% O<sub>2</sub>, and 400 ppm SO<sub>2</sub> (when used), 300 mg of catalyst weight. The catalytic performances were tested from 150 to 250 °C, which corresponded to a GHSV of 18,000 h<sup>-1</sup> and flue gas velocity of approximately 1.8 cm/s.

## 3. Results and discussion

### 3.1. Characterization

The XPS measurements of the 15 wt.% V<sub>2</sub>O<sub>5</sub>/SiC catalysts are shown in Fig. 1. The V and O peaks indicate the presence of vanadium species. As shown in Fig. 1(a), there are two main V2p peaks at 517.0 eV and 524.7 eV, which correspond to the V<sup>5+</sup>(2p<sub>3/2</sub>) and V<sup>5+</sup>(2p<sub>1/2</sub>) of V<sub>2</sub>O<sub>5</sub> [21], respectively. The V species of the catalysts were V<sup>5+</sup>. The O 1s peaks are displayed in Fig. 1(b). The O 1s spectrum has a main peak at 530.7 eV, which is attributed to O 1s in V<sub>2</sub>O<sub>5</sub>. Based on the XPS results, the V<sub>2</sub>O<sub>5</sub>/SiC catalysts of vanadium-containing species are V<sub>2</sub>O<sub>5</sub>.

The XRD patterns of SiC and V<sub>2</sub>O<sub>5</sub>/SiC are shown in Fig. 2. The peaks at 2 $\theta$  = 21.95°, 35.68°, 41.45°, 71.82° and 75.93° are the diffraction peaks of SiC [22]. The XRD pattern and intensity of 15 wt.% V<sub>2</sub>O<sub>5</sub>/SiC are similar to those of SiC, and no vanadium species were detected using XRD. The results indicate that vanadium species in 15 wt.% V<sub>2</sub>O<sub>5</sub>/SiC are well dispersed.

Fig. 3 shows the SEM images of the SiC and V<sub>2</sub>O<sub>5</sub>/SiC catalysts. It is seen that the sample mainly consists of irregular particles with size from tens to hundreds nanometers. The SEM images of the V<sub>2</sub>O<sub>5</sub>/SiC catalyst are similar to those for SiC, and V<sub>2</sub>O<sub>5</sub> particles were not observed. This observation suggests that the vanadium species are highly dispersed.

### 3.2. Catalytic activity

#### 3.2.1. SO<sub>2</sub> effect

The SO<sub>2</sub> effect on the V<sub>2</sub>O<sub>5</sub>/SiC catalysts with different vanadium loading levels was investigated at 250 °C (Fig. 4). At the initial state stage, there was no SO<sub>2</sub> in the reaction atmosphere. NO conversion reached 25.5% when only SiC, without loading V<sub>2</sub>O<sub>5</sub>, was used as a catalyst. NO conversion increased with increased V<sub>2</sub>O<sub>5</sub> loading when the loading ranged from 1 wt.% to 15 wt.%. NO conversion reached 87.7% when V<sub>2</sub>O<sub>5</sub> loading was 15 wt.%. However, NO conversion decreased when V<sub>2</sub>O<sub>5</sub> loading continued to increase. The decrease in the catalytic activity might be from aggregation of vanadium particles on the silicon surface. When SO<sub>2</sub> was added into the reaction gas, SO<sub>2</sub> has no visible effect on the activity of the SiC that was not loaded with V<sub>2</sub>O<sub>5</sub>. However, SO<sub>2</sub> demonstrated a significant increase in activity with the

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