DRIFTS study of a Ce–W mixed oxide catalyst for the selective catalytic reduction of NO\textsubscript{x} with NH\textsubscript{3}

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A systematic study has been conducted on the reactivity of the selective catalytic reduction of NO\textsubscript{x} with NH\textsubscript{3} (NH\textsubscript{3}-SCR) in a wide range of NO/NO\textsubscript{2} feed ratios (from 0 : 1 to 1 : 0) over a CeWO\textsubscript{4} catalyst prepared by a homogeneous precipitation method. By using in situ diffuse reflectance infrared Fourier transform spectroscopy (in situ DRIFTS), the roles of NO and NO\textsubscript{2} at low temperatures during the fast SCR reaction have been revealed. NO\textsubscript{2} adsorption results in the formation of surface nitrates, which participate in the NH\textsubscript{3}-SCR reaction through two pathways: one path where the nitrates react with NH\textsubscript{3} to form ammonium nitrate (NH\textsubscript{4}NO\textsubscript{3}), then NO reduces NH\textsubscript{4}NO\textsubscript{3} below its melting point to form N\textsubscript{2} (the NH\textsubscript{4}NO\textsubscript{3} path); the other path where the surface nitrates are reduced by NO to form active nitrite species that further react with NH\textsubscript{3} to produce N\textsubscript{2} (the nitrate path). “The NH\textsubscript{4}NO\textsubscript{3} path” and “the nitrate path” contributed simultaneously to the standard and the fast SCR reaction at low temperatures. Both the surface nitrates and NO in the gas phase were suggested to be necessary for the excellent performance of the fast SCR reaction over the CeWO\textsubscript{4} catalyst.

1. Introduction

NO\textsubscript{x}, a major source of air pollution, causes photochemical smog and acid rain, which are detrimental to human health. NO\textsubscript{x} mainly comes from industrial combustion of fossil fuels and automobile exhaust gas, and NO\textsubscript{x} removal from diesel engine exhaust remains a challenge in environmental catalysis.\textsuperscript{1,2} The selective catalytic reduction of NO\textsubscript{x} with NH\textsubscript{3} (NH\textsubscript{3}-SCR) is one of the most effective technologies for NO\textsubscript{x} removal from diesel engines.\textsuperscript{3} The catalysts for NH\textsubscript{3}-SCR can be divided into the following groups, V-based oxide catalysts, Cu or Fe zeolite catalysts, and vanadium-free oxide catalysts. Among these catalysts, the non-toxic vanadium-free oxide catalysts, such as FeTiO\textsubscript{3},\textsuperscript{4,6} WO\textsubscript{3}/CeO\textsubscript{2}–ZrO\textsubscript{2},\textsuperscript{7} and CeO\textsubscript{2}–MnO\textsubscript{2}/TiO\textsubscript{2},\textsuperscript{8} show good NH\textsubscript{3}-SCR performance and H\textsubscript{2}O/SO\textsubscript{2} durability over a wide temperature range from 200 to 500 °C. CeO\textsubscript{2} has long been applied as a promoter and carrier for low temperature NH\textsubscript{3}-SCR catalysts.\textsuperscript{9–11} The use of cerium oxide as a main catalyst for the NH\textsubscript{3}-SCR reaction was first reported by Xu et al.,\textsuperscript{12} and then many other researchers developed Ce-based catalysts applicable for the NH\textsubscript{3}-SCR process, e.g. CeO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3},\textsuperscript{13} CeO\textsubscript{2}/TiO\textsubscript{2},\textsuperscript{14–16} Ce–W mixed oxides,\textsuperscript{17–19} Ce–W–Ti mixed oxides,\textsuperscript{20–23} and CeO\textsubscript{2}–MoO\textsubscript{3}/TiO\textsubscript{2}.\textsuperscript{24} It should be noted that CeTiO\textsubscript{3},\textsuperscript{15,16} CeWO\textsubscript{4},\textsuperscript{20} and CeWTiO\textsubscript{4} (ref. 19) could eliminate NO completely over a wide temperature range of 250–425 °C, even under a rather high gas hourly space velocity (GHSV) of 500 000 h\textsuperscript{–1}. The prominent performance under high GHSV of the Ce-based catalysts made it worthwhile to further investigate the NH\textsubscript{3}-SCR mechanism in detail.

The mechanism of NH\textsubscript{3}-SCR over different types of catalysts has been studied by many researchers. Some researchers reported that the NH\textsubscript{3}-SCR reaction followed the Langmuir–Hinshelwood (L–H) mechanism at low temperatures (≤200 °C), whereas the Eley–Rideal (E–R) mechanism might take place at high temperatures (>200 °C), e.g. on FeTiO\textsubscript{4} (ref. 25) or CeO\textsubscript{2}/TiO\textsubscript{2}.\textsuperscript{18} The reaction might also proceed through the E–R mechanism over the whole temperature range, such as on CeWTiO\textsubscript{4} catalysts.\textsuperscript{18} In other studies, both E–R and L–H mechanisms took place over the whole temperature range simultaneously, such as on CeWO\textsubscript{4} catalysts.\textsuperscript{21} However, in these reports, the authors mainly focused on the reaction between NO, O\textsubscript{2}, and NH\textsubscript{3}. It is widely accepted that the oxidation of NO to NO\textsubscript{2} is an important step in the NH\textsubscript{3}-SCR reaction. Long and Yang\textsuperscript{26} reported that the higher activity of NO oxidation to NO\textsubscript{2} on Fe–ZSM-5 led to improved SCR performance. Similarly, Fe–Mn/TiO\textsubscript{2} showed higher SCR activity than Mn/TiO\textsubscript{2} due to the higher rate of NO oxidation to NO\textsubscript{2}.\textsuperscript{27} In our previous studies, NO\textsubscript{2} production by NO oxidation was also suggested to be responsible for...
the promoted SCR activity on CeTiO$_3$ (ref. 15) or on CeWTiO$_x$ at temperatures below 300 °C. The formation of NO$_2$ might facilitate the fast SCR reaction, resulting in higher SCR activity. Therefore, NO$_2$ has a great effect on the reaction between NO, O$_2$, and NH$_3$. However, to the best of our knowledge, no publications have ever reported the effect of NO/NO$_2$ feed ratios on the NO$_x$ conversion systematically over the CeWO$_x$ catalyst.

The promotional role of NO$_2$ in the SCR reaction over V$_2$O$_5$–WO$_3$/TiO$_2$ and zeolite-based catalysts has been intensively investigated in the last decade. Koebel et al. suggested that NO$_2$ accelerated the SCR reaction over V$_2$O$_5$–WO$_3$/TiO$_2$ by reoxidizing the V sites. Yeom et al. suggested that N$_2$O$_3$ formed by equimolar NO/NO$_2$ reacted with water and NH$_3$ to produce ammonium nitrite over the BaNa-Y catalyst, which is an unstable species above 100 °C. Others suggested that the fast SCR reaction at low temperatures involved the reduction of nitric acid, surface nitrates and/or ammonium nitrate (NH$_4$NO$_3$) by NO. At present, it is still a controversial issue how the presence of NO$_2$ in the feed mixture promotes NO$_x$ elimination. By comparing the mechanisms of standard SCR and fast SCR in the meantime, one can gain a clear view of the NH$_3$-SCR mechanism, which is helpful to guide the practical application of the studied catalysts. So far, unfortunately, a detailed study of the mechanism of the fast SCR reaction over Ce-based catalysts is still lacking.

In the present study, the SCR reaction has been studied over a wide range of NO/NO$_2$ feed ratios from 0:1 to 1:0. The mechanism of the fast SCR reaction over CeWO$_x$ in the low temperature range was investigated by in situ DRIFTS. The roles of NO and NO$_2$ in the SCR reaction have been revealed comprehensively, and for the first time, the reactions between NO and NH$_4$NO$_3$ or the surface nitrates have been studied systematically on the CeWO$_x$ catalyst at low temperatures.

2. Experiments

2.1 Catalyst synthesis and activity test

The Ce–W mixed oxide catalyst, with a Ce/W molar ratio of 1:1, was prepared by a homogeneous precipitation method, as described in the previous report. Briefly, cerium nitrate (Ce(NO$_3$)$_3$·6H$_2$O) was first added into a mixed solution containing ammonium tungstate ([NH$_4$]$_{10}$W$_{12}$O$_{41}$) and an equal weight of oxalic acid (H$_2$C$_2$O$_4$·2H$_2$O), and then an aqueous urea solution was added into the mixture, with a urea/(Ce + W) molar ratio of 10:1. The mixed solution was then heated at 90 °C for 12 h under vigorous stirring. After filtration and washing, the sample was dried at 100 °C overnight and successively calcined at 500 °C for 5 h. The obtained catalyst was denoted as CeWO$_x$. The powder CeWO$_x$ catalyst was pressed and crushed to 40–60 mesh before the activity tests.

The SCR activity tests were performed in a fixed-bed quartz flow reactor at atmospheric pressure using 100 mg of catalyst. The reaction conditions were as follows: 500 ppm NO, 500 ppm NH$_3$, 5 vol.% O$_2$, and balance N$_2$ for the standard SCR reaction with a NO/NO$_2$ ratio of 1:0, and 500 ppm NO, with NO/NO$_2$ ratios y (y = 4:1, 3:2, 1:1, 2:3, 1:4), 500 ppm NH$_3$, 5 vol.% O$_2$, and balance N$_2$ for the fast SCR reaction with different NO/NO$_2$ ratios. The NO$_2$/SCR reaction was tested in 500 ppm NO$_2$, 500 ppm NH$_3$, 5 vol.% O$_2$, and balance N$_2$. The total flow rate was 500 ml min$^{-1}$, and the effluent gas, including NO, NH$_3$, NO$_2$, and N$_2$O, was quantitatively detected by an online NEXUS 670-FTIR spectrometer. The spectra were collected at the steady state, and the NO$_x$ conversion and N$_2$ selectivity were calculated according to the equations:

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

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

2.2 Characterization

The in situ DRIFTS experiments were conducted using an FTIR spectrometer (Nicolet Nexus 670) with an MCT/A detector cooled with liquid nitrogen and a smart collector. The experimental temperature was precisely controlled by an Omega programmable temperature controller. Before each adsorption experiment, the catalyst was first pretreated at 400 °C for 0.5 h in a flow of 20 vol.% O$_2$/N$_2$ and then cooled down to comparatively low temperature (150 °C). The DRIFTS experiments of the fast SCR and standard SCR reactions were performed at 150 °C. The background spectrum was collected in flowing N$_2$ and was subtracted from the sample spectrum automatically. Both the adsorption and the reaction experiments were tested with a total flow rate of 300 ml min$^{-1}$. The adsorption conditions were as follows: 500 ppm NH$_3$ or 500 ppm NO or 500 ppm NO$_2$, and N$_2$ balance for adsorption experiments. The reaction conditions were: 500 ppm NO, 500 ppm NH$_3$, 5 vol.% O$_2$, and balance N$_2$ for the standard SCR reaction, and 500 ppm NO$_x$ with a NO/NO$_2$ ratio of 1:1, 500 ppm NH$_3$, 5 vol.% O$_2$, and balance N$_2$ for the fast SCR reaction. All DRIFTS spectra were recorded by accumulating 100 scans with a resolution of 4 cm$^{-1}$.

3. Results

3.1 NH$_3$-SCR activity

To gain a deep insight into the effect of the NO/NO$_2$ ratio on the NH$_3$-SCR activity, a systematic study was conducted by varying the NO/NO$_2$ ratio over a range spanning from 1:0 to 0:1 in the feed gas. Fig. 1 illustrates the NO conversion and N$_2$ selectivity as a function of reaction temperature under different gas compositions with NO/NO$_2$ ratios of 1:0; 4:1, 3:2; 1:1, 2:3, 1:4, and 0:1 over CeWO$_x$. As shown in Fig. 1(a) and (b), the CeWO$_x$ catalyst showed more than...
90% NO\textsubscript{x} conversion from 250 to 450 °C under a GHSV of ~600,000 h\textsuperscript{-1} in the absence of NO\textsubscript{2}, and the NO\textsubscript{x} conversion was less than 60% below 250 °C. It should be noted that the NO\textsubscript{x} conversion increased significantly with increasing NO\textsubscript{2} content until the NO/NO\textsubscript{2} ratio was 1:1 at low temperatures (≤200 °C), as shown in Fig. 1(a). Both the highest low temperature NO\textsubscript{x} conversion and the widest operation temperature window were obtained when the NO/NO\textsubscript{2} ratio was 1:1. As seen in Fig. 1(b), further increase of the NO\textsubscript{2} concentration to an NO/NO\textsubscript{2} ratio of 1:4 decreased the NO\textsubscript{x} conversion dramatically below 200 °C. However, in comparison with standard SCR, the NO\textsubscript{x} conversion was higher at low temperatures (≤200 °C) as long as both NO\textsubscript{2} and NO were present in the feed. The activity results on the CeWO\textsubscript{x} catalyst clearly showed that the presence of NO\textsubscript{2} indeed promoted greatly the low temperature NO\textsubscript{x} elimination, and this promotional effect was closely related to the NO\textsubscript{2} concentration in the feed gas. Similar conclusions have also been drawn for zeolite and V-based oxides.\textsuperscript{35–38} However, when the NO/NO\textsubscript{2} ratio was 0:1 (NO\textsubscript{2}-SCR), the NO\textsubscript{2} conversion was below 60% over the whole temperature range, indicating that both NO and NO\textsubscript{2} in the feed were necessary for obtaining high NO\textsubscript{x} conversion.

As seen in Fig. 1(c), N\textsubscript{2} selectivity was higher than 98% when the NO/NO\textsubscript{2} ratio was higher than 1:1, and the increase in NO\textsubscript{2} concentration decreased the N\textsubscript{2} selectivity slightly to 92%, due to the facilitation of N\textsubscript{2}O formation by the reaction between NO\textsubscript{2} and NH\textsubscript{3}.\textsuperscript{36} It has to be pointed out that the NO/NO\textsubscript{2} ratio had a negligible effect on N\textsubscript{2} selectivity below 200 °C, therefore, the present study focused on the effect of NO/NO\textsubscript{2} ratio on NO\textsubscript{x} conversion instead of N\textsubscript{2} selectivity.

### 3.2 In situ DRIFTS studies

#### 3.2.1 NO adsorption on pre-adsorbed NO\textsubscript{2}
In order to confirm whether NO could interact with the adsorbed NO\textsubscript{2} species, an in situ DRIFTS study was performed on the NO\textsubscript{2}-pretreated CeWO\textsubscript{x} catalyst at 150 °C. The catalyst was first purged with NO\textsubscript{2} until saturation, followed by N\textsubscript{2} purging to remove the physisorbed NO\textsubscript{2} molecules. Then NO/N\textsubscript{2} was introduced, and the spectra were recorded as a function of time. The resulting spectra are shown in Fig. 2(a), and the simultaneous detection results of the effluent gases by an
online NEXUS 670-FTIR spectrometer are shown in Fig. 2(b). After NO₂ adsorption, bands at 1019, 1233, 1527, 1581, and 1604 cm⁻¹ were observed. The bands at 1019 and 1581 cm⁻¹ could be ascribed to bidentate nitrate,¹⁸ whereas the bands at 1233 and 1604 cm⁻¹ could be ascribed to bridging nitrate, and 1527 cm⁻¹ was assigned to monodentate nitrate.²⁰ After NO was introduced into the cell, the wavenumbers of the nitrate species did not change, while all peak intensities of nitrate species decreased. As seen in Fig. 2(b), NO₂ produced by the reaction between NO and the surface oxygen atoms or the reaction between NO and the surface nitrates, evolved simultaneously. The decrease in the peak intensities within 10 min was insignificant, which could be ascribed to the effect of the surface nitrates formed by NO adsorption. These results indicated that NO could react with the surface nitrate species to form NO₂. Similar results have been obtained for Fe-ZSM-5 during fast SCR.²⁰

3.2.2 NO₂ adsorption on pre-adsorbed NO. The DRIFTS results of NO₂ adsorption on pre-adsorbed NO were also obtained so as to make a comparison with the results of NO adsorption on pre-adsorbed NO₂. As shown in Fig. 3(a), after NO adsorption, bands at 1019, 1230, 1527, 1581, and 1604 cm⁻¹ were observed, and the wavenumbers of the bands were almost identical to those after NO₂ adsorption, suggesting that NO could react with surface oxygen to form surface nitrates. On the other hand, the peaks of the nitrate species increased dramatically after the successive adsorption of NO₂, indicating that more nitrate species formed on the CeWO₄ surface. However, the successive treatment of NO and O₂ after NO adsorption did not increase the amount of surface nitrates, as shown in Fig. 3(b), indicating that no oxygen vacancies were present on the surface after the pretreatment of CeWO₄ by O₂ at 400 °C. These results also showed that the oxidation of NO by O₂ at 150 °C could not produce enough NO₂ to adsorb the surface nitrates on the surface of CeWO₄, indicating that the NO₂ formation by NO oxidation was slow over the CeWO₄ catalyst. Therefore, the amount of surface nitrate species formed by NO₂ was much greater than that by NO alone or the mixture of NO and O₂.

3.2.3 NO₂ adsorption on pre-adsorbed NH₃. To confirm if the adsorbed NH₃ could react with NO₂, the catalyst was first treated with NH₃ until saturation and purged with N₂. NO₂ was then introduced into the cell for 30 min, and the spectra recorded at different time intervals are shown in Fig. 4. After NH₃ adsorption, bands at 1181, 1256, 1423, 1590, 1671, and 3000–3400 cm⁻¹ were observed. The bands at 1671 and 1423 cm⁻¹ could be ascribed to the Brønsted ammonia
species (NH$_4^+$-B),$^{20}$ whereas the bands at 1590, 1256, and 1181 cm$^{-1}$ could be ascribed to Lewis ammonia species (NH$_3^+$)-L.$^{15,16,18,20}$ After NO$_2$ was introduced into the cell, the band of NH$_3$-L species at 1181 cm$^{-1}$ disappeared completely within 3 min, and the peaks of NH$_4^+$-B species decreased gradually with time on stream. The bands of the nitrate species at 1604, 1578, and 1230 cm$^{-1}$ increased, indicating that NO$_2$ reacted with both the surface NH$_3$-L and NH$_4^+$-B species. These results were consistent with what was reported in the literature$^{21}$ by Chen et al. that both the Lewis and the Bronsted ammonia species on the Ce-W catalyst could participate in the NH$_3$-SCR reaction. It has to be noted that new bands at 1337, 1320, 1305, and ~3218 cm$^{-1}$ were observed, indicating that NH$_4$NO$_3$ could be formed on CeWO$_4$ by the reaction between ammonia and surface nitrites. It has to be pointed out that a shift in the NH$_3$NO$_3$ band was observed from 1337 (Fig. 4(a)) to 1320/1332 (Fig. 4(b) and 5(b)) and 1305 cm$^{-1}$ (Fig. 4(b) and 5(a)), which might be due to the differences in coverage or different phases$^{40}$ of NH$_4$NO$_3$ caused by the different formation procedures. Therefore, it was reasonable to suggest that the bands at 1337, 1320, 1305, and ~3218 cm$^{-1}$ in Fig. 4 were representatives of the NH$_4$NO$_3$ intermediate on the surface of the CeWO$_4$ catalyst. The results in Fig. 4 and 5 indicate that the surface ammonia species might react with NO$_2$ gas according to the following equation:

$$2\text{NH}_3 + 2\text{NO}_2 \rightarrow \text{NH}_4\text{NO}_3 + \text{N}_2 + \text{H}_2\text{O} \quad (3)$$

This reaction has been reported by Grossale et al.$^{41,42}$ to take place below 250 °C on Fe/zeolite catalysts. It has been reported that reaction (3) was a result of the combination of the following steps:$^{41}$

$$2\text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{HNO}_3 + \text{HONO} \quad (4)$$

$$\text{NH}_3 + \text{HONO} \rightarrow [\text{NH}_4\text{NO}_3] \rightarrow \text{N}_2 + 2\text{H}_2\text{O} \quad (5)$$

$$\text{NH}_3 + \text{HNO}_3 \rightarrow \text{NH}_4\text{NO}_3 \quad (6)$$

These reactions might also take place in the reaction between NO$_2$ and NH$_3$ on CeWO$_4$.

As seen in Fig. 4(b), NH$_4$NO$_3$ was produced within 3 min when the NO$_2$ concentration was 500 ppm, whereas decreasing the concentration of NO$_2$ to 250 ppm led to the formation of NH$_3$NO$_3$ after 3 min. It has to be noted that no peak of NH$_4$NO$_3$ could be observed within 10 min when the NO$_2$ concentration was further decreased to 100 ppm, indicating that the lower NO$_2$ concentration resulted in the smaller amount of NH$_3$NO$_3$ within the same time period.

3.2.4 The decomposition of NH$_3$NO$_3$ at 150 °C. To study the stability of NH$_3$NO$_3$ at low temperature, an in situ DRIFTS study was also conducted over the NH$_3$NO$_3$-impregnated CeWO$_4$ catalyst at 150 °C. As shown in Fig. 5c, the band at 1271 cm$^{-1}$ could be assigned to the contribution of both NH$_3$-L (at 1256 cm$^{-1}$) and NH$_3$NO$_3$ (at 1305 cm$^{-1}$), and the new bands at 1513 and 1673 cm$^{-1}$ at 150 °C could be ascribed to the surface monodentate nitrate and NH$_4^+$-B, indicating that the adsorbed ammonia and nitrates appeared simultaneously on the surface of the NH$_3$NO$_3$-impregnated

\[ \text{NH}_3 + \text{HONO} \rightarrow [\text{NH}_4\text{NO}_3] \rightarrow \text{N}_2 + 2\text{H}_2\text{O} \]

\[ \text{NH}_3 + \text{HNO}_3 \rightarrow \text{NH}_4\text{NO}_3 \]
catalyst at 150 °C. In addition to the changes above, the simultaneous slight decrease in the band at 3200 cm\(^{-1}\) demonstrated that NH\(_4\)NO\(_3\) decomposed to surface nitrates and ammonia following the equation:

\[
\text{NH}_4\text{NO}_3 \rightarrow \text{NH}_3 + \text{HNO}_3
\]

This is the reverse reaction of reaction (6). It is widely accepted that NH\(_4\)NO\(_3\) is solid below 170 °C and could decompose to NH\(_3\) and HNO\(_3\) in the melt above 170 °C.\(^{33}\) However, Koebel \textit{et al.}\(^{43}\) found that ammonium nitrate deposited on a monolith catalyst at 150 °C decomposed to NH\(_3\) and HNO\(_3\) soon after the temperature started to rise, due to the presence of H\(_2\)O in the feed. Similarly, Madany and Burnet\(^{44}\) pointed out in their paper that the presence of H\(_2\)O could promote the reverse reaction of eqn (6). Although the NH\(_4\)NO\(_3\)-impregnated CeWO\(_x\) catalyst had been dried in air overnight and purged with N\(_2\) for 1 h at room temperature before collecting the spectra, adsorbed H\(_2\)O might still have remained on the surface of the catalyst. Therefore, it is possible that a small part of NH\(_4\)NO\(_3\) decomposed to NH\(_3\) and HNO\(_3\) at 150 °C in the present study.

In order to make clear whether the surface NH\(_4\)NO\(_3\) participates in the NH\(_3\)-SCR reaction, \textit{in situ} DRIFTS studies were conducted on the decomposition of NH\(_4\)NO\(_3\) both in N\(_2\) and in NO/N\(_2\). The peaks of NH\(_4\)NO\(_3\) had no obvious change with the time on stream in N\(_2\), as shown in Fig. 6(a), indicating that the decomposition of NH\(_4\)NO\(_3\) in N\(_2\) is a slow process at 150 °C. Nevertheless, the treatment of the NH\(_4\)NO\(_3\)-impregnated CeWO\(_x\) catalyst in NO/N\(_2\) resulted in a dramatic reduction of the peaks of NH\(_4\)NO\(_3\) at 1271, 1426, 2810, 3020, 3180, and 3250 cm\(^{-1}\) within 30 min, as shown in Fig. 6(b). The reduction of the band at 1271 cm\(^{-1}\) to the bands of 1305 and 1256 cm\(^{-1}\) proved that the peak at 1271 cm\(^{-1}\) was indeed the contribution of both NH\(_4\)NO\(_3\) and NH\(_3\)-L. Compared with Fig. 6(a), the consumption of NH\(_4\)NO\(_3\) was much faster in NO/N\(_2\) than in N\(_2\), indicating that NO in the gas phase could react with NH\(_4\)NO\(_3\). To investigate the products of the NH\(_4\)NO\(_3\) reduction by NO, the effluent gases were simultaneously analyzed by an online NEXUS 670-FTIR spectrometer.

NO\(_2\) was evolved accompanied by the reduction of NH\(_4\)NO\(_3\) by NO, as shown in Fig. 6(c). The facilitation of NH\(_4\)NO\(_3\) decomposition by NO was suggested to proceed according to the following equation over many catalysts, e.g., V\(_2\)O\(_5\)-WO\(_3\)/TiO\(_2\) (ref. 31) and Fe/ZSM-5.\(^{41}\)

\[
\text{NH}_4\text{NO}_3 + \text{NO} \rightarrow \text{N}_2 + \text{NO}_2 + 2\text{H}_2\text{O}
\] (7)

### 3.2.5 Co-adsorption of NO\(_2\) and NO on pre-adsorbed NH\(_3\).

In order to study the effect of NO on the reaction between the adsorbed NH\(_3\) and NO\(_2\) gas, the following experiment was conducted. Similar to the experimental procedure for the study of NO\(_2\) adsorption on pre-adsorbed NH\(_3\), the catalyst was first treated with NH\(_3\) until saturation and then purged with N\(_2\). Afterwards, the mixture of NO\(_2\) and NO was introduced for 30 min. The spectra are shown in Fig. 7. After the mixture of NO\(_2\) and NO was introduced into the cell, all the adsorbed ammonia species decreased quickly with time on stream, and disappeared completely after 2 min, leaving only the bands of nitrate species at 1604, 1581, 1230, and 1020 cm\(^{-1}\) in the spectra. Compared with Fig. 4(a), it can be observed that the mixture of NO\(_2\) and NO reacted faster with the surface NH\(_3\) and NH\(_4^+\) species than NO\(_2\) alone. These results were consistent with the activity result that fast SCR in the presence of NO\(_2\) showed better performance than NO\(_2\)-SCR (NO/NO\(_2\) = 0:1). Additionally, no bands at 1337 and ~3218 cm\(^{-1}\) were observed in the presence of NO, indicating...
that the presence of NO might accelerate the decomposition of NH₄NO₃ species, although it was not easy for the NH₄NO₃ intermediate on the surface of the catalyst to decompose to NH₃ and HNO₃ below 170 °C. Another reasonable explanation for the absence of NH₄NO₃ was that the reduction of the surface nitrates by NO is faster than the formation of NH₄NO₃.

### 3.2.6 Fast SCR and standard SCR

To identify the species present on CeWO₄ catalysts during fast SCR and standard SCR, an in situ DRIFTS study was conducted at 150 °C. As seen in Fig. 8, bridging nitrate (the band at 1604 cm⁻¹) was formed after the introduction of the reactant gas for 1 min, and then the bridging nitrate peak decreased with time on stream after 5 min accompanied by the increase in the adsorbed NH₃ species, indicating that the surface nitrates formed by NO or NO₂ could participate in the NH₃-SCR reaction. Under steady state conditions, NH₃-L and NH₄⁺-B were present on the surface of the CeWO₄ catalyst during both standard and fast SCR. It should be noted that no NH₄NO₃ was observed during either standard or fast SCR, indicating that either NH₄NO₃ decomposed rapidly, or was not formed from the beginning due to the faster reaction between NO and the surface nitrates. However, the results in the present study show that if reaction (7) took place, the reaction between NO and NH₄NO₃ during standard SCR and fast SCR was extremely fast.

### 4. Discussion

#### 4.1 Formation of surface nitrates and nitrite

Based on previous reports, CeO₂ was suggested to be the main active site for the NH₃-SCR reaction. It can be suggested that NO activation on the CeWO₄ catalyst follows the equations:

\[
NO + [\text{Ce}^{4+}]\text{–O} \leftrightarrow [\text{Ce}^{4+}]\text{–ONO(nitrite)} \quad (8)
\]

\[
2[\text{Ce}^{4+}]\text{–O} + NO \rightarrow [2\text{Ce}^{4+}]\text{–O}_2\text{NO (bridging nitrate)} \quad (9)
\]

\[
\text{O–}[\text{Ce}^{4+}]\text{–O} \rightarrow [\text{Ce}^{4+}]\text{–O}_2\text{NO (bidentate nitrate)} \quad (10)
\]

and the adsorption of NO₂ on the catalyst follows the equation:

\[
[\text{Ce}^{4+}]\text{–O} + \text{NO}_2 \rightarrow [\text{Ce}^{4+}]\text{–ONO}_2\text{(monodentate nitrate)} \quad (11)
\]

It is clear that NO₂ can be adsorbed on one [Ce⁴⁺]–O site to form one monodentate nitrate ([Ce⁴⁺]–ONO₂), whereas the adsorption of NO needs two [Ce⁴⁺]–O sites to produce one bidentate nitrate ([Ce⁴⁺]–O₂NO) or one bridging nitrate ([2Ce⁴⁺]–O₂NO). In addition, the presence of NO could reduce the amount of surface nitrates, as shown in Fig. 2. Since no surface nitrite species ([Ce⁴⁺]–ONO) was observed in the present study, it can be concluded that the surface nitrite species was extremely active and was desorbed too fast to be detected by DRIFTS. Therefore, NO gas reacted with the surface nitrates to form NO₂ gas according to the equations:

\[
[\text{Ce}^{4+}]\text{–ONO}_2\text{(monodentate nitrate)} + \text{NO} \rightarrow [\text{Ce}^{4+}]\text{–ONO} + \text{NO}_2 \quad (12)
\]

\[
[2\text{Ce}^{4+}]\text{–O}_2\text{NO (bridging nitrate)} + \text{NO} \rightarrow [\text{Ce}^{4+}]\text{–ONO} + \text{NO}_2 + [\text{Ce}^{3+}]\square \quad (13)
\]
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\[ [\text{Ce}^{4+}] = \text{O}_2\text{NO} \text{ (bidentate nitrate)} + \]
\[ \text{NO} \rightarrow [\text{Ce}^{4+}] - \text{ONO} + \text{NO}_2 \] (14)

\[ [\text{Ce}^{4+}] - \text{ONO} \rightarrow [\text{Ce}^{3+}] - \square + \text{NO}_2 \] (15)

The mutual transformation between the monodentate, bridging and bidentate nitrate follows the equations:\n
\[ [2\text{Ce}^{4+}] = \text{ONO}_2\text{(bridging nitrate)} \rightarrow [\text{Ce}^{4+}] - \text{ONO}_2\text{(monodentate nitrate)} + [\text{Ce}^{3+}] - \square \] (16)

\[ [\text{Ce}^{4+}] = \text{O}_2\text{NO} \text{ (bidentate nitrate)} \rightarrow [\text{Ce}^{4+}] - \text{ONO}_2\text{(monodentate nitrate)} \] (17)

These transformations made it possible for the monodentate, bridging and bidentate nitrate species to all be present on the surface of the CeWO₄ catalyst after the adsorption of NO or NO₂.

After the surface was saturated with the nitrates originating from NO adsorption, NO₂ could still be adsorbed on the surface according to the equation:\n
\[ [\text{Ce}^{3+}] - \square + 2\text{NO}_2 \rightarrow [\text{Ce}^{4+}] - \text{ONO}_2\text{(monodentate nitrate)} + \text{NO} \] (18)

This equation is a combination of the reverse reaction of eqn (12) and (15). The presence of NO₂ could reoxidize the low valence Ce species, and the saturated adsorption of NO cannot inhibit the adsorption of NO₂.

4.2 Mechanism of SCR reactions

Many researchers reported that NH₄NO₃ is reducible by NO above its melting point of 170 °C, and in the melt, NH₄NO₃ can decompose to NH₃ and HNO₃. NO could reduce HNO₃ to HNO₂ at a comparatively lower temperature, i.e. at 50 °C. However, it is obvious that NO was able to reduce NH₄NO₃ significantly at 150 °C in the present study, and this reaction rate was faster than that of NH₄NO₃ decomposition to NH₃ and HNO₃ in N₂, as shown in Fig. 6. Therefore, it could be suggested that NO gas reduced NH₄NO₃ directly according to eqn (7), rather than reacting with the nitrates formed by the decomposition of NH₄NO₃. It is widely accepted that the formation of NH₃NO₂ blocks the active site of the NH₃-SCR reaction, and eqn (7) has been suggested to be crucial in the NH₃-SCR reaction by many researchers, since it consumes NH₄NO₃ on the surface of the catalysts. Koebel et al. suggested that eqn (7) was more important at lower temperature, and this reaction governed the whole NO₂ conversion at 140 °C over the V₂O₅-WO₃/TiO₂ catalyst. Wang et al. observed the presence of NH₄NO₃ during the fast SCR reaction instead of the standard SCR reaction over the Cu-SAPO-34 catalyst, and suggested that the reaction between NO and NH₄NO₃ was important for fast SCR. Iwasaki and Shinjoh reported that eqn (7) was the rate-limiting step for the fast SCR reaction over the Fe-ZSM-5 catalyst. A similar conclusion has been drawn by Grossale et al. In the present study, no NH₄NO₃ was present on the surface of the CeWO₄ catalyst under standard and fast SCR reaction conditions at 150 °C, as seen in Fig. 8, indicating that if reaction (7) occurred, it must be very fast. This might be the reason why CeWO₄ performed excellently during both standard and fast SCR.

Nevertheless, NO could still react with the surface nitrate species according to eqn (12)–(14). In this case, NH₄NO₃ could not be formed due to the faster reaction between the surface nitrates and NO. As shown by eqn (12)–(14), NO could react with the surface nitrates to produce NO₂ gas and nitrite intermediates. These nitrites, which might be too active to be observed during DRIFTS studies, will either desorb from the surface of the catalyst to produce NO₂ gas, or react with the adsorbed ammonia to form N₂ in the SCR reaction. The importance of eqn (12)–(14) in the NH₃-SCR reaction has been reported by many groups. Nova et al. found that NO could react with nitric acid at 200 °C on the commercial V₂O₅-WO₃/TiO₂ catalyst, forming NO₂ and nitric acid (HONO), and the fast SCR reaction is limited by this reaction at low temperatures. Additionally, Ruggeri et al. suggested that the reduction of nitrates/nitric acid by NO was a crucial step in the fast SCR reaction over Fe/ZSM-5 based on the results of a DRIFTS study. Grossale et al. proposed that the surface nitrates were the key intermediates for oxidizing NO during fast SCR, which could be reduced by ammonia during the NO₂-SCR reaction over Cu- or Fe-zeolites. The present results are consistent with those reported in the literature for V-based oxides and zeolite catalysts. Therefore, it could be proposed that eqn (12)–(14) are important, and both the surface nitrate and NO in the gas phase are necessary for the formation of active nitrites.

The SCR reaction might proceed according to the following equations at low temperatures (≤200 °C):

1. The formation of surface nitrates from NO or NO₂ adsorption:

\[ \text{NO} + [\text{Ce}^{4+}] - \text{O} \rightarrow [\text{Ce}^{4+}] - \text{ONO} \] (8)

\[ \text{NO}_2 + [\text{Ce}^{4+}] - \square \rightarrow [\text{Ce}^{4+}] - \text{ONO} \] (15)

2. The formation of surface nitrates from NO or NO₂ adsorption:

\[ 2[\text{Ce}^{4+}] - \text{O} + \text{NO} \rightarrow 2[\text{Ce}^{4+}]\text{ONO}_2 \] (9)

\[ \text{O} - [\text{Ce}^{4+}] - \text{O} \rightarrow [\text{Ce}^{4+}] = \text{O}_2\text{NO} \] (10)

\[ [\text{Ce}^{4+}] - \text{O} + \text{NO}_2 \rightarrow [\text{Ce}^{4+}] - \text{ONO}_2 \] (11)

3. Reactions between NO and surface nitrates:

\[ [\text{Ce}^{4+}] - \text{ONO}_2 + \text{NO} \rightarrow [\text{Ce}^{4+}] - \text{ONO} + \text{NO}_2 \] (12)

\[ 2[\text{Ce}^{4+}] = \text{O}_2\text{NO} + \text{NO} \rightarrow [\text{Ce}^{4+}] - \text{ONO} + \text{NO}_2 + [\text{Ce}^{3+}] - \square \] (13)
[Ce⁴⁺]⁺O₂NO + NO ↔ [Ce⁴⁺]⁻ONO + NO₂

4. Reactions between surface nitrites and adsorbed ammonia:

[Ce⁴⁺]⁻ONO + NH₃⁻L → [Ce⁴⁺]⁻OH + NH₃NO → N₂ + H₂O + [Ce⁴⁺]⁻OH

[Ce⁴⁺]⁻ONO + NH₄⁺⁻B → [Ce³⁺]⁻□ + NH₄NO₂ → N₂ + 2H₂O + [Ce³⁺]⁻□

5. Reaction between surface NH₄NO₃ and NO gas:

NH₄NO₃ + NO → N₂ + NO₂ + 2H₂O

For standard SCR, the surface nitrates originated mainly from direct NO adsorption on the surface, or from the adsorption of NO₂ produced by NO oxidation. Therefore, the amount of NO₃ produced during NO oxidation over CeWO₄ was determined. As seen in Fig. 9, the amount of NO₂ produced below 200 °C was less than 10 ppm, indicating that the reaction of NO oxidation to NO₂ was slow, which was consistent with the results shown in Fig. 3(b). Therefore, the surface nitrates mainly came from the adsorption of NO on the surface of the catalyst according to eqn (9) and (10). Since NO₃ adsorption led to the formation of more surface nitrates than NO adsorption, as seen in Fig. 3, NO tended to play the role of reducing NH₄NO₃ or nitrates. Consequently, it could be suggested that there was a close correlation between NO adsorption and the amount of surface nitrates. The surface nitrates, mainly originating from NO₂, were essential intermediates for forming NH₄NO₃ or surface nitrates. The NO₂ conversion depended on the concentration of NO in the reactant gas, as shown in Fig. 1. For NO₂-SCR, the concentration of surface nitrates and NH₄NO₃ must be the highest (see Fig. 4(b)). However, the lack of NO resulted in the accumulation of NH₄NO₃, which would block the surface active sites for activating NH₃ or NO₂, resulting in the lowest NO₂ conversion. Both NO and NO₂ were necessary for higher NO₂ conversion, which confirmed that there was an optimized NO/NO₂ ratio of 1/1 for the SCR reaction when the overall amount of NO₂ was fixed.

5. Conclusions

The NO conversion on CeWO₄ catalysts followed the order of fast SCR > standard SCR > NO₂-SCR at low temperatures (<200 °C). An optimal NO/NO₂ feed ratio was suggested for the SCR reaction, and the best deNO₂ efficiency was achieved at a NO/NO₂ feed ratio of 1:1. The DRIFTS study showed that the adsorption of NO or NO₂ resulted in the formation of the same surface nitrates, whereas NO₂ adsorption led to much more surface nitrates than NO adsorption. NO₂ is responsible for the formation of surface nitrates, which may further react with adsorbed NH₃ to form NH₄NO₃. NO participates in the reaction by following two pathways: one is to reduce NH₄NO₃ to form N₂ directly; the other is to reduce the surface nitrates to active nitrite species, which will react with the adsorbed NH₃ species to produce N₂. Both Lewis and Brønsted amonia species on the CeWO₄ catalyst could participate in the fast SCR reaction. NH₄NO₃ was also observed during the reaction between NO₂ and NH₃, and it was suggested that NO could reduce NH₄NO₃ directly below its melting point.

In comparison with standard SCR, more surface nitrates were formed during the fast SCR reaction, leading to a higher NO₂ conversion. For NO₂-SCR, although the amount of surface nitrates was higher, the lack of NO gas resulted in the blockage of the active sites by NH₄NO₃ on CeWO₄, and consequently, a lower NO₂ conversion. The reactions between NO and NH₄NO₃ or surface nitrates at low temperatures were important for the NH₃-SCR reaction. Therefore, both NO in the gas phase and surface nitrates were important for the NH₃-SCR reaction.

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