Review

Recent Understanding of Low-Temperature Copper Dynamics in Cu-Chabazite NH₃-SCR Catalysts

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Abstract: Dynamic motion of NH₃-solvated Cu sites in Cu-chabazite (Cu-CHA) zeolites, which are the most promising and state-of-the-art catalysts for ammonia-assisted selective reduction of NO_x (NH₃-SCR) in the aftertreatment of diesel exhausts, represents a unique phenomenon linking heterogeneous and homogeneous catalysis. This review first summarizes recent advances in the theoretical understanding of such low-temperature Cu dynamics. Specifically, evidence of both intra-cage and inter-cage Cu motions, given by ab initio molecular dynamics (AIMD) or metadynamics simulations, will be highlighted. Then, we will show how, among others, synchrotron-based X-ray spectroscopy, vibrational and optical spectroscopy (diffuse reflection infrared Fourier transform spectroscopy (DRIFTS) and diffuse reflection ultraviolet-visible spectroscopy (DRUVS)), electron paramagnetic spectroscopy (EPR), and impedance spectroscopy (IS) can be combined and complement each other to follow the evolution of coordinative environment and the local structure of Cu centers during low-temperature NH₃-SCR reactions. Furthermore, the essential role of Cu dynamics in the tuning of low-temperature Cu redox, in the preparation of highly dispersed Cu-CHA catalysts by solid-state ion exchange method, and in the direct monitoring of NH₃ storage and conversion will be presented. Based on the achieved mechanistic insights, we will discuss briefly the new perspectives in manipulating Cu dynamics to improve low-temperature NH₃-SCR efficiency as well as in the understanding of other important reactions, such as selective methane-to-methanol oxidation and ethene dimerization, catalyzed by metal ion-exchanged zeolites.

Keywords: Cu mobility; in situ spectroscopy; simulation; reaction mechanism

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1. Introduction

Nitrogen oxide emissions (mainly NO and NO₂) from power plants and automobiles not only harm the human respiratory system but also participate in atmospheric reactions to form, among others, fine particulate matter (PM), ground-level ozone (O₃), and photochemical smog [1]. Cu-loaded small-pore chabazite (Cu-CHA) zeolites, including Cu-SSZ-13 and Cu-SAPO-34, have been successfully commercialized as catalysts to reduce nitrogen oxide emissions (NO_x) from automotive exhausts by selective catalytic reduction with ammonia (NH₃-SCR) [2–6] via the following route:

The unique small-pore feature of the CHA framework allows for the prevention of hydrocarbons (HCs) in exhausts from entering the zeolite cages, thereby avoiding damage to the framework structure caused by high temperatures due to HC combustion.

Therefore, Cu-CHA zeolites possess excellent hydrothermal stability, which is crucial for their application in diesel exhaust aftertreatment often involving high-temperature operations in combination with high water content in the exhaust [7–16]. However, the activity of Cu-CHA at low temperatures (i.e., <200 °C) is still relatively low, restricting the high-efficiency removal of NO_x from exhausts at cold-start or idle conditions [17–26]. It therefore requires a deeper understanding of the reaction mechanisms and of the structure–reactivity relationships of Cu-CHA catalysts to further improve their low-temperature NH₃-SCR performance for meeting increasingly stringent emission regulations.

CHA zeolite has a three-dimensional cage structure composed of alternately arranged 4-, 6-, and 8-membered rings (4-, 6-, and 8-MRs) of tetrahedral primary building units [27–33]. Both SSZ-13 and SAPO-34 zeolites, sharing the same CHA topology but having different elemental compositions, are employed as NH₃-SCR catalysts in real applications [34–36]. While a fraction of Si T-sites (crystallographically distinct positions) is replaced by Al atoms in SSZ-13, Si atoms substitute P T-atoms in the AlPO₄ framework of SAPO-34. The characteristic variance in framework composition leads to significant differences in acidic properties, charge density, and so on [36,37]. The majority of findings presented in this review are related to Cu-SSZ-13, corresponding to the markedly higher number of available investigations on Cu-SSZ-13 than on Cu-SAPO-34 in literature.

It has been well recognized that the active sites of Cu-CHA in NH₃-SCR catalysis are isolated Cu²⁺ ions coordinated to paired Al atoms in 6-MRs and [Cu²⁺(OH)] coordinated to a single Al center in 8-MRs [38–48]. The state of Cu sites (e.g., location, oxidation state, coordination, etc.) in CHA depends on both the framework composition (i.e., Si/Al ratio and Cu/Al ratio) and the reaction conditions (e.g., gas composition, temperature, etc.) [38–42]. Both, isolated Cu²⁺ and [Cu²⁺(OH)] can participate in the NH₃-SCR redox cycle, which consists of the reduction half-cycle, driven by the interaction with co-adsorbed NH₃ and NO, and the re-oxidation half-cycle, driven by reactions with O₂, NO + O₂, or NO₂ [42,49–52]. Under typical NH₃-SCR conditions, Cu ions can be “solvated” by molecules, which bear free electron pairs to form strong coordinative bonds, such as H₂O and NH₃, and migrate from the original equilibrium position to a location closer to the cage center at low temperatures (i.e., 150–200 °C) [44,53–55]. Although the solvation of Cu ions by H₂O also weakens the attractive forces between Cu and the framework oxygen and allows Cu ions to migrate into CHA cages, the “solvating” effect of NH₃ is even more pronounced according to the spectrochemical series, which attribute H₂O to weak-field ligand, while NH₃ belongs to the group of strong-field ligands [38]. Hence, NH₃ solvation has a stronger effect on Cu mobility and thus plays a dominant role in NH₃-SCR catalysis. We therefore mainly focus on NH₃-supported Cu dynamics in this mini-review. However, several methods to study H₂O-coordinated Cu species will also be mentioned here to provide a more comprehensive picture of the dynamic migration processes.

According to density functional theory (DFT) and ab initio molecular dynamics (AIMD) results, the local migration of Cu ion active sites is restricted mainly by electrostatic tethering of the framework [38,56]. Additionally, factors such as the number of coordination molecules and the presence of framework hetero-atoms or extra-framework cations could also change the local coordination environment of Cu sites and thus considerably affect local Cu migration [36,56–59]. Apart from theoretical simulations, there are few characterization methods that can be used to directly assess the Cu dynamics. Hence, most of the knowledge gained so far about these in situ-formed species stems from indirect observations, such as monitoring of the coordination state or the location change with operando X-ray absorption spectroscopy (XAS) techniques. A combination of optical spectroscopy techniques, such as diffuse reflection infrared Fourier transform spectroscopy (DRIFTS) and diffuse reflection ultraviolet-visible spectroscopy (DRUVS), also allows for the extraction of characteristic features that might be altered by dynamic Cu transformation. Recently, impedance spectroscopy, an electric perturbation-based technique, was employed to track reaction-driven Cu mobilization by monitoring the dynamic variation of dielectric properties caused by ion migration processes [60–68]. As suggested repeat-

edly, the migratory NH_3 -solvated copper species can travel through the 8-MR windows between CHA cages to form Cu dimers in order to activate oxygen molecules to complete the oxidation half-cycle [38,56,57,69]. Due to steric hindrance, the inter-cage diffusion of NH_3 -solvated Cu species is often considered as the rate-limiting step in cyclic reaction paths for low-temperature NH_3 -SCR, particularly for Cu-CHA catalysts with low Cu density [57,70]. Such reaction-driven dynamic Cu motion represents a unique phenomenon embodying features of heterogeneous and homogeneous catalysis and might serve as the basis for enhancing the low-temperature performance of Cu-CHA toward cold-start NO_x abatement.

In this review, we will first present the results from computational studies on the highly complex and condition-dependent nature of NH_3 -solvated and -mobilized Cu species as well as limitations on inter- and intra-cage Cu migration. Then, we will show how a coordinative environment and the local structure of Cu centers during low-temperature NH_3 -SCR reactions can be revealed by a combination of multiple and complementary spectroscopy techniques, such as synchrotron-based Extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES), vibrational and optical spectroscopy (DRIFTS and DRUVS), electron paramagnetic spectroscopy (EPR), impedance spectroscopy (IS), etc. The essential role of Cu dynamics in the tuning of low-temperature Cu redox, the preparation of highly dispersed Cu-CHA catalysts by the solid-state ion exchange method, and the direct monitoring of NH_3 storage and conversion will be presented in the third part. Finally, we will discuss briefly the new perspectives in manipulating Cu dynamics to improve low-temperature NH_3 -SCR efficiency as well as in understanding other important reactions over metal ion-exchanged zeolites, in particular, selective methane-to-methanol oxidation and ethene dimerization.

2. Theoretical Prediction

2.1. Nature of Dynamic Cu Species

In Cu-CHA, the presence of Brønsted acidity, which originates from the Al substitution of Si T-atoms in the CHA framework and the subsequent charge compensation by protons, allows for strong NH_3 adsorption even at high temperatures (above 400 °C) [38–42,71–73]. The introduction of Cu ions, enabled by electrostatic attraction between metal ions and the polyanionic zeolite framework, provides additional sites for NH_3 adsorption with a relatively lower binding enthalpy compared with that on Brønsted sites [74]. The coexistence of Brønsted sites, Cu sites, and other weaker Lewis acidic sites (such as extra-framework Al sites) leads to a condensed phase of adsorbed NH_3 molecules within the zeolite structure, generating a unique solution-like environment at low temperatures [50,75,76].

Even if only NH_3 adsorption is considered, the Cu species formed at two sites of different Al coordination are still very complex in nature, as shown in Figure 1. Paolucci et al. calculated the free energy of NH_3 adsorption in the presence of NH_3 (300 ppm) and H_2O (2%) using first-principles thermodynamic analysis and obtained phase diagrams of Cu speciation by taking the coordination Al of the framework, temperature, and O_2 partial pressure into consideration [38]. It can be clearly seen that, with the increase in temperature, the NH_3 ligands are gradually desorbed and Cu ions eventually bind to the framework in the form of isolated Cu ions (Z represents a negative charge of the zeolite framework). Further calculations show that the proportion of Cu^+ on the 1Al site (a single Al atom in the 6-MR) is higher than that in the 2Al (paired Al atoms in proximity of the 6-MR) in reducing atmosphere, indicating that the Cu ions in the former are more easily reduced, which is consistent with temperature-programmed reduction with H_2 (H_2 -TPR) results in the literature [77–80]. During low-temperature NH_3 -SCR reactions (200 °C), the major species at 1Al sites were found to be $[\text{Cu}^+(\text{OH})(\text{NH}_3)_3]^+$ and $[\text{Cu}^+(\text{NH}_3)_2]^+$, while $[\text{Cu}^{2+}(\text{NH}_3)_4]^{2+}$ species dominated at 2Al sites. When NH_3 ligands pull the Cu species from the framework oxygen coordination positions into the CHA cage, the NH_3 -solvated Cu species migrate dynamically between cages due to the low inter-cage diffusion barrier, as shown in Figure 2. Considering that the diameter of 4-MR is too small to allow molecules

to pass through, Chen et al. investigated the possible diffusion limitations for the complex encountering through 8-MRs by DFT calculations and obtained a diffusion barrier of only 0.29 eV [81]. Paolucci et al. [38] performed AIMD simulations to visualize the diffusion trajectories of $[\text{Cu}^+(\text{NH}_3)_2]^+$ and $[\text{Cu}^{2+}(\text{NH}_3)_4]^{2+}$ species in CHA cages and confirmed that both NH_3 -ligated species are mobile enough to allow Cu to move away from the equilibrium position. Relatively, $[\text{Cu}^+(\text{NH}_3)_2]^+$ species move within a larger volume and thus farther from the original equilibrium position, suggesting that the linear and less sterically hindered $[\text{Cu}^+(\text{NH}_3)_2]^+$ species are more mobile and thus could diffuse through the 8-MR windows between adjacent CHA cages.

Figure 1. Phase diagrams for 1Al (left) and 2Al (right) sites with varying T and P_{O_2} at 300 ppm of NH_3 and 2% H_2O : reproduced with permission from [38], copyright American Chemical Society, 2016.

Figure 2. Diffusion barrier across an eight-membered ring in SSZ-13 for $[\text{Cu}^+(\text{NH}_3)_2]$: the bottom left and right structures show the initial and final configurations, respectively. TS: transition-state structure. Reproduced with permission from [81], copyright American Chemical Society, 2016.

2.2. Inter-Cage Motion of Cu Sites

To further assess the characteristics of $[\text{Cu}^+(\text{NH}_3)_2]$ migration between cages, Paolucci et al. calculated the free energy changes of $[\text{Cu}^+(\text{NH}_3)_2]$ at different positions by the metadynamics method and by taking Cu–Al distance as a variable [56]. As shown in Figure 3, in the simulation of $[\text{Cu}^+(\text{NH}_3)_2]$ diffusion between two adjacent CHA cages, the free energy was found to reach a minimum at a Cu–Al distance of 4.7 Å, that is, at the initial

equilibrium position marked as (1). When the $[\text{Cu}^+(\text{NH}_3)_2]$ passes through 8-MR, the free energy value reaches a peak and decreases immediately after the crossing. With the further increase of Cu–Al distance to more than 9 Å, free energy increases due to an increase of electrostatic tethering of $[\text{Cu}^+(\text{NH}_3)_2]$ by the framework Al center, which means that the maximum distance for dynamic diffusion of Cu species was about 9 Å [56].

Figure 3. Simulated $\text{Cu}^+(\text{NH}_3)_2$ diffusion up to 11 Å from charge-compensating Al: (a) the meta-dynamics-computed free energy at 473 K of $\text{Cu}^+(\text{NH}_3)_2$ in the 72-T site CHA supercell versus Cu–Al distance and (b) the corresponding representative $\text{Cu}^+(\text{NH}_3)_2$ configurations from the trajectories in (a). Reproduced with permission from [56], copyright American Association for the Advancement of Science, 2017.

This inter-cage dynamic motion of Cu sites is considered a key step affecting the NH_3 -SCR efficiency of low Cu-loaded CHA zeolites because two Cu sites are required for dissociation of O_2 in the re-oxidation half-cycle [38,56,57,69]. Therefore, the higher the transport efficiency in the cage, the easier it is to form dimeric Cu species, which can promote NH_3 -SCR activity at low temperatures. As proposed by Paolucci et al., the inter-cage Cu motion is determined by electrostatic tethering of Cu to the framework. Therefore, change in the coordinative environment around Cu sites may cause losses in transport efficiency, which will eventually affect the low-temperature performance of the Cu-CHA catalyst. Recently, O'Malley et al. investigated the diffusion trajectory of Cu species in zeolite with different topologies (LEV and CHA) by molecular dynamics (MD) simulations and quasi-elastic neutron scattering (QENS) experiments [82]. Although QENS experiments indicated that the rates of NH_3 migration within the two zeolite cages are the same, MD simulations (see Figure 4 for the molecular diffusion trajectories of NH_3 in LEV and CHA) suggested that the inter-cage motion frequency of NH_3 molecules in the CHA cage is twice that in the LEV because the former contains more 8-MR windows for NH_3 transport between chabazite cages. Although only NH_3 molecules were considered in this study, the results provide a theoretical and experimental basis for a deeper understanding of local dynamics of NH_3 -solvated Cu species.

Figure 4. Center-of-mass trajectory plots of a NH_3 molecule during the MD simulations, viewed from (a) the side of a selected combined building unit and (b) above the combined building unit: reproduced with permission from [82], copyright The Royal Society of Chemistry, 2018.

3. Experimental Detection

The dynamic formation of multi-nuclear active sites, such as NH_3 -solvated dimeric Cu complexes, provides different and important perspectives for understanding the NH_3 -SCR reaction mechanisms at low temperatures. However, challenges remain in the experimental study of such dynamic reaction processes and such transiently existing active sites. The ligating details of the NH_3 -solvated Cu sites are too complicated (Figure 1) to be resolved unambiguously, which results in an obstacle to explore the dynamic reaction process. Recently, substantial advances have been achieved by applying combinatory and complementary characterizations techniques (such as XAS, DRIFTS, and EPR) to track the dynamic change in Cu coordination environment, which will be discussed in the following.

3.1. X-ray Absorption Spectroscopy Based Techniques

XAS mainly obtains relevant coordination information of active Cu sites, e.g., the type and number of ligands, by monitoring absorption at the K-edges [48,83–86], and is one of the few techniques that can accurately analyze the complex structures of NH_3 -solvated Cu species at an atomic scale. Considering that NH_3 desorption on Cu ions at high temperature is expected to affect SCR reaction activity, Lomachenko et al. explored the dependence between temperature and migration molecules in NH_3 -SCR atmosphere in the temperature range of 150–400 °C by operando XAS (Figure 5a) [84]. Characteristic peaks in the XAS spectra were identified and explained by comparing with standard references, and the Cu speciation was further quantified by linear combination fitting (LCF) analysis. The XANES spectra showed a significant edge-rising peak at 8982.5 eV during exposure at 150 °C in NH_3 -SCR atmosphere, which was assigned to a linear $[\text{Cu}^+(\text{NH}_3)_2]$ complex. LCF analysis showed that, at low temperature (150 °C), two transient species, m- Cu^+ and m- Cu^{2+} (m represents “mobile”), were the dominant active sites, accounting for 46% and 25% of the total Cu species, respectively, while Z-Cu (Z represents framework-interacting) species account for only 26%. With the increase in temperature, NH_3 molecules adsorbed on the Cu ions were gradually desorbed, and more and more Cu ions were finally anchored on the framework, corresponding to the reduction in dynamic species. The two different active Cu sites at high temperatures and low temperatures contributed to two different mechanisms for the NH_3 -SCR reaction on Cu-CHA, resulting in a “seagull” type of temperature–activity curve [56–58,84,87].

Figure 5. (a) Operando XANES collected during SCR at temperatures of 150, 250, 300, and 400 °C and (b) comparison between temperature-dependent NH_3 -SCR conversion rate and Cu-speciation in Cu-CHA: structural snapshots of the dominant (highest relative abundance over the total number of Cu sites) model Cu species evidenced by linear combination fitting (LCF) analysis of operando XANES for each probed temperature are also reported. Reproduced with permission from [84], copyright American Chemical Society, 2016.

In addition to the significant influence of temperature on NH_3 -solvated copper, there are other factors that can cause notable interference in the distribution of dynamic species, such as pretreatment atmosphere and the properties of the material itself [87,88]. Borfecchia's group analyzed the XANES spectra of NH_3 -solvated species in samples activated in N_2 or in vacuum and found that the latter contained more Cu^+ species [88]. This is because some Cu sites (mainly $[\text{Cu}^{2+}(\text{OH})]$) were reduced to Cu^+ when pretreated in vacuum or under high-temperature reducing atmosphere (i.e., so-called self-reduction), and the proportion of NH_3 -solvated species in the catalyst changed accordingly.

3.2. Optical Spectroscopy Techniques

DRIFTS is generally used to identify the characteristic vibrations of probe molecules (such as NH_3 , NO, and CO) adsorbed on the surface of catalysts. Additionally, DRIFTS can be also used to monitor vibrations of the zeolite framework, such as the -Al-O(H)-Si- and asymmetric T-O-T vibrations [55,89]. The two IR features of framework T-O-T vibrations, at ca. 900 cm^{-1} and ca. 950 cm^{-1} , respectively, are sensitive to the existence and perturbation of Cu ions, i.e., Cu^{2+} in the 6-MR and $[\text{Cu}^{2+}(\text{OH})]$ in 8-MR [38,43,46,49]. After NH_3 solvation, the Cu ions gradually migrate away from the original equilibrium position, weakening the interaction between the cations and zeolite framework and, consequently, leading to an obvious change in the T-O-T vibration peaks. On the basis of T-O-T vibration change, Yasser et al. tracked the poisoning of SO_2 to NH_3 -solvated Cu active sites at low temperature by DRIFTS [90]. Two negative peaks located at 900 cm^{-1} and 950 cm^{-1} assigned to T-O-T vibration around Cu^{2+} and $[\text{Cu}^{2+}(\text{OH})]$, respectively, increased in intensity versus time (Figure 6A), indicating that the two Cu active sites were gradually solvated by the adsorbed NH_3 molecules. In the subsequent step of $\text{NO} + \text{O}_2$ adsorption (Figure 6B), the NH_3 ligands on the dynamic Cu species were consumed by the SCR reaction and the negative IR bands returned to baseline because of the weakened local motion. The dynamic local migration process still existed even after suffering from SO_2 poisoning (Figure 6C). However, the migration of $[\text{Cu}^{2+}(\text{OH})]$ species was obviously inhibited. The SCR rates over isolated Cu^{2+} and $[\text{Cu}^{2+}(\text{OH})]$ sites can be calculated by integrating the time-dependent evolution of respective IR band area.

Figure 6. In situ diffuse reflection infrared Fourier transform spectroscopy (DRIFT) spectra of T-O-T vibrations of Cu-SSZ-13 during experiments with/without sulfur: (A) $\text{NH}_3 + \text{O}_2$ adsorption followed by a purging phase in He, (B) $\text{NO} + \text{O}_2$ adsorption at 200 °C, (C) $\text{NH}_3 + \text{O}_2 + \text{SO}_2$ adsorption at 200 °C followed by a purging phase in He, and (D) $\text{NO} + \text{O}_2$ adsorption at 200 °C. Reproduced with permission from [90], copyright American Chemical Society, 2018.

DRUVS is often used as an auxiliary technique for exploring the dynamics of transient Cu species. Unlike DRIFTS, DRUVS does not monitor the vibration of probe molecules adsorbed on the surface but directly detects the charge transfer around the active site and, thus, can work even at high temperatures. Many researchers used the DRUVS technique to obtain information about the coordination and oxidation state of active sites during dehydration [91–93]. The gradual loss of H_2O ligands in hydrated Cu ions upon high-temperature pretreatment, which makes the electronic exchange between Cu ion and framework oxygen more frequent, can be followed by monitoring the typical DRUVS spectral features in the range of $50,000\text{--}30,000\text{ cm}^{-1}$ ($200\text{--}350\text{ nm}$) originating from ligand-to-metal charge transfer (LMCT) processes. Recently, Oda et al. demonstrated that the characteristic DRUVS features at 370 nm were assigned to Cu dimerization of two mobile NH_3 -solvated Cu ions [94]. The features of Cu dimers were observed in different zeolites, including Cu-CHA and Cu-AEI with different Si/Al ratios, as shown in Figure 7, indicating that the formation and dynamic migration of dimeric Cu species is a common phenomenon in Cu-zeolite materials. Apart from the LMCT feature, the characteristic d-d electron transition bands of Cu^{2+} ions at $400\text{--}600\text{ nm}$ are often employed to identify the oxidation states of Cu ions [95]. The O_2 -activated Cu-CHA catalyst shows a broad d-d band, even after the adsorption of NH_3 . Nevertheless, the d-d transition peak only disappears after continuous exposure to NO, indicating that the reduction of Cu^{2+} ions in Cu-CHA at low

temperatures cannot be achieved by NH_3 solvation alone and requires the co-adsorption of NH_3 and NO [96].

Figure 7. (a) In situ diffuse reflection ultraviolet-visible spectroscopy (DRUVS)-NIR spectra of Cu/CHA (12 and 3.2), Cu/AEI (10 and 3.4), and Cu/AEI (5.5 and 3.4) samples under a mixture of 1000 ppm of NO , 1000 ppm of NH_3 , and 10% O_2 gas at 473 K: reproduced with permission from [94], copyright American Chemical Society, 2020. (b) In situ DRUVS spectra of Cu-CHA at 200 °C: the catalyst was first oxidized under 10% O_2/Ar (100 mL min^{-1}), followed by exposure to 0.1% NH_3/Ar flow (100 mL min^{-1}) for 0.5 h and then to 500 ppm NO/Ar flow (100 mL min^{-1}). Reproduced with permission from [96], copyright ChemCatChem, 2020.

3.3. Electron Paramagnetic Resonance (EPR)

EPR is an ideal technique to investigate the nature of Cu^{2+} species even in trace amounts and can provide valuable information about oxidation state and local coordination of the Cu sites. The intensity of an EPR signal has a significant linear relationship with Cu loading, and different Cu species can be identified and even quantified according to the hyperfine splitting peaks in low magnetic fields. However, the resolution of low-field characteristic peaks was significantly reduced by the increased mobility of Cu^{2+} , as confirmed by a comparison of the EPR spectra of the dehydrated and hydrated samples (Figure 8a), which means that it might be inaccurate to attribute the reduced EPR signal to $\text{Cu}^{2+} \rightarrow \text{Cu}^+$ reduction after NH_3 adsorption onto Cu-CHA [93,97–99]. Based on DFT calculations with the Breit–Pauli Hamiltonian, Fernandez et al. simulated EPR spectra by adding adsorbate molecules to optimized geometric structures of zeolites and by comparing it with the experimental data [100]. The results show that the addition of a NH_3 molecule can break a $\text{Cu}-\text{O}_f$ bond (O_f represents oxygen in the zeolite framework) and can drive the Cu ion moving away from the 6-MR plane. With the increase in adsorbed NH_3 molecules, the connection between the Cu ions and framework gradually weakens, which causes Cu ions to migrate further into the CHA cage. Such an atomic study reveals that the restriction of zeolite framework on Cu ions is an important factor affecting the dynamic motion of Cu– NH_3 complexes. In a recent study, Godiksen et al. found that the different features in the hyperfine quadruplet of EPR spectra in Figure 8b (A and B are assigned to para- and meta-configurations, respectively, originating from different Al distributions) can be clearly visualized after the dehydration of Cu-CHA under O_2/He atmosphere but were quickly transformed into a single feature of new species after NH_3 adsorption [101]. This observation indicates that, despite the existence of various active sites, the EPR spectra of transient Cu– NH_3 species formed upon NH_3 solvation are identical.

Figure 8. (a) In situ Electron Paramagnetic Resonance (EPR) spectra of Cu-CHA after dehydration at 250 °C in an O₂/He flow (black line) and successive spectra during the slow exposure to trace water at room temperature: the anisotropic spectrum after 1.5 h is outlined in green, and the final spectrum after exposure to moist ambient conditions without flow for several days is shown in blue. Reproduced with permission from [99], copyright American Chemical Society, 2014. (b) In situ EPR spectra of the reaction of dehydrated Cu/Al = 0.09 with 1000 ppm NH₃ at 100 °C: thin lines are intermediate spectra spaced by 45 s. Reproduced with permission from [101], copyright Wiley-VCH, 2018.

3.4. Impedance Spectroscopy

In impedance spectroscopy (IS), the electrical properties of the sample are studied by applying an alternating voltage (U^*) of known amplitude and frequency (f) and by measuring the sample electric response in terms of alternating electrical current [102,103]. When applied to solids such as zeolites, in which extra-framework ions are present, the measured current arises from ion conduction within the zeolite crystal while the zeolite lattice itself is an electronic insulator with a wide bandgap of several electron volts [104–106]. Depending on the applied frequency, different ion motion modes are activated and can be followed by means of complex impedance-based in situ modulus spectroscopy (Figure 9). While the low-frequency range (LF, 10^{-1} – 10^3 Hz) is dominated by the long-range ion transport (e.g., NH₃-supported proton mobility), resonance peaks due to local displacement of charges or short-range ion movement can be detected in the high-frequency range (HF, 10^3 – 10^6 Hz) [106,107]. According to the abovementioned AIMD results [56], the inter-cage mobility of NH₃-solvated Cu species belongs to this second class of ion motion modes, leading to a resonance peak in the frequency range of 10^4 – 10^6 Hz. The high-frequency ion motion can be tracked by means of multi-frequency in situ IS measurements, which allow the collection of modulus plots, as shown in Figure 10 (more details about the so-called modulus spectroscopy may be found elsewhere in the literature) [103,106]. Investigations on a series of Cu-SSZ-13 samples prepared by ion exchange with the same H-form starting material revealed a correlation between Cu ion exchange level and the position of the HF resonance peak and that a higher Cu/Al ratio corresponds to a more pronounced HF shift of the resonance peak corresponding to enhanced ion mobility [108]. This trend was only observed when the samples were flushed with NH₃ and not during exposure to an inert atmosphere (i.e., N₂). Therefore, it could be concluded that the ion-motion phenomenon causing the peak shift is strictly correlated to NH₃ solvation of the Cu ions. The following IS studies confirmed the contribution of the dynamic Cu sites to HF resonance by performing in situ IS under SCR-related gas and temperature conditions [74,109]. During standard SCR (200 °C, NH₃/NO/O₂), the Cu sites are present both as Cu²⁺ and Cu⁺ species, and the latter one is expected to be more mobile than the former. The formation of such highly mobile NH₃-solvated complexes can be detected by IS according to the shift in the HF resonance peak compared to the same sample exposed to NH₃ after oxidative pretreatment (Figure 10a,b, red and black). In the absence of O₂, the re-oxidation of Cu⁺ to Cu²⁺ was

instead inhibited, and therefore, a complete reduction of the Cu sites was favored. As a consequence, the overall ion conductivity substantially increased, causing a further HF shift in the resonance peak (Figure 10a,b, blue). Similar effects were observed not only on Cu-SAPO-34 but also on other zeolites (e.g., Cu-ZSM-5 and Cu-SSZ-13) [74,109]. The simultaneous measurement of IS and DRIFTS (IS-DRIFTS) also allowed for the interpretation of the dielectric behaviors of different zeolites by the identification of key SCR-related intermediates, such as NH_4^+ intermediates [74].

Figure 9. Schematic representation of impedance-based in situ modulus spectroscopy for monitoring the long- and short-range motion of cations within Cu-zeolite catalysts: reproduced with permission from [110], copyright The Royal Society of Chemistry, 2019.

Figure 10. High-frequency resonance peaks in the modulus plots of (a) Cu-SAPO-34 and (b) Cu-ZSM-5 exposed to different gas atmospheres at 175 °C. NH_3 : 100 ppm in N_2 ; NO : 100 ppm in N_2 ; and O_2 : 10 vol% in N_2 . Cu-ZSM-5: Si/Al 13.5, Cu/Al 0.136; Cu-SAPO-34: [Al + P]/Si 11.2, Cu/Si 0.131. Reproduced with permission from [74], copyright American Chemical Society, 2018.

4. Role of Cu Mobility in NH_3 -SCR Catalysis

4.1. Regulating Low-Temperature Cu Redox

It is widely recognized that the NH_3 -SCR reaction mechanisms on Cu-CHA catalysts are different at low and high temperatures. As verified by in situ XAS, the dominant Cu species at low temperatures are in the form of Cu- NH_3 complexes [84]. Gao et al. proposed that two Cu sites were needed to participate in the rate-limiting step for SCR reaction at low temperatures, based on the facts that the SCR rate was correlated linearly with the square of Cu/Al ratio at a low temperature of 200 °C and linearly with the Cu/Al

ratio at a high temperature of 350 °C (Figure 11a). In the re-oxidation half-cycle ($\text{Cu}^+ \rightarrow \text{Cu}^{2+}$) of NH_3 -SCR catalysis, O_2 dissociation is well recognized as a rate-determining step [38,49,97,111–113]. Recently, it was found that the $[\text{Cu}^+(\text{NH}_3)_2]^+ - \text{O}_2 - [\text{Cu}^+(\text{NH}_3)_2]^+$ intermediate as the most likely transient Cu dimer species plays a crucial role in O_2 activation and dissociation [56,114,115]. Using DFT calculations, Lin et al. proved that the energy barrier for O_2 dissociation is much lower on a NH_3 -solvated Cu pair than on a single NH_3 -solvated Cu site [111]. However, the structure of the Cu dimer formed by the combination of O_2 molecules with two $[\text{Cu}^+(\text{NH}_3)_2]^+$ complexes is still controversial. Two highly similar structures, namely mono-(μ -oxo) dicopper(II) and bis(μ -oxo) dicopper(III), are frequently proposed in the literature. Based on operando spectroscopic evidence and DFT calculations, several recent studies proposed the bis(μ -oxo) dicopper(III) structure as a model, which means that the O_2 molecule is dissociated after adsorption by the Cu centers [56,94,111,114,115]. As suggested by the simulated diffusion area of dynamic Cu species within the CHA unit (the green spherical space shown in the Figure 11b) [56], the transport and pairing of $[\text{Cu}^+(\text{NH}_3)_2]^+$ between CHA cages is the rate-limiting step for Cu-CHA catalysts with low Cu loadings. As described in Section 2.2, due to electrostatic tethering to the framework Al centers, the dynamic diffusion distance of individual Cu– NH_3 species is limited to less than 9 Å, so only in the overlapping parts of the diffusion space is it feasible to form Cu dimers for O_2 activation. It is speculated that the low-temperature NH_3 -SCR efficiency at low Cu loadings can be improved by reinforcing the dynamic local motion of Cu– NH_3 species and by accordingly promoting the dissociation of O_2 [56,57,68]. With the increase of Cu loading, however, formation of Cu dimers is enabled by high Cu density and no longer limited by the long-distance migration process.

Figure 11. (a) SCR rate versus Cu/Al ratio results obtained at two reaction temperatures: 200 °C (upper panel) and 380 °C (lower panel). Reproduced with permission from [57], copyright American Chemical Society, 2017. (b) Snapshots taken from simulated initial (time = 0) and final (time → ∞) Cu^+ spatial distributions for three Cu-SSZ-13 samples with different compositions: reproduced with permission from [56], copyright American Association for the Advancement of Science, 2017.

4.2. Promoting Solid-State Cu Ion Exchange

The dynamics of Cu– NH_3 complexes can also be utilized to facilitate Cu ion exchange in solid-state synthesis [116]. Compared with the aqueous-phase method in the synthesis of metal ion-exchange zeolites, solid-state ion-exchange (SSIE) is relatively simple and generates no wastewater and other pollutants. Traditional SSIE synthesis of Cu-CHA catalysts requires thermal treatment of zeolite-copper oxide mixture powders at high temperatures of 700–800 °C for prolonged duration to introduce Cu ions into zeolites. Zeolite frameworks might be damaged during this continuous high-temperature treatment,

which restricts the wide application of SSIE. Vennestrom et al. found that the temperature required to initiate the exchange process can be significantly reduced in NH_3 -SCR-related atmosphere (such as NH_3 , NO , etc.) and that the Cu loading in the SSIE-synthesized Cu-zeolites are similar to those obtained by the traditional aqueous-phase ion-exchange method [117]. In the SSIE synthesis of Cu-CHA using Cu_2O and CuO as precursors, a mixture of $\text{NH}_3 + \text{NO}$ was found to promote the Cu ion introduction process, especially more pronounced in the case of CuO as a precursor, which indicates that the $[\text{Cu}^+(\text{NH}_3)_x]^+$ ($x \geq 2$) complexes are the main “transport carriers” for Cu ions to migrate into the zeolite framework [116]. They also found that the SSIE rate, i.e., the diffusion rate of transient Cu species, varied in different zeolite structures, in agreement with the simulation results described in Section 2.2. To explore the nature of SSIE-introduced Cu ions and their effects in NH_3 -SCR catalysis, Clemens et al. synthesized a series of Cu-SSZ-13 with different Cu loadings and characterized them using multiple techniques such as HD-XRD, XPS, and DRUVS [118]. They concluded that Cu^+ and Cu^{2+} are present inside zeolite pores at the same time and that there are more Cu^+ species in the SSIE-synthesized samples than those obtained by the aqueous ion-exchange method. Meanwhile, there are also more CuO species on the external surface of SSIE-synthesized zeolites, which can migrate into the framework pores during NH_3 -SCR to increase NO_x conversion. Recently, Vennestrom et al. verified the formation and dynamic migration of key “transport carriers” $[\text{Cu}^+(\text{NH}_3)_2]^+$ during the NH_3 -SSIE process by XANES [119].

4.3. Monitoring NH_3 Storage and Conversion

In addition to their traditional function as catalysts for NH_3 -SCR, zeolites can play another important role as impedimetric sensors for monitoring NH_3 storage and conversion levels. Such application of zeolites, which is based on NH_3 -supported proton transport, has been widely studied and even practically developed [61,120,121]. Precise sensing devices are needed in NH_3 -SCR systems in order to achieve the highest possible NO_x conversion without NH_3 slip [122]. The NH_3 -sensing properties of zeolites are of particular interest for collecting real-time information about the storage and conversion levels of NH_3 within SCR catalysts. The NH_3 -storage capacity, for example, decreases with the increase in temperature due to thermal desorption. Consequently, proton conductivity of the zeolite catalyst, which can be measured by impedance spectroscopy, decreases due to a lower content of NH_3 serving as “vehicle-like” molecules for proton transport [123,124]. However, in light of the recently discovered Cu mobility in Cu-CHA, the influence of mobilized Cu- NH_3 complexes must be taken into account. A comparison of Cu-SSZ-13 and Cu-SAPO-34 revealed that the NH_3 -solvated and -mobilized Cu species actually considerably altered the NH_3 -sensing response [109]. In absence of NO , the ionic conductivity signals (I_{IS}) of both catalysts followed the stepwise drop of NH_3 concentration, demonstrating a semiquantitative relationship between the two variables (Figure 12a). However, while the overall ion conductivity of Cu-SSZ-13 was stepwise lowered with the increase of the NO/NH_3 ratio in the gas mixture at 350 °C, the formation of highly mobile Cu^+-NH_3 complexes appeared to compensate NH_3 consumption by SCR conversion and led to a delayed decrease of I_{IS} signal in the case of Cu-SAPO-34 (Figure 12b). In situ modulus spectroscopy studies confirmed that the prevalence of short-range ion conduction (to which the Cu ions contribute) over the long-range one (dominated by the NH_3 -supported proton transport) was responsible for the unexpected NH_3 -SCR sensing behavior of Cu-SAPO-34. The mechanistic insights into the Cu-CHA catalyst as a sensor implied that tracking the condition-dependent Cu dynamics also provides new perspectives to understand the NH_3 -SCR reaction mechanisms.

Figure 12. (a) NH₃ sensing performance (in terms of I_{IS} change with the NH₃ concentration) over the Cu-SSZ-13 (red traces) and Cu-SAPO-34 (blue traces) catalysts at 200 and 350 °C and (b) sensing behavior (in terms of I_{IS} change with the NO/NH₃ ratio in the fed gas mixture) under NH₃-SCR conditions over Cu-SSZ-13 (red traces) and Cu-SAPO-34 (blue traces) commercial catalysts at 200 and 350 °C: reproduced with permission from [109], copyright American Chemical Society, 2018.

5. Summary and Perspectives

Under low-temperature NH₃-SCR reaction conditions, the Cu active sites in Cu-CHA catalysts mainly exist as NH₃-solvated and -mobilized complexes, which are different from traditional homogeneous or heterogeneous catalysts. Following the dynamics of these transiently formed Cu–NH₃ species can help to reconcile some of the controversies in NH₃-SCR catalysis, including the “seagull” profile of NO conversion as a function of temperature and the nonlinear relationship of Cu density and SCR rates. By summarizing recent studies on the unique reaction-driven Cu dynamics in Cu-CHA during low-temperature NH₃-SCR catalysis, this minireview aims to inspire new considerations for improving the DeNO_x activity of Cu-zeolite catalysts. Theoretical simulations by AIMD, DFT, etc. are essential to unveil the dynamics of Cu active species at the molecular level. According to the simulation results, the diffusion of mobile Cu species is determined by electrostatic tethering generated by the zeolite framework, and the maximum diffusion distance of the Cu–NH₃ species is predicted to be about 9 Å. This explains why the zeolite topology significantly influences the local movements of Cu species. While conventional spectroscopic techniques, such as in situ or operando XANES, DRIFTS, DRUVS, EPR, etc., could provide indirect evidence for the NH₃ solvation of Cu sites by detecting changes in the Cu coordination environment, the recently applied dielectric measuring technique, namely impedance-based in situ modulus spectroscopy, allows for direct tracking of the relaxation of Cu sites under relevant reaction conditions. Interestingly, the NH₃-solvated Cu species have been identified as essential participants not only in low-temperature NH₃-SCR catalysis but also in solid-state ion-exchange synthesis and have complicated the sensing properties of Cu-CHA zeolite as a sensor for direct monitoring of NH₃ storage and conversion.

In addition to being active centers in NH₃-SCR reaction, the dynamically formed, reversible, and temperature-dependent Cu sites have also been found to be potentially important in the selective methane-to-methanol oxidation reaction [125]. In addition, such transiently formed dynamic metal sites were also observed in ethene dimerization reactions over Ni ion-exchanged zeolites and may even exist more broadly in a wide variety of chemical reactions [126]. Although several advanced techniques, such as operando optical spectroscopy or X-ray-based micro-spectroscopy, have been developed to detect, mainly indirectly, the formation of transient active sites, their dynamic nature in zeolite cavity poses a challenge for the design of computational models and precise identification by spectroscopic techniques. Due to the complex dynamics, the transient species cannot be treated either as fixed sites or as unbound free molecules in calculations; therefore, more suitable models for mimicking such reaction systems need to be explored. A more accurate

computational model can also help to eliminate the interference of ion mobility on the spectrum and can improve the resolution of spectroscopic identification. It is expected that detailed understanding of dynamic species will help establish more reliable guidelines for the development of low-temperature NH_3 -SCR catalysts or even develop new concepts for a certain class of reaction systems with dynamic metal species as active centers.

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References

1. Unger, N.; Zheng, Y.; Yue, X.; Harper, K.L. Mitigation of ozone damage to the world's land ecosystems by source sector. *Nat. Clim. Chang.* **2020**, *10*, 134–137. [\[CrossRef\]](#)
2. Yu, T.; Hao, T.; Fan, D.; Wang, J.; Shen, M.; Li, W. Recent NH_3 -SCR Mechanism Research over Cu/SAPO-34 Catalyst. *J. Phys. Chem. C* **2014**, *118*, 6565–6575. [\[CrossRef\]](#)
3. Li, Y.; Deng, J.; Song, W.; Liu, J.; Zhao, Z.; Gao, M.; Wei, Y.; Zhao, L. The Nature of Cu Species in Cu-SAPO-18 Catalyst for NH_3 -SCR: Combination of Experiments and DFT Calculations. *J. Phys. Chem. C* **2016**, *120*, 14669–14680. [\[CrossRef\]](#)
4. Lezcano-Gonzalez, I.; Deka, U.; Arstad, B.; Deyne, Y.D.; Hemelsoet, K.; Waroquier, M.; Speybroeck, V.V.; Weckhuysen, B.M.; Beale, A.M. Determining the storage, availability and reactivity of NH_3 within Cu-Chabazite-based Ammonia Selective Catalytic Reduction systems. *Phys. Chem. Chem. Phys.* **2013**, *16*, 1639–1650. [\[CrossRef\]](#) [\[PubMed\]](#)
5. Brandenberger, S.; Kröcher, O.; Wokaun, A.; Tissler, A. The role of Brønsted acidity in the selective catalytic reduction of NO with ammonia over Fe-ZSM-5. *J. Catal.* **2009**, *268*, 297–306. [\[CrossRef\]](#)
6. Maier, S.M.; Jentys, A.; Janousch, M.; Bokhoven, J.A.V.; Lercher, J.A. Unique dynamic changes of Fe cationic species under NH_3 -SCR conditions. *J. Phys. Chem. C* **2012**, *116*, 5846–5856. [\[CrossRef\]](#)
7. Fickel, D.W.; D'Addio, E.; Lauterbach, J.A.; Lobo, R.F. The ammonia selective catalytic reduction activity of copper-exchanged small-pore zeolites. *Appl. Catal. B Environ.* **2011**, *102*, 441–448. [\[CrossRef\]](#)
8. Kumar, A.; Smith, M.A.; Kamasamudram, K.; Currier, N.W.; Yezerets, A. Chemical deSO_x: An effective way to recover Cu-zeolite SCR catalysts from sulfur poisoning. *Catal. Today* **2016**, *267*, 10–16. [\[CrossRef\]](#)
9. Olsson, L.; Wijayanti, K.; Leistner, K.; Kumar, A.; Joshi, S.Y.; Kamasamudram, K.; Currier, N.W.; Yezerets, A. A kinetic model for sulfur poisoning and regeneration of Cu/SSZ-13 used for NH_3 -SCR. *Appl. Catal. B Environ.* **2016**, *183*, 394–406. [\[CrossRef\]](#)
10. Wijayanti, K.; Leistner, K.; Chand, S.; Kumar, A.; Kamasamudram, K.; Currier, N.W.; Yezerets, A.; Olsson, L. Deactivation of Cu-SSZ-13 by SO₂ exposure under SCR conditions. *Catal. Sci. Technol.* **2016**, *6*, 2565–2579. [\[CrossRef\]](#)
11. Zheng, Y.; Harold, M.P.; Luss, D. Effects of CO, H₂ and C₃H₆ on Cu-SSZ-13 catalyzed NH_3 -SCR. *Catal. Today* **2016**, *264*, 44–54. [\[CrossRef\]](#)
12. Schmidt, J.E.; Oord, R.; Guo, W.; Poplawsky, J.D.; Weckhuysen, B.M. Nanoscale tomography reveals the deactivation of automotive copper-exchanged zeolite catalysts. *Nat. Commun.* **2017**, *8*, 1666. [\[CrossRef\]](#) [\[PubMed\]](#)
13. Usui, T.; Liu, Z.; Ibe, S.; Zhu, J.; Anand, C.; Igarashi, H.; Onaya, N.; Sasaki, Y.; Shiramata, Y.; Kusamoto, T.; et al. Improve the Hydrothermal Stability of Cu-SSZ-13 Zeolite Catalyst by Loading a Small Amount of Ce. *ACS Catal.* **2018**, *8*, 9165–9173. [\[CrossRef\]](#)
14. Usui, T.; Liu, Z.; Igarashi, H.; Sasaki, Y.; Shiramata, Y.; Yamada, H.; Ohara, K.; Kusamoto, T.; Wakihara, T. Identifying the Factors Governing the Early-Stage Degradation of Cu-Chabazite Zeolite for NH_3 -SCR. *ACS Omega* **2019**, *4*, 3653–3659. [\[CrossRef\]](#) [\[PubMed\]](#)
15. Selleri, T.; Nova, I.; Tronconi, E.; Schmeisser, V.; Seher, S. The impact of light and heavy hydrocarbons on the NH_3 -SCR activity of commercial Cu- and Fe-zeolite catalysts. *Catal. Today* **2019**, *320*, 100–111. [\[CrossRef\]](#)
16. Ruggeri, M.P.; Nova, I.; Tronconi, E.; Collier, J.E.; York, A.P.E. Structure-Activity Relationship of Different Cu-Zeolite Catalysts for NH_3 -SCR. *Top. Catal.* **2016**, *59*, 875–881. [\[CrossRef\]](#)

17. Beale, A.M.; Gao, F.; Lezcano-Gonzalez, I.; Peden, C.H.F.; Szanyi, J. Recent advances in automotive catalysis for NO_x emission control by small-pore microporous materials. *Chem. Soc. Rev.* **2015**, *44*, 7371–7405. [CrossRef]
18. Gao, F.; Wang, Y.; Washton, N.M.; Kollar, M.; Szanyi, J. Effects of Alkali and Alkaline Earth Cations on the Activity and Hydrothermal Stability of Cu/SSZ-13 NH₃-SCR Catalysts. *ACS Catal.* **2015**, *5*, 6780–6791. [CrossRef]
19. Wang, J.; Zhao, H.; Haller, G.; Li, Y. Recent advances in the selective catalytic reduction of NO_x with NH₃ on Cu-Chabazite catalysts. *Appl. Catal. B Environ.* **2017**, *202*, 346–354. [CrossRef]
20. Xie, L.; Liu, F.; Ren, L.; Shi, X.; Shou, F. Excellent Performance of One-Pot Synthesized Cu-SSZ-13 Catalyst for the Selective Catalytic Reduction of NO_x with NH₃. *Environ. Sci. Technol.* **2014**, *48*, 566–572. [CrossRef]
21. Damma, D.; Ettireddy, P.R.; Reddy, B.M.; Smirniotis, P.G. A Review of Low Temperature NH₃-SCR for Removal of NO_x. *Catalysts* **2019**, *9*, 349. [CrossRef]
22. Shan, W.; Song, H. Catalysts for the selective catalytic reduction of NO_x with NH₃ at low temperature. *Catal. Sci. Technol.* **2015**, *5*, 4280–4288. [CrossRef]
23. Colombo, M.; Nova, I.; Tronconi, E.; Schmeisser, V.; Weibel, M. Mathematical modelling of cold start effects over zeolite SCR catalysts for exhaust gas aftertreatment. *Catal. Today* **2014**, *231*, 99–104. [CrossRef]
24. Su, W.; Chang, H.; Peng, Y.; Zhang, C.; Wi, J. Reaction Pathway Investigation on the Selective Catalytic Reduction of NO with NH₃ over Cu/SSZ-13 at Low Temperatures. *Environ. Sci. Technol.* **2015**, *49*, 467–473. [CrossRef] [PubMed]
25. De Prins, M.; Verheyen, E.; Hoffmann, A.; Vanbutsele, G.; Sree, S.P.; Kerkhofs, S.; Van Tendeloo, L.; Schuetze, F.-W.; Martens, J. Structural parameters governing low temperature activity of small pore copper zeolites in NH₃-SCR. *J. Catal.* **2020**, *390*, 224–236. [CrossRef]
26. Fan, C.; Ming, S.; Chen, Z.; Pang, L.; Guo, W.; Dong, C.; Liu, P.; Li, T. Cold Start Wetting Effect on the Catalytic Property and Hydrothermal Stability of a Cu-SSZ-13 Catalyst for NH₃-SCR. *Ind. Eng. Chem. Res.* **2020**, *59*, 12304–12312. [CrossRef]
27. Liu, Z.; Wakihara, T.; Oshima, K.; Nishioka, D.; Hotta, Y. Widening Synthesis Bottlenecks: Realization of Ultrafast and Continuous-Flow Synthesis of High-Silica Zeolite SSZ-13 for NO_x Removal. *Angew. Chem. Int. Ed.* **2015**, *54*, 5683–5687. [CrossRef]
28. Baerlocher, C.; McCusker, L.B. Database of Zeolite Structures. Available online: <http://www.iza-structure.org/databases/> (accessed on 25 November 2020).
29. Moreno-Gonzalez, M.; Millan, R.; Concepcion, P.; Blasco, T.; Boronat, M. Spectroscopic Evidence and Density Functional Theory (DFT) Analysis of Low-Temperature Oxidation of Cu⁺ to Cu²⁺NO_x in Cu-CHA Catalysts: Implications for the SCR-NO_x Reaction Mechanism. *ACS Catal.* **2019**, *9*, 2725–2738. [CrossRef]
30. Astala, R.; Auerbach, S.M.; Monson, P.A. Density functional theory study of silica zeolite structures: Stabilities and mechanical properties of SOD, LTA, CHA, MOR, and MFI. *J. Phys. Chem. B* **2004**, *108*, 9208–9215. [CrossRef]
31. Burton, A.W.; Lee, G.S.; Zones, S.I. Phase selectivity in the syntheses of cage-based zeolite structures: An investigation of thermodynamic interactions between zeolite hosts and structure directing agents by molecular modeling. *Microporous Mesoporous Mater.* **2006**, *90*, 129–144. [CrossRef]
32. Nakatsuka, A.; Okada, H.; Fujiwara, K.; Nakayama, N.; Mizota, T. Crystallographic configurations of water molecules and exchangeable cations in a hydrated natural CHA-zeolite (chabazite). *Microporous Mesoporous Mater.* **2007**, *102*, 188–195. [CrossRef]
33. Liang, J.; Su, J.; Wang, Y.; Lin, Z.; Mu, W.; Zheng, H.; Zou, R.; Liao, F.; Lin, J. CHA-type zeolites with high boron content: Synthesis, structure and selective adsorption properties. *Microporous Mesoporous Mater.* **2014**, *194*, 97–105. [CrossRef]
34. Lok, B.M.; Messina, C.A.; Patton, R.L.; Gajek, R.T.; Cannan, T.R.; Flanigen, E.M. Silicoaluminophosphate molecular sieves: Another new class of microporous crystalline inorganic solids. *Chem. Inf.* **1985**, *106*, 6092–6093. [CrossRef]
35. Chen, Z.; Fan, C.; Pang, L.; Ming, S.; Guo, W.; Liu, P.; Chen, H.; Li, T. One-pot synthesis of high performance Cu-SAPO-18 catalyst for NO reduction by NH₃-SCR: Influence of silicon content on the catalytic properties of Cu-SAPO-18. *Chem. Eng. J.* **2018**, *348*, 608–617. [CrossRef]
36. Paolucci, C.; Di Iorio, J.R.; Ribeiro, F.H.; Gounder, R.; Schneider, W.F. Catalysis Science of NO_x Selective Catalytic Reduction With Ammonia Over Cu-SSZ-13 and Cu-SAPO-34. *Adv. Catal.* **2016**, *59*, 1–107.
37. Fan, C.; Chen, Z.; Pang, L.; Ming, S.; Zhang, X.; Albert, K.B.; Liu, P.; Chen, H.; Li, T. The influence of Si/Al ratio on the catalytic property and hydrothermal stability of Cu-SSZ-13 catalysts for NH₃-SCR. *Appl. Catal. A Gen.* **2018**, *550*, 256–265. [CrossRef]
38. Paolucci, C.; Parekh, A.A.; Khurana, I.; Di Iorio, J.R.; Li, H.; Albarracin Caballero, J.D.; Shih, A.J.; Anggara, T.; Delgass, W.N.; Miller, J.T. Catalysis in a cage: Condition-dependent speciation and dynamics of exchanged Cu cations in SSZ-13 zeolites. *J. Am. Chem. Soc.* **2016**, *138*, 6028–6048. [CrossRef]
39. Gao, F.; Washton, N.M.; Wang, Y.; Kollar, M.; Szanyi, J.; Peden, C.H.F. Effects of Si/Al ratio on Cu/SSZ-13 NH₃-SCR catalysts: Implications for the active Cu species and the roles of Bronsted acidity. *J. Catal.* **2015**, *331*, 25–38. [CrossRef]
40. Kwak, J.H.; Zhu, H.; Lee, J.H.; Peden, C.H.; Szanyi, J. Two different cationic positions in Cu-SSZ-13? *Chem. Commun.* **2012**, *48*, 4758–4760. [CrossRef]
41. Andersen, C.W.; Bremholm, M.; Vennestrom, P.N.R.; Blichfeld, A.B.; Lundegaard, L.F.; Iversen, B.B. Location of Cu²⁺ in CHA zeolite investigated by X-ray diffraction using the Rietveld/maximum entropy method. *IUCr* **2014**, *1*, 382–386. [CrossRef]
42. Borfecchia, E.; Beato, P.; Svelle, S.; Olsbye, U.; Lamberti, C.; Bordiga, S. Cu-CHA—A model system for applied selective redox catalysis. *Chem. Soc. Rev.* **2018**, *47*, 8097–8133. [CrossRef] [PubMed]
43. Korhonen, S.T.; Fickel, D.W.; Lobo, R.F.; Weckhuysen, B.M.; Beale, A.M. Isolated Cu²⁺ ions: Active sites for selective catalytic reduction of NO. *Chem. Commun.* **2011**, *47*, 800–802. [CrossRef] [PubMed]

44. Deka, U.; Juhin, A.; Eilertsen, E.A.; Emerich, H.; Green, M.A.; Korhonen, S.T.; Weckhuysen, B.M.; Beale, A.M. Confirmation of isolated Cu^{2+} ions in SSZ-13 zeolite as active sites in NH_3 -selective catalytic reduction. *J. Phys. Chem. C* **2012**, *116*, 4809–4818. [\[CrossRef\]](#)
45. Bates, S.A.; Verma, A.A.; Paolucci, C.; Parekh, A.A.; Anggara, T.; Yezerets, A.; Schneider, W.F.; Miller, J.T.; Delgass, W.N.; Ribeiro, F.H. Identification of the active Cu site in standard selective catalytic reduction with ammonia on Cu-SSZ-13. *J. Catal.* **2014**, *312*, 87–97. [\[CrossRef\]](#)
46. Leistner, K.; Xie, K.; Kumar, A.; Kamasamudram, K.; Olsson, L. Ammonia Desorption Peaks Can Be Assigned to Different Copper Sites in Cu/SSZ-13. *Catal. Lett.* **2017**, *147*, 1882–1890. [\[CrossRef\]](#)
47. Concepcion, P.; Boronat, M.; Millan, R.; Moliner, M.; Corma, A. Identification of Distinct Copper Species in Cu-CHA Samples Using NO as Probe Molecule. A Combined IR Spectroscopic and DFT Study. *Top. Catal.* **2017**, *60*, 1653–1663. [\[CrossRef\]](#)
48. Martini, A.; Alladio, E.; Borfecchia, E. Determining Cu-Speciation in the Cu-CHA Zeolite Catalyst: The Potential of Multivariate Curve Resolution Analysis of In Situ XAS Data. *Top. Catal.* **2018**, *61*, 1396–1407. [\[CrossRef\]](#)
49. Janssens, T.V.W.; Falsig, H.; Lundegaard, L.F.; Vennestrom, P.N.R.; Rasmussen, S.B.; Moses, P.G.; Giordanino, F.; Borfecchia, E.; Lomachenko, K.A.; Lamberti, C.; et al. A Consistent Reaction Scheme for the Selective Catalytic Reduction of Nitrogen Oxides with Ammonia. *ACS Catal.* **2015**, *5*, 2832–2845. [\[CrossRef\]](#)
50. Marberger, A.; Petrov, A.W.; Steiger, P.; Elsener, M.; Krocher, O.; Nachtegaal, M.; Ferri, D. Time-resolved copper speciation during selective catalytic reduction of NO on Cu-SSZ-13. *Nat. Catal.* **2018**, *1*, 221–227. [\[CrossRef\]](#)
51. Zhang, T.; Qiu, F.; Chang, H.; Li, X.; Li, J. Identification of active sites and reaction mechanism on low-temperature SCR activity over Cu-SSZ-13 catalysts prepared by different methods. *Catal. Sci. Technol.* **2016**, *6*, 6294–6304. [\[CrossRef\]](#)
52. Gao, F.; Peden, C.H.F. Recent Progress in Atomic-Level Understanding of Cu/SSZ-13 Selective Catalytic Reduction Catalysts. *Catalysts* **2018**, *8*, 140. [\[CrossRef\]](#)
53. McEwen, J.S.; Anggara, T.; Schneider, W.F.; Kispersky, V.F.; Miller, J.T.; Delgass, W.N.; Ribeiro, F.H.J.C.T. Integrated operando X-ray absorption and DFT characterization of Cu-SSZ-13 exchange sites during the selective catalytic reduction of NO_x with NH_3 . *Catal. Today* **2012**, *184*, 129–144. [\[CrossRef\]](#)
54. Li, X.; Zhao, Y.; Zhao, H.; Liu, M.; Ma, Y.; Yong, X.; Chen, H.; Li, Y. The Cu migration of Cu-SAPO-34 catalyst for ammonia selective catalytic reduction of NO_x during high temperature hydrothermal aging treatment. *Catal. Today* **2019**, *327*, 126–133. [\[CrossRef\]](#)
55. Kwak, J.H.; Varga, T.; Peden, C.H.F.; Gao, F.; Hanson, J.C.; Szanyi, J. Following the movement of Cu ions in a SSZ-13 zeolite during dehydration, reduction and adsorption: A combined in situ TP-XRD, XANES/DRIFTS study. *J. Catal.* **2014**, *314*, 83–93. [\[CrossRef\]](#)
56. Paolucci, C.; Khurana, I.; Parekh, A.A.; Li, S.; Shih, A.J.; Li, H.; Di Iorio, J.R.; Albarracin-Caballero, J.D.; Yezerets, A.; Miller, J.T.; et al. Dynamic multinuclear sites formed by mobilized copper ions in NO_x selective catalytic reduction. *Science* **2017**, *357*, 898. [\[CrossRef\]](#) [\[PubMed\]](#)
57. Gao, F.; Mei, D.; Wang, Y.; Szanyi, J.; Peden, C.H.F. Selective Catalytic Reduction over Cu/SSZ-13: Linking Homo- and Heterogeneous Catalysis. *J. Am. Chem. Soc.* **2017**, *139*, 4935–4942. [\[CrossRef\]](#)
58. Beale, A.M.; Lezcano-Gonzalez, I.; Slawinski, W.A.; Wragg, D.S. Correlation between Cu ion migration behaviour and deNO(x) activity in Cu-SSZ-13 for the standard NH_3 -SCR reaction. *Chem. Commun.* **2016**, *55*, 1667. [\[CrossRef\]](#)
59. Andersen, C.W.; Borfecchia, E.; Bremholm, M.; Jorgensen, M.R.V.; Vennestrom, P.N.R.; Lamberti, C.; Lundegaard, L.F.; Iversen, B.B. Redox-Driven Migration of Copper Ions in the Cu-CHA Zeolite as Shown by the In Situ PXRD/XANES Technique. *Angew. Chem. Int. Ed.* **2017**, *56*, 10367–10372. [\[CrossRef\]](#)
60. Chen, P.; Jablonska, M.; Weide, P.; Caumanns, T.; Weirich, T.; Muhler, M.; Moos, R.; Palkovits, R.; Simon, U. Formation and Effect of NH_4^+ Intermediates in NH_3 -SCR over Fe-ZSM-5 Zeolite Catalysts. *ACS Catal.* **2016**, *6*, 7696–7700. [\[CrossRef\]](#)
61. Chen, P.; Schönebaum, S.; Simons, T.; Rauch, D.; Moos, R.; Simon, U. In situ monitoring of DeNO_x-SCR on zeolite catalysts by means of simultaneous impedance and DRIFT spectroscopy. *Procedia Eng.* **2015**, *120*, 257–260. [\[CrossRef\]](#)
62. Chen, P.; Schoenebaum, S.; Simons, T.; Rauch, D.; Dietrich, M.; Moos, R.; Simon, U. Correlating the Integral Sensing Properties of Zeolites with Molecular Processes by Combining Broadband Impedance and DRIFT Spectroscopy—A New Approach for Bridging the Scales. *Sensors* **2015**, *15*, 28915–28941. [\[CrossRef\]](#) [\[PubMed\]](#)
63. Chen, P.; Simboeck, J.; Schoenebaum, S.; Rauch, D.; Simons, T.; Palkovits, R.; Moos, R.; Simon, U. Monitoring NH_3 storage and conversion in Cu-ZSM-5 and Cu-SAPO-34 catalysts for NH_3 -SCR by simultaneous impedance and DRIFT spectroscopy. *Sens. Actuators B Chem.* **2016**, *236*, 1075–1082. [\[CrossRef\]](#)
64. Simons, T.; Chen, P.; Rauch, D.; Moos, R.; Simon, U. Sensing catalytic conversion: Simultaneous DRIFT and impedance spectroscopy for in situ monitoring of NH_3 -SCR on zeolites. *Sens. Actuators B Chem.* **2016**, *224*, 492–499. [\[CrossRef\]](#)
65. Chen, P.; Rauch, D.; Weide, P.; Schoenebaum, S.; Simons, T.; Muhler, M.; Moos, R.; Simon, U. The effect of Cu and Fe cations on NH_3 -supported proton transport in DeNO(x)-SCR zeolite catalysts. *Catal. Sci. Technol.* **2016**, *6*, 3362–3366. [\[CrossRef\]](#)
66. Simons, T.; Simon, U. Zeolites as nanoporous, gas-sensitive materials for in situ monitoring of DeNO(x)-SCR. *Beilstein J. Nanotechnol.* **2012**, *3*, 667–673. [\[CrossRef\]](#) [\[PubMed\]](#)
67. Chen, P.; Moos, R.; Simon, U. Metal Loading Affects the Proton Transport Properties and the Reaction Monitoring Performance of Fe-ZSM-5 and Cu-ZSM-5 in NH_3 -SCR. *J. Phys. Chem. C* **2016**, *120*, 25361–25370. [\[CrossRef\]](#)

68. Rizzotto, V.; Chen, D.; Tabak, B.M.; Yang, J.-Y.; Ye, D.; Simon, U.; Chen, P. Spectroscopic identification and catalytic relevance of NH_4^+ intermediates in selective NO_x reduction over Cu-SSZ-13 zeolites. *Chemosphere* **2020**, *250*, 126272. [CrossRef]
69. Paolucci, C.; Verma, A.A.; Bates, S.A.; Kispersky, V.F.; Miller, J.T.; Gounder, R.; Delgass, W.N.; Ribeiro, F.H.; Schneider, W.F. Isolation of the Copper Redox Steps in the Standard Selective Catalytic Reduction on Cu-SSZ-13. *Angew. Chem. Int. Ed.* **2014**, *53*, 11828–11833. [CrossRef]
70. Paolucci, C.; Di Iorio, J.R.; Schneider, W.F.; Gounder, R. Solvation and Mobilization of Copper Active Sites in Zeolites by Ammonia: Consequences for the Catalytic Reduction of Nitrogen Oxides. *Acc. Chem. Res.* **2020**, *53*, 1881–1892. [CrossRef]
71. Liu, K.; Yan, Z.; Shan, W.; Shan, Y.; Shi, X.; He, H. Quantitative determination of the Cu species, acid sites and NH_3 -SCR mechanism on Cu-SSZ-13 and H-SSZ-13 at low temperatures. *Catal. Sci. Technol.* **2020**, *10*, 1135–1150. [CrossRef]
72. Luo, J.; Gao, F.; Kamasamudram, K.; Currier, N.; Peden, C.H.F.; Yezerets, A. New insights into Cu/SSZ-13 SCR catalyst acidity. Part I: Nature of acidic sites probed by NH_3 titration. *J. Catal.* **2017**, *348*, 291–299. [CrossRef]
73. Chen, L.; Janssens, T.V.W.; Skoglundh, M.; Gronbeck, H. Interpretation of NH_3 -TPD Profiles from Cu-CHA Using First-Principles Calculations. *Top. Catal.* **2019**, *62*, 93–99. [CrossRef]
74. Chen, P.; Khetan, A.; Jablonska, M.; Simboeck, J.; Muhler, M.; Palkovits, R.; Pitsch, H.; Simon, U. Local dynamics of copper active sites in zeolite catalysts for selective catalytic reduction of NO_x with NH_3 . *Appl. Catal. B Environ.* **2018**, *237*, 263–272. [CrossRef]
75. Xu, L.; Wang, C.; Chang, H.; Wu, Q.; Zhang, T.; Li, J. New Insight into SO_2 Poisoning and Regeneration of $\text{CeO}_2\text{-WO}_3/\text{TiO}_2$ and $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ Catalysts for Low-Temperature NH_3 -SCR. *Environ. Sci. Technol.* **2018**, *52*, 7064–7071. [CrossRef]
76. Moreno-González, M.; Hueso, B.; Boronat, M.; Blasco, T.; Corma, A. Ammonia-containing species formed in Cu-Chabazite as per in situ EPR, solid-state NMR, and DFT calculations. *J. Phys. Chem. Lett.* **2015**, *6*, 1011–1017. [CrossRef]
77. Wu, Z.; Ran, R.; Ma, Y.; Wu, X.; Si, Z.; Weng, D. Quantitative control and identification of copper species in Cu-SAPO-34: A combined UV-vis spectroscopic and H-2-TPR analysis. *Res. Chem. Intermed.* **2019**, *45*, 1309–1325. [CrossRef]
78. Villamaina, R.; Liu, S.; Nova, I.; Tronconi, E.; Ruggeri, M.P.; Collier, J.; York, A.; Thompsett, D. Speciation of Cu Cations in Cu-CHA Catalysts for NH_3 -SCR: Effects of $\text{SiO}_2/\text{Al}_2\text{O}_3$ Ratio and Cu-Loading Investigated by Transient Response Methods. *ACS Catal.* **2019**, *9*, 8916–8927. [CrossRef]
79. Xie, K.; Woo, J.; Bernin, D.; Kumar, A.; Kamasamudram, K.; Olsson, L. Insights into hydrothermal aging of phosphorus-poisoned Cu-SSZ-13 for NH_3 -SCR. *Appl. Catal. B Environ.* **2019**, *241*, 205–216. [CrossRef]
80. Xie, K.; Wang, A.; Woo, J.; Kumar, A.; Kamasamudram, K.; Olsson, L. Deactivation of Cu-SSZ-13 SCR catalysts by vapor-phase phosphorus exposure. *Appl. Catal. B Environ.* **2019**, *256*. [CrossRef]
81. Chen, L.; Jansson, J.; Skoglundh, M.; Gronbeck, H. Mechanism for Solid-State Ion Exchange of Cu^+ into Zeolites. *J. Phys. Chem. C* **2016**, *120*, 29182–29189. [CrossRef]
82. O'Malley, A.J.; Sarwar, M.; Armstrong, J.; Catlow, C.R.A.; Silverwood, I.P.; York, A.P.E.; Hitchcock, I. Comparing ammonia diffusion in NH_3 -SCR zeolite catalysts: A quasielastic neutron scattering and molecular dynamics simulation study. *Phys. Chem. Chem. Phys.* **2018**, *20*, 11976–11986. [CrossRef]
83. Guenter, T.; Doronkin, D.E.; Carvalho, H.W.P.; Casapu, M.; Grunwaldt, J.D. HERFD-XANES and XES as complementary operando tools for monitoring the structure of Cu-based zeolite catalysts during NO_x -removal by ammonia SCR. *J. Phys. Conf. Ser.* **2016**, *712*, 012071. [CrossRef]
84. Lomachenko, K.A.; Borfecchia, E.; Negri, C.; Berlier, G.; Lamberti, C.; Beato, P.; Falsig, H.; Bordiga, S. The Cu-CHA deNO(x) Catalyst in Action: Temperature-Dependent NH_3 -Assisted Selective Catalytic Reduction Monitored by Operando XAS and XES. *J. Am. Chem. Soc.* **2016**, *138*, 12025–12028. [CrossRef]
85. Pankin, I.A.; Martini, A.; Lomachenko, K.A.; Soldatov, A.V.; Bordiga, S.; Borfecchia, E. Identifying Cu-oxo species in Cu-zeolites by XAS: A theoretical survey by DFT-assisted XANES simulation and EXAFS wavelet transform. *Catal. Today* **2020**, *345*, 125–135. [CrossRef]
86. Lomachenko, K.A.; Borfecchia, E.; Bordiga, S.; Soldatov, A.V.; Beato, P.; Lamberti, C. Active sites in Cu-SSZ-13 deNO(x) catalyst under reaction conditions: A XAS/XES perspective. *J. Phys. Conf. Ser.* **2016**, *712*, 012041. [CrossRef]
87. Fahami, A.R.; Guenter, T.; Doronkin, D.E.; Casapu, M.; Zengel, D.; Vuong, T.H.; Simon, M.; Breher, F.; Kucherov, A.V.; Brueckner, A.; et al. The dynamic nature of Cu sites in Cu-SSZ-13 and the origin of the seagull NO_x conversion profile during NH_3 -SCR. *React. Chem. Eng.* **2019**, *4*, 1000–1018. [CrossRef]
88. Borfecchia, E.; Negri, C.; Lomachenko, K.A.; Lamberti, C.; Janssens, T.V.W.; Berlier, G. Temperature-dependent dynamics of NH_3 -derived Cu species in the Cu-CHA SCR catalyst. *React. Chem. Eng.* **2019**, *4*, 1067–1080. [CrossRef]
89. Zhu, H.; Kwak, J.H.; Peden, C.H.F.; Szanyi, J. In situ DRIFTS-MS studies on the oxidation of adsorbed NH_3 by NO_x over a Cu-SSZ-13 zeolite. *Catal. Today* **2013**, *205*, 16–23. [CrossRef]
90. Jangjou, Y.; Do, Q.; Gu, Y.; Lim, L.-G.; Sun, H.; Wang, D.; Kumar, A.; Li, J.; Grabow, L.C.; Epling, W.S. Nature of Cu Active Centers in Cu-SSZ-13 and Their Responses to SO_2 Exposure. *ACS Catal.* **2018**, *8*, 1325–1337. [CrossRef]
91. Negri, C.; Signorile, M.; Porcaro, N.G.; Borfecchia, E.; Berlier, G.; Janssens, T.V.W.; Bordiga, S. Dynamic $\text{Cu}^{2+}/\text{CuI}$ speciation in Cu-CHA catalysts by in situ Diffuse Reflectance UV-vis-NIR spectroscopy. *Appl. Catal. A Gen.* **2019**, *578*, 1–9. [CrossRef]
92. Goltl, F.; Conrad, S.; Wolf, P.; Muller, P.; Love, A.M.; Burt, S.P.; Wheeler, J.N.; Hamers, R.J.; Hummer, K.; Kresse, G.; et al. UV-Vis and Photoluminescence Spectroscopy to Understand the Coordination of Cu Cations in the Zeolite SSZ-13. *Chem. Mater.* **2019**, *31*, 9582–9592. [CrossRef]

93. Giordanino, F.; Vennestrom, P.N.R.; Lundegaard, L.F.; Stappen, F.N.; Mossin, S.; Beato, P.; Bordiga, S.; Lamberti, C. Characterization of Cu-exchanged SSZ-13: A comparative FTIR, UV-Vis, and EPR study with Cu-ZSM-5 and Cu-beta with similar Si/Al and Cu/Al ratios. *Dalton Trans.* **2013**, *42*, 12741–12761. [[CrossRef](#)] [[PubMed](#)]
94. Oda, A.; Shionoya, H.; Hotta, Y.; Takewaki, T.; Sawabe, K.; Satsuma, A. Spectroscopic Evidence of Efficient Generation of Dicopper Intermediate in Selective Catalytic Reduction of NO over Cu-Ion-Exchanged Zeolites. *ACS Catal.* **2020**, *10*, 12333–12339. [[CrossRef](#)]
95. Liu, L.; Wu, X.; Ma, Y.; Zhang, X.; Ran, R.; Si, Z.; Weng, D. Potassium deactivation of Cu-SSZ-13 catalyst for NH₃-SCR: Evolution of salts, zeolite and copper species. *Chem. Eng. J.* **2020**, 383. [[CrossRef](#)]
96. Liu, C.; Kubota, H.; Amada, T.; Kon, K.; Toyao, T.; Maeno, Z.; Ueda, K.; Ohyama, J.; Satsuma, A.; Tanigawa, T.; et al. In Situ Spectroscopic Studies on the Redox Cycle of NH₃-SCR over Cu-CHA Zeolites. *Chemcatchem* **2020**, *12*, 3050–3059. [[CrossRef](#)]
97. Gao, F.; Walter, E.D.; Karp, E.M.; Luo, J.; Tonkyn, R.G.; Kwak, J.H.; Szanyi, J.; Peden, C.H.F. Structure–activity relationships in NH₃-SCR over Cu-SSZ-13 as probed by reaction kinetics and EPR studies. *J. Catal.* **2013**, *300*, 20–29. [[CrossRef](#)]
98. Godiksen, A.; Vennestrom, P.N.R.; Rasmussen, S.B.; Mossin, S. Identification and Quantification of Copper Sites in Zeolites by Electron Paramagnetic Resonance Spectroscopy. *Top. Catal.* **2017**, *60*, 13–29. [[CrossRef](#)]
99. Godiksen, A.; Stappen, F.N.; Vennestrom, P.N.R.; Giordanino, F.; Rasmussen, S.B.; Lundegaard, L.F.; Mossin, S. Coordination Environment of Copper Sites in Cu-CHA Zeolite Investigated by Electron Paramagnetic Resonance. *J. Phys. Chem. C* **2014**, *118*, 23126–23138. [[CrossRef](#)]
100. Fernandez, E.; Moreno-Gonzalez, M.; Moliner, M.; Blasco, T.; Boronat, M.; Corma, A. Modeling of EPR Parameters for Cu(II): Application to the Selective Reduction of NO_x Catalyzed by Cu-Zeolites. *Top. Catal.* **2018**, *61*, 810–832. [[CrossRef](#)]
101. Godiksen, A.; Isaksen, O.L.; Rasmussen, S.B.; Vennestrom, P.N.R.; Mossin, S. Site-Specific Reactivity of Copper Chabazite Zeolites with Nitric Oxide, Ammonia, and Oxygen. *Chemcatchem* **2018**, *10*, 366–370. [[CrossRef](#)]
102. Barsukov, Y.; Macdonald, J. *Impedance Spectroscopy: Theory, Experiment, and Applications*; John Wiley & Sons: Hoboken, NJ, USA, 2005.
103. Lvovich, V.F. *Impedance Spectroscopy: Applications to Electrochemical and Dielectric Phenomena*; John Wiley & Sons: Hoboken, NJ, USA, 2012.
104. Beattie, I.R. The electrical conductivity of analcite and ion-exchanged forms of analcite and chabazite. *Trans. Faraday Soc.* **1954**, *50*, 581–587. [[CrossRef](#)]
105. Freeman, D.; Stamires, D. Electrical Conductivity of Synthetic Crystalline Zeolites. *J. Chem. Phys.* **1961**, *35*, 799–806. [[CrossRef](#)]
106. Simon, U.; Flesch, U. Cation-cation interaction in dehydrated zeolites X and Y monitored by modulus spectroscopy. *J. Porous Mater.* **1999**, *6*, 33–40. [[CrossRef](#)]
107. Franke, M.E.; Simon, U. Characteristics of proton hopping in zeolite H-ZSM5. *Phys. Status Solidi B Basic Res.* **2000**, *218*, 287–290. [[CrossRef](#)]
108. Rizzotto, V.; Chen, P.; Simon, U. Mobility of NH₃-Solvated Cu-II Ions in Cu-SSZ-13 and Cu-ZSM-5 NH₃-SCR Catalysts: A Comparative Impedance Spectroscopy Study. *Catalysts* **2018**, *8*, 162. [[CrossRef](#)]
109. Chen, P.; Rizzotto, V.; Khetan, A.; Xie, K.; Moos, R.; Pitsch, H.; Ye, D.; Simon, U. Mechanistic Understanding of Cu-CHA Catalyst as Sensor for Direct NH₃-SCR Monitoring: The Role of Cu Mobility. *ACS Appl. Mater. Interfaces* **2019**, *11*, 8097–8105. [[CrossRef](#)] [[PubMed](#)]
110. Chen, P.; Rizzotto, V.; Xie, K.; Simon, U. Tracking mobile active sites and intermediates in NH₃-SCR over zeolite catalysts by impedance-based in situ spectroscopy. *React. Chem. Eng.* **2019**, *4*, 986–994. [[CrossRef](#)]
111. Chen, L.; Falsig, H.; Janssens, T.V.W.; Grönbeck, H. Activation of oxygen on (NH₃-Cu-NH₃)⁺ in NH₃-SCR over Cu-CHA. *J. Catal.* **2018**, *358*, 179–186. [[CrossRef](#)]
112. Wallin, M.; Karlsson, C.J.; Skoglundh, M.; Palmqvist, A. Selective catalytic reduction of NO_x with NH₃ over zeolite H-ZSM-5: Influence of transient ammonia supply. *J. Catal.* **2003**, *218*, 354–364. [[CrossRef](#)]
113. Chen, L.; Falsig, H.; Janssens, T.V.W.; Jansson, J.; Skoglundh, M.; Grönbeck, H. Effect of Al-distribution on oxygen activation over Cu-CHA. *Catal. Sci. Technol.* **2018**, *8*, 2131–2136. [[CrossRef](#)]
114. Liu, C.; Kubota, H.; Toyao, T.; Maeno, Z.; Shimizu, K.-i. Mechanistic insights into the oxidation of copper(i) species during NH₃-SCR over Cu-CHA zeolites: A DFT study. *Catal. Sci. Technol.* **2020**, *10*, 3586–3593. [[CrossRef](#)]
115. Negri, C.; Sella, T.; Borfecchia, E.; Martini, A.; Lomachenko, K.A.; Janssens, T.V.W.; Cutini, M.; Bordiga, S.; Berlier, G. Structure and Reactivity of Oxygen-Bridged Diamino Dicopper(II) Complexes in Cu-Ion-Exchanged Chabazite Catalyst for NH₃-Mediated Selective Catalytic Reduction. *J. Am. Chem. Soc.* **2020**, *142*, 15884–15896. [[CrossRef](#)]
116. Clemens, A.K.S.; Shishkin, A.; Carlsson, P.A.; Skoglundh, M.; Martinez-Casado, F.J.; Matej, Z.; Balmes, O.; Hareld, H. Reaction-driven Ion Exchange of Copper into Zeolite SSZ-13. *ACS Catal.* **2015**, *5*, 6209–6218. [[CrossRef](#)]
117. Vennestrom, P.N.R.; Janssens, T.V.W.; Kustov, A.; Grill, M.; Puig-Molina, A.; Lundegaard, L.F.; Tiruvalam, R.R.; Concepción, P.; Corma, A. Influence of lattice stability on hydrothermal deactivation of Cu-ZSM-5 and Cu-IM-5 zeolites for selective catalytic reduction of NO_x by NH₃. *J. Catal.* **2014**, *309*, 477–490. [[CrossRef](#)]
118. Shwan, S.; Skoglundh, M.; Lundegaard, L.F.; Tiruvalam, R.R.; Janssens, T.V.W.; Carlsson, A.; Vennestrom, P.N.R. Solid-State Ion-Exchange of Copper into Zeolites Facilitated by Ammonia at Low Temperature. *ACS Catal.* **2014**, *5*, 16–19. [[CrossRef](#)]

-
119. Vennestrom, P.N.R.; Lundegaard, L.F.; Tyrsted, C.; Bokarev, D.A.; Mytareva, A.I.; Baeva, G.N.; Stakheev, A.Y.; Janssens, T.V.W. The Role of Protons and Formation $\text{Cu}(\text{NH}_3)_2^+$ During Ammonia-Assisted Solid-State Ion Exchange of Copper(I) Oxide into Zeolites. *Top. Catal.* **2019**, *62*, 100–107. [[CrossRef](#)]
 120. Rauch, D.; Kubinski, D.; Simon, U.; Moos, R. Detection of the ammonia loading of a Cu Chabazite SCR catalyst by a radio frequency-based method. *Sens. Actuators B Chem.* **2014**, *205*, 88–93. [[CrossRef](#)]
 121. Wales, D.J.; Grand, J.; Ting, V.P.; Burke, R.D.; Edler, K.J.; Bowen, C.R.; Mintova, S.; Burrows, A.D. Gas sensing using porous materials for automotive applications. *Chem. Soc. Rev.* **2015**, *44*, 4290–4321. [[CrossRef](#)]
 122. Moos, R. Catalysts as sensors—A promising novel approach in automotive exhaust gas aftertreatment. *Sensors* **2010**, *10*, 6773–6787. [[CrossRef](#)]
 123. Li, S.; Zheng, Y.; Gao, F.; Szanyi, J.; Schneider, W.F. Experimental and computational interrogation of fast SCR mechanism and active sites on H-form SSZ-13. *ACS Catal.* **2017**, *7*, 5087–5096. [[CrossRef](#)]
 124. Mao, Y.; Wang, Z.; Wang, H.-F.; Hu, P. Understanding catalytic reactions over zeolites: A density functional theory study of selective catalytic reduction of NO_x by NH_3 over Cu-SAPO-34. *ACS Catal.* **2016**, *6*, 7882–7891. [[CrossRef](#)]
 125. Narsimhan, K.; Iyoki, K.; Dinh, K.; Roman-Leshkov, Y. Catalytic oxidation of methane into methanol over copper-exchanged zeolites with oxygen at low temperature. *ACS Cent. Sci.* **2016**, *2*, 424–429. [[CrossRef](#)] [[PubMed](#)]
 126. Brogaard, R.Y.; Kmurcu, M.; Dyballa, M.M.; Botan, A.; Van Speybroeck, V.; Olsbye, U.; De Wispelaere, K. Ethene dimerization on zeolite-hosted Ni ions: Reversible mobilization of the active site. *ACS Catal.* **2019**, *9*, 5645–5650. [[CrossRef](#)] [[PubMed](#)]