



A superior Ce-W-Ti mixed oxide catalyst for the selective catalytic reduction of NO_x with NH₃

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ABSTRACT

A superior Ce-W-Ti mixed oxide catalyst prepared by a facile homogeneous precipitation method showed excellent NH₃-SCR activity and 100% N₂ selectivity with broad operation temperature window and extremely high resistance to space velocity, which is a very promising catalyst for NO_x abatement from diesel engine exhaust. The excellent catalytic performance is associated with the highly dispersed active Ce and promotive W species on TiO₂. The introduction of W species could increase the amount of active sites, oxygen vacancies, and Brønsted and Lewis acid sites over the catalyst, which is also beneficial to improve the low temperature activity by facilitating “fast SCR” reaction and enhance both of the high temperature activity and N₂ selectivity simultaneously by inhibiting the unselective oxidation of NH₃ at high temperatures.

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1. Introduction

With the rising challenges from energy crisis and global warming, diesel engines become more and more competitive due to its high fuel efficiency. However, the removal of NO_x from diesel engine exhaust, under oxygen-rich conditions, remains one of the major challenges in environmental catalysis [1,2].

Selective catalytic reduction of NO_x with NH₃ (NH₃-SCR), using V₂O₅-WO₃/TiO₂ or V₂O₅-MoO₃/TiO₂ as catalyst, has been widely used for the removal of NO_x from stationary sources. This technology is also introduced into the market for diesel vehicles and is thought to be one of the best technologies for meeting the severe NO_x reduction goals [1,3]. However, the toxicity of active vanadium species together with the narrow operation temperature window restrained the practical applications of the V-based catalysts for diesel vehicles. Some other transition metal-based oxide catalysts (such as Fe, Cu, Mn and Ce) were reported as potential substitutions of V-based catalyst for diesel vehicles [4–7]. Nevertheless, these catalysts were mainly tested under relatively low GHSV below 100,000 h⁻¹ using sieved powders, and some of them also suffer from low N₂ selectivity [5,6].

The reduction of NH₃-SCR catalyst volume is one of the main challenges of diesel vehicle with limited space on board [1]. Therefore, Fe (or Cu)-exchanged zeolites, especially ZSM-5, have received much attention due to their superior NH₃-SCR activity under high GHSV [8–12]. However, the insufficient low-temperature activity of Fe-ZSM-5 and the poor hydrothermal stability of Cu-ZSM-5 are neither satisfactorily solved [8]. Recently, some Cu-containing small-pore zeolites, such as Cu-SSZ-13 and Cu-SAPO-34, have been discovered as NH₃-SCR catalysts with excellent catalytic activity even after severe hydrothermal aging [13–15]. There are continuing efforts to develop new NH₃-SCR catalysts for controlling the NO_x emission from diesel engines.

In our previous study, we have developed a promising Ce/TiO₂ catalyst prepared by impregnation method showing high SCR activity at 275–400 °C [16]. Afterwards, Gao et al. [17] compared the NH₃-SCR activity of CeO₂/TiO₂ catalysts prepared by three methods, and they found that the catalyst prepared by single step sol-gel method shows higher activity than that prepared by impregnation method due to better dispersion of active nano-crystalline ceria. WO₃ was used as stabilizer and promoter of the traditional V₂O₅-WO₃/TiO₂ catalyst for many years [18,19]. Chen et al. [20] found that addition of W could enhance the activity of CeO₂/TiO₂ catalyst prepared by co-impregnation method. However, in their work the catalytic activity was measured mainly under a relatively low GHSV of 28,000 h⁻¹, and the NO_x conversion of the catalyst dramatically decreased at higher GHSV. Recently, we reported a remarkable improvement of Ce-Ti based catalyst, with highly dispersed CeO₂

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on TiO₂, prepared by a facile homogeneous precipitation method. This Ce-Ti mixed oxide catalyst presented prominent performance even under a high GHSV of 150,000 h⁻¹ [21].

In this study, after further optimization of the homogeneous precipitation method, the prepared Ce-Ti mixed oxide powder catalyst (Ce_{0.2}TiO_x) exhibited rather good activity under a high GHSV of 250,000 h⁻¹ (equal to about 25,000 h⁻¹ for a monolith catalyst). More importantly, a W doped Ce-Ti mixed oxide (Ce_{0.2}W_{0.2}TiO_x) powder catalyst present excellent NH₃-SCR activity together with 100% N₂ selectivity in a broad temperature range even under an extremely high GHSV of 500,000 h⁻¹ (equal to about 50,000 h⁻¹ for a monolith catalyst), which is a promising catalyst for NO_x abatement from diesel engine exhaust.

2. Experimental

2.1. Catalyst synthesis and activity test

The Ce-Ti mixed oxide catalyst, with a Ce/Ti molar ratio of 0.2, was denoted as Ce_{0.2}TiO_x. The transition metal doped catalysts were denoted as Ce_{0.2}M_{0.1}TiO_x (M = W, Mo, Fe, Co, Cu; M/Ti molar ratio = 0.1) and Ce_{0.2}W_aTiO_x ("a" represents the W/Ti molar ratio; a = 0.1, 0.2, 0.3, 0.5). The catalysts were all prepared by the optimized homogeneous precipitation method. The aqueous solutions of Ce(NO₃)₃·6H₂O, Ti(SO₄)₂ and relevant transition metal precursor ((NH₄)₁₀W₁₂O₄₁, (NH₄)₆Mo₇O₂₄·4H₂O, Fe(NO₃)₃·9H₂O, Co(NO₃)₂·6H₂O, or Cu(NO₃)₂·3H₂O) were mixed with required molar ratios (H₂C₂O₄·2H₂O was used to facilitate the solution of (NH₄)₁₀W₁₂O₄₁ and (NH₄)₆Mo₇O₂₄·4H₂O). Excessive urea aqueous solution was then added into the mixed solution. The solution was heated to 90 °C and held there for 12 h under vigorous stir. After filtration and washing with deionized water, the resulting precipitant was dried at 100 °C overnight and subsequently calcined at 500 °C for 5 h in air condition. Before NH₃-SCR activity test, the powder catalysts were pressed, crushed and sieved to 40–60 mesh.

The SCR activity tests of the sieved powder catalysts were carried out in a fixed-bed quartz flow reactor at atmospheric pressure. The reaction conditions were controlled as follows: 500 ppm NO (or 250 ppm NO and 250 ppm NO₂), 500 ppm NH₃, 5 vol.% O₂, 5 vol.% CO₂ (when used), 5 vol.% H₂O (when used), 100 ppm SO₂ (when used), balance N₂, and 500 ml/min total flow rate. Different GHSV were obtained by changing the volume of catalyst. The effluent gas, including NO, NH₃, NO₂ and N₂O was continuously analyzed by an online NEXUS 670-FTIR spectrometer equipped with a gas cell with 0.2 dm³ volume. The FTIR spectra were collected after 1 h when the SCR reaction reached a steady state, and the NO_x conversion and N₂ selectivity were calculated accordingly [6,21].

$$\text{NO}_x \text{ conversion} = \left(1 - \frac{[\text{NO}]_{\text{out}} + [\text{NO}_2]_{\text{out}}}{[\text{NO}]_{\text{in}} + [\text{NO}_2]_{\text{in}}}\right) \times 100\% \quad (1)$$

$$\text{N}_2 \text{ selectivity} = \frac{[\text{NO}]_{\text{in}} + [\text{NH}_3]_{\text{in}} - [\text{NO}_2]_{\text{out}} - 2[\text{N}_2\text{O}]_{\text{out}}}{[\text{NO}]_{\text{in}} + [\text{NH}_3]_{\text{in}}} \times 100\% \quad (2)$$

2.2. Characterizations

The surface areas of the catalysts were obtained from N₂ adsorption/desorption analysis at 77 K using a Quantachrome Quadrasorb SI-MP. Prior to the N₂ physisorption, the catalysts were degassed at 300 °C for 4 h. Surface areas were determined by BET equation in 0.05–0.35 partial pressure range.

Powder X-ray diffraction (XRD) measurements of the catalysts were carried out on a computerized PANalytical X'Pert Pro diffractometer with Cu Kα (λ = 0.15406 nm) radiation. The data of

2θ from 20° to 80° were collected at 8°/min with the step size of 0.07°.

Visible Raman spectra of the catalysts were collected at room temperature on a Spex 1877 D triplemate spectrograph with spectral resolution of 2 cm⁻¹. A 532 nm DPSS diode-pump solid semiconductor laser was used as the excitation source and the power output was about 40 mW. Before measurements, the samples were well ground and mounted into a spinning holder to avoid thermal damage during the scanning. The Raman signals were collected with conventional 90° geometry and the time for recording each spectrum was about 30 s. All Raman spectra used in the paper were original and unsmoothed.

The XPS of Ce_{0.2}TiO_x and Ce_{0.2}W_{0.2}TiO_x were both recorded on a Scanning X-ray Microprobe (Axis Ultra, Kratos Analytical Ltd.) using Al Kα radiation (1486.7 eV). Binding energies of Ce 3d, Ti 2p and O 1s were calibrated using C 1s peak (BE = 284.8 eV) as standard.

The *in situ* DRIFTS experiments were performed on an FTIR spectrometer (Nicolet Nexus 670) equipped with a smart collector and an MCT/A detector cooled by liquid nitrogen. The reaction temperature was controlled precisely by an Omega programmable temperature controller. Prior to each experiment, the sample was pretreated at 400 °C for 0.5 h in a flow of 20 vol.% O₂/N₂ and then cooled down to 200 °C. The background spectrum was collected in flowing N₂ and automatically subtracted from the sample spectrum. The reaction conditions were controlled as follows: 300 ml/min total flow rate, 500 ppm NH₃ or 500 ppm NO + 5 vol.% O₂, and N₂ balance. All spectra were recorded by accumulating 100 scans with a resolution of 4 cm⁻¹.

3. Results and discussion

3.1. NH₃-SCR activity of different transition metal doped catalysts

As shown in Fig. 1A, the Ce_{0.2}TiO_x catalyst showed more than 90% NO_x conversion from 250 to 400 °C under a GHSV of 250,000 h⁻¹. Several transition metals including W, Mo, Fe, Co and Cu were doped into the Ce_{0.2}TiO_x catalyst. The addition of Mo to the Ce-Ti mixed oxide catalyst has no obvious influence on the catalytic activity. Other transition metal (W, Fe, Co and Cu) doped catalysts all presented enhanced low temperature SCR activity. However, the medium and high temperature NO_x conversions over Ce_{0.2}Co_{0.1}TiO_x and Ce_{0.2}Cu_{0.1}TiO_x decreased sharply, and the high temperature NO_x conversion over Ce_{0.2}Fe_{0.1}TiO_x decreased significantly. Only Ce_{0.2}W_{0.1}TiO_x clearly showed both enhanced low temperature activity and high temperature activity simultaneously combined with enhanced N₂ selectivity (Fig. 1B), compared with those over undoped Ce_{0.2}TiO_x.

3.2. Influence of W doping molar ratio

With the increase of W doping molar ratio from 0.1 to 0.2, the high temperature NO_x conversion was maintained at 100% even up to 450 °C, while the low temperature NO_x conversion did not show any decrease (Fig. 2). However, further increasing the relative doping amount of W to 0.3 and 0.5 resulted in an obvious decline of low temperature SCR activity, although the high temperature NO_x conversions still maintained being 100%. Therefore, in short summary, the Ce_{0.2}W_{0.2}TiO_x catalyst presented an optimal NH₃-SCR performance with Ce:W molar ratio being 1:1.

3.3. Influence of GHSV and stability test

The NO_x conversions over Ce_{0.2}W_{0.2}TiO_x catalyst under different GHSV are shown in Fig. 3. Obviously, the increase of GHSV only resulted in some decrease of low temperature SCR activity, but no clear influence on high temperature activity. The catalyst

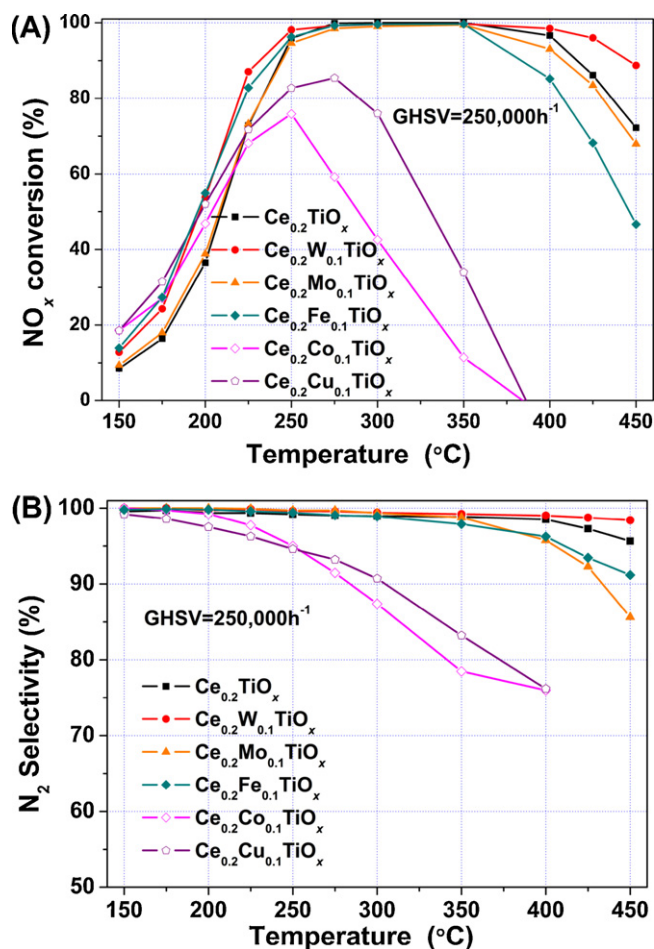


Fig. 1. (A) NO_x conversions and (B) N₂ selectivity over Ce_{0.2}TiO_x and transition metal (W, Mo, Fe, Co, Cu) doped catalysts. Reaction conditions: [NO]=[NH₃]=500 ppm, [O₂]=5 vol.%, N₂ balance and GHSV=250,000 h⁻¹.

even showed over 90% NO_x conversion in a wide temperature range from 275 to 450 °C under a rather high GHSV of 500,000 h⁻¹, suggesting that this Ce_{0.2}W_{0.2}TiO_x catalyst is highly resistant to large space velocity, which is very important for its practical use on diesel vehicles with limited space on board.

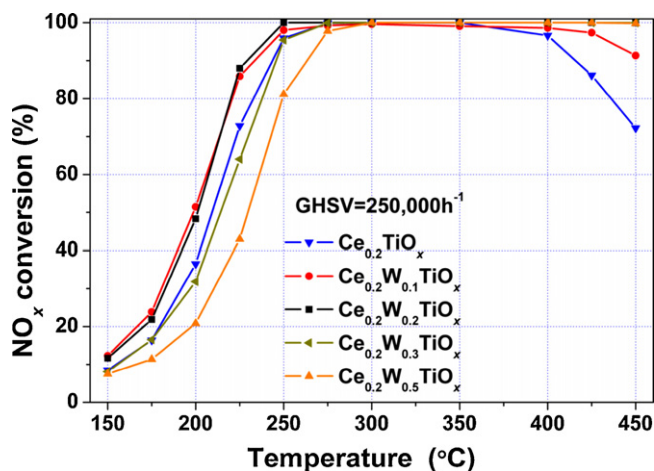


Fig. 2. NO_x conversions over Ce_{0.2}W_αTiO_x (α=0, 0.1, 0.2, 0.3, 0.5) catalysts. Reaction conditions: [NO]=[NH₃]=500 ppm, [O₂]=5 vol.%, N₂ balance and GHSV=250,000 h⁻¹.

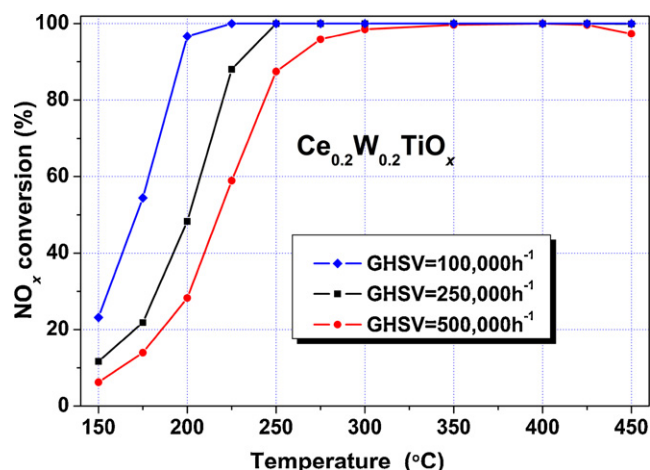


Fig. 3. NO_x conversions over Ce_{0.2}W_{0.2}TiO_x catalyst under different GHSV. Reaction conditions: [NO]=[NH₃]=500 ppm, [O₂]=5 vol.% and N₂ balance.

The stability of the Ce_{0.2}W_{0.2}TiO_x catalyst was also tested under a GHSV of 250,000 h⁻¹ (Fig. 4). Clearly, there was no deactivation occurred, and the NO_x conversion and N₂ selectivity both maintained at 100% during the tested 100 h at 300 °C. After the stability test, the NH₃-SCR activity of the aged catalyst was tested again, and no change was observed at each temperature point comparing with the activity of fresh catalyst, indicating a high stability of Ce_{0.2}W_{0.2}TiO_x.

3.4. Influence of CO₂, H₂O, SO₂ and NO₂

We also tested the effects of CO₂, H₂O, SO₂ and NO₂ on the SCR activity of Ce_{0.2}W_{0.2}TiO_x under a GHSV of 250,000 h⁻¹ (Figs. 5 and 6). The coexistence of 5 vol.% H₂O just showed a slight influence on the SCR activity below 250 °C. The inhibiting effect of water on the SCR reaction is a common phenomenon. It is usually explained as an effect of a competition between H₂O and NH₃/NO_x on the reaction sites or as modification of the structure of active sites, e.g. the transformation of Lewis acid sites into Brønsted acid sites [18,22–25]. The NO_x conversion under the coexistence of 5 vol.% CO₂ and 5 vol.% H₂O was almost the same as that with only 5 vol.% H₂O in the feeding gas, suggesting that no synergistic inhibition effect between CO₂ and H₂O was present on the SCR activity.

In the presence of 100 ppm SO₂ at 300 °C, there was almost no change of NO_x conversion over the catalyst in 12 h. However,

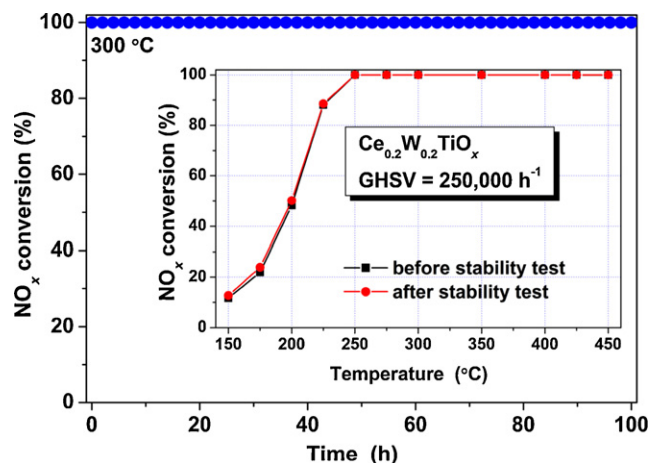


Fig. 4. Stability test result of Ce_{0.2}W_{0.2}TiO_x catalyst. Reaction conditions: [NO]=[NH₃]=500 ppm, [O₂]=5 vol.%, N₂ balance and GHSV=250,000 h⁻¹.

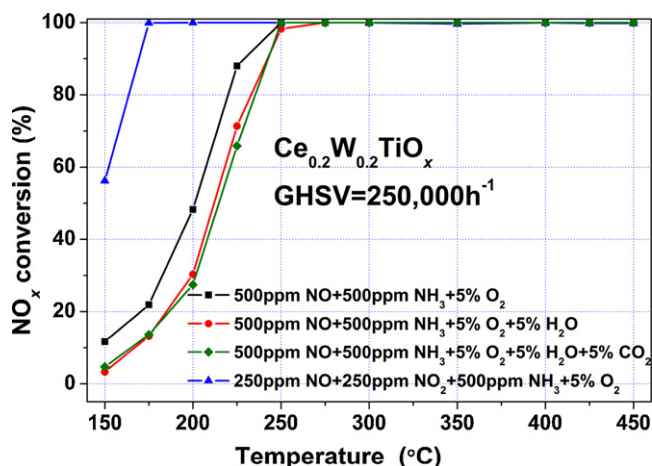


Fig. 5. NO_x conversions over $\text{Ce}_{0.2}\text{W}_{0.2}\text{TiO}_x$ catalyst in the presence of CO_2 , H_2O and NO_2 . Reaction conditions: 500 ppm NO (or 250 ppm NO and 250 ppm NO_2), 500 ppm NH_3 , 5 vol.% O_2 , 5 vol.% CO_2 (when used), 5 vol.% H_2O (when used), N_2 balance and $\text{GHSV} = 250,000 \text{ h}^{-1}$.

the coexistence of 100 ppm SO_2 and 5 vol.% H_2O induced a gradually decrease of NO_x conversion at 300 °C (Fig. 6). After stopping $\text{SO}_2 + \text{H}_2\text{O}$, the NO_x conversion was recovered with a sharp increase from ca. 60% to 100%. It is speculated that the loss of SCR activity might be mainly associated with the deposit of ammonium sulfate on the catalyst surface [26,27].

When NO_2 was added to the feeding gas ($\text{NO}_2:\text{NO} = 1:1$), the low temperature NO_x conversion over $\text{Ce}_{0.2}\text{W}_{0.2}\text{TiO}_x$ was significantly enhanced due to the “fast SCR” effect, and 100% NO_x conversion was obtained even in a broad temperature range from 175 to 450 °C.

3.5. Separated NO oxidation and NH_3 oxidation

In order to investigate the effects of W species in $\text{Ce}_{0.2}\text{W}_{0.2}\text{TiO}_x$ catalyst, the separate NO oxidation ($\text{NO} + \text{O}_2$) and separate NH_3 oxidation ($\text{NH}_3 + \text{O}_2$) experiments were also carried out (Fig. 7). The NO_2 production in the separate NO oxidation reaction over $\text{Ce}_{0.2}\text{W}_{0.2}\text{TiO}_x$ is obviously higher than that over $\text{Ce}_{0.2}\text{TiO}_x$ in the low temperature range (Fig. 7A). Many studies have shown that, if the SCR catalyst can oxidize NO to NO_2 *in situ*, its low temperature SCR activity will be significantly enhanced due to the effect of “fast SCR” [1,21]. Therefore, the introduction of W could enhance the low

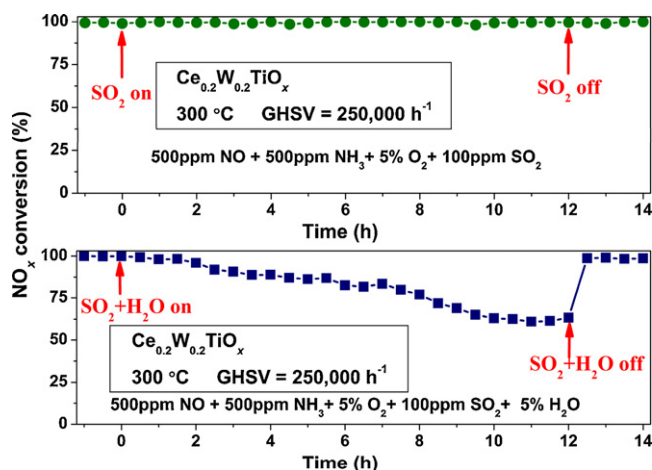


Fig. 6. NO_x conversions over $\text{Ce}_{0.2}\text{W}_{0.2}\text{TiO}_x$ catalyst in the presence of SO_2 and $\text{SO}_2 + \text{H}_2\text{O}$ at 300 °C. Reaction conditions: $[\text{NO}] = [\text{NH}_3] = 500 \text{ ppm}$, $[\text{O}_2] = 5 \text{ vol.}\%$, 100 ppm SO_2 (when used), 5 vol.% H_2O (when used), N_2 balance and $\text{GHSV} = 250,000 \text{ h}^{-1}$.

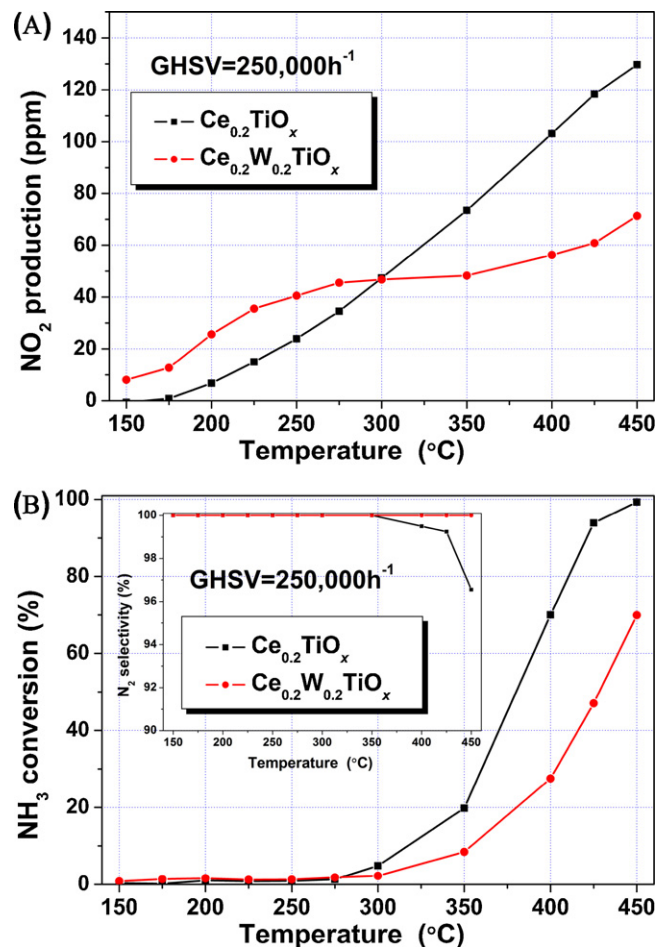


Fig. 7. (A) NO_2 productions during separate NO oxidation reaction and (b) NH_3 conversions and N_2 selectivity during separate NH_3 oxidation reaction over $\text{Ce}_{0.2}\text{TiO}_x$ and $\text{Ce}_{0.2}\text{W}_{0.2}\text{TiO}_x$ catalysts. Reaction conditions: (A) $[\text{NO}] = 500 \text{ ppm}$, (B) $[\text{NH}_3] = 500 \text{ ppm}$, $[\text{O}_2] = 5 \text{ vol.}\%$, N_2 balance and $\text{GHSV} = 250,000 \text{ h}^{-1}$.

temperature activity of the $\text{Ce}_{0.2}\text{W}_{0.2}\text{TiO}_x$ catalyst by promoting NO oxidation to NO_2 to facilitate the “fast SCR” reaction.

The high temperature NH_3 oxidation ability of $\text{Ce}_{0.2}\text{W}_{0.2}\text{TiO}_x$ is obviously lower than that of $\text{Ce}_{0.2}\text{TiO}_x$ (Fig. 7B), which means that the addition of W could inhibit the unselective oxidation of NH_3 and thus promote the high temperature activity of $\text{Ce}_{0.2}\text{W}_{0.2}\text{TiO}_x$. Besides, some NO, NO_2 and N_2O were detected at high temperatures in the NH_3 oxidation reaction over $\text{Ce}_{0.2}\text{TiO}_x$, while none of these by-products was observed over $\text{Ce}_{0.2}\text{W}_{0.2}\text{TiO}_x$, suggesting that the introduction of W species into $\text{Ce}_{0.2}\text{W}_{0.2}\text{TiO}_x$ is also beneficial to the enhancement of N_2 selectivity in NH_3 -SCR reaction.

A catalytic cycle for the SCR reaction involving both acid and redox reactions was proposed by Topsøe et al. [28,29], and the promotion effects of W species in $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalysts were attributed to the increase of both catalyst redox properties and acid sites [25,30–33]. Previous studies by Lietti et al. [25,30,31] have indicated that the catalyst redox functions (especially the reoxidation process of catalytic sites) govern the catalytic reactivity in the low-temperature region, whereas the SCR reaction in the high-temperature region is likely controlled by the surface acid properties. Therefore, in this study, we can expect that the promoted NO oxidation activity at low temperatures (<300 °C) and the inhibited unselective oxidation of NH_3 (as well as the decreased NO oxidation) at high temperatures (>300 °C) is strongly associated with the impact of W addition on the redox and acid properties of $\text{Ce}_{0.2}\text{W}_{0.2}\text{TiO}_x$, respectively.

Table 1
Surface atomic concentrations and BET surface areas of $\text{Ce}_{0.2}\text{TiO}_x$ and $\text{Ce}_{0.2}\text{W}_{0.2}\text{TiO}_x$ catalysts.

Sample	Surface atomic concentration ^a (%)				BET surface area (m^2/g)
	Ce	W	Ti	O	
$\text{Ce}_{0.2}\text{TiO}_x$	4.6	–	19.1	76.3	125.7
$\text{Ce}_{0.2}\text{W}_{0.2}\text{TiO}_x$	6.1	4.6	16.1	73.2	107.9

^a According to XPS analysis.

3.6. BET surface area, XRD and Raman spectra

As shown in Table 1, the BET surface area of $\text{Ce}_{0.2}\text{W}_{0.2}\text{TiO}_x$ ($107.9 \text{ m}^2/\text{g}$) is lower than that of $\text{Ce}_{0.2}\text{TiO}_x$ ($125.7 \text{ m}^2/\text{g}$), yet the SCR performance of $\text{Ce}_{0.2}\text{W}_{0.2}\text{TiO}_x$ is actually much higher than that of $\text{Ce}_{0.2}\text{TiO}_x$, indicating that some synergistic effect must exist between the Ce and W species [34].

No Ce or W species was observed in $\text{Ce}_{0.2}\text{W}_{0.2}\text{TiO}_x$ either in XRD or in Raman analysis (Fig. 8), while only anatase TiO_2 was detected. Although the Ce-W containing species might already exceed the monolayer dispersion on TiO_2 , the multi-layer active species probably only contained amorphous phase or crystallite phase with very small particle size (such as Ce-W solid solution without long-range order). In such case, it is still reasonable to see no diffraction peaks of Ce or W species. In the XRD analysis, a slightly higher crystallization degree of anatase TiO_2 in the bulk phase was observed in $\text{Ce}_{0.2}\text{W}_{0.2}\text{TiO}_x$ than that in $\text{Ce}_{0.2}\text{TiO}_x$. However, the Raman spectra apparently showed that the introduction of W species strongly inhibited the crystallization of anatase TiO_2 on the catalyst surface, probably leading to a much higher dispersion degree of active Ce species.

3.7. XPS results

It was reported that highly dispersed nano-crystalline CeO_2 is the active phase in Ce-Ti mixed oxide catalyst [16,17,20,21]. According to the XPS results, there are more surface Ce atoms dispersed on $\text{Ce}_{0.2}\text{W}_{0.2}\text{TiO}_x$ than those on $\text{Ce}_{0.2}\text{TiO}_x$ (Table 1), which indicate that the introduction of W could induce more abundant CeO_2 crystallite and thus increase the amount of active sites on the catalyst surface. Furthermore, the existence of tungsten species could also contribute to the NH_3 -SCR reaction by their promotion effects [20,33–35]. In addition, more Ce species dispersed on the surface of $\text{Ce}_{0.2}\text{W}_{0.2}\text{TiO}_x$ will induce a strong inhibition effect on the crystallization of surface TiO_2 . Contrastively, less Ce species

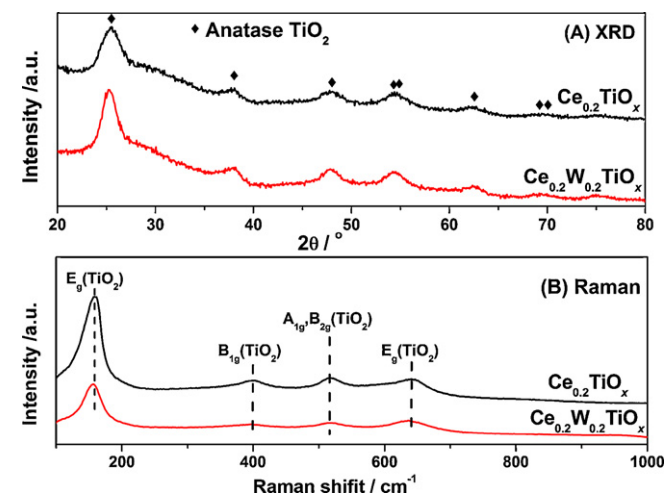


Fig. 8. (A) XRD patterns and (B) Raman spectra ($\lambda_{\text{ex}} = 532 \text{ nm}$) of $\text{Ce}_{0.2}\text{TiO}_x$ and $\text{Ce}_{0.2}\text{W}_{0.2}\text{TiO}_x$ catalysts.

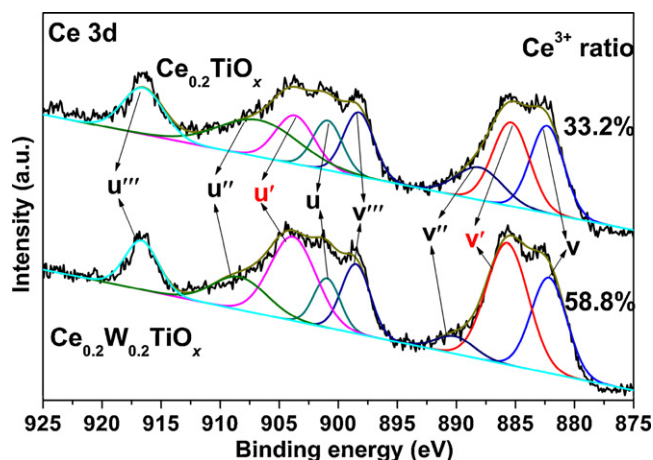


Fig. 9. XPS results of Ce 3d of $\text{Ce}_{0.2}\text{TiO}_x$ and $\text{Ce}_{0.2}\text{W}_{0.2}\text{TiO}_x$ catalysts.

existed in the bulk phase of catalyst will cause a weak inhibition effect on the crystallization of bulk TiO_2 . This might be an important reason for the contradictory trends of TiO_2 crystallization on the surface and in the bulk phase between $\text{Ce}_{0.2}\text{W}_{0.2}\text{TiO}_x$ and $\text{Ce}_{0.2}\text{TiO}_x$, as shown by the XRD results and Raman spectra in Fig. 8.

The Ce 3d peaks were fitted by searching for the optimum combination of Gaussian bands with the correlation coefficients (r^2) above 0.99 (Fig. 9). The sub-bands labeled u' and v' represent the $3d^{10}4f^1$ initial electronic state corresponding to Ce^{3+} , and the sub-bands labeled u, u'', u''', v, v'', and v''' represent the $3d^{10}4f^0$ state of Ce^{4+} . The Ce^{3+} ratio, calculated by $\text{Ce}^{3+}/(\text{Ce}^{3+} + \text{Ce}^{4+})$, of $\text{Ce}_{0.2}\text{W}_{0.2}\text{TiO}_x$ (58.5%) was significantly higher than that of $\text{Ce}_{0.2}\text{TiO}_x$ (33.2%), indicating the presence of more surface oxygen vacancies on $\text{Ce}_{0.2}\text{W}_{0.2}\text{TiO}_x$.

The O 1s peak was fitted into two sub-bands by searching for the optimum combination of Gaussian bands with the correlation coefficients (r^2) above 0.99 (Fig. 10). The sub-bands at 529.5–530.0 eV could be attributed to the lattice oxygen O^{2-} (denoted as O_β). Two shoulder sub-bands at 531.0–531.6 eV and 532.8–533.0 eV are assigned to the surface adsorbed oxygen (denoted as O_α), such as O_2^{2-} and O^- belonging to defect-oxide or hydroxyl-like group, and chemisorbed water (denoted as $\text{O}_{\alpha'}$), respectively [36,37]. Surface adsorbed oxygen (O_α) is often thought to be more reactive in oxidation reactions due to its higher mobility than lattice oxygen (O_β), so many researchers considered that high O_α ratio is beneficial for the NO oxidation to NO_2 in the SCR reaction and thereafter facilitate the “fast SCR” reaction [38–40]. Interestingly, in this study the calculated O_α ratio, calculated by $\text{O}_\alpha/(\text{O}_\alpha + \text{O}_{\alpha'} + \text{O}_\beta)$, of

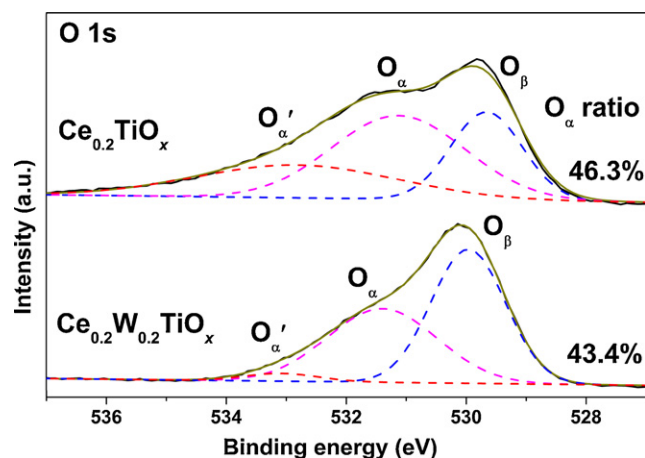


Fig. 10. XPS results of O 1s of $\text{Ce}_{0.2}\text{TiO}_x$ and $\text{Ce}_{0.2}\text{W}_{0.2}\text{TiO}_x$ catalysts.

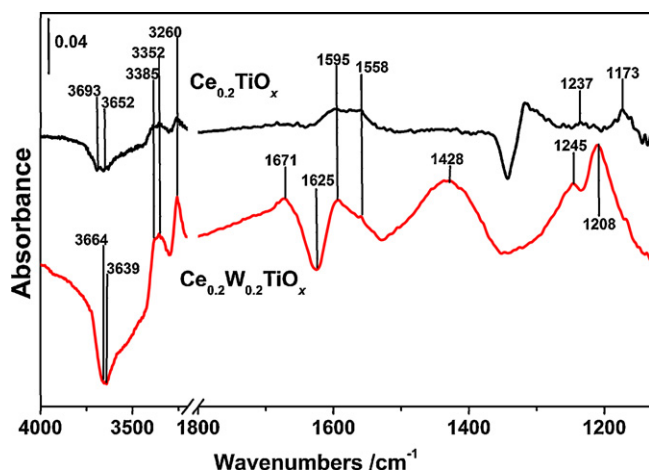


Fig. 11. *In situ* DRIFTS of NH_3 adsorption at 200 °C.

$\text{Ce}_{0.2}\text{W}_{0.2}\text{TiO}_x$ (43.4%) is slightly lower than that of $\text{Ce}_{0.2}\text{TiO}_x$ (46.3%), which means that some other important changes (such as the increase of active CeO_2 crystallite, redox properties, and surface acid sites) but not the changes of O_α ratio induced by W addition caused the enhancement of low temperature NO oxidation ability of $\text{Ce}_{0.2}\text{W}_{0.2}\text{TiO}_x$. However, the inhibited high temperature oxidation of NH_3 over $\text{Ce}_{0.2}\text{W}_{0.2}\text{TiO}_x$ might be associated with the low O_α ratio.

3.8. *In situ* DRIFTS

The *in situ* DRIFTS of NH_3 adsorption at 200 °C were measured to examine the change of acidity on the catalyst after W addition (Fig. 11). The bands at 1671 cm^{-1} and 1428 cm^{-1} are assigned to the symmetric and asymmetric bending vibrations of ionic NH_4^+ [6,28,41]; the bands at 1595 cm^{-1} and 1245, 1208/1237, 1173 cm^{-1} are assigned to the asymmetric and symmetric bending vibrations of coordinated NH_3 [42–44]; the band at 1558 cm^{-1} is assigned to the scissoring vibration mode of NH_2 species [43,45]; the bands at 3260, 3352 and 3385 cm^{-1} are assigned to the N–H stretching vibration modes [6,43]; and the bands at 1625 cm^{-1} and 3639, 3664/3652, 3693 cm^{-1} are assigned to the hydroxyl consumption due to the interaction with NH_3 to form NH_4^+ [6,42].

After NH_3 adsorption, obviously stronger NH_3 (1595 and 1208 cm^{-1}) and NH_4^+ (1671 and 1428 cm^{-1}) bands were observed on $\text{Ce}_{0.2}\text{W}_{0.2}\text{TiO}_x$, despite its low surface area, than those on $\text{Ce}_{0.2}\text{TiO}_x$, indicating that the introduction of W species tremendously increased both of the Lewis and Brønsted acid sites on the catalyst. Based on some previous studies, we can speculate that the increased Lewis acid sites are mainly composed of unsaturated W^{n+} cations, while the increased Brønsted acid sites are mainly composed of W–OH sites arising from partially hydrated tungsten species, such as W=O, W–O–W, and Ce–W–O [18,35,46,47]. It is worthy to note that the adsorbed H_2O on the surface of $\text{Ce}_{0.2}\text{W}_{0.2}\text{TiO}_x$ showed an obvious consumption at 1625 cm^{-1} , and at the same time much more hydroxyl groups were consumed on $\text{Ce}_{0.2}\text{W}_{0.2}\text{TiO}_x$ than those on $\text{Ce}_{0.2}\text{TiO}_x$ owing to the interaction with NH_3 adsorbed species to form NH_4^+ . This result clearly indicates that H_2O can be readily activated on the W doped catalyst to form Brønsted acid sites, participating in the NH_3 -SCR reaction. When the $\text{Ce}_{0.2}\text{W}_{0.2}\text{TiO}_x$ catalyst was subsequently exposed to $\text{NO} + \text{O}_2$ afterwards, all of the NH_4^+ and NH_3 bands vanished in 2 min and some bands ascribed to bridging nitrate (1625 and 1269 cm^{-1}), bidentate nitrate (1603 cm^{-1}) and monodentate nitrate (1581 cm^{-1}) appeared [6,48] (Fig. 12), suggesting that both types of acid sites are involved in NH_3 -SCR reaction. It has been

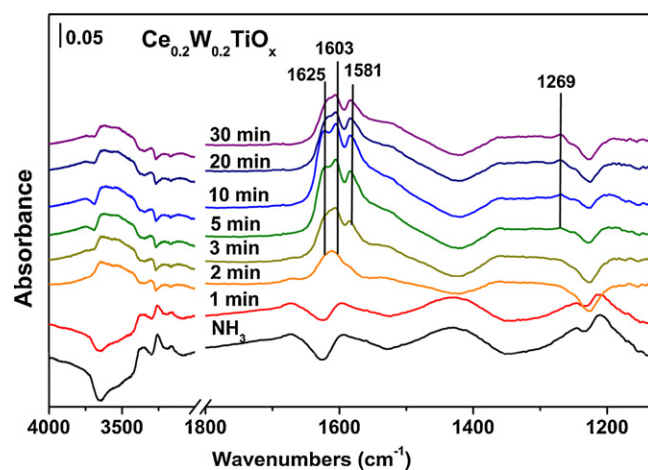


Fig. 12. Pre-adsorbed NH_3 species reacted with $\text{NO} + \text{O}_2$ over $\text{Ce}_{0.2}\text{W}_{0.2}\text{TiO}_x$ catalyst.

indicated that surface acidity plays an important role in the adsorption and activation of NH_3 , and thus affects the occurrence of SCR reaction, especially at high temperature range [31,35]. Therefore, the increased Brønsted and Lewis acid sites by W addition should be an important reason for the enhanced catalytic activity, especially high temperature activity.

4. Conclusions

Several transition metals including W, Mo, Fe, Co and Cu were doped into the $\text{Ce}_{0.2}\text{TiO}_x$ catalyst prepared by a facile homogeneous precipitation method. Among the doped catalysts, $\text{Ce}_{0.2}\text{W}_{0.2}\text{TiO}_x$ with Ce:W molar ratio being 1:1 showed excellent NH_3 -SCR activity and 100% N_2 selectivity in a broad temperature range. Besides, the $\text{Ce}_{0.2}\text{W}_{0.2}\text{TiO}_x$ catalyst even showed over 90% NO_x conversion in a wide temperature range from 275 to 450 °C under a rather high GHSV of 500,000 h^{-1} , suggesting that this $\text{Ce}_{0.2}\text{W}_{0.2}\text{TiO}_x$ catalyst is highly resistant to large space velocity, which is advantageous to the application for diesel engines with limited installing space for exhaust after-treatment systems.

Although the BET surface area of $\text{Ce}_{0.2}\text{W}_{0.2}\text{TiO}_x$ was lower than that of $\text{Ce}_{0.2}\text{TiO}_x$, the introduction of W species could lead to a much higher dispersion degree of active Ce species and increase the amount of active CeO_2 crystallite, oxygen vacancies, and both Brønsted and Lewis acid sites on the catalyst. Furthermore, the low temperature activity of NO oxidation to NO_2 was promoted by W addition and the high temperature activity of NH_3 unselective oxidation was inhibited, which are beneficial to improve the NH_3 -SCR activity in the whole temperature range and enhance the N_2 selectivity in the high temperature range simultaneously.

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