

## Influence of ceria modification on the properties of TiO<sub>2</sub>-SnO<sub>2</sub> supporting V<sub>2</sub>O<sub>5</sub> catalysts for selective catalytic reduction of NO by NH<sub>3</sub>

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A series of V<sub>2</sub>O<sub>5</sub>-CeO<sub>2</sub>/TiO<sub>2</sub>-SnO<sub>2</sub> catalysts were prepared with different CeO<sub>2</sub> content to investigate the effect of Ce modification for selective catalytic reduction of NO by NH<sub>3</sub>. The obtained samples were characterized by BET, XRD, HRTEM, H<sub>2</sub>-TPR and FT-IR. The catalytic test was also investigated on a fixed bed reactor under the condition of simulated composition of flue gas. The results revealed that the V<sub>2</sub>O<sub>5</sub>-CeO<sub>2</sub>/TiO<sub>2</sub>-SnO<sub>2</sub> catalyst with 10% CeO<sub>2</sub> content (i.e. the molar ratio of Ce to Ti) showed the highest catalytic activity within the wide temperature range of 290°C to 430°C, even higher than V<sub>2</sub>O<sub>5</sub>-10wt. %WO<sub>3</sub>/TiO<sub>2</sub>-SnO<sub>2</sub>. Larger BET specific surface area and average pore volume, better dispersion of CeO<sub>2</sub> on support and lower degree of crystallinity would enhance the performance of selective catalytic reduction. Furthermore, Ce modifier could strengthen redox properties of catalysts, which was beneficial for decreasing reduction temperature. Finally, FT-IR demonstrated that significant amounts of Lewis and Brønsted acidity also contributed to the catalytic reaction process.

*Keywords:* Ceria; V<sub>2</sub>O<sub>5</sub>; TiO<sub>2</sub>-SnO<sub>2</sub>; Selective Catalytic Reduction.

### 1. Introduction

Nitrogen oxides (NO<sub>x</sub>) is one of the main cause to produce atmospheric pollution such as acid rains, photochemical smog, stratospheric ozone depletion and greenhouse effect. Selective catalytic reduction (SCR) is widely used worldwide among the flue gas treatment methods for its high efficiency, selectivity and economy. V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub>-MoO<sub>3</sub>/TiO<sub>2</sub> are extensively used as commercial catalysts for SCR of NO with NH<sub>3</sub> currently. Yet, the TiO<sub>2</sub> support is limited by its low catalytic activity within a low temperature range, easily to be influenced by other components in flue gas, low resistance to sintering and crystal transformation forming rutile TiO<sub>2</sub> at high temperature [1].

Supports consisted of mixed oxides has drew people's attention. In recent years, researches of  $\text{TiO}_2\text{-SnO}_2$  supporting metallic oxides catalysts develop fast. Chien-Tsung Wang et al [2] demonstrated that the bridging dopant-O-Sn bond in  $\text{TiO}_2\text{-SnO}_2$  support acted as active sites and influences product distribution. The advance of  $\text{TiO}_2\text{-SnO}_2$  solid solution were also proved by other researchers. As Kairong Li [3] pointed out,  $\text{CuO/TiO}_2\text{-SnO}_2$  showed higher catalytic activity than  $\text{CuO/TiO}_2$  and  $\text{CuO/SnO}_2$  samples, due to a large amount of active site formed by CuO on the  $\text{TiO}_2\text{-SnO}_2$  support.

$\text{CeO}_2$  is one of the promising oxides industrially because oxygen vacancy defects can be rapidly formed and eliminated, giving it a high "oxygen storage capacity"[4]. Many researchers reported that with the modification of Ce, catalysts showed high activity and selectivity for reduction of NO with  $\text{NH}_3$  because of its acidic and redox properties [5]. In addition,  $\text{CeO}_2$  exhibited outstanding water and  $\text{SO}_2$  resistant performance. Xu et al [6] claimed that  $\text{Ce/TiO}_2$  still had high De-NOx efficiency in the water presence and remained 85% De-NOx efficiency by the combined aucton of water and  $\text{SO}_2$ . Therefore, the investigation of a combined catalyst consisting of  $\text{V}_2\text{O}_5$  and  $\text{CeO}_2$  over the  $\text{TiO}_2\text{-SnO}_2$  support is significant.

In the present work, ceria was introduced to the  $\text{V}_2\text{O}_5/\text{TiO}_2\text{-SnO}_2$  catalysts and series of  $\text{V}_2\text{O}_5\text{-CeO}_2/\text{TiO}_2\text{-SnO}_2$  catalysts were prepared by the impregnation method with different  $\text{CeO}_2$  content. The catalytic performance of these catalysts was investigated on a fixed bed reactor under the condition of simulated composition of flue gas for  $\text{NH}_3\text{-SCR}$ . Multiple characterization techniques of BET, XRD,  $\text{H}_2\text{-TPR}$  and FT-IR were employed to study the micro-scale constructions, dispersion of surface species and the correlation between catalytic activity and surface state.

## 2. Experimental

### 2.1. Catalyst preparation

The  $\text{TiO}_2\text{-SnO}_2$  (1:1 mole ratio) mixed oxide was prepared by a co-precipitation method from  $\text{TiCl}_4$  and  $\text{SnCl}_4$  aqueous solutions. Ammonium hydroxide was dropped slowly to the mixture on the condition of ice-water bath and then the obtained solution was kept in stirring for 30 minutes until  $\text{pH}=9.0$ . The mixture kept overnight was filtered and washed by deionized water until no  $\text{Cl}^-$  was detected. The precipitate was dried at  $110^\circ\text{C}$  for 12h and finally calcined in a muffle stove at  $450^\circ\text{C}$  under continuous airflow ( $150\text{ml}\cdot\text{min}^{-1}$ ) for 4h.

$\text{V}_2\text{O}_5\text{-CeO}_2/\text{TiO}_2\text{-SnO}_2$  catalyst with the 10%, 20%, 30% loading of  $\text{CeO}_2$  (i.e. the molar ratio of Ce to Ti) and 1wt. %  $\text{V}_2\text{O}_5$  was prepared by impregnating  $\text{TiO}_2\text{-SnO}_2$  support with an aqueous solution containing the required amount of

Ce (NO<sub>3</sub>)<sub>3</sub>•6H<sub>2</sub>O and NH<sub>4</sub>VO<sub>3</sub> (A•R) step by step. Then the mixture was kept stirring at 20 °C for 2h. Continuing stirring lasted at 85 °C until it was close to dry. The precipitate was dried at 110 °C for 12h and finally calcined in a muffle stove at 450 °C under continuous airflow (150ml·min<sup>-1</sup>) for 4h.

V<sub>2</sub>O<sub>5</sub>-10wt. % WO<sub>3</sub>/TiO<sub>2</sub>-SnO<sub>2</sub> was prepared by the impregnation method as well. For short, TiO<sub>2</sub>-SnO<sub>2</sub> support was denoted as Ti-Sn, V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub>-SnO<sub>2</sub> as V/Ti-Sn, V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub>-SnO<sub>2</sub> as V-W/Ti-Sn, V<sub>2</sub>O<sub>5</sub>-CeO<sub>2</sub>/TiO<sub>2</sub>-SnO<sub>2</sub> catalyst with 10 % (20%, 30%) CeO<sub>2</sub> content (i.e. the molar ratio of Ce to Ti) as V-0.1(0.2,0.3) Ce/Ti-Sn.

## **2.2. Catalysts characterization**

X-ray diffraction (XRD) patterns were obtained with Beijing PEPSEE XD-3 diffraction meter using nickel-filtered Cu K $\alpha$  (0.15406nm) radiation source and a scintillation counter detector. The BET surface area and BJH pore size distribution were measured by nitrogen adsorption at 77 K using F-Sorb 3400 (Beijing Jin Aipu) instrument. High resolution transmission electron microscope (HRTEM) was measured with a JEM-2100 (JEOL, Japan). H<sub>2</sub>-Temperature-programmed reduction (H<sub>2</sub>-TPR) was carried out in a quartz U-tube reactor connected to a TCD with H<sub>2</sub>-Ar mixture as reductant. A Nicolet 5700 FT-IR instrument (Thermo Electron Corporation, USA) was employed to record the in situ FT-IR spectra.

## **2.3. Catalytic activity tests**

The catalytic activity for the SCR of NO by NH<sub>3</sub> was measured in a fixed bed, stainless steel reactor with 7mm inside diameter at atmospheric pressure. 300 mg of the catalysts (20–40 mesh) was used. The reaction temperature was measured by a type K thermocouple inserted directly into the catalyst bed. The inlet gas typically consisted of 800 ppm NO, 800 ppm NH<sub>3</sub>, 5% O<sub>2</sub> and balance N<sub>2</sub>. The total flow rate was set 100 ml/min, and hence the gas hourly space velocity (GHSV) equaled 24000 h<sup>-1</sup>. The reactants were all sent out from gas cylinder and pre-mixed in a gas mixer, and then the mixed gas was sent to the reactor. The tubing of the reactor system was heat traced to prevent formation and deposition of ammonium sulfate/bisulfate and ammonium nitrate. The NO and NO<sub>2</sub> concentrations were continually monitored by a gas analyzer (Testo 330-2 LL).

### 3. Results and Discussion

#### 3.1. Activity tests

##### 3.1.1. Influence of ceria loading to SCR activity

From Figure 1, we could see that in the temperature range of 200 ~ 290°C, the activity increased with the incremental cerium oxide concentration, indicating that cerium oxide could promote the De-NO<sub>x</sub> activity at lower temperature. The De-NO<sub>x</sub> efficiency of V-0.1Ce/Ti-Sn reached nearly to 100% in the temperature range of 300 ~ 400°C. Cerium oxide made a relatively obvious modification on V/ Ti-Sn. In the temperature range of 290 ~ 430°C, V-0.1Ce/Ti-Sn and V-0.2Ce/Ti-Sn had higher De-NO<sub>x</sub> efficiency than V/ Ti-Sn. As shown in Figure 2, we concluded that cerium oxide made a much higher modification than WO<sub>3</sub> on V/ Ti-Sn.

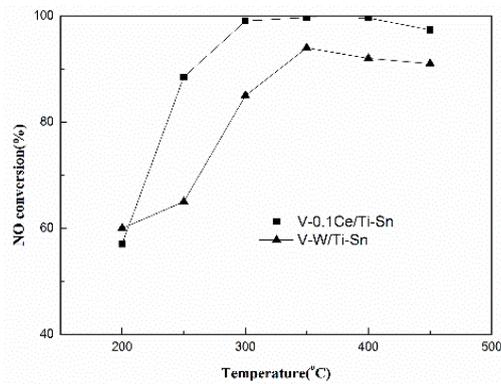


Fig. 1. The NO conversion for different catalysts.

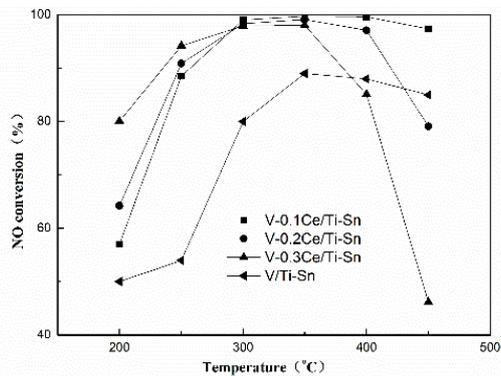


Fig. 2. Comparison of V-Ce/Ti-Sn with V-W/Ti-Sn in De-NO<sub>x</sub> efficiency.

### 3.1.2. Effect of SO<sub>2</sub> on SCR activity over V-0.1Ce/Ti-Sn and V/Ti-Sn

As shown in Figure 3, the De-NO<sub>x</sub> efficiency of V-0.1Ce/Ti-Sn and V/Ti-Sn both decreased immediately after introducing SO<sub>2</sub>. But the lowest efficiency of V-0.1Ce/Ti-Sn was more than 75%, while that of V/Ti-Sn declined to nearly 60%. It came to the normal or even higher degree after stopping adding SO<sub>2</sub>, which was consistent with Wu's research [7]. He argued that the formation of Ti(SO<sub>4</sub>)<sub>2</sub> and Mn(SO<sub>4</sub>)<sub>x</sub> was prevented and the depositions of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and NH<sub>4</sub>HSO<sub>4</sub> were inhibited with the doping of ceria.

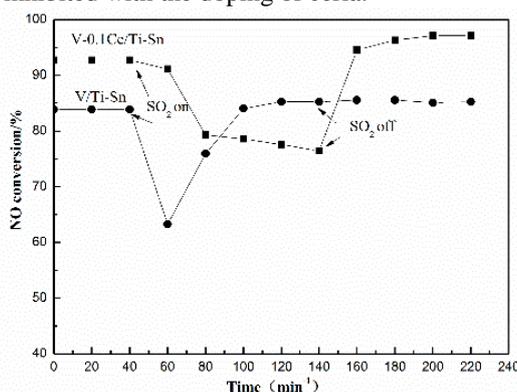


Fig. 3. The NO conversion after adding SO<sub>2</sub>.

Based on the results above, we could conclude that the competitive adsorption between SO<sub>2</sub> and NO and the deposition of ammonium sulphate might be the main cause of the decrease of the catalytic activity. V-0.1Ce/Ti-Sn manifested good resistant of SO<sub>2</sub> due to the adding of Ce and the positive effect of Ti-Sn support.

## 3.2. Catalysts characterization

### 3.2.1. Structural characterization (XRD spectroscopy and BET)

The powder XRD profiles of different samples are presented in Figure 4. The significant peak at  $2\theta = 28.4^\circ$  could not be noted when the catalyst was with 10% or 20% CeO<sub>2</sub> content, while it began to be clear in V-0.3Ce/Ti-Sn. The results showed that CeO<sub>2</sub> was in an X-ray amorphous form and highly dispersed on the surface of the Ti-Sn support since the loading of CeO<sub>2</sub> was low. Better dispersion and lower crystallinity of CeO<sub>2</sub> on the support was beneficial to the SCR reaction, which corresponded with the SCR performance results we obtained above. Meanwhile, characteristic peaks due to crystalline TiO<sub>2</sub> and binary compounds such as Ti<sub>6</sub>Sn<sub>5</sub> were weakened with the increase of cerium oxide, indicating that the introduction of cerium oxide reduced the crystallinity

of the support and there was a strong interaction among Ce, Ti and Sn. No independent diffraction lines due to crystalline  $V_2O_5$  were observed for all samples, suggesting that  $V_2O_5$  was in an X-ray amorphous form.

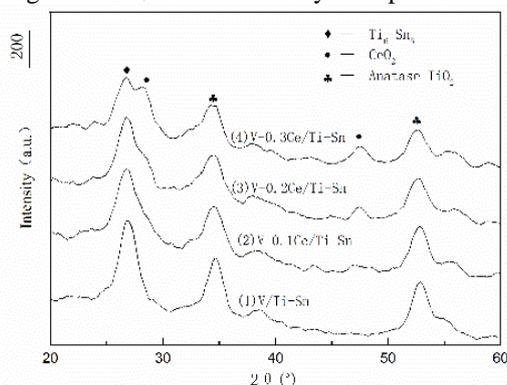


Fig. 4. X-ray powder diffractions of different catalysts.

Table 1 showed that with the increase of cerium oxide loading, BET surface area and the pore volume decreased on the whole. In addition, BET surface area and the pore volume of V-0.1Ce/Ti-Sn was larger than V-W/Ti-Sn, which explained the higher catalytic activity of V-0.1Ce/Ti-Sn compared with V-W / Ti-Sn from the micro-structure respect.

Table 1. BET surface area and pore volume of samples

Sample	$S_{BET}(m^2/g)$	$V_p (cm^3/g)$
TiO <sub>2</sub> -SnO <sub>2</sub>	74.13	0.20
V <sub>2</sub> O <sub>5</sub> /TiO <sub>2</sub> -SnO <sub>2</sub>	73.29	0.17
V <sub>2</sub> O <sub>5</sub> -0.1 CeO <sub>2</sub> /TiO <sub>2</sub> -SnO <sub>2</sub>	67.81	0.17
V <sub>2</sub> O <sub>5</sub> -0.2 CeO <sub>2</sub> /TiO <sub>2</sub> -SnO <sub>2</sub>	50.94	0.15
V <sub>2</sub> O <sub>5</sub> -0.3 CeO <sub>2</sub> /TiO <sub>2</sub> -SnO <sub>2</sub>	62.69	0.17
V <sub>2</sub> O <sub>5</sub> -WO <sub>3</sub> /TiO <sub>2</sub> -SnO <sub>2</sub>	57.48	0.14

$S_{BET}$ : BET surface area;

$V_p$ : porous volume;

### 3.2.2. Reducible properties of the catalysts

Figure 5 showed the TPR profiles of a series of Ce/Ti-Sn. A strong peak at around 585°C and a relatively weak one at about 250°C could be seen in cerium-contained samples, while there was no reduction peak in Ti-Sn support. The reduction temperature decreased with the synergy of Ti-Sn support, thus the reduction ability of the catalyst strengthened.

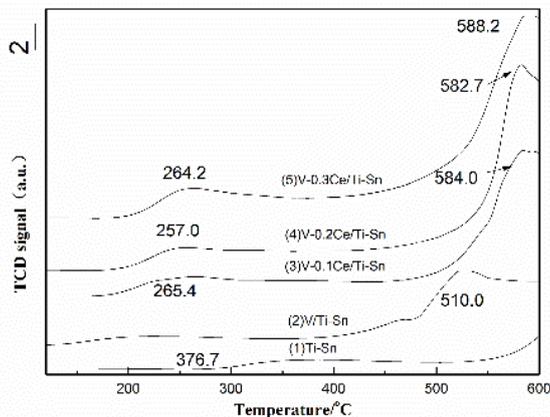


Fig. 5. The TPR profiles of different samples.

$V_2O_5$  reduction peaks were around 853, 1004 and 1008°C, respectively due to  $V_2O_5 \rightarrow V_6O_{13}$ ,  $V_6O_{13} \rightarrow V_2O_4$  and  $V_2O_4 \rightarrow V_2O_3$ , studied by Benjaram M. Reddy et al[8]. An obvious reduction peak appeared at 510°C after loading vanadium oxide to Ti-Sn. Ti-Sn support had also strengthened the reduction ability of  $V_2O_5$  by decreasing its reduction temperature. Similarly, there was a peak at around 260°C after the introduction of cerium oxide, owing to removal of absorbed oxygen on ceria.

### 3.2.3. HRTEM results

V-0.1Ce/Ti-Sn and V-0.3Ce/Ti-Sn were selected to analyze their micro-scale constructions, using high-resolution transmission electron microscopy. Figure 6 showed the HRTEM profiles of them. It could be seen from the HRTEM images that the average particle size of the prepared nano-size catalysts was about 9nm. 0.1Ce/Ti-Sn was in a highly dispersed state with more uniform particles, while particles in the 0.3Ce/Ti-Sn sample agglomerated easily. Better dispersion of V-0.1Ce/Ti-Sn than V-0.3Ce/Ti-Sn could be observed obviously.

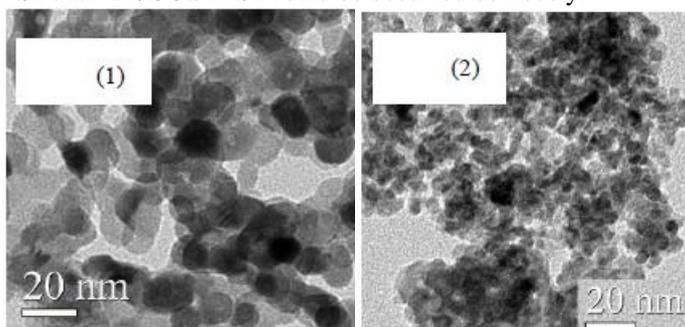


Fig. 6. The HRTEM profile of (1)V-0.1Ce/Ti-Sn(2)V-0.3Ce/Ti-Sn

### 3.2.4. $NH_3$ -adsorbed in situ FT-IR

FT-IR spectra of various samples at  $50^\circ C$  were presented in Figure 7. For V/Ti-Sn, V-0.1Ce/Ti-Sn and V-0.3Ce/Ti-Sn, it could be found that both Lewis acid and Brønsted acid sites existed, as indicated by the bands at 1582, 1176, 1075, 1036  $cm^{-1}$  (Lewis acid sites) and 1662, 1458  $cm^{-1}$  (Brønsted acid sites). The peak at 1748  $cm^{-1}$  was ascribed to the weakly adsorbed  $NH_3$  or gas-phase  $NH_3$ . Ti-Sn and V/Ti-Sn exhibited less acid sites and weaker peak intensity compared with cerium loading catalysts. As for Ti-Sn, there was only a quite weak band at 1458  $cm^{-1}$ . We could conclude that these acid sites were attributed to the interaction of the mixed oxides. Moreover, bands of V-0.1Ce/Ti-Sn at  $50^\circ C$  were much stronger than that of V-0.3Ce/Ti-Sn at the whole wave range, indicating the connection between catalytic activity and acid sites.

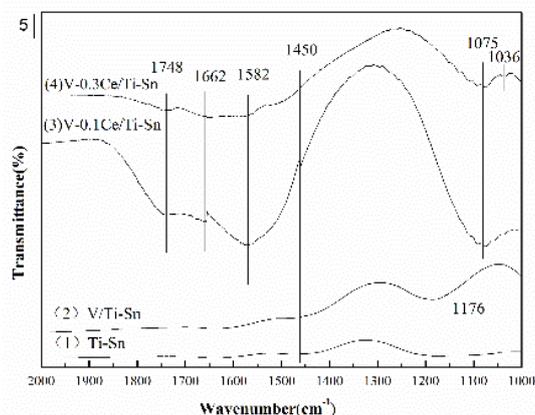


Fig. 7. Ammonia adsorption FT-IR spectra of different catalysts at  $50^\circ C$ .

## 4. Conclusions

The  $V_2O_5$ - $CeO_2$ / $TiO_2$ - $SnO_2$  catalyst with 10%  $CeO_2$  content (i.e. the molar ratio of Ce to Ti) showed the highest catalytic activity within the above-mentioned temperature range, with better performance within the wider temperature range, better thermal stability, and the ability to resist the influence of  $SO_2$  in a short time to some extent. Compared with the  $V_2O_5$ -10wt.%  $WO_3$ / $TiO_2$ - $SnO_2$ ,  $V_2O_5$ -0.1 $CeO_2$ / $TiO_2$ - $SnO_2$  had a higher De- $NO_x$  efficiency.  $V_2O_5$ -0.1 $CeO_2$ / $TiO_2$ - $SnO_2$  had higher de-nitrification efficiency because of its larger BET specific surface area and average pore volume, smaller average pore diameter, better dispersion of  $CeO_2$  on support and lower degree of crystalline, as revealed by means of BET, XRD and HRTEM.  $H_2$ -TPR results indicated that redox properties of catalysts were strengthened after loading cerium oxide, and therefore, better de-nitrification efficiency was obtained. V-0.1Ce/Ti-Sn exhibited significant

amounts of Lewis and Brønsted acidity as well as stronger intensity of dominating acid sites for the NH<sub>3</sub>-SCR reaction.

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