



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.



Experiment title: Development of zeolite supported polynuclear ruthenium complexes and their applications for controlled release of NO

Experiment number:
26-01-776

Beamline: BM26A	Date of experiment: from: 18/06/07 to: 22/06/07	Date of report: 22/08/07
Shifts: 9	Local contact(s): Dr. Serge Nikitenko	<i>Received at ESRF:</i>

Names and affiliations of applicants (* indicates experimentalists):

Kirschhock Christine (main proposer)

Smeekens Sylvia*

Verlooy Pieter*

Stuyven Bernard*

Department of Microbial and Molecular systems, Centre for Surface Chemistry and Catalysis, Kasteelpark Arenberg 23 B-3001 Heverlee

Report:

In order to describe the coordination number of the three Ru atoms in the complex and their ligands, EXAFS measurements were done in transmission mode on the Ru-K-edge (22,117 keV). The adsorption spectra of the samples were acquired between about 300 eV below and 1700 eV above the Ru-K-edge. Data analysis was done with an IFFEFIT package containing FEFF 6.0 and in collaboration with Dr. Ir. Moniek Tromp (University of Southampton). All the spectra were normalised after pre-edge and post-edge background removal. The EXAFS function $\chi(k)$ was then calculated from the remaining oscillations in the EXAFS range and Fourier transformed with respect to the distance to the absorbing Ru atom resulting in an atomic radial quasi distribution around Ru with maxima corresponding to the neighbouring shells of the Ru atoms. This EXAFS spectrum was fitted with one-shell or two-shell models to derive the local structure around Ru: the number of the nearest neighbours (N), the mean distance to them (R), and the distance mean-square fluctuation (σ^2) around R, as an indication of the degree of the structural disorder around the Ru atoms.

The samples were first measured in sealed capillaries but the amount of sample in these capillaries was too small to obtain sufficient signal to noise ratios. Therefore, larger amounts of sample were pressed into pellets. These were placed into an unsealed sample holder with kapton film as an X-ray transparent window. The experiments were performed at room temperature.

As reference samples served RuCl₃, RuO₂, RuO₂.H₂O, Ru-red, Ru(NH₃)₆Cl₃ and Ru(NO)(NO₃)₃.H₂O and Ru(5%) on alumina. The reference samples were diluted with dry CVB760.

The ruthenium complex in zeolite Y, obtained after an ion-exchange with RuCl₃ or Ru-red, were measured in several process stages (after pretreatment, after saturation with NO and after NO release). These samples were not diluted with CVB760.

The Fourier transform of $k^3\chi(k)$ for the RuO₂ is shown in Figure 1. The first main maximum corresponds to the nearest neighbours of Ru: two O atoms at 1.942 Å and four O atoms at 1.986 Å in the TiO₂-like structure of RuO₂. The EXAFS standard characteristics of Ru-O were theoretically calculated with the FEFF code. The

Fourier transforms for the RuNaY samples after pretreatment are shown in Figure 1. The similarity of the Fourier Transform for RuO₂ and the same position of the first maximum suggest a RuO₂-like environment around Ru in the zeolite. When these Fourier transforms are back-transformed to *k*-space, the EXAFS spectra could be successively fitted with a two-shell model. This two-shell model consists of a Ru-O and a Ru-Ru contact. The contact distance of Ru-O is 1.972 ± 0.016 Å, the coordination number is 6.24 ± 0.894 and $\delta\sigma^2$ is 0.003 ± 0.0017 . The contact distance of Ru-Ru is 3.561 ± 0.012 Å, the coordination number is 5.239 ± 0.226 and $\delta\sigma^2$ is 0.002 ± 0.001 .

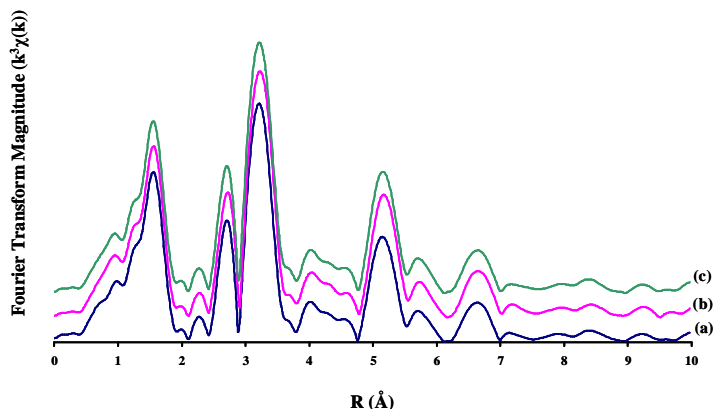


Figure 1: FT ($k^3\chi(k)$) of the EXAFS spectra of Ru(3%)NaY after pretreatment started with RuCl₃ as Ru source (a), Ru-red as Ru source (b) and the reference material RuO₂ (c).

Figure 2 shows the Fourier transforms of the RuNaY samples after NO adsorption and after NO release. The spectra after NO release are the same as the spectra after NO adsorption. There is also no difference between the samples started with RuCl₃ or Ru-red as Ru source. When these Fourier transforms are back-transformed to *k*-space, the EXAFS spectra could be totally fitted with a one-shell model consisting of Ru-Ru contact. The contact distance is 2.678 ± 0.0018 Å, the coordination number is 10.32 ± 0.08 and $\delta\sigma^2$ is 0.005 ± 0.0001 . This Ru-Ru distance is in agreement with that of Ru metal particles. Because the whole *k*-space spectra could be fitted with this model, we can conclude the ruthenium complex is no longer present in the zeolite. It is known the complex is stabilized by water. Activation / deactivation diffraction studies have shown that increased temperatures in the absence of water lead, depending on the oxidizing conditions at the sample, either to RuO₂ or Ru-metal. Measurement of the samples in an unsealed environment, obviously has the same effect as thermal treatment under dry conditions. The EXAFS study could thus verify the reason of deactivation of the material but failed to characterize the active complex. Measurements in improved sample environment will have to be performed to fully characterize the active species.

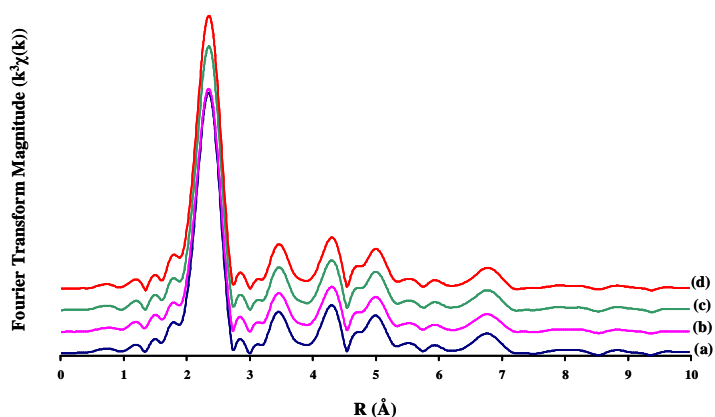


Figure 2: FT ($k^3\chi(k)$) of the EXAFS spectra of RuNaY with RuCl₃ as Ru source after NO adsorption (a) after NO release (b) and with Ru-red as Ru source after NO adsorption (c) and after NO release (d).

