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## Selective catalytic reduction of $\text{NO}_x$ with $\text{NH}_3$ over copper-based catalysts: recent advances and future prospects

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Selective catalytic reduction of NO with  $\text{NH}_3$  ( $\text{NH}_3\text{-SCR}$ ) is a promising technology to reduce the emission of nitrogen oxides ( $\text{NO}_x$ ) from diesel engines and industrial flue gases. Due to their advantages of variable valence and high stability, Cu-based catalysts exhibit superior activity and have been widely employed in the  $\text{NH}_3\text{-SCR}$  reaction. Herein, we expound the reaction mechanism of  $\text{NH}_3\text{-SCR}$ , and summarize the comprehensive advances of Cu-based catalysts (Cu-based small-pore zeolites and Cu-containing metal oxides) developed in the last decade. In this review, the challenges and prospects for Cu-based catalysts are presented to meet the industrial need, and efficient design strategies for promoting the  $\text{NH}_3\text{-SCR}$  performance of Cu-based catalysts through support derivation, precursor optimization engineering, secondary metal doping, crystal structure regulation, preparation method modification and interaction and interface engineering are comprehensively proposed and discussed. These proposed strategies are confirmed to be beneficial for enhancing catalysis by accelerating acid and redox cycles. Besides, we sum up the poisoning mechanism of impurities from flue gas on active sites, and provide the corresponding anti-inactivation measures to inhibit the deactivation of catalysts. Finally, we hope to focus on the current opportunities and challenges faced by Cu-based catalysts, further promoting their development and achieving practical applications.

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### Broader context

Faced with the growing consumption of fossil fuels and consequent environmental crisis, nitrogen oxides ( $\text{NO}_x$ ) remarkably influence the atmospheric environment and have become the main cause of the greenhouse effect, acid rain, photochemical smog, and  $\text{PM}_{2.5}$ . The selective catalytic reduction process using  $\text{NH}_3$  ( $\text{NH}_3\text{-SCR}$ ) is a promising technology to reduce the emission of  $\text{NO}_x$  from stationary and mobile sources, and Cu-based catalysts have been widely investigated as an important representative for  $\text{NO}_x$  removal. Based on the features of the  $\text{NH}_3\text{-SCR}$  reaction, this review reveals the reaction mechanisms and expounds on the design strategies of Cu-based catalysts with high catalytic activity in a targeted way, such as support derivation, precursor optimization engineering, secondary metal doping, crystal structure regulation, preparation method modification and interaction and interface engineering. Specifically, the challenges and opportunities of Cu-based SCR catalysts are presented in view of the increasing demand for  $\text{SO}_2$ /alkali metal resistance and high hydrothermal stability of catalysts. In this regard, the relevant poisoning mechanisms and anti-inactivation measures are summarized to meet industrial needs, which will indicate the future research directions and stimulate the development of novel Cu-based catalysts.

## 1. Introduction

### 1.1 $\text{NO}_x$ pollution

Nitrogen oxides ( $\text{NO}_x = \text{NO} + \text{NO}_2$ ) emitted from activities such as coal burning, motor vehicles and industrial operations are

major contributors to environmental pollution,<sup>1–3</sup> and are associated with various forms of air pollution, including greenhouse effects, acid rain, photochemical smog, and particulate matters (PMs).<sup>4–7</sup> Of greater concern,  $\text{NO}_x$  will also harm the alveolar structures and capillaries of the lungs, leading to respiratory diseases in humans.<sup>8–10</sup> To address this issue and minimize the impact of exhaust emissions on societal development, the United States has taken initiatives to exploit technologies for reducing nitrogen oxide emissions and refine relevant laws and regulations (Clean Air Act, Sec. 407, USA, 2004). At the same time, with the rapid development of society in China, the problem of environmental pollution cannot be overlooked.

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Therefore, China has established stricter emission laws and standards for nitrogen oxides (GB13223-2011, China, 2011), regulating the emissions of power plants, natural gas-fired boilers and turbines to reach the limited emission standards. The implementation of robust policies has provided a solid foundation for reducing  $\text{NO}_x$  emissions from stationary and mobile sources.<sup>11</sup>



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## 1.2 Reaction mechanism of $\text{NH}_3$ -SCR

Recently, there have been several methods including fuel pre-treatment technology, fuel combustion technology and combustion post-treatment technology to reduce  $\text{NO}_x$  emissions. Among the various aftertreatment systems, selective catalytic reduction (SCR) has emerged as the most advanced technology under investigation.<sup>12,13</sup> This technology utilizes suitable reducing agents such as ammonia, hydrogen<sup>14</sup> and hydrocarbon<sup>15-17</sup> to catalyze the conversion of nitrogen oxides to harmless nitrogen molecules and water. Notably, selective catalytic reduction with ammonia ( $\text{NH}_3$ -SCR) is widely employed to remove  $\text{NO}_x$  due to the advantages of wide operating temperature, superior redox properties and high thermodynamic stability.<sup>18-22</sup> In particular, in the real application of diesel vehicle systems (Fig. 1a), the  $\text{NH}_3$ -SCR unit is located at the downstream position of the system comprising multiple processing units. The exhaust gas traverses a complex aftertreatment system, where carbon monoxide (CO) and hydrocarbons (HCs) are oxidized and eliminated in the diesel oxidation catalyst (DOC) unit, while PMs are trapped and filtered by the diesel particulate filter (DPF).<sup>23</sup> Subsequently, NO molecules are converted to  $\text{N}_2$  with reducing agents, and an ammonia oxidation catalyst (AOC) unit is used to remove the unreacted  $\text{NH}_3$  and prevent air pollution. More and



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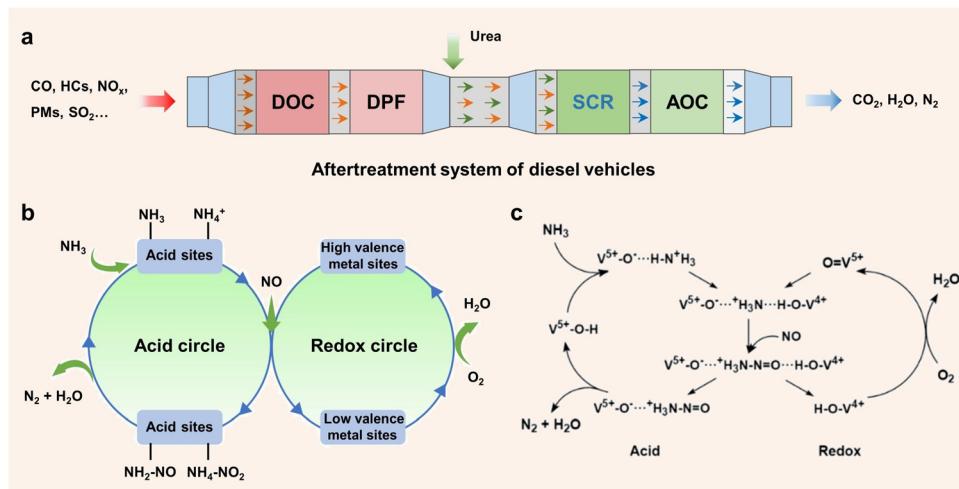
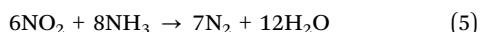
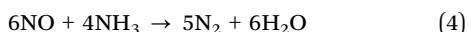
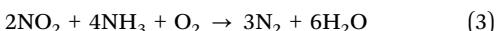


Fig. 1 (a) The after-treatment system of diesel vehicles. (b) Efficient methods for enhancing the acid cycle and redox cycle over de- $\text{NO}_x$  catalysts. (c) The catalytic reaction diagram revealing the double cycles of the  $\text{NH}_3$ -SCR process over vanadia/titania catalysts. Copied with permission from ref. 32. Copyright 1995, Elsevier.

more studies have been focused on the  $\text{NH}_3$ -SCR process to reveal the complex reaction mechanism. In general, the reaction is generally classified into standard SCR reaction (SSCR, reaction (1)) and fast SCR reaction (FSCR, reaction (2)) based on the different ratios of  $\text{NO}/\text{NO}_x$  involved.<sup>23–25</sup> In the SSCR process, the N atom in  $\text{NH}_3$  transfers  $8\text{e}^-$  and  $4\text{e}^-$  to  $\text{NO}$  and  $\text{O}_2$ , respectively. Oxygen molecules participate in the redox cycle and react with H atoms to form  $\text{H}_2\text{O}$ . However, the N atom in  $\text{NH}_3$  will transfer  $2\text{e}^-$  and  $4\text{e}^-$  to  $\text{NO}$  and  $\text{NO}_2$  in the FSCR reaction, in which equal amounts of  $\text{NO}$  and  $\text{NO}_2$  are required. Besides, several main reactions may occur in the process of  $\text{NH}_3$ -SCR, as shown in eqn (3)–(5):



Moreover, there have been many studies concerning the catalytic path of the  $\text{NH}_3$ -SCR reaction. In general, the  $\text{NH}_3$ -SCR reaction at low temperature mainly defers to the Langmuir–Hinshelwood (L–H) mechanism. In this case, the acid sites are used for adsorbing  $\text{NH}_3$ , while  $\text{NO}$  molecules are oxidized by high-valence metal sites, leading to the formation of active nitrates or nitrites. Subsequently,  $\text{NH}_4\text{NO}_2$  or  $\text{NH}_4\text{NO}_3$  species are generated, which will decompose into  $\text{N}_2$  and  $\text{H}_2\text{O}$ . During the reaction, the high-valence redox sites are firstly reduced to the low valence state and then re-oxidized by  $\text{O}_2$ , thus completing the redox cycle. Different from the L–H mechanism, researchers have suggested that the  $\text{NH}_3$ -SCR process at high temperature is more likely to follow the Eley–Rideal (E–R) mechanism. In this pathway, only  $\text{NH}_3$  molecules are adsorbed and activated on the acidic sites of the catalysts to form  $\text{NH}_3$  or  $\text{NH}_4^+$  species, and then gas phase  $\text{NO}$  molecules

will react with  $\text{NH}_3$  or  $\text{NH}_4^+$  species to form transition intermediates ( $\text{NH}_2\text{NO}$  or  $\text{NH}_3\text{NO}$ ) and decompose into  $\text{N}_2$  and  $\text{H}_2\text{O}$ .<sup>26</sup> It is found that the reactive intermediates formed by the L–H and E–R pathways are different, indicating that the specific reaction path can be determined by the capture of intermediates.

The double-cycle mechanisms including the redox cycle ( $\text{NO}_x$ ) and acid cycle ( $\text{NH}_3$ ) are of great importance in the  $\text{NH}_3$ -SCR reaction (Fig. 1b). Therefore, excellent redox properties and strong acidity are two crucial factors that determine the catalytic performance of catalysts.<sup>27–29</sup> In general, the redox properties of catalysts determine the low-temperature activity, while acid properties affect the activity at high temperature.<sup>30,31</sup> In terms of the redox cycle, efficient catalytic performance can be achieved by generating more active  $\text{NO}_3^-$ ,  $\text{NO}_2^-$  and  $\text{NO}_2$  intermediates based on the excellent redox ability. Meanwhile, strong acidity is beneficial for adsorbing and activating  $\text{NH}_3$  molecules, facilitating the active intermediates ( $\text{NH}_3$  or  $\text{NH}_4^+$ ) to participate in the subsequent reaction with activated  $\text{NO}$  species (nitrates or nitrites species). In 1995, Topsøe *et al.* put forward a reaction mechanism involving an acid cycle and a redox cycle over  $\text{V}_2\text{O}_5/\text{TiO}_2$  catalysts (Fig. 1c).<sup>32,33</sup> In the acid cycle,  $\text{V}^{5+}-\text{OH}$  sites acting as Brønsted acid sites were used for the adsorption of  $\text{NH}_3$  molecules, and then the active H atom from  $\text{NH}_3$  molecules was transferred to vanadium species. In this step,  $\text{V}^{4+}-\text{O}-\text{H}$  species were generated through the reduction of  $\text{V}^{5+}=\text{O}$  species, which were subsequently re-oxidized to  $\text{V}^{5+}=\text{O}$  species by  $\text{O}_2$  in the redox cycle. The whole acid cycle was completed by the formation of  $\text{N}_2$  and  $\text{H}_2\text{O}$  through the reaction between activated  $\text{NH}_3$  molecules and adsorbed  $\text{NO}$  molecules. Therefore, the design of efficient SCR catalysts needs to focus on both redox and acidity properties.

### 1.3 Common $\text{NH}_3$ -SCR catalysts

In view of the increasingly serious problem of environmental pollution, the use of catalytic means for effective treatment and



remediation has an important strategic significance for environmental improvement and ecological sustainable development. In this case, the application of easy and eco-friendly nanotechnology is of great significance in the process of industrialization. Nano-scale materials including oxide materials and compounds have been examined by scholars because of their unique nanostructures and extraordinary attributes.<sup>34–37</sup> These compounds are technologically a very beneficial kind of material because of their usage in environmental remediation.<sup>38–40</sup> For the NH<sub>3</sub>-SCR reaction, catalysts such as single metal oxides, mixed metal oxides and supported metal oxides, and pure or metal-exchanged zeolites have consistently demonstrated superior de-NO<sub>x</sub> performance and N<sub>2</sub> selectivity under oxygen-rich conditions, preventing the formation of secondary pollution in the NH<sub>3</sub>-SCR.<sup>41–45</sup> Different catalysts have been developed to varying degrees because of their different characteristics, which are influenced by multiple effect factors (Fig. 2).<sup>46–49</sup> Since the late 1970s, V-based oxide catalysts have been widely explored and industrially used. However, these catalysts have several drawbacks, including a narrow working temperature window, vanadium toxicity, low SO<sub>2</sub>-resistance performance, excessive oxidation of NH<sub>3</sub>, and poor alkali-resistance.<sup>50</sup> It is well known that the SCR unit in flue gas is located before dust removers and desulfurization devices to reduce the cost of waste gas reheating. In this case, the catalyst in the flue gas is easily deactivated due to the SO<sub>2</sub> and flue gas poisoning. Hence, developing V-free catalysts with a broad operating window, moderate redox capacity, and high SO<sub>2</sub>-resistance is of significance for the commercial application of NH<sub>3</sub>-SCR technology.

Among the V-free catalysts, CeO<sub>2</sub>-based catalysts are widely investigated owing to the superior ability to store and release oxygen, leading to the superior redox property. However, pure CeO<sub>2</sub> catalysts exhibit relatively weak surface acidity, which limits the activation of NH<sub>3</sub> and inhibits the catalytic activity.<sup>51–53</sup>

Additionally, the superior low-temperature SCR performance of MnO<sub>x</sub>-based catalysts has also garnered significant attention. The variable valence states of Mn species contribute to the exceptional redox ability of MnO<sub>x</sub>-based catalysts, while pure MnO<sub>2</sub> catalysts have not been generalized in the industry due to their narrow operating temperature window, poor N<sub>2</sub> selectivity at high temperatures, and low SO<sub>2</sub> resistance.<sup>54,55</sup> Moreover, Fe<sub>2</sub>O<sub>3</sub>-based catalysts not only show excellent medium-high performance and SO<sub>2</sub>-resistance at high temperatures, but also show superior thermal stability and N<sub>2</sub> selectivity. Nevertheless, pure Fe<sub>2</sub>O<sub>3</sub> catalysts also have certain drawbacks such as a narrow operating window and relatively poor activity at low temperatures.<sup>24,56</sup> Consequently, substantial efforts have been made to address the limitations of current catalysts, such as introducing other transition or rare earth metal oxides to form mixed metal oxides and optimizing the structure–activity relationship, which have proven to be effective strategies.<sup>57–59</sup>

#### 1.4 Cu-Based catalysts and active Cu species

Recently, Cu-based catalysts, including Cu-containing metal oxides and Cu-based small-pore zeolites, have been extensively explored in NH<sub>3</sub>-SCR owing to the good low-temperature activity in the NH<sub>3</sub>-SCR process.<sup>60–62</sup> As a transition metal, Cu species show better redox properties based on the variable valence of Cu<sup>2+</sup> and Cu<sup>+</sup>, which have been potential supports to combine with other foreign elements. Zhu *et al.* reported that the introduction of Nb species in CuNb binary oxide catalysts accelerated the redox reaction (Cu<sup>2+</sup> + Nb<sup>4+</sup> → Cu<sup>+</sup> + Nb<sup>5+</sup>) and achieved near 100% NO conversion and N<sub>2</sub> selectivity (180–330 °C), resulting from increased acid amount and improved NO adsorption ability.<sup>63</sup> By comparison, taking CHA-type (Cu-SSZ-13 and Cu-SAPO-34), AEI-type (Cu-SAPO-18 and Cu-SSZ-39) and MFI-type (Cu-ZSM-5) zeolites as examples, Cu-based small-pore zeolites have already been applied in the commercial field due to the excellent adsorption capacity of molecule gas and enhanced catalytic performance. Generally, the small-pore CHA-type framework comprised large cavities (8.35 Å × 8.35 Å × 8.23 Å) and eight-membered ring pore windows (3.8 Å × 3.8 Å),<sup>64</sup> which are employed as the state-of-the-art catalysts in NH<sub>3</sub>-SCR due to their high activity, N<sub>2</sub> selectivity, and excellent hydrothermal stability under harsh conditions.<sup>65–67</sup> Besides, AEI-type zeolites have the properties of superior low-temperature performance, wide operating windows and high N<sub>2</sub> selectivity. They possess a similar structure to CHA-type zeolites, characterized by an identical framework density, the presence of double six-membered ring units, and the eight-membered ring pore system with cages located at channel intersections.<sup>68–70</sup> For Cu-exchanged MFI-type zeolites, such as Cu-ZSM-5, they have also attracted much attention for the application of NO<sub>x</sub> removal due to the superior stability, low cost and low toxicity.

In the catalysts mentioned above, isolated Cu species rather than CuO<sub>x</sub> clusters are considered to be the active sites, the valence states of which have a significant effect on NH<sub>3</sub>-SCR performance. For Cu-containing metal oxides, it is generally accepted that the interconversion between Cu<sup>+</sup> and Cu<sup>2+</sup> through a redox process is related to the catalytic activity.<sup>71</sup>

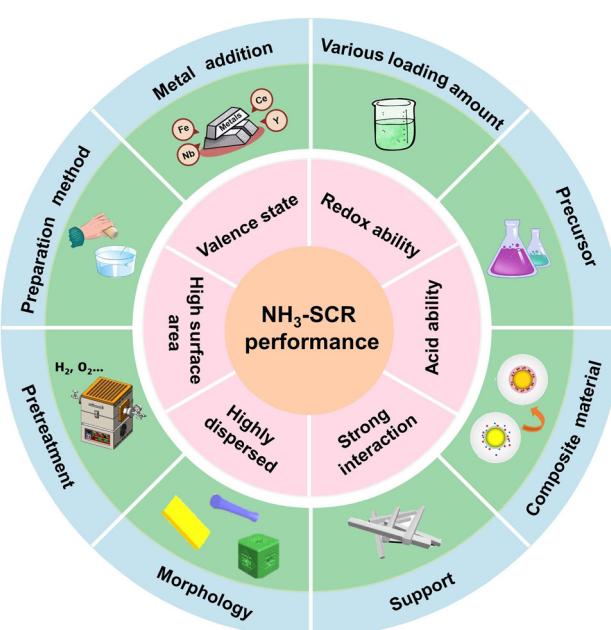


Fig. 2 Effect factors of NH<sub>3</sub>-SCR activity.



Differently, owing to the ion exchange ability of small-pore zeolites, the Cu species will be transferred to the zeolites in the form of an ionic state. Some  $\text{Cu}^{2+}$  ions interacted with two Al atoms and located at the six-membered rings of the framework (denoted as  $\text{Z}_2\text{Cu}^{2+}$ , where Z represented a zeolite framework negative charge), while the other  $\text{Cu}^{2+}$  ions formed  $[\text{ZCu}^{2+}(\text{OH})]^+$  species with a single Al atom at eight-membered rings.<sup>72-74</sup> Both of these Cu species attached to the zeolite framework were considered active sites in the catalytic process, with  $\text{Cu}^{2+}$  easily being reduced to monovalent  $\text{Cu}^+$  ions, leading to the generation of new Brønsted acid sites. Thereafter, the redox cycle was completed through the oxidation process from  $\text{Cu}^+$  species to  $\text{Cu}^{2+}$  and  $[\text{Cu}(\text{OH})]^+$  species.<sup>75</sup> Therefore, it was concluded that both  $\text{Cu}^{2+}$  and  $\text{Cu}^+$  species coexisted and interconverted *via* a redox mechanism in  $\text{NH}_3$ -SCR. Although Cu-based catalysts have lots of attractive advantages presented above in the  $\text{NH}_3$ -SCR reaction, the complex operating environment still brings great challenges to the high activity, stability and anti-toxicity of catalysts.

In this work, efficient strategies for enhancing  $\text{NH}_3$ -SCR performance of Cu-based catalysts through support derivation, precursor optimization engineering, secondary metal doping, crystal structure regulation, preparation method modification and interaction and interface engineering are comprehensively summarized and discussed, and the reaction mechanisms and degradation paths of  $\text{NO}_x$  on Cu-based catalysts are pointed out. Moreover, we further conclude the toxic mechanisms of impurities on the catalysts under real applications, and put forward relevant countermeasures to improve hydrothermal resistance and poisoning-resistance ( $\text{SO}_2$  and alkali metals) performance. In particular, for Cu-based small-pore zeolites, the hydrothermal stability needs to be further promoted because their activity always decreases significantly in the presence of water vapor at high temperatures due to the dealumination and the zeolite structure collapse. In this regard, the aim is to present an easy-to-read and comprehensive review of Cu species in  $\text{NH}_3$ -SCR, thereby highlighting the opportunities and challenges associated with Cu-based catalysts.

## 2. Design strategies of Cu-based catalysts and corresponding reaction mechanisms

Based on the reported research, efficient design strategies to improve the  $\text{NH}_3$ -SCR performance of Cu-based catalysts could

be divided into six categories such as support derivation, precursor optimization engineering, secondary metal doping, crystal structure regulation, preparation method modification and interaction and interface engineering. Herein, we summarized the influence of each strategy on the catalytic activity and analysed the reaction mechanism and investigation status.

### 2.1 Support derivation

Due to the different configuration, specific surface area, electronic properties, interfacial properties, physicochemical properties, *etc.*, the supports have different effects on the chemical valence states and dispersion of Cu active species. This effect was closely related to the adsorption and activation capacity of the reactant gas molecules, which played a crucial role in the  $\text{NH}_3$ -SCR reaction (Table 1). For instance, SSZ-13, SAPO-18, SSZ-39, metal oxides, *etc.* have been widely explored as the support for efficient  $\text{NO}_x$  removal. In particular, for the commercial Cu-SSZ-13 zeolites, it had been confirmed that both monovalent- and divalent-copper sites are active centers.<sup>76</sup> Great efforts have been devoted to revealing the catalytic mechanism through the determination of active sites, which was helpful to provide a basis for guiding and optimizing the structure of catalysts to achieve high performance. At the same time, since the  $\text{NH}_3$  was a gaseous reactant and  $\text{H}_2\text{O}$  was the main reaction product, a comparison was made among water-solvated and ammonia-solvated and bare Cu species to examine the impact of solvents on the activity of active Cu species (Fig. 3a). The results showed that nitrate species were more likely to be generated on solvated Cu sites during the oxidation process compared to in the absence of solvent molecules, while the reduction process of  $\text{NH}_3$ -SCR was inhibited by solvent molecules. Notably, the experimental observation of Cu-nitrate and Cu-nitrosamine ( $\text{H}_2\text{NNO}$ ) spectroscopic signatures provided insights into the reaction mechanisms (Fig. 3b), and reaction mechanisms based on theoretical calculations were performed to reveal the activity of solvated active centers (Fig. 3c). Additionally,  $\text{NH}_3$ -SCR was found to follow the multisite mode on ammonia-solvated Cu species  $[\text{Cu}(\text{NH}_3)]^+$  and Brønsted acid sites, emphasizing the importance of constructing adjacent active sites to promote the catalytic process. The solvation of  $\text{NH}_3$  was found to assist in the generation and dispersion of Cu pairs, activating  $\text{O}_2$  molecules and inducing the generation of  $\text{HONO}$  and  $\text{H}_2\text{NNO}$  intermediates, which were subsequently decomposed by nearby Brønsted acid sites to  $\text{N}_2$  and  $\text{H}_2\text{O}$  (Fig. 4a).<sup>77</sup>

Table 1 Typical Cu-based catalysts with various supports reported in the literature

| Catalysts                   | Reaction conditions  | NO conversion   | Ref. |
|-----------------------------|--|---|------|
| Cu <sub>1.8</sub> -SSZ-13   | $[\text{NO}] = [\text{NH}_3] = 500 \text{ ppm}$ , $[\text{O}_2] = 5\%$ , GHSV = $400\ 000 \text{ h}^{-1}$  | >40% ( $\sim 240\text{--}550^\circ\text{C}$ )         | 78   |
|                             | $[\text{NO}] = [\text{NO}_2] = 250 \text{ ppm}$ , $[\text{NH}_3] = 500 \text{ ppm}$ , $[\text{O}_2] = 5\%$ , GHSV = $400\ 000 \text{ h}^{-1}$                              | >90% ( $\sim 240\text{--}550^\circ\text{C}$ )         |      |
| Cu <sub>1.8</sub> -SSZ-39   | $[\text{NO}] = [\text{NH}_3] = 500 \text{ ppm}$ , $[\text{O}_2] = 5\%$ , GHSV = $400\ 000 \text{ h}^{-1}$  | $\sim 100\%$ ( $\sim 240\text{--}550^\circ\text{C}$ ) | 78   |
|                             | $[\text{NO}] = [\text{NO}_2] = 250 \text{ ppm}$ , $[\text{NH}_3] = 500 \text{ ppm}$ , $[\text{O}_2] = 5\%$ , GHSV = $400\ 000 \text{ h}^{-1}$                              | >80% ( $\sim 260\text{--}550^\circ\text{C}$ )         |      |
| Cu-SSZ-39                   | $[\text{NO}] = [\text{NH}_3] = 500 \text{ ppm}$ , $[\text{O}_2] = 5\%$ , $[\text{H}_2\text{O}] = 5 \text{ vol\%}$ , GHSV = $19\ 000 \text{ h}^{-1}$                        | $\sim 90\%$ ( $\sim 250\text{--}550^\circ\text{C}$ )  | 79   |
| Cu <sub>2.49</sub> -SAPO-18 | $[\text{NO}] = 1000 \text{ ppm}$ , $[\text{NH}_3] = 1100 \text{ ppm}$ , $[\text{O}_2] = 5\%$ , $[\text{H}_2\text{O}] = 10 \text{ vol\%}$ , GHSV = $30\ 000 \text{ h}^{-1}$ | >80% ( $\sim 225\text{--}575^\circ\text{C}$ )         | 80   |
| CuO/PRM                     | $[\text{NO}] = [\text{NH}_3] = 500 \text{ ppm}$ , $[\text{O}_2] = 5\%$ , GHSV = $120\ 000 \text{ h}^{-1}$  | >80% ( $\sim 275\text{--}400^\circ\text{C}$ )         | 86   |
| Cu-SAPO-34                  | $[\text{NO}] = [\text{NH}_3] = 500 \text{ ppm}$ , $[\text{O}_2] = 5\%$ , $[\text{H}_2\text{O}] = 5 \text{ vol\%}$ , GHSV = $400\ 000 \text{ h}^{-1}$                       | >80% ( $\sim 200\text{--}550^\circ\text{C}$ )         | 88   |
| Cu-ZSM-5                    | $[\text{NO}] = [\text{NH}_3] = 500 \text{ ppm}$ , $[\text{O}_2] = 5\%$ , GHSV = $180\ 000 \text{ h}^{-1}$  | >90% ( $\sim 240\text{--}350^\circ\text{C}$ )         | 105  |



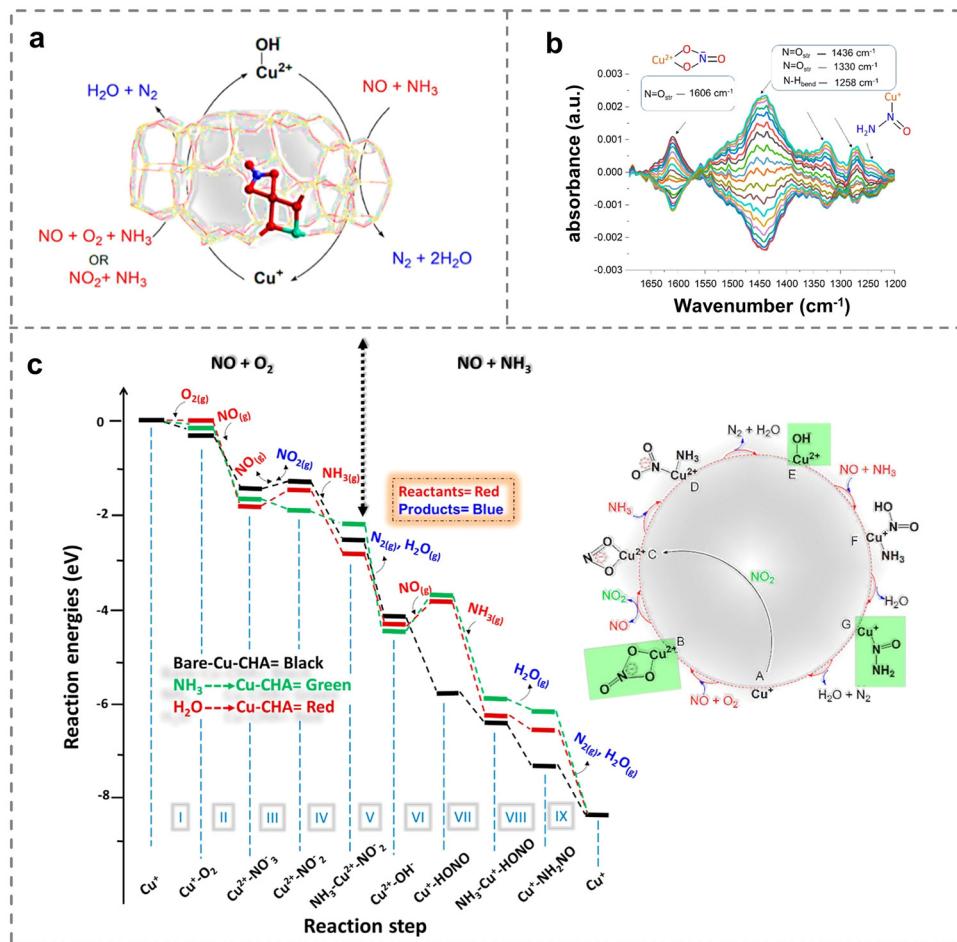


Fig. 3 (a) Schematic of the NH<sub>3</sub>-SCR reaction mechanism on Cu-SSZ-13 zeolites. (b) Concentration modulation ME DRIFTS experiment with the corresponding phase-resolved spectrum. (c) Reaction mechanisms on the bare active site (black), ammonia-physisorbed active site (green) and water-physisorbed active site (red). Copied with permission from ref. 76. Copyright 2022, American Chemical Society.

Consequently, the researchers proposed two possible cycles to reveal the reaction path, with the difference that NO was adsorbed on ammonia-solvated Cu<sup>+</sup> species in cycle I while on activated oxygen in cycle II (Fig. 4b). The studies of the influence on solvated Cu-based catalysts provided a solid understand for revealing the catalytic mechanism in NH<sub>3</sub>-SCR reactions.

Besides, Zhu *et al.* observed that Cu-SSZ-13 demonstrated excellent standard SCR performance, but they noted that the low reactivity and accumulation of NH<sub>4</sub>NO<sub>3</sub> intermediates hindered NO<sub>x</sub> conversion.<sup>78</sup> Particularly in the presence of NO<sub>2</sub>, it had an inhibiting effect on the reduction of NO<sub>x</sub> on Cu-SSZ-13, thereby limiting the process of fast SCR (Fig. 4c–e). The studies revealed that Cu-SSZ-13 catalysts exhibited fewer surface Brønsted acid sites interacting with NO<sub>2</sub> molecules, affecting the formation of HNO<sub>3</sub> species and thus decelerating the reduction of NH<sub>4</sub>NO<sub>3</sub> intermediates. In contrast, a comparison with Cu-SSZ-13 catalysts demonstrated that NO<sub>2</sub> had the opposite effect on Cu-SSZ-39, promoting fast SCR reactions due to an abundance of surface Brønsted acid sites. The findings indicated that the choice of support played an important role in regulating the activity of the catalysts. As a result, a mass of

research studies have also been devoted to improving the SCR activity of other types of Cu-based small-pore zeolites.<sup>65,66</sup> Fu *et al.* firstly revealed the mutual integration of framework Al atoms and Cu ions in Cu-SSZ-39 zeolites, confirming the stabilization mechanism of framework Al by Cu<sup>2+</sup> ions on double six-membered ring units (Fig. 4f).<sup>79</sup> The content of Cu was confirmed to be closely related to the hydrothermal stability of the catalysts. Materials with higher Cu contents showed superior activity even after hydrothermal treatments at 750 and 800 °C, resulting from the framework Al being well retained by the protective effect of isolated Cu<sup>2+</sup> species. However, Du *et al.* reported an unexpected promotion in the NO<sub>x</sub> removal of aging Cu-SSZ-39 with moderate Cu contents at low temperatures. The enhancement was related to the generation of Cu<sub>x</sub>O<sub>y</sub> species from Cu<sup>2+</sup>, facilitating the generation of nitrate species, which was different from other studies that required Cu ions for the activation of O<sub>2</sub> molecules and NO molecules.

Furthermore, Ming *et al.* proposed that the isolated or paired framework Al sites and Si/Al ratio were key factors determining the characteristics and the position of Cu ions in Cu-exchanged zeolites, and the catalytic performance was affected in turn. They systematically investigated the influence

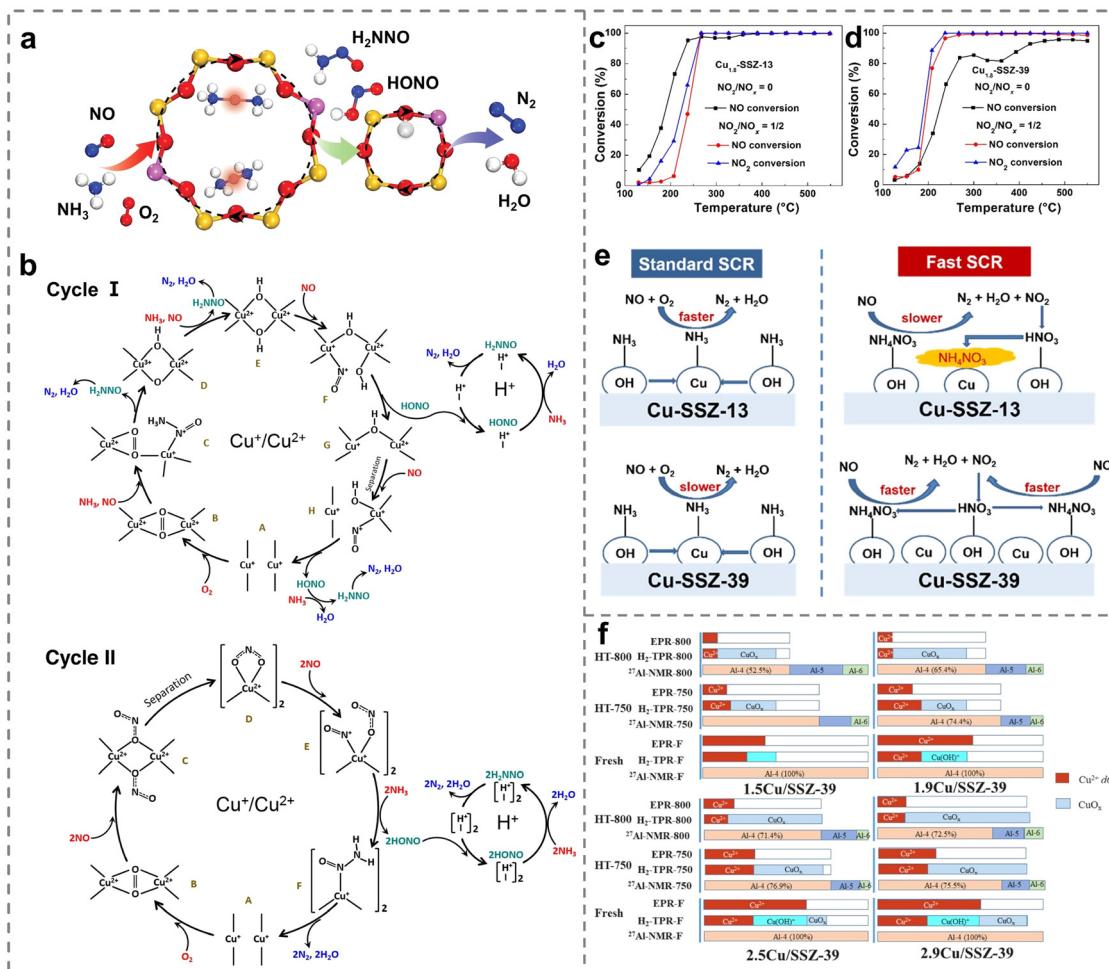


Fig. 4 (a) The reaction route in the multisite fashion for NH<sub>3</sub>-SCR over Cu-CHA. (b) Two possible reaction mechanisms of NH<sub>3</sub>-SCR. Copied with permission from ref. 77. Copyright 2020, American Chemical Society. (c) and (d) NH<sub>3</sub>-SCR activity over (c) Cu<sub>1.8</sub>-SSZ-13 and (d) Cu<sub>1.8</sub>-SSZ-39 catalysts. (e) The influences of NO<sub>2</sub> on NH<sub>3</sub>-SCR processes on Cu-SSZ-13 and Cu-SSZ-39. Copied with permission from ref. 78. Copyright 2020, American Chemical Society. (f) The contents of Al and Cu species quantified on Cu/SSZ-39 zeolites. Copied with permission from ref. 79. Copyright 2021, Elsevier.

of Cu loading and Si content on the catalytic performance of Cu-SAPO-18 catalysts.<sup>80</sup> By optimizing the Cu loading (1.53–3.51 wt%) and Si content (0.084–0.204), they found that the catalysts with a Cu loading of 2.49 wt% and Si content of 0.173 exhibited superior activity and hydrothermal stability. This was attributed to the generation of more acid sites and isolated Cu<sup>2+</sup> ions. It was observed that when the Si content was maximum, the Cu-SAPO-18 zeolites had a large number of Si(0OAl) structures, which was not conducive to stabilizing the extra framework Cu<sup>2+</sup> ions in the process of hydrothermal treatment thus leading to structural destruction. Although Cu-based small-pore zeolites had shown superior NH<sub>3</sub>-SCR activity, complex synthesis measures and the high cost inevitably limited their further commercial application. In contrast, Cu-containing metal oxide catalysts were hopeful to be ideal candidates due to their simple preparation methods and low cost, and they have attracted significant attention for NH<sub>3</sub>-SCR applications in recent years.<sup>81,82</sup> In this regard, various selections of supports were expected to enhance the catalytic performance in the NH<sub>3</sub>-SCR process.<sup>83–85</sup> For instance, pretreated

raw mud (PRM) was used as a support, and then CuO/PRM catalysts were synthesized by introducing varying CuO contents.<sup>86</sup> The results showed that 7 wt% CuO promoted the redox equilibrium of Cu<sup>2+</sup> + Fe<sup>2+</sup> ↔ Cu<sup>+</sup> + Fe<sup>3+</sup> and induced more Cu<sup>+</sup> and surface oxygen active species. The enhanced Eley-Rideal mechanism was further facilitated by the competitive adsorption between NO<sub>x</sub> and NH<sub>3</sub> molecules, as the dispersed CuO improved NH<sub>3</sub> adsorption but weakened NO<sub>x</sub> adsorption. Therefore, the role of the support in affecting the active sites and reaction mechanism could not be ignored, so choosing a suitable support was an effective strategy to regulate the performance of active centers, optimize the reaction path and maximize the activity.

## 2.2 Precursor optimization engineering

The synthesis of zeolites was closely related to different types of Si sources and Cu sources of the precursors. It had been well verified that the formation of different sizes of aluminosilicate intermediates and primary nucleus would be greatly regulated by optimizing the Si source precursor, which further affected

the nucleation and crystallization process. For instance, the structural characteristic of the SSZ-13 support would be significantly tuned by precursor optimization engineering (Fig. 5a), in which various Si sources such as colloidal silica (Si sol), gelatinous silica (Si gel) and tetraethyl orthosilicate (TEOS) were chosen as the precursors, thus leading to variations in acidity and the distribution of Cu species over Cu-SSZ-13.<sup>87</sup> Cu-SSZ-13 zeolites prepared with silica sol (CS-Si sol) showed more uniform sizes and high surface areas, which promoted the adsorption of reactants. Meanwhile, more Cu<sup>2+</sup> active species were detected on the CS-Si sol catalysts, resulting in superior hydrothermal stability after the same hydrothermal treatment. Moreover, different Cu sources had significant effects on the type and distribution of active sites in the NH<sub>3</sub>-SCR reaction. Then, the influence of various Cu precursors on the catalytic activity of Cu-SAPO-34 zeolites was further explored. The physicochemical properties of various Cu-SAPO-34 catalysts with different precursors of Cu (A: Cu-acetate; N: Cu-nitrate; Cl:

Cu-chloride; and S: Cu-sulfate) were employed to reveal the underlying phenomena and essence of the catalytic process.<sup>88</sup> This study demonstrated that Cu(A)-SAPO-34 zeolites exhibited the best catalytic performance compared to Cu(N, Cl or S)-SAPO-34 zeolites. This would be attributed to the presence of a higher proportion of isolated Cu<sup>2+</sup> species and fewer CuO species on the Cu(A)-SAPO-34 catalysts. Unfortunately, all aged catalysts experienced a decrease in activity after hydrothermal treatment, as a portion of isolated Cu<sup>2+</sup> ions became unstable and then transformed into CuO species, resulting in catalyst deactivation. In this regard, submicron Cu-SAPO-34 catalysts, prepared by combining Cu-TEPA and morpholine as templates, exhibited superior catalytic performance and hydrothermal stability compared to the reference catalysts using Cu-TEPA, diethylamine and tetraethylammonium bromide as templates.<sup>89</sup> The presence of Si(*n*OAl) (*n* = 1–4) structures in Cu-SAPO-34 triggered the generation of a significant number of Brønsted acid sites and enhanced NO<sub>x</sub> reduction. Besides, the isolated

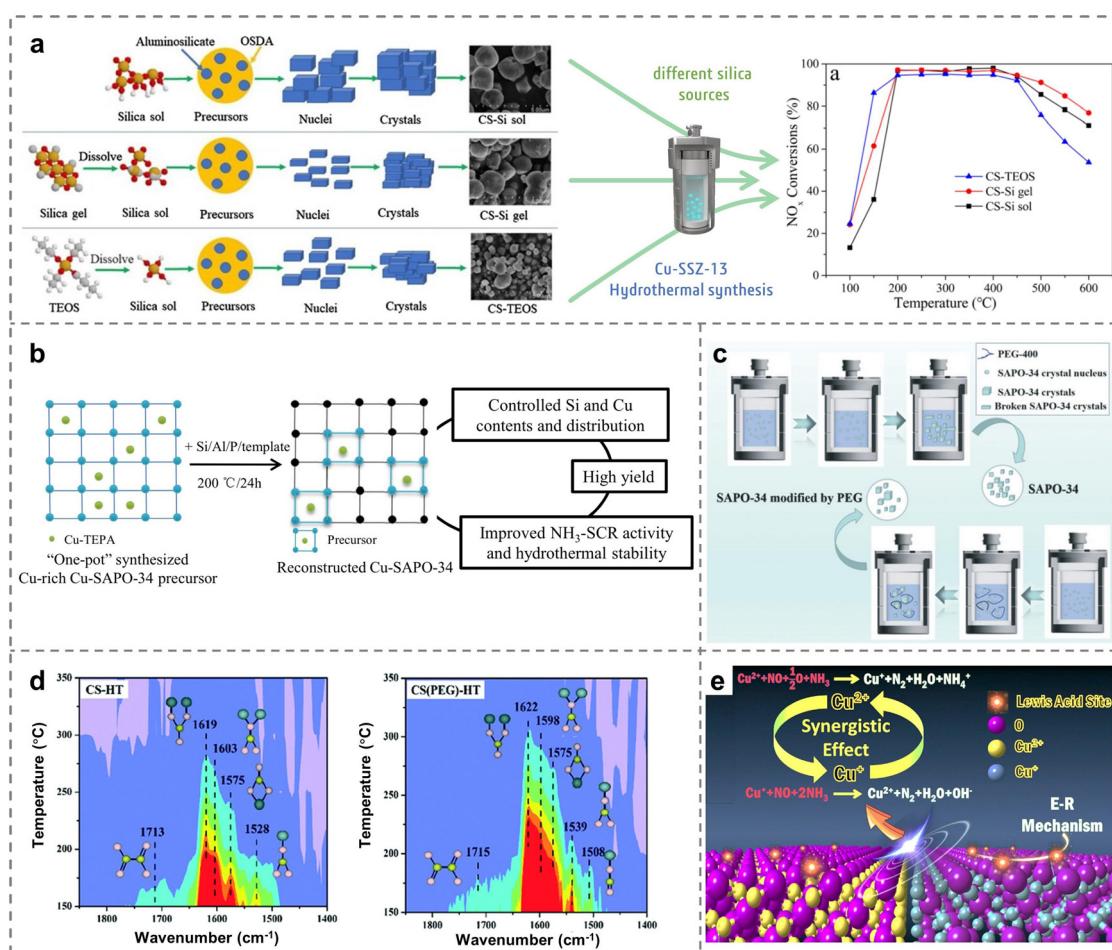


Fig. 5 (a) Schematic diagram of the proposed pathways of SSZ-13 crystallization (Si: yellow, O: red, C: gray, H: white) and NH<sub>3</sub>-SCR performance of Cu-SSZ-13 prepared through using different Si sources. Copied with permission from ref. 87. Copyright 2020, Elsevier. (b) The reconstruction approach for the preparation of Cu-SAPO-34. Copied with permission from ref. 94. Copyright 2020, Elsevier. (c) The crystallization of SAPO-34 and the process induced by PEG. Copied with permission from ref. 95. Copyright 2021, Royal Society of Chemistry. (e) Catalytic mechanism of catalysts prepared with Cu-MOFs as the precursor. Copied with permission from ref. 96. Copyright 2019, Elsevier.



$\text{Cu}^{2+}$  ions were effectively preserved and stabilized by  $\text{Si}(n\text{OAl})$  components, which was critical in the development and manufacture of Cu-SAPO-34 SCR catalysts to achieve superior activity and hydrothermal stability for commercial applications.

Although Cu-SAPO-34 zeolites with CHA framework topology have garnered considerable attention because of the remarkable  $\text{NH}_3$ -SCR performance across a broad operating temperature range and high-temperature hydrothermal stability,<sup>90,91</sup> the crystallinity of Cu-SAPO-34 zeolites tended to decline during the process of traditional metal ion loading in the repeated ion exchange. The other main issue arrived when copper-tetraethylenepentamine (Cu-TPEA) was used as the structure-directing agent, as it often led to the production of high Si contents and numerous Si islands on Cu-SAPO-34 through the one-pot method, significantly reducing the catalytic activity and hydrothermal stability.<sup>68,92,93</sup> In response, Sun *et al.* proposed a reconstruction approach for synthesizing Cu-SAPO-34 *via* using Cu-rich SAPO-34 as the Cu precursor.<sup>94</sup> This approach offers advantages such as a wider crystallization phase region, high yield and adjustable contents of Si and Cu components compared to the traditional “one-pot” means (Fig. 5b). The resulting Cu-SAPO-34 zeolites exhibited a higher content of isolated  $\text{Cu}^{2+}$  after undergoing high-temperature hydrothermal treatment. Notably, the low-silica catalysts retained their acid sites, which contributes to superior hydrothermal stability.

Additionally, polyethylene glycol (PEG) was of great importance to the nucleation and crystal growth of zeolites, and thus intact hierarchical PEG-modified Cu/SAPO-34 catalysts were prepared to enhance the hydrothermal stability for  $\text{NH}_3$ -SCR.<sup>95</sup> The chain-like PEG micelles synthesized by the traditional hydrothermal method would provide sufficient space for crystal growth by adhering to and wrapping SAPO-34, forming large SAPO-34 crystals of 3–7  $\mu\text{m}$  (Fig. 5c). The key intermediates of bridged nitrates ( $1598/1622\text{ cm}^{-1}$ ) induced by NO activation were detected on adjacent isolated Cu sites, which was beneficial for the dissociation of  $\text{O}_2$  and promoted the reduction of  $\text{NO}_x$  on PEG-modified catalysts after the hydrothermal aging (800 °C for 12 hours with 10 vol%  $\text{H}_2\text{O}$ ) (Fig. 5d). Except for Cu-based small-pore zeolites, Wang *et al.* prepared Cu metal organic frameworks (MOFs) with a porous  $\text{CuO}/\text{Cu}_2\text{O}$  heterostructure by regulating Cu precursors.<sup>96</sup> On the one hand, the amount of oxygen defects increased in the  $\text{CuO}/\text{Cu}_2\text{O}$  heterostructure, enabling efficient  $\text{O}_2$  adsorption. On the other hand, the synergistic effect between  $\text{Cu}^+$  and  $\text{Cu}^{2+}$  led to the presence of more Lewis acid sites compared to bulk  $\text{CuO}$ .

and  $\text{Cu}_2\text{O}$ , facilitating the E-R mechanism of the  $\text{NH}_3$ -SCR reaction (Fig. 5e). Therefore, the preparation of catalysts with high performance through precursor optimization engineering was of great significance to the promotion of Cu-based catalysts in industrial applications.

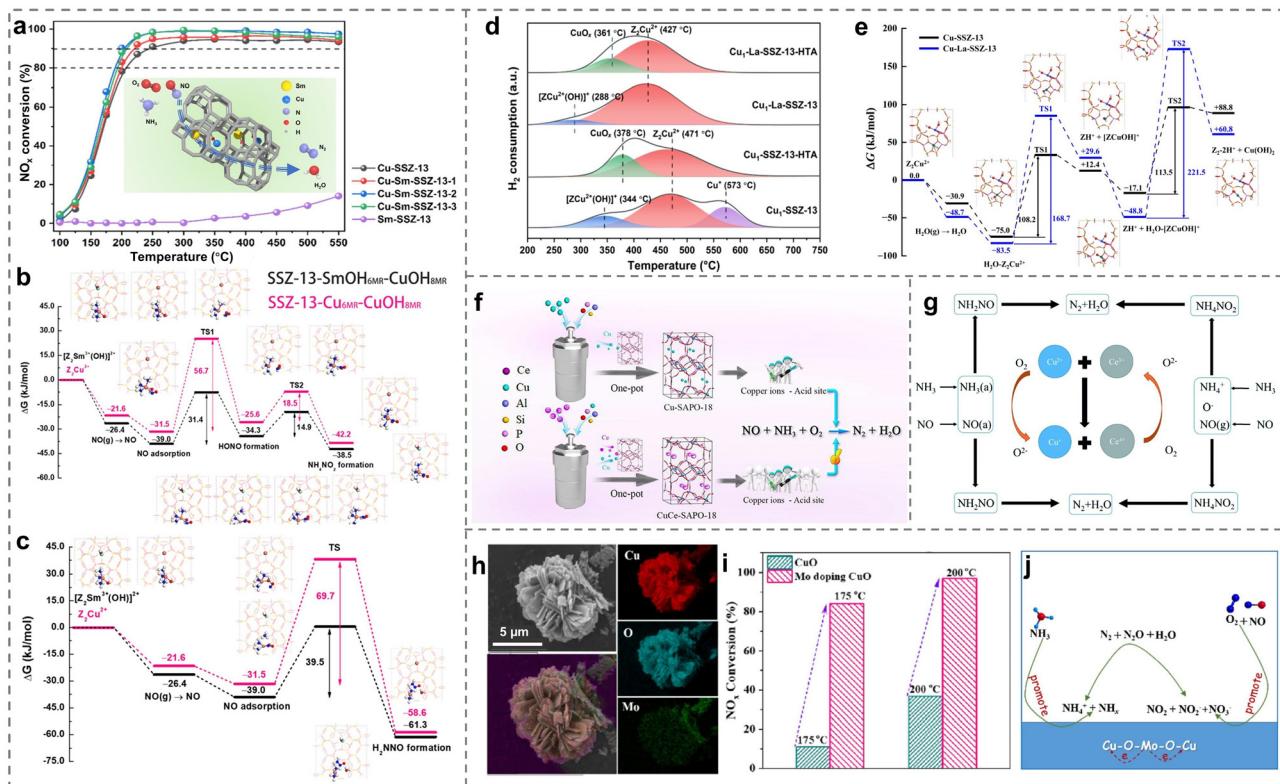
### 2.3 Secondary metal doping

Due to being limited to the sole Cu active sites, the strategy of doping secondary metals was efficient to improve the catalytic activities of Cu-based catalysts (Table 2). For example, the low-temperature activity on Cu-SSZ-13 could be promoted through the introduction of Nb species.<sup>97</sup> After Nb species entered the exchange sites of the framework, both Lewis acid sites and Brønsted acid sites were enhanced, promoting the adsorption of  $\text{NH}_3$  molecules. Meanwhile, more  $\text{NO}_x$  species could adsorb on Nb-modified Cu-SSZ-13 catalysts and react with  $\text{NH}_4^+$  species adsorbing on Brønsted acid sites *via* the Langmuir–Hinshelwood mechanism. It is well-known that the rare earth metals acting as promoters had a superior regulation function on the reactivity of active centers and performance of catalysts. As expected, a crucial study discovered that a series of Cu-Sm-SSZ-13 catalysts exhibited enhanced low-temperature activity (Fig. 6a).<sup>98</sup> Sm ions were observed to be present at six-membered rings of SSZ-13, and then the influence of Sm ions was thoroughly investigated. The theoretical results revealed that the introduction of Sm species facilitated the formation of  $[\text{ZCu}^{2+}(\text{OH})]^+$  ions and promoted their activity, further reducing the formation energies of active  $\text{NH}_4\text{NO}_2$  (14.9 vs. 18.5  $\text{kJ mol}^{-1}$ ) and  $\text{H}_2\text{NNO}$  (39.5 vs. 69.7  $\text{kJ mol}^{-1}$ ) components in the  $\text{NH}_3$ -SCR process (Fig. 6b and c). Notably, the strong electrostatic interaction between  $\text{Sm}^{3+}$  and  $[\text{ZCu}^{2+}(\text{OH})]^+$  also restrained the formation of inactive  $\text{CuO}_x$  species, resulting in the high stability of Cu-Sm-SSM-13 catalysts. Similarly, after the introduction of La species into the Cu-SSZ-13 zeolites, the Cu-La-SSZ-13 exhibited a higher hydrothermal stability (aging in the flowing air containing 10 vol%  $\text{H}_2\text{O}$  at 750 °C for 16 h) than that of Cu-SSZ-13, resulting from the incorporation of La ions inhibiting the transformation from  $\text{Z}_2\text{Cu}^{2+}$  to inactive  $\text{CuO}_x$  species and protecting the framework of zeolites (Fig. 6d).<sup>99</sup> To further reveal the promotion effect of La species, the transition process from  $\text{Z}_2\text{Cu}^{2+}$  to  $\text{Cu}(\text{OH})_2$  by the damage of water was carried out with DFT calculations. When La species existed, the formation barrier of  $\text{Cu}(\text{OH})_2$  was higher (221.5  $\text{kJ mol}^{-1}$ ) than that of 113.5  $\text{kJ mol}^{-1}$  in the absence of La species (Fig. 6e), indicating that the generation of  $\text{CuO}_x$  inactive species was well inhibited.

Table 2 Representative Cu-based catalysts modified with secondary metal doping for the SCR reaction

| Catalysts  | Reaction conditions   | NO conversion      | Ref. |
|--|---|--------------------|------|
| Nb/Cu-SSZ-13                                     | $[\text{NO}] = [\text{NH}_3] = 500\text{ ppm}$ , $[\text{O}_2] = 5\%$ , $[\text{H}_2\text{O}] = 10\text{ vol\%}$ , GHSV = 60 000 $\text{h}^{-1}$                    | >80% (~175–650 °C) | 97   |
| Cu-Sm-SSZ-13                                     | $[\text{NO}] = [\text{NH}_3] = 500\text{ ppm}$ , $[\text{O}_2] = 5\%$ , $[\text{H}_2\text{O}] = 5\text{ vol\%}$ , GHSV = 200 000 $\text{h}^{-1}$                    | >90% (~200–550 °C) | 98   |
| Cu-Sm-SSZ-13                                     | $[\text{NO}] = [\text{NH}_3] = 500\text{ ppm}$ , $[\text{O}_2] = 5\%$ , $[\text{H}_2\text{O}] = 5\text{ vol\%}$ , GHSV = 200 000 $\text{h}^{-1}$                    | >90% (~200–550 °C) | 99   |
| $\text{Cu}_x\text{Ce}_{1-x}\text{W}_5\text{O}_x$ | $[\text{NO}] = [\text{NH}_3] = 500\text{ ppm}$ , $[\text{O}_2] = 5\%$ , GHSV = 36 000 $\text{h}^{-1}$   | >80% (~240–390 °C) | 102  |
| Cu/Y-SSZ-39                                      | $[\text{NH}_3] = 220\text{ ppm}$ , $[\text{NO}] = 200\text{ ppm}$ , $[\text{O}_2] = 10\%$ , $[\text{H}_2\text{O}] = 5\text{ vol\%}$ , GHSV = 40 000 $\text{h}^{-1}$ | >70% (~200–550 °C) | 103  |
| MnCu-SSZ-39                                      | $[\text{NO}] = [\text{NH}_3] = 500\text{ ppm}$ , $[\text{O}_2] = 5\%$ , GHSV = 150 000 $\text{ml g}^{-1} \text{h}^{-1}$   | >80% (~250–550 °C) | 104  |
| FeCu-ZSM-5                                       | $[\text{NO}] = [\text{NH}_3] = 500\text{ ppm}$ , $[\text{O}_2] = 5\%$ , GHSV = 180 000 $\text{h}^{-1}$  | >90% (~230–500 °C) | 105  |
| Mo/CuO   | $[\text{NO}] = [\text{NH}_3] = 500\text{ ppm}$ , $[\text{O}_2] = 3\%$ , GHSV = 45 000 $\text{h}^{-1}$   | >80% (~175–275 °C) | 84   |





**Fig. 6** (a) NH<sub>3</sub>-SCR performance of Cu-SSZ-13 and Sm-doped Cu-SSZ-13 catalysts. (b) and (c) Generation of (b) NH<sub>4</sub>NO<sub>2</sub> and (c) H<sub>2</sub>NNO on Cu<sup>2+</sup>(OH)(NH<sub>3</sub>)<sub>3</sub> with [Z<sub>2</sub>Sm<sup>3+</sup>(OH)]<sup>2+</sup> and Z<sub>2</sub>Cu<sup>2+</sup>, and corresponding intermediates. Copied with permission from ref. 98. Copyright 2022, American Chemical Society. (d) H<sub>2</sub>-TPR profiles of the as-prepared catalysts before and after hydrothermal ageing. (e) The conversion of Z<sub>2</sub>Cu<sup>2+</sup> species in the absence or presence of [ZLa<sup>3+</sup>(OH)<sub>2</sub>]<sup>2+</sup> under hydrothermal treatment. Copied with permission from ref. 99. Copyright 2023, Springer Nature. (f) The schematic diagram regarding the catalyst synthesis process. Copied with permission from ref. 100. Copyright 2022, Elsevier. (g) The interaction of Cu and Ce species over Cu<sub>y</sub>Ce<sub>1-y</sub>W<sub>5</sub>O<sub>x</sub> composite materials. Copied with permission from ref. 102. Copyright 2019, Royal Society of Chemistry. (h) Mapping images of Mo-doped CuO catalysts. (i) NH<sub>3</sub>-SCR performance of the as-prepared catalysts. (j) The mechanism of Mo-doped CuO catalysts. Copied with permission from ref. 84. Copyright 2022, Elsevier.

Notably, as the metal dopants, Ce species exerted a remarkable modifying effect on Cu-SAPO-18 zeolites. Therefore, plenty of effort has been made to explore the promotion mechanism of Ce ions. Wu *et al.* reported that the doping of Ce and Cu in SAPO-18 catalysts (CuCe-SAPO-18) influenced the distribution of Si atoms and the coordination of Al atoms in the skeleton structure,<sup>100</sup> which increased the quantity of active Cu<sup>2+</sup> ions and the acid sites of the catalysts (Fig. 6f), leading to the significant increase of catalytic activity at low temperatures (<200 °C). In one similar study, Han *et al.* proposed that the rate of Langmuir–Hinshelwood and Eley–Rideal route accelerated by doping Ce might be the main reason for superior performance.<sup>101</sup> Importantly, the synergistic effects between Cu and Ce were revealed to enhance the reducibility and surface acid property of the composite materials (Cu<sub>y</sub>Ce<sub>1-y</sub>W<sub>5</sub>O<sub>x</sub>), which was facilitated by the conversion of Cu<sup>2+</sup>/Ce<sup>3+</sup>–Cu<sup>+</sup>/Ce<sup>4+</sup> coupled redox ion pairs (Fig. 6g).<sup>102</sup>

Moreover, other transition metals such as yttrium ions (Y<sup>3+</sup>) were found to be conducive to improving the hydrothermal stability of Cu/SSZ-39 at higher temperatures (>800 °C).<sup>103</sup> Y<sup>3+</sup> ions were confirmed to enter into the cages of SSZ-39 zeolites on the modified catalyst (Cu/Y-SSZ-39), which induced more

isolated Cu ions in the double six-membered rings of SSZ-39 zeolites, showing remarkably higher NO<sub>x</sub> conversion and hydrothermal stability than Cu/SSZ-39. Wang *et al.* even confirmed that Mn species were more beneficial in improving the catalytic activity of Cu-SSZ-39 than Ce species after the hydrothermal treatment.<sup>104</sup> Compared to pure Cu-SSZ-39, the introduction of Mn not only inhibited cluster aggregation but also accelerated the formation of isolated Cu<sup>2+</sup> species. Meanwhile, the structure and acid density were well preserved on MnCu-SSZ-39 even after hydrothermal treatment at temperatures as high as 850 °C, thus improving NH<sub>3</sub>-SCR performance. Similarly, the addition of Fe species would broaden the temperature window and promote the hydrothermal stability of FeCu-ZSM-5 compared to reference catalysts (Cu/ZSM-5 and Fe/ZSM-5).<sup>105</sup> This improvement could be attributed to the hierarchical micro-mesoporous structures exhibited by the FeCu-ZSM-5 catalysts prepared *via* the one-pot method, which facilitated the dispersion of Cu active sites on the surface. In addition, various contents of Ag were employed to dope on Cu/ZSM-5 catalysts to regulate defects by utilizing the synergistic effect between Ag and Cu atoms.<sup>106</sup> On the one hand, Ag<sub>1.5</sub>-Cu/ZSM-5 catalysts enhanced the adsorption of NH<sub>3</sub> molecules owing to the

enhanced surface acidity resulting from the introduction of Ag. On the other hand, the interaction between Ag and Cu species was revealed, leading to the generation of more active oxygen species on the catalysts and consequently contributing to improved redox performance.

Besides, for Cu-based metal oxides, the introduction of Mo to the CuO support induced the formation of the Mo–O–Cu structure, and then a large number of acidic sites and oxygen vacancies were produced through the electron interaction between Mo and Cu species.<sup>84</sup> This promoted the adsorption of NH<sub>3</sub> and NO, thereby forming active intermediates such as nitrate, nitrite, NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup>, which improved the SCR performance (Fig. 6h–j). The results well explained the important role of secondary metal doping on the enhanced performance of Cu-based catalysts.

#### 2.4 Crystal structure regulation

Different crystal structures such as crystallite size, exposed crystal plane and morphology would affect the active site, electronic structure, acidity and redox properties of the catalysts, which was closely related to the catalytic performance. Therefore, the efficient removal of NO<sub>x</sub> would be realized through regulation engineering of the crystal structure on the Cu-based catalysts, and it was of guiding significance for the in-depth understanding of the reaction mechanism and the development of high-performance catalysts.

Recently, it was generally believed that the smaller the size of the active centers, the higher the utilization of atoms, which would better promote the catalytic performance. In this regard, Huang *et al.* regulated Cu-SAPO-34 zeolites with different crystallite sizes (1–13 μm) and confirmed that the rate of NH<sub>3</sub>-SCR reaction tended to decrease with the increase of the Cu-SAPO-34 crystallite size. In addition, a battery of Cu-ZSM-5 catalysts possessing micro-fibrous structures has been shown to help improve the acidic properties when the molar ratio of Si/Al was 100.<sup>107</sup> And the utilization of mesoporous ZSM-5 zeolite (MZ) for supporting Cu and Ce atoms (Cu–Ce/MZ) led to the detection of more highly distributed active sites and abundant oxidation species, thus yielding better performance compared to conventional Cu–Ce/ZSM-5 and Cu–Ce/SBA-15.<sup>108</sup> Therefore, the crystal structure regulation of ZSM-5 zeolite is important in tailoring SCR catalysts for effective removal of NO<sub>x</sub>. Besides, the morphologies of ZSM-5 zeolites has also been confirmed to be associated with the catalytic performance of NH<sub>3</sub>-SCR.<sup>109</sup> Distinct differences in SCR behaviour were observed between traditional Cu-ZSM-5 and specialized Cu-ZSM-5 zeolites with various morphologies (nanoparticles, nanosheets and hollow spheres) (Fig. 7a). Among them, nanosheet-like Cu-ZSM-5 catalysts exhibited the most superior activity, with a T<sub>50</sub> as low as 130 °C and almost 100% NO<sub>x</sub> conversions from 200 to 400 °C (Fig. 7b). It was discovered that adequate mesoporous and framework Al atoms existed on the

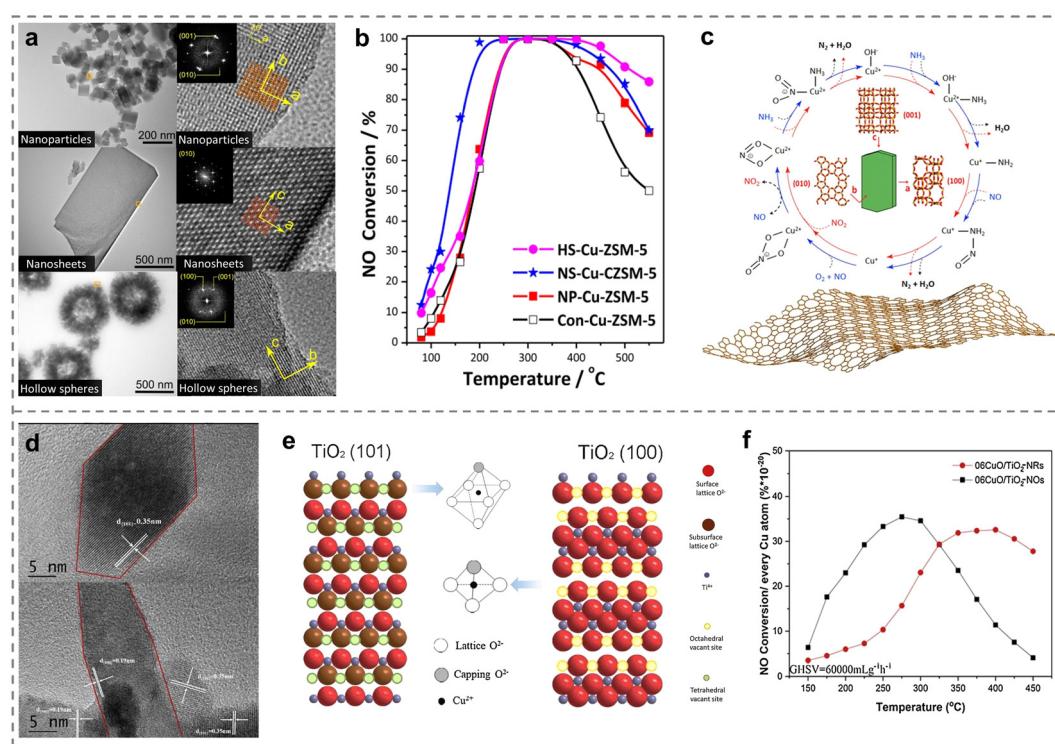


Fig. 7 (a) TEM images of Cu-exchanged catalysts with different morphologies (NP, NS and HS). (b) NO<sub>x</sub> conversion over various as-prepared catalysts. (c) Catalytic mechanism of the NH<sub>3</sub>-SCR process on NS-Cu-ZSM-5. Copied with permission from ref. 109. Copyright 2021, American Chemical Society. (d) HRTEM and (e) schematic diagram for TiO<sub>2</sub> with different exposed facets: TiO<sub>2</sub> (101), TiO<sub>2</sub> (100), and Cu cation in octahedral vacant sites and in tetrahedral vacant sites. (f) NH<sub>3</sub>-SCR performance over different TiO<sub>2</sub> supports modified by CuO (06CuO/TiO<sub>2</sub>-NOs and 06CuO/TiO<sub>2</sub>-NRs). Copied with permission from ref. 110. Copyright 2020, Elsevier.



nanosheet-like Cu-ZSM-5, which influenced the local environment of Cu through rapid switching between  $\text{Cu}^+$  and  $\text{Cu}^{2+}$  ions in the catalytic process, thereby resulting in the best SCR activity. Furthermore, they revealed the reaction mechanism that the  $\text{NH}_3$ -SCR reaction over Cu-ZSM-5 nanosheets mainly followed the Eley-Rideal pathway (Fig. 7c). Different exposed crystal planes on metal oxides would affect the number and distribution of interfacial active species and defects of catalysts, and then regulated the coordination structure of the active sites. The loading of CuO phase onto the surface of the  $\text{TiO}_2$  nano-octahedra (06CuO/ $\text{TiO}_2$ -NOS) and nano-rods (06CuO/ $\text{TiO}_2$ -NRs) using the impregnation method has been reported.<sup>110</sup> The different coordination environments of Cu species induced by various exposed crystal facets of  $\text{TiO}_2$  nano-octahedra and nano-rods played a crucial role. Specifically, Cu ions were present at tetrahedral vacant sites on the (101) plane of the  $\text{TiO}_2$  nano-octahedra and bonded to four O atoms, while on the (100) facet of  $\text{TiO}_2$  nano-rods, they occupied octahedral vacant sites and coordinated with six oxygen atoms (Fig. 7d and e). The unique nano-octahedron structure enhanced de- $\text{NO}_x$  activity by promoting the redox cycle of  $\text{Cu}^{2+} + \text{Ti}^{3+} \leftrightarrow \text{Cu}^+ + \text{Ti}^{4+}$  and generating more acid sites (Fig. 7f). Based on these cases, it was urgent to develop the strategy of crystal structure regulation to controllably synthesize Cu-based catalysts to understand the relationship of structure and activity deeply, expanding the applications in  $\text{NH}_3$ -SCR reaction.

## 2.5 Preparation method modification

Generally, the metal dispersions, valence states and de- $\text{NO}_x$  activity were related to the preparation method. Therefore, the modification and optimization of the synthetic techniques directly tuned the structure–activity relationship of Cu-based catalysts, and thus maximized the catalytic performance (Table 3).<sup>111</sup> The synthesis strategies of incipient wetness impregnation (IWI), ion exchange (IE) and hydrothermal synthesis (HTS) have been extensively explored by Han *et al.* for obtaining Cu-SSZ-13 catalysts (Fig. 8a).<sup>112</sup> Comprehensive results demonstrated that a larger number of stable  $\text{Cu}^{2+}$  active sites was located in the six-membered rings on Cu-SSZ-13 (HTS) catalysts compared to catalysts prepared by the other two methods, leading to the highest  $\text{NH}_3$ -SCR activity (above 90%  $\text{NO}_x$  removal at 215–600 °C) because of the better abilities for  $\text{NH}_3$  and NO adsorption. However, the traditional hydrothermal preparation methods were difficult to control the composition and structure of the samples. An alternative route called

the microwave-assisted hydrothermal method was employed to synthesize  $\text{Cu}^{2+}$  exchanged SSZ-13 catalysts,<sup>113</sup> which was helpful to obtain the target products with small size, superior activity and adjustable crystal orientation. The temperature and time of the microwave synthesis were critical factors in determining the nucleation and growth process of SSZ-13. The optimal Cu-SSZ-13 zeolites were successfully prepared at the temperature of 175 °C and a synthesis time of 9 hours, resulting in more stable Al-O-Si structures of framework, larger specific surface area, and increased  $\text{Cu}^{2+}$  isolated species, thereby promoting the de- $\text{NO}_x$  performance and hydrothermal stability (Fig. 8b).

Besides, a number of Fe-Cu-ZSM-5 zeolites synthesized through solid-state ion-exchanged (Fe-Cu-Z-SS), aqueous ion-exchanged (Fe-Cu-Z-AQ) and impregnation methods (Fe-Cu-Z-IM) were studied to investigate the impact of preparation methods on catalytic performance in  $\text{NH}_3$ -SCR.<sup>114</sup> The higher metal contents were reserved over Fe-Cu-Z-SS and Fe-Cu-Z-IM catalysts, and the mass of metal was significantly lost during the aqueous ion-exchanged method. However, the metal loss would not cause a decrease of performance, because the reserved Cu and Fe species metals existed in a more highly dispersed form on the Fe-Cu-Z-AQ zeolites, avoiding the ammonia peroxidation. By contrast, Fe-Cu-Z-SS and Fe-Cu-Z-IM zeolites showed a decreased high-temperature activity because of the peroxidation of ammonia, resulting from the presence of aggregated oxides. Other preparation methods focused on Cu-exchanged zeolites (Cu/SAPO-34) using mechanical mixing (Cu/SAPO-34-M) and ball milling (Cu/SAPO-34-B) methods were also explored for  $\text{NH}_3$ -SCR performance.<sup>115</sup> Characterization results suggested that ball milling was a more appropriate approach for achieving superior activity as it increased the number of isolated  $\text{Cu}^{2+}$  species over Cu/SAPO-34-B catalysts, which was beneficial for the activation of  $\text{NO}_x$  and the formation of Lewis acid sites, simultaneously promoting the redox property of the catalysts.

Copper species, including isolated  $\text{Cu}^{2+}$  ions, Cu dimers and  $\text{CuO}_x$  clusters, coexisted on the Cu-based catalysts. It was an important means to adjust the physicochemical characteristics of Cu species through changing the pretreatment method in the process of catalyst synthesis. Compared with isolated  $\text{Cu}^{2+}$  ions, most studies reported that  $\text{CuO}_x$  clusters cannot contribute to the low-temperature de- $\text{NO}_x$  activity, and might even decrease the performance at high temperatures. Therefore, the high-temperature hydrogen treatment was beneficial for the reduction of Cu dimers to isolated Cu ions, thus providing a promising avenue for improving the activity of Cu-exchanged

Table 3 Representative Cu-based catalysts prepared by various methods for the SCR reaction

| Catalysts   | Preparation method             | Reaction conditions  | NO conversion       | Ref. |
|-------------|--------------------------------|--|---------------------|------|
| Cu-SSZ-13   | Incipient wetness impregnation | $[\text{NO}] = [\text{NH}_3] = 500 \text{ ppm}$ , $[\text{O}_2] = 5\%$ ,<br>$\text{GHSV} = 180\,000 \text{ h}^{-1}$  | >80% (~250–500 °C)  | 112  |
|             | Ion exchange                   |  | >80% (~250–600 °C)  |      |
|             | Hydrothermal synthesis         |  | >90% (~215–600 °C)  |      |
| Fe-Cu-ZSM-5 | Solid-state ion-exchanged      | $[\text{NO}] = [\text{NH}_3] = 1000 \text{ ppm}$ , $[\text{O}_2] = 8\%$ ,<br>$[\text{H}_2\text{O}] = 3.5 \text{ vol\%}$ , $\text{GHSV} = 333 \text{ h}^{-1}$ | >50% (above 270 °C) | 114  |
|             | Aqueous ion-exchanged          |  | >50% (above 280 °C) |      |
|             | Impregnation method            |  | >50% (above 265 °C) |      |
| Cu-SAPO-34  | Mechanical mixing              | $[\text{NO}] = [\text{NH}_3] = 500 \text{ ppm}$ , $[\text{O}_2] = 5\%$ ,<br>$\text{GHSV} = 200\,000 \text{ h}^{-1}$  | <60% (~100–500 °C)  | 115  |
|             | Ball mixing                    |  | >60% (~200–450 °C)  |      |



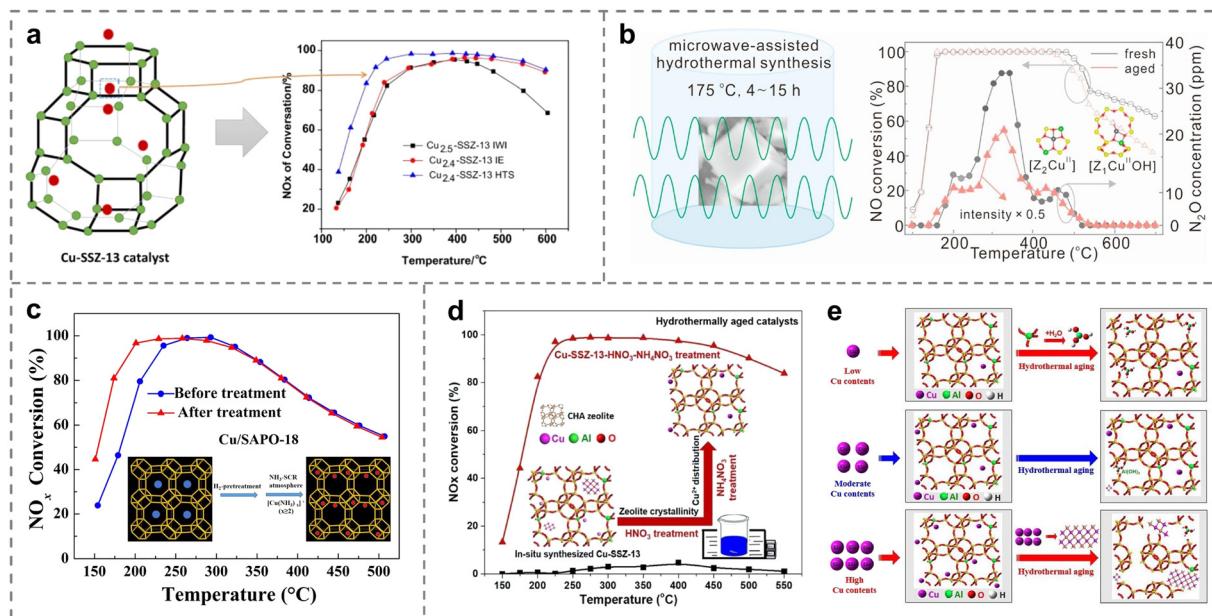


Fig. 8 (a) NH<sub>3</sub>-SCR performance of various as-prepared catalysts with different preparation methods. Copied with permission from ref. 112. Copyright 2019, Springer Nature. (b) Microwave synthesis conditions and hydrothermal performance of the catalysts. Copied with permission from ref. 113. Copyright 2021, Elsevier. (c) NH<sub>3</sub>-SCR activity of various Cu/SAPO-18 catalysts with different treatments. Copied with permission from ref. 116. Copyright 2019, Elsevier. (d) NH<sub>3</sub>-SCR performance of various Cu-SSZ-13 zeolites with different treatments. (e) The deactivation mechanism of Cu-SSZ-13 with different Cu loadings during hydrothermal treatment. Copied with permission from ref. 117. Copyright 2020, Elsevier.

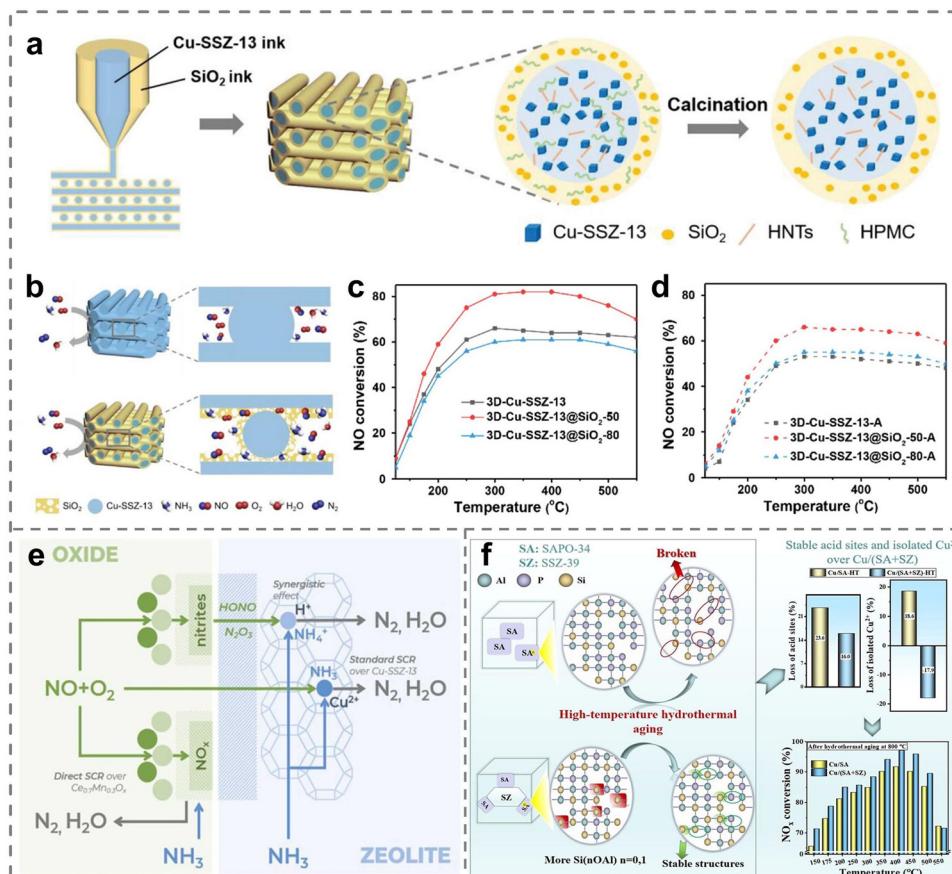
zeolites at low temperatures. Recent reports suggested that the low-temperature SCR activity would be related to the Cu<sup>+/Cu<sup>2+</sup></sup> ratio. With the treatment of H<sub>2</sub> reduction, Cu<sup>+</sup> or [Cu(OH)]<sup>+</sup> species were formed by the reduction of Cu dimers and the Cu<sup>+/Cu<sup>2+</sup></sup> ratio increased,<sup>116</sup> and then the resulting isolated Cu active sites exchanged into Cu-SAPO-18 catalysts. Notably, Cu ions would generate the mobile intermediates of ion-pairs after NH<sub>3</sub> solvation, promoting NO<sub>x</sub> conversion at low temperatures (Fig. 8c). Another method was to pretreat the catalyst with HNO<sub>3</sub> and NH<sub>4</sub>NO<sub>3</sub> to improve the performance of Cu-SSZ-13 zeolites in NH<sub>3</sub>-SCR through adjusting the distribution and electronic properties of active Cu ions. Shan *et al.* firstly synthesized Cu-SSZ-13 zeolites with the treatment of HNO<sub>3</sub> and NH<sub>4</sub>NO<sub>3</sub>, employing Cu-TEPA as the template, achieving above 90% NO<sub>x</sub> removal (250–450 °C), even after hydrothermal aging at 750 and 800 °C (Fig. 8d).<sup>117</sup> The optimal Cu/Al ratios (from 0.22 to 0.31) on the Cu-SSZ-13 zeolites was revealed to inhibit the dealumination of catalysts and the generation of CuO<sub>x</sub> clusters, leading to the superior activity and hydrothermal stability. However, excessive amounts of Cu<sup>2+</sup> species were easily transferred to form CuO<sub>x</sub> clusters, leading to the destruction of the framework structure (Fig. 8e).

## 2.6 Interaction and interface engineering

The performance of SCR catalysts would be greatly modified by the combination of Cu-based catalysts with other materials owing to the regulation of interaction and interface. The interaction and interface engineering could give full play to the advantages of different components, influence the bonding and electron transfer at the atomic level, so as to optimize the adsorption and activation of gas molecules.<sup>118,119</sup> To improve

the catalytic activity and hydrothermal stability of Cu-SSZ-13, Wei *et al.* designed core-shell catalysts with interconnected honeycomb structures by 3D printing strategies, in which the hydrophilic noncompact SiO<sub>2</sub> acted as shells and Cu-SSZ-13 zeolites served as cores (Fig. 9a).<sup>120</sup> In contrast, since pure Cu-SSZ-13 zeolites were limited by the interfacial diffusion, the interaction between SiO<sub>2</sub> shells and Cu-SSZ-13 cores increased the accessibility of Cu active centers on Cu-SSZ-13@SiO<sub>2</sub> (Fig. 9b), leading to superior de-NO<sub>x</sub> performance (Fig. 9c). Notably, the thicker SiO<sub>2</sub> shells further promoted hydrothermal stability because of the inhibition of the dealumination process and the generation of CuO<sub>x</sub> during the hydrothermal treatment (Fig. 9c and d). Similar observations were reported by Qu *et al.*, where the introduction of BaMnO<sub>3</sub> perovskite to mesoporous Cu-SSZ-13 generated small-scale nanocrystals (5–10 nm).<sup>121</sup> The doping of BaMnO<sub>3</sub> accelerated its synergistic effect with Cu ions thus leading to a higher Mn<sup>4+</sup> proportion and stronger redox capacity on BaMnO<sub>3</sub>-Cu-SSZ-13 catalysts, promoting the adsorption and activation of reactant gas molecules based on *in situ* DRIFT spectra. Moreover, the low-temperature performance was revealed to be enhanced by the interaction between Cu-SSZ-13 and doped Ce<sub>0.7</sub>Mn<sub>0.3</sub>O<sub>x</sub> oxides.<sup>122</sup> The reason was that HONO and N<sub>2</sub>O<sub>3</sub> intermediates were firstly formed on the surface of the oxide phase, and then the intermediates could transfer and react with Brønsted acid sites of Cu-SSZ-13 zeolites (Fig. 9e).

Recently, lots of effort has been focused on the hybrid zeolites for enhancing NH<sub>3</sub>-SCR reaction, and utilizing the interfacial interactions between different components was proved to be effective in promoting the catalytic activity. It is well known that Cu-SAPO-34 (Cu-CZC) catalysts show higher



**Fig. 9** (a) The preparation process of 3D-printed materials. (b) Schematic illustration of the diffusion of reactant/product gas over the catalysts in catalytic reaction. (c) and (d) NH<sub>3</sub>-SCR performance of (c) fresh and (d) aged 3D-printed catalysts with various shell thicknesses. Copied with permission from ref. 120. Copyright 2023, Wiley. (e) The mechanism of enhanced catalytic activity of composite catalysts. Copied with permission from ref. 122. Copyright 2023, Elsevier. (f) Schematic diagram of Cu<sub>2</sub>O/CuO interaction in the NH<sub>3</sub>-SCR reaction. Copied with permission from ref. 124. Copyright 2020, Elsevier.

NO<sub>x</sub> removal at lower temperatures (<300 °C) and Fe-Mordenite (Fe-MOR) is beneficial for eliminating NO<sub>x</sub> at higher temperatures (>350 °C).<sup>123</sup> Based on this case, the mechanical mixture of the same amount of Cu-CZC and Fe-MOR was investigated to improve activity over a broad temperature range. Compared with the catalysts prepared with only one metal (Cu-CZC or Fe-MOR), the resulting mechanical mixture exhibited a larger number of acid sites, favorable redox properties, and higher NH<sub>3</sub>-SCR performance when exposing to excess ammonia (NH<sub>3</sub>/NO<sub>x</sub> = 1.3). Moreover, stable SSZ-39 seeds were introduced to the precursors of SAPO-34 to synthesize the composite structure of SAPO-34 + SSZ-39 materials (SA + SZ).<sup>124</sup> With the modification of SSZ-39 zeolites, the interface of the Cu/(SA + SZ) samples induced higher contents of stable Si(nOAl) ( $n = 0, 1$ ) structures and acid sites, accompanied by the formation of more Cu isolated species (Fig. 9f). To a certain degree, these enhancements of physical and chemical properties on Cu/(SA + SZ) samples was confirmed to be beneficial for achieving better activity and hydrothermal stability compared to Cu/SA. Generally, it was well-known that the SCR performance of highly dispersed Cu cations demonstrated satisfactory performance in the catalytic process, but the influence of the electronic properties of Cu species on NH<sub>3</sub>-SCR reactions remained unclear. In this case, the electron transfer between Cu<sup>+</sup>

and Cu<sup>2+</sup> had been widely explored with interfacial engineering by constructing composite materials. CuAl-LDO/CNTs catalysts with the controllable valence states of Cu ions were prepared by combining CuAl-layered double oxide and various mass fractions of carbon nanotubes,<sup>125</sup> revealing the synergistic effect between Cu<sub>2</sub>O and CuO at the atomic level. The results demonstrated that the CuO species were used for the adsorption of NO and NH<sub>3</sub>, which was beneficial to activate NH<sub>3</sub> molecules and promote the generation of NO<sup>+</sup> species. Meanwhile, the Cu<sub>2</sub>O centers served as active sites for adsorbing O species, thereby enhancing the generation of active O<sup>-</sup> species. Therefore, the flexible and adjustable structure of Cu-based catalysts enabled them to form rich interfaces with other materials, and optimized the structure-activity relationship of the composite materials, resulting in the enhancement of the catalytic performance.

### 3. The reaction mechanism and strategies for enhanced poisoning-resistant and hydrothermal stability

As we all know, SO<sub>2</sub> and alkali metals exist in real flue gas, which could directly or indirectly affect the active centers of Cu-

based SCR catalysts, leading to the deactivation of de- $\text{NO}_x$  catalysts.<sup>126–128</sup> For SCR catalysts, they were positioned in close proximity to the diesel particulate filter and were exposed to a temperature above 650 °C, thereby experiencing harsh hydrothermal aging conditions during practical use. Therefore, it was important to investigate the effect of  $\text{SO}_2$  and alkali metals and to design Cu-based catalysts with superior resistance and hydrothermal stability for the  $\text{NH}_3$ -SCR catalytic process. In this part, we provide a comprehensive summary of the catalyst deactivation mechanisms caused by these components and propose several viable strategies.

### 3.1 $\text{SO}_2$ poisoning-resistance

Inevitably, even low levels of  $\text{SO}_2$  from ultra-low sulfur fuel could deactivate catalysts under practical conditions, posing limitations on the development of Cu-based catalysts.<sup>129–132</sup>  $\text{SO}_2$  molecules reacted with  $\text{NH}_3$  and  $\text{H}_2\text{O}$  at appropriate

temperatures to form ammonium bisulfate, which further reacted with catalyst components to generate metal sulfates. Generally, low temperature and high concentrations of  $\text{SO}_2$  would accelerate the deposition of ammonium sulfate on the surface of catalysts, thus reducing the denitrification efficiency. The generation of metal sulfates would fill micropores of catalysts, causing a decrease in specific surface area and pore volume, which hindered the adsorption and activation of gas reactants.<sup>133,134</sup> To address this issue, Wang *et al.* employed acidic  $\text{NbOPO}_4$  species to mitigate the  $\text{SO}_2$  poisoning effect of mixed CuCe oxides.<sup>135</sup> The strong interaction between  $\text{NbOPO}_4$  and CuCe mixed oxides restrained the oxidation process of interfacial oxygen atoms and  $\text{SO}_2$ , thus exhibiting superior NO conversion on CuCe/Nb-P samples when exposed to the conditions of  $\text{SO}_2$  (100 ppm) and  $\text{H}_2\text{O}$  (5 vol%) for 10 hours. Additionally, the CuZ-Ce<sub>n</sub> catalysts modified with the thin CeO<sub>2</sub> film were prepared using liquid deposition, and the

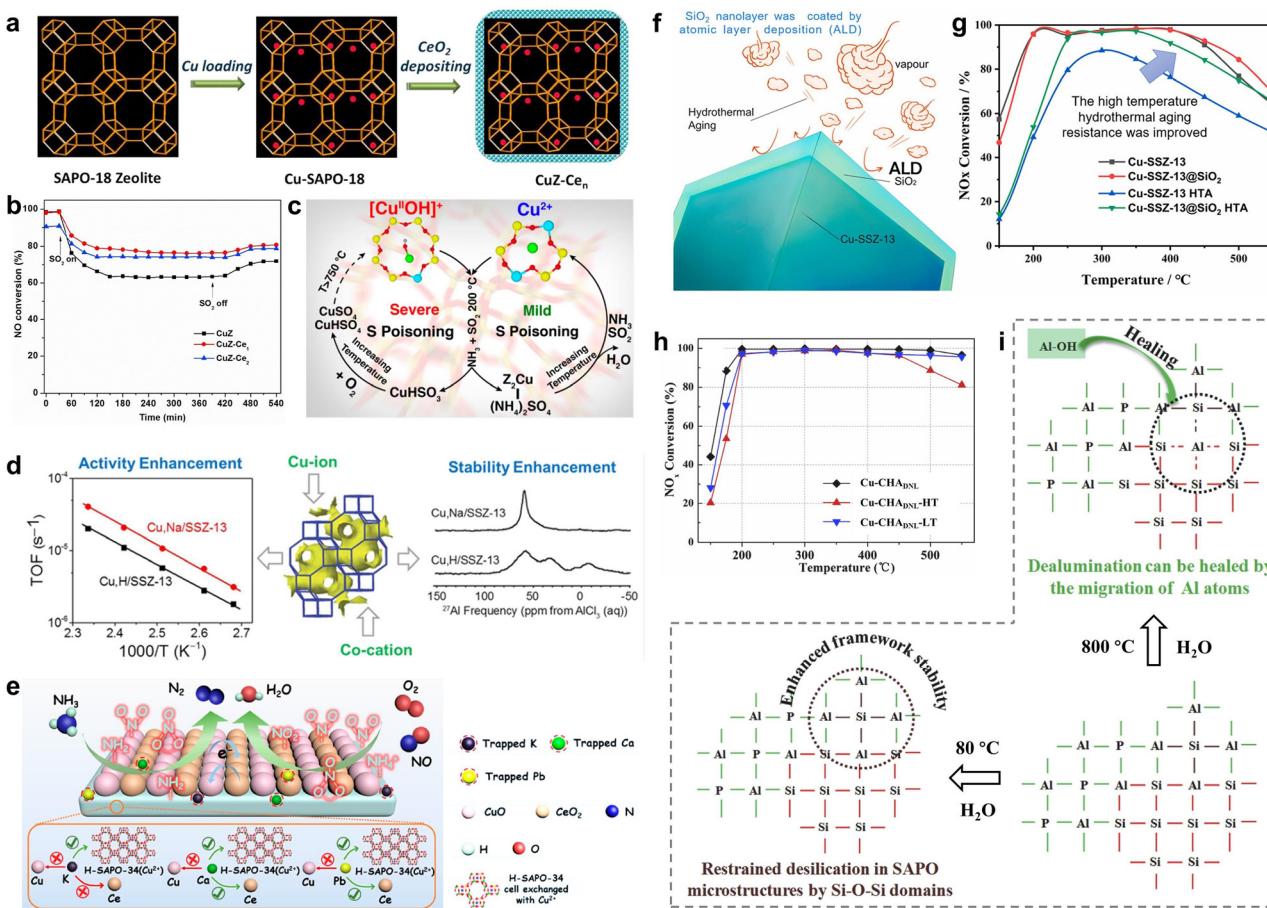


Fig. 10 (a) The schematic diagram for the synthesis of CuZ-Ce<sub>n</sub> catalysts. (b) NH<sub>3</sub>-SCR performance of as-prepared catalysts with the exposure of 100 ppm SO<sub>2</sub>. Copied with permission from ref. 69. Copyright 2017, Elsevier. (c) Proposed formation of sulphates during adsorption of SO<sub>2</sub> on [Cu(OH)]<sup>+</sup>-Al and Cu<sup>2+</sup>-2Al sites. Copied with permission from ref. 137. Copyright 2017, American Chemical Society. (d) The activity enhancement and stability enhancement on Cu-SSZ-13 by co-cations. Copied with permission from ref. 144. Copyright 2015, American Chemical Society. (e) Schematic diagram of enhanced alkaline-resistance and heavy metal-resistance on CuCe/H-SAPO-34. Copied with permission from ref. 147. Copyright 2020, American Chemical Society. (f) The protection mechanism of the ALD effect of SiO<sub>2</sub>. (g) NH<sub>3</sub>-SCR performance of the as-prepared catalysts. Copied with permission from ref. 156. Copyright 2021, Elsevier. (h) NH<sub>3</sub>-SCR performance on Cu-CHA<sub>DNL</sub> catalysts before (black) and after hydrothermal treatment (HT: red; LT: blue). (i) Proposed mechanism for the enhanced hydrothermal stability over Cu-CHA<sub>DNL</sub> catalysts at high and low temperatures. Copied with permission from ref. 157. Copyright 2020, Elsevier.



protective effect of the  $\text{CeO}_2$  thin film was revealed to promote the resistance to  $\text{H}_2\text{O}$  and  $\text{SO}_2$  on Cu-SAPO-18 (Fig. 10a).<sup>69</sup> The enhancement of  $\text{H}_2\text{O}$ -resistant ability was attributed to the fact that  $\text{CeO}_2$  inhibited the aggregation of isolated  $\text{Cu}^{2+}$  species into Cu clusters and inhibited the infection of  $\text{H}_2\text{O}$  molecules on Cu active species and acid centers. Meanwhile, the presence of thin  $\text{CeO}_2$  film restrained the generation and deposition of sulfates, thus preventing the blocking of active centers over CuZ- $\text{Ce}_n$  catalysts and resulting in higher resistance to  $\text{SO}_2$  compared to Cu-SAPO-18 (Fig. 10b).

Moreover, from the studies of Chen *et al.*, three  $\text{Cu}^{2+}$  active sites (named  $\text{Cu}_1$ ,  $\text{Cu}_2$  and  $\text{Cu}_3$ ) were identified to occupy different positions of I, III and IV on Cu-SSZ-13, respectively.<sup>136</sup>  $\text{Cu}_1$  species were located near the window of the eight-membered rings,  $\text{Cu}_2$  species were positioned in the super cage deviated from the double six-membered rings, and  $\text{Cu}_3$  species were present at the center of the hexagonal prism. Among them, the content of  $\text{Cu}_2$  (1.81%) was higher than that of  $\text{Cu}_1$  (0.98%) and  $\text{Cu}_3$  (0.46%). The results demonstrated that  $\text{Cu}_1$  species played a crucial role in enhancing the performance of catalysts at low temperatures, and  $\text{Cu}_3$  species contributed to the excellent  $\text{SO}_2$  resistance because of the high stability. Notably, Jangjou *et al.* carried out a study on the impact of  $\text{SO}_2$  on two types of active Cu species ( $\text{Cu}^{2+}$ -2Al and  $[\text{Cu}(\text{OH})]^{+-}$ -Al) over Cu-SSZ-13 catalysts.<sup>137</sup> From this research, the activity of both active Cu sites for low-temperature SCR functionality was significantly inhibited by  $\text{SO}_2$ , but their behavior of desulfation differed. Compared to the  $\text{Cu}^{2+}$ -2Al structure, ZCuOH species were more likely to suffer severe  $\text{SO}_2$  poisoning at low temperatures, as it led to the blocking of active sites by the generation of unbreakable bisulfite and bisulfate products. This finding suggested that Cu-SSZ-13 with a larger number of  $[\text{Cu}(\text{OH})]^{+-}$ -Al components required higher desulfation temperatures (above 550 °C) (Fig. 10c). To promote the service life and  $\text{SO}_2$  resistance of the catalysts, efforts have been made to prevent the sulfation of active sites. Previous studies have focused on the enhancement of  $\text{SO}_2$ -resistance on SCR catalysts through the incorporation of individual components. For instance, hybrid catalysts combining Cu-SSZ-13 zeolite with metal oxides (Mn, Co, Ni, and Zn) demonstrated excellent  $\text{SO}_2$  resistance compared to pure Cu-SSZ-13 zeolites.<sup>138</sup> Among them, the addition of  $\text{ZnTi}_{10}\text{O}_x$  had the most significant effect on improving performance by acting as the sacrificial component that reacted with  $\text{SO}_2$ , thereby protecting  $\text{Cu}^{2+}$  from sulfur deactivation. Similarly, yttrium-modified Cu-SSZ-39 also exhibited significantly higher  $\text{NO}_x$  conversion after exposure to  $\text{SO}_2$ ,<sup>139</sup> and the reason was that the doping of Y species stabilized  $\text{Cu}^{2+}$  species from six-membered rings and reduced the sensitivity of the reaction between  $\text{Cu}^{2+}$  and  $\text{SO}_2$ . These strategies provided a general and straightforward approach to decrease the sensitivity of active centers towards  $\text{SO}_2$  in catalytic processes. Except for the Cu-based small-pore zeolites, the design of  $\text{Cu}_y\text{AlO}_x$  mixed oxide materials derived from Cu-Al LDHs precursors was confirmed to have a superior  $\text{SO}_2$  resistance compared with  $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$ . And the enhancement of tolerant ability for poisoning might be attributed to the

presence of highly dispersed  $\text{CuO}$  nanoparticles, which induced that the acidic sites and redox property remained and were less influenced by the poisoning of  $\text{SO}_2$ .<sup>140</sup> Another similar catalyst with the chemical composition of  $\text{Cu}_w\text{Mn}_y\text{Ti}_{1-y}\text{O}_x$  showed significant resistance to 100 ppm  $\text{SO}_2$  after copper oxides was introduced, which was associated with the excellent surface acidity and the generation of more  $\text{MnO}_2$  and  $\text{CuO}$  species, indicating the greater potential for industrial applications.<sup>141</sup>

### 3.2 Alkali metal poisoning-resistance

Alkali metal ions mainly originated from the flue gas or aerosol particles of glass furnaces, biomass power generation and urea solutions, would deposit on catalysts and strongly affect their catalytic activity.<sup>142,143</sup> However, the effect of alkali metals on Cu-based catalysts has not been well understood. Gao *et al.* demonstrated that co-cations helped reduce the hydrolysis of Cu-SSZ-13 zeolites in the hydrothermal treatment, as evidenced by  $^{27}\text{Al}$  NMR. In particular,  $\text{Li}^+$  and  $\text{Na}^+$  ions significantly promoted the rate of SCR at low temperatures (Fig. 10d).<sup>144</sup> Nevertheless, several studies have shown that alkali metal ions would volatilize and diffuse to the catalyst surface at high temperatures, resulting in catalyst poisoning. Fundamental research has revealed the mechanisms of alkali metal poisoning on Cu-based catalysts, indicating that the deactivation might be attributed to the pore blockage or damage to the acidic and redox sites caused by alkali metal impurities. From systematic research, Fan *et al.* explored the influence of alkali metal and alkaline earth metals ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ ) on the catalytic performance of Cu-SSZ-13 zeolites.<sup>145</sup> The results showed that the introduction of Mg and Ca caused more serious destruction to the framework structures, resulting in the replacement of more isolated  $\text{Cu}^{2+}$  species and the formation of extra-framework  $\text{CuO}_x$  clusters. For Cu-SSZ-39 zeolites, the toxicity degree of alkali and alkaline earth metals to catalyst deactivation was  $\text{K} > \text{Mg} > \text{Ca} > \text{Na}$ .<sup>146</sup> The presence of the above impurities (at a concentration of 1 mmol per gram of catalyst) significantly decreased the specific surface area, isolated  $\text{Cu}^{2+}$  species and acid centers of the catalysts after poisoning. Thus, the development of a novel catalyst with superior resistance to alkali and alkaline earth metal poisoning is of great concern for de- $\text{NO}_x$  applications.

Based on the understanding of the deactivation mechanism, a potential method for designing alkali-resistant catalysts was to increase the number of active sites or develop sacrificial sites that could trap alkali metals. For instance, the H-SAPO-34 support, which possessed abundant acid centers, protected the activity of active copper components through reacting with alkali metals (K), alkaline earth metals (Ca) and heavy metals (Pb) (Fig. 10e). Furthermore, the introduction of Ce species enhanced the low-temperature performance by facilitating the redox process with Cu active centers and assisting H-SAPO-34 to capture Pb and Ca impurities, resulting in excellent de- $\text{NO}_x$  performance and resistance against the alkaline metal and heavy metal on CuCe/H-SAPO-34 zeolites.<sup>147</sup> Similarly, Nb-OH and Nb=O structures were preferentially link to K atoms on CuNbTi oxides, which resulted in more active Cu species being



protected and the weak acid sites were preserved, contributing to the superior alkali metal resistance.<sup>148</sup> And Li *et al.* utilized the interaction of V, Ce and Cu species to develop excellent alkali metal poisoning-resistant  $\text{VWCeCuTi}$  catalysts, and the results suggested that the addition of Cu species would increase the acidic sites and improve the redox property, which contributed to the superior K resistance.<sup>149</sup> Besides, the construction of the core–shell structure was confirmed to have practical value.<sup>150</sup> By increasing the crystalline sizes of SSZ-13, the active Cu species were regulated to be located in the subsurface or inner core, thereby buffering alkali metal poisoning on the outer layer of zeolites. The dispersion of acid centers could be adjusted through changing the crystalline sizes, which provided a simple and easy approach to enhance performance against alkali metals.

### 3.3 Hydrothermal stability

Cu-Based SCR catalysts, particularly small-pore zeolites, were prone to hydrothermal aging and deactivation when exposed to the harsh tail gas atmosphere in real applications.<sup>151–153</sup> This led to the efflux of alumina to the surface of the catalysts at high temperature. The deactivation would be relevant to the aggregation of  $\text{Cu}^{2+}$  ions into  $\text{CuO}_x$  oxide species or dealumination occurring in Cu-based small-pore zeolites upon exposure to the tail gas.<sup>154,155</sup> These findings highlighted the need to efficiently promote hydrothermal stability of de- $\text{NO}_x$  catalysts at high temperatures. From the destruction mechanism, utilizing the Al-rich support for stabilizing Cu species is effective to promote hydrothermal stability. Moreover, Tian *et al.* successfully enhanced the catalytic activity of  $\text{NO}_x$  reduction through using the atomic layer deposition (ALD) approach to coat the surface of Cu-SSZ-13 catalysts with  $\text{SiO}_2$  nanolayers (Fig. 10f).<sup>156</sup> The integrity of the Cu-SSZ-13 framework was well preserved even after 16 hours of hydrothermal treatment at 800 °C with 12.5 vol%  $\text{H}_2\text{O}$ , owing to the protection of  $\text{SiO}_2$  layers. The layers effectively slowed down the formation of CuO clusters by inhibiting the accumulation of Cu and stabilizing the positions of  $\text{Cu}^{2+}$  ions in the zeolite frameworks by suppressing dealumination, thereby promoting the hydrothermal aging resistance of the Cu-SSZ-13@ $\text{SiO}_2$  HTA catalysts (Fig. 10g).

Moreover, there was evidence supporting the notion that the preparation of zeolite–zeolite composites would effectively promote high-temperature hydrothermal stability. It was acknowledged that Cu-SSZ-13 was prone to dealumination and deactivation after hydrothermal aging at high temperatures. Conversely, SAPO-34 zeolites exhibited irreversible framework degradation during repeated ion-exchange (Cu species) processes or exposure to low-temperature moisture atmospheres, which was avoided in the case of SSZ-13 zeolites. Thus, it was highly desirable to design Cu-based composites that combined the advantages of both Cu-SAPO-34 and Cu-SSZ-13. Sun *et al.* synthesized novel Cu-CHA composites (Cu-CHA<sub>DNL</sub>) by interlacing SAPO and aluminosilicate parts, utilizing Cu-SSZ-13 as the compounds to promote the crystallization of SAPO-34.<sup>157</sup> As displayed in Fig. 10i, the Si–O–Al framework of SAPO was closely linked to Si–O–Si structures in aluminosilicate, resulting in increased difficulty of desilication in

the SAPO part. This effectively restrained framework degradation over Cu-CHA<sub>DNL</sub> catalysts when exposed to  $\text{H}_2\text{O}$ . Meanwhile, adjacent Al–O–P groups facilitated the healing of dealumination in the aluminosilicate parts through migration to defects at high temperatures, thereby promoting high-temperature hydrothermal stabilities. In this work, the high-temperature hydrothermal treatment was carried out at 800 °C for 16 hours, which contained 10 vol% water, and the low-temperature hydrothermal treatment was performed through immersing the catalyst at 80 °C deionized water for 24 hours in a closed vessel. Consequently, Cu-CHA<sub>DNL</sub> compounds with the microstructural properties of both Cu-SSZ-13 and Cu-SAPO-34 demonstrated excellent catalytic activity and robust high-temperature and low-temperature hydrothermal stability (Fig. 10h). Additionally, mechanically mixed samples containing Cu-SSZ-13 and Cu-SAPO-34 zeolites were found to significantly improve hydrothermal stability compared to single-component catalysts. Ma *et al.* proposed that the strong interaction between Cu-SAPO-34 and Cu-SSZ-13 was beneficial in suppressing the dealumination of SSZ-13 and preserving framework structures.<sup>158</sup> Thereafter, the migration of extra-framework P atoms in SAPO-34 would occupy Al atoms in the fragmented SSZ-13 framework, inhibiting further damage of the Si–O–Al structure in hydrothermal treatments. Therefore, synthesizing zeolite–zeolite composites through two-phase intergrowth is of great significance, as it aims to leverage the advantages of individual zeolites while harnessing specific synergistic properties.

## 4. Conclusions

### 4.1 Summary

$\text{NH}_3$ -SCR reaction will effectively remove  $\text{NO}_x$  and convert them into the harmless gases, which is of great significance to environmental protection and has high application value. Herein, we present an in-depth overview of the latest advancements in catalytic reaction mechanisms over Cu-based SCR catalysts (including Cu-based small-pore zeolites and Cu-containing metal oxides). Meanwhile, the review gives a valuable summary of new insights about the essence of  $\text{NH}_3$ -SCR catalytic reaction and the design strategies of Cu-based catalysts, and then efficient solutions against harmful components encountered in real applications are further proposed. This is helpful to provide insights into catalytic mechanisms on various catalysts in the  $\text{NH}_3$ -SCR reaction, thereby facilitating the development of highly active and resistance-enhanced catalysts to deal with complex environmental problems by designing reasonable modification strategies.

Based on the mechanism of the  $\text{NH}_3$ -SCR reaction, the adsorption and activation of  $\text{NH}_3$  and NO molecules are the initial and crucial steps in the catalytic process. In this regard, both excellent redox properties and strong acidity are important factors that contribute to the activity enhancement of SCR catalysts. The reason is that the enhanced redox performance will be beneficial to the activation of NO gas at the active centers, thus promoting the catalytic activity of the catalysts



at low temperature. Besides, abundant strong acid centers help to enhance the activation of  $\text{NH}_3$  molecules, forming  $\text{NH}_3$  (Lewis acid sites) and  $\text{NH}_4^+$  (Brønsted acid sites) species, which will react with active nitrate and nitrite intermediates formed by NO activation in the subsequent reaction. For efficient  $\text{NO}_x$  removal, one feasible design is introducing components which have excellent redox properties such as Ce, Nb or Zr for the oxidation of NO molecules, combined with acid components including W, Mo or zeolites providing adsorption sites to improve the activation of  $\text{NH}_3$  molecules, thus accelerating the  $\text{NH}_3$ -SCR process.

Recently, Cu-based SCR catalysts (Cu-based small-pore zeolites and Cu-containing metal oxides) have been rapidly developed in the field of  $\text{NH}_3$ -SCR, but their further application is limited due to their own shortcomings. Cu-based small-pore zeolites always have better catalytic performance at low temperatures, while their high-temperature activity and hydrothermal stability are not satisfactory. In addition, due to the high price of Cu-based small-pore zeolites, the development of Cu-containing metal oxides is of great significance. The main challenge of these catalysts is that their operating temperature window is too narrow. In this case, improving the temperature window will be an important research direction in the future. Therefore, a large number of optimization studies have been carried out on the design and development of Cu-based catalysts, aiming to explore novel Cu-based small-pore zeolites and Cu-containing metal oxides through common modifications of the catalyst structure and active sites, so as to achieve higher activity and hydrothermal stability.

Specifically speaking, there are great differences in specific active sites and redox routeways in  $\text{NH}_3$ -SCR reaction catalysed by various systems of Cu-based catalysts, which leads to the complexity of the reaction mechanism. Therefore, it is meaningful to develop catalysts with a specific reaction path to optimize the reaction kinetics and facilitate the  $\text{NH}_3$ -SCR process from the perspective of catalyst design, further promoting the reaction activity of Cu-based catalysts. Firstly, due to the different physicochemical properties and specific surface area, the supports had different effects on the chemical valence states and dispersion of Cu active species, so selecting an appropriate support and in-depth understanding of the reaction mechanism have guiding significance to enhance catalysis. Secondly, the growth of the zeolite framework, and the number and location of active Cu species play an important role in the catalytic performance, redox and acid ability of the catalysts. Controllable regulation will be achieved through strategies including precursor optimization engineering and preparation method modification, which can also induce the generation of more isolated Cu ions and promote the adsorption/activation of reactant gas molecules on the catalyst surface. Moreover, the structure-activity relationship needs to be further revealed. Crystal structure regulation, secondary metal doping (Fe, Ce, Y, *etc.*), and interaction and interface engineering (the composite between molecular sieves, the composite between molecular sieve and metal oxides, *etc.*), directly affecting the redox/acid properties of the catalysts and accelerating the electron transfer

between foreign components and active Cu species, will be efficient strategies to design high-performance Cu-based catalysts.

Although great efforts have been made in the design and development of Cu-based SCR catalysts, there are still many serious challenges in industrial applications. Due to the complex composition of flue gas, the chemical poisoning resistance ( $\text{SO}_2$  and alkali metals *etc.*) and hydrothermal resistance for  $\text{NH}_3$ -SCR catalysts should be enhanced. An efficient strategy to promote  $\text{SO}_2$ -resistance is to optimize the redox property of the catalysts, which will weaken the oxidation of  $\text{SO}_2$  on the catalyst surface and promote the decomposition of ammonium bisulfate. To avoid the poisoning of alkali ions, choosing strongly acidic supports or metals should be effective, which will interact with alkali ions and reduce the poisoning effect of alkali metals on the active sites. For Cu-based small-pore zeolites, the generation of  $\text{CuO}_x$  induces dealumination and collapse of the zeolite framework during hydrothermal aging. In this case, constructing a stable structure of the zeolite framework, and utilizing an Al-rich support for stabilizing Cu species is necessary to promote hydrothermal stability. Notably, the addition of other components to design composite materials with separated catalytically active sites and sacrificial centers should be a universal way to increase the hydrothermal stability and resistance to  $\text{SO}_2$  and alkali metals, which is helpful to realize the industrial application of Cu-based catalysts.

#### 4.2 Future perspectives

As summarized above, selective catalytic reduction of  $\text{NO}_x$  with ammonia constitutes a vital component within the complicated aftertreatment system for flue gas removal. This process encompasses the efficient adsorption and activation of NO and  $\text{NH}_3$  molecules, as well as the precise formation and transfer of various intermediates. Therefore, acting as the widely used de- $\text{NO}_x$  catalyst, the optimization of the catalyst structure and active centers of Cu-based catalysts significantly impacts the regulation of catalytic activity. Meanwhile, the exploration of catalyst synthesis and preparation at the atomic scale plays a pivotal role in practical production. However, there remains a need for a deeper understanding of fundamental mechanisms governing interactions among various active components, particularly under realistic reaction conditions, which poses a challenge to further catalyst optimization. Therefore, achieving a comprehensive understanding of the interplay between active components holds immense importance for enhancing the reliability and long-term economic viability of catalyst design and processes. Moreover, to advance the industrialization of Cu-based catalysts, superior resistance to toxicity is imperative, given the presence of numerous toxic constituents in industrial production processes. Subtle adjustments to the catalyst structure and active sites or alterations in reaction pathways can mitigate the combination of active sites with harmful components under the complex flue gas environment, which is of paramount significance for future practical applications. Consequently, the optimization of catalysts and processes to attain outstanding activity and toxicity-resistance represents a foremost research direction, offering promising prospects in future industrial production.



## Conflicts of interest

The authors declare no competing interests.

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