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Progress in Metal-Organic Framework Catalysts for Selective Catalytic Reduction of NO_x: A Mini-Review

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Abstract: Nitrogen oxides released from the combustion of fossil fuels are one of the main air pollutants. Selective catalytic reduction technology is the most widely used nitrogen oxide removal technology in the industry. With the development of nanomaterials science, more and more novel nanomaterials are being used as catalysts for the selective reduction of nitrogen oxides. In recent years, metal-organic frameworks (MOFs), with large specific surface areas and abundant acid and metal sites, have been extensively studied in the selective catalytic reduction of nitrogen oxides. This review summarizes recent progress in monometallic MOFs, bimetallic MOFs, and MOF-derived catalysts for the selective catalytic reduction of nitrogen oxides and compares the reaction mechanisms of different catalysts. This article also suggests the advantages and disadvantages of MOF-based catalysts compared with traditional catalysts and points out promising research directions in this field.

Keywords: nitrogen oxide; selective catalytic reduction; metal organic framework; catalyst

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1. Introduction

Nitrogen oxides (NO_x) are mainly derived from the combustion process of fossil fuels and are the main pollutants that form acid rain and photochemical smog, which bring serious harm to human life and the environment. Commonly, NO_x includes nitrous oxide (N_2O), nitric oxide (NO), nitrogen dioxide (NO_2), nitrous oxide (N_2O_3), nitrous oxide (N_2O_4), and nitrous oxide (N_2O_4, N_2O_5), etc. [1]. Selective catalytic reduction (SCR) is currently the most widely used and most efficient NO_x removal technology. SCR technology mainly uses reducing agents (such as ammonia, urea, etc.) to react with NO_x to generate nitrogen and water chemically [2,3]. This has the advantages of lower secondary pollution, higher purification efficiency, and the use of mature technologies. NH_3-SCR reaction mechanisms are generally divided into the following two types: (1) the Langmuir–Hinshelwood (L–H) mechanism, wherein NH_3 and NO_x adsorbed on the same or adjacent active sites react to generate N_2 and H_2O; (2) the Eley–Rideal (E–R) mechanism, in which the adsorbed NH_3 reacts with NO_x in the gas phase to generate N_2 and H_2O [4]. NH_3-SCR reactions can be divided into medium and high-temperature SCR and low-temperature SCR according to the reaction temperature. Medium and high-temperature SCR mean that the reaction temperature of the catalytic system is generally in the range of 250 to 425 °C, and that the reaction temperature of the low-temperature SCR process is generally lower than 250 °C. V_2O_5-$WO_3(MoO_3)/TiO_2$ is currently the most commonly used denitration catalyst, using NH_3 as a reducing agent to reduce NO_x to N_2 and H_2O [5]. This catalyst has good denitrification ability at high temperatures (300–400 °C), but has the disadvantages of poor activity and sulfur and water resistance at low temperatures. Usually, the sulfur-containing compounds generated by the reaction of the soot and SO_2 in the flue gas to be denitrated

will wear or block the gaps of the catalyst, shortening the service life of the catalyst [6]. Therefore, the development of SCR catalysts with low reaction temperatures and strong SO_2 resistance has always been a research hotspot.

Metal-organic frameworks (MOFs) are porous crystalline materials synthesized by the coordination of metal ions and organic ligands. They have the advantages of a large specific surface area, large pore volume, regular structure, and highly dispersed metal active sites. MOFs with different pore sizes and pore structures can be tuned by using different metal and organic ligands. According to the skeletal structure of the material, MOFs can be divided into three categories: one-dimensional linear chain materials, two-dimensional layered materials, and three-dimensional network materials [7]. Methods that can successfully prepare MOFs materials include the solvothermal method, ultrasonic method, electrochemical method, and vapor deposition method, etc. [8]. MOFs have a wide range of applications in photocatalysis, chemical sensors, drug loading, and fluorescent probes [9]. In addition, MOFs can be converted into metal oxides or porous carbon materials through simple annealing treatments such as calcination [10]. The unique structure and good catalytic activity of MOFs have been extensively studied in the field of SCR in recent years. In this paper, the research progress and catalytic reaction mechanism of MOFs and their derived catalysts in the field of NO_x SCR are reviewed.

2. MOFs as Catalysts in NO_x SCR

2.1. Monometallic MOFs as Catalysts for NO_x SCR

Metal-organic frameworks are usually formed by linking metal ions and organic ligands, as shown in Figure 1. During synthesis, metal ions, organic groups, solvents, templates, and reaction conditions, etc., will affect the crystal structure and size of the final MOFs. The stability of single-metal MOFs largely depends on the strength of the metal–ligand bonds. Strong metal–ligand bonds will make the MOF more stable and less prone to hydrolysis. COO-Lewis bases form stronger linkages with Lewis acids formed by trivalent and tetravalent metal salts than divalent metals.

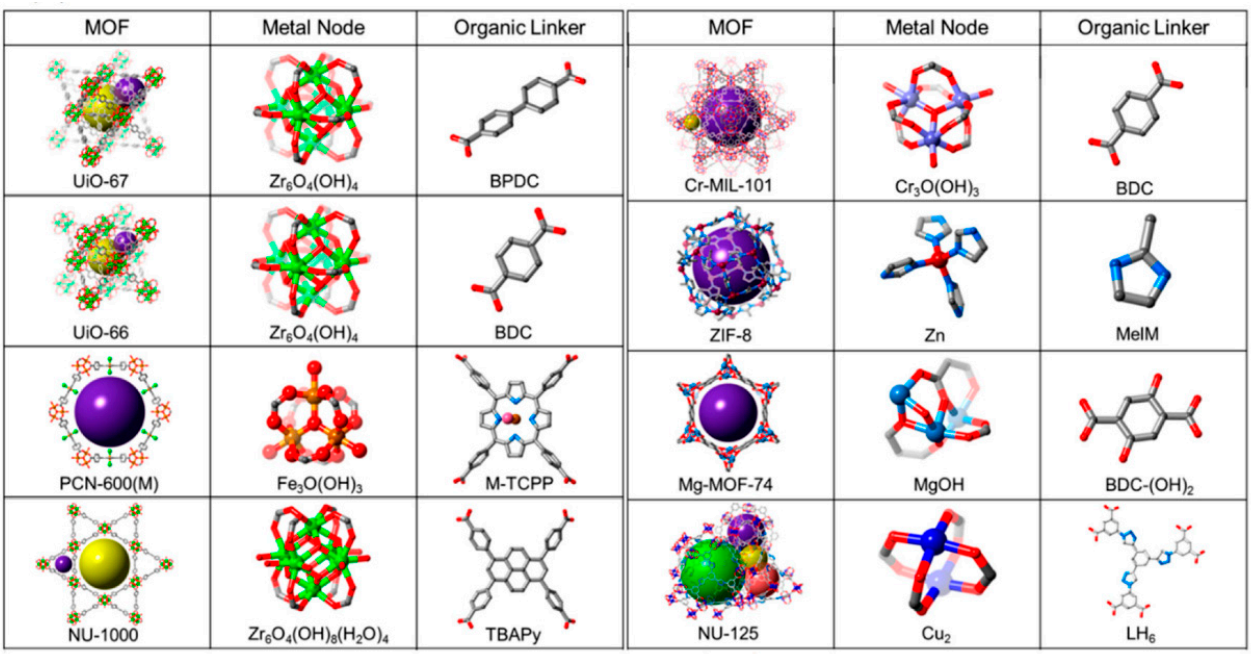

Figure 1. Different MOFs and the organic linkers [11] (copyright 2020 MDPI).

Mn, Cu, Fe, and Ni-based MOFs are the most common monometallic MOFs used for NO_x SCR (Figure 1). Manganese oxide is a traditional SCR catalyst with good low-temperature NO_x SCR activity. Jiang et al. reported a hollow spherical Mn-MOF-74 catalyst

that could achieve 99% NO_x conversion at 220 °C, as shown in Figure 2a [12]. The good catalytic activity of this catalyst comes from its good reactant adsorption and activation properties. To improve the stability of the catalyst under aqueous conditions, P123 was used to modify Mn-MOF-74, enhancing its water resistance [13]. However, in a study of sulfur and water resistance, the coexistence of moisture and sulfur dioxide caused the NO_x conversion to drop to 85% [13]. DFT calculations showed that the high activity of Mn-MOF-74 in NO_x SCR comes from its strong adsorption and activation of NO and NH_3. Furthermore, the carboxyl oxygen vacancies and hydroxyl oxygen vacancies in Mn-MOF-74 can also promote the desorption of NO_2 molecules from metal sites for subsequent rapid SCR reactions. It has also been found that water molecules can weaken Mn-O bonds and influence NO_x reduction performance [14].

In the MOF-74 family, Co-MOF-74 also exhibits good catalytic activity in NO_x SCR; the NO_x conversion rate can reach 70% at a low temperature of 210 °C, and the catalyst has higher catalytic activity than Mn-MOF-74, as well as better water and sulfur resistance [12]. Cu-MOF-74 was also used as a catalyst for NO_x SCR. Studies have shown that the solvent and synthesis temperature have significant effects on the activity of this catalyst in NO_x SCR. Solvothermal synthesis of Cu-MOF-74 from isopropanol at 230 °C exhibited 97.8% NO_x conversion and 100% N_2 selectivity, and the catalyst had good water and sulfur resistance [15]. In addition to adjusting the synthesis temperature, solvent, and other preparation conditions, adding modifiers can also improve the catalytic performance of Cu-MOF. Chen et al. added acetic acid in the synthesis of Cu-MOF-199 to control the growth rate of different crystal planes and to build a hierarchical pore structure [16]. Li et al. studied the effects of activation conditions on the catalytic activity of Cu-MOF in NO_x SCR. The results showed that Cu-MOF activated under vacuum conditions at 230 °C had the best catalytic activity, with NO_x conversion being close to 100%. However, higher activation temperatures were not always better. When the activation temperature was higher than 250 °C, the structure of the Cu-MOF was destroyed, and the catalyst's performance was reduced or even lost [17]. Recently, Yu et al. used CuO as a core to epitaxially grow a layer of Cu-MOF on CuO using the in-situ growth method and obtained the CuO-Cu-MOF catalyst [18]. This catalyst exhibited higher catalytic activity than CuO and Cu-MOFs because the catalyst possessed the advantages of both CuO and Cu-MOFs, showing a high adsorption capacity for NO and a large number of acidic sites, as shown in Figure 2b.

Iron oxides are also common NO_x SCR catalysts. Fe-MOF with ferric iron as the metal center has also been used as a catalyst for NO_x SCR—the most representative of which is Fe-MIL-100. Fe-MIL-100 has abundant pores and Lewis acid sites, which is favorable for the adsorption of reactants, thereby accelerating the NO_x reduction reaction rate. Wang et al. found that Fe-MIL-100 had a higher activity than conventional V_2O_5-WO_3/TiO_2 catalysts, with a NO_x conversion rate of up to 90% at 225 °C, as shown in Figure 2c [19]. Moreover, this catalyst had a stable structure and catalytic activity, and had good water and sulfur resistance.

Most of the time, the synthesis temperature of MOFs is lower than their use temperature in NO_x SCR, so the stability of the MOFs at the SCR reaction temperature is very important for their catalytic performance. Existing studies have shown that the structure of MOFs is stable under most low-temperature SCR reaction conditions. For example, Tang et al. used TG to study the thermal stability of vanadium-based MOFs and found that the V-MOFs were stable at temperatures as high as 320 °C. Sun et al. synthesized Ni-MOF via the hydrothermal method for denitration reactions [20]. Ni-MOF showed higher thermal stability than Cu-MOF and Fe-MOF, and the crystal structure of Ni-MOF remained stable at 440 °C, as shown in Figure 2d. MOFs with high thermal stability are beneficial for broadening the reaction temperature window. The characterization results showed that after activation in a N_2 atmosphere at 220 °C, Ni-O on the catalyst surface increased and became more dispersed, which promoted the adsorption of NH_3; the conversion efficiency of NO_x was higher than 92% at 275–440 °C.

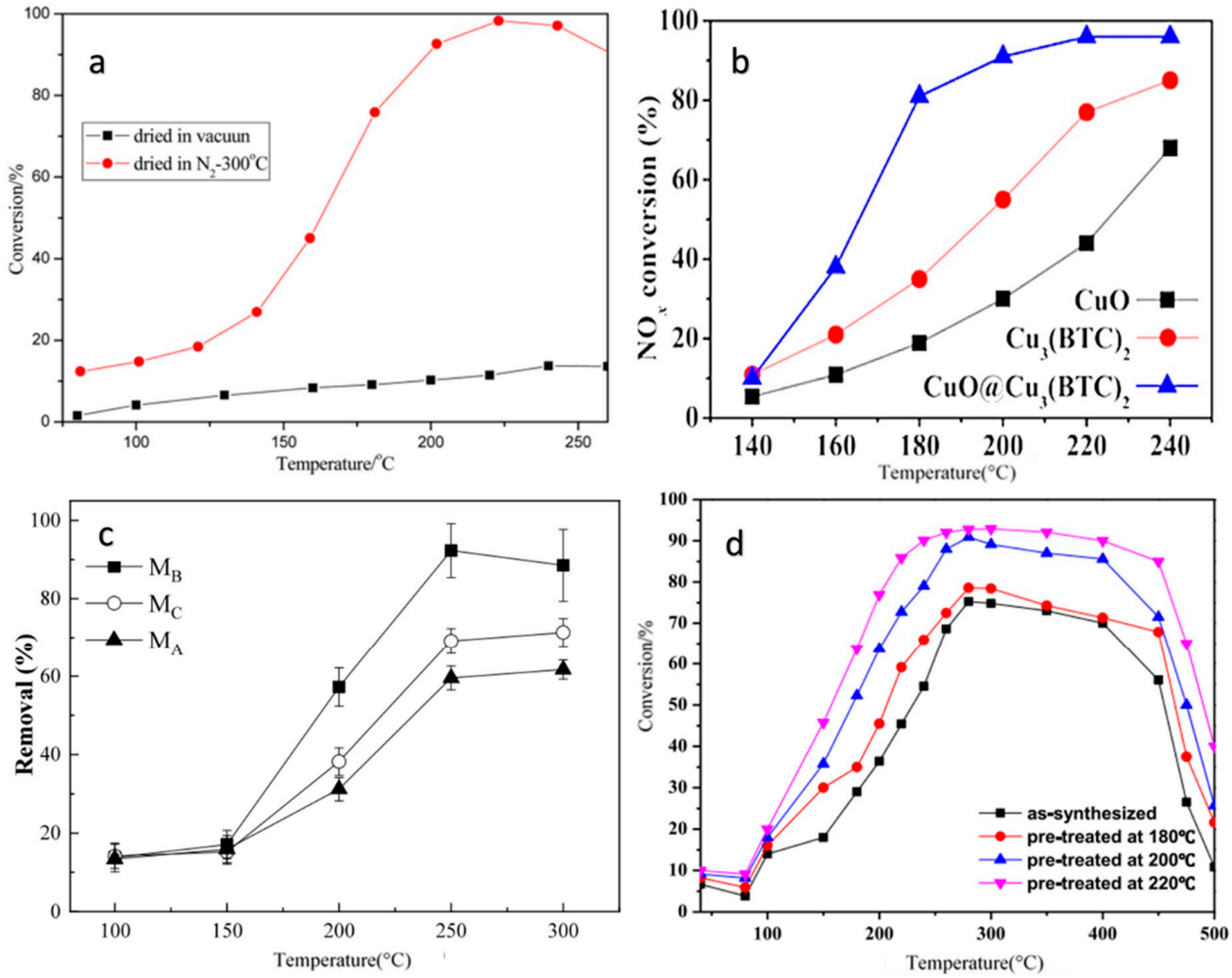

Figure 2. Monometallic MOFs catalysts for NO_x SCR, (**a**) Mn-MOF [12] (copyright 2016 American Chemical Society), (**b**) Cu-MOF [18] (copyright 2017 American Chemical Society), (**c**) Fe-MOF [19] (copyright 2021 Elsevier) and (**d**) Ni-MOF [20] (copyright 2018 Elsevier).

2.2. Bimetallic MOFs as NO_x SCR Catalysts

In the process of synthesizing MOFs, if two metal center species exist simultaneously, there is an opportunity to synthesize bimetallic MOFs. Bimetallic MOFs can be prepared using a similar synthetic approach to monometallic MOFs, but using two metal salts as the reactants in the solvothermal process. In order to form bimetallic MOFs, two metal cations should be able to react with ligands simultaneously, avoiding the formation of single-metal cation MOFs. Another way to synthesize bimetallic MOFs is through the post-synthetic exchange method. This method can synthesize some MOFs that cannot be synthesized by the one-pot method. One MOF is usually immersed in a solution of nitrate or chloride of another metal for a period of time at room temperature or elevated temperature for ion exchange. Zhang et al. synthesized Fe-Mn-MIL-100 via the hydrothermal method for NO_x SCR [21]. Figure 3a shows the application of an Fe and Mn bimetallic MOF (Fe-Mn-MIL-100) in NO_x SCR. The Fe-Mn-MIL-100 shared a common crystal structure with monometallic Fe-MIL-100 or Mn-MIL-100, but exhibited higher catalytic activity in NO_x reduction than Fe or Mn monometallic MOFs. The denitration efficiency of Fe-Mn-MIL-100 was as high as 96% at 280 °C, and the conversion of NO_x was above 90% in the temperature range of 260–330. In contrast, the NO_x conversion was far below 90% for either Fe or Mn single-metal MOFs. This suggested that the synergistic effect between Fe and Mn enhances the catalytic activity of Fe–Mn bimetallic MOFs in NO_x SCR. More interestingly, in the presence of SO_2 and

H_2O, the denitrification capacity of the catalyst increased by 6% instead of decreasing; this is because SO_2 and H_2O formed SO_4^{2-} under the reaction conditions, which enhanced the acidity of the catalyst surface. Similarly, Co-Mn-MOF-74 was hydrothermally synthesized and used as a catalyst for NO_x SCR, and despite having the same crystal structure as Mn-MOF-74, its activity and sulfur resistance were significantly improved. At 180–240 °C, the NO_x conversion was greater than 96% and was not affected by SO_2 introduction into the reactant gases [22].

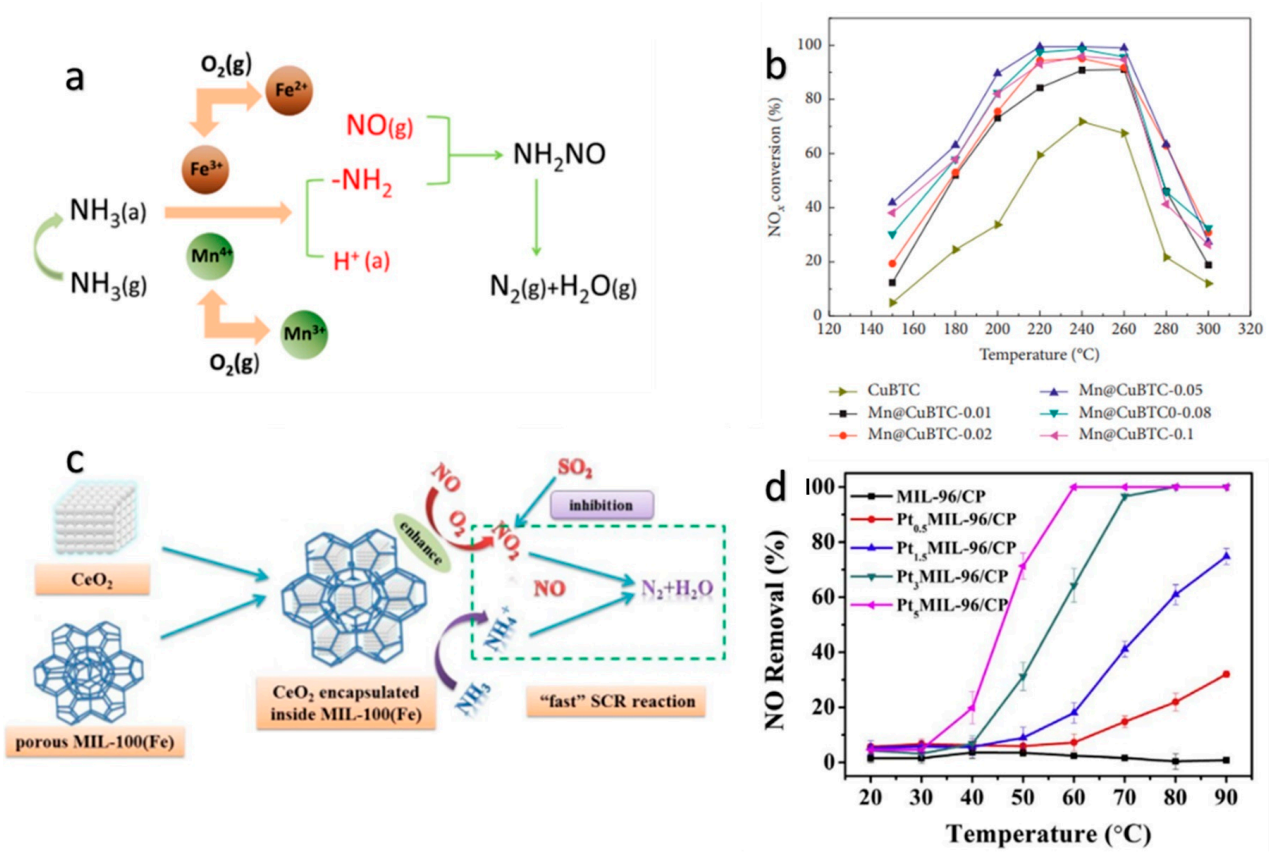

Figure 3. Bimetallic MOFs catalysts for NO_x SCR, (**a**) Fe-Mn [21] (copyright 2022 Springer Nature), (**b**) Mn-Cu [23] (copyright 2019 Hindawi), (**c**) Ce-Fe [24] (copyright 2016 Elsevier), (**d**) Pt-Al [25] (copyright 2018 Elsevier).

Ion exchange is one of the most effective methods for synthesizing bimetallic MOFs. Yao et al. first synthesized Cu-MOF and then incorporated Mn ions into the Cu-MOF through ion exchange in order to obtain Mn/Cu-BTC (BTC = 1,3,5-benzenetricarboxylic acid) [23]. The introduction of Mn changed the pore size of the Cu-MOF, and the synergistic effects of Mn and Cu enhanced its redox activity. The optimum temperature range for NO_x SCR was 230–260 °C, as shown in Figure 3b, and within this temperature range, the NO_x conversion was near 100%. Similarly, Shi et al. used an ion exchange method to incorporate metallic Ag into the framework of Cu-BTC (BTC = 1,3,5-benzenetricarboxylic acid), and the NO_x conversion efficiency was able to reach 92% at temperatures higher than 180 °C.

In addition, impregnation or deposition methods are also effective strategies for preparing bimetallic MOFs-based catalysts. Want et al. immersed Fe-MIL-100 in a cerium precursor solution and successfully prepared a CeO/Fe-MIL-100 catalyst encapsulated with CeO_2 nanoparticles, as shown in Figure 3c [24]. The results showed that the size of CeO_2 nanoparticles was comparable to the pore size of Fe-MIL-100. CeO_2 was embedded into the pores of the Fe-MIL-100, which promoted the oxidation efficiency of NO to NO_2 and improved the low-temperature activity of the catalyst, broadening the temperature window. NO_x conversion was over 90% in the range of 196–300 °C. Similarly, dispersing Pt uniformly

over Al-MIL-96 can also improve the denitration performance of the catalyst. Xue et al. used hydrogen to reduce NO_x, and the Pt_5MIL-96/carbon paper (CP) catalyst was able to achieve almost 100% NO_x removal efficiency at 60 °C, as shown in Figure 3d [25]. Huang et al. compared the performance of the impregnation method and the in-situ deposition method in the preparation of MOF-based SCR catalysts and found that the MNO_x/UiO-66 prepared by the in-situ deposition method had better catalytic performance, which was mainly because the in-situ deposition method was more beneficial for improving the dispersibility of MNO_x than the impregnation method [26]. Li et al. deposited CuO onto Ni-MOF to form Cu-Ni-MOF catalysts with different loadings. The results indicated that all bimetallic catalysts showed a better low-temperature denitration ability than single-metallic catalysts. The catalytic performance was improved by 30% at 320 °C, demonstrating the synergistic effects of Cu and Ni in NO_x reduction [27].

2.3. MOF-Derived NO_x SCR Catalyst

Although MOF catalysts can be directly used as catalysts for NO_x reduction and have good performance, compared with traditional metal oxide catalysts, MOFs have poor stability. The structure of MOFs may be decomposed or collapsed, resulting in a decrease or even loss of catalytic activity. Therefore, researchers have developed a series of post-treatment methods to obtain stable NO_x SCR catalysts with porous structures by calcining MOFs. The treatment temperature and atmosphere during calcination have a great influence on the structure and properties of the final catalyst. Calcination in the air will yield the corresponding metal oxide, and calcination in an inert atmosphere can usually yield a composite of metal oxide and carbon (Figure 3).

Bai et al. obtained a series of CoO_x@PC (PC = porous carbon) catalysts with Co_3O_4 embedded in porous carbon by calcining ZIF-67 in a limited oxygen atmosphere at 800 °C for 2 h with a heating rate of 5 °C/min in N_2, as shown in Figure 4a [28]. The catalyst achieved 90% denitration efficiency in the temperature range of 150–175 °C. Wang et al. prepared a CuO/Cu_2O multilayer catalyst by calcining Cu-MOF at 250 °C for 30 with a heating rate of 10 °C/min in nitrogen, which showed ultra-high denitration activity in the temperature range of 170–220 °C [29]. Gong et al. used Fe-MIL-100 as a precursor and produced an Fe_2O_3 catalyst via calcination. The catalyst showed excellent activity at 250–325 °C, and the NO_x conversion rate was as high as 100% [30]. Kwak et al. calcined Mn-MOF in air to obtain manganese oxide with a layered structure [31]. The catalyst exhibited higher activity than Mn_2O_3 or Mn_3O_4 at low temperatures of 100–200 °C. Dong et al. prepared a CrO_x/C catalyst derived from Cr-MIL-101 via the calcination of MOFs at 450 °C for 4 h in nitrogen for NO_x SCR. The catalyst showed excellent NO reduction activity at low temperatures ranging from 150 to 200 °C; with high SO_2 tolerance, and its superior activity could be resorted by a simple heat treatment [32].

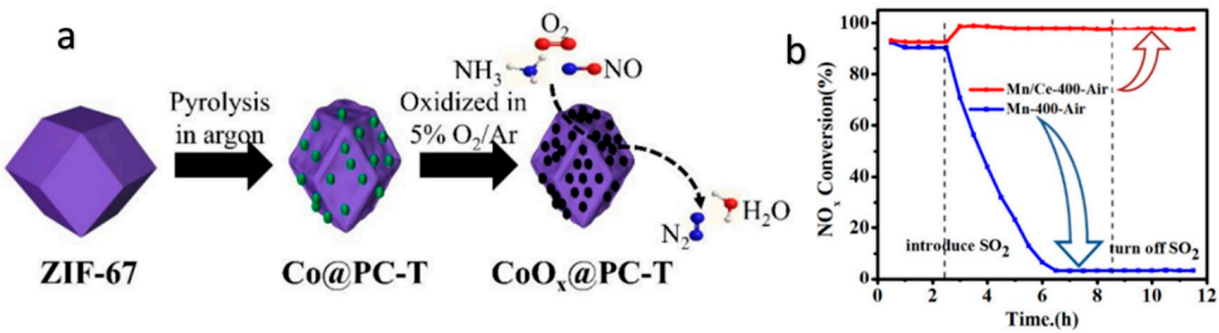

Figure 4. MOF-derived catalysts for NO_x SCR, (**a**) CoOx@PC-T [28] (copyright 2019 Elsevier), (**b**) Ce-Mn oxide [33] (copyright 2021 Elsevier).

Bimetallic oxide catalysts can be obtained by calcining bimetallic MOFs. For example, Fan et al. calcined Mn-Fe-MOF at 350 °C for 2 h with a heating rate of 1 °C/min in air to

obtain an MNO_x-FeOx catalyst, which achieved 100% denitration efficiency at 120–240 °C and had excellent water resistance [33]. Chen et al. synthesized Ce-Mn-MOF via the solvothermal method, and then prepared a Ce-Mn oxide catalyst by the calcination of Ce-Mn-MOF at 400 °C, which exhibited over 90% denitration efficiency at 150–310 °C [34]. It is worth mentioning that the catalyst exhibits an unusual tolerance to SO_2. When 200 ppm SO_2 was introduced into the reaction gas, the conversion rate of NO_x increased from 92.6 to 97.8%, as shown in Figure 4b. $Mn_xCo_{3-x}O_4$ nanocages were prepared through a similar method by Zhang et al.; the bimetal organic framework-derived catalyst showed high activity and improved SO_2 tolerance. The NO conversion was above 90% in the temperature window range from 125 to 300 °C [35]. Li et al. prepared Fe, Mn, and Co catalysts on N-doped carbon nanotubes for NO_x SCR via the pyrolysis of Fe-Mn-MOF-74 at 800 °C [36]. These series catalysts have better water resistance and sulfur resistance. Wang et al. used Uio-66-NH_2 as a template to obtain Pt/ZrO_2/Carbon by impregnating a Pt precursor and thermally decomposing it for NO_x reduction at 800 °C for 150 min, with a heating rate of 5 °C/min in nitrogen gas [37]. At 90 °C, the NO_x conversion rate was close to 100%, using H_2 as a reducing agent.

3. Reaction Mechanism of MOF Catalysts in NO_x SCR

The SCR reaction mechanism of traditional metal oxide catalysts is generally believed to follow the Eley–Rideal (E–R) and Langumuir–Hinshelwood (L–H) mechanisms. In the NO_x reduction reaction catalyzed by MOFs, the catalytic mechanism is mostly studied by in-situ infrared absorption spectroscopy and DFT calculation.

The NO_x SCR process includes three stages: the adsorption of NO_x and/or NH_3, the reaction between the adsorbed species, and the desorption of the produced gas. Martin et al. studied the adsorption of NO_2 in V-MOF; it was found that the V-MOF showed a high isothermal NO_2 uptake of 13.0 mmol g^{-1} [38]. Zhou et al. synthesized a CuO/Cu_2O catalyst derived from Cu-MOFs for NO_x SCR and studied the NH_3 and O_2 adsorption on the catalysts. It was found that the oxygen vacancies in the catalyst enhanced oxygen adsorption, favoring the E–R mechanism and the Cu^+/Cu^{2+} recycle reaction [29].

Sun et al. used NH_3-TPD to study the distribution of acid sites on the surface of Ni-MOF catalysts [20] and speculated that the catalysts combined the E–R mechanism in NO_x reduction:

$$NH_3(g) \rightarrow NH_3(a) \quad (1)$$

$$NH_3(a) + Ni^{2+} \rightarrow NH_2(a) + H + Ni^{3+} \quad (2)$$

$$NH_2(a) + NO(g) \rightarrow NH_2NO(a) \rightarrow N_2(g) + H_2O(g) \quad (3)$$

$$Ni^{3+} + O_2(g) \rightarrow Ni^{2+} + O(a) \quad (4)$$

where "g" indicates the gas phase; "a" indicates the species to be adsorbed.

Zhang et al. used in-situ FT-IR to study the catalytic reaction mechanism of a Fe-Mn-MIL-100 catalyst in NO_x reduction [21]. As a result, Fe-Mn-MIL-100 also followed the E–R mechanism. Xie et al. prepared a series of monometallic and bimetallic MOF-74 (Mn, Co, Ni, Zn, MnCo, MnNi, and MnZn) for NH_3-SCR. The authors used in-situ DRIFTS to study the reaction mechanism of these catalysts for NO_x reduction [39]. The IR spectrum of MOF-74 MoCo/Mn showed that the ammonia adsorption only existed at low temperatures, and both the vibration peak of ammonia adsorption and nitrogen and oxygen appeared at high temperatures, while the vibration peak of ammonia, nitrogen, and oxygen adsorption can be observed throughout the temperature range for MOF-74-Zn. These results indicated that for MOF-74-MnCo, in the low-temperature region, the reaction mainly followed the E–R mechanism—while in the high-temperature region, the reaction mainly followed the L–H mechanism (Figure 5a). Meanwhile for MOF-74-Zn, the catalyst always followed the L–H mechanism from low temperatures to high temperatures (Figure 5b). During the reaction, the high valence metal ions were reduced by NO to low valence metal ions, and then, the low valence meta ions could be oxidized by oxygen and become high valence metal ions.

The various valences of Mn ensure its excellent redox properties, which were the major influential factor for the catalytic activity. MOF-74-Mn had a much higher catalytic activity than MOF-74-Zn.

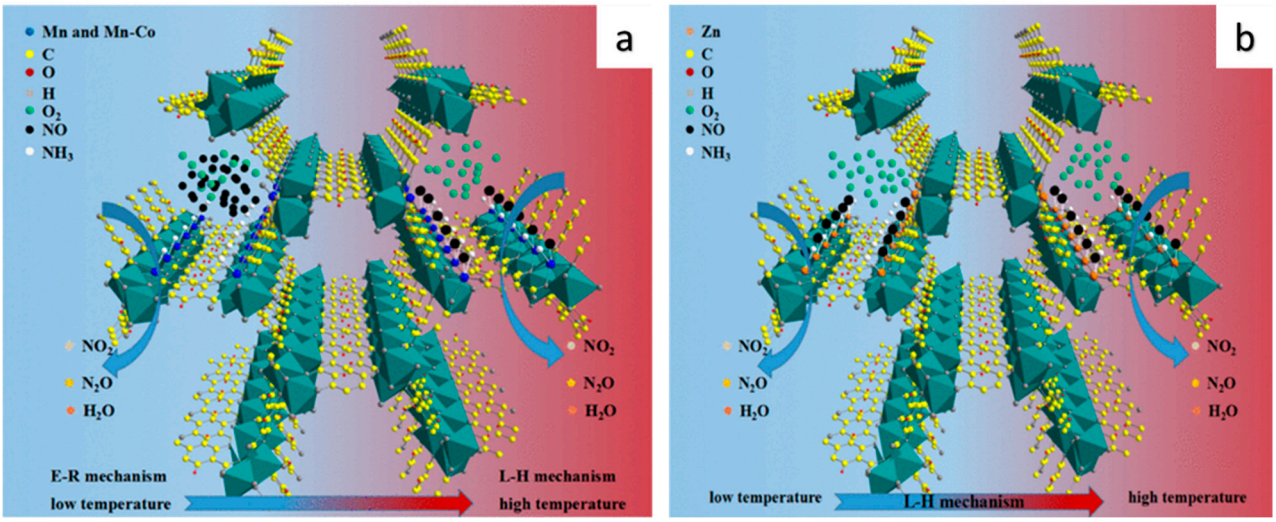

Figure 5. Schematic diagram of (**a**) MOF-74-MnCo, (**b**) MOF-74-Zn NO_x SCR mechanism [38] (copyright 2016 American Chemical Society).

The E–R mechanism dominates at low temperatures:

$$NH_3(g) \rightarrow NH_3(a) \rightarrow NH_2(a) \quad (5)$$

$$NH_2(a) + NO(g) \rightarrow N_2(g) + H_2O(g) \quad (6)$$

The L–H mechanism dominates at high temperatures:

$$NO(g) \rightarrow NO_2(a) \quad (7)$$

$$NH_3(g) \rightarrow NH_3(a) \rightarrow NH_4^+(a) \quad (8)$$

$$NH_4^+(a) + NO_2(a) \rightarrow N_2(g) + H_2O(g) \quad (9)$$

where "g" indicates the gas phase; "a" indicates the species to be adsorbed.

Ko et al. prepared a Mn-Co-BTC (BTC = 1,3,5-benzenetricarboxylic acid)-derived catalyst for NO_x reduction. The catalyst has a honeycomb-like porous structure, which provides a sufficient reaction area; the interactions between Mn and Co further enhanced its catalytic activity [40]. After in-situ DRIFT experiments, it was found that Mn-Co-BTC-500 complies with both the L–H mechanism and E–R mechanism.

4. Conclusion and Future Prospects

The development of MOF catalysts draws on the research of traditional catalysts, which can be seen from the metal-center elements of MOFs. Traditional metal oxide catalysts include Mn-based, Fe-based, Cu-based, and Ni-based catalysts, and these metal elements are also commonly found in MOF catalysts. MOF materials and their derived catalysts usually have higher specific surface areas and highly dispersed metal sites, as well as more acid wash sites, which are beneficial for enhancing the adsorption and activation of reactants—thus exhibiting a better performance than traditional catalysts. With the continuous development of MOF material preparation technologies and the continuous deepening of research into their material properties, the application of MOFs in the field of denitrification is bound to increase. However, the industrial application of MOFs in NO_x reduction still needs to be further explored, especially the following aspects:

(1) Compared with traditional denitration catalysts, the high-temperature stability of MOF materials is still insufficient, which affects the lifetime of MOF catalysts; thus, it is necessary to further improve the structural stability of MOF materials;

(2) Most of the current MOF catalytic denitrification experiments are carried out with artificially simulated flue gas, and there is a lack of research conducted under actual flue gas conditions;

(3) Multimetallic MOFs and their composites with other types of nanomaterials are effective strategies for enhancing the denitration activity of MOF catalysts and enhancing their water and sulfur resistance;

(4) The structures of MOF materials need to be specially designed according to the denitration reaction mechanism—including their pore size, metal sites, shell-core structure, etc.—to promote the diffusion of reactants and reaction products and to strengthen the interactions between different metal sites and between metal sites and the carrier, for the further improvement of the SCR efficiency.

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