A Review on the Catalytic Decomposition of NO by Perovskite-Type Oxides

Qiuwan Shen, Shuangshuang Dong, Shian Li, Guogang Yang and Xinxiang Pan

Abstract: Direct catalytic decomposition of NO has the advantages of being a simple process, producing no secondary pollution, and being good for the economy, which has attracted extensive research in recent years. Perovskite-type mixed oxides, with an ABO$_3$ or A$_2$BO$_4$ structure, are promising materials as catalysts for NO decomposition due to their low cost, high thermal stability, and, of course, their good catalytic performances. In this review, the influence factors, such as A-site substitution, B-site substitution and reaction conditions on the catalytic performance of catalysts have been expounded. The reaction mechanisms of direct NO decomposition are also discussed. Finally, major conclusions are drawn and some research challenges are highlighted.

Keywords: NO direct decomposition; perovskite-type oxides; A-site substitution; B-site substitution

1. Introduction

NO$_x$ is one of the main pollutants that can seriously endanger human health and the ecological environment. It is the main pollutant in the formation of acid rain: NO$_x$ and HC react chemically under the action of sunlight to generate photochemical smog. NO$_x$ can destroy the ozone layer causing global climate change, therefore, the harm caused by NO$_x$ cannot be ignored [1,2].

Direct catalytic decomposition of NO has the advantages of being a simple process, producing no secondary pollution, and being good for the economy, which has attracted extensive research in recent years [3,4].

$$2\text{NO}(g) = \text{N}_2(g) + \text{O}_2(g)$$
$$\Delta H^0_{(298K)} = -90.2 \text{ kJ/mol}$$

As can be seen from the above equation, the reaction is thermodynamically favorable. This decomposition reaction has highly negative Gibbs free energy ($\Delta G_m = -86 \text{ kJ/mol}$), and the tendency of NO decomposition to generate N$_2$ and O$_2$ is large. Although it is thermodynamically feasible, the reaction needs to overcome the high activation energy of the reaction ($\sim 335 \text{ kJ/mol}^{-1}$) [5,6]. Accordingly, NO can decompose smoothly under a catalyst and certain temperature conditions, and the development of greatly active and stable catalysts have always been a popular research direction and challenging task. The process is free of secondary pollution and does not require a reducing agent, which largely reduces the operating costs.

Most of the studies of NO direct catalytic decomposition catalysts focus on six types of catalysts, including noble metals, metal oxides, perovskite-type mixed oxides, ion-exchange ZSM-5 type molecular sieves, multi-compounds, and hydrotalcite type materials [6]. Although some noble metals and metal oxides have high activity, there is catalyst poisoning during NO decomposition. Besides, metal oxide catalysts are also very sensitive to SO$_2$. When SO$_2$ is present it is easy to generate sulfate, which will poison and deactivate the
catalyst. Noble metals are expensive and resources are scarce, whereas perovskite-type mixed oxides have the advantages of good thermal stability and stable oxygen vacancies on the surface. Therefore, the removal of NO by perovskite-type composite oxides has become one of the research hotspots of catalytic decomposition denitrification technology. The research progress and the current state of direct catalytic decomposition of NO by perovskite-type oxides will be reviewed, and the future developmental direction will be discussed.

2. Mechanism of NO Decomposition on Perovskite-Type Oxides

The perovskite-type oxide structure is ABO$_3$, which is a cubic crystal with A-site or B-site cations as nodes, and is consistent with the perovskite (CaTiO$_3$) structure. In general, the metal ions at position A are mostly rare earth metal, alkaline earth metal, and lanthanide metal, which are located at the center of the structure and coordinate with the surrounding 12 oxygen atoms. The metal ions at position B are mostly transition metal ions, which are located in the body center of the octahedral structure and coordinate with the surrounding six oxygen atoms [7]. Among them, metal ion B determines the catalytic performance of the catalyst, and the role of metal ion A is mainly to stabilize the crystal structure. The ideal crystal structure of ABO$_3$ perovskite is shown in Figure 1.

![A schematic of the ideal ABO$_3$ perovskite unit cell.](image)

There are defects in perovskite oxide crystals like most crystals. According to the electric neutral principle, ABO$_3$ can be composed of three kinds: A$^{+1}$B$^{+5}$O$_3$, A$^{+2}$B$^{+4}$O$_3$, A$^{+3}$B$^{+3}$O$_3$. In the perovskite structure, the larger radius of the A ion can be partially or completely lost, so A-site ion defects are common. The B-site ions have a relatively large charge and small ionic radius. From a thermodynamic point of view, the B-site is unfavorable. There are several ways to generate ionic defects:

1. Substitution of high valence ions (rare earth elements) with low valence ions A$'$ (generally alkaline earth metals). According to the principle of electroneutrality, high valence B-site ions and oxygen vacancies can be generated;
2. Substitution of low valence ion A with high valence ion A$'$ can generate low B valence ion and A vacancy;
3. Substitution of high valence B ions with low valence B$'$ ions.

The changes and catalytic reactions of various valence states and oxygen defects of A and B above can generally occur simultaneously.

Zhu et al. [8] believed that oxygen vacancy played a crucial role in the decomposition of NO, and the active center of NO decomposition was composed of oxygen vacancy and...
transition metal with low oxidation state. A large number of oxygen vacancies generally exist in the perovskite-type oxide structure, which provides space and convenience for the adsorption and decomposition of NO. The adsorbed NO obtains an electron from the transition metal with a lower oxidation state. Meanwhile, it is activated by the electron to participate in the reaction.

For the decomposition mechanism of NO on perovskite-type catalysts, Shin et al. [9] thought that, at first, two molecules of NO attached on the Fe\(^{3+}\) with some oxygen vacancies, and then the NO molecules coordinated with the iron ions. At the same time, the iron atoms changed their valence state from Fe\(^{3+}\) to Fe\(^{4+}\), giving one electron per one coordinating NO molecule. The N–O bond in the coordinating nitrosyl ion (NO\(^{-}\)) is so weak that cleavage of the N–O bond may occur, yielding a free molecule of N\(_2\). Subsequently, the thermal energy supplied to the reaction system at a certain temperature will cause the release of the oxygen atoms from the Fe\(^{4+}\). Then, an oxygen molecule will be also isolated from the reaction system, and again the Fe\(^{3+}\), with accompanying oxygen vacancies, are regenerated, and the reaction mechanism is shown in Figure 2. This scheme is thought to be credible for the thermal decomposition of NO over an oxygen-deficient perovskite SrFeO\(_{3-x}\) because the unique lattice of SrFeO\(_{3-x}\) itself easily stabilizes an unusual valence state of +4 for the irons, and it also tends to accommodate appreciable oxygen defects with increasing temperature.

![Figure 2. A possible mechanism of NO decomposition on the perovskite-type catalyst. Adapted with permission from [9], 2021, Elsevier.](image)

Teraoka et al. [10] proposed the reaction mechanism of direct decomposition of NO on perovskite oxides. A pair of NO molecules was first adsorbed onto the adjacent oxygen vacancies on the surface of the catalyst, and then the two adjacent N–O bonds were dissociated to form a free N\(_2\) molecule, and finally released into the gas phase, as shown in Figure 3. Since the adsorption of the second NO molecule at the paired position is a rate-determined step, the important characteristics of this reaction are NO adsorption capacity and oxygen ion vacancy. Besides, the cation activity of the B-site greatly affects the catalytic activity, because B-site ions are adjacent to oxygen anions, and O\(_2\) desorption plays an important role in the regeneration of cation vacancies.
Zhu et al. [11] explored the decomposition mechanism of NO on perovskite-like oxides by studying the O\textsubscript{2}-TPD experiment and NO decomposition activity. The NO was first absorbed and dissociated into N\textsubscript{2} and atomic oxygen, which then reacted with another NO to form the adsorbed NO\textsubscript{2} and, after that, the adsorbed NO\textsubscript{2} desorbed and dissociated into NO and O\textsubscript{2}. In this process, NO\textsubscript{2} acted as an intermediate of O\textsubscript{2} formation. The results showed that the decomposition of NO on perovskite-like oxides was carried out in a cycle manner, in which the cycle (generation and decomposition) of NO\textsubscript{2} played an important role in the reaction and was closely related to the activity.

(a) NO\textsubscript{2} is mainly generated on the surface of the catalyst:

$$\text{NO} + (\text{[ } \text{[ } \text{] } ) \xrightarrow{K_1} \frac{\text{K}_1}{K_{-1}} (\text{[O]} \cdot [\text{ ] }) \quad (I)$$

(b) Oxygen desorption step:

$$\text{O} (\text{[ ] }) + \text{O} (\text{[ ] }) \xrightarrow{K_2} \frac{\text{K}_2}{\text{K}_{-2}} (\text{O} \cdot [\text{ ] }) \quad (II)$$

$$N (\text{[O]} \cdot [\text{ ] }) \xrightarrow{\text{K}_{3, \text{fast}}} N_2 + (\text{[O]} \cdot [\text{O}]) \quad (III)$$

$$\frac{\text{K}_4}{\text{K}_{-4}} (\text{[O]} \cdot [\text{O}]) \xrightarrow{\text{K}_4} \text{O}_2 \cdot (\text{[ ] }) \quad (IV)$$

Figure 3. A possible reaction mechanism for the direct decomposition reaction of NO on perovskite-type oxides. Adapted with permission from [10], 2021, Royal Society of Chemistry.

NO\textsubscript{2} dissociation reaction (2NO\textsubscript{2} = 2NO + O\textsubscript{2}) is an important step in the process of NO decomposition as the catalytic activity of NO decomposition on perovskite-like oxides only occurs at high temperatures. The cyclic decomposition mechanism of NO on perovskite-like oxides with NO\textsubscript{2} as intermediate species is shown in Figure 4.
substitution of A-site atoms by other valence atoms can change the valence of B-site ions and the content of oxygen vacancies in the structure. For example, the content of Fe$^{2+}$ and intermediate species.

Figure 4. The mechanism of cyclic decomposition of NO on perovskite-like oxides with NO$_2$ as an intermediate species.

A large number of oxygen vacancies or oxygen excess in perovskite-like oxides favor the decomposition of NO; NdSrCu$_{1-x}$Co$_x$O$_{4-\delta}$ has a higher density of oxygen vacancies and a stronger Cu$^{3+}$/Cu$^{2+}$ redox capacity, which is more likely to activate NO and is responsible for the enhancement of catalytic performance [12–14].

Perovskite composite oxides have good thermal stability and oxygen defects, so they have been considered promising catalysts for catalytic NO decomposition [15]. On the one hand, oxygen vacancies provide vacancies for NO adsorption, while on the other, electrons generated in the structure can activate NO. The existence of oxygen vacancies and redox properties of B-site ions are two main factors affecting NO adsorption and activation, which play an important role in the reaction process. In recent years, perovskite catalysts have become a research hotspot in the field of catalytic decomposition of NO due to their good direct decomposition performance [16,17].

It is generally believed that the catalytic activity mainly depends on the B-site ions, while the A-site ions mainly play a role in stabilizing the crystal structure. However, the substitution of A-site atoms by other valence atoms can change the valence of B-site ions and the content of oxygen vacancies in the structure. For example, the content of Fe$^{2+}$ and Fe$^{3+}$ ions and oxygen vacancy ($\delta$) in La$_{1-x}$Sr$_x$FeO$_{4-\delta}$ can be changed by the substitution of Sr$^{2+}$ with La$^{3+}$. Due to the unique structural characteristics of perovskite, the original crystal structure of perovskite will not be destroyed by doping different valence metal ions at A- or B-site within the allowable range of the tolerance factor. Therefore, the decomposition activity of NO can be improved by doping different metal ions [18].

3. Effect of A-Site Substitution

The A-site ions of perovskite are larger radius ions. The ions on the A-site will indirectly promote catalytic activity. When the A-site ions are substituted, there are more defects produced and they will affect the electronic state of the B-site ions [19]. Meanwhile, A-site doping can change the oxidation state of B-site ions, and B-site ions are easily reduced to highly disperse metal centers [20–22]. A- and B-sites play different roles in the reaction process. B-site mainly affects the temperature range of the reaction, and A-site mainly affects the selectivity of the reaction. Higher lattice oxygen mobility and lower active oxygen adsorption are also the key factors to determining catalyst activity. Divalent alkaline earth ions are often used to partially replace the A-site ions to increase the alkalinity and generate anion oxide vacancies through charge compensation.

3.1. Effect of Dopants

Zhu et al. [23] found that if external A-site cations could not change the oxidation state of B-site cations, the effect of A-site substitution on catalytic performance was indirect, i.e., by changing the oxidation state of B-site cations or generating oxygen vacancies. This
indicates that although Sr$^{2+}$ had no activity on the decomposition of NO, it could affect the reaction rate by changing the average oxidation of B-site cations.

Yasuda et al. [24] studied the effect of Sr substitution on NO decomposition by La$_{2-x}$Sr$_x$CuO$_4$ and demonstrated that the substitution influence was caused by changing the average oxidation state of Cu. The catalytic activity is closely related to the average oxidation state of Cu, and its value is closely related to the amount of Sr$^{2+}$ substitution. He et al. [25] prepared La$_{1-x}$Sr$_x$FeO$_3$ perovskite composite oxides. After La was partially replaced by Sr, more oxygen vacancies were generated and the catalytic performance was improved. In recent years, barium has been considered as a promising A-site ion for perovskite catalysts because it not only has a low oxidation state (+2), it also has the potential to capture NO$_x$, thus ensuring the supply of NO in the reaction.

An A-site cation does not necessarily have no catalytic activity, but as long as the A-site cation has a variable oxidation state, it can indeed participate in the reaction process. Notably, Ce enters the structural framework of La$_{1-x}$Sr$_x$Ce$_y$NiO$_3$ up to 30% ($x = 0.3$), which is much higher than the reported ABO$_3$ structure of perovskite-type oxides (La$_{1-x}$A$^+$BO$_3$ is usually below 10%) [26–28]. Belessi et al. [29] found that the substitution of Ce in La$_{0.8}$Sr$_{0.2}$FeO$_{0.5}$ was very difficult. No perovskite oxide containing Ce was detected in this system.

Zhu et al. [30] added Sr in La$_2$CuO$_4$ and the NO decomposition conversion rate was low (34.3%, $t = 850$ °C). For a La$_{2-x}$Th$_x$CuO$_4$ (0 ≤ $x$ ≤ 0.4) catalyst, Zhu et al. [22] showed that Cu$^+$ was easily oxidized in the redox cycle of Cu$^+\leftrightarrow$Cu$^{2+}$, so that the active adsorption rate of Cu$^+$ at 850 °C was the highest, reaching about 42%. Chen et al. [31] prepared a La$_{1.6}$Ba$_{0.4}$NiO$_{1-x}$%BaO ($x = 0, 5, 10, 15, 20, 25, 30$) catalytic by heating a mixture of Ba(NO$_3$)$_2$ and La$_{1.6}$Ba$_{0.4}$NiO$_4$, and evaluated their catalytic performance. The results showed that the activity of the La$_{1.6}$Ba$_{0.4}$NiO$_{1-x}$%BaO catalysts increased with the increase of the amount of BaO.

Iwakuni et al. [32] showed that La$_{1.6}$Ba$_{0.4}$NiO$_{1-0.2}$%BaO had the highest activity, and the yield of nitrogen increased from 51.7% to 98.8% at 600–850 °C. The results showed that the addition of BaO increased the number of oxygen vacancies and the mobility of lattice oxygen. Besides, BaO played an important role in the transport and storage of NO and facilitated the reconstruction of active centers. Zhang et al. [33] prepared a series of perovskite-type La$_{1-x}$Ce$_y$FeO$_3$ ($x = 0–0.5$) nanocomposites by sol-gel method and studied the effect of Ce doping ratio on NO conversion rate. When the doping amount is 0.3, the conversion of NO can reach 80% at low temperatures.

Li et al. [34] prepared a series of perovskite La$_{1-x}$Ce$_y$MnO$_3$ ($x = 0–0.2$) nanocomposites by sol-gel method and studied the effect of a Ce$^{4+}$ doping ratio on NO conversion. The results showed that the catalytic activity of active perovskite species was improved by adding the appropriate amount of Ce$^{4+}$ to the La$^{3+}$ site.

Dong et al. [35] prepared a series of La$_{0.7}$Sr$_{0.3}$MnO perovskite catalysts by the sol-gel method under different synthesis conditions. The results showed that the initial pH value of the precursor solution had a great influence on the shape and size of the catalyst, which directly related to the NO$\_x$ storage capacity of the catalyst. Also, the oxidation capacity of the NO was determined by the amount of excess oxygen in the perovskite.

Gao et al. [36] further found that after a reduction in H$_2$ (H$_2$/He = 1/9, flow rate: 20 mL·min$^{-1}$) at 300 °C, the catalytic performance of La$_{1.867}$Th$_{0.133}$CuO$_4$ was effectively improved, and 91% NO conversion (converted to N$_2$) was obtained at 650 °C.

In addition, sometimes the substitution of A-site cations changes the crystalline phase from an ordered structure to a disordered structure, thus affecting the catalytic performance. Shin et al. [25] reported that Ca$_2$Fe$_2$O$_{5+\delta}$ with ordered oxygen vacancies had no activity to decompose NO even at 900 °C, while Sr was substituted for Ca, i.e., Sr$_2$Fe$_2$O$_{5+\delta}$ with disordered oxygen vacancies. Besides, a Ce$^{3+/4+}$ partial substitution of site ions facilitated the regeneration of the active site due to the redox properties of the cerium ion, which can release oxygen adsorbed on the oxide anion defects. This redox effect is more obvious in K$_2$NiF$_4$ perovskite oxides deposited alternately between the ABO$_3$ layer and AO layer, but...
not in ABO₃ type oxides. Because the cavity space of the K₂NiF₄ lattice is larger than that of the ABO₃ lattice, larger Ce ions can replace some A-site ions. Besides, Sr²⁺ can compensate charge at the B-site.

3.2. Effect of Coexisting Gases

In the absence of coexisting gases, the N₂ yield of the NO decomposition of a perovskite catalyst was over 70%. However, the reaction was strongly inhibited by the presence of O₂ and CO₂. Ba₀.₈La₀.₂Mn₀.₈Mg₀.₂O₃, the most active catalyst among the ABO₃-type oxides, gave about 80% N₂ yield for NO decomposition at 850 °C and in the absence of coexisting gases. In contrast, under the presence of 5% CO₂, the concentration was reduced to less than 20% due to the dissociative adsorption of CO₂ on the catalyst surface and the strong adsorption of the resulting CO on the active site [37]. CO₂ poisoning has an enormous negative impact on the catalytic performance of NO decomposition. In addition, when the catalyst was heated at 700 °C, the adsorbed CO molecules were desorbed from the surface, without desorption at a lower temperature of 600 °C.

For La₀.₈Sr₀.₂CoO₃, CO₂ inhibited NO decomposition through carbonate formation, which is different from the poisoning mechanism observed in Ba₀.₈La₀.₂Mn₀.₈Mg₀.₂O₃, although they are similar perovskite oxides [38]. A La₀.₈Sr₀.₂CoO₃ catalyst needs to be heated above 750 °C to decompose carbonate. Therefore, to effectively decompose NO in the presence of CO₂, a new and advanced catalyst is needed, which can inhibit the reaction with CO₂ and limit the adsorption of CO₂.

4. Effect of B-Site Substitution

The substitution effect of B-site cations is much more complex than that of A-site cations. Because B-site cations can not only change their oxidation state, but also an important part of the active site.

4.1. Effect of Dopants

LaMO₃ lanthanide is a common B-site substituted perovskite system. It is generally believed that La³⁺ mainly fixes the crystal structure of the catalyst, and the main catalytic effect is controlled by B-site ions. Yokoi and Uchida [39] studied the reactivity of different B-site cations to NO decomposition directly in LaMO₃ (M = Cr, Mn, Fe, Co, and Ni).

Figure 5 compares the NO decomposition catalytic activity of some LaMO₃-based perovskite [30–43].

![Figure 5. NO decomposition catalytic activity of some LaMO₃-based perovskite.](image_url)

For BaMnO₃-based perovskite oxides, Iwakuni et al. [37] studied the effect of dopants on NO direct decomposition activity. Goto et al. [44] investigated the effect of B-site
substitution on the NO decomposition activity of SrFe$_{0.7}$M$_{0.3}$O$_3$ activity in the order of Mg > Sn > Ni > Ce > Zr. The NO decomposition activity was Mg > Sn > Ni > Ce > Zr. Notably, Kazuya [45] found that Ba$_3$Y$_{3.4}$Sc$_{0.6}$O$_9$ with a perovskite structure composed of alkaline earth metals and rare earth ions exhibited high NO decomposition activity in the temperature range of 600–850 °C.

The application of lanthanide-free perovskite catalysts in NO decomposition reactions has been studied by many researchers. Traditional three-way catalysts (TWCs) in reducing NO$_x$, CO, and HC are very effective, considering the need for the development of high-efficiency catalyst. Glisenti et al. [46] studied the effect of rare-earth element (typically lanthanum) perovskite oxides on the activity of the catalyst: Co and Cu were doped active cations and the results showed that Co appeared to be active in oxidation, while Cu was necessary for reduction. Strontium titanates (Sr$_{1-x}$K$_x$TiO$_3$, $x = 0.1–0.5$), partially replaced with potassium, were prepared by the citric acid sol-gel method [47]. The promoting effect of potassium on the formation of oxygen vacancy and surface alkalinity was discussed, in which molecular oxygen or (NO, NO$_2$) was absorbed to form basic surface oxygen species soot oxidation.

Carlotto et al. [48] studied the NO reduction in a CO-NO atmosphere at the Co and Cu-doped SrTiO$_3$ surface by density function theory. They found that the step to determine the rate is the formation of oxygen vacancy, which is beneficial to the doping of Cu- and Co. Due to its higher ability to stabilize oxygen vacancy, the catalytic performance of the Cu-doped surface was improved at the same time. While the solubility of Cu was low in SrTiO$_3$, Cu-doping is predicted to be particularly effective.

4.2. Effect of Coexisting Gases

To improve the oxygen resistance of the catalyst, Zhu et al. [49] added an appropriate amount of Ce in LaSrNiO$_4$. Among these La$_{1-x}$Ce$_x$SrNiO$_4$, La$_{0.7}$Ce$_{0.3}$SrNiO$_4$ showed high direct decomposition activity at 900 °C even in the presence of 6.0% O$_2$. At 800 °C, the yield of nitrogen reached about 75%. In the presence of 1.0% and 4.0% oxygen, the yield of nitrogen reached 50.5% and 39.8%, respectively [50]. The results of Zhu et al. [51] showed that the NO decomposition activity of laser crystal could be improved by replacing manganese with nickel. LaSrMn$_{1-x}$Ni$_x$O$_{4+\delta}$ ($x = 0.8$) had the highest nitrogen yield at about 85% at 850 °C and about 75% even in the presence of 2.5% oxygen. XPS characterization showed that the stronger the catalyst bonded to oxygen, the lower the catalytic decomposition activity. Ma et al. [52] studied nickel-containing A$_2$BO$_4$ oxide catalysts. Through research, it was found that these catalysts have excellent catalytic performance at low temperatures, which is very suitable for simultaneous removal of NO$_x$ and diesel soot.

Gao et al. [53] synthesized a special structure of La$_2$CuO$_4$ nanofibers using single-walled carbon nanotubes (CNT) as a template. At temperatures above 300 °C, 100% NO conversion could be obtained without other by-products. Wang et al. [54] combined a BaBi$_{0.05}$Co$_{0.8}$Nb$_{0.15}$O$_{3–\delta}$ (BBCN) hollow fiber membrane with a nickel silicate hollow sphere catalyst to fabricate a novel bifunctional catalytic peroxide hollow fiber membrane reactor. Using this new catalytic membrane reactor, the oxygen in the NO decomposition reaction system was instantaneously removed, and NO was completely converted to N$_2$ at low temperatures (675 °C). Dhal et al. [55] applied the solution of combustion synthesis technology to the production of LaFeO$_3$ and improved its NO purification activity by increasing the specific surface area of LaFeO$_3$ with high exothermic and self-sustaining reactions.

Using these efficient composite materials, combined with the existing knowledge of structure, the catalytic activity of perovskite oxide was analyzed. It is hoped that an efficient perovskite oxide catalyst can be successfully found to remove NO and meet the requirements of a large-scale application.

As can be seen from Table 1, the BaMnO$_3$-based perovskite shows low catalytic activity. Meanwhile, the catalytic activity increased after loading Pt, indicating that the adsorption strength of surface oxygen was weakened by Pt. The adsorption capacity and efficiency of
oxygen vacancy could be improved by doping Ba in perovskite catalyst. The difference of the activity between Ce-doped perovskite in the presence of 1% O₂ and the absence of oxygen was very slight, which indicates that the Ce-doped perovskite sample had a strong resistance to oxidation. The direct decomposition capacity of perovskite oxide doped with Sr was greatly affected by Fe doping. Fe was replaced by a low valence cation in SrFeO₃. Moreover, the SO₂ resistance of perovskite oxide doped with oxygen was very slight, which indicates that the Ce-doped perovskite sample had a strong resistance to oxidation. The direct decomposition capacity of perovskite oxide doped with oxygen could be improved by doping Ba in perovskite catalyst. The difference of the activity between Ce-doped perovskite in the presence of 1% O₂ and the absence of oxygen was very slight, which indicates that the Ce-doped perovskite sample had a strong resistance to oxidation. The direct decomposition capacity of perovskite oxide doped with Sr was greatly affected by Fe doping. Fe was replaced by a low valence cation in SrFeO₃.

In conclusion, there has been much research done on the doping of a perovskite oxide catalyst with La. The high activity of a perovskite oxide catalyst can be obtained by doping La and the catalytic performance of the catalyst can be improved by doping Ba, Ni, Ce, etc.

Table 1. A summary of the reaction conditions and maximum nitrogen yield of major perovskite catalysts.

| Catalysts                  | N₂ Yield (%) | Reaction Conditions         | Refs. |
|---------------------------|--------------|-----------------------------|-------|
| La₁.₄Sr₀.₆NiO₄             | 80           | 1.0% NO, 1.34 g cm⁻³, 850 °C | [7]   |
| La₁.₂Sr₀.₈NiO₄             | 20           | 1.0% NO, 1.34 g cm⁻³, 700 °C | [7]   |
| La₁.₆Ba₀.₄NiO₄·20%BaO      | 98.8         | 1.0% NO, 1.2 g cm⁻³, 850 °C | [31]  |
| Ba₀.₇La₀.₁Mn₀.₈La₀.₂O₃     | 74.1         | 1.0% NO, 3.0 g cm⁻³, 850 °C | [32]  |
| Ba₀.₇Pr₀.₁Mn₀.₈Pr₀.₂O₃     | 69.6         | 1.0% NO, 3.0 g cm⁻³, 850 °C | [32]  |
| Ba₀.₈La₀.₂Mn₀.₈Mg₀.₂O₃     | 75           | 1.0% NO, 3.0 g cm⁻³, 850 °C | [32]  |
| BaMn₀.₈Mg₀.₂O₃             | 66.8         | 1.0% NO, 3.0 g cm⁻³, 850 °C | [32]  |
| BaMn₀.₈Zr₀.₂O₃             | 51.6         | 1.0% NO, 3.0 g cm⁻³, 850 °C | [32]  |
| BaMnO₃                     | 16.0         | 1.0% NO, 3.0 g cm⁻³, 850 °C | [32]  |
| SrMn₀.₈Mg₀.₂O₃             | 37.8         | 1.0% NO, 3.0 g cm⁻³, 850 °C | [32]  |
| SrMn₀.₈Fe₀.₂O₅             | 39.7         | 1.0% NO, 3.0 g cm⁻³, 850 °C | [32]  |
| La₁.₂Ba₀.₄NiO₄             | 90           | 4.0% NO, 1.2 g cm⁻³, 850 °C | [41]  |
| La₁.₂Ba₀.₄NiO₄             | 76           | 4.0% NO, 0.75 g cm⁻³, 850 °C | [41]  |
| La₁.₆Ba₀.₄NiO₄·BaCO₃       | 98           | 4.0% NO, 1.2 g cm⁻³, 850 °C | [41]  |
| La₀.₈Sr₀.₁₃Mn₀.₂Ni₀.₈O₃    | 40           | 1.0% NO, 1.2 g cm⁻³, 650 °C | [41]  |
| La₀.₈Ce₀.₅NiO₄             | 70           | 1.0% NO, 1.2 g cm⁻³, 800 °C | [41]  |
| La₁.₆Th₀.₁CuO₄·0.₀₅       | 65           | 1.0% NO, 1.33 g cm⁻³, 500 °C | [42]  |
| La₁.₆Th₀.₁CuO₄             | 42           | 1.0% NO, 1.33 g cm⁻³, 850 °C | [42]  |
| SrFe₀.₂Mg₀.₃O₅             | 47.3         | 1.0% NO, 3.0 g cm⁻³, 850 °C | [43]  |
| Pt/SrFe₀.₇Mg₀.₃O₃          | 56           | 1.0% NO, 3.0 g cm⁻³, 850 °C | [43]  |
| SrFe₀.₂Sr₀.₃O₃             | 42.7         | 1.0% NO, 3.0 g cm⁻³, 850 °C | [43]  |
| SrFe₀.₂Ni₀.₃O₃             | 41.6         | 1.0% NO, 3.0 g cm⁻³, 850 °C | [43]  |
| La₀.₅Ce₀.₅SrNiO/MgO        | 75           | 1.0% NO, 2.4 g cm⁻³, 800 °C | [52]  |
| LaSrMn₀.₂Ni₀.₄O₄·5         | 85           | 1.0% NO, 1.2 g cm⁻³, 850 °C | [53]  |

5. Conclusions

The regeneration of surface oxygen defects in the perovskite catalyst system is an important factor affecting the reaction; the oxygen defects in peroxide-based catalysts are more stable and easily regenerated at high temperatures. However, due to its stability, the initial activity of NO catalytic decomposition on perovskite-type oxide catalysts is also relatively high. On the other hand, because the formation of perovskite requires a high temperature and long calcination time, while the specific surface area of perovskite oxide is small, it can limit the catalytic ability of the catalyst in catalytic reactions. In general, catalysts require a relatively large specific surface area to effectively adsorb and activate the reactants. Presently, work in this area has focused on changing the composition, structure, and specific surface area of the system to obtain catalysts with high activity for NO decomposition at low temperatures. Moreover, the SO₂ resistance of perovskite-type oxides catalysts needs to be further improved.

Perovskite oxide is a promising NO removal catalyst. Its high activity and low cost make it competitive. Therefore, the search for an efficient perovskite-type catalyst is a subject of great interest. In this paper, the structure, catalytic mechanism and research status...
of perovskite oxides were reviewed, and the developmental direction of perovskite oxides was discussed. The possibility of modifying the catalyst and the method of screening the active catalyst was also indicated.

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