Insights into Reaction Conditions for Selective Catalytic Reduction of NO_x with a MnAl Oxide Catalyst at Low Temperatures

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ABSTRACT

MnO_x catalysts have been proven to have superior activity at low temperatures (LT) for selective catalytic reduction (SCR) of NO_x. In this study, spherical mesoporous MnAl_x catalysts with different molar ratios were prepared using a simple precipitation method. In addition, their NO_x catalytic performance, along with relevant main factors (reaction temperature, molar ratio, particle size, space velocity, and O₂ content), was investigated in a simulated fixed bed reactor. The relationship between the main factors and DeNO_x efficiency was evaluated by analyzing two parameters: the NO_x conversion rate and N₂ selectivity. The results showed that the MnAl_{0.1} catalyst had the optimal low temperature DeNO_x performance and had a relatively stable NO_x conversion rate of more than 92% in a space velocity range of 14331 h⁻¹ to 23885 h⁻¹, where smaller catalyst particle size led to higher NO_x conversion rate and N₂ selectivity as high as 100%. In addition, the appropriate oxygen concentration was found to increase NO_x conversion and N₂ selectivity. This work would be beneficial to further optimization of LT SCR catalyst systems for practical applications.

Keywords: NO_x, SCR, Low temperature, MnAl_x oxide, Spherical mesoporous

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1 INTRODUCTION

Nitrogen oxides (NO_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_{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_x emissions. Alternative post-combustion NO_x reduction techniques, including selective catalytic reduction and selective non-catalytic reduction (SNCR), have been used for NO_x elimination. Among them, the SCR process using NH₃ as the reductant is the most widely applied in post-NO_x abatement and has been shown to have high NO_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_x catalysts exhibit excellent activity at low temperature owing to their excellent redox properties and variable valence states. However, poor SO₂ tolerance and low N₂ selectivity relatively restrict their practical applications. Mixing or doping MnO_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. Al_2O_3 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 NO_x (Wang and Lin 1998; Liu *et al.*, 2016). Zhao *et al.* (2014) found that Al_2O_3 modified $\text{CeO}_2/\text{TiO}_2$ can improve the acidity of the catalyst, thereby reducing SO_2 adsorption. Mejía-Centeno *et al.* (2015) reported that Al_2O_3 doped TANs enhances activity at high temperatures due to the Lewis acidity and the multiwalled morphology of the TNTs.

Since Mn-based bimetal oxide catalysts are more active and selective than other alternatives, Al_2O_3 -supported Mn-based oxide catalysts have been intensively reported. Singoredjo *et al.* (1992) first prepared $\text{MnO}_x/\text{Al}_2\text{O}_3$ as SCR catalysts, and the results showed that Mn induced better dispersion on an Al_2O_3 support, resulting in higher catalyst activity. Kapteijn *et al.* (1994) studied the surface acidity of an $\text{MnO}_x\text{-Al}_2\text{O}_3$ catalyst and the adsorption capacity of NO_x and NH_3 on a surface. Cao *et al.* (2014, 2015) found that the high surface area of Al_2O_3 was the key to increasing the number of active catalytic sites by modifying $\text{MnO}_x\text{-Al}_2\text{O}_3$ with well-dispersed Fe, Ag, and Zr. The appropriate introduction of Al_2O_3 into MnO_x can reduce the thermal stability of the adsorbed SO_2 species and facilitate the decomposition of NH_4HSO_4 (Fan *et al.*, 2020). Kijlstra *et al.* (1997) proposed that the Lewis acid center is Mn^{3+} dispersed on the surface of $\text{MnO}_x/\text{Al}_2\text{O}_3$, where NO or an activated nitrite intermediate adsorbed on the surface reacts with NH_2^- 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 NO_x 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 MnAl_x catalyst and aimed to explore the effects of various technological conditions on the NO_x conversion performance of the catalysts. MnAl_x oxide catalysts with different molar ratios were prepared using a simple precipitation method, and their NO_x catalytic performance was investigated in the simulated fixed bed reactor, along with relevant main factors (reaction temperature, molar ratios, particle sizes, space velocity, and O_2 content). The relationship between the main factors and DeNO_x efficiency was evaluated by analyzing the NO_x conversion rate and N_2 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 MnAl_x mixed oxides were synthesized using a simple precipitation method. A specific amount of $\text{Mn}(\text{NO}_3)_2$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ at a total mole amount of 5 mmol was dissolved in 30 mL deionized water under magnetic stirring. After that, an aqueous $(\text{NH}_4)_2\text{CO}_3$ 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 MnAl_x oxides ($x = 0.1, 0.3, 0.5, 0.7$ and 0.9 , where x is the mole ratio of $\text{Al}/(\text{Mn} + \text{Al})$).

2.2 Catalyst Characterization

X-ray diffraction (XRD) was carried out with a BRUKER-AXS D8 Advanced X-ray Diffractometer with Cu K α 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 (H_2 -TPR) tests were performed on a gas chromatograph (SP-6800, Shandong Lunan Ruihong, China) with a thermal conductivity detector (TCD) under a 5% H_2/N_2 gas flow (50 mL min^{-1}).

at a rate of $10^{\circ}\text{C min}^{-1}$ up to 800°C . Temperature-programmed desorption of NH_3 (NH_3 -TPD) was carried out using the same instrument as that used for the H_2 -TPR. 100 mg of the sample saturated with adsorbed NH_3 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 N_2 atmosphere. The feed gas mixture contained NO, NH_3 , and O_2 , with He as the balance. When the reaction reached a stable state at each temperature, the concentrations of NO and NO_2 were continually monitored with the TH-990S NO and NO_2 analyzers, and N_2O in the outlet gas was detected with a Antaris™ IGS Gas Analyzer from Thermo Fisher Scientific Inc. The N_2 concentration was analyzed using a thermal conductivity detection method. The NO_x conversion rate and N_2 selectivity were calculated as follows:

$$\text{NO}_x \text{ conversion (\%)} = \left(1 - \frac{[\text{NO}_x]_{\text{out}}}{[\text{NO}_x]_{\text{in}}} \right) \times 100\%, \quad (1)$$

$$\text{N}_2 \text{ selectivity (\%)} = \left(1 - \frac{2[\text{N}_2\text{O}]_{\text{out}}}{[\text{NO}_x]_{\text{in}} + [\text{NH}_3]_{\text{in}} - [\text{NO}_x]_{\text{out}} - [\text{NH}_3]_{\text{out}}} \right) \times 100\% \quad (2)$$

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 MnAl_x catalysts, XRD measurements were carried out, for which the results are shown in Fig. 1. It can be observed that the $\text{MnAl}_{0.1}$ oxide mainly exhibited the characteristic peaks of Mn_2O_3 (JCPDS PDF: 73-1826). The main diffraction peak located at 32.9° was ascribed to the reflection of (222) plane in Mn_2O_3 . Furthermore, the reflection peaks at 23.1° , 55.1° , and 65.8° , corresponded to the (211), (440) and (662) planes of the Mn_2O_3 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 Mn_5O_8 planes (JCPDS PDF: 39-1218) were also detected on the $\text{MnAl}_{0.1}$. The intensity of the Bragg reflections decreased with increases in the

Fig. 1. XRD patterns of $\text{MnAl}_{0.1}$, $\text{MnAl}_{0.3}$, $\text{MnAl}_{0.5}$, $\text{MnAl}_{0.7}$, and $\text{MnAl}_{0.9}$.

Al doping amount, which could be obviously observed in the $\text{MnAl}_{0.5}$ sample. In addition, when the Al doping amount reached 0.7, the peak generated at 36.9° attributed to Mn_2O_3 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_2O_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_2O_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 $\text{MnAl}_{0.1}$. The SEM images (Figs. 2(a–c)) revealed that the $\text{MnAl}_{0.1}$ oxide exhibited a regular, spherical morphology. The diameters of the spherical particles in the $\text{MnAl}_{0.1}$ 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 $\text{MnAl}_{0.1}$ 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 micro-sphere, which confirmed that Al_2O_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 $\text{MnAl}_{0.1}$, $\text{MnAl}_{0.3}$, and $\text{MnAl}_{0.5}$ 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 (Arandiyana *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 $\text{MnAl}_{0.1}$ exhibited a specific surface area similar to that of $\text{MnAl}_{0.5}$. However, their pore volumes obviously increased from $0.292 \text{ cm}^3 \text{ g}^{-1}$ ($\text{MnAl}_{0.1}$) to $0.549 \text{ cm}^3 \text{ g}^{-1}$ ($\text{MnAl}_{0.5}$), 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 $\text{MnAl}_{0.1}$.

Fig. 3. (a) N₂ adsorption–desorption isotherm, (b) Pore size distribution of the MnAl_{0.1}, MnAl_{0.3} and MnAl_{0.5} catalysts.

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

Samples	S_{BET} (m ² g ⁻¹) ^a	V_p (cm ³ g ⁻¹) ^b	D_p (nm) ^c
MnAl _{0.1}	124.5	0.292	6.5
MnAl _{0.3}	126.1	0.431	5.6
MnAl _{0.5}	125.4	0.549	3.8

^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_x composite oxide showed a regular micro-sphere morphology with a mesoporous structure.

3.4 H₂-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, H₂-TPR of the prepared MnAl_x catalysts with different molar ratios was carried out. As can be seen in Fig. 4, MnAl_{0.1} 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 MnAl_{0.5}, indicating an improvement in the redox ability. This promoted reducible nature of MnAl_x 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, MnAl_{0.9} 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 NH₃-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 NH₃ (Ali *et al.*, 2018; Wu *et al.*, 2021). NH₃-TPD was carried out to explore the surface acid properties of the prepared catalysts. As shown in Fig. 5,

Fig. 4. H₂-TPR profiles of the MnAl_x catalysts.

Fig. 5. NH₃-TPD profiles of the MnAl_x ($x = 0.1, 0.2, 0.3, 0.4, 0.5$) catalysts.

two distinct desorption processes were exhibited in the NH₃ 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 NH₃ adsorbed at Brønsted acid sites is lower than that of the NH₃ molecules coordinated on Lewis acid sites (Kang *et al.*, 2019). Thus, the peaks at temperatures above 300°C were attributed to desorption of NH₃ coordinated at the Lewis acid sites, and the peaks at low temperatures were attributed to desorption of the NH₄⁺ ion from the Brønsted acid sites. All of the MnAl_x micro-spheres showed that the intensity of the NH₃ 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

Fig. 6. Catalytic activity of MnAl_{0.3} at different temperatures. Reaction conditions: C_{NO} = 1100 ppm; SV = 11942 h⁻¹; O₂ = 8%.

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_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_x conversion rates were 78.1%, 89.2%, 98.2% and 99.5%, respectively. However, the N₂ 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_x conversion rate was as high as 99.5% at 150°C, the N₂ selectivity decreased to 56.8%, which was due to the fact that the oxidation reaction of NH₃ was promoted with increases in the reaction temperature, causing the DeNO_x efficiency to decrease. Madia *et al.* (2002) suggested that at low temperatures, N₂O 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 N₂O + 2H₂O or HNO₃ + NH₃ at fast heating rates, and the absence of H₂O could favor the formation of N₂O. Also, Tang *et al.* (2010) reported that NH₃ can be changed into adsorbed N species on β-MnO₂, which reacted with gaseous NO to form N₂O. It can be seen that the MnAl_{0.3} catalyst had good LT catalytic activity, but the N₂ 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_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_x conversion rates were 97.4%, 72.3%, 78.1%, 79.5% and 50.9% for MnAl_{0.1}, MnAl_{0.3}, MnAl_{0.5}, MnAl_{0.7}, and MnAl_{0.9}, respectively, and where the selectivity of N₂ was 64.2%, 58.1%, 57.9%, 72%, and 47.7%, respectively. Interestingly, the N₂ selectivity also exhibited variations similar to those in the NO_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_{0.1} showed the highest NO_x conversion rate among these catalysts. Combined with the previous H₂-TPR and NH₃-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_x removal.

Fig. 7. The catalytic activity of the MnAl_x catalysts at different molar ratios. Reaction conditions: C_{NO} = 1000 ppm, SV = 17914 h⁻¹, T = 80°C, O₂ = 8%.

Fig. 8. Catalytic activity of MnAl_{0.1} under different space velocities. Reaction conditions: C_{NO} = 1000 ppm, T = 80°C, O₂ = 8%.

Fig. 8 displays the DeNO_x performance of the MnAl_{0.1} catalyst at different space velocities. As the space velocity was increased from 14331 h⁻¹ to 23885 h⁻¹, the DeNO_x rate only dropped slightly from 95.3% to 92.1%. When the space velocity was increased to 35828 h⁻¹, the catalytic activity drastically dropped to 56.8%. This may have been due to the fact that as the space velocity increases, the external diffusion resistance decreases, which facilitates NO_x adsorption. However, in the meantime, the residence time of the gas on the surface of the catalyst becomes shorter, and the adsorbed NO_x cannot fully react with NH₃, resulting in a lower DeNO_x rate. Increases in the space velocity led to decreases in the N₂ selectivity. When the space velocity was 14331 h⁻¹, 17914 h⁻¹, 23885 h⁻¹, and 35828 h⁻¹, the corresponding N₂ selectivity was 76.13%, 64.2%, 60.5%, and 43.5%, respectively. The space velocity showed a similar trend of influence on the NO_x conversion rate, supporting the conclusions discussed above.

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 denitration performance. Fig. 9(a) shows the NO_x conversion curve as a function of time. As the catalyst particles became smaller, the NO_x removal rate increased. When the catalyst particles were 20–40 mesh, 40–60 mesh, and 60–100 mesh,

Fig. 9. Catalytic activity of MnAl_{0.1} catalyst with different particle sizes. Reaction conditions: C_{NO} = 1000 ppm, T = 80°C, SV = 35828 h⁻¹, O₂ = 8%.

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 NO_x 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 NO_x 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 MnAl_{0.1} catalyst. It can be seen that the MnAl_{0.1} catalyst exhibited poor catalytic activity with a NO_x conversion rate of 26.0% in the absence of O₂. The NO_x conversion rate changed significantly in the presence of 4% O₂, and when the O₂ concentration was further increased to 8%, the conversion

Fig. 10. Catalytic activity of the MnAl_{0.1} catalyst with different O₂ content. Reaction conditions: C_{NO} = 1000 ppm, T = 80°C, SV = 17914 h⁻¹.

rate increased slightly to 87.6%. With the further increase in the O_2 content, the catalytic activity remained basically unchanged. In the absence of O_2 , the reaction had almost no N_2 selectivity. As the O_2 content was increased, the N_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_2 does not easily occur in the absence of O_2 , where only isolate NO could react slowly with NH_3 . NO_2 has been proven to be a more effective oxidant than O_2 and NO (Zhu *et al.*, 2017). In the presence of O_2 , more NO_2 is generated and participates in the reduction reaction, resulting in a “Fast SCR.” However, when the O_2 content is further increased to 12%, no more NO_2 can be produced because the oxidation reaction is also limited by the reaction temperature. It is worth noting that the N_2 selectivity increased and tended to be stable with increases in the O_2 concentration, indicating that a “Fast SCR” reaction is beneficial for NO_x to be more fully reduced by NH_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 $MnAl_{0.1}$ catalyst surface and the results were shown in Fig. 11.

Fig. 11. DRIFT spectra of (a) NH_3 adsorption (b) $NO + O_2$ adsorption (c) the reaction of pre-adsorbed NH_3 with $NO + O_2$ and (d) the reaction of preadsorbed $NO + O_2$ with NH_3 on the $MnAl_{0.1}$ catalyst at $150^\circ C$. The reactant gases contained 500 ppm NH_3 , N_2 balance (a, d) and a 500 ppm $NO + 5\% O_2$, N_2 balance in (b, c).

The DRIFT results for NH_3 adsorption on the $\text{MnAl}_{0.1}$ catalyst recorded at 150°C over time are illustrated in Fig. 11(a). In the range of $1000\text{--}1650$ and $3200\text{--}3700\text{ cm}^{-1}$, several bands were observed after introducing NH_3 . With increases in adsorption time, these bands became more prominent, resulting from the generating of more adsorbed NH_3 species. The bands at 1609 cm^{-1} and 1192 cm^{-1} were ascribed to the asymmetric and symmetric NH_3 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 $-\text{NH}_2$ originating from the deprotonation of ammonia via partial oxidation of NH_3 (Fan *et al.*, 2017; Ma *et al.*, 2018), and the bands at 1429 cm^{-1} were ascribed to the ionic NH_4^+ 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 NH_3 on the Lewis acid sites, and the negative bands around 3624 were regarded as the hydroxyl consumption by NH_3 (Wu *et al.*, 2007; Ding *et al.*, 2016).

Fig. 11(b) shows the DRIFT results of $\text{NO} + \text{O}_2$ co-adsorption on the catalyst. Two strong bands centered at 1565 and 1283 cm^{-1} were observed for the $\text{MnAl}_{0.1}$ catalyst after the NO adsorbed, which were attributed to bridging nitrate and monodentate nitrate species (Ramis *et al.*, 1990; 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 NH_3 and $\text{NO} + \text{O}_2$ species on $\text{MnAl}_{0.1}$ was performed at 150°C is shown in Fig. 11(c). Compared with the spectra obtained for the NH_3 adsorption, similar spectra were observed while the band intensity was slightly reduced after N_2 purging. After $\text{NO} + \text{O}_2$ 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 NH_3 adsorbed on the Lewis acid sites and the ionic NH_4^+ 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 NH_3 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 $\text{NO} + \text{O}_2$ species and NH_3 on $\text{MnAl}_{0.1}$ catalyst. After introducing NH_3 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 NH_3 were adsorbed on the Lewis acid sites. In addition, the N-H stretching vibrations of coordinated NH_3 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 NO_x species were reduced by the adsorbed NH_3 species to N_2 and H_2O 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 $\text{NO} + \text{O}_2$ and reductant NH_3 can be adsorbed on the surface of MnAl_x oxide catalysts. Gaseous NH_3 can be adsorbed on the surface of MnAl_x oxide catalysts or react with hydroxyl species to form NH_4^+ , which can react with gaseous NO_x to produce N_2 . On the other hand, NO can react with O_2 to form NO_2 , and the adsorbed NO_2 can be further converted into various nitrate and nitrite species, which can easily react with the adsorbed NH_3 species to generate N_2 .

4 CONCLUSIONS

In this study, spherical mesoporous MnAl_x catalysts with different molar ratios were prepared using a simple precipitation method. Their NO_x catalytic reduction performance and relevant main factors were investigated in a simulated fixed bed reactor. The $\text{MnAl}_{0.1}$ catalyst exhibited the optimal low temperature DeNO_x performance, where the highest catalytic efficiency was obtained at a temperature of 120°C . The MnAl catalyst had a relatively stable NO_x 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_x conversion rate, with N_2 selectivity as high as 100%. The appropriate oxygen

concentration is beneficial to increasing NO_x conversion and N₂ selectivity. The NH₃-SCR process carried out on the MnAl_x oxide 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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