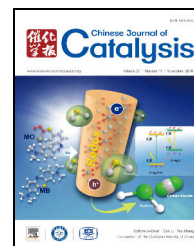


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## Article

# Promotional roles of ZrO<sub>2</sub> and WO<sub>3</sub> in V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub>-ZrO<sub>2</sub> catalysts for NO<sub>x</sub> reduction by NH<sub>3</sub>: Catalytic performance, morphology, and reaction mechanism

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## ABSTRACT

V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub>-ZrO<sub>2</sub> catalysts containing various amounts of WO<sub>3</sub> were synthesized. The catalyst morphologies, catalytic performances, and reaction mechanisms in the selective catalytic reduction of NO<sub>x</sub> by NH<sub>3</sub> were investigated using in situ diffuse-reflectance infrared Fourier-transform spectroscopy, temperature-programmed reduction (TPR), X-ray diffraction, and the Brunauer-Emmett-Teller (BET) method. The BET surface area of the triple oxides increased with increasing ZrO<sub>2</sub> doping but gradually decreased with increasing WO<sub>3</sub> loading. Addition of sufficient WO<sub>3</sub> helped to stabilize the pore structure and the combination of WO<sub>3</sub> and ZrO<sub>2</sub> improved dispersion of all the metal oxides. The mechanisms of reactions using V<sub>2</sub>O<sub>5</sub>-9%WO<sub>3</sub>/TiO<sub>2</sub>-ZrO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub>-9%WO<sub>3</sub>/TiO<sub>2</sub> were compared by using either a single or mixed gas feed and various pretreatments. The results suggest that both reactions followed the Eley-Rideal mechanism; however, the dominant acid sites, which depended on the addition of WO<sub>3</sub> or ZrO<sub>2</sub>, determined the pathways for NO<sub>x</sub> reduction, and involved [NH<sub>4</sub><sup>+</sup>-NO-Brønsted acid site]<sup>+</sup> and [NH<sub>2</sub>-NO-Lewis acid site]<sup>+</sup> intermediates, respectively. NH<sub>3</sub>-TPR and H<sub>2</sub>-TPR showed that the metal oxides in the catalysts were not reduced by NH<sub>3</sub> and O<sub>2</sub> did not reoxidize the catalyst surfaces but participated in the formation of H<sub>2</sub>O and NO<sub>2</sub>.

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## 1. Introduction

The conventional technique for the control of NO<sub>x</sub> emissions is selective catalytic reduction (SCR) of NO<sub>x</sub> by NH<sub>3</sub> [1] using various commercial catalysts containing V<sub>2</sub>O<sub>5</sub>, WO<sub>3</sub>, and TiO<sub>2</sub>. However, the use of such commercial catalysts is limited because of their low activities (300–400 °C, 85%) [2]. Cheap transition-metal-doped catalysts with exceptional catalytic performances are now widely used in several industrial processes [3]. Previous studies have shown that TiO<sub>2</sub>-ZrO<sub>2</sub> supports have

higher thermal stabilities and amounts of acid sites than do pure TiO<sub>2</sub> and ZrO<sub>2</sub> [4]. In this study, we investigated and compared the NH<sub>3</sub>-SCR mechanisms (above 300 °C) over V<sub>2</sub>O<sub>5</sub>-x%WO<sub>3</sub>/TiO<sub>2</sub>-ZrO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub>/9%WO<sub>3</sub>-TiO<sub>2</sub> catalysts.

Although the NH<sub>3</sub>-SCR mechanism has been widely studied, it is still the subject of much debate. This is because (1) different catalysts have been used, resulting in different active sites and (2) different temperatures have been used in NH<sub>3</sub>-SCR reactions over different catalysts. Recently, the reactions NH<sub>3(ads)</sub> → NO<sub>(g)</sub> + O<sub>2(g)</sub> and NO<sub>(ads)</sub> + O<sub>2(ads)</sub> → NH<sub>3(g)</sub> over dif-

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ferent catalysts at different temperatures have been studied and possible reaction pathways have been proposed [5–8]. However, the adsorption behaviors of  $\text{NH}_3$  and  $\text{NO}$  at different temperatures were not clear, e.g., whether and how  $\text{NH}_{3(\text{g})}$ ,  $\text{NO}_{(\text{g})}$ , and  $\text{NO}_{(\text{g})} + \text{O}_{2(\text{g})}$  are adsorbed on the catalyst surface above 300 °C. The differences among the adsorption intensities of these gases are also unclear. Most previous theories have indicated that the reaction involves sequential H abstraction (or oxidation) of  $\text{NH}_3$  species to give the coordinated form of  $\text{NH}_3$  or the protonated form, i.e.,  $\text{NH}_4^+$ , followed by partial oxidation by metal oxides ( $\text{V}_2\text{O}_5$ ,  $\text{WO}_3$ , and  $\text{TiO}_2$ ) [5–8]. The catalyst surface could therefore be reduced by  $\text{NH}_3$  or  $\text{NH}_4^+$ . However, temperature-programmed reduction by  $\text{NH}_3$  ( $\text{NH}_3$ -TPR) of the catalysts has not been investigated, and the proposed catalyst surface reduction by  $\text{NH}_3$  is controversial. All these points have important implications for the  $\text{NH}_3$ -SCR mechanism, and intensive research to clarify these issues is needed.

In this study,  $\text{V}_2\text{O}_5$ - $\text{WO}_3/\text{TiO}_2$ - $\text{ZrO}_2$  catalysts with various  $\text{WO}_3$  loadings were synthesized and used in  $\text{NH}_3$ -SCR. The effects of the amounts of  $\text{WO}_3$  and  $\text{ZrO}_2$  on the catalytic performances and reaction mechanisms over  $\text{V}_2\text{O}_5$ - $\text{WO}_3/\text{TiO}_2$ - $\text{ZrO}_2$  were investigated using the Brunauer-Emmett-Teller (BET) method, X-ray diffraction (XRD), TPR, and in situ diffuse-reflectance infrared Fourier-transform spectroscopy (DRIFTS).

## 2. Experimental

### 2.1. Catalyst preparation

The  $\text{V}_2\text{O}_5$ - $x\%\text{WO}_3/\text{TiO}_2$ - $\text{ZrO}_2$  catalysts were prepared by impregnation of a  $\text{TiO}_2$ - $\text{ZrO}_2$  solid solution with ammonium tungstate hydrate and ammonium vanadate.

A  $\text{TiO}_2$ - $\text{ZrO}_2$  solid solution (Ti:Zr molar ratio 1:1) was prepared using a precipitation method.  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  and  $\text{TiCl}_4$  (Sinopharm Chemical Reagent) were used as precursors. Ammonia water (25%–28%) was added dropwise to the metal precursor solution at 25 °C until the pH was between 9 and 10. The obtained milky slurry was aged in the solution at 25 °C for 24 h. The hydroxide was filtered off, washed with deionized water, and dried at 110 °C for 12 h. The samples were calcined at 450 °C in air for 3 h before milling and screening to 60 mesh.

An incipient wetness impregnation method was used to synthesize  $x\%\text{WO}_3/\text{TiO}_2$ - $\text{ZrO}_2$  ( $x = 0, 6, 9, 12$ , weight ratio).  $(\text{NH}_4)_{10}\text{W}_{12}\text{O}_{41} \cdot x\text{H}_2\text{O}$  (Sinopharm Chemical Reagent) was added to the  $\text{TiO}_2$ - $\text{ZrO}_2$  carrier and the mixture was stirred at 35 °C for 2 h. The residue obtained by evaporation at 80 °C was dried at 110 °C for 12 h. The samples were calcined at 450 °C in air for 3 h, and milled and screened to 60 mesh. The same procedure was used to synthesize  $9\%\text{WO}_3/\text{TiO}_2$  with anatase  $\text{TiO}_2$  as the carrier.

A wet impregnation method was used to synthesize  $1\%\text{V}_2\text{O}_5$ - $x\%\text{WO}_3/\text{TiO}_2$ - $\text{ZrO}_2$  and  $1\%\text{V}_2\text{O}_5$ - $9\%\text{WO}_3/\text{TiO}_2$  as follows.  $\text{NH}_4\text{VO}_3$  (Sinopharm Chemical Reagents) was added to  $x\%\text{WO}_3/\text{TiO}_2$ - $\text{ZrO}_2$  powder and  $9\%\text{WO}_3/\text{TiO}_2$  powder; the rest of the process was the same as that used to prepare  $x\%\text{WO}_3/\text{TiO}_2$ - $\text{ZrO}_2$ .

We denote  $1\%\text{V}_2\text{O}_5$ - $x\%\text{WO}_3/\text{TiO}_2$ - $\text{ZrO}_2$  by  $x\%\text{WO}_3$ , where  $x$  represents the amount of  $\text{WO}_3$  in the catalyst.

### 2.2. Catalyst characterization

XRD patterns of the catalysts were obtained using an XD-3 diffractometer (Beijing PEPSEE, China) with  $\text{Cu } K_\alpha$  radiation ( $\lambda = 0.15406 \text{ nm}$ ). The specific surface areas of the catalysts were measured based on  $\text{N}_2$  adsorption-desorption at liquid  $\text{N}_2$  temperature (−196 °C) using a Micromeritics F-sorb 3400 adsorption apparatus (Beijing Jinaipu, China).  $\text{NH}_3$ -TPR was performed in a quartz U-tube reactor connected to a thermal conductivity detector, using an  $\text{NH}_3$ -He mixture (0.503 vol%  $\text{NH}_3$ ) as a probe. TPR was performed from 25 to 700 °C at a rate of 10 °C/min.

In situ (DRIFTS) was performed using a Nicolet 6700 FT-IR instrument (Thermo Electron Corporation, USA) with a Harrick accessory (HTC-3, Harrick Scientific Corporation, USA) in the wavenumber range 400–4000  $\text{cm}^{-1}$  at a 4  $\text{cm}^{-1}$  resolution.  $\text{NH}_3$ -adsorbed in situ DRIFTS was performed as follows. (1) A thin, intact, self-supporting wafer of the catalyst (10 mg) was prepared and mounted inside a high-temperature cell (HTC-3, Harrick Scientific Corporation, USA) and subjected to a high-purity  $\text{N}_2$  stream at 400 °C for 1 h. (2) After cooling to room temperature, the wafer was exposed to an  $\text{NH}_3$  (99.999%) stream at a flow rate of 5 mL/min for 30 min. (3) The wafer was flushed with a high-purity  $\text{N}_2$  stream for 30 min. (4) IR spectra were recorded at various target temperatures in a high-purity  $\text{N}_2$  stream; the temperature was increased at a rate of 10 °C/min.

### 2.3. Catalyst activity test

The catalytic activity was investigated in a fixed-bed stainless-steel reactor (i.d. 6 mm) at 200–450 °C, using 300 mg of catalyst. A gas mixture of 0.08%  $\text{NO}$ , 0.08%  $\text{NH}_3$ , and 5%  $\text{O}_2$  (by volume) was fed into the reactor and  $\text{N}_2$  was used to give a total flow rate of 100 mL/min (gas hourly space velocity (GHSV) = 20000  $\text{h}^{-1}$ ). The  $\text{NO}$  and  $\text{NO}_2$  concentrations were continually monitored using a flue gas analyzer (Testo 350-XL).

## 3. Results and discussion

### 3.1. Specific surface area and pore size

The specific surface areas and pore size distributions of the catalysts are shown in Table 1 and Fig. 1. The pore size distributions clearly show that the amounts of pores of sizes 384.2–8.3 nm and 3.1–1.7 nm were unchanged by  $\text{WO}_3$  addition, but the amounts of pores of size 8.3–3.9 nm increased greatly. This indicates that  $\text{WO}_3$  addition enhanced the thermal stability of the pore structure, especially of pores of size 8.3–3.9 nm. The BET surface areas ( $S_{\text{BET}}$ ) decreased with increasing  $\text{WO}_3$  loading. The XRD patterns (Fig. 2) show that no crystalline tungsten oxide was present on the catalyst surfaces. This suggests that amorphous  $\text{WO}_3$  was dispersed on the surface of the  $\text{TiO}_2$ - $\text{ZrO}_2$  support and occupied the pores, decreasing the sur-

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