JOURNAL OF ENVIRONMENTAL SCIENCES XX (2017) XXX–XXX

Available online at www.sciencedirect.com

ScienceDirect

www.elsevier.com/locate/jes

JES
JOURNAL OF ENVIRONMENTAL SCIENCES

www.jesc.ac.cn

Alkali resistance promotion of Ce-doped vanadium-titanic-based NH_3-SCR catalysts

Zidi Yan[1,2], *Xiaoyan Shi*[1,2,*], *Yunbo Yu*[1,2,3], *Hong He*[1,2,3]

1. *State Key Joint Laboratory of Environment Simulation and Pollution Control, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China*
2. *University of Chinese Academy of Sciences, Beijing 100049, China*
3. *Center for Excellence in Regional Atmospheric Environment, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen 361021, China*

ARTICLE INFO

Article history:
Received 18 December 2017
Revised 23 January 2018
Accepted 26 January 2018
Available online xxxx

Keywords:
Selective catalytic reduction
Ammonia
Nitrogen oxides
V_2O_5/WO_3-TiO_2
Alkali deactivation

ABSTRACT

The effect of K deactivation on V_2O_5/WO_3-TiO_2 and Ce-doped V_2O_5/WO_3-TiO_2 catalysts in the selective catalytic reduction (SCR) of NO_x by NH_3 was studied. Ce-doped V_2O_5/WO_3-TiO_2 showed significantly higher resistance to K deactivation than V_2O_5/WO_3-TiO_2. Ce-doped V_2O_5/WO_3-TiO_2 with $K/V = 4$ (molar ratio) showed 90% NO_x conversion at 350°C, whereas in this case V_2O_5/WO_3-TiO_2 showed no activity. The fresh and K-poisoned V_2O_5/WO_3-TiO_2 and Ce-doped V_2O_5/WO_3-TiO_2 catalysts were investigated by means of *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), NH_3-temperature progress decomposition (NH_3-TPD), X-ray photoelectron spectroscopy (XPS) and H_2-temperature program reduction (H_2-TPR). The effect of Ce doping on the improving resistance to K of V_2O_5/WO_3-TiO_2were discussed.

Introduction

Selective catalytic reduction (SCR) of nitrogen oxides (NO_x) by NH_3 is one of the most successful technologies for the control of NO_x emission from power plant flue gas and diesel exhaust. The SCR system for coal-fired power plants is commonly in the high-dust (HD) configuration, in which the SCR catalyst is upstream of the electrostatic dust precipitator and processes high dust flue gas with a temperature range of 300–400°C. Vanadium-titanic-based catalysts (*e.g.*, V_2O_5-WO_3/TiO_2), the most widely used SCR catalysts, can provide high performance NO_x reduction in the temperature range 300–400°C (Pârvulescu et al., 1998; Xu et al., 2017; Zhu et al., 2017). However, a major problem in practical application of V_2O_5-WO_3/TiO_2 catalysts has been their strong deactivation by deposition of alkali and alkaline earth metals in fly ash. For example, 1% K_2O-doped V_2O_5-WO_3/TiO_2 gives almost no SCR activity at temperatures from 250 to 400°C (Kamata et al., 1999). The effect of alkali and alkali earth metals on both tungsten-free and tungsten-containing vanadium-titanic-based catalysts has been well studied (Chen et al., 2010; Due-Hansen et al., 2009; Kamata et al., 1999; Klimczak et al., 2010; Lietti et al., 1993; Lisi et al., 2004; Nicosia et al., 2007, 2008; Tang et al., 2010; Wu et al., 2013). The Brønsted acidity of catalysts and the amount of NH_3 adsorbed on the surface can be decreased by alkali metals like K, which cause the decrease of SCR activity (Kamata et al., 1999; Lietti et al., 1993). Nicosia et al. (2008) explained the deactivation of V_2O_5/WO_3-TiO_2 catalysts by alkali and alkali earth metals by a

---

* *Corresponding author. E-mail:* xyshi@rcees.ac.cn (Xiaoyan Shi).

https://doi.org/10.1016/j.jes.2018.01.024

Please cite this article as: Yan, Z., et al., Alkali resistance promotion of Ce-doped vanadium-titanic-based NH_3-SCR catalysts, J. Environ. Sci. (2017), https://doi.org/10.1016/j.jes.2018.01.024

mechanism whereby the poisoning element (Ca, K) occupies the non-atomic hole sites of the (010) V_2O_5 surface, such that both Brønsted acid and $V^{5+} = O$ sites are blocked.

Besides the effect on surface acidity, the reducibility of V_2O_5/TiO_2 catalysts could be another reason for the poisoning effect of Na^+ and Ca^{2+} (Tang et al., 2010). Yu et al. (2013) found that the isolated vanadia species over the $V_2O_5–WO_3/TiO_2$ catalyst were more reactive with potassium than polymeric vanadia spices. Chen et al. (2010) proposed that decreases in NH_3 adsorption, surface chemisorbed oxygen and reducibility of surface vanadium species could be the main factors in the poisoning effect of alkali metal.

In our previous study, cerium–titanium (Ce/TiO_2, $CeTiO_x$, $CeWTiO_x$) catalysts were developed and showed high activity for NH_3-SCR (Shan et al., 2011, 2012; Xu et al., 2008). Chen et al. (2009) and Peng et al. (2012) reported that substitution part of W by Ce in V_2O_5/WO_3-TiO_2 (0.1 or 0.4 wt.% of V_2O_5) can promote SCR activity in the temperature range 200–450°C and enhance the catalyst's alkali poisoning resistance. Xu et al. (2015) studied the addition of Ce and Sb to the V_2O_5/TiO_2 (5 wt.% of V) can improve the low temperature activity for NH_3-SCR of NO_x. Here, the promotional effect of Ce-doping on the alkali metal resistance of the V_2O_5/WO_3-TiO_2 catalyst was investigated. The effect of K-poisoning on V_2O_5/WO_3-TiO_2 and Ce-doped V_2O_5/WO_3-TiO_2 were studied by means of activity measurements, X-ray photoelectron spectroscopy (XPS), NH_3-temperature progress decomposition (NH_3-TPD), *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), and H_2-temperature program reduction (H_2-TPR).

1. Experimental

1.1. Catalyst preparation

The catalysts were prepared by a wet impregnation method. TiO_2 powder containing 5 wt.% WO_3 was used in this work. Ammonium metavanadate was dissolved in an oxalic acid solution. The TiO_2 powder was impregnated in the mixed solution by stirring for 1 hr. After rotary evaporation, the sample was dried at 110°C overnight and then calcined at 500°C in air for 3 hr. V_2O_5/WO_3-TiO_2 catalysts with 1 wt.% V_2O_5 were prepared and denoted as VWTi. Ce-doped V_2O_3/WO_3-TiO_2 catalysts with 6 wt.% Ce were prepared by adding a cerium nitrate solution into the solution of ammonium metavanadate and oxalic acid, and followed by a process similar to the preparation of V_2O_5/WO_3-TiO_2 catalysts. Ce-doped V_2O_3/WO_3-TiO_2 catalysts were denoted as Ce-VWTi. The K-containing samples were prepared by impregnating the dry powder with KNO_3 solution for 8 hr, then dried in air at 100°C overnight and calcined at 500°C for 3 hr. The Ca and Mg poising samples were prepared by the same procedures according to the molar ratio of Ca/V = Mg/V = 4. All catalysts were ground and sieved to 40–60 mesh for activity testing.

1.2. Catalytic activity measurements

The reaction conditions were controlled as follows: 500 ppm NO, 500 ppm NH_3, 5 vol.% O_2, N_2 balance; 150 mg catalyst, total flow rate of 500 mL/min and gas hourly space velocity (GHSV) = 100,000 hr^{-1}. The effluent gas was analyzed using an FTIR spectrometer (Nexus 670, Nicolet, USA) equipped with a heated, low volume multiple-path gas cell (2 m), which can continuously analyze the NO, NO_2, N_2O and NH_3 in the effluent gas. The spectra were collected when the SCR reaction reached a steady state. NO_x conversion was calculated as follows (Liu et al., 2009):

$$NO_x \text{ conversion} = \left(1 - \frac{[NO]_{out} + [NO_2]_{out}}{[NO]_{in}}\right) \times 100\% \quad (1)$$

1.3. Catalyst characterization

The *in situ* DRIFTS experiments were performed on an Fourier Transform infrared spectroscopy (FTIR) spectrometer (Nexus 670, Nicolet, USA) equipped with an mercury cadmium telluride (MCT) detector cooled by liquid nitrogen and an *in situ* DRIFTS reactor cell with ZnSe window connected to a purging/adsorption gas control system, collecting 100 scans at spectral resolution of 4 cm^{-1}. The reaction temperature was controlled precisely by an Omega programmable temperature controller. Each sample was pretreated at 350°C in a flow of 20 vol.% O_2/N_2 for 1 hr, and cooled down to 50°C in N_2. The sample was saturated at 50°C with 0.5% NH_3 in N_2 for about 30 min, and purging with N_2 at 50°C for 1 hr, then heating up to 150°C. The spectra were recorded at 150°C.

Ammonia temperature-programmed desorption (NH_3-TPD) experiments were used to determine the NH_3 storage capacity of SCR catalysts. The test sample (100 mg) was pretreated at 400°C for 30 min by 20 vol.% O_2/N_2, and then cooled down to 150°C. NH_3 was introduced until the adsorption on the sample was saturated. The sample was then sufficiently purged with N_2 to remove excess absorbate from the surface of the sample. The TPD was conducted by heating the sample in N_2 from 150 to 500°C at a rate of 10°C/min and the NH_3 in the outlet gas was analyzed by an online NEXUS 670-FTIR (Nexus 670, Nicolet, USA) spectrometer.

The catalysts were analyzed using X-ray photoelectron spectroscopy (XPS) to identify the surface nature. The XPS data were taken on using Al Ka radiation (AXIS Ultra, Kratos, Japan). The binding energy was corrected using the energy of adventitious carbon (284.7 eV).

H_2-TPR experiments were performed in a flow of 10% H_2/Ar mixture (50 cm^3/min) over 50 mg of catalyst using a heating rate of 10°C/min. The consumption of H_2 was detected by thermal conductivity detector (TCD) (AutoChem II 2920, Micromeritics, USA).

2. Results and discussion

2.1. SCR activity evaluation

Commonly, the operating temperature window of vanadium based catalysts for reducing NO_x from stationary sources is between 300 and 400°C. To investigate the effect of K doping on the VWTi and Ce-VWTi catalysts, the NH_3-SCR activity of fresh and K-doped catalysts was tested. Fig. 1a–b shows the NH_3-SCR activity and of VWTi and Ce-VWTi catalysts with different K loadings at the temperature range from 275 to 450°C under a fixed GHSV of 100,000 hr^{-1}. As can be seen in

Please cite this article as: Yan, Z., et al., Alkali resistance promotion of Ce-doped vanadium-titanic-based NH_3-SCR catalysts, J. Environ. Sci. (2017), https://doi.org/10.1016/j.jes.2018.01.024