



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>

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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

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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: Propane total oxidation over CuO-CeO₂/Al₂O₃ catalyst. Structural and kinetic characterization: Energy dispersive X-ray absorption spectroscopy coupled with mass spectrometry.

Experiment number:
MA-317

Beamline: ID 24	Date of experiment: from: 2-5-2007 to: 8-5-2007	Date of report: 31-8-2007 <i>Received at ESRF:</i>
Shifts: 18	Local contact(s): Dr. Mark Newton	

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Report:

The aim of the experiment was to investigate the dynamic behavior of the CuO-CeO₂/Al₂O₃ catalyst under working conditions, using as a probe reaction the total oxidation of propane and focusing on the transient regime of the catalytic reaction. Basically, the experiment consists of imposing step impulses on the catalytic system using fast switching 4-way valves and to follow the reactor effluent as a function of time by on-line mass spectrometry, while simultaneously probing the catalyst structure using energy dispersive XANES in transmission mode at the copper K edge.

To carry out these measurements, an in-situ/operando cell was constructed in our laboratory with a design that resembles the operation of a reactor under plug flow conditions^[i, ii]. A scheme of this microreactor cell is given in Figure 1 together with the flow sheet of the experimental setup. The “heart” of this experimental cell consists of two capillary tubes mounted horizontally on the setup. One of the reactor tubes is used for the catalyst sample, while in the other one a reference material can be loaded. In this experiment, the capillaries used were made out of either beryllium (ID = 2mm, OD = 6.35mm) or quartz (ID = 1mm, OD = 1.2mm).

Before starting the reaction experiments, the grounded catalyst (< 20 μm) was loaded in the experimental cell and was generally pre-treated as follows. First, the catalyst was heated under He flow from room temperature to 413 K. Next, the catalyst was kept at 413 K under air or oxygen flow during approximately one hour. At last, the catalytic system was further heated in a He flow until it reached the first reaction temperature. Depending on the sequence of the step impulses, the isothermal transient experiments that were attempted can be divided in the following categories:

- He|→5% C₃H₈/He : reduction of the catalyst under flow of propane
- He|→5% O₂/He : re-oxidation of the catalyst under flow of oxygen in He
- He|→{0.83% C₃H₈-4.17% O₂}/He : reaction under simultaneous flow of propane and oxygen in He

These experiments were performed at four different temperatures (namely 623K, 673K, 723K, 773K) under atmospheric pressure and with typical flow rates of 5% C₃H₈/He between 30 to 50 ml/min. The amu's that were followed with the mass spectrometer during the experiment were 4, 12, 18, 22, 28, 29, 32, 41, 42, and 44. For the XANES analysis, as the raw XAS data were in pixels of the camera, energy calibration was done using a Cu foil measured in eV (with edge position at 8979 eV). Determination of the edge position, background subtraction and normalization of the calibrated raw data was done with Athena^[iii]. Moreover, a linear combination fit (LCF) has been applied for the region around the edge (-20 eV to 50 eV) to quantify the ratio of Cu²⁺/Cu¹⁺/Cu⁰, using the spectra of the oxidized and reduced catalyst sample (after the treatment with propane) and additionally a Cu₂O reference taken from another beamline (i.e. BM26).

As this was the first attempt to combine the use of a reactor cell with energy dispersive XAS measurements, some important preliminary technical observations were made concerning the performance of the experimental setup.

- At ID24 energy dispersive XANES spectra were obtained for the catalytic system within a timescale of 0.1s (see Figure 2a, 9wtCu_01). The noise that appears in the spectrum is of statistical nature as an increase of the accumulation time of the final spectrum leads to a decreased noise (see Figure 2a, 9wtCu_02). Although the catalyst could be loaded as such (i.e. no dilution) in the quartz capillaries of 1mm inner diameter, obtaining spectra of good quality for this configuration, this was not the case for the beryllium capillaries of 2mm inner diameter (too much absorption from the catalyst, self absorption effect), and the catalyst had to be diluted in a ratio of at least 1:1 cat/BN (see Figure 2b). However, as the quartz tubes were very fragile, it was only possible to use the beryllium capillaries in the transient experiments, thus making necessary the dilution of the catalyst.
- In order to pass the X-ray beam through the reactor, beryllium windows were placed on both sides of the reactor oven. However, as it can be seen in Figure 3b, the use of beryllium windows resulted in a decreased signal-to-noise ratio. Therefore, it was decided to remove the beryllium windows and to replace them with kapton foil, which proved to have no negative effect on the spectra.
- Energy dispersive measurements are usually normalized using air as reference (I₀) measurement. A reference material, 10% CeO₂/Al₂O₃, was also tested. As it is observed in Figure 3a, although the noise of the spectrum using this technique is less, some important features at the XANES region are diminished while in other regions (further from XANES) some other features in the spectra are introduced by normalizing the signal of the catalyst with that from the reference material. As these effects could not be easily accounted for, it was decided not to use a reference material.

Nonetheless, for the transient experiments the following findings can be reported. As it can be seen in Figure 4, the reduction and reoxidation evolution of the catalyst was visible in the XANES spectra, for the isothermal transient experiments. Moreover, these XANES spectra show the reversability of the redox cycles. Based on the LCF analysis, a small amount of Cu¹⁺ (below 10 %) appears in the transient regime during the transition from Cu²⁺ to Cu. Additionally, from this analysis it is found that the reoxidation of the catalyst occurs faster than its reduction for the investigated temperature range and this becomes more pronounced at lower temperatures (at 773 K $t_{2/3(\text{red})}/t_{2/3(\text{ox})} \approx 3$, while at 673 K $t_{2/3(\text{red})}/t_{2/3(\text{ox})} \approx 6$). Finally, it has to be mentioned that during the last type of experiments, a simultaneous flow of oxygen and propane could not be established over the catalyst bed mainly due to the large backpressure that existed after the mass flow controllers.

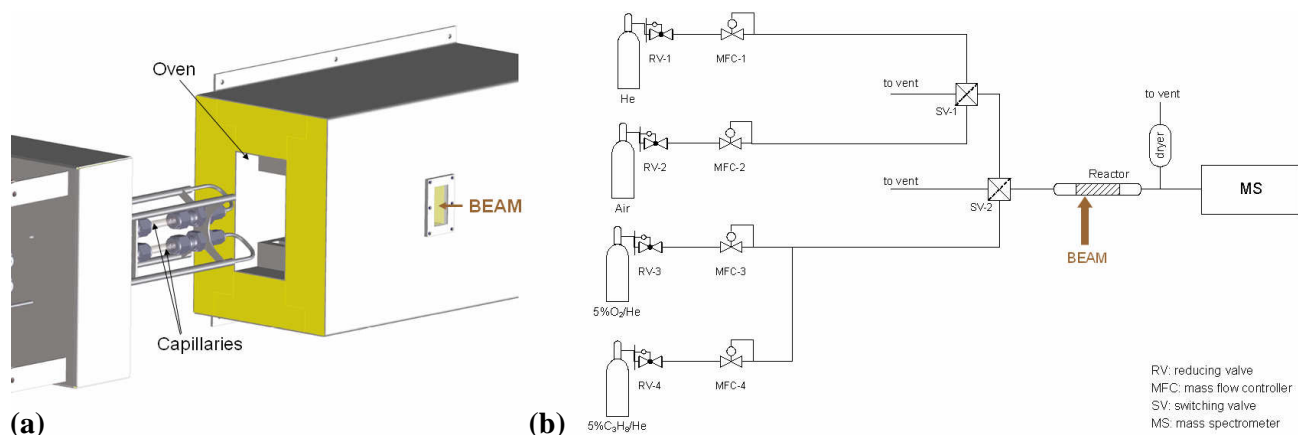


Figure 1. (a) Scheme of the in situ XAS cell. (b) Flow diagram of the experiment.

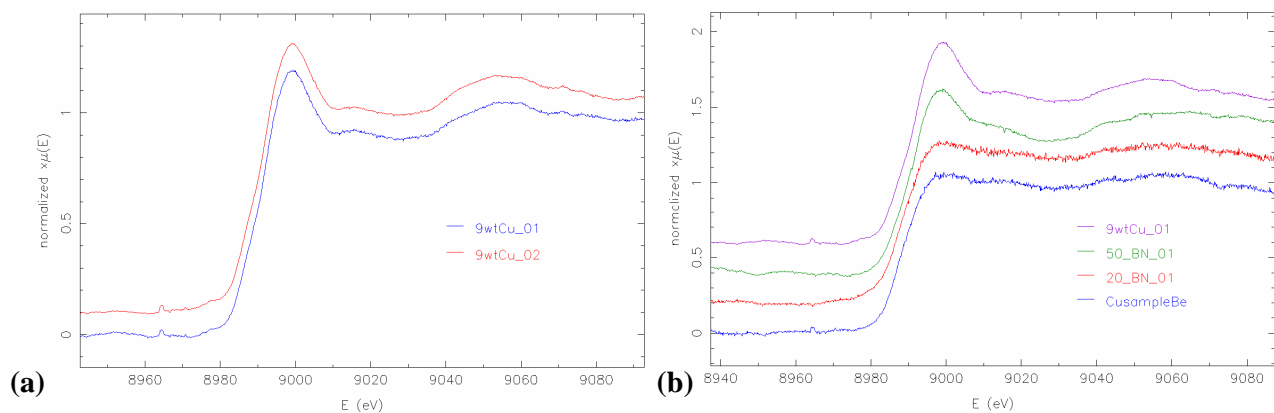


Figure 2. XANES spectra of the catalyst (RT, atmospheric pressure); (a) as such in quartz capillary tube, accumulation time: 0.1s (9wtCu_01), 1 s (9wtCu_02); (b) as such in quartz capillary (9wtCu_01) and in beryllium capillary (CusampleBe), diluted in 1/5 BN:cat. ratio and loaded in the beryllium capillary (20_BN_01), diluted in 1/1 BN:cat. ratio and loaded in the beryllium capillary (50_BN_01)

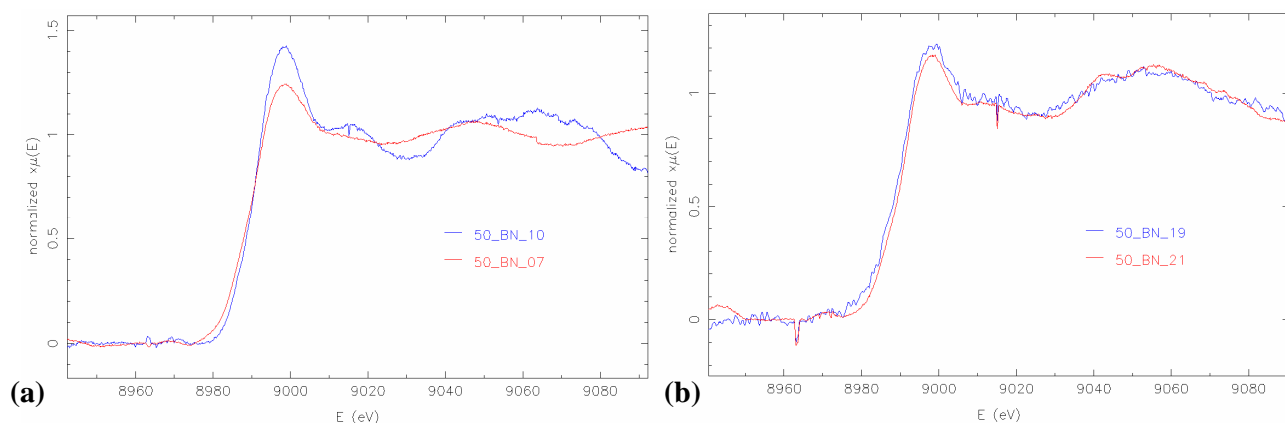


Figure 3. XANES spectra of the catalyst (RT, atmospheric pressure) loaded diluted (1/1 BN:cat. ratio) in beryllium capillary; (a) normalized against air (50_BN_10) and against a reference sample (50_BN_07, also diluted in the same ratio); (b) mounted on the reactor with (50_BN_19) and without (50_BN_21) the beryllium windows

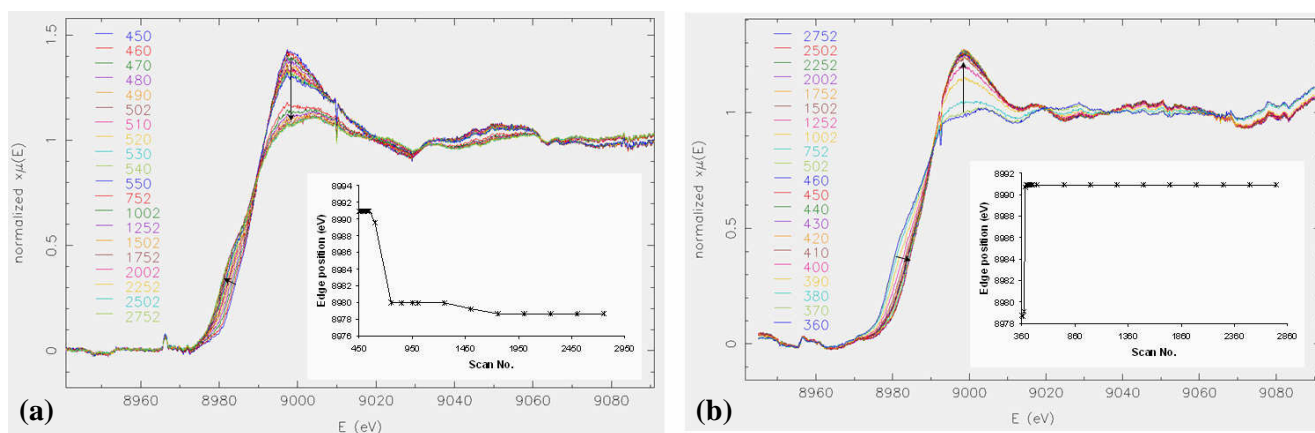


Figure 4. XANES spectra for the diluted catalyst sample (450°C, atmospheric pressure); (a) during reduction, He|→ 5%C3H8/He sequential experiment: 50BN9Cu_68; (b) during oxidation, He|→ 5%O2/He sequential experiment: 50BN9Cu_127

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