Redox behaviour of over-exchanged Fe/ZSM5 zeolites studied with *in-situ* soft X-ray absorption spectroscopy†

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The oxidation and reduction behaviour of calcined over-exchanged Fe/ZSM5 has been studied using soft X-ray absorption by measuring the average iron valence under (2 mbar) helium, oxygen and deNOx (HC-SCR) conditions between room temperature and 350 °C. The results (probing depth of approximately 4 nm) show that Fe/ZSM5 is an extremely flexible redox system. The calcination procedure (severe calcination: heating rate 5 °C min^{-1}, as normally used in the literature; mild calcination: heating rate 0.5 °C min^{-1}) is proven to be important to optimise the reducibility of iron. Upon mild calcination Fe/ZSM5 has an average valence of 2.9 under oxygen (5% in helium), of 2.5 under pure helium at room temperature (RT), and of 2.1 under pure helium at 350 °C. Upon severe calcination Fe/ZSM5 shows higher average valences, in agreement with the assumption that part of the iron in this sample is positioned in small iron-oxide nanoparticles at the outer surface of the zeolite crystals. During heating in helium, the valence reaches a minimum value before slightly rising again (re-oxidation) when the temperature is kept constant. It is also found that the X-ray irradiation is able to affect the average valence by values up to 0.10. This study confirms that iron in 'over-exchanged' Fe/ZSM5 consists dominantly of highly reactive iron complexes, where the iron is (distorted) octahedral Fe^{III} in the oxidised state. The implications for the reaction mechanism for the N$_2$O decomposition and the nature of the α-oxygen sites are discussed, in relation to recent developments in the understanding of iron non-heme enzymes.
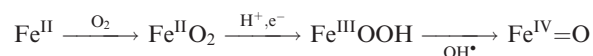
Introduction

Over the past years, Fe containing ZSM5 has been the subject of an extensive body of research. ZSM5 with an iron loading below 1 wt.% is an active catalyst for the decomposition N$_2$O[1,2] and for the selective oxidation of hydrocarbons, for example benzene to phenol, using N$_2$O as oxidant.[3,4] Over-exchanged Fe/ZSM5, with an iron loading up to around 5 wt.%, is an effective catalyst for the reduction of nitrogen oxides in the presence of excess oxygen, as the hydro-carbon assisted selective catalytic reduction (HC-SCR) of NO.[5,6]

Recently, much attention has been paid to the identification and characterisation of the active iron phases in FeZSM5. A complex factor in the discussions is the large diversity of the studied FeZSM5 materials. A variety of synthesis and activation routes are used and there are qualitative differences in the Si/Al ratio, iron loading, parent ZSM5 materials and iron precursors.

The activation of framework substituted Fe-ZSM5 is performed by calcination *in vacuo* or by steaming at high temperature. During these procedures, different Fe-containing species are formed.[4,7] These species vary from isolated extra-framework Fe oxo-ions (Fe$_1$), binuclear oxo-iron complexes (Fe$_2$) and oligonuclear oxo-iron complexes (Fe$_N$) located in the zeolite channels, to larger iron-oxide nanoparticles on the external surface of the zeolite (FeO$_x$). These FeO$_x$ nanoparticles have been shown to be inactive. The selective oxidation properties of Fe-ZSM5 are indeed ascribed to dispersed Fe-containing species in the zeolite channels. According to Panov and co-workers steam treatments cause the formation of extra-framework binuclear iron species by extraction of iron from the zeolite matrix into the micropores. Upon reaction with nitrous oxide these iron centres are believed to generate a particularly reactive oxygen species.[3] This species, so-called α-oxygen, is believed to be capable of the oxidation of benzene to phenol, already at room temperature. Sachtler and co-workers have performed a number of isotopic exchange studies on Fe/ZSM5.[8,9] They have shown that Fe/ZSM5, previously reduced at temperatures above 500 °C and re-oxidised by N$_2$O, exchanges oxygen very rapidly at 250 °C. This oxygen exchange involves fairly isolated oxygen atoms as can be inferred from the R^1 mechanism, resulting in the production of ^{18}O^{16}O oxygen molecules. The authors speculate that Fe^{III} first needs to be reduced to Fe^{II}, where these Fe^{II} sites are brought into a situation of coordinative unsaturation. Reaction with N$_2$O then possibly creates mononuclear [Fe=O]$^{2+}$ sites or diamond core [Fe$_2$O$_2$]$^{2+}$ sites as possible 'α-oxygen' sites. These speculations are partly originating from recent developments in iron non-heme enzymes, where such diamond core sites play a crucial role. An important route to create active oxygen species in iron non-heme enzymes can be written as:

$$Fe^{II} \xrightarrow{O_2} Fe^{II}O_2 \xrightarrow{H^+,e^-} Fe^{III}OOH \xrightarrow[OH^\bullet]{} Fe^{IV}=O$$

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This and related routes are the subject of much research and evidence for such reaction schemes in iron non-heme enzymes and their model compound analogues is building quickly.[10–13] In relation to Fe/ZSM5, it should be mentioned that in both systems the $Fe^{IV}=O$ state seems to be generated from a starting situation containing reduced Fe^{II}, *i.e.* the $Fe^{IV}=O$ state does not seem to be directly obtainable from a Fe^{III} state.

In general, substitution of Fe in the framework of ZSM5 results in a maximum iron loading of 1 wt.%. By introducing iron in extra-framework positions by post-synthesis methods, on the contrary, a higher iron loading is possible, with either ion exchange or sublimation. Binuclear Fe oxo/hydroxo species located at the Brønsted sites position of the framework have been proposed to be the active phase also in Fe/ZSM5 prepared by the sublimation of anhydrous $FeCl_3$.[5] Iron species are sensitive towards washing, calcination, steaming, reduction and oxidation treatments. In particular, Fe-binuclear complexes can undergo agglomeration during calcination, finally resulting in the formation of inactive goethite and hematite crystals on the external surface of the zeolite. It has been demonstrated in a previous study by our group[14] that the agglomeration of iron in Fe/ZSM5 can be controlled by adequately tuning the conditions applied during calcination. As such, Fe/ZSM5 with an estimated amount of binuclear Fe species higher than 70% can be obtained by applying a mild calcination procedure, using a moderate temperature ramp (heating rate $0.5\,°C\ min^{-1}$) and a high specific gas flow-rate (800–1000 $ml\ min^{-1}\ g^{-1}$). A severe calcination procedure (heating rate: $5\,°C\ min^{-1}$) as often applied to Fe/ZSM5 samples studied in the literature leads to a significant agglomeration of the iron complexes towards the formation of iron-oxide clusters at the outer surface of the zeolite crystals.

The autoreduction ability of iron in Fe/ZSM5 is observed by several authors[7,15–18] and has been investigated by our group for mildly calcined Fe/ZSM5 using Fe K-edge X-ray absorption spectroscopy (XAS).[19] In an additional study[20] we have shown that *in-situ* soft X-ray absorption spectroscopy can be applied to determine the structural and electronic properties of the Fe species present in zeolites. The Fe $L_{2,3}$ XAS spectral shape can be simulated in detail, using a charge transfer multiplet code.[21,22] This yields precise information on the electronic ground state of iron, including its number of 3d-electrons, (*i.e.* its valence state), its spin state, crystal field value, local geometry and degree of covalence. In the same contribution it has been shown that, by optimizing the procedure applied for the collection of the $L_{2,3}$-edge XAS spectrua, a precise determination of the iron valence can be obtained with a time resolution of approximately one minute.[20]

The objective of this work is to study the reduction and oxidation properties of the iron species present in Fe/ZSM5, calcined via both the mild and severe calcination procedures. The changes in the iron oxidation state, related to the reactivity of the weakly bound oxygen is of particular interest since it represents the key-step for the decomposition of N_2O, as well as for the HC-SCR of NO.[23] The oxidation state of iron and its local environment in calcined Fe/ZSM5 samples have been followed during heating treatments in helium by *in-situ* soft X-ray absorption spectroscopy measurements at the iron $L_{2,3}$ edge and the oxygen K-edge.

Experimental

Catalyst preparation and characterisation

Over-exchanged Fe/ZSM5 was prepared following the $FeCl_3$ sublimation technique (also called chemical vapour deposition (CVD)), proposed by Chen and Sachtler,[5] and described in more detail in a previous publication.[14] The H^+ removal efficiency (98%), determined by HCl titration, indicated that

during the Fe-exchange procedure nearly all the Brønsted acid sites were removed from the H/ZSM5.

Particular attention was paid to the calcination procedure. Fe/ZSM5 was calcined in two different ways. In the case of the *mild calcination* procedure (further denoted by 'mc'), the sample was heated to $200\,°C$ in a PFR-reactor under a specific He flow of $800\ ml\ min^{-1}\ g^{-1}$ and with a moderate temperature ramp ($0.5\,°C\ min^{-1}$). At this temperature, $200\ ml\ min^{-1}\ g^{-1}$ of O_2 was added to the He flow while, under the same temperature ramp, heating was continued to $550\,°C$. After 3 h at $550\,°C$, the temperature was decreased to $30\,°C$. The *severely calcined* sample (further denoted by 'sc') was heated under $120\ ml\ min^{-1}\ g^{-1}$ flowing oxygen in a tubular oven using a temperature ramp of $5\,°C\ min^{-1}$ and was calcined at $550\,°C$ for 3 h. The crystalline fingerprint of the zeolitic support was monitored after each synthesis step by XRD. On the basis of these measurements lattice damage or formation of large iron oxides phases could be excluded, even upon calcination. Elemental analysis by inductively coupled plasma (ICP) was carried out to determine the silicon/aluminium ratio (Si/Al = 17.0) and the iron loading (Fe/Al = 0.97) of the obtained Fe/ZSM5.

In-situ soft X-ray absorption spectroscopy

Sample treatments. Soft X-ray absorption experiments were carried out to investigate the valence of Fe and the nature of the evolving gasses during various chemical and heat treatments. The Fe/ZSM5 samples investigated in this study and the treatments performed during the collection of the data are indicated in Table 1. All the measurements were performed under dynamic atmospheres (flowing gases). The severely calcined sample (Fe/ZSM5-sc) was inserted into the chamber, which was subsequently pumped down to vacuum. After approximately 15 min the chamber was brought under 5% O_2 in helium (O_2-25). After stabilisation at the maximum Fe-valence, the atmosphere was first switched to pure helium ($t = 0$; He-25) to study the autoreducibility of the sample at room temperature. After 150 min, the temperature was increased from $25\,°C$ to $350\,°C$ with a ramp of $2.7\,°C\ min^{-1}$ at 2 mbar helium. At a time of 280 min the temperature of $350\,°C$ was reached (He-350) and the sample was kept under these conditions for one hour. At a time of 340 min we switched to 5% O_2 in helium again (O_2-350), to study the re-oxidation behaviour at $350\,°C$, followed by switching to helium at a time of 410 min (He-350) in order to study the reversibility of the auto-reduction behaviour. Fe/ZSM5-mc and α-FeOOH were treated in exactly the same manner as Fe/ZSM5-sc. A second Fe/ZSM5-mc sample (from the same batch) was also investigated. To distinguish between the two samples, the second one has been given a subscript 2 (see Table 1). The same treatment was applied also to this second sample,

Table 1 Overview of the Fe/ZSM5 samples; O_2-25 indicates 5% O_2/He at $25\,°C$; the deNOx (HC-SCR) conditions are 0.2 vol% NO, 0.2 vol% i-C_4H_{10}, 3 vol% O_2 balanced with He to $100\ ml\ min^{-1}$

Sample	Measurement conditions
Fe/ZSM5-sc	O_2-25 → He-25 → He-ramp to 350 → He-350 → O_2-350 → He-350
Fe/ZSM5-mc$_1$	O_2-25 → He-25 → He-ramp to 350 → He-350 → O_2-350 → He-350
Fe/ZSM5-mc$_2$	He-25 → He-ramp to 350 → He-350 → He-ramp to 25 → O_2-25 → He-25 → ramp to 350 → He-350 → deNOx-350
α-FeOOH	O_2-25 → He-25 → He-ramp to 350 → He-350 → O_2-350 → He-350

but upon preheating in helium at 350 °C and cooling to room temperature. In addition, the Fe/ZSM5-mc$_2$ sample was measured under deNOx (HC-SCR) conditions (0.2 vol% NO, 0.2 vol% i-C$_4$H$_{10}$, 3 vol% O$_2$ balanced with He to 100 ml min^{-1}; deNOx-350) instead of under 5% O$_2$ in helium. Table 1 outlines the step-by-step treatments of the four samples.

Data collection. The soft X-ray absorption spectra of the iron L$_{2,3}$ edge (700–730 eV) and the oxygen K edge (525–550 eV) were measured at BESSY (Berlin), beamlines U49/2-PGM-1 and UE56/2-PGM-1. The spectral resolution of the monochromators was approximately 0.2 eV. The instrumentation for *in-situ* low energy XAS experiments has been developed by Knop-Gericke and co-workers and is described in detail elsewhere.[24–27] A stainless steel *in-situ* cell was used in which the powdered zeolite sample was fixed in a sample holder. The flow rates of helium and of 5% oxygen in helium were 100 ml min^{-1}, of which approximately half entered the *in-situ* cell. A homemade gas mixing system regulated the flow and the total pressure at the sample position was about 2 mbar during the experiments. A molecular sieve was used in order to remove traces of oxygen when a pure helium flow was flushed (see Table 1). The temperature was increased from room temperature to the reaction temperature of 350 °C with a heating rate of 2.7 °C min^{-1}. The X-ray absorption spectral shape was measured with two collector plates. Both detectors measure the ionised gas due to the created electrons in the X-ray absorption process and the subsequent non-radiative decay of the core hole, *i.e.* they measure the ionised-gas-conversion total-electron-yield. Detector A measures the gas phase while a detector B close to the sample surface detects both the gas phase and surface signal. By subtraction of the signal of detector A from detector B, the surface signal can be revealed. This ionised-gas-conversion total-electron yield based method has a probing depth of approximately 4 nm.[28]

Data processing. For the determination of the iron valence state and the representation of the changes therein during activation treatments and reaction, we measure the L$_3$ X-ray absorption spectrum.

Fig. 1 shows the L$_{2,3}$ X-ray absorption spectra of the oxidised (top) and reduced (bottom) mildly calcined Fe/ZSM5 sample. The oxidised sample was measured after re-oxidation under 5% oxygen in helium and the reduced sample was measured under pure helium (see Table 2). The spectra can be simulated well with charge transfer multiplet calculations of respectively Fe^{III} and Fe^{II}, which implies that these spectra represent pure Fe^{III} and Fe^{II} samples respectively. We estimate
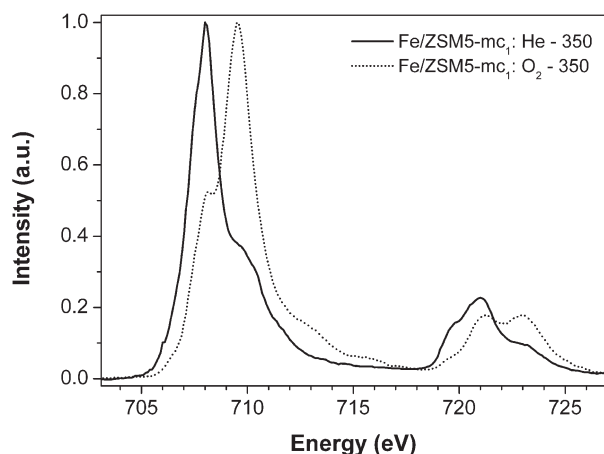
Fig. 1 Experimental L$_{2,3}$ X-ray absorption spectra of reduced (solid line) and oxidized (dotted line) mildly calcined Fe/ZSM5. See Table 2 for details about the samples.

Table 2 The average valence of iron in the Fe/ZSM5 samples; O$_2$-25 indicates 5% O$_2$/He at 25 °C, *etc.*; the sample overview of Fe/ZSM5-sc is indicated with sc, *etc.*; the mc$_2$ sample is measured through two temperature ramps as discussed in the text; the boldface valences of 2.00 and 3.00 indicate the spectra that have been used for calibration

	sc	mc$_1$	mc$_2$	FeOOH	
He-ramp to 350			2.02		
He-350			2.14		
He-ramp to 25			2.40		
He-25	2.82	2.78	2.59	2.97	
O$_2$-25	2.94	2.92	2.92	3.00	
He-25	2.64	2.61	—	3.00	Minimum value
	2.67	2.61	—		Final value
	2.49	2.44	2.43		Fresh spot
He-ramp to 350	2.16	**2.00**	2.16	2.91	
He-350	2.25	2.10	2.20	2.94	Re-oxidation
O$_2$-350	2.91	2.89		2.99	
DeNOx-350			**3.00**		
He-350	2.54	2.44			

that the absolute (maximum) error in the average valence to pure Fe^{III} and Fe^{II} is less than 0.05. A more detailed description of the procedure to determine the average valence of Fe is given in our previous paper,[20] where also the charge transfer multiplet calculations have been discussed; they show that the Fe^{III} site is octahedral with weak bonding between iron and oxygen. The Fe^{II} site is found to be (distorted) tetrahedral. Under the assumption that all the iron sites will be similar to either the oxidised site or the reduced site, each Fe L$_{2,3}$ spectrum is a linear combination of these oxidised Fe^{III} and reduced Fe^{II} samples. Although there will be some variation in iron sites, the calculations show that these are expected to be too small to significantly affect the analysis method. It can be shown[20] that the procedure of valence determination can be simplified by employing a procedure that uses the intensity ratio at the peak positions for Fe^{II} (707.9 eV) and Fe^{III} (709.5 eV). This is important since it allows significantly faster measurement times. By using only the energy range between 702.5 eV and 714.5 eV, the average valence state can be determined with a time interval of 50 s. Periodically, we recorded the complete Fe L$_{2,3}$ spectral shape to check for potential variations in the background. By applying this analysis method, we have monitored the average valence state of the iron present in Fe/ZSM5 during treatments at temperatures between 25 and 350 °C and with gas flows of He, O$_2$ and under deNOx conditions. The relative uncertainty in the average valence of iron could be established to be approximately 0.02.

Results

Fig. 2 (up to $t = 0$ min) shows the variation of the average valence state of iron under an O$_2$ (5% in He) flow of the Fe/ZSM5-sc and Fe/ZSM5-mc samples at room temperature and a pressure of 2 mbar. The samples were subsequently exposed to helium for 2 h. To facilitate the comparison between the redox behaviour of the different Fe/ZSM5 samples the time for switching from O$_2$ to He was set to be $t = 0$ min. The average valence of Fe/ZSM5-sc under O$_2$ (5% in He) at room temperature shows a value of 2.94 ± 0.01 and stays constant at this value for 50 min. After switching to pure He the sample reduces in 15 min to a minimum valence of 2.64, followed by a slight re-oxidation to a value of approximately 2.67 after 110 min. This slight overshooting behaviour has also been observed with hard X-ray absorption,[19] which rules out
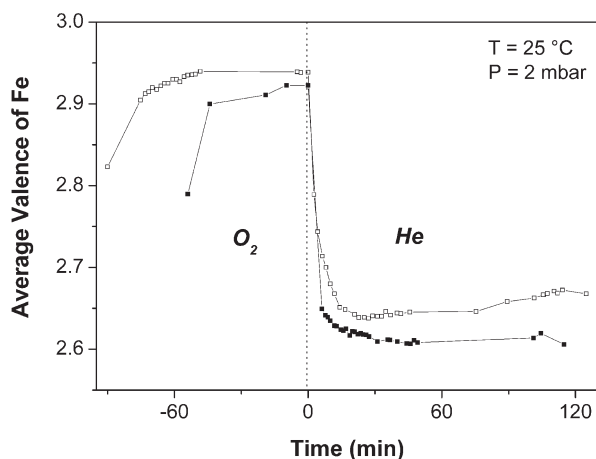
Fig. 2 Oxidation in O_2 (5% in He) and autoreduction in He at room temperature of Fe/ZSM5, severe (open square) and mildly calcined (filled square).

any specific surface effect (see discussion). The mildly calcined sample, Fe/ZSM5-mc, shows an oxidation to 2.92, which is less than for the severely calcined sample. It should nevertheless be noted that for this sample the oxidation time was 60 min instead of the 90 min for the Fe/ZSM5-sc sample. The reduction in helium shows a similar behaviour to that of Fe/ZSM5-sc but with a minimum valence of 2.61. It is clear from Fig. 2 that already at room temperature, both the calcined Fe/ZSM5 samples are subject to significant autoreduction.

During the experiments depicted in Fig. 2 the samples were exposed to soft X-rays all the time. To check whether the X-rays may have had an influence on the average Fe-valence, we compared the difference between the X-ray irradiated part of the sample and a fresh spot. In the case of the Fe/ZSM5-sc sample the average valence of the spot that was irradiated for 200 min is 2.67, while a fresh spot turned out to have an average valence of 2.49. Apparently, an irradiated area has a higher average valence.

Fig. 3 shows the changes in the average valence state of iron, while heating the Fe/ZSM5 samples from 25 °C to 350 °C at 2 mbar He with a ramp of approximately 2.7 °C min^{-1}. A temperature of 350 °C was chosen as it corresponds to the optimal working temperature of Fe/ZSM5 for the HC-SCR reaction with iso-butane. During heating in helium from room temperature to 350 °C the average valence of the severely calcined sample Fe/ZSM5-sc reduced from 2.49 to 2.16. The gap between 225 min and 255 min is related to a re-injection of electrons into the storage ring. After reaching the final temperature of 350 °C, we observe a slight re-oxidation from 2.16 to 2.25. The average oxidation state of Fe/ZSM5-mc is reduced from
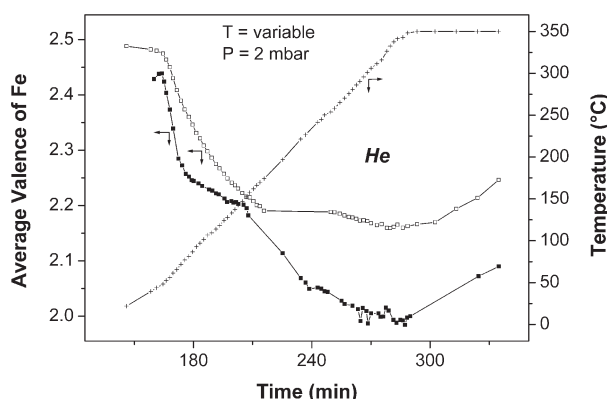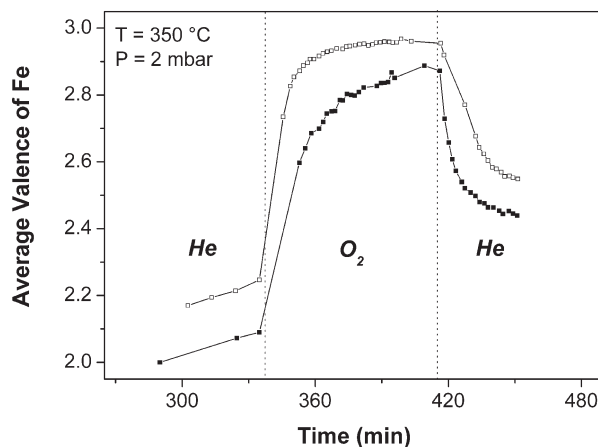
2.44 to 2.00 as a result of heating in He from room temperature to 350 °C. Also in the case of the mildly calcined sample a small re-oxidation to a value of 2.10 is observed while keeping the temperature constant at 350 °C.

Fig. 4 shows an oxidation/reduction cycle at 350 °C of the previously autoreduced samples (Fig. 2). Re-oxidation of Fe/ZSM5-sc in O_2 (5% in He) at 350 °C yields a Fe-valence above 2.90 after 10 min. The re-oxidation with oxygen of the autoreduced Fe/ZSM5-mc is slower and leads to an average valence of 2.89 only after one hour. For the Fe/ZSM5-sc sample the rise of the valence upon oxidation with oxygen is much faster than for the mildly calcined sample. After applying an oxygen (5% in He) atmosphere to the samples for 70 min, we switched back to helium, inducing a drop of the average iron valence to 2.54 and 2.44 for Fe/ZSM5-sc and Fe/ZSM5-mc respectively. The reduction is more pronounced and occurs faster for the mildly calcined Fe/ZSM5 sample. Although this reduction (at $t = 450$ min) is significant, for both the severely and mildly calcined samples the valence state of iron is higher than the minimum valence reached upon autoreduction in helium during the experiments described in Fig. 3. Most of this difference is attributed to the fact that in this case the measurements were interrupted before reaching the steady state.

Fig. 5 shows the effect of the temperature on the valence of iron in a continuously flushed helium atmosphere. As already mentioned, this experiment was carried out with a new mildly calcined sample (Fe/ZSM5-mc$_2$). During heating in helium the autoreduction of iron follows the same pathway, within a deviation of 0.02, as in the equivalent experiment with sample Fe/ZSM5-mc$_1$. Flushing the sample with helium for one hour at 350 °C again results in a re-oxidation, from a minimum valence of 2.02 to 2.14. Upon cooling, the sample further re-oxidises to a final valence of 2.59 (room temperature). An almost complete and very fast oxidation is observed upon switching from helium to oxygen (5% in helium) at room temperature, yielding a final average valence of 2.92, i.e. the same value as obtained during the experiment shown in Fig. 3.

After the heating cycle in helium (RT → 350 °C → RT) and subsequent room temperature oxidation with O_2 (5% in He) as depicted in Fig. 5, the Fe/ZSM5-mc$_2$ sample was heated in helium (same gas flow, heating ramp) as shown in Fig. 6. The gap between 330 min (Fig. 5) and 380 min (Fig. 6) is due to re-injection of electrons in the storage ring. The change of the valence is exactly the same as for the first heating ramp shown in Fig. 5, but there is a 'delay' and the same average valence is reached at some 50 °C higher. In addition, from 200 to 350 °C the average valence of iron is hardly changing and the minimum valence does not go below 2.16. After the

Fig. 3 Autoreduction in He from room temperature to 350 °C (+) of Fe/ZSM5, severe (open square) and mildly calcined (filled square).
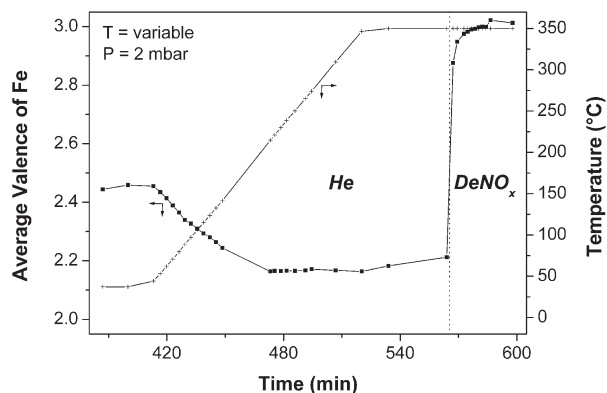

Fig. 4 Reversible oxidation in O_2 (5% in He) at 350 °C after autoreduction in He of Fe/ZSM5, severe (open square) and mildly calcined (filled square).
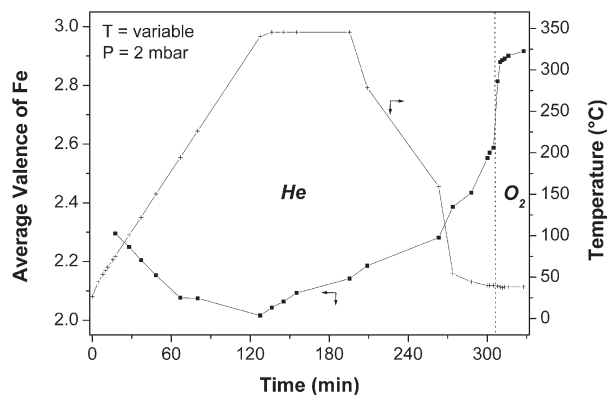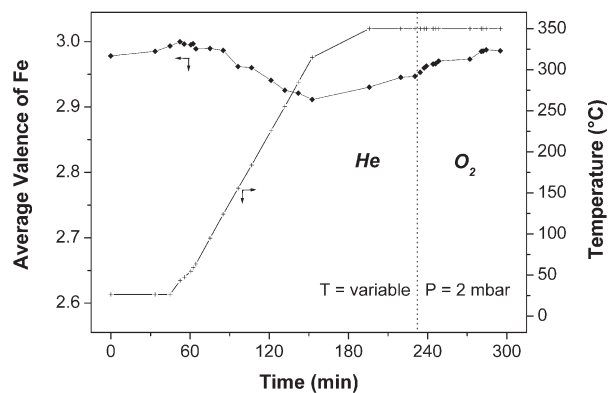
Fig. 5 Reversible autoreduction in He of Fe/ZSM5, mildly calcined (bold square), upon heating to 350 °C and cooling down to RT and subsequent oxidation in O_2 (5% in He) at RT.

Fig. 7 Changes in the average valence state of iron during surface dehydroxylation of FeO(OH) to Fe_2O_3 while heating in He from RT to 350 °C, and subsequent oxidation of the surface by O_2 (5% in He) at 350 °C.

second heating ramp in He to 350 °C, the (auto)reduced Fe-ZSM5-mc$_2$ sample was flushed with a gas mixture with the same composition as that used during deNOx (HC-SCR) catalytic tests previously performed in our laboratory and described elsewhere.[29] The gas flow contained 0.2 vol% NO, 0.2 vol% i-C$_4$H$_{10}$, 3 vol% O_2 balanced with He to 100 ml min^{-1}. Upon switching to the deNOx gas mixture the valence of iron is rapidly increased to 3.00 (within 15 min). Despite the lower oxygen concentration (3% *vs.* 5%) and notwithstanding the presence of iso-butane the observed re-oxidation is faster recorded under HC-SCR conditions than that measured with just oxygen (compare Figs. 1 and 3).

In previous studies on the nature of the iron phases in over-exchanged Fe/ZSM5, α-goethite was suggested to be present. Indeed, small Fe-containing particles on the external surface of severely calcined Fe/ZSM5 samples were investigated by electron microscopy and turned out to contain a crystallised iron oxide phase with a *d*-spacing similar to α-goethite. However, the *d*-values were also close[14] to those of both β-goethite and hematite (α-Fe_2O_3).[18] To investigate the redox behaviour of goethite, pure α-goethite (FeO(OH)) was treated in the same way as the Fe/ZSM5 samples. In Fig. 7 the changes in the average iron valence state of goethite are shown while heating in He from room temperature to 350 °C and subsequent oxidation by O_2 (5% in He). Upon heating two neighbouring surface iron-hydroxyl groups may condense, resulting in the formation of a water molecule, a single surface iron–oxygen group and a coordinatively unsaturated iron atom. The formation of such coordinatively unsaturated iron species at the surface causes a slight decrease in the average valence state of iron to 2.9 (*t* = 152 min). Reoxidation by exposure to oxygen yields
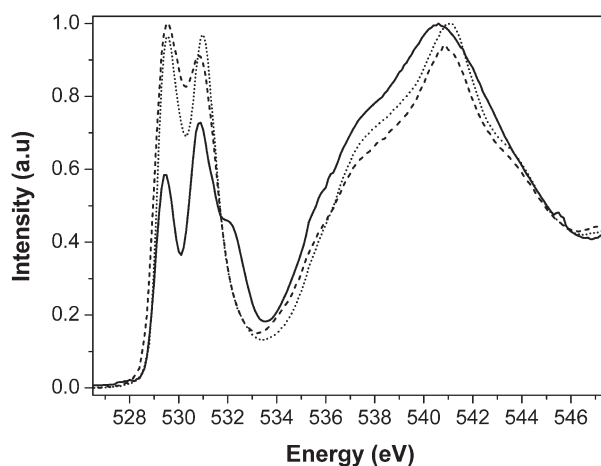
almost exclusively trivalent iron. We note again that soft X-ray absorption (in the electron-yield mode) probes only a top layer of approximately 4 nm, implying that the valence change from 3.0 to 2.9 reflects a slight reduction of the surface iron species only.

Fig. 8 shows the oxygen K-edge spectra of goethite at room temperature and at 350 °C in pure He and of hematite at room temperature in pure He. The change in the nature of the surface oxygen groups in the iron oxy-hydroxide structure of goethite upon heating is clearly visible in these O K-edge spectra. Before the heating cycle the well-known three peaked pre-edge of hydroxyls such as in goethite is visible.[30] After the heating cycle and re-oxidation the three-peaked spectrum is modified to a two-peaked spectrum, identical to the spectrum of pure hematite. The complete absence of the third peak at 532.5 eV indicates that at least the top 10 nm of the goethite sample has been changed into hematite.

Discussion

The oxidation-reduction behaviour

Table 2 collects the average valences of the Fe/ZSM5 samples and goethite measured under various conditions. One can summarise the major features of Table 2 as follows. The valence of all Fe/ZSM5 samples measured under oxygen (5% in helium) is approximately 2.9, in other words the Fe/ZSM5 samples are

Fig. 6 Reversible oxidation in deNOx (HC-SCR) gas mixture (3% O_2, 0.2% NO and 0.2% i-C$_4$H$_{10}$ in He) at 350 °C after autoreduction in He of Fe/ZSM5, mildly calcined (filled square).

Fig. 8 O 1s X-ray absorption spectrum of FeO(OH) at RT in He (solid line), FeO(OH) at 350 °C in He (dashed line) and Fe_2O_3 at RT in He (dotted line).

almost completely oxidised under this condition. Only under deNOx (HC-SCR) conditions does the average valence reach its (assumed) maximum value of 3.0 ± 0.1. Note that if the average valence under oxygen (5% in helium) is set to 3.0, the average valence under deNOx conditions would reach a value slightly larger than 3.0, thereby suggesting the existence of some Fe^{IV} sites, as will be dwelled upon below in relation to the active site in Fe/ZSM5. The average valence under helium depends on the temperature. At $25\,^{\circ}C$ a value around 2.6 is found for irradiated samples, 2.5 for fresh spots. At $350\,^{\circ}C$ an average valance of 2.2 emerges. All these values are almost independent of the sample measurement history. There are however small variations and trends visible that will be discussed below.

At the switching point between Figs. 2 and 3 we moved to a fresh spot, in order to test the effects of the X-rays on the average valence. The effects are a reduction in the average value from 2.67 to 2.49 for the Fe/ZSM5-sc sample and from 2.61 to 2.44 for Fe/ZSM5-mc. The cause of the lower average valence for the non-irradiated spots is not obvious. On the one hand, one would expect the X-rays to have an *oxidative effect*: due to the ionising Auger decay of the iron sites, *i.e.* an absorption process at a Fe^{II} ($3d^6$) site creates a Fe^{II} ($2p^5 3d^7$) site that loses one or more electrons via Auger decay. Although the Auger decay is largely screened by other electrons, one may still expect an effective oxidation. On the other hand, one would expect the temperature at the irradiated spot to be higher than at the non-irradiated spot and as shown above, an increased temperature leads to a decrease of the average valence of iron in Fe/ZSM5. Apparently this temperature effect is more important, at least at room temperature. Exactly the opposite effect is observed for the situation with a temperature of $350\,^{\circ}C$. In those cases the non-irradiated part of the sample tends to have a higher average valence, in other words in those cases the ionising effect seems to dominate over the temperature effect. This is most likely due to the fact that at $350\,^{\circ}C$ the temperature effect of the X-rays will be negligible. From this discussion it is clear that upon irradiation the average valence state of iron will be slightly affected, which should be kept in mind for all the results shown.

Next, we would like to focus on the *overshoot* effects. In Fig. 2 it can be observed that during treatment in helium at room temperature, the average valence of the Fe/ZSM5-sc sample goes down to 2.64 after 30 min, before rising again to 2.67. One could imagine that this effect could be due to the surface sensitivity of soft X-ray absorption, *i.e.* to the fact that the surface of the system reduces more quickly than iron deeper inside the zeolite. When the system then reaches a steady state situation, the surface recovers the average valence of the system. This would be a valid interpretation, however, a similar re-oxidation was observed by our group also during hard X-ray absorption experiments.[19] A possible explanation is that the observed phenomenon is due to dynamical effects: depending on the conditions at hand, a steady state situation is often approached via an overshoot situation. The detailed mechanism by which this occurs is difficult to establish, but it will need to increase the iron average valence. Fig. 3 shows a much stronger overshoot-situation in that during heating to $350\,^{\circ}C$ the valence goes down to 2.16 for the Fe/ZSM5-sc sample (2.00 for Fe/ZSM5-mc) and after keeping the temperature constant at $350\,^{\circ}C$ the systems re-oxidise again to respectively 2.25 for Fe/ZSM5-sc and 2.10 for Fe/ZSM5-mc. In this case the situation is different in the sense that during heating a dynamical situation occurs, with temperature and average valence gradients throughout the sample. In such a dynamic situation, it is very likely that the surface reduces more quickly and maintains this reduced state until the temperature becomes constant, thereby allowing also the average valence gradients to establish a steady state situation. Note that this overshoot effect during heating is much larger than the case when the

temperature is not changed at room temperature, *i.e.* 0.09 and 0.03 respectively for the Fe/ZSM5-sc sample.

Although the redox behaviour of the severely and mildly calcined Fe/ZSM5 samples is similar, by taking a closer look to the path of the curves in the Figs. 2 through 4 some important differences can be observed. The Fe/ZSM5-sc has in all curves a slightly higher average valence than the Fe/ZSM5-mc samples. This observation is in agreement with the earlier findings[14] that there are larger iron-oxide nanoparticles at the outer surface of the zeolite crystals. These nanoparticles are likely to behave similarly to the goethite sample and to have a valence that is close to 3.0 under most conditions. In addition, the reduction in He is slower for the Fe/ZSM5-sc sample, while the oxidations of severely calcined samples are faster. Both the slower reduction and faster oxidation indicate the higher affinity for oxygen of severely calcined Fe/ZSM5. This suggests that the amount of flexible iron complexes in severely calcined samples is less than in the mildly calcined samples. One can also conclude, nevertheless, that even in a severely calcined Fe/ZSM5 sample the fraction of iron located in inactive species can not be high,. *i.e.* given that a bulk oxide such as goethite reaches an valence of 2.9, a value of 2.2 indicates that this amount must be below 20%. The difference in average valence between the first (2.02) and second (2.16) heating indicates that some of the iron could not be reduced from Fe^{III} to Fe^{II} in the second heating run. From this observation we conclude that after autoreduction in He at temperatures up to $350\,^{\circ}C$ followed by a re-oxidation with oxygen, some stable trivalent iron oxide species are formed that are hard to autoreduce.

In order to obtain a reference for the behaviour of the most aggregated iron species, we studied iron at the surface of a crystalline iron oxide particle. We showed that heating to $350\,^{\circ}C$ of pure FeO(OH) results in the dehydroxylation of the surface and the formation of Fe_2O_3. The calcination of over-exchanged Fe/ZSM5 results in the formation of larger iron oxide and/or oxo-hydroxides clusters at the surface. Goethite-like species may be present as intermediates in the formation of stable hematite crystalline structures. However, upon heating to higher temperatures, for instance the deNOx (HC-SCR) operation temperature of $350\,^{\circ}C$, small clusters of goethite will be converted into hematite particles. Although the position of particular features for oxygen–iron bonds in the oxygen K edge spectra are separated from the main edge we were not able to monitor directly the formation of iron oxides as goethite and hematite in calcined Fe/ZSM5. The abundance of the Fe–O bonds and the changes within them were too small compared to the dominating contribution of the oxygen of the zeolite matrix to the overall intensity.

Implications for the structure and bonding of the active site in Fe/ZSM5

The precise structure of the iron in 'over-exchanged' Fe/ZSM5 is still under debate. A possible structure is that the hydroxo-bridged Fe atoms are bound via one (or two) oxo-ions to the ZSM5 framework, where they balance the charge of one (or two) aluminium atom(s).[14,19] Upon calcination (using the temperature ramp of $5\,^{\circ}C$ min^{-1}) agglomeration of the binuclear Fe-complexes towards inactive oxide/hydroxide clusters can be significant. Part of the iron can be present in the form of iron oxide clusters instead of binuclear clusters. We showed, as discussed below, that also upon performing reduction/oxidation cycles at $350\,^{\circ}C$ additional clustering of binuclear iron complexes to larger agglomerates is likely.

The iron in the oxidised iron oxide clusters is octahedral Fe^{III} and also the binuclear complexes contain octahedral Fe^{III}, bound with one (or two) oxygen atom(s) to the zeolite framework, via two oxo(hydroxo) bridges to each other and by three (or two) hydroxide groups and/or water molecules

to make up the five-fold or six-fold coordinated (distorted) octahedral sites.[19] The charge transfer multiplet analysis of the iron $L_{2,3}$ edge (not shown) indicates that the crystal field splitting of 1.0 eV is significantly smaller than for Fe_2O_3, implying on average a rather weak iron–oxygen bond. The chemical origin behind this weak bonding is that the structure of the binuclear sites is for a significant part determined by the zeolite structure and the positions of the aluminium atoms therein. In our opinion, the aluminium sites in ZSM5 can better be understood as randomly distributed than as positioned at special sites,[31] though some site preference might occur. The consequence is that the binuclear iron clusters have to adapt to the different Al locations. This adaptation will lead without doubt to constraints in the chemical bonding and to coordinatively unsaturated situations, completely different from binary oxides where the structure is essentially determined, and optimised for bonding, by the iron atoms.

We return now to the generation of $Fe^{IV}=O$ (*i.e.* α-oxygen) states from coordinatively unsaturated Fe^{II} sites. Fe^{II} sites have essentially a $S = 2$ $3d^6$ ground state and when bound to four neighbours in a distorted tetrahedron, they have an extra spin-down e_g electron in addition to their five spin-up electrons. This spin-down electron is easily accessible to bonding. In contrast Fe^{III} sites have a $S = 5/2$ $3d^5$ ground state within a distorted octahedron and its five spin-up electrons are strongly bound together. One could imagine that the oxygen atom of N_2O tends to bind to such an Fe^{II} site. An isolated Fe^{II} site will not be able to loosen the oxygen from its N_2 counterpart, but the other Fe^{II} site originating from the binuclear iron-cluster can be imagined to bind to the N_2 π-states. The N_2O of the intermediate then breaks its N–O bond neutrally, thereby generating N_2 (bound to an Fe site initially) and O bonded to Fe^{II}. The electronic structure of the Fe^{II} state can be written as $3d^6 + 3d^7\mathbf{L}$, where $\mathbf{L}$ denotes a hole on an oxygen neighbour. The extra oxygen has two holes and can be written as $\mathbf{LL'}$. These oxygen holes are strongly bonding to iron, thereby creating strong π-bonding, hence short bonds. Effectively, the Fe^{II}–O bond formed as such is able to reorganise to a $3d^4 + 3d^5\mathbf{L} + 3d^6\mathbf{LL'}$ configuration, where both the σ and π-bonding channels are strong, *i.e.* there will be large contributions from $3d^5\mathbf{L}$ and $3d^6\mathbf{LL}$ into the formally Fe^{IV} $3d^4$ ground state, possibly leaving its actual number of 3d-electrons close to that of the original Fe^{II} site. During this process the $S = 2$ spin state of the Fe^{II} site is not changed. The created $Fe^{IV}=O$ state contains the α-oxygen that can act in the oxidation of hydrocarbons. An important difference between iron non-heme enzymes and Fe/ZSM5 is that the former use O_2 as their α-oxygen source, while Fe/ZSM5 cannot be activated by O_2, but needs N_2O. A reason could be that O_2 cannot be stabilised on the binuclear iron centres, while the N_2-part of N_2O can use the second iron atom for stabilisation. If the impossibility of using O_2 as a source is further confirmed, this points to a major difference in the oxidation behaviour of Fe/ZSM5 compared with the iron non-heme enzymes.

One could imagine that NO can act similarly to N_2O in the sense that the NO bond gets broken, ending with the $Fe^{IV}=O$ state in combination with a Fe–N site. In the case of NO this process needs to be assisted by an activity of the hydrocarbon, for example by stabilising the Fe–N site. If such a phenomenon should occur, it would suggest that the average valence of iron could reach a value larger than 3.0, which would imply that the calibration point for the iron valence would be different. The fact that $NO + O_2$ brings the iron to a valence of 3.0, whereas only O_2 reaches a maximum valence of 2.9, could then also suggest that $NO + O_2$ brings the system to an average valence slightly larger than 3.0.

In our previous paper, using soft X-ray absorption spectroscopy at the oxygen K edge (probing separately the gas-phase and the surface signal), we showed for Fe/ZSM5-sc that, at 2 mbar pressure, molecular oxygen and water are released dur-

ing autoreduction in helium, at room temperature already and during heating to 350 °C.[20] Similar qualitative results are obtained for Fe/ZSM5-mc. This observation suggests that the bridging oxygen atoms might have been lost leading to isolated Fe^{II} sites that are spatially close together. As we show in Fig. 4 a re-oxidation can readily restore the bridging oxygen atoms between these Fe^{II} sites. Re-oxidation in O_2 (5% in He) at 350 °C creates two (distorted) octahedral Fe^{III} sites within a matter of minutes.

Comparison with Fe K edge XAS

The application of *in-situ* soft X-ray absorption spectroscopy is relatively new in the field of catalysis, whereas the hard XAS technique is more often used to determine the valence. The energy position of the (iron) K edge varies with the valence, at least if the structure and the nature of the neighbours do not vary too much.[32] The procedure to determine the edge position is not uniformly defined and for some systems it is difficult to define the exact edge position. With the use of appropriate references, the edge position can be used to determine the average valence, but because of the complications mentioned above, the quantitative accuracy in valence determination that can be achieved is not good. In addition, the pre-edge region gives valuable information for the determination of the average valence and site symmetry of the iron sites. Wilke *et al.*[33] and Westre *et al.*[34] have proved that the energy position of the centroid and its integrated intensity are good parameters to characterize the pre-edge feature, provided that the pre-edge peak is carefully isolated. The subtraction of the main edge contribution is essential. They showed that the centre-of-gravity of the pre-edge scales with the valence of iron and that the integrated intensity of the pre-edge is related to the site symmetry of the iron, where octahedral sites have the lowest intensity and the tetrahedral sites the highest. Also our group[14,19] and many other groups have employed Fe K edge XAS to study Fe/ZSM5 and related systems.[15–18,35–37] In these studies the analysis of the pre-edges is, in most cases, only qualitative and untreated pre-edge peak maxima are used.

The application of soft X-ray absorption spectroscopy for catalysis research benefits from the much higher resolution of soft X-rays together with the relatively large, systematic variation of the spectral features in the – well defined – Fe L_3 edge with the iron oxidation state and the detailed simulation of their spectral shape. It is evident that these factors enable a considerably higher precision in the determination of the average valence of iron, for Fe/ZSM5 and other (catalytic) systems.

Concluding remarks

We have shown that the Fe/ZSM5 system is an extremely flexible system, with regard to the valence of iron under various conditions. We find that, at a total pressure of 2 mbar, mildly calcined Fe/ZSM5 has an average valence of 2.9 in oxygen (5% in helium) – both at room temperature and at 350 °C, of 2.5 under helium at room temperature, and of 2.1 under helium at 350 °C. These values are only slightly dependent on the sample measurement history. Severely calcined Fe/ZSM5 shows values that are approximately 0.03 to 0.05 higher in the (partly) oxidised states, and 0.10 to 0.15 higher in the reduced states. This higher average valence is in agreement with previous observations that part of the iron in this case is positioned in small iron-oxide nanoparticles at the outer surface of the zeolite crystals. Such iron-oxide nanoparticles, which are more difficult to reduce than the iron clusters inside the Fe/ZSM5, must nevertheless constitute only a minor part

of the total Fe amount, also upon application of a severe calcination procedure.

Changes in the iron valence are accompanied by overshoot effects. During heating in helium, the valence typically reaches a minimum value before slightly rising again (re-oxidation) while keeping the temperature constant. A similar, though smaller, effect occurs during autoreduction in helium at a fixed temperature of 25 °C. These overshoot effects are ascribed to local surface–bulk re-equilibration phenomena (kinetic effects) occurring between the iron complexes and the zeolite matrix. Long exposition to soft X-rays can locally affect the average Fe-valence by amounts up to 0.10. At room temperature this is essentially due to the heating effects of the X-rays.

The conclusions of this study are in agreement with the model of 'over-exchanged' Fe/ZSM5 as outlined in our previous contributions.[14,19] Iron in the oxidised Fe-complexes is present in a five-fold or six-fold coordinated (distorted) octahedral configuration. Based also on the spectral simulations that were discussed in detail in a previous paper,[20] we find in the case of the Fe-complexes a ligand field value of only 1.0 eV, i.e. much less than bulk iron oxides. This indicates (on average) a weak bonding between iron and oxygen and is coherent with the low affinity of the Fe-complexes for oxygen. In addition, the spectral simulations imply that the completely reduced Fe/ZSM5 has lost the bridging oxygen atoms and some of the coordinating water molecules/hydroxide groups and contains almost exclusively Fe in tetrahedral Fe^{II} sites.

Acknowledgements

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