EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

ESRF

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

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

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.

ESRF	**Experiment title:** Probing important interactions between NOx species and the active sites within Cu based zeolite samples leading to better insight into the SCR deNOx process	**Experiment number**: CH-3160
Beamline: BM01B	**Date of experiment**: from: 10/2/2011 to: 15/2/2011	**Date of report**: 1/6/2012
Shifts: 15	**Local contact(s)**: Hermann Emmerich	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Dr A. M. Beale (University of Utrecht)*

Mr U. Deka (University of Utrecht)*

Dr I. Dacil González (University of Utrecht)*

Report:

NH_3-Selective Catalytic Reduction (NH_3-SCR) is a widely used technology for NO_x reduction in the exhaust of heavy duty diesel vehicles. Recently, it has been reported that Cu containing chabazite (Cu-CHA) shows both exceptional activity and hydrothermal stability as compared to other available zeolite supports for such purposes. Owing to its structure, CHA possesses one ion exchange site for Cu in the zeolite and thus simplifies active site interrogation. In this work, we examined the origin of SCR activity of Cu-CHA as evidenced from a combination of synchrotron based X-ray (absorption/diffraction) techniques.

Ex situ EXAFS experiments performed by us in the past already showed that isolated mononuclear Cu^{2+} cations located on the plane and slightly distorted from the center of the *d6r* sub-units of SSZ-13 are active sites of the catalyst after calcination. To study the active sites under realistic reaction conditions, we performed combined in situ XAFS/XRD experiments. These in situ studies show that these isolated copper active sites are maintained even under active SCR reaction conditions at 300^{o}C. However, XAFS and XRD data (Figure 1) revealed together a conformational change (from a square planar to a distorted tetrahedral type environment) as a result of a direct interaction of NH_3 with copper is seen at lower temperatures (125 ^{o}C) and correlates to a lower catalytic activity of the system at these temperatures. Figure 2 illustrates in more detail the changing environment for the active site at different temperatures under SCR conditions. This change in the co-ordination geometry is reversible at higher temperatures and was concurrent with observing maximum catalytic activity. The importance of this 'blocking' interaction in the catalytic cycle however is yet to be addressed. Combined spectroscopic studies focused within these (lower) temperature ranges and with altering reactant gas concentrations could reveal further valuable information on maximizing activity under these conditions.

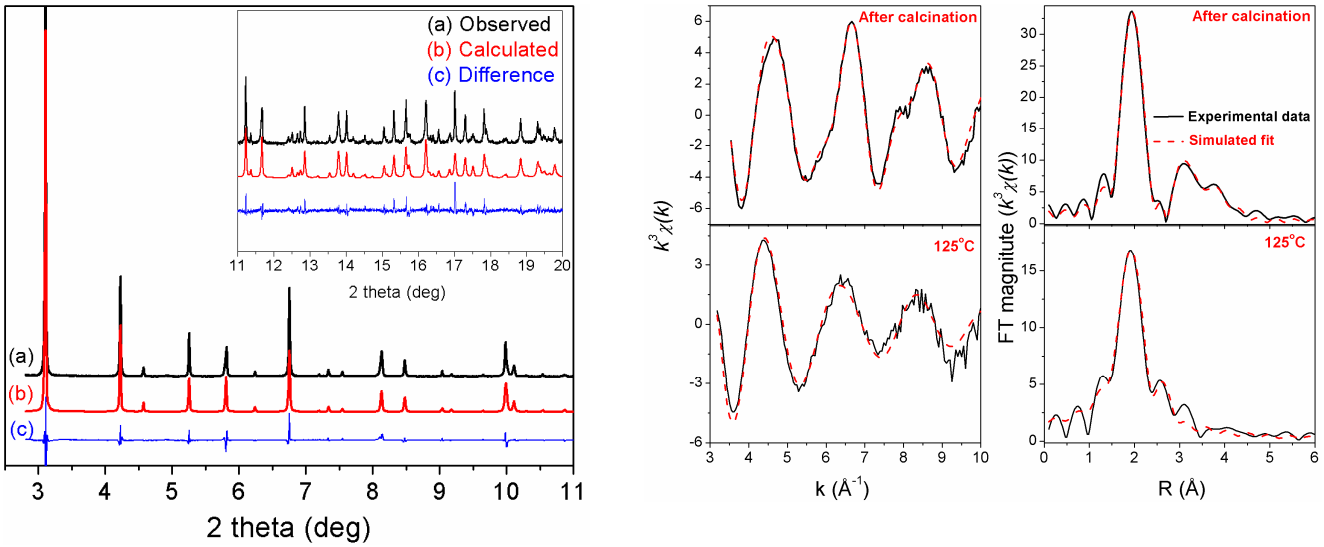

Figure 1. Left) Observed (black), calculated (red) and difference (blue) patterns obtained from the Rietveld refinement of X-ray diffraction collected on Cu-SSZ-13 under SCR reaction conditions at 300°C. The pattern has been magnified for clarification (inset) between 11-20 2theta. X-ray synchrotron radiation λ = 0.50117 Å; Space group: *R-3m*; Refined unit cell: a = b = 13.530 Å, c = 14.792 Å; Vol.: 2345.2 Å^3. Right) In situ Cu K-edge k^3-weighted EXAFS data (left) and corresponding Fourier transforms of the k^3 data (right) collected on Cu-SSZ-13 after calcination and at 125°C under NH_3-SCR conditions. Black solid lines represent experimental data and red dashed lines represent the simulated fits.

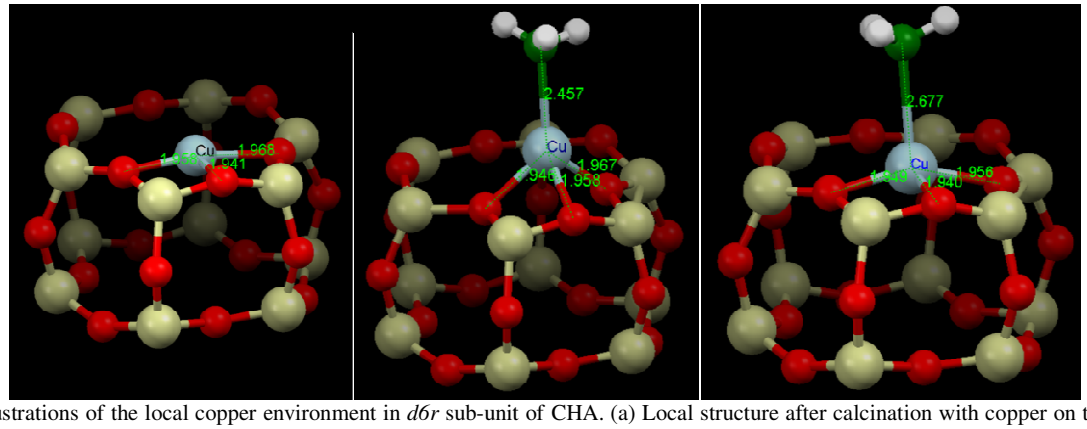

Figure 2. Illustrations of the local copper environment in *d6r* sub-unit of CHA. (a) Local structure after calcination with copper on the plane and slight distorted from the center of the *d6r* sub-unit of CHA; (b) interaction with NH_3 at ~125°C under SCR conditions resulting in a coordination geometry change; (c) under SCR conditions above 250°C.

The following publication resulted from this study:

Confirmation of Isolated Cu^{2+} Ions in SSZ-13 Zeolite as Active Sites in NH_3-Selective Catalytic Reduction
U.Deka et al. JOURNAL OF PHYSICAL CHEMISTRY C Volume: 116 Issue: 7 Pages: 4809-4818

In addition, data from this study were also used in the publication

Changing active sites in Cu–CHA catalysts: deNO_x selectivity as a function of the preparation method
U.Deka et al. Microporous and Mesoporous Materials http://dx.doi.org/10.1016/j.micromeso.2012.04.056