An in Situ X-ray Absorption Spectroscopy Study of N$_2$O Decomposition over Fe-ZSM-5 Prepared by Chemical Vapor Deposition of FeCl$_3$

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The pretreatment conditions (temperature, medium) have a strong influence on the N$_2$O decomposition activity of Fe–ZSM-5 catalysts (J. Jia et al., *J. Catal.* **2002**, *210*, 453). We used X-ray absorption spectroscopy to follow in situ the structural changes of the iron oxide clusters in an Fe–ZSM-5 sample, which was prepared by chemical vapor deposition of FeCl$_3$, during different pretreatments and during N$_2$O decomposition. Reductive pretreatment in H$_2$ always decreased the Fe–Fe coordination number; i.e., it broke the iron oxide clusters into smaller units by removing bridging oxygen atoms. When reduction was carried out at low temperatures (673 K), this process was reversed during reoxidation by N$_2$O. When reduction was carried out at high temperatures (873 K), the smaller fragments were stabilized by forming strong bonds to the zeolite matrix and did not agglomerate during reoxidation. An analysis of the Fe–O coordination numbers showed that temperatures above 673 K are required to dehydroxylate the iron oxide clusters. Reduction at 673 K did not significantly change the Fe–O coordination number because the oxygen remained adsorbed on the iron cluster in the form of H$_2$O (or as a hydroxy group). This is an important result because the degree of (de)hydroxylation of the iron oxide clusters has implications on their catalytic activity. During N$_2$O decomposition the catalyst was in a fully oxidized state. The EXAFS spectra of the samples before and after reaction with N$_2$O were identical, indicating that only a very small concentration of sites, which is not detectable by EXAFS, is responsible for the N$_2$O decomposition activity.

Introduction

Fe–ZSM-5 materials are efficient and stable catalysts for the decomposition of N$_2$O. Because their activity is not strongly affected by the presence of other components such as H$_2$O, SO$_2$, NO, and O$_2$, they can be used for N$_2$O abatement in industrial nitric acid or adipic acid plants, which produce very high N$_2$O emissions.[1] Several methods are suited for preparing Fe–ZSM-5 catalysts, like addition of iron during the hydrothermal synthesis of ZSM-5, ion exchange in the liquid phase,[2,3] solid-state ion exchange,[4] or sublimation[5] (chemical vapor deposition, CVD) of FeCl$_3$. With the latter method an Fe/Al ratio close to 1.0 is obtained; i.e., the iron loading is high. The structure of these catalysts has been intensively investigated. Originally, it was proposed that they contain mainly binuclear iron clusters, whose structure is similar to that of the iron core in the enzyme in methane mono oxygenase.[6] More recent evidence indicates, however, that the iron clusters in these materials are larger than binuclear. Oligomeric, structurally heterogeneous iron clusters seem to be the dominating species.[7,8]

The reactivity is strongly influenced by the size of the iron oxide clusters. A comparative study of different iron zeolites showed that isolated iron atoms, obtained by controlled aqueous ion exchange, have the highest turnover frequency in N$_2$O decomposition.[9] Small iron oxide clusters also contribute to the activity, but have a lower turnover frequency. This can be understood from the mechanism of the reaction. N$_2$O deposits its oxygen atom in a vacant site of the iron cluster. The deposited oxygen atom migrates over the iron cluster by exchanging with other oxygen atoms and finally recombines with another oxygen

atom to O$_2$.[10] This process has an important contribution to the overall activity in catalysts prepared by CVD of FeCl$_3$, but its turnover frequency is rather low because many iron atoms are involved.

The structure of the iron sites does not depend only on the preparation method. Postsynthesis treatments at high temperature can dramatically change the reactivity of the iron catalyst.[11–15] We studied the effect of different pretreatment conditions on the reactivity of Fe–ZSM-5 CVD and observed the following trends:[16] (i) Reductive pretreatment increases the steady-state activity of the catalyst. The effect increases when the reduction is carried out at high temperatures, i.e., at 873 K vs 673 K. (ii) Pretreatment in inert gas at high temperatures leads to a very high initial N$_2$O decomposition activity. Because the high initial rate slowly decays to steady state, the effect is called transient reaction. Exposure to water vapor before the reaction with N$_2$O annihilated the transient activity, suggesting that the transient is related to strongly dehydroxylated iron sites. The results show that treatment with H$_2$ and/or He at high temperatures strongly affects the reactivity of the iron sites. The in situ X-ray absorption study described here was performed to correlate these changes in reactivity with changes in the coordination of the iron sites. Moreover, in situ X-ray Absorption Spectroscopy (XAS) allowed us to follow the oxidation state of the iron clusters under reaction conditions. Determination of the oxidation state of the iron clusters is an important issue because it was proposed that the N$_2$O decomposition activity of iron zeolites is related to their autoreduction behavior.[17] Step response experiments indicated that autoreduction at 673 K is very small and that the catalysts operate in a fully oxidized state. That contrasts with EXAFS studies of others who observed

TABLE 1: Overview over the in Situ XAS Experiments. A Fresh Catalyst Was Used for Each Series (except nr. 4)

experiment	temp (K)	treatment[a]	duration	comment
1	300−873 (10 K/min)	H_2		temperature programmed reduction
2	673	H_2	1 h	
	673	He	10 min	
	673	N_2O	2 h	step from He to N_2O
3	873	H_2	1 h	
	873	He	30 min	
	673	N_2O	2 h	
4[b]	673−798 (5 K/min)	N_2O		temperature programmed N_2O decomposition
5	873	H_2	1 h	
	873	He	30 min	
	573	H_2O	1 h	step from He to H_2O
	573	He	30 min	
	673	N_2O	2 h	step from He to N_2O

[a] Reactant gases were diluted in He: 3% H_2, 0.5% N_2O, 1% H_2O.
[b] Continuation of experiment nr. 3.

extensive autoreduction of Fe−ZSM-5 CVD catalysts at temperatures lower than 673 K.[18,19] The in situ XAS data shown in this work prove that strong autoreduction of the iron does not take place if contamination of the sample and of the EXAFS cell are carefully avoided.

Experimental Section

Fe−ZSM-5 was prepared by sublimation (CVD) of $FeCl_3$ onto H−ZSM-5 (PZ 2−40, Zeochem, Si/Al = 25),[20] as described in detail before.[17] After the sublimation the sample was thoroughly washed with water, dried, and calcined in flowing O_2 at 773 K, using a very low heating ramp (1 K/min). The iron loading of the sample was 4.0 wt %, corresponding to Fe/Al = 1.1. 25 mg of sample were pressed into a self-supporting pellet inside a stainless steel sample holder. Following the design of Ressler et al.,[21] the sample holder was put into a stainless steel cell equipped with Kapton windows. The cross-section of the cell was rectangular, its volume being ∼4 cm³. The gas mixture entered the cell on one end and flowed through the catalyst pellet, which filled the whole cross-section. The reactor was heated with an external coil placed at the position of the sample. The windows were cooled with water. Test experiments showed that when switching from one gas mixture to another it took 70 s to reach 95% of the final concentration at a flow of 15 mL_{NTP}/min. This compares favorably with the response of the conventional plug flow reactor used in our laboratory.

Gases were fed to the EXAFS cell via a gas mixing station, which allowed fast switching from one gas mixture to another. Water was fed to the gas stream via a saturator at 283 K, corresponding to a vapor pressure of 1.2 kPa. The effluent of the EXAFS cell was analyzed by a quadrupole mass spectrometer (Balzers Omnistar). Masses m/e = 2 (H_2), 4 (He), 18 (H_2O), 28 (N_2 and N_2O), 32 (O_2), and 44 (N_2O) were monitored. Because all gas mixtures were highly diluted in He, the signal of He (m/e = 4) could be used as a reference for calculating the concentrations of the other components.

In all experiments, the Fe−ZSM-5 catalyst was first treated in 3% O_2 in He at 773 K, to remove organic contaminants. After the initial treatment in O_2 the reaction of the catalyst with H_2, H_2O, or N_2O was followed in situ by XANES or (Q)EXAFS. Details can be found in Table 1. Each treatment was followed until no changes in the XAS spectra and/or the MS signals could be observed any more, typically between 30 min and 2 h.

Most EXAFS spectra were recorded at the X1 station at Hasylab, Hamburg, which uses a Si(111) double monochromator. Higher order reflections were rejected by detuning the monochromator to 70% of its maximum reflectivity. The Fe−K edge was scanned from 6800 to 8100 eV. A step size of 0.25 eV was used in the edge region and gradually increased to obtain constant steps of Δk = 0.05 Å⁻¹ at high energies. QEXAFS spectra were recorded with a constant step size of 0.5 eV, from 7050 to 8100 eV. An iron foil was used as reference for energy calibration. One of the experiments described hereafter (no. 2 in Table 1) was measured at the Swiss-Norwegian Beamline, ESRF Grenoble. In these experiments a single Si(111) monochromator was used in combination with a Cr-mirror to reject harmonics and other high-order diffractions. The spectra measured at the two beamlines were fully compatible with each other.

EXAFS analysis was carried out using the IFEFFIT software package.[22] The background function was calculated from ∼20 to 1080 eV above the absorption edge. Fitting was performed in R space, with a Hanning window (Δk = 0.4 Å⁻¹) applied before the forward Fourier transformation. The χ data between the first node (k = 2.6 to 3.0 Å⁻¹) and k = 12 to 15 Å⁻¹ (depending on the quality of the data) was transformed. The fitting interval in R space was 1.0−3.0 Å. A Hanning window with Δr = 0.4 Å was applied to cut off low and high R contributions. Fitting was usually performed using the k^2-weighted χ data. The best fits in k^2 usually also led to good representations of the experimental spectra in k^1 and k^3 weighting. Occasionally, the spectra were fit simultaneously in all three k weightings. The parameters obtained in this multi-dimensional fit never deviated strongly from those in k^2 weighting.

Fe_2O_3 was chosen as a reference compound. The reference paths were calculated using the FEFF8.1 algorithm.[23] The Fe−O backscattering path at 1.946 Å and the Fe−Fe backscattering path at 2.971 Å were selected to fit the spectra of Fe−ZSM-5. To calibrate S_0^2, the experimental spectrum of Fe_2O_3 was fit with all theoretical single-scattering paths below 4 Å, using the same ΔE_0, σ^2, and S_0^2 for all shells. After optimization of these three parameters, a good fit of the experimental spectrum of Fe_2O_3 was obtained in the interval 1−3 Å. At larger distances the fit deviated from the experiment because multiple scattering paths had not been taken into account. The three fit parameters converged to the values ΔE_0 = −4.3 eV, σ^2 = 0.0039, and S_0^2 = 0.75. S_0^2 was fixed to this value in all subsequent fits.

Results

Treatment in O_2 and H_2. Figure 1 shows the QEXAFS spectra of Fe−ZSM-5 during the first heating in O_2 from room temperature to 773 K. Two effects were observed. (i) The intensity at the absorption maximum (the whiteline) decreased and the absorption edge became less steep. (ii) The intensity of the preedge peak at 7113 eV increased. Similar differences in the XANES spectra have been observed before for hydrated and dehydrated Fe−ZSM-5 samples.[24] The effects were therefore attributed to the desorption of H_2O from the iron cluster, associated with the change from an octahedral-like to a distorted tetrahedral coordination.

The QEXAFS spectrum of Fe−ZSM-5 in O_2 atmosphere at 773 K could be fitted with one Fe−O shell with an average coordination number of 3.4 at a distance of 1.91 Å and one Fe−Fe shell with an average coordination number of 1.4 at a distance of 2.97 Å (Table 2). When two distinct Fe−O backscattering shells were used to fit the data, they converged
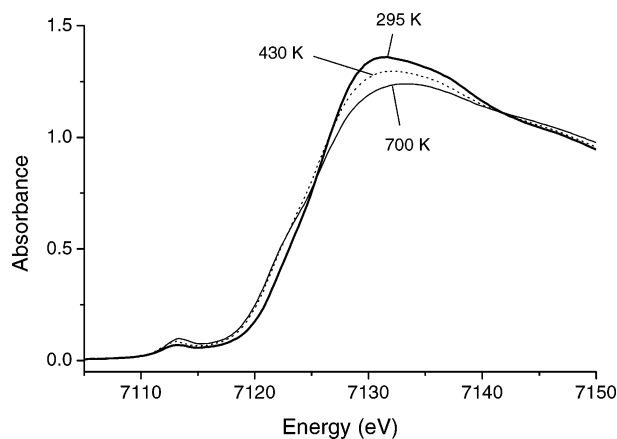
Figure 1. QEXAFS spectra during heating of Fe−ZSM-5 from room temperature to 773 K in a flow of 3% O_2 in He, at 295 K (bold), 430 K (dotted), 700 K (solid).

TABLE 2: Fit Parameters of the (Q)EXAFS Spectra of Fe-ZSM-5[a]

shell	R (Å)	CN	σ^2 (Å^2)	ΔE_0 (eV)
		O_2 773 K[b]		
Fe−O	1.91	3.4 ± 0.5	0.010	−8.0
Fe−Fe	2.97	1.4 ± 1.2	0.014	
		H_2 673 K		
Fe−O	1.94	1.5 ± 0.4	0.005	−6.4
Fe−O	2.07	1.5 ± 0.4	0.005	
Fe−Fe	3.01	1.0 ± 0.6	0.012	
		H_2 873 K		
Fe−O	1.90	1.0 ± 0.2	0.002	−8.0
Fe−O	2.04	1.1 ± 0.2	0.002	
Fe−Fe	3.00	0.9 ± 0.8	0.015	
		H_2 673 K, N_2O 673 K		
Fe−O	1.83	1.6 ± 0.2	0.003	−6.4
Fe−O	1.98	1.7 ± 0.2	0.003	
Fe−Fe	2.98	1.7 ± 1.3	0.017	
		H_2 873K, He 873 K, N_2O 673 K		
Fe−O	1.82	1.2 ± 0.2	0.002	−7.1
Fe−O	1.98	1.3 ± 0.2	0.002	
Fe−Fe	3.03	0.9 ± 0.7	0.012	
		H_2 873 K, H_2O 573 K		
Fe−O	2.01	3.1 ± 0.3	0.009	−7.2
Fe−Fe	3.01	1.0 ± 0.6	0.012	
		H_2 873 K, H_2O 573 K, N_2O 673 K		
Fe−O	1.82	1.3 ± 0.2	0.002	−6.9
Fe−O	1.98	1.4 ± 0.2	0.002	
Fe−Fe	2.98	1.0 ± 0.8	0.012	

[a] CN = coordination number, R = distance, σ^2 = Debye−Waller factor, ΔE_0 = shift of E_0. [b] Values averaged from the fits of two samples.

to coordination numbers of 1.3 at a distance of 1.83 Å and 1.5 at a distance of 1.98 Å. The quality of the fit did not significantly improve by introducing the second oxygen shell. The total oxygen coordination number in the two-shell fit was 2.8, i.e., lower than in the one-shell fit. This phenomenon was generally observed.

After 1 h at 773 K the sample was cooled to room temperature and the EXAFS was recorded. The fit parameters of the spectrum (Table 3) show that both the oxygen and the iron coordination number increased upon cooling to room temperature. The error of the Fe−Fe coordination number was large, due to a strong correlation with the Debye−Waller factor.

After completing the EXAFS scans at room temperature, a temperature programmed reduction (TPR) was started and followed by QEXAFS (Figure 2). Between room temperature

TABLE 3: Fit Parameters of the EXAFS Spectra of Fe-ZSM-5 Measured at Room Temperature[a]

shell	R (Å)	CN	σ^2 (Å^2)	ΔE_0 (eV)
		After Treatment in O_2 at 773 K		
Fe−O	1.86	1.7 ± 0.2	0.0025	−6.4
Fe−O	2.00	2.1 ± 0.3	0.0025	
Fe−Fe	2.99	2.2 ± 0.9	0.013	
		After Treatment in H_2 at 873 K		
Fe−O	1.99	1.6 ± 0.5	0.0045	−6.7
Fe−O	2.07	1.8 ± 0.6	0.0045	
Fe−Fe	3.03	1.6 ± 0.8	0.013	
		After Treatment in H_2 at 673 K, and N_2O at 673 K		
Fe−O	1.86	1.7 ± 0.2	0.003	−6.1
Fe−O	2.00	2.3 ± 0.3	0.003	
Fe−Fe	3.00	2.4 ± 1.2	0.015	

[a] CN = coordination number, R = distance, σ^2 = Debye−Waller factor, ΔE_0 = shift of E_0.
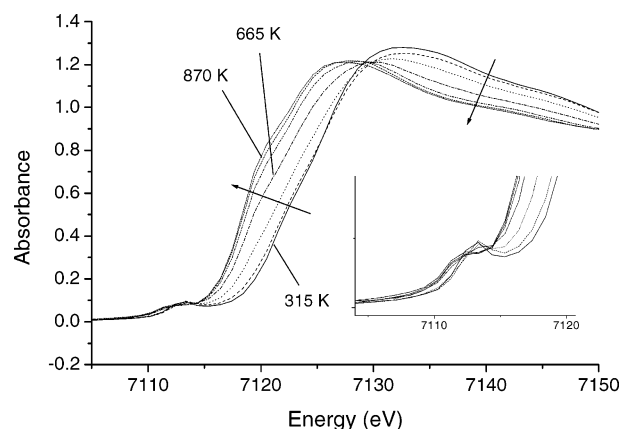
Figure 2. QEXAFS spectra of Fe−ZSM-5 during temperature programmed reduction with 3% H_2 in He. Spectra were taken, in the direction of the arrow, at 315 K (solid), 540 K (dashed), 590 K (dotted), 665 K (dot−dash), 720 K (dot-dot dash), 775 K (dashed), and 870 K (dotted). The inset shows an enlargement of the preedge peak.

and 540 K (dashed curve) the intensity of the whiteline of Fe−ZSM-5 decreased slightly, but the position of the edge did not change. The decrease of the whiteline is ascribed to the removal of H_2O, which had adsorbed on the iron sites at room temperature. Above 540 K the Fe K-edge moved to lower energies, indicating that reduction of the iron oxide clusters took place. Reduction was completed at 870 K (dotted curve). The QEXAFS spectra had a reasonable signal-to-noise ratio up to $k = 11-12$ Å^{-1} and could be fitted with one oxygen and one iron backscattering shell. The evolution of the coordination numbers and distances with temperature is shown in Figure 3b,c. The coordination numbers of the oxygen and iron shell decreased gradually with temperature. When reduction of the iron sites set in at ~550 K, the oxygen coordination number did not change significantly. Reduction did not lead to a removal of oxygen from the coordination shell of the iron atom, but the oxygen remained adsorbed to the iron cluster in the form of H_2O (or as a hydroxy group). The average Fe−O and Fe−Fe distances increased significantly above 550 K, i.e., as soon as reduction set in. To obtain a quantitative measure for the degree of reduction, a least-squares fit of the XANES region was performed, using the XANES spectra of a fully reduced and of a fully oxidized Fe−ZSM-5 at 673 K as references. Each measured spectrum was approximated by a linear combination x*ref(Fe^{II}) + y*ref(Fe^{III}), with x and y being nonnegative. The coefficients obtained in these fits are shown in Figure 3a. The sum of x and y was always between 1.00 and 1.05; i.e., the fits
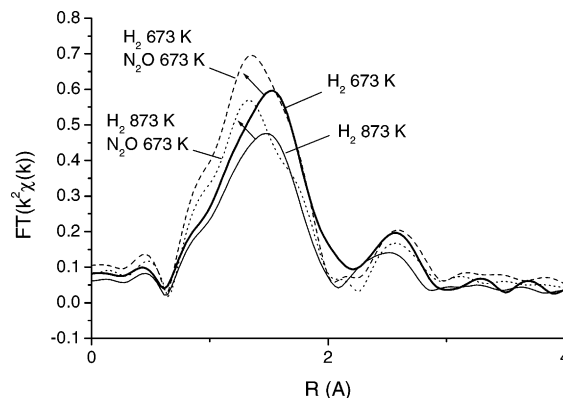
In situ XAS of Fe−ZSM-5/N₂O

J. Phys. Chem. B, Vol. 108, No. 36, 2004 **13749**
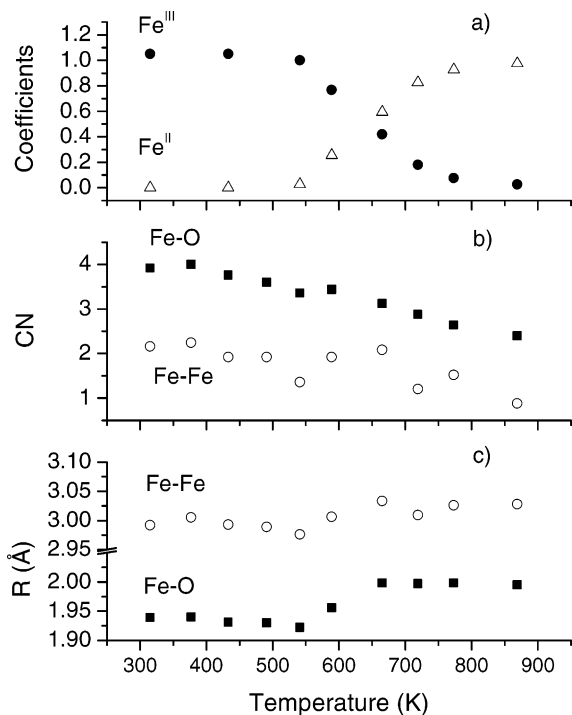
Figure 3. TPR of Fe−ZSM-5. (a) Fraction of Fe^{III} (full circle) and Fe^{II} (open triangle) in the sample obtained by least-squares fitting. (b) Coordination numbers and (c) distances as a function of temperature. Fe−O: full squares. Fe−Fe: open circles.
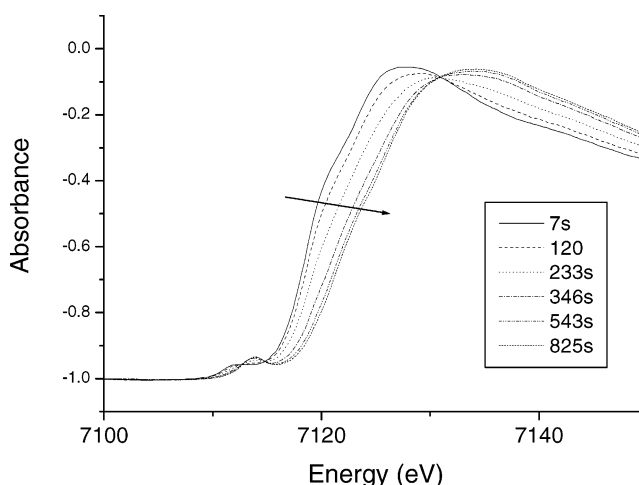

Figure 4. QEXAFS or EXAFS spectra of Fe−ZSM-5 (a) in H_2, at 673 K (bold) and (b) after subsequent reoxidation by N_2O, at 673 K (dash); (c) after reduction in H_2 at 873 K, measured at 873 K in He (solid) and (d) after subsequent reoxidation by N_2O, at 673 K (dotted). Shown is the magnitude of the k^2-weighted Fourier transform of $\chi(k)$ in the range ∼2.8−12.5 Å.


Figure 5. XANES spectra of Fe−ZSM-5 measured during step from He to N_2O at 673 K, after pretreatment in H_2 at 873 K.

were fairly self-consistent. Comparison of the graphs in Figure 3a,c shows that the increase of oxygen and iron distances coincides with the reduction of the iron clusters. The reduction was also reflected in the preedge peak, which decreased in intensity and shifted to lower energies (see inset of Figure 2).[15,18,25,26]

The Debye−Waller factor of the oxygen shell showed a surprising trend. Starting at a value of 0.010 Å² at low temperatures, it increased to 0.013 Å² when the reduction from Fe^{III} to Fe^{II} took place and then decreased to 0.010 Å² again. The expected increase with temperature was not observed. Because our fits did not resolve the oxygen shell into single components, the Debye−Waller factor mainly originates from structural and not from thermal disorder. Under this premise, the evolution of the Debye−Waller factor with temperature can be understood as follows: because not all Fe−O distances in the iron oxide clusters are equal (vide infra) the catalyst has a high structural Debye−Waller factor. At low temperature, coordinating H_2O molecules, which are bound at a slightly larger distance, further increase the spread of the Fe−O distances and, thus, σ^2. When the temperature increased, H_2O desorbed and the structural Debye−Waller factor decreased whereas the thermal Debye−Waller factor increased. Obviously, the two effects nearly compensated each other. The highest Debye−Waller factors were observed during the transition from Fe^{III} to Fe^{II}, when a mix of short and long Fe−O distances was present in the catalyst. The Debye−Waller factor of the Fe−Fe shell remained constant at 0.015 Å² until ∼600 K and then increased to 0.020 Å².

After the TPR, the sample was kept for 1 h at 873 K in H_2/He and then cooled to room temperature to record the EXAFS. The fit parameters of the spectrum are given in Table 3. The total oxygen coordination number decreased slightly from 3.8 to 3.4, compared to the spectrum after treatment in O_2. The iron coordination number decreased from 2.2 to 1.6.

Reduction of Fe−ZSM-5 at Different Temperatures and Reoxidation with N_2O. It was mentioned in the Introduction that reductive pretreatment at high temperatures increased the N_2O decomposition activity of the Fe−ZSM-5 catalyst. The largest effect was observed after reduction at 873 K.[16] Figure 4 compares the (Q)EXAFS spectra of Fe−ZSM-5 in H_2 at 673 K (experiment 2 in Table 1) and 873 K (experiment 3 in Table 1), respectively. In both cases, iron was fully reduced to Fe^{II}, as indicated by the position of the Fe K-edge. The intensity of the oxygen backscattering shell was lower at 873 K. Fitting confirmed that the number of oxygen neighbors indeed decreased. The spectrum at 873 K could be fitted with two Fe−O backscattering shells having a total coordination number of 2.1 (Table 2). For the spectrum at 673 K, a coordination number of 3.0 was obtained (or 3.2 if only one oxygen shell was used for fitting). Moreover, the Fe−O distances were shorter at 873 K. The cluster was more contracted. The Fe−Fe coordination number was approximately 1.0 at both temperatures, i.e., lower than in the oxidized catalyst.

Reaction with N_2O at 673 K led to a quick reoxidation of both catalysts from Fe^{II} to Fe^{III} (Figure 5). The MS analysis of the reactor effluent showed that the production of N_2 due the reoxidation reaction $2Fe^{II} + N_2O \rightarrow 2Fe^{III} + N_2$ ceased after about 20 min (Figure 6 and 7). In accordance, the XANES spectra indicated that conversion of Fe^{II} to Fe^{III} was completed after ∼15 min. It should be noted that the amount of N_2
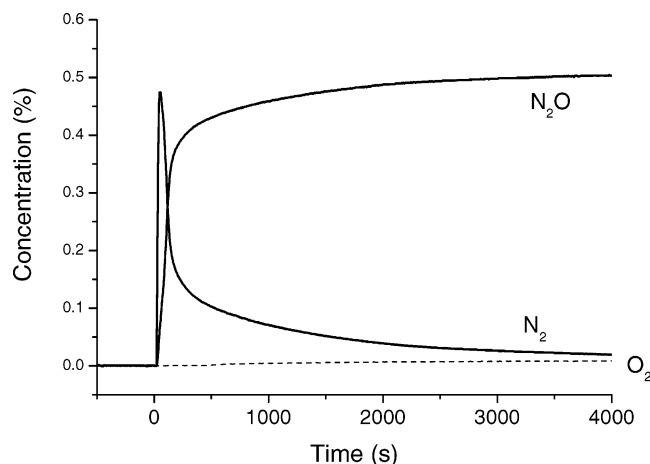
Figure 6. Response of Fe−ZSM-5 to a step from 0 to 5000 ppm N_2O, after pretreatment in H_2 at 673 K. Concentrations of N_2O, N_2, and O_2 determined by MS.
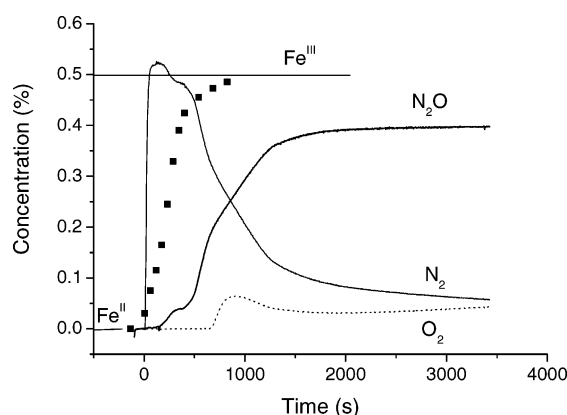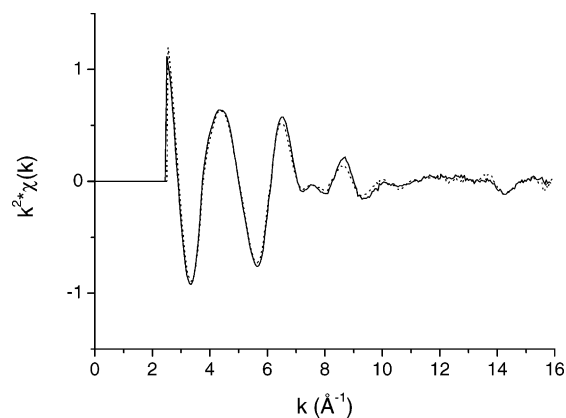

Figure 7. Response of Fe−ZSM-5 to a step from 0 to 5000 ppm N_2O, after pretreatment in H_2 at 873 K. Concentrations of N_2O, N_2, and O_2 determined by MS. Average oxidation state (squares) of the iron species determined by least-squares fitting.

Figure 8. k^2-weighted EXAFS of Fe−ZSM-5 after treatment in O_2 at 773 K (solid) and after subsequent reduction and reoxidation in N_2O at 673 K (dotted), both measured at room temperature.

Figure 9. XANES spectra of Fe−ZSM-5, which was reduced at 873 K in H_2, measured at 573 K before (solid) and after (dashed) exposure to 1.2 kPa H_2O.
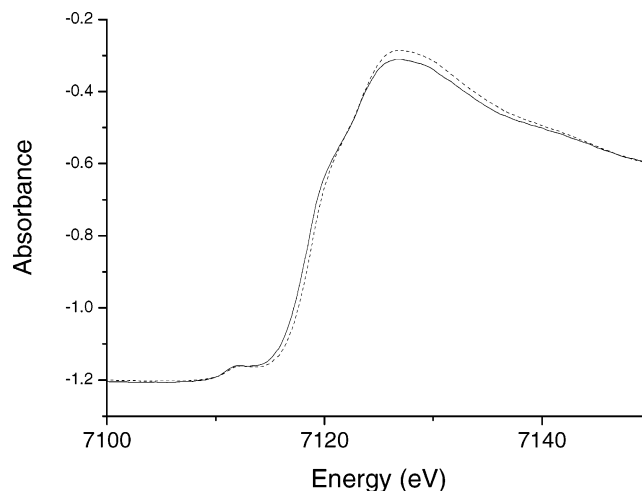
produced during the reoxidation of the catalyst after reduction at 873 K was 4 times higher than the stoichiometrically expected amount. A blank experiment showed that the H_2 treatment at 873 K also reduced the walls of the EXAFS cell. When the feed was switched to N_2O, the cell produced a peak of N_2. After correcting for this blank response, the peak of N_2 in Figure 7 corresponded roughly to the stoichiometrically expected amount (N_2/Fe = 0.5).

Once all the iron sites of the catalyst were converted to Fe^{III}, the activity stabilized at a constant N_2O conversion of ∼4% after reduction at 673 K and ∼12% after reduction at 873 K. The spectra measured during steady-state N_2O decomposition at 673 K are shown in Figure 4. The oxygen coordination number of both catalysts increased during the reoxidation but was lower for the Fe−ZSM-5 reduced at 873 K (Table 2). Also the Fe−Fe coordination number of this catalyst remained low (∼0.9), whereas it increased to 1.7 for the catalyst reduced at 673 K. The fitting parameters obtained for this catalyst were similar to those of the spectrum measured in O_2 at 773 K. To make sure that subtle differences between the parent Fe−ZSM-5 and the N_2O-treated material (reduced at 673 K) were not obscured by the thermal disorder, we also compared the spectra measured after cooling to room temperature (Figure 8). The $\chi(k)$ functions of both samples were almost identical and could be fitted with similar parameters.

Effect of (De)Hydroxylation. When Fe−ZSM-5 was pretreated in inert gas at temperatures above 773 K and then reacted

with N_2O at 673 K, it exhibited very high initial N_2O decomposition activity.[16] The very high initial activity slowly decayed to steady state and was therefore called transient reaction. In our EXAFS cell we could observe transient activity as a shoulder in the N_2 curve between 600 and 1200 s and a peak in the O_2 curve in the same time interval, when the catalyst was pretreated in H_2 and He at 873 K (Figure 7). The extent and rate of the transient reaction were much weaker than in the conventional plug flow reactor, probably due to the different flow pattern in the EXAFS cell. In the conventional plug flow reactor, we had observed that exposure to water vapor annihilated the transient activity, suggesting that the transient was related to the dehydroxylation of the iron sites at high temperatures. To confirm that hypothesis, the effect of exposure to water was studied by in situ XAS (experiment 5 in Table 1): Figure 9 shows the effect of exposure to H_2O (at 573 K) on the near-edge structure of Fe−ZSM-5 (reduced at 873 K). Adsorption of H_2O increased the intensity at the peak of the absorption edge. The edge became steeper but did not change its position. The reverse effect had been observed when H_2O was desorbed from the iron sites during heating from room temperature to 773 K (Figure 1). Fitting of the QEXAFS spectra in water vapor at 573 K showed that the adsorption of H_2O increased the Fe−O coordination number from 2.1 to 3.1 (see Table 2 and Figure 10). Also the average Fe−O distance increased slightly. The Fe−Fe shell was not affected. The changes in the near-edge

In situ XAS of Fe−ZSM-5/N₂O

J. Phys. Chem. B, Vol. 108, No. 36, 2004 **13751**
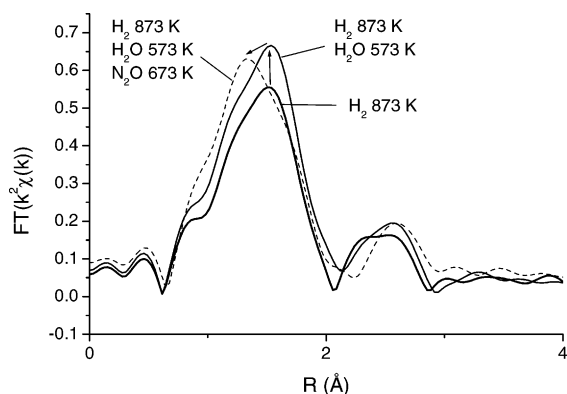
Figure 10. QEXAFS spectra of Fe−ZSM-5 at 573 K, after pretreatment in H_2 at 873 K (bold), after exposure to H_2O at 573 K (solid), and after reaction with N_2O at 673 K (dashed). Shown is the magnitude of the k^2-weighted Fourier transform of $\chi(k)$ in the range ∼2.8−12.5 Å.

and the EXAFS region show that H_2O bound to the Fe^{II} sites but did not change their oxidation state or the degree of clustering.

In the subsequent reaction with N_2O at 673 K, the Fe−O coordination number did not increase, as observed when the water treatment was omitted (Figure 4), but even decreased slightly (Figure 10). This is not surprising, because the iron coordination shell had already been saturated with H_2O before. The oxidation of Fe^{II} sites to Fe^{III} could be followed by the shift of the Fe K-edge to higher energies and the contraction of the Fe−O and Fe−Fe distances. Reoxidation took about 15 min and the catalyst reached steady state (∼12% N_2O conversion) immediately, once reoxidation was completed. No transient activity was observed. The spectrum measured during steady-state N_2O decomposition was fitted and compared with the one where water treatment had been omitted. The Fe−O coordination number of the former catalyst was a bit higher, indicating that some H_2O was still adsorbed to the iron sites. The Fe−Fe coordination number was close to 1.0 for both catalyst.

Decomposition of N_2O at High Temperatures. The catalyst, which was pretreated in H_2 at 873 K and then reoxidized by N_2O at 673 K, was heated from 673 to 798 K in a flow of N_2O. The N_2O conversion increased from 12 to 88% in that temperature range. The position of the Fe K-edge hardly changed. Even at almost full N_2O conversion, the catalyst operated in a fully oxidized state. At 798 K, the feed stream was switched from N_2O to He. A small shift of the edge by 0.5 eV to lower energies was observed, corresponding to ∼7% reduction from Fe^{III} to Fe^{II}. This is in good agreement with the extent of autoreduction measured in our previous kinetic experiments.[9]

Discussion

Fitting of the EXAFS Spectra. Several EXAFS studies of Fe−ZSM-5 CVD catalysts were already reported in the literature.[6−8,18,27,28] In most of them two or three oxygen shells and one or two iron shells are used for the fitting of the spectra. Although allowed by information theory,[29] it may be questioned whether the use of so many parameters is justified. If two types of oxygen atoms with different Fe−O distances are present in the first coordination shell of iron, they will lead to a beat node in the EXAFS amplitude at 15.7 Å^{-1} if the two oxygens are 0.1 Å apart and at 10 Å^{-1} if they are 0.15 Å apart.[30] In our EXAFS spectra, reasonable signal-to-noise ratios were obtained up to k values of 12−15 Å^{-1} (worst and best case). The

resolution of shells, which are at least 0.11−0.13 Å apart should be possible. The EXAFS spectra in Figure 8, which are representative examples, show that the amplitude of the EXAFS oscillations was dampened between 11 and 12 Å^{-1} and then rose again. This suggests that two oxygen shells might be present in the catalyst, which are about 0.14 Å apart. The shape of the Fe−O backscattering peak in the Fourier transform corroborates that suspicion. The peak is asymmetric and has a shoulder at higher R values, which indicates the presence of two shells. An exploration of the χ^2 map also confirmed the existence of two shells. We therefore used two Fe−O shells to fit the spectra. They converged to distances that were 0.13−0.16 Å apart, in agreement with our expectations. The correlation between the oxygen shells was, however, very strong, and many pairs of coordination numbers and Debye−Waller factors gave equally good fits. To reduce that correlation, the Debye−Waller factors of both shells were fixed to the same value. In this way better confidence levels of the parameter fits could be obtained. Spectra where a beat node was not present (or not detectable) could be very well fitted with only one Fe−O backscattering path. Even so, a second Fe−O shell was sometimes used to fit these spectra, to facilitate comparison with other data. The total oxygen coordination number obtained in our fits was always low. It never exceeded a value of 4.0. Others have reported coordination numbers close to 6.0.[7,8,18] In these data analyses a very low S_0^2 factor was used, which leads to higher coordination numbers. We observed that the Fe−O coordination numbers increased when the first negative oscillation of the EXAFS amplitude was cut off by the Fourier transform window. That procedure did, however, lead to inconsistencies in the fits of other spectra and was not adopted as standard.

The Fe−Fe backscattering peak in the Fourier transform was usually weak and overlapped with the peak of oxygen. The shell was fitted with only one Fe−Fe backscattering path, which led to a coordination number of 2.2 in the parent material after O_2 treatment, with a very high Debye−Waller factor of 0.013 Å^2. The high Debye−Waller factor was attributed to a large structural disorder of the iron clusters, i.e., a large spread of the Fe−Fe distances. The coordination number was significantly higher than reported before. We therefore looked for other possible backscattering paths, which might be obscured in the Fe−Fe shell. A distant oxygen shell at about 2.5 Å, attributed to lattice oxygen, was sometimes included in fits reported in the literature.[6,31] If a hypothetical iron cluster is placed in the pore of ZSM-5, one can see that the distances of the iron atoms to nonbonding lattice oxygen atoms vary strongly between 2.3 and 2.7 Å. A coherent EXAFS signal of these lattice oxygen atoms can therefore not be expected. We also verified the possibility that Al contributes to the backscattering.[32] The EXAFS oscillations of an Fe and Al atom at similar distances are, however, out of phase and introducing Al in the fits led to unrealistically high coordination numbers for both Fe and Al. Fitting with two separate Fe−Fe shells was possible, but the total Fe−Fe coordination number did not change. We therefore come to the conclusion that the iron clusters in Fe−ZSM-5 CVD are larger than the binuclear clusters proposed before. Recent XAS and Mössbauer studies arrive at similar results.[7,8,27] The Fe−Fe coordination numbers obtained in our EXAFS analysis are similar to those reported by Heinrich et al.,[27] but significantly lower than the values in two other recent studies cited above.[7,8] It is not clear whether this discrepancy is real, i.e., due to larger iron oxide clusters in our material as a result of the more severe calcination conditions,[7] or simply caused by a different approach to the data analysis.

**SCHEME 1: Hypothetical Iron Tetramer Is Split into Two Binuclear Clusters upon Reduction[a]**
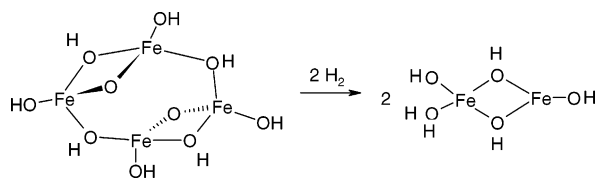
[a] In the zeolite one or two of the terminal OH groups can be replaced by lattice oxygen atoms.

The ambiguities that exist concerning the interpretation of the EXAFS data of Fe−ZSM-5 CVD show how delicate the analysis of this system is. The results may depend on the method used for the calibration of S_0^2, the background subtraction, the data range, and the number of parameters chosen for the fitting. The rather high disorder of the system adds to the difficulty of the fitting. If the distribution of distances around the average value is asymmetric, EXAFS can underestimate the coordination numbers.[33] Our approach to the EXAFS analysis was to not overinterpret the data and to use a minimum number of parameters to obtain reasonable fits. In this respect we would like to express the opinion that the use of ΔE_0 as a free parameter for each shell, as frequently applied,[6−8,18,31] is not justified by physics. ΔE_0 shifts the Fermi level of the measured substance vs that of the reference. If all reference backscattering paths are generated from the same compound (in our case Fe_2O_3), the same ΔE_0 value has to be used for all shells. The fits of some representative spectra of Fe−ZSM-5, in oxidized and reduced forms, are shown in the Supporting Information.

Effect of High-Temperature Treatments on the Structure of the Iron Sites. Fitting of the EXAFS spectrum of the parent Fe−ZSM-5 CVD, after treatment in O_2, led to two oxygen shells at distances of 1.86 and 2.00 Å, with a coordination number of two each, and an iron shell at a distance of 2.99 Å, with a coordination number of 2 (see Table 3 and Figure S2). It was claimed that the iron oxide clusters in ZSM-5 have a structural resemblance to goethite.[7] Scheme 1 shows a fragment of the goethite structure with four iron atoms, similar to the one proposed by Joyner and Stockenhuber.[34] The average Fe−O and Fe−Fe coordination numbers of this cluster are 4 and 2.5, respectively, i.e., similar to the values found in our EXAFS analysis. The two short Fe−O distances found in the fits can be assigned to the µ-O bridges and the terminal OH groups, the longer Fe−O distance to the µ-OH bridges.[35] The cluster drawn in Scheme 1 is just one of many possible structures that can be brought in accordance with our EXAFS data, but it can be used as a plausible model structure, to guide our imagination.

Reduction of the Fe−ZSM-5 catalyst in H_2 reduced the Fe−Fe coordination number to 1 (see Table 2). Scheme 1 gives an idea how that structural rearrangement could take place. The bridges between the two iron dimers are broken and saturated with H_2O. The formation of smaller iron oxide clusters upon reduction is in accordance with the rule[36] that low valent ions require a smaller lattice energy for stabilization, i.e., a smaller cluster size.

Reoxidation by N_2O restored the initial Fe−Fe coordination number if the catalyst was reduced at 673 K; i.e., the reaction in Scheme 1 was reversible. If the material was reduced at 873 K, the binuclear clusters remained intact during the reaction with N_2O (Figure 11). We can only speculate as to why the reduction at 873 K can stabilize the smaller iron oxide clusters, whereas reduction at 673 K cannot. A possible explanation is that the iron cluster compensates for the loss of coordinating water molecules or hydroxy groups at 873 K by forming stronger
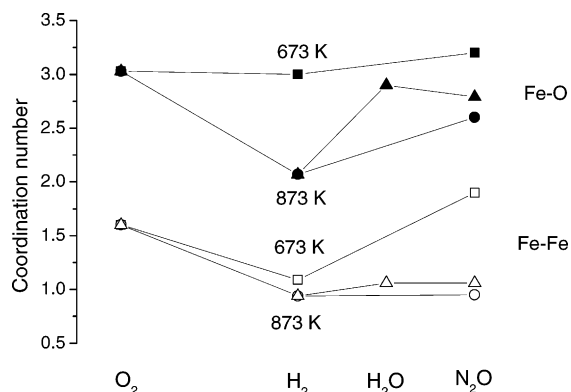

Figure 11. Fe−O (full symbols) and Fe−Fe (open symbols) coordination numbers of Fe−ZSM-5 during treatment in O_2 at 773 K, reduction at 673 K (squares) or 873 K (circles), and treatment with water vapor at 573 K (triangles) and after reoxidation with N_2O at 673 K.
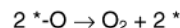
SCHEME 2: Mechanism of N_2O Decomposition

Deposition of oxygen atom on an active site

$$* + N_2O \rightarrow N_2 + *\text{-}O$$
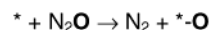
Exchange with other Fe-O atoms

$$*\text{-}O + \#\text{-}O \rightleftharpoons *\text{-}O + \#\text{-}O$$
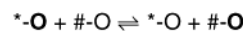
Recombination and desorption as O_2

$$2 *\text{-}O \rightarrow O_2 + 2 *$$

bonds to the oxygen atoms of the zeolite matrix. Once the strong bonds to the matrix are formed, the iron oxide clusters do not merge any more during reoxidation by N_2O. This idea is supported by recent NMR and IR data, which indicate that the Fe_xO_y clusters in Fe−ZSM-5 CVD break into isolated FeO^+ species, which interact with framework or nonframework aluminum, when the samples are treated at high temperatures.[8,37] We tried to identify such Fe−O−Al bonds in the EXAFS spectra of the samples, which were reduced at 873 K. The spectra can be fitted with a mixed backscattering by Fe and Al, but the two shells are strongly correlated. EXAFS can therefore not give a proof for the formation of Fe−O−Al clusters.

The Fe−ZSM-5, which was reduced in H_2 at 673 K, returned to its original structure after reoxidation by N_2O: its EXAFS signal was identical to the parent Fe−ZSM-5 after treatment in O_2. That result was surprising. Catalytic experiments had shown that prereduced catalysts are more active in N_2O decomposition if they incorporate a high concentration of oxygen atoms from N_2O.[17] The oxygen atoms, which N_2O deposits on the catalyst, have a higher reactivity and should, therefore, be bound in a manner different from that of the iron oxide cluster. We could, however, not detect any significant difference between the parameters of the oxygen shell of the samples, which were reduced at 673 or 873 K and then reoxidized with N_2O, and those of the parent material. A very short Fe−O distance, attributable to oxygen from N_2O, as reported in ref 28, could not be confirmed by our EXAFS analysis. Our results suggest that the concentration of active surface oxygen atoms, which originate from N_2O, is very low and can therefore not be detected by EXAFS. That conclusion seems to contradict recent isotope labeling experiments. They showed that the O_2 produced in N_2O decomposition is formed from a pool of surface oxygen atoms, which readily exchange with each other, i.e., according to the mechanism shown in Scheme 2.[10] The pool size was found to be large, on the order of $O_{pool}/Fe = 1$, suggesting that all iron atoms are involved in the reaction. The results of in situ

XAS and isotope labeling can be reconciled if we assume that all iron atoms are involved in the exchange reaction (step 2) but not in the deposition and desorption of oxygen atoms (steps 1 and 3). The oxygen atoms are highly mobile on the surface at 673 K and move and exchange over the whole iron oxide cluster, but only a few iron sites are responsible for the adsorption and desorption of oxygen atoms, which keeps the catalytic cycle running.

Comparison to Earlier Work. Several in situ XAS studies of Fe−ZSM-5 have been reported before.[15,18,19,27,28] Our approach was mainly inspired by the work of Jia et al., who studied the structure of Fe−ZSM-5 after reduction in H₂ at 873 K, followed by reoxidation with N₂O at 523 K.[28] In agreement with our results, they observed a decrease of the Fe−Fe coordination number after the treatment in H₂. The fit parameters contained, however, an unusually short Fe−Fe distance in the sample (2.47 Å), indicating that this EXAFS analysis may not be reliable. Reoxidation of the sample by N₂O led to a different result than observed here: The preedge peak and the Fe−Fe coordination number increased significantly and a very short Fe−O distance was observed in the EXAFS analysis. The variation may be due to the different temperature at which N₂O was reacted with the catalyst: At 673 K the deposited oxygen atoms are more mobile than at 523 K. They can quickly exchange with other oxygen atoms of the iron cluster and lose a distinct spectroscopic signature.

Origin of the Transient Reaction. When Fe−ZSM-5 CVD catalysts were pretreated at high temperatures, they exhibited a very high initial activity in N₂O decomposition.[16,38] The effect is most probably related to the presence of Fe^{II} sites produced by autoreduction at high temperatures. Exposure to water vapor, however, poisoned the sites responsible for the transient reaction. This suggested that the occurrence of the transient reaction was related to the dehydroxylation of the iron clusters (see also ref 11). Our in situ XAS measurements allowed for a direct observation of the deyhdroxylation and hydroxylation of the iron clusters. Treatment at 873 K removed all coordinating H₂O molecules from the iron oxide cluster and created unsaturated iron atoms with a coordination number of 2. These unsaturated iron atoms exhibited transient activity during the reoxidation with N₂O. If the unsaturated iron atoms were exposed to water before the reaction with N₂O, the water filled the open coordination sites and no transient reaction was observed with N₂O. The coordinating water molecules are very strongly bound to the iron cluster and can only be removed by treatment at temperatures above 673 K. That explains why the transient reaction was never observed when the catalysts were pretreated at 673 K.[17] Our conclusion that water molecules bind very strongly to the iron oxide clusters even at very high temperatures is supported by the observation that the addition of H₂O to the feed decreased the N₂O decomposition activity of Fe−ZSM-5 even at 773 K.[37]

Autoreduction of Fe−ZSM-5. Two recent in situ XAS studies reported that Fe−ZSM-5 autoreduces in a stream of He already at very low temperatures.[18,19] Because the samples were not subjected to an oxidative treatment at the beginning of the in situ experiments the observed autoreduction may have been caused by contaminants.[15] Recent transient response experiments (nonspectroscopic) showed that hydrocarbons, which are adsorbed on the iron zeolites, lead to a significant extent of autoreduction, which almost disappears if the samples are first treated in oxygen.[17] After oxidative pretreatment, the extent of autoreduction in He is less than 10%, even at temperatures as high as 773 K.[9,39] In agreement with the nonspectroscopic data,

our in situ XAS experiments never showed an extensive autoreduction of the catalyst in He at high temperatures, after treatment in neither O₂ nor N₂O. In contrast to that, Battiston et al.[18] observed a reduction of their sample in He below 623 K, which was followed by a slow reoxidation. This strongly suggests that the reduction at low temperatures was caused by contaminations of the EXAFS cell or the sample. Our in situ XAS data prove that the Fe−ZSM-5 CVD catalyst operates in an almost fully oxidized state, even at very high temperatures and conversions. It is, however, not ascertained that this conclusion can be extended to iron zeolites prepared by other methods, i.e., hydrothermal synthesis or ion exchange.

Conclusions

EXAFS analysis shows that CVD of FeCl₃ on ZSM-5 creates small iron oxide clusters with 3−4 metal atoms in the ZSM-5 support. Reduction breaks the clusters into smaller (binuclear) units. If reduction is carried out at high temperatures (873 K), the small clusters are strongly dehydroxylated. They stabilize themselves by a strong bonding to the zeolite matrix. The formation of these small iron oxide clusters is probably responsible for the increase in N₂O decomposition activity, which was observed for Fe−ZSM-5 samples pretreated at high temperatures. The dehydroxylation of the iron clusters takes place only at temperatures above 673 K. That explains why the so-called transient reaction, a very high initial N₂O decomposition activity, which is catalyzed by the dehydroxylated iron sites, is only observed after pretreatment of Fe−ZSM-5 at temperatures above 673 K.

Concerning the mechanism of N₂O decomposition, the in situ XAS data confirm conclusions, which had been indirectly derived from kinetic data: In steady state the Fe-ZSM-5 is fully oxidized. Only a very small concentration of Fe^{II}-sites, which is undetectable by XAS, keeps the catalytic cycle running. Extensive autoreduction of the catalyst (>10%) was not observed even at 798 K. Prereduced catalysts are first reoxidized by N₂O before steady-state N₂O decomposition sets in. The incorporation of oxygen atoms from N₂O into the catalyst surface increases its catalytic activity, but the EXAFS signature of such a material is not different from the parent. This suggests that, although the oxygen atoms of all iron oxide clusters can exchange with each other, only a few specific sites are responsible for adsorption and desorption of oxygen, i.e., for the catalytic activity.

Supporting Information Available: EXAFS spectra and corresponding fits of Fe−ZSM-5 at 773 K in O₂, at room temperature after treatment in O₂ at 773 K, at 873 K in H₂, at 673 K in N₂O after reduction in H₂ at 873 K as well as comments on the error margins of the fit parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Perez-Ramirez, J.; Kapteijn, F.; Mul, G.; Moulijn, J. A. *Appl. Catal. B* **2002**, *35*, 227.

(2) Yamada, K.; Kondo, S.; Segawa, K. *Microporous Mesoporous Mater.* **2000**, *35−36*, 227.

(3) Joyner, R.; Stockenhuber, M. *J. Phys. Chem. B* **1999**, *103*, 5963.

(4) Lobree, L. J.; Hwang, I. C.; Reimer, J. A.; Bell, A. T. *J. Catal.* **1999**, *186*, 242.

(5) Chen, H. Y.; Sachtler, W. M. H. *Catal. Lett.* **1998**, *50*, 125.

(6) Marturano, P.; Drozdová, L.; Kogelbauer, A.; Prins, R. *J. Catal.* **2000**, *192*, 236.

(7) Battiston, A. A.; Bitter, J. H.; de Groot, F. M. F.; Overweg, A. R.; Stephan, O.; van Bokhoven, J. A.; Kooyman, P. J.; van der Spek, C.; Vanko, G.; Koningsberger, D. C. *J. Catal.* **2003**, *213*, 251.

(8) Hensen, E. J. M.; Zhu, Q.; Hendrix, M.; Overweg, A. R.; Kooyman, P. J.; Sychev, M. V.; van Santen, R. A. *J. Catal.* **2004**, *221*, 560.

(9) Pirngruber, G. D.; Luechinger, M.; Roy, P. K.; Cecchetto, A.; Smirniotis, P. *J. Catal.* **2004**, *224*, 429.

(10) Pirngruber, G. D.; Roy, P. K. *Catal. Lett.* **2004**, *93*, 75.

(11) Jia, J. F.; Wen, B.; Sachtler, W. M. H. *J. Catal.* **2002**, *210*, 453.

(12) Hensen, E. J. M.; Zhu, Q.; van Santen, R. A. *J. Catal.* **2003**, *220*, 260.

(13) Hensen, E. J. M.; Zhu, Q.; Hendrix, M.; Overweg, A. R.; Kooyman, P. J.; Sychev, M. V.; van Santen, R. A. *J. Catal.* **2004**, *221*, 560.

(14) Kiwi-Minsker, L.; Bulushev, D. A.; Renken, A. *J. Catal.* **2003**, *219*, 273.

(15) Berlier, G.; Spoto, G.; Bordiga, S.; Ricchiardi, G.; Fisicaro, P.; Zecchina, A.; Rossetti, I.; Selli, E.; Forni, L.; Giamello, E.; Lamberti, C. *J. Catal.* **2002**, *208*, 64.

(16) Roy, P. K.; Pirngruber, G. D. *J. Catal.* **2004**, *227*, 164.

(17) Pirngruber, G. D. *J. Catal.* **2003**, *219*, 456.

(18) Battiston, A. A.; Bitter, J. H.; Koningsberger, D. C. *J. Catal.* **2003**, *218*, 163.

(19) Heijboer, W. M.; Battiston, A. A.; Knop-Gericke, A.; Havecker, M.; Mayer, R.; Bluhm, H.; Schlogl, R.; Weckhuysen, B. M.; Koningsberger, D. C.; de Groot, F. M. F. *J. Phys. Chem. B* **2003**, *107*, 13069.

(20) Chen, H. Y.; Sachtler, W. M. H. *Catal. Today* **1998**, *42*, 73.

(21) Ressler, T.; Wienold, J.; Jentoft, R. E.; Neisius, T. *J. Catal.* **2002**, *210*, 67.

(22) Newville, M. *J. Synchotron Rad.* **2001**, *8*, 322.

(23) Ankudinov, A. L.; Ravel, B.; Rehr, J. J.; Conradson, S. D. *Phys. Rev. B* **1998**, *58*, 7565.

(24) Chen, H. Y.; El-Malki, E. M.; Wang, X.; van Santen, R. A.; Sachtler, W. M. H. *J. Mol. Catal. A* **2000**, *162*, 159.

(25) Westre, T. E.; Kennepohl, P.; DeWitt, J. G.; Hedman, B.; Hodgson, K. O.; Solomon, E. I. *J. Am. Chem. Soc.* **1997**, *119*, 6297.

(26) Petit, P. E.; Farges, F.; Wilke, M.; Sole, V. A. *J. Synchrot. Radiat.* **2001**, *8*, 952.

(27) Heinrich, F.; Schmidt, C.; Loffler, E.; Menzel, M.; Grunert, W. *J. Catal.* **2002**, *212*, 157.

(28) Jia, J. F.; Sun, Q.; Wen, B.; Chen, L. X.; Sachtler, W. M. H. *Catal. Lett.* **2002**, *82*, 7.

(29) Brillouin, L. *Science and Information Theory*, 2nd ed.; Academic Press: New York, 1962.

(30) Lee, P. A.; Citrin, P. H.; Eisenberger, P.; Kincaid, B. M. *Rev. Mod. Phys.* **1981**, *54*, 769.

(31) Marturano, P.; Drozdova, L.; Pirngruber, G. D.; Kogelbauer, A.; Prins, R. *Phys. Chem. Chem. Phys.* **2001**, *3*, 5585.

(32) Choi, S. H.; Wood, B. R.; Ryder, J. A.; Bell, A. T. *J. Phys. Chem. B* **2003**, *107*, 11843.

(33) Shido, T.; Prins, R. *J. Phys. Chem. B* **1998**, *102*, 8426.

(34) Joyner, R. W.; Stockenhuber, M. *Catal. Lett.* **1997**, *45*, 15.

(35) Cornell, R. M.; Schwertmann, U. *The Iron Oxides: Structure, Properties, Reactions, Occurrence and Uses*; VCH Verlagsgesellschaft: Weinheim, 1996.

(36) Pauling, L. *Nature of the Chemical Bond*; Cornell University Press: Ithaca, NY, 1960.

(37) Zhu, Q. Ph.D. Thesis, Eindhoven University of Technology, 2004.

(38) Zhu, Q.; van Teeffelen, R. M.; van Santen, R. A.; Hensen, E. J. M. *J. Catal.* **2004**, *221*, 575.

(39) Voskoboinikov, T. V.; Chen, H. Y.; Sachtler, W. M. H. *Appl. Catal. B-Environ.* **1998**, *19*, 279.