A review of Mn-containing oxide catalysts for low temperature selective catalytic reduction of NO\textsubscript{x} with NH\textsubscript{3}: reaction mechanism and catalyst deactivation

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Atmospheric pollutants of nitrogen oxides (NO\textsubscript{x}) can be reduced by selective catalytic reduction (SCR). SCR of NO\textsubscript{x} with ammonia (NH\textsubscript{3}) at low temperatures has attracted much interest for high nitric oxide (NO) conversion, and this method is dominated by catalysts. Manganese (Mn)-containing oxide catalysts exhibit high activity and selectivity for the unique redox property of manganese oxides (MnO\textsubscript{x}). The reaction mechanisms and deactivation processes are summarized in this review. SCR of NO\textsubscript{x} with NH\textsubscript{3} follows both the Langmuir–Hinshelwood and the Eley–Rideal mechanisms, which also contribute to the nitrous oxide formation. Fast SCR has a higher reaction rate than standard SCR. Mn-containing catalysts could also be deactivated by sulfur oxides and water vapor. The deactivation process of sulfur dioxide can be classified into two categories: deposition of (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} and sulfation of active sites. The deactivation caused by water vapor can be attributed to the competitive adsorption. The adsorption of water on catalysts’ surface blocked the active sites, which are provided for the adsorption of NH\textsubscript{3} and NO. Alkali, alkaline earth and heavy metal ions existing in fine fly ash can also damage the catalysts’ acid sites. A notable improvement on performance was obtained when Mn-containing catalysts were doped with a transition metal, for these enhanced its adsorption capacity and oxidation ability. Furthermore, this review gives a comprehensive discussion of the synergistic mechanism between bi-metal or multi-metal oxides. Major conclusions and several possible directions for further research are presented finally.

1. Introduction

Nitrogen oxides (NO\textsubscript{x}) are a series of active gases, and include nitrogen dioxide (NO\textsubscript{2}), nitrogen oxide (NO) and nitrous oxide (N\textsubscript{2}O), and so on. Human activities cause a huge emission rate of NO\textsubscript{x}, which is double that of the biotic and abiotic nitrogen fixation rates. Released NO\textsubscript{x} can cause a series of environmental issues, such as photochemical smog, acid rain, and ozone depletion, and it can affect global tropospheric chemistry.\textsuperscript{1-4} Great efforts have been devoted to abating the emission of NO\textsubscript{x}.

The technologies used to control NO\textsubscript{x} emission can be categorized as combustion controls and post-combustion controls.\textsuperscript{5,6} Combustion controls, which aim to control the production of NO\textsubscript{x}, include low NO\textsubscript{x} burners,\textsuperscript{7} air graded burning and staged fuel combustion.\textsuperscript{8} Post-combustion controls aim to decrease the NO\textsubscript{x} produced by reducing active N to fixed nitrogen gas (N\textsubscript{2}). The technologies for reducing NO\textsubscript{x} from flue gas can be divided into: direct decomposition,\textsuperscript{9,10} selective catalytic reduction (SCR),\textsuperscript{11,12} selective non-catalytic reduction (SNCR),\textsuperscript{13,14} hybrid SNCR/SCR\textsuperscript{15} and NO\textsubscript{x} storage-reduction catalysis.\textsuperscript{16} With the advantages of high efficiency and low cost, NO\textsubscript{x} emitted from stationary sources (e.g., thermal plants or industrial boilers) has been predominantly controlled by SCR of NO with ammonia (NH\textsubscript{3}-SCR) in the presence of excess oxygen (O\textsubscript{2}) for decades.\textsuperscript{17}

The catalyst to be used is a decisive factor in the process of decreasing NO\textsubscript{x} (deNO\textsubscript{x}). The common catalysts include noble metal catalysts,\textsuperscript{18} metal-exchanged zeolite catalysts,\textsuperscript{19} metal oxide catalysts,\textsuperscript{20,21} heteropoly acid catalysts,\textsuperscript{22} and so on. Metal oxide catalysts are widely applied in NH\textsubscript{3}-SCR. Nowadays, the most widely used catalysts are vanadium(v)-based catalysts and tungsten trioxide (WO\textsubscript{3}) and/or molybdenum trioxide (MoO\textsubscript{3}) doped vanadium(v) oxide (V\textsubscript{2}O\textsubscript{5})/titanium dioxide (TiO\textsubscript{2}) catalysts. These are usually installed at the upstream of flue gas because they require a higher working temperature of 300–400 °C.\textsuperscript{23} However, some tough problems have not been solved, such as the effect of excessive dust pollution to the catalysts upstream of the flue, the deactivation by sulfur dioxide (SO\textsubscript{2}) and alkali metal ions, the poor thermal stability at high temperatures and the toxicity of vanadium from the disabled catalysts.\textsuperscript{24} One of the efficient ways to overcome these obstacles is transferring the SCR reactor from upstream to downstream of
the flue gas, where there is relatively less dust and sulfur oxides in the flue gas but a lower temperature below 300 °C.\textsuperscript{27}

A series of metal oxide catalysts have been investigated to adapting low temperature, such as cerium (Ce), cobalt (Co), copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo), nickel (Ni) and V.\textsuperscript{26–30} Of these, manganese oxides (MnO\textsubscript{x}) catalysts show a notable NO conversion and N\textsubscript{2} selectivity for its multi oxidation state, high valence state and characteristic crystallinity. Peña \textit{et al.}\textsuperscript{26} advocated that MnO\textsubscript{x}/TiO\textsubscript{2} had the highest activity among Co, chromium (Cr), Cu, Fe, Mn, Ni and V oxides supported on TiO\textsubscript{2} at low temperatures. Manganese dioxide (MnO\textsubscript{2}) and manganese(III) oxide (Mn\textsubscript{2}O\textsubscript{3}) show the highest activity and N\textsubscript{2} selectivity, respectively, among several MnO\textsubscript{x}.\textsuperscript{31} The activity and poison tolerance can be improved by doping with other transition metals. Ceria (CeO\textsubscript{2}) provides sufficient oxygen in the reaction of redox NO\textsubscript{x}, and improves the activity of MnO\textsubscript{x} catalysts.\textsuperscript{32–34} Mn–Fe spinel shows an excellent SCR performance at low temperature.\textsuperscript{35} Other Mn containing catalysts, such as MnO\textsubscript{x}/CoO\textsubscript{x}/TiO\textsubscript{2},\textsuperscript{28,36} MnO\textsubscript{x}/CrO\textsubscript{x}/TiO\textsubscript{2},\textsuperscript{37,38} MnO\textsubscript{x}/CuO,\textsuperscript{39,40} lanthanum manganite (LaMnO\textsubscript{3}),\textsuperscript{41} have been investigated by many researchers. Mn containing catalysts have been recognized as the potential alternative for industrial applications.

To date, advances in low temperature NH\textsubscript{3}-SCR of NO\textsubscript{x} have been reviewed.\textsuperscript{5,6,42} A review by Li \textit{et al.}\textsuperscript{43} summarized the use of metal oxides and zeolite catalysts and focused on the catalysts’ components, preparation process and catalytic performance, however, the reaction mechanisms were not clarified clearly. A recent review in 2016 by Liu \textit{et al.}\textsuperscript{44} summarized the use of MnO\textsubscript{x}-based catalysts and concentrated on the technological processes and improvement methods, however, little effort was made to summarize the reaction mechanisms and catalyst deactivation processes.

In this review, the advances in the use of Mn containing oxide catalysts are summarized. The focal point of this review is to address the reaction mechanisms and deactivation processes of Mn containing oxide catalysts. The N\textsubscript{2} selectivity and side reactions are discussed together. This review gives a comprehensive discussion of the synergistic effects between bi-metal or multi-metal oxides. The deactivation process using sulfur oxides, water vapor, alkali metal and heavy metal ions and the regeneration methods are summarized. Finally, the major conclusions and several possible directions of research are presented.

2. Reaction mechanisms

To meet the newest and stringent emission standards, (NO\textsubscript{x} concentration \leq 50 mg m\textsuperscript{-3}),\textsuperscript{45} academic researchers and engineers are more interested in use of low temperature SCR, which is one of the efficient ways to install a processor downstream of the flue. A number of metal oxide catalysts have been investigated so far. Transition metal oxides play an important role in low temperature SCR catalysts, such as V\textsubscript{2}O\textsubscript{5}, MnO\textsubscript{2}, CeO\textsubscript{2} and copper oxide (CuO). Of these, MnO\textsubscript{2} shows an excellent performance because of its different crystallinity, special surface area and multi oxidation. It is vital to elucidate the reaction mechanisms for future research. In this section, the reaction mechanisms of NH\textsubscript{3}-SCR over Mn-containing oxide catalysts are summarized.

2.1 Standard SCR

The NH\textsubscript{3}-SCR of NO aims to reduce active N to fixed N\textsubscript{2}, which is harmless to the atmosphere. In the presence of excess O\textsubscript{2}, the main overall reaction is eqn (1).\textsuperscript{46} A number of studies have proposed that eqn (1) shows the reaction stoichiometry in typical SCR conditions.\textsuperscript{47–50} In the absence of O\textsubscript{2}, reaction in eqn (1) would convert into the reaction in eqn (2):\textsuperscript{51}

\[ 4\text{NH}_3 + 4\text{NO} + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} (g), \Delta G_{298} = -1651 \text{ kJ mol}^{-1} \]  (1)

\[ 4\text{NH}_3 + 6\text{NO} \rightarrow 5\text{N}_2 + 6\text{H}_2\text{O} (g), \Delta G_{298} = -1821 \text{ kJ mol}^{-1} \]  (2)

Because the content of NO is more than 90% among NO\textsubscript{x}, eqn (1) is proposed as the standard SCR reaction and dominates the reaction stoichiometry. It is reported widely that the NH\textsubscript{3}-SCR of the NO reaction when comparing the stoichiometric conditions follows both the Langmuir–Hinshelwood (L–H) mechanism and the Eley–Rideal (E–R) mechanism.\textsuperscript{52–55} Through the L–H mechanism, both NH\textsubscript{3} and NO are adsorbed on the surface of catalysts. However, via the E–R mechanism, adsorbed NH\textsubscript{3} reacts with gaseous NO. It is suggested that the gaseous NH\textsubscript{3} could be adsorbed on both Lewis acid sites and Bronsted acid sites, however, the gaseous NO is mainly adsorbed by a physical adsorption process.\textsuperscript{54} The adsorption of NH\textsubscript{3} has been recognized as the first step of the SCR reaction because it is easier for NH\textsubscript{3} to be adsorbed on acid sites rather than NO\textsubscript{2} and the reaction products.\textsuperscript{53}

The SCR process over MnO\textsubscript{2} catalysts via the L–H mechanism can be approximately described as follows:\textsuperscript{25,53,56}

\[ \text{NH}_3(g) \rightarrow \text{NH}_3(ad) \]  (3)

\[ \text{NO}(g) \rightarrow \text{NO(ad)} \]  (4)

\[ \text{Mn}^{n+} = \text{O} + \text{NO(ad)} \rightarrow \text{Mn}^{(n-1)+} - \text{O} - \text{NO} \]  (5)

\[ \text{NH}_3(ad) + \text{Mn}^{(n-1)+} - \text{O} - \text{NO} \rightarrow \text{Mn}^{(n-1)+} - \text{O} - \text{NO} - \text{NH}_3 \rightarrow \text{Mn}^{(n-1)+} + \text{OH} + \text{N}_2 + \text{H}_2\text{O} \]  (6)

\[ \text{Mn}^{(n-1)+} - \text{OH} + 1/2\text{O}_2 \rightarrow \text{Mn}^{n+} = \text{O} + 1/2\text{H}_2\text{O} \]  (7)

Eqn (3) and (4) are the adsorption of gaseous NH\textsubscript{3} and NO. NH\textsubscript{3} is usually adsorbed on the Lewis acid sites and Bronsted acid sites to form adsorbed NH\textsubscript{3}, species of coordinated NH\textsubscript{3} and ionic NH\textsubscript{4}\textsuperscript{+}, respectively.\textsuperscript{57} Nevertheless, the coordinated NH\textsubscript{3} on the Lewis acid sites possesses a higher thermal stability than the ionic NH\textsubscript{4}\textsuperscript{+} on Bronsted acid sites. Manganese cations can provide a great number of Lewis acid sites.\textsuperscript{48,58}

Fang \textit{et al.}\textsuperscript{59,60} investigated the adsorption of NH\textsubscript{3} on the Mn\textsubscript{3}O\textsubscript{4} (222), manganese[III] oxide (Mn\textsubscript{3}O\textsubscript{4}) (211) and MnO\textsubscript{2} (110) surfaces using density functional theory. It is claimed that, with more negative adsorption energy values and the shorter
Coordinated NH3 could be deprived of a hydrogen and be cations are reduced as Mn (MnO2 13 14 16 19 21 et al. Eigenmann NH4NO2 could be decomposed to NH2NO and H2O, and is then followed by Mn5O8,Mn2O3 and Mn3O4.

Activated NH2 species on the catalysts’ surface reacted with oxides to form an amine (NH2) species [eqn (9)]. Labile oxygen activated by the labile oxygen or the lattice oxygen of metal

The adsorbed NO is oxidized by the high valency state Mn1+ cations, (e.g., Mn4+) on the catalysts’ surface to form adsorbed monodentate nitrite (Mn(¿1–)–O–NO) and the very metal cations are reduced as Mn(¿1+) [eqn (5)]. Furthermore, Mn(¿1–)–O–NO reacts with adsorbed NH3 species to form Mn(¿1–)–O–NO–NH3, which decomposes subsequently to N2 and water (H2O) [eqn (6)]. Then, the reduced Mn(¿1+) ions are regenerated by gaseous O2 [eqn (7)].

The SCR process over MnOx catalysts via the E–R mechanism can be described approximately as follows:35,48,61

NH3(g) → NH3(ad) (8)

NH3(ad) + Mn(¿x–)=O → NH2(ad) + Mn(¿1–)+–OH (9)

NH2(ad) + NO(g) → NH2NO → N2 + H2O (10)

Mn(¿1–)+–OH + 1/4O2 → Mn(¿x–)=O + 1/2H2O (11)

The adsorption of NH3 on the Lewis acid sites is recognized as the first step of NO reduction via the E–R mechanism. Coordinated NH3 could be deprived of a hydrogen and be activated by the labile oxygen or the lattice oxygen of metal oxides to form an amine (NH2) species [eqn (9)]. Labile oxygen can be released via the change of the valence states of Mn. Activated NH2 species on the catalysts’ surface reacted with gaseous NO to form the most important intermediate of NH2NO, which subsequently decomposes to N2 and H2O [eqn (10)]. Then, the reduced Mn(¿1+) cations could be oxidized by O2.

Furthermore, the formation of NH4NO2 is a typical SCR mechanism for Mn-containing catalysts. Qi and Tang,66 and Eigenmann et al.62 proposed an amide–nitrilamine type mechanism, which is actually similar to the E–R mechanism. An extra species of NH4NO2 was presented in this mechanism. NH4NO2 could be decomposed to NH2NO and H2O, and is then decomposed to N2 and H2O [eqn (12)–(14)]:

OH(ad) + NO2(ad) → O(ad) + HNO2(ad) (12)

NH3(ad) + HNO2(ad) → NH4NO2(ad) → NH2NO(ad) + H2O (13)

NH2NO(ad) → N2 + H2O (14)

In accordance with the transient eqn (3)–(11), Mn4+–O–NO–NH3 and NH2NO are the most important intermediate in the reaction of the L–H mechanism and E–R mechanism, respectively. There is a quite similarity between these two different mechanisms. A comproportionation, (i.e., N4+ and N3–, N2+ and N2–) occurs on both the L–H and E–R mechanism (eqn (6) and (10)).25,63

2.2 Fast SCR

A fast SCR reaction of NH3 with NO + NO2 over Mn-containing oxide catalysts has been reported. It is suggested that the fast SCR has a higher reaction rate than standard SCR.64 Fast SCR was firstly investigated by Koebel et al., and Madia et al.65–67 The general reaction can be described as follows:56,69

4NH3 + 2NO2 + O2 → 3N2 + 6H2O(g), ΔG298° = −1412 kJ mol−1 (15)

4NH3 + 2NO + 2NO2 → 4N2 + 6H2O, ΔG298° = −1581 kJ mol−1 (16)

In the presence of O2, NO can be oxidized by active oxygen to form NO2 [eqn (17)].70 Judged by the Gibbs free energy, the reaction shown in eqn (15) does not occur easily and consequently limits the rate of eqn (15) or (16). Mn-containing metal oxide catalysts could catalyze this reaction in some extent:71,72

2NO + O2 → 2NO2, ΔG298° = −70 kJ mol−1 (17)

NO2 is the difference between fast SCR standard SCR. NO2 acts as a more efficient oxidizing agent than O2 in the redox process of the SCR reaction. NO2 can form surface nitrates and nitrates via dimerization:73

2NO2 → N2O4 (18)

N2O4 + H2O → HNO2 + HNO3 (19)

NH4NO3 is formed by the reaction between NH3 and HNO3. NH4NO3 or its related surface species is the key intermediate in the fast SCR process. The reaction processes can be described as follows:

2NH3 + 2NO2 → N2 + NH4NO3 + H2O (20)

NH4NO3 + NO → N2 + NO2 + 2H2O (21)

Many researchers considered that NH4NO3 would be solid below 170 °C. NH4NO3 could be reduced by NO at a higher temperatures [eqn (21)].54,74 It is pointed out that NH3 can restrain fast SCR by inhibiting the formation of NO2 at 150–170 °C.75 Actually, eqn (21) can be described as two intermediate reactions:

Table 1 The NO conversion of pure MnOx samples

<table>
<thead>
<tr>
<th>MnOx</th>
<th>NO conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>353</td>
</tr>
<tr>
<td>MnO2</td>
<td>13</td>
</tr>
<tr>
<td>Mn3O4</td>
<td>14</td>
</tr>
<tr>
<td>MnO4</td>
<td>18</td>
</tr>
</tbody>
</table>

* Reaction conditions: [NO] = 720 ppm, [NH3] = 800 ppm, [O2] = 3%.

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There is a chemical equilibrium in the fast SCR process [eqn (22)]. The formation of HNO3 will be restrained while the NH3 concentration is raised, and that inhibits the formation of NO2 [eqn (23)]. Among the fast SCR processes, the vital process is the redox reaction between NO and HNO3, which dominates the rate of fast SCR.

The performance of low temperature SCR has been extensively investigated. Excellent NO conversion and N2 selectivity has been observed using simulated flue gas in the laboratory. Qi and Yang observed nearly 100% NO conversion on the MnOxFeOx catalyst sintered at 120 °C. Long et al. investigated the Fe–Mn-based catalysts. These catalysts showed nearly 100% NO conversion at 100–180 °C. Recently, France et al. studied the CeO2 modified FeMnOx catalysts, and more than 95% NO conversion was obtained at 90–135 °C without the influence of SO2 and H2O. Zhu et al. studied the holmium (Ho) modified Fe-Mn/TiO2 catalysts, which revealed good performance for NO conversion and high SO2 tolerance. However, more attempts need to be made to understand the fundamental mechanism of low temperature SCR, such as surface chemistry, crystal structure, kinetics and scientific reaction mechanism. These have a great influence on the performance of catalysts and knowledge of them would be beneficial in designing a new catalyst.

2.3 Side reactions

As the reductant, NH3 is a vital resource in the SCR reaction. NH3 is consumed mainly via N2 and N2O formation and the oxidation of the catalyst to NOx. The wastage of NH3 is a huge additional cost of the deNOx process. To decrease the wastage of NH3, an appropriate NH3/NO ratio is necessary. Authors agree that a NH3/NO ratio near to 1 is good. Furthermore, undesired reactions can occur during the SCR process. Eqn (24) and (25) show the undesired ammonia loss:

\[ 4\text{NH}_3 + 4\text{O}_2 \rightarrow 2\text{N}_2\text{O} + 6\text{H}_2\text{O}(g), \Delta G^{298} = -1102 \text{ kJ mol}^{-1} \] (24)

\[ 4\text{NH}_3 + 3\text{O}_2 \rightarrow 2\text{N}_2 + 6\text{H}_2\text{O}(g), \Delta G^{298} = -1310 \text{ kJ mol}^{-1} \] (25)

These are the thermodynamically favored reactions but they occur rarely in practice.\textsuperscript{51} In addition, there is another undesired reaction during the NH3-SCR process:

\[ 4\text{NH}_3 + 5\text{O}_2 \rightarrow 4\text{NO} + 6\text{H}_2\text{O}, \Delta G^{298} = -964 \text{ kJ mol}^{-1} \] (26)

Wang et al.\textsuperscript{49} claim that eqn (26) may replace eqn (1) as the dominant reaction over MnOx/TiO2 catalysts when the temperature was raised higher than 175 °C. This was proved by the determination of the components of outlet flue gas. This oxidation of NH3 gives a decline in NO conversion and extra consumption of NH3.

When the concentration of NH3 is appropriate, the formation of N2O is the primary waste of NH3 and this decreases the N2 selectivity [eqn (27)].\textsuperscript{52}

\[ 4\text{NH}_3 + 4\text{NO} + 3\text{O}_2 \rightarrow 4\text{N}_2\text{O} + 6\text{H}_2\text{O}(g), \Delta G^{298} = -1240 \text{ kJ mol}^{-1} \] (27)

Adsorbed NH3 is oxidized on the catalyst surface to form an amine species (NH3\textsuperscript{+}), which subsequently reacts with NO to form N2 and H2O. However, when a further hydrogen atom is abstracted from NH3 to form an NH species, a N2O species will be formed by the reaction of the NO and NH species.\textsuperscript{53} Both the L–H mechanism and the E–R mechanism pathways contribute to N2O formation.

As previously mentioned, in the L–H mechanism, physically adsorbed NO can be oxidized by Mn\textsuperscript{++} to Mn\textsuperscript{(n-1)+}–O–NO\textsuperscript{2-}, which can be further oxidized to monodentate nitrate (Mn\textsuperscript{(n-1)+}–O–NO\textsuperscript{2-}) [eqn (28)]. The Mn\textsuperscript{(n-1)+}–O–NO\textsuperscript{2-} can react with adsorbed NH\textsubscript{3} to form Mn\textsuperscript{(n-1)+}–O–NO\textsubscript{2}–NH\textsubscript{3}. Subsequently, Mn\textsuperscript{(n-1)+}–O–NO\textsubscript{2}–NH\textsubscript{3} will be decomposed to N2O [eqn (29)].

\[ \text{Mn}^{(n-1)+}–\text{O}–\text{NO} + (1/2)\text{O}_2 \rightarrow \text{Mn}^{(n-1)+}–\text{O}–\text{NO}_2 \] (28)

\[ \text{Mn}^{(n-1)+}–\text{O}–\text{NO}_2 + \text{NH}_3(ad) \rightarrow \text{Mn}^{(n-1)+}–\text{O}–\text{NO}_2–\text{NH}_3 \rightarrow \text{Mn}^{(n-1)+}–\text{OH} + \text{N}_2\text{O} + \text{H}_2\text{O} \] (29)

As previously mentioned in Section 2.2, the reaction of NH3 with NO is a vital step in the fast SCR process. Zhu et al.\textsuperscript{74} speculated that NH4NO3 could be decomposed to N2O and H2O via the L–H mechanism [eqn (30)]. Referring to eqn (28) and (29), the formation of N2O could be attributed to the better capacity for NH3 activation and adsorbed active nitrate species.

\[ \text{NH}_3\text{NO}_3 \rightarrow \text{N}_2\text{O} + 2\text{H}_2\text{O} \] (30)

As mentioned previously, in the E–R mechanism, NH3 species can react with gaseous NO to form N2 and H2O. While the NH3 species is further oxidized on the metal cation to NH species, N2O will be formed by the reaction of the NH species and gaseous NO [eqn (31) and (32)].\textsuperscript{55,56,64} It is obvious that the formation of NH3NO3 is a crucial step of NO reduction, which is directly related to the NO conversion and N2 selectivity.\textsuperscript{58}

\[ \text{NH}_2 + \text{Mn}^{n+} = \text{NH} + \text{Mn}^{(n-1)+}–\text{OH} \] (31)

\[ \text{NH} + \text{NO}(g) \rightarrow \text{N}_2\text{O} + \text{H}^+ \] (32)

Whether the adsorbed NO is oxidized to monodentate nitrate or the NH3 species is dehydrated to NH, the N2 selectivity will be restrained and N2O is formed.\textsuperscript{45} This is an important difference from the standard SCR. The formation of N2 and N2O during the SCR process is illustrated in Fig. 1.

Hints at by the previous equations, it is obvious that the two N atoms in N2O originate from NO and NH3, respectively. Suárez et al.\textsuperscript{56} pointed out that N2O did not primarily originate from the NH3 oxidation reaction. The feasible main reaction path is that between the coordinated NO3\textsuperscript{−} (generated from NO/
Nitric oxide (NO) in the presence of O₂ and the adsorbed NH₃. Tang et al. demonstrated that the N₂O selectivity of the SCR reaction over β-MnO₂ was higher than that over z-Mn₃O₄ at 150 °C. The N₂O is generated directly from the reaction of NO with NH₃ via the E–R mechanism. Use of calcium (Ca) modification improves the performance of N₂ selectivity for Mn-containing catalysts.

It is suggested that N₂O formation mainly resulted via the E–R mechanism. Yang et al. studied the mechanism of N₂O formation over Mn–Fe spinel catalysts. N₂O formation via the E–R mechanism was much more than via the L–H mechanism over the Mn–Fe spinel catalysts. In addition, N₂O selectivity was not promoted by increasing the NO concentration, but it was increased with the increase in NH₃ concentration. N₂O selectivity is also related to the gas hourly space velocity (GHSV). It was also found that N₂O in the SCR reaction over Mn–Ce catalysts was generated via the E–R mechanism, not the L–H mechanism. The choice of E–R or L–H mechanisms will vary with the changes of temperature. It is reported that the L–H mechanism plays the main role below 150 °C, and the E–R mechanism way dominates the SCR reaction at higher temperatures.

2.4 Synergistic effect

A pure metal oxide may not be suitable for practical applications because of its defects. However, the property of one metal oxide can be improved by introducing foreign metal cations into its lattice. There will also be an interaction between different metal oxides. For example, reports in the literature indicate that Mn–Ce mixed oxide catalysts demonstrated the best performance among a multitude of metal oxide catalysts. Ceria can enhance the adsorption of NO and O₂, which benefits the oxidation of NO to NO₂ and improve sulfur resistance. Qi and Tang found that the oxidation of NO to NO₂ was increased significantly after addition of ceria to MnO₂ and that it speeded up the overall process. Actually, pure CeO₂ cannot be applied in industry because of its small specific surface area and low thermal stability. Meanwhile, as is reported, modification with titanium (Ti) or tin (Sn) can improve the SCR property of cerium oxides. Qi et al. and Imamura et al. found using X-ray diffraction patterns that there was no manganese oxide phase in the calcined Mn–Ce catalyst prepared by a co-precipitation method. This indicated that strong interactions exist between manganese and cerium oxides, because MnO₂ and MnO₃ can be detected in pure manganese oxide calcined at the same temperature.

The redox property of catalysts is the key factor of the NH₃-SCR processes. Electronic transfer, showing as oxidation and reduction, plays quite an important role in catalytic reactions. The redox couples exist over the metal oxide catalysts, such as Mn⁴⁺/Mn³⁺, Ce⁴⁺/Ce³⁺ and Fe³⁺/Fe²⁺, which provide the redox cycles with excess oxygen. The activity of bi-metal and multi-metal oxide catalysts could be promoted by dual redox cycles. The general formula can be described as follows:

\[ M^{n+} + N^{m+} \leftrightarrow M^{(n-1)+} + N^{(m+1)+} \]  \hspace{1cm} (33)

There is a typical SCR reaction process via the E–R mechanism on Mn–Ce/TiO₂ and Mn–Ce/aluminium oxide (Al₂O₃) catalysts. Manganese oxides and ceria oxides also interact. They can form a solid solution because of the similarity of their structure. Ceria has a superior oxygen storage performance. Thus, the process of oxidizing Mn⁷⁺ to Mn⁴⁺ is enhanced by using ceria.

Liu et al. investigated a Mn–Ce–Ti mixed oxide catalyst prepared using a hydrothermal method, and found that there were dual redox cycles, such as Mn⁴⁺ + Ce³⁺ → Mn³⁺ + Ce⁴⁺ and Mn³⁺ + Ti³⁺ → Mn⁵⁺ + Ti⁴⁺. These dual redox cycles can promote each other and facilitate the electron transfer between Mn, Ce and Ti active sites by decreasing the migration energy. The proposed schemes are as follows (Fig. 2).

The scheme shows that Mn cation sites may be the main active site for the adsorption of N. Furthermore, the addition of Ce, Fe, Cu, Ni and so on, may show a synergistic effect, which

![Fig. 1](image1.png) The scheme of the SCR reaction through L–H and E–R mechanisms over Mn–Fe spinel catalyst. (Reprinted with permission from ref. 35. Copyright 2014 American Chemical Society.)

![Fig. 2](image2.png) The scheme of dual redox cycle during SCR process. (Reprinted with permission from ref. 96. Copyright 2014 American Chemical Society.)
facilitates the generation of Mn$^{4+}$ from Mn$^{3+}$. Kwon et al.\textsuperscript{97} studied the MnO$_x$/CeO$_2$–TiO$_2$ catalyst system. When Ce was added to Mn/Ti, an oxygen bridge of Mn–O–Ce was formed and, thus enhanced the binding between Mn and O$_2$. This oxygen bridge provided a channel for the electron transfer between manganese and cerium cations, and particularly accelerated the oxidation of Mn$^{3+}$ to Mn$^{4+}$ by Ce$^{4+}$\textsuperscript{23}.

\[
\text{Mn}_2\text{O}_3 + 2\text{CeO}_2 \rightarrow 2\text{MnO}_2 + \text{Ce}_2\text{O}_3
\]  

Among the Mn–Fe mixed oxide catalysts, electronic transfer occurs between the different oxidation states of Fe$^{3+}$, Fe$^{2+}$, Mn$^{4+}$ and Mn$^{3+}$\textsuperscript{98}. The performance of the Mn/TiO$_2$ catalyst was improved by the addition of Fe\textsuperscript{99}. The process can be described approximately as follows:

\[
\text{Fe}^{3+} + \text{Mn}^{3+} \leftrightarrow \text{Fe}^{2+} + \text{Mn}^{4+}
\]  

\[
\text{NO} + \text{Mn}^{4+} \rightarrow \text{NO}^+ (\text{ad}) + \text{Mn}^{3+}
\]  

\[
\frac{1}{2}\text{O}_2 + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{O}^- (\text{ad})
\]  

\[
\text{NO}^+ (\text{ad}) + \text{O}^- (\text{ad}) \rightarrow \text{NO}_2
\]  

\[
\text{Fe}^{2+} + \equiv\text{Mn}^{4+} \rightarrow \equiv\text{Fe}^{3+} + \equiv\text{Mn}^{3+}
\]  

Liu et al.\textsuperscript{100,101} investigated a series of WO$_3$-doped Mn–zirconium (Zr) mixed oxide catalysts. Using catalyst performance measurements, the SCR performance and poisoning tolerance of the Mn–Zr catalyst doped with WO$_3$ was higher than that for the Mn–Zr catalyst alone. There were redox couples of Mn$^{4+}$/Mn$^{3+}$ and W$^{6+}$/W$^{5+}$, (i.e., W$^{5+}$ + Mn$^{4+}$ $\leftrightarrow$ W$^{6+}$ + Mn$^{3+}$). The redox property and the electron transfer was improved using these dual redox couples (Fig. 3). Thus, the electron transfer between Mn and W active sites was promoted and this contributes to the activation of NH$_3$ and an improvement of the NO conversion (Fig. 4).

Metal oxides could catalyze the reduction of NO with NH$_3$ \textit{via} the transfer of electrons.\textsuperscript{102,103} As is known, catalysts play a role in accelerating the reaction rate. Referring to Fig. 2, it can be seen that metal cations provide the adsorption sites and function as the transfer station of electrons in the SCR process. Manganese mainly acts as the adsorption center for nitrogen. Mn$^{4+}$ receives an electron from NO or NH$_3$ and will be reduced into Mn$^{3+}$. Then the reduced Mn$^{3+}$ would be restored to Mn$^{4+}$ by an extra oxygen and then the next redox cycle starts. However, a faster pathway is \textit{via} the transfer of an electron between metal oxides, such as Ce, Fe, W and so on. Therefore, to design a catalyst, it is necessary to introduce an element for the role of the adsorption and oxidation of nitrogen. Simultaneously, another element is required for superior oxygen storage to quickly restore the reduced element. The coordination of these two types of elements will improve the performance of SCR.

It is essential to characterize the catalysts’ structure in order to design an excellent catalyst. The current technology for treating the exhaust gas is supported vanadium-based catalysts
In this section, the reaction mechanisms have been summarized. It was supposed originally that NO₂ could be the main reactant for the SCR process. However, it is widely agreed that the primary cause for the deactivation of metal oxide catalysts at low temperature is the decomposition temperature of ammonium sulfate [(NH₄)₂SO₄] and (NH₄)₂SO₄ salts is higher than the operation temperature of the catalysts. Most researchers regard the poisoning of SO₂ as a major problem. The deactivation of SO₂ can be classified into two categories: deposition of (NH₄)₂SO₄ and sulfation of active sites. The undesired metal sulfates and (NH₄)₂SO₄ would occupy active sites on the surface and gradually deactivate the catalyst. The deactivation caused by water vapor can contribute to the competitive adsorption. The adsorption of H₂O on the catalysts’ surface blocks the active sites, which are provided for the adsorption of NH₃ and NO.

### 3.1 SO₂ and H₂O

Sulfur oxides are mainly generated from the combustion of fossil fuels and the sintering of ore. Residual SO₂ after desulfurization can still damage the metal oxide catalysts. The deposition of ammonium sulfates, such as ammonium bisulfate [(NH₄)HSO₄] and ammonium sulfate [(NH₄)₂SO₄], is the primary cause for the deactivation of metal oxide catalysts at low temperature. The decomposition temperature of ammonium sulfate [(NH₄)₂SO₄] and (NH₄)₂SO₄ salts is higher than the operation temperature of the catalysts. Most researchers regard the poisoning of SO₂ as a major problem. The deactivation of SO₂ can be classified into two categories: deposition of (NH₄)₂SO₄ and sulfation of active sites. The undesired metal sulfates and (NH₄)₂SO₄ would occupy active sites on the surface and gradually deactivate the catalyst. The deactivation caused by water vapor can contribute to the competitive adsorption. The adsorption of H₂O on the catalysts’ surface blocks the active sites, which are provided for the adsorption of NH₃ and NO.

#### 3.1.1 Deposition of ammonium sulfates

The harm caused by (NH₄)SO₃ and (NH₄)₂SO₄ is to mainly block the active sites. The micropore surface area and volume was decreased after SO₂ was introduced in to a simulated flue gas. When excess O₂ exists in the flue gas, the trace residual SO₂ can be oxidized to SO₃, a reaction catalyzed by the metal active sites [eqn (34)]. Furthermore, it was proved that the SO₂ could be easily oxidized on the MnOₓ catalysts’ surface. Also, NOₓ would further facilitate the oxidation of SO₂ to SO₃ [eqn (35)].

\[
\text{SO}_2 + 1/2\text{O}_2 \rightarrow \text{SO}_3 \quad (40)
\]

\[
\text{NO}_2 + \text{SO}_2 \rightarrow \text{NO} + \text{SO}_3 \quad (41)
\]

Gaseous NH₃ was assisted by the Bronsted acid sites to form NH₄⁺, which could react with SO₂ or SO₃ to form (NH₄)₂SO₄ or (NH₄)HSO₄, respectively. In addition, NH₄HSO₄ species were also generated in the flue gas. The formation of NH₄HSO₄, (NH₄)₂SO₃ and (NH₄)₂SO₄ can be described as follows:

\[
\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 \quad (42)
\]

\[
\text{H}_2\text{SO}_4 + \text{NH}_3 \rightarrow \text{NH}_4\text{HSO}_4 \quad (43)
\]

\[
2\text{NH}_3 + \text{SO}_2 + \text{H}_2\text{O} \rightarrow (\text{NH}_4)_2\text{SO}_3 \quad (44)
\]

\[
2\text{NH}_3 + \text{SO}_3 + \text{H}_2\text{O} \rightarrow (\text{NH}_4)_2\text{SO}_4 \quad (45)
\]

Actually, (NH₄)₂SO₃ and (NH₄)₂SO₄ can be decomposed at a relatively higher temperature. However, low temperature SCR of NOₓ is usually requested at a low operation temperature, which is lower than the decomposition temperature of the (NH₄)₂SO₃ and (NH₄)₂SO₄. Therefore, removing the undesired side-products of (NH₄)₂SO₄ salts is a big challenge to researchers.

Table 2: Brunauer–Emmett–Teller (BET) surface area and TOF of different loadings of Mn/TiO₂ catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>BET surface area (m² g⁻¹)</th>
<th>TOF at different GHSV (h⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5% Mn/TiO₂</td>
<td>238</td>
<td>139.5</td>
</tr>
<tr>
<td>11.1% Mn/TiO₂</td>
<td>229</td>
<td>60.1</td>
</tr>
<tr>
<td>16.7% Mn/TiO₂</td>
<td>196</td>
<td>32.3</td>
</tr>
<tr>
<td>20% Mn/TiO₂</td>
<td>183</td>
<td>27.8</td>
</tr>
<tr>
<td>24% Mn/TiO₂</td>
<td>165</td>
<td>22.0</td>
</tr>
</tbody>
</table>

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3. Catalyst deactivation

Because of the demands of high temperature operation, conventional SCR catalysts suffer a huge amount of damage from the sulfur oxides, water vapor, heavy metal ions and alkali and alkaline earth metal ions in the upstream of the flue gas. Installing the reactor downstream of the desulfurizer and precipitator is an excellent way to avoid deactivation. Many metal oxide catalysts have been reported as being low temperature SCR catalysts, however, commercial low temperature SCR catalysts have narrow fields of application because they are not immune to the residual SO₂ and H₂O contained in real flue gas. The poor tolerance of SO₂ and H₂O has been a major obstacle for practical applications. Therefore, it is significant to illuminate the poisoning mechanisms of SO₂, H₂O and so on.

---

**Table 2** Brunauer–Emmett–Teller (BET) surface area and TOF of different loadings of Mn/TiO₂ catalysts

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<thead>
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decrease of NO conversion over the Mn–Ce metal oxide catalysts supported on carbon nanotubes. Lu et al.\textsuperscript{117} fed 200 ppm SO\textsubscript{2} to the flue gas, and then the NO\textsubscript{2} conversion of Mn–Ce/TiO\textsubscript{2} catalyst decreased from an initial value of 99% to about 78%. Jiang et al.\textsuperscript{118} investigated the effect of SO\textsubscript{2} on MnO\textsubscript{2}(0.4)/TiO\textsubscript{2} catalysts prepared by three methods, sol–gel, impregnation and co-precipitation. The NO conversions had an apparent decrease for these catalysts (Fig. 5a).

Yu et al.\textsuperscript{111} prepared MnO\textsubscript{2}–Fe\textsubscript{2}O\textsubscript{3}–CeO\textsubscript{2}–TiO\textsubscript{2} catalysts. The performance of this catalyst was decreased by introducing SO\textsubscript{2}. The NH\textsubscript{4}\textsuperscript{+} species and the SO\textsubscript{2}\textsuperscript{2−} species were determined from Fourier-transform infrared spectra. The NH\textsubscript{4}\textsuperscript{+} species were chemisorbed on to the Bronsted acid sites.\textsuperscript{119} This means that the poisoning of SO\textsubscript{2} can be via the formation and deposition of (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4}, which blocks the active channels of the catalyst. The NO conversion was decreased to 50% from 90% (Fig. 5b).

Xu et al.\textsuperscript{120} also found that NH\textsubscript{4}HSO\textsubscript{3} and NH\textsubscript{4}HSO\textsubscript{4} formed via the reaction of SO\textsubscript{2} and NH\textsubscript{3} could be deposited on catalysts’ surface and blocked the active sites [eqn (34)–(39)]. Furthermore, more Bronsted acid sites will be generated while the sulfates are formed by SO\textsubscript{2} adsorption on surface. The Lewis acid site could be transformed to the Bronsted acid site by adsorption of a water molecule.\textsuperscript{121} This means that a wet atmosphere would promote the formation of the Bronsted acid sites, which facilitates the sorption of NH\textsubscript{4}\textsuperscript{+}.\textsuperscript{122} In terms of diffuse reflectance infrared Fourier transform (DRIFT) spectra, Jiang et al.\textsuperscript{123} proved that the formation of NH\textsubscript{4}\textsuperscript{+} was promoted after introducing SO\textsubscript{2}. However, even though Bronsted acid sites were formed by the sulfatization, NO conversion was decreased because SO\textsubscript{2} occupied the NO adsorption sites.

Therefore, to obtain high NO conversion, it is necessary to prevent the formation of (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4}. Actually, it is nearly impossible to eliminate the residual SO\textsubscript{2} completely. Efficient ways to do it may be preventing the oxidation of SO\textsubscript{2} and decreasing the decomposition temperature of (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} and NH\textsubscript{4}HSO\textsubscript{4} on the catalysts’ surface.

Jin et al.\textsuperscript{25} studied the Mn–Ce/TiO\textsubscript{2} and Mn/TiO\textsubscript{2} catalysts. In terms of the thermogravimetry/differential scanning calorimetry (TG/DSC) results, the decomposition temperatures of (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} and NH\textsubscript{4}HSO\textsubscript{4} on the Mn/TiO\textsubscript{2} catalyst was determined to be 213 °C and 361 °C, respectively. However, in the case of the Mn–Ce/TiO\textsubscript{2} catalyst, the decomposition temperature of NH\textsubscript{4}HSO\textsubscript{4} was approximately 286 °C, which was much lower than 361 °C. This indicated that the thermal stability of NH\textsubscript{4}HSO\textsubscript{4} on the catalyst was greatly reduced after introducing cerium. This inference was also proved by the DRIFT results. Therefore, ceria improved the performance of Mn/TiO\textsubscript{2} catalyst.

There is a universal agreement that residual SO\textsubscript{2} damages the metal oxide catalysts and decreases the NO conversion. (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{3} and (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} were formed on catalysts’ surface by the reaction of SO\textsubscript{2}. Researchers found that the NO conversion would increase for a while when SO\textsubscript{2} was introduced and then finally decrease. The adsorption of SO\textsubscript{2} improved the amount of Lewis acid sites, and thus the capacity of NH\textsubscript{3} was improved. However, the sulfation damages the manganese cations, which are the active sites of NO.

3.1.2 Sulfation of active sites. The presence of SO\textsubscript{2} could trigger the sulfation of the dominating active phase of metal oxide catalysts. Furthermore, the harm caused by the sulfation would be permanent and irreversible.\textsuperscript{124} Jiang et al.\textsuperscript{125} described a proposed mechanism of SO\textsubscript{2} deactivation effect for a Fe–Mn/ Ti catalyst. The scheme in Fig. 6a shows the formation of Lewis acid sites. Mn cations are the active sites for the adsorption of NO to form bidentate or monodentate nitrates (Fig. 6b), however, when both NO and SO\textsubscript{2} exist in the flue gas, NO and SO\textsubscript{2} were adsorbed competitively. The adsorption ability of SO\textsubscript{2} was much higher than that of NO (Fig. 6c), so SO\textsubscript{2} occupied the active sites and the catalyst was sulfated. Furthermore, Fig. 6d shows that NH\textsubscript{3} could be adsorbed on the Lewis acid site of the Mn cations. When the active sites were sulfated, the Lewis acid sites could be transformed to the Bronsted acid sites via bonding of a water molecule. Therefore, this did not affect the adsorption of NH\textsubscript{3}, because NH\textsubscript{3} could also be adsorbed on the Bronsted acid sites (Fig. 6e). It is therefore, proposed that the effect of SO\textsubscript{2} was mainly on the adsorption of NO rather than on the adsorption of NH\textsubscript{3}.

Yu et al.\textsuperscript{111} investigated the formation of metal sulfation on fresh Mn–Fe–Ce–Ti catalyst impregnated (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4}. In terms of
MnO metal oxide catalysts. Ceria may trap SO2 for NO Lewis acid sites than Mn/TiO2 catalysts. This result implied that

cation species on MnO pre-treatment with SO2, Ce doped Mn/TiO2 catalysts had more

et al. (MnSO4). They claimed that the MnSO4 could not be formed and then combined with Mn species to form manganese sulfate directly by the reaction of oxidized SO2 and Mn species.57 Kijistra et al.123 proved that the transformation of MnO to MnSO4 on MnO2/Al2O3 catalyst significantly deactivated the catalyst’s activity.

Efforts have been made to facilitate the SO2 tolerance of metal oxide catalysts. Ceria may trap SO2 for NOx storage catalysts to limit the sulfation of the dominating active phase and inhibit the formation of (NH4)2SO4 and NH4HSO4.117,126 After pre-treatment with SO2, Ce doped Mn/TiO2 catalysts had more Lewis acid sites than Mn/TiO2 catalysts. This result implied that the addition of ceria could prevent the Lewis acid sites from the sulfation of SO2.

Liu et al.127 compared the performance of Mn–Ce mixed oxide catalysts prepared using the surfactant template method and the conventional co-precipitation method. Referring to the catalytic activity measurement, the Mn1–Ce5 catalyst prepared using the surfactant template method showed the highest NOx conversion whether SO2 and H2O were introduced or not. The catalysts prepared using the surfactant template method possessed a higher surface area and smaller active sites, which contributed to a higher NOx reduction.

In terms of in situ DRIFT analysis, Jin et al.25 found that the Lewis acid sites could be preserved effectively with the doping of Ce while the SO2 was added. SO2 was oxidized to SO3, or sulfation species on MnO2, however, SO3 and sulfation species move into ceria to form bulk like sulfate species. Therefore, ceria trapped SO3 and protected the dominant active manganese cations (Fig. 7). Furthermore, in terms of the DRIFT and TG-DSC results, it was indicated that the thermal stability of sulfation species over the Mn–Ce catalyst was lower than that over the MnO2 catalyst. Referring to the study of Kylhammar et al.,128 it is assumed that the bulk sulfation species in ceria reveals a high mobility, which facilitates their desorption.

Wang et al.,113 Xu et al.,129 and Shi et al.130 proved that the active manganese cation was reserved for ceria, which finally sulfated it. Ce4+ distributed on the catalysts’ surface transformed into Ce3+ after sulfation. The reaction can be described as follows:

$$2\text{CeO}_2 + 3\text{SO}_2 + \text{O}_2 \rightarrow \text{Ce}_4(\text{SO}_4)_3$$ (46)

Furthermore, it is reported that Zr could optimize the redox property and strengthen SO2 tolerance.49 Chang et al.130,131 reported that Sn modification could further improve the tolerance of the Mn–Ce catalyst to SO2 and H2O. They compared the NO conversion of Sn(0.1)–Mn(0.4)–Ce(0.5)–O and Mn(0.4)–Ce(0.6)–O mixed oxide catalysts. It was obvious that the NO conversion of the Mn(0.4)–Ce(0.6)–O catalyst was decreased more significantly than that of the Sn(0.1)–Mn(0.4)–Ce(0.5)–O catalyst when 200 ppm of SO2 and 3% O2 was fed in to the system at 220 °C.

Shi et al.132 compared the resistance of the Mn/TiO2 catalyst and the hierarchically macro-mesoporous Mn/TiO2 (HM-Mn/TiO2) catalyst prepared by the sol–gel method. After feeding 30 ppm SO2 to the system, the NO conversion of the Mn/TiO2 catalyst decreased sharply from 57% to 15%, however, the NO conversion of the HM-Mn/TiO2 catalyst kept a higher value of more than 84%. The result indicated that maybe the SO2 resistance could be improved by using a hierarchically macro-mesoporous structure.

As previously, because NH3 could be adsorbed on both the Lewis acid sites and the Brønsted acid sites, there is little influence on the adsorption of NH3. However, the adsorption ability of SO2 was higher than that of NO. Residual SO2 would be adsorbed on Mn cations, which are the active sites for the adsorption of NO. The damage caused by sulfation would be permanent and irreversible. Doping with ceria should be a good choice to divert this damage from Mn. More research should be done to investigate the reaction mechanism between SO2 and

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**Fig. 6** The proposed mechanism of SO2 deactivation effect on the SCR reaction. (Reprinted with permission from ref. 123. Copyright (2010) American Chemical Society.)

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**Fig. 7** The formation schematic of bulk like sulfate on Mn–Ce/Ti catalysts. (Reprinted from ref. 25. Copyright 2013, with permission from Elsevier.)
Mn cations. The correlations should be established between the extent of sulfation and the degree of dispersion of MnO₂ species at the surface.

3.1.3 Effect of H₂O. Water vapor could decrease the activity and show a notable inhibition on low temperature SCR. H₂O can be generated from the original flue gas or the reaction of SCR of NO. Even though there is no H₂O in the original flue gas, H₂O vapor will be generated during the SCR reaction, as shown in eqn (1). This means that the presence of H₂O is nearly inevitable. Therefore, many efforts have been made to evaluate the durability of metal oxide catalysts in the presence of H₂O vapor. As mentioned previously, trace SO₂ could still decrease SCR of NO. Even though there is no H₂O in the original gas, the catalyst’s active sites deprived the sites of NH₃ adsorption, hydrogenation, programmed desorption (TPD) procedures have been made to evaluate the competitive adsorption of H₂O. Many researchers reported that the adsorption of H₂O on the catalyst’s surface blocked the active sites, which are provided for the adsorption of NH₃ and NO.

The main reason for the decrease of activity can be attributed to the competitive adsorption of H₂O. Many researchers reported that the adsorption of H₂O on the catalyst’s surface blocked the active sites, which are provided for the adsorption of NH₃ and NO. They proposed that the effect of H₂O can be attributed to the competitive adsorption, the decrease of oxidation ability and the inhibition of interface reactions. The temperature programmed desorption (TPD) profiles of NH₃ and NO were obtained, and the NOₓ and NH₃ adsorption capacity of Mn–Fe spinel in the absence of H₂O and in the presence of 5% H₂O are shown in Table 3.

Table 3 Capacity of Mn–Fe spinel for NH₃ and NOₓ adsorption at 150 °C μmol⁻¹ g⁻¹

<table>
<thead>
<tr>
<th>Condition</th>
<th>NH₃ (μmol⁻¹ g⁻¹)</th>
<th>NOₓ (μmol⁻¹ g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>In the absence of H₂O</td>
<td>122</td>
<td>82</td>
</tr>
<tr>
<td>In the presence of 5% H₂O</td>
<td>105</td>
<td>46</td>
</tr>
</tbody>
</table>

Fig. 8 shows that the NOₓ conversion apparently decreased when 5% H₂O was fed in to the flue gas, especially at the lower temperature, e.g., below 160 °C. The adsorption of H₂O vapor on the catalyst’s active sites deprived the sites of NH₃ adsorption, which apparently decreased the NO conversion. There is a summary of Mn-containing catalysts’ performance in the presence and in the absence of SO₂ and H₂O (Table 4).

3.1.4 Regeneration. Many articles reported that the deactivated (NH₄)₂SO₄ could be regenerated after use. Water washing, thermal regeneration, thermal reduction regeneration and reductive regeneration were the usual methods to regenerate the deactivated catalysts. Yu et al. investigated the regeneration of the SCR catalyst using dilute sodium hydroxide solution. The catalyst was deactivated by the deposition of sulfates on the surface. The catalyst was deactivated by the deposition of sulfates on the surface. The deactivated MnO₂ catalysts via heating at 350 °C for 2 h. This was a reversible process because of (NH₄)₂SO₄ salts can be decomposed, regenerating Mn/Ti and Mn–Ce/Ti catalysts with water washing (Fig. 9a). Shi et al. regenerated the CeO₂ catalysts using a thermal treatment (Fig. 9b).

Huang et al. investigated a series of Fe–Mn oxide catalysts supported on mesoporous silica (MPS), which showed good activity. When H₂O and SO₂ was fed in to the system at 190 °C, the NO conversion over Mn–Fe/MPS was finally decreased to 85.3% from 99.2%. This was attributed to the formation of the NH₄HSO₄ and (NH₄)₂SO₄ in the presence of both H₂O and SO₂. However, the deactivated catalyst could be regenerated using a heating treatment, because the deactivation was because of the catalyst pore plugging and surface area loss by the deposition of (NH₄)₂SO₄. When the temperature is above 140 °C, H₂O has no negative effect on its activity.

Guan et al. investigated the resistance to deactivation by H₂O and SO₂ of Ti₀.₉Ce₀.₀₅V₀.₀₅O₂₋ₓ catalysts, which showed a high NO conversion and N₂ selectivity. After feeding 400 ppm SO₂ for 26 h at 150 °C, the surface of catalyst was deposited with significant agglomeration and bulk NH₄NO₃ and (NH₄)₂SO₄ with a size of 30–50 μm. Then, the NH₄NO₃ and (NH₄)₂SO₄ was decomposed when the catalyst was calcined at 200 °C and 400 °C, because the decomposition temperatures were 170 °C and 300 °C, respectively. The surfaces were scanned using scanning electron microscopy (SEM), and the transformation of the surface is shown in Fig. 10.

3.2 Alkali and alkaline earth metal ions

Fine fly ash still exists in the downstream of the flue gas after desulfurizing and dedusting. Amounts of alkali and alkaline earth metals were released from the raw materials or coal, such
### Table 4  Summary of Mn-containing catalysts performance in the absence/presence of SO₂ and H₂O

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Reaction gas mixture and GHSV</th>
<th>NO conversion (%), SO₂ conversion (%), H₂O conversion (%)</th>
<th>Reaction conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnₓCeₓZnₓO</td>
<td>Co-precipitation/500 • C/6 h</td>
<td>&gt;90% (180 • C)</td>
<td>MnₓCeₓZnₓO-3</td>
</tr>
<tr>
<td>MnₓCeₓZnₓO</td>
<td>Co-precipitation/500 • C/6 h</td>
<td>&gt;90% (180 • C)</td>
<td>MnₓCeₓZnₓO-4</td>
</tr>
<tr>
<td>MnₓCeₓZnₓO</td>
<td>Co-precipitation/500 • C/6 h</td>
<td>&gt;90% (180 • C)</td>
<td>MnₓCeₓZnₓO-5</td>
</tr>
<tr>
<td>MnₓCeₓZnₓO</td>
<td>Co-precipitation/500 • C/6 h</td>
<td>&gt;90% (180 • C)</td>
<td>MnₓCeₓZnₓO-6</td>
</tr>
<tr>
<td>MnₓCeₓZnₓO</td>
<td>Co-precipitation/500 • C/6 h</td>
<td>&gt;90% (180 • C)</td>
<td>MnₓCeₓZnₓO-7</td>
</tr>
<tr>
<td>MnₓCeₓZnₓO</td>
<td>Co-precipitation/500 • C/6 h</td>
<td>&gt;90% (180 • C)</td>
<td>MnₓCeₓZnₓO-8</td>
</tr>
<tr>
<td>MnₓCeₓZnₓO</td>
<td>Co-precipitation/500 • C/6 h</td>
<td>&gt;90% (180 • C)</td>
<td>MnₓCeₓZnₓO-9</td>
</tr>
<tr>
<td>MnₓCeₓZnₓO</td>
<td>Co-precipitation/500 • C/6 h</td>
<td>&gt;90% (180 • C)</td>
<td>MnₓCeₓZnₓO-10</td>
</tr>
</tbody>
</table>

**Note:** The concentration of SO₂ and H₂O introduced on the basis of reaction gas.
as in the cement production process. Alkali salts are important components in fly ash, which not only plugs the pores of catalysts, but also decreases SCR activity by reacting with the active phase. In addition, because of the water solubility or ion exchange, alkali metal has a high liquidity to neutralize the acid sites. For the traditional V2O5-based SCR catalysts, alkali metal deactivated these by affecting the acid sites on the surface. Alkali metals could lower MnOx reducibility, decrease specific surface areas and damage the acid sites of low temperature catalysts.

Zhou et al. reported that sodium sulfate, used to simulate the combined effects of alkali metal and SO2 in the flue gas, had strong effects on the activity of the Mn–Ce/TiO2 catalyst, such as simultaneous pore occlusion and sulfation effect. Guo et al. investigated the deactivation effect of sodium (Na) and potassium (K) on a Mn/TiO2 catalyst. The catalyst was prepared using a sol–gel method and Na and K were doped via an impregnation method. The Mn/TiO2 catalysts exhibited a high activity of 90% NO conversion. However, when Na or K was doped, the conversion was decreased from 95% to 78% and 27%, respectively. In this study, the effect of K was apparently more serious than that of Na. Furthermore, Chen et al. found that on the catalysts' surface chemisorbed oxygen was reduced by alkali and alkaline earth ions together with a decrease of SCR activity. The downward trend was K > Na > Ca > Mg.

Shen et al. studied the effects of K, Na and Ca on a Mn–Ce/Zr catalyst. From the NH3-TPD measurements, the adsorption of NH3 was decreased when the catalyst was doped with alkali metal ions. This may indicate that the alkali metal on the surface of the catalysts may destroy the surface acidic sites, and decrease the redox property and chemisorbed oxygen. Furthermore, they also found that K was more harmful to the catalyst compared to Na or Ca. However, Kustov et al. found that V2O5 supported on sulfated zirconium dioxide showed a good resistance towards alkali ions. Chen et al. reported that the K resistance of the Mn/TiO2 catalyst could be improved by doping it with Co, which increased the adsorption of NH3 and NOx species.

3.3 Heavy metal ions

Heavy metal ions, regarded as hazardous pollutants, can deactivate the SCR catalysts. Heavy metal ions in the flue gas are mainly generated from coal used as fuel. It has been proved that heavy metals could lead to the deactivation of vanadium-based SCR catalysts. Kong et al. found that the Brønsted acid sites of a V–W/TiO2 catalyst were impacted when mercury chloride was introduced. Actually, there is little heavy metal ions found in the downstream of the precipitator because the heavy metal ions usually exist in the fly ash. Moreover, water...
vapor exists in the flue gas all along. For the water solubility of heavy metal ions, it is necessary to take the effect of heavy metals into consideration.

Lead (Pb) and zinc (Zn) are typical heavy metals found in the flue gas of coal fired power plants. Guo et al. and Li et al. compared the poisoning effect of Pb and Zn on a Mn/TiO2 catalyst. The Pb or Zn was loaded on to the Mn/TiO2 catalyst using impregnation. As a result, both Pb and Zn were found to have a negative effect on the Mn/TiO2 catalyst (Fig. 11a). From the characterization experiments, the redox ability of Zn–Mn/TiO2 and Pb–Mn/TiO2 was found to be decreased because of the drop of Mn4+ and chemisorbed oxygen. Zhou et al. investigated the deactivation effects of lead(II) oxide (PbO) on the Mn–Ce/TiO2 catalyst. It was proposed that the surface area, the concentration of Mn4+, Ce3+ and chemisorbed oxygen was decreased after introducing PbO. Consequently, the performance of the Mn–Ce/TiO2 catalyst was greatly decreased because of the poisoning of PbO (Fig. 11b).

Mercury (Hg0) is a toxic trace element in the atmosphere and has a high concentration in coals used in China, such as anthracite, bituminous coal and lignite. Researchers have attempted to remove the NO and Hg0 simultaneously. However, Hg0 is harmful to the catalysts of SCR of NO because it will compete with NH3 for adsorption on the active sites. Xu et al. investigated the influence of Hg0 on the NO conversion over a LaMnO3 catalyst. The NO conversion had a slight decrease in the presence of Hg0 (Fig. 12).

4. Conclusions and perspectives

NH3-SCR of NO2 in the presence of O2 is one of the important strategies in controlling NOx emissions. Low temperature SCR has been investigated for several decades. Mn-containing metal oxide catalysts generally gave the preferable performance. SCR of NO2 with NH3 follows both the L–H and the E–R mechanisms. There is quite a similarity between these two different mechanisms. A comproportionation occurs in both the L–H and E–R mechanisms. Fast SCR has a higher reaction rate than standard SCR and it depends on the formation of NO2, N2O formation can mainly be explained using the E–R mechanism. A synergistic mechanism is vital for designing a remarkable metal oxide catalyst. Multi-metal cations will promote the performance mutually. Manganese cations mainly serve as the adsorption center for nitrogen. Thus, it is necessary to introduce an element for the adsorption of oxygen and to provide a redox cycle.

A big challenge in the industrial use of Mn-containing oxide catalysts is their durability. They are vulnerable to the effects of both SO2 and H2O. Sulfur oxides and water vapor cause the deactivation of Mn-containing catalysts. Alkali metals could lower manganese oxide reducibility, decrease specific surface areas and damage the acid sites of low temperature catalysts. The poisoning process of SO2 can be classified into two categories: deposition of (NH4)2SO4 and sulfation of the active sites. For the low temperature downstream of the flue gas, the deposition of (NH4)2SO4 or NH4HSO4 occurs more easily and NH3 is evidently adsorbed by H2O in comparison with the
operation upstream. Many efforts have been made to improve the durability. Nonetheless, few techniques have been useful in practical industrial applications.

On the basis of the previous analysis, some conclusions can be drawn as follows:

(1) Most research is related to the performance of the catalysts, such as NO conversion, N₂ selectivity and poisons’ tolerance, as well as the mechanism of this process. An excellent NO conversion of catalysts has been obtained, however, the N₂ selectivity is not satisfactory.

(2) Less effort has been made in determining the relationship of metal oxide crystal structure and its performance, which is required for the design of catalysts. More attention should be given to the relationship between the catalysts’ structure and its reaction mechanism, which guides us exactly to design a low temperature SCR catalyst for different flue gases.

(3) Mn-containing metal oxide catalysts show a notable SCR performance at low temperature. However, the single manganese oxide catalysts have a poor tolerance of SO₂ and H₂O, which has been improved by modifying other elements in bench scale experiments. Researchers have been engaged in improving Mn-containing catalysts by modifying them with different metal oxides. Ce can enhance the adsorption of NO and O₂ which benefits the oxidation of NO to NO₂ and improves sulfur resistance, and inhibits the formation of (NH₄)₂SO₄ and NH₄HSO₄. Ce has good selectivity for improving the catalysts’ performance. More research efforts should be made on the activity and poisoning tolerance.

(4) Most catalysts were powder rather than monolith catalysts, such as honeycomb or slab. A laboratory study is a small scale test that will react differently to industrial tests. Specific surface area is important to the activity and closely related to the particles’ size, shape and aggregation. The preparation method is also important to the catalysts’ performance. Researchers should give more attention to pilot scale tests or industrial tests.

(5) The low temperature SCR catalysts have been investigated for several decades. Lots of elements have been studied in the catalysts. To avoid repetitive work and waste of resources, a low temperature SCR catalysts’ materials database should be built.

(6) Heaps of disabled SCR catalysts should be regenerated and reused. The regeneration and recycling of SCR catalysts is another big task for researchers. This problem should be taken into consideration while researchers are designing new SCR catalysts.

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