Insights into Reaction Conditions for Selective Catalytic Reduction of NO\textsubscript{x} with a MnAl Oxide Catalyst at Low Temperatures

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ABSTRACT

MnO\textsubscript{x} catalysts have been proven to have superior activity at low temperatures (LT) for selective catalytic reduction (SCR) of NO\textsubscript{x}. In this study, spherical mesoporous MnAl\textsubscript{x} catalysts with different molar ratios were prepared using a simple precipitation method. In addition, their NO\textsubscript{x} catalytic performance, along with relevant main factors (reaction temperature, molar ratio, particle size, space velocity, and O\textsubscript{2} content), was investigated in a simulated fixed bed reactor. The relationship between the main factors and DeNO\textsubscript{x} efficiency was evaluated by analyzing two parameters: the NO\textsubscript{x} conversion rate and N\textsubscript{2} selectivity. The results showed that the MnAl\textsubscript{x} catalyst had the optimal low temperature DeNO\textsubscript{x} performance and had a relatively stable NO\textsubscript{x} conversion rate of more than 92\% in a space velocity range of 14331 h\textsuperscript{-1} to 23885 h\textsuperscript{-1}, whereas smaller catalyst particle size led to higher NO\textsubscript{x} conversion rate and N\textsubscript{2} selectivity as high as 100\%. In addition, the appropriate oxygen concentration was found to increase NO\textsubscript{x} conversion and N\textsubscript{2} selectivity. This work would be beneficial to further optimization of LT SCR catalyst systems for practical applications.

Keywords: NO\textsubscript{x}, SCR, Low temperature, MnAl oxide, Spherical mesoporous

1 INTRODUCTION

Nitrogen oxides (NO\textsubscript{x}) as air pollutants are primarily emitted from coal-fired power plants and automobiles and are regarded as the major source of many environmental and health problems, including photochemical smog, acid rain, greenhouse gases, and PM\textsubscript{2.5} (Paolucci et al., 2017; Han et al., 2019). In response to environmental protection requirements, stricter emission standards have been adopted by governments around the world to control NO\textsubscript{x} emissions. Alternative post-combustion NO\textsubscript{x} reduction techniques, including selective catalytic reduction and selective non-catalytic reduction (SNCR), have been used for NO\textsubscript{x} elimination. Among them, the SCR process using NH\textsubscript{3} as the reductant is the most widely applied in post-NO\textsubscript{x} abatement and has been shown to have high NO\textsubscript{x} removal efficiency (Forzatti et al., 2009; Imanaka and Masui, 2012). Although commercial vanadium (V)-based oxide catalysts have been widely studied and used, the main drawbacks (narrow temperature window and the toxicity of V components) limit their usage (Brandenberger et al., 2008; Kang et al., 2018). Also, V-based catalysts are not suitable for glass, cement, and steel plants due to the low-temperature flue gas (< 250°C). Recently, a great deal of effort has been made to explore LT V-free SCR high efficient catalysts.

MnO\textsubscript{x} catalysts exhibit excellent activity at low temperature owing to their excellent redox properties and variable valence states. However, poor SO\textsubscript{2} tolerance and low N\textsubscript{2} selectivity relatively restrict their practical applications. Mixing or doping MnO\textsubscript{x} with other metal oxides to obtain polymetal composites with various excellent properties is an effective method to overcome these shortcomings. A great deal of effort has been devoted to constructing bimetallic Mn-based
catalysts, including MnCe, MnCo, MnFe, MnNb, and MnNi, due to the synergistic effects resulting from their complementary advantages (Liu et al., 2013; Lei et al., 2014; Lian et al., 2014; Wan et al., 2014; Fan et al., 2017). Catalysts with high catalytic performance have also been obtained by adjusting the morphology and pore structure of the catalysts and promoting the dispersion of active components. Al2O3 is widely used in SCR catalysts because of its high thermal stability, moderate acidity, and high specific surface area, which can prevent the catalyst from sintering and improve the adsorption of NOx (Wang and Lin 1998; Liu et al., 2016). Zhao et al. (2014) found that Al2O3 modified CeO2/TiO2 can improve the acidity of the catalyst, thereby reducing SO2 adsorption. Mejía-Centeno et al. (2015) reported that Al2O3 doped TANs enhances activity at high temperatures due to the Lewis acidity and the multilaw morphology of the TNTs.

Since Mn-based bimetal oxide catalysts are more active and selective than other alternatives, Al2O3-supported Mn-based oxide catalysts have been intensively reported. Singoredo et al. (1992) first prepared MnOx/Al2O3 as SCR catalysts, and the results showed that Mn induced better dispersion on an Al2O3 support, resulting in higher catalyst activity. Kapteijn et al. (1994) studied the surface acidity of an MnOx-Al2O3 catalyst and the adsorption capacity of NOx and NH3 on a surface. Cao et al. (2014, 2015) found that the high surface area of Al2O3 was the key to increasing the number of active catalytic sites by modifying MnOx-Al2O3 with well-dispersed Fe, Ag, and Zr. The appropriate introduction of Al2O3 into MnO can reduce the thermal stability of the adsorbed SO2 species and facilitate the decomposition of NH4HSO4 (Fan et al., 2020). Kijlstra et al. (1997) proposed that the Lewis acid center is Mn+ dispersed on the surface of MnOx/Al2O3, where NO or an activated nitrite intermediate adsorbed on the surface reacts with NH2− on these acid centers, namely, two types of mechanisms (E-R and L-H) work together.

Previous reports have shown that Mn-based catalysts have high NOx conversion rates, but the working conditions of catalysts are complex and changeable, which creates more requirements for these catalysts in practical application. Thus, in this study, we prepared a novel spherical mesoporous MnAlx catalyst and aimed to explore the effects of various technological conditions on the NOx conversion performance of the catalysts. MnAlx oxide catalysts with different molar ratios were prepared using a simple precipitation method, and their NOx catalytic performance was investigated in the simulated fixed bed reactor, along with relevant main factors (reaction temperature, molar ratios, particle sizes, space velocity, and O2 content). The relationship between the main factors and DeNOx efficiency was evaluated by analyzing the NOx conversion rate and N2 selectivity. This work should be beneficial to the further optimization of LT SCR catalyst systems developed for practical applications.

2 EXPERIMENTAL PROCEDURE

2.1 Preparation of Catalysts

The MnAlx mixed oxides were synthesized using a simple precipitation method. A specific amount of Mn(NO3)2 and Al(NO3)3·9H2O at a total mole amount of 5 mmol was dissolved in 30 mL deionized water under magnetic stirring. After that, an aqueous (NH4)2CO3 solution containing solute of over-stoichiometric ratio to the above metal ions were added dropwise and stirred for 4 h. The obtained flocculent precipitate was subsequently washed with water and ethanol three times and dried at 120°C overnight, calcined in a tube furnace at 300°C for 1 h, and then heated to 500°C for 6 h to obtain MnAlx oxides (x = 0.1, 0.3, 0.5, 0.7 and 0.9, where x is the mole ratio of Al/(Mn + Al)).

2.2 Catalyst Characterization

X-ray diffraction (XRD) was carried out with a BRUKER-AXS D8 Advanced X-ray Diffractometer with Cu Ka radiation at a scanning angle (2θ) ranging from 10°–90° and a scan rate of 8° min⁻¹. Scanning electron microscopy (SEM) and corresponding energy dispersive spectroscopy (EDS) mapping analyses were carried out using a JEOL SU8200 microscope at an acceleration voltage of 200 kV. The surface properties (BET specific surface area and pore size) of the samples were measured with a Micromeritics ASAP 2020 surface area analyzer. Temperature-programmed reduction (H2-TPR) tests were performed on a gas chromatograph (SP-6800, Shandong Lunan Ruihong, China) with a thermal conductivity detector (TCD) under a 5% H2/N2 gas flow (50 mL min⁻¹).
at a rate of 10°C min⁻¹ up to 800°C. Temperature-programmed desorption of NH₃ (NH₃-TPD) was carried out using the same instrument as that used for the H₂-TPR. 100 mg of the sample saturated with adsorbed NH₃ was monitored at temperatures ranging from 20–700°C in a He flow.

2.3 Activity Measurement

The catalytic activity measurement was performed in a fixed-bed quartz tube reactor with an internal diameter of 8 mm. The catalyst was placed in the reactor and pretreated at 200°C for 1 h in an N₂ atmosphere. The feed gas mixture contained NO, NH₃, and O₂, with He as the balance. When the reaction reached a stable state at each temperature, the concentrations of NO and NO₂ were continually monitored with the TH-990S NO and NO₂ analyzers, and N₂O in the outlet gas was detected with a Antaris™ IGS Gas Analyzer from Thermo Fisher Scientific Inc. The N₂ concentration was analyzed using a thermal conductivity detection method. The NO₃ conversion rate and N₂ selectivity were calculated as follows:

\[
\text{NO₃ conversion (\%)} = \left(1 - \frac{\text{[NO₃]_{out}}}{\text{[NO₃]_{in}}} \right) \times 100%,
\]

(1)

\[
\text{N₂ selectivity (\%)} = \left(1 - \frac{2\text{[N₂O]_{out}}}{\text{[NO₂]_{in}} + \text{[NH₃]_{in}} - \text{[NO₃]_{out}} - \text{[NH₃]_{out}}} \right) \times 100%
\]

(2)

where the subscripts “in” and “out” refer to the inlet concentration and outlet concentration at steady state, respectively.

3 RESULTS AND DISCUSSION

3.1 XRD

In order to obtain the crystal structure information for the MnAlₓ catalysts, XRD measurements were carried out, for which the results are shown in Fig. 1. It can be observed that the MnAl₀.₁ oxide mainly exhibited the characteristic peaks of Mn₂O₃ (JCPDS PDF: 73-1826). The main diffraction peak located at 32.9° was ascribed to the reflection of (222) plane in Mn₂O₃. Furthermore, the reflection peaks at 23.1°, 55.1°, and 65.8°, corresponded to the (211), (440) and (662) planes of the Mn₂O₃ phase, respectively. The characteristic Bragg reflections at 18.1°, 21.6°, 28.7°, 36.9°, 47.8°, 49.1° and some weak peaks ascribed to the Mn₃O₈ planes (JCPDS PDF: 39-1218) were also detected on the MnAl₀.₁. The intensity of the Bragg reflections decreased with increases in the

![Fig. 1. XRD patterns of MnAl₀.₁, MnAl₀.₃, MnAl₀.₅, MnAl₀.₇, and MnAl₀.₉.](image-url)
Al doping amount, which could be obviously observed in the MnAl$_{0.5}$ sample. In addition, when the Al doping amount reached 0.7, the peak generated at 36.9° attributed to Mn$_5$O$_8$ became the main diffraction peak. These results showed that the amount of Al doping adjusted the crystal growth due to the synergistic interaction between Mn oxide and Al oxide. It should also be noted that no clear Al$_2$O$_3$ crystalline peaks appeared in the XRD patterns of these catalysts even with Al doping amounts as high as 0.9, indicating that the doped Al oxide may have selectively interacted with the MnO$_x$ in the mixed oxides, where the amorphous Al$_2$O$_3$ acted as a carrier to stabilize and disperse the Mn active sites (Li et al., 2016).

### 3.2 SEM Analysis
The microstructure of the representative catalyst was further evaluated using SEM. Fig. 2 shows the morphologies of the MnAl$_{0.1}$. The SEM images (Figs. 2(a–c)) revealed that the MnAl$_{0.1}$ oxide exhibited a regular, spherical morphology. The diameters of the spherical particles in the MnAl$_{0.1}$ sample were ca. 500–1000 nm. As can be seen in EDS elemental mapping images (Fig. 2(d)) of single spherical particle, the spherical particles were mainly composed of Mn and O species. The Al elements were highly dispersed in the MnAl$_{0.1}$ at the same locations, demonstrating that the Al species were incorporated into the MnO$_x$, corresponding with the results of the XRD patterns. In addition, the highly amorphous Al species also distributed homogeneously around the microparticle, which confirmed that Al$_2$O$_3$ can act as a carrier to stabilize the Mn active sites.

### 3.3 Pore Structure and Surface Area
The N$_2$ adsorption-desorption isotherms of the MnAl$_{0.1}$, MnAl$_{0.3}$, and MnAl$_{0.5}$ catalysts are plotted in Fig. 3. Table 1 summarizes the corresponding results for the textural properties. As shown in Fig. 3(a), the isotherms of the catalysts were displayed as type IV isotherms with H2-type hysteresis loops based on the IUPAC classification, indicating the existence of a mesoporous structure (Arandiyan et al., 2013; Aziz et al., 2014). This was confirmed by the pore size distribution centered at 4–10 nm shown in Fig. 3(b). There was an interesting phenomenon where MnAl$_{0.1}$ exhibited a specific surface area similar to that of MnAl$_{0.5}$. However, their pore volumes obviously increased from 0.292 cm$^3$ g$^{-1}$ (MnAl$_{0.1}$) to 0.549 cm$^3$ g$^{-1}$ (MnAl$_{0.5}$), and the corresponding pore diameter decreased from 6.5 nm to 3.8 nm. This demonstrated that the increase in Al doping may have the contribution to generating a greater number of small-diameter mesopores in the catalysts.

![Fig. 2. (a–c) SEM images and (d) EDS mapping images of MnAl$_{0.1}$.](https://example.com/fig2)
Fig. 3. (a) N₂ adsorption–desorption isotherm, (b) Pore size distribution of the MnAl₀.₁, MnAl₀.₃ and MnAl₀.₅ catalysts.

Table 1. Parameters of the porous structure of the catalysts.

<table>
<thead>
<tr>
<th>Samples</th>
<th>( S_{\text{BET}} ) (m² g⁻¹)ᵃ</th>
<th>( V_\text{p} ) (cm³ g⁻¹)ᵇ</th>
<th>( D_\text{p} ) (nm)ᶜ</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnAl₀.₁</td>
<td>124.5</td>
<td>0.292</td>
<td>6.5</td>
</tr>
<tr>
<td>MnAl₀.₃</td>
<td>126.1</td>
<td>0.431</td>
<td>5.6</td>
</tr>
<tr>
<td>MnAl₀.₅</td>
<td>125.4</td>
<td>0.549</td>
<td>3.8</td>
</tr>
</tbody>
</table>

ᵃ BET specific surface area.ᵇ Total pore volume.ᶜ Average pore diameter.

In general, for gas-solid heterogeneous catalysis, a high surface area and developed pore structure can facilitate easy access of a reactant gas to the active sites and the diffusion of products from the catalyst (Yu et al., 2006), which is favorable for catalytic activity. Summarizing the analyses discussed above, the as-prepared MnAl composite oxide showed a regular micro-sphere morphology with a mesoporous structure.

3.4 \( \text{H}_2 \)-TPR

Reducibility is an important factor by which to evaluate the activity of SCR catalysts. To better understand the effect of Al elements on catalytic activity, \( \text{H}_2 \)-TPR of the prepared MnAlₓ catalysts with different molar ratios was carried out. As can be seen in Fig. 4, MnAl₀.₁ exhibited two successive reduction peaks at 320°C and 450°C, which were believed to be associated with the two-step reductions of Mn⁴⁺ via Mn³⁺ to Mn²⁺, concurring with previous literature suggesting that the reduction of MnO₂ and/or Mn₂O₃ occur via a well-defined two-step reduction profile (Trawczyński et al., 2005; Wan et al., 2014). It can be seen that the reduction peaks obviously shifted to lower temperature region with an increase in Al from 0.1 to 0.3. Meanwhile, the intensities of the two-step reduction peak gradually increased, which could be observed on the MnAl₀.₅, indicating an improvement in the redox ability. This promoted reducible nature of MnAlₓ was attributed to the interaction between manganese species and carriers brought about by the doping of Al cations. It should be noted that the reduction peaks shifted to a higher temperature, and the corresponding peak intensity continually decreased when the Al doping content exceeded 0.7. Specifically, MnAl₀.₉ exhibited a very weak peak at about 470°C. This result indicates that Al species are not active substances, where the introduction of excessive Al inhibits the synergistic interaction between manganese species and Al species, thereby weakening the reducibility.

3.5 \( \text{NH}_3 \)-TPD

It is known that the surface acidity of a catalyst is an important index of the SCR activity because it is responsible for the adsorption and activation of \( \text{NH}_3 \) (Ali et al., 2018; Wu et al., 2021). \( \text{NH}_3 \)-TPD was carried out to explore the surface acid properties of the prepared catalysts. As shown in Fig. 5,
two distinct desorption processes were exhibited in the NH$_3$ desorption profiles. The peaks at low temperatures (100–200°C) originated from weak acid sites, and the peaks at higher temperatures (>500°C) were due to strong acid sites (Fan et al., 2017). It is widely believed that the thermal stability of NH$_3$ adsorbed at Brønsted acid sites is lower than that of the NH$_3$ molecules coordinated on Lewis acid sites (Kang et al., 2019). Thus, the peaks at temperatures above 300°C were attributed to desorption of NH$_3$ coordinated at the Lewis acid sites, and the peaks at low temperatures were attributed to desorption of the NH$_4^+$ ion from the Brønsted acid sites. All of the MnAl$_x$ micro-spheres showed that the intensity of the NH$_3$ desorption peak centered at low temperatures were much stronger than those at high temperature, indicating that Brønsted acid could be the main acid species. The Brønsted acid sites of the catalysts increased to various degrees, and the Lewis acid sites increased first and then decreased with increases in the Al doping amount. This result confirmed that Al plays a positive role in regulating acidic sites on the mixed oxide.

3.6 The Effect of Reaction Temperature

The catalytic activity of Mn-Al$_{0.3}$ at different temperatures was tested. As shown in Fig. 6(a), the catalytic activity curve changed slightly over time. To obtain accurate experimental data for
the stable catalyst, the activity experiment was carried out for 180 min at each corresponding reaction temperature. As shown in Fig.6(b), the DeNO\textsubscript{x} activity increased with increases in the temperature. When the bed reaction temperatures were 80°C, 100°C, 120°C, and 150°C, the corresponding NO\textsubscript{x} conversion rates were 78.1%, 89.2%, 98.2% and 99.5%, respectively. However, the N\textsubscript{2} selectivity showed a trend toward a sudden change, for which the values were 58.1%, 69.5%, 85.9% and 56.8%, respectively, with increasing temperatures. The selective catalytic reduction efficiency of this catalyst was the highest at 120°C. Although the NO\textsubscript{x} conversion rate was as high as 99.5% at 150°C, the N\textsubscript{2} selectivity decreased to 56.8%, which was due to the fact that the oxidation reaction of NH\textsubscript{3} was promoted with increases in the reaction temperature, causing the DeNO\textsubscript{x} efficiency to decrease. Madia et al. (2002) suggested that at low temperatures, N\textsubscript{2}O formation is probably derived from nitroamine or ammonium nitrate intermediate species. They showed that the thermal decomposition of the generated ammonium nitrate may form either N\textsubscript{2}O + 2H\textsubscript{2}O or HNO\textsubscript{3} + NH\textsubscript{3} at fast heating rates, and the absence of H\textsubscript{2}O could favor the formation of N\textsubscript{2}O. Also, Tang et al. (2010) reported that NH\textsubscript{3} can be changed into adsorbed N species on β-MnO\textsubscript{2}, which reacted with gaseous NO to form N\textsubscript{2}O. It can be seen that the MnAl\textsubscript{0.3} catalyst had good LT catalytic activity, but the N\textsubscript{2} selectivity requires improvement.

### 3.7 The Effect of Mole Ratios

In order to determine the effects of the Al doping amount on the LT activity, the catalytic activity of the MnAl\textsubscript{x} catalysts at different molar ratios was investigated at 80°C, as shown in Fig. 7(a). Fig. 7(b) shows that increases in the Al doping amounts cause the catalytic activity to develop a wave-like trend, where the NO\textsubscript{x} conversion rates were 97.4%, 72.3%, 78.1%, 79.5% and 50.9% for MnAl\textsubscript{0.1}, MnAl\textsubscript{0.3}, MnAl\textsubscript{0.5}, MnAl\textsubscript{0.7}, and MnAl\textsubscript{0.9}, respectively, and where the selectivity of N\textsubscript{2} was 64.2%, 58.1%, 57.9%, 72%, and 47.7%, respectively. Interestingly, the N\textsubscript{2} selectivity also exhibited variations similar to those in the NO\textsubscript{x} conversion rate. This may have been due to the fact that although Al oxides with moderate acidity increase the number of acid sites in a catalyst, where more Mn active sites can disperse easily on Al oxides, the Al oxides were the non-catalytic active species, thereby leading to a decrease in catalytic activity. It should be noted that MnAl\textsubscript{0.1} showed the highest NO\textsubscript{x} conversion rate among these catalysts. Combined with the previous H\textsubscript{2}-TPR and NH\textsubscript{3}-TPD results, an increase in the Al doping led to the redox performance and acidity first increasing and then decreasing. These results indicated that the active sites played a decisive role in the low-temperature SCR reaction for the obtained catalysts, and the other properties played a certain regulatory role.

### 3.8 The Effect of Space Velocity

In practical applications, space velocity is the ratio of the volumetric flue gas flow to the reference volume of catalysts (He et al., 2015), which is an important factor for NO\textsubscript{x} removal.
Fig. 7. The catalytic activity of the MnAl\textsubscript{x} catalysts at different molar ratios. Reaction conditions: $C_{NO} = 1000$ ppm, $SV = 17914$ h\textsuperscript{-1}, $T = 80^\circ C$, $O_2 = 8\%$.

Fig. 8 displays the DeNO\textsubscript{x} performance of the MnAl\textsubscript{0.1} catalyst at different space velocities. Reaction conditions: $C_{NO} = 1000$ ppm, $T = 80^\circ C$, $O_2 = 8\%$.

Fig. 8. Catalytic activity of MnAl\textsubscript{0.1} under different space velocities. Reaction conditions: $C_{NO} = 1000$ ppm, $T = 80^\circ C$, $O_2 = 8\%$.

3.9 The Effect of Particle Size

The size of the catalyst particles affects the catalytic performance, so the catalyst was sieved into particles of different sizes to study its denitrification performance. Fig. 9(a) shows the NO\textsubscript{x} conversion curve as a function of time. As the catalyst particles became smaller, the NO\textsubscript{x} removal rate increased. When the catalyst particles were 20–40 mesh, 40–60 mesh, and 60–100 mesh,
the corresponding removal efficiencies were 56.7%, 71.2%, 86.4%, respectively, and the N₂ selectivities were 43.5%, 93.1%, and 100%, respectively. In the case of a gas-solid heterogeneous reaction, after the catalyst particles are reduced to a certain degree, due to an increase in residence time and exposure to more reaction sites, the reaction gas can be more efficiently adsorbed onto the surface active sites of the catalyst, resulting in more NOₓ being fully reduced by NH₃ instead of directly escaping or generating by-products from an incomplete reaction. As shown in Fig. 9, a smaller the catalyst particle size led to a higher NOₓ conversion rate and higher N₂ selectivity. In turn, in practical applications, a catalyst with a small particle size will increase the gas flow resistance and easily cause blockage of the gas path, thereby affecting the continuous, effective progress of subsequent reactions.

3.10 The Effect of O₂ Concentration

Fig. 10 shows the relationship between the O₂ content and the catalytic activity of the MnAl₀.₁ catalyst. It can be seen that the MnAl₀.₁ catalyst exhibited poor catalytic activity with a NOₓ conversion rate of 26.0% in the absence of O₂. The NOₓ conversion rate changed significantly in the presence of 4% O₂, and when the O₂ concentration was further increased to 8%, the conversion
rate increased slightly to 87.6%. With the further increase in the O\textsubscript{2} content, the catalytic activity remained basically unchanged. In the absence of O\textsubscript{2}, the reaction had almost no N\textsubscript{2} selectivity. As the O\textsubscript{2} content was increased, the N\textsubscript{2} selectivity first increased and then stabilized at about 90.1%. Based on the “Standard SCR” reaction mechanism combined with the “Fast SCR” proposed by Arnarson et al. (2017), two cycles, including an NO activation cycle and a “Fast SCR” cycle, were suggested, which shared the same reduction cycle. Thus, the oxidation reaction of NO to NO\textsubscript{2} does not easily occur in the absence of O\textsubscript{2}, where only isolate NO could react slowly with NH\textsubscript{3}. NO\textsubscript{2} has been proven to be a more effective oxidant than O\textsubscript{2} and NO (Zhu et al., 2017). In the presence of O\textsubscript{2}, more NO\textsubscript{2} is generated and participates in the reduction reaction, resulting in a “Fast SCR.” However, when the O\textsubscript{2} content is further increased to 12%, no more NO\textsubscript{2} can be produced because the oxidation reaction is also limited by the reaction temperature. It is worth noting that the N\textsubscript{2} selectivity increased and tended to be stable with increases in the O\textsubscript{2} concentration, indicating that a “Fast SCR” reaction is beneficial for NO\textsubscript{x} to be more fully reduced by NH\textsubscript{3}.

3.11 In situ DRIFTS

In situ DRIFTS were carried out to further explore the SCR reaction mechanism by clarifying the adsorbed species and intermediates over the MnAl\textsubscript{0.1} catalyst surface and the results were shown in Fig. 11.

**Fig. 11.** DRIFT spectra of (a) NH\textsubscript{3} adsorption (b) NO + O\textsubscript{2} adsorption (c) the reaction of pre-adsorbed NH\textsubscript{3} with NO + O\textsubscript{2} and (d) the reaction of preadsorbed NO + O\textsubscript{2} with NH\textsubscript{3} on the MnAl\textsubscript{0.1} catalyst at 150°C. The reactant gases contained 500 ppm NH\textsubscript{3}, N\textsubscript{2} balance (a, d) and a 500 ppm NO + 5% O\textsubscript{2}, N\textsubscript{2} balance in (b, c).
The DRIFT results for NH₃ adsorption on the MnAl₀.₁ catalyst recorded at 150°C over time are illustrated in Fig. 11(a). In the range of 1000–1650 and 3200–3700 cm⁻¹, several bands were observed after introducing NH₃. With increases in adsorption time, these bands became more prominent, resulting from the generating of more adsorbed NH₃ species. The bands at 1609 cm⁻¹ and 1192 cm⁻¹ were ascribed to the asymmetric and symmetric NH₃ stretching mode adsorbed on the Lewis acid sites, respectively (Ramis et al., 1995; Zhan et al., 2014). The bands at 1547 and 1515 cm⁻¹ were ascribed to the NH₃ originating from the deprotonation of ammonia via partial oxidation of NH₃ (Fan et al., 2017; Ma et al., 2018), and the bands at 1429 cm⁻¹ were ascribed to the ionic NH₃⁺ formed on the Brønsted acid sites (Liu et al., 2012; Liu et al., 2014). The bands at 3361 and 3260 cm⁻¹ were attributed to the N-H stretching vibration of coordinated NH₃ on the Lewis acid sites, and the negative bands around 3624 were regarded as the hydroxyl consumption by NH₃ (Wu et al., 2007; Ding et al., 2016).

Fig. 11(b) shows the DRIFT results of NO + O₂ co-adsorption on the catalyst. Two strong bands centered at 1565 and 1283 cm⁻¹ were observed for the MnAl₀.₁ catalyst after the NO adsorbed, which were attributed to bridging nitrate and monodentate nitrate species (Ramis et al., 1996; Larrubia et al., 2001; Ma et al., 2018). In addition, these two nitrate species had similar peak areas, and the adsorption capacity increased with time.

The reaction between the preadsorbed NH₃ and NO + O₂ species on MnAl₀.₁ was performed at 150°C is shown in Fig. 11(c). Compared with the spectra obtained for the NH₃ adsorption, similar spectra were observed while the band intensity was slightly reduced after N₂ purging. After NO + O₂ was introduced, the bands at 1609, 1547, and 1515 cm⁻¹ still existed, but the peak area was further decreased. The bands at 1429 and 1192 cm⁻¹ ascribed to NH₃ adsorbed on the Lewis acid sites and the ionic NH₃⁺ formed on the Brønsted acid sites disappeared, implying that these adsorbed species could be the significantly reactive intermediate species participating in the SCR reaction. Meanwhile, a new band at 1320 cm⁻¹ appeared and increased over time, which was attributed to monodentate nitrate species. This indicates that NH₃ first adsorbed on both the Brønsted and Lewis acid sites and subsequently reacted with gas-phase NO following an Eley-Rideal (E-R) mechanism.

Fig. 11(d) shows the reaction between the preadsorbed NO + O₂ species and NH₃ on MnAl₀.₁ catalyst. After introducing NH₃ into the IR cell, the bridging nitrate at 1565 cm⁻¹ quickly disappeared, and the band at 1283 cm⁻¹ assigned to monodentate nitrate species barely changed, meaning that the bridging nitrate was more active than the monodentate nitrate. The peak at 1600 cm⁻¹ became more prominent, and a round peak appeared at 1192 cm⁻¹, which indicated that the asymmetric and symmetric stretching modes of NH₃ were adsorbed on the Lewis acid sites. In addition, the N-H stretching vibrations of coordinated NH₃ appeared at 3361 and 3260 cm⁻¹. The negative bands around 3624 cm⁻¹ ascribed to the hydroxyl consumption were also found. These results indicated that the adsorbed NO₂ species were reduced by the adsorbed NH₃ species to N₂ and H₂O following a Langmuir-Hinshelwood (L-H) mechanism.

Based on the above analysis and catalytic activity results, it was deduced that the SCR reaction could simultaneously follow the E-R and L-H mechanisms. Both NO + O₂ and reducant NH₃ can be adsorbed on the surface of MnAl₂O₃ catalysts. Gaseous NH₃ can be adsorbed on the surface of MnAl₂O₃ oxide catalysts or react with hydroxyl species to form NH₃, which can react with gaseous NO to produce N₂. On the other hand, NO can react with O₂ to form NO₂, and the adsorbed NO₂ can be further converted into various nitrate and nitrite species, which can easily react with the adsorbed NH₃ species to generate N₂.

4 CONCLUSIONS

In this study, spherical mesoporous MnAl₂O₃ catalysts with different molar ratios were prepared using a simple precipitation method. Their NOₓ catalytic reduction performance and relevant main factors were investigated in a simulated fixed bed reactor. The MnAl₀.₁ catalyst exhibited the optimal low temperature DeNOₓ performance, where the highest catalytic efficiency was obtained at a temperature of 120°C. The MnAl catalyst had a relatively stable NO conversion rate of more than 92% at a space velocity range of 14331 h⁻¹ to 23885 h⁻¹. A smaller catalyst particle size led to a higher NO conversion rate, with N₂ selectivity as high as 100%. The appropriate oxygen
concentration is beneficial to increasing NOx conversion and N2 selectivity. The NH3-SCR process carried out on the MnAl2O3 catalyst reflected both the E-R and LH mechanisms. This work should be beneficial to the further optimization of LT SCR catalytic system developed for practical applications.

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