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# PAPER



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# Simultaneous removal of elemental mercury and NO from simulated flue gas using a CeO<sub>2</sub> modified $V_2O_5$ -WO<sub>3</sub>/TiO<sub>2</sub> catalyst<sup>+</sup>

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To provide insight into optimizing flue gas treatment, simultaneous removal of elemental mercury (Hg<sup>0</sup>) and NO using a CeO<sub>2</sub> modified V<sub>2</sub>O<sub>5</sub>–WO<sub>3</sub>/TiO<sub>2</sub> catalyst was investigated. The results show that a novel V<sub>2</sub>O<sub>5</sub>–WO<sub>3</sub>/TiO<sub>2</sub>–CeO<sub>2</sub> catalyst exhibits excellent Hg<sup>0</sup> oxidation efficiency (88%) and NO conversion efficiency (89%) at 250 °C. Furthermore, CeO<sub>2</sub> modified V<sub>2</sub>O<sub>5</sub>–WO<sub>3</sub>/TiO<sub>2</sub> not only exhibits enhanced catalytic activity but also good resistance in SO<sub>2</sub> and H<sub>2</sub>O. These catalysts were also characterized using BET, SEM, XRD, XPS, and H<sub>2</sub>-TPR. We found lower crystallinity, more reduced species and better texture properties to be presented, which were all ascribed to CeO<sub>2</sub> doping. Also, the redox cycle (V<sup>4+</sup> + Ce<sup>4+</sup>  $\leftrightarrow$  V<sup>5+</sup> + Ce<sup>3+</sup>) plays a key role in promoting Hg<sup>0</sup> oxidation and NO conversion. In tune with the experimental results, a mechanism for the simultaneous removal of Hg<sup>0</sup> and NO was proposed for the V<sub>2</sub>O<sub>5</sub>–WO<sub>3</sub>/TiO<sub>2</sub>–CeO<sub>2</sub> catalysts.

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## 1. Introduction

Nitrogen oxides  $(NO_x)$  and gas-phase mercury emitted from coal-fired power plants are major air pollutants.  $NO_x$  emissions can contribute significantly to various environmental problems such as acid rain, photochemical smog, ozone depletion and greenhouse effects. Mercury has seriously harmful effects on the central nervous system and can cause many diseases, such as pulmonary and renal failure, respiratory damage, blindness, and chromosome damage.<sup>1</sup> Many countries have taken steps to reduce emissions of  $NO_x$  and gas phase mercury. For example, on December 21, 2011, the US Environmental Protection Agency (USEPA) announced standards to limit mercury, acid gases and other toxic pollution from power plants.<sup>2,3</sup>

To comply with environmental and pollutant emission control regulations, various methods and technologies have been proposed/practised to regulate emissions of  $NO_x$  and gas phase mercury. Among them, selective catalytic reduction of  $NO_x$  with  $NH_3$  ( $NH_3$ -SCR) is regarded as one of the most effective technologies for the removal of  $NO_x$ , and  $V_2O_5/TiO_2$ -

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based catalysts have been widely used for this process.<sup>4,5</sup> Catalysts used in the SCR process, especially V2O5-WO3/TiO2 catalysts, could facilitate the catalytic oxidation of elemental mercury (Hg<sup>0</sup>) to oxidized mercury (Hg<sup>2+</sup>) when NO is reduced by NH<sub>3</sub>.<sup>6</sup> Subsequently, the highly water soluble Hg<sup>2+</sup> can be captured efficiently in a wet flue gas desulfurization (WFGD) system.<sup>7</sup> Since single pollutant control technologies result in high investment and operating cost, we illustrate that SCR technology for the simultaneous removal of Hg<sup>0</sup> and NO<sub>x</sub> paves the way to low-cost treatment of coal-fired flue gas. However, the ability to overcome the limitations of SCR technology, whether the narrow operating temperature window of 300-400 °C or the low surface areas of TiO<sub>2</sub> supports,<sup>8,9</sup> remains a challenge. In addition, V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> (VWTi) catalysts are not effective enough for Hg<sup>0</sup> oxidation under flue gas without or with low HCl concentrations.<sup>10</sup>

Luckily, a lot of work has been carried out to find new SCR catalyst systems. Ceria based oxides with the advantages of high oxygen storage capacities (OSC), d-electron orbitals, good sulfur resistance, and excellent redox properties have attracted more and more attention.<sup>11</sup> The most important property of ceria in those studies is as an additive or support for the catalysts, which stores and releases oxygen *via* a redox shift between Ce<sup>4+</sup> and Ce<sup>3+</sup> under oxidizing and reducing conditions, respectively.<sup>12,13</sup> Significantly, many researchers have focused on the development of ceria based catalysts for NH<sub>3</sub>-SCR.<sup>14–20</sup> The results of their experiments suggest that optimized ceria based catalysts exhibit excellent catalytic performance in the NH<sub>3</sub>-SCR reaction. Interestingly, ceria based

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catalysts have also been studied as potential catalysts for Hg<sup>0</sup> oxidation.<sup>21-26</sup> In other words, a ceria based SCR catalyst can also serve as a catalyst for Hg<sup>0</sup> oxidation. For example, He et al.<sup>27</sup> reported that MnO<sub>x</sub>/CeO<sub>2</sub>-TiO<sub>2</sub> catalysts were effective for both Hg<sup>0</sup> oxidation and low temperature SCR of NO<sub>x</sub>. Moreover, Ce-doped V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalysts synthesized by an ultrasound assisted impregnation method were also employed to investigate the simultaneous removal of Hg<sup>0</sup> and NO in lab-scale experiments. However, deactivation by SO2 and H<sub>2</sub>O, and low surface area of TiO<sub>2</sub> support<sup>28</sup> are slightly taken into account in these studies. This has also led to new inspired ideas. For example, Liu et al.<sup>29</sup> suggested that the enhancement of catalytic activity could be attributed to the synergetic interaction between V<sub>2</sub>O<sub>5</sub> (V) and CeO<sub>2</sub> (Ce). It was found that the synergetic effect between V and Ce could result in superior SCR performance and alkali resistance. Furthermore, in our previous work,<sup>30</sup> because of the synergetic effect between cerium and vanadium species, modification of VWTi catalysts with Ce not only improved the surface area of the TiO<sub>2</sub> support but also obviously enhanced the activity of Hg<sup>0</sup> oxidation. Therefore, we anticipate that, regarding the deactivation by SO<sub>2</sub> and H<sub>2</sub>O, a strategy focusing on simultaneous removal of Hg<sup>0</sup> and NO in simulated flue gas using a CeO<sub>2</sub> modified VWTi catalyst will be desirable for practical applications.

Accordingly, in the present study,  $TiO_2$ -CeO<sub>2</sub> as a nanostructured material was used as a support to synthesize VW/ TiCe catalysts, which is considered a promising catalyst for the simultaneous removal of Hg<sup>0</sup> and NO. Catalytic activity tests were performed under simulated flue gas at 100–400 °C in the absence of HCl. The series of VW/TiCe catalysts was characterized using X-ray diffraction (XRD), Brunauer– Emmett–Teller (BET), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FT-IR) and temperature-programmed reduction of H<sub>2</sub> (H<sub>2</sub>-TPR). Furthermore, the detailed reaction mechanism of the simultaneous removal of Hg<sup>0</sup> and NO was also studied.

## 2. Experimental section

### 2.1. Catalyst preparation

 $TiO_2$  and  $TiO_2$ -CeO<sub>2</sub> supports were synthesized using a solgel method, which is similar to our previous study.<sup>30</sup> All of the reagents used in this work were analytically pure grade (AR). A solution of anhydrous ethanol (2.3 mol) and butyl titanate (0.1 mol) was added dropwise to another solution of deionized water (1.9 mol), anhydrous ethanol (0.6 mol), nitric acid (0.1 mol) and a certain amount of cerium nitrate with vigorous stirring at room temperature for 5 h. After continuous stirring, a yellowish transparent sol was yielded. Subsequently, the sol was concentrated in a 40 °C water bath for 2 h and then dried at 80 °C for 24 h to form a xerogel. After being crushed and sieved to 100–120 mesh, the xerogel was calcinated at 500 °C for 5 h with air. The obtained supports were denoted as  $TiCe_x$ , where *x* represents the molar ratio of  $CeO_2/TiO_2$  (*x* = 0.02; 0.05; 0.08; 0.11; 0.15).

The catalysts used in this study were prepared by the ultrasound-assisted impregnation of  $\text{TiCe}_x$  powder with an aqueous solution of ammonium metavanadate (0.80 wt% V<sub>2</sub>O<sub>5</sub> in catalyst) and ammonium tungstate (8.0 wt% WO<sub>3</sub> in catalyst) in oxalic acid. The mixed solution was stirred completely in a water bath at 80 °C for 2 h. Then, the mixture was exposed to an ultrasonic bath for 2 h. Finally, the catalyst was dried at 105 °C for 12 h, followed by calcination at 500 °C for 3 h. The catalysts are denoted as VWTiCe<sub>x</sub> ("x" represents the CeO<sub>2</sub>/TiO<sub>2</sub> molar ratio; x = 0.02; 0.05; 0.08; 0.11; 0.15). Typically, the molar loadings of V<sub>2</sub>O<sub>5</sub> and WO<sub>3</sub> on all catalysts were 0.80% and 8.0%, respectively.

#### 2.2. Catalyst characterization

The morphologies and surface structure of the samples were determined using a Hitachi S-4800 (Hitachi Limited, Japan) scanning electron microscope (SEM). The separated areas for each sample were magnified to 10 000× and 100 000×.

The Brunauer-Emmett-Teller (BET) surface area, pore volume and average pore diameter of catalysts were obtained from  $N_2$  adsorption isotherms using a Micromeritics Tristar II 3020 analyzer (Micromeritics Instrument Crop, USA). The specific surface area was calculated using the standard Brunauer-Emmett-Teller (BET) equation. Prior to the analysis, all samples were degassed under vacuum at 120 °C for 5 h.

X-ray diffraction (XRD) patterns of the samples were recorded at room temperature with Cu-K $\alpha$  radiation (l = 1.5406 Å) in a Rigaku Rotaflex D/Max-C powder diffractometer (Rigaku, Japan). Data were collected for scattering angles ( $2\theta$ ) ranging from 10 to 80° with a step of 0.02° for 1 s per point.

X-ray photoelectron spectroscopy (XPS) data were obtained on a K-alpha 1063 X-ray photoelectron spectrometer (Thermo Fisher Scientific, UK) using an Al  $K_{\alpha}$  X-ray source operated at 12 kV and 6 mA. The observed spectra were calibrated with a carbon 1s electron binding energy (BE) value of 284.6 eV.

Fourier transform infrared spectroscopy (FT-IR) was performed on a SHIMADZU FT-IR-8400S IRPrestige-21 apparatus with a resolution of 2 cm<sup>-1</sup>, accumulating 20 scans. A self-supported wafer was prepared by pressing 2 mg of sample mixed with KBr (200 mg, spectroscopically pure) and then loaded into an IR cell. The pretreatment process was as follows: the samples were treated at 250 °C in N<sub>2</sub> for 30 min to remove any adsorbed species. After the sample was cooled to room temperature, several combinations of different gases including NH<sub>3</sub>, NO + O<sub>2</sub>, NO + O<sub>2</sub> + SO<sub>2</sub> and NO + O<sub>2</sub> + SO<sub>2</sub> + H<sub>2</sub>O, were introduced to the reaction tube for 60 min, then FT-IR experiments were conducted immediately.

Temperature-programmed reduction of  $H_2$  ( $H_2$ -TPR) was performed on a AutoChem 2920 automated chemisorption analyzer (Micromeritics Instrument Crop, USA) using approximately 0.1 mg of sample. The  $H_2$ -Ar mixer (5%  $H_2$  by volume) was switched to a flow rate of 40 mL min<sup>-1</sup>. The temperature was increased linearly from 50 to 750 °C at a rate of 10 °C min<sup>-1</sup> while  $H_2$  consumption was recorded continuously.

#### 2.3. Catalytic performance test

The activities of various catalysts for the simultaneous removal of Hg<sup>0</sup> and NO were analyzed in a fixed bed quartz reactor (i.d. 20 mm) containing 500 mg of catalyst, as shown in Fig. 1. Gas-phase Hg<sup>0</sup> was generated using a Hg<sup>0</sup> permeation tube (VICI Metronics, USA). The simulated flue gas (SFG) components including 700 ppm NO, 700 ppm NH<sub>3</sub>, 5 vol%  $O_2$ , 70 µg m<sup>-3</sup> Hg<sup>0</sup> and 400 ppm SO<sub>2</sub> were precisely controlled by mass flow controllers (MFC). 8 vol% H<sub>2</sub>O (when used) was exactly controlled by a peristaltic pump and injected into a Teflon tube that was wrapped with temperature-controlled heating tape. Then, water vapor was generated. 100 mL min<sup>-1</sup> pure  $N_2$  took along the water vapor to mix with the flue gas. All the Teflon tubes that Hg<sup>0</sup> and water vapor passed through were heated up to 120 °C by heating belts to limit Hg<sup>0</sup> and water vapor condensation. A total flow rate of 500 mL min<sup>-1</sup> was maintained for all experiments with N2 as the balance gas. The tests were completed from 100 to 400 °C at a gas hourly space velocity (GHSV) of 50 000  $h^{-1}$ . The concentration of NO<sub>x</sub> in the inlet (NO<sub>in</sub>) and outlet (NO<sub>out</sub>) gas was measured using a flue gas analyzer (MGA5, Germany). The inlet (Hg<sup>0</sup><sub>in</sub>) and outlet (Hg<sup>0</sup><sub>out</sub>) Hg<sup>0</sup> concentrations were measured using an online RA-915M mercury analyzer (LUMEX Ltd, Russia). Meanwhile, a mercury conversion system was employed to measure the outlet Hg<sup>0</sup> and total Hg<sup>0</sup> concentrations when it was necessary. The mercury conversion system was described in our previous study.<sup>31</sup> After the catalytic process had reached equilibrium, all of the catalysts were kept on stream at each temperature for 2 h. In other words, the inlet gas was monitored until the desired inlet NO/Hg<sup>0</sup> concentration variation less than 5% had been obtained at least 30 min. According to previous studies,<sup>2,32-34</sup> the catalysts were firstly saturated with the established  $Hg_{in}^0$  under a  $N_2$  atmosphere at room temperature to avoid possible bias because of Hg<sup>0</sup> physical adsorption. Less than 10 min was needed for Hg<sup>0</sup> saturation, demonstrating that the Hg<sup>0</sup> physical adsorption capacity of the VWTiCe $_x$  catalysts is negligible. Hence, the Hg<sup>0</sup> oxidation efficiency ( $\eta_{Hg}$ ) and the NO conversion efficiency  $(\eta_{NO})$  can be defined as follows:

$$\eta_{\rm Hg}(\%) = \frac{\Delta {\rm Hg}^{0}}{{\rm Hg}^{0}_{\rm in}} = \frac{{\rm Hg}^{0}_{\rm in} - {\rm Hg}^{0}_{\rm out}}{{\rm Hg}^{0}_{\rm in}} \times 100\%$$
(1)

$$\eta_{\rm NO}(\%) = \frac{\rm NO_{in} - \rm NO_{out}}{\rm NO_{in}} \times 100\%$$
(2)

All or part of the  $\Delta Hg^0$  (Hg<sup>2+</sup>) was captured on the samples in the solid phase and the rest escaped as the outlet gas in the gas phase. Note that in this study, the total Hg<sup>0</sup> concentrations were always higher than the Hg<sup>0</sup> concentrations in



Fig. 1 Schematic diagram of the experimental setup.

the outlet flue gas (in Table S1<sup>†</sup>), indicating that a small portion of the  $Hg^{2+}$  exists in the outlet flue gas, and the rest was captured on the catalysts (approximately 80%  $Hg^{2+}$  captured efficiently).

## 3. Results and discussion

#### 3.1. Catalytic activity tests

3.1.1. Effect of the molar ratio of Ce/Ti. The main objective of this study was to achieve the simultaneous removal of Hg<sup>0</sup> and NO using CeO<sub>2</sub> promoted V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> materials. In real applications, in addition to gas phase mercury, NO and SO<sub>2</sub> are two typical components of flue gas. Hence, the simultaneous removal of NO and Hg<sup>0</sup> was tested in the presence of 400 ppm SO<sub>2</sub>. Table 1 shows the effect of the molar ratio of CeO<sub>2</sub>/TiO<sub>2</sub> (Ce/Ti) on the performance of the VWTiCe catalysts. Obviously, a higher Ce doping enhances catalytic activity and widens the temperature range, showing increasing NO conversion and Hg<sup>0</sup> oxidation until the molar ratio of Ce/Ti reaches 0.08. At 250 °C, Hg<sup>0</sup> oxidation efficiency and NO conversion efficiency are 88% and 89%, respectively. However, further increasing the Ce doping leads to a decrease in catalytic activity. It has been reported that sintering would take place in the catalyst when the loading of the active component increased beyond a certain value.<sup>35</sup> Hence, further increasing the Ce doping might sinter Ce, resulting in lower activity.

**3.1.2. Effect of GHSV.** GHSV is a crucial parameter for practical applications, especially for the system to be used for the selective catalytic reduction of  $NO_x$  with  $NH_3$ . The activity of the VWTiCe<sub>0.08</sub> catalyst was measured at different reaction temperatures in the GHSV range of 25 000–100 000 h<sup>-1</sup>, and the results are shown in Fig. 2. Obviously, the catalytic activity decreases over the whole temperature window as GHSV increases from 25 000 to 100 000 h<sup>-1</sup>. It can be seen that the temperature window at a GHSV of 25 000 h<sup>-1</sup> is broader than at a GHSV of 100 000 h<sup>-1</sup>. This may be due to a longer contact time for reactant gases to react on the catalysts as the GHSV decreases.<sup>18</sup>

**3.1.3. Effect of NH**<sub>3</sub>/NO ratio. It is very important to identify the effect of NH<sub>3</sub> on the NH<sub>3</sub>-SCR reaction and Hg<sup>0</sup> oxidation. A shortage of NH<sub>3</sub> could result in a low NO conversion. In contrast, an excess of NH<sub>3</sub> not only pollutes the environment but also reacts with SO<sub>2</sub> to form sulfate.<sup>18</sup> The effect of



**Fig. 2** The effect of GHSV on the simultaneous removal of Hg<sup>0</sup> and NO over VWTiCe<sub>0.08</sub>: (a) Hg<sup>0</sup> oxidation efficiency and (b) NO conversion efficiency (reaction conditions: 70  $\mu$ g m<sup>-3</sup> Hg<sup>0</sup>, 700 ppm NO, NH<sub>3</sub>/NO: 1, 5 vol% O<sub>2</sub>, 400 ppm SO<sub>2</sub>, 500 mg of sample, total flow rate 250 mL min<sup>-1</sup>, 500 mL min<sup>-1</sup>, 1000 mL min<sup>-1</sup>; GHSV 25 000 h<sup>-1</sup>, 50 000 h<sup>-1</sup>, and 100 000 h<sup>-1</sup>).

NH<sub>3</sub>/NO ratio on Hg<sup>0</sup> oxidation and NO conversion was investigated and the results are shown in Fig. 3. The Hg<sup>0</sup> oxidation efficiency decreased quickly from 95% to 79% with an increase of the NH<sub>3</sub>/NO ratio from 0 to 1.2. On the contrary, NO conversion increased with increasing the NH<sub>3</sub>/NO ratio. Qi *et al.*<sup>12</sup> proposed that gaseous NH<sub>3</sub> is adsorbed on the catalyst surface to form coordinated NH<sub>3</sub> and NH<sub>2</sub>. The possible reactions take place according to the following steps:

$$NH_3(g) \rightarrow NH_3(ad)$$
 (3)

**Table 1** Effect of the molar ratio of  $CeO_2/TiO_2$  (Ce/Ti) on the performance of VW/TiCe (reaction conditions: 70 µg m<sup>-3</sup> Hg<sup>0</sup>, 700 ppm NO, NH<sub>3</sub>/NO: 1, 5 vol%  $O_2$ , 400 ppm SO<sub>2</sub>, 500 mg of sample, total flow rate 500 mL min<sup>-1</sup>, GHSV 50 000 h<sup>-1</sup>)

			η <sub>Hg</sub> /%						$\eta_{ m NO}/\%$				
T∕°C	VWTi	VW/Ti Ce <sub>0.02</sub>	VW/Ti Ce <sub>0.05</sub>	VW/Ti Ce <sub>0.08</sub>	VW/Ti Ce <sub>0.11</sub>	VW/Ti Ce <sub>0.15</sub>	VWTi	VW/Ti Ce <sub>0.02</sub>	VW/Ti Ce <sub>0.05</sub>	VW/Ti Ce <sub>0.08</sub>	VW/Ti Ce <sub>0.11</sub>	VW/Ti Ce <sub>0.15</sub>	
100	23	56	58	62	63	59	10	13	16	18	18	20	
150	28	57	67	77	76	67	26	30	40	43	46	54	
200	34	66	74	80	79	70	35	56	60	64	70	76	
250	41	69	83	88	86	71	53	81	84	89	86	87	
300	49	67	76	82	78	68	82	82	84	89	85	83	
350	45	56	66	68	64	55	83	84	85	86	81	79	
400	35	55	61	61	59	51	82	84	83	86	80	78	

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Fig. 3 Effect of NH<sub>3</sub>/NO ratio for the simultaneous removal of Hg<sup>0</sup> and NO over VWTiCe<sub>0.08</sub> catalysts at 250 °C (reaction conditions: 70  $\mu$ g m<sup>-3</sup> Hg<sup>0</sup>, 700 ppm NO, 5 vol% O<sub>2</sub>, 400 ppm SO<sub>2</sub>, 500 mg of sample, 500 mL min<sup>-1</sup> total flow rate, GHSV 50 000 h<sup>-1</sup>; NH<sub>3</sub>/NO: 0, 0.2, 0.4, 0.8, and 1.2).

$$NH_3(ad) + O^*(ad) \rightarrow NH_2(ad) + OH(ad)$$
 (4)

where  $O^*$  is active surface oxygen of the catalyst. On one hand,  $NH_3$  consumes surface oxygen which is responsible for  $Hg^0$  oxidation. This results in a significant decrease of  $Hg^0$ oxidation efficiency. On the other hand, the formation of  $NH_2$  is considered to be the key step in the process of NO reduction on V–TiO<sub>2</sub>.<sup>36</sup> Combined with the FT-IR results discussed later, it could be inferred that gaseous NO is first adsorbed on the catalyst and then reacts with  $NH_2$  to form a nitrosamine ( $NH_2NO$ ) that decomposes into  $N_2$  and  $H_2O$ . Besides, NO molecules are also adsorbed on the catalyst and then oxidized to nitrate and nitrite in the presence of oxygen.

3.1.4. Effect of H<sub>2</sub>O and SO<sub>2</sub>. SO<sub>2</sub> and H<sub>2</sub>O<sub>(g)</sub> are the main components of coal-fired flue gases. Therefore, the influence of SO<sub>2</sub> and H<sub>2</sub>O<sub>(g)</sub> on catalytic performance over VWTiCe<sub>0.08</sub> must be considered. Fig. 4a illustrates the activity performance of VWTiCe<sub>0.08</sub> as a function of SO<sub>2</sub> concentration. It is observed that a low concentration of SO<sub>2</sub> promotes Hg<sup>0</sup> oxidation, while a high concentration of SO<sub>2</sub> suppresses Hg<sup>0</sup> oxidation. Obviously, when 200 ppm SO<sub>2</sub> was added to the flue gas flow, Hg<sup>0</sup> oxidation efficiency increased from 65% to 73%. Besides, an increase of Hg<sup>0</sup> oxidation efficiency was observed when the concentration of SO<sub>2</sub> is further increased from 200 to 400 ppm. However, with a further increase in  $SO_2$  concentration, the  $Hg^0$  oxidation efficiency decreases. The results indicate that SO<sub>2</sub> possesses both promotional and inhibitive effects on Hg<sup>0</sup> oxidation over the VWTiCe<sub>0.08</sub> catalyst, and the specific effect depends on the SO<sub>2</sub> concentration in the flue gas. In addition, NO conversion decreases slightly with an increase of SO<sub>2</sub> concentration from 200 to 800 ppm. This suggests that the VWTiCe catalysts have excellent SO<sub>2</sub> resistance performance.

It has been reported that  $H_2O$  inhibits  $Hg^0$  oxidation and removal over metal or metal oxide-based catalysts due to competitive adsorption on active sites.<sup>25,37</sup> However, the Ce-based catalysts exhibited strong resistance to  $H_2O$  poisoning.<sup>24,38</sup>



Fig. 4 Simultaneous removal of Hg<sup>0</sup> and NO over VWTiCe<sub>0.08</sub> at 250 °C in flue gas consisting of (a) 70  $\mu$ g m<sup>-3</sup> Hg<sup>0</sup>, 700 ppm NO, 700 ppm NH<sub>3</sub>, 5 vol% O<sub>2</sub>, 0–800 ppm SO<sub>2</sub> and N<sub>2</sub> as a balance; (b) 70  $\mu$ g m<sup>-3</sup> Hg<sup>0</sup>, 700 ppm NO, 700 ppm NH<sub>3</sub>, 5 vol% O<sub>2</sub>, 400 ppm SO<sub>2</sub> (when used) 8 vol% H<sub>2</sub>O vapor (when used) and N<sub>2</sub> as a balance gas.

The effects of H<sub>2</sub>O and SO<sub>2</sub> on the catalytic activity of the VWTiCe<sub>0.08</sub> catalysts are illustrated in Fig. 4b. The instantaneous value of the simultaneous removal of Hg<sup>0</sup> and NO was measured to see how the catalytic activity of the VWTiCe<sub>0.08</sub> catalysts changes over time. After 400 ppm SO2 was introduced to the SCR atmosphere (700 ppm NO, NH<sub>3</sub>/NO: 1, 5 vol% O<sub>2</sub>, 70 µg m<sup>-3</sup> Hg<sup>0</sup>) at 250 °C, NO conversion decreased slightly while Hg<sup>0</sup> oxidation efficiency increased during 12 h of testing. Besides, when 8 vol% H<sub>2</sub>O was added to the simulated flue gas (700 ppm NO, 700 ppm NH<sub>3</sub>, 5 vol% O<sub>2</sub>, 70 µg m<sup>-3</sup> Hg<sup>0</sup> and 400 ppm SO<sub>2</sub>), NO conversion efficiency on VWTiCe<sub>0.08</sub> decreased from 89% to 85% in 7 h. Meanwhile, Hg<sup>0</sup> oxidation efficiency decreased slightly from 87% to 83%. However, compared with the previous literature,<sup>39,40</sup> VWTiCe<sub>0.08</sub> was relatively less affected by H<sub>2</sub>O, indicating that the VWTiCe catalyst has good resistance to H<sub>2</sub>O. After excluding H<sub>2</sub>O from the reactant feed, the activity was quickly restored to its original level. This indicates that the decrease of activity by H<sub>2</sub>O results from the competing adsorption of  $H_2O.$ 

**3.1.5. Effect of O\_2 concentration.** To obtain higher catalytic oxidation, the presence of  $O_2$  is normally necessary,

especially for metal oxide catalysts.<sup>2</sup> The effect of  $O_2$  on the catalytic activity of VWTiCe<sub>0.08</sub> is shown in Fig. 5.  $O_2$  exhibits a promotional effect on catalytic activity. The addition of 2 vol% gas phase  $O_2$  to a gas flow containing 400 ppm SO<sub>2</sub> balanced in  $N_2$  results in a significant increase in Hg<sup>0</sup> oxidation efficiency and NO conversion efficiency. A further increase in  $O_2$  concentration to 5 vol% results in an even higher Hg<sup>0</sup> oxidation efficiency and NO conversion efficiency, implying that  $O_2$  is beneficial to the catalytic activity of the catalyst. Gas phase  $O_2$  regenerates lattice oxygen and replenishes chemisorbed oxygen,<sup>33</sup> which facilitates Hg<sup>0</sup> oxidation and NO conversion.

#### 3.2. Catalyst characterization

**3.2.1. BET and XRD.** The physical properties of the catalysts including BET surface area, total pore volume and average pore size are summarized in Table 2. The surface area, total pore volume and average pore diameter increased markedly with an increase of the Ce/Ti molar ratio from 0 to 0.08, but further adding Ce led to decreasing texture properties. This experimental phenomenon might be related to the state of Ce dispersion, which exists as an amorphous species or crystallite phase with very small particle size. Thus, the physical properties of the catalysts were improved. When the addition of Ce is further increased, it might be assembled or sintered on the surface of the carriers which results in a decline in texture properties. VWTiCe<sub>0.08</sub> has excellent physical properties, which might result from its best activity.

The XRD spectra of the VWTi and VWTiCe<sub>x</sub> catalysts are displayed in Fig. 6. For VWTi, diffraction peaks of both anatase titania and rutile titania were obtained, with anatase titania being the dominant phase. When CeO<sub>2</sub> was added into VWTi, only that of the anatase phase was observed. This result means that the addition of CeO<sub>2</sub> into the support of VWTi could effectively stabilize the anatase phase and inhibit the phase transition from anatase to rutile.<sup>15</sup> Besides, compared with VWTi, the diffraction of TiO<sub>2</sub> over VWTiCe<sub>x</sub> was much weaker, which indicates that Ce and Ti oxide had a



Fig. 5 The effect of O<sub>2</sub> concentration on the simultaneous removal of Hg<sup>0</sup> and NO over VWTiCe<sub>0.08</sub> at 250 °C (reaction conditions: 70  $\mu$ g m<sup>-3</sup> Hg<sup>0</sup>, 700 ppm NO, NH<sub>3</sub>/NO: 1, 400 ppm SO<sub>2</sub>, 0-10 vol% O<sub>2</sub>, 500 mg of sample, 500 mL min<sup>-1</sup> total flow rate and GHSV 50 000 h<sup>-1</sup>).

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Table 2 BET surface and pore parameters of the different catalysts

Catalysts	BET surface area $(m^2 g^{-1})$	Pore volume $(cm^3 g^{-1})$	Average pore diameter (nm)
VW/Ti	45	0.12	11
VW/TiCe <sub>0.02</sub>	90	0.21	9.4
VW/TiCe <sub>0.05</sub>	104	0.26	9.9
VW/TiCe <sub>0.08</sub>	107	0.28	10
VW/TiCe <sub>0 11</sub>	106	0.26	10
VW/TiCe <sub>0.15</sub>	104	0.25	9.7



Fig. 6 XRD patterns of various catalysts.

strong interaction in these catalysts. Modification by Ce led to a decrease in TiO<sub>2</sub> crystallinity. Obviously, no cubic CeO<sub>2</sub> phase was observed. It was inferred that ceria exists as an amorphous phase or crystallite phase with very small particle size in the bulk of the TiO<sub>2</sub> support, which results in a significant increase of catalytic activity.<sup>30</sup> Likewise, VWTi and VWTiCe<sub>0.08</sub> were evaluated using the Scherrer equation, and the small particle sizes for VWTi and VWTiCe<sub>0.08</sub> were 20 nm and 9 nm, respectively, from the scattering angles (2 $\theta$ ) at 25.34°.

3.2.2. SEM. SEM images of selected samples are shown in Fig. 7. The SEM images show that the microstructure of VWTi was influenced by the addition of Ce. It was seen that active components could disperse on the surface of the catalysts (Fig. 7a-d). However, agglomerations formed on the surface of the catalyst (Fig. 7e and f). The particles first decreased with an increase of Ce/Ti molar ratio, and then increased when the Ce/Ti molar ratio was further increased from 0.08 to 0.15. For the VWTiCe $_{0.08}$  (Fig. 7d), higher porosity and larger average pore size were observed. From Fig. 7(B), it is clear that the prepared catalyst is nanoparticles and its size was about 5-25 nm in length. Meanwhile, the particle size of VWTiCe<sub>0.08</sub> was slightly smaller than that of VWTi, indicating that Ce doping could somewhat decrease the particle size of the catalyst. These results are in agreement with the size estimated by XRD analysis. It has been reported that the catalyst particles in nanoscale can exhibit high activity.<sup>41</sup>

**3.2.3.** H<sub>2</sub>-**TPR**. The redox properties of the catalyst were characterized using H<sub>2</sub>-TPR as shown in Fig. 8. TiCe<sub>0.08</sub> exhibits two reduction peaks at around 532 °C and 650 °C. The



Fig. 7 SEM photographs of the catalysts: (a) VWTi, (b) VWTiCe<sub>0.02</sub>, (c) VWTiCe<sub>0.05</sub>, (d) VWTiCe<sub>0.08</sub>, (e) VWTiCe<sub>0.11</sub>, and (f) VWTiCe<sub>0.15</sub>. (A) 10 000 multiplier and (B) 100 000 multiplier.

former peak was assigned probably to the reduction of the surface oxygen of ceria and the second one was due to the reduction of dispersed CeO<sub>2</sub>, bulk CeO<sub>2</sub> and TiO<sub>2</sub>.<sup>19,42</sup> VWTi exhibits two reduction peaks at around 532 and 700 °C, which could be assigned to the reduction of surface oxygen and lattice oxygen, respectively.<sup>19</sup> Typically, the addition of Ce to the VWTi catalyst caused some changes in the TPR profiles. According to the literature,<sup>29,43,44</sup> the overlapped reduction peak in the temperature range of 350–560 °C could result from the reduction of surface Ce<sup>4+</sup> to Ce<sup>3+</sup> and V<sup>5+</sup> to V<sup>4+</sup> because of interaction between vanadium and cerium oxide. Be-

sides, the TPR profiles of the VWTiCe<sub>0.08</sub> present multireduction peaks at 250–350 °C and 600–750 °C. These multireduction peaks arise from the interaction between V and Ce, which may be ascribed to the reduction of surface oxygen and lattice oxygen respectively.<sup>19</sup> This indicates that modification of the support of VWTi results in better texture properties and more reduced species.

**3.2.4. XPS.** In order to determine the chemical state and the relative proportion of elements on the surface of the catalysts, XPS analysis was conducted on fresh and used VWTiCe<sub>0.08</sub> catalysts. Analysis of the used VWTiCe<sub>0.08</sub> catalysts



Fig. 8  $H_2$ -TPR profiles of various catalysts.

was carried out in the fixed bed reaction system under an SCR atmosphere with or without SO<sub>2</sub> at 250 °C, as shown in Fig. 9. A series of peaks denoted by "*u*" and " $\nu$ " represent the contributions of the Ce  $3d_{3/2}$  and Ce  $3d_{5/2}$  states, respec-

tively.<sup>45</sup> The bands labeled  $u^1$  and  $v^1$  represent the  $3d^{10}4f^1$ initial electronic state corresponding to Ce<sup>3+</sup>, whereas the peaks labelled  $u, u^2, u^3, v, v^2$ , and  $v^3$  represent the  $3d^{10}4f^0$ state of Ce<sup>4+</sup> ions.<sup>46</sup> Apparently, as shown in Fig. 9a, the ratio of Ce<sup>4+</sup>/Ce<sup>3+</sup> decreased from 2.0 to 1.8 after the addition of VWTiCe<sub>0.08</sub> under an SCR atmosphere without SO<sub>2</sub>. The increase of Ce<sup>3+</sup> could create a charge imbalance, vacancies, and unsaturated chemical bonds on the catalyst surface, leading to more surface oxygen forming over the VWTiCe<sub>0.08</sub> catalyst. The XPS results for V 2p are shown in Fig. 9b. The V 2p spectra could be divided into two characteristic peaks at 516.2 and 517.3 eV, which are ascribed to  $V^{4+}$  and  $V^{5+}$ , respectively.<sup>47,48</sup> It is obvious that the ratio of  $V^{5+}/V^{4+}$  increases from 0.91 to 1.1 after the test without SO<sub>2</sub>. The redox couple Ce4+/Ce3+ could transfer electrons to V5+, thus leading to more reducible V<sup>5+</sup>.

The O1s spectra were fitted to two characteristic peaks at 529.6 and 531.7 eV, which were ascribed to lattice oxygen (denoted as  $O_{\beta}$ ) and chemisorbed oxygen (denoted as  $O_{\alpha}$ ),



**Fig. 9** XPS spectra of VWTiCe<sub>0.08</sub> over the spectral regions of Ce 3d, V 2p and O 1 s before the test, and Ce 3d, V 2p, O 1s, Hg 4f, and S 2p after the test with or without SO<sub>2</sub>, (a) Ce 3d, (b) V 2p, (c) O 1s, (d) Hg 4f, and (e) S 2p (reaction conditions: 70  $\mu$ g m<sup>-3</sup> Hg<sup>0</sup>, 700 ppm NO, NH<sub>3</sub>/NO: 1, 0/400 ppm SO<sub>2</sub>, 5 vol% O<sub>2</sub>, 500 mg of sample, 500 mL min<sup>-1</sup> total flow rate and GHSV 50 000 h<sup>-1</sup>).

respectively<sup>49</sup> (see Fig. 9c). In the absence of SO<sub>2</sub>, the content of O<sub>β</sub> was 46% and 49% before and after the reaction, while that of O<sub>α</sub> was 54% and 51%, respectively. These observations suggest that the increase of lattice oxygen species results from the increase of Ce<sup>3+</sup> after testing. Similarly, it could also be seen that V<sup>4+</sup> and Ce<sup>4+</sup> still exist on the used VWTiCe<sub>0.08</sub> catalyst. This fact further confirms that the two redox couples (V<sup>5+</sup>/V<sup>4+</sup> and Ce<sup>4+</sup>/Ce<sup>3+</sup>) were present on the catalyst.

The effect of SO<sub>2</sub> on the simultaneous removal of Hg<sup>0</sup> and NO by VWTiCe<sub>0.08</sub> was also studied using XPS analysis. In comparison with the reaction without SO<sub>2</sub>, there were no obvious changes in the atomic ratios of Ce<sup>4+</sup>/Ce<sup>3+</sup>, V<sup>5+</sup>/V<sup>4+</sup> and  $O_{\beta}/O_{\alpha}$ . In the absence of SO<sub>2</sub>, the peak at 99.8 eV was ascribed to Hg<sup>0</sup> (the binding energy at about 102.7 eV was attributed to Si 2p of SiO<sub>2</sub> in quartz wool).<sup>31,50</sup> The peaks at 101.9 and 103.8 eV correspond to the characteristic peaks of Hg  $4f_{7/2}$  and Hg  $4f_{5/2}$  for HgO (shown in Fig. 9d).<sup>22,50,51</sup> This indicates that the main product formed on the surface of VWTiCe<sub>0.08</sub> was HgO. According to our previous study,<sup>30</sup> Hg<sup>0</sup> oxidation mainly follows the Mars-Maessen mechanism. Furthermore, in the presence of  $SO_2$ , the Hg 4f peaks for the VWTiCe<sub>0.08</sub> catalyst after testing still appear at about 101.9 and 103.5 eV, indicating that the oxidized mercury formed was still mainly HgO. In addition, the S 2p peaks observed at approximately 168.8 and 170.0 eV correspond to SO<sub>4</sub><sup>2-</sup> and HSO<sub>4</sub>, respectively (shown in Fig. 9e).<sup>50</sup> However, combined with FT-IR analysis, the content of sulfate was too small to significantly affect the SCR reaction.

**3.2.5.** FT-IR. Fig. 10 shows FT-IR spectra of the VWTiCe<sub>0.08</sub> catalyst after being exposed to different gases for 60 min. As shown in Fig. 10a, several bands at 1065, 1126, 1196, 1270, 1425, 1511 and 1627 cm<sup>-1</sup> were observed after the catalyst was treated with NH<sub>3</sub> at room temperature. The bands at 1126, 1196 and 1627 cm<sup>-1</sup> were assigned to the symmetric and asymmetric bending vibrations of N–H bonds in NH<sub>3</sub> coordinately linked to Lewis acid sites, <sup>12,52,53</sup> and the band at 1425 cm<sup>-1</sup> may be attributed to the asymmetric and symmetric and symmetric and symmetric bending vibrations of NH<sub>4</sub><sup>+</sup> species on Brønsted acid sites. <sup>19,54,55</sup> Tsyganenko *et al.*<sup>56</sup> proposed that a NH<sub>2</sub> deformation mode was observed in the range of 1505–1580 cm<sup>-1</sup>.



Fig. 10 FT-IR spectra taken of VWTiCe<sub>0.08</sub>

Accordingly, the band at 1511 cm<sup>-1</sup> is attributed to amide  $(-NH_2)$  species. Moreover, the band at 1065 cm<sup>-1</sup> belongs to neither Lewis or Brønsted acid sites, which might be caused by ammonia hydrogen bonding to the surface oxygen atoms of cerium oxide.<sup>55,57</sup> Thus, both the coordinated NH<sub>3</sub> bound to Lewis acid sites and NH4<sup>+</sup> bound to Brønsted acid sites could participate in the NH<sub>3</sub>-SCR reaction. In the NO +  $O_2$  FT-IR curve, the band at 1623 cm<sup>-1</sup> is assigned to gas phase or weakly adsorbed NO<sub>2</sub> species.<sup>58</sup> The broad peaks in the range of 1500-1560 cm<sup>-1</sup> could be regarded as a series of successive peaks, which are attributed to NO<sub>2</sub>-containing species, such as nitrito (O-bound NO<sub>2</sub>) and nitrato (NO<sub>3</sub>) species.<sup>59,60</sup> Meanwhile, bidentate nitrates (1270 cm<sup>-1</sup>)<sup>46</sup> and monodentate nitrite species (1413 cm<sup>-1</sup>)<sup>54,55</sup> were also discernible on the catalysts. Anionic nitrosyl NO<sup>-</sup> species have been observed on CeO<sub>2</sub> giving rise to absorption in the region of 1200-1000 cm<sup>-1</sup>.<sup>61</sup> Accordingly, the bands at 1044 and 1131 cm<sup>-1</sup> are assigned to anionic nitrosyl NO<sup>-</sup> species, which could be oxidized to nitrate or nitrite species in the presence of oxygen. At the same time, in order to understand the effects of  $SO_2$  and  $H_2O$  on the SCR of NO, the  $SO_2$  + NO +  $O_2$  and  $H_2O + SO_2 + NO + O_2$  FT-IR spectra of VWTiCe<sub>0.08</sub> are depicted. As shown in Fig. 10c and d, when SO<sub>2</sub> was introduced, the bands that are attributed to NO<sub>2</sub>-containing species (1500-1560 cm<sup>-1</sup>) diminished while the absorption in the region of 1200-1000 cm<sup>-1</sup> strengthened. Herein, a new weak band at 1337 cm<sup>-1</sup> could be mainly related to the vibrations of chelating bidentate sulfates (SO<sub>4</sub><sup>2-</sup>).<sup>42</sup> However, most of the bands ascribed to nitrate or nitrite species stayed unchanged when SO<sub>2</sub> was introduced, indicating that SO<sub>2</sub> has little influence on the SCR of NO. In addition, in spite of the very weak band at 1209 cm<sup>-1</sup>, which could be assigned to stretching motion of adsorbed bisulfate or sulfate on the surface of the catalyst,<sup>62,63</sup> more NO<sub>2</sub>-containing species (1500-1560 cm<sup>-1</sup>) were formed when SO<sub>2</sub> was added with H<sub>2</sub>O. Therefore, it can be concluded that the activity of the catalyst was slightly affected by H<sub>2</sub>O and SO<sub>2</sub>.

#### 3.3. Mechanism discussion

For the VWTiCe<sub>0.08</sub> catalyst, the reactions on the surface include both  $Hg^0$  oxidation and NO conversion.  $Hg^0$  was oxidized to  $Hg^{2+}$  while NO was reduced by NH<sub>3</sub>. H<sub>2</sub>-TPR and XPS analyses suggest that  $Hg^0$  oxidation and NO conversion were aided by a synergistic mechanism between Ce and V, which is consistent with the literature.<sup>29,30,43</sup>The synergistic mechanism can be described as follows:

$$V_2O_4 + 2CeO_2 \leftrightarrow V_2O_5 + Ce_2O_3$$
(5)

$$\operatorname{Ce}_{2}\operatorname{O}_{3} + \frac{1}{2}\operatorname{O}_{2(g)} \to 2\operatorname{CeO}_{2} \tag{6}$$

The redox cycle  $(V^{4+} + Ce^{4+} \leftrightarrow V^{5+} + Ce^{3+})$  plays an important role in promoting Hg<sup>0</sup> oxidation and NO conversion. Cerium can occupy two oxidation states  $[CeO_2 (Ce^{4+}) \leftrightarrow Ce_2O_3]$   $(Ce^{3+})$ ], allowing ceria from the  $CeO_2$ -TiO<sub>2</sub> support to accommodate more surface lattice oxygen species.<sup>27</sup> Consequently, the presence of CeO<sub>2</sub> increased the redox properties of V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub>, favoring catalyst re-oxidation by gas phase oxygen. In addition, the redox cycle results in a decrease of the energy that is required for electron transfer between Ce and V active sites, promoting the adsorption and activation of NH<sub>3</sub> and NO.<sup>29</sup> Thus, the existence of the redox cycle could greatly improve Hg<sup>0</sup> oxidation and NO conversion. Combing the results obtained in this work with those reported earlier,<sup>12,53</sup> the SCR reaction of NO by NH<sub>3</sub> on the VWTiCe<sub>0.08</sub> catalyst most probably takes place according to the following steps. Gaseous NH3 is first adsorbed on the VWTiCe0.08 catalyst to form coordinated NH<sub>3</sub>(ad) and NH<sub>2</sub>(ad), with NO largely adsorbed on VWTiCe<sub>0.08</sub> catalyst. Then NO(ad) reacts with NH<sub>2</sub>(ad) to form ammonium nitrite (NH<sub>2</sub>NO), which subsequently decomposes into N<sub>2</sub> and H<sub>2</sub>O. Meanwhile, NO is also oxidized to nitrate and nitrite. The re-oxidation reaction (10) or disproportionation of 2NO2 with H2O may produce nitrous acid,<sup>12,64</sup> which reacts with ammonia to form ammonium nitrite. The unstable ammonium nitrite is the probable intermediate in the proposed NH<sub>3</sub>-SCR mechanisms.

$$NH_3(g) \rightarrow NH_3(ad)$$
 (3)

$$NH_3(ad) + O^*(ad) \rightarrow NH_2(ad) + OH(ad)$$
 (4)

$$NO(ad) + NH_2(ad) \rightarrow NH_2NO(ad)$$
 (7)

$$NH_2NO(ad) \rightarrow N_2(g) + H_2O(g)$$
 (8)

$$2NO(g) + O_2(g) \rightarrow 2NO_2(ad)$$
(9)

$$NO_2(ad) + OH(ad) \rightarrow O(ad) + HNO_2(ad)$$
 (10)

$$\begin{split} HNO_2(ad) + NH_3(ad) &\rightarrow NH_4NO_2(ad) \rightarrow NH_2NO(ad) + H_2O \\ &\rightarrow N_2(g) + 2H_2O(g) \end{split} \tag{11}$$

At the same time, based on the results obtained in this study and the literature,<sup>30,65,66</sup> the likely reaction pathway for  $Hg^0$  oxidation is related to the Mars–Maessen mechanism. Gaseous  $Hg^0$  is firstly adsorbed on the active sites of the catalyst. Then, the lattice oxygen of  $V_2O_5$  reacts with adjacently absorbed  $Hg^0$  to form  $HgO_{(ad)}$ . Part of  $HgO_{(ad)}$  is captured on the samples as the binary oxide and the rest re-emitted to the gas phase. A possible mechanism for  $Hg^0$  oxidation can be proposed as follows:

$$Hg^{0}_{(g)} + surface \rightarrow Hg^{0}_{(ad)}$$
 (12)

 $Hg^{0}_{(ad)} + V_2O_5 \rightarrow HgO_{(ad)} + V_2O_4$  (13)

$$HgO_{(ad)} \rightarrow HgO_{(g)}$$
 (14)

$$HgO_{(ad)} + V_2O_5 \to HgV_2O_6$$
(15)

Although the simultaneous removal of  $Hg^0$  and NO in a single unit has the potential to lower the capital and operating costs of the process, the capacity of  $Hg^0$  on the catalyst is critical from a commercialization standpoint, which needs to be considered in future studies.

## 4. Conclusions

TiO<sub>2</sub>-CeO<sub>2</sub> as a nanostructured material was used as a support to synthesize VWTiCe which presents a low cost option for the simultaneous removal of Hg<sup>0</sup> and NO compared with activated carbon injection. The catalytic activity for the simultaneous removal of Hg<sup>0</sup> and NO over V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/CeO<sub>2</sub>-TiO<sub>2</sub> catalysts was significantly enhanced after doping Ce into a TiO<sub>2</sub> support. Hg<sup>0</sup> oxidation efficiency and NO conversion efficiency over the V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/CeO<sub>2</sub>-TiO<sub>2</sub> catalyst reached 88% and 89% respectively at 250 °C. The superior performance of catalysts might be attributed to lower crystallinity, more reduced species and better texture properties, resulting from the addition of Ce. The catalyst exhibited good resistance to SO<sub>2</sub> and H<sub>2</sub>O. Moreover, the presence of gaseous O<sub>2</sub> plays an essential role in Hg<sup>0</sup> oxidation and NO conversion, and the redox cycle ( $V^{4+} + Ce^{4+} \leftrightarrow V^{5+} + Ce^{3+}$ ) has an important role in promoting both Hg<sup>0</sup> oxidation and NO conversion.

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