Novel TiO$_2$ catalyst carriers with high thermostability for selective catalytic reduction of NO by NH$_3$

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**A B S T R A C T**

A series of TiO$_2$ catalyst carriers with ceria additives were prepared by a precipitation method and tested for selective catalytic reduction (SCR) of NO by NH$_3$. These samples were characterized by XRD, N$_2$-BET, NH$_3$-TPD, H$_2$-TPR, TEM, XPS and **in situ** DRIFTS, respectively. Results showed that the appropriate addition of ceria can enhance the catalytic activity and thermostability of TiO$_2$ catalyst carriers significantly. The maximum catalytic activity of Ti-Ce-O$_x$-500 is 98.5% at 400 °C with a GHSV of 100 000 h$^{-1}$ and the high catalytic activity still remains even after the treatment at high temperature for 24 h. The high catalytic performance of Ti-Ce-O$_x$-500 can be attributed to a series of superior properties, such as larger specific surface area, more Brunsted acid sites, more hydrogen consumption, and the higher proportion of chemisorbed oxygen. Ceria atoms can inhibit the crystalline grain growth and the collapse of small channels caused by high temperatures. Furthermore, **in situ** DRIFTS in different feed gases show that the SCR reaction over Ti-Ce-O$_x$-500 follows both E-R and L-H mechanisms.

1. Introduction

Nitrogen oxides (NO$_x$) are major contributors to certain worsening environment problems such as acid rain and photochemical smog [1–3]. Selective catalytic reduction of NO$_x$ with NH$_3$ (NH$_3$-SCR) is a well-established and widely employed technology to reduce NO$_x$ from stationary sources [4,5]. According to its reaction temperature window, the NH$_3$-SCR technology can be divided to low-, medium- and high-temperature reactions [6]. The reaction temperatures from 250 °C to 450 °C are often classified as the medium-temperature region. In heat-engine plants and coal-fired boilers, the most commercially used catalysts are V$_2$O$_5$/TiO$_2$ and CeO$_2$/TiO$_2$ catalysts [7]. However, both the V$_2$O$_5$/TiO$_2$ and CeO$_2$/TiO$_2$ catalysts still suffer a lot from their poor thermostability. In other words, their catalyst carriers can be sintered when the reaction temperature is too high (usually higher than 600 °C) at times, which leads to the decrease of their catalytic activity permanently. Moreover, the sublimation of V$_2$O$_5$ occurs at high temperatures even after modification with molybdenum and tungsten species for the V$_2$O$_5$-based catalyst [8]. Therefore, developing novel medium-temperature catalyst carriers with high thermostability to overcome these disadvantages is an urgent demand.

Owing to its chemical inertness, long-term stability and environmental friendliness, TiO$_2$ has been applied in many fields, such as gas sensor application [9], coating [10] and photocatalysis [11]. TiO$_2$ is often used as a catalyst carrier for the NH$_3$-SCR, and has been employed to develop many catalysts, such as CeO$_2$/TiO$_2$ [12,13], V$_2$O$_5$/TiO$_2$ [14–17], Ce-W-O$_x$/TiO$_2$ [18–20], Ce-Zr-O$_x$/TiO$_2$ [21,22], Mn-Ce-O$_x$/TiO$_2$ [23–25] and so on. Along with TiO$_2$, CeO$_2$ is a widely used catalytic material on account of its unique redox properties in many fields such as photocatalysis [26], fuel cell [27] and oxygen permeation membrane [28]. It is well known that the unit cell volume of TiO$_2$ swells after the process at high temperatures. On the other hand, the ionic radius of Ce$^{3+}$ is larger than that of Ti$^{4+}$ [29]. The swell action of anatase TiO$_2$ might be suppressed with the appropriate addition of CeO$_2$, thus improved the thermostability.

With this hypothesis, to investigate the effect of CeO$_2$, the pure TiO$_2$ powder (the general commercial catalyst carrier prepared by the precipitation method) and the unpurified TiO$_2$ (from Shandong Gemsky
Environmental Technology Corporation) were used as the blank samples. The unpurified TiO$_2$ often contains a small amount of WO$_3$ (Ti: W molar ratio = 100:3). Therefore, WO$_3$ can be replaced by CeO$_2$ in the production of TiO$_2$ to improve the thermostability. Guided by this hypothesis, a novel TiO$_2$ catalyst carrier with high thermostability was synthesized by a precipitation method, which can attract more attention in addressing environmental issues [30]. Through a series of characterization, it was found that ceria atoms can inhibit the collapse of the small channels caused by high temperatures. The large specific surface area, abundant Brunsted acid sites, and the high proportion of chemisorbed oxygen of the TiO$_2$/CeO$_2$ warrant excellent catalytic performance even after the process of high temperatures.

2. Experiment

2.1. Catalyst carrier preparation

The TiO$_2$ powder (general commercial catalyst carrier, blank sample) was prepared by a precipitation method. In a typical preparation, the appropriate hydrous titanium oxides and distilled water were mixed under vigorous stirring. Then the aqua ammonia was added into a fi

2.2. Catalytic activity and thermostability measurement

The catalyst carriers (0.5 mL, particle sizes of 0.3–0.45 mm) were added into a fixed-bed quartz reactor (6 mm inner diameter) to investigate the NH$_3$-SCR catalytic activities. The 833 mL min$^{-1}$ gas flow rate corresponded to a GHSV of 100 000 h$^{-1}$. The reacting gas was composed of 600 ppm NO, 600 ppm NH$_3$, 6 vol.% O$_2$ and balance N$_2$. The NO concentrations at the inlet and outlet of the reactor were obtained by the flue gas analyzer (MRU VarioPlus, Germany). The catalytic activity ($X_{\text{NO}}$) was calculated by Eq. (1). Data were recorded after the reaction was stabilized.

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

2.3. Characterization of catalyst carriers

X-ray diffraction (XRD) patterns were obtained from an X-ray diffractometer (Smartlab TM 3Kw, Rigaku, Japan). The scan speed was 5’ min$^{-1}$ and the 2θ scans covered 10–80°. The X-ray photoelectron spectroscopy (XPS) patterns were acquired by an AXIS ULTRA DLD instrument (Al-Ka radiation, 1486.6 eV), and the vacuum degree was maintained at 10$^{-7}$ Pa. The samples were dried at 100°C for 24 h to remove moisture and then were tested without surface treatment. The curve fitting was performed by using XPSPEAK 4.1 with a Shirley-type background. The N$_2$ adsorption/desorption isotherms of the samples were obtained by a surface area analyzer (Micromeritics, 2020 M V3.00 H). After the samples were treated at 350°C under vacuum for 3 h, the samples were measured at -196°C. The microstructural nature of the catalysts was investigated using a transmission electron microscopy (JEOL, JEM-2010UHR).

The temperature programmed desorption of ammonia (NH$_3$-TPD) was conducted on the CHEMBET-3000 (Quantachrome) to obtain the surface acid properties. All the catalyst carriers were preheated at 450°C under a helium stream for 1 h, and then cooled to 60°C for the ammonia adsorption. Afterwards, ammonia was desorbed from 60°C to 550°C at a heating rate of 10°C min$^{-1}$. The Semiautomatic Micromeritics TPD/TPR 2900 instrument was used for the temperature programmed reduction of hydrogen (H$_2$-TPR). All the catalyst carriers were preheated to 400°C under an argon stream for 1 h, and cooled to 50°C. Then 5% H$_2$/Ar flow was switched, and the temperature increased from 50°C to 800°C at a 10°C min$^{-1}$ heating rate. The data were collected throughout the whole temperature range.

In situ Diffuse Reflectance Infrared Fourier Transform Spectra (in situ DRIFTS) were also collected by a Nicolet is50 spectrometer. All the catalyst carriers were preheated at 300°C under a N$_2$ stream for 2 h, and then cooled to the desired temperature. For the NH$_3$-adsorption and the NO + O$_2$ adsorption, 600 ppm NH$_3$ and 600 ppm NO + 5% O$_2$ were pumped into the system for 30 min, respectively, when the temperature was cooled to 150°C. Then the in situ DRIFT spectra were collected as the temperature increased. For the reaction between NH$_3$ and adsorbed NO + O$_2$, 600 ppm NO + 5% O$_2$ was pumped into the system for 30 min. After the temperature was increased to 450°C, the flow of NO + O$_2$ was stopped and 600 ppm NH$_3$ started to be pumped into the system. The in situ DRIFT spectra were collected at different times. For the reaction between NO + O$_2$ and adsorbed NH$_3$, the order of gas was inverse but the steps were similar with that of the reaction between NH$_3$ and adsorbed NO + O$_2$.

3. Results and discussion

3.1. Structural and textural characteristics

The XRD patterns of different catalyst carriers were analyzed, and the results were shown in Fig. 1 and Fig. S1. All the reflections of the catalyst carriers provided diffraction patterns for the anatase TiO$_2$ (2θ = 25.3°, 37.8°, 48.0°, 53.9°, 55.1°) (PDF-ICDD 78-2486). The diffraction peak intensities of TiO$_2$-CA and TiO$_2$-SA were similar, but much higher than that of TiO$_2$-500, which indicated that the prepared TiO$_2$-500 by the precipitation method had poorer crystallinity. As shown in Fig. 1(b), the peaks of ceria was not observed obviously in the spectra of the catalysts, indicating that the ceria species were well dispersed in the TiO$_2$ carriers, entered into the lattice of TiO$_2$ or were present as amorphous species. In addition, the TiO$_2$ peak positions shifted to a lower-angle region (Fig. S1), which implied that the unit cell volume of TiO$_2$ swelled after the process at high temperatures. However, after the doping of ceria, the diffraction peaks of TiO$_2$ shifted to a higher-angle region after the process at high temperatures. In other words, the ceria atom inhibited the swelling of TiO$_2$ caused by high temperatures. The average particle sizes of TiO$_2$ were calculated based on the Scherrer formula and the results were shown in Table 1. The average particle sizes of TiO$_2$-SA and TiO$_2$-CA were higher than those of TiO$_2$-500, indicating that the crystallinity of TiO$_2$ prepared by the precipitation method was suppressed. Moreover, the crystalline grain growth with the increase of temperature and the appropriate addition of ceria inhibited this phenomenon. In a word, ceria atoms inhibit the grain growth and the swelling of TiO$_2$ caused by high temperatures. This would neutralize the negative effect of high temperature on the TiO$_2$ catalyst carrier.

The microstructural nature of the catalysts was investigated by TEM, and the results were shown in Fig. 2 and Fig. S2. Both the average sizes of TiO$_2$-500 and Ti-Ce-O$_x$-500 increased obviously after the process at high temperatures. On the other hand, the appropriate addition of ceria inhibited the grain growth, which was consistent with the XRD results. In addition, the lattice fringes with an interplanar spacing of 0.35 nm and 0.235 nm were consistent with the d-spacing of (101) and...
distribution with appropriate addition of ceria. That is, the addition of ceria inhibited the collapse of small channels caused by the high temperature. The textural characteristics of different catalyst carriers were summarized in Table 2. The increase of the TiO₂ crystallite size could reduce the specific surface area. Consequently, the specific surface area of TiO₂-500 decreased seriously after the process of high temperature and the specific surface areas of TiO₂-500 and TiO₂-600 were 129.7 m² g⁻¹ and 55.3 m² g⁻¹, respectively. With the addition of ceria, the catalyst carrier increased to 144.3 m² g⁻¹ and 77.9 m² g⁻¹, respectively. Furthermore, the specific surface areas of TiO₂-CA and TiO₂-SA were significantly lower than that of TiO₂-500, implying that the TiO₂ prepared by the precipitation method had higher specific surface area.

### 3.2. Surface acid property

It was well known that the surface acid property of a denitration catalyst played an important role in the NH₃ adsorption [32]. The surface acid properties of these catalyst carriers were tested by NH₃-TPD, and their corresponding profiles were presented in Fig. 4. Previous literatures had proved that the area and position of the NH₃ desorption peaks corresponded to the amount and strength of acid sites [33, 34]. All of the ammonia desorption from the catalyst carriers displayed at least two desorption peaks: one desorption peak spanned at 100–300 °C representing the weak acid sites, and one desorption peak spanned at 300–550 °C representing the strong acid sites [35]. As shown in Fig. 4(a), there were no great difference among the peak positions of TiO₂-500, TiO₂-SA and TiO₂-CA, meaning that the TiO₂-500 prepared by the precipitation method had similar strength of acid sites to these two commercial catalyst carriers. As depicted in Fig. 4(b), both the peak positions shifted to lower temperatures when the catalyst carriers were heated at 600 °C for 24 h, indicating that the strength of acid sites decreased after the treatment of high temperature. In addition, the appropriate addition of ceria contributed to the slight decrease of the strength of strong acid sites for TiO₂-500. However, the strength of acid sites was enhanced with the addition of ceria for TiO₂-600. In other words, the effect of the ceria addition on the strength of acid sites was not obvious for TiO₂.

The stability of NH₄⁺ ions bonded on Brønsted acid sites was inferior to that of NH₃ molecules coordinated to Lewis acid sites, so the desorption peaks at low temperature (300 °C <) could be ascribed to Brønsted acid sites [34], while the desorption peaks at high temperature (> 300 °C) could be related to Lewis acid sites [36]. The amount of acid sites was calculated and the related result was shown in Table 3. The process of high temperature had no effect on the amount of Brønsted acid sites, but it would reduce obviously the amount of Lewis acid sites. On the other hand, the amount of Lewis acid sites and total amount of acid sites decreased and the amount of Brønsted acid sites increased with the addition of ceria. Moreover, the amounts of acid sites of both TiO₂-CA and TiO₂-SA were far less than that of TiO₂-500.

### 3.3. Reduction behavior

Fig. 5 showed the H₂-TPR results of different catalyst carriers to evaluate the redox properties. The peak temperature and hydrogen consumption obtained by H₂-TPR patterns were also listed in Table 4. All of the hydrogen reduction of the catalyst carriers displayed one broad peak spanned at 400–600 °C, which was attributed to the reduction of the TiO₂ surface. For Ti-Ce-Oₓ-500 and Ti-Ce-Oₓ-600, the relative content of CeO₂ was so low that there was no obvious reduction peak representing CeO₂. The peak position shifted to lower temperatures, whether the catalyst carrier was treated by high temperature or the addition of ceria. Therefore, the redox properties of TiO₂-500 could be enhanced by the treatment of high temperature and the addition of ceria. As shown in Table 4, the hydrogen consumption of TiO₂-500, TiO₂-600, Ti-Ce-Oₓ-500 and Ti-Ce-Oₓ-600 was 0.383 mmol g⁻¹.
0.268 mmol g\(^{-1}\), 0.561 mmol g\(^{-1}\) and 0.933 mmol g\(^{-1}\), respectively. It can be speculated that the hydrogen consumption of TiO\(_2\) was reduced by the treatment of high temperature. However, the hydrogen consumption of pure CeO\(_2\) was much higher than that of TiO\(_2\), and more crystalline CeO\(_2\) were formed after the treatment of high temperature rather than existed in the amorphous form. This was the reason why the hydrogen consumption of Ti-Ce-Ox-500 increased after treatment of high temperature. In addition, the hydrogen consumption of TiO\(_2\)-CA and TiO\(_2\)-SA was 0.298 mmol g\(^{-1}\) and 0.100 mmol g\(^{-1}\), respectively. The peak temperatures were also higher than those of other catalyst carriers. Therefore, the addition of ceria enhances the redox properties and increases the hydrogen consumption of TiO\(_2\)-500, presenting better properties than that of TiO\(_2\)-CA and TiO\(_2\)-SA.

### 3.4. Surface analysis

The surface composition and oxidation states of catalyst carriers play an important role in the SCR reaction, so XPS was performed to investigate the surface properties of these catalyst carriers. Fig. 6 showed the O 1s, Ti 2p and Ce 3d XPS high-resolution scan spectra of different catalyst carriers. The O 1s peaks can be fitted into two peaks referred as the chemisorbed oxygen (hereafter denoted as O\(_\alpha\)) and the lattice oxygen (hereafter denoted as O\(_\beta\)) [37]. The O 1s peaks of TiO\(_2\) showed a shift toward the lower binding energy with the addition of ceria, indicating strong interactions between Ce and O atoms. In addition, it was reported that the chemisorbed oxygen was the most active oxygen and played a significant role in oxidation of NO to NO\(_2\) [38]. It could also promote the progress of the SCR reaction through a ‘fast SCR’ route [39]. Therefore, the content of O\(_\alpha\)/(O\(_\alpha\) + O\(_\beta\)) was calculated and listed in Table 5. The content of O\(_\alpha\)/(O\(_\alpha\) + O\(_\beta\)) on the surface of TiO\(_2\)-500, TiO\(_2\)-600, Ti-Ce-Ox-500 and Ti-Ce-Ox-600 were 0.47, 0.38, 0.67, and 0.43 respectively. It could be seen that the addition of ceria would increase the proportion of O\(_\alpha\) while the treatment of high temperature decreased the proportion.

As shown in Fig. 6(b), the Ti 2p can be divided into two contributions of Ti\(^{3+}\) and Ti\(^{4+}\) [40]. The change of binding energy corresponded well to a similar law that the addition of ceria resulted in the negative shift of binding energy peak, implying that the electron transfer between Ce and Ti ions in Ti-Ce-O\(_x\) catalyst carriers existed. By comparing with the intensity of Ti 2p, Ti-Ce-O\(_x\) decreased dramatically, which indicated that the amount Ti of the catalyst carrier surface decreased with the addition of Ce. Additionally, the atomic ratio of Ti\(^{3+}\) was calculated and shown in Table 5. It can be found that the atomic ratio of Ti\(^{3+}\) decreased obviously after the treatment of high temperature while there was no significant difference between TiO\(_2\) and Ti-Ce-O\(_x\) catalyst carriers. The TiO\(_2\) grain growth was completed gradually, so the amount of Ti\(^{3+}\) defect reduced after the treatment of high temperature.

Fig. 6(c) showed the Ce 3d XPS spectra of Ti-Ce-Ox-500 and Ti-Ce-Ox-600 catalyst carriers. Both of the spectral peaks were observed at binding energies of 903 eV and 884 eV [41–43]. Therefore, the Ce 3d spectra can be ascribed to Ce\(^{4+}\) and Ce\(^{3+}\). The intensity of Ce 3d peaks increased obviously after the treatment of high temperature. In other words, the CeO\(_2\) existed mainly in an amorphous form when the calcination temperature was 500 °C. The high temperature treatment resulted in the growth of CeO\(_2\) grain and the content of amorphous CeO\(_2\) decreased. For the Ti-Ce-O\(_x\) catalyst carrier, the existence of Ce\(^{3+}\) meant the formation of oxygen vacancy conducive to the improvement of the catalytic performance for SCR reactions [44]. In addition, it could be seen from Table 5 that the high temperature had no effect on the atomic ratio of Ce\(^{3+}\).

### 3.5. Catalytic performance

Fig. 7 displayed the NO conversion obtained from TiO\(_2\)-500, TiO\(_2\)-SA and TiO\(_2\)-CA catalyst carriers. As shown in Fig. 7, the TiO\(_2\)-500 exhibited the best catalytic performance, which showed the maximum catalytic activity (98.7%) at 500 °C. The maximum catalytic activity decreased in the following order TiO\(_2\)-500 > TiO\(_2\)-CA > TiO\(_2\)-SA. As mentioned earlier, TiO\(_2\)-500 prepared by the precipitation method had
poorer crystallinity, larger specific surface area, more acid sites and H$_2$ consumption than these two commercial catalyst carriers. All of these were beneficial to the improvement of catalytic performance.

Fig. 8 displayed the catalytic activity obtained from TiO$_2$-500, TiO$_2$-600, Ti-Ce-Ox-500 and Ti-Ce-Ox-600 catalyst carriers. The initiation temperature (the temperature of X$_{500} = 50\%$) of TiO$_2$-500 was 365 °C and its maximum catalytic activity was 98.7% at 500 °C with a GHSV of 100 000 h$^{-1}$. The appropriate addition of ceria enhanced the catalytic activity significantly. The initiation temperature of Ti-Ce-Ox-500 decreased to 280 °C, and its maximum catalytic activity was 98.5% at 400 °C with a GHSV of 100 000 h$^{-1}$. Furthermore, comparing with TiO$_2$-500, TiO$_2$-600 showed obvious decrease of the catalytic activity, especially when the reaction temperature was higher than 400 °C (decreased 16% at 400 °C). On the other hand, there were no significant changes in the catalytic activity between Ti-Ce-Ox-600 and Ti-Ce-Ox-500 in the whole testing temperatures. Ti-Ce-Ox-500 exhibited excellent thermostability and its catalytic performance remained high even after the treatment of high temperatures for 24 h. As described above, the ceria atom could inhibit the crystalline grain growth and the collapse of small channels caused by high temperatures. Moreover, the addition of ceria also enhanced the redox properties, increased the hydrogen consumption and the proportion of O$_\alpha$. These advantages warranted the excellent thermostability of Ti-Ce-Ox-500.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area/(m$^2$ g$^{-1}$)</th>
<th>Pore volume/(cm$^3$ g$^{-1}$)</th>
<th>Average pore diameter/nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$-CA</td>
<td>78.3</td>
<td>0.378</td>
<td>15.10</td>
</tr>
<tr>
<td>TiO$_2$-SA</td>
<td>79.9</td>
<td>0.339</td>
<td>14.29</td>
</tr>
<tr>
<td>TiO$_2$-500</td>
<td>129.7</td>
<td>0.344</td>
<td>8.61</td>
</tr>
<tr>
<td>TiO$_2$-600</td>
<td>55.3</td>
<td>0.308</td>
<td>17.52</td>
</tr>
<tr>
<td>Ti-Ce-Ox-500</td>
<td>144.3</td>
<td>0.358</td>
<td>8.23</td>
</tr>
<tr>
<td>Ti-Ce-Ox-600</td>
<td>77.9</td>
<td>0.337</td>
<td>14.39</td>
</tr>
</tbody>
</table>

Table 2

Physical properties of different catalyst carriers.

<table>
<thead>
<tr>
<th>Sample</th>
<th>weak acidity/(mmol NH$_3$/g-catalyst)</th>
<th>strong acidity/(mmol NH$_3$/g-catalyst)</th>
<th>Total acidity/(mmol NH$_3$/g-catalyst)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$-CA</td>
<td>0.168</td>
<td>1.085</td>
<td>1.253</td>
</tr>
<tr>
<td>TiO$_2$-SA</td>
<td>0.209</td>
<td>0.327</td>
<td>0.536</td>
</tr>
<tr>
<td>TiO$_2$-500</td>
<td>0.407</td>
<td>1.630</td>
<td>2.037</td>
</tr>
<tr>
<td>TiO$_2$-600</td>
<td>0.415</td>
<td>0.447</td>
<td>0.862</td>
</tr>
<tr>
<td>Ti-Ce-Ox-500</td>
<td>0.883</td>
<td>0.864</td>
<td>1.747</td>
</tr>
<tr>
<td>Ti-Ce-Ox-600</td>
<td>0.751</td>
<td>0.346</td>
<td>1.097</td>
</tr>
</tbody>
</table>

Table 3

Surface acid property of different catalyst carriers.

Fig. 3. (a) N$_2$ adsorption-desorption isotherms and (b) pore diameter distribution of different catalyst carriers.

(a)

(b)

Fig. 4. NH$_3$-TPD profiles of different catalyst carriers.
As shown in Fig. 8, the catalytic activity increases at low temperatures, which may be resulted from the increased effective collision frequency with the increase of temperature [45]. The ammonia oxidation occurred when the reaction temperature was too high, which reduced the reducing agent content, leading to the catalytic activity to decrease gradually. Furthermore, Fig. 9 presented the thermal stability of TiO$_2$-500 and Ti-Ce-Ox-500 catalyst carriers. The catalytic activities of TiO$_2$-500 and Ti-Ce-Ox-500 maintained high at 96.8% and 98.5% at 400 °C for 40 h, respectively.

3.6. Interaction with reactants (in situ DRIFTS)

To investigate the NH$_3$-SCR reaction mechanism over Ti-Ce-Ox-500, the in situ DRIFT spectra were collected and the related results were shown in Fig. 10. As shown in Fig. 10(a), the bands at 3361 cm$^{-1}$,
Symmetric bending vibrations of NH\(_4\)Ti-Ce-Ox-500 catalyst carrier surface, which implies that NH\(_3\) molecules obviously, the Lewis acid sites coexist with Brønsted acid sites on the temperature, indicating that less and less NH\(_3\) species were adsorbed on the peaks gradually decreased in intensity with the increase of the temperature, indicating that less and less NH\(_3\) species were adsorbed on the catalyst carrier surface. As shown in Fig. 10(a), the peak attributed to Brønsted acid sites has disappeared and the peak attributed

<table>
<thead>
<tr>
<th>Sample</th>
<th>O(_2)/(O(_3)+O(_2))</th>
<th>Ti(^{3+})/(Ti(^{3+})+Ti(^{4+}))</th>
<th>Ce(^{3+})/(Ce(^{3+})+Ce(^{4+}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO(_2)-500</td>
<td>0.47</td>
<td>0.09</td>
<td>—</td>
</tr>
<tr>
<td>TiO(_2)-600</td>
<td>0.38</td>
<td>0.04</td>
<td>—</td>
</tr>
<tr>
<td>Ti-Ce-Ox-500</td>
<td>0.67</td>
<td>0.10</td>
<td>0.49</td>
</tr>
<tr>
<td>Ti-Ce-Ox-600</td>
<td>0.43</td>
<td>0.04</td>
<td>0.48</td>
</tr>
</tbody>
</table>

3250 cm\(^{-1}\) and 3169 cm\(^{-1}\) can be assigned to NH stretching vibration of coordinated NH\(_3\) [46,47]. The bands at 1601 cm\(^{-1}\) and 1181 cm\(^{-1}\) can be ascribed to asymmetric and symmetric bending of NH bonds in coordinated NH\(_3\) on Ti-O-Ti Lewis acid sites [48], and the band at 1284 cm\(^{-1}\) corresponds to the coordinated NH\(_3\) on Ti-O-Ce Lewis acid sites [49]. The band at 1446 cm\(^{-1}\) is attributed to asymmetric and symmetric bending vibrations of NH\(_4\)\(^{+}\) on Brønsted acid sites [50,51]. Obviously, the Lewis acid sites coexist with Brønsted acid sites on the Ti-Ce-Ox-500 catalyst carrier surface, which implies that NH\(_3\) molecules can be adsorbed on both Lewis acid sites and Brønsted acid sites. All the peaks gradually decreased in intensity with the increase of the temperature, indicating that less and less NH\(_3\) species were adsorbed on the Ti-Ce-Ox-500 catalyst carrier surface. As shown in Fig. 10(a), the peak attributed to Brønsted acid sites has disappeared and the peak attributed

Combined with aforementioned reactions, the NH\(_3\)-SCR over Ti-Ce-Ox-500 catalyst carrier followed both L-H and E-R mechanisms. The in situ DRIFT spectra has proven that both the reaction of adsorbed monodentate NO\(_2\) with adsorbed NH\(_4\)\(^{+}\) and that of adsorbed NH\(_4\)\(^{+}\) with gas-phase NO existed over the Ti-Ce-Ox-500 catalyst carrier surface. Thus, the reaction mechanism of Ti-Ce-Ox-500 was proposed and displayed in Scheme 1. The ceria atoms entered into the lattice of TiO\(_2\), inhibiting the shrinkage of lattice and the collapse of small channels caused by high temperatures. Therefore, the Ti-Ce-Ox-500 is more suitable for the catalyst carrier for the NH\(_3\)-SCR reaction.

For the reaction between NH\(_3\) and pre-adsorbed NO+O\(_2\) species, the bands attributed to adsorbed NH\(_3\) species (coordinated NH\(_3\) and NH\(_4\)\(^{+}\)) existed within 1 min and the monodentate NO\(_2\) disappeared. In addition, the adsorption of NH\(_3\) was stronger than that of NO+O\(_2\).
It can be speculated that the adsorption of NH3 was obligatory for the NH3-SCR reaction \[57\]. Therefore, the NH3-SCR occurred by the following reaction:

\[
\text{NH}_4^+ + \text{NO}_2^- \rightarrow \text{NH}_4\text{NO}_2 \quad (2)
\]

\[
\text{NH}_4\text{NO}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O} \quad (3)
\]

As to the reaction between NO+O2 and pre-adsorbed NH3 species, the bands attributed to monodentate NO2− gradually appeared and strengthened after the NH4+ disappeared, and the reaction time lasted for 5 min, which indicated that the reaction of NH4+ and gas-phase NO was the rate-controlling step. In other words, the NH3-SCR reaction occurred via the following reaction mechanism:

\[
\text{NH}_4^+ + \text{NO} \rightarrow \text{NH}_3 + \text{NO} \quad (4)
\]

\[
\text{NH}_3 + \text{NO} \rightarrow \text{N}_2 + \text{H}_3\text{O}^+ \quad (5)
\]

4. Conclusions

In this work, a series of TiO2 catalyst carriers with the modulation of CeO2 were synthesized by a precipitation method, and then used as catalyst carriers to study the thermostability and catalytic performance in the selective catalytic reduction of NO by NH3. It was found that appropriate addition of CeO2 can enhance the catalytic activity and thermostability of TiO2. This is mainly because ceria atoms inhibit the crystalline grain growth and the collapse of small channels caused by high temperatures. All these factors contributed to the enhanced thermostability of TiO2, as evidenced by a series of characterizations by XRD, N2-BET, NH3-TPD, H2-TPR, XPS, TEM and in situ DRIFTS. Furthermore, the addition of ceria also enhanced the redox properties, and increased the hydrogen consumption and the proportion of surface chemisorbed oxygen, which guaranteed superior catalytic activity of the Ti-Ce-Ox-500 at low temperatures. At the last, the reaction mechanism was discussed based on the in situ DRIFT spectra. It was found

As to the reaction between NO+O2 and pre-adsorbed NH3 species, the bands attributed to monodentate NO2− gradually appeared and strengthened after the NH4+ disappeared, and the reaction time lasted for 5 min, which indicated that the reaction of NH4+ and gas-phase NO was the rate-controlling step. In other words, the NH3-SCR reaction occurred via the following reaction mechanism:

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\text{NH}_4^+ + \text{NO} \rightarrow \text{NH}_3 + \text{NO} \quad (4)
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\text{NH}_3 + \text{NO} \rightarrow \text{N}_2 + \text{H}_3\text{O}^+ \quad (5)
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that the SCR reaction over Ti-Ce-Ox-500 followed both E-R and L-H mechanisms. With enhanced thermostability and excellent catalytic performance for NH₃-SCR, Ti-Ce-Ox-500 has great potential for wide industrial applications.

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