Promotion Effect and Mechanism of the Addition of Mo on the Enhanced Low Temperature SCR of NOx by NH3 over MnOx/γ-Al2O3 Catalysts

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Promotion Effect and Mechanism of the Addition of Mo on the Enhanced Low Temperature SCR of NO\textsubscript{x} by NH\textsubscript{3} over MnO\textsubscript{x}/\gamma-Al\textsubscript{2}O\textsubscript{3} Catalysts

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Abstract

A series of Mn/\gamma-Al\textsubscript{2}O\textsubscript{3} and MnMo/\gamma-Al\textsubscript{2}O\textsubscript{3} catalysts were prepared by using Incipient Wetness Impregnation (IWI) method. The catalytic performance tests showed that the Mn\textsubscript{3}Mo\textsubscript{1.25}/\gamma-Al\textsubscript{2}O\textsubscript{3} demonstrated a higher SCR performance (NO conversion of around 96\%) at a broad low temperature range (150 to 300\degree\ C). The characterization showed that the addition of Mo to the Mn/\gamma-Al\textsubscript{2}O\textsubscript{3} catalysts could promote the dispersion of MnO\textsubscript{x} on the surface of \gamma-Al\textsubscript{2}O\textsubscript{3}. The adsorption of NO could form two different species, nitrites and nitrates on the surface of the catalyst. The presence of nitrites is beneficial to low temperature SCR. It is also found that the existence of Mo in the catalyst favours the formation of Mn\textsuperscript{3+}, which plays a critical role in the adsorption of NH\textsubscript{3} and therefore improves NH\textsubscript{3} adsorption capacity of the MnO\textsubscript{x}/\gamma-Al\textsubscript{2}O\textsubscript{3} catalysts. The low temperature SCR of the Mn\textsubscript{3}Mo\textsubscript{1.25}/\gamma-Al\textsubscript{2}O\textsubscript{3} catalyst was found to mainly follow L-H mechanism, but E-R mechanism also plays a role to some extent. Moreover, it is also found that the addition of Mo not only mitigates the deactivation of catalysts, but also broadens the effective temperature range of the SCR catalyst.

Keywords: Low temperature SCR; MnMo/\gamma-Al\textsubscript{2}O\textsubscript{3}; Mo addition; Promotion effects; Mechanism
1. Introduction

The emission of nitrogen oxides (NO\textsubscript{x}) from combustion processes is associated with a series of severe environmental problems, such as acid rain and ozone depletion, has become an issue of great concern for decades [1-3]. To address this problem, the selective catalytic reduction (SCR) of NO\textsubscript{x} by NH\textsubscript{3} has been applied to treat flue gas from stationary and mobile sources [4, 5]. At coal-fired power stations, V\textsubscript{2}O\textsubscript{5}-WO\textsubscript{3}/TiO\textsubscript{2} is the most commonly used SCR catalyst. However, the high operating temperature window of 300 - 400°C is associated with a variety of problems [6, 7], such as the possible oxidation of SO\textsubscript{2} and the high energy consumption [8, 9]. Therefore, there is a need for the development of low temperature SCR catalysts, which has attracted a wide attention in recent years [10, 11].

The manganese-based catalyst is a good alternative to vanadium-based SCR catalysts, which has demonstrated high catalytic activity and selectivity at low temperature [9, 12-20]. Mn-based oxides catalysts, such as MnO\textsubscript{x}-CeO\textsubscript{y}/meso-TiO\textsubscript{2}[21], MnO\textsubscript{2}-(Co\textsubscript{3}O\textsubscript{4})/TiO\textsubscript{2}[22] and nano-flaky MnO\textsubscript{x} supported on carbon nanotubes [16], have outstanding SCR activity at low temperatures. The addition of transition and/or rare earth metals, such as Fe, Ce and Sb etc, has been found to have positive effects on the performance of these Mn-based catalysts [20, 23-26]. However, their operating temperature window was narrow. The development of novel SCR catalysts, which are highly efficient at different temperature levels for different applications is highly desirable but remains very challenging [14].

Previous studies have shown that Mo can promote the distribution of active constituents on the support and subsequently enhances the activity of the catalyst [27]. Moreover, most researchers believed that low temperature SCR reaction follows Eley-Rideal (E-R) mechanism [28, 29]. However, to date, very little work has been carried out on the addition of molybdenum to manganese-based catalysts (MnMo/γ-Al\textsubscript{2}O\textsubscript{3}) to improve its low temperature SCR performance [30].
In this study, Mo was doped on the Mn/\(\gamma\)-Al\(_2\)O\(_3\) catalysts via Incipient Wetness Impregnation (IWI) method aiming at improving its low temperature SCR performance. Systematic characterisation and testing were carried out to show the effects of Mo addition on catalytic performance of the Mn\(_x\)Mo\(_y\)/\(\gamma\)-Al\(_2\)O\(_3\). Moreover, the mechanism of the SCR process over the Mo-modified catalyst at low temperature was investigated.

2 Experimental

2.1 Preparation of catalysts

In this research, a series of Mn-based catalysts with different Mo and Mn loadings supported on \(\gamma\)-Al\(_2\)O\(_3\) were prepared via IWI method (binary metal catalysts were prepared with a two-step IWI method).

Chemicals of AR grade, such as \(\text{Mn(NO}_3\text{)}_2\cdot4\text{H}_2\text{O}\) and \((\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot4\text{H}_2\text{O}\), were acquired from Sinopharm Chemical Reagent Co., Ltd and used as precursors for the preparation of the catalysts. To prepare a Mn\(_x\)Mo\(_y\)/\(\gamma\)-Al\(_2\)O\(_3\) catalyst, a controlled amount of \((\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot4\text{H}_2\text{O}\) was loaded on \(\gamma\)-Al\(_2\)O\(_3\) via IWI method, followed by drying at 120°C for 24h and calcination at 520°C for 12h. The sample prepared was then impregnated again with certain quantity of the Mn precursor, followed by drying at 120°C for 24h and calcination at 520°C for 12h. The detailed procedure for the preparation of these catalysts was described elsewhere in our previous research [31, 32].

In this study, the Mn\(_x\)/\(\gamma\)-Al\(_2\)O\(_3\) catalysts means x wt% of Mn in the catalyst, while the Mn\(_x\)Mo\(_y\)/\(\gamma\)-Al\(_2\)O\(_3\) suggests y wt% of Mo in the catalyst.

2.2 Characterization of catalysts

The specific area of samples prepared in this study was characterised by N\(_2\) adsorption/desorption at -196 °C using a Micromeritics ASAP 2020, the procedure of which is described elsewhere in literature [31]. The crystal phases of the catalysts were analysed by using an X-Ray Diffraction (XRD, Bruker D8 Advance) with Cu K\(\alpha\) radiation. Oxidation states of metal species in the catalysts were also analysed using an X-Ray Photoelectron Spectroscopy (XPS Axis Ultra DLD
Multifunctional) [33]. The C\textsuperscript{1s} peak at 284.8eV was used as the standard for calibration. The element compositions of catalysts were analysed by X-Ray Fluorescence (XRF, Bruker s8 TIGER). Morphology, nanostructures and elemental distribution of catalysts were examined using Transmission Electron Microscopy (TEM, FEI Tecnai G2F20). The H\textsubscript{2}-temperature programmed reduction (H\textsubscript{2}-TPR) was performed to investigate the redox of the samples. Ammonia (NH\textsubscript{3}) Temperature Programmed Desorption (NH\textsubscript{3}-TPD) method was also carried out to show the quantity and strength of acidic sites on the surface of the catalysts, which was carried out in a Micromeritics AutoChem II 2920 with a heating rate of 10\textdegree C/min and NH\textsubscript{3} adsorption for 30min at a flowrate of 30mL/min. NH\textsubscript{3} adsorptions on the surface of catalysts were carried out on a Fourier Transform Infrared Spectroscopy (FTIR, Bruker vertex 70). NO-TPD was performed in a specially designed reactor with gas composition measured by a flue gas analyser (Vario Plus, MRU, Germany).

2.3 Measurement of catalytic activity

The prepared sample was loaded into a fixed-bed reactor and exposed to a simulated flue gas containing NO\textsubscript{x} (500 ppm), NH\textsubscript{3} (500 ppm), O\textsubscript{2} (3vol%), and N\textsubscript{2}. The gas hourly space velocity (GHSV) adopted in this study was 3 5000·h\textsuperscript{-1}. Prior to each test, NO\textsubscript{x} concentration at the inlet ([NO\textsubscript{x}]\textsubscript{in}) was measured to confirm the initial concentration and to minimise experimental errors. The concentration of NO\textsubscript{x} at the outlet ([NO\textsubscript{x}]\textsubscript{out}) was continuously monitored by the Flue Gas Analyser (MRU Vario Plus and Testo 350, Germany). The NO\textsubscript{x} removal efficiency is therefore determined by following equation:

\[
NO_x \text{ removal efficiency (\%)} = \frac{[NO_x]_\text{in} - [NO_x]_\text{out}}{[NO_x]_\text{in}} \times 100\% 
\]

3 Results and discussion

3.1. Catalytic performance

Low temperature catalytic activity of the Mn\textsubscript{x}/\gamma-Al\textsubscript{2}O\textsubscript{3} and Mn\textsubscript{x}Mo\textsubscript{y}/\gamma-Al\textsubscript{2}O\textsubscript{3} catalysts was tested in a downflow fixed-bed reactor. NO\textsubscript{x} removal efficiency of the four catalysts is illustrated in Fig.
In Fig. 1(b), Mn3/γ-Al2O3 showed outstanding low temperature NH3-SCR activities, but the optimal operation temperature was at 250°C. In order to further improve the low temperature NH3-SCR activity of the Mn3/γ-Al2O3 catalysts, Mo was added to modify the Mn3/γ-Al2O3 catalysts. In Fig. 1(a), γ-Al2O3 and Mo3/γ-Al2O3 did not show any SCR activity in a broad temperature range. It is obvious that the NO conversion of Mn3/γ-Al2O3 was below 90% at 150°C, above 90% when temperature was raised to 200 and 250°C, but deteriorated when temperature was raised to higher levels. However, the impregnation of Mo significantly improved the low temperature catalytic performance of the Mn3Mo1.25/γ-Al2O3 catalyst, which showed a remarkable promoting effect at 150°C (NO conversion of 96%), and expanded the effective temperature window to 150-300°C. It was found that at higher Mo loadings, the optimal SCR temperature window started to shift to high temperature levels as shown in Fig. 1(c), which suggests that Mo is a good moderator for the adjustment of effective temperature of SCR reaction. Therefore, it can be concluded that the addition of Mo not only promotes the SCR activity of the Mn3/γ-Al2O3 catalyst, but also adjusts the effective temperature range of the catalyst.

The effect of H2O and SO2 on the activity of Mn3Mo1.25/γ-Al2O3 catalysts is in Fig. 1(d). When 100ppm SO2 and 5% H2O were introduced into the reactant gas mixture, the NO conversion of the Mn3Mo1.25/γ-Al2O3 dropped to 81% after 2h, which is similar as what is reported by other researchers [34-36]. However, when the supply of SO2 and H2O was stopped, the NO conversion increased to about 91%. The decrease of NO conversion could be responsible for the deposit of sulphate on the catalyst surface[24]. The results indicated that the Mn3Mo1.25/γ-Al2O3 has resistance to SO2 and H2O. In Fig. 1(d), the durability of Mn3Mo1.25/γ-Al2O3 and Mn3Mo1.25/γ-Al2O3 was also conducted at 150°C. The durability performance of the Mn3Mo1.25/γ-Al2O3 was much better than that of Mn3/γ-Al2O3. NO conversion of Mn3Mo1.25/γ-Al2O3 decreased slightly to 95% after 20h, which indicated that Mo enhanced the durability of Mn3/γ-Al2O3 catalysts.
Fig. 1 NO conversion over different catalysts under different gas atmosphere. Reaction condition: (a), (b), (c), (d), [NH$_3$] = [NO] = 500 ppm, O$_2$=3%, N$_2$ balance, GHSV=35 000 h$^{-1}$. (d), SO$_2$=100 ppm, H$_2$O=5%, Temperature 150° C.

3.2. Characterization of the catalysts

3.2.1. Effects of Mo addition on Mn dispersion

Structural and morphological properties of the catalysts were investigated by BET and XRD analyses. As shown in Table 1, the specific surface area of the Mn$_3$Mo$_{1.25}$/γ-Al$_2$O$_3$ catalyst is larger than that of the Mn$_3$/γ-Al$_2$O$_3$ catalyst, which provides more active sites for low temperature NH$_3$-SCR reaction. In comparison with pure γ-Al$_2$O$_3$, the surface area of the γ-Al$_2$O$_3$ loaded with Mo
decreased slightly. When the Mo loading was below 5 wt %, the surface area of catalysts increased with the increase in Mo loading, which means that the addition of Mo contributes to the dispersion of active component on the support. However, further increase in Mo loading content prevents this trend. It is clear from Table 1 that when Mo loading was greater than 5 wt %, surface areas of the catalysts decreased with the increase in Mo loading. The low temperature SCR activity dropped with the increase in Mo loading. Therefore, 1.25 wt % of Mo loading was found to be the optimal that not only enhanced the dispersion of Mn on the surface of the catalysts, but also promoted the surface area to certain extent.
Table.1 The surface properties of the catalysts

| Catalyst                        | BET surface area (m²/g) | Pore volume (cm³/g) | Pore size (Å) |
|--------------------------------|-------------------------|---------------------|--------------|
| γ-Al₂O₃                        | 242.2                   | 0.48                | 79.7         |
| Mn₂/γ-Al₂O₃                    | 190.02                  | 0.47                | 99.36        |
| Mn₃/γ-Al₂O₃                    | 216.4                   | 0.45                | 82.7         |
| Mn₄/γ-Al₂O₃                    | 164.90                  | 0.46                | 112.33       |
| Mn₆/γ-Al₂O₃                    | 172.18                  | 0.40                | 88.08        |
| Mn₂Mo₁/γ-Al₂O₃                 | 194.45                  | 0.44                | 90.86        |
| Mn₂Mo₁.25/γ-Al₂O₃              | 207.61                  | 0.46                | 89.08        |
| Mn₂Mo₂.₅/γ-Al₂O₃               | 209.65                  | 0.45                | 86.38        |
| Mn₂Mo₅/γ-Al₂O₃                 | 209.91                  | 0.42                | 81.16        |
| Mn₂Mo₇.₅/γ-Al₂O₃               | 209.53                  | 0.42                | 80.42        |
| Mn₂Mo₁₀/γ-Al₂O₃                | 189.67                  | 0.37                | 78.93        |
| Mn₃Mo₁.₂₅/γ-Al₂O₃              | 225.7                   | 0.46                | 80.7         |
| Mn₄Mo₁.₂₅/γ-Al₂O₃              | 219.70                  | 0.45                | 88.11        |
| Mn₆Mo₁.₂₅/γ-Al₂O₃              | 192.38                  | 0.41                | 85.81        |
| Mo₁/γ-Al₂O₃                    | 221.93                  | 0.48                | 86.69        |
| Mo₁.₂₅/γ-Al₂O₃                 | 221.18                  | 0.52                | 94.70        |
| Mo₂.₅/γ-Al₂O₃                  | 223.33                  | 0.46                | 82.94        |
| Mo₅/γ-Al₂O₃                    | 227.67                  | 0.45                | 78.85        |
| Mo₇.₅/γ-Al₂O₃                  | 220.37                  | 0.41                | 75.49        |
| Mo₁₀/γ-Al₂O₃                   | 211.06                  | 0.40                | 75.00        |

XRD spectrum of the Mn₃Mo₁.₂₅/γ-Al₂O₃, Mn₃/γ-Al₂O₃, Mo₁.₂₅/γ-Al₂O₃ and γ-Al₂O₃ are shown in Fig 2(a). It is clear that the XRD patterns showed four different compounds: γ-Al₂O₃ (JCPDS 04-0880), β-MnO₂ (JCPDS 24-0735), α-Mn₂O₃ (JCPDS 24-0508), while the MoOₓ did not exist, which was due to its low content. Pijun Gong’s et al. [37] claimed that β-MnO₂ has the worst SCR activity in among different MnO₂ species, while α-Mn₂O₃ was found to demonstrate high SCR activity and selectivity by many researchers[38, 39]. Except for γ-Al₂O₃, the intensity of diffraction peaks of Mn compounds was weak. However, in Fig 2(b), when Mn loading varied from 0 to 6 wt%, the diffraction peaks of α-Mn₂O₃, MnO, β-MnO₂, especially that of α-Mn₂O₃, started to
appear when Mn loading raised to 3 wt%, and the peaks intensity became higher with the increase in Mn loadings, which means bulk MnOx species began to form and accumulated on the surface of the catalyst. However, bulk MnOx species occupied great amount of surface space but performed poor low temperature SCR activity[40]. While doping Mo first on the support, the intensity of diffraction peaks intensity of Mn species decreased, as shown in Fig 2 (a) and (b). It can be concluded that Mo species could improve the dispersion of MnOx species on the support surface, prevent the formation of large MnOx bulks, and strengthen the interaction between MnOx and the support.

![Graphical representation of diffraction peaks intensity](image)

(a) 

(b) 

Zoom
Fig.2 XRD patterns of catalysts. a. Mn$_2$/γ-Al$_2$O$_3$, b. Mn$_2$Mo$_{1.25}$/γ-Al$_2$O$_3$, c. Mn$_3$/γ-Al$_2$O$_3$, d. Mn$_3$Mo$_{1.25}$/γ-Al$_2$O$_3$, e. Mn$_4$/γ-Al$_2$O$_3$, f. Mn$_4$Mo$_{1.25}$/γ-Al$_2$O$_3$, g. Mn$_6$/γ-Al$_2$O$_3$, h. Mn$_6$Mo$_{1.25}$/γ-Al$_2$O$_3$

3.2.2. XPS, XRF and TEM-EDX

The XPS of Mn 2p (a), Mo 3d (b) are shown in Fig. 3. Different MnO$_x$ species have specific and unique spectrums. In Fig. 3(a), Mn3p$_{3/2}$ peaks consist of three MnO$_x$ species, Mn$^{4+}$ (641.5-641.7eV), Mn$^{3+}$ (541.5-541.7eV) and satellite[41]. The area ratio, respectively, represent the relative amount of species on the surface. A significant decrease in area ratio of Mn$^{4+}$/Mn$^{3+}$ from 1.26 to 1.08 was observed as a result of Mo addition, which is consistent with the results of XRD analysis. It can be seen from Table 2 that the Mn$_3$Mo$_{1.25}$/γ-Al$_2$O$_3$ catalyst had a lower Mn/Al atomic ratio. Moreover, XRF and TEM/EDX tests were carried out to show the existence of different species in the catalysts. In Table 3, the mass percentage of Mn, Mo, Al and O is consistent with these species during the preparation of catalysts. Thus, it can be concluded that the Mn was well loaded on the support. In Fig. 4(a) and (b), Mn$_3$Mo$_{1.25}$/γ-Al$_2$O$_3$ is of a more uniform morphology and structure as compared with Mn$_3$/γ-Al$_2$O$_3$. No aggradation of MnO$_x$ was formed on the surface of Mo$_3$Mo$_{1.25}$/γ-Al$_2$O$_3$, which means MnO$_x$ species have a better dispersion on the surface of Mo$_3$Mo$_{1.25}$/γ-Al$_2$O$_3$. The surface Mn content had a significant increase after the doping Mo, as shown in Fig. 4(c) and (d). It implied that the addition of Mo strengthens the interactions between MnO$_x$ species and the γ-Al$_2$O$_3$, promotes the dispersion of MnO$_x$ on the surface of support. In Fig. 3(b), it can be seen that Mo was loaded on the catalysts surface in the form of MoO$_3$, which was proved by Mo 3d XPS peak at 232.6 eV. In addition, it is speculated that Mo might just act as an accelerant responsible for the formation of active components, itself state does not alter on the surface of the support.
Fig. 3 XPS spectra of MnO$x$/$\gamma$-Al$_2$O$_3$ catalysts before and after Mo addition

Table 2. Binding energy values and surface atomic ratio between Mn 2p for MnO$x$/$\gamma$-Al$_2$O$_3$ catalysts before and after modified by Mo addition

| Catalyst                     | Binding Energy (eV) | PWHH | Mn$^{4+}$/Mn$^{3+}$ | Mn/Al atomic ratio (PP) | Mo/Al atomic ratio (PP) |
|------------------------------|---------------------|------|---------------------|------------------------|------------------------|
| Mn$_3$Mo$_{1.25}$/$\gamma$-Al$_2$O$_3$ | Mn$^{4+}$ 642.97     | 2.8  | 1.08                | 0.046                  | 0.018                  |
|                              | Mn$^{3+}$ 641.56     | 2.4  |                     |                        |                        |
| Mn$_3$/$\gamma$-Al$_2$O$_3$  | Mn$^{4+}$ 642.84     | 2.7  | 1.26                | 0.062                  | 0                      |
|                              | Mn$^{3+}$ 641.46     | 2.0  |                     |                        |                        |

Table 3. The composition (wt.%) of catalysts measured by X-ray fluorescence (XRF)
| Catalyst                  | Mn  | Mo  | Al   | Mn/Al atomic ratio | Mo/Al atomic ratio |
|---------------------------|-----|-----|------|--------------------|--------------------|
| Mn₃Mo₁.₂₅/γ-Al₂O₃         | 3.17| 1.33| 49.7 | 0.0313             | 0.0075             |
| Mn₃/γ-Al₂O₃              | 3.2 | 0   | 50.7 | 0.0310             | 0                  |

Fig. 4. TEM micrographs (a and b) and EDX (c and d) spectra of Mn₃/γ-Al₂O₃ (b and d) and Mn₃Mo₁.₂₅/γ-Al₂O₃ (a and c)

3.2.3. H₂-TPR

The H₂-TPR results of the γ-Al₂O₃, Mo₁.₂₅/γ-Al₂O₃, Mn₃/γ-Al₂O₃, Mn₃Mo₁.₂₅/γ-Al₂O₃ are shown in Fig. 5. There are four distinct reduction peaks, τ₁, τ₂, τ₃, τ₄, which are corresponding to the reduction of MnO₂ to Mn₂O₃, Mn₂O₃ to Mn₃O₄, Mn₃O₄ to MnO and MoO₃ to MoO₂.
respectively[42]. Additionally, the curve of γ-Al$_2$O$_3$ did not change significantly except a noticeable drift at the high temperatures.

![H$_2$-TPR profiles over Mo modified MnO$\delta$/γ-Al$_2$O$_3$ catalysts](image)

**Fig.5** H$_2$-TPR profiles over Mo modified MnO$\delta$/γ-Al$_2$O$_3$ catalysts

Comparing Mn$_3$Mo$_{1.25}$/γ-Al$_2$O$_3$ with Mn$_3$/γ-Al$_2$O$_3$, the temperature of $\tau_2$, $\tau_3$ decreased, which suggests that Mn$_2$O$_3$ has a stronger interaction with the support in Mn$_3$Mo$_{1.25}$/γ-Al$_2$O$_3$. The intensity of $\tau_2$ and $\tau_3$ also increased. Based on observations, it is speculated that the Mo in catalysts promotes the formation of Mn$_2$O$_3$, which is consistent with the results of XRD and XPS analyses.

Normally, only the NH$_3$ being adsorbed on the Lewis acid site of Mn$^{3+}$ shows low temperature SCR activity and can activate the ammonia to -NH$_2$ [5]. The -NH$_2$ takes part in the SCR reaction which suggests that the more Mn$_2$O$_3$ the catalyst has, the more Mn$^{3+}$ Lewis acid sites are formed, which subsequently promotes low temperature SCR, while the MnO$_2$ plays a less important role in the low temperature SCR reaction. In contrast, Mn$_2$O$_3$ dominated the selective catalytic reduction performance at low temperature, which agreed well with the theory proposed by De Fang[43]. Therefore, it could be concluded that the addition of Mo could promote low temperature SCR activity of the Mn/γ-Al$_2$O$_3$ catalyst by enabling the formation of more Lewis acid sites.

**3.2.4. NH$_3$-TPD and FTIR**
The amount and strength of surface acid sites of Mn$_3$/γ-Al$_2$O$_3$ catalyst before and after Mo addition was investigated using NH$_3$-TPD, which is shown in Fig. 6. There are three distinct peaks, which could be divided into weak, medium and strong acid sites, respectively. The temperature range of $\tau_1$, $\tau_2$ and $\tau_3$ is 150-250°C, 250-400°C and 400-500°C respectively. The Mn$_3$Mo$_{1.25}$/γ-Al$_2$O$_3$ had higher intensity at all peaks, which suggests more medium and strong acid sites.

Fig. 6. NH$_3$-TPD profiles of Mn$_3$/γ-Al$_2$O$_3$ catalysts before and after modified by Mo addition

Fig. 7. NH$_3$-TPD profiles over Mn$_2$/γ-Al$_2$O$_3$ catalysts with different Mo loadings
Moreover, catalytic activity of the Mnₓ/γ-Al₂O₃ with different Mo loadings was investigated as shown in Fig. 7. The strong and medium acid sites of catalyst increased significantly with the increase in Mo loadings. It is also found that a higher Mo loading led to a higher catalytic temperature of the catalysts in Fig. 1(c). Therefore, the low Mo content (1.25 wt%) favoured the low temperature SCR.

Fig. 8. FTIR spectra of Mn₃/γ-Al₂O₃ and Mn₃Mo₁.25/γ-Al₂O₃ treated in flowing 500ppm NH₃ at 100°C until saturation and then purged by N₂.

Fig. 8 shows the FTIR spectra of NH₃ adsorption over Mn₃/γ-Al₂O₃ and Mn₃Mo₁.25/γ-Al₂O₃ catalysts at 100°C. For Mn₃Mo₁.25/γ-Al₂O₃, two strong bands at 1266 and 1465 cm⁻¹ and two relatively weaker bands at 1616 and 1681 cm⁻¹ were observed. The bands at 1230, 1251, 1266, 1616 cm⁻¹ can be assigned to bending vibrations of N-H bonds in the NH₃ linked to Lewis acidic sites[44]. The bands at 1397 cm⁻¹ were almost same, resulted from over NH₃ adsorption on γ-Al₂O₃[45]. The bands at 1459 and 1479 cm⁻¹ were observed due to NH₃ adsorbed on Brönsted acidic sites. What’s more, an amide(-NH₂) species also was observed at 1510 cm⁻¹. The bands at 1616 cm⁻¹ (assigned to Lewis acidic sites) and 1681 cm⁻¹ (assigned to Brönsted acidic sites mainly) are mainly came from NH₃ adsorption on γ-Al₂O₃. In previous report[46], molybdenyl species
were unsaturated on the catalyst surface and were deranged easily by adsorption of ammonia. In
Fig. 8, it can be seen that Lewis and Brönsted acidic sites at 1266 and 1465 cm\(^{-1}\) were significantly
enhanced after the modification of Mo. This confirms what was found in NH3-TPD analysis.

3.2.5. NO-TPD

Fig. 9 shows the NO-TPD profiles of the Mn\(_3\)/γ-Al\(_2\)O\(_3\) catalyst before and after Mo addition. Two
desorption peaks can be observed in Fig. 9, which contained a broad peak in the low temperature
region (LT-peak) and a strong peak at higher temperature region (HT-peak). The nitroso species
formed from the adsorbed NO at LT-peak will react with ammonia [45]. In contrast, the nitro
compounds formed from the NO adsorbed at HT-peak only decomposed at high temperature and
reacted with –NH\(_2\)[47]. Therefore, the area ratio between LT-peak and HT-peak could be utilized
to evaluate the activity of SCR catalyst and investigate the mechanism of catalytic process. In Fig.
9, after the addition of Mo, there is a shift in LT-peak and HT-peak toward lower temperature
region and the height of peak decreased, which indicates that the Mn\(_3\)Mo\(_{1.25}\)/γ-Al\(_2\)O\(_3\) had a lower
SCR activity temperature. In addition, the area ratio between LT-peak and HT-peak increased from
4.6 to 5.13, which means that more nitroso species formed on the Mn\(_3\)Mo\(_{1.25}\)/γ-Al\(_2\)O\(_3\) so that higher
low temperature SCR activity.

![Fig. 9. NO-TPD profiles of the Mn\(_3\)/γ-Al\(_2\)O\(_3\) and Mn\(_3\)Mo\(_{1.25}\)/γ-Al\(_2\)O\(_3\)](image-url)
Fig. 10. NO-TPD profiles of the Mn$_2$Mo$_x$/γ-Al$_2$O$_3$

Fig. 10 shows that the LT-peak of Mn catalyst shifted to lower temperature region with the Mo loading increased to 2.5 wt% and a new desorption peak formed below 200°C. With the increase in Mo loading to 10 wt%, the center of the new peak shifted to below 100°C. Meanwhile, the intensity of HT-peaks weakened gradually and disappeared when the Mo loading was 7.5 wt%. This suggests that the addition of Mo had a significant influence on the adsorption of NO.

3.2.6. Mechanism of low temperature SCR over Mo-modified Mn-based catalyst

Four sets of NO adsorption and desorption experiment were carried out to investigate the adsorption of NH$_3$ and NO on the Mn$_3$Mo$_{1.25}$/γ-Al$_2$O$_3$ catalysts.

I: The adsorption of NH$_3$ (500ppm) +NO (500ppm) +O$_2$ (3%) at 25°C for 1h, and then purged with N$_2$ until outlet concentration of NO became below 5ppm, followed by performing TPD process at 10°C/min;
II: The adsorption of NH\textsubscript{3} (500ppm) + O\textsubscript{2} (3\%) at 25°C for 1h, switched to the adsorption of NO (500ppm) + O\textsubscript{2} (3\%) at 25°C for 1h, and then purged with N\textsubscript{2} until outlet concentration of NO became below 5ppm, followed by performing TPD process at 10°C /min;

III: The adsorption of NO (500ppm) +O\textsubscript{2} (3\%) at 25°C for 1h, switched to the adsorption of NH\textsubscript{3} (500ppm) + O\textsubscript{2} (3\%) at 25°C for 1h, and then purged with N\textsubscript{2} until outlet concentration of NO became below 5ppm, followed by performing TPD Process at 10°C /min;

IV: The adsorption of NO (500ppm) +O\textsubscript{2} (3\%) at 25°C for 1h, and then purged with N\textsubscript{2} until outlet concentration of NO became below 5ppm, followed by performing TPD Process at 10°C /min.

In Fig. 11, Curve III coincided with Curve IV resulted from the adsorption of NO on the fresh catalyst. However, Curve I shifted as compared with Curves III and IV when NH\textsubscript{3} and NO were simultaneously introduced, which indicates that NH\textsubscript{3} adsorbs on certain sites competitively with NO. Curve II shifted up significantly in the first 25 min, and then shifted down to the level of curve III and IV. It can therefore be concluded that some of the adsorption sites are occupied randomly by NH\textsubscript{3} owing to NH\textsubscript{3} preferentially adsorbed on the catalyst. According to the calculation, the adsorption capacity of Curve I was larger than that of Curve II, which is attributed to gas phase NH\textsubscript{3} being competitively adsorbed with NO on the catalyst surface. Therefore, the adsorption sites of the catalysts could be classified into four types: Type 1, adsorbs NH\textsubscript{3} preferentially; Type 2, adsorbs NO preferentially; Type 3, adsorbs NH\textsubscript{3} competitively, and Type 4, random adsorption sites, on which both NH\textsubscript{3} and NO can be adsorbed depending on their molecular movement.

As shown in Fig. 12, TPD Curves i and ii did not show high temperature desorption peak of NO and NO\textsubscript{2}. TPD Curves iii and iv are similar, but low temperature desorption peaks of curve iii for NO are weak and high temperature desorption peaks also shifted. Compared Curve i with iii, TPD results did not show high temperature desorption peaks, which indicated that bidentate nitrate and bridge nitrate were not easy to form on the surface treated by NH\textsubscript{3}[5]. It is speculated that O\textsubscript{2} will
accelerate the formation of these stable NO complexes, which only react with NH$_3$ at high temperature and are responsible for the deactivation of SCR catalysts.

![Fig. 11 NO adsorption over the Mn$_3$Mo$_{1.25}$/γ-Al$_2$O$_3$ catalyst](image1)

**Fig. 11 NO adsorption over the Mn$_3$Mo$_{1.25}$/γ-Al$_2$O$_3$ catalyst**

It is generally believed that SCR reaction starts with the adsorption of NH$_3$. But the mechanisms of low temperature SCR for catalysts with different active components and support are different. Marban et al. [48] suggested that there are two different SCR mechanisms associated with different NH$_3$ species. In Fig. 12, NO-TPD peaks disappeared in Curves i and ii, which is attributed to the reaction between NO and ad-NH$_3$ on the catalyst surface. As shown in Fig. 13, the Mn$_3$Mo$_{1.25}$/γ-Al$_2$O$_3$ catalyst adsorbed NO for 1h and then carried out TPD test from 25°C to 150°C (Process I), followed by purging with N$_2$ for 1h (Process II). In Process III, NH$_3$ and O$_2$ were introduced, and temperature was kept at 150°C. In Process IV, TPD test was carried out from 150°C to 630°C. In
order to compare, a similar test without Process III was taken into consideration, which is also shown in Fig. 13 (dashed line). The amount of NOx being adsorbed at low temperature around 250°C decreased, even disappeared, and high temperature species were also reduced to some extent, which directly proves that low temperature SCR proceeds between the adsorbed NH₃ species and the adsorbed NO species via Langmuir-Hinshelwood (L-H) mechanism.

![Fig. 13 TPD profiles of NO adsorption over the Mn₃Mo₁.25/γ-Al₂O₃ catalyst, Process I: TPD from 25-150°C; Process II: N₂ purging for 60min; Process III: adsorbed NO reacted with NH₃; Process IV: TPD from 150°C-630°C](image)

In this study, the addition of Mo was found to improve NH₃ adsorption capacity of the catalyst. With the increase in Mo loadings, the amount of surface acid sites increased, which was vital to SCR reaction. In Fig. 14, when in the presence of gas phase O₂, the adsorption peaks of NO and NO₂ decreased. Therefore, it can be concluded that the addition of Mo could reduce NO adsorption on the catalysts surface but did not result in a lower low temperature SCR activity. Instead, the low temperature SCR efficiency of the Mn₃Mo₁.25/γ-Al₂O₃ was much higher than that of the Mn₃/γ-Al₂O₃ catalyst. Additionally, in Fig.12, Curve II showed a small desorption peak at 100°C as compared with Curve III. This means that the NOx being desorbed reacted with the NH₃ that is adsorbed on the catalyst when the temperature was raised. Therefore, it is illustrated that low temperature SCR reaction could proceed via Eley-Rideal (E-R) path.
Fig. 14 Effect of O2 on the NO adsorption over the Mn3/γ-Al2O3 and Mn3Mo1.25/γ-Al2O3 catalyst

It is clear that the Mn3Mo1.25/γ-Al2O3 catalyst performed outstanding low temperature SCR activity as a result of Mo addition. It can be concluded that the addition of Mo improves the properties of the catalysts in several aspects. Firstly, the addition of Mo species to the catalyst inhibits the growth of MnOx clusters, therefore leading to the good dispersion of MnOx on the γ-Al2O3 surface. Secondly, the addition of Mo enhances the formation of Mn2O3 on the catalyst, which accelerates the formation of intermediates, whereafter the -NH3 is transformed into -NH2 via H-abstraction. Thirdly, the addition of Mo on the catalyst mitigates the deactivation of the catalysts. In Fig. 13, NO adsorbed species at HT-Peak region were very difficult to react with NH3 at 150°C. The reason is that these NO formed some complexes (bridged and bidentate nitrates) that are thermally stable. However, the addition of Mo could inhibit the transformation of nitrites into nitrates thus slow down the self-deactivation of the catalysts.

Therefore, the low temperature SCR reaction is composed of 4 steps as shown in Fig. 15: Step 1, the adsorption of NH3 and NO on the surface of the catalysts; Step 2, the H-abstraction of adsorbed NH3, resulting in the formation of -NH2 species as well as the formation of reactive nitrites from the adsorbed NO species; Step3, the -NH2 species reacted with nitrites or gas phase NO via L-H and E-R mechanism, forming intermediate products -NH2NO, and Step4, -NH2NO decomposed into N2 and H2O.
4. Conclusions

In this study, the Mn₃Mo₁.25/γ-Al₂O₃ catalyst achieved a high NO conversion of around 96% at 150-300°C. It is found that the addition of Mo to Mn-based SCR catalyst could not only inhibit the growth of MnOₓ bulks, favour the formation of Mn³⁺ state and promote the NH₃ adsorption capacity of the catalyst, but also act as a moderator to adjust the effective operating temperature window of the SCR reaction, which could be achieved by adjusting Mo loading. Moreover, the addition of Mo was found to mitigate the deactivation of the catalysts. The study on SCR mechanism showed that the low temperature SCR starts from the adsorption of NH₃ on Mn³⁺ sites. The low temperature SCR followed mainly E-R mechanism, but L-H mechanism also plays a role to some extent.

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