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MINIREVIEW

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A review on selective catalytic reduction of NO_x by supported catalysts at 100–300 $^{\circ}$ C—catalysts, mechanism, kinetics

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Removing NO_x by supported catalysts is important for industrial flue gases and exhaust fumes of diesel engines at low temperature (100–300 °C). However, it is still a challenge to develop the low-temperature catalyst (LTC) for selective catalytic reduction of NO_x, especially at temperatures below 200 °C. This paper reviews the effect of the different carriers with different active centres. Most supported metal oxide catalysts are prepared by impregnation method. But under the same condition, catalysts perform better if they were prepared by sol–gel method. Also, this paper described and compared the research progress of reaction mechanism and kinetics of the supported catalysts which were used for the selective catalytic reduction of NO_x at low temperature. There are different mechanisms because of the different reducing agents and active centres. The L–H and E–R mechanisms, or both of them coexisting, can explain the overall mechanism. In order to research the mechanism thoroughly, the exploration of the reactions of the surface chemical process may be a direction to develop low temperature supported catalysts for removing NO_x.

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1 Introduction

Nitrogen oxides (NO_x, x = 1, 2) are the major causes of photochemical smog, acid rain, ozone depletion and the greenhouse effect.¹⁻⁴ NO_x emits into the atmosphere from natural sources and anthropogenic sources. Furthermore, the combustion of coal and fossil fuels is the primary source of anthropogenic NO_x emissions. In China, 24 043 000 tons of NO_x had been emitted in 2011, which increased by 5.73%

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compared to that of 2010 (the state of environment situation bulletin in 2011). It is estimated that China's coal resources are to be 5570 billion tons with 1018 billion tons of proven reserves and 4552 billion tons of forecasted reserves, and the production of coal in 2008 ranked first in the world with 42.5% of the world's total.^{5,6} The NO_x emissions are mainly from power stations, cogeneration plants, industrial heaters, and the exhaust gas of gasoline and diesel engines.^{3,7,8} Therefore, it is necessary to develop advanced technology and seek for better catalysts to control NO_x emissions.

As for the obvious harm of NO_x , it is known from legislations and policies that reducing the emission of NO_x is getting more and more strict. For example, the NO_x emission



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limits are 100 mg m⁻³ for most power plants (GB13223-2011) and 150 mg m⁻³ for gas, oil, and coal-fired industrial boilers (DB11139-2007) in the capital of China, Beijing.

In order to adapt to the stringent regulations, new technologies emerged to displace the old technologies. A number of NO_x control technologies in thermal power plants and industry furnaces had been taken, including combustion control and post-combustion control technologies. Combustion controls can reduce NO_x emission by altering or modifying the combustion conditions during the combustion process by means of low NO_x burners, fuel reburning and flue gas recirculation (FGR). Post-combustion controls mean the selective reduction of NO_x to N_2 . Three major post-combustion processes are available: selective catalytic reduction (SCR), selective non-catalytic reduction (SNCR), and hybrid SNCR-SCR technologies.9-13 The major products of post-combustion processes are harmless nitrogen and water vapour. Post-combustion technologies were first applied in Japan in the 1970's and have now been installed in the US and several European countries.¹⁴ SCR, which utilizes NH₃ as the reducing agent and heterogeneous reaction of NO on a catalyst, can achieve over 95% of the conversion. For practical implementation of SCR of NOx from coal-fired combustion sources, NH₃ slip ranged from 2 to 5 Vppm.⁵ These technologies are currently experiencing unprecedented growth and development in China. Nowadays, the catalyst of TiO₂-supported V₂O₅, promoted with WO₃, is the main catalyst for SCR in industry.¹⁵ However, there are some problems with it; the catalyst should be installed upstream of the particulate collector and flue gas desulfurization and it has only a narrow and high working temperature window (300-400 °C)¹⁵⁻¹⁷ to ensure a high conversion of NO_x, otherwise the effect of particles and sulfur can lead to deactivation and poisoning.8

There are two methods to solve these problems. One is to install the catalyst downstream of the particulate collector and flue gas desulfurization, which requires an additional heat source to heat the catalyst, and that will make the cost increase significantly. The second one is to develop new low temperature catalysts that can work well around 250 $^{\circ}$ C or even lower.



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Long Qu

Up to now, researchers have studied single metal oxide catalysts. Such as the many SCR catalysts containing a transitional metal (Fe, V, Cr, Cu, Co and Mn), which have good low temperature SCR activity, and the nano-MnO_x catalyst that has excellent temperature performance.^{1,18,19} Multi-metal oxide catalysts were also studied. For example, synergetic catalysis of ceria and titania,²⁰ Fe–Ti spinel for the selective catalytic reduction of NO,²¹ and binary metal oxide solid solutions might be formed between Mn and Cu or Ce, *etc.*^{3,8,22–24} Al₂O₃, TiO₂, zeolites, ACF as the main support and metal oxides supported on carbon materials and zeolite catalysts have also been researched.^{25–30}

Some works have been done in researching the low temperature selective catalytic reduction of NO_x in our team.^{25,28,31–37} In this paper, we review the catalysts which were prepared by different carriers, and the performance of the catalysts at low temperature. The developed mechanism and kinetics have also been discussed. It will be useful for future research.

2 Catalysts

Up to now, low temperature catalysts (LTC) have been studied without carriers or using ACF, Al₂O₃, TiO₂, zeolites and SAPO as the carriers. Taking into consideration the influence of components and environmental temperature on the formation of (NH)₂SO₄, NH₄NO₃, N₂O and other by-products in flue gas, the main goal of these studies is to develop new SCR catalysts with high selectivity and stability, good activity and a broad operating temperature range, which make it possible to place the SCR reactor downstream of the electrostatic precipitator and desulfurizer. However, since most of the catalysts were just researched in the lab, more studies into practical application are needed.

2.1 Catalysts without carriers

According to the literature, many catalysts have been studied to remove NO_x . Some catalysts without carriers have been

researched.^{38–42} It showed that the Mn–Ce mixed-oxide catalyst had the best performance. Gongshin Qi and Ralph T. Yang,^{3,43} researched the performance and mechanism of the MnO_x–CeO₂ catalyst, and indicated that the best Mn–Ce mixed-oxide catalyst yielded nearly 100% NO conversion at 120 °C at a high space velocity of 42 000 h⁻¹. Based on the past investigation, the authors indicated that there may exist a synergistic mechanism between the manganese and cerium oxides by the following chain of reactions:

$$2MnO_2 \rightarrow Mn_2O_3 + O \tag{1}$$

$$Mn_2O_3 + 2CeO_2 \rightarrow 2MnO_2 + Ce_2O_3$$
 (2)

$$Ce_2O_3 + 12O_2 \rightarrow 2CeO_2 \tag{3}$$

The SCR reaction of NO by NH_3 on the MnO_x -CeO₂ catalyst most probably takes place according to the following steps.

$$O_2(g) \rightarrow 2O$$
 (4)

$$NH_3(g) \rightarrow NH_3(a)$$
 (5)

$$NH_3(a) + O(a) \rightarrow NH_2(a) + OH(a)$$
(6)

$$NO(g) + 1/2O_2(g) \rightarrow NO_2(a) \tag{7}$$

$$NH_2(a) + NO(g) \rightarrow NH_2NO(a) \rightarrow N_2(g) + H_2O(g)$$
 (8)

$$OH(a) + NO_2(a) \rightarrow O(a) + HNO_2(a)$$
 (9)

$$\begin{aligned} \mathrm{NH}_3(\mathbf{a}) + \mathrm{HNO}_2(\mathbf{a}) &\to \mathrm{NH}_4\mathrm{NO}_2(\mathbf{a}) \to \mathrm{NH}_2\mathrm{NO}(\mathbf{a}) \\ &+ \mathrm{H}_2\mathrm{O} \to \mathrm{N}_2(\mathrm{g}) + 2\mathrm{H}_2\mathrm{O}(\mathrm{g}) \end{aligned} \tag{10}$$

The meaning of (g) and (a) are gaseous and adsorbed state, respectively.

The effect of different dopants including tin, niobium, iron, tungsten and zirconium oxide of MnO_x -CeO₂ catalysts for SCR has been studied.^{44,45} Although these catalysts can improve NO_x reduction, the high cost and difficulty in forming a fixed shape limited their commercial applicability. In order to solve this problem, more research should be done in modifying the catalysts.

2.2 ACF as the carrier

Active carbon fiber (ACF) is widely utilized in water purification and air purification and separation as a superior adsorbent because of its large number of well distributed micropores, high adsorption speed and high surface area $(1000-2000 \text{ m}^2 \text{ g}^{-1})$.^{46,47} As listed in Table 1, coal-tar pitchbased ACF has over 10 times the physical surface area compared to GAC. Some researchers have studied the NO conversions by ACF in the last few decades. Mochida et al.48 reported that the heat treatment of pitch-based activated carbon fibres of moderate surface area markedly increased the conversion of NO to 87% in dry air, 62% in air of 80% relative humidity and 24% in wet air (100% r.h.) at 25 °C and a ratio of fibre mass to gas flow rate of 1.0×10^{-2} g min mL⁻¹. Sudhakar Adapa et al.49 studied the surface characteristics of ACFs synthesized from raw carbonaceous non-activated fibers under varying activation conditions, and analyzed the adsorptive and catalytic properties of ACF for the control of NO only. They indicated that the extent of conversion depended upon the reaction temperature, inlet O2 and NO concentrations, the types and the preparation methods of ACF. They also showed the phenolic resin-based ACF was more effective in the oxidation of NO in comparison to the pitch and viscose rayon-based ACFs.

ACF as the carrier has been generally researched in the laboratory. The large physical surface area can make metal-oxides highly dispersed on ACF during the preparation process of the catalyst. Masaaki Yoshikawa⁴⁶ researched the three transition-metals, Fe₂O₃, Co₂O₃ and Mn₂O₃, as catalytic components. The result showed that Mn₂O₃ had the best activity, and CeO₂,^{27,33} V₂O₅,⁵⁰ Ni⁵¹ have also been researched. It was indicated that Mn and Ce had the best effects as the active component in ACF. Maybe low temperature SCR of NO based on MnO_x–CeO₂/ACF, or MnO_x–CuO–CeO₂/ACF and so on can be investigated to achieve higher selectivity and stability, and better activity at low temperature.

2.3 Metal oxide as the carrier

2.3.1 Al_2O_3 as the carrier. Al_2O_3 as an atomic crystal, owns high temperature resistance, withstands wear and tear, is easy to form into a fixed shape, and has a surface area below 200 m² g⁻¹, so it has attracted some researchers' attention. The performance of removing NO_x with the metal oxides and preparation of the catalysts by different methods have been studied. Some research showed a similar reaction mechanism by promoted and unpromoted catalysts, and the sol-gel method can produce the most active catalysts.

A series of Pt/Al₂O₃ catalysts promoted by metal oxides (Ba, Ce, Co, Cs, Cu, K, La, Mg, Mo, Ti) or noble metals (Ag, Au, Pd, Rh) was prepared and tested for the lean NO_x reaction using C₃H₆ as the reductant. There was a significant effect (beneficial or otherwise) on the activity and the operation temperature range of Pt/Al₂O₃ (Fig. 1), but a major shortcoming was their high selectivity towards N₂O, a currently unregulated but very undesirable oxide of nitrogen.⁵² Zhang et al.⁵³ tested the catalyst of MnO_x/CeO₂-ZrO₂-Al₂O₃(MnO_x/ CZA), almost 90% NO was transformed to N₂ in the temperature range of 143-300 °C. Erol Seker⁵⁴ prepared alumina supported silver catalysts by co-precipitation, impregnation and single step sol-gel methods, to study the selective NO_x reduction by propene in the presence of oxygen. The catalysts prepared by sol-gel method had the highest activation for selective reduction of NOx, with almost 100%

Table 1 Properties of examined supports⁴⁶

Material	BET surface area $(m^2 g^{-1})$	Pore volume (ml g^{-1})	Size	Physical surface area $(m^2 g^{-1})$
ACF	740	0.342	$D_1 = 20 \ \mu \text{m}^b$ $L = \text{over 50 } \text{mm}^d$	0.5-1
GAC^{a}	831	0.414	$D_2 = 1 \text{ mm}^c$	0.01-0.03

^a GAC: granular active carbons. ^b D₁: diameter of active carbon fibers. ^c D₂: diameter of particles. ^d L: length of active carbon fibers.



Fig. 1 The effect of metal oxide promoters on NO_x conversion over Pt/Al₂O₃ based catalysts. (a): ◆ No promoter, \circ Ce, * Co, \Box Cs, \bullet Mo, \blacksquare Ti; (b) ◆ No promoter, \diamond Ba, \blacktriangle Cu, \times K, + La, \triangle Mg.⁵²

selectivity to N₂. R. Lanza⁵⁵ researched three catalysts (Pt, Rh and Ag on alumina). The Pt/Al₂O₃ and Rh/Al₂O₃ were active at low temperature ($T_{50} = 200-250$ °C) but had quite high selectivity towards NO₂. Meanwhile, Ag/Al₂O₃ was active at higher temperature, but it showed very high selectivity towards N₂. A strong boosting effect on NO conversion was recorded if H₂ was added to the gas mixture. Derek Creaser⁵⁶ showed that feed concentrations of NO and hydrogen had significant effects on the NO_x conversion, indicating that nitrates poisoned the catalytic sites and hydrogen's role was to reduce nitrate species over the Ag–Al₂O₃ catalyst.

2.3.2 TiO₂ as the carrier. Titania has stable physical and chemical properties, it is not a poison and its surface area is under 100 m² g⁻¹.⁵⁷ V₂O₅-WO₃/TiO₂ is the most prevalent commercial catalyst, exhibiting high activity, but it is active only in a narrow temperature window of 300-400 °C.^{58,59} Maybe this shortcoming can be made up for by modifying the carriers and catalysts.

Ruihua Gao *et al.*⁶⁰ modified the V_2O_5 -WO₃/TiO₂ catalysts by iron oxides, and these combination metal oxide catalysts

show not only high catalytic activities but also good resistance to SO₂. According to other research, the catalysts of Mn and Ce oxide supported on TiO2 had better performance for removing NO_r. Wu *et al.*⁶¹ prepared the catalyst of MnO_r/TiO₂ by sol-gel method. Under the optimal conditions, the efficiency of NO removal could exceed 90% at a temperature of 150 °C. It was found that the transition metal had significant effects on the catalytic activity. The temperature could be reduced to 88 °C by using Fe(0.1)-Mn(0.4)/TiO₂⁶² to achieve 90% NO conversion. At the same time, a series of cerium modified MnO_x/TiO₂ catalysts revealed that NO conversion could be improved from 39% to 84% at 80 °C.63 Jin Ruiben et al.64 prepared the catalyst of Mn-Ce/TiO₂ by sol-gel method with NH_3 as the reducing agent, removing NO_x by SCR at different temperatures (100-200 °C). This suggested that the unrecoverable SO₂ deactivation can be greatly retarded if the lowtemperature SCR process over Mn-Ce/TiO2 is operated at about 100 °C. Shen Boxiong et al.⁶⁵ found that 96.8% NO conversion was obtained over Fe(0.1)-Mn-Ce/TiO₂ at 180 °C at a space velocity of 50 000 h⁻¹. Sichem Guerrero⁶⁶ observed a dramatic improvement was achieved by the addition of Na when the Cu/TiO₂ was used as NO adsorbent. The idea may open new possibilities for the use of inexpensive NO adsorbents. Also Ma Zhaoxia¹⁶ found that approximately 90% NO conversion could be achieved at a reaction temperature as low as 150 °C by the catalyst of iron-copper oxides supported on TiO₂ and carbon nanotubes (CNTs).

Different methods can produce different catalysts which have different performances on activity and SO₂ resistance. Zhang Zhixiang *et al.*⁶⁷ reported that the optimal catalyst of Pt/TiO₂ was 0.5 wt.% Pt and provided excess O₂. And bimetallic Pt–Ir/TiO₂ exhibited high activity in H₂–SCR reaction and NO_x conversion exceeding 80%, with N₂ selectivity >80%, could be obtained in the temperature range of 140–200 °C.⁶⁸ Jiang *et al.*⁶⁹ prepared the catalysts of MnO_x/TiO₂ by sol–gel, impregnation, and coprecipitation methods, among these catalysts, the sample prepared by sol–gel method had the best performance in terms of both activity and SO₂ resistance.

2.4 Molecular sieves as the carrier

2.4.1 Zeolites as the carrier. There are different types of zeolites, but ZSM-5 has been widely used because of its thermostability, acid and water resistance and the ease of fixing its shape. The surface area was between $200-500 \text{ m}^2 \text{ g}^{-1.70}$ Katariina Rahkamaa-Tolonen⁷¹ verified that the zeolite-based catalysts were very promising for the SCR reaction with ammonia. Especially, the activities at low and high

temperature were higher than the activities of commercial vanadia-based catalysts. The first time of using Cu-ZSM-5 to catalyze the decomposition of NO to its elements was in 1989.⁷² Choong-Kil Seo et al.⁷³ researched the Cu-ZSM-5 catalyst on which ZrO₂ acted as the additive to improve the low-temperature activity and durability of the SCR catalyst for diesel vehicles. The authors pointed out the NO_x conversion of the Cu-ZSM-5-ZrO₂ (2 wt%) catalyst was improved by 10-20%, compared to that of the Cu-ZSM-5 or Fe-zeolite catalyst. Other catalysts were researched. For instance, Liu Huayan et al.74 researched the high silica content Na-ZSM-5 molecular sieves, which exhibited high catalytic activity at ambient temperature. Sandro Brandenberger et al.75 used different methods to prepared the Fe-ZSM-5 catalysts and the research groups showed that the preparation method is not a decisive factor in determining catalytic activity. The available data indicated that both isolated and bridged iron species participate in the NH₃-SCR reaction over Fe-ZSM-5, with isolated species being the most active. H- β zeolites modified with calcium oxide (Ca- β) have been developed by Chang Xiaofei et al.76 The results displayed that CaO was located inside the pores of H- β and also indicate that NO_x can be easily absorbed on Ca- β samples with the NO_3^- , NO_2^- and NO^+ species.

2.4.2 SAPO as the carrier. Silico-alumino-phosphate (SAPO) is a microporous crystal composed of three kinds of tetrahedral elements, namely PO_4^+ , AlO_4^- and SiO_2 . It can be prepared by introducing the silicon into the skeleton of aluminum phosphate, which is a electronegative framework with small pore structure. SAPO can be used as adsorbent and carrier, has exchangeable cations and enough acid centers (with proton acid) on the surface. Now the research application focuses on the use of its surface acidity; the surface acidity and amount of acid can be regulated by the introduction of various kinds of impurity atoms. The performances of different impurity atoms that were introduced into SAPO have been studied.77-81 They demonstrated that copper can improve the activity and life of the SAPO-34, with great potential for industrial application. Dustin W. Fickel et al.⁸² showed that the NO conversion reached nearly 100% between 200-400 °C. Jun Wang et al.⁸³ studied the effect of Si content in SAPO-34 on NO selective catalytic reduction over Cu/SAPO-34 catalyst. The Si and Al contents affect the contents of Cu^{2+} species. The contents of active sites and the number of acid sites affect the activity over Cu/SAPO-34 samples with various Si contents. Although SAPO is a potential catalyst for removing NO_x, it needs more attention in terms of synthesis process, cost control of the synthesis and reasonable modifications, which include tunable pore size, high stability and ordered arrangement.

In conclusion, much research has comprehensively studied the carriers and achieved high NO_x conversion. But it needs more exploration for industrial applications. Ammonia, as the main reducing agent, has been researched using different kinds of catalysts. Gongshin Qi *et al.*⁸⁴ suggested that the initial step was adsorption of NH₃ onto the acid sites, and then it further reacts with NO_x to produce N_2 and H_2O . So the number of acid sites is important in catalysts. It is known that ammonia adsorbs on acid catalysts and yields two strong bands near 1600 and 1200 cm⁻¹. And some researchers^{46,77,85–87} studied the contents in ACF, Al_2O_3 , TiO₂, zeolites, SAPO.

3 Effect of reaction conditions

With the deepening of the research, the catalysts with high selectivity and stability, good activity and broad range of operating temperature make great progress. However, there is still a burning question regarding catalyst poisoning.

3.1 Effects of H₂O and SO₂

Water vapor is one of the main components in flue gases and often leads to catalyst deactivation. Even in dry conditions, the catalysts can be affected by the water vapor produced in the SCR reaction. It causes a reduction in activity for both non-supported metal oxide catalysts³ and carbon based catalysts.⁸⁸ The effect of H₂O can be divided into two results, reversible and irreversible. It is reversible when H₂O adsorption competes with that of NH₃ and NO. If H₂O were removed, this effect will disappear. However, the hydroxyl created by H₂O adsorption and decomposition on the surface of the catalysts will result in irreversible deactivation of the catalysts.¹

H₂O and SO₂ have a critical influence on the catalyst for NO reduction at low temperature. Huang et al.⁸⁹ studied the effect of SO₂ and H₂O on a catalyst of V₂O₅/AC, in which the AC was obtained by the industrial semi-coke treatment (Fig. 2). The results indicated that the effect of SO₂ was positive in the absence of H₂O. The reason for this is the transference from SO_2 to SO_4^{2-} on the surface of the catalyst, which can improve the acidity of the catalyst surface and enhance the adsorption capacity of NH₃. The experiment also revealed that the effect of the water vapor was small, which may be attributed to competitive adsorption of H₂O and reactants (NO and/or NH_3). But the co-existence of H_2O and SO_2 resulted in an obvious decrease. The phenomenon was possibly caused by sulfate particles formed from H₂O and SO₂, which deposit on the surface of the catalyst in the reaction process.

3.2 Effect of alkali and heavy metal

The fly ash in coal-fired power contains some alkali metal oxide, which will gather in the catalyst surface or react with the active substances in the catalyst and poison the catalyst during the long-term contact with catalyst. In the study of commercial vanadium and tungsten titanium catalyst, a small amount of alkali metal can have a great influence on the activity of the catalyst. Asa Kling *et al.*⁹⁰ Wenchao Yu,⁹¹ and Liang Chen⁹² studied the influence of K, Na, Ca, Mg on the catalysts, indicating the influence rank



Fig. 2 The effect of SO₂ and H₂O on V₂O₅/AC catalytic performance. Reaction conditions: 500 ppm NO, 600 ppm NH₃, 500 ppm SO₂ (when used), 3.4% O₂, 2.5% H₂O (when used), balance Ar, space velocity of 90 000 h⁻¹, reaction temperature of 250 °C.⁸⁹

was K > Na > Ca > Mg. Some researchers^{93–95} suggested that the submicrometer aerosol particles which form in the process of burning alkali and alkaline earth metals, accumulate on the surface of the catalyst, and react with the catalyst causing deactivation. They could decrease the amount and stability of the Brönsted acid sites, and affect the catalytic efficiency.⁹⁶⁻⁹⁸ Maybe an increased resistance to alkali and the regeneration performance of catalysts are better solutions. Researchers^{97,99,100} studied the resistance to alkali by the catalysts of Cu-zeolite, Ag-Al₂O₃, vanadia on sulphated-ZrO₂ and got an ideal result. Shen Boxiong et al.⁹⁶ reported that washing with both water and sulfuric acid solution could partly reverse the catalyst deactivation by alkali metals. And washing with water was the best method for regenerating catalysts that were not greatly deactivated by alkali metals.

Heavy metals are easy to volatilize into metallic vapor during the combustion processes because of their high saturation vapor pressure. And they condense to form fine particles after the temperature drops.¹⁰¹ A few studies have investigated the effects of heavy metals on the activity of catalysts. Researchers^{102–104} attribute the inhibition effect by heavy metals to the formation of alloys from the reaction with active metals.

4 SCR mechanism

At present, many catalysts have been researched, but most of them lack enough clear knowledge of the reaction mechanism. In this paper, the development progress of the mechanisms which remove NO_x by different reducing agents was summarized.

4.1 H₂ and CO as the reducing agent

Some researchers use H_2 and CO as the reducing agent to remove NO_x in SCR,^{105–107} which can get a high conversion rate. According to a study, the effect of CO and NO is to reduce the bond length and separate the bond of N–O. The mechanism is as follows:¹⁰⁵

$$NO(a) + CO(a) \rightarrow N(a) + CO_2(a)$$
(11)

$$NO(a) + H(a) \rightarrow N(a) + OH(a)$$
(12)

$$N(a) + N(a) \rightarrow N_2(g) \tag{13}$$

Another possibility is:

$$CO(a) + NO(a) + H-H(a) \rightarrow CO-O(a) + NH_2(a)$$
 (14)

4.2 Hydrocarbons as the reducing agent

Some researchers studied the mechanism of a hydrocarbon as the reducing agent, because of the practicability and cost-effectiveness. We can use the unburned hydrocarbons already present in the exhaust gas. In the process of catalytic reduction, " NO_y ",¹⁰⁸ CH₃NO¹⁰⁹ or CH₃NON₂^{109,110} can be formed from NO_x. Due to the effect of the catalysts of Y₂O₃, the first step is the formation of CH₃ radicals from CH₄, then these will react with NO_x to form CH₃NO₂, finally, CH₃NO₂ will become N₂ *via* the intermediates of CH₂NOH, CN, NCO and N₂O.¹⁰⁹ At present, the hydrocarbons used as a reducing agent to remove NO_x mainly include methane, propane, propylene.

Aylor *et al.*¹¹¹ analyzed the mechanism using Mn–ZSM-5 as the catalyst and methane as the reducing agent. First, the NO was oxidized to NO₂, then NO₂ adsorbed on the surface of the catalyst and reacted with CH_4 . In the process of the reaction, CN and NCO were formed, and CN would react with NO₂ quickly to generate N₂ and CO₂. They suggested that cyanide is the active intermediate.

Lobree *et al.*¹¹² studied the mechanism that removed NO_x with C_3H_8 as the reducing agent (Fig. 3), but they did not explain the detailed reaction process between C_3H_8 and nitrates, and did not reveal the rate controlling steps in the process of the reaction.



Fig. 3 Proposed mechanism for the reduction of NO by C_3H_8 over Fe–ZSM-5. 112

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Satsuma *et al.*¹¹³ researched the catalysts involving Al_2O_3 as the carrier, including Cu– Al_2O_3 and Ag– Al_2O_3 , for the removal of NO_x. They reported that the NO was oxidized by O₂ to NO₂, and then formed a nitrate species which had a stronger oxidizing ability that could be adsorbed on the catalyst's surface. At the same time, C_3H_6 was partially oxidized to an acetic salt species or other oxide. Then the species will react with nitrate to form NCO and CN, which will continue to react with nitrate to finally form N₂ and CO₂. The author pointed out that the generated N₂ was the rate controlling step. Yu Yunbo *et al.*¹¹⁴ did similar research and got similar results, but Yu thought the NCO's reaction was the rate controlling step.

In practice, hydrocarbons are composed of many kinds of alkanes, alkenes and alkynes. However, in the laboratory, we generally use one of them to test and analyse. Different possible synergistic effects or antagonistic effects would happen with the hydrocarbons during the catalysis. This can change the path which the catalysts react with NO_x , so it needs further research. Of course, it is difficult to completely simulate the physical truth, but it is also important to reveal active intermediates in the process of the reaction and the rate controlling steps, taking into account the key factors which affect the rate controlling step.

4.3 3NH₃ as the reducing agent

Many researchers have studied the mechanism of SCR by NH_3 . Concerning the reaction pathway over metal oxide catalysts, most researchers suggested that NH_3 was adsorbed to the Lewis acid center and intermediates like $NH_2^{115,116}$ or adsorbed $NH_3^{117,118}$ formed, then they reacted with aerial NO and NO₂ through an E–R (Eley-Rideal) mechanism producing N_2 and H_2O . They can also react with activated nitrite intermediate adsorbed on the surface of the catalysts through a L–H (Langmuir-Hinshelwood) mechanism. Marban *et al.*¹¹⁸ proposed an E–R mechanism over carbon-supported Mn_3O_4 catalyst, in which surface-active NH_3 species reacted with NO_2 , and to a lesser extent NO, from the gas phase (see Fig. 4).

Richter *et al.*¹¹⁹ supposed symmetric O=N-O-N=O species formed on the MnO_x/NaY catalyst after contact with NO. They suggested a "diazotization" mechanism, in which NH₃ was protonated to NH₄⁺, NO interacts with the catalyst, and nitrite and nitrate surface species formed in the presence of O₂. Followed by NH₄⁺ reacting with NO₂⁻ to produce N₂ and H₂O. However, a parallel "amide/nitrosamide" SCR reaction route was possible since prevailing Lewis acid sites on these catalysts should enable NH₃ activation *via* amide species.

Meanwhile, some researchers investigated the mechanisms of Cu and Fe on zeolite catalysts. For Fe/zeolite catalysts, it is supposed that Fe^{3+} ions with oxo-Fe³⁺ sites,²⁹ binuclear ions [HO-Fe-O-Fe-OH]²⁺¹²⁰ and others were the active sites for the SCR reaction. Schwidder *et al.*¹²¹ established that mononuclear Fe ions are active sites for SCR reactions, but oligomers



Fig. 4 Mechanism of the steady-state SCR reaction: (I) in the absence of oxygen; (II) in the presence of oxygen.¹¹⁸

contribute as well. Brandenberger et al.^{122,123} supported and further developed these views that oligomers have high oxidation potential, causing undesired total oxidation of the reductant, particularly in the case of isobutene. Authors suggested that the SCR of NO by NH₃ is primarily caused by monomeric iron sites at temperatures below 300 °C. A reaction mechanism which describes NO or NO2 reduction by NH₃ over H-form zeolites was most developed and accepted (see Fig. 5).^{124,125} It suggested that adsorbed NH₃ is the most reactive agent when it is bonded to the Brønsted acid sites in zeolites through three hydrogen bonds. An NO₂-type intermediate is formed on the zeolite surface during the SCR reaction. Formation of this NO₂-type species appears to be a necessary step in the SCR reaction mechanism, since the concentration of adsorbed NH₃ does not decrease (*i.e.*, react) until a band corresponding to this NO₂-type species appears. Grossale^{126,127} presented a systematic study of the chemical steps in the NO/NO2-NH3 fast SCR reaction over a commercial Fe-ZSM-5 catalyst.

The schematic summary of the fast SCR chemistry in terms of surface species is displayed in Fig. 6. Results were demonstrated *via* a global sequence involving NH_4NO_3 or related surface species as intermediates, which is the same as that proposed previously for the fast SCR chemistry over



Fig. 5 Reaction mechanism of SCR of ${\rm NO}_x$ with ${\rm NH}_3$ over H-form zeolites. 124,125



V-based catalysts and other zeolite catalysts and thus is considered a general mechanism. It further showed that the redox reaction between NO and nitrates is the ratecontrolling step and is inhibited by ammonia. Remarkably, the same strongly enhanced de-NO_x activity observed in the fast SCR reaction was also observed in the absence of gaseous NO₂, but in the presence of surface nitrates. Accordingly, they propose a general summary of the fast SCR chemistry over V-based and zeolite catalysts that emphasizes the key role of surface nitrates.

The fast SCR chemistry¹²⁶ basic reaction steps in NO/ NO₂-NH₃ SCR chemistry over V-based and zeolite catalysts are as follows.

Involving NO₂ only

$$2NO_2 \leftrightarrow N_2O_4 \tag{15}$$

$$N_2O_4 + O^{2-} \leftrightarrow NO_2^- + NO_3^-$$
(16)

In the presence of NH₃

$$2NH_{2} + H_{2}O \leftrightarrow 2H_{4}^{+} + O^{2-}$$
(17)

Minireview

$$NH_4^+ + NO_2^- \leftrightarrow [NH_4NO_2] \rightarrow N_2 + 2H_2O$$
(18)

$$NH_4^+ + NO_3^- \leftrightarrow NH_4NO_3$$
 (19)

In the presence of NO

$$NO + NO_3^- \leftrightarrow NO_2 + NO_2^-$$
(20)

Global reactions observed in this work, and their relationship with the basic reactions above

$$3NO_2 + O^{2-} \leftrightarrow NO + 2NO_3^-$$
 (21)

$$2\mathrm{NO}_2 + 2\mathrm{NH}_3 \rightarrow \mathrm{NH}_4\mathrm{NO}_3 + \mathrm{N}_2 + \mathrm{H}_2\mathrm{O}$$
 (22)

$$NO + NH_4NO_3 \rightarrow NO_2 + N_2 + 2H_2O$$
(23)

$$NO + NH_3 + 1/2NH_4NO_3 \rightarrow 2/3N_2 + 5/2H_2O$$
 (24)

$$2NH_3 + NO + NO_2 \rightarrow 2N_2 + 3H_2O \tag{25}$$

5 Kinetics

A lot of work had been done for researching the mechanism and kinetics of removing the NO_x at low temperature. The research of kinetics for SCR reaction at low temperature was based on empirical equations (as power-law kinetics) and obtained from mechanistic analysis or both of them.

Yang *et al.*¹²⁸ studied the kinetics of the catalyst of MnO_x -CeO₂ based on the kinetic equation of power function in eqn (26). They got some data from the result: the reaction orders of NO, NH₃, and O₂ ([O₂] < 1%) were 1, 0 and 0.5 at 120 °C, respectively. This was consistent with the results from Wu *et al.*¹²⁹ The kinetics of MnO_x/TiO_2 was researched based on the kinetic equation of power function.

$$r_{\rm NO} = k[\rm NO]^{x}[\rm NH_{3}]^{y}[\rm O_{2}]^{z}$$
(26)

But different results were reported by Richter *et al.*¹³⁰ using the same equation to obtain the experimental data of MnO_x/NaY at low temperature. The reaction orders were 2 and 0.3 for NO and O₂, respectively. The reaction order of 2 means that two molecules of NO were involved in the rate controlling step of the reaction. It corresponded to the reaction model that they proposed: it was the oxidation of NO to NO₂, and the intermediate was similar to the N₂O₃ by NO and NO₂ formed from reaction with NH₃.

Kijlstra *et al.*¹¹⁵ proved the existence of L–H and E–R mechanisms immediately *via* some experiments. The authors supposed a low temperature SCR reaction model of the MnO_x/Al_2O_3 catalyst below 230 °C, as in eqn (27–34). They

thought that the mechanisms of L–H and E–R happened in parallel, but the formation of N_2 was most attributed to the E–R mechanism. This reaction model was supported and proved by subsequent studies.

$$O_2 + 2^* \rightleftharpoons 2O^{-*} \tag{27}$$

$$NH_3 + * \rightleftharpoons NH_3 - * (Lewis acid Mn^{3+} site) \quad K_3 = K_3/K_{-3} \quad (28)$$

NO + O-*
$$\rightleftharpoons$$
 NO-O-* bridged and monodentate nitrites K_4 (29)

$$NO-O^{*} + O^{*} \rightarrow NO_{3}^{*} + * \text{ bidentate nitrate } K_{5}$$
 (30)

$$NO_3^{-*} + O^{-*} \rightarrow NO_2^{-*} + OH^{-*} K_6$$
 (31)

$$NO_2^{-*} + NO \rightarrow N_2 + H_2O + * ER$$
 mechanism K_7 (32)

$$NO_2^{-*} + NO_{-}O^{-*} \rightarrow N_2 + H_2O + O^{-*}$$

+ * LH mechanism K_8 (33)

$$2OH^* = H_2O + O^* + K_9$$
 (34)

They deduced the kinetic equation in eqn (35) based on the mechanism of L–H and E–R.¹³¹

$$r_{\rm NO} = \frac{(k'*p_{\rm NO}p_{\rm NH_3})}{(1+K_3p_{\rm NH_3}+K_6p_{\rm NO}+K_9p_{\rm H_2O})^2} + \frac{(k'p_{\rm NO}p_{\rm NH_3})}{(1+K_3p_{\rm NH_3}+K_4p_{\rm NO}+K_9p_{\rm H_2O})^2}$$
(35)

Where

$$k' = K_7^* N_t^* K_3$$

$$k'' = K_8^* N_1^* s^* K_3^* K_4$$

The researchers¹³¹ indicated that the reaction order of NO is less than 1, which can be explained by the fact that the NO joining the SCR reaction in a form other than gaseous, may be adsorbed on the catalyst. It means both E–R and L–H mechanisms existed. But if just the E–R mechanism exists, it can also be explained that there exists a rate-controlling step —the activation of NH_3 . Or maybe a composite exists that is formed from NO and NH_3 . Further research should be done on this point.

6 Conclusions and perspective

The supported catalysts are crucial in the removal of NO_x from the flue gas of power plants and diesel engines at low temperature. A lot of supported catalysts have been

researched in the past decade. The catalysts using Mn–Ce as the active sites have a better effect than other metals, with ACF, Al_2O_3 , TiO_2 , zeolites and SAPO as the carriers or without carriers for SCR of NO_x at low temperature. But the high selectivity, stability and resistance of H_2O and SO_2 , alkali and heavy metals require further improvement. Maybe it can be achieved with catalysts by compounding the transition metals and doping rare earth elements into appropriate carriers, such as ACF, γ -Al₂O₃ and so on. At the same time, due to the development of analytical methods and analog computation, the synergistic effect of supported catalysts is a hot topic in recent years.

Some research has been done to study the mechanism. The phenomena of the E-R, L-H mechanisms or both of them coexisting in the progress of the removal NO_x reaction is the main theory. But there are some debates in the research of the reaction order of NO. Different reaction orders will give different analysis results. Some models to study the kinetics of the SCR NO_x have been established at low temperature. The main point of the kinetics research is based on empirical equations (as power-law kinetics) and obtained from mechanistic analysis or both of them. Although de-NO_x by SCR has been studied for a long time, the low-temperature efficiency, especially practical application efficiency, was undesirable. Besides, the mechanism was also not very clear and cannot effectively control the poisoning of the catalyst. The catalyst was limited for wide applications and cannot lower the huge cost. According to the exploration of the surface chemical process, the mechanism of the de-NO_x can be proved, and the root cause of the poisoning and deactivation of the catalyst can be found. Therefore, the surface chemical process is a very worthy subject to study in-depth.

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