# Effect of SO<sub>2</sub> on vanadium-modified Fe/AC catalysts for the NH<sub>3</sub>-SCR of NO<sub>2</sub> at low temperatures

Weiwei Yang, Fudong Liu, Lijuan Xie, Zhihua Lian, Hong He\* Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, 100085, China. \*corresponding author: honghe@rcees.ac.cn

#### Introduction

Nitrogen oxides (NO<sub>x</sub>) from stationary sources contribute greatly to air pollution. Selective catalytic reduction (SCR) of NO<sub>x</sub> with NH<sub>3</sub> has been an effective way to abate NO<sub>x</sub> emissions throughout the world. For power station boilers, a low temperature SCR catalyst with good resistance to SO<sub>2</sub> is needed, because it can avoid re-heating of the flue gas and enable retrofitting the SCR device into existing systems, saving energy and reducing cost. Carbon-based catalysts have received great attention due to their high surface area and ease of modification. A carbon-supported vanadium oxide catalyst was reported to show excellent NH<sub>3</sub>-SCR activity in the presence of SO<sub>2</sub> when the V<sub>2</sub>O<sub>5</sub> loading was less than 5% [1]. However, this V<sub>2</sub>O<sub>5</sub>/AC catalyst is not recommended for practical applications on account of its limited activity at low temperature and bio-toxicity. Iron-based catalysts have been studied widely due to their good NH<sub>3</sub>-SCR activity at medium temperatures [2]. In this study, we report an Fe/AC catalyst modified by a small amount of V<sub>2</sub>O<sub>5</sub> with the aim of developing a catalyst with good activity as well as SO<sub>2</sub> durability at low temperatures. The influence of V<sub>2</sub>O<sub>5</sub> on the SCR activity and SO<sub>2</sub> deactivation is elucidated in detail using results from multiple characterization methods.

### **Materials and Methods**

The activated carbon support was ground to 40-60 mesh and pre-oxidized with HNO<sub>3</sub> before use. Vanadium-modified iron catalysts supported on carbon were prepared by a co-impregnation method. Briefly, the pretreated carbon was impregnated with the required amount of solution containing iron nitrate, ammonium vanadate and oxalic acid. Subsequently, the mixture was evaporated using a rotary evaporator at 60 °C until the excess water was removed, dried at 110 °C overnight and then calcined at 500 °C for 5h. The catalysts are denoted 3% Fe-xV/AC, where *x* represents the mass ratio of V<sub>2</sub>O<sub>5</sub> to AC. Reaction tests were carried out in a fixed-bed quartz tube reactor at a space velocity of 30,000 h<sup>-1</sup>. Detailed characterization was conducted including X-ray diffraction (XRD), Temperature programmed desorption (TPD), Scanning electron microscopy (SEM), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS).

### **Results and Discussion**

The BET surface area and pore structure distribution of catalysts are listed in **Table 1**. The textural loss observed for activated carbon oxidized with HNO<sub>3</sub> is possibly due to the blockage of the entrance of micropores by oxygen functional groups, as well as collapse of the pore structure [3]. After loading with active components, the BET area and micropore volume increased, especially with addition of  $V_2O_5$ . These results indicate that  $V_2O_5$  may contribute to the dispersion of Fe<sub>2</sub>O<sub>3</sub> on the surface of the activated carbon and the XRD results are consistent with this point of view.

Table 1. Surface and pore volume of raw AC, HNO3-oxidized AC and Fe-V/AC catalysts.

Catalyst	BET surface area(m <sup>2</sup> g <sup>-1</sup> )	micropore volume(cm <sup>3</sup> g <sup>-1</sup> )	micropore area(m <sup>2</sup> g <sup>-1</sup> )	mesopore volume(cm <sup>3</sup> g <sup>-1</sup> )
AC(raw)	839	0.370	762	0.103
AC(HNO <sub>3</sub> )	665	0.283	600	0.083
3%Fe	976	0.447	883	0.316
3%Fe-0.3%V	1006	0.443	840	0.161
3%Fe-0.5%V	1004	0.453	942	0.247
3%Fe-0.7%V	1177	0.510	1073	0.302

Figure 1 a) shows the results of NO<sub>x</sub> reduction over AC-supported Fe<sub>2</sub>O<sub>3</sub> with  $V_{2}O_{5}$ addition varying from 0 to 0.7 wt% as a function of temperature. It can be seen that the pristine Fe/AC catalyst without modification by  $V_2O_5$  already possesses good activity. After the addition of  $V_2O_5$  at 0.3 wt% and 0.5 wt%, the activity of catalysts decreases by 5% at low temperature and varies slightly above 200°C. When the content of  $V_2O_3$  is further increased to 0.7 wt%, the catalyst activity decreases more markedly. The results indicate that Fe contributes the dominant active sites, which are covered by vanadium species when the  $V_2O_5$  loading is overly high. Figure 1 b) shows the effect of  $SO_2$  on  $NO_x$  reduction over the vanadiummodified Fe/AC catalysts. All these catalysts demonstrate similar activity without SO<sub>2</sub>, and the activity of all catalysts decreases immediately once SO<sub>2</sub> is introduced. The addition of different amounts of vanadium improves the SO<sub>2</sub> durability of catalysts to different extents. The activity gradually increases in the presence of SO<sub>2</sub> as a function of time with vanadium loading increasing from 0 to 0.5 wt%. However, the SO<sub>2</sub> tolerance is not further enhanced when the vanadium is increased to 0.7 wt%. Overloading of  $V_2O_5$  may result in formation of excessive sulfuric acid, which will be transferred to Fe<sub>2</sub>O<sub>3</sub>, thus sulfurizing the active components and resulting in loss of activity.



**Figure 1**. a) Steady-state  $NO_x$  conversion over Fe-V/AC catalysts as a function of temperature. b) Effect of  $V_2O_5$  addition on the SO<sub>2</sub> tolerance of catalysts.

### Significance

Addition of a small amount of  $V_2O_5$  to  $Fe_2O_3$  loaded on active carbon influenced the NH<sub>3</sub>-SCR activity slightly, yet decreased the SO<sub>2</sub> deactivation to a certain extent. Overloading of  $V_2O_5$  is not beneficial to SCR activity and SO<sub>2</sub> tolerance.

# References

- [1]. Z. P. Zhu, Z. Y. Liu, J Catal 187, 245-248 (1999).
- [2]. F. Liu, H. He, C. Zhang, Chem. Commun. 2043 2045 (2008).
- [3]. A. Boyano, M.E. Galvez, R. Moliner, M.J. Lazaro. Fuel 87, 2058 2068 (2008)