RSC Advances



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

Effects of WO_3 and SiO_2 doping on CeO_2 -TiO₂ catalysts for selective catalytic reduction of NO with ammonia

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A series of CeO_2-WO_3/SiO_2-TiO_2 (CeW_xTiSi_y) catalysts with different loading amounts of WO_3 were synthesized by wet co-impregnation of ammonium metatungstate and cerium nitrate on a SiO_2-TiO_2 support, and were employed for the selective catalytic reduction (SCR) of NO by NH₃. The catalytic activity of the CeO_2/SiO_2-TiO_2 (CeSiTi) catalyst was enhanced by the addition of WO_3 , and the W-containing catalysts showed higher hydrothermal stability especially between 550 and 600 °C. The introduction of WO_3 to the CeSiTi catalyst could produce more chemisorbed oxygen species, reducible subsurface oxygen species, acid sites and ad-NO_x species. Moreover, the modification of CeO_2-WO_3/TiO_2 (CeWTi) by 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

1. Introduction

Nitrogen oxides (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.¹⁻³ The emission of 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 NO_x emissions. Among these technologies, selective catalytic reduction (SCR) of NO_x using reductants such as NH₃ or hydrocarbons (HC) is one of the most promising technologies to reduce NO_x. The issue of catalyst deactivation by HC poisoning needs to be resolved for the commercial application of HC–SCR.⁴ Currently, the SCR of NO_x with NH₃ (NH₃–SCR) is the favored method of denoxification (deNO_x), which has also been widely employed commercially for diesel vehicles to meet the ever tightening emission standards.⁵⁻⁸

Many types of catalysts, including oxides and zeolites based on transition metals have been investigated for the NH₃–SCR reaction.⁹ 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.¹⁰ V₂O₅-based oxide catalysts have been used commercially for SCR due to its high catalytic activity and resistance to SO₂ poisoning, whereas the toxicity of vanadium, the easy sublimation of V_2O_5 and narrow catalytic temperature window (300–400 °C) of this catalyst limit their wide application.^{11,12} Therefore, great efforts have been made to develop environmental friendly SCR catalysts to replace V_2O_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.^{13,14}

As an important component of rare-earth catalytic materials, CeO_2 is a potential substitute for V_2O_5 due to its high oxygen storage capacity and redox ability when Ce species shift between Ce4+ and Ce3+.15,16 Various studies have been conducted to develop SCR catalysts using CeO₂, and several catalyst systems have been developed, including CeO2/TiO2,17 CeO2/TiO2-SiO2,18 CeO₂/WO₃,¹⁹ CeO₂/ZrO₂,²⁰ 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 Al₂O₃,²¹ medicinal stone,²² Ti-pillared clays,²³ TiO₂,²⁴ have been used in environmental catalytic reactions of photocatalysis, catalytic oxidative desulfurization and organic pollutants degradation. Among them, TiO₂ is a favorable candidate as the support for SCR catalysts due to its good SO2 durability and stability,²⁵ hence CeO₂/TiO₂ catalyst exhibits higher SCR catalytic activity. Moreover, WO₃ is widely used as a promotional additive to enhance the catalytic activity of V₂O₅/ TiO₂ catalyst. It was reported that introduction of WO₃ to $V_2O_5/$ TiO₂ increased the amount and the strength of Brönsted acid

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sites on the catalyst surface.²⁶ CeO₂/WO₃ catalyst also exhibits very high efficiency for the reduction of NO_x.²⁷ Shan *et al.* examined the promotional effects of a tungsten-doped CeO₂/ TiO₂ catalyst and the excellent catalytic performance of the CeO₂-WO₃/TiO₂ catalyst was associated with the highly dispersed CeO₂ and primitive WO₃ species on TiO₂.²⁸ Furthermore, SiO₂ is widely used as catalyst supports due to their high mechanical strength and excellent thermal stability.^{29,30} TiO₂ is usually mixed with SiO₂ as the support to enhance the thermal stability and prevent the deactivating during exposure to SO₂.³¹ However, seldom studies focus on CeO₂-WO₃/TiO₂-SiO₂ catalyst.

In this paper, a series of CeO_2-WO_3/TiO_2-SiO_2 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 WO₃ and SiO₂ introduction and the active species for the reaction were proposed and elucidated in detail.

2. Experimental

2.1 Catalyst preparation

A series of CeO₂–WO₃/TiO₂–SiO₂ catalysts with different WO₃ loading amount (denoted as CeW_xSi_yTi; *x* represents the weight percent of WO₃, x = 0–8%; *y* represents the weight percent of SiO₂, y = 0 or 5%) were prepared by the co-impregnation method. Cerium nitrate ((CeNO₃)₃·6H₂O), ammonium metatungstate ((NH₄)₆W₇O₂₄·6H₂O), and TiO₂–SiO₂/TiO₂ support were used for the experiment. All the chemicals with purity \geq 99.7% are from Sinopharm Chemical Reagent Co., Ltd, China. Firstly, cerium nitrate and ammonium metatungstate were dissolved in deionized water. TiO₂–SiO₂ or TiO₂ 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. CeO₂ contents in all the catalysts were 20 wt%.

The fresh catalyst was thermally aged in 10% H_2O 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 NH₃, 200 ppm CO, 50 ppm C_3H_6 , 12 vol% O_2 , 5 vol% H_2O , 4.5 vol% CO_2 , and N_2 as balance gas. The total flow rate was 300 mL min⁻¹, corresponding to GHSV of 300 000 h⁻¹. The effluent gas, including NO, NO₂, and O₂ 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_x conversion was calculated as follows, whereas NO_x = NO + NO₂.

NO_x conversion =
$$\frac{c[NO_x]inlet - c[NO_x]outlet}{c[NO_x]inlet} \times 100\%$$

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 α radiation. The 2θ 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 α 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_2 temperature programmed reduction (H_2 -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⁻¹. A mixture gas flow of 5 vol% H_2 / Ar was used as reductant at a flow rate of 60 mL min⁻¹. Before detection by the TCD, the gas was purified by a trap containing CaO + NaOH materials in order to remove the H_2O and CO_2 .

The temperature-programmed desorption (TPD) of NH_3 or NO_x 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⁻¹) in He flow at 60 mL min⁻¹ for 2 h, then cooled down to 40 °C and purged with 5 vol% NH_3/He (500 ppm NO + 3% O₂) until adsorption saturation, followed by flushing with 20 mL min⁻¹ 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⁻¹.

3. Results and discussion

3.1 SCR catalytic activity

The effect of WO₃ and SiO₂ addition on the deNO_x performance of CeTi catalyst is illustrated in Fig. 1. As shown in Fig. 1a, CeTi and CeW₄Ti showed higher NO_x conversion than CeSiTi and CeW₄SiTi, respectively, indicating that the catalytic activity was even suppressed by SiO₂. While the negative effect on CeW₄SiTi was less obvious for catalysts with WO₃ loaded, suggesting that WO₃ had a promotional impact on activity, which can also be seen from CeTi and CeWTi catalyst. NO_x conversion over CeW₄Ti was higher than CeTi at 150–550 °C. Furthermore, CeW_xSiTi catalysts with different WO₃ loadings were prepared to investigate the effect of WO₃. It was clear that the addition of WO₃ to CeSiTi could significantly enhance the catalytic activities and broaden reactivity window. CeSiTi catalyst exhibited



Fig. 1 Effect of WO₃ and SiO₂ over CeW_xTiSi_y catalysts on deNO_x performance. (a) and (c) Fresh samples; (b) and (d) thermally aged samples.

relatively low activities in the whole temperature range, with maximum NO_x conversion of 84% at 400 °C. After the addition of WO₃, NO_x conversion of CeW₂SiTi was ~20% greater at 250–350 °C and ~10% at 250 or 400 °C than CeSiTi, and the maximum NO_x conversion reached to 92%. With the increasing of WO₃ loading from 2% to 7%, NO_x conversion especially at 250 °C was greatly improved from 22% to 72%. For CeW₇SiTi catalyst, nearly 100% NO_x conversion was obtained in the temperature range of 300–450 °C. Further increasing the WO₃ loading to 8%, CeW₈SiTi showed nearly the same catalytic activity as CeW₇SiTi. This suggested that the WO₃ addition amount is close to its distributed capacity.³²

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_x conversion appearing at 300 °C was up to 50%, indicating that hydrothermal aging had a severe impact on CeTi catalyst. In contrast, NO_x conversion of CeSiTi decreased slightly with only 7% drop at 300 °C, demonstrating that SiO₂ could greatly enhanced thermal stability of catalysts. For catalysts with WO₃ doped (CeW₄Ti and CeW_xSiTi), catalytic activities were remained after hydrothermally treated. Remarkably, compared with the fresh samples, NO_x conversions of these catalysts at temperature 550–600 °C were even higher. For example, NO_x conversion of aged CeW₄Ti and CeW_xSiTi at 550 °C were 22% and 16% higher than that of their fresh samples, respectively. Therefore, WO_3 and SiO_2 were synergistically beneficial for hydrothermal stability of the catalysts.

To evaluate the stability of the catalyst, CeW_7 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 CeW₇SiTi catalyst.

3.2 XRD and BET results

The XRD patterns of CeW_xSi_yTi catalysts are shown in Fig. 3. Only diffraction peaks attributed to cubic CeO₂ crystallites (ICDD PDF#34-0394) and anatase phase (ICDD PDF# 21-1272) of TiO₂ were detected, no WO₃ or SiO₂ phase was observed,¹⁶ which suggested that W and Si species probably exist in an amorphous phase or as highly dispersed species.33 The intensities of CeO₂ peak slowly increased with the WO₃ content increasing, indicating that CeO2 crystallites grown slowly, which may be due to the blocking effect of the CeO₂ by the impregnated tungsten oxide.34 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 WO3 loadings of CeWxSiTi 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.³⁵ The lattice constant and *d*-spacing of CeO₂ increased a little by impregnating tungsten oxide. For CeW_xSiTi, *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 CeWrTi catalysts, from CeTi to CeW4Ti, 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 Ce^{3+} (0.110 nm)/ Ce^{4+} (0.087 nm).³⁴ Therefore, the increasing lattice constant may be result from more Ce³⁺ species brought by WO₃ 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 CeW4Ti catalysts were about 10-20 nm. For CeTi, lattice fringes of 0.272 nm and 0.351 nm matched CeO₂ (200) and anatase (101) phase, respectively.² After addition of WO3, lattice fringe of CeO2 (200) increase to 0.278 nm, which was consistent with the XRD results.

The BET surface areas of CeW_xTiSi_y catalysts as well as total pore volumes and average pore diameters are presented in Table 2. It is clear that with WO₃ content increasing, a slight decrease in BET surface area is observed. This may be due to the growing cluster of CeO₂ crystallites causing the agglomeration of the catalyst surface according to the XRD results.36



Fig. 3 XRD patterns of CeW_xSi_yTi catalysts with different WO₃ loadings.

Table 1 Crystallite size and lattice parameter of the catalysts

Catalysts	Crystallite size of CeO ₂ (nm)	<i>d</i> -spacing (nm)	Lattice constant of CeO ₂ (nm)
CeTi	16.3	0.267	0.532
CeW ₄ Ti	17.3	0.271	0.534
CeSiTi	15.4	0.268	0.533
CeW ₂ SiTi	15.9	0.268	0.534
CeW₄SiTi	16.5	0.268	0.534
CeW ₇ SiTi	16.5	0.268	0.534
CeW ₈ SiTi	17.0	0.272	0.535

Compared with that of their fresh counterpart, the total pore volumes and average pore diameters of aged CeW_xTiSi_y catalysts increased, while BET surface area decreased. Notably for CeTi, BET surface area drastically dropped from 67 to 42 m² g⁻¹ (a 37.3% decrease). Whereas the surface area loss of CeW₄Ti and CeW_x TiSi were much lower (7.8–13.6%), indicating hydrothermal stability was improved by addition of WO3 and SiO2. Remarkably, the BET surface area of aged CeSiTi (80 m² g⁻¹) is almost the same as the fresh sample (81 $m^2 g^{-1}$), showing excellent hydrothermal stability. All these indicated that the addition of active component WO3 and SiO2 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 CeW_xTiSi_v 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 3d¹⁰4f¹ initial electronic state, corresponding to Ce³⁺, whereas the peaks labeled u, u2, u3, v, v2, and v3 represent the $3d^{10}4f^0$ state of Ce^{4+} ions. $Ce^{3+}/(Ce^{3+} +$ Ce⁴⁺) ratio was calculated according to the area ratio of Ce peaks and displayed in Table 3. It can be seen that the addition of WO_3 to the catalyst slightly increased Ce3+ ratio on the surface of the catalysts. Hence, it is likely that W promote the transformation from Ce⁴⁺ to Ce³⁺ ions. Ce³⁺ 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 O_{α}). And the sub-bands from 529.5 to 530.0 eV are attributable to the lattice O^{2-} oxygen (denoted as O_{β}). 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.*³⁷ have insisted that a high O_{α} ratio is beneficial for the oxidation of NO to NO₂ in the SCR reaction, resulting in an improvement to a "fast SCR" reaction. According to Table 3, $O_{\alpha}/(O_{\alpha} + O_{\beta})$ ratio of CeW_xTiSi elevated from 29.2% to 48.1% as the WO₃ content increasing, thereby improving the activity of the catalysts. Similar results were obtained in CeTi & CeW₄Ti catalysts. Additionally, for CeTi and CeW₄Ti catalysts,



Fig. 4 TEM images of (a), (b) CeTi and (c), (d) CeW_4Ti catalysts.

 SiO_2 doping increased the $O_{\alpha}/(O_{\alpha} + O_{\beta})$ ratio. However, the activities of SiO_2 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_2 support.

3.4 NO_x adsorption

To investigate the influence of WO₃ on the NO_x adsorption/ desorption of the catalysts, NO_x-TPD was performed. Fig. 6 displays the TPD profiles of NO_x on the catalysts. The NO_x 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_x. The NO_x peak at 218–258 °C were mainly due to the decomposition of chemisorbed NO_x 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.³⁸ The NO_x adsorption capacity of CeW₄SiTi and CeW₄Ti calculated in Table 4 were

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Table 2 BET surface area (S_{BET}), total pore volume (V_P), average pore diameter (D_P) of CeW<sub>x</sub>Si<sub>y</sub>Ti catalysts
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	$V_{\rm P} \left(\rm cm^3 g^{-1} \right)$		$D_{\mathrm{P}}\left(\mathrm{nm}\right)$		$S_{\rm BET}$ (m ² g ⁻¹)		
	Fresh sample	Aged sample	Fresh sample	Aged sample	Fresh sample	Aged sample	$\Delta S_{ m BET}^{a}$ (%)
CeTi	0.2685	0.2471	15.98	23.51	67	42	37.3
CeW ₄ 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 ₂ SiTi	0.2302	0.2821	11.99	14.91	77	71	7.8
CeW ₄ SiTi	0.2326	0.2541	12.48	15.91	75	68	9.3
CeW ₇ SiTi	0.2328	0.2599	12.82	15.90	73	65	11.0
CeW ₈ SiTi	0.2331	0.2547	13.31	15.60	70	63	10.0

 $^{a}\Delta S_{
m BET}= rac{S_{
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m BET}({
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m BET}({
m fresh})} imes 100\%.$



XPS spectra of (a) Ce 3d and (b) O 1s for CeW_xSi_vTi catalysts.

Table 3 XPS results of CeW, TiSi, catalysts

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



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.39,40 The total areas of peaks

attributed to nitrate species over WO3-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 NH₃-SCR. This elucidates the promotional effect of WO₃ on the activity of the catalysts in terms of the adsorption perspective.

Surface acidity 3.5

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 NH₃-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 NH₃ desorbed by weak (150-350 °C), medium (350-500 °C) and strong (500-800 °C) acid sites.37 CeTi catalyst mainly showed a single broad peak at 160 °C ascribed to NH3 desorbed by weak acid sites. While except the first peak at around 140 °C, CeW4Ti 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 NH₃ desorption amount was 1.01 mmol g⁻¹ according to Table 5, higher than 0.61 mmol g^{-1} of CeTi. CeW_xTiSi catalysts exhibited peaks at 160, 272 and 440 °C, mainly assigned to NH₃ desorption by weak and medium acid sites. With WO₃ loading amounts increasing from 0% to 8%, NH₃ desorption amount increased from 0.14 mmol g^{-1} to 2.02 mmol g^{-1} . All these results implied that the addition of WO3 could increase amounts of acid sites of the catalysts, bringing more NH3 adsorption sites, which plays an important role in the SCR reaction.10

3.6 Redox properties

H₂-TPR analysis was performed to investigate the presence of reducible species in the addition of WO₃ and SiO₂ to CeO₂/ TiO_2 -SiO₂. Fig. 8 illustrates the H₂-TPR profiles of CeW_xTiSi_y catalysts. All catalysts showed broad peak around 495 °C, ascribed to surface oxygen reduction of ceria.34 CeTi catalyst presented a sharp reduction peak at 680 °C, attributing to

Table 4 NO _x adsorption	capacity	of	cataly	sts
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	Integral areas				
Catalysts	Peak 1 (164–181 °C)	Peak 2 (218–258 °C)	Peak 3 (315–390 °C)	Peak 4 (511–620 °C)	Total NO _x desorption (mmol g^{-1})
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_3 -TPD profiles of CeW_xSi_yTi catalysts.

reduction of bulk oxygen in ceria. For CeWTi and CeW_xTiSi catalysts, it is observed that reduction peaks of CeO₂ and WO₃ overlapped on the catalysts in the temperature range of WO₃ reduction. The broad overlapping peaks ranged from 665 to 702 °C are attributed to the reduction of WO₃ to WO₂ as well as bulk oxygen of CeO₂,^{2,27} 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 WO₂ to W.²⁹ The second reduction peak of the WO_x-containing catalysts shifted to higher temperatures, revealing a strong interaction between CeO₂ and WO₃ species with WO₃ addition. For CeW_xTiSi catalysts, with WO₃ content increasing, H₂ consumption increased from 1.47 mmol g⁻¹ to 8.65 mmol g⁻¹ as shown in Table 5, indicating that the addition of WO₃ could bring more reducible subsurface

Table 5 Calculated amount of ammonia desorption in $\rm NH_3-TPD$ tests and hydrogen consumption in the $\rm H_2-TPR$

Catalysts	$NH_3 \ desorption \ (mmol \ g^{-1})$	H_2 consumption (mmol g ⁻¹)
CeSiTi	0.14	1.47
CeW ₂ SiTi	0.38	5.44
CeW ₄ SiTi	1.38	6.68
CeW ₇ SiTi	1.50	8.17
CeW ₈ SiTi	2.02	8.65
CeTi	0.61	4.41
CeW ₄ Ti	1.01	4.70



Fig. 8 H₂-TPR profiles of CeW_xSi_yTi 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_3 was doped into CeO_2/TiO_2 and CeO_2/TiO_2 -SiO₂ catalysts by impregnation method. WO_3 has a promotional effect

on the activity of the catalysts and the optimal loading of WO₃ species was 7%. After hydrothermal aging treatment, 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 WO₃ could promote CeO₂ and WO₃ crystallites disperse better over the catalyst surface. XPS results prove that WO₃ bring more appearance of Ce³⁺ and surface chemisorbed oxygen species so that more NO would be oxidized to NO₂, which was a benefit for the SCR process. NH₃ and NO_x-TPD results indicate that WO₃ provide more acid sites and more adsorbed NO_x and NH₃ species, which was also beneficial for the SCR reaction. TPR results suggest that WO₃ improve redox property of the catalysts.

Introduction of SiO₂ lower the catalytic activities of the catalysts. While after hydrothermally treating, the surface area of SiO₂-containing catalysts mostly preserved, hence enhancing the hydrothermal stability of the catalysts. There is synergistic effect between SiO₂ and WO₃ on keeping hydrothermal stability of the catalysts. From the results of XPS, TPD and H₂-TPR, the strong interaction between ceria, tungsten and silica could contribute to the excellent deNO_x performance of CeW_xTiSi_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).

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