



**DUTCH-BELGIAN BEAMLINE  
AT ESRF**

**EUROPEAN  
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## **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.

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	<b>Experiment title:</b> Combining XAS with on-line GC catalytic studies for in situ characterization of Volatile Organic Compounds (VOCs) elimination over a CuO-CeO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> catalyst	<b>Experiment number:</b> 26-01-760
<b>Beamline:</b> BM26A	<b>Date(s) of experiment:</b> From: 07-12-2006 To: 12-12-2006	<b>Date of report:</b> 22- 12 -2006
<b>Shifts: 15</b>	<b>Local contact(s): Dr. Serge NIKITENKO</b>	
<b>Names and affiliations of applicants (* indicates experimentalists):</b> <b>Dr. Maria OLEA *</b> (main proposer), <b>Professor Guy B. Marin, Philippe Heynderickx *, Konstantinos Alexopoulos *, Hilario Miguel Castresana Ardanza *</b> <b>Laboratorium voor Petrochemische Techniek, Department of Chemical Engineering, Ghent University, Krijgslaan 281 S5, 9000 Belgium</b>  <b>Dr. Hilde POELMAN*, Professor Roger De Gryse, Professor Dirk Poelman</b> <b>Surface Physics and Thin Films Division, Department of Solid State Sciences, Ghent University, Krijgslaan 281 S1, 9000 Belgium</b>  <b>Dr Mickael CAPRON*, Dr Sylvain CRISTOL*</b> <b>UCCS - Unité de Catalyse et de Chimie du Solide - UMR CNRS 8181</b> <b>Université des Sciences et Technologies de Lille</b> <b>Cité Scientifique - Bâtiment C3</b> <b>59655 Villeneuve d'Ascq Cedex, France</b>		

## Report: (max. 2 pages)

The aim of the experiment was to study the changes in the structure and catalytic activity of the CuO-CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst in propane total oxidation by an *in situ* method, which combined X-ray absorption spectroscopy (XAS) and on-line catalytic measurements by gas chromatography ( $\mu$ -GC). The XAS study was performed in transmission mode, at the Cu K edge (8979 eV) and was coupled with kinetic measurements, performed under steady-state conditions in temperature steps, from 300°C to 500°C, for three different space times, namely 114, 142 and 176 kg<sub>cat</sub> s mol<sup>-1</sup>, respectively. The expected outcomes of data analysis, which are in progress now, are the dynamic structural changes of the catalyst and steady-state intrinsic kinetic data as functions of different reaction conditions.

To reach our goal, the following strategy was proposed. Reaction mixture will contain propane and oxygen in different ratios, but not higher than 1:17, balanced with helium. Propane concentration will be within a range of 0.5 to 5 mol%, close to the industrial flue gas compositions. By changing the propane inlet molar flow rate, a wide range of space times and hence a wide range of conversions can be obtained. After loading, the catalyst will be heated from room temperature to 140°C under helium flow. Then, the flow will be switched to an air flow, under which the catalyst will be kept for one hour. Next, the flow will be switched back to helium flow and the catalyst will be heated from 140°C to first reaction temperature, with a heating rate of 10<sup>0</sup>/min. At reaction temperature, the He flow will be switched to reaction flow, with a pre-set propane inlet molar flow rate. Then, consecutive 20 min EXAFS spectra will be taken concomitant with  $\mu$ -GC sampling till constant conversion of propane will be reached. At this moment, three new XAS and GC measurements will be done and GC values will be averaged to get the mean conversion value for the set space time and temperature. A new value will be set for the space time and the EXAFS and kinetic measurements will be repeated, following the same procedure. After obtaining at least 3 values for propane steady-state conversion, the catalyst will be re-oxidized if necessary, by switching the flow from the reaction one to a 50% O<sub>2</sub> in helium under which the catalyst will be kept to allow a complete oxidation. Then, the flow will be switched to He flow and the catalyst will be heated to the next reaction temperature, 20<sup>0</sup>C higher. Once the new reaction temperature is reached, the above described procedure for the first temperature will be repeated.

To perform the experiments a new type experimental cell was used which also served as a catalytic reactor and therefore simultaneously had to satisfy XAS and catalytic reactor criteria. The cell consists of several boron nitride and stainless steel plates linked together using graphite seals. It allows the measurement of XANES and EXAFS spectra of heterogeneous catalysts within a wide range of photon energies in transmission mode under the flow of various oxidative, reductive or reaction gas mixtures at elevated temperatures. The catalyst in the form of compacted powder is loaded into the cell, in fact in an oval-shaped hollow drilled in the central boron nitride plate, which is equipped with a vertical system of gas circulation, thermocouple and heating elements as well. The size of the catalyst particle and the amount and thickness of the sample were determined such as to satisfy XAS criteria, namely uniformity and homogeneity of the sample and good transmission signal. In addition, the length of the catalytic bed and the flow rate were chosen so as to maintain plug flow conditions and to ensure that the reaction rate is not controlled by external diffusion. Moreover, owing to the high thermal conductivity of boron nitride, the heat is supplied uniformly to the catalyst.

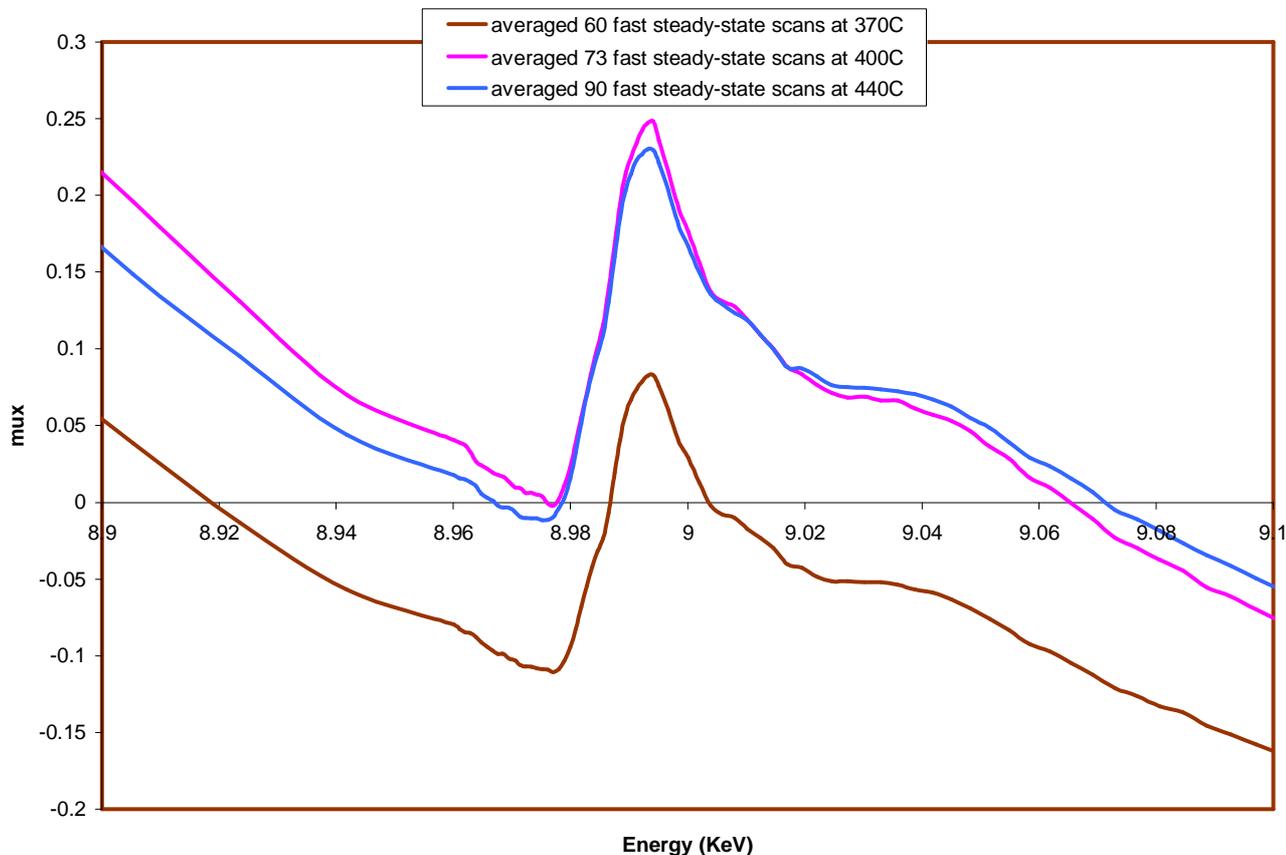
The proposed strategy was adapted during the experimental campaign. The propane to oxygen ratio was kept constant at 5, for all steady-state experiments. Some changes were done. The most important change was the fact that during steady-state measurements, only 1 min fast XANES scans were taken and averaged within one hour. Unfortunately, at the beginning of the experiment, the quality of EXAFS spectra was not the expected one. The signal-to-noise ratio was very low therefore we decided to give up taking and averaging at least three 20 min EXAFS spectra. Moreover, as the control of the temperature was very stable ( $\pm 1^0$ ), at the end of the experiment, the opportunity to follow the kinetics of the reduction of the catalyst and the oxidative dehydrogenation of propane was taken. Therefore, changes in the catalysts state and catalytic activity were monitored for at least one hour, at the following temperatures: 340, 360, 380, 400, 440, 460 and 500°C, respectively.

Meanwhile, the Cu references, Cu foil, CuO and Cu<sub>2</sub>O, were measured through repeated fast XANES scans as well, the later two being measured in the same cell as the one used for main experiments.

A preliminary analysis of data show slight differences at different temperatures for a fixed space time (see Fig.1). A complete analysis of XANES data is in progress now.

As concerning the evolution of the reduction of the catalyst, Fig. 2 presents the dynamic structural changes at 460°C.

**Fig. 1. mux variation as a function of temperature for a space time of 142 kgcat s/ mol**



**Fig. 2. Fast scan spectra under propane 5% in He flow, at 460°C, at t=0, 10, 30, and 60 min, respectively.**

