



**DUTCH-BELGIAN BEAMLINE
AT ESRF**

**EUROPEAN
SYNCHROTRON
RADIATION FACILITY**



Experiment Report Form

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.

(next page)

**Experiment title:****Investigation of the copper and cerium surroundings in CuO-CeO₂/Al₂O₃ catalyst by XANES and EXAFS****Experiment****number:****26-01-732**

Beamline:	Date(s) of experiment: From: 09-11-2005 To: 14-11-2005	Date of report: 30-08-2006
Shifts:	Local contact(s): Dr. Serge NIKITENKO	
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Report: (max. 2 pages)

The main goal of our proposal was to determine the local structure of Cu and Ce in the CuO-CeO₂/Al₂O₃ commercial catalyst and their structural and electronic changes during in-situ oxidation and reduction. Therefore, a XAS study in transmission mode, for Cu K and Ce L_{III} edge (8979 and 5723 eV, respectively) was envisaged.

To reach the goal, the following strategy was proposed:

- 1) catalyst as such;
- 2) after full oxidation (675 K, 5 or 10 vol% O₂/He, 100ml/min, 15 min);
- 3) during reduction with propane: 2 series (5 and 10 vol% C₃H₈/He, 100ml/min), at increasing temperature from 500 K to 675 K, 25 K per step;
- 4) re-oxidized catalyst (675 K, 5 or 10 vol% O₂/He, 100ml/min, 15 min).

This proposed strategy was adapted during the experimental campaign. Some changes were done, regarding the composition of reducing and re-oxidizing mixtures and temperature window for reduction. Eventually, different mixtures of propane in He and oxygen in He were used. Moreover, taking the advantage of Quick-scan XAFS mode (1 or 5 min), more experiments were performed within an enlarged temperature window for reduction. For the Cu K edge, beside the influence of temperature for in-situ reduction under propane flow, other influences were studied as follows:

- Influence of different pre-treatment procedures:
 - Heating and cooling under He flow;
 - Pre-adsorbed propane;
 - Pre- and re-oxidation.
- Influence of heating rate under reducing conditions
- Influence of partial pressure of propane
- Influence of propane space time.

The analysis of obtained data was performed and the following findings can be reported.

Firstly, a visual comparison of the shape of the spectra obtained for catalyst as such and references, at RT, under air, was done. The references measured were Cu foil, Cu₂O, and CuO for Cu K edge, while for Ce L_{III} edge Ce powder (in mineral oil), CeO₂ and CeF₃ were available.

Results are presented in Fig. 1 and 2. As it can be seen, for the studied catalyst the possible oxidation state of Cu is 2+, while for Ce is 4+.

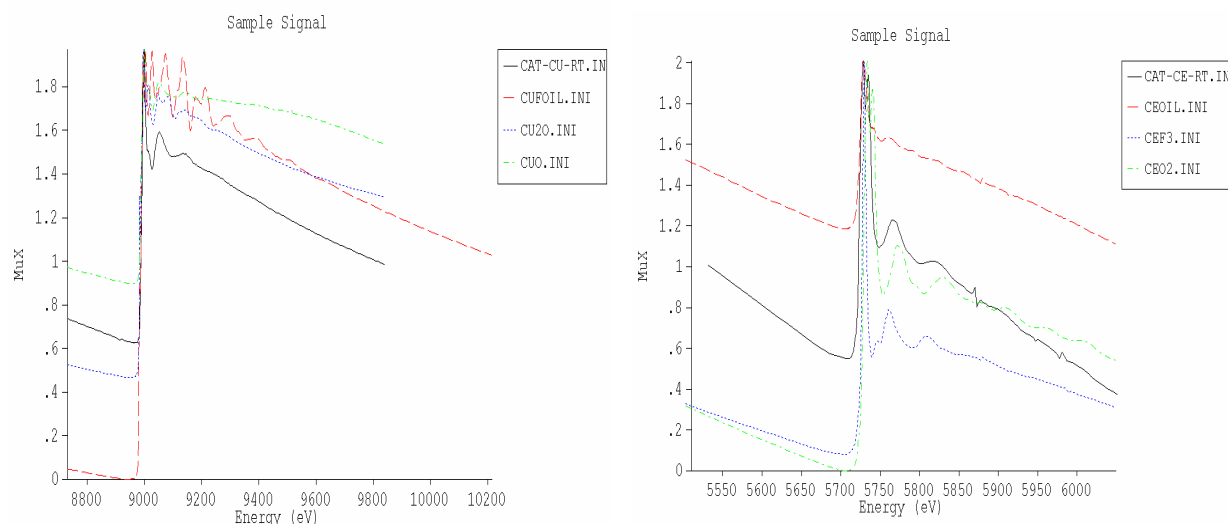


Fig. 1. Cu K edge: catalyst as such and references at RT under air

Fig. 2. Ce L_{III} edge: catalyst as such and references at RT under air

The heating and the cooling under He flow do not affect the state of the catalyst.

The temperature at which the copper species can be reduced seems to depend on the heating rate, on the amount of the pre-adsorbed propane on the surface, on the partial pressure of propane, and on the initial state of the catalyst (fresh or re-oxidized). Fig. 3 presents the changes of a re-oxidized catalyst, over which a mixture of 2vol% propane in He was flushed for 15 min at 150°C, followed by a very fast heating, 15 min from 150°C to 400°C, under the same mixture.

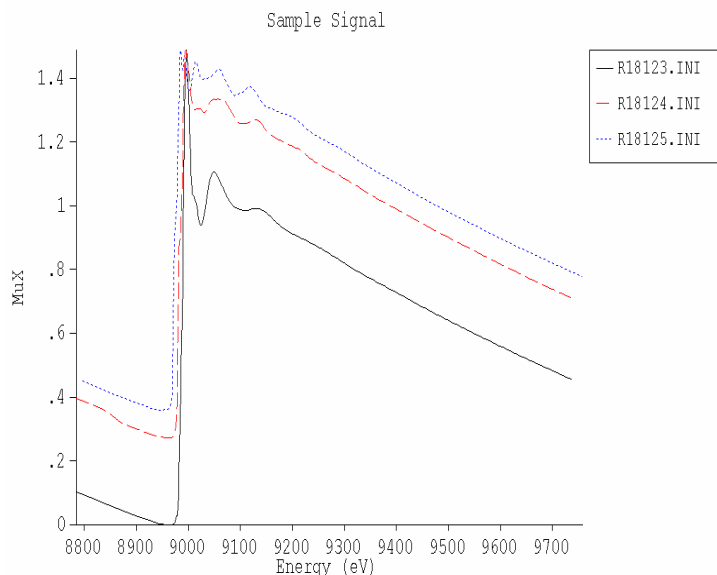


Fig.3. Cu K edge: Sample 8 after flushing (PA 2% in He), 15 min at 150°C, followed by very fast heating to 400°C (about 15 min), 3 fast scans; R18123.INI was taken at 225°C, R18124.INI at 369°C, while R18125.INI was taken at 400°C.

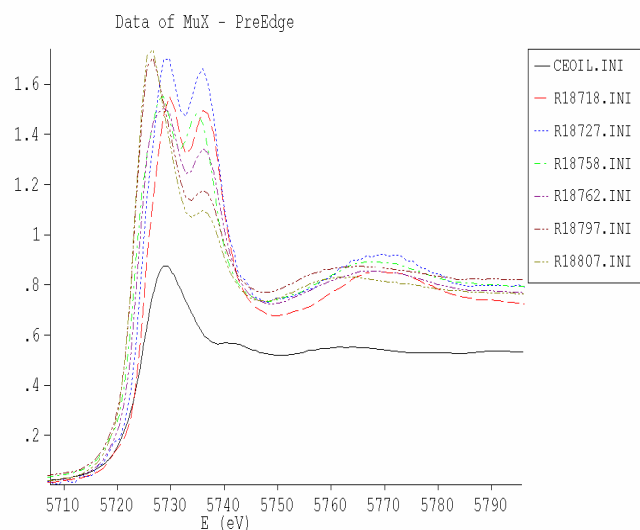


Fig. 4. Ce L_{III} edge- catalyst sample under He flushing at RT for 15 min, heating from RT to 150°C manually (very fast) under He flow, flushing with 1.431 l/min (PA 2% in He) flow for 15 min, heating under 460 ml/min (PA 2% in He) flow , with 5°/min, plus Ce oil reference.

As regarding the cerium reduction, Fig. 4. presents the changes suffered by the catalyst sample when it was heated under a 2vol% propane in He flow from 150°C to 600°C, with a heating rate of 5°/min.

As it can be seen, spectra start to change between curves R18758.INI and R18762.INI (corresponding sample temperatures 340 and 363°C, respectively).

Concerning the re-oxidation of the catalyst, this occurs very fast (almost instantaneously) under the XAS experimental conditions.

Secondly, the EXAFS data reduction was performed with the XDAP software. The pre-edge background was subtracted using a modified Victoreen curve whilst the atomic background was subtracted using a cubic spline routine. The spectra were normalized by division of the absorption data by the value of the edge step at 50 eV above the edge position. Results on local Cu structure as prepared, after propane reduction, and during the propane reduction were presented during the 13th International Conference on X-ray Absorption Fine Structure (XAFS13), held in Stanford, CA, USA, July 9-14, 2006 and are in press in the Proceedings published by The American Institute of Physics. The abstract of this paper was as follows:

“A CuO_x-CeO_x/Al₂O₃ catalyst was studied with in-situ transmission Cu K XAS for the total oxidation of propane as model reaction for the catalytic elimination of volatile organic compounds. The local Cu structure was determined for the catalyst as such, after pre-oxidation and after reduction with propane. The catalyst as such has a local CuO structure. No structural effect was observed upon heating in He up to 600°C or after pre-oxidation at 150°C. A full reduction of the Cu²⁺ towards metallic Cu⁰ occurred, when propane was fed to the catalyst. The change in local Cu structure during propane reduction was followed with a time resolution of 1 min. The $\chi(k)$ scans appeared as linear combinations of start and end spectra, CuO and Cu structure respectively. However, careful examination of the XANES edge spectra indicates the presence of a small amount of additional Cu¹⁺ species.”

The corresponding Cu K-edge XANES spectra are given in Figure 5.

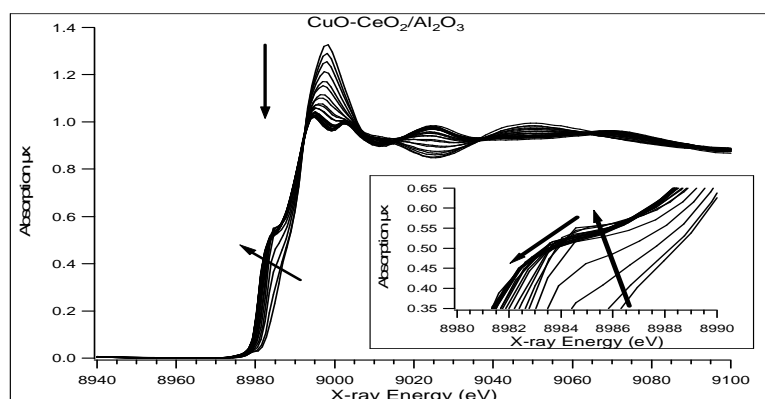


Fig. 5. XANES spectra for the CuO_x-CeO_x/Al₂O₃ catalyst during propane reduction, 1 minute measuring time per spectrum. The inset shows a detail around the edge structure (evidence for the presence of Cu¹⁺).