A Review of Low Temperature NH$_3$-SCR for Removal of NO$_x$

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Abstract: The importance of the low-temperature selective catalytic reduction (LT-SCR) of NO$_x$ by NH$_3$ is increasing due to the recent severe pollution regulations being imposed around the world. Supported and mixed transition metal oxides have been widely investigated for LT-SCR technology. However, these catalytic materials have some drawbacks, especially in terms of catalyst poisoning by H$_2$O or/and SO$_2$. Hence, the development of catalysts for the LT-SCR process is still under active investigation throughout seeking better performance. Extensive research efforts have been made to develop new advanced materials for this technology. This article critically reviews the recent research progress on supported transition and mixed transition metal oxide catalysts for the LT-SCR reaction. The review covered the description of the influence of operating conditions and promoters on the LT-SCR performance. The reaction mechanism, reaction intermediates, and active sites are also discussed in detail using isotopic labelling and in situ FT-IR studies.

Keywords: low-temperature selective catalytic reduction; NH$_3$-SCR; de-NO$_x$ catalysis; SO$_2$/H$_2$O tolerance; transition metal-based catalysts

1. Introduction

The non-renewable fossil fuels are continuing to remain the dominant energy source in power plants and automobiles to satisfy the ever-growing energy demands. However, the combustion of fossil fuels mainly generates nitrogen oxide (NO$_x$) pollutants (NO, NO$_2$, and N$_2$O and their derivatives) which can cause acid rain, photochemical smog, ozone depletion, and eutrophication problems [1–4]. Due to the negative impacts of NO$_x$, the mitigation of NO$_x$ emissions is of paramount importance for environmental protection. Several technologies are available to reduce NO$_x$ emissions by using catalytic materials and among them, selective catalytic reduction of NO$_x$ with NH$_3$ (NH$_3$-SCR) has been widely applied due to its high NO$_x$ removal efficiency [5–7]. Usually, the flue gas temperature of the industrial process is as low as 300 °C and, thus, the SCR catalyst must be active in the low-temperature regime (100–300 °C). V$_2$O$_5$–WO$_3$(MoO$_3$)/TiO$_2$ is the typical and efficient catalyst and has been commercialized for NH$_3$-SCR technology for medium temperature process [8,9]. However, this catalyst has some intrinsic drawbacks such as narrow and high working temperature window (350–400 °C), and low N$_2$ selectivity in the high-temperature range [3,10,11]. Therefore, many researchers continue to develop highly active catalysts for low-temperature NH$_3$-SCR in a wide temperature window.

With this perspective, several transition metal oxide-based catalysts have been extensively investigated for low-temperature NH$_3$-SCR reaction due to their excellent redox properties, low price,
and high thermodynamic stability. Especially, the easy gain and loss of electrons in the $d$ shell of the transition metal ions could be responsible for the facile redox properties [12–14]. For example, the Cr/TiO$_2$ [15], Cr-MnO$_x$ [8], Fe-MnO$_x$ [16], Mn/TiO$_2$ [17,18], Fe$_3$TiO$_2$ [19], MnO$_x$/CeO$_2$ [20], and Cu/TiO$_2$ [21] catalysts were shown to exhibit good SCR activity in the low temperature range. In our earlier work, we investigated the low-temperature NH$_3$-SCR in the presence of excess O$_2$ on the TiO$_2$ supported V, Cr, Mn, Fe, Co, Ni, and Cu oxides and found the catalytic performance decreased in the following order of Mn $>$ Cu $>$ Cr $>$ Co $>$ Fe $>$ V $>$ Ni [16]. Particularly, manganese-containing catalysts have attracted much attention due to its variable valence states and excellent redox ability [2,5].

In the recent past, we published a series of papers on Mn-based SCR catalysts that showed a highly promising deNO$_x$ potential in the low-temperature region [5,22–26]. However, these catalysts are very sensitive to the presence of SO$_2$ in the feed and exhibit lower N$_2$ selectivity [8,27–29]. Hence, the development of catalysts that show both good low-temperature activity and high SO$_2$/H$_2$O durability is of great importance for the NH$_3$-SCR reaction. In general, there are two plausible strategies available to enhance low-temperature NH$_3$-SCR performance. One strategy is to modify the transition metal oxide with one or multiple metal oxides, which could enhance the active sites for the reaction by inducing the synergistic effect [30–33]. The other approach is to synthesize the supported materials to disperse the transition metal-based oxides which can increase the activity by metal-support interactions [26,34–37]. Recently, many supported and mixed transition metal catalyst formulations have been studied to improve the low-temperature SCR performance, as well as resistance to SO$_2$/H$_2$O.

In this study, we systematically reviewed the recent advancements in developing the transition metal-based catalysts for low-temperature NH$_3$-SCR reaction. This review also demonstrated the action of different promoters and supports on the catalytic performance and SO$_2$/H$_2$O tolerance of the transition metal-based catalysts in NH$_3$-SCR of NO$_x$. The reported catalysts were divided into four categories, such as binary, ternary/multi, supported single, and supported binary/multi-transition metal-based catalysts.

2. Binary Transition Metal-Based Catalysts

Various transition-metal oxides have been proved to be active for the NH$_3$-SCR at low-temperature. However, the catalytic performance on single transition metal oxide is far from satisfactory due to their low specific surface area and thermal instability [38–41]. The addition of dopants is a common method to improve the drawbacks associated with pure transition metal oxide. Hence, much progress has done to improve the low-temperature SCR activity of transition metal oxides by mixing or doping with other metal oxides. In recent years, Mn, Fe, Co, Ni, and Cu-based binary oxide catalysts have been extensively studied for low-temperature NH$_3$-SCR reaction due to their attractive catalytic performance [19,33,41–49]. Particularly, Mn-based binary oxides are popular and proven to be effective catalysts for low-temperature NH$_3$-SCR reaction [42,50,51]. Recently, Xin et al. [52] designed bifunctional V$_a$-MnO$_x$ (where a represents the molar ratios of V / (V + Mn)) catalysts composed of Mn$_2$O$_3$ and Mn$_5$V$_2$O$_7$ phases that significantly improved both NO$_x$ conversion and N$_2$ selectivity in comparison with Mn$_2$O$_3$ at low-temperature (Figure 1). Although Mn$_2$V$_2$O$_7$ showed an excellent N$_2$ selectivity, the NO$_x$ conversion is much lower on it. Especially, above 90% NO$_x$ conversion and 80% N$_2$ selectivity was observed in the temperature region of 120–240 °C over the V$_{0.05}$-MnO$_x$ catalyst. The V$_{0.05}$-MnO$_x$ catalyst also found to be exhibit higher NO$_x$ conversion to N$_2$ as compared to the mechanically mixed Mn$_2$O$_3$ + Mn$_2$V$_2$O$_7$ sample which has the same component content to V$_{0.05}$-MnO$_x$ (Figure 1). This finding indicated that the synergism between Mn$_2$O$_3$ and Mn$_2$V$_2$O$_7$ exists in the chemically prepared V$_{0.05}$-MnO$_x$ rather than the mechanically mixed Mn$_2$O$_3$ + Mn$_2$V$_2$O$_7$ sample. Moreover, the mechanically mixed Mn$_2$O$_3$ + Mn$_2$V$_2$O$_7$ sample showed higher activity in comparison to mechanically mixed Mo$_2$O$_3$ + Mn$_2$V$_2$O$_7$ sample, suggesting that the presence of Mn$_2$O$_3$ phase in the catalyst is necessary for NH$_3$-SCR reaction. In conjunction with in situ IR characterization and DFT (density functional theory) calculation results, the authors concluded that the Mn$_2$O$_3$ phase of the
catalyst could activate NH$_3$ into NH$_2$ intermediate, which then transferred to the Mn$_2$V$_2$O$_7$ phase of the catalyst and reacted with gaseous NO into NH$_2$NO. Finally, the generated NH$_2$NO intermediate on the Mn$_2$V$_2$O$_7$ phase exclusively decomposed to the N$_2$ rather than the undesired byproduct, N$_2$O, which is formed due to the deep oxidation of adsorbed NH$_3$ on Mn$_2$O$_3$.

Figure 1. (a) NO$_x$ conversion and (b) N$_2$ selectivity for V$_x$-MnO$_x$, Mn$_2$O$_3$, Mn$_2$V$_2$O$_7$, and reference samples. Reprinted from Reference [52]. Copyright 2018, with Permission from American Chemical Society.

Han and co-workers [53] fabricated triple-shelled NiMn$_2$O$_4$ hollow spheres (Figure 2a,b) by using a solvothermal method and tested their ability for low-temperature NH$_3$-SCR reaction. As shown in Figure 2c, the prepared NiMn$_2$O$_4$ hollow spheres (NiMn$_2$O$_4$-S) showed the best catalytic activity with NO$_x$ conversion of above 90% over a wide temperature range from 100 °C to 225 °C as compared to the NiMn$_2$O$_4$ nanoparticles (NiMn$_2$O$_4$-P). The triple-layer shell structure of the NiMn$_2$O$_4$-S catalyst generates a larger surface area (165.3 m$^2$ g$^{-1}$) that exposes more active sites (such as surface Mn$^{4+}$ and surface adsorbed oxygen species), which are responsible for its superior activity. Additionally, the NiMn$_2$O$_4$-S catalyst displayed outstanding stability and good tolerance to H$_2$O and SO$_2$ (Figure 2d).
Gao et al. [54] investigated the low-temperature NH$_3$-SCR reaction over the hydroxyl-containing Me-Mn binary oxides (Me = Co, Ni) prepared by a combined complexation–esterification method. It was found that the NO$_x$ conversion decreased in the order of Mn$_3$O$_4$-Co$_3$O$_4$-OH (Co-MnO$_x$ binary oxide) > Mn$_2$O$_3$-NiMnO$_3$-OH (Ni-MnO$_x$ binary oxide) > Mn$_2$O$_3$-OH, while the N$_2$ selectivity increased in the sequence of Mn$_3$O$_4$-Co$_3$O$_4$-OH < Mn$_2$O$_3$-OH < Mn$_2$O$_3$-NiMnO$_3$-OH. Although the Co and Ni elements in the catalysts delay the poisoning of SO$_2$ as compared to MnO$_x$ sample, the Co-MnO$_x$ and Ni-MnO$_x$ binary oxides are deactivated by SO$_2$ over the postponement due to the formation of metal sulfate and ammonia hydrogen sulfite species. In another study, Sun and co-workers [55] prepared Mn$_{0.66}$M$_{0.33}$O$_x$ catalysts (M = Fe, Zn, Cu) and a series of Fe$_x$Mn$_{1-x}$O$_x$ ($\alpha = 1, 0.25, 0.33, 0.50, 0$ mol%) catalysts and examined for NH$_3$-SCR at low-temperatures. The results demonstrated that the Fe$_{0.33}$Mn$_{0.66}$O$_x$ catalyst displayed the superior NH$_3$-SCR activity (NO$_x$ removal efficiency > 90%) in a wide temperature range (75–225 °C) among the Cu$_{0.33}$Mn$_{0.66}$O$_x$, Zn$_{0.33}$Mn$_{0.66}$O$_x$, and Fe$_{\alpha}$Mn$_{1-\alpha}$O$_x$ ($\alpha = 1, 0.25, 0.50, 0$ mol%) catalysts. The authors proposed that the distortion of the catalyst structure by Fe doping could play a key role in improving the NH$_3$-SCR performance over the Fe$_{0.33}$Mn$_{0.66}$O$_x$ catalyst.
Rare-earth metal oxides have been frequently adopted to modify the MnO$_x$ as an efficient low-temperature NH$_3$-SCR catalyst due to their incomplete 4f and empty 5d orbitals [50,51,56]. Fan et al. [57] synthesized Gd-modified MnO$_x$ catalysts with Gd/Mn molar ratio of 0.05, 0.1, and 0.3 to improve the catalytic performance and sulfur resistance in the NH$_3$-SCR reaction at low-temperature. The MnGdO-2 catalyst (the mole ratio of Gd/Mn = 0.1) found to show the optimal NO conversion and N$_2$ selectivity among the investigated catalysts. The addition of a proper amount of Gd into MnO$_x$ could enhance the concentrations of surface Mn$^{4+}$ and chemisorbed oxygen species, and increase the amount and the strength of surface acid sites, which lead to better low-temperature catalytic performance than the others. Furthermore, the MnGdO-2 catalyst had an excellent tolerance to SO$_2$/H$_2$O as compared to pure MnO$_x$ sample (Figure 3). Their results demonstrate that the doping of Gd could restrain the transformation of MnO$_2$ to Mn$_2$O$_3$ and the generation of MnSO$_4$, obstructs the decrease in Lewis acid sites and the increase in Brønsted acid sites, and eases the competitive adsorption between the NO and SO$_2$ and, thus, improves the resistance to SO$_2$.

Figure 3. The (a) resistance to water vapor poisoning test and (b) resistance to sulfur poisoning test. (Reaction condition: [NO] = [NH$_3$] = 500 ppm, [O$_2$] = 5 vol%, balanced with N$_2$, [H$_2$O] = 5 vol%, [SO$_2$] = 100 ppm, and GHSV = 36,000 h$^{-1}$). Reprinted from Reference [57]. Copyright 2018, with Permission from Elsevier.

Li et al. [58] developed hollow MnO$_x$-CeO$_2$ binary nanotubes as efficient low-temperature NH$_3$-SCR catalysts via an interfacial oxidation-reduction process using KMnO$_4$ aqueous solution and Ce(OH)CO$_3$ nanorod as both template and reducing agent without any other intermediate. They reported that the MnO$_x$-CeO$_2$ hollow nanotube catalyst with 3.75 g of Ce(OH)CO$_3$ template (denoted it as MnO$_x$-CeO$_2$-B) exhibited outstanding performance with more than 96% NO$_x$ conversion in the temperature range of 100–180 °C. The best activity of the MnO$_x$-CeO$_2$-B catalyst was due to its ample number of surface Mn$^{4+}$ and O species, and hollow and porous structures that provide abundant Lewis acid sites and large surface area. Additionally, MnO$_x$-CeO$_2$-B catalyst showed an excellent resistance to H$_2$O and SO$_2$ (Figure 4) and especially, the great SO$_2$ tolerance was ascribed to the hierarchically porous and hollow structure that inhibits the deposition of ammonium sulfate species, and the doping of ceria that acts as an SO$_2$ trap to limit sulfation of the main active phase.
Fe-based binary catalysts have also been studied as NH$_3$-SCR catalysts due to their high activity, excellent resistance to H$_2$O and SO$_2$, outstanding environmentally friendly performance, lower cost, and higher abundance [59–62]. Mu et al. [63] synthesized a series of vanadium-doped Fe$_2$O$_3$ catalysts and evaluated the effect of V on the low-temperature NH$_3$-SCR activity of hematite. The NH$_3$-SCR activity and N$_2$ selectivity are greatly enhanced after the incorporation of vanadium into Fe$_2$O$_3$ and the Fe$_{0.75}$V$_{0.25}$O$_3$ catalyst with a Fe/V mole ratio of 3/1 showed the best catalytic performance over a wide temperature window and strong resistance to H$_2$O and SO$_2$. They found that the charge transfer from Fe to V due to the electron inductive effect between Fe and V which could enhance the redox ability and surface acidity thereby superior NH$_3$-SCR activity at low-temperature. The in situ DRIFTS and kinetic studies suggested that the SCR reaction followed the Langmuir–Hinshelwood mechanism below 200 °C, while an Eley–Rideal mechanism dominated at and above 200 °C. Li and co-workers [64] reported novel iron titanium (CT-FeTi) catalyst, prepared by a CTAB-assisted process, showing good deNO$_x$ efficiency and H$_2$O resistance at low-temperature as compared to the FeTi catalyst that prepared without adding CTAB. The addition of CTAB during the CT-FeTi catalyst preparation not only promotes to form the uniform mesoporous structure to avoid being excessively enlarged in the presence of H$_2$O, but also enhances the adsorption of bridging nitrate and NH$_3$ species on Lewis acid sites. Thus, the authors concluded that the CTAB acted as a “structural” and “chemical” promoter in improving the NH$_3$-SCR activity and H$_2$O resistance at low-temperature.

Recently, Co-based spinel catalysts have shown to exhibit a remarkable low-temperature NH$_3$-SCR activity, N$_2$ selectivity, and tolerance to SO$_2$/H$_2$O [30,65–67]. Meng et al. [48] synthesized a highly efficient Co$_a$Mn$_b$O$_x$ (where a/b is the molar ratio of Co/Mn) mixed oxide catalysts and investigated the effects of the Co/Mn molar ratio on the low-temperature NH$_3$-SCR reaction. The Co$_a$Mn$_b$O$_x$ mixed oxides showed higher NH$_3$-SCR activity than either MnO$_x$ or CoO$_x$ alone due to their improved redox properties and surface acid sites by the synergistic effects between the Co and Mn species. Particularly, the catalyst with Co/Mn molar ratio of 7:3 (Co$_7$Mn$_3$O$_x$) exhibited the greatest activity (>80% NO$_x$ conversion) in a temperature window of 116–285 °C as compared to the catalysts with Co/Mn molar ratio of 5:5 (Co$_5$Mn$_5$O$_x$) and 3:7 (Co$_3$Mn$_7$O$_x$). They considered that the high NO + O$_2$ adsorption ability and enhanced redox properties of the Co$_7$Mn$_3$O$_x$ catalyst, emerging from its MnCo$_2$O$_{4.5}$ spinel phase and higher surface area, were beneficial to augment the NH$_3$-SCR performance by forming...
nitrate species on the catalyst surface. Although Co7Mn3Ox catalyst had better resistance to H2O/SO2 than the Co3Mn7Ox and MnOx, the tolerance to SO2 poisoning still need to be improved for practical use. Nevertheless, it was found that the deactivated Co7Mn3Ox, Co3Mn7Ox, and MnOx catalysts in SO2 stream can be regenerated simply by washing with water. Based on their results, the authors also proposed the NH3-SCR reaction mechanism over the Co7Mn3Ox catalyst, which is shown in Scheme 1. The reaction was initiated by adsorption and activation of gaseous oxygen on oxygen vacancies (symbol □), which was then transformed into lattice oxygen O2− (Step 1); This lattice oxygen was diffused to the catalyst surface and then it had become surface active oxygen (O*) (Step 2); Gaseous NO was adsorbed and subsequently reacted with O* to form NO2/NO3− intermediates (Step 3); Meanwhile, NH3 was activated to −NH2 and NH4+ species by Mn4+ (Step 4); Finally, NO2/NO3− intermediates reacted with the NH species to produce reaction products, N2, and H2O (Step 5); By the electron transfer from Mn3+ to Co3+ (Step 6); the catalyst was recovered to its original state (Step 7); Thus, the synergistic effect between the Co and Mn plays a key role in improving the NH3-SCR activity over Co7Mn3Ox catalyst.

Mesoporous materials have been proved as promising catalysts for NH3-SCR reaction since they can facilitate to promote effective diffusion of reactants towards the active sites [30,65,66,68]. With this perspective, Hu et al. [47] developed mesoporous 3D nanosphere-like Mn-Co-O catalysts through a template-free approach and evaluated for low-temperature NH3-SCR reaction. It was found that the synthesized Mn-Co-O samples showed excellent NH3-SCR activity in a broad working temperature window of 75 to 325 °C (NOx conversion above 80%). They ascribed this outstanding performance to the strong and abundant acid sites, the strong adsorption of NOx, robust redox properties, the formation of more oxygen vacancies and metal-metal interactions between the cobalt and manganese species.

Besides Mn, Fe, and Co oxides, CuOx has also been considered in the bimetallic catalyst formulations for low-temperature NH3-SCR reaction [69,70]. For instance, Ali et al. [71] reported the Cu0.25-Nb0.85 catalyst and found that the Cu/Nb ratio was crucial in enhancing the NH3-SCR activity. As shown in Figure 5a,b, all binary Cu0.25-Nb1-x oxides exhibited significantly higher activity than the CuOx and Nb2O5, and among the Cu0.25-Nb1-x samples, Cu0.25-Nb0.85 catalyst displayed the best performance in a wide temperature window of 180–330 °C (>90% NO conversion). Even at a high GHSV of 105,000 h−1, the optimal Cu0.25-Nb0.85 catalyst
showed a good NO removal efficiency (above 90% NO conversion) from 210 °C to 360 °C (Figure 5c).

Although the SO2/H2O streams in the feed gas have some adverse impact on Cu0.25-Nb0.85, still the catalyst showed excellent resistance to SO2/H2O with reversible deactivation (Figure 5d). The superior NH3-SCR performance and SO2/H2O tolerance of Cu0.25-Nb0.85 catalyst were attributed to its high acid amount and NO adsorption capacity.

![Figure 5](image-url)

**Figure 5.** (a) NO conversion; (b) N2 selectivity over Cu0-x-Nb1.1-x (x = 0.45, 0.35, 0.25, 0.15) as a function of temperature under a GHSV of 35,000 h⁻¹; (c) effect of GHSV on NO conversion over Cu0.25-Nb0.85, and (d) effect of SO2, H2O, and SO2 + H2O on NO conversion over Cu0.25-Nb0.85 at 200 °C under a GHSV of 35,000 h⁻¹. (Reaction conditions: [NO] = [NH3] = 1000 ppm, [O2] = 3% and N2 balance), and Effect of SO2, H2O, and SO2 + H2O on NO conversion over Cu0.25-Nb0.85 at 200 °C under a GHSV of 35,000 h⁻¹. Reprinted from Reference [71]. Copyright 2018, with Permission from Elsevier.

3. Ternary and Multi-Transition Metal-Based Catalysts

The catalytic performance of single transition metal oxides can also be improved by mixing with two or multi other metal oxides. Thus, transition metal oxides are widely reported to fabricate ternary-or multi-metal-based low-temperature NH3-SCR catalysts, which could improve the catalytic activity by the enlarged synergetic interactions [14,72–87]. Fang et al. [88] investigated the low-temperature NH3-SCR reaction over the Fe0.3Mn0.5Zr0.2 catalyst and found that it showed an excellent deNOx activity with 100% NO conversion in the temperature range of 200–360 °C as compared to the Fe0.5Zr0.5 and Mn0.5Zr0.5 samples. Moreover, the Fe0.3Mn0.5Zr0.2 catalyst had outstanding stability and good tolerance to SO2 (Figure 6), which they attributed to the strong interactions among Fe, Mn, and Zr species. However, the durability of the catalyst in the presence of both SO2 and H2O need to be tested to investigate its feasibility in practical use.
Guo and co-workers [89] studied the effect of Sb doping on the activity of MnTiO₅ catalyst for NH₃-SCR reaction. The results showed that Sb modification has greatly improved the NH₃-SCR performance of MnSbTiOₓ catalysts in comparison to the MnTiOₓ and SbTiOₓ samples. Particularly, the MnSbTiOₓ-0.2 (Sb/Mn molar ratio = 0.2) catalyst exhibited the best activity with above 90% NOₓ conversion in the temperature range of 138–367 °C as it had good adsorption and activation properties for NH₃ and NOₓ reactants in SCR. It can be seen from Figure 7 that the addition of Sb dramatically improved the SO₂ and H₂O resistance of MnTiOₓ catalyst. Although the NOₓ conversion over the MnSbTiOₓ-0.2 catalyst slightly decreased in the presence of SO₂ and H₂O, it recovered to almost the original level after stopping the SO₂/H₂O supply.

Shi et al. [90] synthesized a series of NiₓCo₁₋ₓMn₂Oₓ microspheres (MSs) (y = 0.1, 0.3, 0.5, 0.7, 0.9) for NH₃-SCR using a hydrothermal method. It was observed that the activity of all ternary MSs was greater than binary CoMn₂Oₓ and NiMn₂Oₓ, and Ni₀.7Co₀.3Mn₂Oₓ showed the best NH₃-SCR performance among the NiₓCo₁₋ₓMn₂Oₓ catalysts. Although the Ni₀.7Co₀.3Mn₂Oₓ catalyst exhibited...
good resistance to H2O, it had poor SO2 tolerance which needs to be improved. Wu and co-workers [91] compared the DeNOx performance of MnO2/CoAl-LDO and CoMnAl-LDO mixed metal oxides prepared from CoAl-MnO2-LDH and CoMnAl-LDH templates by ion-exchange/redox reaction and hexamethylenetetramine (HMT) hydrolysis methods, respectively. The CoAl-MnO2-LDH showed higher NH3-SCR activity in a broad temperature window of 90–300 °C (Figure 8a) as well as better stability and SO2/H2O resistance (Figure 8b) than the CoMnAl-LDO, which was attributed to its larger specific surface area, stronger redox ability, more quantitative acid sites, and abundant active components.

Figure 8. (a) NOx conversion and N2 selectivity over MnO2/CoAl-LDO and CoMnAl-LDO catalysts prepared by calcination at 500 °C; and (b) the stability and SO2/H2O resistance test (inset) of MnO2/CoAl-LDO and CoMnAl-LDO catalysts at 240 °C. Reaction conditions: [NH3] = 600 ppm, [NO] = 600 ppm, [O2] = 5 vol%, 100 ppm SO2 (when used), 10 vol% H2O (when used) balanced by N2. Reprinted from Reference [91]. Copyright 2019, with Permission from Elsevier.
Leng and collaborators [92] synthesized Mn$_{0.2}$TiO$_x$, Ce$_{0.3}$TiO$_x$ and series of Mn$_a$Ce$_{0.3}$TiO$_x$ ($a = 0.1, 0.2, 0.3$) catalysts and investigated their applicability for low-temperature NH$_3$-SCR reaction. They demonstrated that the low-temperature NH$_3$-SCR activity of Mn$_a$Ce$_{0.3}$TiO$_x$ was greatly improved after incorporation of Mn, and the Mn$_{0.1}$Ce$_{0.3}$TiO$_x$ catalyst displayed the best performance (with 100% NO conversion and above 90% N$_2$ selectivity) in the temperature range of 175–400 °C even at high GHSV of 80,000 h$^{-1}$. The outstanding performance of Mn$_{0.1}$Ce$_{0.3}$TiO$_x$ catalyst in NH$_3$-SCR resulted from its enhanced acidity and chemisorbed oxygen, and suitable redox property derived from Ce$^{3+}$ ↔ Ce$^{4+}$ + Mn$^{3+}$ ↔ Mn$^{4+}$ reaction. Furthermore, the NO conversion over the Mn$_{0.1}$Ce$_{0.3}$TiO$_x$ catalyst decreased and stabilized at 82% after the introduction of 100 ppm SO$_2$ and 6% H$_2$O and restored to almost 100% NO conversion after stopping the supply of SO$_2$ and H$_2$O (Figure 9), suggesting that the catalyst had excellent resistance to SO$_2$/H$_2$O and the effects were reversible.

![Figure 9](image-url)  
**Figure 9.** Effect of H$_2$O and SO$_2$ on NO conversion over the Mn$_{0.1}$Ce$_{0.3}$TiO$_x$ catalyst at 200 °C (1000 ppm NO, 1000 ppm NH$_3$, 3% O$_2$, balance N$_2$, GHSV = 40,000 h$^{-1}$). Reprinted from Reference [92]. Copyright 2018, with Permission from Elsevier.

Ali et al. [93] developed a series of Nb-promoted Fe$_x$-Nb$_{0.5-x}$-Ce$_{0.5}$ ($x = 0.45, 0.4, 0.35$) oxides for NH$_3$-SCR. The best activity (>90% NO conversion and near 100% N$_2$ selectivity) in the broad temperature window of 180–400 °C as well as excellent SO$_2$/H$_2$O resistance (Figure 10) was observed for Fe$_{0.4}$-Nb$_{0.1}$-Ce$_{0.5}$ catalyst. The authors considered the strong interaction among Nb, Fe, and Ce oxides leading to the enhancement of BET surface area, redox ability, acid amount, and NO adsorption capacity, which could be responsible for the outstanding performance of the catalyst.
with reversible inhibition effect (Figure 12). It was concluded that the interactions among Ce, Co, Mn, and Ti oxides led to more surface Brønsted acid and Lewis acid sites, NOx adsorption sites and modest redox ability which could play a crucial role to improve the NH3-SCR activity of Co0.2Ce0.35Mn0.45Ti10.

Sun and co-workers [94] reported the multimetallic Sm- and/or Zr-doped MnOx-TiO2 catalysts for NH3-SCR reaction. As shown in Figure 11, the Sm and Zr co-doped MnOx-TiO2 (MSZTOx) catalyst had better activity (=100% NO conversion and >95% N2 selectivity) in a wide temperature range (125–275 °C) with an excellent H2O/SO2 tolerance than the MSTOx (MnOx-SmOx-TiO2), MZTOx (MnOx-ZrOx-TiO2) and MTOx (MnOx-TiO2) catalysts. The authors claimed that the enhanced redox properties and acidic sites play a crucial role in improving the NH3-SCR performance of MSZTOx catalyst. Yan and co-workers [95] fabricated Cu0.5Mg1.5Mn0.5Al0.5Ox catalyst from layered double hydroxides and found that it showed better activity in a wide temperature range together with superior SO2 and H2O tolerance than conventional Mn/γ-Al2O3. The improved performance of Cu0.5Mg1.5Mn0.5Al0.5Ox was attributed to the high specific surface area, high reducibility of MnO2 and CuO species, an abundance of acid sites, and the good dispersion of MnO2 and CuO species.

Chen et al. [96] investigated the NH3-SCR reaction over a series of Co0.2Ce0.8-xMn0.8-xTi10 (x = 0, 0.05, 0.15, 0.25, 0.35, and 0.40) oxides catalysts and observed that the Co0.2Ce0.35Mn0.45Ti10 catalyst exhibited the best catalytic performance with 100% NO conversion and over 91% N2 selectivity in a broad temperature window of 180–390 °C. Although NOx conversion decreased to some extent after introducing SO2 and H2O, the Co0.2Ce0.35Mn0.45Ti10 catalyst showed excellent resistance to SO2/H2O with reversible inhibition effect (Figure 12). It was concluded that the interactions among Ce, Co, Mn, and Ti oxides led to more surface Brønsted acid and Lewis acid sites, NOx adsorption sites and modest redox ability which could play a crucial role to improve the NH3-SCR activity of Co0.2Ce0.35Mn0.45Ti10.

Figure 10. Effect of SO2, H2O, and SO2 + H2O on NO conversion over the Fe0.4-Nb0.1-Ce0.5 catalyst at 220 °C. Reprinted from Reference [93]. Copyright 2018, with Permission from Elsevier.
Figure 11. (a) NO conversions and (b) N\textsubscript{2} selectivities of the catalysts in the NH\textsubscript{3}-SCR reaction as a function of temperature; (c) SO\textsubscript{2} (100 ppm) resistance tests, and (d) H\textsubscript{2}O + SO\textsubscript{2} (2.5 vol\%, 100 ppm) resistance tests at 200 °C over the catalysts. Reproduced from Reference [94]. Copyright 2018, with Permission from Elsevier.

Figure 12. Effects of H\textsubscript{2}O and/or SO\textsubscript{2} on NO\textsubscript{x} conversion over the Co\textsubscript{0.2}Ce\textsubscript{0.35}Mn\textsubscript{0.45}Ti\textsubscript{10} catalyst. Reproduced from Reference [96]. Copyright 2018, with Permission from Elsevier.
4. Supported Single Transition Metal-Based Catalysts

Support materials have proved to be highly beneficial for enhancing the activity and durability of catalysts as they possess high surface area and good thermal stability. In virtue of the fine dispersion of the active component on the surface of the support and the synergistic effect between active component and support, supported catalysts exhibit improved NH₃-SCR performance than the unsupported transition metal oxide. Therefore, a lot of attention has been focused to increase the de-NOₓ efficiency by dispersing the transition metal oxides over different support materials such as TiO₂, Al₂O₃, SiO₂, carbon nanotubes (CNTs), etc. TiO₂ supported transition metal oxides, especially manganese oxides, have been widely reported as promising catalysts for NH₃-SCR reaction at low temperature [17,24,97–105]. Smirniotis and co-workers [17,106,107] first reported the transition metal oxides (V, Cr, Mn, Fe, Co, Ni, and Cu) supported on Hombikat TiO₂ for NH₃-SCR reaction at low-temperature. Among the investigated samples, the Mn/Hombikat TiO₂ catalyst found to exhibit the highest activity even in the presence of water. They also studied the effect of different supports on the NH₃-SCR performance and observed that the Mn/Hombikat TiO₂ (anatase, high surface area) had the best activity as compared to the Kemira TiO₂ (rutile), Degussa P25 TiO₂ (anatase, rutile), Aldrich TiO₂ (anatase, low surface area), Puralox γ-Al₂O₃. Aldrich SiO₂ supported Mn catalysts.

It was concluded that the Lewis acidity, redox behavior, and a high surface concentration of MnO₂ could play a key role in improving the NH₃-SCR activity. Later, they investigated the effect of Mn loading on the NH₃-SCR performance of Mn/Hombikat TiO₂ and reported that the catalyst with 16.7 wt% Mn had optimal activity and excellent tolerance to H₂O during 10 days of the reaction [108]. In another work, they also proposed the NH₃-SCR reaction mechanism over the Mn/TiO₂ catalyst using transient isotopic labeled and in-situ FT-IR studies. As shown in Figure 13, the reaction proceeds via a Mars-van-Krevelen-like mechanism, in which NH₃ and NO species were first adsorbed onto the Mn⁴⁺ sites (Lewis acid sites), followed by the formation of nitrosamide and azoxy intermediate species. Finally, these intermediates converted into N₂ and H₂O products [24].

![Figure 13. Plausible SCR mechanism over the surface of Mn/TiO₂ catalyst. Adapted from Reference [24]. Copyright 2012, with Permission from Elsevier.](image-url)
In the aspect of catalyst structure design, Smirniotis and co-workers [26] developed a series of manganese confined titania nanotube (Mn/TNT-X) catalysts using different TiO$_2$ precursors (X = Ishihara (I), Kemira (K), Degussa P25 (P25), Sigma–Aldrich (SA), Hombikat (H), TiO$_2$ synthesized from titanium oxysulfate (TOS)) for low-temperature NH$_3$-SCR reaction. As can be observed from the Figure 14, all Mn/TNT-X catalysts exhibited an excellent NO$_x$ conversion in broad temperature window, and especially, Mn(0.25)/TNT-H sample obtained the superior activity in the temperature range of 100–300 °C as compared to other catalysts. They believed that the better performance of Mn(0.25)/TNT-H catalyst was due to the high surface area (421 m$^2$/g) of the TNT-H support, and high dispersion of active components. The Mn(0.25)/TNT-H catalyst also showed greater catalytic performance than the conventional Mn-loaded titania nanoparticles (Mn/TiO$_2$), suggesting that the unique multiwall nanotube with open-ended structure could be advantageous to promote the reaction. Besides, the Mn (0.25)/TNT-H displayed outstanding tolerance to 10 vol% H$_2$O in the feed (Figure 15), which might be attributed to the preferential existence of highly active and redox potential pairs of Mn$^{4+}$ and Mn$^{3+}$ in the tubular framework.

Figure 14. Catalytic evaluation of the Mn(0.25)/TNT-X (X = Hombikat, Ishihara, P25 Degussa, Kemira, Sigma–Aldrich, and Titania oxysulfate) family of catalyst for the SCR of NO$_x$ by NH$_3$, in the presence of 900 ppm NO, 100 ppm NO$_2$, 1000 ppm NH$_3$, 10 vol% O$_2$ with He balance under a GHSV of 50,000 h$^{-1}$ in the temperature range from 100–300 °C. Reproduced from Reference [26]. Copyright 2016, with Permission from Elsevier.
Recently, Boningari et al. [109] extended this work by comparing the NH\textsubscript{3}-SCR activity of various metal oxide confined titania nanotubes M/TNT (M = Mn, Cu, Ce, Fe, V, Cr, and Co) based on the Hombikat TiO\textsubscript{2} support. As shown in Figure 16, the Mn-, V-, Cr-, and Cu-oxide confined titania nanotubes had excellent low-temperature activity and meanwhile, vanadium oxide confined titania nanotubes showed a broad operation temperature window for the NH\textsubscript{3}-SCR reaction.

Sheng et al. [100] synthesized core-shell MnO\textsubscript{x}/TiO\textsubscript{2} nanorod catalyst, showed high activity, stability, and N\textsubscript{2} selectivity in NH\textsubscript{3}-SCR. They concluded that the abundant mesopores, Lewis-acid sites, and high redox capability could be beneficial to improve catalytic performance. Although the MnO\textsubscript{x}/TiO\textsubscript{2} catalyst exhibited excellent resistance to H\textsubscript{2}O, it was deactivated in the presence of SO\textsubscript{2} and SO\textsubscript{2}/H\textsubscript{2}O. Jia et al. [110] reported the low-temperature NH\textsubscript{3}-SCR efficiency of MnO\textsubscript{x}/TiO\textsubscript{2}, MnO\textsubscript{x}/ZrO\textsubscript{2}, and MnO\textsubscript{x}/ZrO\textsubscript{2}-TiO\textsubscript{2} catalysts, and found that MnO\textsubscript{x}/ZrO\textsubscript{2}-TiO\textsubscript{2} obtained good activity at a temperature of 80–360 °C and excellent resistance to H\textsubscript{2}O at 200 °C. However, all the catalysts showed poor tolerance to SO\textsubscript{2} and SO\textsubscript{2}/H\textsubscript{2}O that caused irreversible deactivation. Similar findings were also observed by Zhang et al. [111] over the Mn/Ti, Mn/Zr, and Mn/Ti-Zr catalysts, in which Mn/Ti-Zr sample exhibited an excellent NH\textsubscript{3}-SCR performance in a wide temperature range due to its high surface area, Lewis acid sites, and surface Mn\textsuperscript{4+} ions.
Poor resistance to SO2 presence of SO2. Bai et al. [117] developed CNTs supported copper oxide catalysts, and found that the 10 wt% CuO/CNTs showed good NH3-SCR activity and excellent stability at 200 °C.

Interestingly, SO2 stream in the feed had promoting effect on the NO conversion (Figure 17b), which could be attributed to the increased acid sites for NH3 adsorption and activation on the catalyst surface in presence of SO2. Bai et al. [117] developed CNTs supported copper oxide catalysts, and found that the 10 wt% CuO/CNTs showed good NH3-SCR activity and excellent stability at 200 °C. The 10 wt% CuO/CNTs also had greater performance in comparison to 10 wt% CuO/TiO2. However, it exhibited poor resistance to SO2 and moderate tolerance to H2O.

Figure 16. Catalytic activity evaluation of metal oxides confined titania (made of Hombikat titania) nanotube catalytic formulations M/TNT where M = Mn, Cu, Ce, Fe, V, Cr, and Co for the selective catalytic reduction of NOx by NH3 in the presence of 900 ppm NO, 100 ppm NO2, 1000 ppm NH3, 10 vol% O2 in He balance, under a GHSV = 50,000 h⁻¹. Reprinted from Reference [109]. Copyright 2018, with Permission from Elsevier.

Carbon nanotubes (CNTs) have been reported as promising catalyst support for NH3-SCR catalysis due to their excellent stability and unique electronic and structural properties [36,112–115]. Qu and co-workers [116] reported that the NH3-SCR performance of Fe2O3 was dramatically enhanced when it supported on CNTs (Figure 17a). It was concluded that the large surface area, fine dispersion of Fe2O3, and interaction between Fe2O3 and CNTs were important factors to improve the NH3-SCR activity. In addition, the Fe2O3/CNTs catalyst showed an excellent tolerance to H2O/SO2. Interestingly, SO2 stream in the feed had promoting effect on the NO conversion (Figure 17b), which could be attributed to the increased acid sites for NH3 adsorption and activation on the catalyst surface in presence of SO2. Bai et al. [117] developed CNTs supported copper oxide catalysts, and found that the 10 wt% CuO/CNTs showed good NH3-SCR activity and excellent stability at 200 °C. The 10 wt% CuO/CNTs also had greater performance in comparison to 10 wt% CuO/TiO2. However, it exhibited poor resistance to SO2 and moderate tolerance to H2O.

Figure 17. (a) NOx conversion as a function of temperature over different catalysts and (b) SO2/H2O tolerance of the Fe2O3/CNTs catalyst. Reprinted from Reference [116]. Copyright 2015, with Permission from Royal Society of Chemistry.
5. Supported Binary and Multi Transition Metal-Based Catalysts

Given that the dispersion of two active components on support enhances the active sites further, researchers have been widely reported the supported binary transition metal-based oxides to improve the performance and SO$_2$/H$_2$O tolerance in NH$_3$-SCR reaction. With this perspective, several composites, such as MnCe/CNTs [118], Mn-Fe/TiO$_2$ [119], MnO$_x$-CeO$_2$/graphene [120], Mg-MnO$_x$/TiO$_2$ [121], CeO$_x$-MnO$_x$/TiO$_2$-graphene [122], Fe-Mn/Al$_2$O$_3$ [123], Mn-Fe/W-Ti [124], MnO$_x$-CeO$_2$/TiO$_2$-1%NG (NG = N-doped graphene) [125], Mn-Ce/CeAPSO-34 [126], etc., were investigated for the NH$_3$-SCR reaction at low-temperature. Smirniotis et al. [22] studied the promotional effect of co-doped metals (Cr, Fe, Co, Ni, Cu, Zn, Ce, and Zr) on the NH$_3$-SCR performance of Mn/TiO$_2$. As shown in Figure 18, except Zn and Zr, all other co-doped metals had a positive impact on the activity of Mn/TiO$_2$, and particularly, the Mn-Ni/TiO$_2$ exhibited the highest NO conversion and N$_2$ selectivity among the other titania-supported bimetallic catalysts.

![Figure 18](image)

Figure 18. N$_2$ selectivity and catalytic performance of Mn-M'/TiO$_2$ anatase (M' = Cr, Fe, Co, Ni, Cu, Zn, Zr, and Ce) catalysts: NH$_3$ = 400 ppm; NO = 400 ppm; O$_2$ = 2.0 vol%; GHSV = 50,000 h$^{-1}$; catalyst wt. = 0.1 g; reaction temperature = 200 °C. Reproduced from Reference [22]. Copyright 2011, with Permission from Elsevier.

They also investigated the influence of Ni loading on the activity of Mn/TiO$_2$ catalyst, and found that the 5wt%Mn-2wt%Ni/TiO$_2$ (Mn-Ni(0.4))/TiO$_2$, where Ni/Mn = 0.4) had the optimal activity with complete NO conversion at the temperature range of 200–250 °C (Figure 19a) and outstanding stability even in the presence of 10 vol% water (Figure 19b,c) [5,23]. The enhanced reducibility of manganese oxide and dominant phase of MnO$_2$ claimed to be responsible for the best activity and stability of Mn–Ni/TiO$_2$ catalyst [5,22,23]. In another study, they compared the de-NO$_x$ performance of high surface texture hydrated titania and Hombikat TiO$_2$ supported Mn-Ce bimetallic catalysts, and observed that the Mn–Ce/TiO$_2$ (Hombikat) showed the better activity and excellent resistance to H$_2$O (Figure 20). The superior performance could be attributed to the enhancement in reduction potential of active components, broadening of acid sites distribution, and the promotion of Mn$^{4+}$/Mn$^{3+}$, Ce$^{3+}$/Ce$^{4+}$ ratios including surface labile oxygen and small pore openings [25].
Figure 19. (a) Influence of Ni/Mn atomic ratio on NO conversion in the SCR reaction at a temperature range (160–240 °C) over Mn-Ni/TiO2 catalysts (XNO% = conversion of NO at 6 h on stream); (b) SCR of NO with NH3 at 200 °C temperature over Mn/TiO2 and Mn-Ni/TiO2 catalysts; (c) Influence of inlet water concentrations (10 vol%) on NO conversion in the SCR reaction over Mn–Ni(0.4)/TiO2 catalyst at 200 °C (GHSV = 50,000 h⁻¹; feed: NO = 400 ppm, NH3 = 400 ppm, O2 = 2 vol%, He carrier gas, catalyst = 0.1 g, total flow = 140 mL min⁻¹). Reprinted from Reference [5]. Copyright 2012, with Permission from Elsevier.

Figure 20. Influence of inlet water concentrations (7 vol%) on NOx conversion in the SCR reaction over Mn–Ce(5.1)/TiO2-Hk (Hombikat) catalyst at 175 °C; feed: NO = 900 ppm, NO2 = 100 ppm NH3/NOx (ANR) = 1.0, O2 = 10 vol%, He carrier gas, catalyst. 0.08 g, GHSV. 80,000 h⁻¹. Reprinted from Reference [25]. Copyright 2015, with Permission from Elsevier.
Xu and co-workers [127] reported Ce-Mn/TiO₂ catalysts with different Ce loadings, and the Ce(20)-Mn/TiO₂ found to show high activity with >90% NO conversion in the temperature range of 140–260 °C (Figure 21a). Their SO₂ tolerance results showed that the resistance ability was decreased in the order of Ce(20)-Mn/TiO₂ > Ce(30)-Mn/TiO₂ > Ce(10)-Mn/TiO₂ (Figure 21b). Although the Ce(20)-Mn/TiO₂ catalyst had reasonable resistance to 100 ppm SO₂ at different reaction temperatures (Figure 21c), it exhibited moderate tolerance to SO₂ poisoning when added higher than 100 ppm SO₂ to the reaction feed (Figure 21d). They ascribed the good SO₂ resistance of Ce(20)-Mn/TiO₂ to the widely distributed elements of Mn and Ce which in turn led to the inability of the sulfate material to remain on the surface.

Lin et al. [128] synthesized Me-Fe/TiO₂ (SD) catalyst via an aerosol-assisted deposition method, showing an excellent NH₃-SCR performance and good tolerance to SO₂/H₂O as compared to its counterparts prepared by co-precipitation and wet impregnation methods. The authors concluded that the enhanced surface reducibility and adsorption ability of NH₃/NOₓ of Mn-Fe/TiO₂ (SD) catalyst could be responsible for its superior activity. Lee and co-workers [129] investigated the poisoning effect of SO₂ as metal sulfate and/or ammonium sulfate deposits on the low-temperature

Figure 21. (a) Catalytic activity of Ce-Mn/TiO₂ catalyst for NH₃-SCR. Catalysts were loaded with 10%, 20% and 30% Ce and denoted as Ce(10), Ce(20) and Ce(30), respectively. Pure TiO₂ was also used for comparison; (b) The effect of various Ce concentrations using a Ce-Mn/TiO₂ catalyst on SO₂ resistance; (c) The effects of reaction temperature on NO conversion of the Ce(20)-Mn/TiO₂ catalyst in the presence of SO₂. The above three types of reactions were performed at: 500 ppm NO, 500 ppm NH₃, SO₂ 100 ppm, 3% O₂, N₂ balance. gas, GHSV = 10 000 h⁻¹; and (d) the effects of SO₂ concentration on NO conversion of Ce(20)-Mn/TiO₂ catalysts (T = 180°C, 500 ppm NO, 500 ppm NH₃, 3%O₂, N₂ balance gas, GHSV = 10 000 h⁻¹). Adapted from Reference [127]. We thank the Royal Society Open Science for this Contribution.

Lin et al. [128] synthesized Me-Fe/TiO₂ (SD) catalyst via an aerosol-assisted deposition method, showing an excellent NH₃-SCR performance and good tolerance to SO₂/H₂O as compared to its counterparts prepared by co-precipitation and wet impregnation methods. The authors concluded that the enhanced surface reducibility and adsorption ability of NH₃/NOₓ of Mn-Fe/TiO₂ (SD) catalyst could be responsible for its superior activity. Lee and co-workers [129] investigated the poisoning effect of SO₂ as metal sulfate and/or ammonium sulfate deposits on the low-temperature
NH₃-SCR activity of MnFe/TiO₂ catalysts. They found that the metal sulfates had a more serious deactivation effect than that of ammonium salts on the MnFe/TiO₂ catalysts. Their results showed that metal sulfates poisoning resulted in lower crystallinity, lower specific surface area, a lower ratio of Mn⁴⁺/Mn³⁺, higher surface acidity, and more chemisorbed oxygen, which in turn led to an adverse effect on the NH₃-SCR activity of the catalyst. Mu et al. [130] prepared Fe-Mn/Ti catalyst by ethylene glycol-assisted impregnation method, showing high NH₃-SCR efficiency over a broad temperature window (100–325 °C) and outstanding tolerance to sulfur poisoning. The formation of the Fe-O-Ti structure with strong interaction strengthened the electronic inductive effect and increased the ratio of surface chemisorption oxygen, thereby the enhancement of NO₃ adsorption capacity and NO oxidation performance, which could be beneficial to improve the NH₃-SCR activity.

Liu and co-workers [131] reported that the addition of Eu had noticeably improved the NH₃-SCR performance of Mn/TiO₂ catalyst even after sulfation process under SCR conditions (Figure 22a). However, both the Mn/TiO₂ and MnEu/TiO₂ catalysts showed poor activity when they sulfated only with SO₂ + O₂ (Figure 22a). Further, the MnEu/TiO₂ catalyst found to show better SO₂ tolerance as compared to the Mn/TiO₂ (Figure 22b). Their results revealed that Eu modification could inhibit the formation of surface sulfate species on the Mn/TiO₂ catalyst during the NH₃-SCR in the presence of SO₂, which could be the reason for improved SO₂ resistance.

![Figure 22.](image)

(a) NH₃-SCR activities of the fresh and sulfated catalysts; and (b) SO₂ tolerances of Mn/TiO₂ and MnEu/TiO₂ in NH₃-SCR reaction. Reprinted from Reference [131]. Copyright 2018, with Permission from Elsevier.

Sun et al. [132] investigated the NH₃-SCR activity over the Nb-doped Mn/TiO₂ catalysts with different Nb/Mn molar ratios, and found that the MnNb/TiO₂-0.12 (where Nb/Mn = 0.12) catalyst had optimal NO₃ conversion and N₂ selectivity in the temperature range of 100–400 °C (Figure 23a,b). The optimal MnNb/TiO₂-0.12 catalyst also exhibited greater SO₂ resistance than Mn/TiO₂ catalyst (Figure 23c). The incorporation of Nb into Mn/TiO₂ catalyst led to increase surface acidity and reducibility as well as generate more surface Mn⁴⁺ and chemisorbed oxygen species along with more NO₂, which results in the better NH₃-SCR activity. In situ DRIFT studies over the Mn/TiO₂ and MnNb/TiO₂-0.12 catalysts disclosed that the NH₃-SCR took place through Eley–Rideal mechanism even in presence of SO₂, in which the reaction mainly occurred between adsorbed NO₂ and gaseous NH₃. Hence, it was concluded that the higher SO₂ tolerance of the MnNb/TiO₂-0.12 catalyst could be due to the existence of more adsorbed NO₂ on its surface.
In another study, they reported the Mo-modified Mn/TiO₂ catalysts, exhibiting improved NH₃-SCR activity from 50 to 400 °C in comparison to Mn/TiO₂ catalyst. Particularly, the optimal MnMo/TiO₂-0.04 (where molar ratio of Mo/Mn = 0.04) catalyst better tolerance to SO₂ poisoning compared with Mn/TiO₂ (Figure 24) [133].

Fan and co-workers [134] fabricated ordered mesoporous titania supported CuO and MnO₂ composites (CuO/MnO₂-mTiO₂) through a facile acetic acid-assisted one-pot synthesis approach, showing high deNOₓ efficiency (>90% NO conversion) and N₂ selectivity (>95%) in a wide operating temperature range of 120–300 °C. They considered that the superior NH₃-SCR performance could be attributed to the unique structure and highly integrated mesoporous TiO₂ supported by the multicomponent system with high surface areas, accessible and homogeneously dispersed CuO and MnO₂ with multivalent nature and good redox activity. Although the CuO/MnO₂-mTiO₂ catalyst had good tolerance to H₂O, the resistance to SO₂ and H₂O/SO₂ poisoning, as well as high space velocity (GHSV), still need to be enhanced for practical use. Li et al. [135] synthesized fly ash-derived SBA-15 mesoporous molecular sieves supported Fe and/or Mn catalysts, and reported that Fe-Mn/SBA-15
catalyst showed notably greater NH3-SCR activity than Mn/SBA-15 or Fe/SBA-15 in the temperature range of 150–250 °C. Moreover, the Fe-Mn/SBA-15 catalyst exhibited good time-on-stream stability (200 h) and water tolerance at 200 °C. The high metal dispersion, Mn⁴⁺/Mn³⁺ ratio, the concentration of adsorbed oxygen, and the redox activity are important features to enhance the NH₃-SCR performance of the Fe-Mn/SBA-15 catalyst. In their subsequent study, the authors investigated the mechanisms of NO reduction and N₂O formation using in-situ DRIFT and transient reaction studies and proposed a possible denitration mechanism over the Fe-Mn/SBA-15 catalyst which is shown in Figure 25. The NH₃-SCR reaction over the Fe-Mn/SBA-15 catalyst proceeded through Langmuir-Hinshelwood, Eley-Rideal, and Mars-van Krevelen mechanisms. Their results also revealed that a large amount of nitrate thereby N₂O being produced over the Fe-Mn/SBA-15 during the reaction due to its strong oxidation ability, low acidity, and high basicity, which resulted in the lower N₂ selectivity [136].

![Figure 24](image-url) 
**Figure 24.** SO₂ tolerance of Mn/TiO₂ and MnMo/TiO₂-0.04 catalysts at 150 °C, Reaction conditions: 600 ppm NO, 600 ppm NH₃, 100 ppm SO₂, 5% O₂, balance Ar, GHSV = 108,000 h⁻¹. Reprinted from Reference [133]. Copyright 2018, with Permission from Elsevier.

![Figure 25](image-url)  
**Figure 25.** Low-temperature NH₃-SCR reaction mechanism on Fe-Mn/SBA-15 catalyst. Adapted from Reference [136]. Copyright 2018, with Permission from American Chemical Society.

Tang and co-workers [137] reported that Mn₂CoO₄/reduced graphene oxide (Mn₂CoO₄/rGO) catalyst with an optimal amount of CoCl₂·6H₂O of 0.3 (millimole) showed excellent NH₃-SCR activity and stability at low-temperature due to its large specific surface area, abundant Lewis acid sites,
and special three-dimensional architecture. When 100 ppm SO2 added to reaction feed, the NOx conversion over the optimal catalyst decreased significantly (96% to 53%), and the NOx conversion was recovered to original level by water-washing after stopping the supply of SO2. However, the decreased activity (100% to 82% NOx conversion) in the presence of H2O was restored to the original level after removing H2O from the feed gas. Wang et al. [138] investigated the honeycomb cordierite-based Mn-Ce/Al2O3 catalyst for NH3-SCR reaction and found that it showed good activity and reasonable resistance to SO2/H2O. The catalyst deactivation in the presence of SO2 was ascribed to the deposition of ammonium hydrogen sulfide and sulfated CeO2 on the catalyst surface during the NH3-SCR process.

Meng et al. [139] synthesized a novel CuAlOx/CNTs (CNTs = carbon nanotubes) catalyst by facile one-step carbothermal reduction decomposition method for low-temperature NH3-SCR. The CuAlOx/CNTs catalyst was found to exhibit higher NOx conversion (>80%) and N2 selectivity (>90%) than the CuAlOx in the temperature range of 180–300 °C (Figure 26a). They concluded that more favorable formation of Cu+ active sites, better dispersion of active CuO species and higher surface adsorbed oxygen were beneficial to enhance the NH3-SCR activity of CuAlOx/CNTs catalyst.

As shown in Figure 26b, the CuAlOx/CNTs catalyst displayed excellent resistance to SO2/H2O at 240 °C during the NH3-SCR. The authors attributed this outstanding SO2/H2O tolerance to the presence of CNTs that could promote the reaction of NH4HSO4 and NO continuously to avoid the formation and accumulation of excess ammonium sulfate salts on the catalyst surface. Li group [140] reported a series of ultra-low content copper-modified TiO2/CeO2 catalysts and observed that the catalyst with a Cu/Ce molar ratio of 0.005 exhibited the high NH3-SCR performance and good tolerance to SO2. Their characterization results disclosed that the addition of Cu into TiO2/CeO2 lead to enhance the Brønsted acid sites, amount of surface adsorbed oxygen and Ce 3+ species, redox, and surface acidic properties, which in turn improve the NH3-SCR activity.

![Figure 26. (a) NH3-SCR activity and N2 selectivity as a function of temperature from 150 °C to 330 °C; and (b) SO2/H2O resistance test of CuAlOx/CNTs catalyst at 240 °C. Reaction conditions: 600 ppm NH3, 600 ppm NO, 5.0 vol% O2, 100 ppm SO2 (when used), 10 vol% H2O (when used) balanced by N2 with a GHSV was 45,000 h−1. Reprinted from Reference [139]. Copyright 2019, with Permission from Elsevier.](image-url)

Recently, supported multi-metal oxide catalysts have been considered as the very promising candidates for low-temperature NH3-SCR reaction because of the enlarged synergetic catalysis effects of different components as well as improved metal-support interactions [141–145]. Wang and co-workers [146] reported a series of Nb modified Cu-Ce-Ti mixed oxide (Nb, x CCT, where y represented the atomic ratio of Nb to Ti) catalysts for low-temperature NH3-SCR reaction. It was found that Nb0.05CCT catalysts demonstrated a better activity than the Cu-Ce-Ti (CCT) and Ce-Ti (CT) samples (Figure 27a). Among all the Nb, x CCT catalysts, Nb0.05CCT showed a higher NO conversion (>90%) in a broad temperature range of 180–360 °C under the GHSV of 40,000 h−1 (Figure 27a). Results indicated that the incorporation of Nb to Cu-Ce-Ti led to strong interactions among the active phases that increased the oxygen vacancies and inhibited the over-oxidation of NH3, which in turn improved the NH3-SCR activity and N2 selectivity in a wide temperature window. DRIFTS studies revealed...
that the introduction of Nb promoted the generation of NO₂, which could improve the activity via “fast” SCR reaction process (Langmuir–Hinshelwood reaction pathway). As shown in Figure 27b, the optimal Nb₀.₀₅CCT catalyst exhibited higher resistance to SO₂/H₂O as compared to the Nb free catalyst. Li et al. [147] investigated the effect of Ho doping on the NH₃-SCR performance and the SO₂/H₂O resistance of Mn-Ce/TiO₂ catalyst. Among the catalysts tested, the catalyst with Ho/Ti of 0.1 (Mn₀.₄Ce₀.₀₇Ho₀.₁/TiO₂) showed the best performance with >90% NO conversion in the temperature range of 150–220 °C, which was attributed to high concentration of chemisorbed oxygen, surface Mn⁴⁺/Mn³⁺ ratio, and acidity, as well as large specific surface area. Although the Mn₀.₄Ce₀.₀₇Ho₀.₁/TiO₂ showed higher resistance to SO₂ and H₂O than the Mn₀.₄Ce₀.₀₇/TiO₂ catalyst, it was deactivated some extent in presence of SO₂/H₂O which is irreversible.

Lu group [148] synthesized a series of activated coke (AC) supported FeₓCoₓCeₓOm catalysts for low-temperature NH₃-SCR, and found that the 3%Fe₀.₆Co₀.₂Ce₀.₂O₁.₅₇/AC catalyst had the best activity at 250–350 °C and good tolerance to H₂O/SO₂ at 250 °C. The superior performance of the catalyst was ascribed to the co-participation of Fe, Co, and Ce species with different valence states, high concentration of chemisorbed oxygen, well dispersed active components, increase of weak acid sites, good redox properties of metallic oxides, and abundant functional groups on the catalyst surface. Their mechanistic and kinetic studies also indicated that the enhanced active sites for the adsorption of NO and NH₃, and the redox cycle among Fe, Co and Ce were responsible for the improved activity. Zhao et al. [149] reported a series of Mn-Ce-V-WOₓ/TiO₂ composite oxide catalysts, exhibiting greater NH₃-SCR activity than the TiO₂ supported single-component catalysts (Figure 28a,b). Particularly, the catalyst with a molar ratio of active components/TiO₂ = 0.2 showed the best performance (>90% NO conversion) from 150 to 400 °C (Figure 28a). As shown in Figure 28c, the optimal Mn-Ce-V-WOₓ/TiO₂ (molar ratio of Mn-Ce-V-WOₓ/TiO₂ = 0.2) showed excellent stability and outstanding tolerance to H₂O/SO₂ at 250 °C. The authors concluded that the better performance of Mn-Ce-V-WOₓ/TiO₂ mainly attributed to the variety of valence states of the four active components and their high oxidation-reduction ability.

![Figure 27](image-url)

**Figure 27.** (a) NH₃-SCR activities of different catalysts [Reaction conditions: [NH₃] = [NO] = 600 ppm, [O₂] = 3%, [H₂O] = 5 vol%, N₂ as balance. GHSV = 40 000 h⁻¹]; and (b) SO₂ and H₂O resistance of the catalysts at 250 °C in SCR reaction process [Reaction conditions: [NH₃] = [NO] = 600 ppm, [O₂] = 3%, [SO₂] = 50 ppm, [H₂O] = 5 vol%, N₂ balance, GHSV = 40 000 h⁻¹]. Reproduced from Reference [146]. Copyright 2018, with Permission from Elsevier.
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Figure 28. (A) Selective catalytic reduction (SCR) activity of Mn-Ce-V-WOx/TiO2 composite catalysts with molar ratio of active components/TiO2 at different values; (a) 0.1; (b) 0.2; (c) 0.3; (d) 0.6; (B) SCR activity of V2O5/TiO2, WO3/TiO2, MnO2/TiO2, CeO2/TiO2 and TiO2. Reaction conditions: [NO] = [NH3] = 1500 ppm, O2 = 3%, gas hourly space velocity (GHSV) = 40,000 h−1; and (C) the lifetime of Mn-Ce-V-WOx/TiO2 catalyst with molar ratio of 0.2 at 250 °C: inset (a-c) H2O and SO2 resistance at 250 °C. Reaction conditions: [NO] = [NH3] = 1500 ppm, [O2] = 3%, [H2O] = 5%, [SO2] = 100 ppm, GHSV = 40,000 h−1. Adapted from Reference [149].

6. Conclusions

Since the emission standards for NOx are becoming more stringent to keep our atmosphere clean, the widespread use of fossil fuel in automobiles and industries require advanced catalytic materials for NOx emission control. The low-temperature SCR of NOx with NH3 would be a promising solution to mitigate the NOx emissions from mobile and stationary sources. Hence, the development of efficient catalysts for the low-temperature NH3-SCR with high deNOx activity, N2 selectivity, and high resistance toward SO2/H2O poisonings is the subject of increasing interest in the field of environmental catalysis. Transition metal-based oxide catalysts have drawn much attention for low-temperature NH3-SCR due to their excellent redox properties, high activity, durability, and relatively low manufacturing costs. In this review, we have summarized the recent progress in the low-temperature NH3-SCR technology over the various transition metal-based catalysts. Over the past decades, significant research efforts have been made to improve the de-NOx efficiency and SO2/H2O tolerance of transition metal-based oxides in NH3-SCR at low-temperatures. Various transition metal-based mixed oxides with and without support have been extensively studied for NH3-SCR reaction and, particularly, MnOx-based catalyst formulations have caught much attention because of their excellent de-NOx efficiency at low-temperatures. The modification of transition metal oxides by doping with other metal oxides led to high redox ability and acidic sites, and consequently, better NH3-SCR performance at low-temperature. The loading of single and multi-transition metal-based oxides on the surface of supports (TiO2, TiO2 nanotubes, carbon nanotubes, etc.) could also enhance the NOx conversion and N2 selectivity in NH3-SCR reaction by the fine dispersion of active component/s and its/their strong interaction with the support. The choice of metal loading and the support
could play a key role in the catalytic function of the supported transition metal-based catalysts. The synergistic redox interaction between the active components of mixed metal oxide/supported metal oxide catalysts was also found to be an important factor to design the efficient denitration catalysts. In spite of the significant progress on the SO\textsubscript{2}/H\textsubscript{2}O tolerance of the catalysts, the durability of catalysts in the presence of both SO\textsubscript{2} and H\textsubscript{2}O still needs to be improved. Most transition metal-based catalysts suffered from low resistance when the reaction feed contains both SO\textsubscript{2} and H\textsubscript{2}O streams simultaneously. Hence, researchers have continuously explored the different options of transition metal-based mixed oxides and active transition metal/s-support combinations in order to develop the better NH\textsubscript{3}-SCR catalysts in terms of SO\textsubscript{2}/H\textsubscript{2}O tolerance at low-temperature. The understanding of the inhibition mechanism of SO\textsubscript{2} and H\textsubscript{2}O could be a promising strategy to develop high SO\textsubscript{2}/H\textsubscript{2}O resistance catalysts for NH\textsubscript{3}-SCR reaction. However, the SO\textsubscript{2}/H\textsubscript{2}O inhibition mechanism was not very clear that needs to be investigated deeply. Especially, the design of transition metal-based catalysts with a combination of high NO\textsubscript{x} conversion and N\textsubscript{2} selectivity in a wide operation temperature window and good resistance to SO\textsubscript{2}/H\textsubscript{2}O have attracted paramount attention, but it is still challenging task. The scope of NH\textsubscript{3}-SCR research is quite vast and a large number of improvements need to be achieved in the near future.

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