

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 via the User Portal:

<https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

Reports supporting requests for additional beam time

Reports can 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.



	Experiment title: X-ray Raman Spectroscopic Studies of Ammonia Synthesis and Decomposition Catalysts	Experiment number: CH4941
Beamline: ID 20	Date of experiment: from: 19.10.2016 to: 25.10.2016	Date of report: 05.03.2017
Shifts: 18	Local contact(s): Christoph Sahle	<i>Received at ESRF:</i>

Names and affiliations of applicants (* indicates experimentalists):

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Dr. Christoph Sahle - ESRF

Report:

The production of ammonia from inert dinitrogen is an essential process for all life forms. However, the detailed mechanism of how the triple bond of dinitrogen is activated by iron surfaces in the Haber-Bosch process has remained elusive and many open questions remain regarding the nature of formed surface nitrides, the oxidation state of the active iron and the role of promoters. XRS measurements allowed to obtain N K- O K- and Fe L-edges which provide information about both the surface and bulk composition of the catalyst studied and how this evolves at different stages of the catalyst lifetime.

During experiment CH4941 at beamline ID20, we obtained X-ray Raman data on series of ammonia synthesis and decomposition catalyst samples synthesized in the group of Prof. Malte Behrens at the University of Duisburg-Essen. The series of samples included calcined, reduced and spent catalyst after ammonia decomposition and after ammonia synthesis. The catalyst was present either in its pure form or was additionally impregnated with KNO_3 in the spinel state.

Figure 1 shows Fe L-edge data of the calcined catalyst in its pure form (cal) and impregnated with potassium (cal_ KNO_3). The spectra look similar and show no measurable influence of KNO_3 impregnation. Fe L-edges of both calcined samples are consistent with iron at Fe(III) oxidation state. Figure 2 shows the Fe L-edges of the catalyst at different stages of the reaction: calcined catalyst (cal), reduced catalyst in its pure form (red) and impregnated with potassium (red_ KNO_3), spent catalyst after NH_3 synthesis in its pure form (sy) and impregnated with potassium (sy_ KNO_3) and spent catalyst after NH_3 decomposition (de). One can see that unfortunately during transfer of the samples to the sample chamber two of the studied samples: red and sy_ KNO_3 partially oxidized to a form similar to the calcined samples. For the red and sy_ KNO_3 samples one can see that the average oxidation state of Fe is much lower, with α -Fe being major component of the sample. In spent catalyst after NH_3 decomposition one can see that Fe is present in oxidized form.

In Figure 3 oxygen K-edges of catalyst at different stages of reaction are presented. Spectrum of calcined sample shows a lot of similarity to the spectra of FeO and Fe₂O₃ suggesting that these two forms are major components of this sample. O K-edge spectra of the spent catalysts have similar shape to the spectrum of calcined sample, which may be another indication that samples oxidized during transfer or measurement. The different O K-edge spectral shapes of the reduced catalyst strongly suggest that FeO and Fe₂O₃ are no longer major forms of oxygen in these samples. The O K-edges of the reduced catalysts are consistent with binding of oxygen to magnesium probably either as MgO or as Mg_(1-x)Fe_xO.

Nitrogen K-edge spectra were hard to measure due to low intensity of incident beam in this energy region and because of low content of nitrogen in the measured samples. In Figure 4 the spectra of spent catalyst after NH₃ decomposition and a selected iron nitride reference (Fe_xN, x=2-4) (which was determined by Moessbauer spectroscopy to be mixture of Fe₃N and Fe₄N) are presented. The presence of N K-edge in spent catalyst is consistent with bulk nitridation in the catalyst during ammonia decomposition.

The presented data are, of our knowledge, the first XRS spectra collected for a real catalyst and they pave a way towards further in-situ studies of low-energy edges in ammonia synthesis and decomposition catalyst. Future studies will focus on optimizing the sample environment for controlled in situ studies.

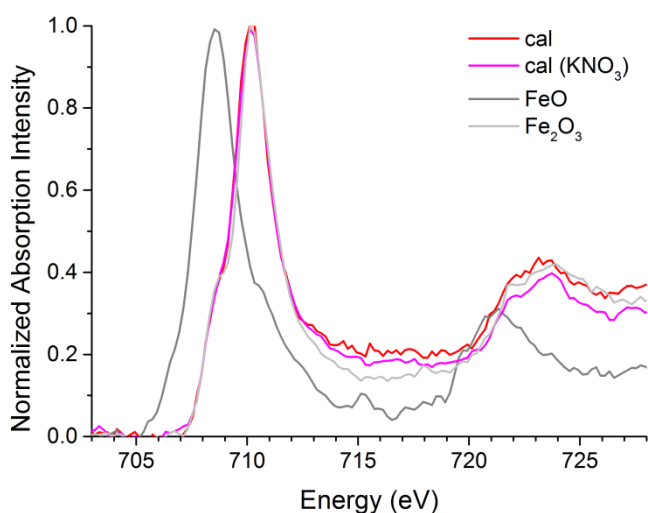


Figure 1. Fe L-edges of calcined catalyst (impregnated with KNO₃ and not impregnated) along with the edges of iron oxides.

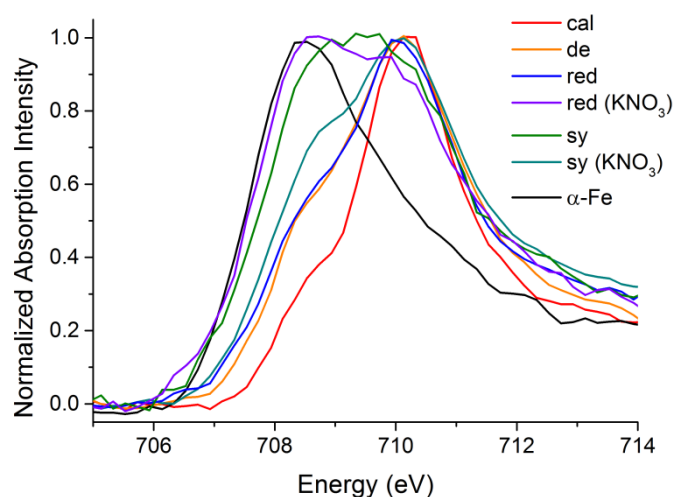


Figure 2. Fe L-edges of calcined, reduced and spent (after NH₃ synthesis and decomposition) catalyst (impregnated with KNO₃ and not impregnated).

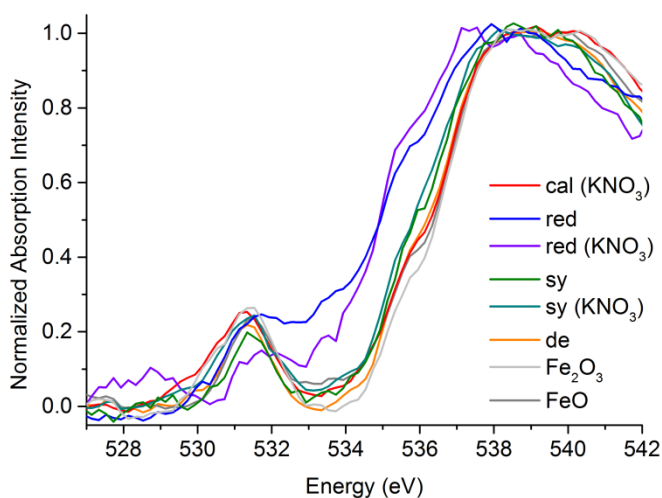


Figure 3. O K-edges of calcined, reduced and spent (after NH₃ synthesis and decomposition) catalyst (impregnated with KNO₃ and not impregnated).

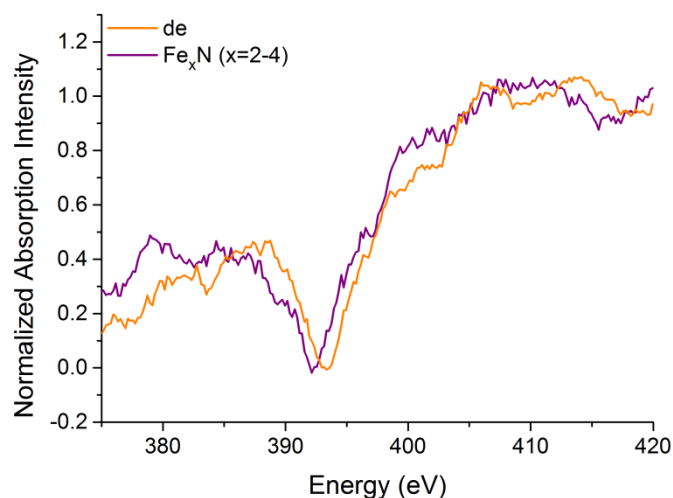


Figure 4. N K-edges of spent catalyst after NH₃ decomposition along with the edge of Fe_xN (x=2-4).