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# Enhanced activity of tungsten modified $CeO_2/TiO_2$ for selective catalytic reduction of NOx with ammonia

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ABSTRACT

A series of W-doped $CeO_2/TiO_2$ catalysts prepared by different impregnation methods assisted with ultrasonic energy were investigated for the selective catalytic reduction (SCR) of NOx (NO and $NO_2$) by $NH_3$. The activity of the $CeO_2/TiO_2$ catalyst was enhanced by the addition of W with all the methods, while the promotional effect was pronounced for catalyst prepared by co-impregnation method. The catalytic activity of 10% $CeO_2/TiO_2$ (CeTi) was greatly enhanced by the addition of 6% $WO_3$ in the broad temperature range of 200–500 °C. BET, XRD, XPS and TPD methods revealed that the co-impregnation method could make $CeO_2$ and $WO_3$ crystallites disperse better over the catalyst surface, and much stronger interaction happened between Ce and W for the more appearance of $Ce^{3+}$. The addition of tungsten could bring more ad-NOx and ad-$NH_3$ adsorption species, and simultaneously enhanced the catalytic activity for $NH_3$-SCR of NOx.

## 1. Introduction

Nitrogen oxide (NOx) emission from automobile exhaust and stationary source poses a serious threat to environment since it can cause acid rain and photochemical smog [1–4]. The selective catalytic reduction (SCR) of nitrogen oxides (NOx) with ammonia remains among the state-of-the-art technologies for abating NOx in the flue gas from stationary sources [5]. Commercial catalysts for the above reaction are based on $V_2O_5$–$WO_3$–$TiO_2$ or $V_2O_5$–$MoO_3$–$TiO_2$ [6,7]. However, this type of catalyst is efficient only within a narrow temperature window of 300–400 °C, the loss of vanadium and formation of $N_2O$ at high temperatures [8,9] are hazardous to the environment and to human health, and the high activity for oxidation of $SO_2$ to $SO_3$, which will be further reacted with $H_2O$ and $NH_3$ to $NH_4HSO_4$, $(NH_4)_2S_2O_7$ and $H_2SO_4$ [10], could cause corrosion of downstream equipments and pore plugging of catalysts. Considering these disadvantages, many researchers continue to modify current catalysts and develop novel catalysts to reduce the vanadium loadings, or replace the vanadium with other metal elements.

Ceria ($CeO_2$) has been studied extensively due to its oxygen storage and redox properties in the Three Way Catalyst (TWC) used for gasoline engine emission control. This compound can store and release oxygen via the redox shift between $Ce^{4+}$ and $Ce^{3+}$ under oxidizing and reducing conditions, respectively [11]. Wu et al. [12] reported a MnOx–$CeO_2$ catalyst which has a high NOx conversion within a low temperature range (80–220 °C). Carja et al. [13] reported a novel catalyst Mn–Ce/ZSM-5, which has high performances in a broad temperature window (517–823 K). As a support or a catalyst, the $CeO_2$–$TiO_2$ mixed oxide was studied in some applications, such as wet air oxidation reactions of organics [14], NO removal [15], etc. Xu et al. [16] reported $CeO_2/TiO_2$ has high activity for $NH_3$-SCR of NOx in the temperature range 275–400 °C at a space velocity of 50,000 $h^{-1}$. Shen et al. [28] also proposed a novel catalyst of $CeO_2$–$Al_2O_3$ supported on an activated-ceramics which has the highest activity in the temperature range 250–350 °C at a space velocity of 3000 $h^{-1}$, and the selective catalytic reduction of NO over $CeO_2/Al_2O_3$ may be an oxidation–reduction process.

$WO_3$ is widely used as the most promotional additive to enhance the NO removal activity of $V_2O_5/TiO_2$ catalyst. Chen and Yang [17] observed that the addition of $WO_3$ improved NO removal activity of $V_2O_5/TiO_2$ catalyst and widened the operating temperature window of SCR reaction. They reported that $WO_3$ on $V_2O_5/TiO_2$ increased the amount and the strength of Brønsted acid sites on the catalyst surface. It should be noted that the surface acidity plays a critical role in SCR reaction [18]. It was also suggested that the higher reducibility of the catalyst due to the electronic interaction of vanadia with tungsten oxide on the surface of $TiO_2$ was respon-

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sible for the high NO removal activity of $V_2O_5$–$WO_3/TiO_2$ catalyst, particularly at low reaction temperatures [7].

As mentioned above, $CeO_2/TiO_2$ is a promising catalyst which may be used for $NH_3$-SCR in the future, further work on investigating this Ce-based catalyst is necessary. In this work, we used impregnation method assisted ultrasonic energy to study W-doped $CeO_2/TiO_2$ catalyst. The main point is to develop a non-vanadium catalyst with high activity in a broader temperature window.

## 2. Experimental

### 2.1. Catalyst preparation

The catalysts were prepared by the wet impregnation method, and three impregnation sequences were taken out. The cerium nitrate, ammonium paratungstate, oxalic acid and Degussa AEROSIL $TiO_2$ P25 support were used for our experiment. WTi was prepared as described previously by impregnating ammonium paratungstate and oxalic acid solution together with $TiO_2$ support, stirred for 30 min, then exposed to ultrasonic energy for 2 h, dried at 110 °C overnight and calcined at 500 °C for 4 h in static air. Ce/WTi was prepared by impregnation of WTi with an aqueous solution of $Ce(NO_3)_4$, stirred for 30 min, exposed to ultrasonic energy for 2 h, dried at 110 °C overnight and calcined at 500 °C for 4 h in static air. And W/CeTi was prepared by impregnation of CeTi and an oxalic acid solution of ammonium paratungstate, which was as the same method as that mentioned above. The cerium oxide content and tungsten oxide content in both catalysts was 10% and 6% by weight, respectively. CeW*x*Ti (*x* represented the weight percentage of $WO_3$, e.g. CeW6Ti.) were prepared by mixing cerium nitrate and ammonium paratungstate in the oxalic acid solution in the desired proportion. To this solution, the calculated amount of $TiO_2$ support was impregnated by stirring for 30 min. The paste obtained was exposed to ultrasonic energy for 2 h, dried overnight at 110 °C and then calcined at 500 °C for 4 h in static air. All the above catalysts were ground and sieved to 40–60 mesh for evaluation. And $CeO_2$ contents in all the catalysts were 10% by weight.

### 2.2. Catalytic activity measurement

The activity measurements were carried out in a fixed-bed quartz reactor (inner diameter 9 mm) using 0.5 g catalyst with 40–60 mesh. The feed gas mixture contained 500 ppm NO, 500 ppm $NH_3$, 3 vol.% $O_2$, 100 ppm $SO_2$ (when used) and 10 vol.% $H_2O$ (when used) and $N_2$ as the balance gas. In all the tests (except of the test about the effect of GHSV), the total flow rate of the feed gas was 300 mL/min, corresponding to a space velocity of about 28,000 $h^{-1}$. The concentration of NOx, $N_2O$ and $NH_3$ in the inlet and outlet gas was measured by FT-IR gas analyzer Gasmet Dx-4000. The activity data were collected when the catalytic reaction substantially reached a steady-state condition for half an hour at each temperature.

### 2.3. Catalyst characterization

BET-surface area, pore size and pore volume were measured by $N_2$ adsorption at 77 K using a Quantachrome Autosorb AS-1 System.

X-ray diffraction (XRD) measurements were performed on a D/MAX-RB system with Cu Kα radiation.

X-ray photoelectron spectroscopy (XPS) data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W Mg Kα radiation. The base pressure was about $3 \times 10^{-9}$ mbar. The binding energies were referenced to the C 1s line at 284.8 eV from adventitious carbon.

Temperature programmed desorption (TPD) experiments of NOx and $NH_3$ were carried out in a fixed-bed quartz reactor. A typical sample mass of 0.5 g and a gas flow rate of 300 mL/min were used during the experiments. The experiment consisted of four stages: (1) degasification of the sample in $N_2$ at 500 °C for 1 h, (2) adsorbed 500 ppm NO + 3% $O_2$ (500 ppm $NH_3$) at room temperature for 1 h, (3) isothermal desorption in $N_2$ at the temperature of the final step-response experiment until no NOx ($NH_3$) was detected, and (4) temperature-programmed desorption in $N_2$ (TPD stage) at 10 °C/min up to 600 °C.

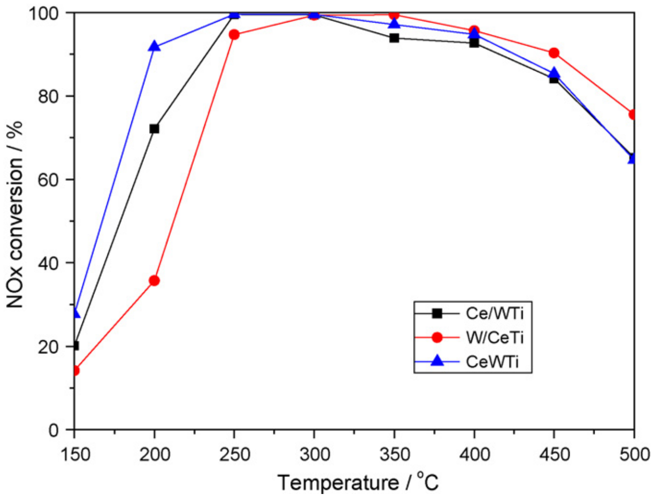

**Fig. 1.** NOx conversion of various catalysts prepared by different impregnation sequences as function of temperatures. Reaction conditions: 500 ppm NO, 500 ppm $NH_3$, 3% $O_2$, $N_2$ as balance gas, and GHSV: 28,000 $h^{-1}$.

## 3. Results and discussion

### 3.1. Catalytic activity evaluation

#### 3.1.1. $NH_3$-SCR activity test

The impregnation sequence is important for the catalyst preparation. It can affect the structure properties and the catalyst activities. Fig. 1 shows the NOx conversion activities of the Ce/WTi, W/CeTi and CeWTi catalysts. And here the amount of $CeO_2$ and $WO_3$ in all the catalysts was 10% and 6%, respectively. All of these three catalysts showed very wide temperature window from 200 to 500 °C, which indicates that W had affirmative effect over CeTi catalyst. And among these catalyst, CeWTi prepared by co-impregnation method showed the best activity, above 80% NOx conversion was obtained in the temperature of 200–500 °C, especially at 200 °C it showed about 92% NOx conversion, which was much higher than the other two catalysts. W/CeTi had higher activity above 450 °C, but only exhibited a low NOx conversion about 35% at 200 °C. Ce/WTi showed nearly the same NOx conversion as CeWTi, while a lower NOx conversion of 72% was obtained at 200 °C. Therefore, in our further work, all the catalysts were prepared by the co-impregnation method.

The effect of various $WO_3$ loadings from 0% to 20% on the performance of CeTi catalyst is shown in Fig. 2. Fig. 2a shows that the addition of W to CeTi by co-impregnation could significantly influence the activity of CeTi catalyst. The maximum NOx conversion activity was greatly improved from 24% to 92% with the increasing of $WO_3$ loading from 0% to 6% at 200 °C. For CeW6Ti catalyst, NOx conversion was greater than 90% in a wide temperature range (200–400 °C). Further increasing the W loading led to a decrease of the activity. As shown in Fig. 2b, the $NH_3$ slip decreased more rapidly when W was added over CeTi catalyst; for CeW6Ti catalyst, $NH_3$ conversion was higher than 80% in the temperature of 200–500 °C. And the remarkable point is that there was few $N_2O$

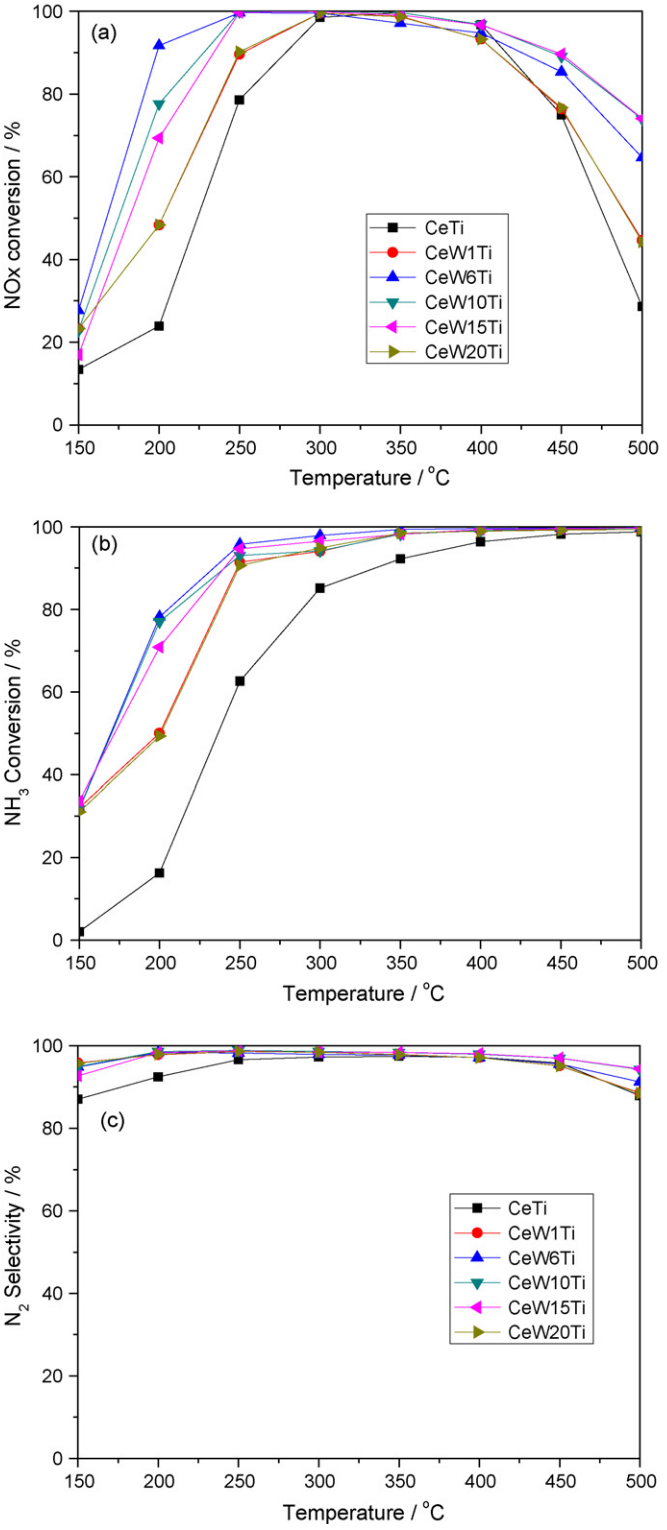

**Fig. 2.** Effect of $WO_3$ loadings over $CeO_2$–$WO_3$/$TiO_2$ catalysts at different temperatures on: (a) NOx conversion; (b) $NH_3$ conversion; (c) $N_2$ selectivity. Reaction conditions: 500 ppm NO, 500 ppm $NH_3$, 3% $O_2$, $N_2$ as balance gas, and GHSV: 28,000 $h^{-1}$.

appeared over all the catalysts, which indicates that this Ce-based catalyst showed excellent $N_2$ selectivity as Fig. 2c shows. In all, we could find that promotional effect was obtained when W was modified over $CeO_2$/$TiO_2$ catalyst, and the 10 wt.%$CeO_2$–6 wt.%$WO_3$/$TiO_2$ (CeW6Ti) had the best activity for the SCR reaction.

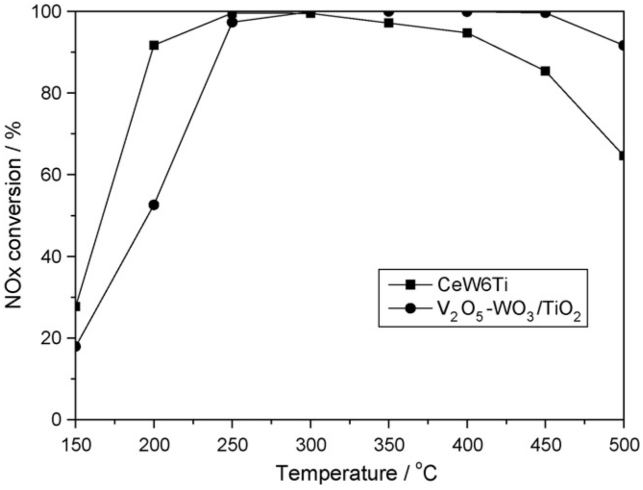

**Fig. 3.** Comparison of NOx conversion over CeW6Ti and 1 wt.% $V_2O_5$–9 wt.% $WO_3$/$TiO_2$ catalyst. Reaction conditions: 500 ppm NO, 500 ppm $NH_3$, 3% $O_2$, $N_2$ as balance gas, and GHSV: 28,000 $h^{-1}$.

Furthermore, we choose CeW6Ti catalyst as a model catalyst to compare with the traditional commercial $V_2O_5$–$WO_3$/$TiO_2$ catalyst under the GHSV = 28,000 $h^{-1}$. As shown in Fig. 3, $V_2O_5$–$WO_3$/$TiO_2$ catalyst showed good activity with nearly 100% NOx conversion at the temperature higher than 250 °C. As for our CeW6Ti catalyst, the low temperature SCR activity was much better than that of $V_2O_5$–$WO_3$/$TiO_2$, especially at 200 °C, although the high temperature SCR activity above 350 °C showed a little decrease. About 27% NOx conversion decreased at 500 °C for CeW6Ti catalyst compared with $V_2O_5$–$WO_3$/$TiO_2$. Another key point was the comparison of the $N_2O$ formation. Few $N_2O$ appeared over all the Ce-based catalyst. And in our previous study [29], we have found that large amount of $N_2O$ would appear over $V_2O_5$–$WO_3$/$TiO_2$ catalyst, especially at higher temperature above 350 °C. Consequently, our CeW6Ti catalyst is possible to be utilized for the removal of NOx from stationary source for its efficient SCR activity and $N_2$ selectivity.

### 3.1.2. *Effect of GHSV on NOx reduction by $NH_3$ over CeW6Ti catalyst*

Space velocity is a very important parameter for the practical application. The activities of the CeW6Ti catalyst in a wide range of GHSV from 28,000 to 113,000 $h^{-1}$ were measured, and the results are shown in Fig. 4. It can be seen that below 200 °C and higher than 350 °C, the NOx conversion dramatically decreased at high GHSV. But the NOx conversion was maintained above 94% in a range of 250–350 °C, even though the GHSV reached 113,000 $h^{-1}$. These results indicate that the CeW6Ti catalyst is highly effective for NOx removal within a wide range of GHSV.

### 3.1.3. *Effect of $O_2$ concentration*

$O_2$ is very important in the SCR reaction [19]. Accordingly, the effect of $O_2$ concentration at 200 °C over CeW6Ti catalyst was also performed and the results are shown in Fig. 5. When $O_2$ was not introduced into the reaction gas, it still showed 50% NOx conversion, which might be due to the participation of lattice oxygen. When a small amount of $O_2$ was added to the feed, there was a great increase of NOx conversion. However, no obvious change was observed when the $O_2$ concentration exceeded above 3%. The results indicate that lattice oxygen created by CeWTi catalyst could partly participate in the SCR reaction, while the $O_2$ gas, which could be adsorbed over catalyst surface to form the chemisorbed oxygen, is the most active oxygen and plays an important role in the SCR reaction.

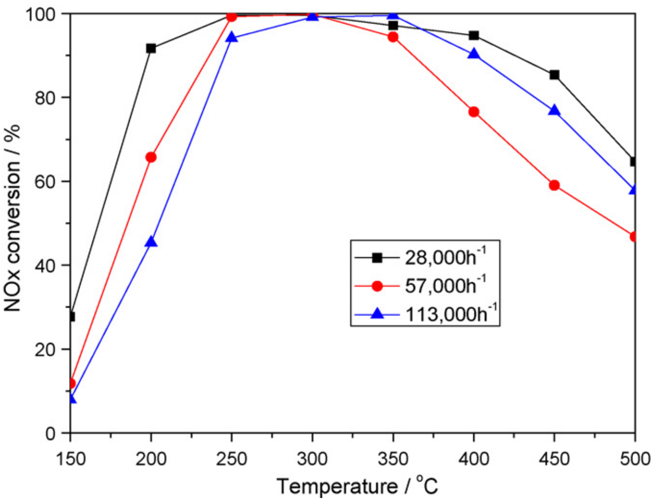

**Fig. 4.** NOx conversion as a function of GHSV for CeW6Ti catalyst. Reaction conditions: 500 ppm NO, 500 ppm $NH_3$, 3% $O_2$, and $N_2$ as balance gas.

### 3.1.4. Effect of $H_2O$ and $SO_2$ over CeTi and CeW6Ti

$H_2O$ and $SO_2$ are unavoidable existed in exhaust and flue gas, so it is very important for industrial application to investigate the effect of $H_2O$ and $SO_2$ on SCR activities of catalysts. Here we discussed the effect of $H_2O$ and $SO_2$, respectively. Furthermore, the co-affection of $H_2O$ and $SO_2$ were also carried out, and the results are shown in Fig. 6. When $H_2O$ was added into the reaction gas, the activity of CeTi catalyst (Fig. 6a) decreased a little in the temperature range of 150–450 °C, while for CeWTi catalyst (Fig. 6b), the addition of $H_2O$ had no inhibition in 250–450 °C. NOx conversion over both catalysts at 500 °C were enhanced. All the results indicate that both catalysts have good resistance against water vapor, and the addition of W could increase the ability to resist the poison of $H_2O$.

The addition of 100 ppm $SO_2$ to the feed gas had different effects over these two catalysts. For CeTi (Fig. 6a), the deactivation happened in the temperature range of 300–400 °C, while in other temperature region, $SO_2$ could even enhance the NOx conversion slightly. But for CeWTi catalyst (Fig. 6b), the addition of $SO_2$ increase the catalytic activity above 300 °C, while the obvious decrease of NOx conversion happened from 90% to 20% at 200 °C. The results indicate that the addition of W could enhance the ability to resist $SO_2$. The process may be explained that sulfate species deposit on catalyst surface at low temperature, and catalytic active center is covered. When temperature is higher, the sulfate species will be decomposed. And it indicates that W can decrease the thermal stability of surface sulfate species such as $Ce(SO_4)_2$ and $Ce_2(SO_4)_3$ [20] at high temperature, which indicate CeWTi catalyst had better $SO_2$ resistance than CeTi.

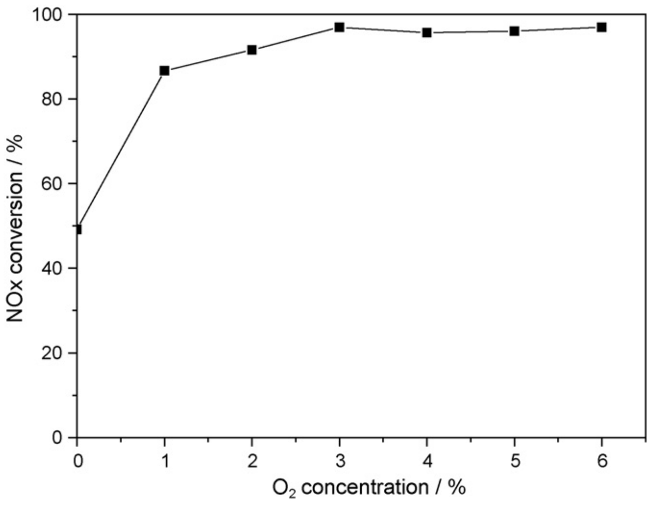

**Fig. 5.** Effect of $O_2$ concentration over CeW6Ti catalyst. Reaction conditions: 500 ppm NO, 500 ppm $NH_3$, $N_2$ as balance gas, and GHSV: 28,000 $h^{-1}$.

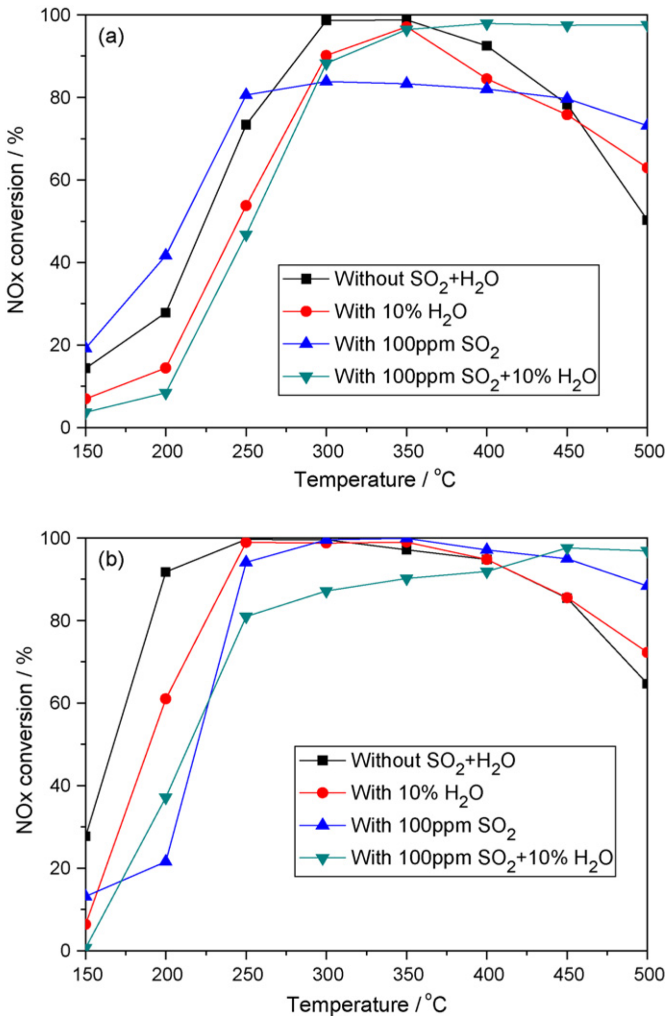

**Fig. 6.** Effect of $H_2O$ and $SO_2$ on the activities of (a) CeTi and (b) CeW6Ti catalyst. Reaction conditions: 500 ppm NO, 500 ppm $NH_3$, 3% $O_2$, 100 ppm $SO_2$, 10% $H_2O$, $N_2$ as balance gas, and GHSV: 28,000 $h^{-1}$.

The addition of 10 vol.% $H_2O$ and 100 ppm $SO_2$ into the reaction gas reduced the catalytic activities of both catalysts below 400 °C, while above 400 °C nearly 100% NOx conversion were both obtained. The NOx conversion over CeTi (Fig. 6a) and CeWTi (Fig. 6b) decreased to 47% (from 74%) and 80% (from 100%) at 250 °C, respectively. Therefore, the CeWTi catalyst still exhibited a higher resistance against $H_2O$ and $SO_2$ than CeTi catalyst with above 80% NOx conversion in the temperature range of 250–500 °C.

## 3.2. Characterization

### 3.2.1. BET and XRD results

The BET-surface area, total pore volume and average pore diameter of various catalysts are summarized in Tables 1 and 2. From Table 1, we could find that the introduction of Ce could make the surface area decrease at different points. The surface area of Ce/WTi, W/CeTi and CeWTi was 48.4, 49.4 and 53.2 $m^2\,g^{-1}$, respectively. Table 2 shows that each element added into $TiO_2$ made the average

**Table 1**
Physical property of CeTi, Ce/WTi, W/CeTi and CeW/Ti catalysts.

| Samples | $S_{BET}$ ($m^2 g^{-1}$) | Vp ($cc g^{-1}$) | Dp (nm) |
|---|---|---|---|
| CeTi | 54.5 | 0.354 | 26.3 |
| Ce/WTi | 48.4 | 0.270 | 22.1 |
| W/CeTi | 49.4 | 0.308 | 26.4 |
| CeW/Ti | 53.2 | 0.400 | 36.5 |

**Table 2**
Physical property of CeWTi catalysts with different $WO_3$ loadings.

| Samples | $S_{BET}$ ($m^2 g^{-1}$) | Vp ($cc g^{-1}$) | Dp (nm) |
|---|---|---|---|
| $TiO_2$ | 50.5 | 0.341 | 3.38 |
| CeTi | 54.5 | 0.354 | 26.3 |
| CeW1Ti | 56.6 | 0.369 | 36.5 |
| CeW6Ti | 53.2 | 0.400 | 36.5 |
| CeW10Ti | 52.7 | 0.356 | 26.3 |
| CeW15Ti | 50.8 | 0.356 | 22.3 |
| CeW20Ti | 45.1 | 0.349 | 21.2 |

pore diameter increase rapidly. The surface area and average pore diameter of CeTi were 54.5 $m^2 g^{-1}$ and 26.3 nm, respectively. After doping with a little tungsten, the surface area and average pore diameter of CeW1Ti catalyst increased to 56.6 $m^2 g^{-1}$ and 36.54 nm, respectively. However, further doping tungsten on CeTi catalyst made the surface area and average pore diameter decrease severely. That may be due to various factors such as the solid-state reactions between cerium oxide and tungsten oxide, or the growing of $CeO_2$ and $WO_3$ crystallites.

XRD patterns of the catalysts prepared by different methods are shown in Fig. 7a. It is clearly that the intensities of $CeO_2$ and $WO_3$ crystallites over CeWTi catalyst prepared by co-impregnation were the weakest, which was consistent with BET results: cluster of $CeO_2$ and $WO_3$ crystallites appeared would cause the agglomeration of the catalyst surface, resulting of the surface area decreasing. Therefore, CeWTi prepared by co-impregnation method exhibited the best activity because this method could make $CeO_2$ and $WO_3$ disperse better over the surface.

Fig. 7b shows the XRD patterns of CeWTi catalysts with different $WO_3$ loadings. For all the $TiO_2$ supported catalysts, the anatase phase was the main phase, with only a little rutile phase. When Ce was doped, a weak peak of cubic $CeO_2$ crystallites was observed ($2\theta = 28.59$). No obvious $WO_3$ phase was observed at low W loadings (<10%). This demonstrates that tungsten existed as a highly dispersed or amorphous surface species. As the W loading increased from 10% to 20%, the XRD patterns of $CeO_2$ grew sharper and the diffraction line of $WO_3$ became apparent. Meanwhile, the peaks of $TiO_2$ were broader and smaller. These results suggest that with the increasing of W loadings, the crystallites of $TiO_2$ became smaller and $CeO_2$ and $WO_3$ crystallites were formed and slowly growing, which may cause the surface area decrease.

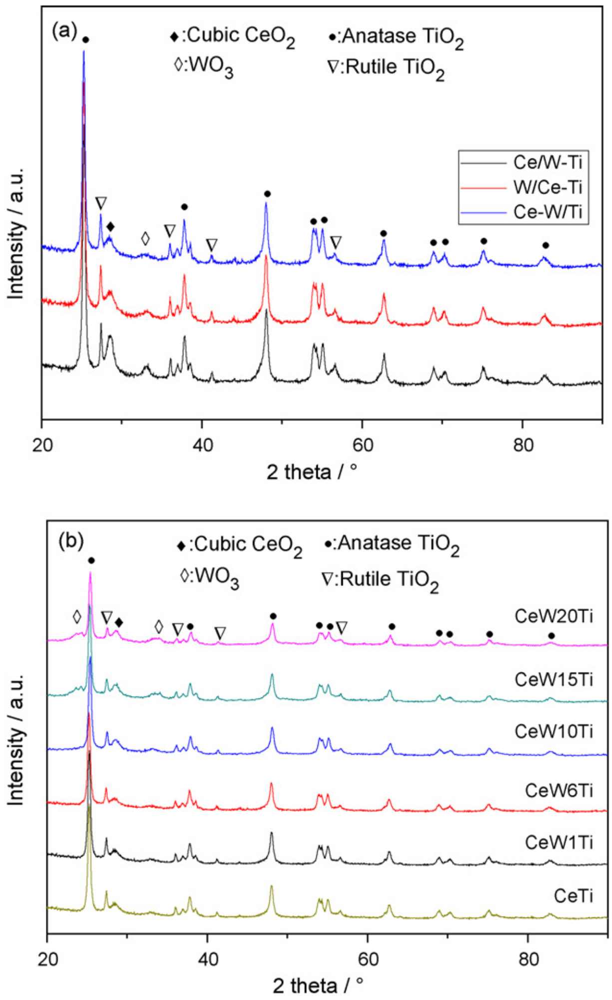

**Fig. 7.** XRD patterns of (a) Ce/WTi, W/CeTi and CeWTi, and (b) CeWTi catalysts with different $WO_3$ loadings.

### 3.2.2. XPS results

Surface atomic concentrations of Ce, W, Ti and O are summarized in Table 3 and photoelectron spectra of Ce 3d levels are displayed in Fig. 8. The ratio of Ce/Ti and W/Ti were slightly higher than the corresponding bulk ratio, indicating the richness of surface Ce and W atoms as shown in Table 3.

The XPS spectra of chemical states of Ce over various catalysts are shown in Fig. 8. The bands labeled u1 and v1 represent the $3d^{10}4f^1$ initial electronic state corresponding to $Ce^{3+}$, while the

**Table 3**
XPS results.

| Samples | Surface atomic concentration (%) | | | | | |
|---|---|---|---|---|---|---|
| | Ti | Ce | W | O | Ce/Ti | W/Ti |
| Pure $TiO_2$ | 28.8 | – | – | 71.2 | – | – |
| CeTi | 24.8 | 3.1 | – | 72.1 | 0.13(0.05[a]) | – |
| CeW1Ti | 20.5 | 3.5 | 0.4 | 75.6 | 0.17(0.05) | 0.02(0.004) |
| CeW6Ti | 21.0 | 4.6 | 2.3 | 72.1 | 0.22(0.03) | 0.11(0.02) |
| CeW10Ti | 16.9 | 5.0 | 2.9 | 75.2 | 0.30(0.06) | 0.17(0.04) |

[a] The number in the brackets is denoted as the corresponding bulk ratio.

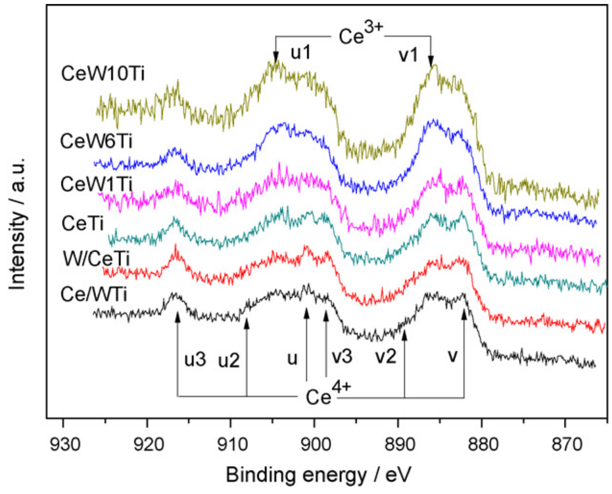

**Fig. 8.** XPS spectra of Ce 3d over various catalysts.

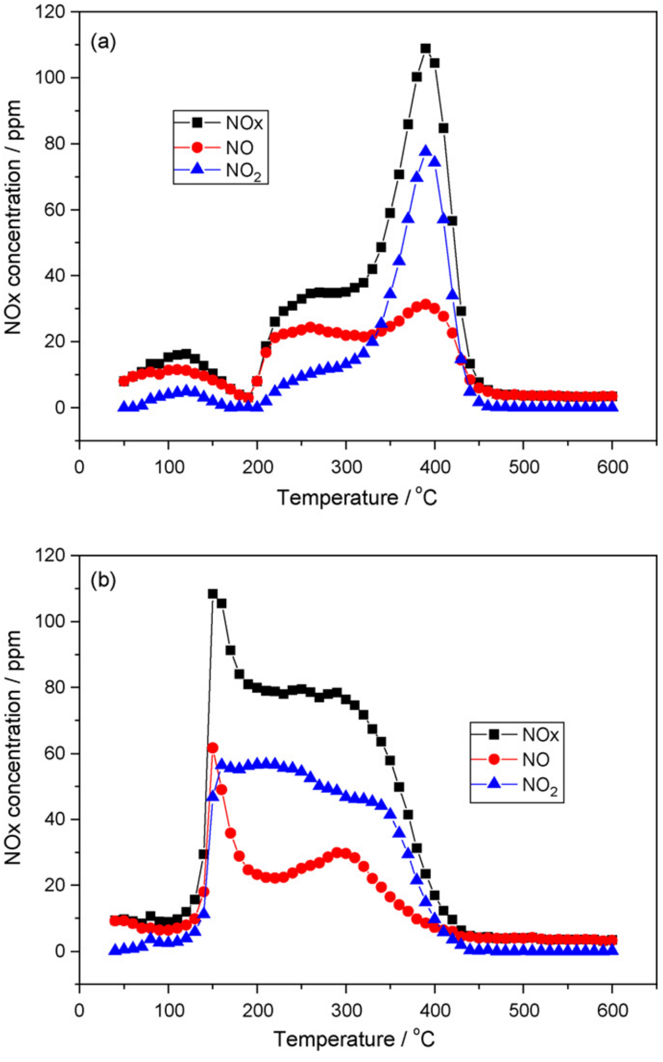

**Fig. 9.** NOx-TPD profiles of (a) CeTi and (b) CeW6Ti.

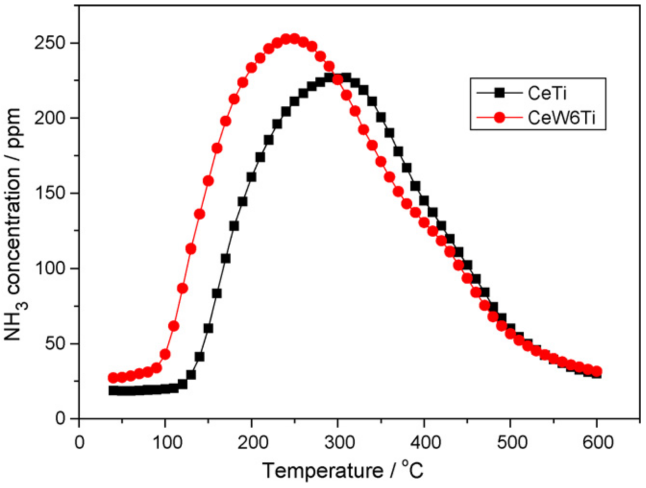

**Fig. 10.** $NH_3$-TPD profiles of CeTi and CeW6Ti.

peaks labeled u, u2, u3, v, v2 and v3 represent the 3d104f0 state of $Ce^{4+}$ ions [21,22]. For Ce/WTi and W/CeTi catalysts, v1 and u1 peaks for $Ce^{3+}$ were much weaker than v and u3 peaks for $Ce^{4+}$ state. These facts suggested that Ce in these two catalysts were mainly in the valence state of 4+, and this situation also happened in CeTi catalyst. For the CeW6Ti catalyst, much stronger v1 and u1 peaks belonging to $Ce^{3+}$ were detected. These results suggest that the co-impregnation method could make Ce mainly stay in the state of 3+, while in the catalysts prepared by the other two methods, $Ce^{4+}$ was predominated. Furthermore, the binding energy of v1 peak belonging to $Ce^{3+}$ for CeW1Ti, CeW6Ti and CeW10Ti was 885.4, 885.6 and 885.0 eV, respectively. The noticeable high binding energy of CeW6Ti could be explained by the addition of W with strong electronegativity that withdraws the electron atmosphere of Ce–O. Hence, it is most likely that W was beneficial for the transformation from $Ce^{4+}$ to $Ce^{3+}$ irons, while the presence of the $Ce^{3+}$ species could create a charge imbalance, the vacancies and unsaturated chemical bonds on the catalysts surface [14], which will lead to the increase of chemisorbed oxygen on the surface.

### 3.2.3. *TPD tests*

Fig. 9 illustrates the TPD profiles of NO + $O_2$ of CeTi and CeW6Ti. Three NOx adsorption peaks were observed at 120, 260 and 390 °C for CeTi (Fig. 9a), and two NOx adsorption peaks appeared at 150 and 290 °C for CeW6Ti (Fig. 9b). According to the literature, the low temperature peak was always due to decomposition of nitrite species (ad-$NO_2{}^-$), but the high temperature peak was ascribed to the strongly bound nitrate species [23–25]. Comparing with these two figures, we could find that more $NO_2$ than NO could be desorbed over CeW6Ti catalyst, while for the CeTi catalyst, the amount of NO and $NO_2$ was nearly the same. It indicated that the NOx adsorbed specie over the catalyst was mainly $NO_3{}^-$, which was beneficial for the $NH_3$-SCR. According to the XPS results, more $Ce^{3+}$ state would appear when W was modified, which could create a charge imbalance, the vacancies and unsaturated chemical bonds over the catalyst surface, and then more NO could be easily oxidized into $NO_2$. Furthermore, larger amount of NOx desorbed over CeW6Ti catalyst in a temperature range of 150–250 °C, while much smaller NOx were desorbed for CeTi. It indicates that unstable nitrates species appeared at low temperature. According to Shimizu et al.'s analysis [26], the stable nitrates occupying the active sites over $Ag/Al_2O_3$ were unfavorable to SCR reactions at low temperatures. So unstable nitrates over CeW6Ti catalyst would result in more effective SCR reactions, especially in the temperature range of 150–250 °C, which was proven by the activity of CeTi and CeW6Ti catalyst.

Fig. 10 shows $NH_3$-TPD curves for CeTi and CeW6Ti. Single broad desorption peak spanned in the temperature range of 100–500 °C for both samples which was attributed to $NH_3$ desorbed by weak and medium acid sites. It was noticeable that the $NH_3$ desorption peak shifted to the low temperature from CeTi (310 °C) to CeW6Ti (250 °C). It indicates that the $NH_3$ adsorbed species could be more easily desorbed at low temperature with the addition of W. Furthermore, the intensity and the area of $NH_3$ over CeWTi is comparatively higher than CeTi catalyst. Many research shows that the surface acidity plays a critical role in SCR reaction [17,27]. Consequently, the addition of W over CeTi catalyst brought more active $NH_3$ adsorbed species, which is believed to be the significantly beneficial to SCR reaction.

## 4. Conclusions

In this work, tungsten was introduced into the $CeO_2/TiO_2$ catalysts by different impregnation sequences. The activity of the $CeO_2/TiO_2$ catalyst was enhanced by the addition of W with all the methods, while the promotional effect was pronounced for catalyst prepared by co-impregnation method. Because the co-impregnation method could make $CeO_2$ and $WO_3$ crystallites disperse better over the catalyst surface, and much stronger interaction happened between Ce and W for the more appearance of

$Ce^{3+}$. The optimal loading of W species was 6% ($WO_3$), and $H_2O$ and $SO_2$ had slight influence under the evaluation condition. The superior performance of this W modified CeTi catalyst could be mainly attributed more appearance of $Ce^{3+}$ state with the introduction of W, which could be beneficial for the SCR reaction such as more NO would be oxidized to $NO_2$. Furthermore, TPD results showed that CeWTi catalyst provided more adsorbed NOx and $NH_3$ species, and simultaneously enhanced the activity of both species resulting in the improvement of SCR activity.

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## References

[1] H. Bosch, F. Janssen, Catal. Today 2 (1988) v.
[2] M. Shelef, Chem. Rev. 95 (1995) 209.
[3] G. Busca, L. Lietti, G. Ramis, F. Berti, Appl. Catal. B 18 (1998) 1.
[4] V.I. Parvulescu, P. Grange, B. Delmon, Catal. Today 46 (1998) 233.
[5] F. Nakajima, I. Hamada, Catal. Today 29 (1996) 109.
[6] L. Casagrande, L. Lietti, I. Nova, P. Forzatti, A. Baiker, Appl. Catal. B 22 (1999) 63.
[7] L. Lietti, P. Forzatti, F. Bregani, Ind. Eng. Chem. Res. 35 (1996) 3884.
[8] S. Djerad, M. Crocoll, S. Kureti, L. Tifouti, W. Weisweiler, Catal. Today 113 (2006) 208.
[9] M. Yates, J.A. Martín, M.Á. Martín-Luengo, S. Suárez, J. Blanco, Catal. Today 107 (2005) 120.
[10] G. Qi, R.T. Yang, Appl. Catal. B 44 (2003) 217.
[11] B.M. Reddy, A. Khan, Y. Yamada, T. Kobayashi, S. Loridant, J.C. Volta, J. Phys. Chem. B 107 (2003) 5162.
[12] Z.B. Wu, R.B. Jin, H.Q. Wang, Y. Liu, Catal. Commun. 10 (2009) 935.
[13] G. Carja, Y. Kameshima, K. Okada, C.D. Madhusoodana, Appl. Catal. B 73 (2007) 60.
[14] S.X. Yang, W.P. Zhu, Z.P. Jiang, Z.X. Chen, J.B. Wang, Appl. Surf. Sci. 252 (2006) 8499.
[15] M.F. Luo, J. Chen, L.S. Chen, J.Q. Lu, Z.C. Feng, C. Li, Chem. Mater. 13 (2001) 197.
[16] W.Q. Xu, Y.B. Yu, C.B. Zhang, H. He, Catal. Commun. 9 (2008) 1453.
[17] J.P. Chen, R.T. Yang, Appl. Catal. A 80 (1992) 135.
[18] E.Y. Choi, I.S. Nam, Y.G. Kim, J. Catal. 161 (1996) 597.
[19] H. Bosch, F. Janssen, Catal. Today 2 (1988) 369.
[20] W.Q. Xu, H. He, Y.B. Yu, J. Phys. Chem. C 113 (2009) 4431.
[21] F.B. Noronha, E.C. Fendley, R.R. Soares, W.E. Alvarez, D.E. Resasco, Chem. Eng. J. 82 (2001) 21.
[22] H. He, H. Dai, C.T. Au, Catal. Today 90 (2004) 245.
[23] J.H. Li, Y.Q. Zhu, R. Ke, J.M. Hao, Appl. Catal. B 80 (2008) 202.
[24] J.H. Li, J.M. Hao, L.X. Fu, T.L. Zhu, Z.M. Liu, X.Y. Cui, Appl. Catal. A 265 (2004) 43.
[25] J.H. Li, J.M. Hao, L.X. Fu, Z.M. Liu, X.Y. Cui, Catal. Today 90 (2004) 215.
[26] K. Shimizu, H. Kawabata, A. Satsuma, T. Hattori, Appl. Catal. B 16 (1998) 319.
[27] L. Lietti, I. Nova, G. Ramis, L. Dall'Acqua, G. Busca, E. Giamello, P. Forzatti, F. Bregani, J. Catal. 187 (1999) 419.
[28] Y.S. Shen, S.M. Zhu, T. Qiu, S.B. Shen, Catal. Commun. 11 (2009) 20.
[29] L. Chen, J.H. Li, M.f. Ge, J. Phys. Chem. C 113 (2009) 21177.