



Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

<http://193.49.43.2:8080/smis/servlet/UserUtils?start>

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Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



	Experiment title: Interaction of N ₂ O with iron catalysts – in situ EXAFS and XANES study	Experiment number: 01-01-606
Beamline: BM01b	Date of experiment: from: 26 september 2002 to 1 october 2002	Date of report: 2 march 2004
Shifts: 15	Local contact(s): Dr. Hermann Emerich	<i>Received at ESRF:</i>

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Report:

Introduction

Iron zeolites can be prepared by different methods, i.e. (i) hydrothermal synthesis, (ii) ion-exchange and (iii) chemical vapour deposition. The preparation method has an influence on the catalytic properties of the materials in N₂O-decomposition, selective catalytic reduction and benzene oxidation. Goal of the present XAS was to compare the structural features of iron zeolites prepared by the three above-mentioned methods and to relate these features to the catalytic activity of the materials in N₂O decomposition.

Experimental

Table 1 shows a list of the samples which were investigated in this XAS study. The samples were pressed into pellets, placed into the EXAFS cell and treated at 673 K in O₂. Subsequently an EXAFS spectrum was recorded at 77 K. EXAFS analysis was carried out using the IFEFFIT software.¹ Reference files were calculated with FEFF 8.1.² S₀² was calibrated using an experimental reference spectrum of Fe₂O₃.

Table 1 Preparation of the iron zeolites

Catalyst	Preparation	Fe %	Fe/Al
ZSM-5 CVD	CVD of FeCl ₃	4.0	1.1
ZSM-5 CVD st	+ steaming		
ZSM-5 IEA	Ion-exchange of FeCl ₂	0.8	0.25
ZSM-5 IEA st	+steaming		
ZSM-5 HT	Hydrothermal synthesis	1.0	0.35
ZSM-5 HT st	+ steaming		
ZSM-12 IEM	Ion-exchange of FeSO ₄	1.6	0.65
ZSM-12 IEM st	+ steaming		

Results

All catalysts exhibited a rather weak EXAFS signal. The spectra were fitted with only one single Fe-O and one single Fe-Fe shell. This two-shell fit enabled a direct comparison of the average Fe-O and Fe-Fe coordination numbers of all the samples. In cases where the data quality allowed the use of a second Fe-O or second Fe-Fe shell, the sum of the Fe-O and Fe-Fe coordination numbers obtained in these fits did not deviate much from the values obtained in the two-shell fit. This assured us that the lumping of all oxygen and iron neighbours into one common backscattering function did not produce erroneous results. The Debye-Waller factors of these lumped shells were very high, however, indicating a large spread of the Fe-O and the Fe-Fe distances, i.e. a high structural disorder. The Fe-O coordination number was between 4 and 5 for all catalysts. The average Fe-O distances were also similar. The Fe-Fe coordination number decreased from Fe-ZSM-12 IEM st and Fe-ZSM-5 HT st (CN ~ 4.0) to Fe-ZSM-5 CVD st (CN ~ 3.5) to Fe-ZSM-5 CVD and Fe-ZSM-5 IEA (CN ~ 2). The steamed catalysts generally had larger Fe-Fe coordination numbers (see Figure 2 and 3). The coordination number can be seen as a measure for the degree of clustering of the iron atoms. The EXAFS spectrum of the as-synthesized Fe-ZSM-5 HT could be fit with only one Fe-O shell. Its coordination number was 2.8. For iron atoms, which are incorporated into the ZSM-5 framework a value of four would be expected. The discrepancy may be due to the fact that a fraction of the iron species was not in framework positions, but in amorphous clusters with a more distorted coordination. An even lower coordination number (CN = 1.5) was obtained for the calcined sample. Similar results were recently found by Berlier et al. and ascribed to the large heterogeneity of the iron species in the calcined sample.³

The fit of Fe-ZSM-5 IEA (st) yielded a rather high Fe-Fe coordination number with a large error margin. Choi et al. recently reported an EXAFS analysis of a very similar sample⁴ and pointed out that the peak between 2.5 and 3.0 Å in the radial distribution function should be attributed to backscattering by Al and not by Fe. We could fit our spectra equally well with an Al-shell, a Fe-shell or a combination of both. Due to the narrow k-range available for fitting, no firm conclusions could be drawn about the type and number of neighbours in the second coordination shell of iron in these samples.

We also analysed the pre-edges of the iron zeolites. Absorption in the pre-edge is due to a dipole-forbidden $1s \rightarrow 3d$ transition. Its intensity and position can yield additional information on the oxidation state and coordination geometry of iron.^{5,6} The as-synthesized Fe-ZSM-5 HT had a very sharp and intense pre-edge peak at 7114.5 eV, due to the tetrahedral coordination of the iron atoms in the zeolite framework. All the other samples had a less intense pre-edge peak, also at 7114.5 eV. Differences between the samples could not be detected. None of the pre-edge peaks had a shoulder at higher energies, which is characteristic for Fe_2O_3 -clusters.⁷ For all catalysts, the intensity of the peak was higher than that of $Fe(acac)_3$, with octahedral coordination. We can infer that the iron atoms in our catalysts did not have centrosymmetric coordination, but an irregular, distorted coordination sphere.

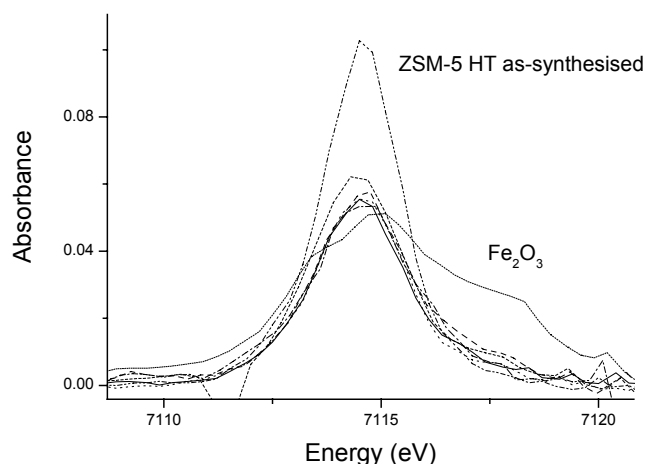


Figure 1 Preedges of the iron zeolites.

Table 2 Fit parameters of the EXAFS spectra: R = average distance, CN = coordination number, σ^2 = Debye-Waller factor, ΔE_0 = shift of E_0 compared to the reference.

Shell	R (Å)	CN	σ^2 (Å ²)	ΔE_0 (eV)
ZSM-5 CVD				
Fe-O	1.96	4.8 ± 0.5	0.011	-10.5
Fe-Fe	3.01	2.5 ± 1.1	0.014	
ZSM-5 CVD st				
Fe-O	1.98	4.3 ± 0.6	0.011	2.6
Fe-Fe	3.02	3.5 ± 1.2	0.011	
ZSM-5 IEA				
Fe-O	1.99	4.9 ± 1.1	0.012	-7.2
Fe-Fe	3.04	(2.1 ± 3.3)	0.016	
ZSM-5 IEA st				
Fe-O	1.99	5.0 ± 1.3	0.018	-5.8
Fe-Fe	3.06	(3.4 ± 3.5)	0.020	
ZSM-5 HT as				
Fe-O	1.84	2.8 ± 0.8	0.002	-11.4
ZSM-5 HT st				
Fe-O	1.97	4.1 ± 0.6	0.010	-4.6
Fe-Fe	3.03	4.1 ± 2.5	0.017	
ZSM-12 IEM st				
Fe-O	2.02	4.8 ± 0.8	0.009	3.8
Fe-Fe	3.04	3.9 ± 2.0	0.012	

Discussion

The iron zeolites prepared by the different methods listed in Table 1 exhibited similar structural features, indicated by the almost identical Fe-O and Fe-Fe distances and the similar pre-edge peak. Differences were only found in the average size of the iron clusters, reflected in the average Fe-Fe coordination number. Steaming always increased the average Fe-Fe coordination number, i.e. it led to a clustering of the iron atoms. The clustering was also observed by an increase of the intensity of bands below 35000 cm⁻¹ in the UV-Vis spectra, but could not be quantified from the visible spectra since the absorption coefficients are not known.⁸

The catalytic tests showed that the activity of the samples in N₂O decomposition increased after steaming.⁸ This cannot be related to the increase in the size of the iron oxide clusters, since larger iron oxide clusters have a lower turn-over-frequency. The increase in activity is attributed to the formation of Fe-O-Al clusters during the steaming process. In our spectra we could not find clear evidence for the existence of such clusters, possibly because they are only present as minority species. Moreover, the short k-range available for fitting did not allow for a very detailed analysis of the spectra.

Reaction of the catalysts with N₂O at 673 K had no effect on the EXAFS spectra. The oxygen atoms, which N₂O deposited on the catalyst surface were quickly exchanged with other surface oxygen atoms and became indistinguishable from each other.

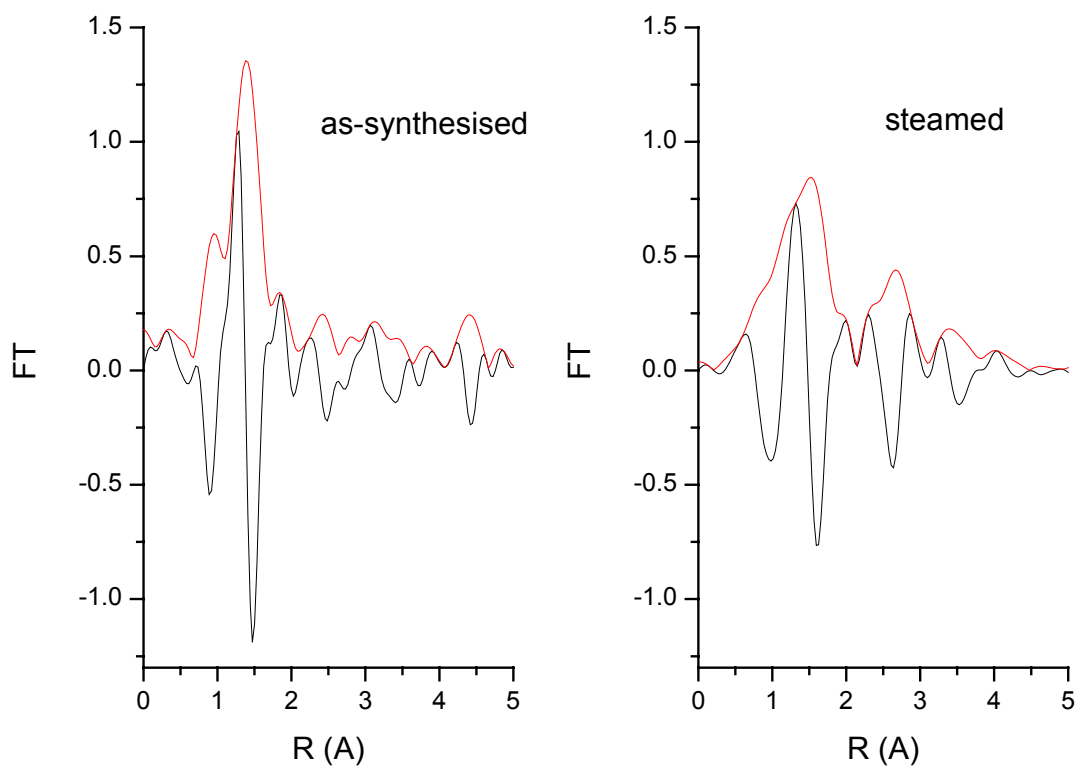


Figure 2 k^2 -weighted FT of Fe-ZSM-5 HT as synthesised and steamed.

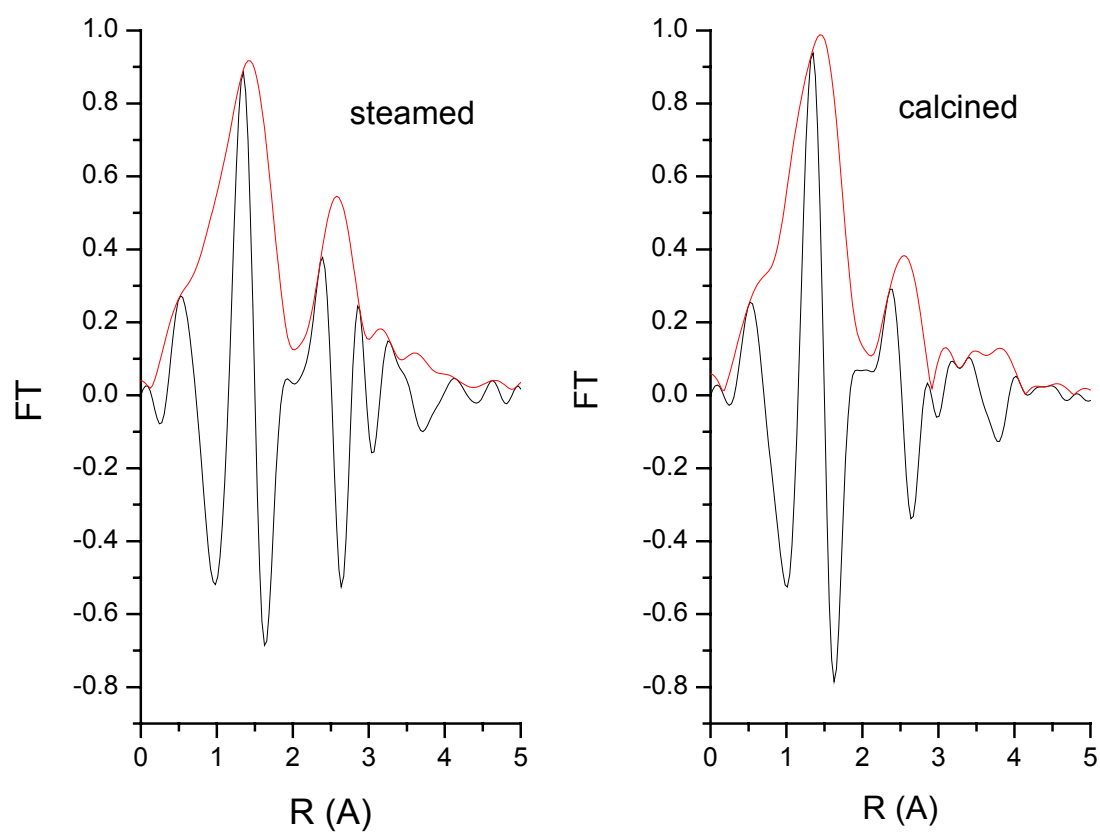


Figure 3 k^2 -weighted FT of Fe-ZSM-5 CVD calcined and steamed.

References:

- ¹ M. Newville, *J. Synchrotron Rad.* 8 (2001) 322.
- ² A.L. Ankudinov, B. Ravel, J.J. Rehr, S.D. Conradson, *Phys. Rev. B* 58 (1998) 7565.
- ³ G. Berlier, G. Spoto, P. Fisticaro, S. Bordiga, A. Zecchina, E. Giamello, C. Lamberti, *Microchem. J.* 71 (2002) 101.
- ⁴ S.H. Choi, B.R. Wood, J.A. Ryder, A.T. Bell, *J. Phys. Chem. B* 107 (2003) 11843.
- ⁵ P.E. Petit, F. Farges, M. Wilke, V.A. Sole, *J. Synchrotron Rad.* 8 (2001) 952.
- ⁶ T.E. Westre, P. Kennepohl, J.G. DeWitt, B. Hedman, K.O. Hodgson, E.I. Solomon, *J. Am. Chem. Soc.* 119 (1997) 6297.
- ⁷ L.X. Chen, T. Liu, M.C. Thurnauer, R. Csencsits, T. Rajh, *J. Phys. Chem. B* 106 (2002) 8539.
- ⁸ G.D. Pirngruber, M. Luechinger, P.K. Roy, A. Cecchetto, P. Smirniotis, submitted to *J. Catal.*