



# **Review Fe-Exchanged Small-Pore Zeolites as Ammonia Selective Catalytic Reduction (NH<sub>3</sub>-SCR) Catalysts**

# Feng Gao

Institute for Integrated Catalysis, Pacific Northwest National Laboratory, P.O. Box 999, Richland, WA 99354, USA; feng.gao@pnnl.gov; Tel.: +1-509-371-7164

Received: 12 October 2020; Accepted: 11 November 2020; Published: 14 November 2020



**Abstract:** Cu-exchanged small-pore zeolites have been extensively studied in the past decade as state-of-the-art selective catalytic reduction (SCR) catalysts for diesel engine exhaust NOx abatement for the transportation industry. During this time, Fe-exchanged small-pore zeolites, e.g., Fe/SSZ-13, Fe/SAPO-34, Fe/SSZ-39 and high-silica Fe/LTA, have also been investigated but much less extensively. In comparison to their Cu-exchanged counterparts, such Fe/zeolite catalysts display inferior low-temperature activities, but improved stability and high-temperature SCR selectivities. Such characteristics entitle these catalysts to be considered as key components of highly efficient emission control systems to improve the overall catalyst performance. In this short review, recent studies on Fe-exchanged small-pore zeolite SCR catalysts are summarized, including (1) the synthesis of small-pore Fe/zeolites; (2) nature of the SCR active Fe species in these catalysts as determined by experimental and theoretical approaches, including Fe species transformation during hydrothermal aging; (3) SCR reactions and structure-function correlations; and (4) a few aspects on industrial applications.

Keywords: Fe-exchanged zeolite; small-pore zeolite; SCR catalyst; deNOx; engine exhaust abatement

# 1. Introduction

From 2008 to 2011, several milestone patents were issued describing the use of copper exchanged chabazite zeolites SSZ-13 and SAPO-34 as ammonia SCR catalysts for vehicle exhaust NOx abatement (even though SAPO-34 is not a zeolite by scientific categorization, it is treated so in this short review for the sake of simplicity) [1–4]. These patents denote arrival of a new era in emission control catalysis, i.e., the remediation of toxic emissions from vehicles by small-pore (pore opening ~0.4 nm) zeolite catalysts. To date, there is strong continuing research enthusiasm on Cu/SSZ-13 and Cu/SAPO-34, as evidenced by some 300 open literature publications addressing various aspects of these SCR catalysts [5–10]. Cu-exchanged small-pore zeolites with other topologies, e.g., SSZ-39 (AEI) [11–13] and high-silica zeolite A (LTA) [14–16], have also been actively investigated.

Prior to this era, metal-exchanged medium- (pore opening ~0.55 nm) and large-pore (pore opening ~0.7 nm and larger) zeolites were the catalysts of choice for the same application, with the most representative ones being exchanged ZSM-5 (MFI) and beta (BEA) zeolites [17–19]. Among these investigations, catalysts containing exchanged iron were studied at least as extensively as those containing exchanged copper, despite the well-known fact that Fe catalysts provide inferior performance at low reaction temperatures for the standard SCR reaction. The driving force for studying Fe/zeolites, at least from an application standpoint, is that they frequently offer improved hydrothermal stability and sulfur tolerance than their Cu/zeolite counterparts [20–25]. Since long-term hydrothermal stability and tolerance to poisoning are such important criteria for commercial use, it is not surprising that much effort was devoted to the more durable Fe/zeolites in the early studies.

Since Cu-exchanged small pore zeolites offer unprecedented hydrothermal stability than any of the medium- and large-pore zeolite SCR catalysts previously studied, as is evidenced by their successful commercialization in 2010, investigating Fe-exchanged small pore zeolites in order to achieve additional durability becomes less significant for application, especially considering that the benefits from potential stability enhancement can be severely compromised by the anticipated poor low-temperature standard SCR performance. Likely because of this, studies on Fe-exchanged small pore zeolite SCR catalysts have been considerably scarcer than those on small pore Cu catalysts. To our knowledge, the first open literature publication describing Fe/SSZ-13 and Fe/SAPO-34 SCR catalysts appeared in 2012 by Yang and coworkers [26]. However, these catalysts only served as a point of comparison for the more active Cu/zeolites in the study; they were not characterized by any means other than SCR light-off tests. The authors also prepared Cu,Fe/SSZ-13 and Cu,Fe/SAPO-34 co-exchanged catalysts, and demonstrated that these display SCR performance between their singly exchanged counterparts. In the same year, Narula and coworkers also studied Cu,Fe/SSZ-13 [27]. In addition to SCR tests, they applied several spectroscopic methods to characterize their catalysts. The authors reported that Fe introduction positively influences activity and stability of Cu/SSZ-13. These initial studies were followed by work from Pacific Northwest National Laboratory (PNNL). From 2015 till more recently, the researchers systemically investigated Fe/SSZ-13 catalysts in terms of Fe loading effects [28,29], hydrothermal aging effects [30–32], comparison between Cu/SSZ-13 and Fe/SSZ-13 [33], as well as Cu,Fe/SSZ-13 co-exchanged catalysts [34]. In 2018, theoretical studies via first principles also appeared in the open literature, in particular studies by Schneider and coworkers [35], and McEwen and coworkers [36]. These studies addressed the nature and location of possible exchanged Fe-ions in Fe/SSZ-13, as well as their interactions with adsorbates relevant to SCR. Regarding Fe/SAPO-34, following the initial work by Yang and coworkers [26], this catalyst was investigated later by a few groups, e.g., work by Olsson and coworkers addressing its stability and SCR performance [37], and work by Wright and coworkers focusing more toward catalyst preparation methods [38]. In additional to chabazite catalysts, Corma and coworkers investigated Fe/SSZ-39 as a SCR catalyst [39-41]; more recently, Hong and coworkers reported Fe-exchanged high-silica LTA catalysts [42].

Despite the very short period of explorations (~10 years), researchers have made important discoveries about small-pore Fe/zeolite SCR catalysts. Even though they have inferior low-temperature activities compared to small-pore Cu/zeolites, these catalysts do display some properties superior to small-pore Cu/zeolites, e.g., high SCR selectivities at temperatures above ~400 °C, and low selectivities to unwanted N<sub>2</sub>O. This short review covers a few aspects of these catalysts, including (1) their preparation, (2) the nature of active sites in these catalysts as probed by chemical titrations, spectroscopic and microscopic methods, and (3) their SCR applications.

## 2. Synthesis of Small-Pore Fe/Zeolites

The traditional solution ion-exchange method can be readily applied to prepare small-pore Fe/zeolites, where efficient Fe-ion diffusion into the zeolite body is critical for successful ion exchange. Based on prior investigations on exchanging  $Fe^{2+}/Fe^{3+}$  into zeolites, care must be taken to avoid formation of bulky Fe-containing moieties (e.g., FeOOH) during the process; some of the latter species are not readily diffused into zeolites with medium- and even large-pores [43–45]. Since small-pore zeolites have pore openings only around 0.4 nm [46], efficient Fe-ion diffusion can become even more challenging. To facilitate ion exchange, the hydration spheres around the Fe-ions must be thin [43]. This can be achieved by applying  $Fe^{2+}$  salts rather than  $Fe^{3+}$  salts, low pH, and high exchange temperatures. When  $Fe^{2+}$  salts are used, however, protection under an inert atmosphere is required to avoid air exposure, which oxidizes  $Fe^{2+}$  to  $Fe^{3+}$ . Please note that even without such precautions, for example by suspending SSZ-13 in an  $Fe^{3+}$  solution at ambient temperature, nominal "exchange" still occurs allowing one to obtain Fe-loaded zeolite catalysts. However, external surface iron oxide agglomerates typically dominate in this case. As will be shown below, this is undesirable for SCR applications. Figure 1 presents UV-Vis spectra for a series of freshly prepared, calcined and

rehydrated Fe/SSZ-13 samples (Si/Al = 12, Fe loadings 0.27–1.20 wt%) synthesized by ion-exchange using NH<sub>4</sub>/SSZ-13 and dilute FeSO<sub>4</sub> solutions at 80 °C; during synthesis, the suspension pH was adjusted to ~3.0 and flowing N<sub>2</sub> protection was applied to avoid Fe<sup>2+</sup> oxidation by air [28]. The line shapes of the spectra (arising from  $O \rightarrow Fe^{3+}$  charge transfer) are rather similar, and their intensity increases with increasing Fe loading. The insert of Figure 1 presents Gaussian peak fitting of the sample with the highest Fe loading (1.20 wt. %). Two strong bands are found below 300 nm that can be assigned to isolated Fe<sup>3+</sup> ions. The ~220 nm band is attributed to tetrahedrally coordinated Fe<sup>3+</sup>; the ~270 nm band is assigned to Fe<sup>3+</sup> with higher coordinations. The band at ~350 nm is due to octahedral Fe<sup>3+</sup> in small oligomeric Fe<sub>x</sub>O<sub>y</sub> clusters. The much weaker band centered at ~470 nm can be assigned to larger Fe-oxide particles [24,47,48]. A few points are worth mentioning based on these spectra: (1) Even though some tetrahedrally coordinated Fe<sup>3+</sup> are present, these are extraframework (rather than framework) species. Solution ion-exchange does not lead to Fe incorporation into the framework [24]. (2) This synthesis method does not generate "single-site catalysts". Even at a very low Fe loading of 0.27 wt%, it is apparent that multiple Fe sites already coexist. However, at low Fe loadings, Fe-oxide particle contents can be considered negligible.



**Figure 1.** UV-vis spectra of the fresh, ambient Fe/SSZ-13 samples with different Fe loadings (loadings are marked adjacent to the spectra). The inset shows the peak fitting results of the Fe loading 1.20% sample. Reprinted with permission from [28]. Copyright © 2016 American Chemical Society.

Alternative small-pore Fe/zeolite synthesis methods have also been actively studied in recent years; the so-called "one-pot synthesis" approach has received the most attention [37–41]. As pointed out by Corma and coworkers, via this approach, not only the successive post-synthetic treatments for the incorporation of the iron species would be avoided, the metal dispersion within the zeolitic crystals could also be improved [39]. This method could be more attractive for the synthesis of Fe/SAPO-34, since the SAPO-34 support is prone to degradation by hydrolysis under typical solution ion-exchange conditions [49,50].

In synthesizing one-pot small-pore Fe/zeolites, the simplest method is to adopt procedures used for the preparation of the corresponding parent zeolites, with the addition of small amounts of Fe salts (e.g., Fe(NO<sub>3</sub>)<sub>3</sub>) to the gel prior to synthesis. Using this method, Andonova et al. prepared Fe/SAPO-34 with various Fe loadings [37]. Following calcination to burn off the templates, Fe/SAPO-34 catalysts were readily obtained. Martín et al. also prepared Fe/SSZ-13, Fe/SSZ-16 and Fe/SSZ-39 using the same method [39–41]. However, since these zeolite materials typically crystallize in alkaline media (e.g., NaOH and KOH), it is sometimes necessary to conduct post-synthesis treatments to remove the alkaline cations. This is readily achieved by ion-exchanging calcined catalysts with an NH<sub>4</sub>Cl solution [39]. Please note that the Fe(III) moieties in the zeolites are not readily leached out in this case

because of the diffusion constraints discussed above. Since these zeolites also crystalize in a fluoride medium, replacing NaOH/KOH with HF avoids the post-synthesis ion-exchange step [39].

Since Fe(III) can adopt tetrahedral coordination, it is possible that some of the Fe<sup>3+</sup> ions added to the synthesis gel incorporate into the zeolite framework during one-pot synthesis. This chemistry is readily probed with UV-Vis spectroscopy. As shown in Figure 2A, the as-synthesized Fe/SSZ-13 by Martín et al. [40] in fluoride media contains two  $O \rightarrow Fe(III)$  charge transfer bands at 215 and 240 nm, both are attributed to Fe(III) with tetrahedral coordinations. After calcination in air at 550 °C for 4 h (Figure 2B), new bands appear at 270 nm attributable to Fe(III) with higher coordinations. Please note that bands at 215 and 240 nm cannot be entirely assigned to framework Fe; as shown in Figure 1, solution ion-exchange also generates bands at ~220 nm which are attributed to extraframework Fe species [28]. However, the 270 nm feature must be extraframework in nature because of the high Fe coordinations. The findings shown in Figure 2 suggest then that at least a portion of the Fe added to the synthesis gel ends up incorporating into the framework, and at least some of that relocates to extraframework positions during calcination. In one-pot Fe/SAPO-34 synthesis by Andonova et al. [37], the authors also found evidence for Fe incorporation into the framework. For their catalysts, particularly the one that contains 1.03 wt% Fe, both (Si + P)/Al ratio calculations from elemental analysis and lattice parameter analysis from XRD suggest framework Al substitution by Fe.



**Figure 2.** Diffuse-reflectance UV/Vis spectra of the iron-containing CHA zeolites synthesized in fluoride media in their as-prepared (**A**) and calcined (**B**) forms. Reprinted with permission from [40]. Copyright © 2017 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

Please note that Fe incorporation into the framework is not an ideal situation for SCR applications. First, it is unlikely that framework Fe sites will contribute to SCR; only extraframework Fe sites are considered SCR active. Second, some framework Fe sites relocate to extraframework positions during calcination (see, for example, Figure 2), this creates lattice defects of the zeolite supports that more than likely will lower long-term stability of the SCR catalysts. An improved one-pot synthesis strategy would be to maintain Fe species in extraframework positions during SSZ-13 [51] and SAPO-34 [52] synthesis, Turrina et al. [38] studied one-pot Fe/SAPO-34 synthesis using Fe<sup>2+</sup>-polyamine complexes as structure directing agents (SDAs), where the following polyamines were used: diethylenetriamine (DETA), N-(2-hydroxyethyl) ethylenediamine (HEEDA), triethylenetetramine (TETA), N,N'-bis(2-aminoethyl)-1,3-propanediamine, 1,2-bis(3-aminopropylamino) ethane, tetraethylenepentamine (TEPA), and pentaethylenehexamine (PEHA). For comparison, Fe<sup>3+</sup>-TEPA, morpholine and TEAOH were also used as SDAs during one-pot synthesis. Even though XRD analysis demonstrated that all of these SDAs led to successful SAPO-34

synthesis, some of the extraframe Fe<sup>2+</sup>-polyamine complexes were not maintained during synthesis. Figure 3 presents UV-Vis spectra of the as-prepared, air-dried samples (i.e., before calcination) by Turrina et al. In the O  $\rightarrow$  Fe charge transfer region, in addition to bands below ~300 nm assigned to isolated Fe(III), strong bands at ~370 nm, assigned to Fe<sub>x</sub>O<sub>y</sub> clusters are also evident for the samples synthesized with Fe-polyamine SDAs. Obviously, these Fe species were not preserved by the polyamine ligands as monomeric Fe during synthesis. Interestingly, however, that some samples display d-d transition bands at ~550 nm, assigned to Fe<sup>2+</sup> complexes involving molecular O<sub>2</sub> in the coordination sphere. Please note that Fe<sup>2+</sup> ions giving rise to such bands remained in extraframe locations during synthesis. Clearly, some polyamines (e.g., TEPA) are more efficient than others in complexing Fe<sup>2+</sup>, allowing Fe to stay in extraframework positions during synthesis. Morpholine and TEAOH, on the other hand, are incapable of this site protection.



**Figure 3.** Solid-state UV-visible spectra of as-prepared Fe-SAPO-34 obtained using (a) DETA, (b) HEEDA, (c) TETA, (d) 232, (e) 323 and (f) TEPA (all with  $Fe^{2+}$ ); (g) TEPA with  $Fe^{3+}$ , (h) PEHA (with  $Fe^{2+}$ ), (i) morpholine (with  $Fe^{3+}$ ) and (j) TEA<sup>+</sup> (with  $Fe^{2+}$ ). Reprinted with permission from [38]. Copyright © 2017 The Royal Society of Chemistry.

Overall, methods commonly used for generating ion-exchanged zeolite materials can be readily adopted to synthesize small-pore Fe/zeolites. Even for catalysts formed via incipient wetness impregnation where large Fe agglomerates are anticipated to dominate, moderate SCR activity is still achieved [53]. It is likely that some levels of solution ion-exchange and solid-state ion exchange occur during the impregnation and calcination processes, respectively, forming Fe sites that are active for SCR. In terms of maximizing Fe atomic efficiency; however, solution ion-exchange and one-pot synthesis clearly have their advantages over impregnation. Regardless of the synthesis method, lowering total Fe loading generally limits formation of  $Fe_xO_y$  clusters and  $Fe_2O_3$  particles, leading to catalysts with lower levels of site heterogeneity.

# 3. Fe Speciation of Small-Pore Fe/Zeolites

#### 3.1. Fe Species in Freshly Prepared Small-Pore Fe/Zeolites

In the previous section, we showed that UV-Vis spectroscopy can be readily applied to distinguish Fe species with different nuclearity. However, as the extinction coefficients for different bands are typically unknown, this method is only qualitative. Next, a few additional characterization techniques, including some quantitative ones, are described. We mainly focus on Fe/SSZ-13 catalysts prepared by solution ion-exchange to avoid complexities caused by the presence of both framework and extraframework Fe species associated with one-pot synthesis. Specific attention will be given to monomeric and dimeric Fe species since these moieties are most relevant to SCR. The summary of the experimental findings is followed by describing DFT simulated Fe structures.

As shown by UV-Vis (e.g., Figure 1), even by following careful ion-exchange procedures, iron oxides can still accumulate as exchange level rises. Even though iron oxide particles are unwanted for SCR applications, it is of interest to understand sizes and locations of such species. Figure 4 displays TEM images for a freshly prepared Fe/SSZ-13 with 1.20 wt% Fe (the highest Fe loaded sample of the series shown in Figure 1) [32]. Fe agglomerates are not observed on most of the SSZ-13 particles (see Figure 4a, for example) suggesting that monomeric, dimeric and larger oligomeric Fe sites locate inside the zeolite particles. However, two types of iron oxide moieties are detected, including occasional Fe enriched thin films at zeolite particle edges (Figure 4b, marked with a dashed oval) and needle-shaped particles that are not attached to the zeolite particles (Figure 4c, marked with dashed cycles). The formation of these unexchanged moieties demonstrates that some Fe species fail to diffuse into zeolite pores during ion exchange. Although these Fe-oxides are not anticipated to contribute to SCR, as will be shown below, they play important roles in trapping Al that leaches out from the zeolite support during hydrothermal aging.



**Figure 4.** TEM images of fresh Fe/SSZ-13 catalyst (1.20 wt% Fe loading): (**a**) representative individual particles; (**b**) occasional individual particles with Fe enrichment at particle edges; (**c**) larger scale image with needle-shaped Fe-oxide particles. Scale bars for (**a**–**c**) are 5, 10 and 100 nm, respectively. Reprinted with permission from [32]. Copyright © 2017 American Chemical Society.

As long as the Fe loadings are maintained at low values, the contents of Fe-oxide particles and even smaller oligomeric  $Fe_xO_y$  clusters can be considered negligible in comparison to the more dominant monomeric and dimeric Fe sites. This notion is readily proven by calculating H<sup>+</sup>/Fe<sup>2+</sup> exchange ratios of ion-exchanged Fe/SSZ-13 formed using Fe<sup>2+</sup> salts. Figure 5 displays NH<sub>3</sub>-TPD data for the same series of low-Fe loaded Fe/SSZ-13 samples as shown in Figure 1 [28]. The inset shows a linear correlation between remaining Brønsted acid sites (probed by NH<sub>3</sub> adsorption) and Fe/Al ratios with a slope of ~-1. Since Fe-oxide particles are charge neutral and oligomeric Fe<sub>x</sub>O<sub>y</sub> clusters have charge densities lower than unity on a per Fe atom basis, high percentages of such species would otherwise substantially deviate this linear correlation. Furthermore, the slope of ~-1 suggests that the dominant monomeric and dimeric Fe sites have a +1 formal charge per Fe, e.g., ZFe(OH)<sub>2</sub> and ZFe(OH)O(OH)FeZ ("Z" represents a -1 framework change). Precise determination of the nature of the monomeric and dimeric Fe sites, however, is rather challenging. From the current state of the art, the most powerful experimental approach that can be applied to quantitatively describe possible Fe sites in small pore zeolites is Mössbauer spectroscopy. Next, selected results obtained with this technique are summarized.



**Figure 5.** NH<sub>3</sub>-TPD curves for the parent H/SSZ-13 and the Fe/SSZ-13 samples. NH<sub>3</sub> adsorption and purging was carried out at 100 °C prior to TPD. The inset shows a linear fit between normalized NH<sub>3</sub> desorption peak areas versus Fe/Al ratios. Reprinted with permission from [28]. Copyright © 2016 American Chemical Society.

Since only recoil-free Fe can be detected with Mössbauer spectroscopy, to increase detectability of Fe species that interact weakly with the zeolite support to fulfill quantification needs, it is important to apply cryogenic measurement temperatures to immobilize such species. This notion is demonstrated by Figure 6, displaying spectra for the 1.20 wt% Fe-loaded Fe/SSZ-13 sample measured at different temperatures [54]. These spectra clearly show that the paramagnetic Fe(II) doublets (marked with a red dashed line) and magnetic Fe(III) sextets (marked with asterisks) only fully develop at liquid N<sub>2</sub> temperatures or lower, demonstrating that low temperatures are essential for quantifying all possible Fe moieties.



**Figure 6.** Mössbauer spectra of the ambient <sup>57</sup>Fe/SSZ-13 (1.20 wt%) sample measured at different temperatures, from 8 K to room temperature. Reprinted with permission from [54]. Copyright © 2017 Elsevier Inc. Magnetic Fe(III) sextets (marked with asterisks).

Figure 7a presents Mössbauer spectra for the same series of samples shown in Figure 1, measured at liquid He temperature [28]. Despite the loading differences, the spectra are qualitatively similar to each other; they mainly differ in the relative contents of doublet (paramagnetic, P) and sextet (magnetic, M) features. Details about spectrum fitting and quantification are not described here; these can be found elsewhere [28]. Figure 7b plots the quantification results: Fe(II)-P denotes Fe(II) species that display doublet signals (i.e., paramagnetic), Fe(III)-P denotes Fe(III) species that display doublet signals (paramagnetic), and Fe(III)-M denotes Fe(III) species that display sextet signals (i.e., magnetic). By examining key Mössbauer parameters, e.g., center shift and quadrupole splitting, the nature of the different Mössbauer signals are assigned as follows: Fe(II)-P contains primarily hydrated, isolated Fe<sup>2+</sup> ions. The high mobility of this species should render it completely invisible at room temperature. However, as shown in Figure 6, a weak Fe(II) signal is indeed detected at RT, suggesting the presence of a small portion of less mobile Fe(II) moieties. This species is tentatively assigned to Fe(III)-O-Fe(II) dimeric species [54]. It is interesting to note from Figure 7b that the Fe(II)-P contents do not vary with Fe loading, suggesting that isolated  $Fe^{2+}$  ions are only stabilized at certain low-concentration exchange positions of the SSZ-13 support. Fe(III)-P, owing to its high quadrupole splitting values, is best attributed to dinuclear Fe<sup>3+</sup> complexes. This species was suggested by Gao et al. as ZFe(OH)O(OH)FeZ [28]. As will be shown below from DFT calculations, other dimeric Fe(III) species are also possible [35]. Fe(III)-M, on the other hand, contains monomeric Fe(III), Fe<sub>x</sub>O<sub>v</sub> clusters and Fe-oxide particles. Please note that the Fe-oxide particles present in SSZ-13 (e.g., Figure 4)

most likely have a stoichiometry as  $Fe_2O_3$ , but the Mössbauer parameters are distinct from those of hematite. It is likely that these Fe-oxide particles are poorly crystalline or amorphous. To summarize, Mössbauer spectroscopy can be considered as the best state-of-the-art quantitative technique that can be applied to quantify different Fe species on Fe/zeolites (e.g., Figure 7b). Even so, it is still incapable of distinguishing the multiple components in Fe(III)-M. With the aid from other characterization techniques (e.g., UV-Vis, Figure 1), it can be ascertained that monomeric Fe(III) sites are the main contributor for Fe(III)-M, i.e., low Fe-loaded chabazite catalysts contain predominately monomeric and dimeric Fe species.



Figure 7. (a) Mössbauer spectra of the ambient 57Fe/SSZ-13 samples measured at 8 K. Spectra are shifted vertically and displayed with different colors, and Fe loadings are marked adjacent to the spectra.
(b) Loadings of the three Fe components determined from Mössbauer spectroscopy as a function of total Fe loading. Reprinted with permission from [28]. Copyright © 2016 American Chemical Society.

Recent theoretical studies by Schneider and coworkers [35], and McEwen and coworkers [36] provided further understanding of the detailed structures and locations of possible monomeric and dimeric Fe species. Similar to Cu/SSZ-13 where Cu(II) ions occupy windows of 6- and 8-membererd rings (6MR and 8MR) with Al substitution [6,55], Al substituted 6MR and 8MR are also sites for exchanged monomeric and dimeric Fe ions to anchor. Figure 8 presents relative energies for the various possible monomeric and dimeric Fe(III) and Fe(II) structures in four different framework charging environments [35]. Some of the lowest energy Fe(III) and Fe(II) structures are presented in Figure 9. It is readily seen from the data that ring size, Al-Al separation and Brønsted acid sites, among other factors, play important roles in stabilizing such structures. Please note that the Fe(III) species are heavily hydroxylated to maintain their +1 charge per Fe, consistent with the experimentally derived  $H^+/Fe^{2+}$  exchange ratios of ~1 (Figure 5). It appears somewhat counterintuitive that the "bulky" dimeric Fe(III) species ZFe(OH)(OH)<sub>2</sub>(OH)FeZ is the most stable in 6MR windows. However, an 8MR window can stabilize this species with almost identical energies (Figure 8). For Fe(II) moieties, the same  $Z_2$ Fe(H<sub>2</sub>O) species display similar energies in varying locations, and all of them are energetically more favorable than ZFeOH. However, in comparison to the most stable Fe(III) species,  $Z_2$ Fe(H<sub>2</sub>O) is clearly energetically less favorable (Figure 8). This is consistent with experimental observations that only limited amounts (~0.1 wt%) of Fe(II) species exist in the series of Fe/SSZ-13 samples prepared by Gao et al. (Figure 7b). It is of interest to note that the chabazite framework can also host Fe species with +4/+5 oxidation states. A particularly important structure is  $Z_2$ Fe=O, located in 6MR windows; this so-called  $\alpha$ -O structure has been found to be active in ambient temperature methane activation [56].

It should be noted that the structures and relative energies for the various possible Fe species shown above are subject to changes under thermal and/or vacuum treatments. One important such change is "autoreduction", i.e., the conversion of Fe(III) to Fe(II) during thermal and/or vacuum

treatments in the absence of purposely introduced reductants. Such a phenomenon is relevant to standard SCR since Fe ions cycle between +3 and +2 oxidation states during standard SCR. Figure 10 presents computed phase diagrams by Li et al. [35], reporting the free-energy minimizing species as a function of temperature and O<sub>2</sub> pressure, at 0.02 atm of H<sub>2</sub>O. Phase diagrams include Fe species of the same nuclearity anchored to the same Al configuration, including Fe monomer phase diagrams for each Al configuration and the dimeric Fe phase at each  $Z_2$  site. Vertical arrows in the figures indicate the expected Fe transformations at a site as the temperature is increased at 0.2 atm  $O_2$  pressure. At room temperature, the most stable species correspond to the energy-minimizing Fe(III) monomers or dimers shown in Figure 8, possibly covered with additional solvating water. As the temperature increases, all sites transition to partially dehydrated equilibrium structures, each at its own distinct temperature. Except for the 8MR 4NN Cu dimer, all Fe(III) sites eventually transition to an "autoreduced" Fe(II) state, where equilibrium autoreduction temperatures vary widely from site to site [35]. If one assumes that the energy barriers for autoreduction positively correlates to the energy barriers for redox cycling during SCR, the phase diagrams shown in Figure 10 suggest at least two points that are likely important to SCR: (1) both monomeric and dimeric Fe(III) species, when located in certain extraframework positions, are SCR active, and (2) Brønsted acid sites in the proximity of Fe(III) sites can greatly promote SCR rates.



**Figure 8.** Relative energies of Fe species calculated using the Heyd-Scuseria-Ernzerhof (HSE) method at isolated (left) and paired ( $Z_2$ ) sites, referenced to an isolated ZFeOH. Colors indicate the Fe formal oxidation state. Solid lines connect monomeric [Fe(OH)<sub>2</sub>]<sup>+</sup> and [Fe(OH)]<sup>+</sup> species at an isolated Al site and 8MR 4NN  $Z_2$  sites. Dashed lines connect analogous species among  $Z_2$  sites. Reprinted with permission from [35]. Copyright © 2018 American Chemical Society.



**Figure 9.** Lowest-relative-energy formal (**a**)  $\text{Fe}^{3+}$  and (**b**)  $\text{Fe}^{2+}$  species optimized via the Perdew-Becke-Erzenhof (PBE) functional. For ease of visualization, only framework atoms of the nearest 6- or 8MR are shown. Reprinted with permission from [35]. Copyright © 2018 American Chemical Society.



**Figure 10.** Compositional Fe-site phase diagrams vs relative O<sub>2</sub> pressure and temperature at 0.02 atm of H<sub>2</sub>O. (**a**–**d**) Monomeric Fe at isolated Al, 8MR 4NN, 6MR 3NN, and 6MR 2NN Z<sub>2</sub> sites, respectively, and (**e–g**) dimeric Fe species. Black vertical arrows correspond to PO<sub>2</sub> = 0.2 atm. Reprinted with permission from [35]. Copyright © 2018 American Chemical Society.

It can be seen in Figure 7b that Fe/SSZ-13 prepared via ion-exchange already contains small amounts of Fe(II) ions after calcination in air. Certain catalyst treatment procedures, e.g., thermal dehydration, further induces Fe(II) formation via Fe(III) autoreduction as shown immediately above. As predicted by theoretical calculations (Figures 8 and 9), Fe(II) sites can occupy more than one extraframework positions. This heterogeneity is readily probed by NO titrations with FTIR. Figure 11 presents IR spectra collected during NO adsorption and desorption on an Fe/SSZ-13 catalyst vacuum annealed at 773 K (i.e., autoreduced) by Szanyi et al. [29]. The system consisted a batch reactor attached to a vacuum system. The powder sample was pressed onto a tungsten net that can be resistively heated or cooled by thermal contact with a liquid nitrogen reservoir. FTIR spectra were acquired via a transmission mode by placing the sample in the IR beam. The measurements were carried out by introducing small doses of NO to the transmission IR cell, and each spectrum was collected after equilibrium was reached following such NO doses. The measurements were continued until the accumulation of ~0.5 Torr of NO in the gas phase. The background was collected prior to NO admission. At very small NO dosage amounts (see the inset in Figure 11a), two overlapping features centered at ~1900 and ~1888 cm<sup>-1</sup> form one broad, asymmetric band in the IR spectra, attributed to adsorbed NO on isolated Fe(II) sites in 8RM and 6MR, respectively. At intermediate NO pressures (when gas phase NO just appears), the ~1888 cm<sup>-1</sup> band saturates, and new bands appear at around 1771 and 1850 cm<sup>-1</sup>, attributed to Fe<sup>2+</sup>(NO)<sub>2</sub> dinitrosyl species. With further increasing NO pressure, the 1900, 1850 and 1771 cm<sup>-1</sup> bands diminish, replaced by simultaneously developed peaks at ~1916, 1812 and 1801 cm<sup>-1</sup>; these latter bands are attributed to Fe<sup>2+</sup>(NO)<sub>3</sub> trinitrosyl species. Desorption experiments (Figure 11b) demonstrate the highly unstable nature of trinitrosyl; however, dinitrosyl is rather stable and only diminishes slowly. Importantly, only Fe(II) sites in 8RM form dinitrosyl and trinitrosyl, whereas Fe(II) sites in 6RM saturate with mono-nitrosyls. Such a difference is readily understood from spatial considerations, i.e., the windows of 6MR cannot accommodate more than one NO adsorbed on the same Fe(II) site. Such experimental findings that Fe(II) sites occupy both 6RM and 8MR windows are fully consistent with DFT simulated Fe(II) structures shown in Figure 9, where ZFeOH prefers to occupy 8MR and  $Z_2$ Fe(H<sub>2</sub>O) can occupy both 6MR and 8MR windows. Via DFT, Zhang et al. [36] calculated mono-, di- and trinitrosyl N-O vibrational frequencies on ZFeOH anchored in 8MR window. The calculated values differ considerably from experimental data, as much as 60–70  $cm^{-1}$ . The likely explanation is that Z<sub>2</sub>Fe(H<sub>2</sub>O), rather than ZFeOH is more dominant as predicted from energy calculations (Figure 8).



Figure 11. Cont.



1900

1800

1700

**Figure 11.** Selected IR spectra collected during the step-wise adsorption of NO on an annealed (773 K) Fe/SSZ-13 (Si/Al = 12, Fe loading = 0.63 wt%) sample at 295 K: (**a**) adsorption and (**b**) desorption. (The inset in panel a highlights the IR spectra recorded at the lowest NO dosages). Reprinted with permission from [29]. Copyright © 2016 by the Owner Societies.

2100

2000

Wavenumbers/cm<sup>-1</sup>

2200

# 3.2. Fe-Ion Transformations during Hydrothermal Aging

(b)

0.24

0.22

0.20 0.18

0.16 0.14 0.12

0.10 0.08 0.06 0.04 0.02

2300

Absorbance/a.u.

Hydrothermal stability and resistance to chemical poisoning (e.g., sulfur and phosphorus) are among the most important criteria for a successful commercial SCR catalyst [6]. Good hydrothermal stability requires that (1) the zeolite support stays intact during aging, i.e., with limited crystallinity, surface area and porosity loss, as well as limited dealumination, and (2) the SCR active sites do not convert to species with no or lower activities. The quality of the support materials, the active site loading and dispersion, and dynamic interactions between the support and the active sites all play important roles on hydrothermal stability. For the well-studied Cu/SSZ-13 catalyst, it has been clearly documented that support stability becomes enhanced when exchanged Cu at intermediate exchange levels are present [57–59], whereas in over-exchanged catalysts, some exchanged Cu species (i.e., ZCuOH) agglomerate to CuO during aging, and the latter species "attack" the supports leading to lowered hydrothermal stability [60,61]. For Fe/SSZ-13, such detailed atomic level understanding is not yet available; however, changes to the supports and Fe sites as a result of hydrothermal aging have been investigated using several standard characterization approaches. Some such data are shown below.

Using the Fe/SSZ-13 (Si/Al = 12, Fe loading = 1.20 wt%) catalyst shown above as an example, we show next how the support and Fe sites evolve with increasing aging temperature [32]. Figure 12a presents <sup>27</sup>Al solid-state MAS NMR spectra for the fresh catalyst, and the ones hydrothermally aged at different temperatures. Please note that framework tetrahedral Al displays signals around 59 ppm and extraframework Al displays signals around 0 ppm. The intensity of framework Al signals rapidly declines with increasing aging temperature. By ratioing the peak areas against that of the fresh catalyst, the remaining framework Al contents in the HTA samples can be readily calculated, and the values are marked adjacent to the corresponding spectra. It is important to note that framework Al signal loss for steamed zeolites is typically attributed to dealumination. As such, extraframework Al with signal intensities comparable to those of the lost framework Al should appear at ~0 ppm for the aged samples. However, this is clearly not the case as Figure 12a shows. It has been well documented in the literature that there exist two, and only two, possibilities for Al being NMR-invisible: (1) the presence of paramagnetic species in proximity; or (2) Al being located in a highly distorted position [62,63]. Accordingly, in addition to dealumination, the framework Al signal loss shown in Figure 12a may also be contributed by paramagnetic Fe sites staying closer to framework Al and the zeolite framework being more defective (i.e., more distorted) as a result of hydrothermal aging. Such ambiguity, however, can be readily clarified by NH<sub>3</sub>-TPD shown in Figure 12b [31]. Desorption above ~350 °C is attributed

to Brønsted acid sites and desorption at lower temperatures to Lewis (e.g., extraframe Al) acid sites. From these data, it is readily concluded that Brønsted acid site density loss shown in Figure 12b and framework Al loss shown in Figure 12a correlate very well for the aged samples, suggesting that it is indeed dealumination, rather than any other possible reasons, that is responsible for framework <sup>27</sup>Al NMR signal loss for the aged samples. In contrast, the absence of extraframework Al signal increase can be safely attributed to (1) such Al species being close to paramagnetic Fe species, and/or (2) such



**Figure 12.** (a) Solid-state <sup>27</sup>Al-NMR spectra for the fresh and hydrothermally aged (HTA) Fe/SSZ-13 samples (Si/Al = 12, Fe loading 1.20 wt%). Tetrahedral Al contents for the HTA samples were normalized against the fresh sample, and the values are marked adjacent to each spectrum. (b) NH<sub>3</sub>-TPD for the fresh and HTA. NH<sub>3</sub> is adsorbed at 100 °C. Ramping rate = 10 °C/min. (c) The corresponding <sup>29</sup>Si-NMR spectra showing gradual conversion of Si(OSi)<sub>3</sub>(OAl) to Si(OSi)<sub>4</sub> with increasing aging temperature. (a,c) reprinted with permission from [32]. Copyright © 2017 American Chemical Society; (b) reprinted with permission from [31]. Copyright © 2016 Springer Science+Business Media New York.

It is interesting to note that in comparison to Cu/SSZ-13 catalysts with the same Si/Al ratio and similar exchange levels, Fe/SSZ-13 catalysts tend to dealuminate more severely under the same aging conditions [33]. Even so, Fe/SSZ-13 catalysts appear to preserve surface area/porosity better than Cu/SSZ-13 catalysts during aging. For the series of Fe/SSZ-13 catalysts studied by Kovarik et al. [32],

hydrothermal aging at 800 °C for 16 h induces more than 80% of dealumination (Figure 12a), yet with less than 7% surface area/porosity loss. Such support integrity preservation is well reflected from <sup>29</sup>Si NMR data shown in Figure 12c. The fresh catalyst contains two framework tetrahedral Si (Q4) features: one at -105 ppm assigned to tetrahedral Si with three Si and one Al neighbors (i.e., Si(OSi)<sub>3</sub>(OAl)) and one at -111 ppm assigned to tetrahedral Si with four Si neighbors (i.e., Si(OSi)<sub>4</sub>) [64]. With increasing hydrothermal aging temperature, the -105 ppm resonance gradually diminishes, and the -111 ppm resonance intensifies and narrows. Please note that the disappearance of Si(OSi)<sub>3</sub>(OAl) during hydrothermal aging is fully consistent with catalyst dealumination found in Figure 12a. It is interesting; however, that sample dealumination is not accompanied by the appearance of Q2 and Q3 features (i.e., Si(OSi)<sub>2</sub>(OH)<sub>2</sub> and Si(OSi)<sub>3</sub>(OH), expected at ~-90 and -100 ppm, respectively [64], or broadening of the -111 ppm signals as a result of crystallinity decrease. These experimental findings strongly suggest that defects created via dealumination are subsequently "self-healed" to sustain structural integrity of SSZ-13 during aging [32].

As a result of support dealumination, it is anticipated that some monomeric and dimeric Fe sites agglomerate during hydrothermal aging to cope with the decreased framework charge density. Next, Mössbauer spectroscopic results by Kovarik et al. [32] on Fe transformations during hydrothermal aging are given. As discussed above, Mössbauer spectroscopy is the best available technique for quantifying various Fe species supported on zeolites. The authors chose an Fe/SSZ-13 catalyst with a low Fe loading of 0.37 wt% that contains negligible Fe-oxide content in its fresh form (Figure 1) to lower ambiguities in Mössbauer spectra simulations and assignments. The Mössbauer spectra for fresh and aged samples are shown in Figure 13. Detailed Mössbauer parameter analysis and quantification of various Fe species can be found elsewhere [32]. Herein, a simplified version of the quantification results is displayed in the table next to the spectra. We note again that Fe(II)-P comprises primarily monomeric Z<sub>2</sub>Fe and small amounts of Fe(III)-O-Fe(II) moieties; Fe(III)-P comprises dimeric Fe(III) species (as shown in Figures 8–10, there exist a few such species with slight differences in structures); and Fe(III)-M contains Fe(III) monomers, Fe<sub>x</sub>O<sub>v</sub> clusters and Fe-oxide particles (all these species show indistinguishable sextet patterns under liquid helium temperature). Important information derived from the spectra analysis includes: (1)  $Z_2$ Fe becomes unstable under hydrothermal aging conditions; these species convert primarily to dimeric Fe(III) moieties. This conversion can be readily understood from the relative energy plots for different Fe species shown in Figure 8. (2) Dimeric Fe(III) moieties are highly stable; their content only decreases very slightly when the aging temperature increases from 700 to 800 °C. (3) Even though Fe(III) monomer agglomeration to Fe<sub>x</sub>O<sub>y</sub> clusters and Fe-oxide particles is difficult to quantify due to their highly similar sextet spectrum lineshapes, the average hyperfine magnetic field for the sextets decreases with increasing HTA temperature, most notably for the HTA-800 sample. This could be due to increasing incorporation of Al into these latter phases (i.e., magnetic dilution), an explanation that is in full agreement with the unusual undetectability of extraframework Al in the aged samples (Figure 12a) [32].

Fe(III) ion agglomeration during hydrothermal aging is readily observed by TEM imaging. Figure 14a presents a representative TEM image for an Fe/SSZ-13 catalyst particle (1.20% Fe loading) after aging at 800 °C. In comparison to Figure 4a, for the fresh catalyst that displays no Fe enrichment anywhere on the particle, the HTA-800 sample contains uniformly dispersed spots ~1–2 nm in size, lighter than the zeolite matrix, that can be readily attributed to  $Fe_xO_y$  clusters. The precise locations for these clusters, i.e., whether these are located on the zeolite surface or embedded within the zeolite particle bulk, is not readily determined from such imaging. However, these clusters are likely embedded (and thus immobilized) within zeolite bulk; if they stayed on external surfaces, it is anticipated that they would have undergone more extensive sintering to form larger particles. As shown in Figure 14b, needle-shaped particles seen on the fresh catalyst in Figure 4c are still present (highlighted with dashed cycles). Figure 14c presents EDS of the SSZ-13 matrix (upper panel) and the needle-shaped particles (lower panel). The SSZ-13 matrix spectrum is expected as it is composed of O, Si, Al, and detectable amounts of Fe. Note specifically that the needle shaped particles in fresh

samples are Fe-oxides, whereas in the HTA-800 sample they are enriched in Al, resulting from apparent conversion to Fe-aluminate-like species during aging. This is direct evidence that upon dealumination, the extraframe Al interacts with Fe-oxides. This is fully consistent with the magnetic dilution of Fe(III)-M Mössbauer signals in hydrothermal aging as discussed immediately above.



sample	Fe(II)-P	Fe(III)-P	Fe(III)-M
Fresh	26.4	12.4	61.2
HTA-600	15.7	27.1	57.2
HTA-700	7.6	31.1	61.4
HTA-800	2.0	30.0	68.0

**Figure 13.** Experimental and simulated Mössbauer results for fresh and HTA Fe/SSZ-13 samples (0.37% Fe loading) measured at 7 K. Reprinted with permission from [32]. Copyright © 2017 American Chemical Society.

Hydrothermal stability of a few other small-pore Fe/zeolites have also been investigated in the past few years. Martín et al. compared hydrothermal stability of Fe/SSZ-39 prepared via both solution ion-exchange and one-pot synthesis with one-pot synthesized Fe/beta, and concluded that both Fe/SSZ-39 catalysts have hydrothermal stability higher than the latter [39]. Such results are consistent with the consensus that catalysts synthesized using small-pore zeolite supports offer improved stability than those formed with zeolite supports with larger pore openings. However, the hydrothermal aging temperature was limited to 600 °C in the study, which is substantially lower than the accelerated aging temperatures of 750–800 °C typically adopted for evaluating industrial SCR catalysts [65]. Therefore, it is not clear whether the Fe/SSZ-39 catalysts synthesized by Martín et al. can withstand such harsher aging temperatures. It is interesting to note that the sodium-free one-pot Fe/beta catalyst prepared by the authors performed poorly after hydrothermal aging at 600 °C, which is somewhat unexpected since Fe/beta was considered one of the most stable zeolite SCR catalysts prior to the small-pore zeolite catalyst era [23,66]. This may be a strong warning sign that the one-pot method, despite its various advantages as described above, is comprised by Fe incorporation into the framework during synthesis; such Fe species migrate from framework to extraframework positions during aging, leading to lowered hydrothermal stability. However, the one-pot Fe/SAPO-34 synthesized by Andonova et al. [37] appears not to suffer from this potential drawback; not only do their one-pot catalysts withstand hydrothermal aging temperature of 800 °C, they appear to be more stable than commercial Cu/SAPO-34 under the same aging conditions. In any case, detailed Fe transformations under hydrothermal aging for one-pot small-pore Fe/zeolites are still largely unexplored and much is still needed to learn regarding (1) mechanisms for framework Fe relocation to extraframework locations, and the associated influences

on SCR performance; (2) the evaluation of such catalysts under industrial accelerated hydrothermal aging conditions to verify their suitability for commercial use.



**Figure 14.** (a) TEM image of a representative HTA-800 Fe/SSZ-13 catalyst (1.20% Fe loading) demonstrating formation of Fe-oxide aggregates; (b) larger-scale image displaying the preservation of needle-shaped particles; (c) EDS of the SSZ-13 matrix (upper panel) and the needle-shaped particles (lower panel). Note that the weak Cu signals at ~8 keV come from the TEM grid rather than the catalyst. Reprinted with permission from [32]. Copyright © 2017 American Chemical Society.

The comparative study between solution ion-exchanged Fe/SSZ-13 and high-silica Fe/LTA by Ryu et al. [42] convincingly proved the higher hydrothermal stability for the latter. After hydrothermally treating the catalysts at 900 °C, the authors then used <sup>27</sup>Al NMR, FTIR and NH<sub>3</sub>-TPD characterizations to confirm the that the LTA supports were better preserved than SSZ-13 during aging; they also applied UV-Vis, EPR and NO titration FTIR spectroscopies to verify the better preservation of Fe ions during aging. Finally, SCR reaction tests demonstrated that aged Fe/LTA display better performance than aged Fe/SSZ-13. The authors suggested that the stability difference of the two catalysts may be due to intrazeolitic location differences of Fe species. Based on the study, the authors concluded that high-silica LTA zeolites have the potential of being used as a stable NH<sub>3</sub>-SCR catalyst support for both Fe and Cu.

In addition to high-temperature hydrothermal stability, stability under lower-temperature SCR reaction conditions, even under ambient temperature storage conditions, is also of importance for

industrial applications of zeolite-based SCR catalysts. For aluminosilicate zeolite supported Fe catalysts, low-temperature stability should not be of any concerns. For Fe/SAPO-34 catalysts; however, their stability under low-temperature (<100 °C) humid conditions may be problematic for applications. Please note that recent studies found stability issues of Cu/SAPO-34 SCR catalysts under such conditions [50,67–69]. At present, low-temperature moisture sensitivity for Fe/SAPO-34 is largely unknown; explorations are clearly needed.

#### 4. Small-Pore Fe/Zeolites as SCR Catalysts: Structure-Function Correlations

For the purpose of facilitating the discussions below, it is useful to briefly summarize target and key side reactions for NH<sub>3</sub>-SCR. Based on NO<sub>2</sub>/NOx ratios of the feed, NH<sub>3</sub>-SCR is categorized into three reactions [5–7]:

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \text{ (standard SCR)}$$
(1)

$$NO + NO_2 + 2NH_3 \rightarrow 2N_2 + 3H_2O \text{ (fast SCR)}$$

$$(2)$$

$$6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O (NO_2 SCR)$$
 (3)

Among the three reactions, R1 is technically the most important since engine exhausts typically contain NO as the primary form of NOx. R2 can become important when a portion of NO in the exhausts is oxidized to  $NO_2$  by, for example, a diesel oxidation catalyst positioned upper stream of the SCR catalyst. R3 is not encountered under normal SCR reaction conditions.

Key side reactions include non-selective  $NH_3$  oxidation by  $O_2$  and reactions leading to  $N_2O$  formation. These are presented as follows [17]:

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O \tag{4}$$

$$2NH_3 + 2NO_2 \rightarrow N_2 + NH_4NO_3 + H_2O \tag{5}$$

$$NH_4NO_3 \rightarrow N_2O + 2H_2O \tag{6}$$

 $NH_3$  oxidation by O<sub>2</sub> lowers deNOx efficiency. Although this can be technically compensated by extra  $NH_3$  (urea) use; this leads to another technical problem " $NH_3$  slip", which must be dealt with by an ammonia oxidation catalyst (AMOX) down stream of SCR. N<sub>2</sub>O formation is particularly unwanted since it is a greenhouse gas with high global-warming impact [54]. It is generally agreed that N<sub>2</sub>O formation during  $NH_3$ -SCR is due to  $NH_4NO_3$  decomposition (R6), and formation of the latter species is directly associated with the presence of NO<sub>2</sub> in engine exhausts (R5) [70].

To discuss small-pore Fe/zeolites as potential commercial SCR catalysts, we first list SCR performance of a few representative catalysts. Due to the lack of detailed SCR selectivity and turnover rate reports, we only compare NOx conversions at a reaction temperature of 300 °C (Table 1). As the data show, all of these catalysts display mediocre NOx conversions at 300 °C (the high NOx conversion of 90% reported in Ref. [40] may be due to the low NO concentration used in the test). Please note that Cu/zeolites readily reach near 100% NOx conversions under similar testing conditions [6]. This activity difference is consistent with earlier studies on medium- and large-pore zeolite catalysts where Fe catalysts were generally found to be inferior to Cu catalysts in catalyzing standard SCR at low temperatures [17].

Catalyst	SCR Test Condition	NOx Conversion at 300 °C	Reference
One-pot Fe/SAPO-34, Fe loading 0.27 wt%, washcoated	Catalyst: monolith with length = 20 mm, diameter = 22 mm and cell density of 400 cpsi, contains ~700 mg of washcoaated Fe/SAPO-34. Reaction feed contains 350 ppm NO, 350 ppm NH <sub>3</sub> , 14% O <sub>2</sub> , 5% H <sub>2</sub> O and 5% CO <sub>2</sub> . The total gas flow is held constant at 3500 mL min <sup>-1</sup> .	~70%	[37]
Solution exchanged Fe/SSZ-13, Fe loading 1.2 wt%	The reactant feed contains 350 ppm of NO, 350 ppm of NH <sub>3</sub> , 14% O <sub>2</sub> , and 2.5% H <sub>2</sub> O balanced with N <sub>2</sub> at a GHSV of 200,000 $h^{-1}$ .	~50%	[28]
Impregnated Fe/SSZ-13, Fe loading 2.5 wt%	Reaction conditions: 400 ppm NO, 400 ppm NH <sub>3</sub> , 14% O <sub>2</sub> , 2% H <sub>2</sub> O, balance helium; 40 mg of catalyst; total flow rate 300 mL min <sup>-1</sup> ; GHSV = $3.45 \times 10^5$ h <sup>-1</sup> .	~65%	[53]
One-pot Fe/SSZ-13, sodium free, Fe loading 1.7 wt%	The reactant feed contains 50 ppm NO, 60 ppm NH <sub>3</sub> , 10% O <sub>2</sub> , and 10% H <sub>2</sub> O; gas flow at 300 mL min <sup>-1</sup> ; 40 mg catalyst.	~90%	[40]
Solution exchanged Fe/SSZ-39, Fe loading 0.9 wt%	Same as above	~75%	[39]
Solution exchanged Fe/LTA, Fe/Al ratio 0.37	A feed gas containing 500 ppm $NH_3$ , 500 ppm $NO$ , 5% $O_2$ and 10% $H_2O$ , balanced with $N_2$ ; 600 mg catalyst; GHSV = $1 \times 10^5 h^{-1}$ .	~80%	[42]

Table 1 SCR	performance	for selected	small-nore	Fe/zeolites	at 300 °C 1
Table L. JUK	periormance	IOI SEIECIEU	sman-pore	re/zeomes	at 500 C.

<sup>1</sup> Standard NH<sub>3</sub>-SCR on fresh catalysts.

To better understand structure-function correlations for small-pore Fe/zeolite SCR catalysts, and to discuss their potentials for industrial applications, we next compare standard NH<sub>3</sub>-SCR light-off behavior over freshly prepared and hydrothermally aged Cu- and Fe/SSZ-13 catalysts. Figure 15a presents a comparison between fresh catalysts with the same Si/Al ratio of 12 and similar ion-exchange levels (Cu(Fe)/Al =  $\sim 0.2$ ) [33]. Please note that Cu/SSZ-13 shows light-off temperature  $\sim 100$  °C lower than that of Fe/SSZ-13. The lower activity for Fe/SSZ-13 in catalyzing standard SCR at low temperatures (<~250 °C) is typically attributed to "ammonia inhibition" [71]. However, this somewhat vague term has not been clearly explained in the literature. Herein, a few possible explanations are discussed. First, ammonia inhibition may be due to strong complexing of ammonia with Fe ions, rendering the Fe-ammine complexes less reactive than Cu-ammine complexes (e.g.,  $[Cu(NH_3)_4]^{2+}$ ). However in terms of metal-ammine complexing strength, ammonia binds Cu(II)/Cu(I) ions much stronger than Fe(III)/Fe(II) ions. In aqueous solutions, Cu(II) ions interact with ammonia solution to form  $[Cu(NH_3)_4]^{2+}$  with a high formation constant of 2.1 × 10<sup>13</sup>, whereas Fe(III)/Fe(II) ions prefer the formation of hydroxide precipitates under similar conditions. Second, ammonia may readily reduce Fe(III) to Fe(II) under low-temperature SCR conditions, thus slowing down redox cycling of the Fe-ion active species. This second explanation appears to be more reasonable, considering the fact that Fe/zeolites are particularly active for low-temperature fast SCR where Fe(III)/Fe(II) redox cycling appears not to be kinetically relevant [72]. In any case, the lower activity for Fe/SSZ-13 than Cu/SSZ-13 in catalyzing standard SCR at low temperatures may be generally interpreted as that efficient Fe(III)/Fe(II) redox cycling requires higher temperatures than that of Cu(II)/Cu(I).

Data in Figure 15a also show another key difference between fresh Fe/SSZ-13 and Cu/SSZ-13, that is, NOx/NH<sub>3</sub> consumption ratios during standard SCR. Over Cu/SSZ-13, NOx and NH<sub>3</sub> conversions maintain essentially identical, indicating that standard SCR (R1) overwhelms any side reactions over the entire temperature range. This is typical for fresh Cu/SSZ-13 catalysts that contain predominately isolated Cu-ions (i.e., no or low concentrations of Cu<sub>x</sub>O<sub>y</sub> clusters). In contrast, as much as ~20% NH<sub>3</sub> overconsumption is registered over fresh Fe/SSZ-13 at temperatures above ~260 °C. During standard SCR, NH<sub>3</sub> overconsumption is typically due to nonselective NH<sub>3</sub> oxidation by O<sub>2</sub> (R4). However, since control experiments demonstrate that R4 does not commence on the Fe/SSZ-13 catalyst used in Figure 15a below 300 °C [28], NH<sub>3</sub> overconsumption in SCR below this temperature cannot be attributed to this reaction. Rather, such low-temperature overconsumption results from NH<sub>3</sub> + NO<sub>2</sub>

$$NO_2 + 2NH_3 + O_2 = NO + N_2 + 3H_2O$$
(7)

In any case, parasitic  $NH_3$  oxidation requires the participation of oxidants with low-temperature reactivity higher than  $O_2$ , and  $NO_2$  appears to be the only molecule that satisfies this requirement under typical SCR reaction conditions. Therefore, this reaction is closely correlated with the capacity for a SCR catalyst to catalyze NO oxidation to  $NO_2$  (R8).

$$2NO + O_2 = 2NO_2 \tag{8}$$

Recent studies demonstrate that freshly prepared Fe/SSZ-13 are much more active in catalyzing this latter reaction than fresh Cu/SSZ-13 at similar exchange levels [33]. Regarding which Fe sites are active for R8, it is conceivable that oligomeric  $Fe_xO_y$  sites (including dimers), owing to their stronger  $O_2$  activation capacities than monomeric Fe(III) ions, are the more active ones. In short, SCR selectivity difference between fresh Fe/SSZ-13 and Cu/SSZ-13 can be understood from an active site nuclearity point of view. Cu/SSZ-13 contains predominately monomeric Cu(II) ions that are weak in catalyzing NO oxidation to NO<sub>2</sub> [58,75]; therefore, this catalyst enables high SCR selectivities over wide temperature ranges. In contrast, Fe/SSZ-13 contains both monomeric and oligomeric Fe(III) sites; the latter species are highly active in oxidizing NO to NO<sub>2</sub>. In this case, SCR pathways with NH<sub>3</sub>/NOx ratios larger than unity are enabled, leading to SCR selectivity decrease even in the absence of nonselective NH<sub>3</sub> oxidation by O<sub>2</sub> (R4).

Herein, the two catalysts are further compared in their hydrothermally aged forms, where aging was conducted at 800 °C for 16 h in flowing air containing 10% water vapor. Figure 15b displays standard SCR light-off behaver for hydrothermally aged Cu/SSZ-13. In comparison to its fresh counterpart (Figure 15a), low-temperature activity decreases due to loss of isolated Cu(II) active sites during aging, and high-temperature (>350  $^{\circ}$ C) selectivity decreases due to the formation of Cu<sub>x</sub>O<sub>y</sub> clusters which are highly active in catalyzing R4 at such high temperatures. As is shown in Figure 15c, the hydrothermally aged Fe/SSZ-13 catalyst also loses some of the low temperate activity, due also to loss of SCR active sites during aging. Interestingly; however, low-temperate SCR selectivities increase as compared to the fresh catalyst as evidenced by the much closer NOx and NH<sub>3</sub> conversions below ~400 °C. Based on the discussions above, this is attributed to activity decrease for aged Fe/SSZ-13 in catalyzing oxidation reactions (R4 and R8 above). A few Fe site transformations during aging can be responsible for such activity loss: (1) the agglomeration of smaller clusters to larger ones (this lowers active site density). This notion is readily supported by TEM imaging (comparison between Figures 4a and 14a). (2) Incorporation of Al into the  $Fe_xO_y$  clusters, i.e., conversion of iron oxides to iron aluminates. The occurrence of this chemistry is strongly supported by a few experimental observations. First, as Figure 12 displays, Fe/SSZ-13 dealuminates heavily during hydrothermal aging; however, the detached extraframework Al is barely detectable by <sup>27</sup>Al NMR. The most likely explanation is the interaction between such detached Al and paramagnetic Fe(III) species in Fe<sub>x</sub>O<sub>v</sub> clusters. Second, EDS analysis shown in Figure 14c clearly shows Al incorporation into Fe<sub>2</sub>O<sub>3</sub> particles in hydrothermally aged samples. Even though  $Fe_xO_v$  clusters embedded within zeolite bulk are too small for reliable EDS analysis, it is only reasonable to postulate that Al incorporates into the structurally more defective Fe<sub>x</sub>O<sub>v</sub> clusters as readily as Fe<sub>2</sub>O<sub>3</sub> particles, if not more. Indeed, Mössbauer analysis of aged Fe/SSZ-13 (Figure 13) reveals that the average hyperfine magnetic field for the sextets decreases with increasing aging temperature, most notably for the HTA-800 sample. This "magnetic dilution" is best attributed to Al diffusion into Fe-rich phases [32]. (3) Finally, the conversion of more active  $Fe_xO_y$  clusters to less active  $Fe_xO_y$  clusters during aging. This postulation lacks experimental support; however based on

DFT simulations shown in Figure 10, the conversion of ZFe(OH)(OH)<sub>2</sub>(HO)FeZ to ZFe(OH)O(HO)FeZ is anticipated to greatly lower redox capacity of Fe-dimers. In short, the SCR performance comparison shown above highlights an important characteristic for hydrothermally aged Fe/SSZ-13: in contrast to aged Cu/SSZ-13 that typically suffer from loss of high-temperature SCR selectivities, aged Fe/SSZ-13 maintain high-temperature SCR selectivities rather well, for the reasons discussed immediately above.



**Figure 15.** NOx/NH<sub>3</sub> conversions as a function of temperature during standard SCR for the (**a**) fresh Cuand Fe/SSZ-13 samples, (**b**) hydrothermally aged Cu/SSZ-13, and (**c**) hydrothermally aged Fe/SSZ-13. Reactant feed contains 350 ppm NO, 350 ppm NH<sub>3</sub>, 14% O<sub>2</sub>, 2.5% H<sub>2</sub>O balanced with N<sub>2</sub> at a GHSV of 200,000 h<sup>-1</sup>. Reprinted with permission from [33]. Copyright © 2015 Elsevier B.V.

From the SCR reaction data shown above, and from previous studies on other Fe/zeolite SCR catalysts [25], it can be generally concluded that both isolated Fe(III) and oligomeric Fe<sub>x</sub>O<sub>y</sub> clusters (including dimers) are active for SCR; however, the latter species are less selective than the isolated sites due to parasitic and non-selective NH<sub>3</sub> oxidation reactions. In attempting to gain further details on intrinsic SCR performance of the Fe monomers and oligomers, Gao et al. [28] studied standard SCR, wet and dry NO oxidation, and wet and dry NH<sub>3</sub> oxidation over the series of Fe/SSZ-13 catalysts characterized above in Figures 1, 5 and 7. Figure 16a presents standard SCR NO light-off curves at a space velocity of 200,000 h<sup>-1</sup>. From this plot, it is seen that low temperature NO conversion increases with increasing Fe loading as one would expect. Figure 16b presents normalized SCR rates as a function of Fe loading at a few reaction temperatures (220–260 °C). Except for the catalyst with the lowest Fe content of 0.27 wt%, good linear rates versus Fe content correlations are registered at these temperatures demonstrating that the Koros-Nowak criterion is obeyed under the reaction conditions, i.e., in the absence of mass and heat transfer limitations [76]. The low activity for the 0.27 wt% Fe sample may be understood from its relatively high content of isolated Fe<sup>2+</sup> sites as shown in Figure 7, if one assumes that such sites are inactive for standard SCR. Indeed, as shown in Figure 16c, a linear correlation for all five catalysts is found by plotting normalized SCR rates as a function of the Fe(III) content of the

catalysts, thus confirming the inactivity for isolated  $Z_2$ Fe(II) ions. Finally, as displayed in Figure 16d, all catalysts display similar apparent reaction activation energies of 51–55 kJ/mol demonstrating the same nature of active sites in all catalysts. This is fully in line with the characterization data shown in Figures 1, 5 and 7.



**Figure 16.** Conversion-temperature curves for standard NH<sub>3</sub>-SCR on Fe/SSZ-13 catalysts. Only NO conversions are shown. Reactant feed contains 350 ppm NO, 350 ppm NH<sub>3</sub>, 14% O<sub>2</sub>, 2.5% H<sub>2</sub>O balanced with N<sub>2</sub> at a GHSV of 200,000 h<sup>-1</sup>. (b) Normalized SCR rates (mol NO g<sup>-1</sup> s<sup>-1</sup>) within the differential regime shown in (a) plotted as a function of the Fe loading at 220, 240 and 260 °C. Note highlighted SCR rates on the Fe 0.27% sample that are abnormally low. (c) Normalized SCR rates (mol NO g<sup>-1</sup> s<sup>-1</sup>) within the differential regime shown in (a) plotted as a function of the Fe(III) loading at 220, 240 and 260 °C. (d) Arrhenius plots for standard SCR in the low-temperature regime ( $\leq$ 280 °C) indicating similar apparent activation energies for different samples. Reprinted with permission from [28]. Copyright © 2016 American Chemical Society.

The inactivity for isolated  $Z_2$ Fe(II) ions for standard SCR is readily understood. As a redox reaction, active Fe sites must cycle between +3 and +2 oxidation states to achieve continuous turnovers. Please note that such isolated  $Z_2$ Fe(II) ions survive during catalyst calcination in air at ~600 °C, demonstrating their inactivity toward O<sub>2</sub>. Therefore, these species are not readily oxidized to Fe(III) and become SCR active during standard SCR reaction conditions. An important indication, then, is that the SCR active isolated Fe(III) species is more likely ZFe(III)(OH)<sub>2</sub> than  $Z_2$ Fe(III)OH, where their reduced Fe(II) counterparts are ZFe(II)OH and  $Z_2$ Fe(II), respectively. Even for ZFe(II)OH, the manner in which this species is oxidized back to Fe(III) under SCR conditions to enable continuous turnovers is not well understood. In particular, previous theoretical calculations indicate that individual isolated Fe(II) cannot active O<sub>2</sub> to form Fe(III) [77]. Since small-pore zeolite supported Cu SCR catalysts also

contain isolated active sites, and individual Cu(I) ions also cannot directly active O<sub>2</sub> [78], these two active sites may share the same redox mechanisms. For isolated Cu(I) ions, there has been general consensus that a pair of mobile ammonia ligated Cu(I) species (i.e., Cu(I)(NH<sub>3</sub>)<sub>2</sub>) are required for low-temperature O<sub>2</sub> activation by forming Cu(I)-O<sub>2</sub>-Cu(I) complexes; this chemistry allows Cu(I) reoxidation back to Cu(II) [79,80]. For Cu(I) sites without ammonia ligands (i.e., immobilized "naked" Cu(I) sites), Cu(I) ions are reoxidized by NO+O<sub>2</sub> to form surface nitrates (Cu(I) + NO + O<sub>2</sub>  $\rightarrow$  Cu(II)-NO<sub>3</sub><sup>-</sup>) [55,81,82]. It is important to note that ammonia ligating is prevalent only at temperatures below ~250 °C [83]. Therefore, there is a strong temperature dependence for the two Cu(I) reoxidation mechanisms. Particularly, (1) the Cu(I)-O<sub>2</sub>-Cu(I) complex formation mechanism is inapplicable at high-reaction temperatures since isolated Cu(I) ions lose ammonia ligands and become immobilized above ~250 °C; and (2) the nitrate formation mechanism is inapplicable at low reaction temperatures for the formation of the nitrate intermediates [7]. Assuming that the same reoxidation mechanisms apply for isolated Fe(II), a likely low-temperature standard SCR mechanism over isolated ZFe(III)(OH)<sub>2</sub> can be formulated as follows:

$$ZFe(III)(OH)_2 + NO \rightarrow ZFe(II)OH + HONO$$
 (9)

$$HONO + NH_3 \rightarrow NH_4NO_2 \rightarrow N_2 + 2H_2O$$
(10)

$$2ZFe(II)OH + \frac{1}{2}O_2 + H_2O \rightarrow 2ZFe(III)(OH)_2$$
(11)

We should note that this mechanism, even though it is considered likely, has not yet received experimental confirmation by in situ (operando) spectroscopic studies, and the energetics have not yet been calculated theoretically. Please note that this mechanism does not involve the formation of NO<sub>2</sub> or Fe-nitrates. From our discussions regarding "parasitic NH<sub>3</sub> oxidation" above, these latter species can lead to NH<sub>3</sub> overconsumption (R3, R7). Therefore, R9-R11 can be considered to dominate under reaction conditions where high SCR selectivities are observed. Importantly, this mechanism requires a pair of mobile, isolated ZFe(II)OH for O<sub>2</sub> activation, which can obviously only occur at relatively low temperatures since all Fe species are anticipated to become immobilized when reaction temperatures become sufficiently high.

During the discussions above, we suggested that NO<sub>2</sub> forms during standard SCR as an important intermediate for the target (R2, 3) or side reactions (R5-7). Two mechanisms have been proposed in the past for NO<sub>2</sub> formation. First, NO is oxidized by extraframework oxygen on oligomeric Fe sites, and oxygen is then replenished by gas phase O<sub>2</sub> (i.e., a redox or Mars–van Krevelen mechanism). These reaction pathways are shown below [17,84]:

$$Fe(III)-O-Fe(III)- + NO \rightarrow -Fe(II)-\Box -Fe(II)- + NO_2$$
(12)

$$Fe(II)-\Box-Fe(II)- + 1/2O_2 \rightarrow -Fe(III)-O-Fe(III)$$
(13)

Second, NO<sub>2</sub> can be generated during the "nitrate" SCR route [85] on monomeric sites as follows:

$$ZFe(III)(OH)_2 + NO + NH_3 \rightarrow ZFe(II)-OH + N_2 + 2H_2O$$
(14)

$$ZFe(II)-OH + NO + O_2 \rightarrow ZFe(III)(OH)-NO_3$$
(15)

$$ZFe(III)(OH)-NO_3^- + NO \rightarrow ZFe(III)(OH)-NO_2^- + NO_2$$
(16)

$$ZFe(III)(OH)-NO_2^- + NH_3 \rightarrow ZFe(III)(OH)_2 + N_2 + H_2O$$
(17)

At this time, it is still not possible to fully ascertain which Fe sites, monomers or oligomers, contribute more toward  $NO_2$  formation. Part of the difficulty lies in the fact that it is difficult to synthesize model catalysts that only contain one of the two Fe sites. Still, considering that the  $NO_2$  formation pathway via nitrate and NO interactions (R16) is only important at high reaction temperatures

over Cu/SSZ-13 (due to high activation barriers) [7], it is conceivable that reactions described in R12-R13 contribute more toward NO<sub>2</sub> formation under standard SCR catalyzed by Fe/SSZ-13. Note particularly that both dry and wet NO oxidation reactions over Fe/SSZ-13 have apparent activation energies of ~35 kJ/mol, considerably lower than those of standard SCR and NH<sub>3</sub> oxidation reactions [28]. Still, much experimental and theoretical work is needed to fully interpret SCR reaction pathways over small-pore Fe/zeolites. For example, the nitrate route shown above is still a postulation; the formation of surface nitrate, and how this species interacts with NO and NH<sub>3</sub>, has not been systematically investigated. Also, how oligomeric sites catalyze standard SCR is not fully understood. In addition to the possible "fast SCR" route where NO oxidation to NO<sub>2</sub> is critically important, other pathways where NO is activated to intermediates with a +3 nitrogen oxidation state, are not well understood.

As discussed above, key side reactions lowering SCR selectivities are non-selective NH<sub>3</sub> oxidation by  $O_2$  (R4), and those that lead to the formation of  $N_2O$  (R5, R6). For R4, considering that this is a redox reaction and monomeric Fe(II) ions are difficult to be reoxidized by  $O_{2}$ , it is reasonable to suggest that only oligometric  $Fe_xO_v$  species and Fe-oxide particles are active for this reaction. This notion is consistent with studies by Brandenberger et al. [25], who found that monomeric Fe sites are completely inactive for NH<sub>3</sub> oxidation up to 500 °C. From an application point of view, it is important to note that small-pore Fe/SSZ-13 has the advantage over Cu/SSZ-13 in maintaining better SCR selectivities at high reaction temperatures (e.g., >400  $^{\circ}$ C) after hydrothermal aging (Figure 15). This difference apparently correlates to intrinsic activity differences for Cu<sub>x</sub>O<sub>y</sub> and Fe<sub>x</sub>O<sub>y</sub> clusters, i.e., Cu<sub>x</sub>O<sub>y</sub> is much more active than  $Fe_xO_y$  in catalyzing NH<sub>3</sub> oxidation. The lower activity for  $Fe_xO_y$  can be understood from the following considerations. (1) Similar to standard SCR, "ammonia inhibition" may also apply to ammonia oxidation over Fe<sub>x</sub>O<sub>y</sub>. Fundamentally, ammonia oxidation is also a redox reaction where  $O_2$  activation over  $Cu_xO_y$  occurs at lower temperatures than over  $Fe_xO_y$ , rendering  $Cu_xO_y$  more active. (2) As TEM imaging demonstrates,  $Fe_xO_v$  clusters tend to be much larger (~1–2 nm, Figure 14a) than  $Cu_xO_y$  clusters (which are too small to detect via scanning TEM [60]). This difference further lowers activity for  $Fe_xO_y$  clusters by lowering relative surface active site exposures. (3)  $Fe_xO_y$  may have higher tendency in incorporating extraframework Al (which lowers oxidation potentials) than  $Cu_xO_y$ . However, this latter notion still awaits further demonstrations.

In terms of N<sub>2</sub>O formation via  $NH_4NO_3$  decomposition (R6), two possible  $NH_4NO_3$  formation routes that are associated with either the monomeric or oligomeric Fe sites, are discussed here. On monomeric Fe sites, the ZFe(III)(OH)- $NO_3^-$  intermediate shown in R16 can undergo the following chemistry to form  $NH_4NO_3$ :

$$ZFe(III)(OH)-NO_3^- + ZNH_4^+ \rightarrow Z_2Fe(III)-OH + NH_4NO_3$$
(18)

Over oligomeric Fe sites,  $NO_2$  formed via R12 can undergo disproportionation reactions to form nitrate and nitrite, where the former interacts with ammonia to generate  $NH_4NO_3$ :

$$2NO_2 + H_2O \rightarrow HNO_3 + HNO_2 \tag{19}$$

$$HNO_3 + NH_3 \rightarrow NH_4NO_3 \tag{20}$$

Reactions R19 and R20 can be considered to occur non-catalytically within the zeolite pores. It is not clear at this time which of the two Fe species, monomers or oligomers, contribute more toward NH<sub>4</sub>NO<sub>3</sub> formation. Please note that NH<sub>4</sub>NO<sub>3</sub> formation does not necessarily always lead to N<sub>2</sub>O formation. Similar to R16 shown above, NH<sub>4</sub>NO<sub>3</sub> can also be reduced by NO as follows:

$$NH_4NO_3 + NO \rightarrow NH_4NO_2 + NO_2$$
 (21)

Finally, even if  $N_2O$  indeed forms, it can still be converted to harmless  $N_2$  by decomposition and  $N_2O$ -SCR pathways shown as follows [86,87]:

$$2N_2O \rightarrow 2N_2 + O_2 \tag{22}$$

$$3N_2O + 2NH_3 \rightarrow 4N_2 + 3H_2O$$
 (23)

From Figure 17, it can be readily seen that N<sub>2</sub>O formation over hydrothermally aged Fe/SSZ-13 under standard SCR is very minor, much less than that over hydrothermally aged Cu/SSZ-13 at similar exchange levels [33]. Particularly, reaction data over a 1/1 physical mixture of Cu/SSZ-13 and Fe/SSZ-13 suggest that N<sub>2</sub>O formed on Cu/SSZ-13 can be partially consumed on Fe/SSZ-13 (i.e., N<sub>2</sub>O formation over the mixture is less than half of that on Cu/SSZ-13), thus demonstrating a synergy between the two catalysts for optimal deNOx efficiency. This notion will be further addressed below.



**Figure 17.** N<sub>2</sub>O formation as a function of temperature during standard SCR for the HTA Cu/SSZ-13, Fe/SSZ-13 and mixed (1/1) samples. Reactant feed contains 350 ppm NO, 350 ppm NH<sub>3</sub>, 14% O<sub>2</sub>, 2.5% H<sub>2</sub>O balanced with N<sub>2</sub> at a GHSV of 200,000 h<sup>-1</sup>. Reprinted with permission from [33]. Copyright © 2015 Elsevier B.V.

#### 5. Small-Pore Fe/Zeolites as SCR Catalysts: Application Aspects

At the onset of this short review, we described the historic findings that medium- and large-pore Fe/zeolites typically display hydrothermal stability better than their Cu-exchanged counterparts [20–25]. This general trend appears to hold for Fe/SSZ-13 catalysts formed via solution ion-exchange. For example, hydrothermal aging at 800 °C for 16 h leads to negligible changes in surface area/porosity of low Fe-loaded Fe/SSZ-13 [32]. In comparing hydrothermal stability of Fe-exchanged SSZ-13 and high-silica LTA catalysts, Ryu et al. [42] demonstrated that their most stable Fe/LTA can sustain an extremely harsh hydrothermal aging condition of 900 °C for 12 h with >60% relative crystallinity maintained; whereas their best Fe/SSZ-13 catalysts tend to collapse completely under such harsh aging conditions [59,65]. For catalysts formed via one-pot synthesis, framework Fe relocation to extraframework positions during aging [39,40] may induce structure instability. Overall, it can be concluded that properly prepared small pore Fe/zeolites, at least via the solution ion-exchange approach, should readily satisfy hydrothermal stability requirements for commercial applications.

Regarding toleration to sulfur poisoning, another key prerequisite for commercial applications, it is to our knowledge that this has not been systematically studied on small pore Fe/zeolites. Based on studies on small pore Cu/zeolites [88–92], there exist two sulfur poisoning mechanisms: zeolite pore blocking by sulfur deposits, and the formation of copper sulfite/sulfate species that do not display SCR activity. Particularly, SO<sub>2</sub> oxidation to SO<sub>3</sub> greatly deteriorates sulfur poisoning because more stable deposits and/or Cu salts form. In this regard, small pore Fe/zeolites may be more prone to sulfur poisoning than their Cu-exchanged counterparts since they appear to be better oxidation catalysts, i.e., they may be more active than Cu/zeolites in catalyzing SO<sub>2</sub> oxidation to SO<sub>3</sub>. However, research efforts are clearly needed in this essentially unexplored area. The same situation holds true for other potential contaminations, e.g., from unburnt hydrocarbons, from engine lubricants, or from noble metals diffused from other components of the emission control system to the SCR bed. More work is needed to understand resistance of small pore Fe/zeolites to such contaminants.

Finally, the low activity for small-pore Fe/zeolites in catalyzing standard SCR at low-temperatures (<300 °C) can be considered the biggest obstacle for their application as commercial catalysts for the transportation industry. It is highly desirable, therefore, to boost low-temperature SCR activity for small-pore Fe/zeolites by choosing the right SCR chemistry (i.e., fast SCR rather than standard SCR), or by the introduction of other active sites to small pore Fe/zeolites. In the following, some of such aspects are discussed.

It is well known that over medium- and large-pore Fe/zeolites, fast SCR proceeds much more efficiently than standard SCR at low temperatures [87]. The origin for such a difference between these two chemistries may lie in the fact that the difficult low-temperature Fe(III)/Fe(II) redox is circumvented during fast SCR. However, this strategy may not work for small-pore Fe/zeolites. Please note that over Cu-exchanged medium- and large-pore zeolites, fast SCR also proceeds faster than standard SCR at low temperatures. Interestingly, however, low-temperature fast SCR is less favorable than standard SCR over small-pore Cu/zeolites. In a recent study, Cui and Gao discovered that this is due to two facts: (1) the high stability of NH<sub>4</sub>NO<sub>3</sub> in small-pore SSZ-13, which accumulates as a poison on the catalyst at temperatures below ~220 °C; (2) the reaction that eliminates NH<sub>4</sub>NO<sub>3</sub>, i.e., R21, shown below, has a high activation barrier of ~160 kJ/mol, which certainly cannot proceed with high efficiency at low temperatures. It is important to note that the high stability of NH<sub>4</sub>NO<sub>3</sub> in small-pore Fe/zeolites will not solve the low NOx conversion efficiency issues associated with slow Fe(III)/Fe(II) redox is in standard SCR at low reaction temperatures.

A viable solution for increasing low-temperature NOx conversion efficiency is to introduce other cations to small-pore Fe/zeolites. At a microscopic level, this can be achieved by co-exchanging different cations during catalyst synthesis, e.g., the formation of co-exchanged Cu,Fe/zeolite catalysts. As described above, Cu,Fe/SSZ-13 and Cu,Fe/SAPO-34 co-exchanged catalysts appeared in literature as early as 2012, albeit they were not systematically investigated in these studies [26,27]. More recently, Wang et al. [34] revisited co-exchanged Cu,Fe/SSZ-13, and made the following discoveries worth mentioning: (1) In terms of NOx conversion rates, no particular synergy is found between Fe and Cu active sites, i.e., Fe sites do not significantly influence SCR turnover rates on Cu sites, and vice versa. (2) Regarding hydrothermal stability, co-exchanged catalyst also does not display greatly improved hydrothermal stability as compared to the single metal counterparts. (3) A clear synergy is observed with regard to N<sub>2</sub>O formation, which is significantly reduced on Cu,Fe/SSZ-13 as compared to Cu/SSZ-13. This can be explained by suggesting that  $N_2O$  formed on Cu sites, is subsequently decomposed on Fe sites. (4) Finally, Cu,Fe/SSZ-13 appears to be more resistance to coking than Cu/SSZ-13 with the presence of hydrocarbon (propylene) in the feed. Based on these findings, the authors suggested that the concept of co-exchanged Cu,Fe/zeolite SCR catalyst can indeed be beneficial, not for significantly improving activity and stability of SCR catalysts, but rather as a means to fine-tune performance of practical SCR catalysts. To our knowledge, there have been no research

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efforts attempting to introduce other low-temperature SCR active phases (e.g., manganese oxides, noble metal cations) into small-pore Fe/zeolites to boost low-temperature NOx conversion efficiency.

#### 6. Future Perspectives

In the section immediately above, it was demonstrated that at least some of the state-of-the-art small-pore Fe/zeolite can be readily employed in commercial diesel engine emission control systems, since their service life expectancy is anticipated to be as good as, if not better than, the current commercial small-pore Cu/zeolites. Because of the inferior low-temperature performance of Fe/zeolites; however, it is unlikely that these catalysts can fully replace Cu/zeolites in future aftertreatment systems. However, the current emission standards are already very stringent worldwide. It is anticipated that future standards will be even more difficult to meet. As such, the "merits" of small-pore Fe/zeolites, i.e., their better performance than Cu/zeolites at temperatures above ~400 °C, and their low selectivity to N<sub>2</sub>O formation, should not be disregarded simply because these catalysts do not show satisfactory low-temperature activity. In particular, diesel engine aftertreatment systems periodically undergo high temperature (>600 °C) soot combustion and desulfation treatments; during such events, small-pore Fe/zeolites are anticipated to provide much better SCR performance than their Cu-exchanged counterparts. Therefore, instead of using Fe/zeolites to replace Cu/zeolites in advanced SCR systems, both catalysts should be employed. In addition to the co-exchanged Cu,Fe/zeolite concept described above, mixed Cu/zeolite and Fe/zeolite SCR catalysts can be engineered in various ways to take advantage of both low-temperature activity of Cu/zeolites and high-temperature selectivity of Fe/zeolites. The simplest approach is to apply physical mixtures of the two catalysts. Studies by Gao et al. [33] demonstrate that this method readily broadens the operational temperature window for high NOx conversions, and in the meanwhile lowers high temperature N<sub>2</sub>O generation. For industrial packed bed or washcoated catalysts, sequential beds or dual layer designs allow for optimized NOx conversions and N<sub>2</sub> selectivities, where the activities of each catalyst for SCR and ammonia oxidation and the extent of washcoat diffusion limitations all influence overall catalyst performance [87,93–95].

On the basis of the considerations discussed above, studies on small-pore Fe/zeolites can be readily justified, and continuous research is strongly encouraged. Below are a few suggested research directions:

(1) This review article described a few catalyst synthesis approaches, including solution ion-exchange, impregnation, and one-pot synthesis. All of these methods have their limitations. For example, Fe site heterogeneity is difficult to control via solution ion-exchange, and incorporation of Fe into the framework appears to be inevitable for one-pot synthesis. More work is needed to improve small pore Fe/zeolite synthesis in order to generate catalysts with further improved stability and site uniformity. To our knowledge, solution ion-exchange in non-aqueous media, or solid-state ion exchange, have not be used to generate such catalysts.

(2) Additional work is needed to better understand standard SCR mechanisms and structure–activity relationships. In this review, we described the use of experimental and theoretical approaches to understand the nature of various Fe species in these catalysts. It can be reasonably concluded that isomeric and dimeric Fe(III) sites are the SCR active species in these catalysts; however, how these active species catalyze standard SCR is only speculated at present. Studies, especially theoretical studies, are strongly encouraged to interpret how catalytic turnovers occur on these sites at a molecular level.

(3) Fast SCR on small-pore Fe/zeolites needs a better understanding. Over medium- and large-pore Fe/zeolites, fast SCR has been repeatedly found to be more efficient than standard SCR at low-temperatures. This trend does not appear to hold for small-pore Fe/zeolites, based on the hypothesis that ammonia nitrate becomes particularly stabilized in small pore zeolites, thus inhibiting low-temperature fast SCR. However, more work is needed to verify this hypothesis and to find solutions to overcome this inhibition.

(4) It is believed that future highly efficient SCR systems should incorporate both Cu and Fe catalysts. Therefore, more work is needed in engineering mixed Cu/zeolite and Fe/zeolite SCR systems to optimize NOx elimination efficiency.

(5) In addition to SCR, recent studies also demonstrated that such catalysts can be used to decompose  $N_2O$  [54,96], and to catalyze methane partial oxidation to methanol [56]. Other catalytic applications are not reported but are highly anticipated.

# 7. Conclusions

This short review covers a few selected topics of the newly emerging small-pore Fe/zeolite SCR catalysts, including Fe/SSZ-13, Fe/SAPO-34, Fe/SSZ-39 and high-silica Fe/LTA. Both solution ion-exchange and one-pot synthesis methods, among others, can be used to prepare these catalysts. In solution ion exchange, care should be taken to facilitate Fe-ion diffusion. One-pot synthesis, despite its various advantages, may lead to catalysts with low hydrothermal stabilities due to incorporation of Fe into the framework. At low Fe loadings, monomeric and dimeric Fe sites dominate in these catalysts. As Fe loading increases, Fe<sub>x</sub>O<sub>y</sub> clusters larger than dimers and Fe-oxide particles also populate. In terms of their contributions to standard SCR, it is generally believed that all Fe sites can contribute to the reaction but with different temperature dependence and selectivities. In particular, monomeric sites can be considered to be highly selective for SCR, whereas dimeric and larger Fe<sub>x</sub>O<sub>y</sub> clusters are considered to be less selective, due to their activity in catalyzing parasitic NH<sub>3</sub> oxidation, believed to occur with the participation of NO<sub>2</sub>, and non-selective NH<sub>3</sub> oxidation by O<sub>2</sub>. Hydrothermal aging leads smaller Fe moieties to agglomerate to larger ones, and extraframework Al incorporation into iron oxide clusters and particles. Such changes lower low-temperature standard SCR activity but increase SCR selectivities.

In comparison to small-pore Cu/zeolites, small-pore Fe/zeolites show inferior low-temperature activity toward standard SCR. However, they display a few advantages over Cu catalysts in hydrothermally aged forms. First, they offer improved high-temperature SCR selectivities. Second, they generate less N<sub>2</sub>O, an unwanted side product. Finally, they appear to be hydrothermally more robust than Cu/zeolites at similar ion-exchange levels. These advantages suggest that these catalysts can be considered for industrial applications. Particularly, future SCR systems should consider applying both small-pore Cu and Fe-exchanged catalysts to optimize both low- and high-temperature activity and selectivity.

**Funding:** This research was funded by the U.S. Department of Energy (DOE), Energy Efficiency and Renewable Energy, Vehicle Technologies Office.

Acknowledgments: The author gratefully acknowledges the U.S. Department of Energy (DOE), Energy Efficiency and Renewable Energy, Vehicle Technologies Office for the support of this work. PNNL is operated for the U.S. DOE by Battelle.

Conflicts of Interest: The author declares no conflict of interest.

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