Selective catalytic reduction of NO with NH₃ over manganese substituted iron titanate catalyst: Reaction mechanism and H₂O/SO₂ inhibition mechanism study

Fudong Liu, Hong He*

State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, PR China

ABSTRACT
Selective catalytic reduction (SCR) of NO with NH₃ over Mn substituted iron titanate catalyst (Fe₀.₇₅Mn₀.₂₅TiOₓ) was fully investigated using in situ diffuse reflectance infrared Fourier transform spectroscopy. At relatively low temperatures, both ionic NH₄⁺ and coordinated NH₃ contributed to the SCR reaction, and both bridging nitrate and monodentate nitrate were confirmed to be the reactive nitrate species. In the SCR reaction condition, surface NH₄NO₃ species was formed as intermediate species and its reactivity was also proved. An NH₃-SCR mechanism over Fe₀.₇₅Mn₀.₂₅TiOₓ at low temperatures was proposed accordingly, in which the reduction of NH₄NO₃ by NO was possibly the rate-determining step. Due to the mild and reversible inhibition effect of H₂O on NH₃/NO adsorption, the SCR activity decline in the presence of H₂O was also slight and recoverable; however, the inhibition effect of SO₂ was much more intense and irreversible, because the formation of nitrate species was totally inhibited by the formation of sulfate, resulting in the cut-off of the SCR reaction pathway at low temperatures.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction
Selective catalytic reduction (SCR) of NO with NH₃ is a well-proven technique for the removal of NOₓ in exhaust gases from stationary and mobile sources, and the most widely used commercial catalyst system is V₂O₅–WO₃ (MoO₃)/TiO₂ [1], of which the operation temperature window is usually at 350–400 ℃. Such a catalyst system cannot be used in the NOₓ removal process for the flue gas after dust removal and desulfurization from coal-fired power plants or the exhaust gas from diesel engines in the cold-start process due to the low exhaust temperature (< 200 ℃). Therefore, many researchers are devoted to the development of low temperature SCR catalysts, such as V₂O₅ loaded on AC (activated carbon)/Al₂O₃/carbon–ceramic [2–4], Fe–Mn oxides loaded on TiO₂/USY zeolite/mesoporous silica [5–7], pure MnOₓ [8–10], MnOₓ loaded on TiO₂/Al₂O₃/SiO₂/AC/USY zeolite [6,11–13], and Mn–Cu, Mn–Ce mixed oxides [14–16].

In our previous study, we have also developed a novel iron titanate catalyst (FeTiO₄) showing high SCR activity, N₂ selectivity and H₂O/SO₂ durability in the medium temperature range (200–400 ℃) [17,18]. In the relatively low and high temperature ranges, Langmuir–Hinshelwood mechanism and Eley–Rideal mechanism mainly dominated in the NH₃-SCR reaction, respectively [19]. Through the substitution of partial Fe by Mn, the low temperature SCR activity was greatly enhanced with more than 90% NOₓ conversion obtained from 150 to 325 ℃; the influence of Mn substitution on the structure and activity of iron titanate catalyst was also fully investigated [20]. In this paper, the SCR reaction mechanism over Fe₀.₇₅Mn₀.₂₅TiOₓ catalyst at low temperatures will be studied using in situ diffuse reflectance infrared Fourier transform spectroscopy (in situ DRIFTS). The inhibition effect of H₂O and SO₂ will also be clarified, which is important to the further improvement of the SCR performance and H₂O/SO₂ resistance for its practical application.

2. Experimental
2.1. Catalyst synthesis and activity test
Fe₀.₇₅Mn₀.₂₅TiOₓ catalyst was prepared by conventional co-precipitation method using Fe(NO₃)₃·9H₂O, Mn(NO₃)₂ and Ti(SO₄)₂ as precursors. The detailed synthesis process was described in our previous study [20]. The influence of H₂O/SO₂ on the NOₓ conversion in the NH₃-SCR reaction over Fe₀.₇₅Mn₀.₂₅TiOₓ catalyst was conducted in a fixed-bed quartz tube reactor at atmospheric pressure. The reaction conditions were controlled as follows: 500 ppm NO, 500 ppm NH₃, 5 vol. % O₂, 10 vol. % H₂O...
from the Ti(SO$_4$)$_2$ precursor, indicating again on the Fe$_{0.75}$Mn$_{0.25}$TiO$_2$N O$^+$O$_2$ and pre-adsorbed NH$_3$ species on the Fe$_{0.75}$Mn$_{0.25}$TiO$_2$.

2.2. Mechanism study

The in situ DRIFTS experiments were performed on an FTIR spectrometer (Nicolet Nexus 670) equipped with an MCT/A detector cooled by liquid nitrogen and an in situ DRIFTS reactor cell with ZnSe window (Nexus Smart Collector) connected to a purging/adsorption gas control system. The reaction temperature was controlled precisely by an Omega programmable temperature controller. Prior to each experiment, the sample was pretreated at 400 °C in a flow of 20 vol.% O$_2$/N$_2$ for 0.5 h and then cooled down to the desired temperature. The background spectrum was collected in flowing N$_2$ atmosphere and was automatically subtracted from the sample spectrum. The total flow rate of the feeding gas was kept at 300 ml/min, and all spectra were recorded by accumulating 100 scans with a resolution of 4 cm$^{-1}$. The reaction conditions were controlled as follows: 500 ppm NO, 500 ppm NH$_3$, 5 vol.% O$_2$, 1 vol.% H$_2$O (when used), 100 ppm SO$_2$ (when used) and N$_2$ balance.

3. Results and discussion

3.1. NH$_3$-SCR mechanism over Mn substituted iron titanate catalyst

3.1.1. In situ DRIFTS of the reaction between NO + O$_2$ and adsorbed NH$_3$ species

Fig. 1 shows the in situ DRIFTS spectra of the reaction between NO + O$_2$ and pre-adsorbed NH$_3$ species on the Fe$_{0.75}$Mn$_{0.25}$TiO$_x$ catalyst at 150 °C. After NH$_3$ pre-adsorption and N$_2$ purge, the catalyst surface was mainly covered by ionic NH$_4^+$ ($\delta_1$ at 1676 cm$^{-1}$ and $\delta_2$ at 1443 cm$^{-1}$) bound to Brønsted acid sites and coordinated NH$_3$ ($\delta_3$ at 1603 cm$^{-1}$ and $\delta_4$ at 1180 cm$^{-1}$) bound to Lewis acid sites [21–23]. N–H stretching vibration modes at 3361, 3255 and 3155 cm$^{-1}$ also showed up, together with the negative bands at 3703 and 3362 cm$^{-1}$ due to the hydroxyl consumption through interaction with NH$_3$ to form NH$_4^+$. The negative band at 1358 cm$^{-1}$ was mainly caused by the coverage of residual sulfate species ($\nu_{asSO_4}$) [23] from the Ti(SO$_4$)$_2$ precursor, indicating again the existence of Brønsted acid sites on the catalyst surface. After the introduction of NO + O$_2$, both the bands attributed to ionic NH$_4^+$ and coordinated NH$_3$ showed an obvious decrease in intensity, and totally disappeared after 10 min. This result implied that both ionic NH$_4^+$ and coordinated NH$_3$ could play the roles as reducing agents to reduce NO$_x$ in the SCR reaction. Only after the pre-adsorbed NH$_3$ species was completely consumed, the nitrate species began to accumulate on the catalyst surface, including bridging nitrate at 1610 cm$^{-1}$ ($\nu_3$ high) and 1232 cm$^{-1}$ ($\nu_3$ low), bidentate nitrate at 1581 cm$^{-1}$ ($\nu_3$ high) and monodentate nitrate at 1552 cm$^{-1}$ ($\nu_3$ high) [24,25]. Besides, the in situ DRIFTS spectra in Fig. S1 (Supporting Information) showed that the nitrate species could not form after the introduction of NO + O$_2$ if NH$_3$ was supplied successively in the simulating gas, indicating that the consumption of active nitrate species was very fast during this process.

3.1.2. In situ DRIFTS of the reaction between NH$_3$ and adsorbed NO$_x$ species

Contrastively, we performed another in situ DRIFTS experiment of the reaction between NH$_3$ and pre-adsorbed NO$_x$ species on the Fe$_{0.75}$Mn$_{0.25}$TiO$_x$ catalyst at 150 °C, of which the results are shown in Fig. 2. As we have known, after the pre-adsorption of NO + O$_2$ and N$_2$ purge, the catalyst surface was mainly covered by three kinds of nitrate species. The subsequent introduction of NH$_3$ resulted in the rapid disappearance of bridging nitrate (1612 and 1230 cm$^{-1}$) and monodentate nitrate (1552 cm$^{-1}$), implying that these two kinds of nitrate species were reducible or reactive in the SCR reaction. Oppositely, the bidentate nitrate species (1581 or 1576 cm$^{-1}$), always existed on the catalyst surface even after 60 min, showing that this species was inactive in the SCR reaction once formed. Similar phenomenon was also observed over our iron titanate catalyst [19] and MnO$_x$/Al$_2$O$_3$ catalyst by other researchers at relatively low temperatures [26]. Simultaneously, adsorbed NH$_3$ species rapidly occurred on the catalyst surface, i.e. ionic NH$_4^+$ at 1676 cm$^{-1}$ and coordinated NH$_3$ at 1603 and 1186 cm$^{-1}$. During this process, additional bands locating at 1524, 1282 and 1254 cm$^{-1}$ showed up, belonging to neither NH$_3$ nor NO$_x$ species separately. Similar bands also showed up after the introduction of NH$_3$ when NO + O$_2$ was supplied successively in the simulating gas (Fig. S2 in Supporting Information).

We assumed that this species was surface ammonium nitrate (NH$_4$NO$_x$), originating from NO$_2$ dimerization, disproportion in the presence of trace of H$_2$O (producing HONO and HNO$_2$) and successive reaction with NH$_3$ [27–29]. In this process, the produced ammonium nitrite (NH$_4$NO$_2$) was easy to decompose even at very low temperatures, giving out N$_2$ and H$_2$O; however, NH$_4$NO$_3$...
could exist on the catalyst surface stably, because its decomposing temperature is ca. 200 °C [27]. Therefore, we performed another experiment at 200 °C to see whether this surface species could form on the catalyst surface, during which NH3 was subsequently introduced with the successive supply of NO + O2. As shown in Fig. 3, this species was indeed absent at 200 °C, suggesting the possible validity of our previous assumption.

3.1.3. Confirmation of the formation of NH4NO3 species

To further confirm the formation of NH4NO3 species, we performed another in situ DRIFTS experiment of NH3 adsorption at 150 °C on the Fe0.75Mn0.25TiOx catalyst pre-impregnated with HNO3, during which NH4NO3 could form directly on the catalyst surface. As the results shown in Fig. 4, besides of the band at 1425 cm\(^{-1}\) ascribed to ionic NH4\(^+\) and negative bands at 1623, 1595 and 1556 cm\(^{-1}\) ascribed to the reduction or coverage of nitrate species by NH3, the bands at 1524, 1286 and 1257 cm\(^{-1}\) showed an obvious increase in intensity with the increasing of adsorption time. These bands were located at the same positions as those in Fig. 2 (i.e. 1524, 1282 and 1254 cm\(^{-1}\)), further proving that the additional bands appeared in Figs. 2 and S2 were indeed due to the formation of adsorbed NH4NO3 species.

3.1.4. In situ DRIFTS of the SCR reaction

To investigate the surface species in the real SCR reaction condition, the in situ DRIFTS spectra were recorded in a flow of NO + O2 + NH3 on the Fe0.75Mn0.25TiOx catalyst at 150 °C. As the results shown in Fig. 5, the bands attributed to ionic NH4\(^+\) (1676 cm\(^{-1}\)), coordinated NH3 (1603 and 1184 cm\(^{-1}\)) and bidentate nitrate (1578 cm\(^{-1}\)) showed up with the increasing of reaction time. Besides, the bands at 1522, 1286 and 1248 cm\(^{-1}\) also appeared, similar as those in Figs. 2 and S2, suggesting that the surface NH4NO3 might be an important intermediate species in the real SCR reaction. In the following section, the reactivity of NH4NO3 species in the SCR reaction will be clarified.

3.1.5. Reactivity of in situ-formed and pre-impregnated NH4NO3 on Fe0.75Mn0.25TiOx

The in situ DRIFTS experiment of reaction at 150 °C between NO + O2 and in situ-formed NH4NO3 species on the Fe0.75Mn0.25TiOx catalyst was firstly conducted. As the results shown in Fig. 6, after 60 min reaction in a flow of NO + O2 + NH3, the surface NH4NO3 species was in situ-formed with the IR bands at 1522, 1286 and 1252 cm\(^{-1}\). Then, the NH3 supply was cut off from the simulating gas, making NO + O2 to react with the surface species. With the increasing of reaction time, not only the bands attributed
to adsorbed NH₃ species (3361, 3257, 3159, 1676, 1603 and 1188 cm⁻¹) but also the bands ascribed to NH₄NO₃ species disappeared, with the remaining of nitrate species on the catalyst surface eventually. This result shows that the in situ-formed NH₄NO₃ was indeed reducible, thus being an important reactive intermediate species in the SCR reaction.

To further confirm the reactivity of NH₄NO₃ species, we also performed another in situ DRIFTS experiment in which NO + O₂ reacted with pre-impregnated NH₄NO₃ on the Fe₀.₇₅Mn₀.₂₅TiOₓ catalyst at 150 °C. During this process, we collected the spectrum of Fe₀.₇₅Mn₀.₂₅TiOₓ catalyst pre-impregnated with NH₄NO₃ and set as background, therefore the negative bands occurred in Fig. 7 indicated the surface species which were consumed in the reaction. As shown in the inserted figure, the bands nearly 1270 cm⁻¹ firstly showed some increase in intensity after the introduction of NO + O₂ possibly due to the formation of partial extra NH₄NO₃ between NOₓ and ionic NH₄⁺, which were later overlapped by the strong negative bands from 1300 to 1500 cm⁻¹. These strong negative bands were caused by the reduction of pre-impregnated NH₄NO₃ by NO following the reaction equation of NH₄NO₃ + NO → NO₂ + N₂ + 2H₂O [29], which could also be confirmed by the N–H consumption bands at 3242, 3045 and 2835 cm⁻¹ and the hydroxyl formation band at 3662 cm⁻¹. Because of different crystallization degrees of pre-impregnated NH₄NO₃ and in situ-formed surface NH₄NO₃, it was reasonable that the bands appeared in Fig. 7 showed some shift in position comparing with those in Figs. 2–6. Besides, the nitrate species including bridging nitrate (1614 or 1624 cm⁻¹ and 1232 or 1219 cm⁻¹) and bidentate nitrate (1583 or 1585 cm⁻¹) also formed on the catalyst surface in this process. These results further confirmed that NH₄NO₃ was reducible by NO on the Fe₀.₇₅Mn₀.₂₅TiOₓ catalyst, playing the role as important reactive intermediate species in the SCR reaction at temperatures below 200 °C.

3.1.6. Proposed NH₃-SCR mechanism

Based on the in situ DRIFTS results in Sections 3.1.1–3.1.5, the NH₃-SCR mechanism over Mn substituted iron titanate catalyst at low temperatures is proposed and presented in Scheme 1. As shown in our previous study [20], the substitution of partial Fe by Mn in iron titanate catalyst greatly enhanced its NO oxidation ability at low temperatures. The in situ-produced NO₂ could strongly adsorb on the surface of Fe₀.₇₅Mn₀.₂₅TiOₓ catalyst, and then come through dimerization and disproportion into HONO and HNO₃ in the presence of H₂O. In the SCR reaction condition, NH₃ could strongly adsorb on the surface of catalyst as ionic NH₄⁺ and coordinated NH₃, reacting with HONO and HNO₃ to form NH₄NO₂ and NH₄NO₃, respectively. Below 200 °C, NH₄NO₃ was very easy to decompose into N₂ and H₂O, while NH₄NO₂ could react with NO to produce NO₂ and NH₄NO₃ simultaneously [29,30]. The produced NO₂ could participate into the SCR reaction in another cycle, and the produced NH₄NO₂ could decompose into N₂ and H₂O directly. Since the surface NH₄NO₃ species was obviously present on the catalyst during this process, the reduction of NH₄NO₃ by NO was possibly the rate-determining step of the SCR reaction. Above 200 °C, NH₄NO₃ could also decompose into N₂O and H₂O [31], resulting in the decrease of N₂ selectivity of the SCR reaction. This was another possible route of N₂O formation besides of the unselective oxidation of NH₃ at relatively high temperatures [32].

Recently, Klukowski et al. [33] proposed an SCR reaction mechanism on dual Fe³⁺ sites over their Fe/HBEA zeolite catalyst using DRIFTS, XANES, TPD and kinetic measurements, in which the adsorbed NH₂ after NH₃ dehydrogenation reacted with adsorbed NO to form N₂ and H₂O. However, no NH₂ species on the Fe³⁺ sites was resolved in their DRIFTS experiments. Therefore, we cannot exclude the possibility that adsorbed NH₃ species over our Fe₀.₇₅Mn₀.₂₅TiOₓ catalyst would undergo dehydrogenation by Fe³⁺ or Mn³⁺ to form NH₂ species and then react with adsorbed NO₂ species to form N₂ and H₂O, although this reaction pathway might not be important in the low temperature range below 200 °C. Besides, Iwasaki et al. [31] and Grossale et al. [34] concluded that the high concentrations of NH₃ on the surface of Fe/ZSM-5 catalyst would inhibit its low temperature SCR activity, because of the inhibition of NO oxidation or the capture of reactive nitrate species by strongly adsorbed NH₃. Similar inhibition effect might also exist over our Fe₀.₇₅Mn₀.₂₅TiOₓ catalyst, although it was not investigated in this study. In our future study, we can optimize the SCR reaction atmosphere (such as the gas phase NH₃ concentration) or modify the acid–base property of the catalyst surface to lower the undesired inhibition effect of NH₃ [34], further improving its low temperature SCR activity.

3.2. H₂O/SO₂ inhibition effect on NH₃-SCR over Fe₀.₇₅Mn₀.₂₅TiOₓ

3.2.1. Influence of H₂O/SO₂ on NOx conversion in the NH₃-SCR reaction

For practical use of this Mn substituted iron titanate catalyst, the influence of H₂O and SO₂ on the SCR activity needs to be investigated. As the results shown in Fig. 8, when 10 vol.% H₂O was added into the flue gas, a sharp decline of the NOx conversion (to ca. 70%) was firstly observed, which then partially recovered and maintained at 90% for the next 48 h; after the removal of H₂O, the NOx conversion recovered to the original level rapidly, indicating that the inhibition effect of H₂O on the SCR activity over Fe₀.₇₅Mn₀.₂₅TiOₓ catalyst was mild and reversible. On the con-
 tertary, the inhibition effect of SO$_2$ was much more intense and irreversible: only ca. 60% NO$_x$ conversion was obtained in the presence of 100 ppm SO$_2$ for 48 h test and no recover was observed after the removal of SO$_2$. The coexistence of H$_2$O and SO$_2$ led to more serious activity decline, yet no synergistic inhibition effect was observed; only the activity loss caused by H$_2$O was recovered after stopping H$_2$O + SO$_2$, implying again that the SO$_2$ poisoning was irreversible. On the one hand, the Mn substitution could obviously enhance the SCR activity of Fe$_{0.75}$Mn$_{0.25}$TiO$_x$ catalyst at low temperatures, yet on the other hand it also resulted in the decrease of SO$_2$ resistance. This catalyst should be used in SO$_2$-free atmosphere, such as flue gas after desulfurization and dust removal. The H$_2$O/SO$_2$ inhibition mechanism will be clarified in the following sections using in situ DRIFTS methods.

3.2.2. Influence of H$_2$O on NH$_3$/NO$_x$ adsorption

As we mentioned above, both NH$_3$ and NO$_x$ adsorbed species existed on the catalyst surface participating into the SCR reaction, therefore the influence of H$_2$O on NH$_3$/NO$_x$ adsorption was firstly investigated. As shown in Fig. 9, after the introduction of H$_2$O, the bands at 1680 and 1448 cm$^{-1}$ attributed to ionic NH$_4^+$ showed some increase in intensity due to the hydroxylation of catalyst surface in the presence of H$_2$O. At the same time, the bands at 1603 and 1178 cm$^{-1}$ (with some blue shift to 1192 cm$^{-1}$) attributed to coordinated NH$_3$ showed some decrease in intensity, mainly due to the transformation of partial Lewis acid sites into Brønsted acid sites in the hydroxylation process. The band at 1632 cm$^{-1}$ ($\delta_{\text{HOH}}$ vibration mode) [35,36] was ascribed to the adsorption of H$_2$O on the surface of catalyst, which totally disappeared after the removal of H$_2$O feed. The hydroxylation effect was also vanished after stopping the H$_2$O supply, accompanied by the simultaneous decrease of ionic NH$_4^+$ bands and increase of coordinated NH$_3$ bands in intensity.

Fig. 10 shows the in situ DRIFTS spectra of influence of H$_2$O on NO$_x$ adsorption on the Fe$_{0.75}$Mn$_{0.25}$TiO$_x$ catalyst at 150 $^\circ$C. After the introduction of H$_2$O, both bridging nitrate (1612 and 1227 cm$^{-1}$) and monodentate nitrate (1552 cm$^{-1}$) showed some decrease in intensity, while bidentate nitrate (1581 cm$^{-1}$) showed no obvious change during the whole process. Due to the adsorption and disturbance of H$_2$O on the surface of catalyst (shoulder band at 1628 cm$^{-1}$ for $\delta_{\text{HOH}}$ vibration mode), the $\nu_3$ low vibration mode of bridging nitrate showed some blue shift to 1248 cm$^{-1}$ due to the reduction of splitting of $\nu_3$ frequency [37]; the $\nu_3$ low vibration mode of monodentate nitrate also appeared at 1284 cm$^{-1}$ [36]. After the removal of H$_2$O feed, the surface nitrate species recovered to the original level, similar as adsorbed NH$_3$ species. Summarizing the results in Figs. 9 and 10 we can conclude that, the inhibition effect of H$_2$O on the adsorption of NH$_3$ and NO$_x$ on the Fe$_{0.75}$Mn$_{0.25}$TiO$_x$ catalyst was mild and reversible, which is in well accordance with the SCR activity results in Fig. 8; the slight activity decline in the presence of H$_2$O was mainly caused by the competitive adsorption of H$_2$O with partial reactive bridging nitrate and monodentate nitrate.

3.2.3. Influence of SO$_2$ on NH$_3$/NO$_x$ adsorption

Comparatively, the influence of SO$_2$ on NH$_3$/NO$_x$ adsorption on the Fe$_{0.75}$Mn$_{0.25}$TiO$_x$ catalyst was also investigated at 150 $^\circ$C. As the results shown in Fig. 11, after the introduction of SO$_2$ + O$_2$, the bands at 1684 and 1437 cm$^{-1}$ attributed to ionic NH$_4^+$ showed strong increase in intensity due to the sulfation of catalyst surface and simultaneous enhancement of surface acidity. The bands at 1603 and 1182 cm$^{-1}$ ascribed to coordinated NH$_3$ showed some decrease in intensity, and the latter one was even overlapped by the growing bands attributed to sulfate species (1240, 1159 and 1051 cm$^{-1}$ for $\nu_3$ band splitting of SO$_4^{2-}$) [38]. In the N–H stretching vibration region, the bands also shifted from 3359, 3251 and 3153 cm$^{-1}$ of coordinated NH$_3$ to 3209, 3049 and 2835 cm$^{-1}$ of ionic NH$_4^+$ [21], indicating the formation of a large amount of extra Brønsted acid sites during the sulfation process. The strongly
adsorbed NH₄⁺ species on these Brønsted acid sites introduced by sulfate species inhibited the further adsorption of reactive coordinated NH₃ on Lewis acid sites, which probably resulted in the decrease of SCR activity to a certain extent. After the removal of SO₂ + O₂, the adsorbed surface species showed no obvious change.

Fig. 12 shows the in situ DRIFTS spectra of influence of SO₂ on NO₃ adsorption on the Fe₀.₇₅Mn₀.₂₅TiOₓ catalyst at 150 °C. After the introduction of SO₂ into the NO + O₂ feeding gas, the surface nitrate species at 1614, 1581, 1554 and 1228 cm⁻¹ quickly disappeared with the increasing of time, replaced by the deposited sulfate species (1363 and 1282 cm⁻¹ for ν₂SO₄ and ν₃SO₄, 1200, 1144 and 1038 cm⁻¹ for ν₁ band splits) [38-40] and adsorbed H₂O (δ₁OH vibration mode) formed in the sulfation process. After the removal of SO₂ from the feeding gas, the nitrate species did not recover at all, suggesting that the inhibition effect of SO₂ on NO₂ adsorption on the Fe₀.₇₅Mn₀.₂₅TiOₓ catalyst was intense and irreversible. Summarizing the results in Figs. 11 and 12 we can conclude that, although the NH₃ adsorption was greatly enhanced with the SCR activity results in Fig. 8, in which the activity decline of the SCR reaction pathway that we proposed.

4. Conclusions

The NH₃-SCR reaction mechanism over Mn substituted iron titanate catalyst was fully investigated using in situ DRIFTS methods. On the Fe₀.₇₅Mn₀.₂₅TiOₓ catalyst at low temperatures, both ionic NH₄⁺ and coordinated NH₃ contributed to the SCR reaction; bridging nitrate and monodentate nitrate were confirmed to be the reactive nitrate species. In the real SCR reaction condition, surface NH₄NO₃ was formed, playing the role as an important intermediate species. The reactivity of NH₄NO₃ was also proved, and the reduction of NH₄NO₃ by NO was possibly the rate-determining step of the whole SCR reaction. At temperatures above 200 °C, the decompositon of NH₄NO₃ might be another source of N₂O formation besides of the unselective oxidation of NH₃. The inhibition effect of H₂O on the SCR activity was mild and reversible, because only slight and reversible inhibition of NH₄NO₃ adsorption by H₂O was observed. On the contrary, the inhibition effect of SO₂ was much more intense and irreversible, because the nitrate formation was totally inhibited by the deposition of sulfate species, resulting in the cut-off of the SCR reaction pathway that we proposed.

Acknowledgements

This work was financially supported by the Chinese Academy of Sciences (KZCX1-YW-06-04) and the National High Technology Research and Development Program of China (2009AA064802 and 2009AA062301).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cattod.2010.02.043.

References