Review of the application of Cu-containing SSZ-13 in NH$_3$-SCR-DeNO$_x$ and NH$_3$-SCO

Magdalena Jabłońska

The reduction of NO$_x$ emissions has become one of the most important subjects in environmental protection. Cu-containing SSZ-13 is currently the state-of-the-art catalyst for the selective catalytic reduction of NO$_x$ with ammonia (NH$_3$-SCR-DeNO$_x$). Although the current-generation catalysts reveal enhanced activity and remarkable hydrothermal stability, still open challenges appear. Thus, this review focuses on the progress of Cu-containing SSZ-13 regarding preparation methods, hydrothermal resistance and poisoning as well as reaction mechanisms in NH$_3$-SCR-DeNO$_x$. Remarkably, the paper reviews also the progress of Cu-containing SSZ-13 in the selective ammonia oxidation into nitrogen and water vapor (NH$_3$-SCO). The dynamics in the NH$_3$-SCR-DeNO$_x$ and NH$_3$-SCO fields make this review timely.

Introduction

Nitrogen oxides (NO$_x$, consisting of >95% NO and <5% NO$_2$) are one of the major atmospheric pollutant gasses emitted from vehicle engines (e.g., automobiles, ships, etc.) and industrial boiler processes. NO$_x$ are formed via different mechanisms such as thermal-NO$_x$, prompt-NO$_x$ and fuel-NO$_x$. Nitrogen oxides affect human health (e.g., lowering the body’s resistance to bacterial infections, eye and respiratory system irritation, causing problems with breathing, allergic diseases, etc.). Furthermore, the hazards of NO$_x$ include the promotion of global warming and the formation of photochemical smog, acid rain, atmospheric haze (fine particle pollution) and ozone depletion, while the control of NO$_x$ emission remains a challenging task in the field of environmental catalysis. The upcoming EU emission legislation challenges researchers and engineers to keep the NO$_x$ emissions at a very low level under various boundary conditions. The selective catalytic reduction with ammonia (NH$_3$-SCR-DeNO$_x$: 4NH$_3$ + 4NO + O$_2$ → 4N$_2$ + 6H$_2$O) is one of the most effective technologies for removing NO$_x$ from diesel engine exhausts with an 80–95% removal efficiency. Catalysts – typically metal-oxides, noble metals, metal exchanged zeolites or hybrid systems – are an integral part of NH$_3$-SCR-DeNO$_x$. Much research has been done on Cu-containing ZSM-5 catalysts since its discovery in 1986 by Iwamoto et al. However, Cu-containing ZSM-5, beta or SAPO-34 suffer from poor hydrothermal stability. Cu-containing SSZ-13 (standard oil synthetic zeolite-thirteen, chabazite (CHA)-type zeolite) catalysts have been commercialized in the US and Europe since 2010 due to their efficient reduction of NO$_x$ and enhanced hydrothermal stability. The CHA framework is composed of four-, six-, and eight-membered rings arranged to form a tridimensional system of channels perpendicular to each other (0.38 × 0.38 nm; R3m (166) space group). Examples of morphology of SSZ-13 are given in Fig. 1a. SSZ-13 was first synthesized by Zones in 1983 applying the very costly template $N_3N,N$-trimethyl-1-adamantammonium hydroxide (TMAdaOH). Nowadays, SSZ-13 can be synthesized by applying a variety of cheaper templates, including choline chloride and $N_3N,N$-dimethylethyclohexylammonium bromide (DMCHABr), etc. Cu-SSZ-13 prepared via ion-exchange showed improved activity and N$_2$ selectivity (i.e., lower amounts of NO$_x$ by-products) compared to Cu-ZSM-5 and Cu-beta (Fig. 1b). The activity of catalysts was maintained even...
after severe hydrothermal treatment at 800 °C for 16 h.\textsuperscript{11,19–21} Still, some challenges remain for Cu-containing SSZ-13, including broadening the reaction temperature window together with improved (thermal) stability against chemical poisons. Although some review articles on the Cu-containing SSZ-13 were already published in 2015–2021,\textsuperscript{22–27} extensive studies on the Cu-containing SSZ-13 catalysts concerning preparations methods, hydrothermal stability and poisoning, the reaction mechanisms as well as the determination of active sites are of great interest. Thus, all these factors constitute the present review, which covers the thorough literature of the last ten years. However, this review did not include patents.

**Preparation methods of Cu-containing SSZ-13**

Kwak \textit{et al.}\textsuperscript{26} first suggested the presence of two different cationic Cu sites in Cu-SSZ-13, while Giordanino \textit{et al.}\textsuperscript{29} first reported the presence of [Cu(OH)]\textsuperscript{+} species in Cu-SSZ-13. Cu-containing SSZ-13 contains two active sites for NH\textsubscript{3}-SCR-DeNO\textsubscript{x}, Cu\textsuperscript{2+} in double-six-membered ring (D6R) cages and [Cu(OH)]\textsuperscript{+} in CHA cages, which are balanced by a pair of negative charges (Z) and a single framework negative charge (Z), respectively\textsuperscript{20–22} (Fig. 2a). The concentration of [Cu(OH)]\textsuperscript{+} ions within the eight-ring windows of Cu-SSZ-13 increases as the \(n\text(Cu)/n\text(Al)\) ratio rises, unlike that of Cu\textsuperscript{2+} ions on D6Rs.\textsuperscript{23} The dehydration of the [Cu(OH)]\textsuperscript{+} ions may lead to the formation of Cu\textsuperscript{+} species ([Cu(OH)]\textsuperscript{+} → Cu\textsuperscript{2+} + H\textsubscript{2}O),\textsuperscript{24} or [Cu–O–Cu]\textsuperscript{2+} oxocations (–Al–O–Cu\textsuperscript{2+}–OH + –Al–O–Cu\textsuperscript{2+}–OH → –Al–O–[Cu–O–Cu]\textsuperscript{2+}–Al– + H\textsubscript{2}O).\textsuperscript{15} Furthermore, Verma \textit{et al.}\textsuperscript{34,37} suggested that when the \(n\text(Cu)/n\text(Al)\) is above 0.2, Cu\textsubscript{2}O\textsubscript{y} are also present. Such aggregated copper oxide species catalyze ammonia oxidation.\textsuperscript{38} Fickel and Lobo\textsuperscript{32} pioneered in the investigation over Cu species in Cu-SSZ-13 with low \(n\text(Si)/n\text(Al)\) and 4.39 wt% of Cu. They proposed that the Cu cations exist exclusively in the form of isolated Cu\textsuperscript{2+} ions and are located in the cages coordinated with three oxygen atoms of the six-membered rings (6MRs). Nowadays it is recognized that the location, as well as the nature of the Cu cations, varies significantly depending on the \(n\text(Si)/n\text(Al)\) ratio and also on the Cu loading. Thus, the copper species can occupy four types of cationic sites in CHA, such as site I – displaced from the six-membered-ring into the ellipsoidal cavity, site II – located near the center of the ellipsoidal cavity, site III – located in the center of the hexagonal prism, and site IV – located near the eight-membered-ring window.\textsuperscript{39,40} The copper species can be introduced into the CHA structure via different techniques, including ion-exchange, one-pot hydrothermal method, solid-state ion-exchange, etc. Table 1 summarizes the catalyst preparation, reaction conditions, and NO\textsubscript{x} conversion in NH\textsubscript{3}-SCR-DeNO\textsubscript{x} above 80% and related by-products in the range. The activity and selectivity of the Cu-containing systems depend on multiple factors, particularly catalyst composition (e.g., \(n\text(Si)/n\text(Al)\) ratio and copper species loading) and treatment history (e.g., degreening and hydrothermal ageing). It is important to note that the reaction conditions are generally different from each other, including the feed gas composition, total flow, catalyst dosage, and even measurement systems. Therefore, it is hard to compare the activity of the various catalysts in detail. However, a rough comparison is still feasible. Other transition metals have been introduced to improve the activity of catalysts (e.g., Fe,\textsuperscript{41–44} Mn,\textsuperscript{45,46} etc.). In the current review, the focus is given mainly on the Cu-containing SSZ-13.

**Ion-exchange**

In the most widely applied preparation method reported in the literature – ion-exchange, the initial Na-SSZ-13 must also be ion-exchanged with NH\textsubscript{4}NO\textsubscript{3} and Cu\textsuperscript{2+} salt solutions to obtain Cu-SSZ-13. The NH\textsubscript{4}\textsuperscript{+}-form has been reported to improve the mobility of Cu\textsuperscript{2+} ions and promote the ion-exchange rates and levels.\textsuperscript{35} However, the ion-exchange properties (thus, the nature and location of copper species) are influenced by the synthesis conditions of SSZ-13, such as silica source, aluminium source, \(n\text(Si)/n\text(Al)\) ratio, organic structure-directing agent, water content, alkalinity, ageing time, crystallization temperature or
time, etc. Furthermore, ion-exchange variables such as the copper precursor, temperature and time are also influencing factors. For example, Gao et al. prepared SSZ-13 with different \( n(\text{Si})/n(\text{Al}) \) ratios (6, 12 and 35) by the traditional synthesis method with \( N,N,N' \)-trimethyl-1-adamantammonium hydroxide as a structure-directing agent. They proposed that the location of \( \text{Cu}^{2+} \) ions and their redox properties can be adjusted through the variation of the \( n(\text{Si})/n(\text{Al}) \) ratio of Cu-SSZ-13. Moreover, the isolated \( \text{Cu}^{2+} \) ions in Cu-SSZ-13 are adjusted by the application of different Cu precursors, i.e., in 6MRs for the catalysts prepared with \( \text{CuCl}_2 \) and \( \text{Cu(CH}_3\text{COO})_2 \) precursors and in 8MRs for the catalysts prepared with \( \text{Cu(NO}_3)_2 \) and \( \text{CuSO}_4 \) precursors. The presence of catalytic centers with different activities can be visualized via the seagull profile, i.e., first, an increase in NO conversion with temperature, followed by a decrease at intermediate temperatures (ca. 250–350 °C), and finally an increase again at higher temperatures (Fig. 2b). The seagull profile is often seen for Cu-SSZ-13 with low Cu content (i.e., 0.5–3 wt.%), \( \text{NH}_3\text{-SCR-DeNO}_x \) with high space velocity, low oxygen concentration (e.g., 2 vol%) as well as in the presence of hydrocarbons. The ion-exchange properties can also be varied for the micro-/mesoporous materials. In the case of SSZ-13, mesopores with diameters of 2–10 nm were introduced into the zeolite H-SSZ-13 after treatment with NaOH. Cu-containing SSZ-13 with the support treated with an aqueous solution of 0.1 M NaOH showed enhanced activity in \( \text{NH}_3\text{-SCR-DeNO}_x \). The use of higher concentrations of NaOH led to a drop in activity. Moreover, lower activity was also reported for the steamed Cu-SSZ-13. Further studies proved Cu-containing SSZ-13, with the support treated with 0.1 M aqueous solution to be the most active catalyst in the series (0–0.3 M concentration of NaOH solution). The copper species loading introduced via ion-exchange was comparable for the catalysts with unmodified and post-modified support; however, they varied significantly between both studies. As can be seen from Table 1, the amount of introduced copper species varies significantly among the samples, i.e., it is uncontrollable. Furthermore, as the ion-exchange requires successive washing, filtering, drying, calcining and solute recycling procedures, many researchers turn to alternative preparation procedures, e.g., the one-pot hydrothermal method.
Table 1  Representative results of NH₃-SCR-DeNOₓ over Cu-containing SSZ-13 reported in the literature

| Pos. | Sample | Preparation method | Reaction conditions | Operation temperature for achieving > 80% NOₓ conversion/C (h) | Ref. |
|------|--------|--------------------|---------------------|---------------------|------|
| 1    | (1.4 wt%)Cu-SSZ-13 \(\text{n(Si)/n(Al) = 4.8}\) monolith catalyst | Commercial; degreening: 14 vol% O₂, 5 vol% H₂O, 5 vol% CO₂, N₂ balance, 600 °C, 4 h | 0.015 vol% NO, 0.035 vol% NH₃, 14 vol% O₂, 5 vol% CO₂, 5 vol% H₂O, N₂ balance, GHSV 30,000 h⁻¹ | 200–500 (<7% N₂O selectivity) | 68   |
| 2    | (1.63 wt%)Cu-SSZ-13 \(\text{n(Si)/n(Al) = 16}\) monolith catalyst | Commercial; degreening: 10 vol% O₂, 7 vol% H₂O, 8 vol% CO₂, N₂ balance, 650 °C, 4 h; *hydrothermal treatment: 10 vol% H₂O, 18.9 vol% O₂, N₂ balance, 650 °C, 100 h | 0.05 vol% NO, 0.05 vol% NH₃, 7 vol% H₂O, 8 vol% CO₂, 10 vol% O₂, N₂ balance, GHSV 60,000 h⁻¹ | 200–500 (not shown), *200–500 (not shown) | 69   |
| 3    | (1.63 wt%)Cu-SSZ-13 \(\text{n(Si)/n(Al) = 16}\) monolith catalyst | Commercial; degreening: 10 vol% O₂, 7 vol% H₂O, 8 vol% CO₂, N₂ balance, 650 °C, 50 h | 0.05 vol% NO, 0.05 vol% NH₃, 7 vol% H₂O, 8 vol% CO₂, 10 vol% O₂, N₂ balance, GHSV 60,000 h⁻¹ | 200–500 (<15 ppm N₂O) | 70   |
| 4    | (2.2 wt%)Cu-SSZ-13 \(\text{n(Si)/n(Al) = 13.6}\) monolith catalyst | Commercial; *hydrothermal treatment: 10 vol% H₂O, air balance, 800 °C, 12 h | 0.1 vol% NO, 0.11 vol% NH₃, 5 vol% O₂, 10 vol% H₂O, N₂ balance, GHSV 30,000 h⁻¹ | 225–550 (not shown) *225–575 (not shown) | 71   |
| 5    | (2.4 wt%)Cu-SSZ-13 \(\text{n(Si)/n(Al) = 15}\) monolith catalyst | Commercial; degreening: 10 vol% O₂, 7 vol% H₂O, 8 vol% CO₂, Ar balance, 550 °C, 4 h | 0.02 vol% NO, 0.02 vol% NH₃, 5 vol% O₂, 5 vol% H₂O, Ar balance, GHSV 40,000 h⁻¹ | 200–450 (<6% NO₂, N₂O concentration) | 72   |
| 6    | (2.7 wt%)Cu-SSZ-13 \(\text{n(Si)/n(Al) = 12}\) monolith catalyst | Commercial; degreening: 10 vol% H₂O, air balance, 650 °C, 12 h; *hydrothermal treatment: 10 vol% H₂O, air balance, 800 °C, 16 h; pre-treatment: 21 vol% O₂, N₂ balance, 600 °C, 20 min | 0.05 vol% NO, 0.05 vol% NH₃, 5 vol% O₂, 3 vol% H₂O, N₂ balance, GHSV 120,000 h⁻¹ | 200–600 (<10 ppm N₂O), *200–500 (<10 ppm N₂O) | 73   |
| 7    | (2.8 wt%)Cu-SSZ-13 \(\text{n(Si)/n(Al) = 35}\) monolith catalyst | Commercial; calcination, 450 °C, 0.5 h; 12.5 vol% H₂O, air balance, 800 °C, 16 h | 0.02 vol% NO, 0.02 vol% NH₃, 10 vol% O₂, 5 vol% H₂O, 8 vol% CO₂, 10 vol% O₂, N₂ balance, GHSV 60,000 h⁻¹ | 250–450 (not shown) | 21   |
| 8    | (3 wt%)Cu-SSZ-13 \(\text{n(Si)/n(Al) = 7}\) monolith catalyst | Commercial; degreening: 10 vol% O₂, 5 vol% H₂O, N₂ balance, 500 °C, 1 h | 0.1 vol% NO, 0.1 vol% NH₃, 10 vol% O₂, 5 vol% H₂O, N₂ balance, GHSV 120,000 h⁻¹ | 200–500 (<15 ppm N₂O) | 52   |
| 9    | Cu-SSZ-13 (Cu content, \(\text{n(Si)/n(Al) not shown}\) monolith catalyst | Commercial; degreening: 10 vol% O₂, 7 vol% H₂O, 8 vol% CO₂, N₂ balance, 550–600 °C, 4 h | 0.02 vol% NO, 0.02 vol% NH₃, 10 vol% O₂, 5 vol% H₂O, Ar balance, GHSV 40,000 h⁻¹ | 200–500 (not shown) | 74   |
| 10   | Cu-SSZ-13 (Cu content, \(\text{n(Si)/n(Al) not shown}\) monolith catalyst | Commercial; hydrothermal treatment: 10 vol% O₂, 8 vol% CO₂, 7 vol% H₂O, N₂ balance, 800 °C, 4 h | 0.02 vol% NO, 0.02 vol% NH₃, 10 vol% O₂, 8 vol% CO₂, 7 vol% H₂O, N₂ balance, GHSV 40,000 h⁻¹ | 200–500 (not shown) | 75   |
| 11   | Cu-SSZ-13 (Cu content, \(\text{n(Si)/n(Al) not shown}\) monolith catalyst | Commercial; hydrothermal treatment: 14 vol% O₂, 5 vol% CO₂, 5 vol% H₂O, N₂ balance, 750 °C, 16 h | 0.035 vol% NO, 0.035 vol% NH₃, 14 vol% O₂, 2 vol% H₂O, N₂ balance, GHSV 140,000 h⁻¹ | 250–500 (not shown) | 76   |
| 12   | Cu-SSZ-13 \(\text{n(Si)/n(Al) = 6}\) (Cu content not shown) | Ion-exchange, calcination, 500 °C, 2 h, air | 0.035 vol% NO, 0.035 vol% NH₃, 14 vol% O₂, 2 vol% H₂O, N₂ balance, GHSV 30,000 h⁻¹ | 200–550 (<10 ppm NOₓ formation, <5 ppm N₂O formation) | 11   |
| 13   | (0.87 wt%)Cu-SSZ-13 \(\text{n(Si)/n(Al) = 6}\) | Ion-exchange, calcination, 550 °C, 8 h, air; *hydrothermal treatment: 10 vol% H₂O, air balance, 880 °C, 12 h | 0.035 vol% NO, 0.035 vol% NH₃, 14 vol% O₂, 2.5 vol% H₂O, N₂ balance, GHSV 100,000 h⁻¹ | 200–500 (not shown) | 77   |
| 14   | (0.98 wt%)Cu-SSZ-13 \(\text{n(Si)/n(Al) = 6}\) | Ion-exchange, calcination, 550 °C, 8 h, air; *hydrothermal treatment: 10 vol% H₂O, air balance, 880 °C, 12 h | 0.035 vol% NO, 0.035 vol% NH₃, 14 vol% O₂, 2.5 vol% H₂O, N₂ balance, GHSV 100,000 h⁻¹ | 200–500 (not shown) *200–500 (not shown) | 77   |
| Pos. | Sample | Preparation method | Reaction conditions | Operation temperature for achieving > 80% NOx conversion/°C (by-product formation) | Ref. |
|------|--------|-------------------|---------------------|--------------------------------|-----|
| 15 | (0.88 wt%)Cu-SSZ-13 \((n(Si)/n(Al) = 16)\) | Ion-exchange, calcination, 550 °C, 8 h, air; pre-treatment: 21 vol% O₂, N₂ balance, 500 °C, 2 h | 0.05 vol% NO, 0.05 vol% NH₃, 5 vol% O₂, 10 vol% H₂O, N₂ balance, GHSV 100,000 h⁻¹ | 200–600 (not shown) | 78 |
| 16 | (0.95–1.38 wt%)Cu-SSZ-13 \((n(Si)/n(Al) = 20)\) | Ion-exchange; pre-treatment: 5 vol% O₂, He balance, 550 °C, 1 h | 0.1 vol% NO, 0.1 vol% NH₃, 5 vol% O₂, He balance, GHSV 100,000 h⁻¹ | 300–450 (not shown) | 79 |
| 17 | (1.04 wt%)Cu-SSZ-13 \((n(Si)/n(Al) = 5.5)\) | Ion-exchange, calcination, 500 °C, 5 h, air; *hydrothermal treatment: 10 vol% H₂O, air balance, 800 °C, 12 h | 0.05 vol% NO, 0.05 vol% NH₃, 10 vol% O₂, 5 vol% H₂O, N₂ balance, GHSV 30,000 h⁻¹ | 200–600 (not shown), *200–550 (not shown) | 80 |
| 18 | (1.00–1.17 wt%)Cu-SSZ-13 \((n(Si)/n(Al) = 23.6–23.8)\) | Ion-exchange, calcination, 550 °C, 6 h, air; pre-treatment: 500 °C, 0.5 h, 5 vol% O₂, N₂ balance | 0.05 vol% NO, 0.05 vol% NH₃, 10 vol% O₂, 3 vol% H₂O, N₂ balance, GHSV 40,000 h⁻¹ | 250–500 (<6 ppm N₂O) | 81 |
| 19 | (2.5 wt%)Cu-SSZ-13 \((n(Si)/n(Al) = 15)\) | Ion-exchange, calcination, 500 °C, 5 h, air; *hydrothermal treatment: 10 vol% H₂O, air balance, 800 °C, 5 h | 0.05 vol% NO, 0.05 vol% NH₃, 10 vol% O₂, 5 vol% H₂O, N₂ balance, GHSV 80,000 h⁻¹ | 175–550 (<15 ppm N₂O), *175–600 (<15 ppm N₂O) | 82 |
| 20 | (1.21 wt%)Cu-SSZ-13 \((n(Si)/n(Al) = 6)\) | Ion-exchange, calcination, 550 °C, 4 h, air; *hydrothermal treatment: 10 vol% H₂O, air balance, 600 °C, 20 h | 0.036 vol% NO, 0.036 vol% NH₃, 10 vol% O₂, N₂ balance, GHSV 400,000 h⁻¹ | 225–550 (not shown), *250–550 (not shown) | 83 |
| 21 | (1.25–1.27 wt%)Cu-SSZ-13 \((n(Si)/n(Al) = 21–24)\) | Ion-exchange, calcination, 500 °C, 6 h, air; pre-treatment: 500 °C, 1 h, 14 vol% O₂, N₂ balance; *hydrothermal treatment: 5 vol% H₂O, N₂ balance, 800 °C, 16 h | 0.005 vol% NO, 0.005 vol% NH₃, 5 vol% O₂, N₂ balance, GHSV 48,000 h⁻¹ | 200–500 (>90% N₂ selectivity), *200–500 (>90% N₂ selectivity) | 84 |
| 22 | (1.3 wt%)Cu-SSZ-13 \((n(Si)/n(Al) = 17.6)\) | Ion-exchange, calcination, 550 °C, 4 h, air; pre-treatment: 5 vol% O₂, He balance, 550 °C, 1 h | 0.01 vol% NO, 0.01 vol% NH₃, 5 vol% O₂, He balance, GHSV 100,000 h⁻¹ | 250–450 (not shown) | 58 |
| 23 | (1.45–1.62 wt%)Cu-SSZ-13 \((n(Si)/n(Al) not shown)\) | Ion-exchange, calcination, 550 °C, 5 h, air; *hydrothermal treatment: 10 vol% H₂O, air balance, 800 °C, 16 h | 0.035 vol% NO, 0.035 vol% NH₃, 14 vol% O₂, 2.5 vol% H₂O, N₂ balance, GHSV 200,000 h⁻¹ | 200–500 (not shown), *225–450 (not shown) | 14 |
| 24 | (1.73 wt%)Cu-SSZ-13 \((n(Si)/n(Al) = 9.5)\) | Ion-exchange, calcination, 550 °C, 4 h, air; *hydrothermal treatment: 10 vol% H₂O, air balance, 800 °C, 16 h | 0.05 vol% NO, 0.05 vol% NH₃, 5 vol% O₂, 5 vol% H₂O, N₂ balance, GHSV 400,000 h⁻¹ | 225–600 (>95% N₂ selectivity), *250–500 (>90% N₂ selectivity) | 85 |
| 25 | (1.8–2 wt%)Cu-SSZ-13 \((n(Si)/n(Al) = 7.8)\) | Ion-exchange, calcination, temperature and time not shown; *hydrothermal treatment: 5 vol% H₂O, N₂ balance, 750 °C, 16 h | 0.05 vol% NO, 0.05 vol% NH₃, 14 vol% O₂, 5 vol% H₂O, N₂ balance, GHSV 48,000 h⁻¹ | 200–600 (>97% N₂ selectivity), *200–500 (>97% N₂ selectivity) | 86 |
| 26 | (1.88–2.16 wt%)Cu-SSZ-13 \((n(Si)/n(Al) = 16.5–20.3)\) | Ion-exchange, calcination, 550 °C, 5 h, air; *hydrothermal treatment: 10 vol% H₂O, air balance, 750 °C, 16 h; pre-treatment: 21 vol% O₂, N₂ balance, 550 °C, 20 min | 0.05 vol% NO, 0.05 vol% NH₃, 5 vol% O₂, 3 vol% H₂O, N₂ balance, GHSV 120,000 h⁻¹ | 200–550 (<5 ppm N₂O), *200–500 (<5 ppm N₂O) | 87 |
| 27 | (2 wt%)Cu-SSZ-13 \((n(Si)/n(Al) = 9)\) | Ion-exchange, calcination, 550 °C, 5 h, air; *hydrothermal treatment: 10 vol% H₂O, air balance, 800 °C, 16 h; **degreening: 10 vol% H₂O, air balance, 700 °C, 4 h | 0.036 vol% NO, 0.036 vol% NH₃, 14 vol% O₂, 2.5 vol% H₂O, N₂ balance, GHSV 100,000 h⁻¹ | *200–550 (not shown), **200–550 (not shown) | 88 |
| Pos. | Sample Preparation method | Reaction conditions | Operation temperature for achieving >80% NO\textsubscript{x} conversion/°C (by-product formation) | Ref. |
|------|--------------------------|---------------------|------------------------------------------------|-----|
| 28   | (2 wt%)Cu-SSZ-13 (n(Si)/n(Al) = 11) Ion-exchange, calcination conditions not shown; degreening: Reaction conditions, 600 °C, 4 h; pre-treatment: 10 vol% O\textsubscript{2}, 7 vol% H\textsubscript{2}O, N\textsubscript{2} balance, 600 °C, 1 h | 0.035 vol% NO, 0.035 vol% NH\textsubscript{3}, 10 vol% O\textsubscript{2}, 7 vol% H\textsubscript{2}O, N\textsubscript{2} balance, GHSV 300,000 h\textsuperscript{-1} | 225–550 (>97% N\textsubscript{2} selectivity) | 89  |
| 29   | (2.08 wt%)Cu-SSZ-13 (n(Si)/n(Al) = 4.5) Ion-exchange, calcination, 550 °C, 4 h, air; hydrothermal treatment: 20 vol% O\textsubscript{2}, 10 vol% H\textsubscript{2}O, N\textsubscript{2} balance, 550 °C, 0.5 h | 0.05 vol% NO, 0.05 vol% NH\textsubscript{3}, 10 vol% O\textsubscript{2}, N\textsubscript{2} balance, 100% N\textsubscript{2} selectivity | 250–300 (not shown), *250–300 (not shown) | 90  |
| 30   | (2.1 wt%)Cu-SSZ-13 (n(Si)/n(Al) = 12) Ion-exchange, calcination conditions not shown; hydrothermal treatment: 10 vol% H\textsubscript{2}O, air balance, 800 °C, 1 h | 0.036 vol% NO, 0.036 vol% NH\textsubscript{3}, 14 vol% O\textsubscript{2}, 2.5 vol% H\textsubscript{2}O, N\textsubscript{2} balance, GHSV 200,000 h\textsuperscript{-1} | 175–500 (not shown), *200–450 (not shown) | 91  |
| 31   | (2.2 wt%)Cu-SSZ-13 (n(Si)/n(Al) = 10.5) Ion-exchange, calcination, 600 °C, 6 h, air; hydrothermal treatment: 10 vol% H\textsubscript{2}O, air balance, 800 °C, 1 h | 0.05 vol% NO, 0.05 vol% NH\textsubscript{3}, 5 vol% O\textsubscript{2}, 5 vol% H\textsubscript{2}O, N\textsubscript{2} balance, GHSV 400,000 h\textsuperscript{-1} | 225–550 (<10 ppm N\textsubscript{2}O), *225–500 (<15 ppm N\textsubscript{2}O) | 92  |
| 32   | (2.23 wt%)Cu-SSZ-13 (n(Si)/n(Al) = 8.8) Ion-exchange, calcination conditions not shown; hydrothermal treatment: 10 vol% H\textsubscript{2}O, 700 °C, 16 h; pre-treatment: 14 vol%, N\textsubscript{2} balance, 500 °C, 1 h | 0.03 vol% NO, 0.03 vol% NH\textsubscript{3}, 5 vol% O\textsubscript{2}, 3 vol% H\textsubscript{2}O, N\textsubscript{2} balance, WHSV 60,000 ml g\textsuperscript{-1} h\textsuperscript{-1} | 250–500 (not shown), *250–500 (not shown), **300–350 (not shown) | 93  |
| 33   | (2.25 wt%)Cu-SSZ-13 (n(Si)/n(Al) = 12) Ion-exchange, calcination, 550 °C, 5 h, air; hydrothermal treatment: 10 vol% H\textsubscript{2}O, 700 °C, 16 h | 0.036 vol% NO, 0.036 vol% NH\textsubscript{3}, 14 vol% O\textsubscript{2}, 2.5 vol% H\textsubscript{2}O, N\textsubscript{2} balance, GHSV 200,000 h\textsuperscript{-1} | 175–500 (<7 ppm N\textsubscript{2}O), *200–500 (<25 ppm N\textsubscript{2}O) | 94  |
| 34   | (2.3 wt%)Cu-SSZ-13 (n(Si)/n(Al) = 15) monolith catalyst Ion-exchange, calcination, 600 °C, 5 h, air; hydrothermal treatment: 10 vol% H\textsubscript{2}O, air balance, 750 °C, 12 h | 0.1 vol% NO, 0.11 vol% NH\textsubscript{3}, 5 vol% O\textsubscript{2}, 10 vol% H\textsubscript{2}O, N\textsubscript{2} balance, GHSV 30,000 h\textsuperscript{-1} | 200–575 (not shown), *200–575 (not shown) | 95  |
| 35   | (2.35 wt%)Cu-SSZ-13 (n(Si)/n(Al) = 12.93) Ion-exchange, calcination, 550 °C, 4 h, air; pre-treatment: 8 vol% O\textsubscript{2}, N\textsubscript{2} balance, 1 h, 500 °C | 0.05 vol% NO, 0.05 vol% NH\textsubscript{3}, 6.5 vol% O\textsubscript{2}, 3 vol% H\textsubscript{2}O, N\textsubscript{2} balance, GHSV 120,000 h\textsuperscript{-1} | 125–400 (>95% N\textsubscript{2} selectivity) | 96  |
| 36   | (2.38 wt%)Cu-SSZ-13 (n(Si)/n(Al) = 6) Ion-exchange, calcination, 600 °C, 6 h, time not shown, air; pre-treatment: 5 vol% O\textsubscript{2}, N\textsubscript{2} balance, 200 °C, 1 h | 0.06 vol% NO, 0.06 vol% NH\textsubscript{3}, 5 vol% O\textsubscript{2}, 5 vol% H\textsubscript{2}O, N\textsubscript{2} balance, GHSV 450,000 h\textsuperscript{-1} | 250–550 (not shown) | 97  |
| 37   | (2.38 wt%)Cu-SSZ-13 (n(Si)/n(Al) = 6) Ion-exchange, calcination, 600 °C, 6 h, air; hydrothermal treatment: 5 vol% O\textsubscript{2}, N\textsubscript{2} balance, 1 h, 600 °C | 0.05 vol% NO, 0.05 vol% NH\textsubscript{3}, 5 vol% O\textsubscript{2}, 5 vol% H\textsubscript{2}O, N\textsubscript{2} balance, GHSV not shown | 250–550 (not shown), *300–400 (not shown) | 98  |
| 38   | (2.5-3 wt%)Cu-SSZ-13 (n(Si)/n(Al) = 12.5) Ion-exchange, calcination, 500 °C, 6 h, air; hydrothermal treatment: 5 vol% H\textsubscript{2}O, air balance, 800 °C, 12 h | 0.1 vol% NO, 0.1 vol% NH\textsubscript{3}, 5 vol% O\textsubscript{2}, N\textsubscript{2} balance, GHSV 130,000 h\textsuperscript{-1} | 200–800 (100% N\textsubscript{2} selectivity), *200–800 (100% N\textsubscript{2} selectivity) | 30  |
| 39   | (2.5 wt%)Cu-SSZ-13 (n(Si)/n(Al) = 8.7) Ion-exchange, calcination, 550 °C, 5 h, air; hydrothermal treatment: 10 vol% H\textsubscript{2}O, air balance, 750 °C, 16 h | 0.05 vol% NO, 0.05 vol% NH\textsubscript{3}, 5 vol% O\textsubscript{2}, 5 vol% H\textsubscript{2}O, N\textsubscript{2} balance, GHSV 200,000 h\textsuperscript{-1} | 200–550 (100% N\textsubscript{2} selectivity), *250–500 (100% N\textsubscript{2} selectivity) | 99  |
| 40   | (2.5 wt%)Cu-SSZ-13 (n(Si)/n(Al) not shown) Ion-exchange, calcination, 550 °C, 6 h, air; one-pot hydrothermal synthesis, calcination, 550 °C, 6 h, air | 0.05 vol% NO, 0.05 vol% NH\textsubscript{3}, 5 vol% O\textsubscript{2}, Ar balance, GHSV 180,000 h\textsuperscript{-1} | 250–600 (not shown), *200–600 (not shown) | 100 |
| Pos. | Sample | Preparation method | Reaction conditions | Operation temperature for achieving > 80% NOx conversion/°C (by-product formation) | Ref. |
|------|--------|-------------------|---------------------|-----------------------------------------------|------|
| 41   | (2.8 wt%)Cu-SSZ-13 (n(Si)/n(Al) = 5) | Ion-exchange, calcination, 550 °C, 5 h, air; *hydrothermal treatment: 10 vol% H2O, air balance, 800 °C, 16 h | 0.05 vol% NO, 0.05 vol% NH3, 10 vol% O2, 5 vol% H2O, N2 balance, WHSV 80,000 h⁻¹ | 175–650 (<15 ppm N2O), *175–550 (<15 ppm N2O) | 101 |
| 42   | (3.0 wt%)Cu-SSZ-13 (n(Si)/n(Al) = 6) | Ion-exchange, calcination, 550 °C, 8 h, air; *hydrothermal treatment: 10 vol% H2O, air balance, 800 °C, 16 h | 0.036 vol% NO, 0.036 vol% NH3, 14 vol% O2, 2.5 vol% H2O, N2 balance, WHSV 100,000 h⁻¹ | 200–450 (not shown) | 102 |
| 43   | (3.4 wt%)Cu-SSZ-13 (n(Si)/n(Al) = 9) | Ion-exchange, calcination, 700 °C, 5 h, air | 0.05 vol% NO, 0.05 vol% NH3, 4 vol% O2, N2 balance, WHSV 60,000 h⁻¹ | 175–500 (<10 ppm N2O) | 103 |
| 44   | (3.43–5.15 wt%)Cu-SSZ-13 (n(Si)/n(Al) = 6) | Ion-exchange, calcination, 550 °C, 8 h, air | 0.035 vol% NO, 0.035 vol% NH3, 14 vol% O2, 2.5 vol% H2O, N2 balance, WHSV 80,000 h⁻¹ | 250–550 (not shown) | 32 |
| 45   | (3.6 wt%)Cu-SSZ-13 (n(Si)/n(Al) = 6.5) | Ion-exchange, calcination, 700 °C, 4 h, air | 0.02 vol% NO, 0.02 vol% NH3, 8 vol% O2, 10 vol% H2O, N2 balance, WHSV 60,000 h⁻¹ | 200–500 (>95% N2 selectivity) | 104 |
| 46   | (3.97 wt%)Cu-SSZ-13 (n(Si)/n(Al) = 13.26) | Ion-exchange, calcination, 550 °C, 6 h, air | 0.05 vol% NO, 0.05 vol% NH3, 10 vol% O2, 5 vol% H2O, N2 balance, WHSV 200,000 h⁻¹ | 200–450 (>95% N2 selectivity) | 64 |
| 47   | (4.0–4.7 wt%)Cu-SSZ-13 (n(Si)/n(Al) = 12.0–12.7) | Ion-exchange, calcination, 500 °C, 6 h, air; *hydrothermal treatment: 10 vol% H2O, air balance, 800 °C, 12 h | 0.05 vol% NO, 0.05 vol% NH3, 10 vol% O2, N2 balance, WHSV 30,000 h⁻¹ | 200–500 (<25 ppm N2O), *200–500 (<25 ppm N2O) | 48 |
| 48   | (4.1 wt%)Cu-SSZ-13 (n(Si)/n(Al) = 6) | Ion-exchange, calcination, 600 °C, 4 h, air | 0.04 vol% NO, 0.04 vol% NH3, 8 vol% O2, 5 vol% H2O, Ar balance, WHSV 22,100 h⁻¹ | 175–500 (<15 ppm NOx, <8 ppm N2O) | 105 |
| 49   | (4.93 wt%)Cu-SSZ-13 (n(Si)/n(Al) = 6.48) | Ion-exchange, calcination, 550 °C, 6 h, air | 0.1 vol% NO, 0.1 vol% NH3, 6 vol% O2, 5 vol% H2O, He balance, WHSV 50,000 h⁻¹ | 150–450 (>70% N2 yield) | 16 |
| 50   | (4.93 wt%)Cu-SSZ-13 (n(Si)/n(Al) = 4.03) | Ion-exchange, vacuum evaporator, calcination, 550 °C, 6 h, air | 0.1 vol% NO, 0.1 vol% NH3, 10 vol% O2, He balance, WHSV 30,000 h⁻¹ | 150–450 (>70% N2 yield) | 17 |

**One-pot hydrothermal synthesis**

| Pos. | Sample | Preparation method | Reaction conditions | Operation temperature for achieving > 80% NOx conversion/°C (by-product formation) | Ref. |
|------|--------|-------------------|---------------------|-----------------------------------------------|------|
| 51   | Cu-SSZ-13 (n(Si)/n(Al) = 14.2) (Cu content not shown) | One-pot hydrothermal synthesis, calcination, 550 °C, time not shown, air; *hydrothermal treatment: 2.2 ml min⁻¹ H2, air balance, 750 °C, 13 h pre-treatment: 550 °C, 1 h, N2 | 0.05 vol% NO, 0.053 vol% NH3, 7 vol% O2, 5 vol% H2, N2 balance, WHSV 450,000 ml g⁻¹ h⁻¹ | 250–500 (not shown), *300–450 (not shown) | 62 |
| 52   | (2.82 wt%)Cu-SSZ-13 (n(Si)/n(Al) = 15) | One-pot hydrothermal synthesis, calcination, 600 °C, 5 h, air; *hydrothermal treatment: 10 vol% H2O, air balance, 850 °C, 12 h | 0.1 vol% NO, 0.11 vol% NH3, 5 vol% O2, 10 vol% H2O, N2 balance, WHSV 30,000 h⁻¹ | 200–550 (not shown), *250–550 (not shown) | 63 |
| 53   | (3.5 wt%)Cu-SSZ-13 (n(Si)/n(Al) = 6.5) | One-pot hydrothermal synthesis, calcination, 600 °C, 6 h, air; *hydrothermal treatment: 10 vol% H2O, air balance, 750 °C, 16 h | 0.05 vol% NO, 0.05 vol% NH3, 5 vol% O2, N2 balance, WHSV 400,000 h⁻¹ | 200–600 (>90% N2 selectivity), *200–550 (>90% N2 selectivity) | 106 |
| Pos. | Sample Preparation method | Reaction conditions | Operation temperature for achieving > 80% NOx conversion/°C (by-product formation) | Ref. |
|------|---------------------------|---------------------|------------------------------------------|------|
| 54   | (3.8 wt%)Cu-SSZ-13 (n(Si)/n(Al) = 8.3) One-pot hydrothermal synthesis, calcination, 600 °C, 6 h, air; *hydrothermal treatment: 10 vol% H2O, air balance, 750 °C, 16 h | 0.05 vol% NO, 0.05 vol% NH3, 5 vol% O2, N2 balance, GHSV 400,000 h⁻¹ | 200–550 (100% N2 selectivity), *250–450 (not shown) | 67 |
| 55   | (4.06–4.11 wt%)Cu-SSZ-13 (n(Si)/n(Al) = 4) One-pot hydrothermal synthesis, calcination, 600 °C, 6 h, air; *hydrothermal treatment: 10 vol% H2O, air balance, 750 °C, 12 h; pre-treatment: 5 vol% O2, N2 balance, 550 °C, 1 h | 0.05 vol% NO, 0.05 vol% NH3, 5 vol% O2, 5 vol% H2O, N2 balance, WHSV 300,000 g⁻¹ h⁻¹ | 175–550 (<10 ppm N2O), *175–450 (<20 ppm N2O) | 107 |
| 56   | (4.92 wt%)Cu-SSZ-13 (n(Si)/n(Al) = 4.36) One-pot hydrothermal synthesis, calcination, 550 °C, 4 h, air; *hydrothermal treatment: 10 vol% H2O, air balance, 750 °C, 16 h; pre-treatment: Reaction conditions, 550 °C, 1 h | 0.05 vol% NO, 0.05 vol% NH3, 5 vol% O2, 5 vol% H2O, N2 balance, GHSV 300,000 h⁻¹ | 200–500 (not shown), *250–500 (not shown) | 108 |
| 57   | (6.31 wt%)Cu-SSZ-13 (n(Si)/n(Al) = 13) One-pot hydrothermal synthesis, calcination, 600 °C, 6 h, air | 0.05 vol% NO, 0.05 vol% NH3, 5 vol% O2, N2 balance, GHSV 100,000 h⁻¹ | 150–550 (not shown) | 65 |
| 58   | (9.5 wt%)Cu-SSZ-13 (n(Si)/n(Al) = 4) One-pot hydrothermal synthesis, calcination, 550 °C, 8 h, air | 0.06 vol% NO, 0.06 vol% NH3, 6 vol% O2, 5 vol% H2O, He balance, GHSV 400,000 h⁻¹ | 200–550 (>98% N2 selectivity) | 109 |
| 59   | (9.7 wt%)Cu-SSZ-13 (n(Si)/n(Al) = 3.82 One-pot hydrothermal synthesis, calcination, 550 °C, 6 h, air | 0.05 vol% NO, 0.05 vol% NH3, 5 vol% O2, 5 vol% H2O, N2 balance, GHSV 400,000 h⁻¹ | 225–400 (not shown) | 110 |
| 60   | (10.0 wt%)Cu-SSZ-13 (n(Si)/n(Al) = 4.5) One-pot hydrothermal synthesis, calcination, 600 °C, 6 h, air | 0.05 vol% NO, 0.05 vol% NH3, 5 vol% O2, 5 vol% H2O, N2 balance, GHSV 400,000 h⁻¹ | 150–400 (>90% N2 selectivity) | 111 |
| 61   | (10.61 wt%)Cu-SSZ-13 (n(Si)/n(Al) = 4.17 One-pot hydrothermal synthesis, calcination, 550 °C, 6 h, air | 0.05 vol% NO, 0.05 vol% NH3, 5 vol% O2, 5 vol% H2O, N2 balance, GHSV 120,000 h⁻¹ | 200–400 (>95% N2 selectivity) | 66 |

**Solid-state ion-exchange**

| Pos. | Sample Preparation method | Reaction conditions | Operation temperature for achieving > 80% NOx conversion/°C (by-product formation) | Ref. |
|------|---------------------------|---------------------|------------------------------------------|------|
| 63   | (1.79 wt%)Cu-SSZ-13 (n(Si)/n(Al) = 10.8) Solid-state ion-exchange, vacuum evaporator, calcination, 300 °C, 0.5 h, air; *hydrothermal treatment: 10 vol% H2O, air balance, 750 °C, 16 h | 0.05 vol% NO, 0.05 vol% NH3, 5 vol% O2, 3 vol% H2O, N2 balance, GHSV 120,000 h⁻¹ | 200–550 (not shown), *200–550 (not shown) | 112 |
| 64   | (3.7 wt%)Cu-SSZ-13 (n(Si)/n(Al) = 13) Solid-state ion-exchange, calcination, 600 °C, 5 h, 800 °C 12 h, air | 0.04 vol% NO, 0.04 vol% NH3, 8 vol% O2, 5 vol% H2O, Ar balance, GHSV 205,000 h⁻¹ | 250–500 (not shown) | 113 |
| 65   | (3.08 wt%)Cu-SSZ-13 (n(Si)/n(Al) = 10.1) monolith catalyst Solid-state ion-exchange, vacuum evaporator, calcination conditions not shown; *hydrothermal treatment: 10 vol% H2O, air balance, 800 °C, 12 h | 0.1 vol% NO, 0.11 vol% NH3, 10 vol% O2, N2 balance, GHSV 80,000 h⁻¹ | 200–550 (>90% N2 selectivity), *200–550 (not shown) | 47 |
| Pos. | Sample | Preparation method | Reaction conditions | Operation temperature for achieving > 80% NO₂ conversion/C (by-)product formation | Ref. |
|------|--------|--------------------|---------------------|---------------------------------------------------------------------------------|-----|
| 66   | (3.9 wt%)Cu-SSZ-13 \((n(\text{Si})/n(\text{Al}) = 5.2)\) | Solid-state ion-exchange, calcination, 600 °C, time not shown, air; *hydrothermal treatment: 10 vol% H₂O, air balance, 750 °C, 16 h | 0.05 vol% NO, 0.05 vol% NH₃, 5 vol% O₂, 5 vol% H₂O, N₂ balance, GHSV 400,000 h⁻¹ | 200–550 (>97% N₂ selectivity), *200–450 (not shown) | 114 |
| 67   | (4.10 wt%)Cu-SSZ-13 \((n(\text{Si})/n(\text{Al}) = 6)\) | Solid-state ion-exchange, calcination, 700 °C, 16 h, dry air; *hydrothermal treatment: 10 vol% H₂O, 10 vol% O₂, N₂ balance, 750 °C, 16 h | 0.05 vol% NO, 0.05 vol% NH₃, 10 vol% O₂, 10 vol% H₂O, N₂ balance, GHSV 240,000 h⁻¹ | 225–550 (not shown), *225–500 (not shown) | 115 |
|      |        |                    |                     |                                                                                |     |
| **Impregnation** | |                      |                     |                                                                                |     |
| 68   | (1.5 wt%)Cu-SSZ-13 \((n(\text{Si})/n(\text{Al}) = 12.6)\) | Impregnation, calcination, 550 °C, 1 h, air | 0.02 vol% NO, 0.02 vol% NH₃, 10 vol% O₂, 3 vol% H₂O, N₂ balance, GHSV 60,000 h⁻¹ | 200–500 (not shown) | 69 |
| 69   | (1.5 wt%)Cu-SSZ-13 \((n(\text{Si})/n(\text{Al}) = 11.5)\) | Impregnation, calcination, 550 °C, 1 h, air; *hydrothermal treatment: 10 vol% H₂O, air balance, 900 °C, 4 h, **8 h | 0.02 vol% NO, 0.02 vol% NH₃, 10 vol% O₂, 3 vol% H₂O, N₂ balance, GHSV 60,000 h⁻¹ | 200–500 (not shown), *200–500 (not shown), **200–500 (not shown) | 116 |
| 70   | (2 wt%)Cu-SSZ-13 \((n(\text{Si})/n(\text{Al}) = 11.4)\) monolith catalyst | Impregnation, calcination, 600 °C, 8 h; 750 °C, 2 h; air; degreening: 0.04 vol% NO, 0.04 vol% NH₃, 5 vol% H₂O, Ar balance, 250 °C, 1 h; 10 vol% O₂, 500 °C; pre-treatment: 10 vol% O₂, 5 vol% H₂O, Ar balance, 500 °C, 20 min | 0.04 vol% NO, 0.04 vol% NH₃, 10 vol% O₂, Ar balance; *0.04 vol% NO, 0.04 vol% NH₃, 10 vol% O₂, 5 vol% H₂O, Ar balance, GHSV 20,400 h⁻¹ | 250–500 (>3 ppm N₂O), *200–500 (<5 ppm N₂O) | 117 |
| 71   | (2.2 wt%)Cu-SSZ-13 \((n(\text{Si})/n(\text{Al}) = 12)\) | Impregnation, 550 °C, 5 h, air; degreening: 10 vol% H₂O, air balance, 650 °C, 4 h; *hydrothermal treatment: 10 vol% H₂O, air balance, 800 °C, 16 h | 0.036 vol% NO, 0.036 vol% NH₃, 14 vol% O₂, 2.5 vol% H₂O, N₂ balance, GHSV 100,000 h⁻¹ | 175–500 (not shown), *175–400 (not shown) | 118 |
One-pot hydrothermal method

Cu-containing SSZ-13 prepared by the one-pot hydrothermal method shows higher content and dispersion of copper species. Ren et al. designed a one-pot synthesis method for Cu-SSZ-13 (with a low \( n(Si)/n(Al) \) ratio of 4) using low-cost copper-tetraethylenepentamine (Cu-TEPA) as a template. The catalyst exhibited superior catalytic activity with more than 80% NO conversion at 150–400 °C. In addition, Martínez-Franco et al. used Cu-TEPA and \( N,N,N,N' \)-trimethyl-1-adamantamonium (TMAdaOH) in one-pot prepared Cu-SSZ-13 with \( n(Si)/n(Al) \) of 14.2 and Cu loading of \( n(Cu)/n(Si + Al) = 0.059 \), i.e., controlled ratios and a Cu loading. Furthermore, in another study, a \( n(Si)/n(Al) \) ratio of 15 was reported to guarantee enhanced NO conversion among \( n(Si)/n(Al) \) ratios of 6, 15 and 30. In other studies, the authors mentioned \( n(Si)/n(Al) \) of 13.26 (among 6.54–33.12) or 13 (among 10.6, 13.0 and 16.0) for Cu-SSZ-13 prepared via the one-pot hydrothermal method, and investigated its activity for the NH\(_3\)-SCR-DeNO\(_x\).

One of the main drawbacks of the one-pot hydrothermal method appears to be a high loading of copper species (i.e., 6.31–11.27 wt% of Cu) as the result of a large amount of metal ions in the corresponding structure-directing agent (Table 1, pos. 57–62). Unfortunately, these copper ions cannot be completely removed, even after an ion-exchange (i.e., reverse ion-exchange) of Cu-SSZ-13 with an aqueous solution of 1 M NH\(_4\)NO\(_3\) for several times, limiting its control. Following these studies, the synthesis was further optimized by decreasing the amount of template required and changing some post-treatment steps (e.g., with dilute HNO\(_3\) solution or with HNO\(_3\) followed by NH\(_4\)NO\(_3\) solution) or even via the introduction of a second transition metal. As a result, materials with a significantly lower amount of copper species (e.g., <3.9 wt%) were achieved, thus, enhancing its activity in NH\(_3\)-SCR-DeNO\(_x\) (Fig. 2c). For example, Liu et al. reported an effective strategy to regulate the nature and distribution of Cu species of a one-pot synthesized Cu-SSZ-13 zeolite via ion-exchange with an aqueous 0.1 M HNO\(_3\) solution (for 4, 8, 12 and 16 h) before removing the template. An optimum time of 4 h guarantees enlarged specific surface area, pore volume, \( n(Si)/n(Al) \) ratio and isolated Cu\(^{2+}\) content, and thus enhanced activity and N\(_2\) selectivity over Cu-SSZ-13.

Solid-state ion-exchange

Relatively limited studies – compared to Cu-SAPO-34, were conducted on Cu-containing SSZ-13 prepared via solid-state ion-exchange (SSIE, Table 1, pos. 63–67). However, it has been reported that SSIE can be carried out either via the physical mixture of CuO and H-SSZ-13 at 700–800 °C (reduction of Cu\(^{2+}\) in CuO to Cu\(^+\)/Cu\(^0\), and reoxidation at the ion-exchange sites of the zeolites) or ammonia-assisted SSIE (below 350 °C, formation of the \([\text{Cu}(\text{NH}_3)_x]^+\) complex via the interaction of Cu\(_2\)O(111) with H– or NH\(_3\)-SSZ-13). In the first approach, framework deteriorations and inadequately reacted CuO was inevitable, while in the second approach the application of ammonia may limit the commercialization of the NH\(_3\)-assisted
SSIE. Moreover, the modification of HT-SSIE (e.g., after 150–500 °C NH3-SCR-DeNOx) due to movement of external CuO to Cu/SSZ-13 pores during hydrothermal treatments. Thus, it can be inserted back into the framework during cooldown (i.e., reversible dealumination) to maintain the integrity of the zeolite structure. The aluminum sites can be protected by adjusting the n(Si)/n(Al) ratio accordingly, thus accommodating the highly hydrothermally stable Cu2+-2Z sites. The Cu-SSZ-13 catalysts (n(Si)/n(Al) = 6–11, <3 wt%) are reported to be resistant to hydrothermal aging with 10 vol% H2O at 800 °C for 16 h (i.e., comparable to the exposure of a 135 000-mile vehicle-aged catalyst30,31,32), which is influenced by the copper species loading (Fig. 3b).33 A high copper loading is attributed to the abundance of [CuOH]−Z sites that tend to gradually transform to Cu2+, upon hydrothermal aging, which further destabilizes the zeolite framework. However, the onset of zeolite-framework occurs above 800–900 °C.32,33 During the hydrothermal aging (>700 °C) of Cu-SSZ-13, [Cu(OH)]−Z (rather than Cu2+-2Z) convert to CuO clusters via [Cu(OH)2]−Z → Cu(OH)− → CuO sequence, where [Cu(OH)2]− is first hydrolyzed to Cu(OH)2, and then the latter agglomerates to form CuO clusters. Furthermore, CuO can interact with Al species without the formation of defined structures. CuO clusters lower NH3-SCR-DeNOx selectivity by catalyzing the NH3 oxidation side reactions, as well as actively promoting the degradation of SSZ-13 during aging. It was observed that hydrothermal aging at 800 °C for 16 h led to a significant increase in mesopores ≤ 4 nm, which is believed to result from increased CuO formation.34,37,38 The hydrothermal treatment causes the zeolite structure to contract in the d direction which then leads to the collapse of the 4MRs.39 Despite this, some of the isolated copper species are still protected in the larger rings. Prodinger et al.40 reported higher hydrothermal stability over submicron Cu/SSZ-13 compared to Cu/SSZ-13 with particle sizes 10 times bigger.

**Co-cation modification**

The introduction of second metal ions into the Cu-containing SSZ-13 catalyst is a facile way to improve its hydrothermal stability. Sodium is a common element found in Cu-SSZ-13 as a result of a strong basic environment provided by NaOH during SSZ-13 synthesis and incomplete exchange between Na-SSZ-13 and NH4NO3 solutions (before Cu-exchange). For example, Gao et al.47 demonstrated that the presence of certain amounts of Na+ (1.7 wt%) or Li+ (0.40 wt%) enhanced the hydrothermal stability of low-Cu loaded (0.87 wt%) Cu-SSZ-13 (n(Si)/n(Al) = 6). Further studies confirmed an optimal loading of 1–1.5 wt% of Na+ in the materials with preserved NOx activity (Fig. 4a).48 The optimized Al-rich (2.7 wt%Cu–(1.7 wt%)Na-SSZ-13 (n(Si)/n(Al) = 4) catalyst exhibits >80% NO conversion between 200–650 °C in NH3-SCR-DeNOx after hydrothermal aging at 750 °C.49 The Na+ cations were reported to compete with Cu ions for catalytic

**Hydrothermal stability and poisoning**

NH3-SCR-DeNOx catalysts used in diesel vehicles operate under high temperature and humid conditions alongside poisons derived from biodiesel and lubricant oil additives. The activity and stability of respective Cu-containing SSZ-13 vary in NH3-SCR-DeNOx depending on the applied hydrothermal aging treatment (Table 1). Both the dealumination of the Cu-containing SSZ-13 catalysts, as well as the transformation of ZCuOH sites to Z2Cu, coupled with the consumption of Bronsted acid sites, were reported during the rather mild hydrothermal aging treatment ≤ 700 °C (ZCuOH + ZH → Z2Cu + H2O).25,73,81,123 confirmed via DFT calculations;35 promoted by other transition metals44,99). Water molecules tend to attack the aluminum sites (e.g., Bronsted acid sites, –Si(OH)−Al–), which causes dealumination and consequently structural amorphization (decomposed to SiO2 and Al(OH)3).37,124,125 Al(OH)3 possesses a kinetic diameter of 0.503 nm, which means that it cannot escape from the SSZ-13 pores during hydrothermal treatments. Thus, it can be inserted back into the framework during cooldown (i.e., reversible dealumination) to maintain the integrity of the zeolite structure. The aluminum sites can be protected by adjusting the n(Si)/n(Al) ratio accordingly, thus accommodating the highly hydrothermally stable Cu2+-2Z sites. The Cu-SSZ-13 catalysts (n(Si)/n(Al) = 6–11, <3 wt%) are reported to be resistant to hydrothermal aging with 10 vol% H2O at 800 °C for 16 h (i.e., comparable to the exposure of a 135 000-mile vehicle-aged catalyst30,31,32), which is influenced by the copper species loading (Fig. 3b).33 A high copper loading is attributed to the abundance of [CuOH]−Z sites that tend to gradually transform to Cu2+, upon hydrothermal aging, which further destabilizes the zeolite framework. However, the onset of zeolite-framework occurs above 800–900 °C.32,33 During the hydrothermal aging (>700 °C) of Cu-SSZ-13, [Cu(OH)]−Z (rather than Cu2+-2Z) convert to CuO clusters via [Cu(OH)2]−Z → Cu(OH)− → CuO sequence, where [Cu(OH)2]− is first hydrolyzed to Cu(OH)2, and then the latter agglomerates to form CuO clusters.41,127,128 Furthermore, CuO can interact with Al species without the formation of defined structures. CuO clusters lower NH3-SCR-DeNOx selectivity by catalyzing the NH3 oxidation side reactions, as well as actively promoting the degradation of SSZ-13 during aging. It was observed that hydrothermal aging at 800 °C for 16 h led to a significant increase in mesopores ≤ 4 nm, which is believed to result from increased CuO formation.40,48,127 The hydrothermal treatment causes the zeolite structure to contract in the d direction which then leads to the collapse of the 4MRs.39 Despite this, some of the isolated copper species are still protected in the larger rings. Prodinger et al.40 reported higher hydrothermal stability over submicron Cu/SSZ-13 compared to Cu/SSZ-13 with particle sizes 10 times bigger.

**Co-cation modification**

The introduction of second metal ions into the Cu-containing SSZ-13 catalyst is a facile way to improve its hydrothermal stability. Sodium is a common element found in Cu-SSZ-13 as a result of a strong basic environment provided by NaOH during SSZ-13 synthesis and incomplete exchange between Na-SSZ-13 and NH4NO3 solutions (before Cu-exchange). For example, Gao et al.47 demonstrated that the presence of certain amounts of Na+ (1.7 wt%) or Li+ (0.40 wt%) enhanced the hydrothermal stability of low-Cu loaded (0.87 wt%) Cu-SSZ-13 (n(Si)/n(Al) = 6). Further studies confirmed an optimal loading of 1–1.5 wt% of Na+ in the materials with preserved NOx activity (Fig. 4a).48 The optimized Al-rich (2.7 wt%Cu–(1.7 wt%)Na-SSZ-13 (n(Si)/n(Al) = 4) catalyst exhibits >80% NO conversion between 200–650 °C in NH3-SCR-DeNOx after hydrothermal aging at 750 °C.49 The Na+ cations were reported to compete with Cu ions for catalytic
exchange sites and provide NH₃ adsorption function as Lewis acids, as well as neutralize Brønsted acid sites (–Si(Oh)–Al; thus preventing dealumination during hydrothermal aging). The K⁺ cations show effects similar to those of Na⁺ and the optimal low-temperature activity for Cu, K-SSZ-13 is also found at n(K)/n(Cu) = 0.7. Cu²⁺ ions occupy windows of 6MRs and co-cations occupy windows of 8MRs. Furthermore, the hydrothermal stability of (3.4–4.1 wt%)Cu-SSZ-13 was remarkably enhanced through loading with a small amount of cerium (i.e., ca. 0.2–0.4 wt%, optimum ca. 0.35 wt%). This can be achieved either via ion-exchange or solid-state ion-exchange. Cerium ions can serve as an oxygen reservoir that can store and release oxygen via the redox shift between Ce⁴⁺ and Ce³⁺ under oxidizing and reducing conditions, which presumably stabilize the zeolite framework. Also, Ce³⁺ ions tend to fill defect sites of zeolites, where they attract water molecules, reducing the probability of them attacking the aluminum sites. Other cations, like Ca²⁺, are detrimental at any loading, according to the order of poisoning effect: Mg > Ca > Na > K. The hydrothermal stability of Cu-SSZ-13 can be further improved via its modification with Fe⁴⁺, Y¹⁺, Sm³⁺, or Zn,⁶⁹ as well as by the passivation of its surface with Al₂O₃ at ⁶⁷ or ZrO₂.⁷⁸ Furthermore, the hydrothermal stability of the composite samples, e.g., Cu-SSZ-13 + Fe-SSZ-13,⁷⁹ H-SAPO-34, Cu-SSZ-13,⁸⁶ Cu-SSZ-13 and Cu-SAPO-34,⁸⁵,¹³⁸ was significantly improved compared to that of the single Cu-SSZ-13.

**Sulfur poisoning**

Thus, in addition to their excellent catalytic activity, hydrothermal stability and high resistance against chemical poisons are also highly required properties for these catalysts. As it also happens with hydrothermal stability, [Cu(OH)]²⁻-Z is more susceptible (than Cu⁴⁺-Z) to SO₂ poisoning (coming from the burning of sulfuric species in fuel). Sulfur species adsorb on the ZCuOH sites (in the presence and absence of NH₃), and exist in bisulfite form (ZCuOH + SO₂ → ZCuHSO₄). Moreover, ammonium sulfate ([NH₄]₂SO₄) blocks the ZCu sites along with Cu sulfate species – CuHSO₄ (in the presence of NH₃ and SO₃) and Cu sulfate (in the presence of only SO₃ in the feed). The lower mobility of sulfated Cu species compared to non-sulfated Cu species led to a drop in catalytic activity.⁶⁹ Ammonium sulfate can be removed at 350 °C,¹⁰⁸,¹³⁹ while in the case of other species temperatures higher than 550 °C were needed (i.e., can be removed via regeneration of the diesel particle filter).¹³⁷,¹⁴⁰ Non-decomposed sulfate species block the pore of Cu-SSZ-13, thus decreasing its catalytic activity. However, many researchers showed that NO₂ conversion can reach its original level after the removal of SO₃ and/or H₂O from the feed gas, i.e., reversible inactivation.⁶³,⁶⁴ A combination of other metals (e.g., Zn,¹⁴¹ Ce,¹⁴²–¹⁴⁴ Fe,¹⁴³,¹⁴⁵,¹⁴⁶ etc.) with Cu-containing SSZ-13 can adequately protect active sites from sulfur poisoning. Furthermore, Cu-SSZ-13 becomes more robust against sulfur as a result of hydrothermal aging.⁶⁶

**Phosphorus poisoning**

Besides poisoning by sulfur-containing species, Cu-containing SSZ-13 is also affected by phosphorus and zinc (coming from engine lubricating oil, e.g., zinc dialkyldithiophosphate (ZDDP) as an additive), alkali and alkaline earth metals (e.g., Na, K, Ca, and Mg, coming from engine lubricating oil), noble metals (coming from the upper stream emission abatement components, e.g., diesel oxidation catalysts (DOC), etc.).¹⁴⁷–¹⁴⁹ Lezcano-Gonzalez et al.¹⁴⁶ gave an overview of the key deactivation mechanism observed for Ca, Zn, (1–2 wt%) Pt and P. Doping of Cu-SSZ-13 with P (2.2 wt%) fully suppressed the catalytic activity as a result of site blocking of the zeolite framework, CuO formation coupled with the reduction in the number of isolated Cu²⁺ ions, between other phenomena. In other studies, the catalyst’s activity with higher P loading of 0.4–1.0 wt%, was significantly lower than that without P between 100 to 300 °C.⁹⁶ The N₂ selectivity was not affected by phosphorus at low temperatures. However, the introduction of Ca and Zn (1.3–5.4 and 2.2–8.8 wt%, respectively) led mainly to pore-blocking/filling together with the formation of CuO species. It has been widely reported that Pt species promote N₂O and NO₂ formation.¹⁰⁷,¹⁵⁰,¹⁵¹ Regarding the P-poisoning studies, Dahlin et al.² investigated the activity of Cu-SSZ-13 exposed to exhaust generated by a biodiesel burner. Cu-SSZ-13 was deactivated at low temperatures, and could not be regenerated until temperatures up to 550 °C when the phosphorous content in the catalysts was above 0.1 wt%. As the main approaches for introducing P into Cu-containing SSZ-13, impregnation with H₃PO₄, (NH₄)₂HPO₄,¹⁰⁵,¹⁰⁸,¹¹⁰ or synthesis of SSZ-13 by using trimethyladamantylaminium hydroxide (TMAdaOH) and tetramethylphosphonium hydroxide (TEPOH) as dual-template agents¹¹⁶,¹⁵² are reported. Further studies on the influence of phosphorus on the catalytic properties of Cu-SSZ-13 for NH₃-SCR-DeNOₓ can be found in ref. 95, 108, 153 and 154. Several researchers suggest that phosphorus tends to poison ZCuOH more easily than Z₃Cu.⁹⁶,¹⁵³ To regenerate the P-poisoned Cu-SSZ-13 catalysts, phosphorous species in the catalysts should be removed. As an example of that approach, Chen et al.⁷¹ successfully applied the combination of washing with hot water (90 °C) and hydrothermal treatment (800 °C for 12 h) to recover the activity of the phosphorous-poisoned Cu-SSZ-13.

**Hydrocarbons poisoning**

The other aspect associated with the application of NH₃-SCR-DeNOₓ is poisoning by hydrocarbons (HCs). The limited DOC activity leads to HCs slipping over the SCR component, which negatively affects its NO₂ reduction activity. Therefore, few works regarding the HCs poisoning (carbonaceous deposit, including formed aliphatic compounds: acrolein, acetate and aceton, and aromatic compounds: hydrogen-deficient) effect on Cu-SSZ-13 were reported mainly over C₃H₆ (a representative low-chain HC in the exhaust).⁷⁶,⁹⁴ For example, Ma et al.⁷⁶ found that Cu-SSZ-13 deactivated in the presence of C₃H₆ due to the competitive adsorption of NH₃ and C₃H₆ on the catalysts as well as blockage of coke in the pore channels. In the case of the aged materials, Wang et al.⁷⁴ found that Cu-SSZ-13 (aged at 700 °C) displayed a more severe NO₂ conversion decline than the fresh sample in the presence of C₃H₆. On the other hand, Zhao et al.⁹⁷ found that less carbonaceous deposit forms in the
hydrothermally aged samples of Cu-SSZ-13 (due to the lower content of Brønsted acid sites). The presence of aromatic compounds increases with higher HTA temperatures (700, 750, and 800 °C) due to a greater generation of mesopores. Based on these studies, aged Cu-SSZ-13 can prevent the deactivation of Cu-containing SSZ-13 due to HCs poisoning, and thus, maintain its NO activity and stability. Other approaches like hybrid catalysts (e.g., Cu-SSZ-13 with CeO₂–SnO₂)⁵⁸ were also reported.

**Reaction mechanisms**

\[ \text{NH}_3\text{-SCR-DeNO}_x \left( 4\text{NH}_3 + 4\text{NO} + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} \right) \] over Cu-containing SSZ-13 can proceed through the adsorption stage of NH₃ and/or NO, according to the Eley–Rideal (E–R; i.e., the gaseous NO reacts with pre-adsorbed NH₃ to produce N₂ and H₂O) and/or Langmuir–Hinshelwood (L–H; both the adsorbed NO and NH₃ simultaneously participate in the reaction) mechanisms.¹³,²⁵,¹⁵⁶ For example, the L–H mechanism was...
proposed over calcined Cu-SSZ-13, while the E-R mechanism was proposed over its aged form (based on in situ DRIFTS analysis). The amount of surface CuO species increased after hydrothermal aging treatment, while the Lewis sites and Bronsted sites (i.e., surface nitrates adsorbed sites and NH3 capacity) decreased, thus, limiting the formation of intermediate products NH3NO3/NH4NO2 (below 350 °C) or NO2−/NH4+ (above 350 °C), which in turn led to the loss of NH3-SCR-DeNOx activity34 (Fig. 5a).

Specifically, NH3-SCR-DeNOx on Cu-SSZ-13 follows a redox reaction mechanism, consisting of a reduction half-cycle (RHC; Cu2+ ↔ Cu+) and an oxidation half-cycle (OHC; Cu+ ↔ Cu2+). The detailed reaction mechanism is still under debate, indicating the complexity of both RHC and OHC.117

Reduction half-cycle

When NH3 is present in the feed, solvation of Z2Cu with NH3 is preferred rather than with H2O,158-160 leading to the formation of Cu-amine coordination complexes, i.e., the principal active sites in the redox cycle.24,161 The NH3 solvation of ZCuOH sites (or [Cu2Z2O4]+ in their O2 activated form162) may lead to the formation of dimeric or two-proximate Cu-amine complexes (i.e., [CuI(1)(OH)(NH3)3]+ units).163 NH3-solvated Z2Cu sites can hydrolyze to NH3-solvated ZCuOH sites in the presence of H2O.164 Furthermore, the complexes containing a mixture of NH3 and NO, i.e., [CuI(1)(OH)(NH3)2−1(NO)], were evidenced for the first time by the application of rapid-scan FT-IR spectroscopy and two-dimensional correlation spectroscopy (2D COS) analysis.165 These solvated Cu moieties were suggested to be active sites in low-temperature NH3-SCR-DeNOx (<250 °C).159,164 The neighboring NH3 and NO ligands rearrange to create N–N bonds via the formation of nitrosamide (NH3NO) or ammonium nitrite (NH4NO2) intermediates.31,165 Subsequently, NH3NO and NH4NO2 decompose into N2 and H2O to complete the reduction part of the NH3-SCR-DeNOx. As an alternative mechanism, Chen et al.164,166 proposed the formation of Cu(H2NNO)2+ and Cu(OHNO)2+ intermediates that decompose over neighboring Bronsted acid sites to complete the catalytic cycle. The formation of the HONO intermediates was reported also by Usberti et al.,168 who found that activated NO reacted with the NH3 adsorbed on the Lewis sites (verified also by DFT calculations). This mechanism consists of two sequential NO oxidative activation processes, consisting of NO oxidative activation to HONO catalyzed by [CuI(1)(OH)(NH3)3]+, HNO reacting with one NH3 ligand to NH3NO2, and NH3NO2 decomposition to N2 and H2O164 (eqn (1)-(6)).

\[
\text{NO + [CuI(OH)(NH3)3] → HONO + CuI(NH3)2 + CuI(OH)(NH3)3; structure A, Fig. 5b}
\]

(1)

\[
\text{HONO + CuI(NH3)2 → CuI(NH3)2 + NH4NO2}
\]

(2)

\[
\text{NH4NO2 → N2 + 2H2O}
\]

(3)

\[
\text{NO + CuI(OH)(NH3)3 → HONO + CuI(NH3)3; structure E, Fig. 5b}
\]

(4)

\[
\text{HONO + CuI(NH3)3 → CuI(NH3)2 + NH4NO2}
\]

(5)

\[
\text{NH4NO2 → N2 + 2H2O}
\]

(6)

Summing up the above steps results in a global reaction (eqn (7)):

\[
2\text{NO} + [\text{CuII(OH)(NH3)3}]_{\text{2}} → 2\text{CuI(NH3)2 + 2N2 + 4H2O}
\]

(7)

Thus, Hu et al.169 and Gramigni et al.168 proved (based on kinetic experimental and DFT calculations) a second-order dependence, suggesting that binuclear reactions between two Cu species could occur during RHC.

The decomposition of NH3NO3 (NH4NO2 can be oxidized into NH3NO4) allows also the side reaction leading to undesired N2O (<300 °C).19 On the other hand, Feng et al.170 claimed that the formation of N2O resulted from the H2NNO decomposition over Cu–OOH–Cu complexes, which explains the enhanced N2O formation with increasing Cu loading. This was further supported by the studies of Xi et al.,79 who claimed that N2O formation occur over Cu-oxo species, such as [CuO–Cu]2+. However, N2O formation has also been reported to mainly occur over [Cu(OH)2]+ located in CHA cages.89,171,172 The high-temperature N2O production (>300 °C), on the other hand, takes place because of unselective ammonia oxidation. The N2O production profiles of the different types of SCR catalysts differ considerably.117

Below 250 °C, a linear SCR rate versus (Cu loading)2 correlation was reported, suggesting that the reaction limiting step involves the participation of two Cu ions.24,164 The activation energy for NH3-SCR-DeNOx over Cu-containing SSZ-13 varies in the range of 32,166 40–41 kJ mol⁻¹ to 54,174 43–57 kJ mol⁻¹,166 also depending on the temperature, i.e., 175–250 °C – 130 kJ mol⁻¹, and 250–300 °C – 60 kJ mol⁻¹.21 Thus, at temperatures above 350 °C, the active sites of Cu-SSZ-13 change from mobile Cu ions coordinated by NH3 into immobilized Cu ions, thus, giving a seagull profile for NO conversion (based on the Gao et al.22 assumptions). Fahami et al.23 attributed the activity decrease at around 350 °C to a more localized structure of monos(oxo) dicopper complexes. At high temperatures (above 350 °C), the activity has instead been measured to have a first-order dependence on copper loading, indicating that the reaction can proceed with other possible Cu sites.24

Oxidation half-cycle

The [Cu(NH3)2]+ complexes become the intermediate starting the oxidation half-cycle. The two [Cu(NH3)2]+ intermediates and an oxygen molecule then combine to form [Cu(NH3)3]−−O2− [Cu(NH3)3]− intermediates (2[Cu(NH3)2]+ + O2 → [Cu(NH3)2]+ − O2−[Cu(NH3)3]−).51,161,175 The mobility of the Cu ions (i.e., one [Cu(NH3)2]+ must migrate to the vicinity of another; enhanced in the presence of H2O176-178) guarantees the formation of these dimeric Cu species,90,166 thus improving the NH3-SCR-DeNOx activity. The 1Al–Cu species (located at isolated single Al sites, i.e., ZCuOH) can form dimeric Cu intermediates more easily than the 2Al–Cu (located at two adjacent Al sites, i.e., Z2Cu).179,180 The ratio of n(1Al–Cu)/n(2Al–Cu) can be controlled through the catalyst’s hydrothermal aging.90 Krishna et al.181 suggested their
| Sample | Preparation method | Reaction conditions | Operation temperature for achieving 100% NH₃ conversion/°C ([by-product formation]) | Ref. |
|--------|-------------------|---------------------|-----------------------------------------------|-----|
| 1      | (2.4 wt%)Cu-SSZ-13 (n(Si)/n(Al) = 15) monolith catalyst | Commercial; degreening: 10 vol% O₂, 7 vol% H₂O, 8 vol% CO₂, Ar balance, 550 °C, 4 h | 0.02 vol% NH₃, 5 vol% O₂, 5 vol% H₂O, Ar balance, GHSV 40,000 h⁻¹ | 400–450 (not shown) | 72 |
| 2      | Cu-SSZ-13 (Cu loading, n(Si)/n(Al) not shown) monolith catalyst | Commercial; degreening: 10 vol% O₂, 7 vol% H₂O, 8 vol% CO₂, N₂ balance, 550–600 °C, 4 h | 0.02 vol% NH₃, 5 vol% O₂, 3 vol% H₂O, N₂ balance, GHSV 120,000 h⁻¹ | 500–600 (<20 ppm N₂O) | 73 |
| 3      | (2.7 wt%)Cu-SSZ-13 (n(Si)/n(Al) = 12) | Commercial; degreening: 10 vol% H₂O, air balance, 650 °C, 12 h; pre-treatment: 21 vol% O₂, N₂ balance, 600 °C, 20 min | 0.05 vol% NH₃, 5 vol% O₂, 3 vol% H₂O, N₂ balance, GHSV 120,000 h⁻¹ | 500–600 (<20 ppm N₂O) | 73 |
| 4      | Cu-SSZ-13 (n(Si)/n(Al) = 6) (Cu content not shown) | Ion-exchange, calcination, 500 °C, 2 h; air; *hydrothermal treatment: 10 vol% H₂O, air balance, 800 °C, 16 h | 0.035 vol% NH₃, 14 vol% O₂, 2 vol% H₂O, N₂ balance, GHSV 30,000 h⁻¹ | 500–550 (not shown) | 11 |
| 5      | (0.88 wt%)Cu-SSZ-13 (n(Si)/n(Al) = 25) | Ion-exchange, calcination, 550 °C, 4 h, air; *hydrothermal treatment: 10 vol% H₂O, air balance, 800 °C, 16 h | 0.05 vol% NH₃, 5 vol% O₂, N₂ balance, GHSV 400,000 h⁻¹ | 500–600 (not shown) | 85 |
| 6      | (2.1 wt%)Cu-SSZ-13 (n(Si)/n(Al) = 12) | Ion-exchange, calcination conditions not shown; *hydrothermal treatment: 10 vol% H₂O, air balance, 550 °C, 16 h | 0.036 vol% NH₃, 14 vol% O₂, 2.5 vol% H₂O, N₂ balance, GHSV 200,000 h⁻¹ | 500–500 (not shown), *500–550 (not shown) | 91 |
| 7      | (2.35 wt%)Cu-SSZ-13 (n(Si)/n(Al) = 12.93) | Ion-exchange, calcination, 550 °C, 4 h, air; pre-treatment: 8 vol% O₂, N₂ balance, 1 h, 500 °C | 0.05 vol% NH₃, 6.5 vol% O₂, 3 vol% H₂O, N₂ balance, GHSV 120,000 h⁻¹ | 350–500 (not shown) | 96 |
| 8      | (1.88–2.16 wt%)Cu-SSZ-13 (n(Si)/n(Al) = 16.5–20.3) | Ion-exchange, calcination, 550 °C, 5 h, air; *hydrothermal treatment: 10 vol% H₂O, air balance, 750 °C, 16 h; pre-treatment: 21 vol% O₂, N₂ balance, GHSV 400,000 h⁻¹ | 0.05 vol% NH₃, 3 vol% O₂, 3 vol% H₂O, N₂ balance, GHSV 120,000 h⁻¹ | 400–550 (<10 ppm NO), *500–550 (<20 ppm NO) | 87 |
| 9      | (4 wt%)Cu-SSZ-13 (n(Si)/n(Al) = 11) | Ion-exchange, calcination conditions not shown; degreening: Reaction conditions, 600 °C, 4 h; pre-treatment: 10 vol% O₂, 7 vol% H₂O, N₂ balance, 600 °C, 1 h | 0.035 vol% NH₃, 10 vol% O₂, 7 vol% H₂O, N₂ balance, GHSV 300,000 h⁻¹ | 400–550 (<120 ppm NO₂) | 89 |
| 10     | (4.5–5 wt%)SSZ-13 (n(Si)/n(Al) = 9) | Ion-exchange, calcination, 550 °C, 5 h, air; *hydrothermal treatment: 10 vol% H₂O, air balance, 800 °C, 16 h; **degreening: 10 vol% H₂O, air balance, 700 °C, 4 h | 0.038 vol% NH₃, 14 vol% O₂, N₂ balance, GHSV 100,000 h⁻¹ | *450–550 (not shown), **400–550 (not shown) | 88 |
| 11     | (4.76 wt%)Cu-SSZ-13 (n(Si)/n(Al) = 4.97) | Ion-exchange, vacuum evaporator, calcination, 550 °C, 6 h, air | 0.1 vol% NH₃, 6 vol% O₂, He balance, GHSV 300,000 h⁻¹ | 400–550 (<3% NOₓ, N₂O yield) | 195 |
**Selective ammonia oxidation (NH$_3$-SCO)**

To achieve the desired NO$_x$ conversion, a stoichiometric or even an excess quantity of NH$_3$ is required, which can result in unreacted NH$_3$ (also known as NH$_3$ slip). Thus, oxidation catalysts (ASC, guard catalysts, AMOX) are usually employed to selectively oxidize the unreacted NH$_3$ (from NH$_3$-SCR-DeNO$_x$) into nitrogen and water vapor. Some researchers investigate NH$_3$-SCO (4NH$_3$ + 3O$_2$ → 2N$_2$ + 6H$_2$O) as a side process of the NH$_3$-SCR-DeNO$_x$ while, there are not many publications dedicated separately to the ammonia oxidation over Cu-containing zeolites. Similar to NH$_3$-SCR-DeNO$_x$, NH$_3$-SCO is enhanced over Cu-containing catalysts, including zeolite-based catalysts (e.g., Cu-ZSM-5, Cu-Y, Cu-Beta, etc.). The aggregated CuO species lead to higher NH$_3$ oxidation, thus, across investigated catalytic systems, mainly 10 wt% of Cu loading was found as the optimal. Progress on selective catalytic ammonia oxidation over Cu-containing zeolite-based catalysts was already published by Jablonska in 2020. Furthermore, NH$_3$-SCO over different catalysts, including proposed reaction mechanisms were reviewed. Thus, in this chapter, there is a focus on the Cu-containing SSZ-13 based-catalysts prepared via different techniques i.e., containing different amounts of Cu species.
Table 2 lists representative results of NH$_3$-SCO over Cu-containing SSZ-13 reported in the literature. For example, Gao et al.\textsuperscript{32} found that NH$_3$ conversion increases with higher Cu loading (exchange level 23–90%), which possibly arises from the weaker interactions between Cu$^{2+}$ ions and the SSZ-13 framework (i.e., more facile Cu$^{2+}$ ↔ Cu$^{+}$ redox-cycling) or higher amount of Cu$^{2+}$ ions placed closer to the pore openings (being more accessible to reactants). Similar to the NH$_3$-SCR-DeNO$_x$, the authors observed the seagull profile of NH$_3$ conversion, which was later also approved by Olsson et al.\textsuperscript{191,192} These two regimes, below and above 250 °C (400 °C in ref. 191) with different values of activation energy over Cu-SSZ-13 were attributed to the change in the catalytic centers resulting in a different activity. Cui et al.\textsuperscript{88} reported a higher activity for Cu/SSZ-13 with increasing Cu loading up to 5 wt% (Fig. 6a). After hydrothermal aging (at 800 °C for 16 h) the full NH$_3$ conversion is shifted about 50 °C higher (Table 2, pos. 10). In another example, NH$_3$ oxidation activity decreases with increasing HTA temperature (550–900 °C). The activity decrease was assigned to the loss of active isolated Cu$^{2+}$ species (active below 400 °C) during aging, and a decrease in NH$_3$ storage capacity.\textsuperscript{91} Both Cu$^{2+}$ ions and CuO coexist in Cu/SSZ-13 (n(Si)/n(Al) = 16–24) prepared by impregnation.\textsuperscript{193} Enhanced activity over Cu/SSZ-13 with n(Si)/n(Al) = 20 (activation energy of 68 kJ mol$^{-1}$) resulted from the highest content of CuO species and acid sites (Fig. 6b). Contrary to that, Han et al.\textsuperscript{80} reported no significant changes for Cu-SSZ-13 with a n(Si)/n(Al) ratio of 5.5 (among 11, 21) in NH$_3$ conversion for the whole temperature range. However, the NOx conversion slightly increased from 10 to 20 ppm at 625 °C after hydrothermal aging at 800 °C. Based on the in situ DRIFTS, the authors claimed that NH$_3$-SCO over Cu/SSZ-13 follows the in situ/internal SCR (i-SCR) mechanism, consisting of two steps. In the first step, NH$_3$ was oxidized to NOx by surface CuO. Subsequently, NOx was reduced to N$_2$ and H$_2$O by unreacted NH$_3$ on isolated Cu$^{2+}$ sites (i.e., NH$_3$-SCR-DeNO$_x$).\textsuperscript{193} Thus, Cu-SSZ-13 revealed higher NH$_3$ oxidation than CuO/SSZ-13 (CuO mechanically mixed with SSZ-13).\textsuperscript{87} A similar conclusion about the reaction mechanism was given over Cu-SSZ-13 (prepared by one-pot hydrothermal synthesis) treated with dilute HNO$_3$ solution.\textsuperscript{186} The reaction mechanism was assigned based on the in situ DRIFTS studies, excluding the hydrazine mechanism (as the N$_2$H$_4$ species were not observed in the spectra). Details on the reaction mechanisms can be found elsewhere.\textsuperscript{188,189,194} The one-pot synthesized Cu-SSZ-13 treated with dilute HNO$_3$ possessed added Cu$^{2+}$ ions that accelerated low-temperature NH$_3$-SCR-DeNO$_x$ (second step of NH$_3$-SCO). Thus, enhanced activity and N$_2$ selectivity over this catalyst were reported (Fig. 6c) compared to non-modified zeolite-based catalysts. One-pot hydrothermally prepared Cu-SSZ-13 (n(Si)/n(Al) = 6.5–12.5, 1.8–3.5 wt% of Cu) did not show significant changes before and after the hydrothermal aging treatment (Table 2, pos. 12) in the whole temperature range.\textsuperscript{106} However, Luo et al.\textsuperscript{74} have shown

![Fig. 6](https://example.com/fig6.png)  
(a) NH$_3$ conversion over degreened Cu/H-SSZ-13. Reproduced from ref. 88 with permission from Elsevier, copyright 2020; (b) NH$_3$ conversion over Cu/SSZ-13 with different n(Si)/n(Al) ratios. Reproduced from ref. 193 with permission from Elsevier, copyright 2020; (c) NH$_3$ conversion over Cu-SSZ-13 post-modified with a solution of HNO$_3$. Reproduced from ref. 186 with permission from ACS Publications, copyright 2018; (d) NH$_3$ conversion over fresh and P-poisoned Cu-SSZ-13. Reproduced from ref. 96 with permission from ACS Publications, copyright 2021.
that NH₃ oxidation activity of commercial Cu-SSZ-13 (detail of composition or preparation not shown) decreases with increased temperature up to 800 °C. Cu-SSZ-13 – prepared via the solid-state ion-exchange method at 700–800 °C, did not reach full conversion. On the other hand, the enhanced activity of bifunctional catalysts was reported, with single examples given as mixed, dual-layer and hybrid layer designs composed of Pt/Al₂O₃ and Cu-SSZ-13, or Ru/Cu-SSZ-13. Similar to Cu-containing SSZ-13 applied in NH₃-SCR-DeNOₓ, also the catalysts applied in NH₃-SCO lost their activity after poisoning, e.g., with P²⁶⁻²⁹ (Fig. 6d). Catalyst activity decreased remarkably with P loading (0.26–1.21 wt%) and especially above 300 °C, because of the interaction between phosphorus with oligomeric CuO₂ especies inside the large cages. As these species are not active in NH₃-SCR-DeNOₓ, the effect is less pronounced, as reported before.²⁹⁵

Conclusions and perspectives

This review summarizes recent progress in the NH₃-SCR-DeNOₓ and the NH₃-SCO over Cu-containing SSZ-13 catalysts, concerning their preparation methods, hydrothermal stability and poisoning, as well as their reaction mechanisms. Various preparation methods have been applied to manipulate the nature and distribution of Cu species in the materials, with continuous efforts aiming at improving the (hydrothermal) stability of the Cu-CHA catalysts. Minimizing [Cu(OH)]²⁻sites, which are more susceptible to hydrothermal aging, sulfur or phosphorus poisoning than Cu²⁺-2Z, will be a challenging task in the following years. Determining the effect of (new) dopants on catalyst stability is a promising research direction. Furthermore, more work should be spent on the application of the degreening and treatment/poisoning strategies closely related to the industrial applications (i.e., degreening at 700 °C in 10 vol% O₂, 5 vol% of CO₂ and H₂O, followed by the aging at 800 °C for 50 h for diesel exhaust applications).²⁸⁰ Besides enhanced activity and stability, N₂ selectivity also indicates the commercialization of catalysts. Despite recent findings, an accurate and experimentally established standard NH₃-SCR-DeNOₓ reaction mechanisms at low temperatures including field aged materials is still missing. Thus, more detailed in situ and operando studies, transient kinetic investigations, as well as molecular-scale computational models, are required to further understand reaction mechanisms.

Furthermore, compared to NH₃-SCR-DeNOₓ, the studies of NH₃-SCO are rather scarce. Mainly, ammonia oxidation is considered as the side process of NH₃-SCR-DeNOₓ above 350–400 °C. The catalytic experiments have been conducted under conditions, which differ far from the ones existing in the diesel aftertreatment system, i.e., minor NH₃ slip (O₂ excess), presence of H₂O, CO₂ or SO₂, etc. Besides, key requirements comprehend high activity and N₂ selectivity up to 600–700 °C (in the cycle of diesel particulate filter regeneration) and stability under application-relevant reaction conditions. A limited amounts of studies focus on the investigation of the reaction mechanisms. Furthermore, there are no systematic studies on the development of bifunctional catalysts. As NH₃-SCO proceeds mainly according to the i-SCR mechanism (i.e., with NH₃-SCR-DeNOₓ as the second step), similar reaction paths can be potentially ascribed for a description of the activity of Cu-containing SSZ-13. Thus, more effort must be spent on studying NH₃-SCO reaction mechanisms in the future. Systematic studies (i.e., careful design, appropriate coupling techniques, etc.) should also cover bifunctional catalysts composed of Cu-containing SSZ-13 (NH₃-SCR-DeNOₓ function) and noble metal-based catalyst (NH₃ oxidation function). A collective understanding of reaction and deactivation mechanisms of both components allows for the design of high-performing NH₃-SCO catalysts with appropriate catalyst promotion strategies. Thus, the development of such hybrid catalysts (in monolith form) for diesel exhaust aftertreatment systems is a topic of interest.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

M. J. acknowledges a DFG Research Grant JA 2998/2-1 and support from Universität Leipzig for Open Access Publishing.

References

1. R. Chen, T. Zhang, Y. Guo, J. Wang, J. Wei and Q. Yu, Chem. Eng. J., 2021, 420, 127588–127631.
2. M. Jabłońska and L. Chmielarz, Zesz. Nauk., 2013, 7, 7–23.
3. T. Boningari and P. G. Smirniotis, Curr. Opin. Chem. Eng., 2016, 13, 133–141.
4. C. Rusznak, S. Jenkins, P. R. Mills, R. J. Sapsford, J. L. Devalia and R. J. Davies, Rev. Fr. d’Allergologie d’Immunologie Clin., 1998, 38, S80–S90.
5. X. Wang, Y. Xu, Z. Zhao, J. Liao, C. Chen and Q. Li, Fuel, 2021, 305, 121482–121501.
6. T. Andana, K. G. Rappé, F. Gao, J. Szanyi, X. Pereira-Hernandez and Y. Wang, Appl. Catal., B, 2021, 120054–120079.
7. Y. Zeng, K.-G. Haw, Y. Wang, S. Zhang, Z. Wang, Q. Zhong and S. Kawi, ChemCatChem, 2021, 13, 491–505.
8. M. Iwamoto, H. Furukawa, Y. Mine, F. Uemura, S. Mikuriya and S. Kagawa, J. Chem. Soc., Chem. Commun., 1986, 1272–1273.
9. A. Wang, Y. Chen, E. D. Walter, N. M. Washton, D. Mei, T. Varga, Y. Wang, J. Szanyi, Y. Wang, C. H. F. Peden and F. Gao, Nat. Commun., 2019, 10, 1–10.
10. Q. Ye, L. Wang and R. T. Yang, Appl. Catal., A, 2012, 427, 24–34.
11. J. H. Kwak, R. G. Tonkyn, D. H. Kim, J. Szanyi and C. H. F. Peden, J. Catal., 2010, 275, 187–190.
12. D. W. Pickel and R. F. Lobo, J. Phys. Chem. C, 2010, 114, 1633–1640.
13. C. Baerlocher, L. B. McCusker and D. H. Olson, Atlas of zeolite framework types, Elsevier, 2007, pp. 96–97.
