

## REVIEW

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# A review of Mn-containing oxide catalysts for low temperature selective catalytic reduction of $\text{NO}_x$ with $\text{NH}_3$ : reaction mechanism and catalyst deactivation

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Atmospheric pollutants of nitrogen oxides ( $\text{NO}_x$ ) can be reduced by selective catalytic reduction (SCR). SCR of  $\text{NO}_x$  with ammonia ( $\text{NH}_3$ ) 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 ( $\text{MnO}_x$ ). The reaction mechanisms and deactivation processes are summarized in this review. SCR of  $\text{NO}_x$  with  $\text{NH}_3$  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  $(\text{NH}_4)_2\text{SO}_4$  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  $\text{NH}_3$  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.

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## 1. Introduction

Nitrogen oxides ( $\text{NO}_x$ ) are a series of active gases, and include nitrogen dioxide ( $\text{NO}_2$ ), nitrogen oxide (NO) and nitrous oxide ( $\text{N}_2\text{O}$ ), and so on. Human activities cause a huge emission rate of  $\text{NO}_x$ , which is double that of the biotic and abiotic nitrogen fixation rates. Released  $\text{NO}_x$  can cause a series of environmental issues, such as photochemical smog, acid rain, and ozone depletion, and it can affect global tropospheric chemistry.<sup>1–4</sup> Great efforts have been devoted to abating the emission of  $\text{NO}_x$ .

The technologies used to control  $\text{NO}_x$  emission can be categorized as combustion controls and post-combustion controls.<sup>5,6</sup> Combustion controls, which aim to control the production of  $\text{NO}_x$ , include low  $\text{NO}_x$  burners,<sup>7</sup> air graded burning and staged fuel combustion.<sup>8</sup> Post-combustion controls aim to decrease the  $\text{NO}_x$  produced by reducing active N to fixed nitrogen gas ( $\text{N}_2$ ). The technologies for reducing  $\text{NO}_x$  from flue gas can be divided into: direct decomposition,<sup>9,10</sup> selective catalytic reduction (SCR),<sup>11,12</sup> selective non-catalytic reduction (SNCR),<sup>13,14</sup> hybrid SNCR/SCR<sup>15</sup> and  $\text{NO}_x$  storage-

reduction catalysis.<sup>16</sup> With the advantages of high efficiency and low cost,  $\text{NO}_x$  emitted from stationary sources (e.g., thermal plants or industrial boilers) has been predominantly controlled by SCR of NO with ammonia ( $\text{NH}_3$ -SCR) in the presence of excess oxygen ( $\text{O}_2$ ) for decades.<sup>17</sup>

The catalyst to be used is a decisive factor in the process of decreasing  $\text{NO}_x$  (de $\text{NO}_x$ ). The common catalysts include noble metal catalysts,<sup>18</sup> metal-exchanged zeolite catalysts,<sup>19</sup> metal oxide catalysts,<sup>20,21</sup> heteropoly acid catalysts,<sup>22</sup> and so on. Metal oxide catalysts are widely applied in  $\text{NH}_3$ -SCR. Nowadays, the most widely used catalysts are vanadium(v)-based catalysts and tungsten trioxide ( $\text{WO}_3$ ) and/or molybdenum trioxide ( $\text{MoO}_3$ ) doped vanadium(v) oxide ( $\text{V}_2\text{O}_5$ )/titanium dioxide ( $\text{TiO}_2$ ) catalysts. These are usually installed at the upstream of flue gas because they require a higher working temperature of 300–400 °C.<sup>23</sup> 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 ( $\text{SO}_2$ ) and alkali metal ions, the poor thermal stability at high temperatures and the toxicity of vanadium from the disabled catalysts.<sup>24</sup> One of the efficient ways to overcome these obstacles is transferring the SCR reactor from upstream to downstream of

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the flue gas, where there is relatively less dust and sulfur oxides in the flue gas but a lower temperature below 300 °C.<sup>25</sup>

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.<sup>26–30</sup> Of these, manganese oxides ( $MnO_x$ ) catalysts show a notable NO conversion and  $N_2$  selectivity for its multi oxidation state, high valence state and characteristic crystallinity. Peña *et al.*<sup>26</sup> advocated that  $MnO_x/TiO_2$  had the highest activity among Co, chromium (Cr), Cu, Fe, Mn, Ni and V oxides supported on  $TiO_2$  at low temperatures. Manganese dioxide ( $MnO_2$ ) and manganese(III) oxide ( $Mn_2O_3$ ) show the highest activity and  $N_2$  selectivity, respectively, among several  $MnO_x$ .<sup>31</sup> The activity and poison tolerance can be improved by doping with other transition metals. Ceria ( $CeO_2$ ) provides sufficient oxygen in the reaction of redox  $NO_x$ , and improves the activity of  $MnO_x$  catalysts.<sup>32–34</sup> Mn–Fe spinel shows an excellent SCR performance at low temperature.<sup>35</sup> Other Mn containing catalysts, such as  $MnO_x$ – $CoO_x/TiO_2$ ,<sup>28,36</sup>  $MnO_x$ – $CrO_x/TiO_2$ ,<sup>37,38</sup>  $MnO_x$ – $CuO_x$ ,<sup>39,40</sup> lanthanum manganite ( $LaMnO_3$ ),<sup>41</sup> 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  $NH_3$ -SCR of  $NO_x$  have been reviewed.<sup>5,6,42</sup> A review by Li *et al.*<sup>43</sup> 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 *et al.*<sup>44</sup> summarized the use of  $MnO_x$ -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  $N_2$  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.

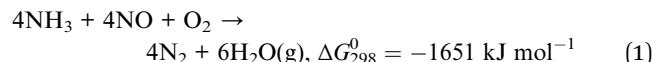
## 2. Reaction mechanisms

To meet the newest and stringent emission standards, ( $NO_x$  concentration  $\leq 50 \text{ mg m}^{-3}$ ),<sup>45</sup> 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  $V_2O_5$ ,  $MnO_x$ ,  $CeO_2$  and copper oxide ( $CuO$ ). Of these,  $MnO_x$  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  $NH_3$ -SCR over Mn-containing oxide catalysts are summarized.

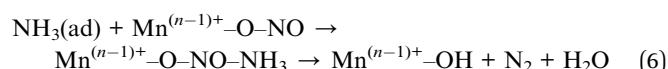
### 2.1 Standard SCR

The  $NH_3$ -SCR of NO aims to reduce active N to fixed  $N_2$ , which is harmless to the atmosphere. In the presence of excess  $O_2$ , the main overall reaction is eqn (1).<sup>46</sup> A great number of studies have proposed that eqn (1) shows the reaction stoichiometry in typical SCR conditions.<sup>47–50</sup> In the absence of  $O_2$ , reaction in eqn (1) would convert into the reaction in eqn (2):<sup>51</sup>



Because the content of NO is more than 90% among  $NO_x$ , eqn (1) is proposed as the standard SCR reaction and dominates the reaction stoichiometry. It is reported widely that the  $NH_3$ -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.<sup>52,53</sup> Through the L–H mechanism, both  $NH_3$  and NO are adsorbed on the surface of catalysts. However, *via* the E–R mechanism, adsorbed  $NH_3$  reacts with gaseous NO. It is suggested that the gaseous  $NH_3$  could be adsorbed on both Lewis acid sites and Brønsted acid sites, however, the gaseous NO is mainly adsorbed by a physical adsorption process.<sup>54</sup> The adsorption of  $NH_3$  has been recognized as the first step of the SCR reaction because it is easier for  $NH_3$  to be adsorbed on acid sites rather than  $NO$ ,  $O_2$  and the reaction products.<sup>55</sup>

The SCR process over  $MnO_x$  catalysts *via* the L–H mechanism can be approximately described as follows:<sup>23,53,56</sup>



Eqn (3) and (4) are the adsorption of gaseous  $NH_3$  and NO.  $NH_3$  is usually adsorbed on the Lewis acid sites and Brønsted acid sites to form adsorbed  $NH_3$  species of coordinated  $NH_3$  and ionic  $NH_4^+$ , respectively.<sup>57</sup> Nevertheless, the coordinated  $NH_3$  on the Lewis acid sites possesses a higher thermal stability than the ionic  $NH_4^+$  on Brønsted acid sites. Manganese cations can provide a great number of Lewis acid sites.<sup>49,58</sup>

Fang *et al.*<sup>59,60</sup> investigated the adsorption of  $NH_3$  on the  $Mn_2O_3$  (222), manganese(II,IV) oxide ( $Mn_3O_4$ ) (211) and  $MnO_2$  (110) surfaces using density functional theory. It is claimed that, with more negative adsorption energy values and the shorter



Table 1 The NO conversion of pure  $\text{MnO}_x$ <sup>59a</sup>

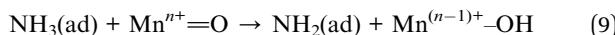
$\text{MnO}_x$	NO conversion (%)				
	353 K	373 K	393 K	413 K	433 K
$\text{MnO}_2$	13	14	16	19	21
$\text{Mn}_2\text{O}_3$	14	17	37	47	44
$\text{Mn}_3\text{O}_4$	18	23	34	44	56

<sup>a</sup> Reaction conditions:  $[\text{NO}] = 720 \text{ ppm}$ ,  $[\text{NH}_3] = 800 \text{ ppm}$ ,  $[\text{O}_2] = 3\%$ . (Reprinted with permission from ref. 59. Copyright 2013 Elsevier.)

Mn–N bonds,  $\text{Mn}_2\text{O}_3$  (222) and  $\text{Mn}_3\text{O}_4$  (211) surfaces were more active for  $\text{NH}_3$  adsorption than the  $\text{MnO}_2$  (110) surface, which contributed to a higher performance (Table 1). Kapteijn *et al.*<sup>31</sup> proposed that the highest NO conversion is exhibited by  $\text{MnO}_2$ , followed by  $\text{Mn}_5\text{O}_8$ ,  $\text{Mn}_2\text{O}_3$  and  $\text{Mn}_3\text{O}_4$ .

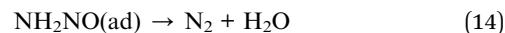
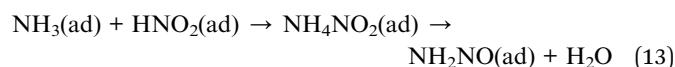
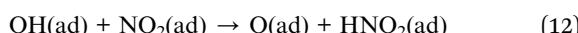
The adsorbed NO is oxidized by the high valency state  $\text{Mn}^{n+}$  cations, (e.g.,  $\text{Mn}^{4+}$ ) on the catalysts' surface to form adsorbed monodentate nitrite ( $\text{Mn}^{(n-1)+}\text{O-NO}$ ) and the very metal cations are reduced as  $\text{Mn}^{(n-1)+}$  [eqn (5)]. Furthermore,  $\text{Mn}^{(n-1)+}\text{O-NO}$  reacts with adsorbed  $\text{NH}_3$  species to form  $\text{Mn}^{(n-1)+}\text{O-NO-NH}_3$ , which decomposes subsequently to  $\text{N}_2$  and water ( $\text{H}_2\text{O}$ ) [eqn (6)]. Then, the reduced  $\text{Mn}^{(n-1)+}$  ions are regenerated by gaseous  $\text{O}_2$  [eqn (7)].

The SCR process over  $\text{MnO}_x$  catalysts *via* the E–R mechanism can be described approximately as follows:<sup>35,48,61</sup>



The adsorption of  $\text{NH}_3$  on the Lewis acid sites is recognized as the first step of NO reduction *via* the E–R mechanism. Coordinated  $\text{NH}_3$  could be deprived of a hydrogen and be activated by the labile oxygen or the lattice oxygen of metal oxides to form an amine ( $\text{NH}_2$ ) species [eqn (9)]. Labile oxygen can be released *via* the change of the valence states of Mn. Activated  $\text{NH}_2$  species on the catalysts' surface reacted with gaseous NO to form the most important intermediate of  $\text{NH}_2\text{NO}$ , which subsequently decomposes to  $\text{N}_2$  and  $\text{H}_2\text{O}$  [eqn (10)]. Then, the reduced  $\text{Mn}^{(n-1)+}$  cations could be oxidized by  $\text{O}_2$ .

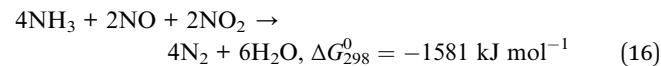
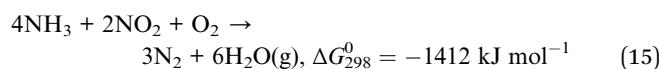
Furthermore, the formation of  $\text{NH}_4\text{NO}_2$  is a typical SCR mechanism for Mn-containing catalysts. Qi and Tang,<sup>56</sup> and Eigenmann *et al.*<sup>62</sup> proposed an amide–nitrosamine type mechanism, which is actually similar to the E–R mechanism. An extra species of  $\text{NH}_4\text{NO}_2$  was presented in this mechanism.  $\text{NH}_4\text{NO}_2$  could be decomposed to  $\text{NH}_2\text{NO}$  and  $\text{H}_2\text{O}$ , and is then decomposed to  $\text{N}_2$  and  $\text{H}_2\text{O}$  [eqn (12)–(14)]:



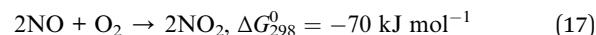
In accordance with the transient eqn (3)–(11),  $\text{Mn}^{3+}\text{O-NO-NH}_3$  and  $\text{NH}_2\text{NO}$  are the most important intermediate in the reaction of the L–H mechanism and E–R mechanism, respectively. There is a quite similarity between these two different mechanisms. A comproportionation, (*i.e.*,  $\text{N}^{3+}$  and  $\text{N}^{3-}$ ,  $\text{N}^{2+}$  and  $\text{N}^{2-}$ ) occurs on both the L–H and E–R mechanism (eqn (6) and (10)).<sup>53,63</sup>

## 2.2 Fast SCR

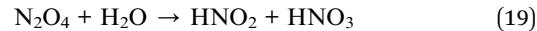
A fast SCR reaction of  $\text{NH}_3$  with  $\text{NO} + \text{NO}_2$  over Mn-containing oxide catalysts has been reported. It is suggested that the fast SCR has a higher reaction rate than standard SCR.<sup>64</sup> Fast SCR was firstly investigated by Koebel *et al.*, and Madia *et al.*<sup>65–67</sup> The general reaction can be described as follows:<sup>68,69</sup>



In the presence of  $\text{O}_2$ , NO can be oxidized by active oxygen to form  $\text{NO}_2$  [eqn (17)].<sup>70</sup> 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.<sup>71,72</sup>



$\text{NO}_2$  is the difference between fast SCR standard SCR.  $\text{NO}_2$  acts as a more efficient oxidizing agent than  $\text{O}_2$  in the redox process of the SCR reaction.  $\text{NO}_2$  can form surface nitrites and nitrates *via* dimerization:<sup>73</sup>

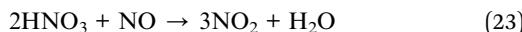


$\text{NH}_4\text{NO}_3$  is formed by the reaction between  $\text{NH}_3$  and  $\text{HNO}_3$ .  $\text{NH}_4\text{NO}_3$  or its related surface species is the key intermediate in the fast SCR process. The reaction processes can be described as follows:



Many researchers considered that  $\text{NH}_4\text{NO}_3$  would be solid below 170 °C.  $\text{NH}_4\text{NO}_3$  could be reduced by NO at a higher temperatures [eqn (21)].<sup>64,74</sup> It is pointed out that  $\text{NH}_3$  can restrain fast SCR by inhibiting the formation of  $\text{NO}_2$  at 150–170 °C.<sup>75</sup> Actually, eqn (21) can be described as two intermediate reactions:



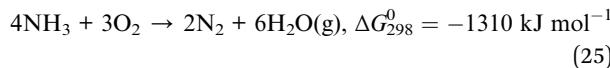
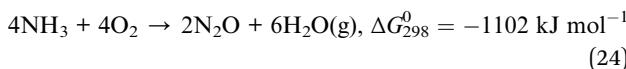


There is a chemical equilibrium in the fast SCR process [eqn (22)]. The formation of  $\text{HNO}_3$  will be restrained while the  $\text{NH}_3$  concentration is raised, and that inhibits the formation of  $\text{NO}_2$  [eqn (23)]. Among the fast SCR processes, the vital process is the redox reaction between  $\text{NO}$  and  $\text{HNO}_3$ , which dominates the rate of fast SCR.

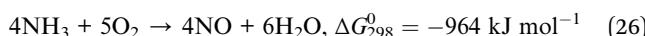
The performance of low temperature SCR has been extensively investigated. Excellent  $\text{NO}$  conversion and  $\text{N}_2$  selectivity has been observed using simulated flue gas in the laboratory. Qi and Yang<sup>76</sup> obtained more than 99% of  $\text{NO}$  conversion on the  $\text{MnO}_x(0.3)\text{-CeO}_2$  catalyst sintered at 120 °C. Long *et al.*<sup>77</sup> investigated the Fe-Mn-based catalysts. These catalysts showed nearly 100%  $\text{NO}$  conversion at 100–180 °C. Recently, France *et al.*<sup>78</sup> studied the  $\text{CeO}_2$  modified  $\text{FeMnO}_x$  catalysts, and more than 95%  $\text{NO}$  conversion was obtained at 90–135 °C without the influence of  $\text{SO}_2$  and  $\text{H}_2\text{O}$ . Zhu *et al.*<sup>79</sup> studied the holmium (Ho) modified Fe-Mn/TiO<sub>2</sub> catalysts, which revealed good performance for  $\text{NO}$  conversion and high  $\text{SO}_2$  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,  $\text{NH}_3$  is a vital resource in the SCR reaction.  $\text{NH}_3$  is consumed mainly *via*  $\text{N}_2$  and  $\text{N}_2\text{O}$  formation and the oxidation of the catalyst to  $\text{NO}_x$ .<sup>52</sup> The wastage of  $\text{NH}_3$  is a huge additional cost of the  $\text{deNO}_x$  process. To decrease the wastage of  $\text{NH}_3$ , an appropriate  $\text{NH}_3/\text{NO}$  ratio is necessary. Authors agree that a  $\text{NH}_3/\text{NO}$  ratio near to 1 is good. Furthermore, undesired reactions can occur during the SCR process. Eqn (24) and (25) show the undesired ammonia loss:

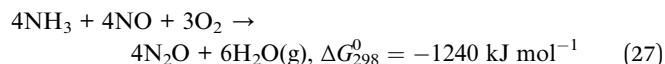


These are the thermodynamically favored reactions but they occur rarely in practice.<sup>80</sup> In addition, there is another undesired reaction during the  $\text{NH}_3$ -SCR process:



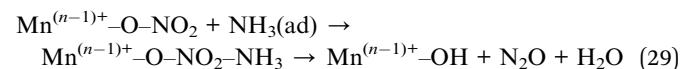
Wang *et al.*<sup>81</sup> claim that eqn (26) may replace eqn (1) as the dominant reaction over  $\text{MnO}_x/\text{TiO}_2$  catalysts when the temperature was raised higher than 175 °C. This was proved by the determination of the components of outlet flue gas. This oxidation of  $\text{NH}_3$  gives a decline in  $\text{NO}$  conversion and extra consumption of  $\text{NH}_3$ .

When the concentration of  $\text{NH}_3$  is appropriate, the formation of  $\text{N}_2\text{O}$  is the primary waste of  $\text{NH}_3$  and this decreases the  $\text{N}_2$  selectivity [eqn (27)].<sup>35</sup>



Adsorbed  $\text{NH}_3$  is oxidized on the catalyst surface to form an amine species ( $\text{NH}_2$ ), which subsequently reacts with  $\text{NO}$  to form  $\text{N}_2$  and  $\text{H}_2\text{O}$ . However, when a further hydrogen atom is abstracted from  $\text{NH}_2$  to form an  $\text{NH}$  species, a  $\text{N}_2\text{O}$  species will be formed by the reaction of the  $\text{NO}$  and  $\text{NH}$  species.<sup>82</sup> Both the L-H mechanism and the E-R mechanism pathways contribute to  $\text{N}_2\text{O}$  formation.

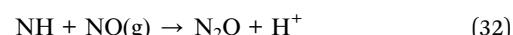
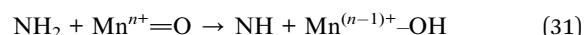
As previously mentioned, in the L-H mechanism, physically adsorbed  $\text{NO}$  can be oxidized by  $\text{Mn}^{n+}$  to  $\text{Mn}^{(n-1)+}\text{-O-NO}$ , which can be further oxidized to monodentate nitrate ( $\text{Mn}^{(n-1)+}\text{-O-NO}_2$ ) [eqn (28)]. The  $\text{Mn}^{(n-1)+}\text{-O-NO}_2$  can react with adsorbed  $\text{NH}_3$  to form  $\text{Mn}^{(n-1)+}\text{-O-NO}_2\text{-NH}_3$ . Subsequently,  $\text{Mn}^{(n-1)+}\text{-O-NO}_2\text{-NH}_3$  will be decomposed to  $\text{N}_2\text{O}$  [eqn (29)]:<sup>17,83</sup>



As previously mentioned in Section 2.2, the reaction of  $\text{NH}_4\text{NO}_3$  with  $\text{NO}$  is a vital step in the fast SCR process. Zhu *et al.*<sup>74</sup> speculated that  $\text{NH}_4\text{NO}_3$  could be decomposed to  $\text{N}_2\text{O}$  and  $\text{H}_2\text{O}$  *via* the L-H mechanism [eqn (30)]. Referring to eqn (28) and (29), the formation of  $\text{N}_2\text{O}$  could be attributed to the better capacity for  $\text{NH}_3$  activation and adsorbed active nitrate species.



As mentioned previously, in the E-R mechanism,  $\text{NH}_2$  species can react with gaseous  $\text{NO}$  to form  $\text{N}_2$  and  $\text{H}_2\text{O}$ . While the  $\text{NH}_2$  species is further oxidized on the metal cation to  $\text{NH}$  species,  $\text{N}_2\text{O}$  will be formed by the reaction of the  $\text{NH}$  species and gaseous  $\text{NO}$  [eqn (31) and (32)].<sup>55,63,84</sup> It is obvious that the formation of  $\text{NH}_2\text{NO}$  is a crucial step of  $\text{NO}$  reduction, which is directly related to the  $\text{NO}$  conversion and  $\text{N}_2$  selectivity.<sup>58</sup>



Whether the adsorbed  $\text{NO}$  is oxidized to monodentate nitrate or the  $\text{NH}_2$  species is dehydrated to  $\text{NH}$ , the  $\text{N}_2$  selectivity will be restrained and  $\text{N}_2\text{O}$  is formed.<sup>85</sup> This is an important difference from the standard SCR. The formation of  $\text{N}_2$  and  $\text{N}_2\text{O}$  during the SCR process is illustrated in Fig. 1.

Hinted at by the previous equations, it is obvious that the two N atoms in  $\text{N}_2\text{O}$  originate from  $\text{NO}$  and  $\text{NH}_3$ , respectively. Suárez *et al.*<sup>86</sup> pointed out that  $\text{N}_2\text{O}$  did not primarily originate from the  $\text{NH}_3$  oxidation reaction. The feasible main reaction path is that between the coordinated  $\text{NO}_3^-$  (generated from  $\text{NO}/$



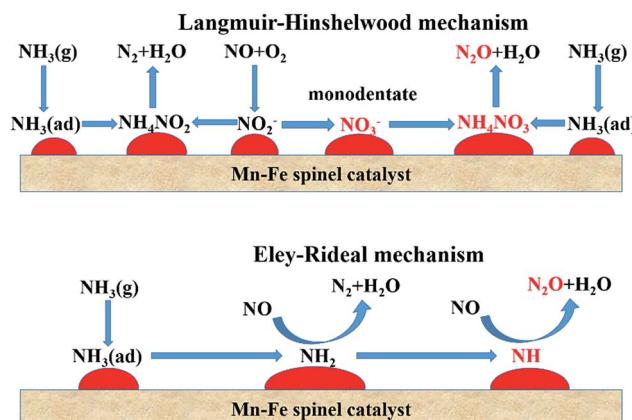


Fig. 1 The scheme of the SCR reaction through L-H and E-R mechanisms over Mn-Fe spinel catalyst. (Reprinted with permission from ref. 35. Copyright 2014 American Chemical Society.)

NO<sub>2</sub> in the presence of O<sub>2</sub>) and the adsorbed NH<sub>x</sub>. Tang *et al.*<sup>63</sup> demonstrated that the N<sub>2</sub>O selectivity of the SCR reaction over  $\beta$ -MnO<sub>2</sub> was higher than that over  $\alpha$ -Mn<sub>2</sub>O<sub>3</sub> at 150 °C. The N<sub>2</sub>O is generated directly from the reaction of NO with NH<sub>3</sub> *via* the E-R mechanism. Use of calcium (Ca) modification improves the performance of N<sub>2</sub> selectivity for Mn-containing catalysts.<sup>87</sup>

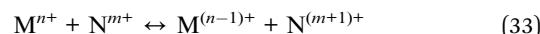
It is suggested that N<sub>2</sub>O formation mainly resulted *via* the E-R mechanism.<sup>53</sup> Yang *et al.*<sup>35</sup> studied the mechanism of N<sub>2</sub>O formation over Mn-Fe spinel catalysts. N<sub>2</sub>O formation *via* the E-R mechanism was much more than *via* the L-H mechanism over the Mn-Fe spinel catalysts. In addition, N<sub>2</sub>O selectivity was not promoted by increasing the NO concentration, but it was increased with the increase in NH<sub>3</sub> concentration. N<sub>2</sub>O selectivity is also related to the gas hourly space velocity (GHSV). It was also found that N<sub>2</sub>O in the SCR reaction over Mn-Ce catalysts was generated *via* the E-R mechanism, not the L-H mechanism.<sup>88</sup> The choice of E-R or L-H mechanisms ways 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.<sup>55,89</sup>

#### 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 O<sub>2</sub>, which benefits the oxidation of NO to NO<sub>2</sub> and improve sulfur resistance. Qi and Tang<sup>76</sup> found that the oxidation of NO to NO<sub>2</sub> was increased significantly after addition of ceria to MnO<sub>x</sub> and that it speeded up the overall process. Actually, pure CeO<sub>2</sub> cannot be applied in industry because of its small specific surface area and low thermal stability.<sup>90</sup> Meanwhile, as is reported,<sup>91</sup> modification with titanium (Ti) or tin (Sn) can improve the SCR property of cerium oxides. Qi *et al.* and Imamura *et al.*<sup>27,92</sup> 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 Mn<sub>2</sub>O<sub>3</sub> and MnO<sub>2</sub> can be detected in pure manganese oxide calcined at the same temperature.

The redox property of catalysts is the key factor of the NH<sub>3</sub>-SCR processes.<sup>29</sup> 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 Mn<sup>4+</sup>/Mn<sup>3+</sup>, Ce<sup>4+</sup>/Ce<sup>3+</sup> and Fe<sup>3+</sup>/Fe<sup>2+</sup>, 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:



There is a typical SCR reaction process *via* the E-R mechanism on Mn-Ce/TiO<sub>2</sub> and Mn-Ce/aluminium oxide (Al<sub>2</sub>O<sub>3</sub>) catalysts.<sup>27,93</sup> Manganese oxides and ceria oxides also interact. They can form a solid solution because of the similarity of their structure.<sup>94</sup> Ceria has a superior oxygen storage performance. Thus, the process of oxidizing Mn<sup>3+</sup> to Mn<sup>4+</sup> is enhanced by using ceria.<sup>95</sup>

Liu *et al.*<sup>96</sup> investigated a Mn-Ce-Ti mixed oxide catalyst prepared using a hydrothermal method, and found that there were dual redox cycles, such as Mn<sup>4+</sup> + Ce<sup>3+</sup>  $\leftrightarrow$  Mn<sup>3+</sup> + Ce<sup>4+</sup> and Mn<sup>4+</sup> + Ti<sup>3+</sup>  $\leftrightarrow$  Mn<sup>3+</sup> + Ti<sup>4+</sup>. 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

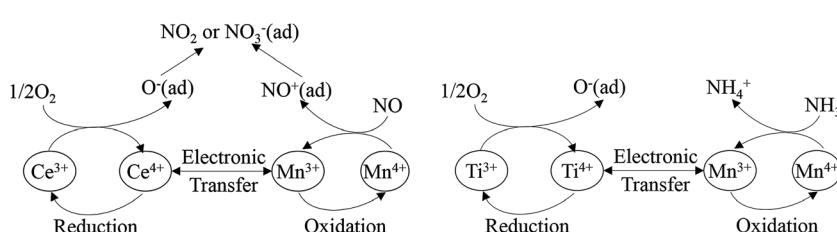


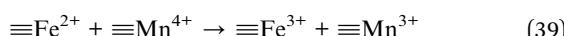
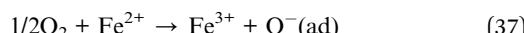
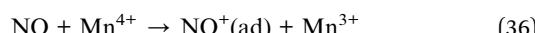
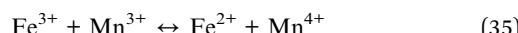
Fig. 2 The scheme of dual redox cycle during SCR process. (Reprinted with permission from ref. 96. Copyright 2014 American Chemical Society.)



facilitates the generation of  $Mn^{4+}$  from  $Mn^{3+}$ . Kwon *et al.*<sup>97</sup> 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<sub>2</sub>. 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<sup>4+</sup>.<sup>23</sup>



Among the Mn–Fe mixed oxide catalysts, electronic transfer occurs between the different oxidation states of Fe<sup>3+</sup>, Fe<sup>2+</sup>, Mn<sup>4+</sup> and Mn<sup>3+</sup>.<sup>98</sup> The performance of the Mn/TiO<sub>2</sub> catalyst was improved by the addition of Fe.<sup>99</sup> The process can be described approximately as follows:



Liu *et al.*<sup>100,101</sup> investigated a series of WO<sub>3</sub>-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<sub>3</sub> was higher than that for the Mn–Zr catalyst alone. There were redox couples of Mn<sup>4+</sup>/Mn<sup>3+</sup> and W<sup>6+</sup>/W<sup>5+</sup>, (*i.e.*, W<sup>5+</sup> + Mn<sup>4+</sup>  $\leftrightarrow$  W<sup>6+</sup> + Mn<sup>3+</sup>). 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<sub>3</sub> and an improvement of the NO conversion (Fig. 4).

Metal oxides could catalyze the reduction of NO with NH<sub>3</sub> *via* the transfer of electrons.<sup>102,103</sup> As is known, catalysts play

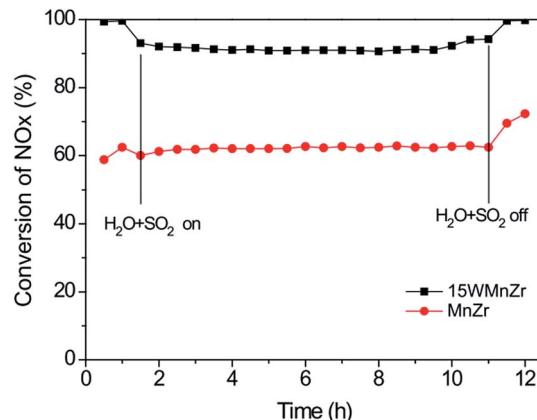


Fig. 4 NO<sub>x</sub> conversion over MnZr and WMnZr catalysts at 300 °C. Reaction conditions: [NO] = [NH<sub>3</sub>] = 500 ppm, [O<sub>2</sub>] = 5%, [H<sub>2</sub>O] = 5%, [SO<sub>2</sub>] = 50 ppm, GHSV = 128 000 h<sup>-1</sup>. (Reprinted from ref. 100. Copyright 2015, with permission from Elsevier.)

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<sup>4+</sup> receives an electron from NO or NH<sub>3</sub> and will be reduced into Mn<sup>3+</sup>. Then the reduced Mn<sup>3+</sup> would be restored to Mn<sup>4+</sup> by an extra oxygen and then the next redox cycle starts. However, a faster pathway is *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

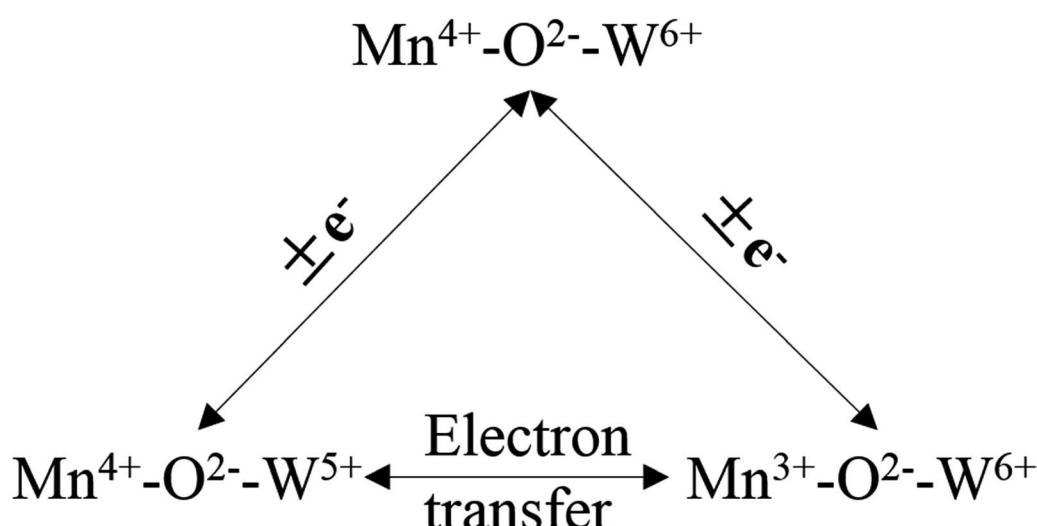


Fig. 3 The electron transfer of redox couples of Mn<sup>4+</sup>/Mn<sup>3+</sup> and W<sup>6+</sup>/W<sup>5+</sup>.



**Table 2** Brunauer–Emmett–Teller (BET) surface area and TOF of different loadings of Mn/TiO<sub>2</sub> catalysts<sup>106a</sup>

Catalyst	BET surface area (m <sup>2</sup> g <sup>-1</sup> )	TOF at different GHSV (h <sup>-1</sup> )	
		50 000	100 000
5% Mn/TiO <sub>2</sub>	238	139.5	127.8
11.1% Mn/TiO <sub>2</sub>	229	60.1	58.7
16.7% Mn/TiO <sub>2</sub>	196	32.3	31.7
20% Mn/TiO <sub>2</sub>	183	27.8	27.5
24% Mn/TiO <sub>2</sub>	165	22.0	21.3

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on TiO<sub>2</sub> modified by W or Mo addition. Depending on the coverage, different polymeric vanadium oxides (VO<sub>x</sub>) could segregate at the surface and these exhibited different turnover frequency (TOF) and selectivity.<sup>104,105</sup> This could be interesting if the same trend existed for MnO<sub>x</sub> species, however, there has been little research proposed on use of different polymeric MnO<sub>x</sub> corresponding to their different performances. Ettireddy *et al.*<sup>106</sup> studied TiO<sub>2</sub> supported manganese oxide catalysts. Different TOFs were obtained on the Mn/TiO<sub>2</sub> loaded with different amounts of manganese (Table 2). It was proposed that the polymeric or microcrystalline form of MnO<sub>x</sub> was envisaged at higher loadings. As a general trend, the TOF and selectivity decreased with the polymeric form increasing at higher loadings. However, further study should be done to confirm which kind of polymeric manganese was formed and its TOF and selectivity should also be determined.

In this section, the reaction mechanisms have been summarized. It was supposed originally that NO<sub>2</sub> could be the reactant of SCR process. However, it is widely agreed that the main reactant for the SCR process is NO, while NO<sub>2</sub> is reduced by the fast SCR process.<sup>107</sup> The synergistic effect among the different metal cations is essential to improve the catalysts' performance, such as NO conversion, selectivity and poisons' tolerance. According to various reports, the low resistance to different poisons is the greatest obstacle for the application of low temperature SCR catalysts.

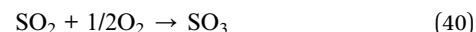
### 3. Catalyst deactivation

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.<sup>108</sup> 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,<sup>99,109,110</sup> however, commercial low temperature SCR catalysts have narrow fields of application because they are not immune to the residual SO<sub>2</sub> and H<sub>2</sub>O contained in real flue gas. The poor tolerance of SO<sub>2</sub> and H<sub>2</sub>O has been a major obstacle for practical applications.<sup>111</sup> Therefore, it is significant to illuminate the poisoning mechanisms of SO<sub>2</sub>, H<sub>2</sub>O and so on.

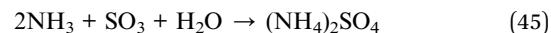
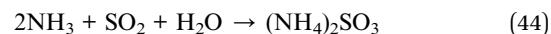
#### 3.1 SO<sub>2</sub> and H<sub>2</sub>O

Sulfur oxides are mainly generated from the combustion of fossil fuels and the sintering of ore. Residual SO<sub>2</sub> after desulfurization can still damage the metal oxide catalysts. The deposition of ammonium sulfates, such as ammonium bisulfate (NH<sub>4</sub>HSO<sub>4</sub>) and ammonium sulfate [(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>], is the primary cause for the deactivation of metal oxide catalysts at low temperature.<sup>112</sup> The decomposition temperature of ammonium sulfite [(NH<sub>4</sub>)<sub>2</sub>SO<sub>3</sub>] and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> salts is higher than the operation temperature of the catalysts. Most researchers regard the poisoning of SO<sub>2</sub> as a major problem. The deactivation of SO<sub>2</sub> can be classified into two categories: deposition of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and sulfation of active sites. The undesired metal sulfates and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> 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 H<sub>2</sub>O on the catalysts' surface blocks the active sites, which are provided for the adsorption of NH<sub>3</sub> and NO.

**3.1.1 Deposition of ammonium sulfates.** The harm caused by (NH<sub>4</sub>)<sub>2</sub>SO<sub>3</sub> and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> is to mainly block the active sites. The micropore surface area and volume was decreased after SO<sub>2</sub> was introduced in to a simulated flue gas.<sup>113</sup> When excess O<sub>2</sub> exists in the flue gas, the trace residual SO<sub>2</sub> can be oxidized to SO<sub>3</sub>, a reaction catalyzed by the metal active sites [eqn (34)]. Furthermore, it was proved that the SO<sub>2</sub> could be easily oxidized on the MnO<sub>x</sub> catalysts' surface. Also, NO<sub>x</sub> would further facilitate the oxidation of SO<sub>2</sub> to SO<sub>3</sub> [eqn (35)].<sup>111</sup> The reaction could be described approximately as follows:



Gaseous NH<sub>3</sub> was assisted by the Brønsted acid sites to form NH<sub>4</sub><sup>+</sup>, which could react with SO<sub>2</sub> or SO<sub>3</sub> to form (NH<sub>4</sub>)<sub>2</sub>SO<sub>3</sub> or (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, respectively. In addition, NH<sub>4</sub>HSO<sub>4</sub> species were also generated in the flue gas. The formation of NH<sub>4</sub>HSO<sub>4</sub>, (NH<sub>4</sub>)<sub>2</sub>SO<sub>3</sub> and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> can be described as follows:<sup>114</sup>



Actually, (NH<sub>4</sub>)<sub>2</sub>SO<sub>3</sub> and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> can be decomposed at a relatively higher temperature. However, low temperature SCR of NO<sub>x</sub> is usually requested at a low operation temperature, which is lower than the decomposition temperature of the (NH<sub>4</sub>)<sub>2</sub>SO<sub>3</sub> and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>. Therefore, removing the undesired side-products of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> salts is a big challenge to researchers.

Almost all of reported MnO<sub>x</sub> catalysts were affected by the introduction of SO<sub>2</sub> in the feed gas.<sup>115</sup> Zhang *et al.*<sup>116</sup> introduced 100 ppm SO<sub>2</sub> in the feed gas, which induced an apparent

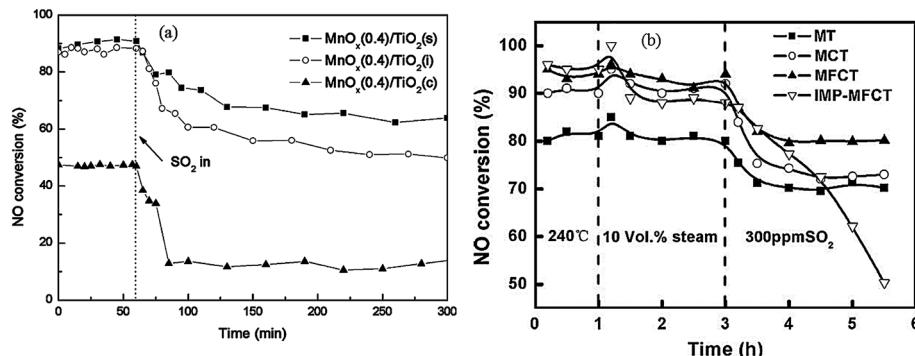


Fig. 5 The effect of  $\text{SO}_2$  on NO conversion. (a) Reaction conditions:  $[\text{NO}] = [\text{NH}_3] = 1000 \text{ ppm}$ ,  $[\text{O}_2] = 3\%$ ,  $[\text{SO}_2] = 200 \text{ ppm}$ , balance  $\text{N}_2$ , temperature:  $150^\circ\text{C}$ ,  $\text{GHSV} = 30\,000 \text{ h}^{-1}$ . (Reprinted from ref. 118. Copyright 2008, with permission from Elsevier.) (b) Reaction conditions:  $[\text{NO}] = 600 \text{ ppm}$ ,  $[\text{NH}_3] = 480 \text{ ppm}$ ,  $[\text{O}_2] = 2\%$ ,  $[\text{SO}_2] = 300 \text{ ppm}$ ,  $[\text{H}_2\text{O}] = 10 \text{ vol\%}$ , balance  $\text{N}_2$ , temperature:  $240^\circ\text{C}$ ,  $\text{GHSV} = 24\,000 \text{ h}^{-1}$ . (Reprinted from ref. 111. Copyright 2009, with permission from Elsevier.)

decrease of NO conversion over the Mn–Ce metal oxide catalysts supported on carbon nanotubes. Lu *et al.*<sup>117</sup> fed 200 ppm  $\text{SO}_2$  to the flue gas, and then the  $\text{NO}_x$  conversion of Mn–Ce/TiO<sub>2</sub> catalyst decreased from an initial value of 99% to about 78%. Jiang *et al.*<sup>118</sup> investigated the effect of  $\text{SO}_2$  on  $\text{MnO}_x(0.4)/\text{TiO}_2$  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.*<sup>111</sup> prepared  $\text{MnO}_2\text{--Fe}_2\text{O}_3\text{--CeO}_2\text{--TiO}_2$  catalysts. The performance of this catalyst was decreased by introducing  $\text{SO}_2$ . The  $\text{NH}_4^+$  species and the  $\text{SO}_4^{2-}$  species were determined from Fourier-transform infrared spectra. The  $\text{NH}_4^+$  species were chemisorbed on to the Brønsted acid sites.<sup>119</sup> This means that the poisoning of  $\text{SO}_2$  can be *via* the formation and deposition of  $(\text{NH}_4)_2\text{SO}_4$ , which blocks the active channels of the catalyst. The NO conversion was decreased to 50% from 90% (Fig. 5b).

Xu *et al.*<sup>120</sup> also found that  $\text{NH}_4\text{HSO}_3$  and  $\text{NH}_4\text{HSO}_4$  formed *via* the reaction of  $\text{SO}_2$  and  $\text{NH}_3$  could be deposited on catalysts' surface and blocked the active sites [eqn (34)–(39)]. Furthermore, more Brønsted acid sites will be generated while the sulfates are formed by  $\text{SO}_2$  adsorption on surface. The Lewis acid site could be transformed to the Brønsted acid site by adsorption of a water molecule.<sup>121</sup> This means that a wet atmosphere would promote the formation of the Brønsted acid sites, which facilitates the sorption of  $\text{NH}_4^+$ .<sup>122</sup> In terms of diffuse reflectance infrared Fourier transform (DRIFT) spectra, Jiang *et al.*<sup>123</sup> proved that the formation of  $\text{NH}_4^+$  was promoted after introducing  $\text{SO}_2$ . However, even though Brønsted acid sites were formed by the sulfatization, NO conversion was decreased because  $\text{SO}_2$  occupied the NO adsorption sites.

Therefore, to obtain high NO conversion, it is necessary to prevent the formation of  $(\text{NH}_4)_2\text{SO}_4$ . Actually, it is nearly impossible to eliminate the residual  $\text{SO}_2$  completely. Efficient ways to do it may be preventing the oxidation of  $\text{SO}_2$  and decreasing the decomposition temperature of  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{NH}_4\text{HSO}_4$  on the catalysts' surface.

Jin *et al.*<sup>25</sup> studied the Mn–Ce/TiO<sub>2</sub> and Mn/TiO<sub>2</sub> catalysts. In terms of the thermogravimetry/differential scanning calorimetry (TG/DSC) results, the decomposition temperatures of

$(\text{NH}_4)_2\text{SO}_4$  and  $\text{NH}_4\text{HSO}_4$  on the Mn/TiO<sub>2</sub> catalyst was determined to be  $213^\circ\text{C}$  and  $361^\circ\text{C}$ , respectively. However, in the case of the Mn–Ce/TiO<sub>2</sub> catalyst, the decomposition temperature of  $\text{NH}_4\text{HSO}_4$  was approximately  $286^\circ\text{C}$ , which was much lower than  $361^\circ\text{C}$ . This indicated that the thermal stability of  $\text{NH}_4\text{HSO}_4$  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<sub>2</sub> catalyst.

There is a universal agreement that residual  $\text{SO}_2$  damages the metal oxide catalysts and decreases the NO conversion.  $(\text{NH}_4)_2\text{SO}_3$  and  $(\text{NH}_4)_2\text{SO}_4$  were formed on catalysts' surface by the reaction of  $\text{SO}_2$ . Researchers found that the NO conversion would increase for a while when  $\text{SO}_2$  was introduced and then finally decrease. The adsorption of  $\text{SO}_2$  improved the amount of Lewis acid sites, and thus the capacity of  $\text{NH}_3$  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  $\text{SO}_2$  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.<sup>124</sup> Jiang *et al.*<sup>123</sup> described a proposed mechanism of  $\text{SO}_2$  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  $\text{SO}_2$  exist in the flue gas, NO and  $\text{SO}_2$  were adsorbed competitively. The adsorption ability of  $\text{SO}_2$  was much higher than that of NO (Fig. 6c), so  $\text{SO}_2$  occupied the active sites and the catalyst was sulfated. Furthermore, Fig. 6d shows that  $\text{NH}_3$  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 Brønsted acid sites *via* bonding of a water molecule. Therefore, this did not affect the adsorption of  $\text{NH}_3$ , because  $\text{NH}_3$  could also be adsorbed on the Brønsted acid sites (Fig. 6e). It is therefore, proposed that the effect of  $\text{SO}_2$  was mainly on the adsorption of NO rather than on the adsorption of  $\text{NH}_3$ .

Yu *et al.*<sup>111</sup> investigated the formation of metal sulfation on fresh Mn–Fe–Ce–Ti catalyst impregnated  $(\text{NH}_4)_2\text{SO}_4$ . In terms of



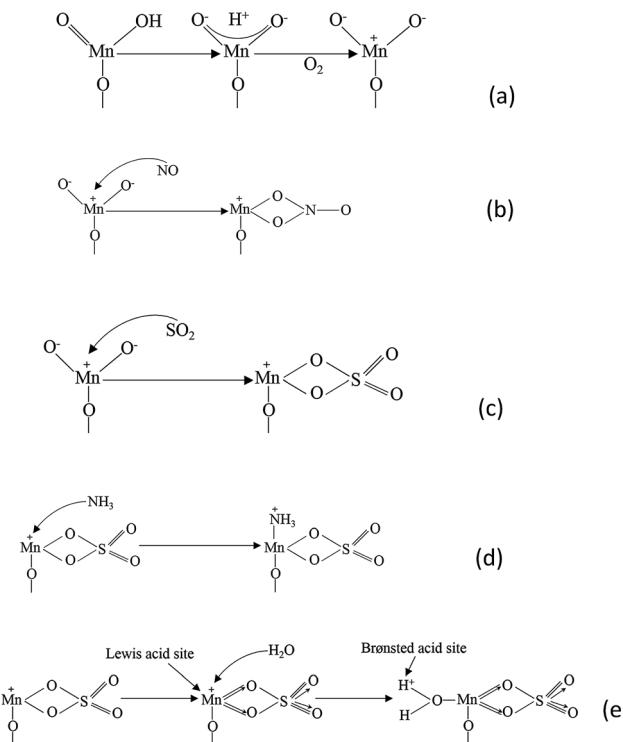


Fig. 6 The proposed mechanism of  $\text{SO}_2$  deactivation effect on the SCR reaction. (Reprinted with permission from ref. 123. Copyright (2010) American Chemical Society.)

the TG curve,  $\text{SO}_3$  was released from  $(\text{NH}_4)_2\text{SO}_4$  decomposition and then combined with Mn species to form manganese sulfate ( $\text{MnSO}_4$ ). They claimed that the  $\text{MnSO}_4$  could not be formed directly by the reaction of oxidized  $\text{SO}_2$  and Mn species.<sup>57</sup> Kijlstra *et al.*<sup>125</sup> proved that the transformation of  $\text{MnO}$  to  $\text{MnSO}_4$  on  $\text{MnO}_x/\text{Al}_2\text{O}_3$  catalyst significantly deactivated the catalyst's activity.

Efforts have been made to facilitate the  $\text{SO}_2$  tolerance of metal oxide catalysts. Ceria may trap  $\text{SO}_2$  for  $\text{NO}_x$  storage catalysts to limit the sulfation of the dominating active phase and inhibit the formation of  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{NH}_4\text{HSO}_4$ .<sup>117,126</sup> After pre-treatment with  $\text{SO}_2$ , Ce doped  $\text{Mn}/\text{TiO}_2$  catalysts had more Lewis acid sites than  $\text{Mn}/\text{TiO}_2$  catalysts. This result implied that the addition of ceria could prevent the Lewis acid sites from the sulfation of  $\text{SO}_2$ .

Liu *et al.*<sup>127</sup> 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  $\text{Mn}_5\text{--Ce}_5$  catalyst prepared using the surfactant template method showed the highest  $\text{NO}_x$  conversion whether  $\text{SO}_2$  and  $\text{H}_2\text{O}$  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  $\text{NO}_x$  reduction.

In terms of *in situ* DRIFT analysis, Jin *et al.*<sup>25</sup> found that the Lewis acid sites could be preserved effectively with the doping of Ce while the  $\text{SO}_2$  was added.  $\text{SO}_2$  was oxidized to  $\text{SO}_3$  or sulfation species on  $\text{MnO}_x$ , however,  $\text{SO}_3$  and sulfation species move

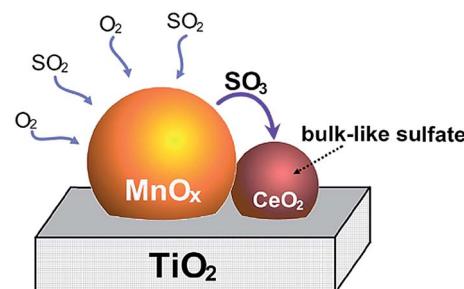


Fig. 7 The formation schematic of bulk-like sulfate on Mn–Ce/Ti catalysts. (Reprinted from ref. 25. Copyright 2013, with permission from Elsevier.)

into ceria to form bulk-like sulfate species. Therefore, ceria trapped  $\text{SO}_2$  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  $\text{MnO}_x$  catalyst. Referring to the study of Kylhammar *et al.*,<sup>128</sup> it is assumed that the bulk sulfation species in ceria reveals a high mobility, which facilitates their desorption.

Wang *et al.*,<sup>113</sup> Xu *et al.*,<sup>120</sup> and Shi *et al.*<sup>129</sup> proved that the active manganese cation was reserved for ceria, which finally sulfated it.  $\text{Ce}^{4+}$  distributed on the catalysts' surface transformed into  $\text{Ce}^{3+}$  after sulfation. The reaction can be described as follows:



Furthermore, it is reported that Zr could optimize the redox property and strengthen  $\text{SO}_2$  tolerance.<sup>89</sup> Chang *et al.*<sup>130,131</sup> reported that Sn modification could further improve the tolerance of the Mn–Ce catalyst to  $\text{SO}_2$  and  $\text{H}_2\text{O}$ . They compared the NO conversion of  $\text{Sn}(0.1)\text{--Mn}(0.4)\text{--Ce}(0.5)\text{--O}$  and  $\text{Mn}(0.4)\text{--Ce}(0.6)\text{--O}$  mixed oxide catalysts. It was obvious that the NO conversion of the  $\text{Mn}(0.4)\text{--Ce}(0.6)\text{--O}$  catalyst was decreased more significantly than that of the  $\text{Sn}(0.1)\text{--Mn}(0.4)\text{--Ce}(0.5)\text{--O}$  catalyst when 200 ppm of  $\text{SO}_2$  and 3%  $\text{O}_2$  was fed in to the system at 220 °C.

Shi *et al.*<sup>132</sup> compared the resistance of the  $\text{Mn}/\text{TiO}_2$  catalyst and the hierarchically macro-mesoporous  $\text{Mn}/\text{TiO}_2$  (HM- $\text{Mn}/\text{TiO}_2$ ) catalyst prepared by the sol–gel method. After feeding 30 ppm  $\text{SO}_2$  to the system, the NO conversion of the  $\text{Mn}/\text{TiO}_2$  catalyst decreased sharply from 57% to 15%, however, the NO conversion of the HM- $\text{Mn}/\text{TiO}_2$  catalyst kept a higher value of more than 84%. The result indicated that maybe the  $\text{SO}_2$  resistance could be improved by using a hierarchically macro-mesoporous structure.

As previously, because  $\text{NH}_3$  could be adsorbed on both the Lewis acid sites and the Brønsted acid sites, there is little influence on the adsorption of  $\text{NH}_3$ . However, the adsorption ability of  $\text{SO}_2$  was higher than that of NO. Residual  $\text{SO}_2$  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  $\text{SO}_2$  and



Mn cations. The correlations should be established between the extent of sulfation and the degree of dispersion of  $\text{MnO}_x$  species at the surface.

**3.1.3 Effect of  $\text{H}_2\text{O}$ .** Water vapor could decrease the activity and show a notable inhibition on low temperature SCR.  $\text{H}_2\text{O}$  can be generated from the original flue gas or the reaction of SCR of NO. Even though there is no  $\text{H}_2\text{O}$  in the original flue gas,  $\text{H}_2\text{O}$  vapor will be generated during the SCR reaction, as shown in eqn (1). This means that the presence of  $\text{H}_2\text{O}$  is nearly inevitable. Therefore, many efforts have been made to evaluate the durability of metal oxide catalysts in the presence of  $\text{H}_2\text{O}$  vapor. As mentioned previously, trace  $\text{SO}_2$  could still decrease the activity of the metal catalyst. The deactivation process of  $\text{SO}_2$  would be enhanced in the case of  $\text{H}_2\text{O}$  vapor.

The main reason for the decrease of activity can be attributed to the competitive adsorption of  $\text{H}_2\text{O}$ . Many researchers reported that the adsorption of  $\text{H}_2\text{O}$  on the catalysts' surface blocked the active sites, which are provided for the adsorption of  $\text{NH}_3$  and  $\text{NO}$ .<sup>109,133</sup> Chen *et al.*<sup>134</sup> studied a  $\text{MnO}_x$ -niobium oxides ( $\text{NbO}_x$ )- $\text{CeO}_2$  catalyst prepared by a sol-gel method and found that the adsorption of  $\text{H}_2\text{O}$  inhibited the adsorption of  $\text{NO}_x$ . Xiong *et al.*<sup>108</sup> compared the SCR performance of Mn-Fe spinel catalysts in the presence and absence of  $\text{H}_2\text{O}$ . They proposed that the effect of  $\text{H}_2\text{O}$  can be attributed to the competitive adsorption, the decrease of oxidation ability and the inhibition of interface reactions.<sup>135,136</sup> The temperature programmed desorption (TPD) profiles of  $\text{NH}_3$  and  $\text{NO}_x$  were obtained, and the  $\text{NO}_x$  and  $\text{NH}_3$  adsorption capacity of Mn-Fe spinel in the absence of  $\text{H}_2\text{O}$  and in the presence of 5%  $\text{H}_2\text{O}$  are shown in Table 3.

Fig. 8 shows that the  $\text{NO}_x$  conversion apparently decreased when 5%  $\text{H}_2\text{O}$  was fed in to the flue gas, especially at the lower temperature, *e.g.*, below 160 °C. The adsorption of  $\text{H}_2\text{O}$  vapor on the catalyst's active sites deprived the sites of  $\text{NH}_3$  adsorption, which apparently decreased the NO conversion. There is

a summary of Mn-containing catalysts' performance in the presence and in the absence of  $\text{SO}_2$  and  $\text{H}_2\text{O}$  (Table 4).

**3.1.4 Regeneration.** Many articles reported that the deactivated  $(\text{NH}_4)_2\text{SO}_4$  could be regenerated after use. Water washing, thermal regeneration, thermal reduction regeneration and reductive regeneration were the usual methods to regenerate the deactivated catalysts.<sup>137,149</sup> Yu *et al.*<sup>150</sup> investigated the regeneration of the SCR catalyst using dilute sodium hydroxide solution. The catalyst was deactivated by the deposition of sulfates on the surface. Pourkhalil *et al.*<sup>151</sup> regenerated the deactivated  $\text{MnO}_x$  catalysts *via* heating at 350 °C for 2 h. This was a reversible process because of  $(\text{NH}_4)_2\text{SO}_4$  salts can be decomposed. Jin *et al.*<sup>25</sup> regenerated the Mn/Ti and Mn-Ce/Ti catalysts with water washing (Fig. 9a). Shi *et al.*<sup>129</sup> regenerated the  $\text{CeO}_2$  catalysts using a thermal treatment (Fig. 9b).

Huang *et al.*<sup>152</sup> investigated a series of Fe-Mn oxide catalysts supported on mesoporous silica (MPS), which showed good activity. When  $\text{H}_2\text{O}$  and  $\text{SO}_2$  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  $\text{NH}_4\text{HSO}_4$  and  $(\text{NH}_4)_2\text{SO}_4$  in the presence of both  $\text{H}_2\text{O}$  and  $\text{SO}_2$ . 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  $(\text{NH}_4)_2\text{SO}_4$ . When the temperature is above 140 °C,  $\text{H}_2\text{O}$  has no negative effect on its activity.

Guan *et al.*<sup>153</sup> investigated the resistance to deactivation by  $\text{H}_2\text{O}$  and  $\text{SO}_2$  of  $\text{Ti}_{0.9}\text{Ce}_{0.05}\text{V}_{0.05}\text{O}_{2-x}$  catalysts, which showed a high NO conversion and  $\text{N}_2$  selectivity. After feeding 400 ppm  $\text{SO}_2$  for 26 h at 150 °C, the surface of catalyst was deposited with significant agglomeration and bulk  $\text{NH}_4\text{NO}_3$  and  $(\text{NH}_4)_2\text{SO}_4$  with a size of 30–50  $\mu\text{m}$ . Then, the  $\text{NH}_4\text{NO}_3$  and  $(\text{NH}_4)_2\text{SO}_4$  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.

Table 3 Capacity of Mn-Fe spinel for  $\text{NH}_3$  and  $\text{NO}_x$  adsorption at 150 °C  $\mu\text{mol}^{-1} \text{g}^{-1}$ <sup>108</sup>

Condition	$\text{NH}_3$ ( $\mu\text{mol}^{-1} \text{g}^{-1}$ )	$\text{NO}_x$ ( $\mu\text{mol}^{-1} \text{g}^{-1}$ )
In the absence of $\text{H}_2\text{O}$	122	82
In the presence of 5% $\text{H}_2\text{O}$	105	46

### 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

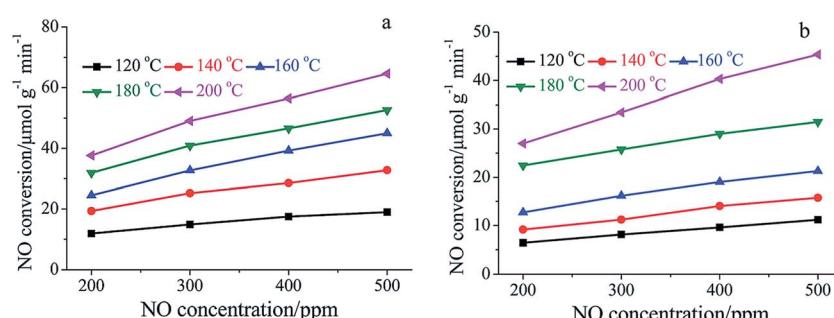


Fig. 8 Dependence of NO conversion rate on gaseous NO concentration over Mn-Fe spinel: (a) in the absence of  $\text{H}_2\text{O}$ ; (b) in the presence of 5%  $\text{H}_2\text{O}$ . (Reproduced from ref. 108 with permission from the Royal Society of Chemistry.)



Table 4 Summary of Mn-containing catalysts' performance in the absence/presence of  $\text{SO}_2$  and  $\text{H}_2\text{O}$ 

Catalysts	Preparation process <sup>a</sup>	Reaction conditions <sup>b</sup>	NO <sub>x</sub> conversion <sup>c</sup>		Poison condition <sup>d</sup>	NO <sub>x</sub> conversion <sup>e</sup>	Ref.
			NO <sub>x</sub> conversion	NO <sub>x</sub> conversion			
$\text{Mn}_{0.4}\text{-Ce}_{0.5}\text{-Sr}_{0.1}\text{-O}$	Co-precipitation/500 °C/6 h	0.1% NO, 0.1% $\text{NH}_3$ , 2% $\text{O}_2$ /35 000 $\text{h}^{-1}$	100%	(110–230 °C)	0.01% $\text{SO}_2$ , 9% $\text{H}_2\text{O}$	62% (110 °C)	130
$\text{Mn}_{0.2}\text{-Ce}_{0.1}\text{-Ti}_{0.7}\text{-O}$	Hydrothermal/500 °C/6 h	0.05% NO, 0.05% $\text{NH}_3$ , 5% $\text{O}_2$ /64 000 $\text{h}^{-1}$	>92%	(150–250 °C)	0.005% $\text{SO}_2$ , 5% $\text{H}_2\text{O}$	~90% (200 °C/10 h)	96
$\text{Mn}_{0.3}\text{-Ce}_{0.7}\text{-O}$	Citric acid/650 °C/6 h	0.1% NO, 0.1% $\text{NH}_3$ , 2% $\text{O}_2$ /42 000 $\text{h}^{-1}$	>95%	(100–150 °C)	0.01% $\text{SO}_2$ , 2.5% $\text{H}_2\text{O}$	~95% (120 °C/4 h)	76
$\text{Mn}_5\text{-Ce}_5\text{-O}$	Surfactant template/500 °C/4 h	0.05% NO, 0.05% $\text{NH}_3$ , 5% $\text{O}_2$ /64 000 $\text{h}^{-1}$	>95%	(100–200 °C)	0.005% $\text{SO}_2$ , 5% $\text{H}_2\text{O}$	>90% (150–200 °C)	127
$\text{Mn}_{0.28}\text{-Ce}_{0.5}\text{-Ti}_{0.67}\text{-O}$	Co-precipitation/400 °C/2 h	0.06% NO, 0.06% $\text{NH}_3$ , 3% $\text{O}_2$ /40 000 $\text{h}^{-1}$	>92%	(120–180 °C)	0.07% $\text{SO}_2$ , 3% $\text{H}_2\text{O}$	35% (120 °C/13 h)	137
$\text{Mn}_{0.4}\text{-Ce}_{0.07}\text{-Ti}_1\text{-O}$	Sol-gel/500 °C/6 h	0.08% NO, 0.08% $\text{NH}_3$ , 3% $\text{O}_2$ /40 000 $\text{h}^{-1}$	~100%	(100–180 °C)	0.01% $\text{SO}_2$ , 3% $\text{H}_2\text{O}$	~60% (100 °C/10 h)	138
$\text{Sh}_{0.1}\text{-Mn}_{0.4}\text{-Ce}_{0.5}\text{-O}$	Co-precipitation/500 °C/6 h	0.1% NO, 0.1% $\text{NH}_3$ , 2% $\text{O}_2$ /35 000 $\text{cm}^3 \text{g}^{-1} \text{h}^{-1}$	~100%	(110–230 °C)	0.01% $\text{SO}_2$ , 12% $\text{H}_2\text{O}$	~70% (110 °C/9 h)	131
$\text{Mn}_{1.3}\text{-Ce}_{0.3}\text{-TiO}_2\text{-graphene}$	Impregnation/500 °C/6 h	0.05% NO, 0.05% $\text{NH}_3$ , 7% $\text{O}_2$ /67 000 $\text{h}^{-1}$	>90%	(140–180 °C)	0.02% $\text{SO}_2$ , 10% $\text{H}_2\text{O}$	~75% (180 °C/3 h)	117
$\text{Mn}_{0.6}\text{/Ce}_{0.5}\text{-Zr}_{0.5}\text{-O}$	Impregnation/500 °C/6 h	0.06% NO, 0.06% $\text{NH}_3$ , 3% $\text{O}_2$ /30 000 $\text{h}^{-1}$	>90%	(140–180 °C)	0.01% $\text{SO}_2$ , 3% $\text{H}_2\text{O}$	~90% (180 °C/3 h)	139
$\text{Mn}_{0.4}\text{-Ce}_{0.07}\text{-Ti}_1\text{-O}$	Sol-gel/500 °C/6 h	0.1% NO, 0.1% $\text{NH}_3$ , 3% $\text{O}_2$ /40 000 $\text{h}^{-1}$	~100%	(120–220 °C)	0.01% $\text{SO}_2$ , 3% $\text{H}_2\text{O}$	~82% (150 °C/7 h)	140
$\text{Mn}_{0.4}\text{-Ce}_{0.5}\text{-W}_{0.1}\text{-O}$	Sol-gel/600 °C/3 h	0.05% NO, 0.05% $\text{NH}_3$ , 5% $\text{O}_2$ /40 000 $\text{h}^{-1}$	>80%	(140–300 °C)	0.006% $\text{SO}_2$ , 5% $\text{H}_2\text{O}$	~55% (150 °C/3 h)	141
$\text{Mn}_{0.3}\text{-Ce}_{0.7}\text{-O}$	Citric acid/550 °C/6 h	0.1% NO, 0.1% $\text{NH}_3$ , 2% $\text{O}_2$ /42 000 $\text{h}^{-1}$	~100%	(120–150 °C)	0.01% $\text{SO}_2$ , 6% $\text{H}_2\text{O}$	~92% (120 °C/4 h)	23
$\text{Mn}_{0.2}\text{-Ce}_{0.1}\text{-Ti}_{0.7}\text{-O}$	Hydrothermal/500 °C/6 h	0.05% NO, 0.05% $\text{NH}_3$ , 5% $\text{O}_2$ /64 000 $\text{h}^{-1}$	>95%	(150–350 °C)	0.005% $\text{SO}_2$ , 5% $\text{H}_2\text{O}$	~90% (200 °C/10 h)	96
$\text{Mn}\text{-Ce}\text{-W}\text{-Ti}\text{-O}$	Impregnation/400 °C/4 h	0.02% NO, 0.02% $\text{NH}_3$ , 8% $\text{O}_2$ /30 000 $\text{h}^{-1}$	~100%	(160–200 °C)	0.01% $\text{SO}_2$ , 8% $\text{H}_2\text{O}$	~85% (180 °C/10 h)	97
$\text{Mn}_{0.4}\text{-Ce}_{0.07}\text{-Ti}_1\text{-O}$	Co-precipitation/400 °C/2 h	0.06% NO, 0.06% $\text{NH}_3$ , 3% $\text{O}_2$ /40 000 $\text{h}^{-1}$	>92%	(120–180 °C)	0.07% $\text{SO}_2$ , 3% $\text{H}_2\text{O}$	61% (120 °C/2.5 h)	142
$\text{Mn}_{0.2}\text{-Fe}_{0.15}\text{-Ce}_{0.3}\text{-Ti}_1\text{-O}$	Sol-gel/500 °C/6 h	0.06% NO, 0.06% $\text{NH}_3$ , 3% $\text{O}_2$ /50 000 $\text{h}^{-1}$	>95%	(160–260 °C)	0.01% $\text{SO}_2$ , 3% $\text{H}_2\text{O}$	~85% (180 °C/6 h)	143
$\text{Mn}_{0.6}\text{-Ce}_{0.5}\text{-Zr}_{0.5}\text{-O}$	Impregnation/500 °C/6 h	0.06% NO, 0.066% $\text{NH}_3$ , 6% $\text{O}_2$ /45 000 $\text{h}^{-1}$	>95%	(140–220 °C)	0.01% $\text{SO}_2$ , 3% $\text{H}_2\text{O}$	~90% (180 °C/7 h)	144
$\text{Mn}_{0.4}\text{-Fe}_{0.1}\text{-Ce}_{0.5}\text{-O}$	Co-precipitation/500 °C/6 h	0.1% NO, 0.1% $\text{NH}_3$ , 2% $\text{O}_2$ /84 000 $\text{h}^{-1}$	>82%	(150–180 °C)	0.01% $\text{SO}_2$ , 2.5% $\text{H}_2\text{O}$	>90% (150 °C/4 h)	27
$\text{Mn}_{0.4}\text{-Ce}_{0.1}\text{-Ti}_1\text{-O}$	Sol-gel/500 °C/6 h	0.08% NO, 0.08% $\text{NH}_3$ , 3% $\text{O}_2$ /40 000 $\text{h}^{-1}$	~100%	(150 °C)	0.01% $\text{SO}_2$ , 3% $\text{H}_2\text{O}$	~60% (150 °C/10 h)	25
$\text{Mn}_{0.6}\text{-Fe}_{0.4}\text{-O}$	Citric acid/500 °C/3 h	0.1% NO, 0.1% $\text{NH}_3$ , 3% $\text{O}_2$ /30 000 $\text{h}^{-1}$	>95%	(90–220 °C)	0.01% $\text{SO}_2$ , 5% $\text{H}_2\text{O}$	~88% (120 °C/6 h)	98
10% Mn/Fe-Ti spinel	Impregnation/500 °C/3 h	0.05% NO, 0.05% $\text{NH}_3$ , 2% $\text{O}_2$ /24 000 $\text{cm}^3 \text{g}^{-1} \text{h}^{-1}$	>95%	(150–250 °C)	0.006% $\text{SO}_2$ , 8% $\text{H}_2\text{O}$	~80% (200 °C/13 h)	53
$\text{Mn}_{0.4}\text{-Fe}_{0.1}\text{-Ti}_{0.5}\text{-Zr}_{0.5}\text{-O}$	Sol-gel/500 °C/6 h	0.1% NO, 0.1% $\text{NH}_3$ , 4% $\text{O}_2$ /30 000 $\text{h}^{-1}$	>95%	(80–180 °C)	0.01% $\text{SO}_2$ , 8% $\text{H}_2\text{O}$	~70% (150 °C/5 h)	89
$\text{Mn}_{0.4}\text{-Fe}_{0.1}\text{-Ti}_{0.5}\text{-O}$	Sol-gel/500 °C/6 h	0.1% NO, 0.1% $\text{NH}_3$ , 3% $\text{O}_2$ /30 000 $\text{h}^{-1}$	~100%	(150 °C)	0.02% $\text{SO}_2$	~65% (150 °C/6 h)	123
$\text{Mn}_{0.6}\text{-Ti}_1\text{-O}$	Sol-gel/500 °C/6 h	0.1% NO, 0.1% $\text{NH}_3$ , 3% $\text{O}_2$ /30 000 $\text{h}^{-1}$	~100%	(110 °C)	0.003% $\text{SO}_2$	~85% (120 °C/9 h)	132
$\text{Mn}_{0.4}\text{-Ti}_1\text{-O}$	Sol-gel/500 °C/6 h	0.1% NO, 0.1% $\text{NH}_3$ , 3% $\text{O}_2$ /30 000 $\text{h}^{-1}$	>90%	(180–250 °C)	0.02% $\text{SO}_2$ , 3% $\text{H}_2\text{O}$	~70% (150 °C/6 h)	118
$\text{Mn}\text{-Fe}\text{-Ce}\text{-Ti}\text{-O}$	Sol-gel/500 °C/6 h	0.06% NO, 0.048% $\text{NH}_3$ , 2% $\text{O}_2$ /24 000 $\text{h}^{-1}$	>80%	(200–300 °C)	0.03% $\text{SO}_2$ , 10% $\text{H}_2\text{O}$	~80% (240 °C/5 h)	111
7% Mn/Ti <sub>1</sub> -graphene	Impregnation/450 °C/6 h	0.05% NO, 0.05% $\text{NH}_3$ , 7% $\text{O}_2$ /67 000 $\text{h}^{-1}$	>80%	(120–180 °C)	0.02% $\text{SO}_2$ , 10% $\text{H}_2\text{O}$	~72% (180 °C/3 h)	115
$\text{Mn}_{0.5}\text{-Zr}_{0.5}\text{-O}$	Citric acid/450 °C/3 h	0.1% NO, 0.1% $\text{NH}_3$ , 3% $\text{O}_2$ /30 000 $\text{h}^{-1}$	~100%	(100–200 °C)	0.01% $\text{SO}_2$ , 5% $\text{H}_2\text{O}$	~40% (150 °C/13 h)	124
$\text{Mn}_{2.5}\text{-Ce}_{0.1}\text{-Ti}_1\text{-O}$	Co-precipitation/350 °C/6 h	0.05% NO, 0.05% $\text{NH}_3$ , 5% $\text{O}_2$ /30 000 $\text{h}^{-1}$	~100%	(60–280 °C)	0.01% $\text{SO}_2$ , 11% $\text{H}_2\text{O}$	~60% (125 °C/10 h)	39
$\text{Mn}_4\text{/Co}_{0.05}\text{-Ce}_{2.7}\text{-Zr}_{2.7}$	Impregnation/500 °C/6 h	0.06% NO, 0.06% $\text{NH}_3$ , 6% $\text{O}_2$ /45 000 $\text{h}^{-1}$	>97%	(120–220 °C)	0.01% $\text{SO}_2$ , 3% $\text{H}_2\text{O}$	~93% (180 °C/7 h)	109
$\text{Mn}_{0.6}\text{-Ce}_{0.4}\text{-O}$	Citric acid/650 °C/3 h	0.1% NO, 0.1% $\text{NH}_3$ , 3% $\text{O}_2$ /30 000 $\text{h}^{-1}$	~100%	(120–220 °C)	0.01% $\text{SO}_2$	~82% (120 °C/5 h)	37
$\text{Mn}_{0.3}\text{-Ce}_{0.7}\text{-O}$	Citric acid/650 °C/6 h	0.05% NO, 0.05% $\text{NH}_3$ , 2% $\text{O}_2$ /52 000 $\text{cm}^3 \text{g}^{-1} \text{h}^{-1}$	>95%	(120–160 °C)	5% $\text{H}_2\text{O}$	~70% (120–140 °C)	61
$\text{Mn}_{0.3}\text{-Ce}_{0.7}\text{-O}$	Citric acid/650 °C/6 h	0.05% NO, 0.05% $\text{NH}_3$ , 2% $\text{O}_2$ /120 000 $\text{cm}^3 \text{g}^{-1} \text{h}^{-1}$	>90%	(140–200 °C)	5% $\text{H}_2\text{O}$	>70% (160–200 °C)	88
$\text{Mn}\text{-Ce}\text{/W}\text{-Zr}\text{-O}$	Impregnation/550 °C/3 h	0.1% NO, 0.1% $\text{NH}_3$ , 5% $\text{O}_2$ /10 000 $\text{h}^{-1}$	>90%	(150–250 °C)	0.01% $\text{SO}_2$ , 10% $\text{H}_2\text{O}$	>80% (140–240 °C)	145
Mn/Ce activated carbon honeycomb	Impregnation/400 °C/3 h	0.05% NO, 0.05% $\text{NH}_3$ , 5% $\text{O}_2$ /19 100 $\text{h}^{-1}$	~84%	(160 °C)	0.03% $\text{SO}_2$	~44% (160 °C/7 h)	113
$\text{Mn}_{0.23}\text{-Nb}_{0.23}\text{-Ce}_{0.54}\text{-O}$	Co-precipitation/650 °C/5 h	0.1% NO, 0.1% $\text{NH}_3$ , 10% $\text{O}_2$ /52 000 $\text{h}^{-1}$	—	5% $\text{H}_2\text{O}$	>80% (200–300 °C)	146	
$\text{Mn}_{0.23}\text{-Nb}_{0.23}\text{-Ce}_{0.54}\text{-O}$	Co-precipitation/650 °C/5 h	0.1% NO, 0.1% $\text{NH}_3$ , 10% $\text{O}_2$ /52 000 $\text{h}^{-1}$	>78%	(200–300 °C)	0.005% $\text{SO}_2$ , 5% $\text{H}_2\text{O}$	~20% (250 °C/0.5 h)	147
$\text{Mn}_{0.25}\text{-La}_{2.5}\text{-Ce}_1\text{-Ni}_1$	500 °C/6 h	0.06% NO, 0.06% $\text{NH}_3$ , 6% $\text{O}_2$ /20 000 $\text{h}^{-1}$	~98%	(150–350 °C)	0.03% $\text{SO}_2$	~85% (200 °C/4 h)	148

<sup>a</sup> Preparation process means of preparation method, calcination temperature and time. <sup>b</sup> Reaction gas mixture and GHSV. <sup>c</sup> NO conversion at a specified temperature. <sup>d</sup> The concentration of  $\text{SO}_2$  and  $\text{H}_2\text{O}$  introduced on the basis of reaction gas. <sup>e</sup> NO conversion at a certain temperature after introducing  $\text{SO}_2$  and/or  $\text{H}_2\text{O}$  for a specified time.

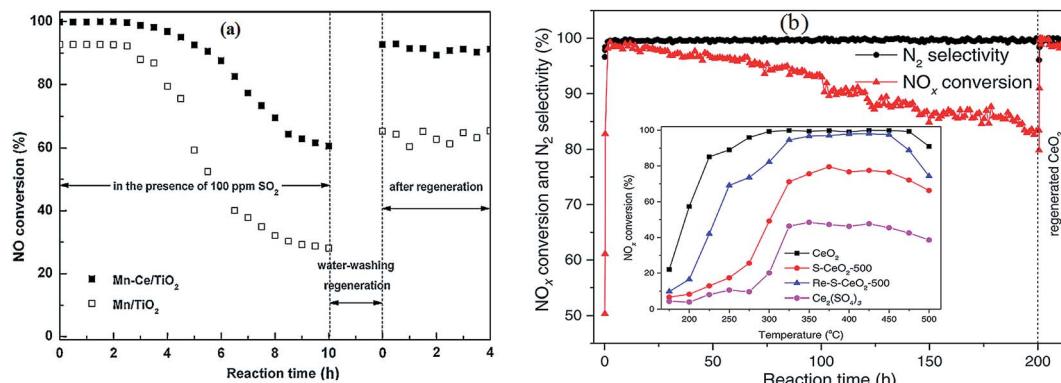


Fig. 9 SCR activities of Mn/Ti and Mn–Ce/Ti in the presence of SO<sub>2</sub>. (a) Reaction conditions: [NO] = [NH<sub>3</sub>] = 800 ppm, [O<sub>2</sub>] = 3%, [SO<sub>2</sub>] = 100 ppm, [H<sub>2</sub>O] = 3 vol%, balance N<sub>2</sub>, temperature: 150 °C, GHSV = 40 000 h<sup>-1</sup>. (Reprinted from ref. 25. Copyright 2013, with permission from Elsevier.) (b) Regeneration of sulfur poisoned CeO<sub>2</sub> catalyst using a thermal treatment. Reaction conditions: [NO] = [NH<sub>3</sub>] = 500 ppm, [O<sub>2</sub>] = 5%, [SO<sub>2</sub>] = 25 ppm, balance N<sub>2</sub>, temperature: 350 °C, GHSV = 175 000 h<sup>-1</sup>. (Reprinted from ref. 129. Copyright 2016, with permission from Elsevier.)

as in the cement production process. Alkali salts are important components in fine fly ash, which not only plugs the pores of catalysts, but also decreases SCR activity by reacting with the active phase.<sup>154–156</sup> In addition, because of the water solubility or ion exchange, alkali metal has a high liquidity to neutralize the acid sites.<sup>157</sup> For the traditional V<sub>2</sub>O<sub>5</sub>-based SCR catalysts, alkali metal deactivated these by affecting the acid sites on the surface.<sup>154,158</sup> Alkali metals could lower MnO<sub>x</sub> reducibility, decrease specific surface areas and damage the acid sites of low temperature catalysts.

Zhou *et al.*<sup>159</sup> reported that sodium sulfate, used to simulate the combined effects of alkali metal and SO<sub>2</sub> in the flue gas, had strong effects on the activity of the Mn–Ce/TiO<sub>2</sub> catalyst, such as simultaneous pore occlusion and sulfation effect. Guo *et al.*<sup>160</sup> investigated the deactivation effect of sodium (Na) and potassium (K) on a Mn/TiO<sub>2</sub> catalyst. The catalyst was prepared using a sol-gel method and Na and K were doped *via* an impregnation method. The Mn/TiO<sub>2</sub> 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.<sup>161</sup> Furthermore, Chen *et al.*<sup>155</sup> 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.*<sup>162,163</sup> studied the effects of K, Na and Ca on a Mn–Ce/Zr catalyst. From the NH<sub>3</sub>-TPD measurements, the adsorption of NH<sub>3</sub> 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.*<sup>164</sup> found that V<sub>2</sub>O<sub>5</sub> supported on sulfated zirconium dioxide showed a good resistance towards alkali ions. Chen *et al.*<sup>70</sup> reported that the K resistance of the Mn/TiO<sub>2</sub> catalyst could be improved by doping it with Co, which increased the adsorption of NH<sub>3</sub> and NO<sub>x</sub> 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.<sup>165</sup> It has been proved that heavy metals could lead to the deactivation of vanadium-based SCR catalysts.<sup>166</sup> Kong *et al.*<sup>167</sup> found that the Brønsted acid sites of a V–W/TiO<sub>2</sub> 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

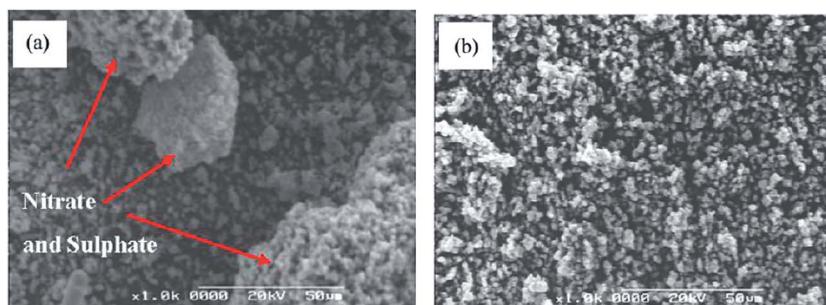


Fig. 10 SEM images (a) feeding with 400 ppm SO<sub>2</sub> at 150 °C for 26 h, (b) calcined at 200 °C and 400 °C for 2 h. (Reprinted from ref. 153. Copyright 2011, with permission from Elsevier.)



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.*<sup>156,168</sup>, and Li *et al.*<sup>169</sup> compared the poisoning effect of Pb and Zn on a Mn/TiO<sub>2</sub> catalyst. The Pb or Zn was loaded on to the Mn/TiO<sub>2</sub> catalyst using impregnation. As a result, both Pb and Zn were found to have a negative effect on the Mn/TiO<sub>2</sub> catalyst (Fig. 11a). From the characterization experiments, the redox ability of Zn-Mn/TiO<sub>2</sub> and Pb-Mn/TiO<sub>2</sub> was found to be decreased because of the drop of Mn<sup>4+</sup> and chemisorbed oxygen. Zhou *et al.*<sup>170</sup> investigated the deactivation effects of lead(II) oxide (PbO) on the Mn-Ce/TiO<sub>2</sub> catalyst. It was proposed that the surface area, the concentration of Mn<sup>4+</sup>, Ce<sup>3+</sup> and chemisorbed oxygen was decreased after introducing PbO. Consequently, the performance of the Mn-Ce/TiO<sub>2</sub> catalyst was greatly decreased because of the poisoning of PbO (Fig. 11b).

Mercury (Hg<sup>0</sup>) 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.<sup>171</sup> Researchers have attempted to remove the NO and Hg<sup>0</sup> simultaneously. However, Hg<sup>0</sup> is harmful to the catalysts of SCR of NO because it will compete with NH<sub>3</sub> for adsorption on the active sites.<sup>172</sup> Xu *et al.*<sup>41</sup> investigated the influence of Hg<sup>0</sup> on the NO conversion over a LaMnO<sub>3</sub> catalyst. The NO conversion had a slight decrease in the presence of Hg<sup>0</sup> (Fig. 12).

#### 4. Conclusions and perspectives

NH<sub>3</sub>-SCR of NO<sub>x</sub> in the presence of O<sub>2</sub> is one of the important strategies in controlling NO<sub>x</sub> emissions. Low temperature SCR has been investigated for several decades. Mn-containing metal oxide catalysts generally gave the preferable performance. SCR of NO<sub>x</sub> with NH<sub>3</sub> 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 NO<sub>2</sub>. N<sub>2</sub>O formation can

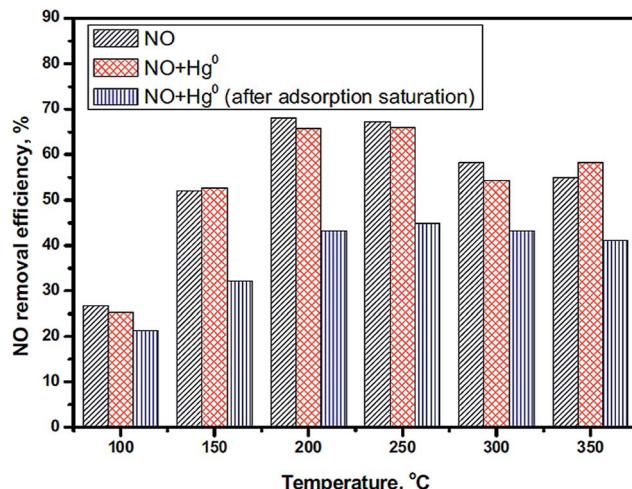


Fig. 12 The effect of Hg<sup>0</sup> on NO conversion. Reaction conditions: [NO] = [NH<sub>3</sub>] = 500 ppm, [Hg<sup>0</sup>] = 500  $\mu\text{g m}^{-3}$ , [O<sub>2</sub>] = 4%, balance N<sub>2</sub>, GHSV = 478 000  $\text{h}^{-1}$ . (Reprinted from ref. 41. Copyright 2016, with permission from Elsevier.)

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 SO<sub>2</sub> and H<sub>2</sub>O. 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 SO<sub>2</sub> can be classified into two categories: deposition of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and sulfation of the active phase. For the low temperature downstream of the flue gas, the deposition of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> or NH<sub>4</sub>HSO<sub>4</sub> occurs more easily and NH<sub>3</sub> is evidently adsorbed by H<sub>2</sub>O in comparison with the

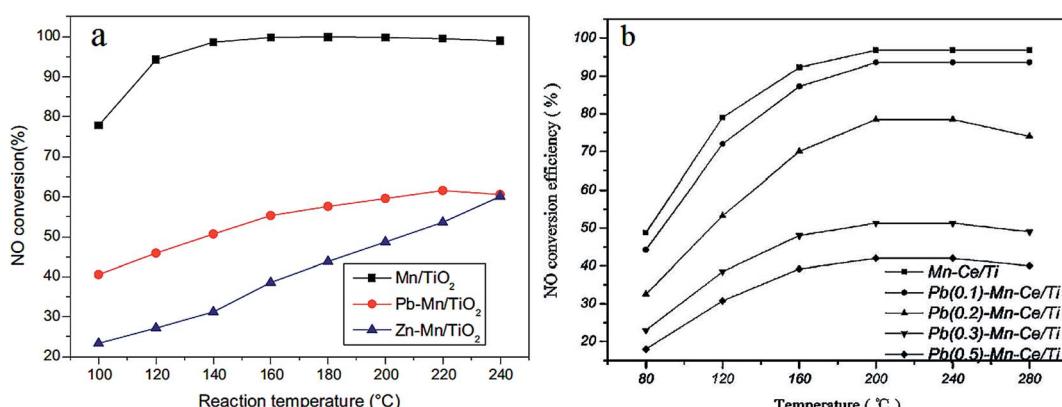


Fig. 11 NO conversion over pure and poisoned catalysts. (a) Reaction conditions: [NO] = [NH<sub>3</sub>] = 600 ppm, [O<sub>2</sub>] = 5%, balance N<sub>2</sub>, GHSV = 108 000  $\text{h}^{-1}$ . (Reprinted from ref. 156. Copyright 2015, with permission from Elsevier.) (b) Reaction conditions: [NO] = [NH<sub>3</sub>] = 800 ppm, [O<sub>2</sub>] = 5%, balance N<sub>2</sub>, GHSV = 200 000  $\text{h}^{-1}$ . (Reprinted from ref. 170. Copyright 2016, with permission from Elsevier.)



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, N<sub>2</sub> selectivity and poisons' tolerance, as well as the mechanism of this process. An excellent NO conversion of catalysts has been obtained, however, the N<sub>2</sub> selectivity is not satisfactory.

(2) Less effort has been made on 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 SO<sub>2</sub> and H<sub>2</sub>O, 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 O<sub>2</sub> which benefits the oxidization of NO to NO<sub>2</sub> and improves sulfur resistance, and inhibits the formation of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and NH<sub>4</sub>HSO<sub>4</sub>. 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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