

# Active sites for NO reduction over Fe-ZSM-5 catalysts

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A study of Fe-ZSM-5 catalysts with variable amounts of isolated, oligomeric and heavily aggregated Fe<sup>3+</sup> oxo sites (as evidenced by UV-Vis and EPR spectroscopic data) and their catalytic properties in the selective catalytic reduction of NO by isobutane or by NH<sub>3</sub> is presented, which allows development of a unified concept of the active Fe sites in these reactions, according to which isolated Fe sites catalyse both SCR reactions while oligomeric sites, though also involved in the selective reduction path, limit the catalyst performance by causing the total oxidation of the reductant.

Iron-modified zeolites, mostly Fe-ZSM-5, are subject to considerable attention due to their catalytic potential in reactions of environmental and commercial interest, among them the selective catalytic reduction (SCR) of NO by hydrocarbons<sup>1</sup> or by ammonia.<sup>2</sup> Much research has been devoted to the identification of the active sites for these reactions, in particular for hydrocarbon-SCR. For this reaction, mostly performed with an isobutane reductant, catalysts of high iron loading (Fe/Al  $\approx$  1, typically  $\approx$  5 wt-%) prepared *via* chemical vapour deposition (CVD) of FeCl<sub>3</sub> into H-ZSM-5<sup>1</sup> are favoured. Based on evidence from TPR and EXAFS studies,<sup>3,4</sup> and inspired by analogy with the methane monooxygenase enzyme, intra-zeolite binuclear Fe oxo complexes have been suggested to be the active sites for isobutane-SCR.<sup>1,4,5</sup> In contrast, Sobalik *et al.* attribute the SCR activity (of Fe-ferrierite) exclusively to mononuclear Fe ions in a well-defined exchange position.<sup>6,7</sup> Our group has concluded from former work that mononuclear sites are active for both isobutane- and NH<sub>3</sub>-SCR, but oligomeric Fe oxo species may be involved as well.<sup>8–10</sup> However, any decision on this problem is severely hindered by the complex structure of the Fe-ZSM-5 materials used where the coexistence of many Fe structures is hard to avoid, which impairs, in particular, the applicability of EXAFS for these materials.

We have now succeeded in preparing a series of Fe-ZSM-5 catalysts with a variable distribution between isolated, oligomeric and strongly aggregated sites (hereafter referred to as particles) which gives a sound basis for decisive conclusions about the nature of the active iron sites. This preparation is a variation of the improved liquid ion exchange (ILIE) introduced recently by Long and Yang.<sup>11</sup> Na-ZSM-5 (Si/Al *ca.* 14), a variable amount of Fe powder, and deionised water were mixed under inert atmosphere and brought to pH = 1 by adding concentrated hydrochloric acid. The Fe<sup>2+</sup> ions formed by dissolution of the metal were allowed to exchange into the zeolites for 5 days under a protecting atmosphere of inert gas and hydrogen resulting from iron dissolution. During the process of Fe dissolution and exchange, the pH value rises to 1.5 ... 5.5 dependent on the Fe amount.

Subsequently, the samples were washed, dried, and calcined in air at 873 K.

The catalysts presented here contain 0.3, 0.7, and 1.2 wt-% Fe (by ICP-OES, see Table 1). Their SCR activity was studied in catalytic micro-flow reactors using gas feeds of 2000 ppm NO, 2000 ppm isobutane, 3% O<sub>2</sub> in He at 42,000 h<sup>-1</sup>, or of 1000 ppm NO, 1000 ppm NH<sub>3</sub>, 2% O<sub>2</sub> in He at 750,000 h<sup>-1</sup>. UV-Vis spectra were measured at room temperature with a Varian Cary 400 spectrometer (samples diluted with  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>) equipped with a diffuse reflectance accessory (Harrick). X-band EPR spectra were recorded in flowing air at 623 K by an ELEXSYS 500-10/12 CW-spectrometer (Bruker) equipped with a special flow reactor. DPPH was used as a magnetic field standard.

In Fig. 1a, NO conversions obtained with the isobutane reactant are presented. Already with 0.3% Fe, conversions of  $\geq$  86% are achieved at 623 K, which to our knowledge exceeds all published data measured under the same conditions with Fe-ZSM-5 made *via* CVD preparations. Remarkably, ILIE-0.3 retains high NO conversions even at higher temperatures where the known catalysts exhibit a much stronger decline, typically to 40–50% at 723–773 K.<sup>4,12</sup> The ILIE catalysts with higher iron content achieve improved NO conversions at low temperature, but upon temperature increase, the decline of the NO conversions starts earlier so that the peak conversions decrease.

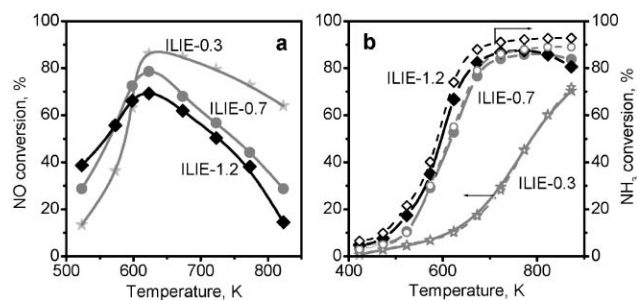
NO conversions achieved with the NH<sub>3</sub> reductant increase monotonously with the iron content (Fig. 1b). At low Fe content, the NH<sub>3</sub> conversions match the NO conversions in the whole temperature range. With increasing Fe content, deviations can be seen in the high-temperature region. Together with the NO conversion maximum of ILIE-1.2, this indicates an increasing tendency to unselective NH<sub>3</sub> oxidation. In the low-temperature range, the activity of ILIE-1.2, which was also studied at 1.1 \* 10<sup>6</sup> h<sup>-1</sup>, equals the best published activities for Fe-ZSM-5 (with 1.9% Fe<sup>11</sup>) within experimental error while it clearly exceeds the known data for high temperatures.

UV-Vis spectra of these catalysts (after calcination at 823 K) are displayed in Fig. 2. They have been deconvoluted into sub-bands representing Fe<sup>3+</sup>  $\leftarrow$  O charge transfer bands (Table 1), the assignment of which has been discussed in refs. 10,13. Briefly, sub-bands  $\leq$  300 nm arise from isolated Fe<sup>3+</sup> sites in tetrahedral and octahedral environments ( $t_1 \rightarrow t_2/t_1 \rightarrow e$  transitions unresolved),

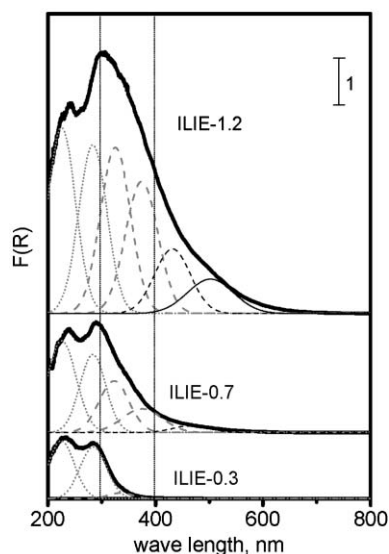
**Table 1** Iron content (wt-%) and speciation (from UV-Vis spectra, Fig. 2) of samples studied

Sample	Total Fe	Fe (mono)	Fe (oligo)	Fe (particle)
ILIE-0.3	0.3	0.28 <sub>5</sub>	0.01 <sub>5</sub>	0
ILIE-0.7	0.7	0.42	0.25	0.03
ILIE-1.2	1.2	0.5	0.5	0.2

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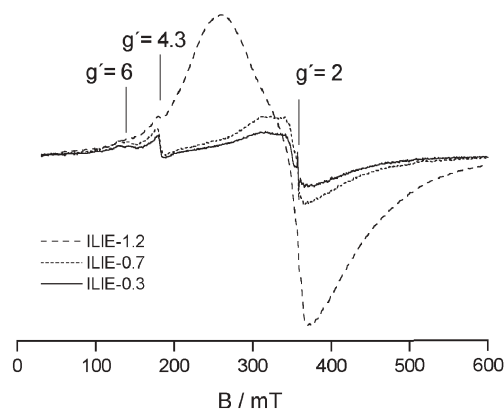
**Fig. 1** Catalytic behaviour of Fe-ZSM-5 containing 0.3–1.2 wt-% Fe in SCR reactions. a) NO conversions using 2000 ppm NO, 2000 ppm isobutane, 3% O<sub>2</sub>, in He, at 42,000 h<sup>-1</sup>, b) NO (filled symbols) and NH<sub>3</sub> conversions (open symbols) using 1000 ppm NO, 1000 ppm NH<sub>3</sub>, 2% O<sub>2</sub> in He at 750,000 h<sup>-1</sup>.



**Fig. 2** UV-Vis spectra of Fe-ZSM-5 catalysts, measured after calcination in air at 823 K. For numerical results see Table 1.

bands at 300 nm <  $\lambda$  < 400 nm are assigned to oligomeric clusters, and sub-bands > 400 nm to particles. From the intensity of the sub-bands, the relative percentage, and by multiplication with the total Fe content, the amount of each kind of Fe species was derived (Table 1). Since the wavelength dependence of the absorption coefficient is not known for this system, the ratio of the different species within the same sample should be regarded as an estimate only. Despite this fact and the intrinsic uncertainty of the deconvolution procedure, the derived values in Table 1 allow a meaningful comparison of approximate amounts of the particular species in different samples. According to this analysis, ILIE-0.3 has 95% of its iron in isolated sites of different coordination. With increasing Fe content, the total amount of the isolated sites grows slightly and levels off while the total amount of oligomers and (in ILIE-1.2) of particles increases dramatically. As we cannot exclude any intensity contribution of the particles to the  $\lambda$  < 200 nm region, one may consider the 0.5 wt-% isolated Fe<sup>3+</sup> in ILIE-1.2 (Table 1) as an upper limit.

The EPR spectra of the catalysts (Fig. 3) qualitatively confirm this analysis. ILIE-0.3 exhibits almost exclusively signals that have to be assigned to isolated Fe<sup>3+</sup> sites. We have assigned them



**Fig. 3** EPR spectra of Fe-ZSM-5 catalysts investigated. Spectra measured at 623 K, for assignment of signals see text.

previously<sup>10,13</sup> to Fe<sup>3+</sup> ions in a distorted tetrahedral environment ( $g \approx 4.3$ ), to penta- or hexacoordinated Fe<sup>3+</sup> ions ( $g \approx 6.0$ ), and to Fe<sup>3+</sup> ions in a highly symmetric, probably octahedral coordination ( $g \approx 2.0$ ). The latter signal is superimposed by a very weak and narrow signal at the same  $g$  value, which is caused by the reactor. There is no signal that could be attributed to a Fe<sub>*n*</sub>O<sub>*x*</sub> site with nuclearity  $n = 2$ . The spectrum of ILIE-1.2 in the range of  $g \approx 2$  is a superposition of two lines. The dominating very broad signal arises from aggregated entities which might show some ferrimagnetic interaction as suggested by the high spectral intensity in comparison to ILIE-0.3 and ILIE-0.7, while the narrow signal at  $g \approx 2$  (an isolated site) can still be well discerned. Here, the signals at  $g \approx 4.3$  and 6 have become rather weak.

Taken together, these data lend strong support to the view that oligomers (including binuclear sites) and particles are not required to achieve a high activity in isobutane-SCR. Indeed, the highly active ILIE-0.3 has its iron almost exclusively in isolated sites. With growing Fe content, the 2–3 fold increase of NO conversion at 523 K does not correlate with the 15–30 fold increase of the oligomer amount (Table 1). On the other hand, this improvement cannot be accounted for exclusively by increasing amounts of isolated sites. At the same time, it is obvious that oligomers and particles deteriorate the overall catalytic behaviour of these materials by catalysing the total oxidation of the isobutane reductant, which causes the NO conversion curves to increase less steeply and bend down at lower peak conversions upon increasing the Fe content. These conclusions are described on a larger basis of samples, and with full account of the characterization results, in ref. 14.

In NH<sub>3</sub>-SCR, the catalytic role of the aggregated entities in the desired SCR reaction is more evident. Again, the capability of isolated sites to catalyse this reaction is obvious from the results of ILIE-0.3, but the increase of the iron content brings about substantial improvements up to 1.2% Fe. Again, clusters and particles have an adverse effect on the reductant but this occurs at much higher temperatures than with isobutane.

In summary, a unified view of the active sites of SCR reactions over Fe-ZSM-5 may be derived: isolated Fe<sup>3+</sup> sites catalyse the SCR of NO by isobutane and by NH<sub>3</sub> with high efficiency. Oligomeric Fe oxo species may contribute to these reactions, in particular in NH<sub>3</sub>-SCR. On the other hand, the oligomeric and Fe oxo species play a negative part by catalysing the unselective

oxidation of the reductant. As isobutane becomes oxidised more easily than NH<sub>3</sub>, narrow limits are imposed on the improvement of activities by increasing the Fe content with isobutane while this is a promising approach possible with NH<sub>3</sub>.

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