In Situ Spectroscopic Studies of Proton Transport in Zeolite Catalysts for NH₃-SCR

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Abstract: Proton transport is an elementary process in the selective catalytic reduction of nitrogen oxides by ammonia (DeNOₓ by NH₃-SCR) using metal-exchanged zeolites as catalysts. This review summarizes recent advancements in the study of proton transport in zeolite catalysts using in situ electrical impedance spectroscopy (IS) under NH₃-SCR reaction conditions. Different factors, such as the metal cation type, metal exchange level, zeolite framework type, or formation of intermediates, were found to influence the proton transport properties of zeolite NH₃-SCR catalysts. A combination of IS with diffuse reflection infrared Fourier transformation spectroscopy in situ (in situ IS-DRIFTS) allowed to achieve a molecular understanding of the proton transport processes. Several mechanistic aspects, such as the NH₃-zeolite interaction, NO-zeolite interaction in the presence of adsorbed NH₃, or formation of NH₄⁺ intermediates, have been revealed. These achievements indicate that IS-based in situ methods as complementary tools for conventional techniques (e.g., in situ X-ray absorption spectroscopy) are able to provide new perspectives for the understanding of NH₃-SCR on zeolite catalysts.

Keywords: proton transport; impedance spectroscopy; DRIFTS; reaction mechanism; NOₓ emission control; NH₄⁺ intermediates

1. Introduction

Selective catalytic reduction (SCR) is one of the key technologies to reduce nitrogen oxide emissions (NOₓ) from “lean-burn” engines and power plants [1–3]. Because of their superior activity and hydrothermal stability, Cu- or Fe-exchanged zeolites are widely applied as SCR catalysts, especially in diesel-powered automobiles [3,4]. To meet the continuously tightening NOₓ emission legislation, it is necessary to further improve the performance of the metal-exchanged zeolite catalysts in SCR, which requires understanding more deeply both the reaction mechanisms and the real-time physico-chemical properties of the zeolite catalysts under operational conditions [2–6].

For SCR reactions using NH₃ as a reductant (NH₃-SCR; see Equations (1)–(3) for different reaction routes depending on the NOₓ composition):

\[ 4\text{NH}_3 + 4\text{NO} + \text{O}_2 \to 4\text{N}_2 + 6\text{H}_2\text{O} \text{ (standard SCR)}, \]
\[ 2\text{NH}_3 + \text{NO} + \text{NO}_2 \to 2\text{N}_2 + 3\text{H}_2\text{O} \text{ (fast SCR)}, \]
\[ 8\text{NH}_3 + 6\text{NO}_2 \to 7\text{N}_2 + 12\text{H}_2\text{O} \text{ (NO}_2\text{ SCR)} \].

One of the fundamental issues is to understand the NH₃-zeolite interaction. This interaction has been known to largely determine the storage capability, the uptake and release energetics,
and the reactivity of NH₃ within zeolite catalysts [3,7], and eventually the catalytic performance of the zeolite catalysts in NH₃-SCR. Considerable advancements have been achieved by means of, for example, temperature-programmed desorption (TPD), infrared spectroscopy, and X-ray based methods such as Extended X-Ray Absorption Fine Structure, X-ray Absorption Near Edge Structure, X-ray Emission Spectroscopy (all using NH₃ as a probe molecule) [7–13]. Nevertheless, more elementary processes associated with the NH₃ storage and conversion, in particular, the proton transport, are not fully understood.

It is known that proton transport, which can take place either from the bridging hydroxyl groups (Brensted acid sites) to reactant molecules or between the reaction intermediates, plays an important role in a series of catalytic reactions such as methylation [14], cracking and methanol-to-olefin [15,16], as well as abatement of NOx emissions [3,4,17]. Comprehensive experimental and theoretical investigations had been performed over zeolites with different framework types (FAU, BEA, MFI, FER, CHA, etc.), in order to understand and take advantage of the proton transport processes for further improving the catalytic performance of zeolites [18–22]. Density functional theory (DFT) calculations revealed that proton transfer takes place in several elementary processes in NH₃-SCR reactions over zeolite catalysts, including NO oxidation, fast SCR, NO₂-SCR, NH₃ oxidation and N₂O decomposition [12,20,22,23]. For Cu-ZSM-5 catalyzed NO decomposition, the presence of protons was found to significantly lower the energy barrier for the NO activation on Cu sites [24]. Although the proton transport processes can be probed by ¹H MAS NMR spectroscopy under well-controlled conditions [12,19,21], studies under technically relevant reaction conditions are practically challenging. In the last years, we applied electrical impedance spectroscopy (IS) to study the proton transport in various zeolites (such as H-ZSM-5, Fe-ZSM-5, Cu-ZSM-5, Cu-SSZ-13, Cu-SAPO-34, etc.) as NH₃-SCR catalysts under in situ or operando conditions [17,25–31]. In NH₃-SCR over zeolite catalysts, the adsorption of NH₃ molecules on Brensted acid sites leads to the formation of ammonium ions (NH₄⁺), which interact further with NH₃ molecules forming NH₄⁺·(NH₃)ₙ complexes at low temperatures [2]. The formed NH₄⁺ and NH₄⁺·(NH₃)ₙ complexes, which can provide additional paths or carriers for proton transport [26,32–34], lead to increased proton conductivities which can be monitored by IS in a broad frequency range (mHz–GHz) [27,32–36]. The consumption of adsorbed NH₃, either by desorption or SCR conversion, leads to decreased conductivity due to a loss of proton carriers [17,26]. A further combination of IS and diffuse reflection infrared Fourier transformation spectroscopy (in situ IS-DRIFTS) allowed us to achieve a molecular understanding of the proton transport processes and their impact in NH₃-SCR catalysis [17,27–29].

In this review, we will briefly introduce the physical background and instrumentation of in situ IS and in situ IS-DRIFTS (Section 2). In Section 3, we will summarize the mechanisms and influential factors of NH₃-supported proton transport in zeolite catalysts, and the impact of proton transport in NH₃-SCR catalysis. The future perspectives, which arise from the achieved understanding, will be discussed at the end (Section 4).

2. Theory and Instruments

2.1. Theory of Impedance Spectroscopy

Impedance spectroscopy is an electric perturbation technique, and can be employed to analyze the mobility of ions in solid materials [37,38]. In a typical IS measurement over zeolite, an alternating voltage U(ω) with angular frequency ω and amplitude U₀ is applied to form an electric field over a zeolite in thermodynamic equilibrium. A response of the system, i.e., a movement of the mobile cations either via translation motion or a local displacement, is induced by the electric perturbation, and can be macroscopically measured as a current I(ω). The complex impedance Z(ω) is defined as

$$Z(\omega) = U(\omega)/I(\omega)$$

(4)
and can be described by a real part $Z'$ and an imaginary part $Z''$. Both depend on the angular frequency $\omega$:

$$Z(\omega) = Z'(\omega) + jZ''(\omega).$$

(5)

In the analysis of complex impedance $Z(\omega)$, low-frequency phenomena such as the sample/electrode interface polarization can be identified from the dominating low-frequency tail of the traditional Argand representation (also known as Nyquist plot; the real part $Z'$ is plotted against the imaginary part $Z''$; see Figure 1a for an example) [39]. The high-frequency processes are more visible in the Modulus plot, which shows the imaginary part of the Modulus $M$, i.e., $M''(\omega)$, against the frequency $f$ (Figure 1b). The modulus $M''(\omega)$ is defined as

$$M''(\omega) = \omega C_0 Z'(\omega),$$

(6)

wherein $C_0$ is the capacity of the empty capacitor, i.e., the geometric capacitance. Thereby, two distinct relaxation processes, i.e., the local dipolar relaxation (as visualized by the maximum at high-frequency range) and the long-range proton transport (as visualized by the maximum at low-frequency range) can be clearly distinguished in one spectral representation.

![Figure 1](image-url)

**Figure 1.** (a) Argand diagram (plot of the imaginary part of the impedance $-Z''$ versus the real part of the impedance $Z'$ in the complex plane) of dehydrated H-ZSM-5 (Si/Al 13.5) at 250 °C; the gray arrow indicates the increase of frequency; (b) modulus spectra of the imaginary part $M''$ versus frequency $f$ of H-ZSM-5 at temperatures 200–450 °C; the gray arrow indicates the increase of temperature; (c) Arrhenius-like plot of logarithmic proton conductivity at resonance frequencies (in low-frequency range) derived from the Modulus spectra in (b). Reproduced with permission from [29]. The Royal Society of Chemistry, 2016.
The long-range proton transport within the zeolites is temperature-dependent, and can be represented using the Arrhenius equation:

$$\ln(Y' \times T) - \ln(\sigma T) = A - E_a / (k_B \times T),$$

(7)

where $Y'$ is the real part of the admittance, i.e., $Y(\omega) = 1/Z(\omega)$, at the resonance frequency $f_{\text{res}}$ (determined according to the low-frequency maximum in the Modulus plot at the respective temperature), $A$ is the pre-exponential factor (which depends on the charge and number of the mobile species, its on-site oscillation frequency and the hopping distance [38]), $E_a$ is the activation energy of the proton transport process, $\sigma$ is the specific conductivity of the zeolite, $k_B$ is the Boltzmann constant, and $T$ is the temperature. An example is shown in Figure 1c for an Arrhenius-like representation of IS results over the zeolite H-ZSM-5.

2.2. Instruments for In Situ IS and In Situ IS-DRIFTS

The measurement configurations for in situ IS and in situ IS-DRIFTS are schematically displayed in Figure 2a,b, respectively. For both methods, the zeolite catalysts were deposited as a thick film on screen-printed interdigital electrodes (IDEs) comprised of an alumina substrate with gold electrodes on the front side and an integrated heater on the reverse side. In this way, an excellent electrical contact between the zeolite film and the IDE structure can be achieved [30]. An external power supply is used for temperature control via resistive heating. Temperature calibration was performed for each sample with a pyrometer for the remote monitoring of temperature on the surface of zeolite film. The gas composition is controlled by mass flow controllers (MFCs) dosing different gases such as NO, O$_2$, NH$_3$ and N$_2$ (carrier gas). Prior to each measurement, the zeolite sample was pretreated at high temperatures (usually at 400 °C in 10 vol. % O$_2$ for 1 h) to remove any adsorbed water or hydrocarbon contaminants. The electrical impedance of the sample is measured with an impedance analyzer range up to $10^{14}$ Ω (±1%). The voltage is set to 0.1 V (rms) for all measurements to stay in the linear response regime.

![Figure 2](image_url)

**Figure 2.** Schematic illustrations of the measurement configurations for (a) in situ impedance spectroscopy (IS) and (b) in situ IS and diffuse reflection infrared Fourier transformation spectroscopy (in situ IS-DRIFTS). (a) Reproduced with permission from [30]; (b) adapted with permission from [28], Elsevier, 2016.

The in situ IS measurements were carried out using a homemade reaction chamber (Figure 2a). For in situ IS-DRIFTS measurements, a commercial high-temperature reaction chamber (Harrick Scientific Products, Pleasantville, NY, USA) was modified to allow the introduction of IDE chips with zeolite catalyst film (Figure 2b). A specially designed holder with electrical contacts was employed to keep the sensor chip inside the reaction chamber in a way that the zeolite film is in the focal point of the infrared beam of the DRIFTS mirror design. Simultaneous IS and DRIFTS measurements were carried out using the same catalyst film, allowing simultaneous monitoring of both the proton conductivity of zeolite catalysts and the vibration modes of the molecules on zeolite catalysts [26,28].
3. Proton Transport in Zeolite Catalysts for NH3-SCR

3.1. NH3-Supported Proton Transport

Zeolites are a class of crystalline, microporous solids consisting of tetrahedral TO4 (T denotes as Si, Al, Ti, etc.) units. The TO4 units serve as primary building blocks forming three-dimensional frameworks with interconnected cages and channels of distinct sizes and shapes. The Brønsted acidity of zeolites, which results from the non-equivalent substitution of T-atoms (e.g., the substitution of Si by Al in TO4 units as shown in Figure 3) and the subsequent charge-balancing by external, exchangeable cations (Na+, NH4+, H+, etc.) at the adjacent oxygen sites within the pore space, enables several characteristic functions, such as ion-exchange capacity, proton donating ability and ionic conductivity [3,40–42]. These properties allow zeolites to be used as adsorbents, separators, ionic conductors, sensors, or catalysts [3,40–42].

![Figure 3. Schematic illustration of the mechanisms of proton transport occurring in NH3-loaded H-form zeolites at different temperature ranges. (i) Grothuss-like proton transport along condensed NH3 molecules, i.e., NH4+(NH3)n chains (below 120 °C); (ii) proton transport along dis-integrated NH4+(NH3)n chains (120–200 °C); (iii) vehicle transport mechanism, where NH4+ serves as “vehicle” like proton carrier (200–340 °C); and (iv) hopping transport of protons by thermal activation (above 340 °C). Adapted with permission from [31]. Copyright American Chemical Society, 2016.]

In NH3-SCR catalysis, protons on Brønsted acid sites of zeolite catalysts could transfer to adsorbed NH3 forming ammonium ions (NH4+), which interact further with NH3 molecules leading to the formation of NH4+(NH3)n complexes at low temperatures [2]. Both NH4+ and NH4+(NH3)n complexes can provide additional paths or carriers for proton transport, which consequently increase the proton conductivity of zeolite catalysts [26,32–34]. The physico-chemical features of NH3-supported proton transport were revealed by in situ studies over NH3-loaded zeolites using techniques combining IS with TPD or quantum chemical calculations [26–29,34,43], and are schematically illustrated in Figure 3 for proton-form zeolites. Four distinct temperature-dependent mechanisms can be distinguished, specifically (i) the Grothuss-like transport along condensed NH4+(NH3)n chains at low temperatures, i.e., below the desorption temperature of NH3; (ii) proton hopping along partially disintegrated chains of NH3 molecules (i.e., in the temperature range, where weakly bound solvent molecules desorb); (iii) vehicle-supported transfer of protons between the neighboring Brønsted sites with NH4+ carriers as “proton vehicles”; and (iv) thermally activated proton hopping along the electron density located at the oxygen atoms of the zeolite lattice in the absence of solvate molecules (above 340 °C) [26,32,33].

3.2. Factors Influencing the Proton Transport in Zeolite Catalysts

As can be seen in Figure 3, the proton transport in zeolites is largely determined by the abundance of Brønsted sites serving as the primary sites for the adsorption of NH3. This was already confirmed
by our previous studies over ZSM-5 zeolites with different Si/Al ratios [32,33]. For metal-exchanged zeolites used as catalysts in NH₃-SCR, several structural or chemical parameters such as framework topology, metal cation type, and metal exchange level also influence considerably the NH₃-supported proton transport by affecting the formation of NH₄⁺-(NH₃)ₙ complexes and/or the affinity between the NH₃ species and the zeolite catalysts.

3.2.1. Metal Cation Type

Based on the NH₃-supported proton transport, the loading and desorption of NH₃ in Fe- and Cu-ZSM-5 can be effectively monitored by means of in situ IS (Figure 4a). Comparative studies revealed that, as compared to Fe-ZSM-5, the Cu-ZSM-5 demonstrated a stronger retention ability against thermal desorption for the adsorbed NH₃ species (i.e., NH₄⁺ on Brønsted as indicated by the IR band at 1457 cm⁻¹, and the NH₃ on metal sites as indicated by the IR band at 1276/1266 cm⁻¹), which is due to a stronger NH₃-zeolite interaction (according to the higher activation energy Eₐ for proton transport by multi-frequency IS experiments; see Figure 4b). During exposure in NO/O₂ mixture for the SCR conversion of stored NH₃ (Figure 5), while the proton conductivity of NH₃-saturated Fe-ZSM-5 decreased rapidly, that of NH₃-saturated Cu-ZSM-5 increased further significantly (Figure 5a). Such unexpected increase of proton conductivity during NO/O₂ exposure was observed in the temperature range of 100–250 °C over NH₃-saturated Cu-ZSM-5 (Figure 6a).

In situ IS-DRIFTS studies revealed that the increased proton conductivity results mainly from NH₄⁺ intermediates (Figure 6b), which formed via the following route: (i) interaction of NO and adsorbed NH₃ on Cu²⁺ sites; (ii) reduction of Cu²⁺ to Cu⁺ and release of a proton on the adjacent Brønsted site (i.e., Cu²⁺ → Cu⁺ + H⁺); and (iii) interaction of the released proton and adsorbed NH₃ on Cu sites (i.e., H⁺ + NH₃ → NH₄⁺) [27,29,44,45]. The enhanced proton transport of NH₃-saturated zeolite catalysts by NO exposure is thus considered to manifest the NO activation ability in the presence of adsorbed NH₃ [29].

![Figure 4.](image-url)

**Figure 4.** (a) Simultaneously measured proton conductivity (Iₜₛ; IS signal at 10 kHz; solid lines) and DRIFTS signals after Kubelka-Munk (KM) transformation (Iₜₛ; symbols) during the loading and thermal desorption of NH₃ over zeolites at 100 °C. The colorful background indicates the period with NH₃ supply to the system. Iₜₛ at 1457 cm⁻¹ (triangles) and 1276/1266 cm⁻¹ (circles) are attributed to the bending vibrations of NH₄⁺ ions on Brønsted acid sites and bending vibrations of NH₃ species on metal sites, respectively; and (b) Arrhenius-like representations for the IS results obtained in flowing N₂ (empty symbols) and NH₃ (100 ppm in N₂; half-filled symbols) over H-ZSM-5 (squares), Fe-ZSM-5 (circles) and Cu-ZSM-5 (triangles). Reproduced with permission from [29]. Copyright The Royal Society of Chemistry, 2016.
3.2.2. Metal Exchange Level

The metal exchange level (estimated according to, for example, the metal to Al ratio in metal-exchange aluminosilicate zeolites) of zeolite catalyst is known to have a strong impact in NH$_3$-SCR catalysis [46–50]. In the case of ZSM-5 with a Si/Al ratio of 13.5, while the Cu species in

Figure 5. (a) time-courses of normalized proton conductivity $I_{IS}$ (at 10 kHz) for Fe-ZSM-5 and Cu-ZSM-5 during exposure to the indicated atmospheres at 175 °C; (b) measured NO conversion in selective catalytic reduction (NH$_3$-SCR) over Fe-ZSM-5 and Cu-ZSM-5 (0.5 g catalyst; a total flow rate of 1 L min$^{-1}$; 500 ppm NH$_3$, 500 ppm NO, 10% O$_2$, 2% H$_2$O). Reproduced with permission from [29]. Copyright The Royal Society of Chemistry, 2016.

Figure 6. (a) time-courses of normalized proton conductivity $I_{IS}$ (at 10 kHz) for Fe-ZSM-5 and Cu-ZSM-5 during exposure to the indicated atmospheres at 100 °C and 250 °C; (b) normalized $I_{IS}$ (line) and $I_{DRIFTS}$ signals (symbols) for Cu-ZSM-5 under SCR-related atmospheres at 250 °C. (a) Reproduced with permission from [29]. Copyright The Royal Society of Chemistry, 2016; (b) Reprinted with permission from [31]. Copyright American Chemical Society, 2016.

It has to be noted that the redox cycle of active metal sites consists of a reduction half-cycle (Cu$^{2+}$ → Cu$^+$ or Fe$^{3+}$ → Fe$^{2+}$) and a re-oxidation half-cycle (Cu$^+$ → Cu$^{2+}$ or Fe$^{2+}$ → Fe$^{3+}$), and the latter one is usually considered to be the rate-determining step in the whole redox processes [10,11]. Therefore, further IS studies on the re-oxidation half-cycle are needed to understand in more detail the very different low-temperature NH$_3$-SCR activities of Cu- and Fe-exchanged zeolite catalysts (Figure 5b) [29].
Cu-ZSM-5 remain mainly in isolated state at a Cu/Al ratio of ca. 0.2, a considerable amount of Fe dimers or oligomers form in Fe-ZSM-5 with a Fe/Al ratio of ca. 0.2 and above [31]. The introduced metal species can adsorb NH$_3$ at an intermediate strength (stronger than the adsorption on Lewis sites, but weaker than that on Brønsted sites), as characterized by the NH$_3$ desorption at temperatures between 130 and 250 °C (Figure 7a) [7]. The influence of metal exchange level on the NH$_3$-zeolite interaction can be examined by analyzing the mobility of adsorbed NH$_3$-species as proton carriers under thermal desorption conditions by means of in situ IS [31]. As indicated by the activation energies for proton transport (i.e., the strength of NH$_3$ adsorption on zeolites), while the increase of Fe loading weakened slightly the NH$_3$-zeolite interaction, a higher Cu loading enhanced significantly the NH$_3$-zeolite interaction (Figure 7b). The weakening interaction between NH$_3$ and Fe-ZSM-5 with increasing Fe/Al ratio can be clearly visualized in DRIFTS (Figure 7c), according to the decreasing band intensity at 1266 cm$^{-1}$ originating from the NH$_3$ species on Fe sites [17,31]. In NH$_3$-SCR catalysis, for the zeolite catalysts shown in Figure 7b, while the low-temperature (below 250 °C) NH$_3$-SCR activity of Fe-ZSM-5 decreased with Fe/Al ratio, that of Cu-ZSM-5 increased with Cu/Al ratio [17,31].

![Figure 7](image-url)

**Figure 7.** (a) NH$_3$-TPD (temperature-programmed desorption using NH$_3$ as a probe molecule) profiles showing the desorption of NH$_3$ species on Lewis sites, metal sites and Brønsted sites in different temperature ranges; (b) activation energy ($E_a$) for proton transport as a function of metal exchange level. The $E_a$ values were derived from the Arrhenius plots of the in situ IS results over NH$_3$-loaded zeolite catalysts under thermal desorption conditions (in N$_2$) at temperatures 130–250 °C; (c) in situ DRIFT spectra for NH$_3$-saturated Fe-ZSM-5 zeolite catalysts with different Fe/Al ratios at 175 °C; (d) in situ DRIFT spectra for a NH$_3$-saturated Fe-ZSM-5 zeolite catalyst (Fe/Al ratio of 0.11) at different temperatures. (a) Reproduced with permission from [29]. Copyright The Royal Society of Chemistry, 2016; (b) Reprinted with permission from [31], American Chemical Society, 2016; (c,d) Reprinted with permission from [17]. Copyright American Chemical Society, 2016.
At high Fe loadings or under harsh conditions (e.g., hydrothermal aging), the Fe species in Fe-zeolites may aggregate forming Fe$_2$O$_3$ dimers or small clusters within the zeolite pores, or even relatively large Fe$_2$O$_3$ particles outside the zeolite pores [31]. At low temperatures, these Fe$_2$O$_3$ species or Fe$_2$O$_3$ particles could provide additional acidic sites for the adsorption of NH$_3$ species, favoring the formation of NH$_4^+$-(NH$_3$)$_x$ chains (as indicated by the broad band centered at ca. 2520 cm$^{-1}$ in the DRIFT spectra in Figure 7d) and consequently the proton transport within the zeolite lattice [28,29]. At high temperatures (175 °C and above), however, the weakly bound NH$_3$ species cannot be retained on the Fe$_2$O$_3$ species or Fe$_2$O$_3$ particles (as indicated by the disappearance of the broad band centered at ca. 2520 cm$^{-1}$) and thus have no (or just negligible) contribution to the proton transport [17,29].

3.2.3. Zeolite Framework Type

Among different zeolite framework types, those with medium or small pore diameters (such as CHA, MFI, MOR, FER, etc.) after metal ion exchange were found to be especially advantageous for NH$_3$-SCR catalysis [2–4]. A comparison of Cu-ZSM-5 (MFI type) and Cu-SAPO-34 (CHA type) zeolites using in situ IS revealed that the framework type influenced significantly the proton transport properties of Cu-zeolite catalysts under NH$_3$-SCR related conditions [27]. At low temperatures, formation of highly proton-conducting NH$_4^+$ intermediates was observed in both zeolites (Figures 6b and 8), which is due to the reduction of Cu$^{2+}$ to Cu$^+$ as a result of the interaction of NH$_3$ and NO [17,25,29,44]. In the monitoring of NH$_3$-SCR using the zeolite catalysts directly as sensors, while the performance of Cu-SAPO-34 can be improved by increasing the temperature to 200 °C and above, that of Cu-ZSM-5 was impeded by the formation of NH$_4^+$ intermediates even at high temperatures as 350 °C (Figure 9). Both zeolites performed similarly in the direct monitoring of NH$_3$-SCR at temperatures above 350 °C. At 200 °C and below, Cu-SAPO-34 also showed higher NH$_3$-SCR activity than Cu-ZSM-5 [27]. The difference in proton transport, NH$_3$-SCR reaction monitoring and NH$_3$-SCR catalysis can be attributed to the different coordinative nature of the metal sites in the two catalysts [4]. Systematic investigations are required to gain more insights into this issue.

Figure 8. Normalized $I_{IS}$ and $I_{DRIFTS}$ signals obtained over Cu-SAPO-34 at 250 °C in different gas mixtures; (I) pure N$_2$; (II) 100 ppm NH$_3$, N$_2$ balance; (III) 70 ppm NH$_3$, 20 ppm NO, 10% O$_2$, N$_2$ balance; (IV) 45 ppm NH$_3$, 45 ppm NO, 10% O$_2$, N$_2$ balance; (V) 20 ppm NH$_3$, 70 ppm NO, 10% O$_2$, N$_2$ balance; (VI) 100 ppm NO, N$_2$ balance. Cu-SAPO-34: 1 wt % Cu, (P + Al)/Si = 12.9. 1457 cm$^{-1}$: NH$_4^+$ ions on Brønsted acid sites; 1273 cm$^{-1}$: NH$_3$ species on Cu sites. Reproduced with permission from [25].
3.2.4. Formation of NH$_4^+$ Intermediates

In zeolite catalyzed NH$_3$-SCR reactions, depending on the used catalysts and reaction conditions, different intermediate species, such as NO$^+$ [51], NO$_3^-$ [45], NO$_2^-$ [52], H$^+$ [11], NH$_4^+$ [44], have been observed forming. As shown in Figures 6b and 8, highly mobile NH$_4^+$ intermediates formed on Cu-ZSM-5 and Cu-SAPO-34 as a result of the NH$_3$-NO interaction [44]. In case of Fe-ZSM-5, due to the well-known NH$_3$-inhibition effect [10,53], formation of NH$_4^+$ intermediates (resulting from the reduction of Fe$^{3+}$ to Fe$^{2+}$ similar as the Cu redox cycle) at low reaction temperatures can only be clearly observed by in situ IS-DRIFTS after a partial desorption of adsorbed NH$_3$ (Figure 10a) [17]. Nevertheless, adsorption and activation of NO did take place on NH$_3$-satured Fe-ZSM-5, leading to the formation of NH$_4^+$ intermediates, clearly enhancing the proton conductivity of NH$_3$-loaded Fe-ZSM-5 in NO (see the higher $I_{IS}$ values during exposure in NO than in N$_2$; Figure 10b). These observations indicate a Fe$^{3+}$↔Fe$^{2+}$ redox cycle in Fe-ZSM-5 catalysts similar as the widely accepted Cu$^{2+}$↔Cu$^+$ redox cycle in Cu-SSZ-13 catalysts (Figure 11a) [3,10,11,44,45,54]. More interestingly, the formed NH$_4^+$ intermediates were found to largely determine the NH$_3$-SCR activity of Fe-ZSM-5 catalysts at low temperatures (Figure 11b). Therefore, the formation of NH$_4^+$ intermediates, indicating the activation of NO in the presence of adsorbed NH$_3$, may potentially serve as a ‘descriptor’ of the activity of Fe-zeolite catalyst for NH$_3$-SCR, especially at low temperatures.

![Figure 9](image-url) Electric signals of Cu-ZSM-5 and Cu-SAPO-34 in SCR-related atmospheres. Cu-SAPO-34: 1 wt % Cu, (P + Al)/Si = 12.9. Cu-ZSM-5: 1 wt % Cu, Si/Al = 13.5. Reproduced with permission from [27]. Copyright Elsevier, 2016.

![Figure 10](image-url) Normalized $I_{IS}$ (green line) and DRIFTS signals (red symbols) at characteristic wavenumbers of NH$_3$-loaded Fe-ZSM-5 (Si/Al 13.5, Fe/Al 0.11) exposed N$_2$ and NO/O$_2$ mixture in sequence (a) and exposed to NO and NO/O$_2$ mixture in sequence (b). $I_{IS}$: absolute value of complex admittance $|Y^*|$ ($Y^*$ is the reciprocal of the complex impedance $Z^*$, i.e., $Y^* = 1/Z^*$) at 10 kHz. 1457 cm$^{-1}$: NH$_4^+$ ions on Brønsted acid sites; 1266 cm$^{-1}$: NH$_3$ species on Fe sites. The catalyst was pre-treated at 450 ºC in 10% O$_2$ for 1 h before each measurement. Reprinted with permission from [17]. Copyright American Chemical Society, 2016.
3.2.5. H₂O Vapor

In real diesel exhausts, a considerable amount of H₂O vapor resulting from the fuel combustion processes and the NH₃-SCR reactions is always present. As revealed previously, H₂O as a solvate molecule could serve as proton carrier as well and consequently enhance the proton conductivity of zeolites in a broad temperature range [33]. As compared to NH₃, H₂O demonstrates a significantly weaker supporting effect for the proton transport in zeolites [16], specifically, 1 vol. % H₂O vapor only has the same effect as 6 ppm of NH₃ in terms of the conductivity change of H-ZSM-5 (at 420 °C) [55]. In the above-mentioned transient IS measurements (in the absence of H₂O), a significant influence of H₂O as the product of NH₃-SCR reaction can thus be ruled out because of the very low concentration. Nevertheless, minor contribution of H₂O to the overall proton conductivity of the respective zeolite catalyst cannot be fully excluded. Further comparative studies (with or without H₂O) are required to achieve a more complete understanding of the influence of H₂O.

3.2.6. Zeolite Crystallite Size

Although the crystallite size of zeolite was found to influence limitedly the intrinsic NH₃-SCR activities of metal-exchanged zeolite catalysts (e.g., Cu-SSZ-13, Cu- SAPO-34, Fe-ZSM-5) [56–58], a decrease of crystal size from several micrometers to 50–100 nm can improve the hydrothermal stability of zeolite catalysts [56,57]. For proton transport in zeolites, the influence of crystallite size (or grain boundary) is negligible with crystallite size at micrometer level, and is noted only with crystallite sizes below 200 nm [59]. Considering that commercially relevant zeolite materials with a broad distribution of crystallite size (0.5–5 μm) were applied in the above-mentioned IS studies [17,25–36], a noticeable influence of the zeolite crystallite size can be excluded.

4. Summary and Perspectives

In summary, by analyzing the proton transport properties of zeolite catalysts under SCR-related reaction conditions using in situ IS, the NH₃-zeolite interaction, NO-zeolite interaction (in the presence of adsorbed NH₃), and formation of proton-conducting intermediates can be probed. A combination of IS with DRIFTS allows for understanding molecularly the proton transport properties of zeolite NH₃-SCR catalysts. Several structural or chemical parameters, such as framework topology, metal cation type and metal exchange level, influenced the proton transport to different degrees by affecting the reactant–zeolite interactions. On the one hand, the mobility of adsorbed NH₃-species as proton
carriers, determined by the NH₃-zeolite interaction, was influenced differently by the type, loading and coordinative environment of the exchanged Fe or Cu species in zeolite catalysts. On the other hand, highly mobile NH₄⁺ intermediates, as identified by IS combined with DRIFTS, can form on zeolite catalysts as general intermediate species resulting from the interaction of co-adsorbed NH₃ and NO on metal active sites. The formed NH₄⁺ intermediates not only significantly influenced the proton transport properties, and consequently the reaction monitoring performance of zeolite catalysts due to the highly proton-conducting nature, but also largely determined the low-temperature NH₃-SCR activity because of their high mobility and reactivity. These findings, which are not easily achievable by conventional methods, thus provide new perspectives to understand mechanistically the NH₃-SCR reaction over zeolite catalysts.

To understand further the role of proton transport in NH₃-SCR catalysis, both chemical nature (e.g., surface acidity, chemical composition) and structural properties (e.g., size, shape, or porosity) of the zeolite catalysts should be taken into account. Substantial improvements, for example the synthesis of zeolites with well-controlled crystal sizes or porosity, have already been achieved using delicately designed bottom-up (i.e., controlling the chemical and structural properties by adjusting the synthetic procedure) or top-down (i.e., post-synthetic modifications) approaches [60,61]. Although the electrical and catalytic properties of zeolites can be correlated to certain specific chemical or structural features in a collective manner, it is still practically challenging to discriminate intrinsic and interfacial effects in the mentioned applications. In recent years, several advanced techniques, such as X-ray based micro-spectroscopy or local-probe measurement, have been developed to analyze in situ the chemical nature, the three-dimensional structure, the electrical properties, and eventually the structure–activity relationship at single-particle levels without the interference of boundary effects [15,62,63]. It is expected that a combination of these new techniques will promote achieving more reliable guidelines for the rational development of zeolite catalysts in the future.

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References


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