

## **Structure/reactivity correlation in Fe/ZSM5 for deNO<sub>x</sub> applications. *In-situ* XAFS characterization and catalysis**

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On the basis of an *in-situ* XAFS spectroscopy study performed at 350°C it will be shown that in Fe/ZSM5 synthesized through the FeC<sub>3</sub> sublimation technique (Si/Al ratio=17) iron is predominantly present in the form of binuclear oxo/hydroxo-complexes. During reaction with *i*-C<sub>4</sub>H<sub>10</sub> a clear reduction in the oxidation state of the iron is detected, accompanied by changes in only one of the three Fe-O shells. The present findings confirm the presence of only one reactive oxygen-shell in the complexes and demonstrate the possibility of XAFS of studying the local environment around iron in Fe/ZSM5 under experimentally realistic conditions (*in-situ*, at 350°C). The same Fe/ZSM5 sample measured with XAFS shows a very high activity towards the selective catalytic reduction of NO with isobutane under excess oxygen.

### **1. INTRODUCTION**

Fe/ZSM5 synthesized through the FeC<sub>3</sub> sublimation technique has been reported to be a superior catalyst for the selective catalytic reduction of NO<sub>x</sub> with butane and isobutane in the presence of excess oxygen under dry and wet conditions [1-4]. Despite several spectroscopic studies [5-8], the nature of the iron phase in the active material is still unclear. The final structure of the iron phase appears to be very sensitive to differences in the starting zeolitic support as well as in the synthesis procedure. In a previous paper [8] we showed the results of a XAFS study (spectra recorded at liquid nitrogen (L.N.) temperature) on a catalyst prepared with the sublimation technique. The objectives of that study were: 1) to unravel the structure of the iron phase in the as-synthesized (calcined) catalyst; 2) to investigate if we could track the changes occurring in the structural parameters of the iron phase after specific treatments. For this purpose a reduction with CO, followed by a reoxidation with O<sub>2</sub>, was chosen as a test-treatment. The results revealed the presence of binuclear oxo/hydroxo iron-complexes, similar to the ones proposed by Chen and Sachtler [1]. Furthermore, a specific reactivity was revealed in one of the three Fe-O shells of the complexes.

On the basis of the success of this experiment we have decided to investigate the structure and the reactivity of the iron complexes *in-situ*: at 350°C under an oxidizing atmosphere (20%O<sub>2</sub> in He) and during a reducing treatment, also at 350°C, performed with a typical HC-SCR reductant (20%*i*-C<sub>4</sub>H<sub>10</sub> in He).

Moreover, in order to have a confirmation of its catalytic activity, the as-synthesized (calcined) Fe/ZSM5 sample has also been tested in a deNO<sub>x</sub> set-up towards the selective catalytic reduction of NO with isobutane with excess oxygen.

The results of the XAFS data analysis and of the catalytic test will be presented in this contribution.

## 2. EXPERIMENTAL

### 2.1 Catalyst preparation

NH<sub>4</sub>/ZSM5 (Si/Al molar ratio=17) provided by Zeolyst was converted into the H<sup>+</sup> form (sample further denoted as H/ZSM5) by calcination in flowing O<sub>2</sub> (100 ml/min) at 500°C for 4h. The iron was introduced in the H/ZSM5 matrix by means of the FeCl<sub>3</sub> sublimation technique, as previously described in [8]. After the sublimation procedure, the obtained Fe/ZSM5 was washed under stirring in doubly deionized water for 30 min, separated by centrifugation, dried overnight under static air at 70°C and calcined in O<sub>2</sub> at 550°C for 3h (Fe/ZSM5 calc).

### 2.2 Catalysts characterization

The elemental composition of the Fe/ZSM5 calc sample and of the starting H/ZSM5 support were obtained through ICP analysis. XRD was used in order to monitor the crystallinity of the Fe/ZSM5 calc sample and to exclude significant formation of large iron oxidic phases during the synthesis. Spectra were recorded for 24 h in order to obtain a good signal-to-noise ratio.

XAFS experiments were performed to characterize the local environment around Fe.

### 2.3 XAFS data collection and analysis

The X-ray absorption spectra of the Fe K edge (7112 eV) were collected at Hasylab (Hamburg) wiggler station X1.1. A Si (111) double crystal monochromator was used after detuning to 50% maximum intensity in order to avoid higher harmonics present in the X-ray beam. The measurements were collected in transmission mode using ionisation chambers filled with Ar to obtain a X-ray absorbance of 20% in the first ion chamber and of 80% of the remaining radiation in the second one. A Fe foil was measured using a third ionisation chamber.

The samples were pressed into self-supporting wafers calculated to have an absorbance ( $\mu x$ ) of 2.5. All the samples were mounted and measured in a controlled atmosphere cell [9].

A list of the measurements together with the description of the chemical pretreatments and the environmental conditions of the sample are shown in Table1.

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Table 1  
XAFS spectra: pretreatments and measuring conditions

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Measurements	Pretreatment	Environment	Temperature
1) Fe/ZSM5calc L.N.	He, 120°C, 50 ml/min	static He	L.N.
2) Fe/ZSM5calc-CO L.N.	5% CO/He 350°C, 50 ml/min	static He	L.N.
3) Fe/ZSM5calc-O <sub>2</sub> -350	20% O <sub>2</sub> /He 350°C, 50 ml/min	20% O <sub>2</sub> /He	350°C
4) Fe/ZSM5calc-iC <sub>4</sub> H <sub>10</sub> -350	20% O <sub>2</sub> /He 350°C, 50 ml/min	20% i-C <sub>4</sub> H <sub>10</sub> /He	350°C

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Following a specific pretreatment (30 min), X-ray absorption spectra were collected: (1,2) at liquid nitrogen temperature under static He; (3) *in-situ* at 350°C under a flowing mixture of 20% O<sub>2</sub> in He (overall flow of 50 ml/min); (4) *in-situ* at 350°C under a flowing mixture of 20% i-C<sub>4</sub>H<sub>10</sub> in He (overall flow of 50 ml/min).

All the *in-situ* spectra were recorded after preconditioning the samples under the flowing reactants at 350°C for 1h.

The analysis of the XAFS data was performed following the procedure described in [8]. Please note that we re-examined the Fe-Fe reference-file used in this previous paper. This lead to different values for the Fe-Fe inner potential correction ( $\Delta E_0$ ) and for the Debye-Waller factor ( $\Delta\sigma^2$ ) in the EXAFS analysis of Fe/ZSM5 calc LN and Fe/ZSM5 calc-CO LN. Errors in the parameters obtained by the analysis are estimated to be 10% in the coordination number (N), 1% in the distance (R), 5% in the Debye-Waller factor ( $\Delta\sigma^2$ ) and 10% in the inner potential correction ( $\Delta E_0$ ) [10].

## 2.4 Catalytic testing

The Fe/ZSM5 sample after calcination (Fe/ZSM5 calc) was tested for the selective catalytic reduction of NO with isobutane in a plug-flow reactor (i.d.=1.2 cm). The catalyst was pelletized, crushed and sieved to 70-100 mesh. An amount of 100 mg of the sample was diluted with 4 g of quartz and charged in the reactor. The sample was preheated to 350°C under a He flow of 100 ml/min with a rate of 5°C/min. The reaction feed was obtained by blending four flows, *i.e.*, 1% NO/He, 1% iC<sub>4</sub>H<sub>10</sub>/He, O<sub>2</sub>, balance He. Each flow-rate was regulated by a digital Brooks mass-flow controller. The resulting inlet composition was 2000 ppm NO, 2000 ppm iC<sub>4</sub>H<sub>10</sub>, 3% O<sub>2</sub>, balance He, with an overall flow of 140 ml/min. Based on an apparent zeolite density of 0.5 g/cm<sup>3</sup>, the calculated gas hourly space velocity (GHSV) was 42000 h<sup>-1</sup>.

A Perkin Elmer Autosystem XL gas chromatograph equipped with a TCD detector was used to monitor the effluent N<sub>2</sub>, iC<sub>4</sub>H<sub>10</sub>, N<sub>2</sub>O, CO and CO<sub>2</sub>. In order to be able to measure NO and NO<sub>2</sub> a Thermo Environmental Instruments 42C NOx chemiluminescence analyzer was connected in parallel with the gas chromatograph. The GC and the NOx analyzer could be operated simultaneously.

## 3. RESULTS

In Table 2 the elemental composition of the starting support and of the Fe/ZSM5 catalyst is shown (ICP analysis). By introducing the iron in a H/ZSM5 support with a Si/Al molar ratio lower than 20 a typical Fe/Al molar ratio of 1 was achieved.

Table 2: elemental composition (ICP)

samples	Si/Al (molar ratio)	Fe/Al (molar ratio)
H/ZSM5	17.0	-
Fe/ZSM5 calc	17.0	0.98

The XRD spectra of the samples H/ZSM5 and Fe/ZSM5 calc were identical, indicating that the crystallinity of the starting support was retained and that no new large oxidic phases were formed during the synthesis procedure.

The results of the catalytic test performed for the selective catalytic reduction of NO with isobutane under excess oxygen are depicted in Fig.1. In agreement with the literature [1] a maximum conversion of NO to  $N_2$  was obtained at a temperature of about 350°C. The

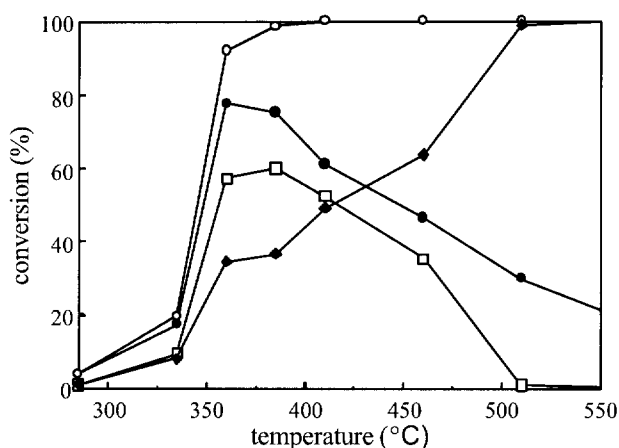


Fig. 1. Selective catalytic reduction of NO over Fe/ZSM5 calc (0.2% $iC_4H_{10}$ +0.2%NO+3% $O_2$ ) GHSV 42000  $h^{-1}$ . Conversion of (●)NO to  $N_2$ , (□) $iC_4H_{10}$  to CO, (◆) $iC_4H_{10}$  to  $CO_2$ , (○) $iC_4H_{10}$  to CO and  $CO_2$ .

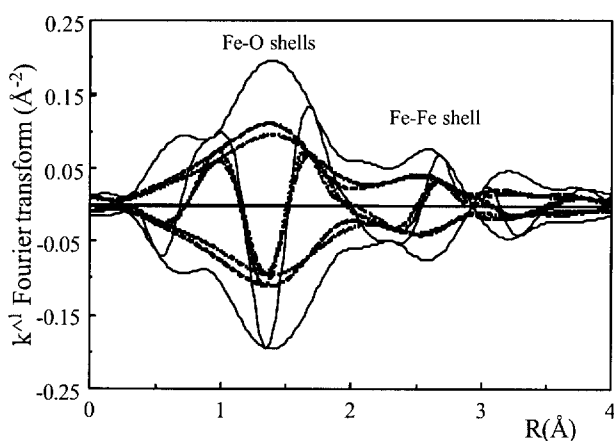


Fig. 2. Fourier Transforms ( $k^1$ ,  $\Delta k=2.7-10\text{\AA}^{-1}$ ) of EXAFS data of Fe/ZSM5 calc-L.N.(solid line), Fe/ZSM5 calc- $O_2$ -350(dashed line) and Fe/ZSM5 calc- $iC_4H_{10}$ -350(dashed-dotted line)

maximum  $N_2$  yield was around 78%, confirming the high activity of this material. Both  $N_2O$  and  $NO_2$  were absent from the products, the selectivity towards  $N_2$  being complete. On the other hand, a considerable amount of CO (60% yield) was formed as a result of the incomplete  $iC_4H_{10}$  combustion.

In Fig.2 a comparison between the Fourier Transforms of the Fe/ZSM5 sample measured under static He at L.N. temperature (Fe/ZSM5 calc L.N.) and *in-situ* at 350°C, in an oxidizing (Fe/ZSM5 calc- $O_2$ -350) and in a reducing atmosphere (Fe/ZSM5-calc- $iC_4H_{10}$ -350), is presented. The Fourier Transforms show two major contributions, one located around 1.4Å and one at 2.6Å. While the latter corresponds to the Fe-Fe contribution, the former represents the oxygen environment around the iron. Both signals (Fe-O and Fe-Fe) appear broadened and decreased in intensity when the spectra were recorded at 350°C. This is ascribed to the large increase of the Debye-Waller factor due to the high measuring temperature.

By comparing the spectrum of Fe/ZSM5-calc- $O_2$ 350 with that of Fe/ZSM5-calc- $iC_4H_{10}$ 350, it appears that after reduction the intensity of the overall Fe-O contribution is lower, and that it is located at a slightly higher distance from the iron. Moreover, noticeable changes are observed in the imaginary part of the

Fourier Transform at around 1.8 Å. The results of the EXAFS data analysis are collected in

Table 3. In the same table also the results of the analysis for the measurement Fe/ZSM5 calc-CO L.N. (see Table 1) are presented.

Table 3: EXAFS data analysis of: Fe/ZSM5calc-LN, Fe/ZSM5calc-CO-LN, Fe/ZSM5calc-O <sub>2</sub> -350, Fe/ZSM5calc-iC <sub>4</sub> H <sub>10</sub> -350						
Shells	N (±10%)	R (Å) (±1%)	$\Delta\sigma^2$ (10 <sup>-3</sup> Å <sup>2</sup> ) (±5%)	$\Delta E_0$ (eV) (±10%)	k <sup>1</sup> variance (%)	
					Im. Part	Abs. Part
Fe/ZSM5 calc L.N.						
					0.4	0.2
Fe-O1	2.0	1.97	-3.4	-0.6		
Fe-O2	1.1	1.85	-3.7	8.5		
Fe-O3	1.1	2.16	-3.0	-8.6		
Fe-Fe	1.1	3.07	-3.8	-7.1		
Fe/ZSM5 Calc-CO-L.N.						
					0.3	0.2
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	3.05	-4.9	-6.2		
Fe/ZSM5 calc-O <sub>2</sub> -350						
					0.8	0.3
Fe-O1	2.0	1.97	3.8	-1.8		
Fe-O2	1.1	1.86	6.1	11.4		
Fe-O3	0.8	2.37	17.3	2.0		
Fe-Fe	1.1	3.06	6.3	-4.9		
Fe/ZSM5 calc-iC <sub>4</sub> H <sub>10</sub> -350						
					0.8	0.3
Fe-O1	2.0	1.97	6.1	-1.8		
Fe-O2	1.1	1.88	14.7	13.8		
Fe-O3	0.5	2.66	8.0	1.5		
Fe-Fe	1.1	3.05	5.8	-7.2		

The effect of the temperature mentioned above is clearly visible in the increased Debye-Waller factors of all the *in-situ* measurements.

Three different Fe-O shells and one single Fe-Fe shell were identified in all cases. The coordination number of the Fe-Fe shell is within the limits of accuracy equal to 1,

demonstrating the presence of stable binuclear iron oxo/hydroxo-complexes. The first oxygen shell of these complexes (Fe-O1) contains two oxygen atoms, while the second (Fe-O2) consists of only one oxygen neighbor. The structural parameters (N and R) of these two Fe-O shells and of the Fe-Fe contribution are not significantly affected by any of the reducing treatments (Fe/ZSM5 calc-CO L.N. and Fe/ZSM5 calc-iC<sub>4</sub>H<sub>10</sub>-350).

On the contrary, the Fe-O3 shell is largely affected by the environmental conditions and by the treatments. While a slight decrease in the Fe-O3 coordination number is visible at 350°C under 20% O<sub>2</sub>, striking changes are caused by the reductants: in both the cases (Fe/ZSM5-calc-CO-LN and Fe/ZSM5-calc-iC<sub>4</sub>H<sub>10</sub>-350) a 50% oxygen removal was detected,

accompanied by a shift in the distance of the remaining Fe-O3 contribution towards a higher distance. This shift appeared to be much larger for the measurement Fe/ZSM5 calc-iC<sub>4</sub>H<sub>10</sub>-350 (Fe-O3 distance =2.66Å) than for Fe/ZSM5-calc-CO-LN (Fe-O3 distance =2.37Å).

In order to be able to correlate the decrease in the Fe-O3 contribution with the changing in the oxidation state of the iron, the recorded XANES spectra have been depicted in Fig.3. The spectra of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (Fe<sup>3+</sup>) and of iron-titanate (Fe<sup>2+</sup>) are also included as internal references ( $\Delta E$  Fe<sup>2+</sup>→ Fe<sup>3+</sup>=4.5 eV). Figure 3 shows that the edge position of the iron (calculated at 60% of the absorption jump) in the as-

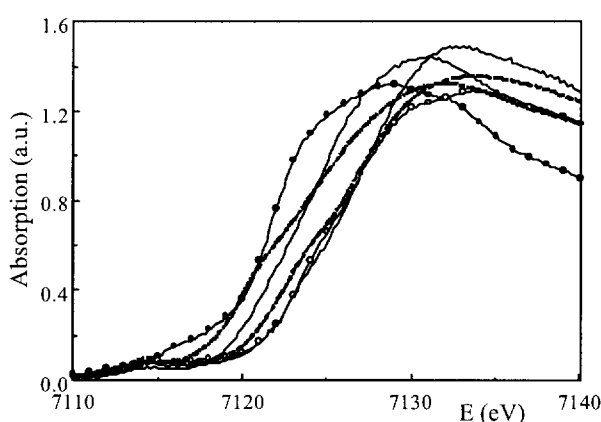


Fig.3. XANES spectra of Fe/ZSM5-calc-LN (thick solid line), Fe/ZSM5-calc-O<sub>2</sub>-350 (dashed line), Fe/ZSM5-calc-iC<sub>4</sub>H<sub>10</sub>-350 (dashed dotted line), Fe/ZSM5-calc-CO-LN (thin solid line); Fe<sup>2+</sup> reference (●), Fe<sup>3+</sup> reference (○)

synthesized Fe/ZSM5-calc sample measured at L.N. temperature overlaps with the one of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, being 3+. By measuring the sample under O<sub>2</sub> at 350°C a slight reduction is detected (note that a precise comparison is complicated by the change in the shape of the spectra with the recording temperature). On the other hand, according to the above-mentioned striking decrease in the intensity of the Fe-O3 shell, both the CO pretreatment and the in situ reduction with iC<sub>4</sub>H<sub>10</sub> caused a Fe-edge shift towards a lower energy of around 2.7 eV. Therefore the oxidation state of iron in both the reduced samples appeared to be slightly higher than 2+.

#### 4. DISCUSSION

The present contribution represents the continuation of a study whose final goal is the determination of the structure of the active iron phase for the selective catalytic reduction of NO with hydrocarbons in Fe/ZMS5 obtained through the FeCl<sub>3</sub> sublimation technique. In a previous paper [8] we demonstrated that the iron in this material is largely present in the form of binuclear oxo/hydroxo complexes. This result was obtained through the analysis of the XAFS spectrum of a calcined Fe/ZSM5 sample (Si/Al molar ratio=17) measured in static He at L.N. temperature. The presence of a single Fe-Fe shell and of three different Fe-O

shells (measurement denoted in the present contribution as Fe/ZSM5-calc-L.N.) was observed (Table 3). Besides, we monitored the reactivity of these complexes by measuring the Fe/ZSM5 sample (also under static He at L.N) after a reduction pretreatment with 5%CO in He at 350°C. The EXAFS data analysis revealed the reactivity of only one of the three oxygen shells (FeZSM5-calc-CO-L.N., see Table 3).

On the basis of the success of these experiments we have decided to continue our study by:

- 1) testing the catalytic activity of the as-synthesized Fe/ZSM5 sample under a typical HC-SCR feed (Selective Catalytic Reduction with HydroCarbons), in order to get a confirmation that our sample was indeed capable of the same performances reported in the literature for this material [1-4];
- 2) investigating the structure and the changes occurring in the iron complexes *in-situ*, i.e., in the presence of the reactants and at reaction temperature. For this purpose, XAFS spectra of the Fe/ZSM5-calc sample have been recorded at 350°C under a net oxidizing atmosphere (20% O<sub>2</sub> in He; sample denoted as FeZSM5-calc-O<sub>2</sub>-350) and in the presence of a typical HC-SCR reductant (20% iC<sub>4</sub>H<sub>10</sub> in He; FeZSM5-calc-iC<sub>4</sub>H<sub>10</sub>-350).

#### 4.1 Catalytic testing

The catalytic test has confirmed the high activity of our sample towards the selective catalytic reduction of NO with isobutane (feed composition and GHSV were chosen in order to be able to compare our results with the ones already available in the literature [1]). As appears in Fig.1, the maximum conversion of NO to N<sub>2</sub> is obtained at a temperature of 350°C, with a maximum N<sub>2</sub> yield of around 78% and a total selectivity towards N<sub>2</sub>. A large amount of CO is typically formed as a result of the incomplete combustion of iC<sub>4</sub>H<sub>10</sub>. The present results are very similar to the ones presented in [1] and confirm that the sample studied through the XAFS spectroscopy is indeed highly active for the selective catalytic reduction of NO.

#### 4.2 *In-situ* XAFS spectroscopy

By comparing the results of the EXAFS analysis (Table 3), a clear increase in the Debye-Waller factor is visible for the measurement performed *in-situ* at 350°C. Nevertheless, the analysis shows that it is indeed possible, by using XAFS spectroscopy, to analyze the structure and to track the changes occurring in the Fe-complexes even at this temperature. This arises by comparing the analysis of the measurements Fe/ZSM5-calc-L.N and Fe/ZSM5-calc-O<sub>2</sub>-350 (as-synthesized Fe/ZSM5 catalyst measured at different temperatures), and the measurements Fe/ZSM5-calc-CO-L.N and Fe/ZSM5-calc-iC<sub>4</sub>H<sub>10</sub>-350 (reduced Fe/ZSM5 catalyst measured at different temperatures).

The analysis of the first two measurements reveals hardly any differences in the structural parameters (N and R) of the binuclear Fe-complexes: only a slight decrease in the coordination number of the most distant (Fe-O3) shell is visible at 350°C, accompanied by a small increase in the shell distance. These slight changes are probably due to an autoreduction process occurring at high temperature in the most reactive shell of the complexes. An autoreduction process for this material has already been reported in the literature [2,5]. In this case this phenomenon is surprisingly detectable even under a net oxidizing atmosphere.

Effects similar to the ones recorded at L.N. after the pretreatment with CO (FeZSM5-calc-CO-L.N) are visible for the sample reduced with isobutane and measured at 350°C (Fe/ZSM5-calc-iC<sub>4</sub>H<sub>10</sub>-350). Also in this case, the Fe-Fe coordination number remains equal to 1, underlining the stability of the binuclear iron-clusters. Furthermore, a reduction in the

oxidation state of the iron is clearly visible in the XANES spectrum, together with a 50% decrease in the coordination number of the most distant (Fe-O3) oxygen shell, while no differences are visible in the two other Fe-O shells. The changes in the Fe-O3 contribution can be ascribed to both a removal of oxygen from this highly reactive shell (note that in the same shell a slight autoreduction process was detected at 350°C even under an oxidizing atmosphere) and to the formation of carbonaceous deposits in the proximity of the iron. This could represent an explanation for the large increase in the Fe-O3 distance after reduction. Note that the carbon deposition in the sample is consistent also with the change of its color: from a starting yellow/brown to a final light gray, after the measurement.

## 5 CONCLUSIONS

The analysis of the EXAFS spectra of a Fe/ZSM5 catalyst prepared through the FeCl<sub>3</sub> sublimation technique (Si/Al molar ratio=17) measured *in-situ* in a net oxidizing atmosphere (350°C, 20%O<sub>2</sub>/He) reveals the presence of binuclear iron oxo/hydroxo-complexes. Three Fe-O shells and a single Fe-Fe shell with a coordination number equal to 1 have been identified. By applying an *in-situ* reduction treatment at 350°C with 20% iC<sub>4</sub>H<sub>10</sub> in He, a decrease of around 50% in the Fe-O3 coordination number is found, accompanied by a clear increase in the Fe-O3 distance, while no other changes in the complexes are visible. This establishes that only the oxygen present in this shell is reactive. The present findings represent a confirmation of previous results (measurements recorded at L.N. temperature) [8] and demonstrate the possibility of XAFS of studying the local environment around iron in Fe/ZSM5 under experimentally realistic conditions (*in-situ*, at 350°C).

The same Fe/ZSM5 sample measured with XAFS shows a very high activity towards the selective catalytic reduction of NO with isobutane with excess oxygen. Both the activity and the selectivity towards N<sub>2</sub> are equal to the ones already measured in other studies under the same experimental conditions.

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