

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>

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

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Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

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: EXAFS characterisation of heterogenised Fe-complexes for methane to methanol oxidation	Experiment number: 01-01-281
Beamline: BM01b	Date of experiment: from: 17 july 2002 to: 20 july 2002	Date of report: 31 march 2003
Shifts: 9	Local contact(s): Dr. Wouter van Beek	<i>Received at ESRF:</i>

Names and affiliations of applicants (* indicates experimentalists):

Roel Prins, Gerhard Pirngruber*, Marco Lüchinger*, Lukas Frunz*, Pavel Kukula*

Institute for Chemical and Bioengineering, ETH Zürich

Wolfgang-Pauli-Str. 10

8093 Zürich, Switzerland

Report:

Introduction

It was reported that Fe-ZSM-5 catalysts, prepared by hydrothermal synthesis followed by steaming, react with N₂O to form an active surface oxygen species, which can even oxidise methane to methanol.¹ Analogies to the iron-based enzyme methane monooxygenase, which catalyses the conversion of methane to methanol in methanotrophic bacteria, were drawn. A later EXAFS analysis of a Fe-ZSM-5 catalyst, which was, however, prepared by a different method, seemed to confirm the structural similarity between the iron cluster in the zeolite and the iron core of the enzyme. It was found that the Fe-ZSM-5 contains, like the enzyme, a binuclear iron-cluster, in which the two iron atoms are connected with a (μ-O)₂-bridge.

In this experiment we studied in situ the interaction of the Fe-ZSM-5 catalyst with N₂O in order to identify the nature of the active surface oxygen species.

Experimental

Fe-ZSM-5 prepared by sublimation of FeCl₃ was pressed into a pellet and placed into the EXAFS cell. It was subjected to a series of treatments in O₂, He, H₂ and 1000 ppm N₂O at 400°C. The treatments were followed in situ with XANES and at the end of each treatment an EXAFS spectrum was recorded at 77 K. EXAFS analysis was carried out using the XDAP 2.3.3. software. Reference files were calculated with FEFF 8.1. Fe(acac)₃ was used for generating the Fe-O shell and Fe₂O₃ for the Fe-Fe shell. S₀² was calibrated using an experimental reference spectrum of Fe(acac)₃.

Results

Figure 1 shows the XANES-spectra after the treatments in O₂, He, H₂ and N₂O. Figure 2 shows the corresponding k²-weighted EXAFS spectra in R-space. Treatment in He led to a shift of the Fe K-edge to lower energies, indicating a slight reduction of Fe³⁺ to Fe²⁺. At the same time the intensity of the Fe-O shell in the EXAFS spectrum seemed to decrease. Treatment in H₂ led to a complete reduction to Fe²⁺. The Fe-O

shell shifted to longer distances and the intensity of the Fe-Fe shell decreased. The final treatment in N₂O reoxidised the iron clusters to Fe³⁺ and the final EXAFS spectrum resembled very much the original one obtained after treatment in O₂. Figure 3 compares the pre-edge peaks of the catalyst with Fe₂O₃. Intensity and shape of the pre-edge of the O₂ and N₂O-treated catalyst are inbetween those expected for a tetrahedral and octahedral coordination. A full analysis of the EXAFS spectra is reported hereafter.

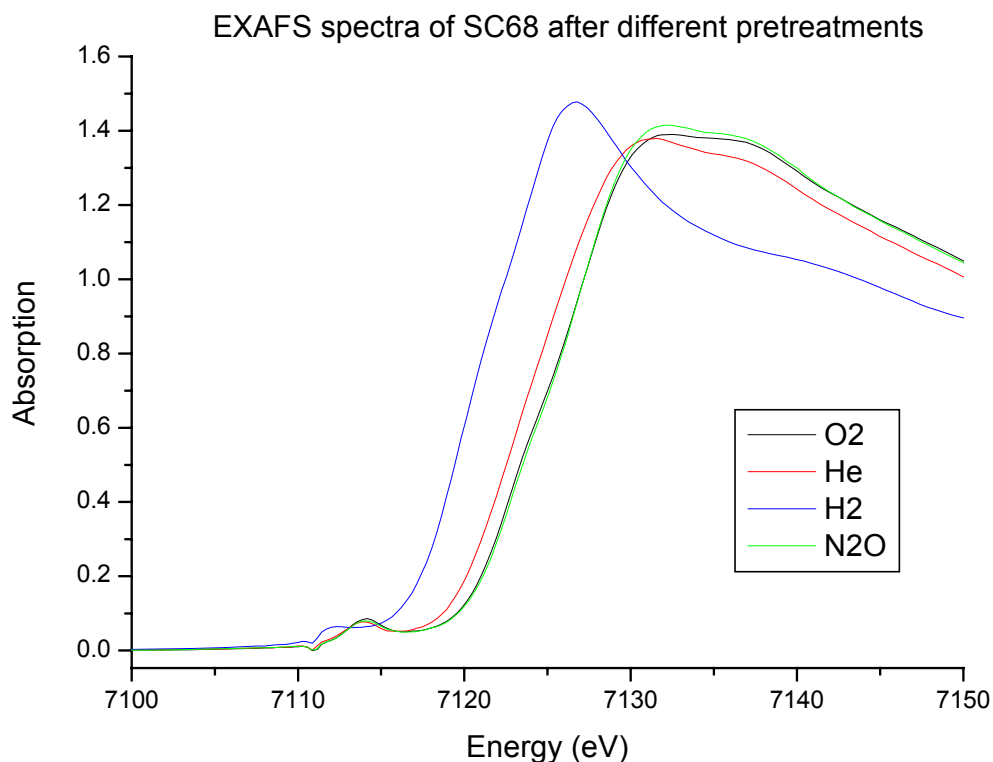


Figure 1 Normalized X-ray absorption of Fe-ZSM-5 after treatment in O₂, He, H₂ and N₂O, measured at 77K.

The EXAFS spectrum of the O₂-treated catalyst was fitted with three different shell combinations, (i) with 2 short-oxygen shells between 1.8 and 2.1 Å, (ii) with only one short oxygen shell and (iii) with one short and one long oxygen shell at 2.5 Å, representing lattice oxygen surrounding the iron cluster. In addition an iron shell at about 3 Å was always present. Model (i) gave the best representation of the data, especially at high k-values. The two short oxygen shells were, however, highly correlated and the distribution of intensity over the long and short distance depended strongly on the conditions used for the fit.¹

Table 1 Fit parameters of the spectrum of Fe-ZSM-5 after O₂-treatment. The k-range from 2.7 to 14 Å⁻¹ was transformed and fit in R-space from 0.8 to 3.0 Å.

Shell	N	σ^2	R	E ₀
Fe-O	2.77	0.0067	1.884	4
Fe-O	1.17	0.0010	2.015	3.85
Fe-Fe	1.32	0.0094	3.001	0

For fitting the EXAFS spectrum of the He-treated catalyst, a Fe-O shell at 2.5 Å was introduced in order to reproduce the features of the spectrum in the overlap region between the Fe-O and the Fe-Fe shells. A fit with short Fe-O shells only, as used above, could not reproduce this region of the Fourier-transform. The fit parameters are shown in Table 2. The quality of the fit is excellent, but a strong correlation between the second Fe-O shell and the Fe-Fe shell was observed.

¹ The presented fit results are fairly consistent since the fit did not run away when all parameter except the E₀ values and the distance of the Fe-Fe shell were left free. Moreover, similar values were obtained by fitting with k² and k³-weighting.

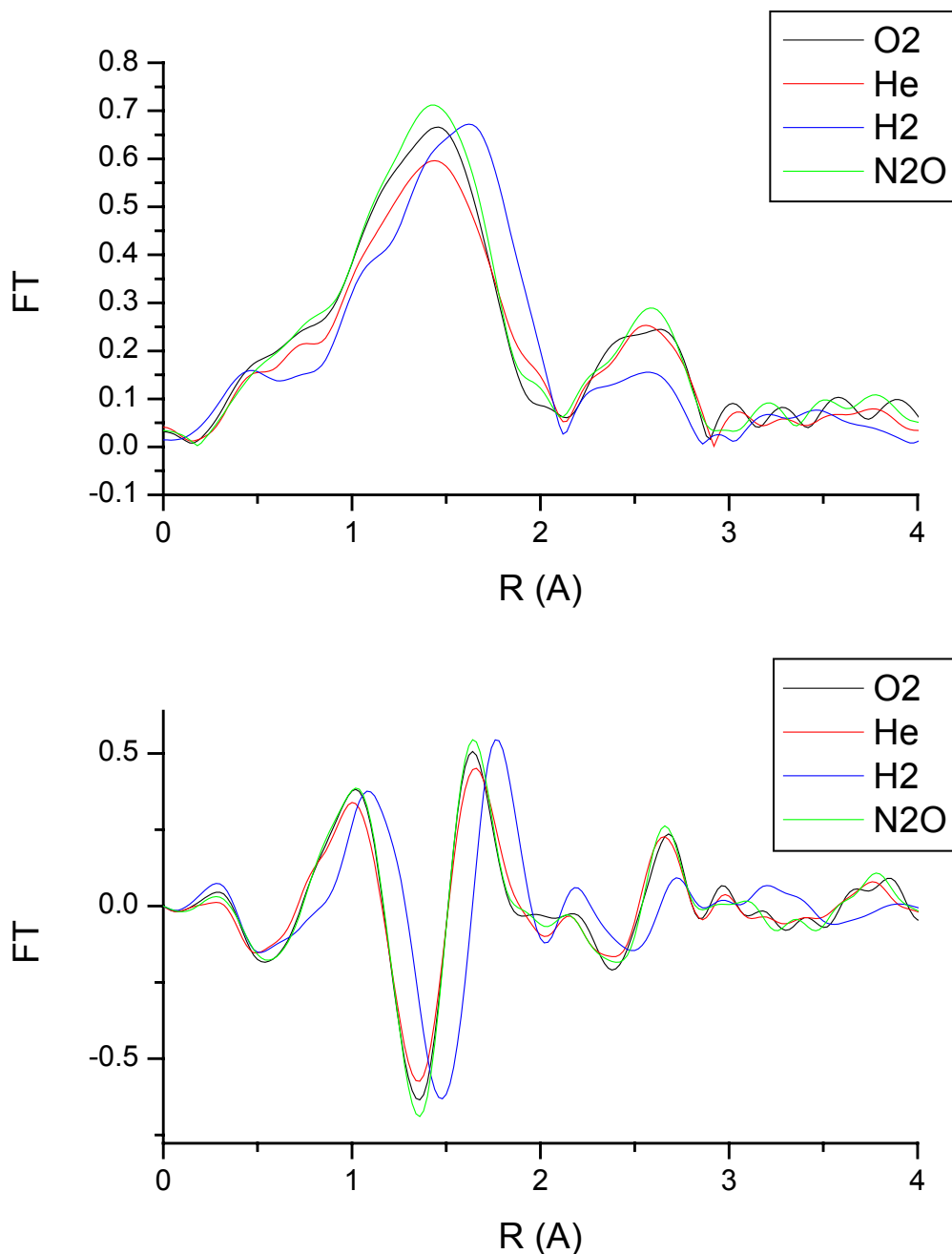


Figure 2 k^2 -weighted Fourier-transform of the spectra of Fe-ZSM-5 after treatment in O₂, He, H₂ and N₂O. Top: magnitude. Bottom: imaginary part.

Table 2 Fit parameters of the spectrum of Fe-ZSM-5 after He-treatment. The k -range from 2.7 to 12 Å⁻¹ was transformed and fit in R-space from 0.8 to 3.0 Å.

Shell	N	σ^2	R	E_0
Fe-O	4.57	0.0143	1.932	4
Fe-O	1.39	0.0107	2.5	4
Fe-Fe	1.61	0.0120	3.03	-5

Also the spectra after H₂- and N₂O-treatment could be fitted with the same shell-combination, i.e. one short and one long oxygen-shell. The H₂-treatment lead to an elongation of the Fe-O and the Fe-Fe distance. The

Fe-O coordination number increased and the Fe-Fe coordination number decreased.² The spectrum after N₂O-treatment could be fitted with almost the same parameters as those given in Table 2.

Table 3 Fit parameters of the spectrum of Fe-ZSM-5 after H₂-treatment. The k-range from 3.2 to 11 Å⁻¹ was transformed and fit in R-space from 0.8 to 3.2 Å.

Shell	N	σ^2	R	E ₀
Fe-O	6.51	0.0146	2.09	0
Fe-O	1.92	0.0075	2.5	4
Fe-Fe	0.94	0.0123	3.13	-5

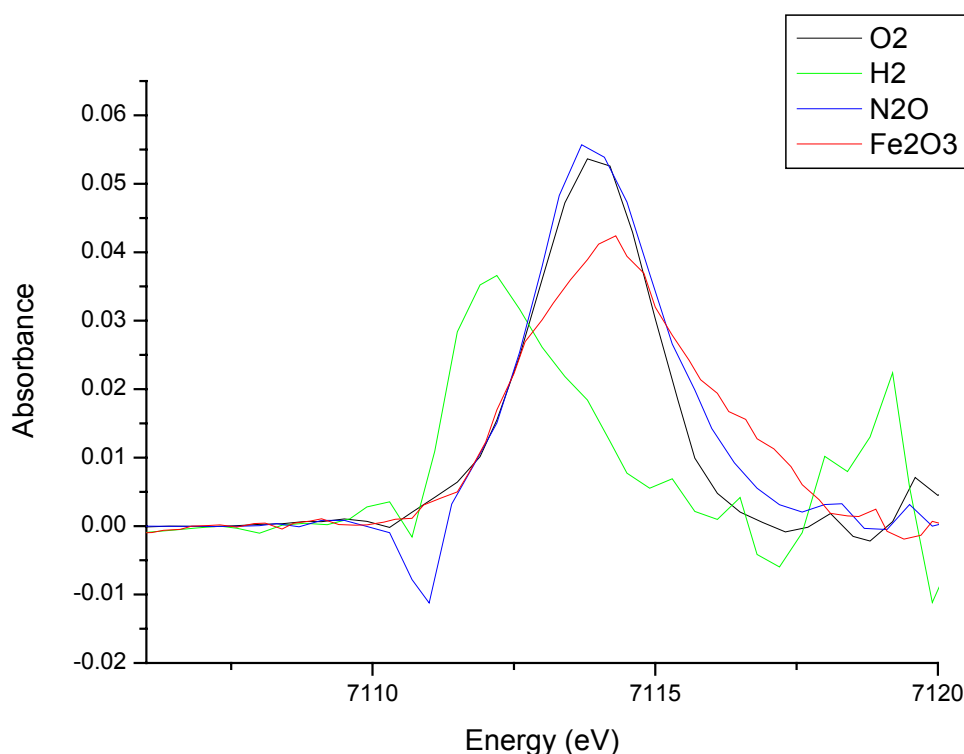


Figure 3 Pre-edge peak of Fe-ZSM-5 after treatment in O₂, H₂ and N₂O and of Fe₂O₃.

Discussion

Catalytic measurements with the Fe-ZSM-5 sample showed that the reactivity of the sample changed after exposure to N₂O.² We tried to correlate this with changes in the structure of the iron sites, in particular in the oxygen coordination. The quality of the data allowed fitting the spectrum of the N₂O-treatment only with one short Fe-O shell. For comparison with the original sample, we forced a second short Fe-O shell into the fit, but significant differences could not be found. EXAFS is therefore not sensitive enough to detect the changes in the structure of the iron clusters induced by the N₂O treatment.

Note that the Debye-Waller factors of all samples except for the original one are very high. That indicates a high structural disorder, i.e. a mix of clusters with different iron coordinations. The chemical treatments can further increase the structural disorder, if not all the iron clusters are affected in the same way. That might also explain why we were not able to track down specific changes in the structure of the oxygen coordination shell.

For the Fe-Fe shell a coordination number of 1.3 – 1.6 was found, which is higher than the coordination of 1, which was previously reported for these catalysts. This indicates that the catalysts does not exclusively contain binuclear clusters, but a mix of small iron clusters or chains. Upon reduction, however, the Fe-Fe coordination number was reduced to one and the Fe-O coordination number increased. Our tentative

² Also here the fit is consistent since all N and σ^2 values were allowed to vary against each other and similar values were obtained by fitting in k² and k³-space.

interpretation is that iron oxide chains, similar to those found in goethite,³ break up during reduction and form single binuclear iron clusters. The oxygen coordination number increased because the water formed during reduction remained bound to the iron cluster. When the H₂-treated catalyst was heated up, intensity shifts in the edge region were observed, which could be attributed to the desorption of water. This supports the explanation given above.

The glitches as well as the bad S/N ratio can be attributed to the fact that the measurements were carried out in 16-bunch mode. It cannot be stated whether a better S/N ratio (i.e. a longer k-range available for fitting) would yield more precise results as the system itself shows large disorder and is therefore difficult to analyse.

References:

¹ G.I. Panov, A.S. Kharitonov, V.I. Sobolev, *Appl. Catal. A* 98 (1993) 1.

² G.D. Pirngruber, "The surface chemistry of N₂O on iron zeolites", submitted to *J. Catal.*

³ A.A. Battiston, J.H. Bitter, F.M.F. de Groot, A.R. Overweg, O. Stephan, J.A. van Bokhoven, P.J. Kooyman, C. van der Spek, G. Vanko, D.C. Koningsberger, *J. Catal.* 213 (2003) 251.