Cu-Zeolite Selective Catalytic Reduction Catalysts for NO_x Conversion
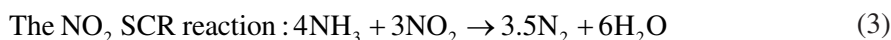
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1 Introduction

Selective catalytic reduction (SCR) of nitrogen oxides (NO_x) is an important technology to reduce environmentally harmful NO_x from exhaust gases, originating from mobile sources, such as cars and ships [1]. NO_x causes acid rain and is a major component in smog. The smog is usually found in big cities, where it is mainly produced by vehicles and power plants. This smog is highly toxic to humans. Forty percent of the total NO_x released into the atmosphere comes from road transport [2]. Newer catalyst formulations were needed because the old two-way exhaust catalysts, consisting of metals such as platinum, palladium, and rhodium supported on a metal oxide, did not meet the new emission standards, including EURO 5, or the 2010 US EPA standards for both light- and heavy-duty diesel trucks, especially on their capability to remove NO_x [3]. The SCR component is one of the catalysts in the typical exhaust emission catalytic system. The total system normally consists of a diesel oxidative catalyst (DOC), diesel particulate filter (DPF), and the NH_3-SCR system, an example of such system is schematically illustrated in Fig. 1.

In the NH_3-SCR reaction NO_x gases are reduced to N_2 and H_2O, by using NH_3 as a reducing agent. Depending on the operating conditions of the engine as well as of the exhaust system, different gas compositions are possible, which has an influence on how the NH_3-SCR reactions proceeds. The three most important reaction pathways of this process are [4]:

$$\text{The standard SCR reaction}: 4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O \tag{1}$$

$$\text{The fast SCR reaction}: 2NH_3 + NO + NO_2 \rightarrow 2N_2 + 3H_2O \tag{2}$$

$$\text{The } NO_2 \text{ SCR reaction}: 4NH_3 + 3NO_2 \rightarrow 3.5N_2 + 6H_2O \tag{3}$$

In the exhaust gases containing NO_x, NO is generally present, while only a small fraction of NO_2 is present. Therefore, reaction (1) is called the standard SCR reaction. The reaction of a 1 to 1 mixture of NO and NO_2 is a lot faster, and is therefore called the fast SCR
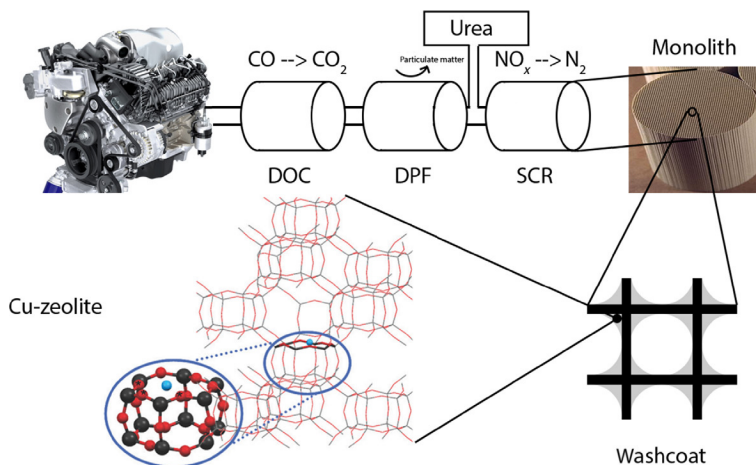
Fig. 1

Schematic of the exhaust catalyst catalytic system. The NH$_3$-SCR takes place in the selective catalytic reactor (SCR) catalyst component. The other components depicted are diesel oxidative catalyst (DOC), diesel particulate filter (DPF), urea, the source of NH$_3$. The active component, most commonly a Cu-exchanged zeolite, is placed as a wash coat on a ceramic monolith.

reaction (reaction (2)). If there is more NO$_2$ than NO present in the exhaust gases, the SCR reaction will be as in reaction (3) and only NO$_2$ will react [4]. Oxidation of NH$_3$ to NO or even NO$_2$ is possible, but Cu-ion exchanged zeolite catalysts are generally very selective for N$_2$ formation, in the right temperature window [4]. In this chapter we discuss briefly the different types of catalysts that are used for the NH$_3$-SCR reaction, with special emphasis on Cu-exchanged zeolites. We will discuss the differences in synthesis methods and their implications, as well as the location of Cu in the zeolite framework. Next we will put the focus on the differences between Cu-SAPO-34 and Cu-SSZ-13. After this we will move to the deactivation mechanisms for Cu-exchanged zeolites. For more details and background on both stationary and mobile catalysts we refer the interested reader to the book entitled *Urea-SCR Technology for deNOx After Treatment of Diesel Exhaust* [5]. For a more mechanistic view on Fe-exchanged zeolites and their role in NH$_3$-SCR we can recommend the review article by Brandenberger et al. [4].

2 Different Catalysts Used for NH$_3$-SCR

Different catalysts capable of performing the NH$_3$-SCR reaction are now being used [5]. For stationary applications, supported base metal catalysts, such as vanadium on titania, are used. However, for mobile applications, Cu- and Fe-exchanged zeolites are normally used, due to their good redox capacity. Zeolites are crystalline aluminosilicates consisting of repeating SiO$_4$ and AlO$_4$ tetrahedral subunits to form porous three-dimensional networks. The negative

charge, which is a result of Al^{3+} replacing Si^{4+} in the zeolite framework, results in giving zeolites both an acid functionality and an ion exchange capacity. Cu-zeolite materials are known to be highly active in the SCR of NO_x with NH_3 (NH_3-SCR) [5]. In this section, we will discuss why different catalysts are being used and which drawbacks they have.

An SCR catalyst needs to be hydrothermally stable, even at elevated temperatures up to 650°C, since the DPF needs to be generated at temperatures above 600°C periodically. Vanadium-based catalysts, which are commonly employed in stationary applications, such as power plants, however, are not stable at these elevated temperatures, while Cu- and Fe-zeolite-based SCR catalysts are much more stable [6]. This is not a problem for stationary operations, since the temperature doesn't reach these temperatures during stationary operations.

Fe-zeolite catalysts are very resistant to the high temperatures and show good SCR activity. The drawback of these catalysts is that they perform less at relatively low temperatures (200–300°C) as the Cu-zeolite catalysts, which are common exhaust operation conditions. This makes Cu-zeolite catalysts the preferred catalyst for mobile diesel NO_x removal [7].

To show the difference in level of activity after aging, Ford Motor Company performed research in which they compared Fe- and Cu-exchanged zeolites as well as a vanadium-supported titania catalyst, normally used in stationary applications [8,9]. After aging for 64 h at 670°C to represent ~120 k miles on a diesel vehicle with a regenerating DPF, they concluded that the vanadium-supported titania catalyst is not the right catalyst formulation for mobile applications, since the activity is very low (in comparison with the Cu- and Fe-exchanged zeolites). A graphical representation of this set of experiments can be found in Fig. 2. This figure also illustrates the better performance of the Cu-zeolite based SCR catalyst material at lower temperatures.

3 Cu-Exchanged Zeolites

If we have a closer look at Cu-exchanged zeolites, one of the features with which we can differentiate types of zeolites is the largest pore size opening of the framework structure. These pores can be small (8-membered ring), medium (10-membered ring), large (12-membered ring), and extra-large (>12-membered ring). Examples of zeolite structures, which are mostly used for catalysis research, are shown in Fig. 3. Medium- and large-pore Cu-zeolites are less stable under severe hydrothermal conditions as their small pore counterparts [10,12–14]. The small pore Cu zeolites have an improved selectivity toward N_2 and a reduced selectivity toward N_2O formation. Small-pore Cu-zeolite SCR catalysts are currently used successfully in diesel engine-powered heavy vehicles. Most research done in the early days was performed on the medium- and large-pore zeolites like ZSM-5 (MFI), mordenite (MOR), zeolite Y (FAU), and beta (BEA). The last couple of years the research
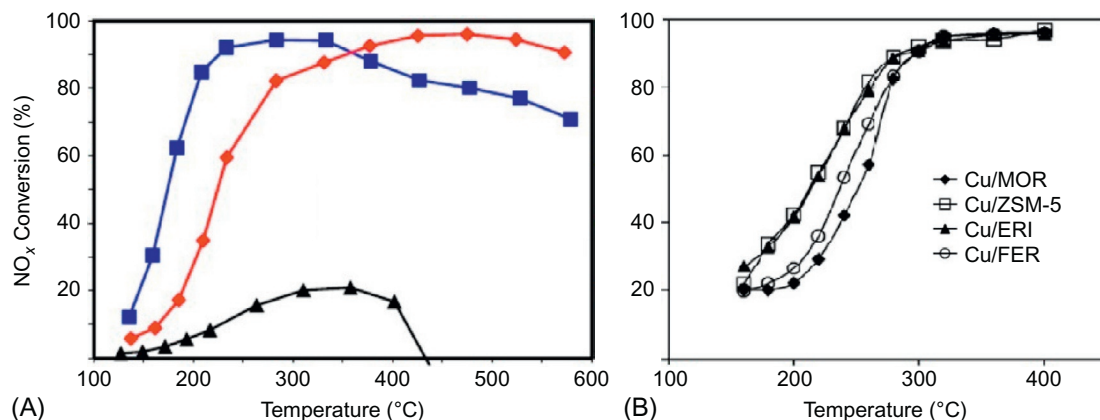
Fig. 2

(A) NO$_x$ conversion over Cu-exchanged zeolites (■), Fe-exchanged zeolites (♦), and vanadium-based (▲) formulation, as a function of temperature. A round sample core of 1 in. diameter was taken from a wash-coated monolith obtained from a supplier and a gas space velocity of 30,000 h^{-1} [8,9]. *Reproduced from Li J, Chang H, Ma L, Hao J, Yang RT. Low-temperature selective catalytic reduction of NO$_x$ with NH$_3$ over metal oxide and zeolite catalysts—a review. Catal. Today 2011;175:147–156. Copyright 2011, with permission of Elsevier.* (B) NO$_x$ conversion over Cu/zeolites and a gas hourly space velocity of 75,000 h^{-1} [10]. *Reproduced from Sultana A, Nanba T, Sasaki M, Haneda M, Suzuki K, Hamada H. Selective catalytic reduction of NO$_x$ with NH$_3$ over different copper exchanged zeolites in the presence of decane. Catal. Today 2011;164:495-499. Copyright 2011, with permission of Elsevier.*

has shifted toward small-pore zeolites; like the microporous aluminosilicate SSZ-13 and the microporous silico-aluminophosphate SAPO-34, which have both the CHA framework topology, and Erionite (ERI). The CHA structure belongs to the ABC-6 family of zeolite structures [15]. The framework is basically built by stacking layers of double 6-membered rings in the order AABBCC…, forming double 6-rings at each apex of the rhombic unit cell. This leads to the formation of large cavities, accessible through a three-dimensional 8-membered ring (8r) structure, with an aperture of 3.8×3.8 Å. The framework topology of the CHA structure type is rhombohedral, R3m, which has also been attributed to chabazite [16]. Fig. 3 shows the cage of the CHA topology viewed normal to the [001] plane. Instead, Erionite (ERI) is a small-pore zeolite, the biggest accessible pore in this system is also an 8-membered ring (3.6×5.1 Å), similar to chabazite. Other small-pore zeolites that are briefly researched in literature are: SSZ-52 (SFW), SSZ-39 (AEI, not a member of the family, but closely related to CHA structure) and SSZ-16. (AFX, stacking sequence AABBCCBB) all show good activity for the NH$_3$-SCR reaction, indicating that other units with d6r units might be promising as future DeNO$_x$ catalysts [15,17,18]. Ferrierite (FER) has both 10-membered ring pores (in the c direction) having an aperture 5.4×4.2 Å, which are interconnected by 8-membered ring pores (in the b direction) having an aperture of 4.8×3.5 Å [19]. Fig. 2
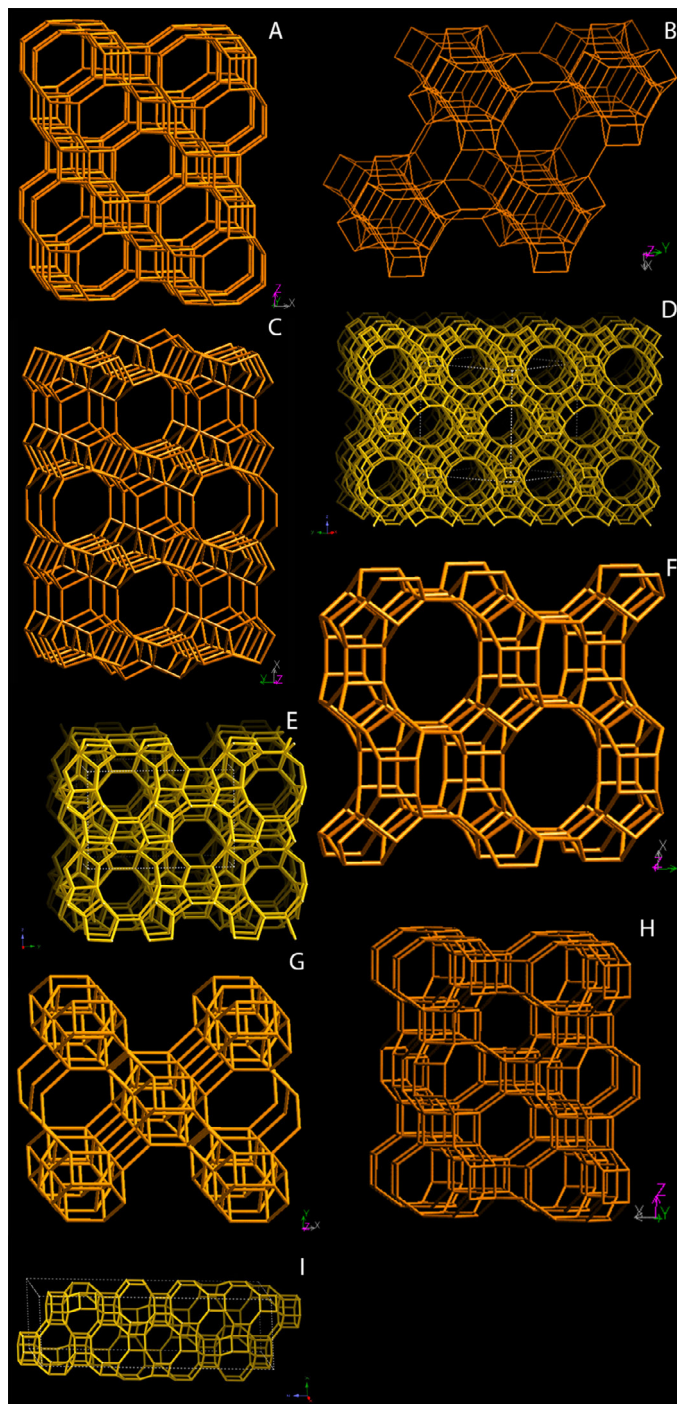
Fig. 3
Different types of framework topologies for the zeolites mentioned in this chapter, topologies are described by their three-letter code. A CHA B ERI C FER D FAU E MFI F MOR G AEI H AFX I SFW [11]. *Modified from IZA. IZA structural database,* http://www.iza-structure.org/databases/. *Copyright 2014, with permission of IZA structural database.*

shows the difference in NO_x conversion over small (ie, Cu-ERI), medium (ie, Cu-MFI), large (ie, Cu-MOR) pore zeolite materials as well as an in-between small and medium (ie, Cu-FER) zeolite material. It can be clearly seen that the small-pore zeolites show a higher activity at lower reaction temperatures.

Both the Brønsted acid sites as the copper sites inside the zeolite are important for the SCR reaction, the acid sides adsorb NH_3 to form NH_4^+ and the Cu is an essential redox center for the NH_3-SCR reaction. To get an optimal NH_3-SCR activity, the Cu exchange level should be well balanced, as both these functions are essential in the catalyst [20]. How the Cu exactly behaves during the SCR reaction is still under debate, but it is generally accepted that Cu should be in its ionic state. CuO clusters, which may appear in the zeolite, because of imperfect synthesis or hydrothermal deactivation, are more active in catalyzing NH_3 oxidation at high temperatures, yielding a negative effect on the selectivity for NO_x in NH_3-SCR [18,21].

The total mechanism of the NH_3-SCR reaction, for small-pore zeolites, is still not fully understood. One thing that is known is that the reaction pathways are different for both the low and high temperature ranges. According to Ma et al. [22] at low temperatures, ammonium nitrates from the reaction between surface NH_3 and nitrates are most important intermediates that are later reduced by gas-phase NO to yield nitrogen and water. At high temperatures, gas phase NO_2 is an important intermediate in the NH_3-SCR reaction. Pre-adsorbed NH_3 reacts gas phase NO_2 to form an intermediate after which it decomposes into nitrogen and water. Kinetic studies are difficult to perform as they are complicated due to the pore diffusion limitation, which is associated especially with the small pore structures of the CHA framework. Furthermore, studying the reaction mechanism under in situ conditions is even more complicated for this reaction system, as $-OH$, H_2O, and NH_3 all have strong ligand effects, which cause mobility and transient interactions among Cu^{2+} ions [23]. A few considerations for the total reaction mechanism, based on the work of Gao et al. [23] are: before full dehydration, isolated Cu^{2+} ions are very mobile; isolated Cu^{2+} ions do not catalyze NO oxidation, if the temperature remains under 400°C; Cu-SSZ-13 follows a Cu^{2+}/Cu^+ redox mechanism. They conclude as well, that for different loadings, different kinds of Cu-dimers play a role in their catalytic system.

4 Differences in Synthesis Methods

Copper-exchanged zeolites can be prepared using different methods and yielding different results; an example of this can be found in Fig. 4 [24]. A few methods are being used in the literature today: conventional wet ion exchange, chemical vapor deposition (CVD), solid-state (SS) ion exchange, and a direct synthesis using a Cu containing precursor, a summary of which can be found in Table 1.

Conventional wet ion exchange is used in all types of fields to exchange metal ions into different kinds of zeolites. Normally, a zeolite material in its proton or ammonia form is
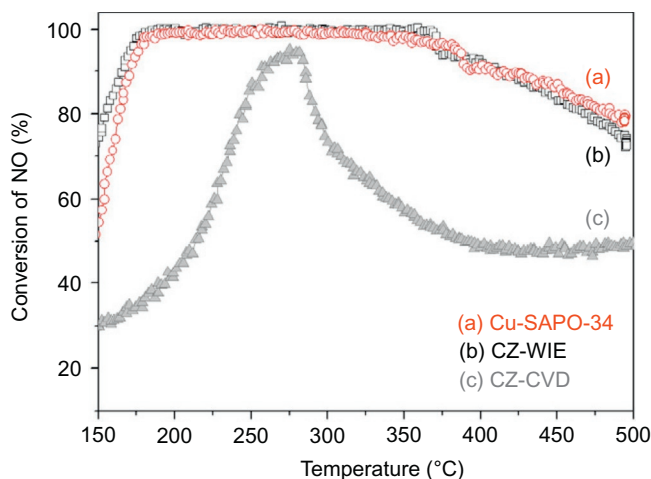
Fig. 4

Conversion of NO over (A) Cu-SAPO-34 (red); (B) CZ-WIE (black), and (C) CZ-CVD (gray). The gas hourly space velocity equals 100,000 h^{-1} [24]. *Reprinted from Deka U, Lezcano-Gonzalez I, Warrender SJ, Lorena Picone A, Wright PA, Weckhuysen BM, Beale AM. Changing active sites in Cu−CHA catalysts: deNO$_x$ selectivity as a function of the preparation method. Microporous Mesoporous Mater. 2013;166:144−152. Copyright 2013 with permission of Elsevier.*

Table 1: Advantages and disadvantages of different synthesis methodologies to prepare Cu-based SCR catalyst materials

Method	Advantages	Disadvantages
Wet ion exchange	– Easiest method experimentally – Copper in the desired cationic locations	– Yields lots of waste
Chemical vapor deposition	– Limits waste – Techniques already available industrially	– Develops CuAlO2 phase which causes bad selectivity
Solid-state ion exchange	– Limits waste – Easy experimental method	– High temperature needed – Sample needs to be dry to avoid damage to zeolite
Direct synthesis	– Limits waste – Good distribution over zeolite	– More expensive structure directing agents

added to a solution containing the desired metal ions, while continuously stirring. The temperature can be varied to get a better distribution over the zeolite. In general for small-pore zeolites, the temperature should be increased to increase the rate of diffusion [4]. After the ion exchange process is done, the sample should be filtered and washed properly. The risk of this procedure is over-exchange of the metal precursor, yielding metal or metal oxide clusters, but by correct timing and correct concentration of exchange

liquid one can get very active catalysts [25]. CVD is a technique mostly used to cover flat surfaces with a few layers of metals. Generally, when correct salts, conditions, and flows are being used, it is also possible to use this method to deposit ions inside the zeolite pore structure. The salts most used for this procedure are chlorine salts. The resulting exchanged zeolite should be washed carefully, to remove all of the chlorine left behind with this procedure, as chlorine is expected to cause a higher mobility of metal species [26]. SS ion exchange is possible for Cu-zeolite systems [27] and is recently applied in the preparation for SCR catalysts [28]. In this method a Cu-containing precursor and the zeolite are mixed and consequently heated to high temperatures in a flow in order to get the metals mobile and inside the zeolite framework. Finally, the last method discussed is a direct synthesis using a Cu-containing precursor. Different groups have been working on this system [29–33]. Instead of using a normal NH_4-zeolite or H-zeolite, a Cu-containing precursor is used to synthesize the zeolite around it, immediately resulting in a Cu-zeolite. The advantage of this one-step synthesis is that after the process, further treatment is no longer necessary, thereby limiting the waste that is generated during ion exchange. By using Cu-containing structure-directing agents, the Cu distribution over crystal should be more homogeneous as a postsynthesis treatment, as the Cu is used as a charge-balancing molecule during synthesis [31].

Of all these methods, the most used method is the conventional wet ion exchange, it is by far the easiest method experimentally and yields copper in the desired cationic locations inside the zeolite. A very good alternative, once the synthesis method using Cu-structure directing agents is optimized to perfection, would be the direct synthesis route, since it limits waste and saves energy in the production of the Cu-materials. SS ion exchange is also an option since it limits waste and is experimentally easy. These synthesized materials have shown that they have excellent activity in the NO_x NH_3-SCR reaction, and also show a good hydrothermal stability [31]. Each of the above-mentioned methods seems to lead a different local environment for Cu inside the zeolite pore system, and not all of them are equally effective for the NH_3-SCR reaction [24]. The CVD method also seems to develop a $CuAlO_2$ phase next to the Cu^{2+} ions, which causes a poor $deNO_x$ activity and high selectivity toward the formation of undesired N_2O [24].

In what will follow we will focus on the most studied small-pore zeolites in NO_x NH_3-SCR reaction, in particularly Cu-SSZ-13 and Cu-SAPO-34. We discuss here the precise Cu location and different deactivation pathways proposed.

5 Cu Location

Different research groups have been investigating the location of the Cu inside small-pore zeolite systems. Both Fickel et al. and Deka et al. have done extensive investigations on the location and redox state of the copper with respect to the zeolite framework. Fickel et al. [17]
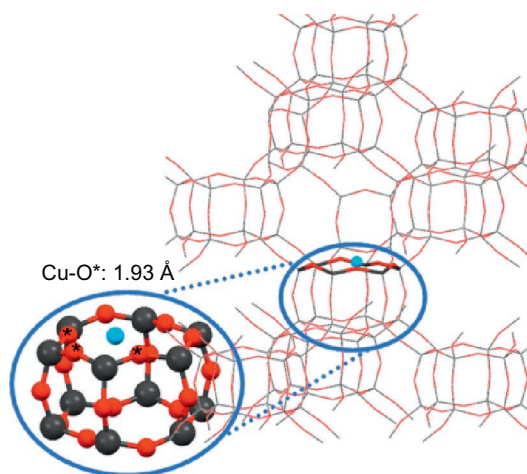
Fig. 5

Local environment of Cu^{2+} in zeolite SSZ-13, the proposed acid site for the NH_3-SCR reaction. The distance between the Cu ion and the oxygen's marked with an asterisk is 1.93 Å [36]. *Reprinted from Deka U, Lezcano-Gonzalez I, Weckhuysen BM, Beale AM. Local environment and nature of Cu active sites in zeolite-based catalysts for the selective catalytic reduction of NO_x. ACS Catal. 2013;3:413–427. Copyright 2013, with permission of American Chemical Society.*

used Rietveld refinement of synchrotron XRD at different temperatures on a Cu-SSZ-13 catalyst and concluded that copper within the SSZ-13 framework is located within the cage, just outside the 6-membered rings of the zeolite. Korhonen et al. [34] demonstrated with their XAFS data that the Cu^{2+} is coordinated by three oxygen atoms of the 6-membered ring. Deka et al. [35] confirmed this location also during NH_3-SCR, the ions located on the plane and slightly distorted from the center of the d6r subunits of SSZ-13, by using in situ XAFS/XRD. The exact location is visible in Fig. 5, the distance between the Cu ion and the oxygen's marked with an asterisk is 1.93 Å. When ion exchange levels reach close to a 100%, the Cu species still exist as isolated ion monomers [34].

Recent papers gave many new insights in other locations for Cu ions inside zeolite framework structures. Andersen et al. [37] concluded that the majority of the Cu^{2+} ions are in a specific site in the 8R of SSZ-13, as well as in the d6R, based on Rietveld and MEM analysis applied to synchrotron pXRD data, on a dehydrated Cu-SSZ-13. They used a system with Si/Al ratio of 15.5 and a Cu/Al ratio of 0.45. By DFT calculations they assigned this specific site in 8R to $[Cu^{2+}OH^-]^+$ close to a Al atom, and Cu^{2+} in the d6r. This was backed up by the work of Godiksen et al. [38] where they used EPR to study their Cu-SSZ-13 system (Si/Al = 14). They explain the loss of EPR signals upon dehydration due to EPR silent species, $[Cu^{2+}OH^-]^+$. Borfecchia et al. [39] concluded that the majority of the dehydrated Cu species are found preferentially in 8R units of the SSZ-13 framework, as tri-coordinated $[CuOH]^+$ species at O_2 activation, and bi-coordinated Cu^+ ions upon
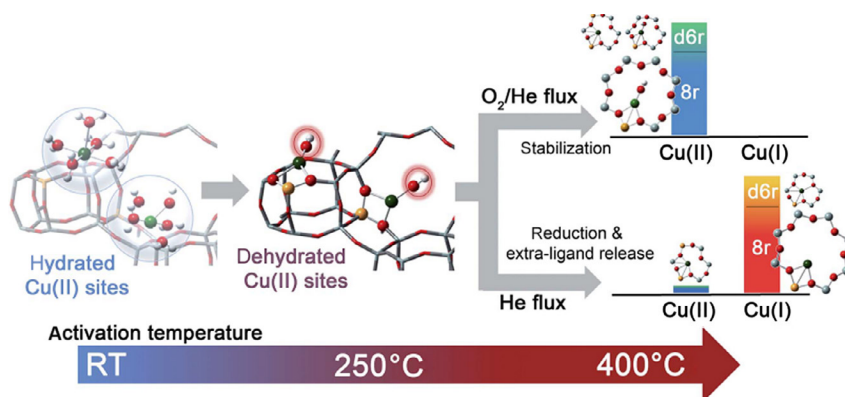
Fig. 6

Schematic representation of Cu-speciation in the Cu-SSZ-13 catalyst as a function of the dehydration temperature and conditions. In the O_2-activated Cu-SSZ-13 no traces of Cu(I). A minor fraction (around 10%) of Cu(II) in the He-activated sample was detectable in HERFD XANES spectra. The right side of the scheme concerns the dominant structural components identified by XAS, XES, and FTIR in the Cu-SSZ-13 sample investigated in the present work [39]. *Reprinted from Borfecchia E, Lomachenko KA, Giordanino F, Falsig H, Beato P, Soldatov AV, Bordiga S, Lamberti C. Revisiting the nature of Cu sites in the activated Cu-SSZ-13 catalyst for SCR reaction. Chem. Sci. 2015;6:548–563. Copyright 2014, with permission of The Royal Society of Chemistry.*

He activation. A schematic representation can be found in Fig. 6. They used a Cu-SSZ-13 zeolite with an Si/Al ratio of 12 and a Cu/Al ratio of 0.44.

Verma et al. [40] using a Cu-SSZ-13 zeolite (Si/Al=4.5, Cu/Al varies) came to slightly other conclusions. They used UV–vis, XAS, catalytic measurements, and a computational kinetic study of dry NO oxidation, to conclude that there are at least two Cu ion configurations within SSZ-13. For Cu/Al ratios below 0.2 the dominant Cu^{2+} ion is a hydrated isolated Cu^{2+} ion. Under dry NO oxidation, these species were converted into dehydrated isolated Cu^{2+} ions close by two framework Al sites, in the d6r unit. For Cu/Al=0.2, all framework Al pairs in the d6r units were exchanged with dehydrated isolated Cu^{2+} ions. For Cu/Al>0.2, Cu_xO_y ($x \geq 2$, $y \geq 1$) species inside the 8r unit, balanced by the Al in the 8r unit, play a major role in NO oxidation. Gao et al. [23], using their Cu-SSZ-13 system (Si/Al=6, Cu/Al varies), studied with TPR, EPR, and catalytic testing with NO oxidation, NH_3-oxidation, and NH_3-SCR, the state of Cu inside the zeolite. They state that for Cu/Al $\leq$ 0.22, transient Cu-dimers are relevant active sites at reaction temperatures under 300°C, which are in equilibrium with monomeric Cu ion complexes. At temperatures above 350°C, at low Cu loadings, the Cu-dimers completely dissociate to isolated Cu^{2+} monomers. At loadings $0.032 \leq$ Cu/Al ≤ 0.22 Cu^{2+} ion monomers next to the 8r become relevant sites for SCR. At Cu loadings above one Cu^{2+} ion per unit cell, stable Cu-dimers form, and they do not dissociate at temperatures above 350°C. Borfecchia et al. [39] however, state that they could not find

a significant fraction of dimeric oxo-Cu species (Cu_xO_y ($x \geq 2$, $y \geq 1$)) and according to them these species are very unlikely.

The major difference between these studies is the Si/Al ratio in the parent zeolite, which apparently has a large influence on the Cu location and coordination inside the zeolite framework, since a single conclusion, which backs up everything is not yet found.

Both Cu-SSZ-13 and Cu-SAPO-34 are more stable during the NH_3-SCR reaction, as the larger pore Cu-zeolites, resulting in an increased activity and selectivity after aging, as can be seen in Fig. 7 [41,42]. Several studies have been carried out to determine the exact location and state of the Cu ions in both Cu-SSZ-13 and Cu-SAPO-34 catalysts. According to Ma et al. [22,43] after hydrothermal treatment at high temperatures, Cu-SSZ-13 was proven to be less stable as Cu-SAPO-34, based on catalyst performance testing. Wang et al. [28] also came to this conclusion, for SS ion exchanged Cu-SSZ-13 and Cu-SAPO-34. The difference can be clearly seen in Fig. 8. Hydrothermal treatment at 800°C caused a significant reduction in the NH_3-SCR performance for Cu-SSZ-13, accompanied by a loss in crystallinity and a loss of active Cu-sites. Cu-SAPO-34 did, however, not lose this activity at these conditions [28]. This difference in hydrothermal stability is not yet properly explained in current literature. Deka et al. did not detect major differences in Cu locations for Cu-SSZ-13 or Cu-SAPO-34 in their extensive study [24]. The chemistry of the framework is different for silico-aluminophosphates (SAPO), and it is reported that SSZ-13 shows a higher acid strength than its SAPO analog SAPO-34[44].
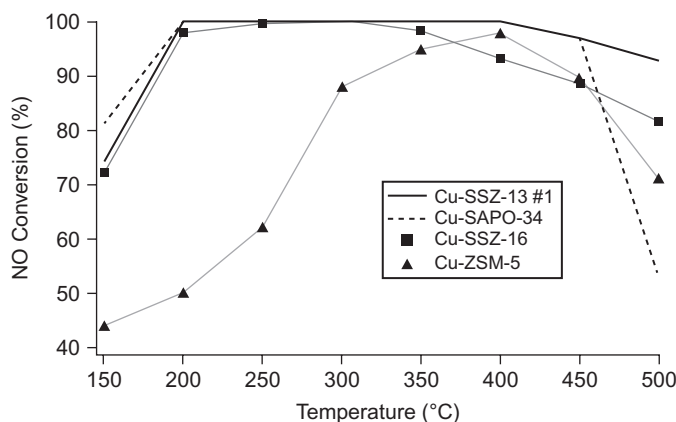

Fig. 7

NH_3-SCR activity after the 14-h hydrothermal treatment of Cu-SSZ-13, Cu- SAPO-34, Cu-SSZ-16, and Cu-ZSM-5 [41]. *Reprinted from Fickel DW, D'Addio E, Lauterbach JA, Lobo RF. The ammonia selective catalytic reduction activity of copper-exchanged small-pore zeolites. Appl. Catal. B 2011;102:441−448. Copyright 2011, with permission of Elsevier.*
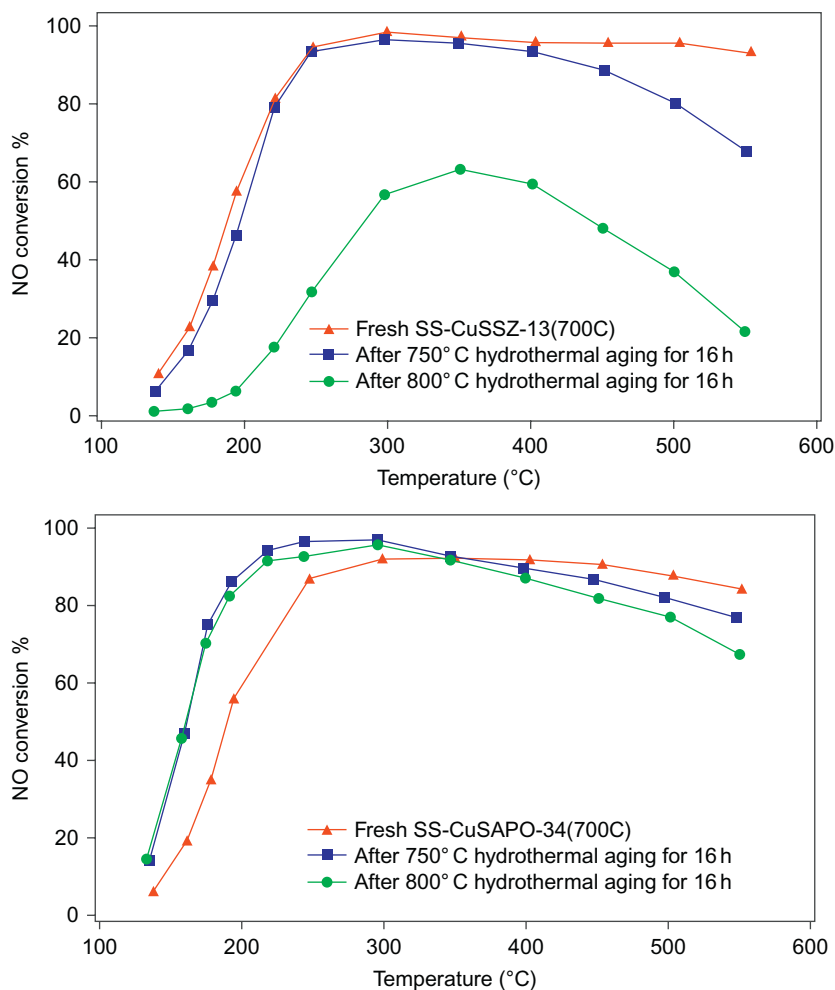
Fig. 8

CR performance of SS-Cu-SSZ-13 (left), and SS-Cu-SAPO-34 (right) before and after hydrothermal aging for 16 h [28]. *Reprinted from Wang D, Jangjou Y, Liu Y, Sharma MK, Luo J, Li J, Kamasamudram K, Epling WS. A comparison of hydrothermal aging effects on NH$_3$-SCR of NO$_x$ over Cu-SSZ-13 and Cu-SAPO-34 catalysts. Appl. Catal. B 2015;165:438−445. Copyright 2014, with permission of Elsevier.*

6 Deactivation

Deactivation of zeolite-based SCR systems can be divided into two main categories: hydrothermal deactivation by steam in the exhaust system or chemical deactivation by different chemicals found in an exhaust stream of typical fossil fuel engine. Steam is present in the exhaust, since it is a by-product of burning fossil fuels, while different chemicals might be present due to lubrication oil, contaminants in the fuel, or they may be originating from a different catalyst in the exhaust system.

6.1 Hydrothermal Deactivation

The main drawback of using zeolites is decreased activity at high temperatures due to hydrothermal deactivation. Especially for the medium- and large-pore zeolites, at temperatures exceeding 700°C and in the presence of steam, the catalysts deactivate quickly and show lower SCR activity [12–14]. The main cause of this deactivation is dealumination of the zeolite framework, the aluminum inside the framework becomes unstable and is removed from the tetrahedral framework locations [13,45–47]. Since aluminum atoms positioned in tetrahedral framework locations are the Brønsted acid sites in the zeolites, the Brønsted acidity is also lost. Furthermore, less charge compensation is needed due to the removal of aluminum, so the Cu also starts to migrate, and forms CuO or copper aluminate clusters [48,49]. For most larger pore zeolites, Cu exchanged zeolites are less stable as the normal zeolites, as can be seen by in situ XRD [5]. For smaller pore zeolites, like SSZ-13, this seems to be not the case. In situ XRD also shows the difference between NH_4-SSZ-13 and Cu-SSZ-13. Clearly the zeolite retains its crystal structure longer, at more severe hydrothermal temperatures [17].

Small-pore zeolites are much less susceptible to this hydrothermal deactivation, although H_2O can still enter the pores easily, the kinetic diameter of H_2O being 2.65 Å, and the pore diameter of the largest pore being the 8-membered ring with dimensions of 3.8×3.8 Å [16]. Fickel at al. [41] hypothesized, in order to get defects in the zeolite because of dealumination, $Al(OH)_3$ units have to leave the zeolite framework, and out of the pores. They estimate the kinetic diameter of $Al(OH)_3$ at 5.03 Å, making it impossible for the $Al(OH)_3$ to escape the pores and locking it inside. They also propose based on other literature about the postsynthesis alumination treatments [50,51], that at low temperatures, the $Al(OH)_3$ is reincorporated into the zeolite framework [41]. Because of these reasons Cu-SSZ-13 displays an improved hydrothermal stability in comparison with bigger pore Cu-zeolite catalysts for NH_3-SCR. The mechanism that deactivates SSZ-13 is still similar to other zeolites, namely dealumination and structural collapse.

6.2 Other Types of Deactivation

Another type of deactivation found under automotive conditions is the storage of hydrocarbons, and sequentially coking of these hydrocarbon molecules inside the zeolite pore system. Hydrocarbons are always present in the exhaust stream, but even more so during cold starts of the engine. The buildup of hydrocarbons inside the zeolite can burn during the regeneration cycle of the DPF filter, creating more heat locally inside the zeolite pore system, which can in turn thermally destroy the zeolite. One of the reasons Cu-SSZ-13 is more stable for this deactivation has to do with the small-pore openings of this zeolite. For hydrocarbon molecules with a kinetic diameter larger than 3.8 Å (methane) it is very difficult to enter the pores, making diffusion very slow [13].

Other types of deactivation are based on the chemical deactivation of the Cu zeolite system. Chemical deactivation of NH_3-SCR catalysts is due to contaminants from oil and fuel and chemicals from different catalysts in the exhaust system, like Pt, originating from the DOC [52–54]. The volatized Pt from the DOC produce severe deactivation of the SCR catalyst, where it is known to oxidize NH_3 toward NO_x and N_2O [52–54]. Other impurities such as phosphorous, calcium, magnesium, and zinc originate lubrication oil in the engine, where they are added as additives [54]. Lezcano-Gonzalez et al. [54] have performed extensive research on the deactivation mechanisms of Ca, Zn, Pt, and P. The main influence on the catalytic performance of Ca and Zn is a decrease in NO conversion, and an increased NH_3 slip. For Pt there is also a decrease in NO conversion, but also a strong influence on the N_2 selectivity and an increase in NO oxidation activity. P is responsible for a complete suppression of the catalytic activity. The main deactivation mechanisms are different for all investigated poisons. For Ca, it is due to pore blocking and filling by CaO and CuO aggregates. For Zn it is also pore blocking and filling, by ZnO and CuO aggregates, but also the decrease of Cu^{2+} sites. Pt species itself promote NO and NH_3 oxidation, and as a secondary effect it also fills the pores with Pt species. P disturbs the zeolite framework, by reacting with the Al species in the framework, it is also responsible for the decrease in the amount of Cu^{2+} ions and the formation of CuO. Furthermore, it forms polyphosphates and CuO, which block the pores of the zeolite system (Table 2) [54].

7 Conclusions and Look into the Future

Compared to medium and large-pore Cu-exchanged zeolite catalysts, small-pore Cu-exchanged zeolite catalysts show an excellent and improved activity, hydrothermal stability, and selectivity toward N_2. Because of the small pores, the small-pore Cu-exchanged zeolite catalysts also show a better resistance against hydrocarbon poisoning, as well as dealumination effects. Different synthesis procedures, however, might result in differences in catalyst performance, so it is key to pick the right synthesis procedure, while taking care of waste treatment. At the moment, these catalysts are already employed in heavy-duty diesel trucks on a commercial level, however, a lot more work is needed to fully understand and employ these new Cu exchanged small-pore zeolites. A full mechanistic catalytic cycle, for example, is still not yet established. New vehicle emission regulations could be expected in the future, and the low temperature activity for Cu-SSZ-13 and Cu-SAPO-34 has to be improved. As mentioned, pore diffusion causes difficulties for both Cu-SSZ-13 and Cu-SAPO-34. To overcome these problems more studies into the synthesis of very small zeolite crystals or mesopores and modified zeolites is necessary. The full mechanism of the NH_3-SCR reaction inside the Cu-SSZ-13 framework is still not known as more research is needed in the field of kinetic studies.

Table 2: Overview of the deactivation mechanisms observed for Ca, Zn, Pt, P, hydrocarbons (HC) and steam for Cu-based zeolite NO_x SCR catalyst materials [54]

Deactivation factor	Influence on catalytic performance	Main deactivation mechanism	Secondary deactivation mechanism
Ca	– Decrease in NO conversion – Increased NH_3 slip	– Pore blocking or filling by CaO and CuO aggregates	– Decrease of isolated Cu^{2+} ions and CuO formation
Zn	– Decrease in NO conversion – Increased NH_3 slip	– Pore blocking or filling by ZnO and CuO aggregates – Decrease of isolated Cu^{2+} ions and CuO formation	
Pt	– Decrease in NO conversion – Strong influence on N_2 selectivity – Increase in NO oxidation activity	– Pt promotes NO and NH_3 oxidation	– Pore blocking or filling by Pt species
P	– Complete suppression of catalytic activity	– Decrease of isolated Cu^{2+} ions and CuO formation – Pore blocking or filling by polyphosphates and CuO aggregates – Disruption of zeolite framework	
HC	– Decrease in NO conversion – Generation of local heat while burning them off	– Thermal destruction of zeolite framework – Pore blocking or filling by HC species (coking)	
Steam	– Decrease in NO conversion	– Dealumination of zeolite framework – Loss of Brønsted acidity – Decrease of isolated Cu^{2+} ions and CuO formation	

Data adapted from Lezcano-Gonzalez I, Deka U, van der Bij HE, Paalanen P, Arstad B, Weckhuysen BM, Beale AM. Chemical deactivation of Cu-SSZ-13 ammonia selective catalytic reduction (NH_3-SCR) systems. Appl. Catal. B 2014;154−155:339−349. Copyright 2014, with permission of Elsevier.

Acknowledgments

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