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The role of NO_2 in the selective catalytic reduction of nitrogen oxides over Fe-ZSM-5 catalysts: Active sites for the conversion of NO and of NO/NO_2 mixtures

Michael Schwidder[a], Sascha Heikens[a], Andrea De Toni[a], Simone Geisler[b], Malte Berndt[b], Angelika Brückner[c], Wolfgang Grünert[a,*]

[a] *Lehrstuhl für Technische Chemie, Ruhr-Universität Bochum, PO Box 102148, D-44780 Bochum, Germany*
[b] *Interkat Catalysts GmbH, D-53639 Königswinter, Germany*
[c] *Leibniz Institute for Catalysis at Rostock University, Berlin Branch, Richard-Willstätter-Str. 12, D-12489 Berlin, Germany*

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ABSTRACT

The selective catalytic reduction by NH_3 of NO (“standard SCR”) and NO/NO_2 mixtures (“fast SCR”) were compared over Fe-ZSM-5 catalysts of different Fe content ranging from 0.2 to 5 wt%. The Fe site structure was monitored by UV–vis spectroscopy. From the response of the reaction rates to the variation of the site structure, it was concluded that standard and fast SCR require different Fe sites; standard SCR proceeds both on isolated and oligomeric Fe oxo sites, whereas a small concentration of isolated Fe sites is sufficient to sustain the high reaction rates of fast SCR, with no discernible contribution of different sites. The response of both reactions to hydrothermal stress (with or without SO_2 present) differs; strong deactivation in standard SCR accompanied by increasing NH_3 oxidation activity being opposed to stable activity in fast SCR, suggesting that those isolated sites, which are responsible for fast SCR are very resistive toward clustering under the conditions of automobile exhaust catalysts. The potential of preparation procedures to improve the activity by increasing the Fe content is very different. The best performance was achieved using solid-state ion exchange with $FeCl_3$, with NO_x conversions >90% between 473 and 773 K obtained over the best catalyst. But if a concomitant increase of the aggregated site abundance cannot be avoided, then NH_3 oxidation will effectively compete with fast SCR already at relatively low temperatures. The role of free NO_2 in the reaction mechanism of standard SCR was assessed by comparing the SCR reaction rate with that of NO oxidation for all catalysts used. NO oxidation was significantly slower than NO reduction in all cases, which excludes free NO_2 produced by NO oxidation as an intermediate of the standard SCR reaction.

1. Introduction

The selective catalytic reduction (SCR) of nitrogen oxides has been in the focus of NO_x abatement research for mobile sources over the past two decades. The discovery of catalysts capable of reducing NO with fuel components [1,2] drew much effort on the hydrocarbon-SCR in the early 1990s, but the failure to identify catalysts with sufficient activity and durability meanwhile has reverted the attention to the ammonia reductant, which is fed into the exhaust gas stream as urea. The technological development takes advantage of the fact that equimolar mixtures of NO and NO_2 are reduced by NH_3 at much lower temperatures than NO or NO_2 alone [3]. This “fast SCR” was first observed on Fe_2O_3/TiO_2 catalysts [4], but it proceeds also over V/W–TiO_2 [5] and over Fe-modified zeolites [6–8].

The reason for the acceleration of NO reduction by gas-phase NO_2 is a matter of debate, which is closely related to the discussion about the mechanism of “standard” SCR, that is, the SCR of NO alone [9]. The presence of NO_2 may provide a shortcut in a mechanism where its formation is rate-limiting, or it may open a reaction channel alternative to a route where it is not included. Such routes have been discussed in the literature, including activation of NH_3 by a redox reaction with Fe(III) [4], V(V) [10], or Cu(II) [11], the amide-nitrosamide mechanism of Ramis et al. [12], which has also been discussed for Fe catalysts [13,14], or a route in which nitrogen in NO is first oxidized, but not beyond the +3 oxidation state [6]. To accelerate the redox routes by NO_2, the reoxidation must be rate-limiting and more rapid with NO_2 than with O_2. For the V/W–TiO_2 system, the former was rejected by Tuenter et al. [5] with reference to the low reaction order in oxygen above 0.5 vol%, although a favorable influence of facilitated reoxidation by surface nitrates was recently reported by Tronconi et al. [15]. Contrary to expectations, Delahay et al. reported that Cu(I) in Faujasite was reoxidized less effectively by NO_2 than by O_2 [16].

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* Corresponding author. Fax: +49 234 321 4115.
E-mail address: w.gruenert@techem.rub.de (W. Grünert).

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Free NO_2 is a crucial intermediate in the mechanism proposed previously [17], in which the catalytic role of the iron is confined to the oxidation of NO and the subsequent fast SCR proceeds exclusively on zeolite Brønsted sites. This mechanism also was supported by Devadas et al. [7], although they noted a catalytic relevance of the Fe sites in the fast SCR step as well. In recent work with iron-free catalysts, Sachtler et al. [18] emphasized the formation of NH_4NO_2, which is easily formed from NO, NO_2, NH_3, and H_2O [18]. Its decomposition to nitrogen and water is very rapid with no catalyst at low temperatures, but enhancement by acidic sites also has been observed [19].

In our recent work, we investigated the relevance of different Fe sites in Fe-ZSM-5 for the SCR of NO by ammonia in some detail, combining structural information from UV–vis, EPR, and X-ray absorption spectroscopy with catalytic data [20–22]. According to these results, all iron sites present, including isolated Fe oxo species, can catalyze this reaction, and at low temperatures (523 K), the reaction rate can even be correlated with the total Fe content for catalysts with well-dispersed iron. At the same time, a particular activity contribution of oligomeric clusters was noted, which would have impeded such correlation at higher temperatures [21].

The present paper reports an attempt to extend this approach on the fast SCR by studying this reaction over Fe-ZSM-5 catalysts of different Fe site structures, characterized by UV–vis spectroscopy. Striking differences in site requirements of fast and standard SCR, as well as in catalyst durability, indicate that the fast SCR proceeded on isolated Fe oxo sites, which is further supported by a successful optimization effort for Fe-ZSM-5 inspired by this conclusion. A clear discrepancy between the rates of oxidation and the selective reduction of NO over the catalysts used suggests no mechanistic relation between the seemingly similar selective catalytic reduction of NO and of NO/NO_2 mixtures.

2. Experimental

The ZSM-5 zeolites used had a Si/Al ratio of 14 and were provided by Chemiewerk Bad Köstritz (Germany; Na-ZSM-5, used for ILIE and CVD preparations, see below) and by Tricat Zeolites GmbH Bitterfeld, now Südchemie Bitterfeld GmbH (Germany; NH_4-ZSM-5, for SSIE samples and study with parent zeolite). H-ZSM-5 was made from these zeolites through standard procedures (i.e., exchange with HCl, calcination at 873 K).

The Fe-ZSM-5 catalysts were prepared through various routes. The improved liquid ion-exchange (ILIE) samples were prepared according to a procedure described in detail elsewhere [21]. In brief, the zeolite was exchanged with Fe^{2+} generated *in situ* from iron powder under an inert gas atmosphere. The chemical vapor deposition (CVD) sample was prepared as described previously [23], with the zeolite in the H form exchanged with vaporized $FeCl_3$ under an inert gas atmosphere. The solid-state ion exchange (SSIE) samples were prepared by heating a mixture of the zeolite in the H form with a suitable amount of $FeCl_3$ in flowing nitrogen according to the following protocol. First, the mixture was heated to 423 K with a temperature ramp of 2 $K\,min^{-1}$ to protect the pore system of the zeolite from being destroyed by vaporizing water. Then the temperature was increased to 573 K at a rate of 5 $K\,min^{-1}$ and maintained there for 1 h. Finally, the sample was washed with deionized water and dried at ambient atmosphere. In what follows, we designate the samples based on their preparation method and their iron content; that is ILIE-0.2 designates a Fe-ZSM-5 prepared by the ILIE method and containing 0.2 wt% iron.

The Fe content of the samples was analyzed by atomic absorption spectroscopy. For digestion, 50 mg of each sample was dissolved in a mixture of concentrated acids: HNO_3 (5 ml), HCl (1 ml), and HF (1 ml). After evaporation of the acid mixture, the residue was redissolved in 1 ml nitric acid, and the liquid was washed into a volumetric flask containing demineralized water. The UV–vis spectra of the catalysts in calcined state (heating in synthetic air to 423 K with 2 $K\,min^{-1}$, after a 15 min isothermal period heating to 873 K with 5 $K\,min^{-1}$, followed by 1 h at this temperature) were recorded with a Cary 400 spectrometer (Varian) equipped with a diffuse reflectance accessory (Harrick). For light absorption reduction, samples were diluted with α-Al_2O_3 (calcined for 4 h at 1473 K) at a ratio of 1:10.

The catalytic data were measured in a catalytic microflow reactor (6 mm i.d.) in the temperature range 423–873 K. In standard SCR, the feed gas consisted of 1000 ppm NO, 1000 ppm NH_3, and 2% oxygen with helium as balance. For fast SCR, 500 ppm NO_2 and 500 ppm NO were used instead of 1000 ppm NO. NO_2 was introduced into the feed gas mixture directly before the reactor inlet, to prevent the formation of ammonium nitrate within the gas lines. For the NO oxidation reaction, only 1000 ppm and 2% oxygen with helium as balance were used. In all reactions, the space velocity applied was 750,000 h^{-1} (catalyst mass, 10 mg; particle size, 250–350 µm; total flow rate, 183.3 $ml\,min^{-1}$). Conversions were determined using calibrated mass spectrometry (Balzers QMS 200). The only nitrogen-containing components detected were NO, NO_2, N_2, and NH_3, N_2O was not found in measurable quantities. In fact, N_2O detection is not very sensitive with our analytical scheme because of rather intense fragmentation, but the N_2O selectivity is known to be low over Fe-ZSM-5 under the conditions applied here [7,24]. Cross-sensitivities between ammonia and water fragments ($m/z = 17$) and between NO and NO_2 fragments ($m/z = 30$) were eliminated by calibrated fragmentation ratios.

This experimental scheme has two problems. First, at temperatures below 500 K, the measurements may have been influenced by the formation of ammonium nitrate. The role of ammonium nitrate in fast SCR is presently under debate. Its formation was first considered as a side reaction [25], and recently its role as an intermediate in the fast-SCR reaction sequence over V/W–TiO_2 catalysts has been proposed [26]. We discuss the extent of this effect over our catalysts later in the paper. The observation of white (ammonium nitrate) powder deposition at inadequately heated reactor walls near the reactor entrance suggests, however, that this reaction can proceed noncatalyzed and parallel to the main reaction. Second, mass spectrometry analysis of coexisting NO and NO_2 is prone to experimental errors in the individual concentration of the oxides, whereas their sum is less affected. Due to the strong fragmentation of NO_2 in the mass spectrometer, measured conversions of both NO and NO_2 depend critically on the correct intensity measurement of the weak NO_2 signal at $m/e = 46$. Underestimation of the NO_2 signal will result in insufficient correction of the NO intensity, that is, overestimation of residual NO. Thus, errors in NO and NO_2 conversion are complementary, leaving the NO_x conversion largely unaffected. The problem disappears when the residual NO_2 concentration tends toward zero, obviously at high temperatures in our experiments. Although evidence also exists suggesting that the divergence between NO and NO_2 conversion may be real in some cases, for now we assign it to undiscovered changes in the mass spectrometry conditions, leading to the aforementioned errors, and confine ourselves to the discussion of total NO_x conversion in what follows.

3. Results and discussion

3.1. Characterization of Fe-ZSM-5 samples by UV–vis spectroscopy

Fig. 1 presents the UV–vis spectra of the Fe-ZSM-5 catalysts used in this study. The Kubelka–Munk function is plotted in normalized form to facilitate comparison of signal shapes. The spectra differ strongly and indicate a widely varying degree of clus-

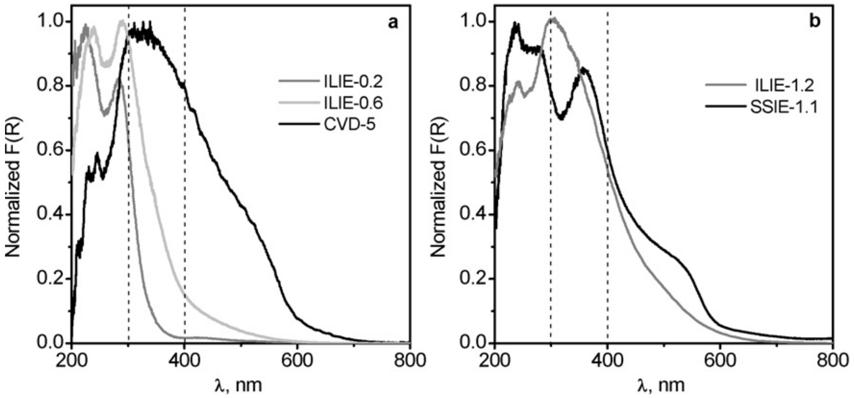

Fig. 1. UV–vis spectra (normalized Kubelka–Munk function) of Fe-ZSM-5 catalysts used in the present study.

tering of the Fe sites present. The signals arise from $Fe^{3+} \leftarrow O$ charge-transfer transitions. It has been proposed that bands below 300 nm indicate isolated Fe ions in tetrahedral and octahedral coordinations, whereas the $t_1 \rightarrow t_2$ and $t_1 \rightarrow e$ transitions remain unresolved [27,28]. Signals between 300 and 400 nm have been assigned to oligomeric Fe oxo entities, and bands above 400 nm have been assigned to Fe oxide aggregates, which may be strongly disordered. The smallest aggregate size that would cause a shift of the band into the region >400 nm is unknown.

Spectra as shown in Fig. 1 may be deconvoluted into subbands that fall into the aforementioned wavelength regions, as has been shown previously [20,21,28]. For our purposes here, a qualitative discussion of this is sufficient. Among the ILIE catalysts, that with the lowest Fe content (ILIE-0.2, Fig. 1a) gave rise to a very narrow spectrum consisting almost completely of bands peaking below 300 nm. In a quantitative analysis of such a spectrum, 95% of the intensity was found to arise from signals below 300 nm [21]. Thus, when changes of the extinction coefficients over the wavelength range are neglected, one may suggest that almost all iron is present in isolated sites, with the remainder present as oligomers [21]. It was recently shown that signals below 300 nm also may arise from binuclear Fe oxo clusters provided that the oxo bridge between the Fe ions is hydroxylated [29]. Such hydroxylation may be questioned for the calcined state in which the spectra shown in Fig. 1 were measured. Moreover, in that previous study [29], only 30% of the iron turned out to be actually paired at a Fe content of 0.4 wt% in magnetic measurements made to differentiate sites identified as isolated by UV–vis. Therefore, we believe that the vast majority of Fe sites in ILIE-0.2 indeed may be considered isolated.

The remaining spectra clearly extended into the range typical of clustered species, but they differed significantly in detail. The spectrum of ILIE-0.6 extended into the 300–400 nm range, assigned to oligomeric clusters, whereas all other samples exhibited significant intensity also beyond 400 nm. In the ILIE series, the intensity near 300 nm increased with increasing Fe content and provided the total intensity maximum in the spectrum of ILIE-1.2. This is a clear difference from the spectrum of SSIE-1.1, which peaked below 250 nm, with a well-separated signal in the oligomer range 300–400 nm and increased intensity above 400 nm. Earlier analyses suggested a distribution of ca. 50% isolated, 25% oligomeric, and 25% particulate species for ILIE-1.2 [21]. For SSIE-1.1, a somewhat higher weight of isolated and of particulate sites the signal shape suggests, with a smaller contribution of oligomeric sites. The spectrum of CVD-5 (Fig. 1a) was clearly dominated by species absorbing above 300 nm; that is, clustering of the Fe oxo species was greatest in this catalyst. But signals below 300 nm contributed to the spectrum as well; thus, even a highly loaded Fe-ZSM-5 contained isolated Fe sites as confirmed previously [29] by magnetic measurements. But one should keep in mind that only relative contributions of species have been considered to date. Due to the increasing Fe content, the absolute abundance of isolated sites still grew from ILIE-0.2 via ILIE-1.2/SSIE-1.1 to CVD-5, although the proportion of total Fe present decreased.

3.2. Fast and standard SCR: Activities

Fig. 2 compares conversions measured during fast SCR and standard SCR for the three catalysts of the ILIE series. As mentioned in the Experimental section, fast SCR conversion data below 500 K may have been affected to some extent by the formation of NH_4NO_3. Above 500 K, where deposited NH_4NO_3 should have disappeared due to melting and decomposition, the time to achieve steady state was extended. To evaluate the influence of ammonium nitrate formation, a full nitrogen balance, including N_2 formed, was conducted in a specific run. In the entire temperature range, the N balance closed between 94% and 104%, with the lowest value of 94% occurring at 423 K. Thus, it may be concluded that even at temperatures below 500 K, the error due to the side reaction was hardly beyond the limits of experimental error. As an additional check, the fast SCR over ILIE-0.2 (cf. Fig. 1a) was measured both with increasing and decreasing sequences of reaction temperatures. The results were very close, confirming an only minor effect of ammonium nitrate formation on the data even below 500 K. Fig. 2a shows the data for the run with decreasing temperature sequence due to some outliers in the increasing temperature series.

Fig. 2 confirms the favorable effect of NO_2 on the NO_x conversion over Fe-ZSM-5. At the same time, it indicates that the reactions in presence and absence of NO_2 were very different and proceeded on different sites. A first indication of this is the dramatic shift in the difference of light-off temperatures (T_{50}) between fast and normal SCR. Over ILIE-0.2, the light-off temperature of normal SCR was as much as 240 K higher than that of fast SCR. Over the remaining catalysts, this difference was only 135 K.

Obviously, the performance in fast SCR is not correlated with the iron content; even 0.2 wt% Fe was sufficient to make a catalyst with very respectable conversions over the entire temperature range. In fact, the catalysts behaved very similarly, with a strong increase in all conversions at low temperatures passed over in a gradual growth around 520 K. Above 700 K, NO_x conversion tended to decrease, due mainly to decreasing NO conversion. This tendency is known from standard SCR [21,28] where it has been ascribed to oxidation of the NH_3 reductant, particularly over clustered sites. The NO_x conversion curves of all three ILIE catalysts were identical within the limits of experimental error below 773 K, with a light-off temperature around 480 K. Above 773 K, NO_x conversion remained somewhat higher with ILIE-0.2, which is almost void of clustered iron species. It should be noted that the diver-

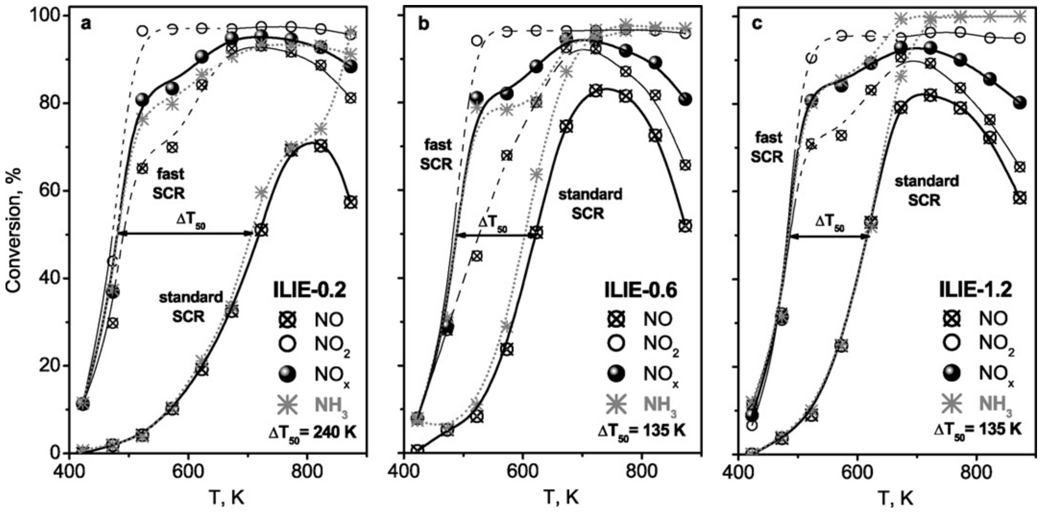

Fig. 2. Comparison of standard SCR and fast SCR over different Fe-ZSM-5 catalysts: (a) ILIE-0.2, $\Delta T_{50} = 240$ K; (b) ILIE-0.6, $\Delta T_{50} = 135$ K; (c) ILIE-1.2, $\Delta T_{50} = 135$ K. Conditions: 1000 ppm NO_x, 1000 ppm NH_3, 2% O_2, at 750,000 h^{-1}, NO_x being NO (standard SCR) or an equimolar NO/NO_2 mixture (fast SCR). Divergence of NO and NO_2 conversions below 650 K in fast SCR possibly measurement artifact (cf. text).

gence between NO and NO_2 conversions at 520–670 K may be an experimental artifact (see Section 2); thus, the corresponding curves are dashed in this region. The overall NO_x conversion data are reliable, however. Indeed, the NO_x conversions were always close to the NH_3 conversions in this temperature range, where NH_3 oxidation is known to be negligible over these catalysts [21,28].

In the standard SCR of NO, the differences between the catalysts were more pronounced (Fig. 2). At higher Fe content (e.g., ILIE-1.2), the NO conversions increased at much lower temperatures than with ILIE-0.2; thus, the difference between the light-off temperatures of ILIE-0.2 and ILIE-1.2 was as much as 100 K. Notably, NO and NH_3 conversions were identical over ILIE-0.2 up to 823 K, only at 873 K, ammonia oxidation was observed over the largely isolated Fe sites of this catalyst. Over the remaining ILIE catalysts, NH_3 conversions exceeded those of NO (i.e., NH_3 was oxidized to N_2) already at 673 K. Analogously, the NO conversions began to decline at much lower temperatures over the latter catalysts than over ILIE-0.2.

These observations confirm earlier conclusions that standard SCR is supported both by isolated and oligomeric Fe oxo species, but with a greater intrinsic activity of the latter [21,22]. Indeed, standard SCR did proceed over ILIE-0.2 (Fig. 2a), which contains almost exclusively isolated sites, but it was much more rapid over the remaining catalysts, which contain oligomeric clusters as well. On the other hand, isolated Fe oxo species appeared to be most effective for fast SCR; the addition of more iron sites to the isolated entities in ILIE-0.2 had no effect on this reaction, except for a deterioration at higher temperatures due to ammonia oxidation over clustered species (Fig. 2). At the same time, it is obvious that not all isolated sites were involved in the fast SCR reaction. Their absolute abundance was greater In ILIE-0.6 and ILIE-1.2 compared with in ILIE-0.2 (*vide supra*), which had no effect on NO_x conversion at low temperatures. Isolated Fe sites are known to exist in different coordinations, which seem to contribute differently to the catalytic behavior of Fe-ZSM-5 in standard SCR [21,22]. Similar differences between isolated sites most likely apply for the fast SCR reaction as well.

The surprising activity of a catalyst with only 0.2 wt% Fe may suggest that the fast SCR proceeds just on acidic sites without involving iron, which is inferred by some SCR mechanisms proposed in the literature [17,19]. Catalytic data for the parent H-ZSM-5 are given in Fig. 3a. H-ZSM-5, which was very poor in standard SCR, exhibited a remarkable performance in fast SCR but without being competitive with ILIE-0.2. Its light-off temperature was 75 K higher than that of the latter, and its peak NO_x conversion was 83%, compared with 96% for the latter. A similar observation was reported previously [7]. Because the H-ZSM-5 used here had a nonnegligible Fe content (ca. 0.05 wt%), one could doubt whether the fast SCR conversions shown in Fig. 3a were caused by reactions on acidic sites, as proposed previously [17,19]. On the other hand, there exists a noncatalytic fast SCR reaction path (over nonacidic Ba-Y [18]), and earlier work by our group found that the Fe species in our H-ZSM-5 were clustered rather than isolated [28] and thus should be poor sites for fast SCR. Irrespective of the sites involved in fast SCR over H-ZSM-5, their contribution can be considered minor compared with the activity of isolated Fe sites deliberately introduced into the zeolite.

Over H-ZSM-5, ammonia conversion equaled NO_x conversion up to 723 K, at which point the declining NO_x conversion indicated the onset of ammonia oxidation. This decline of NO_x conversion above 723 K most likely was due to the considerable oxidation activity of the Fe oxo clusters contained in the zeolite [28], as confirmed by the steep onset of NH_3 conversion in standard SCR (Fig. 3a). Significantly, NH_3 conversion did not reach 100% at high temperatures despite the increasing NH_3 oxidation. A weaker temperature dependence of the fast SCR proceeding on acidic sites (compared with the Fe-catalyzed reaction) may explain this finding.

Fig. 3 also reports activity data for two catalysts prepared via dry interaction of $FeCl_3$ with H-ZSM-5. Although the general course of the conversion-temperature curve in fast SCR was very similar to those for the ILIE samples (Fig. 2), the NO_x conversions achieved at low temperatures were somewhat higher. Over SSIE-1.1 (Fig. 3b), NO_x conversion exceeded 70% already at 473 K, whereas with ILIE-1.2, it remained well below 40% at this temperature (Fig. 2c). CVD-5 achieved 68% NO_x conversion at 473 K; however, at higher temperatures, the NO_x conversion curves became rather similar to those of the ILIE samples and remained at 80%–95%, whereas above 800 K, the NO_x conversion over SSIE-1.1 and CVD-5 dropped below that of ILIE-1.2. In standard SCR, SSIE-1.1 was less active than ILIE-1.2, apparently due to its higher content of isolated Fe sites (Fig. 1b). Its light-off temperature was 640 K (vs 620 K), it achieved a peak conversion of 77% (vs 82%), and it had a significantly greater tendency toward ammonia oxidation. Therefore, the difference in light-off temperatures between standard and fast SCR (195 K) was rather high with SSIE-1.1, possibly reflecting the im-

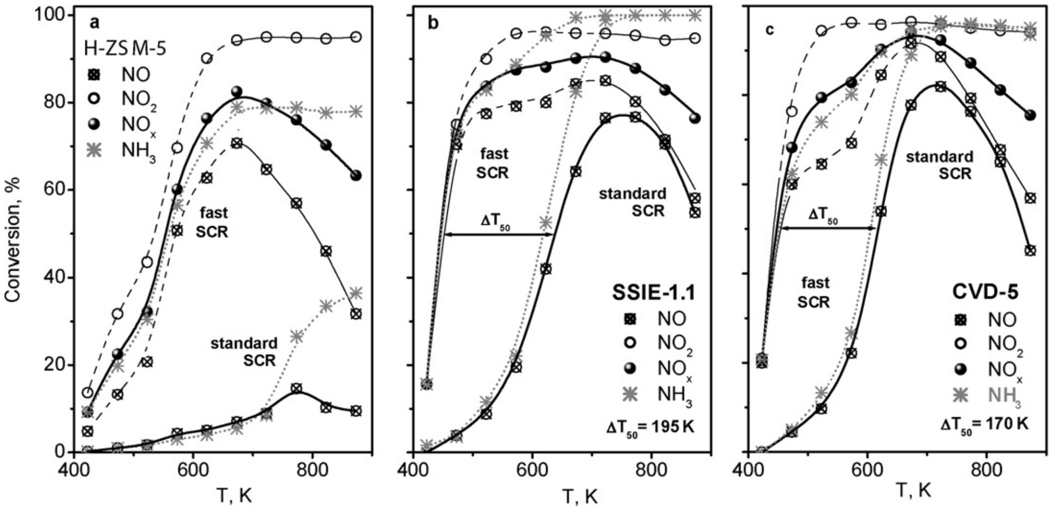

Fig. 3. Comparison of standard SCR and fast SCR over H-ZSM-5 and over Fe-ZSM-5 made by dry interaction of $FeCl_3$ with H-ZSM-5: (a) H-ZSM-5; (b) SSIE-1.1, $\Delta T_{50} = 195$ K; (c) CVD-5, $\Delta T_{50} = 170$ K. Conditions: 1000 ppm NO_x, 1000 ppm NH_3, 2% O_2, at 750,000 h^{-1}, NO_x being NO (standard SCR) or an equimolar NO/NO_2 mixture (fast SCR). Divergence of NO and NO_2 conversions below 650 K in fast SCR possibly measurement artifact (cf. text).

portance of the isolated sites to its catalytic behavior. The activity of CVD-5 in standard SCR was of comparable to that of ILIE-1.2.

Whereas the latter observations confirm that fast SCR and standard SCR rely on different actives sites, the improved fast SCR activity through the use of a different preparation procedure is an encouraging result. From the ILIE series, one might conclude that the amount of active sites for fast SCR cannot be increased above the level in ILIE-0.2; however, this applies apparently only to this specific preparation route. The preparations involving $FeCl_3$ vapors seemed to achieve a higher population of the active site or to create another site that was not accessible via ILIE. At present, the nature of this site can only be speculated. From the UV–vis spectra shown in Fig. 1, it is obvious that in the ILIE series, the relative contribution of the signal at ≈240 nm (which most likely arises from tetrahedrally coordinated sites [27,28]) decreased with increasing Fe content, whereas the intensity in all other wavelength regions increased. Thus, because the abundance of active sites appeared to remain constant in this series, one might be tempted to search for the active site among these isolated tetrahedral sites. Indeed, SSIE-1.1, which is more active than ILIE-1.2, exhibited more intensity in the 240 nm region (Fig. 1b). Other sites cannot be ruled out, however. Thus, the prominent band at 360 nm, assigned to Fe oxo trimers by Pirngruber et al. [29], seems to be completely missing in the ILIE preparations and thus might arise from a candidate species.

3.3. *Optimization of Fe-ZSM-5 for fast SCR*

The results presented so far suggest that dry interaction with $FeCl_3$ may be a promising preparation route, resulting in activities that exceeded those obtained with the ILIE series already at 1.1 wt% Fe. Although the example of CVD-5 may subdue the optimism, because this catalyst is similar to SSIE-1.1 despite its much higher Fe content, a series with Fe concentrations ranging from 0.2 to 3.2 wt% was prepared by SSIE. According to the widely accepted concepts of gas-phase preparation of Fe-ZSM-5 from $FeCl_3$ and H-ZSM-5, mononuclear $Z^-FeCl_2^+$ species are formed in the first step and are hydrolyzed on washing. Although these isolated species may become mobile and aggregate as in other preparations [30], the greater abundance of isolated sites in SSIE-1.1 compared with ILIE-1.2 (Fig. 1b) was the rationale behind this attempt.

Fig. 4 displays the UV–vis spectra of these catalysts (SSIE-1.1 included, Kubelka–Munk function not normalized). From the intensity trend below 300 nm, it is obvious that the concentration of isolated sites indeed parallels the total Fe content. On the other hand, extensive clustering of Fe sites also is obvious in these samples. A quite unexpected finding is that this occurred at Fe content as low as 0.2 wt% where the route via mononuclear $FeCl_2^+$ intermediates should have led to a site structure similar to that of ILIE-0.2 (Fig. 1b). Instead, significant intensity was seen even beyond 400 nm, and the 360-nm band of Fe oxo oligomers (trimers?) was well developed. A tentative explanation for this finding refers to an observation of a study in which CVD was performed in a fluidized bed instead of a fixed bed to prepare partially exchanged Fe-ZSM-5 [31]; the materials thus obtained were strongly surface-enriched in Fe even at low Fe content, as detected by XPS, suggesting that the reaction between H-ZSM-5 and $FeCl_3$ proceeded in zones not only in a fixed bed, but also in a crystallite. Therefore, local Fe concentrations, and thus clustering tendencies, might be high in all cases.

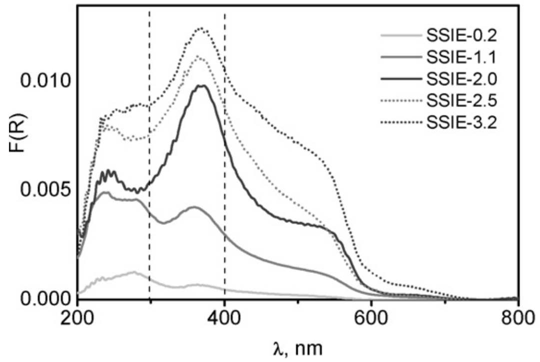

Fig. 4. UV–vis spectra (absolute Kubelka–Munk function) of Fe-ZSM-5 catalysts prepared by solid-state ion exchange.

Fig. 5 illustrates the temperature dependence of total NO_x conversion measured over the catalysts described above. The low-temperature conversion data show that the activity increased monotonously with the Fe content in the samples. NO_x conversions of almost 90% were achieved at temperatures as low as 423 K (SSIE-3.2), and the very low conversions measured with SSIE-0.2 in the same type of experiment proves without the need for further explanation that noncatalytic NH_4NO_3 formation did not contribute to this conversion to any significant extent. On the other hand, NH_3 oxidation activity increased dramatically above 2 wt% Fe, and the useful temperature range became very narrow

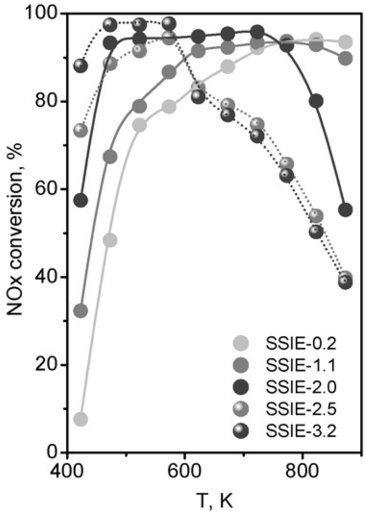

Fig. 5. Fast SCR over Fe-ZSM-5 catalysts prepared by solid-state ion exchange: temperature dependence of total NO_x conversion.

(SSIE-2.5). However, with the optimum Fe content of 2.0 wt%, NO_x conversions >90% were achieved in a broad temperature range of 473–773 K.

The enhanced activity of the SSIE catalysts (Fig. 5) correlates well with the increasing amount of isolated sites in these catalysts (Fig. 4); however, the abundance of other sites also grew with increasing iron content. Although clustered sites are undesirable due to their ammonia oxidation activity, they might catalyze fast SCR as well as they do standard SCR [21]; however, comparing the catalytic behavior and UV–vis spectra of ILIE-0.2 (Figs. 1a and 2a) and SSIE-0.2 (Figs. 4 and 5) supports the notion that fast SCR required only isolated sites. SSIE-0.2 clearly contained a significant amount of clustered species, among them the oligomer giving rise to the 360-nm UV–vis band. Consequently, ILIE-0.2 had a greater abundance of isolated sites. If the new site that caused the superior activity of the SSIE preparations had been a clustered site (e.g., the site absorbing at 360 nm), then SSIE-0.2 should have been more active than ILIE-0.2. This clearly was not the case, however; instead, SSIE-0.2 was slightly inferior to ILIE-0.2. Consequently, further work which is needed to identify the active sites for fast SCR more precisely, should concentrate on the various isolated (extra-framework) Fe sites in the Fe zeolites.

3.4. *Fast and standard SCR: durability*

Fig. 6 characterizes the affects of aging on the two reactions under study, showing the catalytic behavior of ILIE-1.2 after two different aging treatments. The first of these treatments involved aging for 2 days in moist air (10% H_2O) at 923 K (Fig. 6a). This clearly led to a significant loss of activity in standard SCR, although the slightly increased conversions below 473 K are somewhat suspicious. The NH_3 conversions exceeded the NO conversions at a lower temperature than occurred in the fresh state, indicating clustering of isolated and/or growth of oligomeric species in the sample. Fast SCR was hardly affected by this hydrothermal stress, which was found for other Fe-ZSM-5 preparations (e.g., SSIE-1.1).

Fig. 6b shows the result of an aging experiment in the presence of SO_2 (5 wt% H_2O, 200 ppm SO_2 at 823 K for 65 h). Here the damage in standard SCR activity was much greater. At low temperatures, NO conversion increased as in the fresh state, but at 623 K, the NH_3 conversion curve dropped sharply and even fell below zero due to drastically increased ammonia oxidation activity. Apparently, SO_2 accelerated the aforementioned clustering processes significantly. Remarkably, in fast SCR, the impact of this harsh treatment was not seen at low temperatures. Only between 550 and 670 K were the NO conversions somewhat short of those measured with the fresh sample.

The very different response of standard and fast SCR to the aging treatments confirms that both reactions proceeded on different sites. The strong changes in ammonia oxidation activity seen in the standard SCR measurements hardly affected the fast SCR reaction, which was much more rapid and apparently won the competition even with the accelerated NH_3 oxidation reaction. Isolated sites are known to be inactive in ammonia oxidation [21] [see also the parallelism of NO and NH_3 activities in ILIE-0.2 (Fig. 2a)]; therefore, the increased ammonia oxidation activity indicates clustering of isolated sites and/or restructuring of clusters into a size favoring the oxidation activity at the expense of standard SCR activity. Fast SCR was little affected by these changes, in agreement with our earlier conclusion that it proceeds in isolated sites. Moreover,

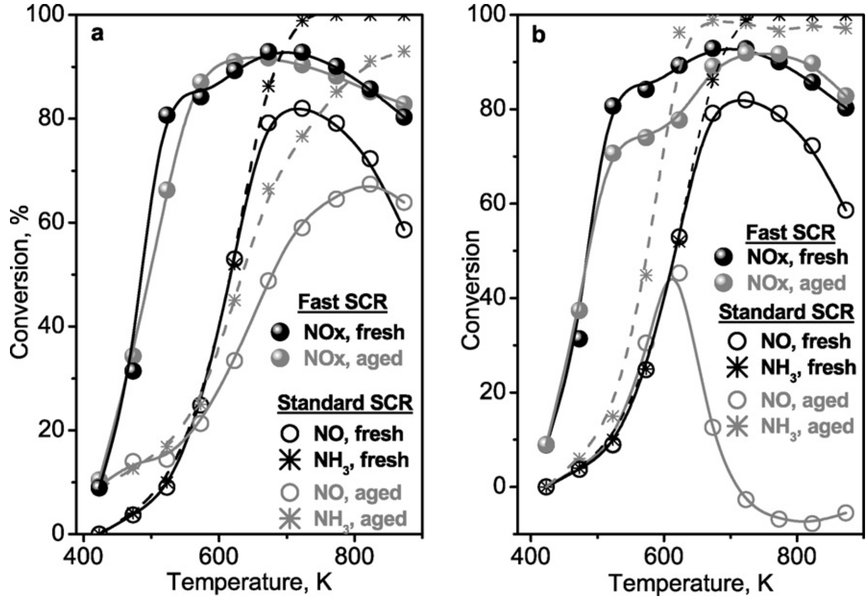

Fig. 6. Deactivation of Fe-ZSM-5 (ILIE-1.2) in standard and in fast SCR: (a) ageing in moist atmosphere, 10 vol% H_2O in air, 923 K, 48 h; (b) ageing in presence of water and SO_2, 5% H_2O, 200 ppm SO_2 in He, at 823 K over 65 h. Measurement conditions as in Figs. 1 and 2.

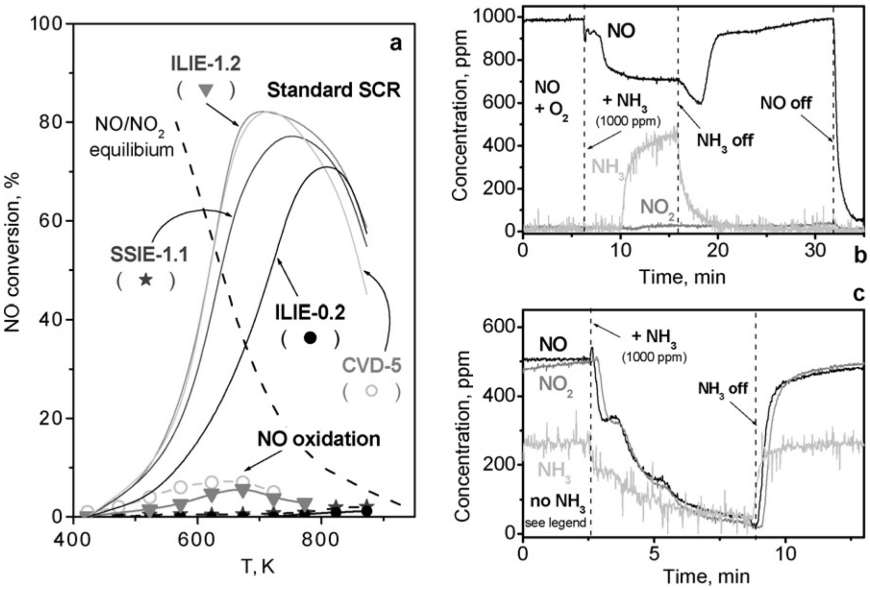

Fig. 7. Conversion of NO in NO oxidation and in standard SCR: (a) Temperature dependence of NO conversion (standard SCR data taken from Figs. 2 and 3), 1000 ppm NO, 2% O_2 in He at 750,000 h^{-1}, (●) ILIE-0.2, (▼) ILIE-1.2, (★) SSIE-1.1, (○) CVD-5. (b) Isothermal comparison between NO oxidation and standard SCR over SSIE-1.1, $T = 573$ K, initial feed 1000 ppm NO, 2% O_2 in He at 750,000 h^{-1}, first switch 1000 ppm NH_3 added, second switch NH_3 removed, third switch NO removed, (d) isothermal comparison between NO oxidation and fast SCR over SSIE-1.1, $T = 573$ K, initial feed 500 ppm NO, 500 ppm NO_2, 2% O_2 in He at 750,000 h^{-1}, first switch 1000 ppm NH_3 added, second switch NH_3 removed. Concentrations measured by non-dispersive IR photometry given without corrections for cross-sensitivities.

those isolated sites that catalyze fast SCR appeared to be very stable under realistic conditions of flue gas catalysis.

3.5. Mechanistic considerations

As mentioned in Section 1, NO oxidation has been considered a crucial step in the reaction mechanism of NO reduction. Therefore, we measured NO conversions to NO_2 over our catalysts at the same gas-phase concentrations and space velocity as the SCR data presented earlier, that is, 1000 ppm NO and 2% O_2 in He (NH_3 missing) at 750,000 h^{-1}. The results are shown in Fig. 7a. For comparison, the NO conversion curves obtained for the standard SCR are repeated as thin lines. The NO oxidation measurements were not very accurate; NO conversions remained very low at the high space velocity applied, as confirmed by the small NO_2 yields found. It appears that samples with a greater degree of clustering (CVD-5, ILIE-1.2) were somewhat more active than those with predominantly isolated Fe sites, but the most important result is that the rates of NO oxidation were inferior to those of standard SCR for all catalysts studied.

For the SSIE-1.1 sample, this finding was confirmed by direct comparison using a different measurement technique (nondispersive IR photometry). In these runs, conducted at 573 K, the ammonia reductant was removed from and switched into the feed without changing the GHSV. For standard SCR (Fig. 7b), this is equivalent to a change from standard SCR feed to NO oxidation feed and *vice versa*. For fast SCR, the feed without NH_3 is an oxygen-containing NO_2/NO (1:1) mixture in which the NO_2/NO ratio should increase over a catalyst of sufficient NO oxidation activity (cf. equilibrium curve in Fig. 7a). Fig. 7b shows that the NO oxidation conversion indeed was below the detection limit, with an apparent NO_2 effluent concentration of ca. 20 ppm due to cross-sensitivity from NO. The NO outlet concentration decreased markedly after addition of the ammonia reductant, demonstrating the superiority of the SCR rate over the NO oxidation rate. When NH_3 was removed from the feed, the NO conversion increased temporarily before gradually returning to the low value characteristic of NO oxidation. The transient increase in NO conversion may be due to a negative reaction order of NH_3 [7,9,24], which would lead to an acceleration of the reaction at moderate decreases in the ammonia surface concentration. In the analogous fast SCR experiment (Fig. 7c), the NO/NO_2 mixture left the catalyst equimolar in the absence of NH_3, again indicating the minor NO oxidation conversion. The apparent NH_3 effluent concentration of almost 300 ppm resulted from a cross-sensitivity effect by NO_2. Adding NH_3 to the feed removed the NO_x from the effluent almost completely, with the concentrations of NO and NO_2 matching over the entire period. When NH_3 was switched off, the NO_x effluent concentrations returned to the feed values without deviating from the 1:1 NO:NO_2 ratio.

Fig. 7 raises serious doubt that NO oxidation was the rate-limiting step avoided by adding NO_2 to the gas phase. This reaction was significantly slower than NO reduction over the catalysts studied, and is therefore not a candidate for an SCR reaction scheme. Our findings do not rule out adsorbed higher oxidized NO_x species as SCR intermediates, but the participation of free NO_2 in standard SCR is unlikely. It has been argued that NO_2 desorption might be the rate-limiting step in NO oxidation over Fe ions. But, in terms of the NO oxidation mechanism over Fe^{3+}/Fe^{2+} ions summarized by Brandenberger et al. [9] this means that NO_2 would accumulate at Fe^{2+} sites in the stationary state, which seems not very likely for the typical reaction conditions for fast SCR applications.

Consequently, we believe that other mechanisms that operate without free NO_2 (e.g., the amide-nitrosamide mechanism [12,13], as well as routes that avoid the N^{4+} oxidation state [6]), deserve more attention. The effect of an NO_2 admixture on the gas phase likely is not so much to shift the rate-determining step in a given reaction sequence, but rather to open up a completely new reaction mechanism. A less efficient SCR mechanism, possibly via Fe amide species, is outperformed by a highly efficient route involving both NO and NO_2. The fast SCR mechanisms proposed for Fe catalysts in the literature do not involve a catalytic role for iron, but differ in terms of the role of Brønsted sites. Their direct participation has been suggested previously [17], where a reaction between NH_4^+ and NO_2 opens the reaction sequence. According to another report [18], NH_4NO_2 is formed and rapidly decomposed noncatalytically, but a participation of Brønsted sites in the decomposition has been proposed later [19]. Thus, these mechanisms can explain only our data for H-ZSM-5 (Fig. 3a). The clear evidence of the participation of Fe sites (Fig. 2a compared with Fig. 3a) demonstrates that more work is needed to identify the actual reaction mechanism.

4. Conclusion

The SCR by NH_3 of NO (standard SCR) and of NO/NO_2 mixtures (fast SCR) over Fe-ZSM-5 was found to proceed over different Fe sites. Whereas standard SCR proceeded on both isolated and oligomeric Fe oxo sites, fast SCR appeared to require only isolated Fe sites, with a small site concentration rendering very high reaction rates. Therefore, the response of Fe-ZSM-5 catalysts to conditions typical of flue gas catalysis (i.e., moist feeds, high temperatures) differed as well. Fast SCR was hardly affected under conditions that strongly deactivated the catalyst for standard SCR and caused significant enhancement of NH_3 oxidation activity, indicating the high stability of those isolated sites responsible for fast SCR. The potential of preparation procedures to improve the activity by increasing the Fe content varied widely. Whereas aqueous exchange H-ZSM-5 with Fe^{2+} ions rendered the best activity at only 0.2 wt% Fe, much better performance could be achieved by increasing the Fe content via solid-state ion exchange with $FeCl_3$, the best catalyst, giving NO_x conversions $>90\%$ at 473–773 K. At high Fe content, clustered sites, which could not be avoided in this preparation, led to decreased NO_x conversion at rather low temperatures, due to competing ammonia oxidation activity.

The standard SCR reaction was significantly faster than NO oxidation. Thus, free NO_2 produced by NO oxidation was not an intermediate of standard SCR. The acceleration of standard SCR by addition of NO_2 to the feed most likely can be interpreted as a switch between different reaction channels, the slower one without participation of NO_2 and the rapid one (which likely is possible on Brønsted sites alone but is strongly accelerated over isolated Fe oxo sites) involving NO_2 and Fe sites.

Acknowledgments

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