

## Promotional effect of CeO<sub>x</sub> for NO reduction over V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub>-carbon nanotube composites

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### ABSTRACT

A series of V<sub>2</sub>O<sub>5</sub>-CeO<sub>x</sub>/TiO<sub>2</sub>-carbon nanotube composites were prepared by sol-gel method and their catalytic activity for the reduction of NO<sub>x</sub> with NH<sub>3</sub> was compared. V<sub>2</sub>O<sub>5</sub>CeO<sub>x</sub>/TiO<sub>2</sub> (Ce/V=9) achieved a NO<sub>x</sub> removal efficiency of 92% and 98% at 200 °C and 250 °C, respectively. SEM, XRD, XPS, BET, Raman, TPD and TPR were employed to probe the promotional effect of CeO<sub>x</sub>. The appearance of Ce<sup>3+</sup> is found to increase chemisorbed oxygen thus facilitates the catalytic reduction of NO<sub>x</sub>. The poisoning effect caused by SO<sub>2</sub> was found to depend on temperatures and gas velocity strongly. Moreover, the existence of excess oxygen was found to be essential (2% of O<sub>2</sub> compared to 500 ppm NO<sub>x</sub>) to keep high SCR activity.

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### 1. Introduction

Nitrogen oxides (NO<sub>x</sub>) discharged from power plants, waste incinerators, industrial boilers, engines, and automobiles can result in acid rain, photochemical smog, and ozone depletion. These detrimental effects to the environment have aroused worldwide attention. Many approaches have been investigated to reduce NO<sub>x</sub> emission. Among them, selective catalytic reduction (SCR) technique has been proven to be one of the most effective methods for reducing NO<sub>x</sub> emissions [1,2]. A large number of SCR catalysts have been explored, including noble metals [3,4], transition metal oxides [5,6] and zeolites [7,8]. Especially, V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> based catalysts have been extensively used in the industry. However, the operating temperature for these catalysts is usually above 300 °C, and the exhaust gases usually contain a large number of fly ash and SO<sub>2</sub>, which can easily deactivate the catalysts. Thus, the development of active SCR catalysts that can be operated at relatively low temperatures (below 250 °C) is needed, so that SCR systems could be installed downstream of the desulfurizer and electrostatic precipitator, where the flue gas temperature is relatively low (below 250 °C). Low-temperature catalysts can also contribute to

lower energy consumption and help simplify the retrofitting of SCR devices for flue gas cleaning [9].

A series of catalysts, including V<sub>2</sub>O<sub>5</sub>/AC [10], V<sub>2</sub>O<sub>5</sub>/CNTs [11], Mn-Ce/TiO<sub>2</sub> [12], V<sub>2</sub>O<sub>5</sub>-MnO<sub>x</sub>/TiO<sub>2</sub>CNTs [13] have been reported to present high activity at relatively low temperatures. Researchers have tried to introduce metal oxides to traditional V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> and MnO<sub>x</sub>-CeO<sub>2</sub> catalysts to further improve NO<sub>x</sub> removal efficiency at low temperatures. Amiridis et al. [14] screened the effect of introducing metal oxides to V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> and found that WO<sub>3</sub> and MoO<sub>3</sub> exhibit the most significant promotion of the catalyst, whereas MnO<sub>2</sub>, Ga<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>, SnO<sub>2</sub>, and ZnO appear to poison the catalyst. Phil et al. [15] reported that Se-, Sb-, Cu-, and S-doped V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalysts show high catalytic activity for NH<sub>3</sub>-SCR of NO<sub>x</sub> at temperatures between 150 and 400 °C. Recently, CeO<sub>2</sub> attracted researchers' interest due to its special structure and property. CeO<sub>2</sub> has fluorite-structure and could store and release oxygen via the redox shift between Ce<sup>4+</sup> and Ce<sup>3+</sup> under oxidizing and reducing conditions, respectively [16–18]. CeO<sub>x</sub> can also be utilized as catalyst support, promoter or even active species. Qi and Yang [19] achieved good catalytic performance in reduction of NO<sub>x</sub> over catalyst MnO<sub>x</sub>-CeO<sub>2</sub>. Chen [18] and Wu et al. [20,21] improved SCR performance for V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> and MnO<sub>x</sub>/TiO<sub>2</sub>, using CeO<sub>x</sub> as promoter, respectively. Moreover, CeO<sub>x</sub> has been used as structure promoter and a buffer in redox cycle to enhance catalytic property of catalyst Pd/Al [16]. And CeO<sub>2</sub>-zeolite was reported to be very active for reduction of NO with NH<sub>3</sub> [22].

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Recently, we found that SCR activity of the traditional  $V_2O_5/TiO_2$  catalyst was significantly promoted by the introduction of CNTs [23]. In the present study,  $CeO_x$  was added into catalyst  $V_2O_5/TiO_2$ -CNTs trying to further improve SCR activity for  $NO_x$  removal. Also, the influences of oxygen,  $SO_2$  and gas velocity on catalyst  $V_2O_5-CeO_x/TiO_2$ -CNTs were examined with respect of its application in large scale.

## 2. Experimental method

### 2.1. Catalyst preparation

Samples were prepared by sol–gel method. The multi-walled CNTs (MWCNTs) purchased from Shenzhen Nanoport Co. Ltd. were purified in concentrated nitric acid for 2 h and then dried and ground for later use. Tetrabutyl titanate, ammonium metavanadate, chromic nitrate, cobalt nitrate, cerium nitrate, nickel nitrate and ammonium molybdate were used as precursors of  $TiO_2$ ,  $V_2O_5$ ,  $Cr_2O_3$ ,  $Co_3O_4$ ,  $CeO_2$ ,  $NiO$  and  $MoO_3$ , respectively.

Details of catalyst synthesis are as follows. First, purified MWCNTs, acetic acid and tetrabutyl titanate were ultrasonically dispersed in ethanol for 30 min, ammonium metavanadate dissolved in oxalic acid, chromic nitrate (cobalt nitrate, cerium nitrate, nickel nitrate and ammonium molybdate) and deionized water were added to above suspension and then ultrasonicated until a sol was formed. The sol was aged in air until it transformed into a gel. The gel was dried at  $100^\circ C$  and finally calcined at  $450^\circ C$  for 2 h in  $N_2$  to obtain  $V_2O_5-MO_x/TiO_2$ -CNTs (M: Cr, Co, Ce, Ni, Mo). The catalysts are denoted as  $VM_xTiC$ , where X represents nominal atomic ratio of M to V.  $V_2O_5/TiO_2$ -CNTs catalyst was also prepared through the same method for comparison. The physicochemical properties of the catalysts are summarized in Table 1.

### 2.2. Catalyst characterization

X-ray diffraction (XRD) patterns were recorded on an X-ray diffractometer (Philips XD-98) using  $Cu K_\alpha$  radiation ( $\lambda = 0.15406$  nm). Brunauer–Emmett–Teller surface areas, pore diameter, and pore volume were measured using an ASAP2000 physical adsorber. Sample morphology and dispersion were characterized by scanning electron microscopy (SEM; Hitachi S-4800). Element analysis of catalysts was done by X-ray photoelectron spectroscopy (XPS), using a Kratos Axis Ultra-DLD. The Raman spectra were obtained on a Labor Raman HR-800 (JDBin Yvon) at 10 mW of the 514.5 nm line of an Ar ion laser to analyze the surface species and the interaction among the metal oxides.

The temperature-programmed reduction ( $H_2$ -TPR) experiment was carried out from 50 to  $800^\circ C$  in a 1690 Gas Chromatograph using 50 mg samples of the catalysts. Prior to the analysis, the catalysts were pretreated at  $300^\circ C$  for 30 min in air. The TPR runs were carried out at a heating rate of  $10^\circ C \text{ min}^{-1}$  using a stream of 5%  $H_2$  in argon at a flow rate of  $40 \text{ mL min}^{-1}$ . The hydrogen consumption was measured by a thermal conductivity detector calibrated with  $CuO$ .

**Table 1**  
Summary of the surface element composition and structure property of catalysts.

Catalysts	Atomic ratio (V, Ce, Ti, V/Ce, V/Ti) <sup>a</sup>	S ( $m^2/g$ )	Pore volume ( $cm^3/g$ )	Pore diameter (nm)
VTiC	(0.0015, –, 0.1194, –, 1:80)	109	0.25	8.1
VCe <sub>3</sub> TiC	(0.0015, 0.0068, 0.1015, 1:4.5, 1:67)	126	0.23	6.4
VCe <sub>6</sub> TiC	(0.0017, 0.0132, 0.0877, 1:7.8, 1:52)	120	0.17	5.0
VCe <sub>9</sub> TiC	(0.0015, 0.0243, 0.0962, 1:16, 1:64)	133	0.19	5.0

<sup>a</sup> The atomic ratio of the composition is determined by XPS. Moreover, the CNTs concentration was approximately 10% in each catalyst.

The  $NH_3$  temperature-programmed desorption ( $NH_3$ -TPD) experiment was performed to determine the acidity of catalysts. A 30 mg sample of each catalyst was loaded in the reactor and was pretreated in a helium stream ( $30 \text{ mL min}^{-1}$ ) at  $550^\circ C$  for 1 h, and then cooled to  $100^\circ C$  in the same stream. The pretreated sample was then exposed to  $NH_3$  (4%) at a flow rate of  $20 \text{ mL min}^{-1}$  for 3 h. The physisorbed  $NH_3$  was removed by flushing the catalysts with  $N_2$  at a flow rate of  $30 \text{ mL min}^{-1}$  for 1 h before starting the TPD experiment. Experimental runs were recorded by heating the samples in  $N_2$  ( $30 \text{ mL min}^{-1}$ ) from 100 to  $600^\circ C$  at a heating rate of  $10^\circ C \text{ min}^{-1}$ .

### 2.3. Catalytic activity characterization

All catalysts were pasted to 10 aluminum plates ( $3 \text{ cm} \times 10 \text{ cm}$ ) with 20% organoclay, which were then inserted into a fixed-bed flow reactor. The distance between each plate was approximately 5 mm. An  $NO-NO_2-NO_x$  analyzer (Testo AG-testo 350) was used to measure the inlet and outlet concentrations of NO and  $NO_2$ . The catalyst temperature was measured using a thermocouple projecting into the center of the reactor. Dry air was used as the source of  $O_2$ , and  $N_2$  was used as the balance gas. The premixed gases (1%  $NO/Ar$ , 1%  $NH_3/Ar$ ) were prepared to formulate the flue gas in the experiments. The reaction conditions were as follows: 500 ppm NO, 500 ppm  $NH_3$ , 6%  $O_2$ , 200 ppm  $SO_2$  (when used). The reacting gases were mixed and preheated at  $100^\circ C$  before being introduced into the reactor. The activity measurements were performed from 100 to  $300^\circ C$ , at increments of  $25^\circ C$  under varied GHSV of  $7500-30,000 \text{ h}^{-1}$ .

## 3. Results and discussion

### 3.1. Catalytic activity

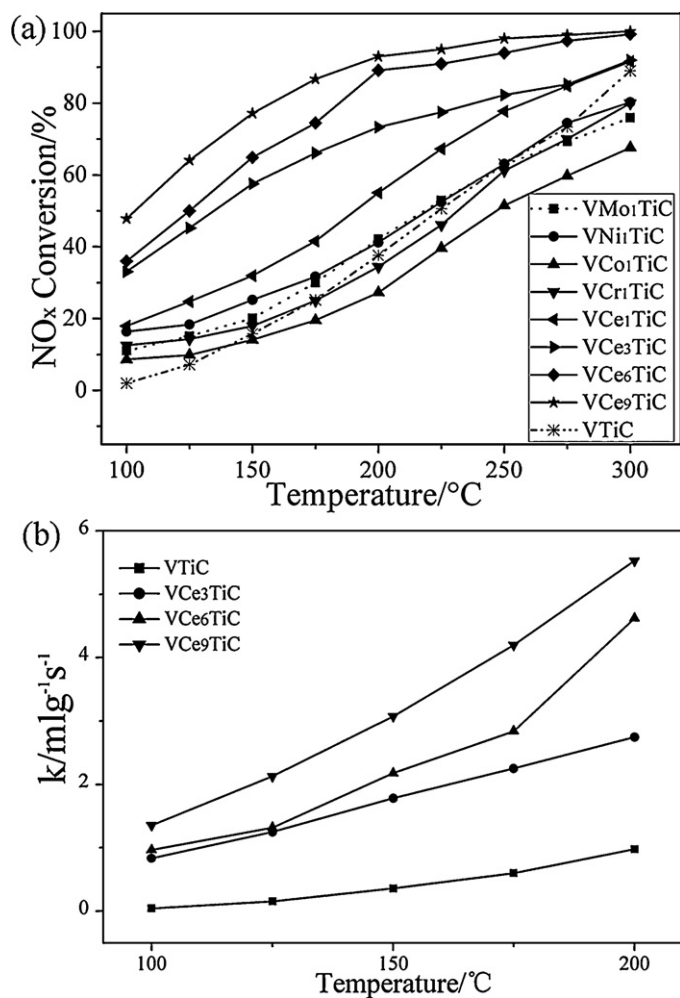
#### 3.1.1. Effect of different dopant on activity of $V_2O_5/TiO_2$ -CNTs

As shown in Fig. 1(a), no great effect was observed on the catalytic property of catalyst VTiC with addition of Ni, Cr and Mo, at temperature between 100 and  $300^\circ C$ , and the Co even had a negative influence on  $NO_x$  reduction. Fortunately, catalytic improvement took place with the addition of  $CeO_x$  to VTiC and the reactivity was further improved by increasing the  $CeO_x$  content (Ni, Cr, Mo, Co and Ce were introduced with the same atomic ratio (M/V = 1, M: Ni, Cr, Mo, Co, Ce)). The  $NO_x$  conversion increased dramatically to 92% at  $200^\circ C$  over catalyst  $VCe_9TiC$  upgraded by  $CeO_x$ . To better evaluate catalytic activity for  $NO_x$  conversion, kinetic parameters were calculated according to Eqs. (1) and (2), which were based on the assumption that the reaction is first-order dependent on  $NO_x$  and zero-order dependent on  $NH_3$  [24,25].

$$k = -\frac{V}{W} \times \ln(1-x) \quad (1)$$

$$k = A \exp\left(\frac{E_a}{RT}\right) \quad (2)$$

where  $k$  is the reaction rate coefficient ( $\text{mL g}^{-1} \text{ s}^{-1}$ ),  $V$  is the total gas flow rate ( $\text{mL s}^{-1}$ ),  $W$  is the mass of the catalyst (g),  $x$  is



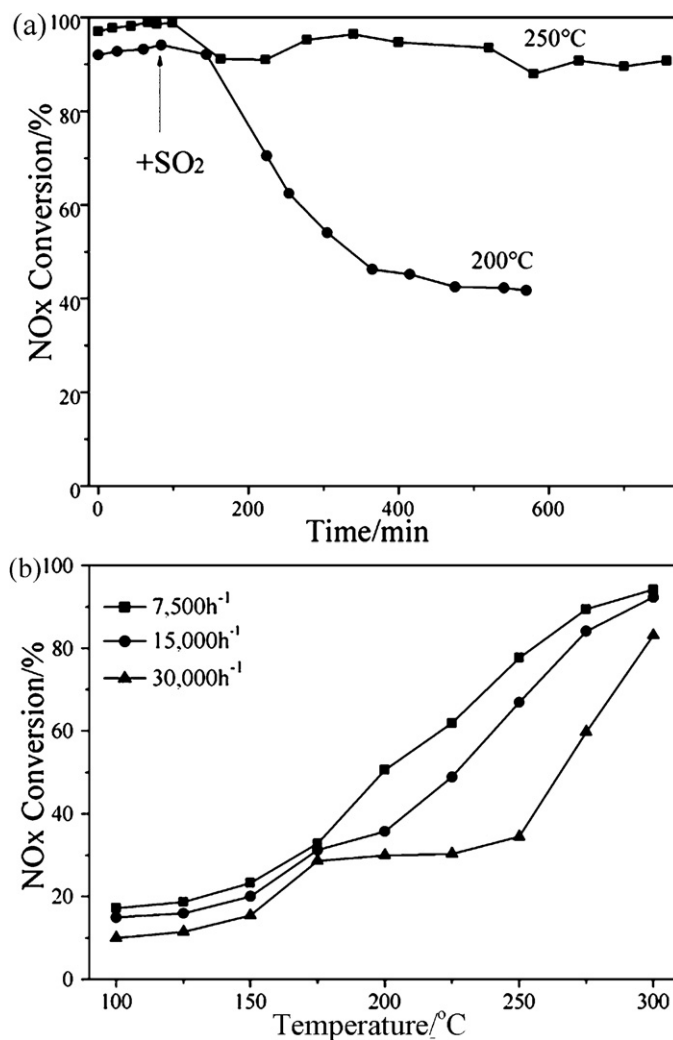
**Fig. 1.** (a) NO<sub>x</sub> conversion at temperatures over different catalysts. (b) The kinetic rate constant *k* at temperatures over different catalysts. Reaction conditions: NO 500 ppm, NH<sub>3</sub> 500 ppm, O<sub>2</sub> 6%, N<sub>2</sub> as the balance gas, GHSV = 7500 h<sup>-1</sup>.

the conversion of NO<sub>x</sub> (%),  $E_a$  is the apparent activation energy (J mol<sup>-1</sup>),  $A$  is the pre-exponential factor,  $R$  is the gas constant (8.3145 J mol<sup>-1</sup> K<sup>-1</sup>), and  $T$  is the temperature (K).

The variation of  $k$  with temperatures is presented in Fig. 1(b). The values of  $k$  for the catalysts VTiC and VCe<sub>9</sub>TiC were found to be 1.0 and 5.5 at 200 °C respectively, which indicates a marked promotion in the reaction rate with the introduction of CeO<sub>x</sub> to VTiC. The apparent activation energy for catalysis by VTiC, VCe<sub>9</sub>TiC was calculated to be 32.95 and 18.9 kJ mol<sup>-1</sup> respectively, according to the Arrhenius plot. These calculations indicate that catalytic reaction was easier over VCe<sub>9</sub>TiC than VTiC.

### 3.1.2. Effect of SO<sub>2</sub> on reduction of NO<sub>x</sub> over catalyst VCe<sub>9</sub>TiC

SO<sub>2</sub> is a common component of industrial exhaust gas, thus it is important to investigate its influence on SCR activity. The catalytic performances with introduction of SO<sub>2</sub> to flue gas over catalyst VCe<sub>9</sub>TiC are presented in Fig. 2. Fig. 2(a) shows experimental results of the time-dependent SO<sub>2</sub> resistance at 200 °C and 250 °C, respectively. Slight decrease of catalytic activity upon addition of SO<sub>2</sub> was observed at 250 °C while the catalyst VCe<sub>9</sub>TiC can still reach 90% NO<sub>x</sub> conversion even after 11 h. To contrast, the NO<sub>x</sub> conversion decreased from 93% to 41% within 8 h upon the introduction of SO<sub>2</sub> at 200 °C. Evidently the poison effect brought by SO<sub>2</sub> depends on the reaction temperature greatly, which was consistent with Goo et al.'s report [24]. According to previous study [26], the balance of sulfate salt formation and consumption is the main mechanism

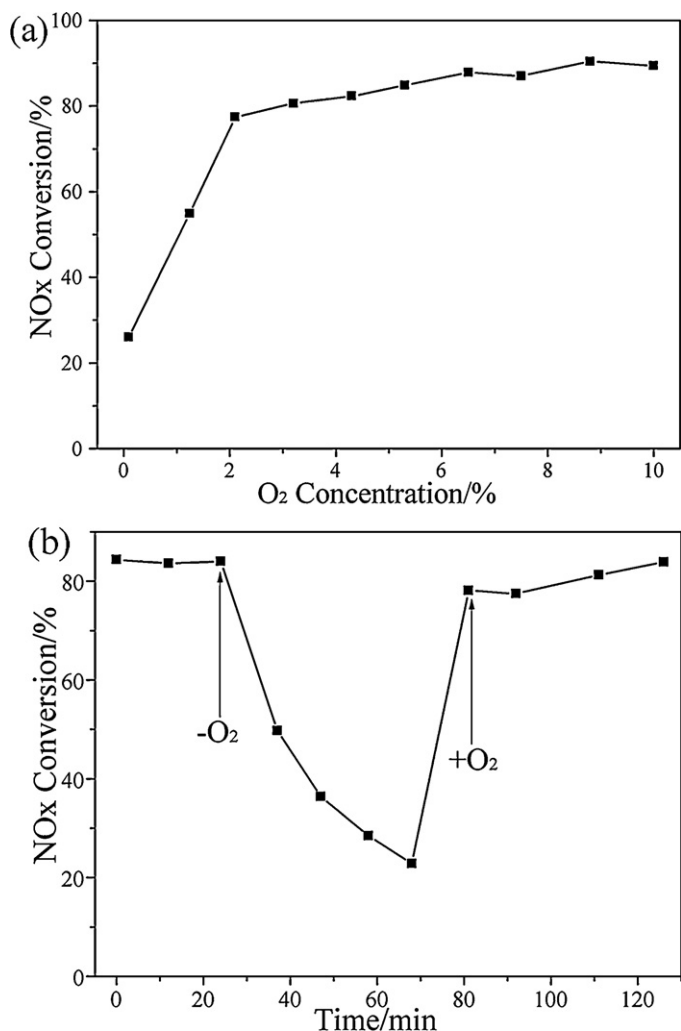


**Fig. 2.** (a) Catalytic reduction of NO<sub>x</sub> at different temperatures over catalyst VCe<sub>9</sub>TiC with SO<sub>2</sub>. Reaction conditions: NO 500 ppm, NH<sub>3</sub> 500 ppm, O<sub>2</sub> 6%, SO<sub>2</sub> 200 ppm (when used), N<sub>2</sub> as the balance gas, GHSV = 7500 h<sup>-1</sup>. (b) Catalytic reduction of NO<sub>x</sub> over catalyst VCe<sub>9</sub>TiC under varied GHSV. Reaction conditions: NO 500 ppm, NH<sub>3</sub> 500 ppm, O<sub>2</sub> 6%, 200 ppm SO<sub>2</sub>, N<sub>2</sub> as the balance gas.

that controls the deactivation of the catalyst. The deposition rate of sulfate is determined by the difference between its formation and reaction with NO<sub>x</sub>. At lower temperature, the deposition rate outweighs the consumption rate of sulfate species thus the sulfate species may deposit on the surface of catalyst and cover the active site, which results in the poison of catalyst. As shown in Fig. 2(b), catalytic reactivity of VCe<sub>9</sub>TiC as a function of temperatures under different gas velocity was examined. On the one hand, the contact time between catalyst and NO<sub>x</sub> molecular reduced with high GHSV. On the other hand, high gas velocity increased the sulfate deposition, which caused an over deposition of sulfate species. These two effects combined to explain the reduction of catalytic activity over catalyst VCe<sub>9</sub>TiC under high gas velocity.

### 3.1.3. Effect of O<sub>2</sub> on catalytic performance over catalyst VCe<sub>9</sub>TiC

O<sub>2</sub> is very essential for the selective catalytic reaction [27]. Accordingly, the effect of O<sub>2</sub> concentration was also performed in the present study and the results are displayed in Fig. 3. As shown in Fig. 3(a), catalytic performance was suppressed greatly with O<sub>2</sub> concentration of 0.09% while can recover to 77% quickly with introduction of 2% O<sub>2</sub> at 175 °C. However, no great increase of catalytic property was observed when the O<sub>2</sub> concentration exceeds 3%,



**Fig. 3.** (a) Effect of O<sub>2</sub> concentration on catalytic performance over VCe<sub>9</sub>TiC at 175 °C. (b) Transient response over catalyst VCe<sub>9</sub>TiC upon switching off and on O<sub>2</sub> at 175 °C. Reaction conditions: NO 500 ppm, NH<sub>3</sub> 500 ppm, O<sub>2</sub> 0–10%, N<sub>2</sub> as the balance gas, GHSV = 7500 h<sup>-1</sup>.

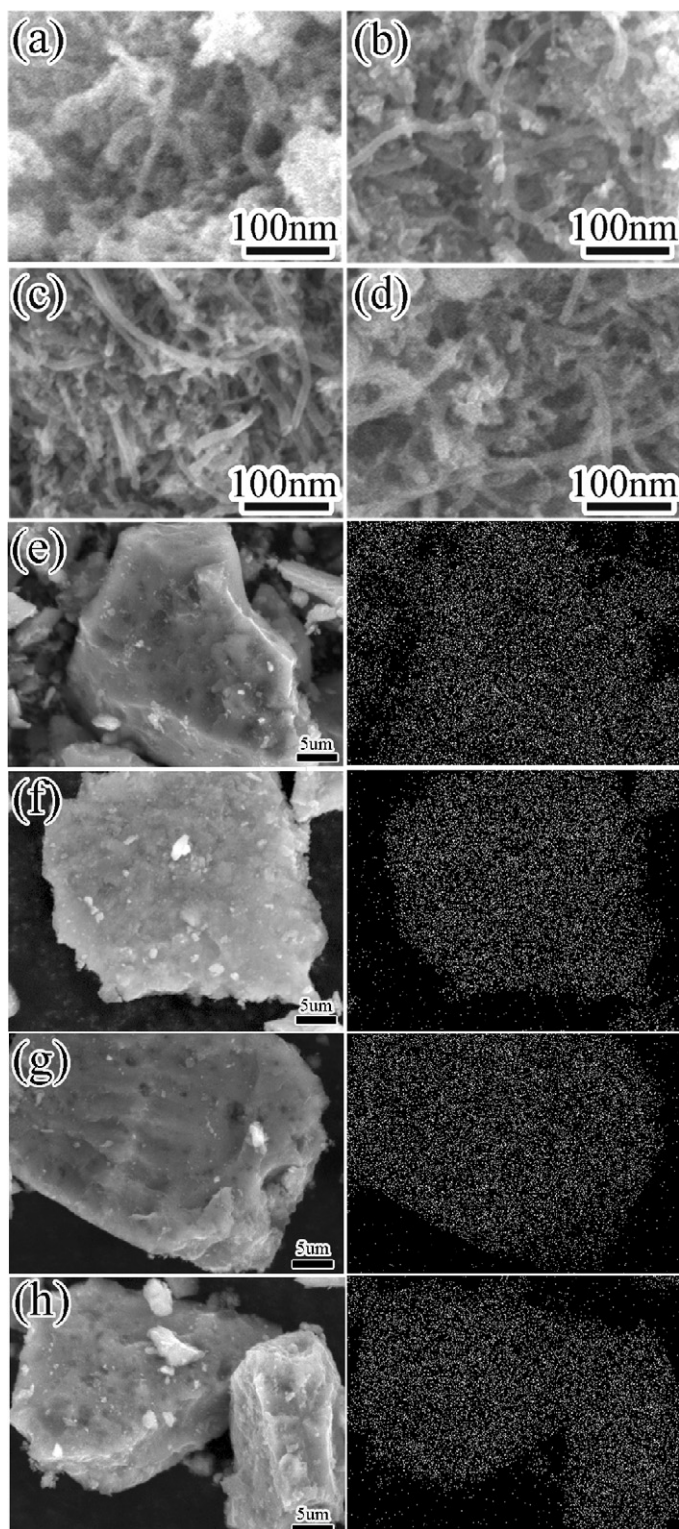
which was consistent with other reports [19,27]. The significance of O<sub>2</sub> concentration can also be verified by another transient experiment presented in Fig. 3(b). The catalytic activity decreased quickly upon turning off O<sub>2</sub> and recovered to original level with switching on O<sub>2</sub> again. These observations indicated the importance of O<sub>2</sub> concentration to SCR reaction especially under low oxygen concentration and that lattice oxygen participated in the reduction of NO<sub>x</sub> when O<sub>2</sub> was shut off.

### 3.2. Catalyst characterization

#### 3.2.1. Microstructure and morphology analysis

Fig. 4(a)–(d) shows the SEM images of the catalysts VTiC, VCe<sub>3</sub>TiC, VCe<sub>6</sub>TiC and VCe<sub>9</sub>TiC. The catalyst particles were dispersedly coated on the surfaces of the CNTs with uniform distribution. Vanadium dispersion was investigated by EDX-mapping as shown in Fig. 4(e)–(h). With the introduction of CeO<sub>x</sub>, the aggregation of V<sub>2</sub>O<sub>5</sub> was further reduced.

The XRD patterns of VTiC, VCe<sub>3</sub>TiC, VCe<sub>6</sub>TiC and VCe<sub>9</sub>TiC are shown in Fig. 5. The peaks corresponding to TiO<sub>2</sub> (anatase PDF# 21-1272) appeared in the patterns of all catalysts. The peak at 26.4° is attributed to the peak for CNTs that overlapped with that of TiO<sub>2</sub> at 25.3° [28]. The peak located at 30.8° was assigned to titanium oxide (PDF# 65-2448) over catalyst VTiC. No peak corresponding



**Fig. 4.** SEM images (a–d) and V<sub>k</sub>-EDX mapping patterns (e–h) for catalysts VTiC, VCe<sub>3</sub>TiC, VCe<sub>6</sub>TiC, VCe<sub>9</sub>TiC, respectively.

to CeO<sub>x</sub> and V<sub>2</sub>O<sub>5</sub> was observed in all catalysts; which indicates that the amount of its crystalline was too small to be detected. Moreover, the peaks of VTiC were much sharper than those of the other catalysts. This indicates that the grain size of the catalysts decreased with the addition of CeO<sub>x</sub>. The crystalline sizes of VTiC, VCe<sub>3</sub>TiC, VCe<sub>6</sub>TiC, and VCe<sub>9</sub>TiC calculated from the XRD peaks at 26.4° were 8.5, 4.9, 4.6, and 3.6 nm, respectively. The addition of

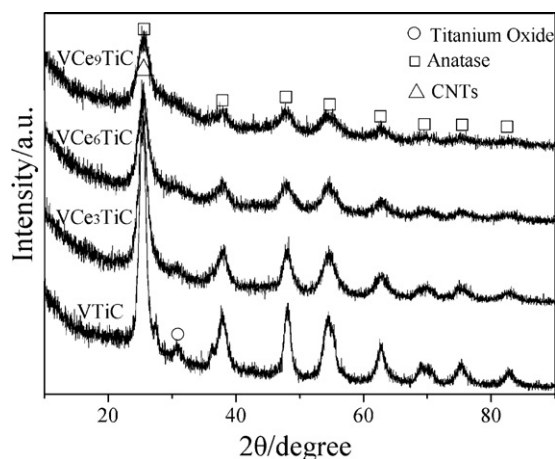


Fig. 5. XRD patterns of catalysts with CeO<sub>x</sub>.

CeO<sub>x</sub> might hinder the sinter and aggregation of nano particles, which was in line with Fig. 4 and other report [16]. Moreover, the intensity of peaks corresponding to TiO<sub>2</sub> reduced with the addition of CeO<sub>x</sub>, though no peaks assigned to CeO<sub>x</sub> appeared. In summary, the introduction of CeO<sub>x</sub> hindered aggregation of nano particles, which contributed to good dispersion of V<sub>2</sub>O<sub>5</sub>.

The specific surface area, pore volume, and pore size of the catalysts are summarized in Table 1. Surface area increased while the pore volume and pore diameter both decreased with the introduction of CeO<sub>x</sub>. Although the surface area of the catalysts may not be the determining parameter in SCR activity [29], the high surface area can promote the catalytic reduction of NO<sub>x</sub> by NH<sub>3</sub>, since high surface area can offer more active sites for reaction.

The V<sub>2</sub>O<sub>5</sub> contents of the surfaces of VTiC, VCe<sub>3</sub>TiC, VCe<sub>6</sub>TiC, and VCe<sub>9</sub>TiC were 0.48, 0.41, 0.43 and 0.39 μmol m<sup>-2</sup>, respectively (assuming that all active components were present on the surface of the catalysts). The surface V<sub>2</sub>O<sub>5</sub> contents are lower than value obtained by monolayer coverage (commonly accepted to be 6–7 μmol m<sup>-2</sup> for vanadia) [11].

### 3.2.2. Surface species analysis

The Raman spectra of the catalysts VTiC, VCe<sub>3</sub>TiC, VCe<sub>6</sub>TiC, and VCe<sub>9</sub>TiC are shown in Fig. 6. Typical Raman peaks of CNTs centered at 1350 (D peak), 1590 cm<sup>-1</sup> (G peak) and 2700 cm<sup>-1</sup> in the spectra of all catalysts were detected [30]. Catalysts VTiC and VCe<sub>3</sub>TiC showed Raman peaks at 144, 196, 395, 511, and 633 cm<sup>-1</sup>, which correspond to the anatase phase of TiO<sub>2</sub> [31]. The intensity of the anatase peaks decreased with the introduction of CeO<sub>x</sub> so that

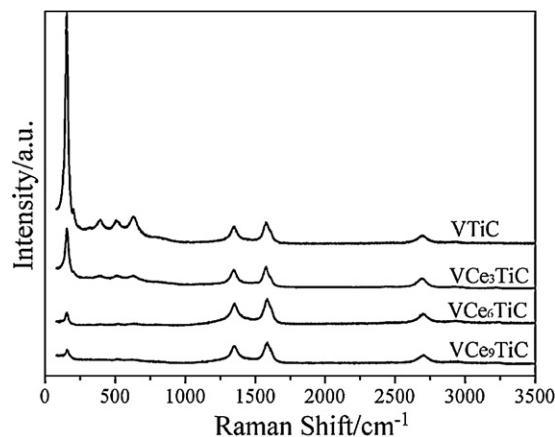


Fig. 6. Raman spectra of catalysts with CeO<sub>x</sub>.

Table 2  
NH<sub>3</sub>-TPD results over catalysts with different CeO<sub>x</sub> content.

Catalysts	$\eta_{\text{NH}_3}$ (μmol g <sup>-1</sup> )		Total	$I_{\text{H}}/I_{\text{H+L}}$
	240 °C (L)	380 °C (H)		
VTiC	40	14	54	0.26
VCe <sub>3</sub> TiC	40	22	62	0.35
VCe <sub>6</sub> TiC	25	12	37	0.32
VCe <sub>9</sub> TiC	34	29	63	0.46

only peak centered at 144 cm<sup>-1</sup> appeared on catalysts VCe<sub>6</sub>TiC, and VCe<sub>9</sub>TiC, which was in line with results of XRD. Moreover, no Raman peak ascribed to V<sub>2</sub>O<sub>5</sub> and CeO<sub>x</sub> was observed on all catalyst spectra, which may be due to the low V<sub>2</sub>O<sub>5</sub> loading on the surface or the interaction of V, Ce, Ti and C [17,31].

The XPS spectra of O1s peaks are displayed in Fig. 7(a). The peak at 529.6–530.0 eV corresponds to lattice oxygen (hereafter denoted as O<sub>β</sub>), whereas the peak at 531.3–531.7 eV corresponds to several O1s states of surface-adsorbed oxygen (hereafter denoted as O<sub>α</sub>) [32]. As shown in Fig. 7(a), the O<sub>β</sub> concentration decreased with the addition of CeO<sub>x</sub>. The relative concentration ratio of O<sub>α</sub>/(O<sub>α</sub> + O<sub>β</sub>) of VTiC and VCe<sub>6</sub>TiC was calculated to be 0.21 and 0.29, respectively. The concentration of chemisorbed oxygen increased with the addition of CeO<sub>x</sub>, which was suggested to be helpful for SCR reaction [18,32]. And the ease of formation of labile oxygen vacancies and particularly the relatively high mobility of bulk oxygen species of CeO<sub>x</sub> may contribute to the improvement of chemisorbed oxygen [17].

V2p peaks for catalysts are presented in Fig. 7(b). V<sup>5+</sup> (517.4 eV), V<sup>4+</sup> (516.2 eV) and V<sup>3+</sup> (515.1 eV) ion [33] all appeared on catalyst VTiC and the intensity of V<sup>3+</sup> declined gradually with the addition of CeO<sub>x</sub>. In addition, the V2p peaks shifted to higher binding energy when CeO<sub>x</sub> was introduced, indicating quantivalence of V species increased thus the V<sup>3+</sup> reduced. The shortened red-ox cycle of V<sup>5+</sup>/V<sup>4+</sup> perhaps favors the catalytic reaction as Zhong and Li [34] thought the formation of V<sup>4+</sup> facilitated to the SCR reaction.

XPS spectra of Ce3d for catalysts are displayed in Fig. 7(c). The peaks labeled u are due to 3d<sub>3/2</sub> spin-orbit states, and those labeled v are the corresponding 3d<sub>5/2</sub> states [17]. The bands labeled u1 and v1 represent the 3d<sup>10</sup>4f<sup>1</sup> initial electronic state, corresponding to Ce<sup>3+</sup>, whereas the peaks labeled u, u2, u3, v, v2, and v3 represent the 3d<sup>10</sup>4f<sup>0</sup> state of Ce<sup>4+</sup> ions [18]. The Ce<sup>3+</sup> ions were predominant for all catalysts and a small fraction of Ce<sup>4+</sup> ions appeared with high Ce/V ratio. It demonstrated that Ce mainly existed in the form of Ce<sup>3+</sup> for catalyst VCe<sub>9</sub>TiC. It was reported [18,27,35] that Ce<sup>3+</sup> could create a charge imbalance, the vacancies and unsaturated chemical bonds on the catalyst surface thus facilitated the formation of chemisorbed oxygen, so a large number of Ce<sup>3+</sup> ions will contribute to the improved catalytic property.

Fig. 7(d) shows the XPS spectra of Ti2p for catalysts VTiC, VCe<sub>6</sub>TiC and VCe<sub>9</sub>TiC. No great change can be drawn from the comparison of the XPS patterns, which indicated that the introduction of CeO<sub>x</sub> did not influence the structure of TiO<sub>2</sub> support. No solid solution was observed for our study, which was consistent with the results of XRD and Raman.

### 3.2.3. Surface acidity

Fig. 8 shows the deconvolution of NH<sub>3</sub>-TPD profiles over catalysts VTiC, VCe<sub>3</sub>TiC, VCe<sub>6</sub>TiC and VCe<sub>9</sub>TiC. Two peaks centered at about 240 °C (L), 380 °C (H) were deconvoluted on all profiles. The quantity analysis of acidic sites over catalysts with different CeO<sub>x</sub> content is summarized in Table 2. The total amount of acid sites increased with addition of CeO<sub>x</sub> except for catalyst VCe<sub>6</sub>TiC. However, the ratio of strong acid and total acid content denoted as  $I_{\text{H}}/I_{\text{H+L}}$  increased remarkably upon the introduction of CeO<sub>x</sub>. This clearly indicated that CeO<sub>x</sub> could increase acidity of

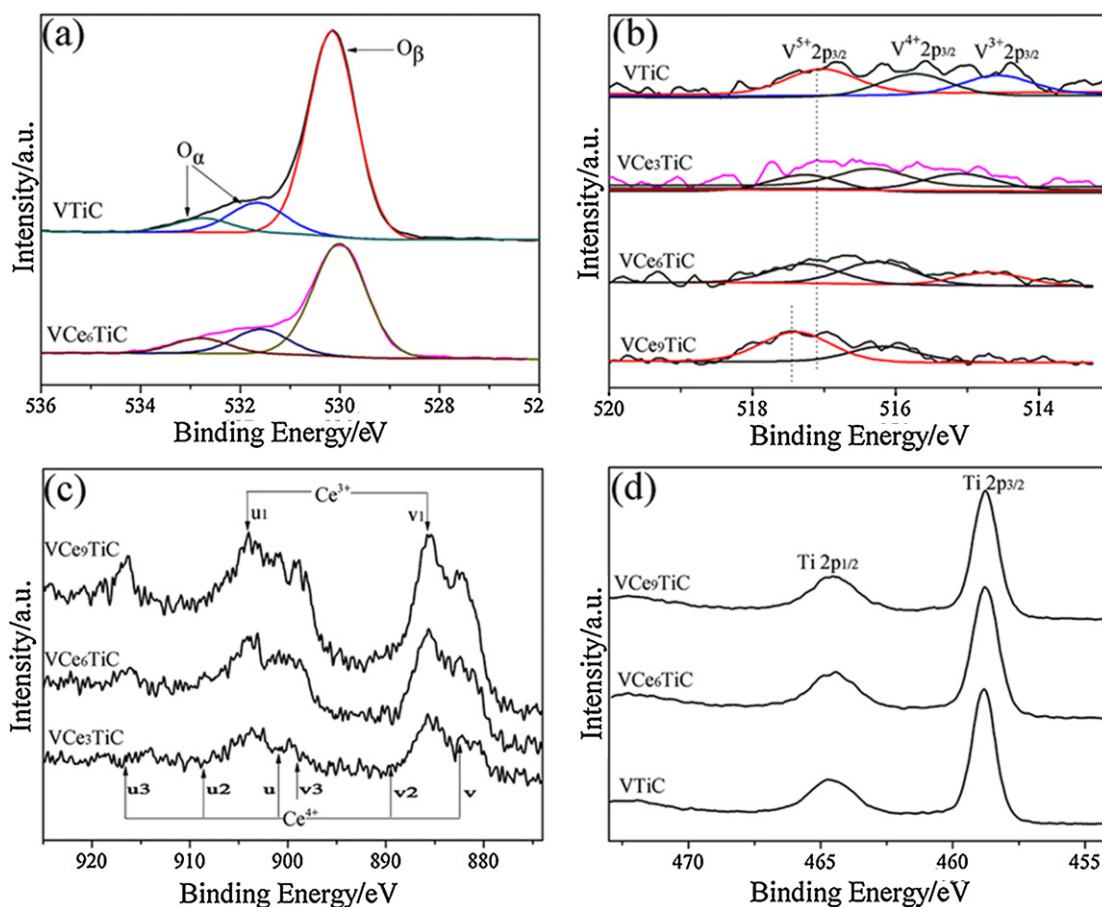


Fig. 7. XPS spectra over catalysts with  $\text{CeO}_x$ . (a): O1 s; (b): V2p; (c): Ce3d; (d): Ti2p.

upgraded catalysts especially for improving strong acid thus facilitates the adsorption and activation of  $\text{NH}_3$  during catalytic reaction. Based on the foregoing analysis, it seems that the enhanced acidity contributes to promotion of  $\text{NH}_3$  adsorption and activation thus enhanced the catalytic activity in  $\text{NH}_3$ -de $\text{NO}_x$  [23,36].

### 3.2.4. Reducibility

Fig. 9 presents the  $\text{H}_2$ -TPR profiles of VTiC, VCe<sub>3</sub>TiC and VCe<sub>9</sub>TiC. A broad peak centered at 550 °C was detected over VTiC, which could be assigned to the reduction of vanadia from  $\text{V}^{5+}$  to  $\text{V}^{3+}$  and

$\text{V}^{4+}$  to  $\text{V}^{3+}$  [37]. Catalysts VCe<sub>3</sub>TiC and VCe<sub>9</sub>TiC both gave rise to one broad peak (380–800 °C), which could be ascribed to overlap of reduction of  $\text{Ce}^{4+}$  to  $\text{Ce}^{3+}$ ,  $\text{V}^{5+}$  to  $\text{V}^{3+}$  and  $\text{V}^{4+}$  to  $\text{V}^{3+}$  [18,37,38]. In contrast to a previous report that several peaks above 627 °C were observed on unsupported  $\text{V}_2\text{O}_5$  [37], only one peak was observed in our study, which was associated with good dispersion of  $\text{V}_2\text{O}_5$  on the support. Note that, the  $\text{H}_2$  consumption peaks over doped catalysts were broadened and the reaction started at relatively low temperatures with introduction of  $\text{CeO}_x$ . Moreover,  $\text{H}_2$  consumption of VTiC, VCe<sub>3</sub>TiC and VCe<sub>9</sub>TiC was calculated to be 302, 688 and 832  $\mu\text{mol g}^{-1}$ , respectively. A large increase in  $\text{H}_2$  consumption was observed upon the addition of  $\text{CeO}_x$ , which probably resulted from

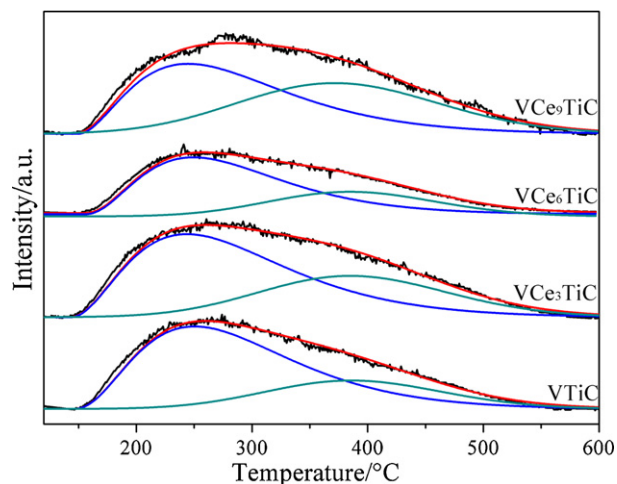


Fig. 8. Typical  $\text{NH}_3$ -TPD curves of  $\text{CeO}_x$  contained catalysts.

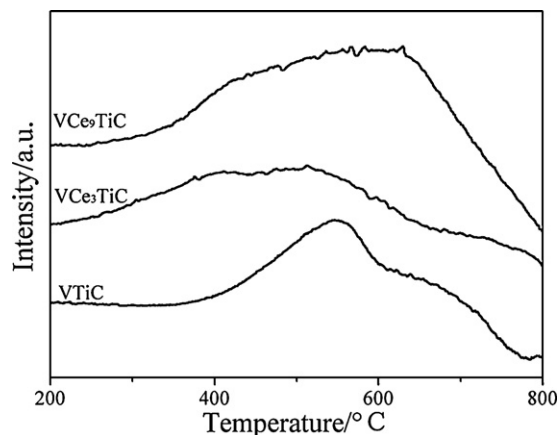


Fig. 9. Typical  $\text{H}_2$ -TPR curves of  $\text{CeO}_x$  contained catalysts.

the large number of chemisorbed oxygen introduced by  $\text{CeO}_x$  as shown in Fig. 7a. These observations indicate that the reducibility of upgraded catalysts is improved upon the addition of  $\text{CeO}_x$ , which could contribute to  $\text{NH}_3$ -SCR activity [13].

#### 4. Conclusion

Co, Ce, Cr, Mo, Ni were introduced to catalyst  $\text{V}_2\text{O}_5/\text{TiO}_2$ -CNTs with sol-gel method and Ce was proved to be most effective to promote  $\text{NH}_3$ -SCR activity. A large number of  $\text{Ce}^{3+}$  contributes to the increase of chemisorbed oxygen, which favors the SCR activity. The aggregation of catalyst might be inhibited by  $\text{CeO}_x$  thus result to the increase of specific surface. Moreover, the increase of surface acidity and reducibility both contribute to the extra  $\text{NO}_x$  conversion upon addition of  $\text{CeO}_x$ . The deactivation of catalyst  $\text{V/Ce}_9\text{Tic}$  caused by  $\text{SO}_2$  depends on reaction temperatures and gas velocity strongly. And at least 2% of oxygen in exhaust gas is essential to keep high SCR activity.

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