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Selective reduction of NO with Fe-ZSM-5 catalysts of low Fe content: Part II. Assessing the function of different Fe sites by spectroscopic in situ studies

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Abstract

A series of Fe-ZSM-5 catalysts prepared by improved liquid ion exchange (see part I [J. Catal. 231 (2005) 314]) containing 0.2–1.2 wt% Fe, with a systematically changing nature of Fe sites, was studied during the selective catalytic reduction (SCR) of NO with NH₃ or isobutane or during the interaction with feed components by various in situ methods (EPR, UV–vis, and FTIR spectroscopy). The results were related to the catalytic behavior. Several types of isolated Fe³⁺ sites with different reducibility were identified. FTIR results revealed that reduction of NO proceeds via intermediate formation of adsorbed nitrato species, which are subsequently reduced. Their formation requires the presence of Fe³⁺. Those Fe³⁺ ions that are permanently reduced to Fe²⁺ under reaction conditions probably do not contribute to catalytic activity. In general, the degree of steady-state Fe site reduction during NH₃ SCR is markedly lower than that during isobutane SCR, which may be a reason for the lower activity of Fe-ZSM-5 in the latter reaction. UV–vis and EPR results suggest that isolated Fe³⁺ sites in octahedral coordination are more easily reduced than tetrahedral Fe³⁺. In contrast to some types of isolated Fe³⁺ species, Fe_xO_y clusters reoxidize much more rapidly than they reduce, and thus remain essentially trivalent under reaction conditions. Due to their higher oxidation potential, they cause undesired total oxidation of the reductant, particularly in the case of isobutane.

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1. Introduction

Recently Fe-ZSM-5 zeolites containing nonframework iron species have become recognized as highly efficient catalysts for a number of reactions, including selective oxidation of benzene to phenol [1,2], N₂O decomposition [3], and selective catalytic reduction (SCR) of NO_x by NH₃ [4] and hydrocarbons [5,6]. But despite extensive studies of structure–reactivity relationships by various characterization techniques, debate on the nature of active Fe sites in these catalysts is ongoing. This is due mainly to the fact that in most cases, depending on the preparation method and the Fe content, various coexisting Fe species are created, ranging from isolated Fe ions via dimers and small oligonuclear Fe_xO_y clusters inside the pores to large Fe_2O_3 particles on the external surface.

The inhomogeneous distribution of Fe species is a major problem hindering a definitive identification of active sites. A possible way to overcome this difficulty would be the dedicated synthesis of Fe-ZSM-5 materials with Fe species of homogeneous and defined nature. With Fe content as low as 0.5%, it has been possible to make some significant strides toward this goal. Fe silicalite prepared by isomorphous substitution and subsequent steam treatment [7] and Fe-ZSM-5 obtained by a mechanochemical route [8] have been shown to contain predominantly isolated Fe species and to have high catalytic performance in the SCR of N₂O by CO and in the SCR of NO by both isobutane and NH₃. Based on these findings, it has been

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proposed that isolated Fe sites may play a major role in the catalytic cycle.

Selective analysis of the role of $Fe_r O_v$ clusters requires a catalyst without isolated Fe sites, the synthesis of which once seemed impossible. However, recently we succeeded in preparing a series of Fe-ZSM-5 catalysts with a systematically decreasing dispersion of Fe sites [9,10] using a variation of the improved liquid ion exchange (ILIE) method introduced by Long and Yang [11]. The nature of the Fe sites in these catalysts has been studied by several techniques, including X-ray absorption spectroscopy (XAFS), electron paramagnetic resonance (EPR), UV-vis spectroscopy, temperature-programmed reduction (H2-TPR), and transmission electron microscopy (TEM); the results have been described in detail in part I of this study [10]. It was found that in samples with 0.2-0.3% Fe, >95% of the total iron was present in form of isolated sites. At intermediate Fe content (0.6-0.7%), the percentage of additional oligonuclear intrazeolitic clusters became substantial, whereas the amount of large oxide particles remained negligible. The latter species were formed in reasonable amounts only at the highest Fe content of 1.2%. These conclusions are based mainly on a combined evaluation of deconvoluted UV-vis spectra showing a red shift of subbands with increasing degree of Fe site agglomeration and of temperature-dependent EPR measurements (77-773 K), allowing differentiation between isolated and agglomerated Fe^{3+} species by their magnetic behavior [10]. The formation of Fe_2O_3 particles in the sample with 1.2% Fe was also confirmed by TEM [10]. This series of samples made it possible to derive a unified concept of the active sites in the SCR of NO demonstrating that isolated Fe sites play major roles in both reactions and that oligomers also contribute, but in differing ways depending on the reducing agent. A detailed discussion of the nature of Fe sites and their relationship to catalytic performance can be found in part I of this work [10].

It must be mentioned, however, that even in samples with almost exclusively isolated Fe ions there exist at least three different kinds of these sites, which have been discriminated by EPR spectroscopy on the basis of their effective g values $(g' \approx 6, 4.3, \text{ and } 2)$. It remains an open question as to whether all of these participate equally in the catalytic cycle. Based on the observation that signals at $g' \approx 5.6$ and 6.5 in Fe-ZSM-5 prepared by sublimation lose intensity on treatment with NO/O₂/C₃H₆ mixtures of increasing propene percentage at 773 K, Kucherov et al. [11] suggested that Fe ions reflected by these lines might be coordinatively unsaturated active sites. Likewise, Ribera et al. [12] suggested that Fe species evidenced by signals at $g' \approx 6.4$ and 5.7 in steam-activated Fe-ZSM-5 participate in the redox process, because they disappeared on contact with β -mercaptoethanol at room temperature. In a recent study, Kubánek et al. [13] correlated the sum intensity of the signals at $g \approx 6.0$ and 5.6 in fresh Fe-ZSM-5 with the rate of phenol formation, observed when these samples were used as catalysts in the direct oxidation of benzene. In the aforementioned studies it was assumed that signals around $g' \approx 6$ were active sites, due to the fact that they decrease more or less in the presence of reactants. However, it is possible that they are

just spectator species, because their disappearance has not been reported to lead to decreased catalytic activity.

Moreover, little is known about whether the different coordination states of Fe species in Fe-ZSM-5 gives rise to changes in reduction and reoxidation behavior, which should be a crucial property in view of these species' participation in the catalytic redox cycle. According to Kucherov et al. [11], there is no doubt that the formation of ferrimagnetic oxidic agglomerates, which is favored by reducing conditions at high temperature, is detrimental to catalytic activity [11]. Wichterlova and co-workers [14] identified three different sites for isolated metal ions in ZSM-5: the straight channels (α), the intersection between the straight and sinusoidal channels (β), and a boatshaped site in the sinusoidal channel (γ) [14]. Although this information was originally derived for Co²⁺ ions from UV-vis data, it has been analogously adopted for Fe ions as well [15]. It was found that Cu and Co ions are most easily reduced when located in α positions and are highly resistant to reduction when in γ positions [16]. Whether the same is true for Fe ions has not been explicitly stated. Moreover, how the observed EPR signals relate to any of these positions remains unknown.

In this work we studied a series of Fe-ZSM-5 catalysts prepared by ILIE and found them to contain almost only isolated Fe sites in tetrahedral and octahedral coordination for low Fe content, small oligonuclear $Fe_x O_y$ clusters besides isolated sites for medium Fe content, and additional Fe₂O₃ particles for the highest Fe content [10]. The goal of our study was to elucidate how the differently coordinated isolated sites, as well as the clusters of different sizes, interact with reactants of the NH3 and isobutane SCR feeds, using in situ methods able to monitor the Fe species (EPR, UV/vis-DRS) as well as surface adsorbates formed on reaction (FTIR spectroscopy). In particular, we explored the reactivity of the various Fe species in both NH₃ SCR and isobutane SCR to identify reasons for previously detected differences in activity and selectivity [10]. Beneficial and detrimental types of Fe species are discriminated as a basis for future catalyst design.

2. Experimental

Spectroscopic in situ studies at elevated temperature and in the presence of reactants were performed with Fe-ZSM-5 samples described in part I of this study [10] labeled Fe-Z(0.2), Fe-Z(0.3), Fe-Z(0.7), and Fe-Z(1.2) (with the Fe iron content in wt% in parentheses). The catalysts were prepared by ILIE as described in part I [10]. In brief, a commercial Na-ZSM-5 and Fe powder was stirred in 0.1 M HCl under a protective gas atmosphere for 5 days, washed with deionized water (separating residual iron with a magnet), dried, and calcined in air at 873 K for 2 h.

In situ EPR spectra in X-band ($\nu \approx 9.5$ GHz) were recorded with a cw-spectrometer (ELEXSYS 500-10/12; Bruker) using a microwave power of 6.3 mW, modulation frequency of 100 kHz, and modulation amplitude of 0.5 mT. The magnetic field was measured with respect to the standard 2,2-diphenyl-1picrylhydrazyl hydrate (DPPH). A homemade quartz plug-flow reactor connected to a gas-dosing system containing mass flow controllers (Bronkhorst) was implemented in the rectangular cavity of the spectrometer. For all in situ experiments, 50 mg of catalyst particles (125–200 µm) were used and exposed to the following sequence of experimental steps: (a) pretreatment in air (20 ml/min) at 773 K and cooling to 623 K; (b) SCR using 0.1% NO, 0.1% reducing agent (NH₃ or isobutane), and 2% O₂/He for 1 h (GHSV = 30,000 h⁻¹ for both NH₃ and isobutane); (c) reoxidation in air (20 ml/min) at 773 K and cooling to 623 K; (d) treatment in 0.1% NH₃/He (34.7 ml/min) or 0.1% isobutane/He (34.7 ml/min) for 1 h; and (f) treatment in 0.1% NO/He (34.7 ml/min) for 1 h.

In situ UV/vis-DRS measurements were performed with a Cary 400 spectrometer (Varian) equipped with a diffuse reflectance accessory (Praying Mantis, Harrick) and a heatable reaction chamber (Harrick). The samples were used as powders and placed in a sample cup of 5 mm diameter and 3 mm depth, at the bottom of which is a small sieve. The temperature was controlled by a thermocouple located on the bottom of the sample cup and connected to a temperature programmer (Eurotherm). Reactant gases were provided by a gas-dosing system as mentioned above and led from top to bottom through the sample layer. The same sequence of experimental steps as in the in situ EPR experiments was used.

Reduction and reoxidation kinetics of the Fe sites were determined by following the absorbance at 241 and 291 nm for isolated Fe³⁺ ions in Fe-Z(0.3) and at 350 nm for oligonuclear Fe_xO_y clusters in Fe-Z(1.2) at 673 K as a function of time. After pretreatment in air (10 ml/min) at 773 K for 1 h, reduction was performed at 673 K in a flow of 1% NH₃/He (10 ml/min) for 2 h, followed by reoxidation in air (10 ml/min) for 2 h at the same temperature. The experimental curves thus obtained were fitted by a pseudo-first-order rate law using

$$Abs_t = Abs_{t=\infty} + (Abs_{t=0} - Abs_{t=\infty})e^{-kt},$$
(1)

in which $Abs_{t=0}$, Abs_t , and $Abs_{t=\infty}$ are the absorbance values at the start of the experiment, at time *t*, and after reaching steady state, respectively.

FTIR spectra (2 cm⁻¹ resolution, 100 scans) were recorded by a Bruker IFS 66 spectrometer equipped with a heatable and evacuable reaction cell with CaF2 windows and connected to a gas dosing and evacuation system. The zeolite powder was pressed into self-supporting wafers with a diameter of 20 mm and a weight of 50 mg. NO adsorption experiments were performed according to the following sequence: (a) oxidative pretreatment in air (30 ml/min) at 673 K for 1 h, followed by cooling to 293 K; (b) adsorption of 1% NO/He (40 ml/min) for 1 h, followed by evacuation for 30 min, with spectra recorded before and after evacuation; (c) heating in air at 673 K for 1 h; (d) reductive pretreatment in 2% NH₃/He (40 ml/min) for 1 h, followed by evacuation at the same temperature for 30 min and cooling to 293 K; and (e) adsorption of 1% NO/He (40 ml/min) for 1 h followed by evacuation for 30 min. Spectra were recorded before and after evacuation.

In situ FTIR experiments during isobutane SCR used the following treatment sequence: (a) oxidation in air (30 ml/min) at 673 K for 1 h; (b) cooling to 623 K and flushing by a mixture of 1% NO/He (30 ml/min), 1% isobutane/He (30 ml/min), and air (30 ml/min) for 1 h, with spectra recorded at 623 K at different time intervals before and after evacuation; and (c) reoxidation in air (30 ml/min) at 623 K for 1 h.

3. Results and discussion

3.1. In situ studies in the presence of NH_3 SCR feed components

3.1.1. In situ UV-vis studies

UV-vis spectra of the catalysts used in this study were given in part I [10] and are summarized here in Fig. 1, to facilitate discussion of the following data. These spectra are characterized by broad, partially overlapping $Fe^{3+} \leftarrow O$ charge-transfer bands (Fig. 1). To facilitate the identification of different Fe species, the experimental spectra were deconvoluted into several subbands, the assignment of which was discussed previously [17,18] based on earlier proposals [19,20]. In brief, subbands around 240 and 290 nm arise from isolated Fe^{3+} sites in tetrahedral and higher coordination (five or six oxygen ligands). respectively, whereas bands at $300 < \lambda < 400$ nm are assigned to oligometric clusters and subbands >400 nm are assigned to large Fe₂O₃ particles (Table 1). The spectra deconvolution shown in Fig. 1 indicates that the apparent broadening of the experimental spectrum above 290 nm with increasing Fe content comes from the contribution of subbands assigned to small oligomeric clusters and Fe₂O₃ particles that partially overlap with the high-wavelength tail of the subband at 290 nm assigned to isolated Fe^{3+} species in fivefold and/or sixfold coordination. The dividing line between oligomeric clusters and Fe₂O₃ particles may be blurred. Theoretical calculations of UV-vis spectra of trimeric Fe³⁺ hydroxo complexes in solution revealed the appearance of CT bands above 400 nm for even this low degree of aggregation [21]. Nevertheless, there is no doubt that light absorbance increases in the visible range, as does the tendency to form $Fe_x O_y$ clusters.

Fig. 1 clearly shows that the Fe-Z(0.2) and Fe-Z(0.3) samples contained almost only isolated Fe sites in both tetrahedral (241 nm) and higher (probably octahedral) coordination (291 nm). Exposure of these catalysts to the feed mixture of NH₃ SCR reduced the intensity of both bands due to the reduction of isolated Fe³⁺ (Fig. 2); this effect was even more pronounced for Fe species with more than four oxygen ligands (291 nm). Treatment in NH₃ slightly enhanced the reduction process even more, whereas subsequent treatment in NO flow led to reoxidation, which was roughly complete for tetrahedral Fe sites (241 nm) but only partial for octahedrally coordinated Fe (291 nm).

With an increasing percentage of oligonuclear clusters and even Fe₂O₃ particles in the Fe-Z(0.7) and Fe-Z(1.2) samples, the effects on treatment in the NH₃-SCR feed, NH₃, and NO became less pronounced. In sample Fe-Z(1.2), which contains more than half of its iron in agglomerated Fe species [10], only a weak intensity decrease was observed for the CT band around 350 nm. This indicates a markedly different redox behavior of Fe_xO_y clusters and particles, but also suggests that redox properties of isolated Fe³⁺ sites (reflected by the band at 241 nm)



Fig. 1. Experimental UV–vis spectra measured at ambient temperature and atmosphere (—) including deconvoluted sub-bands, which are assigned to the following Fe species: isolated Fe³⁺ (---), oligonuclear Fe_xO_y clusters inside pores (—), Fe oxide particles (—).

Table 1		
Assignments	of spectroscop	ic signals

	UV–vis subbands					
λ (nm)	nm) Assignment of Fe bands in as-received samples					
≈240	$Fe^{3+}O_4$	[17-20]				
≈ 290	$Fe^{3+}O_{4+x}$ (x = 1 or 2)	[17–20]				
300-400	small oligonuclear $Fe_x O_y$ clusters inside pores	[17–20]				
>400 nm	Fe_2O_3 particles in the nm range	[17–20]				
<400	C/N-containing deposits in Fe-Z(0.2) during					
	isobutane-SCR (Fig. 7)	[44,45]				
>400	carbon deposits in Fe-Z(0.2) during treatment with isobutane (Fig. 7)	[46,47]				
>500	$Fe^{2+} \rightarrow Fe^{3+}$ ICVT in Fe-Z(1.2) during treatment with isobutane (Fig. 7)	[8,36]				
	EPR signals					
<i>g</i> ′	Assignment	Ref.				
≈4.3	isolated $Fe^{3+}O_4$ in strong rhombic distortion)				
≈6	isolated $Fe^{3+}O_6$ in strong axial distortion	19 10 17 41 421				
≈ 2	isolated $Fe^{3+}O_x$ in high symmetry	[0,10,17,41-43]				
≈ 2	$Fe_x^{3+}O_y$ clusters	J				
	FTIR bands					
Wavenumber (cm ⁻¹)	Assignment	Ref.				
2193	$[NO^{+}][N_{2}O_{4}]$	[23]				
2134	NO ⁺	[25,28]				
1745	N_2O_4	[23]				
1880, 1575	N_2O_3	[23,30]				
1601	adsorbed NO ₂	[23]				
1608, 1628, 1618, 1576	differently bound nitrato species	[26,29]				
1437	adsorbed nitrite and ammonium species	[29]				
2240	C/N-containing species (nitrile, cyanate and/or isocyanate) [29]					
1690, 1723, 1765	carbonyl-containing species of different structure [29]					



Fig. 2. In situ UV-vis spectra measured at 623 K during sequential treatment in a flow of (1) air, (2) 0.1% NO, 0.1% NH₃, 2% O₂/He, (3) 0.1% NH₃/He (after reoxidation at 773 K) and (4) 0.1% NO/He. Each spectrum measured after 1 h exposure time.

might change when they coexist with dominating clusters in the same sample. Kucherov et al. [11] has demonstrated that isolated Fe³⁺ can migrate out of position and be incorporated into $Fe_r O_v$ clusters during calcination. Others have shown that agglomeration of isolated Fe³⁺ into clusters is particularly favored for easily reducible Fe species [22,23]. Thus, it can be assumed that in samples with higher Fe content, those Fe^{3+} sites may preferentially withstand the tendency to form clusters that are rather resistant against reduction. This could explain why the band at 241 nm in Fe-Z(1.2) was by far less sensitive against redox treatment than those in Fe-Z(0.2) and Fe-Z(0.3). It also means that different isolated tetrahedral Fe³⁺ sites coexist in Fe-ZSM-5 and contribute to the 241 nm band depending on the Fe loading, which cannot be distinguished by UV-vis-DRS. However, as discussed in part I [10], oxide clusters and/or particles may also contribute to a certain extent to the UV-vis absorbance below 300 nm, particularly when they show a shortrange order similar to that of γ -Fe₂O₃. EXAFS data for these samples suggested that the γ -Fe₂O₃ structure is not typical for these clusters, but rather the short-range order of the agglomerated species in Fe-Z(1.2) resembles that of α -Fe₂O₃, for which a negligible contribution to UV-vis absorbance below 300 nm was shown [10]. Nevertheless, the possibility that oxide clusters contribute to a certain extent to the band at 241 nm cannot be completely excluded. Given that the clusters are more difficult to reduce than isolated Fe^{3+} , this could be an additional reason for the smaller changes of the UV band at 241 nm in the Fe-Z(0.7) and Fe-Z(1.2) samples.

To further analyze the differences in the reduction/reoxidation behavior of the various Fe species, absorbance in the band maximum representing isolated tetrahedral (241 nm) and isolated octahedral Fe^{3+} (291 nm) was followed as a function of time for sample Fe-Z(0.3), and the absorbance at 350 nm in sample Fe-Z(1.2) was used to elucidate redox kinetics for oligonuclear $Fe_x O_y$ clusters. The resulting time dependencies were fitted using the pseudo-first-order rate law of Eq. (1). As examples, Fig. 3 shows the reduction/reoxidation curves for the 241 and 350 nm positions in Fe-Z(0.3), and Table 2 summarizes the corresponding rate constants. Note that the experimental kinetic curves for isolated sites could not be fitted assuming only one single process. Two processes with different rate constants, a faster one (I) and a slower one (II), had to be superimposed for a satisfactory fit (Table 2), whereby the difference of the rate constants was larger for reduction. This suggests that at least two kinds of isolated Fe^{3+} sites (I and II) with different reducibility contribute to each of the two bands below 300 nm. Considering the negligible change of the 241nm band in sample Fe-Z(1.2) (Fig. 2), it is likely that this band arises only from the hardly reducible species II. Generally, it appears that isolated octahedral Fe^{3+} species I (band at 291 nm) are significantly more rapidly reduced but more slowly reoxidized than isolated tetrahedral Fe³⁺ species I (band at 241 nm) (Table 2). Comparing the rate constants for oligonu-



Fig. 3. Time dependence of (A) the absorbance at 241 nm in sample Fe-Z(0.3) and (B) at 350 nm in sample Fe-Z(1.2) during reduction in 1% NH₃/N₂ and during reoxidation in air at 673 K. Fits are superimposed as dashed black lines (reduction) and solid black lines (reoxidation). UV–vis spectra at the start and end of the reduction as well as at the end of reoxidation at 673 K are also shown.

Table 2

Pseudo-first order rate constants derived from the time dependence of the UV-vis absorbance during reduction in 1% NH₃/N₂ and reoxidation in air

Sample	Species	Treatment	λ	t (min)	k
			(nm)	(mm)	(10 11111)
Fe-Z(0.3)	Ι	NH ₃	241	0-25	10.3
	II			25-120	1.2
	Ι	Air	241	0-10	16.6
	II			10-120	15.9
Fe-Z(0.3)	Ι	NH ₃	291	0–25	17.5
	II	-		25-120	2.4
	Ι	Air	291	0-45	8.4
	II			45-120	8.8
Fe-Z(1.2)		NH ₃	350	0-120	1.2
		Air	350	0-120	65.0

clear $Fe_x O_y$ clusters (350 nm) with those of isolated Fe^{3+} ions clearly shows that the former are markedly more slowly reduced but much more rapidly reoxidized. Interestingly, the reduction/reoxidation curves could be fitted assuming one single process, suggesting a more uniform nature and/or position of the clusters compared with isolated Fe sites.

3.1.2. In situ EPR studies

EPR spectra of the Fe-Z(0.2) and Fe-Z(0.3) samples show signals at effective g-values of $g' \approx 6$, 4.3, and 2, which are known from earlier studies (Fig. 4) [8,10,17]. Based on their behavior during dehydration/rehydration experiments [17], the $g' \approx 4.3$ and 6 signals were assigned to isolated Fe³⁺ in strongly distorted tetrahedral and octahedral coordination, respectively, whereas the $g' \approx 2$ line in samples containing only isolated Fe was attributed to Fe³⁺ in sites of high symmetry, for which a discrimination between tetrahedral and octahedral symmetry was not possible. In samples containing $\text{Fe}_x \text{O}_y$ clusters and particles, the latter species also contribute to the $g' \approx 2$ signal (Table 1) [10,17].

Switching from air to the SCR feed mixture and further to NH_3 flow in the Fe-Z(0.2) and Fe-Z(0.3) samples gave rise to a marked decrease in the signals of octahedral Fe^{3+} ($g' \approx 6$) and a lesser decrease in the signals of tetrahedral Fe^{3+} at $g' \approx 4.3$. In contrast, almost no change was observed for the $g' \approx 2$ line. Only when the experiment was performed at 773 K did the EPR signal at $g' \approx 2$ decrease, and then only slightly (not shown). This agrees very well with the UV-vis results described above (Fig. 2, Table 2), in which a more rapid reduction of isolated octahedral Fe³⁺ in comparison to tetrahedral Fe³⁺ was observed. This finding also indicates differing reduction stabilities for the various kinds of isolated Fe ions, with those with the highest reduction resistance reflected by the EPR signal at $g' \approx 2$. Furthermore, the fact that the same trend was observed for the behavior of UV-vis and EPR signals at 241 nm/g' \approx 4.3 and 291 nm/g' \approx 6 further supports assignment of the EPR signals to the aforementioned coordination, which would not be possible solely from their positions in the magnetic field. On subsequent treatment in NO/He flow, the changes observed during reduction were only partly reversible, whereas complete restoration of both EPR and UV/vis signals could be achieved in NO/He at 773 K (not shown). This means that under SCR conditions in the low-temperature range, only a certain percentage of isolated Fe species remained trivalent, mainly those giving rise to the $g' \approx 2$ EPR line. Comparing these with the UV-vis spectra recorded under the same conditions (Fig. 2) reveals that these Fe³⁺ sites are reflected by the (less-intense) bands at 241 and 290 nm remaining under SCR conditions. This suggests that the reduction-resistant EPR signal at $g' \approx 2$ reflects isolated Fe³⁺ sites in both tetrahedral and higher coordination.



Fig. 4. In situ EPR spectra measured at 623 K during sequential treatment in a flow of (1) air, (2) 0.1% NO, 0.1% NH₃, 2% O₂/He, (3) 0.1% NH₃/He (after reoxidation at 773 K) and (4) 0.1% NO/He. Each spectrum measured after 1 h exposure time.

Comparing the EPR spectra of sample Fe-Z(0.7) with those of samples Fe-Z(0.2) and Fe-Z(0.3) recorded under the same conditions reveals rather similar behavior for the signals at low magnetic field (Fig. 4). However, it must be noted that the total intensity of the lines at $g' \approx 6$ and 4.3 in sample Fe-Z(0.7) is similar to that in samples Fe-Z(0.2) and Fe-Z(0.3), even though the iron content is more than twice as high. This clearly shows that the relative percentage of (more easily reducible) isolated Fe³⁺ species represented by the signals at $g' \approx 6$ and 4.3 decreases with rising iron content. This effect is even more pronounced for sample Fe-Z(1.2), in which these signals are hardly visible (Fig. 4). This result supports the conclusion derived from the UV–vis measurements (Fig. 2) that with increasing Fe content only reduction-resistant isolated Fe³⁺ sites may survive.

As mentioned above, oligonuclear $Fe_x O_y$ clusters and particles also contribute to the EPR signal at $g' \approx 2$. This is most significant for sample Fe-Z(1.2), in which the $g' \approx 2$ signal is much more intense than in the other samples and represents a superposition of at least two contributions, an intense broad line and a less-intense narrower line. The two signals in the $g' \approx 2$ range may arise from oxidic clusters of different sizes. Isolated Fe³⁺ sites may contribute to the line at $g' \approx 2$ as well, but these cannot be distinguished from the cluster signals in this case. Switching from air to NH₃ SCR feed has virtually no effect on the EPR spectra, suggesting that cyclic reduction/reoxidation keeps the mean valence state of the iron oxide clusters and particles unchanged at +3. This agrees nicely with the UV-vis results showing slow reduction and rapid reoxidation of agglomerated oxide species (Fig. 2, Table 2). On a further change to NH₃/He flow, the intensity of the narrow line in the $g' \approx 2$ range decreases, whereas that of the broad line increases. The latter effect is characteristic for the formation of Fe₃O₄-like areas with ferrimagnetic ordering of spins [8,11]. Because the EPR intensity of ferrimagnetic species is usually larger than that of paramagnetic species by orders of magnitude, the rather small increase of the broad $g' \approx 2$ subsignal of sample Fe-Z(1.2) in Fig. 4 suggests that only a few of the Fe species that form agglomerates (probably those located on the outer surface of the particles) contribute to the ferrimagnetic signal. This may be why only a very slight reduction of the band intensity around 350 nm in the UV-vis spectrum was observed (Fig. 2). In sample Fe-Z(0.7), no increase, but rather a slight decrease, in the intensity at $g' \approx 2$ occurred on partial reduction, probably because this sample contains only oligonuclear $Fe_x O_y$ clusters inside the pores that are partially reduced on NH₃/He treatment (intensity decrease at $g' \approx 2$). Obviously, these species are not large enough to demonstrate ferrimagnetic ordering of sufficient extension.

Switching from NH₃/He to NO/He flow causes a marked increase of the $g' \approx 2$ line in sample Fe-Z(0.7) that may arise from ferrimagnetic ordering of clusters grown on reduction. Based on the knowledge that reductive treatment can favor the agglomeration of Fe sites [11,22,23], this signal likely arises from



Fig. 5. In situ FTIR spectra after adsorption of NO at 293 K on (a) H-ZSM-5 and (b) Fe-Z(1.2) after preoxidation (1 h at 673 K in air, —) and prereduction (1 h at 673 K in 2% NH₃/He, …) before evacuation of the IR cell. Difference spectra are shown.

partially reoxidized Fe₃O₄-like species that have agglomerated during reduction in NH₃/He flow. A similar explanation can be given for the increase of the narrow $g' \approx 2$ subsignal in sample Fe-Z(1.2) during NO/He treatment even above its original value (Fig. 4).

The observation that Fe species reflected by EPR signals around $g' \approx 6$ are preferentially reduced was previously made by others [11,12] and taken as an indication that these sites determine the catalytic activity. When this is true, Fe²⁺ should interact with NO equally well or even better than Fe³⁺. In contrast to Cu-ZSM-5, in which adsorption of NO on reduced diamagnetic Cu⁺ centers could be detected by EPR [24], this would not be expected for either Fe³⁺ or Fe²⁺, because both of these ions are paramagnetic. Dipolar interaction with paramagnetic NO would render the EPR signal undetectable. Therefore, the adsorption of NO was studied by in situ FTIR spectroscopy on the best NH₃-SCR catalyst of the ILIE series, Fe-Z(1.2) [10], after preoxidation in air and after prereduction in NH₃.

3.1.3. In situ FTIR measurements

FTIR spectra of sample Fe-Z(1.2) and of the bare H-ZSM-5 matrix after oxidative pretreatment and 30 min adsorption of 1% NO/He showed bands at around 2193, 2134, 1880, 1744, 1601–1628, and 1576 cm⁻¹ (Fig. 5). Others have observed similar bands on adsorption of NO (Table 1) [25–28]. Based on these studies, bands around 2193 and 2134 cm⁻¹ are assigned to $[NO^+][N_2O_4]$ and NO⁺, respectively, whereas the band at 1745 cm⁻¹ is ascribed to adsorbed N₂O₄. The latter can form easily already at room temperature on oxidation of NO to NO₂ followed by subsequent dimerization [29]. The NO used for the experiments in the present work contained traces of NO₂ and was not purified further. This is one possible explanation for the formation of N₂O₄, besides oxidation of NO by the Fe sites. For NO⁺, different formation routes must be considered [30], including

$$N_2O_4 \rightarrow NO_3^- + NO^+ \tag{2}$$

and

$$NO + NO_2 + 2H^+ \rightarrow 2NO^+ + H_2O.$$
 (3)

Because no bands for purely ionic nitrate (around 1380 cm⁻¹ [31]) were detected in this study, NO⁺ is most likely formed via Eq. (3) by the reaction of NO and NO₂ with Brønsted sites [32]. This is also supported by changes in the OH region (not shown). The OH bands around 3610 cm⁻¹ disappeared after NO adsorption, whereas the Si–OH bands around 3740 cm⁻¹ remained unaffected.

The intense band at 1880 cm^{-1} (Fig. 5) can, in principle, arise from two sources: (a) NO adsorbed on an Fe site, whereby higher band intensities have been found for prereduced Fe-MFI [22,25] and (b) N₂O₃ [32]. In the latter case, another equally intense band at around 1575 cm⁻¹ must be found that also belongs to N_2O_3 . This is true for the spectra shown in Fig. 5. On evacuation, both bands disappear completely in H-ZSM-5, whereas a certain rest of intensity remains at around 1574 cm⁻¹ after sample Fe-Z(1.2) is evacuated (cf. Fig. 6). This suggests that the bands around 1880 and 1575 cm^{-1} belong to the same compound; therefore, they are assigned to N₂O₃ that may arise from dimerization of NO and NO₂. As mentioned above, NO₂ is contained as an impurity in the NO used for this study. However, the markedly higher intensity of the bands of N₂O₃ and N_2O_4 in sample Fe-Z(1.2) compared with H-ZSM-5 indicates that the main source of NO₂ (which contributes to N₂O₃ and N₂O₄ formation) is oxidation of NO by the Fe sites of the catalyst, and that the NO₂ impurity may play a minor role because of its low concentration. Moreover, it must be taken into account that the commercial H-ZSM-5 used in this study contains traces of Fe as an impurity (ca. 500 ppm), which could also react with NO.

Surprisingly, no bands below 1700 cm^{-1} were detected on NO adsorption when thoroughly purified NO was used [22]. In this case only bands in the range of $1800-1900 \text{ cm}^{-1}$ were observed, and these were assigned to mononitrosyl and dinitrosyl complexes of iron. This is in good agreement with results of



Fig. 6. In situ FTIR spectra after adsorption of NO at 293 K on (a) H-ZSM-5 and (b) Fe-Z(1.2) after preoxidation (1 h at 673 K in air, —) and prereduction (1 h at 673 K in 2% NH₃/He,) after evacuation of the IR cell. Difference spectra are shown.

Long and Yang [33], who observed that Fe-ZSM-5 reacts much more strongly with a mixture of NO and NO_2 than with NO alone.

Bands above 1700 cm^{-1} disappear on evacuation for 30 min (cf. Figs. 5 and 6). This suggests that the aforementioned nitrogen oxide species to which they have been assigned are only weakly adsorbed. In contrast, bands below 1700 cm⁻¹ remain after evacuation, although there appear to be differences in intensity. Thus, the band at 1601 cm^{-1} is no longer observed, probably due to weakly adsorbed NO₂, because it is close to the asymmetric stretching frequency of gaseous NO2 (1610 cm^{-1}) [25]. Bands at 1634, 1625, and 1570 cm⁻¹ have been assigned to adsorbed nitrato species [25-28]. It is well known that NO₃⁻ and NO₂⁻ anions give rise to bands at 1380 and 1260 cm⁻¹, respectively [29]. For adsorbed nitrate and nitrite species that are not purely ionic, an increase in bond strength and change in symmetry cause a blue shift of the bands. This is in agreement with the results of Davydov [31], who reported bands of differently bound nitrate species at 1480- 1650 cm^{-1} and those of nitrite species at $1205-1520 \text{ cm}^{-1}$. Based on these findings, bands at 1628, 1618, and 1576 cm^{-1} in the spectra of evacuated samples (Fig. 5) can be assigned to differently bound nitrato species. Interestingly, the band at 1576 cm^{-1} is missing on the bare H-ZSM-5 and observed only on Fe-Z(1.2). This suggests that nitrato species reflected by this band are preferably adsorbed on Fe species. The fact that a weak band of nitrato species is also seen on the bare H-ZSM-5 can be explained by the presence of traces of Fe (ca. 500 ppm) as impurities.

To learn more about the influence of the Fe valence state on the interaction with NO, we performed the same experiments with reductively pretreated samples. Similar bands were observed, although with lower intensity (Fig. 5). Over H-ZSM-5, the bands for $[NO^+][N_2O_4]$ (2204 cm⁻¹), NO⁺ (2136 cm⁻¹), and N₂O₃ (1875 and 1577 cm⁻¹) were very weak, whereas the band for N₂O₄ (1745 cm⁻¹) can hardly be seen (Fig. 5). The decrease in these bands was also obvious on prereduced

Fe-Z(1.2) with a markedly higher Fe content, although not as pronounced as on prereduced H-ZSM-5. That the severity of the reductive pretreatment was only moderate must also be taken into account. In situ UV-vis and EPR experiments revealed that complete reduction of Fe^{3+} was not possible even after 1 h at 773 K in NH₃/He flow. Thus, two superimposing effects can account for the presence of NO₂ and its secondary products reflected by the aforementioned bands: (a) reaction of the NO₂ impurity in the NO gas, which should not depend on the pretreatment and should be comparable over both samples, and (b) oxidation of NO to NO_2 by the Fe³⁺ that persisted the reductive pretreatment. Effect (a) may have been dominant on prereduced H-ZSM-5 (Fig. 5); however, because it is not completely Fefree, and it is not known whether all of the Fe^{3+} sites were reduced by the pretreatment, effect (b) cannot be completely excluded. Certainly, effect (b) is more important over reduced Fe-Z(1.2) and dominant over preoxidized samples. In general, the decreased band intensities in the in situ FTIR spectra after reductive pretreatment are obvious, at least for the weakly adsorbed nitrogen oxide species. The stronger interaction of Fe³⁺ with NO suggests that trivalent iron is required to oxidize NO to NO₂ and further to adsorbed nitrate that accumulates on the surface. The more weakly interacting Fe^{2+} is probably less active (if at all) for this reaction; a redox cycle with this ion would involve low-valent Fe species that should be highly unstable.

3.2. In situ studies in the presence of isobutane-SCR feed components

Spectroscopic in situ studies during NH₃-SCR revealed obvious differences between the samples with the highest and lowest Fe content. Therefore, samples Fe-Z(1.2) and Fe-Z(0.2), respectively, Fe-Z(0.3) were selected for in situ studies in isobutane-SCR to elucidate the influence of the different reducing agents.



Fig. 7. In situ UV–vis spectra measured at 623 K during sequential treatment in a flow of (1) air, (2) 0.1% NO, 0.1% isobutane, 2% O₂/He, (3) 0.1% isobutane/He (after reoxidation at 773 K) and (4) 0.1% NO/He. Each spectrum measured after 1 h exposure time.

3.2.1. In situ UV-vis studies

In contrast to the NH₃-SCR feed mixture (Fig. 2), treatment of sample Fe-Z(0.2) under isobutane-SCR conditions caused not a decrease, but rather a marked increase in UV-vis absorbance below 600 nm (Fig. 7). This effect may be due to the formation of C/N-containing organic deposits in the pores, which has been discussed for the SCR of NO by hydrocarbons [26,34–37]. Based on in situ FTIR results, the formation of several C/N-containing organic species, including alkyl nitrites, nitrates and nitriles, cyanates, and isocyanates, has been proposed. Almost all of these species are UV-vis active and give rise to bands below 400 nm; thus, it is not possible to identify particular species from UV-vis spectra alone. Therefore, additional in situ FTIR measurements were performed, as discussed below. When the preoxidized sample Fe-Z(0.2) was exposed to a stream of only isobutane/He, a rather different behavior was observed (Fig. 7): The intensity of the bands below 300 nm decreased, whereas light absorption increased above 400 nm. The former effect is due to the reduction of isolated Fe species, whereas the enhanced absorption in the visible range arises from the formation of carbonaceous deposits. This may occur preferentially on acidic sites and is due to incomplete oxidation of isobutane. Most probably, those carbonaceous deposits also contribute to the UV-vis absorbance below 300 nm and partly compensate for the loss of intensity caused by reduction of Fe^{3+} . This is suggested by comparing the total intensity losses during treatment in NH₃/He (Fig. 2) and in isobutane/He (Fig. 7). On subsequent treatment in NO/He flow, the UV-vis band intensity again increased below 400 nm but decreased above 400 nm. This points to a reaction of NO with the carbonaceous deposits on which C/N-containing species are formed, as was also observed in the total isobutane-SCR feed mixture. In addition, the reoxidation of Fe^{2+} to Fe^{3+} by NO should also contribute to the increased absorption below 400 nm.

In sample Fe-Z(1.2), which is dominated by $Fe_x O_y$ clusters and particles of different sizes, treatment with the isobutane-SCR feed mixture had virtually no effect on the intensity of the UV–vis bands (Fig. 7). As for NH₃SCR, this suggests that most of the Fe species remain trivalent under isobutane-SCR conditions and also that insufficient C/N-containing deposits detectable by UV–vis-DRS are formed on Fe-Z(1.2). This might be due to the strong oxidizing power of the $Fe_x^{3+}O_y$ clusters that are abundant in this sample, which prevents C/N deposit formation. Even in a flow of isobutane/He containing no oxidizing agent, no carbon deposits are formed, in contrast to sample Fe-Z(0.2) (Fig. 7), suggesting that isobutane is oxidized to CO_x by the iron oxide clusters. The related partial reduction of Fe³⁺ is reflected in a slight decrease of the CT band intensity around 350 nm and a concomitant increase in absorbance above 500 nm. The latter originates from the low-wavelength tail of an intervalence charge-transfer transition (IVCT) between Fe²⁺ and Fe³⁺ that is characteristic for mixed-valence iron oxides and has been observed in Fe₃O₄ nanoparticles in the NIR range [8,38]. The spectrum is restored on NO/He treatment, indicating that NO is able to reoxidize the clusters.

3.2.2. In situ EPR studies

In the EPR spectrum of sample Fe-Z(0.2), the signal at $g' \approx 6$ disappeared and the signal at $g' \approx 4.3$ lost much of its intensity as soon as the preoxidized catalyst came in contact with the isobutane-SCR feed mixture (Fig. 8), indicating rapid reduction of the isolated Fe³⁺ species represented by these lines. In contrast, the line at $g' \approx 2$, which is also due to isolated Fe³⁺, decreased only marginally. This behavior is comparable to that under NH₃-SCR conditions (Fig. 4), although the reduction of the Fe³⁺ sites reflected by the low-field signals is much more pronounced in isobutane-SCR. In addition, a narrow singlet is superimposed in the $g' \approx 2$ range, indicating the formation of some kind of carbon radical that may be connected with the formation of C/N deposits, as evidenced by UV–vis results described above.

In the presence of isobutane/He, the $g' \approx 4.3$ line decreased even more, and the intensity loss is almost nonreversible on treatment with NO/He. In addition, the $g' \approx 6$ line does not reappear in NO/He, whereas the Fe³⁺signal at $g' \approx 2$ remains roughly unchanged during all steps of this sequential treatment.

In general, the EPR spectrum of sample Fe-Z(1.2) (Fig. 8) showed changes similar to those observed during sequential treatment with NH₃-SCR feed components (Fig. 4). Under the total isobutane-SCR mixture, virtually no changes were observed for the broad signal at $g' \approx 2$ due mainly to iron oxide clusters and particles in this sample, because the reduc-



Fig. 8. In situ EPR spectra measured at 623 K during sequential treatment in a flow of (1) air, (2) 0.1% NO, 0.1% isobutane, 2% O₂/He, (3) 0.1% isobutane/He (after reoxidation at 773 K) and (4) 0.1% NO/He. Each spectrum measured after 1 h exposure time.



Fig. 9. In situ FTIR spectra measured at 623 K. Treatment: (1) 1 h in air at 673 K + 1 h in a flow of 1% NO/He (30 ml/min), 1% isobutane/He (30 ml/min) and air (30 ml/min) at 623 K (-); (2) subsequent air treatment at 673 K for 1 h and cooling to 623 K (--). Difference spectra after evacuation are shown.

tion/reoxidation process keeps the average steady-state Fe valence at +3. However, due to the stronger reducing power of isobutane compared with NH₃, partial reduction to ferrimagnetically ordered iron oxide clusters and/or particles was more pronounced in isobutane/He (Fig. 8) than in NH₃/He (Fig. 4). This is reflected by the much higher intensity of the EPR signal in isobutane/He (Fig. 8). On subsequent treatment by NO/He, the line shape was modified, but the intensity gain was only partially reversible, suggesting a change in the ferrimagnetic ordering but not complete reoxidation. Interestingly, no carbon radical signal was observed in the EPR spectra of Fe-Z(1.2) as was the case for Fe-Z(0.2). This suggests that such radicals are indeed part of the C/N-containing deposits formed in significant amounts on the latter catalyst but not on the former catalyst.

3.2.3. In situ FTIR studies

To gain more information about the nature of adsorbates detected during the in situ UV–vis experiment described above, in situ FTIR spectra were recorded after 1 h of treatment in isobutane-SCR feed at 623 K followed by evacuation and after subsequent 1 h of reoxidation at 673 K. For comparison, the same experiment was also performed with the bare H-ZSM-5 (Fig. 9).

It can be seen that the FTIR spectra after SCR feed treatment are rather similar for H-ZSM-5 and Fe-Z(0.3). The strong band at 1608 cm⁻¹ clearly indicates the formation of adsorbed nitrate species [28,31], and bands around 1437 cm⁻¹ point to the formation of adsorbed nitrite species [31]. However, it must be mentioned that bands in the latter range can also arise from deformation vibrations of adsorbed ammonium species. In particular, this possibility cannot be excluded for the Fe-ZSM-5 samples, because an additional weak and broad band was observed at 3340/3132 cm⁻¹ (not shown) in the range for ν (N–H) vibrations, which is not visible for H-ZSM-5. Moreover, it is known that the intermediate formation of NH₃ can occur during SCR of NO with hydrocarbons [39,40].

The band at 2240 cm⁻¹ is certainly due to the C–N stretching vibration of nitrile, cyanate, and/or isocyanate species, which

can be formed only in the presence of both NO and *i*-butane. Interestingly, this band was not observed over H-ZSM-5, suggesting that this reaction requires the presence of a sufficient amount of Fe species, probably for the intermediate oxidation of NO to NO₂ and/or adsorbed NO_x species, which then react with *i*-butane to C/N-containing intermediates. Obviously, the amount of adsorbed nitrates formed by the very low level of Fe impurities (0.05%) present in the commercial H-ZSM-5 is not sufficient to produce C/N-containing deposits with detectable surface concentrations.

After subsequent treatment in air at 673 K, the band at 2240 cm^{-1} decreased due to the oxidative degradation of nitrile, cyanate and/or isocyanate species. The bands around 1600 and 1430 cm⁻¹ were markedly diminished in samples Fe-Z(0.3) and Fe-Z(1.2) but remained almost unchanged in H-ZSM-5. This suggests that in the former two samples those bands may arise in large part from oxidizable organic (alkyl) nitrates and nitrites, whereas in H-ZSM-5 they may originate from inorganic nitrate and nitrite species, the thermal degradation of which is probably not favored at this temperature.

Moreover, a band around 1690 cm⁻¹ was observed in all samples along with additional bands at 1723 and 1765 cm⁻¹ occurring only in sample Fe-Z(1.2), characterized by abundant Fe_xO_y clusters. These bands were all in the range of ν (C=O) and diminished on reoxidation. They may have arised from carbonyl-containing species of different structures formed on partial oxidation of *i*-butane by Fe³⁺ species and burned to CO_x in air flow.

3.3. Active sites and catalytic behaviour

Comparing the results of in situ UV-vis and EPR measurements during sequential treatment with components of the NH₃-SCR feed reveals some crucial differences (Figs. 2 and 4). Isolated Fe³⁺ ions in samples free of oxidic clusters [Fe-Z(0.2) and Fe-Z(0.3)] were partially reduced under steady-state SCR conditions, albeit to different extents. Octahedral Fe³⁺, reflected by EPR signals around $g' \approx 6$ and a UV–vis band at 291 nm, were the most sensitive to reduction, followed by tetrahedral Fe³⁺ ($g' \approx 4.3$ and 241 nm), whereas Fe³⁺ ions indicated by the EPR signal at $g' \approx 2$ were hardly reduced. For these Fe species, the coordination geometry cannot be easily specified; however, with respect to the UV-vis spectra under steadystate SCR conditions showing bands of both reduction-resistant tetrahedral and octahedral Fe^{3+} , it is likely that the EPR signal at $g' \approx 2$ also reflects Fe sites of both coordinations. The amounts of these barely reducible isolated Fe³⁺ sites increased with increasing Fe content, as can be seen by comparing the UV-vis intensity below 300 nm under steady-state conditions (Fig. 2). Regarding the relative intensities of the different EPR signals (Fig. 4), it appears that the barely reducible sites compose the majority of the isolated Fe species and are reflected mainly by the signal at $g' \approx 2$. In contrast, easily reducible sites give rise to the line at $g' \approx 6$ and also partly to the signal at $g' \approx 4.3$ and seem to be much less abundant.

In situ FTIR spectra suggest that, in the presence of even traces of NO₂ and/or oxygen, weakly adsorbed N_2O_3 , N_2O_4 ,

and strongly adsorbed nitrate intermediates are readily formed (Figs. 5 and 6). They were present in lower amounts on prereduced Fe-ZSM-5, suggesting that nitrogen oxides interact more strongly with trivalent iron. Hence, active sites for NO oxidation should be Fe³⁺ species. Fe–NO adsorption complexes, as detected in the complete absence of NO₂ and O₂ [22,25], were not found. This suggests that under SCR conditions in the common presence of NO, NO₂, and O₂, the reaction proceeds via the intermediate formation of adsorbed nitrate intermediates, which might then be reduced by NH₃ to N₂. This is in agreement with the reaction mechanism proposed by Long and Yang [33] involving initial oxidation of NO to adsorbed NO_x ($x \ge 2$) and further reduction to N2 by NH4+ ions. Clearly, the intermediate oxidation of NO may be favored by Fe³⁺ but not by Fe^{2+} . Thus, it seems likely that, among the isolated Fe species, those that are not permanently reduced under steady-state SCR conditions are active sites in the SCR of NO by NH₃. This is also supported by the fact that in used Fe-ZSM-5 catalysts, the $g' \approx 6$ signal disappears completely, although no deactivation is observed during the SCR reaction [17]. Because the amount of barely reducible isolated Fe increases with increasing Fe content, it is not surprising that the activity of the Fe-Z samples has been observed to increase as well [10].

Despite these findings, however, attempts to correlate the rate of the SCR reaction with the number of Fe sites in the Fe-Z catalysts [10] were most successful when assuming that not only isolated Fe ions, but also oligonuclear Fe_xO_y clusters and probably even Fe ions accessible on the surface of oxide particles, are redox-active species in NH₃-SCR of NO. In situ UV–vis studies, including those of the redox kinetics (Table 2), have shown that Fe_xO_y agglomerates reoxidize much more rapidly than isolated Fe sites and thus can immediately enter into another redox cycle. Therefore, it is plausible to assume that they contribute to the selective catalytic process at lower reaction temperatures as well. At higher temperatures (>700 K), these agglomerates, due to their higher oxidation potential in comparison to isolated Fe³⁺ species, give rise to unselective total oxidation of NH₃, thus limiting NO conversion [10].

In general, the behavior of isolated Fe sites during isobutane-SCR, as evidenced by in situ EPR results, is similar to that under NH₃-SCR conditions (Fig. 8). This agrees with the observation that at low reaction temperature, catalytic activity increases with increasing Fe content [10]. A major difference arises from the fact that isolated Fe sites are more strongly reduced under isobutane-SCR conditions (Fig. 8). Note that the EPR signal at $g' \approx 6$ is no longer present and that the one at $g' \approx 4.3$ is much smaller than during NH₃-SCR. However, the exposed Fe sites of oxidic clusters are more strongly reduced, too, giving rise to more pronounced formation of ferrimagnetic species; compare the EPR spectra of Fe-Z(1.2) in Figs. 4 and 8. This stronger reduction in steady state can explain the fact that the overall activity of the Fe-Z samples in isobutane-SCR is much lower than in NH₃-SCR under the same reaction conditions [10], because the intermediate oxidation of NO is not as effectively catalyzed due to the lower amount of accessible trivalent Fe species. Another obvious difference that depends on the nature of the reductant is evident from the behavior of the oxide clusters. In contrast to NH₃-SCR, where they are selective up to temperatures of about 700 K, $Fe_x O_y$ agglomerates play a detrimental role in isobutane-SCR because they oxidize the isobutane reductant to CO_x at temperatures as low as 623 K. This is evident from carbonyl-containing species detected by in situ FTIR preferentially on Fe-Z(1.2) but not on Fe-Z(0.3) (Fig. 9). Recently we showed that the commercial H-ZSM-5 matrix used for the preparation of the Fe-Z samples contains about 500 ppm of Fe impurities in the form of clusters rather than as isolated sites [17], demonstrating why a carbonyl band at 1690 cm⁻¹ is also observed on this sample (Fig. 9).

Carbonyl-containing adsorbates are considered as intermediates in the total oxidation of isobutane. As a result of this unselective oxidation behavior of the Fe_xO_y agglomerates, NO conversion decreases dramatically above 600 K, and this undesired effect becomes more and more pronounced as the content of oxide clusters increases with increasing Fe content [10]. In contrast, the formation of C/N-containing species, such as nitriles, cyanates, and isocyanates, seems to proceed preferentially on isolated Fe sites, the amount of which increases from sample Fe-Z(0.3) to sample Fe-Z(1.2) (Fig. 9). Some have claimed that these species are active intermediates in NO_x reduction [35,38– 40], which can be considered another reason for the superior catalytic performance of isolated Fe sites in isobutane-SCR.

4. Conclusion

A series of Fe-ZSM-5 catalysts with a tailored dispersion of Fe sites ranging from almost exclusively isolated Fe ions (Fe content ≤ 0.3 wt%) via some additional oligonuclear Fe_xO_y clusters (0.6–0.7 wt% Fe) to abundant oligonuclear Fe_xO_y clusters and large Fe₂O₃ particles were studied by in situ UV–vis, EPR, and FTIR spectroscopy during interaction with feed components of the SCR of NO by NH₃ and *i*-butane, respectively. A certain part of the isolated Fe³⁺ species reflected by UV and EPR signals at 241 nm and $g' \approx 4.3$ (Fe³⁺O₄), respectively, at 290 nm and $g' \approx 6$ (Fe³⁺O_{4+x}, x = 1-2) was irreversibly reduced under steady-state SCR conditions. For both NH₃- and *i*-butane-SCR, this reduction was more pronounced for Fe sites coordinating to more than four oxygen ligands (290 nm and $g' \approx 6$), and the total extent of permanent reduction was highest in *i*-butane-SCR.

In situ FTIR results suggest that the reduction of NO to N_2 in the presence of NO₂ and/or O₂ proceeds via the formation of higher oxidized intermediates, such as adsorbed N₂O₄, N₂O₃, and nitrates, which are subsequently reduced. In *i*-butane-SCR, this reduction proceeds via the formation of C/N-containing intermediates and possibly organic nitrates detected by FTIR spectroscopy.

The formation of nitrogen oxide intermediates in higher oxidation states requires the presence of trivalent active Fe sites, which must undergo a periodic Fe^{3+}/Fe^{2+} redox cycle. Fe sites that are permanently reduced to Fe^{2+} under SCR conditions and cannot be reoxidized are likely not active, because a Fe^{2+}/Fe^+ redox cycle should be energetically unfavorable. These Fe sites are reflected by EPR signals at $g' \approx 6$ and partially also at $g' \approx 4.3$, whereas the EPR signal at $g' \approx 2$ (in samples with Fe content $\leq 0.3 \text{ wt\%}$) represents isolated reduction-resistant and thus probably active Fe³⁺ sites. Permanent reduction of isolated Fe³⁺ was more pronounced during SCR with *i*-butane than with NH₃, which may be why the catalysts were markedly less active in the former case.

In contrast to certain isolated Fe³⁺ sites, oxidic clusters of different sizes, reflected by UV–vis signals above 300 nm and an EPR line at $g' \approx 2$ (in samples with Fe content ≤ 0.6 wt%), remained essentially trivalent during SCR of NO with both NH₃ and *i*-butane, due to their slow reduction and very rapid reoxidation. Consequently, these species have a higher oxidizing power than isolated Fe³⁺ sites. This leads to undesired total oxidation of the reducing agent at higher temperatures, an effect that is most detrimental for *i*-butane but not as crucial for NH₃.

As a rule for knowledge-based catalyst design, the results of this study indicate that for both NH₃- and *i*-butane-SCR, the concentration of accessible Fe³⁺ that can participate in a reversible redox cycle should be maximized, whereas the formation of Fe_xO_y clusters must be completely (*i*-butane-SCR) or largely (NH₃-SCR) avoided.

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