

Review

# Research Progress of the Selective Catalytic Reduction with NH<sub>3</sub> over ZSM-5 Zeolite Catalysts for NO<sub>x</sub> Removal

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**Abstract:** Nitrogen oxides (NO<sub>x</sub>) are very common air pollutants that are harmful to the environment and human bodies. Selective catalytic reduction with ammonia (NH<sub>3</sub>-SCR) is considered an effective means to remove NO<sub>x</sub> emissions due to its good environmental adaptability, high catalytic activity, and remarkable selectivity. In this paper, the preparation methods, types, advantages, and challenges of ZSM-5 catalysts are reviewed. Special attention is paid to the catalytic properties and influence factors of ZSM-5 catalysts for NH<sub>3</sub>-SCR. The SCR performances of ZSM-5 catalysts doped with single or multiple metal ions are also reviewed. In addition, the environmental adaptabilities (sulfur resistance, alkali resistance, water resistance, and hydrothermal stability) of ZSM-5 catalysts are discussed, and the development of ZSM-5 catalysts in denitrification is summarized.

**Keywords:** NH<sub>3</sub>-SCR; ZSM-5; catalyst; NO<sub>x</sub> removal



**Citation:** Pan, W.; He, J.; Huang, G.; Zhang, W.; Fang, D. Research Progress of the Selective Catalytic Reduction with NH<sub>3</sub> over ZSM-5 Zeolite Catalysts for NO<sub>x</sub> Removal. *Catalysts* **2023**, *13*, 1381. <https://doi.org/10.3390/catal13101381>

Academic Editor: Roman Bulánek

Received: 14 September 2023

Revised: 11 October 2023

Accepted: 14 October 2023

Published: 19 October 2023



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## 1. Introduction

### 1.1. Denitration and Its Necessity

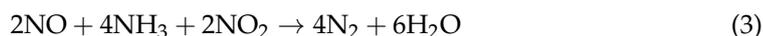
Nitrogen oxides, including nitric oxide, nitrous oxide, nitrogen dioxide, and other compounds, are very common air pollutants. They cause a series of problems such as the greenhouse effect, acid rain, acid deposition, and soil acidification, and may induce a series of diseases in humans such as cough, chest tightness, and pulmonary edema. With the improvement in people's living standards, the popularity of cars has increased, and, thus, has the emission of nitrogen oxides. In addition, the boilers that are used in most industrial installations, such as power plants and factories, are also an unavoidable source of nitrogen oxides. From the currently available "China Ecological and Environmental Statistics Annual Report 2021", the nitrogen oxide emission data obtained in 2021 in China, only within the scope of emission sources, was 9.884 million tons. In 2019, China's annual emissions of nitrogen oxides were second only to the United States, and the annual emissions have remained above the level of 10 million tons. The treatment of nitrogen oxides can prevent acid rain and the greenhouse effect, and all of society can better obtain sustainable development with a long-term solution for NO<sub>x</sub> removal [1,2].

There are many methods for treating nitrogen oxides. The emergence and maturity of denitrification make this method widely used throughout the world. Denitration technology can be divided into wet denitration (acid absorption, alkali absorption, oxidation absorption, etc.) and dry denitration (selective catalytic reduction flue gas denitration and selective non-catalytic reduction denitration). A total of 90% of the flue gas from the combustion is nitric oxide, whose nature makes it difficult to dissolve in water, so the dry denitration method receives more attention in academic and industrial circles.

## 1.2. NH<sub>3</sub>-SCR Technology

Selective catalytic reduction technology is also named SCR, and its essence is to add a reducing agent to flue gas to remove the nitrogen oxides with the help of a suitable catalyst. The catalyst can convert the nitrogen oxides into non-toxic and harmless nitrogen and water within a certain temperature range [3–6]; if the reducing agent is ammonia, the technology is named NH<sub>3</sub>-SCR. There are several advantages of SCR technology for the flue gas denitration method. Firstly, the product is non-toxic and harmless nitrogen which can be directly put into the atmosphere without subsequent recovery operations and will not cause secondary pollution. Moreover, denitration efficiency is terribly remarkable and can reach more than 85%. Secondly, the SCR technology is relatively mature and reliable in popular use.

SCR can be divided into three types according to its reaction equation, standard SCR, NO<sub>2</sub> SCR, and fast SCR. Most of the SCR catalytic reactions are based on the standard SCR reaction (1) because the ratio of NO and NO<sub>2</sub> in the exhaust is generally more than 9:1. When the concentration of NO<sub>2</sub> is larger than NO (NO<sub>2</sub>/NO ratio is more than 1), the NO<sub>2</sub> can react via the NO<sub>2</sub> SCR routes (2). The fast SCR reaction (3) involves an equimolar mixture of NO and NO<sub>2</sub> at lower temperatures, and its reaction rate is over 10 times that of the standard SCR reaction. Furthermore, the oxidation process of NO to NO<sub>2</sub> by O<sub>2</sub> is the rate-limiting step that separates standard SCR from fast SCR [7,8].



The key to SCR technology is the catalyst, and there are many kinds of catalysts for NH<sub>3</sub>-SCR. Precious metal catalysts were investigated earlier than others. Generally, platinum and palladium are used as active ingredients, and aluminum oxide, titanium oxide, and molecular sieves are used as carriers. Metal oxide catalysts are widely used at present, mostly vanadium, tungsten, cerium, manganese, iron, copper, and others. Metal oxide catalysts can promote the reaction activity of ammonia, and their denitrification rates are considerable. For molecular sieve catalysts, most of them have certain adsorption properties and exhibit excellent NH<sub>3</sub>-SCR activity and N<sub>2</sub> selectivity.

## 1.3. Classification of SCR Catalysts

In general, SCR catalysts for commercial use can be divided into several types, such as precious metal catalysts, metal oxide catalysts, metal salt catalysts, molecular sieve catalysts, and carbon-based catalysts [9–13].

### 1.3.1. Precious Metal Catalysts

The earliest SCR catalysts appeared in the 1970s, and the active ingredients were basically precious metal catalysts. Precious metal catalysts are made by dispersing small amounts of precious metals, such as Pt [14] and Ag [15], on the supports (such as TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, etc.). The denitrification efficiency of this kind of catalyst is high, but the reaction temperature needs to be accurately controlled. Due to the expensive price and limited production of precious metals, the related catalysts cannot be used widely in industry, so partial or complete replacement of the precious metals has become a major area of research.

### 1.3.2. Metal Oxide Catalysts

There are many kinds of metal oxide catalysts, such as vanadium oxides [16], manganese oxides [17], copper oxides [18], iron oxides [19], cerium oxides [20], nickel oxides, cobalt oxides, chromium oxides [6], samarium oxides [21], etc. The advantages of metal oxide catalysts are their high catalytic efficiency, good stability, strong renewable ability, and low cost. However, at the same time, they have a certain toxicity, poor selectivity, and limited service life. These disadvantages also limit their use. At present, researchers are mainly investigating the

synergistic effect of composite oxides on SCR, since the activity of catalysts with composite oxides was found to be significantly higher compared with that of single oxide catalysts.

### 1.3.3. Metal Salt Catalysts

Among the metal salt catalysts, ferric sulfate, cerium phosphate, and cupric sulfate catalysts are the main ones [22–25]. The  $\text{Fe}_2(\text{SO}_4)_3/\text{TiO}_2$  catalyst showed about 90%  $\text{NO}_x$  conversion in the temperature range between 350 and 450 °C, and was synthesized by a solid-state impregnation method [22]. Zr, Co, Mo, or Cu-doped  $\text{CePO}_4$  catalysts were prepared via the co-precipitation method for  $\text{NH}_3$ -SCR for  $\text{NO}_x$  removal. Mo-doped  $\text{CePO}_4$  catalysts exhibited about 99%  $\text{NO}_x$  conversion at 300 °C, illustrating excellent low-temperature activity,  $\text{N}_2$  selectivity, long stability, and  $\text{SO}_2$  and  $\text{H}_2\text{O}$  resistances [23]. The catalyst with a 10 wt%  $\text{CuSO}_4$  displayed excellent  $\text{NH}_3$ -SCR activity, a broad temperature window, and remarkable  $\text{SO}_2$  and  $\text{H}_2\text{O}$  tolerance, suggesting great potential for  $\text{NH}_3$ -SCR at low temperatures [24]. The 0.3 Mn-FeV catalyst showed a superior  $\text{NH}_3$ -SCR performance (100%) at 250 °C. However, the crystal size, acidity, and redox of the catalyst could be improved and the V species with higher valence states could also be obtained due to the addition of Mn [25]. Metal salt catalysts have a wide range of applications and they are not as susceptible to toxic inactivation as metal oxides.

### 1.3.4. Carbon-Based Catalysts

At present, the main research scope of carbon-based catalysts includes activated carbon [26], graphene [27], carbon nanotubes [28], and other carbon materials. Carbon-based catalysts have remarkable and beneficial properties for the  $\text{NH}_3$ -SCR process, which are large specific surface areas, developed pore structures, oxygen-containing functional groups, and good adsorption capacity. Meanwhile, carbon-based catalysts are ideal for use in industrial production because they are low-cost due to their rich storage and wide sources. However, there are some unavoidable disadvantages for carbon-based catalysts during the  $\text{NH}_3$ -SCR process, such as low strength and combustibility.

### 1.3.5. Molecular Sieve Catalysts

A molecular sieve catalyst, also known as a zeolite catalyst, is a ceramic-based catalyst made of water with alkaline ions and a porous crystalline substance of aluminum silicate in the form of a pellet or honeycomb. There are various classification methods for molecular sieve catalysts, such as 3A (potassium type A), 4A (sodium type A), 5A (calcium type A), 10Z (calcium type Z), 13Z (sodium type Z), Y (sodium type Y), sodium mercerite type, etc., according to the differences in the molecular ratio of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ . Molecular sieve catalysts demonstrate excellent  $\text{NH}_3$ -SCR performance and good hydrothermal stability, using ZSM-5, SSZ-13, SAPO, ZK-5, KFI, and CHA molecular sieves as the supports.

A molecular sieve is a kind of artificially synthesized hydrated silicoaluminate (bubble zeolite) or natural zeolite with the function of screening molecules. It has many pores with a uniform size that are neatly arranged in the structure; molecular sieves with different pore sizes can separate molecules of different sizes and shapes. A molecular sieve has the characteristics of a large specific surface area, rich pore structure, and strong stability. The thermal stability of a molecular sieve catalyst can be optimized by changing the type and proportion of added materials when constructing the core–shell structure. By controlling the content of the supported metal elements, the temperature window of the catalyst can be adjusted to achieve denitrification at different temperatures [29]. The pore size of molecular sieves with small grains is shorter than that of large-grain molecular sieves, and its pore utilization rate and catalytic activity are greatly improved [30]. The molecular sieve catalyst has good denitrification performance and  $\text{N}_2$  selectivity [31,32], but the pore size of the molecular sieve can cause certain restrictions on the diffusion of some molecules, thus affecting its pore utilization rate and catalytic performance.

In different molecular sieve catalyst systems, the active species of metal ions or oxides show different physical and chemical properties, affecting the complexity of the redox

reaction mechanism in  $\text{NH}_3$ -SCR. For Cu-based molecular sieve catalysts, the Si/Al ratio in zeolite and the metal loadings are the key factors for the distribution of active metal species, while the main active sites for the standard SCR reaction are  $\text{Cu}^{2+}$  species at low temperatures. For the standard  $\text{NH}_3$ -SCR process over a Fe/SSZ-13 catalyst, isolated  $\text{Fe}^{3+}$  species are the primary active sites at low temperatures ( $<300\text{ }^\circ\text{C}$ ) while  $[\text{HO-Fe-O-Fe-OH}]^{2+}$  species are the primary active sites at high temperatures ( $\geq 300\text{ }^\circ\text{C}$ ). NO oxidation was caused by dinuclear  $\text{Fe}^{3+}$  species and  $\text{NH}_3$  oxidation was caused by highly aggregated  $\text{Fe}_x\text{O}_y$  species [33,34]. For the  $\text{NH}_3$ -SCR process over Fe/ZSM-5 zeolites, the main active sites for standard SCR were  $\text{Fe}^{3+}$  species at the  $\alpha$  site, while the fast SCR reaction was promoted by  $\text{Fe}^{3+}$  species at the  $\beta$  sites and  $\gamma$  sites [35]. Moreover, due to the presence of rich metal species with higher value states and oxygen vacancies over the surfaces of catalysts, the oxidation of NO to  $\text{NO}_2$  can be accelerated to promote the fast SCR reaction, causing higher SCR activity at low temperatures.

Due to the high Si–Al ratio and the structurally stable five-membered ring in its skeleton, ZSM-5 zeolite has high thermal stability. Its acid resistance is also very good, so it can resist a variety of acids other than hydrofluoric acid corrosion. At the same time, ZSM-5 does not easily accumulate ash, because there is no large cavity in the ZSM-5 skeleton, limiting the formation and accumulation of large condensates. ZSM-5 has good stability in water steam while the structures of other zeolites are destroyed and irreversibly deactivated when they are subjected to water steam and heat. Therefore, the ZSM-5 molecular sieve catalyst for  $\text{NH}_3$ -SCR has been a hot topic in recent years [36,37].

## 2. Preparation Method of ZSM-5 Catalysts

### 2.1. Catalyst Prepared with the Impregnation Method

The impregnation method is a common method for the preparation of solid catalysts. For example, the Mg/ZSM-5 catalyst was prepared by impregnation [38]. The carrier ZSM-5 was placed in contact with an aqueous solution of a certain metal salt (MgX) as the carrier of the active component so the metal salt solution could be adsorbed or stored in the capillary tube of the carrier. After filtrating, drying, grinding, activation, and immersing in the solution containing the co-catalyst precursor, the catalyst was finally obtained after drying.

The principle of the impregnation method is that the active component is impregnated on the porous carrier in the form of a salt solution and permeates into the inner surface to form a high-efficiency catalyst. Most of the active components are permeated to the inner surface, and only a small number of active components are loaded on the carrier surfaces. The salt of the active component is left on the inner surface of the carrier when the water evaporates and escapes. The impregnated metal and metal oxide salts are evenly distributed in the pores of the carrier, and then the highly dispersed carrier catalyst can be obtained after heating decomposition and activation. The specific surface, pore size, and strength of the molecular sieve play a significant role in the properties of catalysts [39], and different active components can also affect the properties of catalysts. For example, Ebrahim Mohiuddin et al. [40] found that the total acidity of Fe-ZSM-5 was higher than that of Cr-ZSM-5, which improved the selectivity of the catalyst.

Impregnation methods are mainly divided into four kinds, namely, excessive impregnation, equal amount overflow, multiple impregnation, and impregnation precipitation methods. Ricardo H. Gil-Horan et al. [41] used multiple impregnation methods to reduce the interference between different components when preparing P, Fe, and Ni-reinforced ZSM-5 zeolite catalysts. Compared with the excessive impregnation method, the impregnation solution enters the void of the carrier with the impregnation precipitation method, and the precipitating agent is added to precipitate the active component on the inner hole and surface of the carrier.

Impregnation methods do not require special equipment and complex processes, reducing the preparation cost and preparation difficulty. By adjusting the concentration of the solution, impregnation time, and temperature, the morphology, size, and distribution

of catalyst particles can be accurately controlled. However, the impregnation method does not easily form a uniform distribution for large-scale production.

### 2.2. Catalyst Prepared with the Ion Exchange Method

Since most of the cations that need to be exchanged can exist in the cation (simple or complex) state in an aqueous solution, the aqueous ion exchange method is commonly used. When the pH value of an aqueous solution is adjusted to the extent that the crystal structure of the molecular sieve cannot be destroyed and the molecular sieve contacts an aqueous solution of a metal salt, the metal cation in the aqueous solution will exchange with the original cation of the molecular sieve (usually sodium ions), and the anionic skeleton of the molecular sieve will be recombined. For example, a Fe-ZSM-5 catalyst was prepared with the aqueous solution exchange method by Yu Shen et al. [42]. The  $\text{Fe}^{3+}$  in ferric chloride hexahydrate is exchanged with the  $\text{Na}^+$  ions in a molecular sieve to obtain the catalyst. If a higher degree of exchange is required in the ion exchange process, intermittent multiple exchange methods or continuous exchange methods could be used.

The multiple exchange method filters and washes the molecular sieve after the first exchange. Then, the above molecular sieve is treated with a second exchange, filtration, and washing. Moreover, the above steps are repeated until the exchange degree reaches the desired requirements. For multiple exchanges, the exchange degree and exchange rate can be improved by alternating ion exchange and high-temperature roasting. A variety of cations can be exchanged into molecular sieves at the same time, and the molecular sieve after the exchange often has better properties. The ratio of each cation exchange capacity can be better controlled by using the mixed solution or by successive exchanges, according to the strength of the selectivity for various cation exchanges.

Regarding molten salt solution technology, the interference of the solvent effect can be eliminated. Molten salts with high ionization, such as alkali metal halides, sulfates, or nitrates, can be used to provide a cation exchange molten salt solution, but the melting point of the molten salt solution must be lower than the destruction temperature of the zeolite molecular sieve structure. According to a previous study, Houda Jouini prepared Fe-Cu-ZSM-5 from CuCl molten salt [43]. In addition to the cation exchange reaction in the molten salt solution, there were some salts contained in the molecular sieve cage, causing the special properties of zeolites. At the same time, external assistance (such as microwaves) could also promote ion exchange. Somayeh Taghavi [44] heated a mixture of copper chloride and zeolite in a microwave oven with a power of 700 W (about 235 °C) for 10 min to assist the molten salt exchange to produce Cu-ZSM-5.

Some salts can be sublimed into a gas at low temperatures, and the ion exchange of zeolites can be carried out in this gaseous environment. For example, ammonium chloride is sublimed into gas at 300 °C, and  $\text{Na}^+$  in a molecular sieve can be exchanged with ammonium chloride vapor. Cuprous chloride can also sublime above 300 °C, and the non-skeleton cation of the molecular sieve can exchange with it to overcome its insolubility in water and instability in aqueous solution.

No special equipment is required for the preparation of the ion exchange method, so the production cost is relatively low. The preparation process is simple, and the operation is convenient. However, the service life of the prepared catalyst is relatively short, and it needs to be replaced frequently. At the same time, its stability is poor, and it is easily affected by environmental conditions and operating factors, which leads to the decline of its catalytic efficiency.

### 2.3. Catalyst Prepared with the Chemical Vapor Deposition Method

Chemical vapor deposition (CVD) uses gaseous or vapor substances to react at the gas phase or gas–solid interface to form solid deposits. For example, a manganese (II) acetylacetonate precursor was used to deposit manganese oxide on a clay-bonded SiC support by an aerosol-assisted metal–organic chemical vapor deposition (AA-MOCVD) technique [45]. The preparation process of chemical vapor deposition is mainly divided into three steps.

First, the reaction gas is diffused on the surface of the body. Second, the reaction gas is adsorbed on the surface of the matrix. Finally, the solid sediment and gaseous by-products formed on the surface of the matrix are separated from the surface of the matrix.

The advantages of CVD are that a smooth deposition on the surface can be obtained, the mean free path of molecules (atoms) is relatively larger, and the spatial distribution of molecules is more uniform. For example, Milad Rasouli introduced ZnO into the HZSM-5 molecular sieve by chemical vapor deposition in their experiment [46]. In addition, it has excellent product performance, but there are some problems of pollution and insufficient precision.

#### 2.4. Catalyst Prepared with the Sublimation Method

Under a certain atmospheric pressure, the vapor pressure of a solid substance is equal to the external pressure, and sublimation occurs not only on the surface of the solid but also in its interior. In related studies, El-Malki et al. [47] sublimed volatile compounds onto HZSM-5 to produce Z/ZSM-5 molecular sieve catalysts with Ga, Fe, and Zn. In addition, the catalytic activity and durability of the Fe/ZSM-5 catalyst prepared by Haiying Chen in a water-rich environment were promoted by sublimation [48]. The advantage of the sublimation method is that it does not use a solvent and the product purity is high. Its disadvantage is that the product loss is larger, and it is generally used for the preparation of a small number of catalysts.

#### 2.5. Catalyst Prepared with the Hydrothermal Method

The hydrothermal method is adopted to prepare materials in a sealed pressure vessel after a powder is dissolved and recrystallized with water as a solvent. A certain form of the precursor is put into an autoclaved aqueous solution, a hydrothermal reaction under high-temperature and high-pressure conditions is performed, and then separation, washing, drying, and other operations are carried out.

The advantage of the hydrothermal method is that the powder prepared with it has complete grain development, a small particle size, and uniform distribution, and it is convenient to design and characterize its stoichiometry and crystal type. However, it usually depends on the equipment because the hydrothermal method requires high temperature and high pressure. At present, some researchers have synthesized ZSM-5 composite membranes by the hydrothermal method [49].

In short, the hydrothermal method can promote the growth of crystals. The catalyst that is prepared by this method has a smaller crystal size and its catalytic activity is very high. Meanwhile, a wide variety of catalysts can be synthesized. However, the reaction rate is slow and there are high temperature and high pressure steps, and a high-precision reactor is needed to ensure that the reaction conditions are well controlled.

According to the above information, ZSM-5 catalysts can be prepared with the impregnation method, ion exchange method, chemical vapor deposition method, sublimation method, hydrothermal method, and so on. The preparation method can have a significant effect on the surface enrichment of active compositions, BET surface area, uniform distribution, acid sites, redox properties, and so on. Therefore, NO conversions especially are dependent on the preparation methods for ZSM-5 catalysts. Among them, the catalysts that are prepared by the impregnation method and ion exchange method have a low cost. The product with the sublimation method has higher purity, but the method is only suitable for the preparation of a small number of catalysts. The quality of the product that is produced by the chemical vapor deposition method is low and the product that is prepared by the hydrothermal method has good SCR performance, but the cost is high.

### 3. Effect of Single Metal Ion on ZSM-5 Catalysts

#### 3.1. ZSM-5-Cu Catalysts

Marzieh Hamidzadeh et al. proved that the hydrothermal impregnation of copper chloride and nitrate on HZSM-5 enhanced its denitrification catalytic activity, although this method could cause the loss of zeolite skeleton. The Cu (Cl)/ZSM-5 catalyst had the



role in the SCR activity of Fe-ZSM-5, and the Fe-oxo-related Lewis sites were important for the low-temperature SCR reaction. Compared to the dimeric  $[\text{OH-Fe-O-Fe-OH}]^{2+}$ , the isolated  $\text{Fe}^{3+}$  species in Fe-ZSM-5 were shown more active during the SCR process at a middle temperature of 500 °C.

According to Wang's research [54], a series of Fe/ZSM-5 catalysts with different iron contents via the impregnation method were prepared to study the effect of iron loading on the performance and structure of the Fe/ZSM-5 catalyst for  $\text{NH}_3$ -SCR of NO. The optimal loading capacity of the Fe active component was 10 wt%. In the experiment, the activities of other catalyst samples under different temperatures were characterized. When the temperature increased from 350 to 450 °C, the conversion rate of the 10 wt% Fe/ZSM-5 catalyst was more than 80% and reached the highest conversion rate (96.91%) at 431 °C. The crystallization of ZSM-5 was not affected by the Fe contents. The more dispersed nanoparticles as active components on the surface of the carrier, the more favorable the  $\text{NH}_3$ -SCR reaction was. The redox performance of the 10 wt% Fe/ZSM-5 catalyst was significant. More  $\text{Fe}^{3+}$  species and easier formation of Lewis acid sites could improve the conversion efficiency of  $\text{NO}_x$ .

### 3.3. ZSM-5-Co Catalysts

Marzieh Hamidzadeh proved that the hydrothermal impregnation of cobalt chloride and nitrate on HZSM-5 enhanced its denitrification catalytic activity. The Co (Cl)/ZSM-5 catalyst showed the highest activity around 300 °C [50]. However, the related research is very limited since many previous works focus on the NO-SCR reaction over Co-containing H-ZSM-5 catalysts with a  $\text{C}_x\text{H}_y$  reductant instead of  $\text{NH}_3$  [55].

### 3.4. ZSM-5-Mn Catalysts

Most Mn in Mn/ZSM-5 exists in the form of oxides. Mn/ZSM-5 molecular sieve catalysts were prepared by Xue Hongyan's team with the impregnation method [56]. Below 200 °C, the conversion of  $\text{NH}_3$  with the Mn/ZSM-5 catalyst is negligible. The conversion rates of  $\text{NH}_3$  on the Mn/ZSM-5 catalyst increase sharply in the range of 250–300 °C, reaching almost 100% at 300 °C. In Xiao's research [57], he found that the Mn/ZSM-5 catalyst had weak sulfur resistance. The addition of Fe significantly improved the conversion rate of  $\text{SO}_2$ - $\text{SO}_3$ , and the presence of appropriate Fe promoted the formation of  $\text{SO}_3$  and enhanced the conversion of  $\text{NO}_x$ .

As shown in Figure 3, this work reveals the relationship between the location of  $\text{MnO}_x$  nanoparticles and the SCR properties, which can provide a new idea for designing low-temperature zeolite catalysts.  $\text{MnO}_x$ -ZSM-5 catalysts with different  $\text{MnO}_x$  loadings were explored for the  $\text{NH}_3$ -SCR reaction. The catalyst exhibited superior low-temperature SCR activity when  $\text{MnO}_x$  was dispersed on the outer surface of ZSM-5. Thus, the confinement effect could influence the redox properties of the catalysts [58].

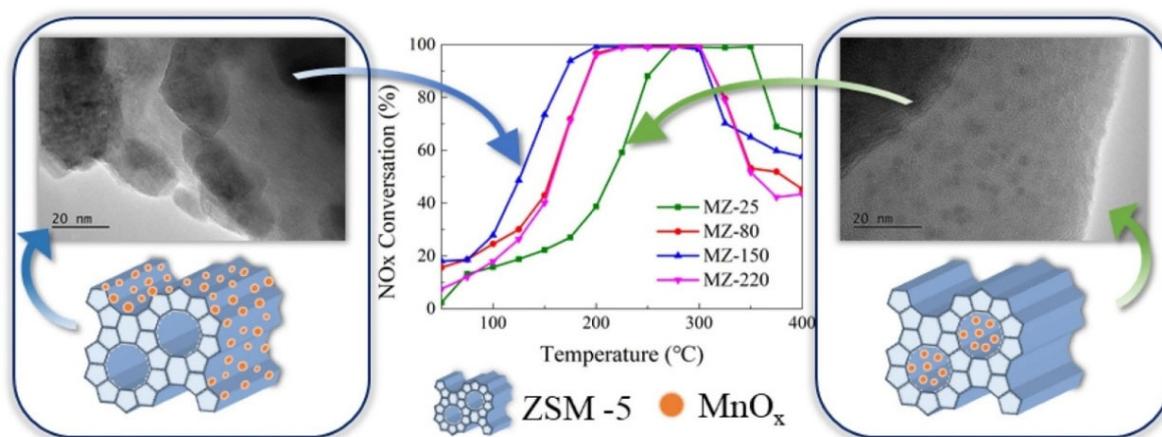


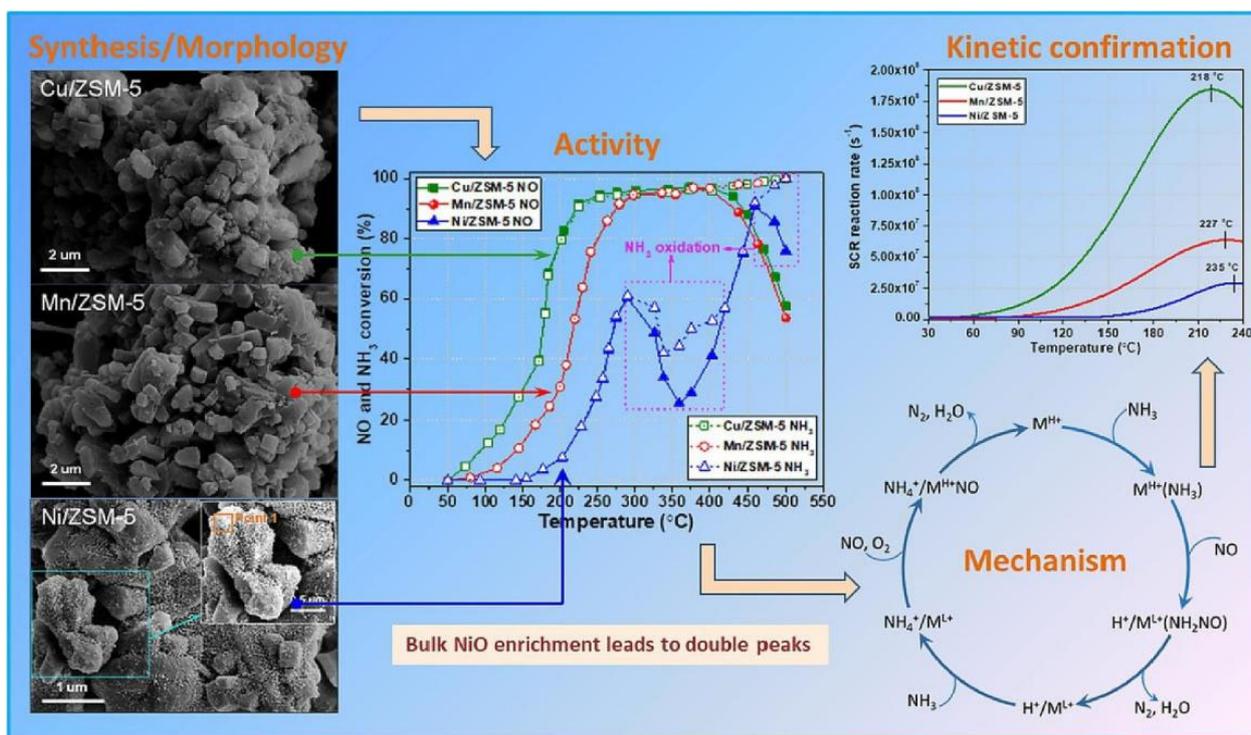
Figure 3. ZSM-5 catalyst with a superior low-temperature SCR activity [58].

### 3.5. ZSM-5-Ni Catalysts

The Ni in Ni/ZSM-5 exists in the form of NiO crystals (3–50 nm) and charge-compensated Ni<sup>2+</sup> cations. After the introduction of Ni by the initial wet impregnation method, Vu's team [59] largely preserved the structure and texture properties of ZSM-5. It was pointed out that the ZSM-5 molecular sieve functionalized with cheap and abundant transition metal Ni (Ni/ZSM-5) was a highly active and cost-effective catalyst. In addition, the excellent (water) thermal stability under harsh operating conditions (e.g., temperature up to 873 K and pressure up to 60 bar) made this silicon-rich zeolite bifocal catalyst more attractive, especially for industrially relevant gas applications.

According to Marzieh Hamidzadeh's study [50], Ni-ZSM5 catalysts were prepared with the hydrothermal impregnation method, using nickel chloride and nitrate as the precursors. The catalyst prepared with the chloride precursor system showed higher activity and higher metal dispersion. However, compared with nickel, copper and cobalt improved the conversion rate of SCR reaction more significantly.

As shown in Figure 4, double active sites are verified by redox ability: Cu/ZSM-5 > Mn/ZSM-5 > Ni/ZSM-5. Copper, manganese, and nickel were introduced into H/ZSM-5 zeolites with the incipient wetness impregnation method. The modified catalysts were evaluated for the NH<sub>3</sub>-SCR of nitric oxides, suggesting that the NH<sub>3</sub>-SCR route over catalysts was through the Langmuir–Hinshelwood mechanism. Metal clusters and bulk oxides were the active sites used to adsorb NO and NH<sub>3</sub> was adsorbed on the acid sites. Nonselective NH<sub>3</sub> oxidation at higher temperatures appeared at higher temperatures due to the double active sites [60].



**Figure 4.** Copper, manganese, and nickel/ZSM-5 catalytic mechanisms for nitric oxide selective reduction with ammonia [60].

According to Table 1, it can be seen that the molecular sieve catalysts Cu(Cl)/ZSM-5, Cu-ZSM-5, Co(Cl)/ZSM-5, Mn/ZSM-5, MnO<sub>x</sub>-ZSM-5, Cu(Cl)/ZSM-5, CO (Cl)/ZSM-5, and MnO<sub>x</sub>-ZSM-5 can achieve a catalytic efficiency of 90% at a low temperature (<300 °C). The Ni(Cl)/ZSM-5 molecular sieve catalyst requires a relatively high reaction temperature (>300 °C) for catalysis, but its conversion is slightly lower than that of other catalysts

at lower temperatures. Meanwhile, the distribution and species of metal elements play important roles in the SCR reaction and NO<sub>x</sub> removal.

**Table 1.** The effect of single metal ions on the performances of ZSM-5 catalysts.

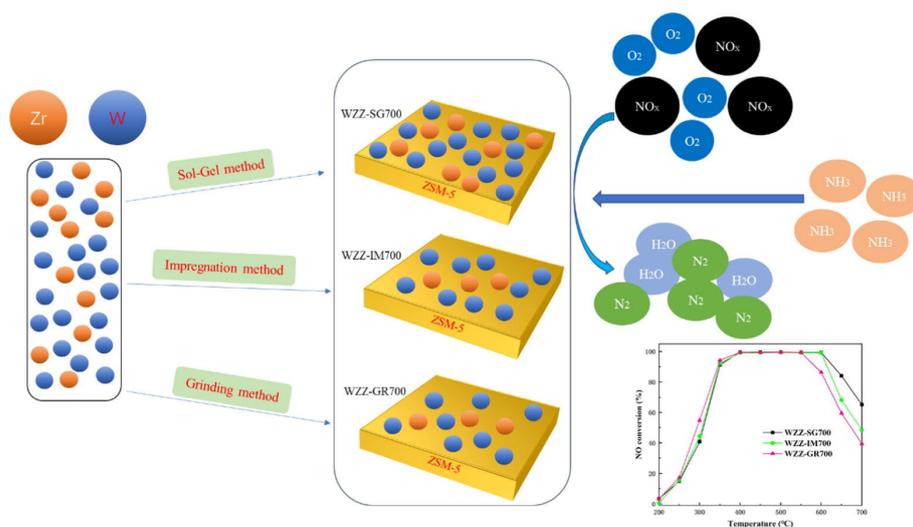
Catalysts	Method	Conditions	Conversion	Ref.
Cu(Cl)/ZSM-5	hydrothermal impregnation method	[NO] = [NH <sub>3</sub> ] = 350 ppm, [O <sub>2</sub> ] = 2.6%, GHSV = 30,000 h <sup>-1</sup>	>90% (300 °C)	[50]
Cu-ZSM-5	polymer-assisted deposition method	[NO] = [NH <sub>3</sub> ] = 600 ppm, [O <sub>2</sub> ] = 5%, GHSV = 45,000 h <sup>-1</sup>	>90% (240–390 °C)	[51]
Fe-ZSM-5	wet incipient impregnation method	[NO] = [NH <sub>3</sub> ] = 500 ppm, [O <sub>2</sub> ] = 8%, GHSV = 50,000 h <sup>-1</sup>	>80% (425–680 °C)	[52]
Fe-ZSM-5	ion exchange method	[NO] = [NH <sub>3</sub> ] = 500 ppm, [O <sub>2</sub> ] = 8%, GHSV = 50,000 h <sup>-1</sup>	>90% (550 °C)	[53]
Fe/ZSM-5	impregnation method	[NO] = [NH <sub>3</sub> ] = 3%, [O <sub>2</sub> ] = 21%, GHSV = 24,000 h <sup>-1</sup>	96.91% (431 °C)	[54]
Co(Cl)/ZSM-5	hydrothermal impregnation	[NO] = [NH <sub>3</sub> ] = 350 ppm, [O <sub>2</sub> ] = 2.6%, GHSV = 30,000 h <sup>-1</sup>	>90% (300 °C)	[50]
Mn/ZSM-5	Mn (NO) impregnation method	[NO] = [NH <sub>3</sub> ] = 500 ppm, [O <sub>2</sub> ] = 5.0%, GHSV = 80,000 h <sup>-1</sup>	>90% (250 °C)	[55]
MnO <sub>x</sub> -ZSM-5	impregnation method T = 150 °C	[NO] = [NH <sub>3</sub> ] = 500 ppm, [O <sub>2</sub> ] = 4%, GHSV = 30,000 h <sup>-1</sup>	>80% (157–315 °C)	[58]
Ni/ZSM-5	incipient wetness impregnation method	[NO] = [NH <sub>3</sub> ] = 500 ppm, [O <sub>2</sub> ] = 5%	90.9% (460 °C)	[60]
Ni(Cl)/ZSM-5	hydrothermal impregnation	[NO] = [NH <sub>3</sub> ] = 350 ppm, [O <sub>2</sub> ] = 2.6%, GHSV = 30,000 h <sup>-1</sup>	>80% (400 °C)	[50]

Ordinary ZSM-5 catalysts cannot meet the needs of denitration in all environments, which is why scholars have repeatedly studied the significance of introducing different metal cations to ZSM-5 catalysts. The introduction of Cu and Co can enhance the denitrification activity over 300 °C. Fe enhances the redox capacity of the catalyst and obtains the maximum conversion rate of nitrogen oxides over 400 °C, Mn expands the range of applications due to its remarkably low temperature (below 300 °C) SCR activity, and the Ni-ZSM-5 catalyst shows excellent SCR activity over 400 °C. Moreover, Fe and Ce can enhance sulfur resistance. Sometimes, adding a single metal ion is not enough to meet the complex conditions of realistic denitrification, so it is necessary to study the effect of multiple metal ions on the performance of a ZSM-5 catalyst.

#### 4. Effect of Multiple Metal Ions on ZSM-5 Catalysts

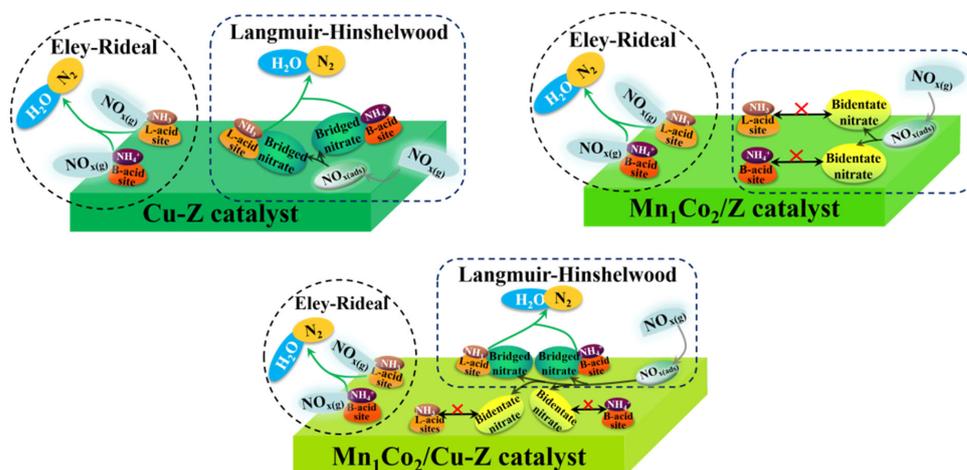
Houda Jouini's team [43] utilized the solid-state ion exchange method to prepare Ce-Fe-Cu-ZSM-5 and Fe-Cu-ZSM-5 catalysts. The Fe-Cu-ZSM-5 catalytic system demonstrated its efficiency in NO<sub>x</sub> emission reduction at a wide temperature window (180 °C–550 °C). The addition of cerium promoted the oxygen transport capacity, and the combination of the three significantly enhanced the low-temperature SCR activity. Cerium, acting as an oxygen storage promoter, facilitated the oxidation of NO to NO<sub>2</sub>, which was a crucial step in NH<sub>3</sub>-SCR. While reducing NO emissions in the presence of O<sub>2</sub>, it also facilitated the oxidation of ammonia. Therefore, the addition of cerium promoted the catalyst's activity at high temperatures.

Furthermore, the catalyst (WZZ-SG700) that was prepared by the sol-gel method had a higher surface enrichment when compared with the impregnation method and grinding method methods, illustrating the highest NO conversion (as shown in Figure 5) [61]. The SCR performance at high temperatures was improved by its remarkable surface acidity and redox property due to the significant interaction between WO<sub>3</sub> and ZrO<sub>2</sub>. Meanwhile, the high resistance against SO<sub>2</sub> and H<sub>2</sub>O and high N<sub>2</sub> selectivity were enhanced for the WZZ-SG700 catalyst. The main reaction intermediates of monodentate nitrite, ad-NO<sub>2</sub> species, NH<sub>4</sub><sup>+</sup>, surface-adsorbed NH<sub>3</sub>, and amide (-NH<sub>2</sub>) were found during the reaction by the in situ DRIFTS tests.



**Figure 5.** The high activity of  $\text{NH}_3$ -SCR at high temperatures compared to W-Zr/ZSM-5 [61].

As shown in Figure 6, Xue's team [62] employed a combination of ion exchange and impregnation methods to prepare a series of  $\text{MnCo}/\text{Cu-ZSM-5}$  ( $\text{MnCo}/\text{Cu-Z}$ ) catalysts with varying Mn/Co ratios for the  $\text{NH}_3$  selective catalytic reduction of  $\text{NO}$ . It was found that the reason for the increase in SCR activity over the  $\text{MnCo}$  catalyst was the improvement of the high-price metal ions on the catalyst surface and the reduction of metal oxides. Below  $200^\circ\text{C}$ ,  $\text{MnCo}/\text{Cu-Z}$  catalysts exhibited higher  $\text{NH}_3$ -SCR activity for  $\text{NO}_x$  compared to  $\text{Cu-Z}$  catalysts, with the highest activity observed for  $\text{Mn}_1\text{Co}_2/\text{Cu-Z}$  catalysts.



**Figure 6.** Proposed reaction mechanism of the  $\text{NH}_3$ -SCR of  $\text{NO}_x$  compared to  $\text{Cu-Z}$ ,  $\text{Mn}_1\text{Co}_2/\text{Z}$ , and  $\text{Mn}_1\text{Co}_2/\text{Cu-Z}$  catalysts at  $150^\circ\text{C}$  [62].

ZSM-5 with Co and Mn was prepared by Zhang's team with the co-precipitation method and they tested their catalysts for the low-temperature  $\text{NH}_3$  selective catalytic reduction of  $\text{NO}_x$ . The optimal catalyst was found to be 5 wt% Co 10 wt% Mn/ZSM-5(2), showing a high  $\text{NO}_x$  conversion (98.8%) and  $\text{N}_2$  selectivity (90.7%) at  $150^\circ\text{C}$  [63].

Wen's team [64] proposed a four-step catalytic mechanism for SCR and fast SCR using Mn/Co-Al/Ce-doped ZSM-5 and conducted a detailed study on the catalytic mechanism using quantum chemical methods. It was concluded that when Ce/Al was doped into ZSM5-Mn/Co and replaced the active center Si, the activation energy for fast SCR was further reduced to about 40–60 kJ/mol. The catalysts for SCR and fast SCR were not only related to the supported transition metals such as Mn and Co but also highly correlated with active centers such as Al and Ce.

As shown in Figure 7, Wentao Mu [65] discovered that the Fe content and metal ion ratio of Fe-Mn/ZSM-5 catalysts must be suitable for optimal catalytic performance at low temperatures. A series of catalysts (Fe-Mn/ZSM-10) were prepared with a different iron content and constant manganese content (5 wt%) by conventional co-precipitation. The addition of Fe may bring about a strong synergistic effect between Fe and Mn to produce a bimetallic active site and establish a multifunctional electron transfer bridge to improve the catalytic performance of Fe-Mn/ZSM-5 catalyst. However, the bridge transfer rate depends on the relative contents of iron and manganese ions, so the content of Fe should be moderate.

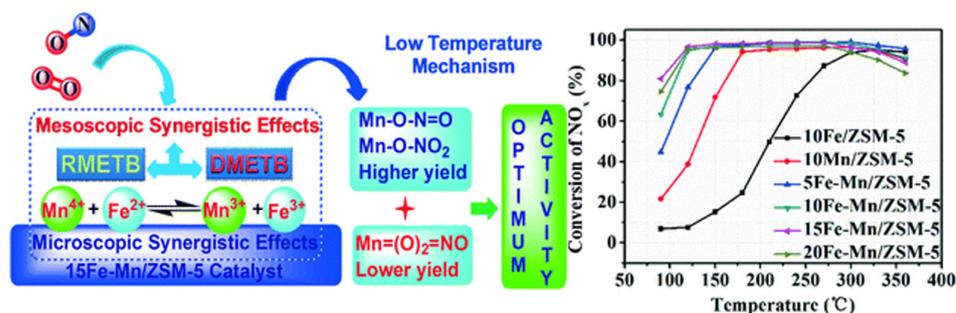


Figure 7. Fe-Mn/ZSM-5 catalyst for the  $\text{NH}_3$ -SCR of  $\text{NO}_x$  at low temperatures [65].

The effects of different La loadings on Ce-Cu/ZSM-5 catalysts were investigated, and their performances on the  $\text{NH}_3$ -SCR of  $\text{NO}_x$  were evaluated. The Ce-Cu/ZSM-5 catalyst doped with 2 wt% La illustrated the best  $\text{NH}_3$ -SCR performance at 200–500 °C, suggesting the promotion of La doping. The redox cycle between Cu and Ce could promote the oxidation of NO, resulting in a “Fast SCR”. The surface acidic and redox properties could be improved by the addition of La, causing an increase in  $\text{NH}_3$ -SCR performance [66]. The related results are shown in Figure 8.

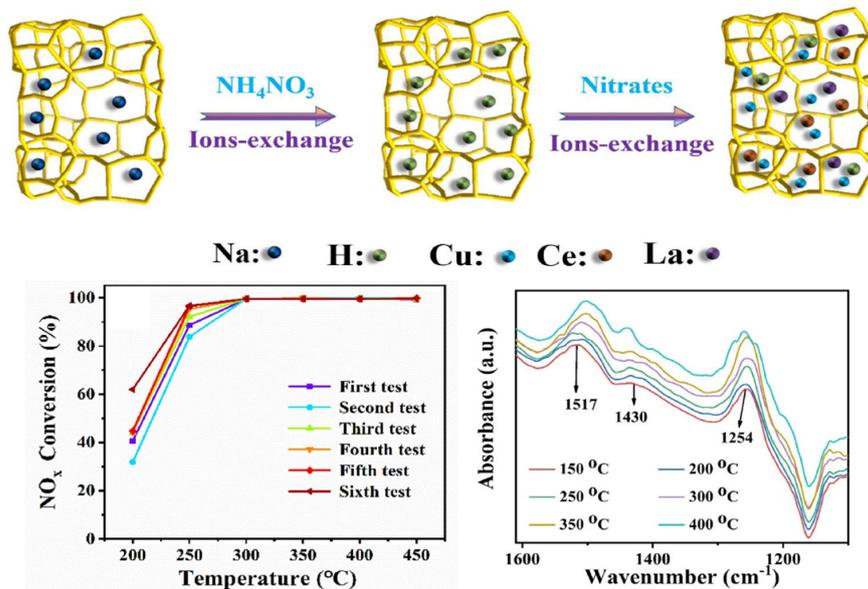


Figure 8. Effect of the V, Cu, and Ce-loading on the simultaneous removal of  $\text{SO}_2$  and NO [66].

Ma’s team [67] investigated the structure and physicochemical properties of Mn-Ce species-loaded mesoporous ZSM-5 (MZ) for the selective catalytic reduction of NO with ammonia. Compared to traditional ZSM-5 and SBA-15, Cu-Ce/MZ exhibited numerous mesopores and more accessible active sites, facilitating diffusion and improving the internal mass transfer during the denitrification process. Cu-Ce/MZ displayed a high NO conversion of 55.9% at

150 °C. At 200 °C, the Cu-Ce/MZ catalyst showed higher activity than Cu-Ce/ZSM-5 and Cu-Ce/SBA-15 for fast SCR, maintaining NO<sub>x</sub> conversion rates of about 92.7%.

According to Xue's study [68], Ca/ZrCu/ZSM-5 catalysts were synthesized with different Zr contents using the initial wet impregnation method. It was concluded that the addition of Zr enhanced the resistance of Cu/ZSM-5 catalysts to calcium poisoning during the SCR process. Additionally, the acidity of Ca/Cu/ZSM-5 did not change significantly after the addition of Zr. The optimal Zr content was found to be 0.10%, resulting in the highest catalytic activity.

MnO<sub>x</sub>-CeO<sub>2</sub>/ZSM-5 catalysts were prepared by Yang's team [69] with the impregnation method. Compared to MnO<sub>x</sub>/ZSM-5, the catalytic performances for the fast SCR reaction and NO oxidation were significantly improved with the addition of CeO<sub>2</sub>. The doping of CeO<sub>2</sub> facilitated the absorption and oxidation of NO and therefore promoted the conversion of NO to NO<sub>2</sub>. MnCe(0.39)/ZSM-5 exhibited the best performance, maintaining fast SCR NO<sub>x</sub> conversion rates above 95% within the temperature range of 150–350 °C. The NO<sub>x</sub> conversion reached 95.4% at 150 °C.

As mentioned above, the introduction of a single metal cation greatly improves the SCR performance of a catalyst. The complex reality often requires all aspects of the properties of the catalyst, and the introduction of multiple ions will improve the many catalytic properties of the catalysts. According to Table 2, it is common to introduce two or more ions into catalysts, such as Ce, Fe, Cu, Mo, La, Zr, W, and Mn, and the impregnation method and ion exchange method are commonly used for their preparation. Fe-Mn/ZSM-5, 5% Co 10% Mn/ZSM-5, Cu-ZSM-5 with Mn-Co, Fe-Mn/ZSM-5, CuCe-La/ZSM-5, Cu-Ce/ZSM-5, Ca/ZrCu/ZSM-5, MnO<sub>x</sub>-CeO<sub>2</sub>/ZSM-5, and K<sub>0.5</sub>/Cu/ZSM-5 showed high activity at low temperature (<300 °C), while (W-Zr-ZSM-5 (WZZ)), W-Zr-ZSM-5 (WZZ), K<sub>0.5</sub>/Cu/ZSM-5 (WZZ), and Ce-Fe-Cu-ZSM-5 showed better catalytic performance at high temperatures (>300 °C). The temperature window is not only an important issue to be considered in the laboratory stage, but also a remarkable factor from the perspective of energy consumption and economy. Moreover, the interaction of multiple ions over the ZSM-5 catalysts usually can change the catalytic active sites and active centers, generating active species. Fe and Mn enhance redox properties, Mn and Ce improve redox activity, Cu and Ce exhibit numerous mesopores and more accessible active sites, and WO<sub>3</sub> and ZrO<sub>2</sub> improve remarkable surface acidity and redox properties.

**Table 2.** Multiple metal ions on the performances of ZSM-5 catalysts.

Catalysts	Method	Conditions	Conversion	Ref.
Ce-Fe-Cu-ZSM-5	solid-state ion exchange method	[NO] = [NH <sub>3</sub> ] = 1000 ppm, [O <sub>2</sub> ] = 8%, GHSV = 333,333 h <sup>-1</sup>	63% (550 °C)	[43]
Fe-Cu-ZSM-5	solid-state ion exchange method	[NO] = [NH <sub>3</sub> ] = 1000 ppm, [O <sub>2</sub> ] = 8%, GHSV = 333,333 h <sup>-1</sup>	72% (550 °C)	[43]
Fe-Mn/ZSM-5	wet impregnation method	[NO <sub>2</sub> ] = [NO] = 250 ppm, [O <sub>2</sub> ] = 5%, GHSV = 37,500 h <sup>-1</sup>	99.44% (250 °C)	[57]
W-Zr-ZSM-5 (WZZ)	sol-gel method, impregnation method, and grinding method	[NO <sub>x</sub> ] = [NH <sub>3</sub> ] = 500 ppm, [O <sub>2</sub> ] = 5% GHSV = 15,000 h <sup>-1</sup>	>90% (300–650 °C)	[61]
Cu-ZSM-5 with Mn-Co	ion-exchange technique	[NO <sub>x</sub> ] = [NH <sub>3</sub> ] = 500 ppm, [O <sub>2</sub> ] = 5%	>90% (185–470 °C)	[62]
5%Co10%Mn/ZSM-5	impregnation method	[NO <sub>x</sub> ] = [NH <sub>3</sub> ] = 500 ppm, [O <sub>2</sub> ] = 5%	98.8% (150 °C)	[63]
Fe-Mn/ZSM-5	conventional co-precipitation method	[NO <sub>x</sub> ] = [NH <sub>3</sub> ] = 600 ppm, [O <sub>2</sub> ] = 5%	100% (90 °C)	[65]
CuCe-La/ZSM-5	ion exchange method	[NO] = [NH <sub>3</sub> ] = 500 ppm, [O <sub>2</sub> ] = 5%, GHSV = 17,000 h <sup>-1</sup>	99.5% (300 °C)	[66]
Cu-Ce/ZSM-5	ion exchange method	[NO] = [NH <sub>3</sub> ] = 500 ppm, [O <sub>2</sub> ] = 5%	>92.7% (200 °C)	[67]
Ca/ZrCu/ZSM-5	impregnation method	[NO] = [NH <sub>3</sub> ] = 500 ppm, [O <sub>2</sub> ] = 5%, GHSV = 80,000 h <sup>-1</sup>	>90% (200–250 °C)	[68]
MnO <sub>x</sub> -CeO <sub>2</sub> /ZSM-5	impregnation method	[NO] = [NO <sub>2</sub> ] = 500 ppm, [NH <sub>3</sub> ] = 1000 ppm, [O <sub>2</sub> ] = 3%, GHSV = 30,000 h <sup>-1</sup>	95.4% (150 °C)	[69]
K <sub>0.5</sub> /Cu/ZSM-5	impregnation method	[NO] = [NH <sub>3</sub> ] = 500 ppm, [O <sub>2</sub> ] = 5%, 80,000 mL/g-h	>90% (200–250 °C)	[70]

## 5. Environmental Adaptability and Future Prospect of ZSM-5 Catalyst

### 5.1. Sulfur Resistance

The sulfur resistance of a catalyst refers to its ability to maintain high denitrification activity in the presence of sulfides (such as hydrogen sulfide or sulfur oxides). The toxicity mechanism of  $\text{SO}_2$  on catalysts can be divided into three ways. The first way is that the competitive adsorption between  $\text{SO}_2$  and reactants ( $\text{NO}$  and  $\text{NH}_3$ ) reduces the adsorption sites, causing poor SC activity. The second way is that the formation of  $\text{SO}_3$  from  $\text{SO}_2$  reacts with  $\text{NH}_3$  to generate the ammonium sulfate salt, covering the active sites. The third way is that the active metal species are consumed by  $\text{SO}_2$  to form metal sulfates or sulfites, reducing the reducibility of metal ions.

ZSM-5 is a commonly used catalyst with excellent denitrification properties. This kind of catalyst illustrates remarkable sulfur resistance due to its special distribution and species of metal ions and its characteristic pore structures. Moreover, the introduction of other specific metal ions or oxides can enhance the sulfur resistance of ZSM-5 [71–73]. Improving the sulfur resistance can prolong the service life of a catalyst by slowing down the reaction between the sulfide and the active site on the catalyst surface. It can also reduce the adsorption of sulfide and improve the selective removal efficiency of the catalyst for nitrogen oxides. The adsorption of sulfide is then reduced and the selective removal efficiency of nitrogen oxides is improved. Wang [54] discovered that Fe-ZSM-5 catalysts with different iron contents exhibited high catalytic activity in SCR, along with good sulfur and water resistance.

### 5.2. Alkali Resistance

Fuel and lubricant additives may contain a large amount of alkali metals, and their deposition could significantly reduce the performance of SCR catalysts. Alkaline substances will competitively adsorb on the active site of ZSM-5, causing the active site to be blocked and reducing the denitrification performance. If ZSM-5 has good alkaline resistance, it can reduce the blocking of the active site, improve the selective removal efficiency of the catalyst for nitrogen oxides, slow down the alkali vapor deactivation rate of the catalyst, and extend the service life of the catalyst.

Hongyan Xue and his team [70] found that the introduction of potassium reduced the exposure of active CuO on ZSM-5. To some extent, it inhibited the adsorption of  $\text{NH}_3$  and  $\text{NO}_x$ , reduced the formation of active bridging nitrates, and promoted the formation of inactive bidentate nitrates. As shown in Figure 9, the alkali metal deposition on the SCR catalyst reduces the specific surface area and pore volume of the catalyst, destroys the active site on the catalyst surface, and eventually leads to catalyst poisoning [74]. The alkali metal compounds present in the exhaust gases of diesel vehicles and certain factories after dust removal could severely poison Fe-Cu-ZSM-5 catalysts and affect their activity [75]. Characterization results revealed that the introduction of alkali metals did not decrease the crystallinity and textural properties (specific surface area and pore volume) of the parent molecular sieve. On the contrary, it induced new mesoporosity in ZSM-5 materials. By comparing the pore size distributions (PSD) of the fresh and alkali-treated catalysts obtained by adsorption branches, the pore size distributions were found to be relatively wide in the poisoned samples.

Meanwhile, the doping of other metal elements, rational design of catalyst structures, and effective use of catalyst supports can effectively improve the anti-poisoning ability of SCR catalysts. Water washing, pickling, and electrophoresis treatment are some common methods for alkaline poisoning catalyst regeneration.



**Figure 9.** Schematic diagram of the poisoning mechanism of alkali metals on different SCR catalysts [74].

### 5.3. Water Resistance

Water will competitively adsorb on the active site of ZSM-5, causing the active site to be blocked, thus reducing the denitrification performance. If ZSM-5 has good water resistance, it can reduce the blocking of the active site, improve the selectivity, slow down the hydrothermal deactivation rate of the catalyst, and extend the service life of the catalyst. Guiying Xu and his team [76] focused on the study of different active metals and carriers on the water resistance and sulfur resistance of Mn-based catalysts and proposed that the different physical and chemical properties of different carriers have a certain impact on the performance of catalysts; so, selecting the right carrier can improve the water resistance and sulfur resistance of the catalyst. At the same time, in the existing research, it is difficult to study the durability of catalysts in regard to water resistance and sulfur resistance, so it is one of the important issues that should be further investigated.

When other molecular sieves are exposed to water vapor and heat, their structures are generally destroyed, leading to irreversible deactivation. However, ZSM-5 was used as a catalyst for methanol conversion (with water being one of the main products). This indicated that ZSM-5 had good stability toward water vapor. ZSM-5 molecular sieves had a high silicon-to-aluminum ratio, resulting in lower surface charge density.  $\text{H}_2\text{O}$ , being a highly polar molecule, was not easily absorbed by ZSM-5 molecular sieves. The core-shell structure Mn-Ce mixed oxide catalyst designed by Honggen Peng and his team [77] improved the water resistance of ZSM-5. Additionally, Wang [54] found that a Fe-ZSM-5 (20, 1:1) catalyst exhibited good water resistance under the conditions of a space velocity of  $55,510 \text{ h}^{-1}$ , 5% ( $\varphi$ ) water vapor, and  $600 \times 10^{-6}$  sulfur dioxide. This indicated that the introduction of other metal ions could alter the water resistance of ZSM-5.

### 5.4. Hydrothermal Stability

Hydrothermal stability is an important property of molecular sieve catalysts that needs to be investigated. Many industrial catalytic reactions have high requirements for hydrothermal stability, which is often the key to determining the catalyst life and reaction process selection. For molecular sieve catalysts, hydrothermal treatment can cause the dealumination of zeolites, reducing the surface area and pore volume, inactivating the active metal species to the aggregation of active metal species, and degrading the structure due to the mobility of metal oxides [78].

In order to obtain molecular sieve catalysts with good hydrothermal stability, several kinds of methods are investigated for the issue. The molecular sieve catalyst can improve the stability of the active center of the catalytic material under water vapor conditions by modifying the active center of the porous material with phospho-oxygen compound assembly and introducing skeleton heteroatoms [79]. Hydrothermal treatment results in chemical and structural changes that are sometimes irreversible, depending on the stability of the zeolite frame. In order to maintain the structural integrity of zeolites and improve the hydrothermal stability of zeolites, high-silicon zeolites have been synthesized. Meanwhile, small-pore zeolites show stronger resistance to dealumination under hydrothermal conditions, preventing the formation of metal oxide species [78,80]. Therefore, appropriate or special molecular sieve catalysts should be selected according to the temperature window of the application situation. Fe-exchanged ZSM-5 catalysts prepared from  $\text{Na}^+$  and  $\text{H}^+$  forms of ZSM-5, by Xiaoyan Shi [81], and better hydrothermal stability could be obtained when Fe-ZSM-5 catalysts had greater quantities of  $\text{Fe}^{3+}$  species in ion-exchanged sites and fewer residual protonic sites. Therefore, modifying the active center, preparing high-silicon zeolites, selecting special molecular sieves, and forming suitable metal species can promote the hydrothermal stability of  $\text{NH}_3$ -SCR.

### 5.5. Future Prospect

The occurrence of side reactions will consume reactants and produce unwanted products, resulting in a waste of resources and secondary pollution.  $\text{N}_2\text{O}$  as the side reaction during the SCR process over molecular sieve catalysts will bring secondary pollution. Therefore, how to reduce the formation of  $\text{N}_2\text{O}$  is also a significant issue for  $\text{NO}_x$  removal. It is very efficient to choose highly selective catalysts by introducing suitable metal ions to ensure selectivity.

Metal ions (such as Cu, Fe, Co, Ni, Cr, Zn, Zr, W, Mo, La, Ce, and Mn) are widely used for preparing ZSM-5 catalysts. During the synthesis and scrapping process, the residual metal ions resulting in environmental pollution are also a major problem. This problem can be solved by obtaining a green approach for  $\text{NO}_x$  removal by designing and selecting an environmentally friendly synthesis and scrapping process. During the synthesis process, we can choose the appropriate ions and control the concentration and temperature to improve the ion exchange efficiency. Meanwhile, using ions with good activity and low toxicity as much as possible can prevent risks to the environment, even if there are metal ions remaining after preparation. For example, between the Fe ion and Cr ion, without considering other factors, the Fe ion with good activity and low toxicity is preferred. Furthermore, in terms of energy, it is important to choose a preparation method with a low cost and low energy consumption. The hydrothermal method is expensive and has high energy consumption, while the lower production cost of the impregnation method and ion exchange method are in line with the theme of green energy. During the scrapping process, catalyst regeneration is an excellent way to solve the problem of residual metal ions in the ZSM-5 catalysts, and acid/alkali washing and thermal treatment are the common regeneration methods for deactivated catalysts [82]. Furthermore, metal ions from waste ZSM-5 catalysts can be extracted and used to prepare new materials, if the catalysts have no regeneration value. In conclusion, the green approach for  $\text{NO}_x$  removal can be further enhanced by controlling the synthesis and scrapping process.

## 6. Conclusions

Most of the molecular sieve catalysts were prepared with the immersion method, and some were prepared with the ion exchange method. The more commonly introduced metal ions are Fe, Co, Ni, Mn, Cr, Cu, Zr, W, Ce, La, and so on. Meanwhile, the SCR activity and environmental adaptability of multiple metal ions over the ZSM-5 molecular sieve catalysts were found to be significantly better compared to that of single metal ions, due to the strong interaction of the multiple metal ions. However, ZSM-5 molecular sieve catalysts still face many challenges in environmental adaptability, including the poisoning of toxic substances,

competitive adsorption of volatile substances, influence of water vapor, changes in reaction conditions, and long-term stability. Overcoming these challenges requires further research and development to improve catalyst stability and performance.

Denitrification, the process of removing nitrogen oxides from flue gas, is still highly regarded by the public and has been sharply raised as a worldwide problem. SCR denitration technology is the most widely used technology in China, and the molecular sieve catalyst is one of the main catalysts that can meet the needs of fixed source denitration in the future. They demonstrate excellent catalytic activity and selectivity in a variety of fields, such as exhaust gas purification, petrochemical, biomass conversion, olefin separation, and conversion. The ZSM-5 molecular sieve catalyst has a highly controllable pore structure and acid site, and its catalytic performance can be optimized by adjusting its composition, morphology, and active center. In addition, the ZSM-5 molecular sieve catalyst also has good environmental adaptability and can resist adverse factors such as sulfur, alkali, and water, so it has a wide application prospect.

**Author Contributions:** Conceptualization, W.P., J.H. and D.F.; methodology, W.P., J.H. and D.F.; software, W.P.; validation, G.H. and W.Z.; formal analysis, D.F.; investigation, W.P., J.H., W.Z. and D.F.; resources, G.H. and W.Z.; data curation, G.H., W.Z. and D.F.; writing—original draft preparation, W.P., J.H. and D.F.; writing—review and editing, D.F., J.H. and G.H.; visualization, D.F.; supervision, D.F.; project administration, D.F.; funding acquisition, D.F. All authors have read and agreed to the published version of the manuscript.

**Funding:** The 2023 program of graduate education and teaching reform at Wuhan University of Technology (construction and research of the teaching case base for the course named Contemporary Analytical Techniques for material characterization).

**Data Availability Statement:** Data will be made available on request.

**Conflicts of Interest:** The authors declare no conflict of interest.

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