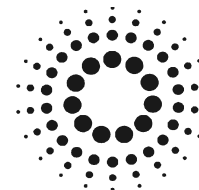


# EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON



## 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. This double-page report will be reduced by ESRF to a one page, A4 format, and will be published in the Annex to the ESRF Annual Report.

Should you wish to make more general comments on the experiment, enclose these on a separate sheet, and send both the Report and comments to the User Office.

When preparing your report, please follow the instructions below:

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- make sure the report does not exceed the space available; tables and figures may be included if you wish.
- for work which is published or which is in press, you may simply include a copy of the abstract together with full reference details. If the abstract is in a language other than English, ensure that you include an English translation.
- bear in mind that the report will be reduced to 71% of its original size. A type-face such as “Times”, 14 points, with a 1.5 line spacing between lines for the text produces a report which can be read easily.

Note that requests for further beam time must always be accompanied by a report on previous measurements.



	<b>Experiment title:</b> EXAFS characterisation of Fe species in zeolites and MCM41 materials	<b>Experiment number:</b> 01-01-272
<b>Beamline:</b> BM01B	<b>Date of experiment:</b> from: 02/11/2001 to: 06/11/2001	<b>Date of report:</b> 26/03/2002
<b>Shifts:</b> 12	<b>Local contact(s):</b> Wouter van Beek	<i>Received at ESRF:</i>

**Names and affiliations of applicants** (\* indicates experimentalists):

Prof. Roel Prins, Dr. Gerhard Pirngruber\*, Marco Lüchinger\*, Viviane Schwartz\*  
Laboratory of Technical Chemistry, ETH Zürich, CH-8093 Zürich, Switzerland

**Report:**

*Introduction*

Iron-zeolites attracted much attention for the removal of NO<sub>x</sub> and/or N<sub>2</sub>O from exhaust streams in the last years. In contrast to other materials, the iron catalysts do not seem to deactivate in the presence of water and SO<sub>2</sub>, which are always present in a real exhaust gas. There has been much discussion about the nature of the active species in iron-zeolites. Binuclear iron complexes, small iron clusters (on the order of a few nm) and also isolated iron ions were proposed to be the active sites. In many cases these conclusions were based on the activity of the catalysts in the selective catalytic reduction (SCR) of NO<sub>x</sub> with hydrocarbons. SCR is, however, not a very suited reaction to probe the intrinsic activity of the iron species. Factors like acid site density, diffusion of the hydrocarbon and coke formation play a big role, and may screen the actual role of the iron.

N<sub>2</sub>O decomposition is a much more suited reaction for probing the activity of the iron species. It is a clean reaction leading to N<sub>2</sub> and O<sub>2</sub>, with no side products and it runs exclusively on the iron-species. The pure zeolite has no or very little activity (this small activity is, in fact, often due to impurities of iron in the framework).

The aim of our work was to shed more light on the interaction of the iron catalyst with N<sub>2</sub>O. The structural changes of the iron sites upon interaction with N<sub>2</sub>O were probed by EXAFS and XANES. In situ XANES measurements were performed to measure the rate of oxidation of the iron sites by N<sub>2</sub>O under reaction conditions.

### Experimental

40 mg sample were placed in the EXAFS cell and reduced in flowing  $H_2$  at  $390^\circ C$  for 1h. The Fe-K edge EXAFS spectrum was then measured at liquid nitrogen temperature. Subsequently, the cell was connected to a flow of 45 ml/min  $N_2O/He$  (1000 ppm) and the temperature was increased from room temperature to  $400^\circ C$  with an increment of  $3^\circ C/min$ . The change in shape and position of the Fe K edge was continuously followed by XANES (stepsize 1 eV). Finally, the sample was cooled down again in He and another EXAFS spectrum of the now oxidised catalyst was measured at liquid nitrogen temperature.

The sample was reduced once more in flowing  $H_2$  at  $390^\circ C$  for 1h and cooled down to room temperature. Then the cell was heated ( $3^\circ C/min$ ) to  $350^\circ C$  in 45 ml/min He. At  $350^\circ C$  the inlet stream of the cell was switched from He to  $N_2O/He$  (1000 ppm) and the oxidation of the sample by  $N_2O$  was continuously followed by XANES. In cases where the oxidation rate at  $350^\circ C$  was very low the sample temperature was carried to  $400^\circ C$  to complete the oxidation.

The change of oxidation state of the samples was determined by the shift of the Fe K edge. The position of the edge was defined as the energy at half height of the edge.

### Results

For all tested samples a shift of the Fe K edge to higher energies was observed during treatment with  $N_2O$ , at temperatures between  $350^\circ C$  and  $400^\circ C$ . The rate of oxidation differed among the samples. Fe-ZSM-5 containing mainly small (binuclear) iron oxide clusters showed the highest oxidation rate, whereas samples containing mainly large hematite clusters reacted only slowly with  $N_2O$ .

Clear differences were also observed in the EXAFS spectra of the reduced and  $N_2O$ -oxidised materials. A detailed structural analysis of the data is under way. Qualitatively, the results indicate a much higher structural inhomogeneity in the reduced state of the iron clusters (see Figure 1). Note that the reduced state is the one, which can react with  $N_2O$  and is, thus, more relevant for catalysis.

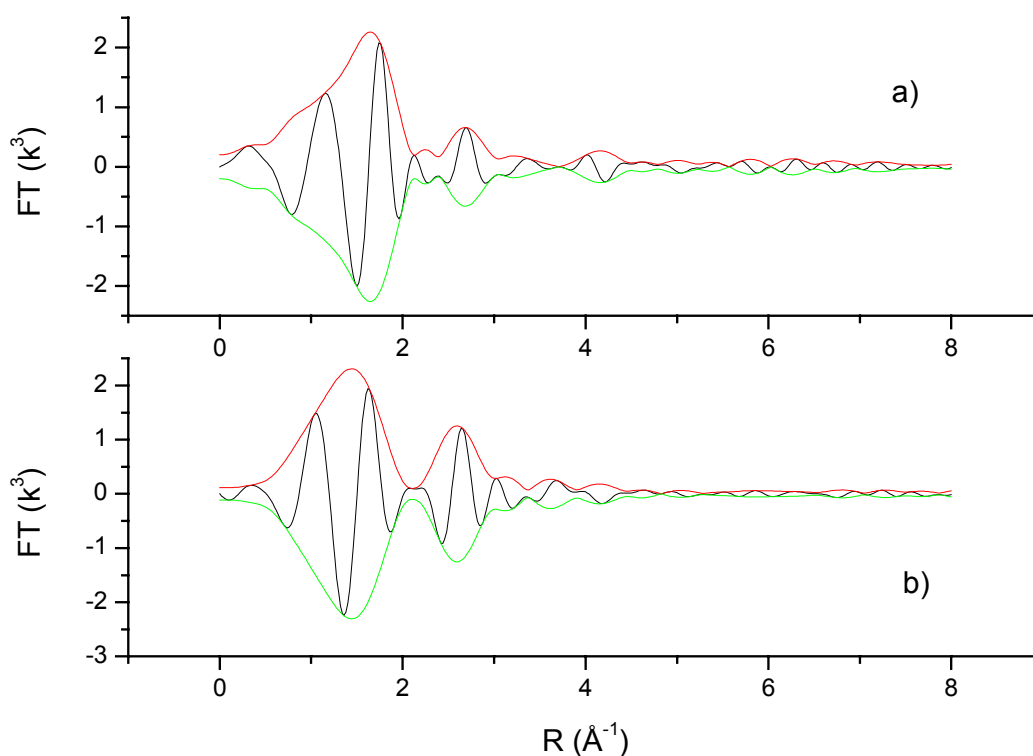


Figure 1) EXAFS spectra of Fe-ZSM-5 after reduction in  $H_2$  (a) and subsequent oxidation by  $N_2O$  (b).

