



Review

Low temperature selective catalytic reduction of NO_x with NH₃ over Mn-based catalyst: A review

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Abstract: The removals of NO_x by catalytic technology at low temperatures (100–300 °C) for industrial flue gas treatment have received increasing attention. However, the development of low temperature catalysts for selective catalytic reduction (SCR) of NO_x with ammonia is still a challenge especially in the presence of SO₂. The current status of using Mn-based catalysts for low temperature SCR of NO_x with ammonia (NH₃-SCR) is reviewed. Reaction mechanisms and effects of operating factors on low temperature NH₃-SCR are addressed, and the SCR efficiencies of Mn-based metal oxides with and without SO₂ poisoning have also been discussed with different supports and co-metals. The key factors for enhancing low temperature NH₃-SCR efficiency and SO₂ resistance with Mn-based catalysts are identified to be (1) high specific surface area; (2) high surface acidity; (3) oxidation states of manganese; (4) well dispersion of manganese oxide metals; (5) more surface adsorbed oxygen; (6) more absorbed NO₃⁻ on the catalyst surface; (7) easier decomposition of ammonium sulfates. Moreover, the regenerative methods such as water washing, acid and/or alkali washing and heat treatment to the poisoned catalysts could help to recover the low temperature SCR efficiency to its initial level.

Keywords: Selective catalytic reduction; SO₂ resistance; poisoning; Fast SCR; low temperature catalysts

1. Introduction

The combustion of fossil fuels in power plants, vehicles and factories are major sources of air pollution, and the exhaust air pollutants containing sulfur oxides, carbon monoxide, particulate matter and nitrogen oxides (NO_x), etc. The NO_x air pollutants cause a series of environmental issues such as photochemical smog, acid rain, ozone depletion, fine particulate pollution and even the global warming problem [1,2].

Increasing concerns on the NO_x emission have stimulated vital development of the NO_x control technologies. Fuel control, combustion control and post-combustion control are three primary techniques for NO_x emission controls. The aim of fuel control technologies is to minimize the nitrogen contained in the fuels before the combustion process. Combustion control technologies are to reduce NO_x formation levels during the combustion process. And the post-combustion control technologies are used to immobilize NO_x by adsorption or absorption, or convert NO_x into less harmful species by plasma processes as well as catalytic or non-catalytic reaction processes.

One of the well-known post-combustion control techniques is the selective catalytic reduction (SCR) process, where ammonia based reagent or hydrocarbons (HCs) are used as the reducing agents. The catalytic technology that uses ammonia as the reducing agent of NO_x is called NH_3 -SCR or simply termed as the SCR technology, which is widely applied for NO_x controls from stationary sources. And the SCR process that employs HCs as the reducing agent is termed as HC-SCR, which is being investigated for the vehicle NO_x emission controls. In this study, the low temperature SCR process for stationary source controls using Mn-based catalysts is reviewed.

The NH_3 -SCR is a commercially available technology applied to convert the NO_x emissions into water vapors and nitrogen gas molecules. The SCR method was firstly applied in Japan in the 1970's and have now been installed in the USA, Europe and several Asian countries, etc. [1]. And the V_2O_5 - WO_3 / TiO_2 -based catalyst is one of the major catalysts used for the SCR process in the industry. However, the V_2O_5 - WO_3 / TiO_2 -based catalyst has a narrow and high working temperature window of 300–400 °C [3-9]. At temperatures lower than 300 °C the activity is too low, while at temperatures higher than 400 °C the NH_3 will be oxidized to form N_2O and NO .

However, the flue gas temperatures for industrial processes including cement, glass and steel manufacture could be as low as 100–200 °C. Thus when using the conventional V_2O_5 - WO_3 / TiO_2 -based catalyst the SCR system needs to be heated to above 300 °C, which consumes a lot of energy. Furthermore, vanadium byproducts formed during catalyst preparation and usage is hazardous to the environment and human health [10].

Therefore more and more researchers have been interested in developing new catalysts that can work well at low temperatures. Singoredjo et al. [11] prepared manganese oxide based catalysts in 1992, which showed both high activity and good selectivity at $T < 250$ °C. Later in 1994 Kapteijn et al. [12] studied the reaction model, kinetics and identification of surface intermediates on Mn/ Al_2O_3 . And in 2001, Smirniotis et al. [13] used Mn, Cr, and Cu oxides supported on Hombikat TiO_2 . It was found that both Cr- TiO_2 , Cu- TiO_2 and Mn- TiO_2 had high activity at 120 °C. And the Mn- TiO_2 even can be active at 100 °C. Since then, studies on low-temperature SCR catalyst increase rapidly. This is demonstrated by Figure 1 that shows the number of published research papers on low temperature SCR from 1990 to 2015 as searched from the Web of Science system using the keyword of “Low

Temperature Selective Catalytic Reduction”. It is observed that there are only a few papers published each year during early 1990’s. But within the year of 2015, the number of papers addressing the low temperature SCR issue has been over 380.

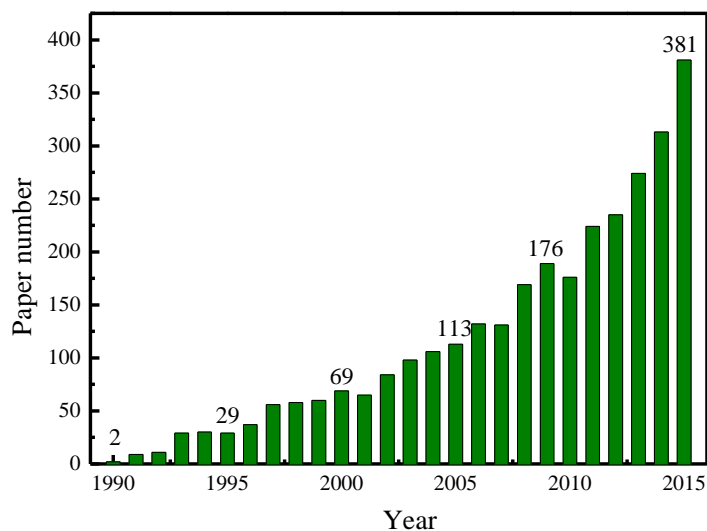


Figure 1. Number of low temperature SCR papers published since 1990. Data are obtained via the Web of Science system using the keyword of “low temperature selective catalytic reduction”.

Up to now, researchers have studied on different active metals and supports for low temperature SCR catalysts such as transition metals (Fe, V, Cr, Cu, Co and Mn) supported on SiO_2 , Al_2O_3 or TiO_2 [14-16], which showed good activity for low temperature SCR reaction. However, the problem of SO_2 poisoning is difficult to be resolved. There are two possible reasons causing deactivation of the catalyst due to the presence of SO_2 . One is that SO_2 could react with NH_3 to form $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 at low temperature which then deposit on the catalyst surface and block the active sites of catalyst [14,17-24]. The other reason is due to the active phase of metal oxides could be sulfated by SO_2 and form stable sulfate species, which are inactive in SCR reaction [17,20]. And there are some researchers studying on regenerating the catalysts by calcination or water-washing treatment [20,25-29].

In this paper, we review the Mn-based SCR catalysts coupled with different active metals and supports, and evaluate their performance at low temperature. The mechanisms of SCR reaction and SO_2 poisoning, the key factors to enhance SCR efficiency and inhibit the SO_2 poisoning are addressed. Finally, the methods to regenerate the catalysts are discussed.

2. SCR Reaction mechanisms

The catalyst for SCR of NO usually is composed of active metals coated on the honeycomb, ceramics or plate supports. The main principle of SCR reaction is to use a reducing agent, e.g. anhydrous ammonia, aqueous ammonia or urea, which is mixed with the flue gas and then flow

through the SCR system. Then the NO_x in the flue gas subsequently reacts with reducing agent to form harmless water vapors and nitrogen [1,30].

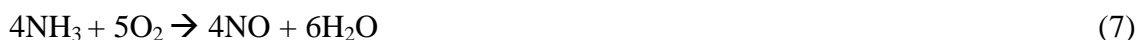
The major desired reactions of SCR reaction are shown as follows [31-33]:



However, the following undesired reactions are occurred during the SCR of NO [34]:



Besides, the nonselective oxidation of ammonia may also react with oxygen [35,36]:



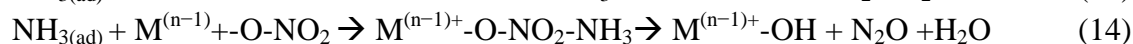
In general, researchers agree that Equation (1) proceeds under typical SCR conditions of NH_3/NO ratio of near 1, few percentages of oxygen and reaction temperature of less than 400 °C. On the other hand, “fast SCR”, first proposed in 1986 [37], proceeds at a much higher reaction rate than “standard SCR” reactions (Equation (1) and (2)) was developed to improve deNO_x efficiency especially at low temperatures [33,38-43]. Wang et al. [42] indicated that Mn catalytic sites can implement the conversion of NO to NO_2 on a Mn mullite (Sm, Gd) Mn_2O_5 catalyst. The result showed that $\text{Mn}_{0.05}\text{Co}_{0.95}\text{O}_x$ had a better NO oxidation ability due to the higher content of O_α .

Unselective behavior occurs when the molar ratio of converted NO and NH_3 is lower than 1 (Equation (4)) or when the reaction temperature is too high (Equation (5)) [1,22]. Some researchers showed that ammonia is converted by ways other than Equation (1) [34]. Among them the low-temperature selective catalytic oxidation (SCO) of ammonia into nitrogen is potentially considered as one of the most efficient technologies for ammonia removal from oxygen-containing waste gases. However, in the NH_3 -SCR case the oxidation of reducing agent (NH_3) to NO or N_2O will cause the decrease in NO conversion. The catalytic oxidation of ammonia, depending on operating conditions and the type of catalysts used, can proceed in the three principal reactions of Equations (6–8) [35]:

The mechanism of SCR reaction and N_2O formation during the low-temperature selective catalytic reduction reaction were studied [41,44]. Many researchers used in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and transient reaction to find out the mechanism of SCR [39,45-47]. They concluded that both the E-R mechanism (Eley-Rideal mechanism, i.e., the reaction of adsorbed NH_3 species with gaseous NO) and the L-H mechanism (Langmuir-Hinshelwood mechanism, i.e., the reaction of adsorbed NH_3 species with adsorbed NO_x species) contribute to N_2O formation.

The reduction of NO through the L-H mechanism can be approximately described as [45,46,48-50]





Equations (9) and (10) are the adsorption of gaseous NH_3 and NO , respectively, on the surface of catalyst. Some researchers agreed that the SCR reaction starts with the adsorption of gaseous NH_3 . Physically adsorbed NO can be oxidized by active metals (e.g., Mn, Ce and Fe) to form monodentate nitrite and monodentate nitrate (Equations (11) and (12)). Yang et al. [45] indicated that adsorbed monodentate nitrite and monodentate nitrate react with adsorbed NH_3 to form NH_4NO_2 and NH_4NO_3 (Equations (13) and (14)). The NH_4NO_2 and NH_4NO_3 are two important reaction intermediates. Furthermore, NH_4NO_2 and NH_4NO_3 are decomposed to N_2 and N_2O , respectively. The reduced active sites can be rapidly regenerated by the reaction with gaseous O_2 (Equation (15)).

On the other hand, NO reduction through the E-R mechanism can be approximately described as [45,49-51]



Adsorbed NH_3 can be oxidized to NH_2 by active metals (M^{n+} , e.g., Mn, Ce and Fe) on the surface (Equation (17)). Furthermore, the active metals can further oxidize NH_2 to NH (Equation (18)). The NH_2 and NH are two important reaction intermediates. They react with gaseous NO and then decompose to N_2 and N_2O , respectively as observed in Equations (19) and (20).

Yang et al. [45] used in situ DRIFTS to find out the mechanism of SCR and N_2O formation during the low-temperature SCR reaction over Mn-Fe spinel. It was observed that lots of N_2O are formed during NO reduction over Mn based low temperature SCR catalyst. On the other hand, only little N_2O is formed during NO reduction over Fe based SCR catalyst, which suggested that NH_2 on the surface cannot be oxidized to NH by Fe^{3+} and the oxidation of NH_2 on 5% Mn-10% Fe/ TiO_2 and 10% Mn/Fe-Ti spinel to NH is mainly related to Mn^{4+} on the surface.

Hu et al. [52] used anatase TiO_2 -supported manganese and cobalt oxide catalysts for selective catalytic reduction of NO_x with NH_3 . Their DRIFT results showed that the adsorption of $NO + O_2$ led to the formation of four NO_x species: gaseous NO_2 , bidentate nitrates, linear nitrites, and monodentate nitrites. After NH_3 was introduced, only the band attributed to gaseous NO_2 started to decrease. Meanwhile, the characteristic peak of coordinated NH_3 did not appear which confirms that NO_2 and NH_3 participated in the fast SCR reaction and the catalysts showed good catalytic performance at low temperature.

Moreover, Smirniotis et al. [53,54] studied the mechanism of Mn/ TiO_2 . Smirniotis et al. [54] used ^{15}N (^{15}NO and $^{15}NH_3$) and ^{18}O ($^{18}O_2$) containing species to investigate the reaction mechanism of the low-temperature SCR of NO over Mn/ TiO_2 . The roles of ammonia oxidation and surface oxygen species for the overall SCR reaction network at low-temperatures was quantified, and their results

showed that oxygen exchange between nitric oxide and the catalyst lattice oxygen was established in the catalytic reduction of NO reaction. And the effect of oxygen on activity and selectivity was noteworthy in both SCR and ammonia oxidation reactions over Mn/TiO₂.

By the review on the reaction mechanisms for low temperature SCR of NO_x with ammonia, it was shown that SCR reactions take place via different mechanisms under different temperatures [21,23,41]. In addition, research results also showed that fast SCR proceeds at a much higher reaction rate than “standard SCR”, especially at low temperatures [33,43,46,55]. Important results regarding the L-H and E-R mechanisms and the condition of fast SCR are summarized in Table 1.

Table 1. Summary of the Langmuir-Hinshelwood and Eley-Rideal mechanisms and the conditions for fast SCR.

Mechanism	Catalyst	Ref.
Langmuir-Hinshelwood and Eley-Rideal	<p>Low temperature SCR activity is inhibited due to the cutting off of the L-H reaction pathway (<200 °C); E-R reaction pathway dominates in the NH₃-SCR reaction at high temperature (>250 °C), which is an important reason for its enhanced SO₂ durability [21,23,41].</p> <p>MnCe/TiO₂ (higher Lewis acid sites) is a superior SCR catalyst to MAce/Al₂O₃ (higher Brønsted acid sites) at low temperature (80–150 °C) [56].</p> <p>N₂O selectivity of NO reduction through the L-H mechanism is much less than that through the E-R mechanism [45,49].</p>	[21,23,33,41,45,49]
Fast SCR	<p>Fast SCR reaction that occurred with equal amounts of NO and NO₂ shows a much higher rate than the standard SCR reaction in the temperature range of 200–350 °C [33].</p> <p>The SCR reaction needs two types of active sites: the Brønsted acid sites for ammonia adsorption and the metal ion sites (e.g., Fe³⁺ ions) for NO oxidation to NO₂ [46].</p> <p>NO₂ adsorption on Fe-ZSM-5 identifies the formation of ferric nitrates as the prevailing and stable terminal products of NO₂ storage [43].</p> <p>Addition of iron results in more Ce³⁺ and chemisorbed oxygen on the catalyst surface, thus increases the amount of Brønsted acid sites and in situ formed NO₂, respectively [41].</p>	[33,43,41,46]

3. Operating factors affecting low temperature SCR efficiency

There are many researchers studied on the effects of operating conditions on the SCR efficiency. The experimental results demonstrated that the SCR reactions are significantly influenced by operating factors such as reaction temperature, space velocity, and the presence of H₂O and SO₂.

3.1. Reaction temperature

The appropriate operating temperature of SCR system is determined by the types of SCR catalysts. The traditional SCR catalysts (e.g., WO_3 and V_2O_5 etc.) are active within a narrow temperature window of 300–400 °C [7]. On the other hand, the low temperature SCR catalysts (e.g., Mn, Fe and Ce metal etc.) are active below 300 °C [57-59]. Kong et al. [58] used TiO_2 supported Mn and W for low-temperature SCR. The result showed that the MnTiO_x and WTiO_x catalysts have high activities in NH_3 -SCR reaction within temperature ranges of 175–300 °C and 350–450 °C, respectively. Kong et al. [58] combined Mn and W metals and the MnWTiO_x catalyst showed the highest activity in NH_3 -SCR reaction within a broad temperature range of 200–400 °C. Xu et al. [60] used WO_3 modified MnO_x - $\text{CeO}_2/\text{ZrO}_2$ monolith catalysts for selective catalytic reduction of NO_x with ammonia. They indicated that MnO_x - CeO_2/WO_3 - ZrO_2 had the best textural properties including a well-dispersed state of WO_3 , the lowest binding energy of $\text{Ce}^{3+} 3d_{5/2}$, the maximum value of $\text{Ce}^{3+}:\text{Ce}^{4+}$, the suitable molar ratio of Mn:Ce, and a co-existence state of MnO_2 - Mn_2O_3 . As a result, MnO_x - CeO_2/WO_3 - ZrO_2 had wider reaction temperature window of 150–380 °C. Pappas et al. [61] found that the Mn/TNT-Hombikat sample demonstrated impressive NO_x conversions in the temperature range 100–300 °C in comparison with Mn/ TiO_2 nanoparticles and other catalysts. This may be attributed to smaller particle size, scattered amorphous Mn over the catalyst surface, higher dispersion, and an abundant MnO_2 phase.

Although literature data revealed that it is possible to have one catalyst which performed well over wide temperature range, however, the operation conditions were different among different literature, hence it is hard to understand which type of catalyst performed better at different temperature ranges. The results of Liu's studies in 2009 [62] and 2013 [63] were conducted under the same operation condition and thus their results are summarized in Figure 2. It was demonstrated that the MnWO_x catalyst had very high activity even at GHSV as high as 50,000 h^{-1} and temperature as low as 60 °C. But at an operation temperature of higher than 200 °C the NO conversion rate of MnWO_x decreased significantly. On the other hand, the MnFe- TiO_2 catalyst performed better at higher temperature range of 150–300 °C.

In general, the SCR catalyst efficiency is increased by increasing the reaction temperature, but after reaching the highest efficiency, the performance of SCR catalyst will then be decreased with increasing temperature. Yu et al. [22] investigated the catalytic behavior of MnO_2 - Fe_2O_3 - CeO_2 - TiO_2 prepared by sol-gel method (MFCT) and impregnation method (imp-MFCT). The result showed that the catalyst MFCT has the widest temperature window of about 200–400 °C, while the imp-MFCT catalyst enables acceptable NO conversions of over 80% only at 200–300 °C. In addition, effluent N_2O concentration over imp-MFCT first increases with increasing temperature and in turn remains constant of about 100 ppmv when the temperature is higher than 250 °C. And the effluent N_2O concentration is less than 20 ppm which appears at 300–400 °C over the sol-gel catalysts. The results indicated that SCR catalyst produces N_2O at relatively higher temperature.

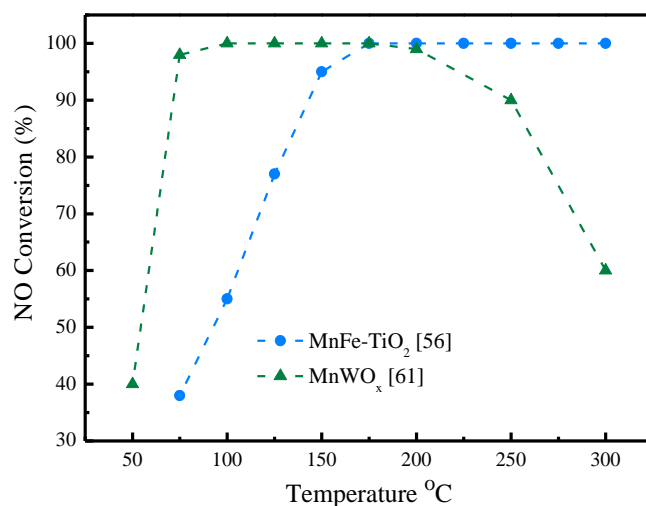


Figure 2. Performance of low-temperature SCR catalysts tested by the same research group of Liu et al. [62,63]. Reaction conditions: $[\text{NO}] = 500 \text{ ppm}$, $[\text{NH}_3] = 500 \text{ ppm}$, $[\text{O}_2] = 5 \%$, and $\text{GHSV} = 50,000 \text{ h}^{-1}$.

There are two reasons for the decrease of NO conversion at high temperatures. The first one is that the reducing agent (NH_3) will be oxidized to NO or N_2O (Equation 7–8) [41,50,64–68]. Magdalena et al. [65] used Cu-containing catalyst to study the SCR and SCO processes. The results showed that ammonia oxidation in the SCO process over Cu catalyst starts at about 275 °C. And conversion of NO in the SCR process is noticed at lower temperatures of about 175 °C. Therefore Magdalena et al. [65] indicated that oxidation of NH_3 into NO (Equation 7) is a rate determining step in the low temperature range. Therefore, it is important to select the appropriate operating temperature of the SCR system for avoiding SCO reaction. Hu et al. [52] used anatase TiO_2 -supported manganese and cobalt oxide catalysts for NH_3 and NO oxidation reaction in the temperature range of 100–400 °C. Hu et al. [52] found that the temperature at which the NH_3 conversion reaches 50% gradually decreased from 245 °C (Mn/TiO_2) to 180 °C ($\text{Co}(8)\text{-Mn}/\text{TiO}_2$) with increasing Co content. This result indicated that the addition of Co promoted the oxidation ability of the catalyst, inducing the occurrence of NH_3 oxidation at lower temperatures. After comparing the SCR activity, Hu et al. [52] indicated that NO_x formed in considerable amounts and can be seen as the main reason for catalyst deactivation. Because NH_3 oxidation will inevitably occur during the SCR process, a certain amount of reducing agent is insufficient to react with NO_x and eventually leads to catalyst deactivation.

The second reason for the decrease of NO conversion at high temperature is that NO will be over oxidized to NO_2 [40,66,69,70]. This is a more complicated situation since the oxidation of NO to NO_2 could lead to either positive or negative result to the NO conversion. When fast SCR reaction occurs at low temperatures, the oxidation of NO to NO_2 is a beneficial effect to the NO conversion [33,38–43]. However, when the NO is over oxidized to NO_2 at higher temperature, it would lead to the decrease of NO conversion. Xu et al. [70] used $\text{MnO}_x\text{-CeO}_2/\text{WO}_3\text{-ZrO}_2$ catalysts with different mass ratios of $\text{Mn}/(\text{Mn}+\text{Ce})$ were prepared and used for the selective catalytic reduction and NO oxidation reaction. They found that the ratio of NO converted to NO_2 showed a slightly increasing trend with the $\text{Mn}/(\text{Mn}+\text{Ce})$ mass ratio below 300 °C. At above 300 °C, the ratio of NO

converted to NO₂ for all catalysts rapidly increased with temperature and then decreased again after reaching the peak value. After comparing the SCR activity, Xu et al. [70] indicated that NO could be more easily reduced to N₂ by NH₃ when there was some NO₂ than with NO alone due to the “fast SCR” reaction. But the NO₂ formed was continuously fed to the NH₃ reducing agent, and thus block NH₃ oxidation reaction at high temperatures.

Zhou et al. [40] studied the individual oxidation effect of NH₃ and NO using Fe–Ce–Mn/ZSM-5 catalyst in the temperature range of 100–500 °C. They observed that NO oxidation occurs at 100 °C. And Fe–Ce–Mn/ZSM-5 catalyst had the highest NO₂ concentration at 300 °C. For the study on the NH₃ oxidation, Zhou et al. [40] indicated that NH₃ is more oxidized to N₂ rather than to NO in temperature range of 100–400 °C. And NH₃ will be mainly oxidized to NO at above 400 °C.

On the other hand, higher operating temperature is one of the key factors for the inhibition of SO₂ poisoning. Liu et al. [71] poisoned the FeTiO_x to clarify the SO₂ effect on NO conversion at different operation temperatures. They found out that active nitrate species could not form effectively after SO₂ poisoning due to the stronger acidity of sulfate species on iron sites. Therefore the low temperature SCR activity is inhibited due to the cutting off of the L-H reaction pathway. When the reaction temperature is higher than 250 °C, Liu et al. [71] showed that only the E-R reaction pathway dominates in the NH₃-SCR reaction over sulfated FeTiO_x catalyst, which is an important reason for its enhanced SO₂ durability at high temperatures. The effect of temperature on SCR reaction and the catalysts used for those studies are summarized in Table 2.

Table 2. Temperature effect on the SCR reaction and catalysts used for the temperature effect studies.

Temperature effect	Catalyst	Ref.
NH ₃ will be oxidized to NO or N ₂ O at high temperature and causes the decrease in NO conversion.	MnCoO _x [39]	[6,22,24,39,40,58,64-70, 72-75]
	W-MnCeTi [68]	
	V/Sb/Ce/Ti [24]	
	V/W/TiO ₂ [6]	
	MnCe/TiO ₂ [72]	
	Cu/Mn/Fe [65]	
	Co-Ce-Mn/TiO ₂ [64]	
	CeNb [67]	
	Ce/MIL-100 [73]	
	Mn-Ce-Zr [74]	
Mn-Fe-Ce-Ti [22]		
NO will be over oxidized to NO ₂ at high temperature and causes the decrease in NO conversion.	Ag-MnCe [69]	
	MnO _x -CeO ₂ /WO ₃ -ZrO ₂ [70]	
	Mn/TiO _x [66]	
Catalysts which are active at different temperatures	Fe-Ce-Mn/ZSM-5 [40]	
Catalysts which are active at different temperatures	Mn/Ti (active in 175–300 °C);	
	W/Ti (active in 350–450 °C) [58]	
	Mn-Nb-Ce (active in 200–350 °C);	
	VWTi (active in 300–450 °C) [75]	

According to the above literature results, we can describe the SCR reaction mechanism at different temperatures without the presence of SO_2 by Figure 3. In the lower temperature range of (A) where the SCR efficiency was low, the NO conversion can be enhanced by increasing reaction temperature, reducing GHSV and promoting NO oxidation (fast SCR reaction). When the temperature reaches range (B), NO conversion is mainly determined by the composition of SCR catalysts including the active metals and supports. And a further increase of the reaction temperature to range (C) tends to decrease the NO conversion due to two reasons: one is that reducing agent (NH_3) is oxidized to form NO or N_2O , the other is NO is over oxidized to NO_2 .

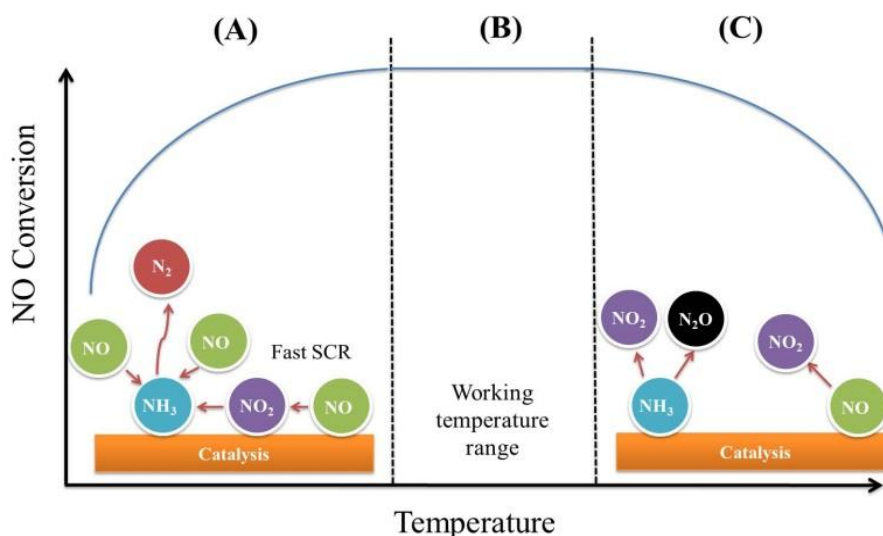


Figure 3. SCR reaction mechanisms at different temperatures without the presence of SO_2 .

3.2. Space velocity

Gas hourly space velocity (GHSV) is most commonly used to represent the retention time of the gas and catalyst. The gas hourly space velocity is the reciprocal of average retention time:

$$\text{GHSV} = \frac{\text{volumetric rate of the gas at STP}}{\text{bed volume}} \quad (21)$$

In general, a smaller space velocity value represents a longer retention time of the gas in the catalyst system, which indicates that the SCR reaction can be more completed with better NO conversion. Zuo et al. [76] tested the effect of different values of GHSV for the low-temperature SCR of NO_x with ammonia in the presence of SO_2 . The results showed that when SO_2 is added to the SCR system, the NO conversion starts to decrease after 8 hours and 1 hour for GHSV of $30,000 \text{ h}^{-1}$ and $200,000 \text{ h}^{-1}$, respectively. The results indicated that a smaller space velocity could inhibit the SO_2 poisoning. This is due to that smaller space velocity means more catalyst amount to tolerate more SO_2 . In addition, the values of GHSV probably affect the N_2O formation. Yang et al. [45] studied on N_2O selectivity with different values of GHSV. The results showed that N_2O selectivity during NO reduction increases with the increase of GHSV from $60,000$ to $1,200,000 \text{ cm}^3\text{g}^{-1}\text{h}^{-1}$. Yang et al. [45] suggested

that the ratio of NO reduction through the L–H mechanism generally increases with the decrease of GHSV. The transient reaction study demonstrated that N₂O selectivity through the L–H mechanism is much less than that through the E–R mechanism. Therefore, N₂O selectivity in the SCR reaction decreases with the decrease of GHSV.

3.3. Effects of H₂O and SO₂

Water vapors and sulfur oxides are the main components in flue gases and often lead to catalyst deactivation. Water vapors could partially occupy and decrease the number of available active sites. Even in dry conditions, the catalysts can be affected by the water vapor produced in the SCR reaction [77,78]. It causes a reduction in activity for low-temperature SCR catalysts. In general, the effect of H₂O can be reversible [79,80]. When H₂O is added into the SCR system, H₂O tends to compete with NO and NH₃ on the active sites, which cause the decrease in NO conversion. And this effect disappears if H₂O vapors are removed. Some researchers showed that the water effect is significant when the operating temperature is below than 200 °C. When operating temperature is above than 200 °C, the water effect becomes negligible because water vapors are not easily adsorbed on the surface of catalyst [71,79-83].

The presence of SO₂ has a critical influence on the catalyst for SCR reaction at low temperature because there are still some residual sulfur oxides after the desulfurization equipment. And the sulfur oxides will react with NH₃ and the SCR catalyst, which generates ammonia sulfate and metallic sulfate, respectively. The salts products are occupied on the active sites of catalysts and resulted in the decrease of NO conversion at low temperature [73,75,84-86].

However, promotion effect of SO₂ was observed by Huang et al. [87,88] and Zhu et al. [89,90], which used V₂O₅/AC and V₂O₅/CNT to study the effect of SO₂ and H₂O at 250 °C. Their results indicated that a small amount of ammonium sulfate salts promotes the SCR activity. Although their catalysts are V₂O₅ supported on carbon materials, similar mechanism could also occur for Mn-based catalysts, and this may be due to that when the reaction temperature is higher than 250 °C only the E-R reaction pathway is dominant in the NH₃-SCR reaction [21,23,41]. Thus the SO₂ promotion phenomenon is attributed to the formation of SO₄²⁻ on the catalyst surface, which increases NH₃ adsorption and promotes NH₃ reaction with NO. On the other hand, Huang et al. [87] indicated that large amounts of ammonium sulfate salts deactivate the catalyst. And the deactivation may be attributed to the deposition of ammonium-sulfate salts such as NH₄HSO₄ and (NH₄)₂S₂O₇ on the catalyst surface, which blocks the pores of the catalyst.

In addition to the deposition of ammonium sulfates, the competitive adsorption between SO₂ and NO on the active sites of the catalysts also contributed to the poisoning effect of SO₂ on the SCR reaction. Jiang et al [91] used Fe-Mn/TiO₂ to carry out the in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) investigation for revealing the mechanism of the SO₂ effect on the SCR reaction. Their results showed that SO₂ could be adsorbed on the surface of the catalyst as the bidentate mononuclear sulfate. The sulfates would retard the formation of NO complex on the surface of catalyst, resulting in the decrease of NO adsorption. On the other hand for NH₃ adsorption, the adsorption of SO₂ had little effect on the coordinated NH₃, but would increase the amount of NH₄⁺

because of the formation of new Brønsted acid sites. Therefore, sulfate was formed on the catalyst, less NO could be adsorbed and thus the SCR efficiency could be decreased.

Moreover, it is well known that alkali metals in the fly ash have a serious deactivation effect on SCR catalysts [92-94]. Alkali metals also deposit on the surface of catalysts, and this not only reduces the surface area and pore volume of the catalysts but also reduces the surface chemisorbed oxygen and causes a decline in Brønsted acid sites [95]. Guo et al. [96] studied the poisoning effect of Na^+ and K^+ on the SCR performance of Mn/TiO₂ catalyst. They indicated that K^+ has a more serious deactivation effect on Mn/TiO₂ catalyst due to that it results in high crystallinity, weak surface acidity, low Mn⁴⁺ concentration, chemisorbed oxygen, and bad redox ability. Yu et al. [97] studied the deactivation and regeneration of selective catalytic reduction catalysts in a coal power plant. They indicated that decrease in specific surface area and acid site numbers should be the main reasons for the deactivation of an SCR catalyst. The formation of Al₂(SO₄)₃ was the main reason for the decrease in specific surface area and the deposit of K, Mg and Ca was mainly responsible for the decrease in acid site numbers.

3.4. Regeneration of catalysts

It seems to be unavoidable for the deactivation of low-temperature catalysts in the presence of SO₂. Therefore the regeneration of low temperature SCR catalysts is important for which to be economically used in the industry. There are only few studies on catalyst regeneration [20,25-29]. A summary on the reaction products of SO₂ poisoning and the catalyst regeneration methods are shown in Table 3.

Table 3. The reaction products of SO₂ poisoning and the methods of regeneration after SO₂ poisoning.

SO ₂ poisoning	Catalyst	Ref.
Products of SO ₂ poisoning	NH ₄ HSO ₄ and/or (NH ₄) ₂ S ₂ O ₇ [20]	[17,18,20,21,
	(NH ₄) ₂ SO ₄ and NH ₄ HSO ₄ [26]	24-29,49,
	(NH ₄) ₂ SO ₄ and NH ₄ HSO ₄ [27]	98-100]
	NH ₄ HSO ₄ and Ce ₂ (SO ₄) ₃ [21,24]	
	NH ₄ HSO ₄ , NH ₄ S ₂ O ₄ and (NH ₄) ₂ SO ₄ [98]	
	(NH ₄) ₂ SO ₄ , Ce ₂ (SO ₄) ₃ and MnSO ₄ [99]	
	Ti(SO ₄) ₂ , Mn(SO ₄) _x , and NH ₄ HSO ₄ [17]; CuSO ₄ [18]	
Regeneration methods	Heat treated 4 h in N ₂ at 400 °C [20]	
	Heat treated 2 h in N ₂ at 280 °C [25]	
	Heat treated 1 h in N ₂ /Ar at 400 °C [18]	
	Heat treated 2 h in N ₂ at 350 °C [28]	
	Heat treated 2 h in He at 350 °C [98]	
	Heat treated 1 h in air, N ₂ and Ar at 400 °C [29]	
	H ₂ and NH ₃ reduction [29]; Water washing [26,27,29,49]	
	Alkali washing, acid washing and acid-alkali combination washing [97]	

Jin et al. [26,27] found that SO_2 reacts with NH_3 to form $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 , which deposit on the catalyst surface. And they are the main reason for the irreversible deactivation of catalyst in SCR reaction. Jin et al. [26,27] showed that the salt could be washed away easily, and the SCR efficiency is reversible after washing regeneration. On the other hand, Huang et al. [20] and Tang et al. [25] used heat treatment to regenerate the catalysts after SO_2 poisoning at 280°C . They found that SCR activity recovers back to the initial level after removing H_2O and SO_2 gases. Sheng et al. [29] checked the effectiveness of water washing, thermal regeneration and reductive regeneration for recovering the catalytic activity of Mn-Ce/TiO_2 . They indicated that most of sulfate and nitrate species deposited on the deactivated catalyst can be removed by water washing. The catalytic activity could reach to fresh catalyst level by water washing with ultrasonic vibration.

Yu et al. [97] used alkali washing, acid washing and acid-alkali combination washing method to regenerate the catalysts. The results indicated that both the single acid and alkali solution regeneration presented inherent disadvantages; for instance, the active metal V was partly dissolved after HNO_3 washing, while the alkali solution had inferior contaminant removal efficiency. Meanwhile, the harmful alkali metal ions would deposit on the catalyst surface. And the acid-alkali combination treatment technique could overcome the drawbacks mentioned above, and it could partly remove the contaminants, minimize V dissolution and alkali metal deposition to form new acid sites. The results of Yu et al. [97] showed that acid-alkali combination treatment could remove the surface contaminants, increase the specific surface area and recover the acid sites of the used catalyst, and hence reactivate the catalytic performance to some degree.

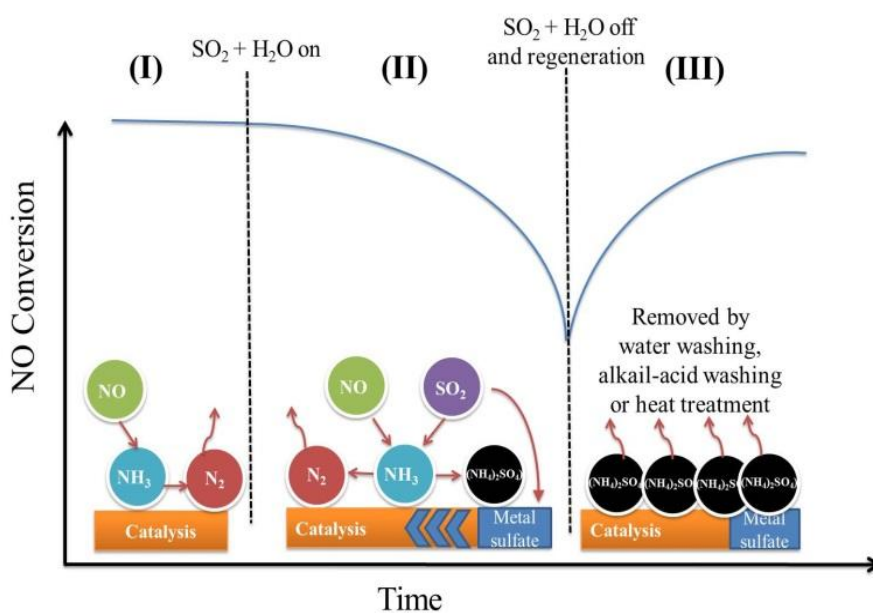


Figure 4. Scheme of SO_2 poisoning effect and the regeneration of catalysts.

According to literature information, we can sketch the SO_2 poisoning and catalyst reactivation by Figure 4. Before the introduction of SO_2 , the SCR can remain at high NO conversion as long as the catalysts and the operation conditions are appropriately selected (period I). But when SO_2 was

added (period II), SO₂ not only reacts with NH₃ to form (NH₄)₂SO₄ and NH₄HSO₄ but also reacts with the active metal and leads to the formation of metal sulfate. The ammonium salts and the metal sulfate salts can cause the decrease in NO conversion. The ideal low temperature SCR catalyst should have good SCR efficiency and better SO₂ resistance. Once the catalysts are poisoned, both water washing and heat treatment might be able to remove some salts, H₂O and SO₂ gases. And SCR activity could be recovered to the initial level after regeneration. Thus future design in the low-temperature SCR might need to include an online catalyst regeneration system.

4. Mn-based catalysts for low-temperature SCR

The goals of recent researches on low-temperature SCR catalysts are to develop catalysts which have good activity, high selectivity, high stability and broad range of operating temperature. Up to now, low temperature SCR catalysts which have been studied include the use of CeO₂, Fe₂O₃, and MnO_x as the active metals. Among them, the MnO_x catalyst has been studied extensively because of its excellent low temperature performance. The key factors affecting the performance of Mn-based catalysts are summarized in Table 4 and Table 5. In summary, the key factors for enhancing SCR efficiency and SO₂ resistance include (1) high specific surface area; (2) high surface acidity; (3) oxidation states of manganese; (4) well dispersion of manganese oxide metals; (5) more surface adsorbed oxygen. The Mn-based catalysts coupled with different supports and active metals for understanding their roles in the SCR process are discussed in details in the followings.

Table 4. Key factors which affect deNO_x performance of Mn-based catalysts with different supports.

Supports	Key factors for enhancing SCR efficiency and SO ₂ resistance	Ref.
Titanium supports	Provide higher surface area [81,115]	[14,15,56,
TiO ₂ and TNTs	Provide higher surface acidity [56,109]	61,72,81-83,
	Provide surface adsorbed oxygen [104]	98,99,
	Affect oxidation states of manganese [103,105,107,122]	103-105,107,
	Good dispersion of manganese oxides on the surface [61]	109,110,
Zeolite and SiO ₂ supports	Provide higher surface acidity [110,124]	114-116,
	Provide surface adsorbed oxygen [15]	121,122,124]
	Affect oxidation states of manganese [82,121]	
Aluminum supports (Al ₂ O ₃ , etc.)	Provide higher surface acidity [109,110]	
	Provide surface adsorbed oxygen [14]	
	Affect oxidation states of manganese [83]	
Carbon supports (AC, CNT, etc.)	Provide higher surface area [116]	
	Good dispersion of manganese oxides on the surface [98]	
Other metal oxide supports (CeO ₂ , ZrO ₂ , etc.)	Provide surface adsorbed oxygen [14]	
	Good dispersion of manganese oxides on the surface [72,99,114]	

4.1. Mn-based catalysts with different supports

Ammonia gas is mainly adsorbed on support of SCR catalyst in the form of ionic NH_4^+ and coordinated NH_3 . The reactive monodentate nitrate on active metal could react with two neighboring NH_4^+ on support to form intermediate species, which could further react with gaseous or weakly adsorbed NO to form N_2 [71,100]. Therefore, supports play important roles to provide the active site for NH_3 adsorption.

Mn-based catalysts with different supports, such as $\text{MnO}_x/\text{TiO}_2$ [66,101-107] [6-8], MnO_x/TNTs [108], $\text{MnO}_x/\text{Al}_2\text{O}_3$ [74,109,110], $\text{MnO}_x/\text{SiO}_2$ [20,111], MnO_x/CNT [98,112,113] and $\text{MnO}_x/\text{metal oxides}$ [14,99,114] have been reported in recent years. And the key factors affecting the performance of these catalysts which focused on the support effect are summarized in Table 4. The titanium supports, zeolite supports and aluminum supports can provide the higher surface acidity for Mn-based catalysts. Jin et al. [56] studied Mn-Ce metals supported on TiO_2 and Al_2O_3 for low-temperature SCR reaction in the absence of SO_2 . From the NH_3 -TPD result, they observed that NH_3 desorption amounts at the lower temperature range by MnCe/TiO_2 and $\text{MnCe}/\text{Al}_2\text{O}_3$ were 43 and $307 \mu\text{M}\cdot\text{g}^{-1}$, respectively. On the other hand, NH_3 desorption amounts at the higher temperature range by MnCe/TiO_2 and $\text{MnCe}/\text{Al}_2\text{O}_3$ were 122 and $109 \mu\text{M}\cdot\text{g}^{-1}$, respectively. Therefore, Jin et al. [56] indicated that TiO_2 and Al_2O_3 led to the formation of Lewis and Brønsted acid sites, respectively. In addition, Jin et al. [56] indicated that MnCe/TiO_2 was active at low temperature (80–150 °C), while $\text{MnCe}/\text{Al}_2\text{O}_3$ provided a relatively higher SCR activity than MnCe/TiO_2 at above 150 °C.

Pan et al. [109] used manganese-copper oxide supported on TiO_2 and Al_2O_3 for low-temperature SCR reaction in the presence of SO_2 . Their results also showed that TiO_2 is helpful for the formation of Lewis acid sites, while Al_2O_3 is favorable to the formation of Brønsted acid sites. And $\text{MnO}_x\text{-CuO}_x/\text{TiO}_2$ has a better NO conversion and SO_2 resistance than that of $\text{MnO}_x\text{-CuO}_x/\text{Al}_2\text{O}_3$. Pan et al. [109] indicated that good SO_2 resistance performance of $\text{MnO}_x\text{-CuO}_x/\text{TiO}_2$ may be resulted from its large surface area and high redox ability at low temperature. Panahi et al. [110] used different metals (Mn, Fe, Co and Cu) and supports (Al_2O_3 , ZSM5 and SAPO-34) for NH_3 -SCR reaction. And they used artificial neural network for modeling the relationship between catalyst composition and catalytic performance. Their results revealed that electro-negativity and ionization energy as transition metal descriptors had the largest significance on catalyst performance and acidic property is the most effective one among the support descriptors.

High surface area of the support is also an important factor for enhancing the NO conversion. As shown in Table 4, both the titanium supports and carbon supports provide higher surface areas for Mn-based catalysts. And researchers indicated that higher specific surface area could provide more active sites to enhance SCR efficiency and inhibit SO_2 poisoning [74,105,106,115-117]. Su et al. [115] added graphene oxide (GO) into Mn- TiO_2 catalyst for low-temperature SCR in the presence of SO_2 . The results showed that adding graphene oxide increased the specific surface area and transfer capability of electrons on the surface. Therefore, Mn/ TiO_2 -GO had better catalytic activity and SO_2 resistance than that of Mn/ TiO_2 .

Fan et al. [116] prepared Mn-Ce- O_x catalysts loaded on TiO_2 , TiO_2 -AC and TiO_2 -CNTs. They found that the BET surface areas increased markedly with the addition of carbonaceous material and

they were measured to be 154, 195, and 218 m²/g for Mn-Ce/Ti, Mn-Ce/Ti-AC and Mn-Ce/Ti-CNTs, respectively. The results showed that SCR efficiency of more than 90% was obtained over the Mn-Ce-O_x/TiO₂-CNTs catalyst at the temperature window of 75–225 °C. Fan et al. [116] indicated that the promoted activity of Mn-Ce-O_x/TiO₂-CNTs catalyst at low-temperatures could be attributed to the increase of the BET surface area, and the occurrence of reaction between adsorbed NO_x and NH₃. Yao et al. [81] used MnO_x/TiO₂ and MnO_x/TNT for the low-temperature selective catalytic reduction of NO. Their BET results showed that surface area of MnO_x/TNT was significantly increased, which reached 200 m²/g, more than three times of MnO_x/TiO₂. And the NO removal rate of MnO_x/TiNT reached 59.2% at 80 °C and 98.2% at 150 °C, which was four times higher than MnO_x/TiO₂.

Pappas et al. [61] used manganese confined to different TiO₂ and TNTs supports for the low-temperature selective catalytic reduction of NO. Pappas et al. [61] found that the titania nanotubes possessed different morphological features such as specific surface area, length and diameter due to the different characteristics of TiO₂ nanoparticles used for their synthesis. Among all the prepared samples, the Mn/TNT-Hombikat catalyst demonstrated remarkable deNO_x performance and a wide temperature window in the temperature range of 100–300 °C. Pappas et al. [61] indicated that the activity of the manganese confined titania nanotube catalysts was attributed to the high surface area of the support. On the other hand, they also indicated that Mn/Ti ratio of the catalytic formulations impacted the low temperature deNO_x potential of the catalysts.

In addition, various MnO_x states played diverse roles in the low-temperature SCR reaction [48,102,118-120]. Manganese oxides attract interest as catalysts since they contain various types of labile oxygen and oxidation states of manganese (Mn²⁺, Mn³⁺ and Mn⁴⁺). Fang et al. [118] indicated that NH₃ adsorption on the MnO_x surfaces plays a significant role in the mechanism of SCR with NH₃. The NH₃-TPD results showed that Mn₂O₃ and Mn₃O₄ had higher NH₃ adsorption capability, while Mn₂O₃ and Mn₃O₄ exhibited higher activity for NO conversion as compared to that of MnO₂. Fang et al. [118] indicated that catalysts calcined in nitrogen are beneficial to NH₃-SCR, which was because low valence MnO_x oxides such as Mn₂O₃ and Mn₃O₄ tended to be formed.

There are some research works indicating that supports would affect the oxidation states of manganese [3,66,83,104,121,122]. As shown in Table 4, the titanium supports, zeolite supports and aluminum supports can affect the oxidation states of manganese for Mn-based catalysts. Qu et al. [83] used Zr, Ti and Si combined with Al as supports for Mn-Ce catalysts. The result showed that MnO_x-CeO_y/Al₂O₃-ZrO₂ has a bigger specific surface area, more amorphous states of Mn₂O₃ and coexisting Ce³⁺/Ce⁴⁺, which leads to the good performance in the low temperature SCR and SO₂ resistance. Boningari et al. [121] used Mn/TiO₂ and Mn/TiO₂-SiO₂ catalysts to study the correlation of surface properties and key components to the activity of NO_x reduction. The XPS results showed that the relative atomic percentage value of Mn⁴⁺/Mn³⁺ was significantly high for the Mn/TiO₂ as compared to Mn/TiO₂-SiO₂ catalysts. Boningari et al. [121] indicated that the catalyst had a higher SCR efficiency which was due to their higher Mn⁴⁺/Mn³⁺ ratio. Boningari et al. [104] prepared Mn-Ce catalysts over different types of TiO₂ supports. The results showed that the promoted or isolated Mn⁴⁺ and Ce³⁺ species located over the surface of TiO₂ are responsible for the high deNO_x efficiency.

Shen et al. [14] compared various supported MnO_x catalysts including Al₂O₃, TiO₂, CeO₂, ZrO₂ and Ce_{0.5}Zr_{0.5}O₂ for the low-temperature SCR of NO_x with ammonia in the presence of SO₂. The

results showed that the resistance ability to sulfur poisoning was as follow: $\text{MnO}_x/\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2 > \text{MnO}_x/\text{Al}_2\text{O}_3 > \text{MnO}_x/\text{CeO}_2 > \text{MnO}_x/\text{TiO}_2 > \text{MnO}_x/\text{ZrO}_2$. In addition, the NO conversion of $\text{MnO}_x/\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ nearly recovered when SO_2 was removed. Shen et al. [14] found that the ZrO_2 provided higher surface acidity and BET specific surface area. On the other hand, CeO_2 enhanced the $\text{Mn}^{4+}/\text{Mn}^{3+}$ ratio and adsorb oxygen species on the surface. Therefore, the combination of the advantages of the two supports (i.e., ZrO_2 and CeO_2) enhanced the SCR activity and inhibited SO_2 poisoning of $\text{MnO}_x/\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$.

The surface adsorbed oxygen is one of the important factors for enhancing SCR efficiency and SO_2 resistance. As shown in Table 4, the titanium support, zeolite support and metal oxide supports provided surface adsorbed oxygen for Mn-based catalysts. Boningari et al. [104] prepared Ce over Mn/TiO_2 NH_3 -SCR catalysts with different active titania carriers for low temperature SCR. They compared four different titanium supports including N1, N2, N3, and Hk, which had surface areas of $620 \text{ m}^2/\text{g}$, $457 \text{ m}^2/\text{g}$, $398 \text{ m}^2/\text{g}$, $309 \text{ m}^2/\text{g}$, respectively. Boningari et al. [104] indicated that the existence of high $\text{O}_\alpha/(\text{O}_\alpha + \text{O}_\beta)$ ratio was beneficial for the NO oxidation to NO_2 in the SCR of NO_x reaction in order to boost the low-temperature activity. From the XPS results, the $\text{O}_\alpha/(\text{O}_\alpha + \text{O}_\beta)$ ratio of $\text{Mn-Ce}/\text{TiO}_2$ (Hk) catalyst calculated from de-convoluted O1s XPS spectrum was significantly higher than those of other catalysts. And this was a reason for high deNO_x efficiency of $\text{Mn-Ce}/\text{TiO}_2$ (Hk) at low temperatures.

For increasing dispersion of manganese oxides [15,72,99,107,123], the TNTs support, CNT support and metal oxide supports can help to do the job as seen in Table 4. Shen et al. [99] employed Mn/CeO_2 , Mn/ZrO_2 and $\text{Mn}/\text{Ce-ZrO}_2$ for low-temperature SCR reaction in the presence of SO_2 . The Scherrer Formula was used to calculate the grain size of Mn_2O_3 in Mn/ZrO_2 , Mn/CeO_2 and $\text{Mn}/\text{Ce-ZrO}_2$, and the results were 305, 212 and 180 \AA , respectively. This suggested that $\text{Mn}/\text{Ce-ZrO}_2$ had the best dispersion of manganese. Shen et al. [99] indicated that $\text{Mn}/\text{Ce-ZrO}_2$ and Mn/CeO_2 had better SCR efficiency and SO_2 resistance due to the higher dispersion of manganese oxides, better redox characteristic and more surface adsorbed oxygen. Lee et al. [72] supported manganese oxides on CeO_2 and found that when using a 4% CeO_2 catalyst support, Mn dispersion could be controlled, NH_3 adsorption could be increased as a result of Mn dispersion control, and excellent catalytic activity in the SCR reaction could be obtained. Lee et al. [72] indicated that $\text{Mn}(20)/\text{Ce}(4)\text{-TiO}_2$ catalyst exhibited the highest catalytic activity in this reaction. The high catalytic activity of the $\text{Mn}(20)/\text{Ce}(4)\text{-TiO}_2$ catalyst was mainly attributed to the large Mn^{4+} dispersion on the surface due to the TiO_2 pore being partially occluded by CeO_2 , which prevented Mn oxides from entering the bulk TiO_2 .

From Table 4 one can conclude that the titanium supports is a good support of Mn-based catalyst as they have all major characteristics for enhancing the low temperature SCR performance. On the other hand, zeolite and aluminum supports can provide higher surface acidity, surface adsorbed oxygen and affect oxidation states of manganese. And the carbon supports usually can provide higher surface area and enhance dispersion of manganese oxides on the surface. And the metal oxide supports usually can provide higher surface adsorbed oxygen and enhance dispersion of manganese oxides on the surface.

4.2. Mn-based catalysts with different metals

Addition or doping other metal oxides such as Ce [17,26,28,64,72,80,125], Fe [41,57,79,123,126], Ni [127], Cu [128] and Li [129] on the Mn-based catalyst is the main way to enhance its activity and stability. Ceria (CeO_2) has been studied extensively as the co-doping metal of Mn-based catalysts because it has many good characteristics as listed in Table 5. The advantages of ceria include that it provides (1) more absorbed NO_3^- on the catalyst surface; (2) easier decomposition of ammonium sulfates; (3) high surface acidity; (4) high surface area; (5) surface adsorbed oxygen (6) well dispersion of manganese oxides; and it also affects (7) the oxidation states of manganese.

Table 5. Key factors which affect deNO_x performance of Mn-based catalysts doping with other metals.

Doping metal	Key factors for enhancing SCR efficiency and SO ₂ resistance	Ref.
Ce	Provide more absorbed NO_3^- on the catalyst surface [28,125] Reduce the binding energy between the NH_4^+ and sulfate ions, which may result in the easier decomposition of ammonium sulfates. [17,26] Good dispersion of manganese oxides on the surface [72,80] Provide surface acidity[26,64] Provide surface adsorbed oxygen [5,130] Provide higher surface area [22,28,117]	[5,17,22,26,28,41,57,62,64,68,72,79,80,117,123,125,126,128-130,133-136]
Fe	Good dispersion of manganese oxides on the surface [57,79,123,126] Provide surface acidity [41] Provide surface adsorbed oxygen[62]	
Ca, Mo, Zr, Cr and La	Good dispersion of manganese oxides on the surface[123,126,133,134]	
Ni and W	Affect oxidation states of manganese[68,135]	
Cu	Decrease the reduction temperature of manganese oxides[128]	
Y and Li	Provide surface adsorbed oxygen [129,136]	

Wang et al. [28,125] added CeO_x to MnO_x/ACH for low-temperature SCR of NO with NH_3 . The results showed that the selectivity to N_2 on MnO_x/ACH (Activated Carbon Honeycomb) was increased by the addition of CeO_2 . Wang et al. [28,125] indicated that the distribution of manganese and cerium oxide on ACH was improved by the addition of CeO_2 , which was because there were strong interactions between these two metal oxides. In addition, adding CeO_x enhanced SCR activity due to it promoted NO oxidation and provided more absorbed NO_3^- on the catalyst surface.

Jin et al. [17,26] used Ce-doped Mn/TiO_2 catalyst for low-temperature SCR in the presence of SO_2 . The results showed that doping of Ce reduced the binding energy between the NH_4^+ and sulfate ions, which might result in the easier decomposition of ammonium sulfates. Therefore, surface sulfates were preferentially formed on Ce metal and less sulfation of the MnO_x active phase was

expected, which caused some portion of the Lewis acid sites on MnO_x was preserved to fulfill the low-temperature SCR cycle. Shen et al. [80] modified cerium to the $\text{MnO}_x/\text{TiO}_2$ -PILC catalysts and showed high activity for the low temperature SCR of NO with NH_3 . Shen et al. [80] found that doped cerium on Mn-based catalyst resulted in a good dispersion of manganese oxides on the surface of the catalysts and provided more Lewis acid sites. Therefore, addition of cerium improved SCR efficiency and SO_2 resistance.

Moreover, ceria provided the surface characteristics including surface acidity, surface area and surface adsorb oxygen. Qiu et al. [64] used in situ IR to study Ce and Co doped Mn/TiO_2 catalyst for low-temperature SCR of NO with NH_3 . The FTIR results suggested that the addition of cobalt and cerium oxides increased the amounts of acid sites and redox sites. And cobalt oxide yielded lots of Brønsted acid sites, which favored the adsorption of coordinated ammonia. On the other hand, cerium oxide possessed strong redox abilities, leading to the increase of NH_2^- species and NO adsorption. Both Co and Ce doped Mn/TiO_2 catalysts enhanced the SCR efficiency below 200 °C. Li et al. [5] used cerium-manganese oxides supported on modified glass-fiber with different Ce/Mn molar ratios for low-temperature SCR (80–180 °C) of NO with ammonia. From the BET and XPS result, Li et al. [5] found that Ce-Mn/GF (0.2) had the highest surface area and surface oxygen (O_β). Therefore, the Ce-Mn/GF(0.2) catalyst showed high activity that over 87% NO conversion was obtained at 150 °C under a space velocity of 50,000 h^{-1} . Wu et al. [130] employed cerium modified $\text{MnO}_x/\text{TiO}_2$ catalysts for low-temperature SCR of NO_x with ammonia. They found that when increasing the molar ratio of Ce to Ti, the surface area and surface oxygen were increased. In the case of $\text{Ce}_{(0.07)}\text{MnTi}$, the BET surface area and pore volume were 50% greater than those of $\text{Ce}_{(0)}\text{MnTi}$. The XPS results indicated that the chemisorbed oxygen concentration on catalyst surface could doubly increase with the introduction of Ce. And the NH_3 -TPD results showed that Ce modified $\text{MnO}_x/\text{TiO}_2$ provided a better NH_3 chemisorption ability and resulted in the improvement of SCR activity.

Iron is also a good doping metal for Mn-based catalysts. As seen in Table 5, the advantages of iron include that it provides well dispersion of manganese oxides, high surface acidity, and more surface adsorbed oxygen. Although the Fe-based catalyst was only active in 350–550 °C [62]. But iron had the strong interaction between manganese and iron species in $\text{Mn-Fe}/\text{TiO}_2$ catalysts, leading to the formation of manganese-iron composite oxides which was in amorphous phase. And those amorphous structures could increase the surface adsorbed oxygen, facilitate the oxygen mobility and enhance the oxidation-reduction ability over catalysts, all of which are crucial factors for the increase of NO oxidation activity [131]. And Liu et al. [131] also found that the introduction of iron to manganese oxides reduced the adsorption of the gas phase water and the formation of sulfates on catalysts surface, and then improved the water and sulfur resistance. Shen et al. [79,132] showed iron-doped $\text{Mn-Ce}/\text{TiO}_2$ had a high SCR efficiency, it also inhibited SO_2 poisoning at low temperature. Shen et al. [79,132] found that the NO conversion over $\text{Fe-Mn-Ce}/\text{TiO}_2$ was obviously improved after iron doping as compared with that over $\text{Mn-Ce}/\text{TiO}_2$. The $\text{Fe-Mn-Ce}/\text{TiO}_2$ catalyst with molar ratio of $\text{Fe}/\text{Ti} = 0.1$ exhibited the highest activity. And the highest activity was due to the increase of specific surface area, NH_3 adsorption capacity, well dispersion of active metals as well as the increased surface oxide (O_a) of the catalysts.

In addition to the cerium and iron doping, the Mn-based catalyst for low-temperature SCR of NO has also been significantly improved after modifying with other metal elements such as Cu, Ni,

Cr, W, Y and Li, etc. As can be observed in Table 5, there could be different reasons for enhancing the SCR efficiency and SO₂ resistance by different metals. The Ca, Mo, Zr, Cr and La metal could enhance dispersion of manganese oxides on the surface. Zhou et al. [126,133] studied on effects of doping different transition metals (Mo, Zr, Cr) in the Mn-Fe catalysts. their results suggested that the addition of Cr significantly improved the low temperature activity of Mn-Fe catalyst, which was due to the better dispersion of active components and less agglomeration and sintering as well as the largest BET surface specific area. In addition to Cr doping, Gu et al. [134] and Zhao et al. [123] also indicated that Ca and La doped on Mn-based catalyst could enhance SCR efficiency. They attributed this to better dispersion of MnO_x.

On the other hand, the Ni and W metal could affect the oxidation states of manganese. Thirupathi et al. [135] employed nickel metal doped on Mn/TiO₂ for the low-temperature SCR of NO with NH₃. The XPS results revealed that MnO₂ was the dominant phase with respect to the Mn₂O₃ phase ($Mn^{4+}/Mn^{3+} = 22.31, 96\%$), thus leading to a large number of Mn⁴⁺ species (Mn⁴⁺/Ti) over the titania support for the Mn–Ni(0.4)/TiO₂ catalyst. The TPR data also showed that the addition of nickel oxide to titania supported manganese resulted in the stabilization of the former in the form of MnO₂ rather than Mn₂O₃. Thirupathi et al. [135] indicated that an increase in reducibility and the extremely dominant MnO₂ phase seemed to be the reason for the high SCR activity of the Mn–Ni/TiO₂ catalysts.

Doping the Cu metal could further decrease the reduction temperature of manganese oxides. Fang et al. [128] used Cu–Mn oxide for the selective catalytic reduction of NO_x with NH₃ at low temperatures. The TPR, XPS and in situ DRIFT results showed that CuMn₂O₄ was responsible for low reduction temperature, strong interaction between manganese oxides and copper oxides, high Mn³⁺ content and numerous acid sites on the surface.

Moreover, the Y and Li metal provided the surface active oxygen of the Mn-based catalysts. Kong et al. [129] modified Li to MnO₂ catalyst for low-temperature SCR in the presence of SO₂. The result showed that the introduction of lithium adjusted the surface acid sites and surface active oxygen of the MnO₂, which improved its NH₃-SCR reaction performance. Zhang et al. [136] used Y-doped TiO₂-supported MnO_x for low-temperature SCR reaction. The XPS results indicated that the superficial O_α concentration of MnTiY was higher than that of MnTi. Zhang et al. [136] showed that Y doping might have better activity for the NO oxidation and it may be due to the increase of oxygen vacancies.

5. Conclusions and future perspectives

In this study we have reviewed the current status of using Mn-based catalysts for low temperature NH₃-SCR. Reaction mechanisms and effects of operating factors were addressed, and the SCR efficiencies of Mn-based metal oxides with and without SO₂ poisoning have also been discussed under different supports and co-doping metals. From the review of reaction mechanisms for low-temperature SCR, it is concluded that the key factors for enhancing SCR efficiency and SO₂ resistance include (1) high specific surface area; (2) high surface acidity; (3) oxidation states of manganese; (4) well dispersion of manganese oxide metals; (5) more surface adsorbed oxygen. (6) more absorbed NO₃⁻ on the catalyst surface; (7) easier decomposition of ammonium sulfates. A good support could provide the first five key factors and help to enhance the SCR performance, while a

good co-doping metal could provide all of the seven characteristics for increasing the NO_x conversion efficiency. However, SO₂ and H₂O poisonings seem to be an unavoidable problem under low temperature SCR, but the poisoned catalysts can be recovered by water washing, acid and/or alkali washing and heat treatment.

For the future research, it is suggested that appropriate supports and metals which have higher deNO_x efficiency, higher N₂ selectivity, wide temperature window and higher SO₂ resistance can be further investigated. One of the challenges for designing new SCR catalysts is to further increase the activity of low temperature SCR catalyst in the broad and low temperature range of 60~400 °C for extensive applications to the fields at high space velocity. The active metals for low temperature NH₃-SCR have already received significant attention, with consistent conclusion that Mn-based catalysts are the most active components for NH₃-SCR at the temperature range of 100~300 °C. However, the supports also play important roles but received less attention than the active metals. The major characteristics of good supports are: (1) to provide high acidity and high surface area for enhancing catalytic reaction; (2) to have high thermal stability and chemical stability; (3) to prevent from the formation of big crystalline and sulfate species. Furthermore, it seems to be unavoidable for the deactivation of low-temperature catalysts in the presence of SO₂. Therefore the regeneration of low temperature SCR catalysts is important. And a novel design of the low-temperature SCR system which includes an online catalyst regeneration device or a new device that can simultaneously remove the SO₂/NO_x might help to facilitate the application of low temperature SCR to the industry.

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Conflict of interest

The authors declare there is no conflict of interest.

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