Catalysis Letters 66 (2000) 75–79

XAFS characterization of the binuclear iron complex in overexchanged Fe/ZSM5 – structure and reactivity

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Received 4 January 2000; accepted 17 March 2000

We have characterized, with emphasis on XAFS spectroscopy, one of the most promising DeNOx catalysts, i.e., Fe/ZSM5 prepared through the $FeCl_3$ sublimation technique. XAFS is a very useful tool for this purpose since it is element specific and can be used *in situ*, namely, in the presence of the reactants and at reaction temperature. In this communication it will be pointed out that the as-synthesized Fe/ZSM5 catalyst contains stable binuclear iron oxo/hydroxo-complexes. The reaction of these complexes with the probe molecule CO clearly shows that only one of the oxygen shells around iron changes while the iron contribution is not affected, the iron complex remaining binuclear.

Keywords: Fe/ZSM5, $FeCl_3$, SCR, DeNOx, XAFS

1. Introduction

Recent results have shown that "overexchanged" Fe/ZSM5 (Fe/Al molar ratio $\sim$1) is a remarkably active and stable catalyst for the selective catalytic reduction of NO_x with i-C_4H_{10} and excess O_2 [1–5]. Its stability and durability, even in the presence of 20% H_2O and 150 ppm SO_2, make it a serious candidate for practical HC-SCR (hydrocarbon-selective catalytic reduction) applications [1,2,4].

The first promising results were obtained on a Fe/ZSM5 catalyst prepared by exchanging $[FeOH^+]$ ions from a saturated aqueous solution of FeC_2O_4 [1,2] onto a Na/ZSM5 support (Si/Al molar ratio $\sim$15). However, the catalysts prepared in this way turned out to be hardly reproducible, probably due to difficulties related to the control of the reaction conditions within the zeolite pores [3–5].

A more easily reproducible method for the preparation of overexchanged Fe/ZSM5 has been proposed by Chen and Sachtler [4,7]. It consists of subliming $FeCl_3$ into the cavities of a H/ZSM5 support, where it chemically reacts with the Brønsted acid sites of the zeolite. This method overcomes the problems related to the complicated chemistry of iron in aqueous solutions. Moreover, an exchange level as high as $Fe/Al = 1$ can easily be achieved starting from different batches of H/ZSM5 ($10 < Si/Al < 25$). The resulting samples have shown a catalytic performance very similar to the one obtained through the above-mentioned oxalate technique, with respect to activity and stability towards poisons [4].

Although the excellent activity and durability of overexchanged Fe/ZSM5 catalysts are well established [2–5,7], the nature of the active site is still a matter of debate. A binuclear iron complex has tentatively been proposed as the active phase in these materials for the HC-SCR reaction [4,5,7].

In this communication we will show that XAFS spectroscopy unambiguously points out that the iron complexes in Fe/ZSM5 prepared by the $FeCl_3$ method are binuclear, i.e., they contain two iron atoms per cluster.

Since XAFS spectroscopy can be applied *in situ*, it is a very powerful tool to track the changes taking place in the coordination parameters of the Fe cluster during (DeNOx) reactions. This ability will be shown by the results obtained during the reaction of the binuclear iron clusters with the probe molecule CO. In this reaction a clear decrease in the oxygen coordination, accompanied by a shift to lower energies of the adsorption edge, was observed. This clearly indicates a reduction of the Fe clusters. These changes appeared to be completely reversible by reoxidation with O_2.

2. Experimental

2.1. Catalyst preparation

Fe/ZSM5 was prepared via the $FeCl_3$ sublimation method proposed by Chen and Sachtler [4]. NH_4/ZSM5 ($Si/Al = 17$), obtained from Zeolyst, was converted into the H^+ form by calcination in an O_2 flow at 550 °C for 3 h. For introducing iron on the zeolite support a special U-shaped reactor was constructed. In each leg of the reactor a porous frit and a Pyrex valve were mounted. 1.0 g of calcined H/ZSM5 was loaded onto one of the frits and flushed overnight in a He flow (40 ml/min) at 300 °C. The temperature was then lowered to 30 °C under the same He flow. The reactor was isolated closing its inlet and outlet valves and moved to a glove bag, where 0.31 g of anhydrous $FeCl_3$ (98%, Acros Organics) were loaded on its second frit. The reactor was then reconnected to the He line

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and sublimation exchange was performed at a temperature of 330 °C for 30 min. The HCl formed during the $FeCl_3$ reaction with the Brønsted acid sites of the H/ZSM5 was absorbed in 100 ml of 0.05 M NaOH solution. After the sublimation procedure, the sample was washed in 1000 ml doubly deionized H_2O for 30 min, dried overnight in air at 70 °C and finally calcined for 3 h in flowing O_2 at 550 °C.

2.2. Catalyst characterization

ICP analysis was performed in order to determine the Si/Al ratio and the iron loading of the starting parent Fe/ZSM5 sample. For this purpose 0.4 g of lithium tetraborate, 0.2 g of lithium metaborate and 0.1 g of the calcined Fe/ZSM5 parent sample were accurately weighed and put together in a platinum cup. The cup was heated up in air to 925 °C for 1 h. After cooling to room temperature, the resulting soluble iron borate was dissolved in 330 ml 1 M HCl. The solution was then diluted up to 1000 ml with doubly deionized water and measured through ICP.

Acid–base titration with 0.1 M HCl of the remaining OH^- in the NaOH solution (see above) was used to quantify the amount of HCl released during the $FeCl_3$ exchange. The H^+ removal efficiency was calculated as the ratio between the HCl produced during the sublimation reaction, according to the equation $Fe_2Cl_6 + 2H^+ \rightarrow 2HCl + [Fe_2Cl_4]^{2+}$, and the H^+ sites theoretically present in the support, i.e., by assuming $Al/H^+ = 1$.

The crystalline fingerprint of the zeolitic support was monitored after each synthesis step using XRD to exclude lattice damage or formation of iron oxides phases. XAFS experiments were performed to characterize the local environment around Fe.

2.3. XAFS data collection

The X-ray absorption spectra of the Fe K edge (7112 eV) were collected at Hasylab (Hamburg) Wiggler Station X1.1, using a Si(111) double crystal monochromator. The monochromator was detuned to 50% maximum intensity to avoid higher harmonics present in the X-ray beam. The measurements were done in transmission mode using ion chambers filled with Ar to have an X-ray absorbance of 20% in the first ion chamber and of 80% of the remaining radiation in the second one. In all the experiments a Fe foil was measured using a third ionisation chamber.

The calcined Fe/ZSM5 sample was pressed into a self-supporting wafer (calculated to have an absorbance (μx) of 2.5) and placed in a controlled atmosphere cell [8]. Spectra were recorded at liquid-nitrogen temperature after: (1) flushing the calcined Fe/ZSM5 sample with He (measurement further denoted by FeZSM5), (2) a subsequent 30 min reduction treatment performed *in situ* at 350 °C with 5% CO/He (FeZSM5-CO), and (3) a final reoxidation for 30 min with 20% O_2/He at 350 °C (FeZSM5-CO–O_2). All the above-mentioned total flows were 50 ml/min.

2.4. XAFS data analysis

The final XAFS spectrum was obtained by averaging three scans. The pre-edge background was approximated by a modified Victoreen curve [9], and the background was subtracted using cubic spline routines [10]. Spectra were normalised by dividing the absorption intensity by the height of the absorption edge at 50 eV above the edge [9]. The edge position was always determined by calibrating the monochromator with an iron foil. Data analysis was performed in R space by using the XDAP software [11]. All fits were performed using k^1-weighted spectra and the results were checked to give satisfactorily results for k^0- and k^2-weighted spectra.

In order to analyse the experimental data, Fe–Fe and Fe–O references were used to fit the Fe–Fe and Fe–O contributions present in the XAFS spectra. The Fe–Fe reference was calculated using the FEFF7 program. The input parameters for FEFF7 (V_r, V_i, $\Delta\sigma^2$, R and S_0^2) were adjusted in such a way that a fit with the resulting reference file produced satisfactorily the Fe–Fe coordination parameters of a measured α-Fe_2O_3 reference compound. A similar procedure was adopted for the Fe–O reference file, using the Fe–O coordination in $Fe(acac)_2$ for calibration. Errors in the parameters obtained by the EXAFS data analysis are estimated to be 10% in coordination number (N), 1% in distance (R), 5% in Debye–Waller factor ($\Delta\sigma^2$) and 10% in inner potential correction (ΔE_0) [12].

3. Results

Table 1 shows the elemental composition of the Fe/ZSM5 catalyst. In the same table the H^+ removal efficiency of the synthesis procedure, as it arises from the HCl titration, is compiled. The $FeCl_3$ sublimation procedure led to an iron content of $Fe/Al = 0.97$. This was consistent with the H^+ removal efficiency also being close to unity, i.e., all the H^+ acid sites were removed from the H/ZSM5 support.

XRD spectra (not shown here) were collected after every synthesis step and compared to the one of the parent H/ZSM5 support. All spectra were identical, indicating that no damage to the structure nor formation of large crystalline Fe phases occurred.

In figure 1 the Fourier transformed EXAFS spectrum of the parent calcined Fe/ZSM5 sample (FeZSM5) is presented, together with the fitted data. The spectrum showed two major contributions, one located around 1.4 Å and one around 2.6 Å. The former corresponds to the oxygen coordination around iron, whereas the latter one is due to

Table 1
Calcined FeZSM5 sample prepared by $FeCl_3$ sublimation: elemental composition (ICP) and H^+ removal efficiency.

	Si/Al (molar ratio)	Fe/Al (molar ratio)	H^+ removal efficiency
Fe/ZSM5	17.0	0.97	0.98

the Fe–Fe contribution. The overall results of the EXAFS analysis of FeZSM5 are compiled in table 2. As can be seen in this table, three different Fe–O shells (it was not possible to obtain an acceptable fit with only two Fe–O shells) and one Fe–Fe shell were identified. The first oxygen shell consists of two oxygen neighbours, while the second and the third Fe–O shells contain only one oxygen atom. The coordination number of the Fe–Fe shell is within the limits of accuracy equal to 1, clearly pointing to the presence of binuclear iron oxo/hydroxo-complexes. The EXAFS analysis showed an interatomic distance of 3.07 Å for the two iron atoms in the clusters.

As is depicted in figure 2, the Fourier transform (both magnitude and imaginary part) of the sample treated with CO showed significant changes, compared to the spectrum of the parent sample, in the Fe–O coordination. In contrast, the Fe–Fe contribution remained almost unaffected. The resulting EXAFS parameters, showing the extent of the oxygen removal, together with the changes occurred in the structural parameters of the iron clusters, are presented in table 2. An average O/Fe removal of 0.5 after the treatment with CO was revealed in the third oxygen shell (Fe–O3), whereas the coordination numbers of the remaining two Fe–O shells were not modified.

Notwithstanding the oxygen removal, both the coordination number of the Fe–Fe shell and the interatomic distance between the two iron atoms were not significantly affected, underlining the stability of the binuclear clusters.

In order to investigate whether the removal of oxygen had indeed been accompanied by a reduction in the oxidation state of Fe, the XANES spectra of the FeZSM5 sample were recorded after the different treatments. They are compiled in figure 3. For comparison, the XANES spectrum of α-Fe_2O_3 is also included. Figure 3 shows that the CO treatment (FeZSM5-CO) caused a decrease of 2.5 eV in the position of the Fe K edge. The edge position of all the other X-ray absorption spectra is the same, irrespective of the history of the sample, and is identical to the one of the spectrum obtained for α-Fe_2O_3.

The influence of the reoxidation treatment on the Fourier transformed EXAFS spectrum of the sample previously reduced with CO is shown in figure 4. As it appears in this

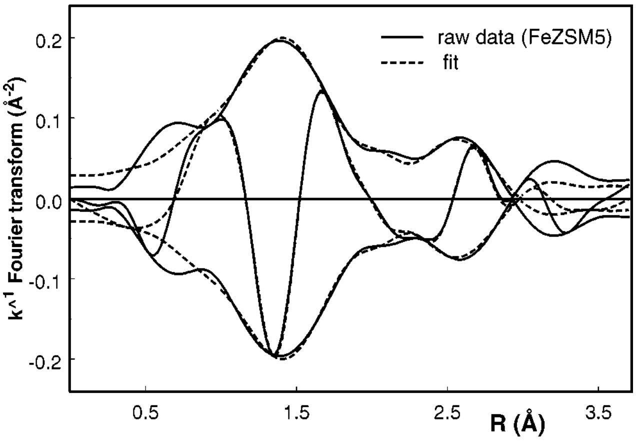

Figure 1. Fourier transform (k^1, $\Delta k = 2.7$–10 Å^{-1}) of EXAFS data of FeZSM5 (—) and fit ($1 < R < 3$ Å) (- - -).

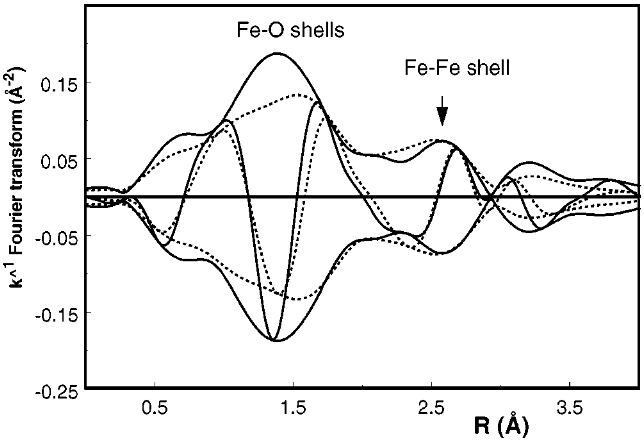

Figure 2. Fourier transform (k^1, $\Delta k = 2.7$–10 Å^{-1}) of EXAFS data of FeZSM5 (—) and FeZSM5-CO (- - -).

Table 2
EXAFS analysis of FeZSM5, FeZSM5-CO and FeZSM5-CO–O_2.

Shells	N (±10%)	R (Å) (±1%)	$\Delta\sigma^2$ (10^{-3} Å^2) (±5%)	ΔE_0 (eV) (±10%)	k^1 variance (%) Im. part.	Abs. part
FeZSM5					0.4	0.1
Fe–O1	2.0	1.97	−3.4	−0.6		
Fe–O2	1.1	1.85	−3.7	8.5		
Fe–O3	1.1	2.15	−3.0	−8.6		
Fe–Fe	1.0	3.07	−1.2	0.6		
FeZSM5-CO					0.3	0.1
Fe–O1	2.0	2.10	−3.2	−0.5		
Fe–O2	1.1	1.87	−5.0	9.1		
Fe–O3	0.5	2.27	−1.1	−10.0		
Fe–Fe	1.2	3.07	−0.6	0.8		
FeZSM5-CO–O_2					0.6	0.2
Fe–O1	1.9	1.98	−3.4	1.4		
Fe–O2	0.9	1.81	−4.7	9.0		
Fe–O3	0.9	2.13	−1.1	−11.3		
Fe–Fe	1.2	3.07	−0.4	0.5		

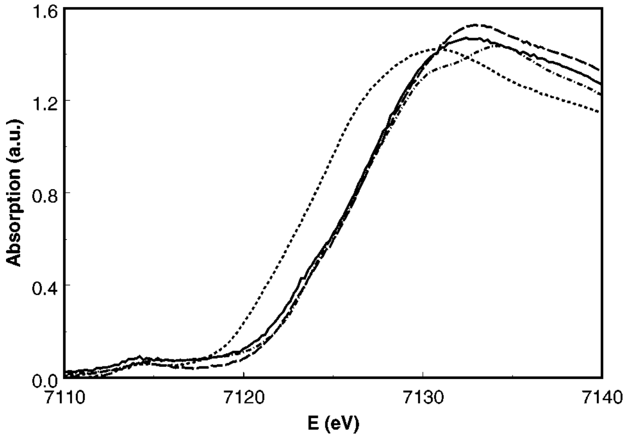

Figure 3. XANES spectra of FeZSM5 (—), FeZSM5-CO (- - -), FeZSM5-CO–O_2 (– – –), Fe_2O_3 as reference (·····).

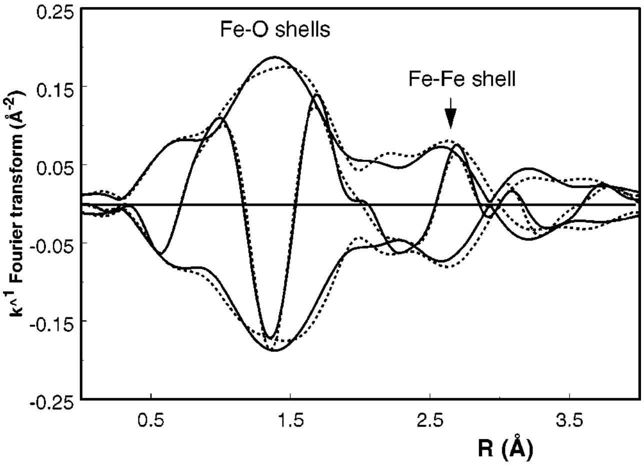

Figure 4. Fourier transform (k^1, $\Delta k = 2.7$–10 Å^{-1}) of EXAFS data of FeZSM5 (—) and FeZSM5-CO–O_2 (- - -).

figure, the Fourier transform of the EXAFS data of the reoxidized sample (FeZSM5-CO–O_2) and the one of the parent sample (FeZSM5) are similar. The loss in the intensity of the Fe–O contribution observed after the CO treatment (see figure 2) appeared to be completely reversible by supplying O_2 (FeZSM5-CO–O_2). In addition, as in the case of FeZSM5-CO, the Fe–Fe shell remained almost unaffected by the treatment. All these observations are further confirmed by the results of the EXAFS analysis shown in table 2. In particular, the coordination number of the third Fe–O shell appears to be restored to its initial value, pointing to a full reversibility of the previous reduction treatment. Besides, almost no difference appears in the parameters of the Fe–Fe shell before (FeZSM5) and after the cycle of treatments (FeZSM5-CO–O_2).

4. Discussion

While there is general agreement that Fe/ZSM5 is very promising for the use in the HC-SCR reaction, there is a debate about the structure of the iron species present in this material. For the overexchanged samples prepared through the $FeCl_3$ sublimation technique (note that these are the most active and stable ones) a binuclear iron complex has been proposed in literature as the active phase [4–7]. This model is based on Fourier transform infrared (FTIR) studies, X-ray diffraction (XRD), H_2 and CO temperature-programmed reduction (TPR) investigation. However, all these techniques lack the ability to visualize the direct coordination around Fe. XAFS spectroscopy, in contrast, is able to do so. It is important to note here that XAFS results on different low loaded Fe samples have already been published [13]. These Fe/ZSM5 samples (Si/Al $= 33$, Fe/Al < 0.5) were obtained through both conventional ion exchange and the already mentioned oxalate technique, and showed the presence of two different iron species: mononuclear ions and oxo-nanoclusters with an average composition of Fe_4O_4. To our best knowledge no XAFS data on highly exchanged Fe/ZSM5 catalysts have been published yet.

The analysis of the XAFS spectrum of a calcined Fe/ZSM5 sample (Si/Al $= 17$, Fe/Al $= 0.97$) prepared via the $FeCl_3$ sublimation technique clearly identifies multiple Fe–O shells and a single Fe–Fe shell (table 2). The Fe–Fe coordination number in the latter shell is equal to 1, thus providing spectroscopic confirmation of the proposed binuclear complex. The analysis of the oxygen contribution for the parent FeZSM5 sample identified three different Fe–O shells, consisting of respectively two, one and one oxygen atom (table 2).

In the literature the existence of different binuclear iron complexes, supported [5,15] or unsupported [16], with different oxo, hydroxo or peroxo coordination of oxygen around iron are suggested. With the current EXAFS results it is not possible yet to unambiguously determine the structure of the iron complexes in FeZSM5. Note that all the calculated Debye–Waller factors are negative, indicating that the Fe–O and Fe–Fe coordination of the iron complexes in the FeZSM5 sample have a lower disorder than those of the reference compounds. Different types of oxygen are claimed to exist on Fe/ZSM5 [14]. The fact that the nature of the oxygen atoms in the cluster is different can also be inferred from the results collected in table 2. The E_0 shifts for the oxygen shells are very different compared to those of the reference compound (if they were similar E_0 should be zero). Moreover, the E_0 shift of the Fe–O contribution runs in opposite directions for the three oxygen shells (e.g., for FeZSM5: Fe–O2 is $+8.5$ and Fe–O3 is -8.6). Therefore, it must be concluded that these oxygens are different in nature. The variation in the E_0 values might be explained by a difference in the covalency of the Fe–O bond, e.g., Fe–O–Fe versus Fe–OH. A more detailed study on this subject and a comparison of the present EXAFS results with molecular modeling calculations will be published in the near future.

In order to explore the specific reactivity of the different oxygen atoms, we performed a reduction treatment on the Fe complex with the probe molecule CO. We also applied a subsequent oxidation treatment to test the reversibility of the changes occurred. The CO treatment resulted in a strong decrease in the intensity of the Fe–O contribution (figure 2), which could in principle have been ascribed to both a lowered Fe–O coordination number (i.e., removal of oxygen) and/or to an increase of the Debye–Waller factor (increase of disorder). The EXAFS analysis revealed a 50% decrease in the oxygen coordination number of the third Fe–O shell (table 2), corresponding to an average removal of 0.5 O atoms per Fe atom. Moreover, the position of the Fe edge of the sample treated with CO appeared at a lower energy compared to the edge of the other samples (figure 3). This clearly indicates that the CO treatment decreases the oxidation state of the iron by removing oxygen from its most distant Fe–O shell. Because the edges of all the XANES spectra, with the exception of the one of the sample treated with CO, are all at the same position of the α-Fe_2O_3 edge, it must be concluded that in all these samples Fe is present in its 3+ oxidation state. Since all the features of the parent FeZSM5 sample (both in EXAFS and XANES) are restored after reoxidizing the CO treated sample, it is concluded that the reduction is fully reversible. Note that the Fe–Fe shell is not significantly affected by any of the treatments. The Fe–Fe coordination number remained always close to unity, pointing to the presence of a stable binuclear complex.

The discrepancy between the present XAFS results and the ones already published in the literature underlines the influence on the final iron phase of both the synthesis technique and the Si/Al ratio of the support. The possibility of having the formation of binuclear iron complexes, i.e., the possibility for two Al centered tetrahedron of the H/ZSM5 to be located within a critical distance of around 6.0 Å, was calculated by Feng and Hall [6]. This probability turned out to be very high for ZSM5 catalysts with a Si/Al ratio <20 while it appeared to be nearly zero starting from supports with Si/Al ratios higher than 30. This could be an explanation for the fact that no iron binuclear complexes [13] were found on samples with a very low Al content.

5. Conclusion

The analysis of the Fe K edge EXAFS spectra obtained from Fe/ZSM5 prepared through the $FeCl_3$ sublimation technique ($Si/Al = 17$, $Fe/Al = 0.97$) clearly shows the presence of a stable binuclear iron oxo/hydroxo-complex. Multiple Fe–O shells, and a single Fe–Fe shell with a Fe–Fe coordination number equal to 1 have been identified. The coordination number of the third Fe–O shell is reversibly altered by *in situ* reduction (5% CO in He, 350 °C) and subsequent *in situ* reoxidation treatment (20% O_2 in He, 350 °C), whereas no major changes occur in the structural parameters of the Fe–Fe shell. The Fe–Fe coordination number remains, within the limits of accuracy, equal to unity, with an interatomic distance of 3.07 Å.

The oxidation state of Fe in the binuclear complexes of the calcined Fe/ZSM5 catalyst is 3+. Treating the sample with CO results in a clear decrease of this initial oxidation state, which is regained by applying the subsequent reoxidation treatment.

These results show clearly that XAFS spectroscopy opens the possibility of determining the structure of the iron phase under real DeNOx reaction conditions. In the near future we will report on a full analysis of the binuclear iron complex, focusing on the stucture of the oxygen atoms around Fe and their behavior under model and real DeNOx conditions.

Acknowledgement

The European Union program for Large Scale Facilities (contract no. ERBFMGECT950059) and NWO (contract no. 326-710) are acknowledged for financial support. We also thank the personnel of Beamline X1.1 at Hasylab (Hamburg) for their assistance during the X-ray absorption measurements.

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