


 Cite this: *RSC Adv.*, 2020, 10, 5845

# Effects of $\text{WO}_3$ and $\text{SiO}_2$ doping on $\text{CeO}_2$ - $\text{TiO}_2$ catalysts for selective catalytic reduction of NO with ammonia

 Rongrong Fan,<sup>ab</sup> Zhaoqiang Li,<sup>\*ab</sup> Yan Wang,<sup>ab</sup> Cheng Zhang,<sup>ab</sup> Yu Wang,<sup>ab</sup> Zhiyong Ding,<sup>ab</sup> Xin Guo<sup>ab</sup> and Rong Wang<sup>ab</sup>

A series of  $\text{CeO}_2$ - $\text{WO}_3$ / $\text{SiO}_2$ - $\text{TiO}_2$  ( $\text{CeW}_x\text{TiSi}_y$ ) catalysts with different loading amounts of  $\text{WO}_3$  were synthesized by wet co-impregnation of ammonium metatungstate and cerium nitrate on a  $\text{SiO}_2$ - $\text{TiO}_2$  support, and were employed for the selective catalytic reduction (SCR) of NO by  $\text{NH}_3$ . The catalytic activity of the  $\text{CeO}_2$ / $\text{SiO}_2$ - $\text{TiO}_2$  ( $\text{CeSiTi}$ ) catalyst was enhanced by the addition of  $\text{WO}_3$ , and the W-containing catalysts showed higher hydrothermal stability especially between 550 and 600 °C. The introduction of  $\text{WO}_3$  to the  $\text{CeSiTi}$  catalyst could produce more chemisorbed oxygen species, reducible subsurface oxygen species, acid sites and ad- $\text{NO}_x$  species. Moreover, the modification of  $\text{CeO}_2$ - $\text{WO}_3$ / $\text{TiO}_2$  ( $\text{CeWTi}$ ) by  $\text{SiO}_2$  could enhance the specific surface area, especially the aged specific surface area, thus improving the hydrothermal stability of the catalyst.

 Received 3rd January 2020  
 Accepted 27th January 2020

DOI: 10.1039/d0ra00053a

[rsc.li/rsc-advances](http://rsc.li/rsc-advances)

## 1. Introduction

Nitrogen oxides ( $\text{NO}_x$ ) are one of the major sources of air pollution, and have caused a series of environmental problems such as acid rain, photochemical smog, and the green-house effect.<sup>1-3</sup> The emission of  $\text{NO}_x$  remains a major problem for diesel vehicles. In recent years, great efforts have been applied to the development and application of available technologies for controlling  $\text{NO}_x$  emissions. Among these technologies, selective catalytic reduction (SCR) of  $\text{NO}_x$  using reductants such as  $\text{NH}_3$  or hydrocarbons (HC) is one of the most promising technologies to reduce  $\text{NO}_x$ . The issue of catalyst deactivation by HC poisoning needs to be resolved for the commercial application of HC-SCR.<sup>4</sup> Currently, the SCR of  $\text{NO}_x$  with  $\text{NH}_3$  ( $\text{NH}_3$ -SCR) is the favored method of denoxification (de $\text{NO}_x$ ), which has also been widely employed commercially for diesel vehicles to meet the ever tightening emission standards.<sup>5-8</sup>

Many types of catalysts, including oxides and zeolites based on transition metals have been investigated for the  $\text{NH}_3$ -SCR reaction.<sup>9</sup> However, these catalysts have intrinsic flaws when it comes to practical applications. Transition-metal (in particular Fe and Cu) ion-exchanged zeolite catalysts have poor water and sulfur resistances.<sup>10</sup>  $\text{V}_2\text{O}_5$ -based oxide catalysts have been used commercially for SCR due to its high catalytic activity and resistance to  $\text{SO}_2$  poisoning, whereas the toxicity of vanadium,

the easy sublimation of  $\text{V}_2\text{O}_5$  and narrow catalytic temperature window (300–400 °C) of this catalyst limit their wide application.<sup>11,12</sup> Therefore, great efforts have been made to develop environmental friendly SCR catalysts to replace  $\text{V}_2\text{O}_5$ -based catalysts. Studies in recent years revealed that the presence of rare-earth components can effectively regulate the surface acidity and alkalinity, modify the structure of catalytic active centers, improve the oxygen storage/release capacities, and enhance the structural stability and active species dispersion of catalysts.<sup>13,14</sup>

As an important component of rare-earth catalytic materials,  $\text{CeO}_2$  is a potential substitute for  $\text{V}_2\text{O}_5$  due to its high oxygen storage capacity and redox ability when Ce species shift between  $\text{Ce}^{4+}$  and  $\text{Ce}^{3+}$ .<sup>15,16</sup> Various studies have been conducted to develop SCR catalysts using  $\text{CeO}_2$ , and several catalyst systems have been developed, including  $\text{CeO}_2$ / $\text{TiO}_2$ ,<sup>17</sup>  $\text{CeO}_2$ / $\text{TiO}_2$ - $\text{SiO}_2$ ,<sup>18</sup>  $\text{CeO}_2$ / $\text{WO}_3$ ,<sup>19</sup>  $\text{CeO}_2$ / $\text{ZrO}_2$ ,<sup>20</sup> etc. The selection of supports is important for the performance of the composite catalysts in environmental catalytic reactions, because the structural properties of supports can affect the dispersion of active sites and the contact between reactants. Various types of supports, such as  $\text{Al}_2\text{O}_3$ ,<sup>21</sup> medicinal stone,<sup>22</sup> Ti-pillared clays,<sup>23</sup>  $\text{TiO}_2$ ,<sup>24</sup> have been used in environmental catalytic reactions of photocatalysis, catalytic oxidative desulfurization and organic pollutants degradation. Among them,  $\text{TiO}_2$  is a favorable candidate as the support for SCR catalysts due to its good  $\text{SO}_2$  durability and stability,<sup>25</sup> hence  $\text{CeO}_2$ / $\text{TiO}_2$  catalyst exhibits higher SCR catalytic activity. Moreover,  $\text{WO}_3$  is widely used as a promotional additive to enhance the catalytic activity of  $\text{V}_2\text{O}_5$ / $\text{TiO}_2$  catalyst. It was reported that introduction of  $\text{WO}_3$  to  $\text{V}_2\text{O}_5$ / $\text{TiO}_2$  increased the amount and the strength of Brønsted acid

<sup>a</sup>State Key Laboratory of Baiyunobo Rare Earth Resource Researches and Comprehensive Utilization, Baotou Research Institute of Rare Earths, Baotou 014030, China. E-mail: li\_brire@163.com

<sup>b</sup>National Engineering Research Center of Rare Earth Metallurgy and Functional Materials, Baotou 014030, China



sites on the catalyst surface.<sup>26</sup> CeO<sub>2</sub>/WO<sub>3</sub> catalyst also exhibits very high efficiency for the reduction of NO<sub>x</sub>.<sup>27</sup> Shan *et al.* examined the promotional effects of a tungsten-doped CeO<sub>2</sub>/TiO<sub>2</sub> catalyst and the excellent catalytic performance of the CeO<sub>2</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalyst was associated with the highly dispersed CeO<sub>2</sub> and primitive WO<sub>3</sub> species on TiO<sub>2</sub>.<sup>28</sup> Furthermore, SiO<sub>2</sub> is widely used as catalyst supports due to their high mechanical strength and excellent thermal stability.<sup>29,30</sup> TiO<sub>2</sub> is usually mixed with SiO<sub>2</sub> as the support to enhance the thermal stability and prevent the deactivating during exposure to SO<sub>2</sub>.<sup>31</sup> However, seldom studies focus on CeO<sub>2</sub>-WO<sub>3</sub>/TiO<sub>2</sub>-SiO<sub>2</sub> catalyst.

In this paper, a series of CeO<sub>2</sub>-WO<sub>3</sub>/TiO<sub>2</sub>-SiO<sub>2</sub> catalysts were prepared by impregnation method and their SCR performance were evaluated in a simulated diesel engine exhaust. According to the characterization, the essence of the activity enhancement arising from the WO<sub>3</sub> and SiO<sub>2</sub> introduction and the active species for the reaction were proposed and elucidated in detail.

## 2. Experimental

### 2.1 Catalyst preparation

A series of CeO<sub>2</sub>-WO<sub>3</sub>/TiO<sub>2</sub>-SiO<sub>2</sub> catalysts with different WO<sub>3</sub> loading amount (denoted as CeW<sub>x</sub>Si<sub>y</sub>Ti; *x* represents the weight percent of WO<sub>3</sub>, *x* = 0–8%; *y* represents the weight percent of SiO<sub>2</sub>, *y* = 0 or 5%) were prepared by the co-impregnation method. Cerium nitrate ((Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O), ammonium metatungstate ((NH<sub>4</sub>)<sub>6</sub>W<sub>7</sub>O<sub>24</sub>·6H<sub>2</sub>O), and TiO<sub>2</sub>-SiO<sub>2</sub>/TiO<sub>2</sub> support were used for the experiment. All the chemicals with purity ≥99.7% are from Sinopharm Chemical Reagent Co., Ltd, China. Firstly, cerium nitrate and ammonium metatungstate were dissolved in deionized water. TiO<sub>2</sub>-SiO<sub>2</sub> or TiO<sub>2</sub> powder was added to the above solution and stirred for 1 h. Secondly, the mixture exposed to ultrasonic for 2 h and then aged for 12 h. At last, the mixture was dried at 110 °C for 2 h and calcined at 550 °C for 3 h in static air. CeO<sub>2</sub> contents in all the catalysts were 20 wt%.

The fresh catalyst was thermally aged in 10% H<sub>2</sub>O in air at 600 °C for 50 h and labeled as aged-600 °C 50 h.

### 2.2 Catalytic activity measurement

The activity test of 0.06 g catalysts was carried out in a fixed-bed quartz reactor (inner diameter = 6 mm). The gas mixture simulates a real diesel exhaust, which contains 200 ppm NO, 200 ppm NH<sub>3</sub>, 200 ppm CO, 50 ppm C<sub>3</sub>H<sub>6</sub>, 12 vol% O<sub>2</sub>, 5 vol% H<sub>2</sub>O, 4.5 vol% CO<sub>2</sub>, and N<sub>2</sub> as balance gas. The total flow rate was 300 mL min<sup>-1</sup>, corresponding to GHSV of 300 000 h<sup>-1</sup>. The effluent gas, including NO, NO<sub>2</sub>, and O<sub>2</sub> was continuously analyzed by an online flue gas analyzer. The results for the steady-state activity were collected after 20 min at each temperature. The NO<sub>x</sub> conversion was calculated as follows, whereas NO<sub>x</sub> = NO + NO<sub>2</sub>.

$$\text{NO}_x \text{ conversion} = \frac{c[\text{NO}_x]_{\text{inlet}} - c[\text{NO}_x]_{\text{outlet}}}{c[\text{NO}_x]_{\text{inlet}}} \times 100\%$$

### 2.3 Catalysts characterization

The BET surface area was measured at -196 °C on an ASAP 2050 physical adsorption instrument (Micromeritics Corp., Norcross, GA, USA) by using the nitrogen adsorption method. The samples were pretreated in a vacuum at 300 °C for 4 h before experiments. The surface area was determined by BET method in 0–0.3 partial pressure range.

X-ray diffraction (XRD) measurement was performed on an X'pert Pro diffractometer (Panalytical Corp., The Netherlands) operating at 40 mA and 40 kV with Cu K $\alpha$  radiation. The 2 $\theta$  data from 10 to 90° were collected with the step size of 0.03°.

Microstructures of the catalyst samples were observed with a FEI Tecnai G2 F20 electron microscope.

X-ray photoelectron spectra (XPS) were obtained with a Thermo ESCALAB 250Xi spectrometer (ThermoFisher Scientific, Waltham, MA, USA) using Al K $\alpha$  radiation (1486.6 eV). Binding energies of Ce 3d and O 1s were calibrated using C 1s peak (B.E. = 284.6 eV) as standard. The composition on catalyst surface according to atomic ratios was calculated, and Shirley background and Gaussian-Lorentzian was used for peak analysis.

H<sub>2</sub> temperature programmed reduction (H<sub>2</sub>-TPR) was carried out on a Quantachrome: Chem BET chemisorption analyzer (Micromeritics, Norcross, GA, USA). Before the experiment, 50 mg of the sample was heated from room temperature to 800 °C at a rate of 10 °C min<sup>-1</sup>. A mixture gas flow of 5 vol% H<sub>2</sub>/Ar was used as reductant at a flow rate of 60 mL min<sup>-1</sup>. Before detection by the TCD, the gas was purified by a trap containing CaO + NaOH materials in order to remove the H<sub>2</sub>O and CO<sub>2</sub>.

The temperature-programmed desorption (TPD) of NH<sub>3</sub> or NO<sub>x</sub> was conducted on a Quantachrome: Chem BET chemisorption analyzer supplied by the Micromeritics Company. 50 mg of the sample was pretreated at 300 °C (10 °C min<sup>-1</sup>) in He flow at 60 mL min<sup>-1</sup> for 2 h, then cooled down to 40 °C and purged with 5 vol% NH<sub>3</sub>/He (500 ppm NO + 3% O<sub>2</sub>) until adsorption saturation, followed by flushing with 20 mL min<sup>-1</sup> He at the same temperature to remove physical absorption species. The desorption was then performed in the range of 40–800 °C at a speed of 10 °C min<sup>-1</sup>.

## 3. Results and discussion

### 3.1 SCR catalytic activity

The effect of WO<sub>3</sub> and SiO<sub>2</sub> addition on the deNO<sub>x</sub> performance of CeTi catalyst is illustrated in Fig. 1. As shown in Fig. 1a, CeTi and CeW<sub>4</sub>Ti showed higher NO<sub>x</sub> conversion than CeSiTi and CeW<sub>4</sub>SiTi, respectively, indicating that the catalytic activity was even suppressed by SiO<sub>2</sub>. While the negative effect on CeW<sub>4</sub>SiTi was less obvious for catalysts with WO<sub>3</sub> loaded, suggesting that WO<sub>3</sub> had a promotional impact on activity, which can also be seen from CeTi and CeWTi catalyst. NO<sub>x</sub> conversion over CeW<sub>4</sub>Ti was higher than CeTi at 150–550 °C. Furthermore, CeW<sub>x</sub>SiTi catalysts with different WO<sub>3</sub> loadings were prepared to investigate the effect of WO<sub>3</sub>. It was clear that the addition of WO<sub>3</sub> to CeSiTi could significantly enhance the catalytic activities and broaden reactivity window. CeSiTi catalyst exhibited



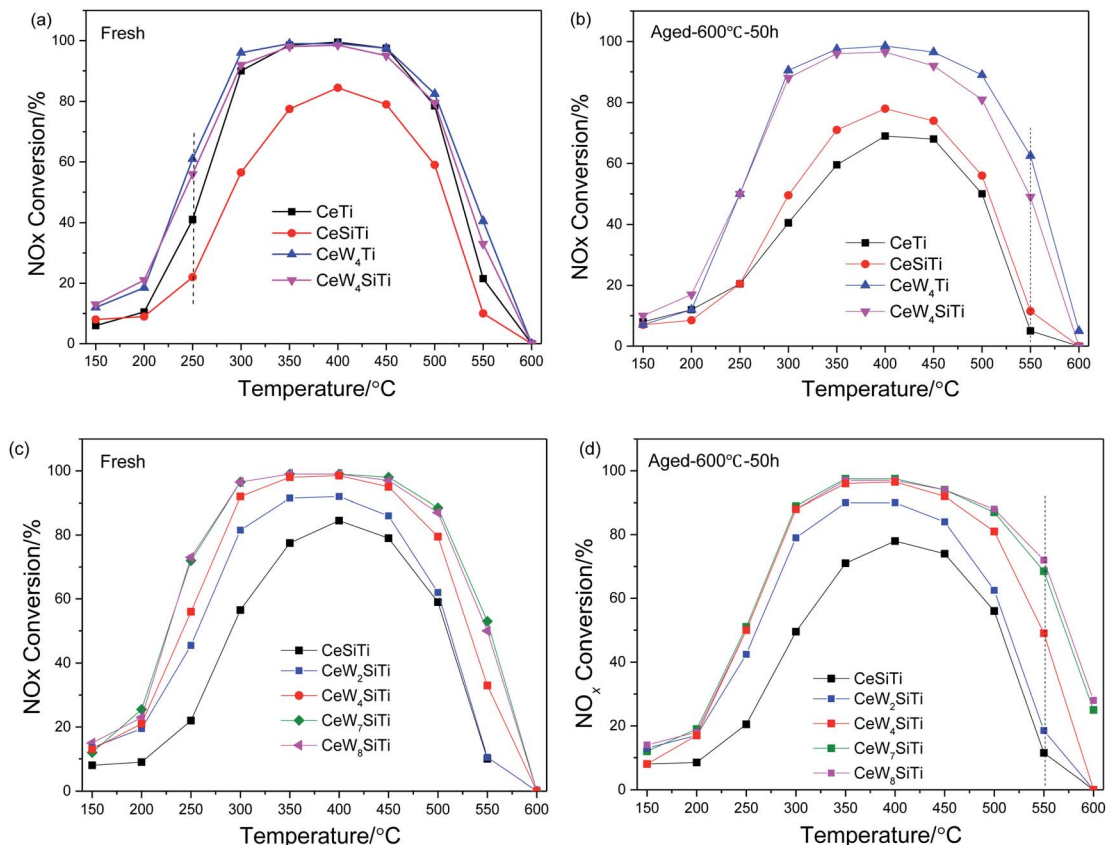


Fig. 1 Effect of WO<sub>3</sub> and SiO<sub>2</sub> over CeW<sub>x</sub>TiSi<sub>y</sub> catalysts on deNO<sub>x</sub> performance. (a) and (c) Fresh samples; (b) and (d) thermally aged samples.

relatively low activities in the whole temperature range, with maximum NO<sub>x</sub> conversion of 84% at 400 °C. After the addition of WO<sub>3</sub>, NO<sub>x</sub> conversion of CeW<sub>2</sub>SiTi was ~20% greater at 250–350 °C and ~10% at 250 or 400 °C than CeSiTi, and the maximum NO<sub>x</sub> conversion reached to 92%. With the increasing of WO<sub>3</sub> loading from 2% to 7%, NO<sub>x</sub> conversion especially at 250 °C was greatly improved from 22% to 72%. For CeW<sub>7</sub>SiTi catalyst, nearly 100% NO<sub>x</sub> conversion was obtained in the temperature range of 300–450 °C. Further increasing the WO<sub>3</sub> loading to 8%, CeW<sub>8</sub>SiTi showed nearly the same catalytic activity as CeW<sub>7</sub>SiTi. This suggested that the WO<sub>3</sub> addition amount is close to its distributed capacity.<sup>32</sup>

SCR performance of the catalysts after hydrothermal aging treatment is shown in Fig. 1b and d. Compared with the fresh sample, activity of aged CeTi dropped dramatically in a wide temperature range of 250–550 °C. The maximum decrease of NO<sub>x</sub> conversion appearing at 300 °C was up to 50%, indicating that hydrothermal aging had a severe impact on CeTi catalyst. In contrast, NO<sub>x</sub> conversion of CeSiTi decreased slightly with only 7% drop at 300 °C, demonstrating that SiO<sub>2</sub> could greatly enhanced thermal stability of catalysts. For catalysts with WO<sub>3</sub> doped (CeW<sub>4</sub>Ti and CeW<sub>x</sub>SiTi), catalytic activities were remained after hydrothermally treated. Remarkably, compared with the fresh samples, NO<sub>x</sub> conversions of these catalysts at temperature 550–600 °C were even higher. For example, NO<sub>x</sub> conversion of aged CeW<sub>4</sub>Ti and CeW<sub>x</sub>SiTi at 550 °C were 22%

and 16% higher than that of their fresh samples, respectively. Therefore, WO<sub>3</sub> and SiO<sub>2</sub> were synergistically beneficial for hydrothermal stability of the catalysts.

To evaluate the stability of the catalyst, CeW<sub>7</sub>SiTi was chosen to carry out the reuse cycle experiment, as described on sub-Section 2.2. After one test cycle finished, the sample was cooled down to room temperature first, then heated to 600 °C for another cycle. Catalytic activities in each cycle were exhibited in Fig. 2. It can be seen that there was no obvious reduction in the catalytic activity after 7 reuse cycles, indicating perfect reusability and good stability of the catalyst.

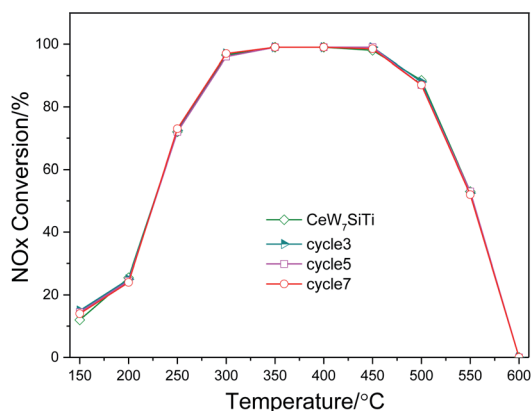


Fig. 2 Reuse cycle experiment of CeW<sub>7</sub>SiTi catalyst.



### 3.2 XRD and BET results

The XRD patterns of  $\text{CeW}_x\text{Si}_y\text{Ti}$  catalysts are shown in Fig. 3. Only diffraction peaks attributed to cubic  $\text{CeO}_2$  crystallites (ICDD PDF#34-0394) and anatase phase (ICDD PDF# 21-1272) of  $\text{TiO}_2$  were detected, no  $\text{WO}_3$  or  $\text{SiO}_2$  phase was observed,<sup>16</sup> which suggested that W and Si species probably exist in an amorphous phase or as highly dispersed species.<sup>33</sup> The intensities of  $\text{CeO}_2$  peak slowly increased with the  $\text{WO}_3$  content increasing, indicating that  $\text{CeO}_2$  crystallites grown slowly, which may be due to the blocking effect of the  $\text{CeO}_2$  by the impregnated tungsten oxide.<sup>34</sup> Accordingly, the average crystallite size calculated using the Scherrer equation is shown in Table 1. The crystallite size increased from 15.4 nm to 17.0 nm with  $\text{WO}_3$  loadings of  $\text{CeW}_x\text{SiTi}$  increasing from 0% to 8%. Moreover, as presented in Table 1, the lattice parameter corresponding to the ceria phase was also calculated *via* Bragg's Law.<sup>35</sup> The lattice constant and  $d$ -spacing of  $\text{CeO}_2$  increased a little by impregnating tungsten oxide. For  $\text{CeW}_x\text{SiTi}$ ,  $d$ -spacing expanded from 0.268 nm to 0.272 nm, and the lattice constant increased from 0.533 nm to 0.535 nm. Likewise for  $\text{CeW}_x\text{Ti}$  catalysts, from CeTi to  $\text{CeW}_4\text{Ti}$ , crystallite size elevated from 16.3 nm to 17.3 nm,  $d$ -spacing from 0.267 nm to 0.271 nm, and lattice constant from 0.532 nm to 0.534 nm. Generally, the lattice constant of ceria is mainly associated with the ratio of  $\text{Ce}^{3+}$  (0.110 nm)/ $\text{Ce}^{4+}$  (0.087 nm).<sup>34</sup> Therefore, the increasing lattice constant may be result from more  $\text{Ce}^{3+}$  species brought by  $\text{WO}_3$  incorporation, as discussed in the following XPS results.

The HR-TEM micrographs of different catalysts are exhibited in Fig. 4. Particle size of CeTi and  $\text{CeW}_4\text{Ti}$  catalysts were about 10–20 nm. For CeTi, lattice fringes of 0.272 nm and 0.351 nm matched  $\text{CeO}_2$  (200) and anatase (101) phase, respectively.<sup>2</sup> After addition of  $\text{WO}_3$ , lattice fringe of  $\text{CeO}_2$  (200) increase to 0.278 nm, which was consistent with the XRD results.

The BET surface areas of  $\text{CeW}_x\text{TiSi}_y$  catalysts as well as total pore volumes and average pore diameters are presented in Table 2. It is clear that with  $\text{WO}_3$  content increasing, a slight decrease in BET surface area is observed. This may be due to the growing cluster of  $\text{CeO}_2$  crystallites causing the agglomeration of the catalyst surface according to the XRD results.<sup>36</sup>

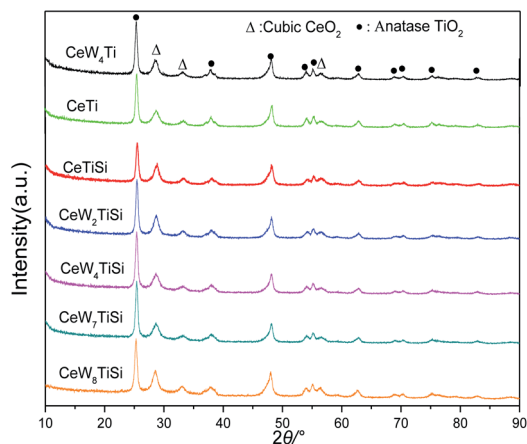


Fig. 3 XRD patterns of  $\text{CeW}_x\text{Si}_y\text{Ti}$  catalysts with different  $\text{WO}_3$  loadings.

Table 1 Crystallite size and lattice parameter of the catalysts

Catalysts	Crystallite size of $\text{CeO}_2$ (nm)	$d$ -spacing (nm)	Lattice constant of $\text{CeO}_2$ (nm)
CeTi	16.3	0.267	0.532
$\text{CeW}_4\text{Ti}$	17.3	0.271	0.534
CeSiTi	15.4	0.268	0.533
$\text{CeW}_2\text{SiTi}$	15.9	0.268	0.534
$\text{CeW}_4\text{SiTi}$	16.5	0.268	0.534
$\text{CeW}_7\text{SiTi}$	16.5	0.268	0.534
$\text{CeW}_8\text{SiTi}$	17.0	0.272	0.535

Compared with that of their fresh counterpart, the total pore volumes and average pore diameters of aged  $\text{CeW}_x\text{TiSi}_y$  catalysts increased, while BET surface area decreased. Notably for CeTi, BET surface area drastically dropped from 67 to 42  $\text{m}^2 \text{g}^{-1}$  (a 37.3% decrease). Whereas the surface area loss of  $\text{CeW}_4\text{Ti}$  and  $\text{CeW}_x\text{TiSi}$  were much lower (7.8–13.6%), indicating hydrothermal stability was improved by addition of  $\text{WO}_3$  and  $\text{SiO}_2$ . Remarkably, the BET surface area of aged CeSiTi (80  $\text{m}^2 \text{g}^{-1}$ ) is almost the same as the fresh sample (81  $\text{m}^2 \text{g}^{-1}$ ), showing excellent hydrothermal stability. All these indicated that the addition of active component  $\text{WO}_3$  and  $\text{SiO}_2$  could coordinatively preserve the BET surface area of hydrothermally aged catalysts, thus enhance hydrothermal stability of the catalysts, which were in good accordance with results demonstrated in Fig. 1.

### 3.3 XPS results

To understand the chemical states of elements over the surface of  $\text{CeW}_x\text{TiSi}_y$  catalysts, XPS spectra of Ce and O are presented in Fig. 5. XPS spectra of Ce 3d are shown as Fig. 5a. The sub-bands labeled u1 and v1 represent the  $3d^{10}4f^1$  initial electronic state, corresponding to  $\text{Ce}^{3+}$ , whereas the peaks labeled u, u2, u3, v, v2, and v3 represent the  $3d^{10}4f^0$  state of  $\text{Ce}^{4+}$  ions.  $\text{Ce}^{3+}/(\text{Ce}^{3+} + \text{Ce}^{4+})$  ratio was calculated according to the area ratio of Ce peaks and displayed in Table 3. It can be seen that the addition of  $\text{WO}_3$  to the catalyst slightly increased  $\text{Ce}^{3+}$  ratio on the surface of the catalysts. Hence, it is likely that W promote the transformation from  $\text{Ce}^{4+}$  to  $\text{Ce}^{3+}$  ions.  $\text{Ce}^{3+}$  could create more charge imbalance, vacancies, and chemisorbed oxygen on the surface, which is beneficial for SCR performance.

Fig. 5b displays the O 1s XPS spectra of different catalysts. The O 1s peaks were fitted into two sub-bands. The bands at 531.0–531.9 eV are assigned to surface-chemisorbed oxygen (denoted as  $\text{O}_\alpha$ ). And the sub-bands from 529.5 to 530.0 eV are attributable to the lattice  $\text{O}^{2-}$  oxygen (denoted as  $\text{O}_\beta$ ). The surface-adsorbed oxygen is considered to be more reactive in oxidation reactions since its mobility is higher than that of lattice oxygen, and Wu *et al.*<sup>37</sup> have insisted that a high  $\text{O}_\alpha$  ratio is beneficial for the oxidation of NO to  $\text{NO}_2$  in the SCR reaction, resulting in an improvement to a “fast SCR” reaction. According to Table 3,  $\text{O}_\alpha/(\text{O}_\alpha + \text{O}_\beta)$  ratio of  $\text{CeW}_x\text{TiSi}$  elevated from 29.2% to 48.1% as the  $\text{WO}_3$  content increasing, thereby improving the activity of the catalysts. Similar results were obtained in CeTi &  $\text{CeW}_4\text{Ti}$  catalysts. Additionally, for CeTi and  $\text{CeW}_4\text{Ti}$  catalysts,



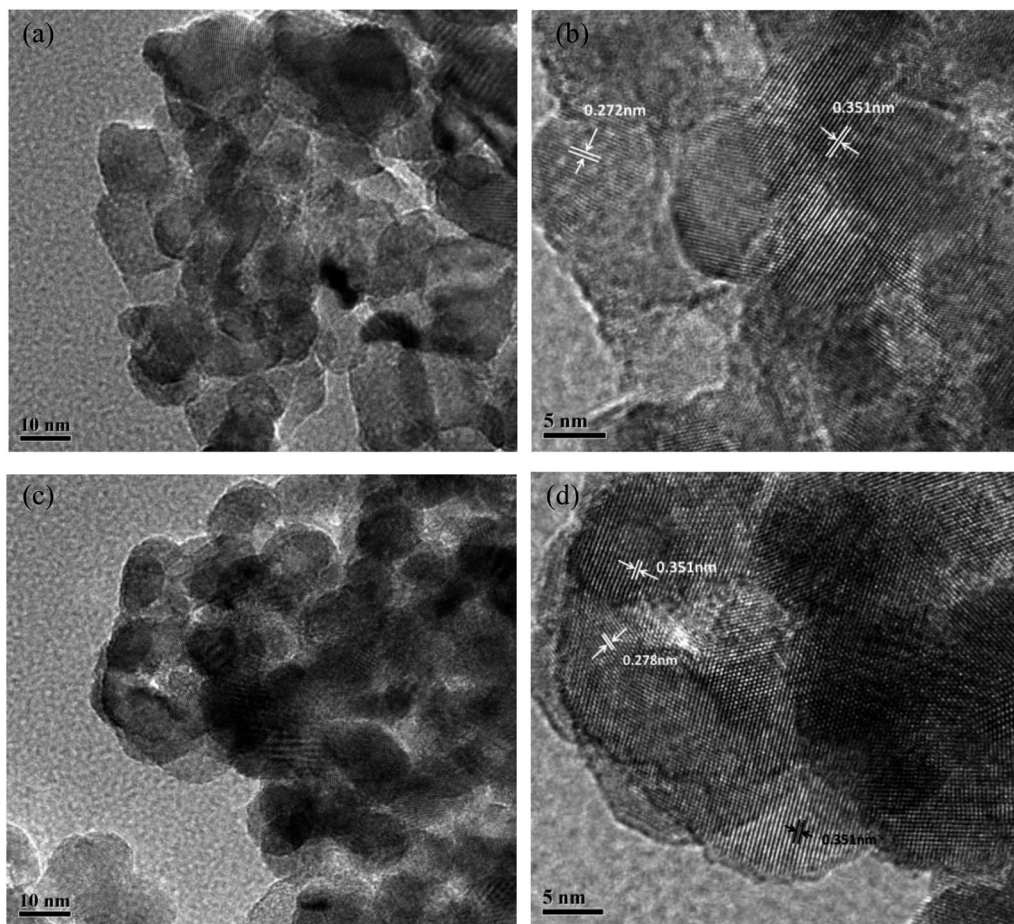


Fig. 4 TEM images of (a), (b) CeTi and (c), (d) CeW<sub>4</sub>Ti catalysts.

SiO<sub>2</sub> doping increased the  $O_{\alpha}/(O_{\alpha} + O_{\beta})$  ratio. However, the activities of SiO<sub>2</sub> free catalysts were better, as shown in Fig. 1. This indicated that some synergistic effect should take place between the Ce, W species and SiO<sub>2</sub> support.

### 3.4 NO<sub>x</sub> adsorption

To investigate the influence of WO<sub>3</sub> on the NO<sub>x</sub> adsorption/desorption of the catalysts, NO<sub>x</sub>-TPD was performed. Fig. 6 displays the TPD profiles of NO<sub>x</sub> on the catalysts. The NO<sub>x</sub>

profiles were mainly divided into four different peaks by peak fitting according to the Gaussian deconvolution method. The first peak at 164–181 °C were associated with the desorption of physisorbed NO<sub>x</sub>. The NO<sub>x</sub> peak at 218–258 °C were mainly due to the decomposition of chemisorbed NO<sub>x</sub> species. The peaks at 315–390 °C and 511–620 °C were probably related to the decomposition of bridging nitrate species and bidentate nitrate species with higher thermal stability.<sup>38</sup> The NO<sub>x</sub> adsorption capacity of CeW<sub>4</sub>SiTi and CeW<sub>4</sub>Ti calculated in Table 4 were

Table 2 BET surface area ( $S_{\text{BET}}$ ), total pore volume ( $V_{\text{P}}$ ), average pore diameter ( $D_{\text{P}}$ ) of CeW<sub>x</sub>Si<sub>y</sub>Ti catalysts

	$V_{\text{P}}$ (cm <sup>3</sup> g <sup>-1</sup> )		$D_{\text{P}}$ (nm)		$S_{\text{BET}}$ (m <sup>2</sup> g <sup>-1</sup> )		$\Delta S_{\text{BET}}^a$ (%)
	Fresh sample	Aged sample	Fresh sample	Aged sample	Fresh sample	Aged sample	
CeTi	0.2685	0.2471	15.98	23.51	67	42	37.3
CeW <sub>4</sub> Ti	0.2489	0.2632	15.19	18.35	66	57	13.6
CeSiTi	0.2487	0.2777	12.30	13.87	81	80	1.2
CeW <sub>2</sub> SiTi	0.2302	0.2821	11.99	14.91	77	71	7.8
CeW <sub>4</sub> SiTi	0.2326	0.2541	12.48	15.91	75	68	9.3
CeW <sub>7</sub> SiTi	0.2328	0.2599	12.82	15.90	73	65	11.0
CeW <sub>8</sub> SiTi	0.2331	0.2547	13.31	15.60	70	63	10.0

$$^a \Delta S_{\text{BET}} = \frac{S_{\text{BET}}(\text{fresh}) - S_{\text{BET}}(\text{aged})}{S_{\text{BET}}(\text{fresh})} \times 100\%$$



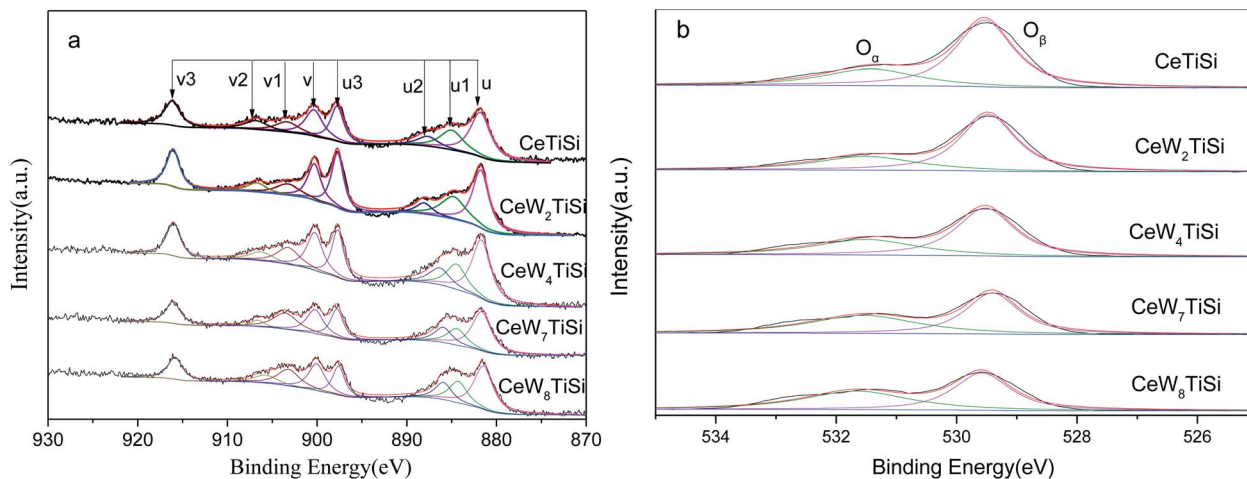


Fig. 5 XPS spectra of (a) Ce 3d and (b) O 1s for  $CeW_xSi_yTi$  catalysts.

Table 3 XPS results of  $CeW_xTiSi_y$  catalysts

Catalysts	$Ce^{3+}/(Ce^{3+} + Ce^{4+})$	$O_\alpha/(O_\alpha + O_\beta)$
CeSiTi	21.2%	29.2%
CeW <sub>2</sub> SiTi	21.2%	30.8%
CeW <sub>4</sub> SiTi	21.9%	36.3%
CeW <sub>7</sub> SiTi	23.9%	47.2%
CeW <sub>8</sub> SiTi	24.4%	48.1%
CeTi	21.1%	23.3%
CeW <sub>4</sub> Ti	23.5%	28.7%

attributed to nitrate species over  $WO_3$ -containing catalysts were larger than that over CeTi and CeSiTi catalyst, indicating the addition of W could bring more ad- $NO_x$  species, which was beneficial for the  $NH_3$ -SCR. This elucidates the promotional effect of  $WO_3$  on the activity of the catalysts in terms of the adsorption perspective.

### 3.5 Surface acidity

Surface acidity plays a critical role in SCR reaction. Surface acid sites promote ammonia adsorption on solid surfaces especially at high temperatures. The amounts and strengths of acid sites of  $CeW_xTiSi_y$  catalysts were measured by  $NH_3$ -TPD and shown in Fig. 7. All the catalysts exhibited several broad peaks in the temperature range of 100–800 °C, which were attributed to  $NH_3$  desorbed by weak (150–350 °C), medium (350–500 °C) and strong (500–800 °C) acid sites.<sup>37</sup> CeTi catalyst mainly showed a single broad peak at 160 °C ascribed to  $NH_3$  desorbed by weak acid sites. While except the first peak at around 140 °C,  $CeW_4Ti$  catalyst displayed a sharp desorption peak at 222 °C and a broad peak at 417 °C, which was ascribed to medium acid sites. Besides, its  $NH_3$  desorption amount was 1.01  $mmol\ g^{-1}$  according to Table 5, higher than 0.61  $mmol\ g^{-1}$  of CeTi.  $CeW_xTiSi_y$  catalysts exhibited peaks at 160, 272 and 440 °C, mainly assigned to  $NH_3$  desorption by weak and medium acid sites. With  $WO_3$  loading amounts increasing from 0% to 8%,  $NH_3$  desorption amount increased from 0.14  $mmol\ g^{-1}$  to 2.02  $mmol\ g^{-1}$ . All these results implied that the addition of  $WO_3$  could increase amounts of acid sites of the catalysts, bringing more  $NH_3$  adsorption sites, which plays an important role in the SCR reaction.<sup>10</sup>

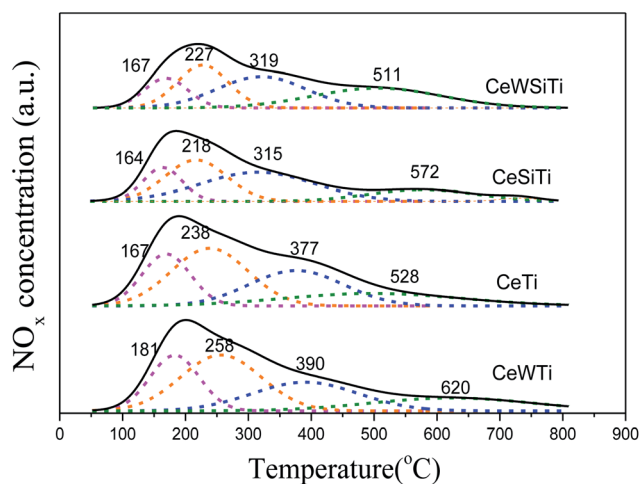


Fig. 6  $NO_x$ -TPD profiles over the  $CeW_xSi_yTi$  catalysts.

1.29 and 2.05  $mmol\ g^{-1}$ , respectively, which were higher than that of CeSiTi (1.02  $mmol\ g^{-1}$ ) and CeTi (1.87  $mmol\ g^{-1}$ ). It indicated that the addition of W increased the amount of  $NO_x$  adsorbed species. Nitrate species (ad- $NO_x$ ), formed on the catalyst surface, are known to play an important role in NO reduction. ad- $NO_x$  species desorbed above 300 °C are presumed to participate in NO reduction.<sup>39,40</sup> The total areas of peaks

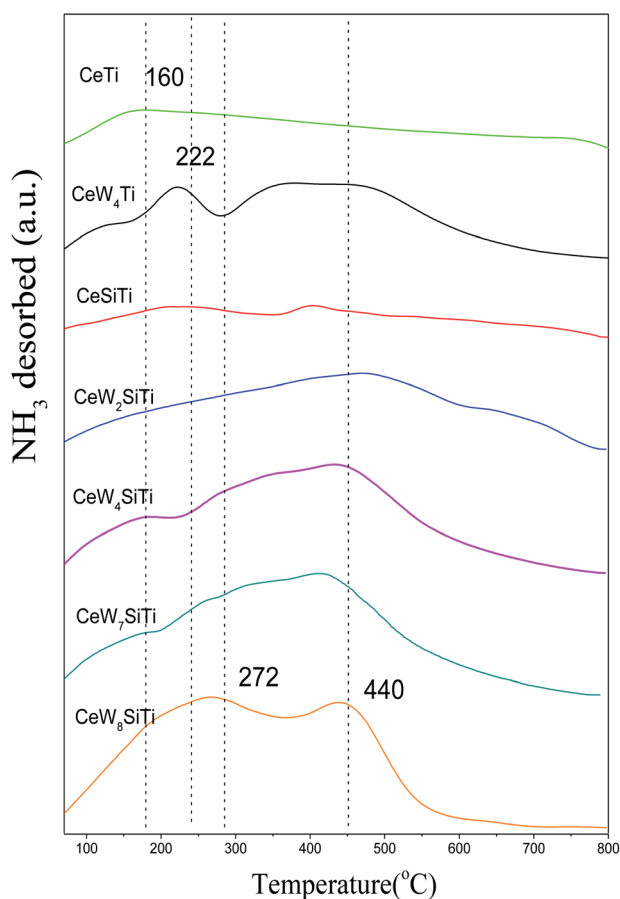
### 3.6 Redox properties

$H_2$ -TPR analysis was performed to investigate the presence of reducible species in the addition of  $WO_3$  and  $SiO_2$  to  $CeO_2/TiO_2-SiO_2$ . Fig. 8 illustrates the  $H_2$ -TPR profiles of  $CeW_xTiSi_y$  catalysts. All catalysts showed broad peak around 495 °C, ascribed to surface oxygen reduction of ceria.<sup>34</sup> CeTi catalyst presented a sharp reduction peak at 680 °C, attributing to



Table 4 NO<sub>x</sub> adsorption capacity of catalysts

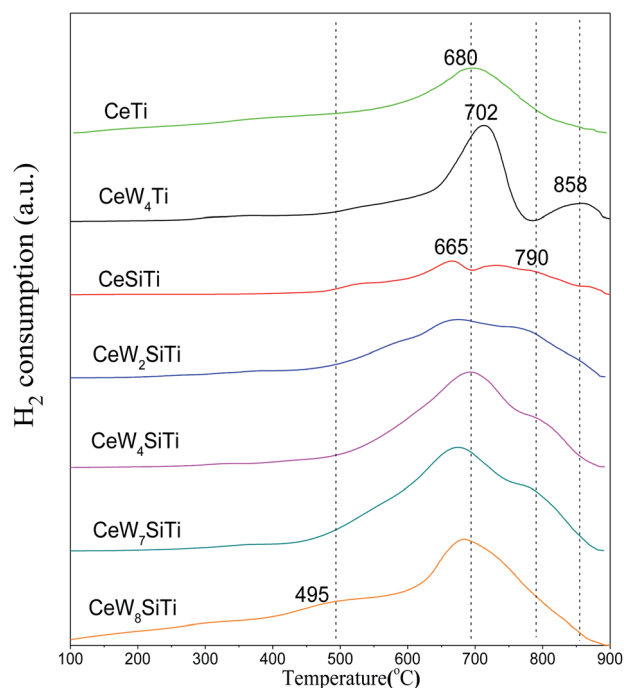
Catalysts	Integral areas				Total NO <sub>x</sub> desorption (mmol g <sup>-1</sup> )
	Peak 1 (164–181 °C)	Peak 2 (218–258 °C)	Peak 3 (315–390 °C)	Peak 4 (511–620 °C)	
CeWTi	1919	3141	2121	1461	2.05
CeTi	1524	2668	2016	1336	1.87
CeWSiTi	786	1531	1991	751	1.29
CeSiTi	540	914	1162	1064	1.02

Fig. 7 NH<sub>3</sub>-TPD profiles of CeW<sub>x</sub>Si<sub>y</sub>Ti catalysts.

reduction of bulk oxygen in ceria. For CeWTi and CeW<sub>x</sub>TiSi catalysts, it is observed that reduction peaks of CeO<sub>2</sub> and WO<sub>3</sub> overlapped on the catalysts in the temperature range of WO<sub>3</sub> reduction. The broad overlapping peaks ranged from 665 to 702 °C are attributed to the reduction of WO<sub>3</sub> to WO<sub>2</sub> as well as bulk oxygen of CeO<sub>2</sub>,<sup>2,27</sup> which is due to the interaction of tungsten with cerium oxide. The reduction peaks ranged from 790–858 °C were ascribed to the reduction of WO<sub>2</sub> to W.<sup>29</sup> The second reduction peak of the WO<sub>x</sub>-containing catalysts shifted to higher temperatures, revealing a strong interaction between CeO<sub>2</sub> and WO<sub>3</sub> species with WO<sub>3</sub> addition. For CeW<sub>x</sub>TiSi catalysts, with WO<sub>3</sub> content increasing, H<sub>2</sub> consumption increased from 1.47 mmol g<sup>-1</sup> to 8.65 mmol g<sup>-1</sup> as shown in Table 5, indicating that the addition of WO<sub>3</sub> could bring more reducible subsurface

Table 5 Calculated amount of ammonia desorption in NH<sub>3</sub>-TPD tests and hydrogen consumption in the H<sub>2</sub>-TPR

Catalysts	NH <sub>3</sub> desorption (mmol g <sup>-1</sup> )	H <sub>2</sub> consumption (mmol g <sup>-1</sup> )
CeSiTi	0.14	1.47
CeW <sub>2</sub> SiTi	0.38	5.44
CeW <sub>4</sub> SiTi	1.38	6.68
CeW <sub>7</sub> SiTi	1.50	8.17
CeW <sub>8</sub> SiTi	2.02	8.65
CeTi	0.61	4.41
CeW <sub>4</sub> Ti	1.01	4.70

Fig. 8 H<sub>2</sub>-TPR profiles of CeW<sub>x</sub>Si<sub>y</sub>Ti catalysts.

oxygen and increase the redox property, which facilitates SCR reaction. The results are in accordance with SCR activities.

## 4. Conclusion

In this work, WO<sub>3</sub> was doped into CeO<sub>2</sub>/TiO<sub>2</sub> and CeO<sub>2</sub>/TiO<sub>2</sub>-SiO<sub>2</sub> catalysts by impregnation method. WO<sub>3</sub> has a promotional effect



on the activity of the catalysts and the optimal loading of  $\text{WO}_3$  species was 7%. After hydrothermal aging treatment,  $\text{NO}_x$  conversion of W-containing catalysts at 500–600 °C even exceeded that of fresh samples, showing excellent hydrothermal stability. XRD and BET results show that the addition of  $\text{WO}_3$  could promote  $\text{CeO}_2$  and  $\text{WO}_3$  crystallites disperse better over the catalyst surface. XPS results prove that  $\text{WO}_3$  bring more appearance of  $\text{Ce}^{3+}$  and surface chemisorbed oxygen species so that more NO would be oxidized to  $\text{NO}_2$ , which was a benefit for the SCR process.  $\text{NH}_3$  and  $\text{NO}_x$ -TPD results indicate that  $\text{WO}_3$  provide more acid sites and more adsorbed  $\text{NO}_x$  and  $\text{NH}_3$  species, which was also beneficial for the SCR reaction. TPR results suggest that  $\text{WO}_3$  improve redox property of the catalysts.

Introduction of  $\text{SiO}_2$  lower the catalytic activities of the catalysts. While after hydrothermally treating, the surface area of  $\text{SiO}_2$ -containing catalysts mostly preserved, hence enhancing the hydrothermal stability of the catalysts. There is synergistic effect between  $\text{SiO}_2$  and  $\text{WO}_3$  on keeping hydrothermal stability of the catalysts. From the results of XPS, TPD and  $\text{H}_2$ -TPR, the strong interaction between ceria, tungsten and silica could contribute to the excellent  $\text{deNO}_x$  performance of  $\text{CeW}_x\text{TiSi}_y$  mixed oxide catalyst.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

This research was funded by the Science and Technology Projects of China Northern Rare Earth (Group) High-tech Co., Ltd. (Grant No. BFXT-2018-D-1) and Natural Science Foundation of Inner Mongolia (Grant No. 2017MS0209).

## References

- J. Chen, Y. Chen, M. Zhou, Z. Huang, J. Gao, Z. Ma, J. Chen and X. Tang, *Environ. Sci. Technol.*, 2017, **51**, 473–478.
- Y. Jiang, Z. Xing, X. Wang, S. Huang, X. Wang and Q. Liu, *Fuel*, 2015, **151**, 124–129.
- S. Liu, X. Feng, J. Liu, Q. Lin, L. Xiong, Y. Wang, H. Xu, J. Wang and Y. Chen, *New J. Chem.*, 2019, **43**, 2258–2268.
- F. Liu, Y. Yu and H. He, *Chem. Commun.*, 2014, **50**, 8445–8463.
- J. Wang, H. Zhao, G. Haller and Y. Li, *Appl. Catal., B*, 2017, **202**, 346–354.
- H. Hu, S. Cai, H. Li, L. Huang, L. Shi and D. Zhang, *J. Phys. Chem. C*, 2015, **119**, 22924–22933.
- D. W. Kwon and S. C. Hong, *Appl. Surf. Sci.*, 2015, **356**, 181–190.
- W. Zhao, Y. Tang, Y. Wan, L. Li, S. Yao, X. Li, J. Gu, Y. Li and J. Shi, *J. Hazard. Mater.*, 2014, **278**, 350–359.
- W. Shan, F. Liu, Y. Yu and H. He, *Chin. J. Catal.*, 2014, **35**, 1251–1259.
- J. Xu, H. Yu, C. Zhang, F. Guo and J. Xie, *New J. Chem.*, 2019, **43**, 3996–4007.
- L. Chen, J. Li and M. Ge, *J. Phys. Chem. C*, 2009, **113**, 21177–21184.
- Z. Yan, X. Shi, Y. Yu and H. He, *J. Environ. Sci.*, 2018, **73**, 155–161.
- G. Zhang, W. Han, H. Zhao, L. Zong and Z. Tang, *Appl. Catal., B*, 2018, **226**, 117–126.
- T. Boningari, A. Somogyvari and P. G. Smirniotis, *Ind. Eng. Chem. Res.*, 2017, **56**, 5483–5494.
- L. Xu, C. Wang, H. Chang, Q. Wu, T. Zhang and J. Li, *Environ. Sci. Technol.*, 2018, **52**, 7064–7071.
- Y. Geng, H. Huang, X. Chen, H. Ding, S. Yang, F. Liu and W. Shan, *RSC Adv.*, 2016, **6**, 64803–64810.
- X. Gao, Y. Jiang, Y. Fu, Y. Zhong, Z. Luo and K. Cen, *Catal. Commun.*, 2010, **11**, 465–469.
- Y. Peng, C. Liu, X. Zhang and J. Li, *Appl. Catal., B*, 2013, **140**, 276–282.
- W. Shan, F. Liu, H. He, X. Shi and C. Zhang, *Chem. Commun.*, 2011, **47**, 8046–8048.
- W. Zhao, Z. Li, Y. Wang, R. Fan, C. Zhang, Y. Wang, X. Guo, R. Wang and S. Zhang, *Catalysts*, 2018, **8**, 375.
- L. Kang, H. Liu, H. He and C. Yang, *Fuel*, 2018, **234**, 1229–1237.
- Q. Luo, Q. Zhou, Y. Lin, S. Wu, H. Liu, D. Cheng, Y. Zhong and C. Yang, *Catal. Sci. Technol.*, 2019, **9**, 6166–6179.
- S. Wu, Y. Lin, C. Yang, C. Du, Q. Teng, Y. Ma, D. Zhang, L. Nie and Y. Zhong, *Chemosphere*, 2019, **237**, 124478.
- L. Qiu, Y. Cheng, C. Yang, G. Zeng, Z. Long, S. Wei, K. Zhao and L. Luo, *RSC Adv.*, 2016, **6**, 17036.
- L. Zong, J. Zhang, G. Lu and Z. Tang, *Catal. Surv. Asia*, 2018, **22**, 105–117.
- L. Chen, J. Li, M. Ge and R. Zhu, *Catal. Today*, 2010, **153**, 77–83.
- W. Shan, Y. Geng, X. Chen, N. Huang, F. Liu and S. Yang, *Catal. Sci. Technol.*, 2016, **6**, 1195–1200.
- W. Shan, F. Liu, H. He, X. Shi and C. Zhang, *Appl. Catal., B*, 2012, **115**, 100–106.
- L. Cao, X. Wu, Y. Xu, Q. Lin, J. Hu, Y. Chen, R. Ran and D. Weng, *Catal. Commun.*, 2019, **120**, 55–58.
- L. Qiu, Y. Wang, D. Pang, F. Ouyang and C. Zhang, *Catal. Commun.*, 2016, **78**, 22–25.
- M. Kobayashi, R. Kuma and A. Morita, *Catal. Lett.*, 2006, **112**, 37–44.
- K. K. Akurati, A. Vital, J. P. Dellemann, K. Michalow, T. Graule, D. Ferri and A. Baiker, *Appl. Catal., B*, 2008, **79**, 53–62.
- Y. Peng, K. Li and J. Li, *Appl. Catal., B*, 2013, **140**, 483–492.
- Z. Ma, D. Weng, X. Wu and Z. Si, *J. Environ. Sci.*, 2012, **24**, 1305–1316.
- Y. Wang, Z. Li, R. Fan, X. Guo, C. Zhang, Z. Ding, R. Wang and W. Liu, *Catalysts*, 2019, **9**, 797.
- L. Chen, D. Weng, J. Wang, D. Weng and L. Cao, *Chin. J. Catal.*, 2018, **39**, 1804–1813.
- Z. Wu, R. Jin, Y. Liu and H. Wang, *Catal. Commun.*, 2008, **9**, 2217–2220.
- F. Liu and H. He, *J. Phys. Chem. C*, 2010, **114**, 16929–16936.
- J. Li, Y. Zhu, R. Ke and J. Hao, *Appl. Catal., B*, 2008, **80**, 202–213.
- J. Li, J. Hao, L. Fu, T. Zhu, Z. Liu and X. Cui, *Appl. Catal., A*, 2004, **265**, 43–52.

