**In Situ** DRIFTS Study of the Low Temperature Selective Catalytic Reduction of NO with NH₃ over MnOₓ Supported on Multi-Walled Carbon Nanotubes Catalysts

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**ABSTRACT**

MnOₓ supported on multi-walled carbon nanotubes (MWCNTs) catalysts were prepared by the pore volume impregnation method and used for low-temperature selective catalytic reduction (SCR) of NO with NH₃. Based on the previous study, 10 wt.% loading MnOₓ/MWCNTs were then selected for investigation of the reaction mechanism by in situ Diffuse Reflectance Infrared Fourier Transform spectroscopy (in-situ DRIFTS). The important intermediates in the SCR of NO process at 210°C were discussed based on the DRIFTS results. Furthermore, the NH₃-SCR reaction pathways over MnOₓ/MWCNTs catalysts were proposed. The results showed that NH₄⁺ species on Brønsted acid sites and coordinate ammonia species on Lewis acid sites existed during the SCR reaction. NH₄⁺ species was more active than coordinate ammonia species over the catalysts at 210°C. Most of NOₓ ad-species would react with NH₃ ad-species. However, nitrite species, bidentate and monodentate nitrates contributed to the SCR reaction over the catalysts mostly. Two possible reaction pathways were proposed. One was that NOₓ ad-species could react with NH₄⁺ to form intermediate of NH₄N₂O₄ (a), NH₄NO₂ (a) or NH₄NO₃ (a), then to produce N₂ and H₂O as the final products. The other pathway was that NH₃ was initially adsorbed on active site and NH₂ was formed, then NH₂ reacted with NOₓ ad-species to produce intermediate NH₂NO₂ or NH₂NO₃ which were unstable and would decompose into N₂ and H₂O.

**Keywords:** Low-temperature SCR; MnOₓ/MWCNTs; In-situ DRIFTS; Reaction pathways.

**INTRODUCTION**

Selective catalytic reduction (SCR) of NOₓ with NH₃ is a well-established technology to abate nitrogen oxides from stationary source (Bosch, 1988; Forzatti, 1996). In power plants, the commercial catalysts (V₂O₅–WO₃ (MoO₃)/TiO₂), with relatively narrow temperature window of 300–400°C, have been widely used. However, due to the drawbacks of these catalysts, such as high catalytic temperature, narrow temperature window and toxicity of vanadium by SO₂ or dust, there has been a continuing effort to develop a highly low-temperature (≤250°C) efficient, stable, environmentally-friendly SCR catalysts for the removal of NOₓ (Lou et al., 2003., Qi et al., 2004; Jiang et al., 2009; Yang et al., 2012; Liu et al., 2013).

Manganese-based catalysts have shown excellent low-temperature SCR activity for NOₓ removal, which have attracted much interest (Wallin et al., 2004; Wu et al., 2008). Furthermore, there are various kinds of labile oxygen in Manganese-based catalysts, which play important roles in completing the SCR reaction cycle (Kijlstra et al., 1997a). It has been reported that Mn-based catalysts, such as MnOₓ/TiO₂ (Jiang et al., 2009), MnOₓ/activated carbon fiber (Pasel et al., 1998), and MnOₓ/activated carbon/ceramic (Tang et al., 2007), have presented good catalytic activity in SCR reaction with excess oxygen at low temperature. In our previous study, we had successfully developed MnOₓ supported on multi-walled carbon nanotubes (MWCNTs) catalysts which showed high active for low-temperature SCR (Wang et al., 2012).

It is well known that catalyst supports not only could make the active components dispersed uniformly on the supports surface, but also provide higher specific surface area. Furthermore, catalyst supports could improve catalytic efficiency of the active components (Jackson and Hargeaves, 2008; Tian et al., 2010). Carbon materials have wide applications as catalyst supports for low-temperature SCR because of their high specific surface areas and chemical stability. Carbon nanotubes (CNTs), as special orderly carbon materials, have been reported to be excellent as catalyst supports due to their unique electronic properties and structure (Planeix et al., 1994; Santillan-Jimenez et al.,...
The mechanism of SCR reaction in the manganese catalysts has been studied and various possible reaction pathways have been proposed. For some manganese catalysts, such as MnO$_2$/TiO$_2$ (Pena et al., 2004; Wu et al., 2007; Wu et al., 2010), unsupported MnO$_x$ (Qi et al., 2004; Chen, 2007), MnO$_x$/Al$_2$O$_3$ (Kijlstra et al., 1997a, b), and perovskite-type manganese oxides (Zhang et al., 2013b), some aspects of the reaction mechanism were similar, but some were distinguishably different, in particular, at the initial step of adsorption of NH$_3$ on these catalysts. It was reported that NH$_3$ adsorbed on the Lewis sites was more active than NH$_4^+$ species in the SCR reaction (Zhu et al., 2013; Fu et al., 2014). On the surface of the manganese catalysts, competition for adsorption between NH$_3$ and NO exists. If the NO adsorbed on the surface before the NH$_3$ was introduced, NO would have blocked the SCR reaction. Especially when bidentate nitrate was formed at the surface of the manganese catalysts, it could not react with NH$_3$ but occupied the activated sites, resulting in deactivation of the catalysts. In general, O$_2$ in atmosphere can improve the oxidation of NO to higher states (such as bidentate nitrate, bridged nitrate, etc.) on the surface of the catalysts and enhance the adsorption of NO. However, in the case of NH$_3$ adsorption, the roles of O$_2$ in atmosphere on the catalysts with various kinds of supports were quite different. In the MnO$_2$/TiO$_2$ catalysts (Wu et al., 2007; 2010), O$_2$ in atmosphere could enhance the absorption of NH$_3$. But in contrast, O$_2$ appeared to have no effects on the adsorption of NH$_3$ on the MnO$_x$/Al$_2$O$_3$ catalysts (Kijlstra et al., 1997a, b). Researchers (Reddy and Khan, 2005; Liu et al., 2007) showed that the catalytic properties of supported catalysts remarkably vary with the nature of the supports possibly due to the different reaction pathways over catalysts with various materials of supports for low-temperature SCR. Lots of work based on FT-IR to study the mechanism of SCR reaction has been done for the low-temperature NH$_3$-SCR, however, to the best of our knowledge, there has been few studies that focused on the reaction mechanism of manganese supported on carbon materials, especially on MWCNTs. In light of this, mechanism of manganese supported on MWCNTs SCR catalysts should be investigated for further development of efficient low-temperature SCR catalysts.

In this work, the important intermediates and possible reaction mechanism in the SCR of NOx process over MnO$_2$/MWCNTs catalysts have been investigated by using a combination of adsorption, transient response, steady-state response and in situ DRIFTS experiments. We proposed two possible reaction pathways that are significant to understand the behaviour of the formed surface compounds, active intermediates and elucidate the potential mechanism for the catalysts with high low-temperature activity in respect to the SCR reaction cycle.

**EXPERIMENT**

**Catalyst Preparation**

The MWCNTs were purchased from Shenzhen Nanotech Port Co., Ltd. Prior to supporting manganese, the MWCNTs were purified with 3 mol/L HNO$_3$ solution at 100°C for 4 h and pretreated in oxygen dielectric barrier discharge plasma at the discharge power of 15 W for 40 min. The detailed process was described in previous study (Wang et al., 2011).

The catalysts were prepared by pore volume impregnation method. According to previous study (Wang et al., 2012), when the manganese loading was 10 wt.%, the catalyst showed the highest SCR activity. Therefore, in this study, a manganese acetate solution was used as the Mn precursor and was controlled to 10 wt.% loading. After the impregnation, the catalysts were dried at 110°C for 12 h followed by the calcination at 400°C in air for 2 h. The detailed information of catalyst preparation was described in previous study (Wang et al., 2012). The catalysts were denoted as MnO$_x$/MWCNTs.

**DRIFTS Experiments**

In situ DRIFTS experiments were conducted on a Nicolet 6700 FTIR spectrometers (2 cm$^{-1}$ resolution with 100 accumulated scans) equipped with a MCT detector cooled by liquid nitrogen and a diffuse reflection accessory with a high temperature reaction cell. The catalysts were first mixed with KBr in a ratio of 1/100 by weight, and it was then loaded into a DRIFTS cell. Prior to each experiment, the sample was pretreated at 350°C in Ar atmosphere for 1 h to remove any adsorbed species, then cooled down to the reaction temperature of 210°C. The background spectrum was recorded in flowing Ar and was automatically subtracted from the sample spectrum during the experiment. Then the Ar flow was switched to a stream containing one or more reactants, such as NH$_3$, NO, and O$_2$.

**RESULTS AND DISCUSSION**

**Adsorption Experiments**

The purpose of the NH$_3$ or NO + O$_2$ adsorption experiments was to learn the main adsorption species on the surface of the catalysts, which could be conducive to the following analysis of the intermediates and reaction pathways.

**NH$_3$ Adsorption on MnO$_x$/MWCNTs**

As shown in Fig. 1, several weak bands at 930, 965, 1549, 1559, 1684 cm$^{-1}$ and a broad band in the range of 3350–3100 cm$^{-1}$ were detected when NH$_3$ was injected at 210°C for various times. After NH$_3$ was fed into the DRIFTS cell for about 10 min, the bands at 1549 cm$^{-1}$, 1559 cm$^{-1}$ due to presence of amide species (–NH$_2$) were detected (Qi and Yang, 2004; Sun et al., 2009), which might be oxidized by...
lattice oxygen on the surface of manganese oxide (Kijlstra et al., 1997a). With the continuous injection of ammonia, the new band at 1684 cm\(^{-1}\) which could be attributed to the ammonium ions bond to Bronsted acid sites was detected (Jin et al., 1986; Pan et al., 2013). It was noted that several adsorbed species were detected after injection of NH\(_3\) for about 25 min. The weak bands corresponding to N–H stretching vibration modes of NH\(_3\), especially for the coordinated ammonia bonded to Lewis acid sites (3345, 3325, 3249 and 3152 cm\(^{-1}\)) (Galvez et al., 2008; Sun et al., 2009; Jin et al., 2010; Liu et al., 2012) were observed at a broad band in the range of 3350–3100 cm\(^{-1}\) (Kijlstra et al., 1997a; Wu et al., 2007; Liu and He, 2010; Zhou et al., 2011). And the bands at 965 and 930 cm\(^{-1}\) attributed to gaseous state or weakly adsorbed NH\(_3\) (Jiang et al., 2010; Jin et al., 2010; Liu et al., 2012) were also observed. However, the intensity of adsorption of ammonia was very weak, which was in agreement with previous studies by Fan et al. (2011) and Chang et al. (2001). On the whole, Fig. 1 reveals that the main ammonia adsorption species were ammonium ions bonded to Brønsted acid sites, coordinated ammonia bonded to Lewis acid sites and weakly adsorbed NH\(_3\) on the surface of MnO\(_x\)/MWCNTs catalysts.

**NO and O\(_2\) Co-Adsorption on MnO\(_x\)/MWCNTs**

The DRIFTS results of feeding NO and O\(_2\) mixture over MnO\(_x\)/MWCNTs catalysts for various times are shown in Fig. 2. With the supply of NO and O\(_2\) mixture, the bands at 1741, 1697, 1648, 1559, 1508, and 1457 cm\(^{-1}\) were clearly observed. These bands could be assigned to N\(_2\)O\(_4\)(a) (1741 and 1697 cm\(^{-1}\)) (Zhou et al., 2011), bridging nitrate species (1648 and 1627 cm\(^{-1}\)) (Kijlstra et al., 1997a; Zhao et al., 2009), bidentate nitrate (1559 cm\(^{-1}\)) (Liu and He, 2010; Wu et al., 2010; Zhou et al., 2011; Zhang et al., 2013a), monodentate nitrate (1539 cm\(^{-1}\)) (Zhang et al., 2013a), and nitrite species (1508 and 1457 cm\(^{-1}\)) (Kijlstra et al., 1997a; Jin et al., 2010). When NO and O\(_2\) were adsorbed onto the surface of MnO\(_x\)/MWCNTs catalysts for about 15 min, the intensity of bands at 2236 and 2221 cm\(^{-1}\) were detected and became larger afterwards. These bands could be attributed to N\(_2\)O in NH\(_3\)-SCR (Liu et al., 2012). After NO-s adsorbed on the surface of MnO\(_x\)/MWCNTs, the NO\(_x\) ad-species formed N\(_2\)O may due to oxygen vacant sites in MnO\(_x\) (Kijlstra et al., 1997a) which were able to dissociate adsorbed NO-s. This could provide a route for the formation of the N\(_2\)O gaseous species (NO-s + N-s → N\(_2\)O + 2s). The gaseous NO bands on the surface of the catalysts at around 1907 cm\(^{-1}\) and 1843 cm\(^{-1}\) (Zhang et al., 2013b) were hardly detected, indicating NO adsorbed on the catalysts quickly then translated to NO\(_x\) ad-species.

Compared to the process of ammonia adsorption (Fig. 1), the rate of the NO\(_x\) adsorption was much faster and more prominent. This result is in agreement with the study of Long and Yang (2001) reported that carbon nanotubes as superior sorbents for nitrogen oxides.

**Transient Reaction Experiments**

The Reaction between NO + O\(_2\) Ad-Species and NH\(_3\) on MnO\(_x\)/MWCNTs

The MnO\(_x\)/MWCNTs catalysts were first purged with NO and O\(_2\) mixture for 30 min, then NO and O\(_2\) were shut down when NH\(_3\) was introduced at 210°C. As shown in Fig. 3, after NH\(_3\) was introduced, the intensity of the bands due to bridging nitrate species (1648 cm\(^{-1}\)), bidentate nitrate (1559 cm\(^{-1}\)) (Liu and He, 2010; Wu et al., 2010; Zhou et al., 2011; Zhang et al., 2013a), monodentate nitrate (1539 cm\(^{-1}\)) (Zhang et al., 2013a), and nitrite species (1508 and 1457 cm\(^{-1}\)) (Kijlstra et al., 1997a; Jin et al., 2010). When NO and O\(_2\) were adsorbed onto the surface of MnO\(_x\)/MWCNTs catalysts for about 15 min, the intensity of bands at 2236 and 2221 cm\(^{-1}\) were detected and became larger afterwards. These bands could be attributed to N\(_2\)O in NH\(_3\)-SCR (Liu et al., 2012). After NO-s adsorbed on the surface of MnO\(_x\)/MWCNTs, the NO\(_x\) ad-species formed N\(_2\)O may due to oxygen vacant sites in MnO\(_x\) (Kijlstra et al., 1997a) which were able to dissociate adsorbed NO-s. This could provide a route for the formation of the N\(_2\)O gaseous species (NO-s + N-s → N\(_2\)O + 2s). The gaseous NO bands on the surface of the catalysts at around 1907 cm\(^{-1}\) and 1843 cm\(^{-1}\) (Zhang et al., 2013b) were hardly detected, indicating NO adsorbed on the catalysts quickly then translated to NO\(_x\) ad-species.

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The Reaction between NO + O\(_2\) Ad-Species and NH\(_3\) on MnO\(_x\)/MWCNTs

The MnO\(_x\)/MWCNTs catalysts were first purged with NO and O\(_2\) mixture for 30 min, then NO and O\(_2\) were shut down when NH\(_3\) was introduced at 210°C. As shown in Fig. 3, after NH\(_3\) was introduced, the intensity of the bands due to bridging nitrate species (1648 cm\(^{-1}\)), bidentate nitrate (1559 cm\(^{-1}\)), and nitrite species (1508 and 1457 cm\(^{-1}\)) on the catalysts surface were consumed rapidly before 10 min. And the bands at 1627 cm\(^{-1}\) attributed to the gaseous or weakly adsorbed NO\(_2\) became weaker afterwards. However, with the continuous injection of ammonia, new bridging nitrate species were formed on the surface of the catalysts, and these active nitrate species kept the dynamic equilibrium. Fig. 3 indicates that the gaseous or weakly adsorbed NO\(_2\) were transformed to bridging nitrate species and nitrite species on MnO\(_x\)/MWCNTs. Additionally, H\(_2\)O with the surface O-H stretching bands at 3800–3500 cm\(^{-1}\) was observed, which is a final product of the SCR reaction.
Furthermore, it also suggested that these nitrate species and nitrite species were active on catalysts surface. In contrast, the bands could be assigned to NH$_3$ ad-species began to grow, including coordinated ammonia bonded to Lewis acid sites (3256 and 1389 cm$^{-1}$) and the gaseous or weakly adsorbed NH$_3$ (966 and 930 cm$^{-1}$). Obviously, the bands due to the coordinated ammonia bonded to Lewis acid sites in this experiment were more remarkable than those in ammonia adsorption experiment (Fig. 1). The results in Fig. 3 indicated that competition for adsorption between NH$_3$ and NO, which would block the SCR reaction, did not occur or might be very weak in this SCR reaction. However, this does not coincide with the works of Kijlstra et al. (1997b) and Chen (2007). The reason might be different in the number of adsorption sites between the catalysts with various kinds of supports.

The Reaction between NH$_3$ Ad-Species and NO + O$_2$ on MnO$_x$/MWCNTs

The catalysts were first purged with NH$_3$ for 30 min, then the NO and O$_2$ mixture was injected when NH$_3$ was shut down simultaneously. The spectra were recorded as a function of time. The variations of adsorption and desorption were recorded and shown in Fig. 4. After injecting NO and O$_2$, the bands could be assigned to the surface O-H stretching (3800–3500 cm$^{-1}$), N$_2$O$_4$(a) (1735 cm$^{-1}$), bridging nitrate species (1684 and 1652 cm$^{-1}$), bidentate nitrate (1559 cm$^{-1}$), monodentate nitrate (1539 cm$^{-1}$) and nitrite species (1457 cm$^{-1}$) were observed. Band intensity increased gradually with time. And it was noted that new bands at 1684 cm$^{-1}$ assigned to the ammonium ions bonded to Bronsted acid sites (Tuo et al., 1986; Pan et al., 2013) was clearly observed and intensified with addition of NO and O$_2$. DRFITS
spectra of ammonia adsorption in Fig. 1 and Fig. 4 have demonstrated that the majority of coordinated ammonia consumed rapidly by NO\textsubscript{x} ad-species, so that the bands due to ammonia adsorption were barely observed. Thus, the water was detected which could be confirm by the surface O-H stretching (3800–3500 cm\textsuperscript{-1}). However, a small portion of adsorbed NH\textsubscript{3} species reacted with water and generated NH\textsubscript{4}\textsuperscript{+} species on Brønsted acid sites. Reversible reaction can be described by the following equation:

\[
\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^- (1)
\]

Because the intensity of the band due to NH\textsubscript{4}\textsuperscript{+} species (1684 cm\textsuperscript{-1}) grow larger gradually, and the reaction is reversible and slow, it turned out that NH\textsubscript{4}\textsuperscript{+} species was still increase in about 30 min.

**SCR Steady-State Response Experiments on MnO\textsubscript{x}/MWCNTs Catalysts**

The formation of surface species on MnO\textsubscript{x}/MWCNTs catalysts under an atmosphere of NH\textsubscript{3}, NO and O\textsubscript{2} mixture is also investigated by DRIFTS. The results were presented in Fig. 5. After all the reaction gases were supplied, the bands due to N\textsubscript{2}O (2241 and 2203 cm\textsuperscript{-1}), nitrosyl NO\textsuperscript{−} (1911 and 1847 cm\textsuperscript{-1}) (Zhou et al., 2011), bridging nitrate (1627 cm\textsuperscript{-1}) (Zhao et al., 2009), bidentate nitrate (1559 cm\textsuperscript{-1}), monodentate nitrate (1539 cm\textsuperscript{-1}), coordinate ammonia species on Lewis acid site (1597 and 1263 cm\textsuperscript{-1}) (Zhao et al., 2009) and the gaseous or weakly adsorbed NH\textsubscript{3} (966 and 928 cm\textsuperscript{-1}) were detected. The bands due to bridging nitrate, coordinate ammonia species on Lewis acid site and the gaseous or weakly adsorbed NH\textsubscript{3} increased obviously with time. However, the bands that could be assigned to bidentate and monodentate nitrates increased only slightly. Considering the sharp peaks of bidentate and monodentate nitrates species in the NO and O\textsubscript{2} co-adsorption experiment, it indicated that these species were favoured in SCR reaction for the catalysts at low-temperature. The bands due to N\textsubscript{2}O\textsubscript{4} (1697–1754 cm\textsuperscript{-1}) and nitrosyls (1508 cm\textsuperscript{-1}) were barely observed in this experiment. Considering that the N\textsubscript{2}O\textsubscript{4} and nitrosyls species could react with NH\textsubscript{3} ad-species in the NH\textsubscript{3} transient reaction experiment (Fig. 3), it could be suggested that the N\textsubscript{2}O\textsubscript{4} and nitrosyls species were also important intermediate during the formation of NO\textsubscript{x} ad-species. Moreover, the band at 1684 cm\textsuperscript{-1} attributed to the ammonium ions bonded to Bronsted acid sites was hardly detected in SCR steady-state response experiments, and considering NH\textsubscript{4}\textsuperscript{+} species on Bronsted acid sites observed in the NH\textsubscript{3} adsorption experiment (Fig. 1), it indicated that the NH\textsubscript{4}\textsuperscript{+} participated in the reaction and NH\textsubscript{4}\textsuperscript{+} species was important intermediate in the SCR reaction cycle at 210°C.

** Shut-off Experiments **

**NO + O\textsubscript{2} Shut-Off after SCR Reaction on MnO\textsubscript{x}/MWCNTs**

Fig. 6 shows the variation of the DRIFTS spectra when the supply of NO and O\textsubscript{2} stopped after SCR reaction with MnO\textsubscript{x}/MWCNTs catalysts at 210°C for various times. It was shown that intensity of the bands due to N-H stretching vibrations modes of NH\textsubscript{3}, the coordinate ammonia species on Lewis acid sites (1597 and 1263 cm\textsuperscript{-1}), and the gaseous or weakly adsorbed NH\textsubscript{3} became stronger with time. However, because the intensity of the bands (928 and 966 cm\textsuperscript{-1}) due to the gaseous or weakly adsorbed NH\textsubscript{3} grew with time very clearly, suggesting that these species might not react with NO\textsubscript{x} ad-species directly. In addition, it is worth noting that the very weak band (1684 cm\textsuperscript{-1}) attributed to Bronsted acid sites could be detected after 25 min. However, due to stopping the supply of NO and O\textsubscript{2} and introducing NH\textsubscript{3} into the DRIFTS cell continuously, it is also observed in Fig. 6 that the band due to bridging nitrate (1627 cm\textsuperscript{-1}) decreased remarkably with time, and the bands due to nitrosyl NO\textsuperscript{−} (1911 and 1847 cm\textsuperscript{-1}), bidentate nitrate (1559 cm\textsuperscript{-1}),
Fig. 5. In situ DRIFTS spectra of adsorbed species in the SCR reaction for various times; Reaction conditions: 1000 ppm NO, 1000 ppm NH₃, 5% O₂, Ar balance, 210°C.

Fig. 6. In situ DRIFTS spectra of MnOₓ/MWCNTs in a flow of 1000 ppm NH₃, 1000 ppm NO, 5% O₂ then removed NO and O₂ at 210°C for various times.

and monodentate nitrate (1539 cm⁻¹) decreased slightly. Moreover, the bands due to Brønsted acid sites can be detected after 25 min, but its intensity was very weak because of the compensation from the gaseous or weakly adsorbed NH₃. Before 25 min, the band attributed to Brønsted acid sites was hardly detected and the bands due to NOₓ ad-species decreased simultaneously. It indicated that the NH₄⁺ bond to Brønsted acid sites could have reacted with bridging nitrate, nitrosyl NO− and other NOₓ ad-species directly. Accordingly, NH₄⁺ species might be important intermediate in the SCR reaction, which was in agreement with conclusion of steady-state response experiments.

NH₃ Shut-Off after SCR Reaction on MnOₓ/MWCNTs

The catalysts were first purged with mixture of NO, O₂ and NH₃ for 30 min at 210°C. Fig. 7 shows the evolution of species on the MnOₓ/MWCNTs surface, when NH₃ was switched off from the NH₃, NO and O₂ mixture. The intensity of the bands could be assigned to NOₓ ad-species, including nitrosyls (1911 and 1847 cm⁻¹), bridging nitrate (1627 cm⁻¹), bidentate nitrate (1559 cm⁻¹), and monodentate nitrate (1539 cm⁻¹). These bands did not vary apparently with the time when ammonia in the feed gases was turned off. In the case of ammonia ad-species, the bands of gaseous or weakly adsorbed NH₃ (966 and 928 cm⁻¹) decreased remarkably once without ammonia. By contrast, the intensity of the bands that could be assigned to coordinate ammonia species on Lewis acid sites (1597 and 1263 cm⁻¹) did not vary firstly, and started to decrease after the gaseous or weakly adsorbed NH₃ disappeared, suggesting the translation of
gaseous or weakly adsorbed NH₃ into coordinate ammonia species on Lewis acid sites. Therefore, the bands intensities due to coordinate ammonia species on Lewis acid sites varied slightly, because of the compensation from the gaseous or weakly adsorbed NH₃. The decrease of intensities of coordinate ammonia species bands with time were observed when the gaseous or weakly adsorbed NH₃ vanished. Considering the increase of gaseous or weakly adsorbed NH₃ in section 3.4.1, it indicated that gaseous or weakly adsorbed NH₃ might not or slightly react with the NOₓ ad-species directly. In addition, the band due to NH₄⁺ species on Brønsted acid sites was disappeared after the gaseous or weakly adsorbed NH₃ vanished, it suggesting that NH₄⁺ species on the surface of catalysts were consumed rapidly by NOₓ ad-species and they were very active in SCR reaction. After adsorbing on the surface of MnOₓ/MWCNTs catalysts, the gaseous or weakly adsorbed NH₃ would translate to NH₄⁺ species on Brønsted acid sites and coordinate ammonia species on Lewis acid site then participate into the SCR reaction. Moreover, NH₄⁺ species on Brønsted acid sites was important intermediates and they significantly contributed to the SCR reaction on MnOₓ/MWCNTs catalysts.

When NO and O₂ mixture was injected to the pre-adsorbed ammonia catalysts, adsorbed ammonia species were consumed rapidly, and H₂O, N₂O₄ (a), bridging nitrate, bidentate nitrate, monodentate nitrate, and nitrite were produced. Fig. 1 and Fig. 2 have indicated that the adsorption of NO and O₂ on the MnOₓ/MWCNTs catalysts was more quickly and remarkable compared to the adsorption of ammonia. The NOₓ ad-species, including bridging nitrate species, bidentate nitrate, and nitrite species, N₂O, N₂O₄ (a), began to grow once NO and O₂ mixture was injected to the MnOₓ/MWCNTs catalysts. Most of the NOₓ ad-species were consumed in the SCR reaction with ammonia. It was different from the results obtained by Kijlstra et al. (1997a, b). In their report, the formation of bidentate nitrates would block the catalytic sites on the surface of the MnOₓ/Al₂O₃ catalysts below 500 K. It further suggested that the activity of bidentate nitrates was improved with MnOₓ/MWCNTs as catalysts in this study. It was worth noting that N₂O₄ (a) and nitrite species were not detected in the SCR steady-state response process (section 3.3). However, these species were observed in other experiments in this study. The disappearance of N₂O₄ (a) and nitrite species might be attributed to the lower generation rates of these species compared to their consumption. Nevertheless, evidence of small amount of N₂O₄ (a) species in the adsorption experiments in section 3.1.2 suggested that the N₂O₄ (a) species did not react with other species and their reaction activity might be damped. For the nitrite species, the result is in good agreement with a previous literature (Liu et al.,
2012) in which nitrite (NO$_2^-$) species were easy to bond with adsorbed NH$_3$ species to form NH$_4$NO$_2$, these species acted as active intermediates in SCR process and were easy to decompose to N$_2$ and H$_2$O. From these results, it is believed that nitrite species are quite active in SCR reaction over MnO$_x$/MWCNTs catalysts. In order to improve the activity of the MnO$_x$/MWCNTs catalysts, and it is important to increase the ability of the forming nitrite species during adsorption of NO and O$_2$ over the catalysts. In conclusion, nitrite species, bidentate and monodentate are the principal NO species which participated in the SCR reaction over MnO$_x$/MWCNTs catalysts.

The mechanism of NH$_3$-SCR of NO over various Mn-based catalysts has been discussed in many literatures (Kijlstra et al., 1997b; Wu et al., 2007; Liu et al., 2012; Zhang et al., 2013b) in which NH$_4^+$ species was reported to react with the active nitrites to produce the unstable ammonium nitrite for a further N$_2$ generation. Kijlstra et al. (1997b) reported the mechanism for NH$_3$-SCR of NO over MnO$_x$/Al$_2$O$_3$ catalysts, proposing both E-R (Eley-Rideal) and L-H (Langmuir-Hinshelwood) mechanisms for this reaction. However, in the case of Mn-based catalysts with carbon materials as catalyst supports, there are rare studies on SCR reaction mechanism with DRIFTS. The main conclusions were drawn as follows:

The ammonia ad-species were probably formed according to the reactions:

\[
\text{NH}_3(a) + \text{O}_2(g) \rightarrow \text{NO}_2(a)/\text{NO}_2^-/\text{NO}_3^- \quad (7)
\]

\[
2\text{NO}_2(a) \rightarrow \text{N}_2\text{O}_4(a) \quad (8)
\]

The reaction between ammonia ad-species and NO$_2$ ad-species are:

\[
\text{NH}_4(a) + \text{NO}_2^- \rightarrow \text{NH}_2\text{NO}_2(a) \rightarrow \text{N}_2(a) + \text{H}_2\text{O} + \text{O}(a) \quad (9)
\]

\[
\text{NH}_4(a) + \text{NO}_3^- \rightarrow \text{NH}_2\text{NO}_3(a) \rightarrow \text{N}_2(a) + \text{H}_2\text{O} + 2\text{O}(a) \quad (10)
\]

\[
2\text{NH}_2(a) + \text{N}_2\text{O}_4(a) \rightarrow 2\text{NH}_2\text{NO}_2(a) \rightarrow \text{N}_2(a) + \text{H}_2\text{O} + \text{O}(a) \quad (11)
\]

The other pathway happened between NH$_4^+$ and NO ad-species. NH$_4^+$ could react with NO ad-species to form NH$_4$NO$_2$, NH$_4$NO$_3$O$_4$ or NH$_4$NO$_3$, and these species were unstable and were further converted to N$_2$ and H$_2$O.

\[
\text{NH}_4(a) + \text{H}^+ \rightarrow \text{NH}_4^+(a) \quad (12)
\]

\[
\text{NH}_4^+(a) + \text{N}_2\text{O}_4(a) \rightarrow \text{NH}_4\text{N}_2\text{O}_4(a) \rightarrow \text{N}_2(a) + \text{H}_2\text{O} + \text{O}(a) \quad (13)
\]

\[
\text{NH}_4^+(a) + \text{NO}_2^- \rightarrow \text{NH}_4\text{NO}_2(a) \rightarrow \text{N}_2(a) + \text{H}_2\text{O} \quad (14)
\]

\[
\text{NH}_4^+(a) + \text{NO}_3^- \rightarrow \text{NH}_4\text{NO}_3(a) \rightarrow \text{N}_2(a) + \text{H}_2\text{O} + \text{O}(a) \quad (15)
\]

The mechanism of the SCR reaction had been studied extensively elsewhere and different hypotheses had been proposed (Li et al., 2011; Zhou et al., 2011; Fu et al., 2014; Yu et al., 2014). Fig. 8 showed that the reaction pathways existed in the NH$_3$-SCR process over the catalysts. However, in this study there are two reaction pathway existing in the NH$_3$-SCR process over the MnO$_x$/MWCNTs catalysts at 210°C.

**CONCLUSIONS**

In this paper, low-temperature NH$_3$-SCR process over the MnO$_x$/MWCNTs catalysts was investigated by \textit{in situ} DRIFTS. The main conclusions were drawn as follows:

Ammonia adsorption species were ammonium ions, coordinated ammonia and weakly adsorbed NH$_3$ on the surface of MnO$_x$/MWCNTs catalysts at 210°C. The gaseous and weakly adsorbed NH$_3$ will translate to NH$_4^+$ species and coordinate ammonia then participate into the SCR reaction. NH$_4^+$ species as one of intermediates in the SCR reaction was more active than coordinate ammonia species on the surface of the catalysts at 210°C. In terms of NO$_2$ ad-species, most of them would react with NH$_3$ ad-species, including N$_2$O$_4$(a), bridging nitrate, bidentate nitrate, monodentate nitrate, and nitrite. And nitrite species, bidentate and monodentate nitrates contributed to the SCR reaction over the catalysts mostly.
Two possible reaction pathways were proposed by the in situ DRIFTS results. One was that NO$_x$ ad-species could react with NH$_4^+$ species and the formed NH$_4$N$_2$O$_4$ (a), NH$_4$NO$_2$ (a), NH$_4$NO$_3$ (a). Also, they are unstable and producing N$_2$ and H$_2$O as the final products. The other way was that NH$_3$ was adsorbed and formed NH$_2$, then reacted with N$_2$O$_4$ (a), NO$_2^-$, NO$_3^-$. The possible intermediates of NH$_2$NO$_2$ and NH$_2$NO$_3$ were unstable and would decompose into N$_2$ and H$_2$O.

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