



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: Propane total oxidation over CuO-CeO₂/Al₂O₃ catalyst: Structure-activity relationships of metal oxide catalysts from time-resolved energy dispersive X-ray absorption spectroscopy and mass spectrometry

Experiment number:
MA-526

Beamline: ID 24	Date of experiment: from: 19-3-2008 to: 26-3-2008	Date of report: 29-8-2008
Shifts: 21	Local contact(s): Dr. Mark Newton	<i>Received at ESRF:</i>

Names and affiliations of applicants (*: experimentalists):

Konstantinos Alexopoulos* (main proposer), **Professor Guy B. Marin**, **Professor Marie-Françoise Reyniers**, **Veerle Balcaen***, **Raf Roelant***, **Quinten Kastelijn***
Laboratorium voor Chemische Technologie, Department of Chemical Engineering, Ghent University, Krijgslaan 281 S5, 9000 Belgium

Dr Hilde Poelman, **Professor Dirk Poelman**
Surface Physics and Thin Films Division, Department of Solid State Sciences, Ghent University, Krijgslaan 281 S1, 9000 Belgium

Dr Sylvain Cristol*
UCCS - Unité de Catalyse et de Chimie du Solide - UMR CNRS 8181
Université des Sciences et Technologies de Lille
Cité Scientifique - Bâtiment C3
59655 Villeneuve d'Ascq Cedex, France

Dr Camille Lafontaine*
Synchrotron SOLEIL
L Orme des Merisiers
Saint-Aubin - BP 48
91192 Gif-sur-Yvette Cedex, France

Report:

The main purpose 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. The experiment consisted of imposing step pulses on the catalytic system using fast switching valves while simultaneously monitoring the reactor effluent as a function of time by on-line mass spectrometry and probing the catalyst's structure using energy dispersive XANES in transmission mode at the copper K edge. In addition to the dynamic response, the catalytic system was allowed to reach its steady state at each reaction temperature and for each reaction mixture.

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]. The “heart” of this experimental cell consists of a quartz capillary tube (ID = 0.9mm, OD = 1mm) mounted horizontally on the setup. The flow sheet of the experimental setup is given in Figure 1.

Before starting the reaction experiments, the grounded catalyst (75-100 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 423 K. Next, the catalyst was kept at 423 K under 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 pulses, the isothermal step-response experiments that were carried out can be divided in the following categories:

- a) He| \rightarrow 2% C₃H₈/He : reduction of the catalyst under flow of propane
- b) He| \rightarrow 10% O₂/He : re-oxidation of the catalyst under flow of oxygen in He
- c) He| \rightarrow {1% C₃H₈ – 5 or 10% O₂}/He : reaction under simultaneous flow of propane and oxygen in He

These experiments were performed at four different temperatures (namely 573K, 623K, 673K, 723K) under atmospheric pressure. During the catalytic red/ox cycles a constant flow rate was used (i.e. $1.5 \cdot 10^{-5}$ mol/s), while under reaction conditions a range of space times (38.3 - 127.7 kg s / mol) was obtained by varying the total flow rate (i.e. 0.5 - $1.5 \cdot 10^{-5}$ mol/s). The amu's that were followed with the mass spectrometer (MS) during the experiment were 4, 12, 14, 18, 28, 29, 32, 41, and 44. Calibration of the MS was performed with mixtures of non overlapping gas components. To obtain quantitative results from the MS (i.e. gas phase compositions), the analysis procedure of the MS-software (QuadstarTM) was followed (i.e. method of elimination according to Givens). 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^[ii]. 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).

No obvious changes were observed in the spectra of the catalyst during heating under He and pre-treating with 10% O₂/He (see Figure 2a). Moreover, no changes were witnessed in the XANES spectra during total oxidation reaction conditions (see Figure 2b), indicating that the copper phase remained fully oxidized under such conditions. From the MS analysis of the reactor effluent, propane conversions were obtained at different space times and temperatures (see Figure 3a). From the propane conversion versus space time curves, initial reaction rates were calculated at different temperatures, yielding an apparent activation energy for the total oxidation of propane of 70.1 kJ/mol (see Figure 3b). Additionally as seen from Figure 3a, a higher O₂/C₃H₈ molar ratio did not have an effect at the initial reaction rate.

For the catalytic red/ox cycles the following findings can be reported. The high spectral resolution that was achieved together with the time resolution of ID24 (i.e. 0.1 s) made possible to follow in great detail the transition of Cu²⁺ to Cu⁰ and to observe the existence of the intermediate Cu¹⁺ phase (40% max). This was evident from both the evolution of the pre-edge feature and the LCF analysis (see Figure 4). In Figure 5, the conversion of the CuO phase during reduction and the conversion of the Cu phase during re-oxidation is given at all temperatures, as obtained from the LCF analysis. The reoxidation of the catalyst occurred much faster (ca. two orders of magnitude) than its reduction for all temperatures and this became more pronounced at lower temperatures. Assuming a first order approximation for the data of Figure 5 (i.e. $X=1-e^{-t/\tau}$), characteristic time constants for the red/ox cycles were obtained at different temperatures, yielding an apparent activation energy for the catalyst's reduction of 70.0 kJ/mol and an apparent activation energy for the catalyst's oxidation of 55.2 kJ/mol (see Figure 6). Therefore, the catalyst's reduction under the applied conditions requires a higher activation energy than the catalyst's oxidation. Finally, it is worth noticing that the activation energy from the MS analysis agrees very well with the activation energy of the LCF analysis for the catalyst's reduction, which indicates that during hydrocarbon oxidation over the CuO-CeO₂/Al₂O₃ catalyst the rate determining step is catalytic reduction.

ⁱ J.-D. Grunwaldt, A.M. Molenbroek, N.-Y. Topsøe, H. Topsøe, B. S. Clausen, J.Catal. 194 (2000) 452

ⁱⁱ B. Ravel, M. Newville, J. Synch. Rad. 12 (2005) 537

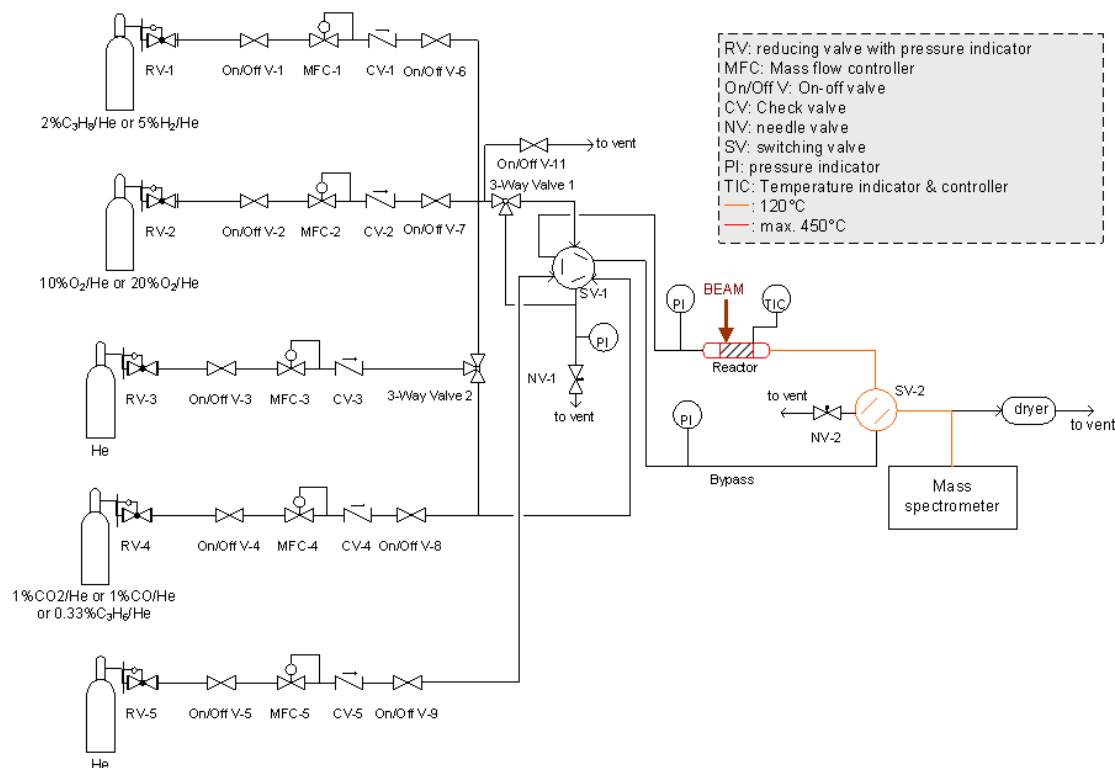


Figure 1. Flow diagram of the experiment

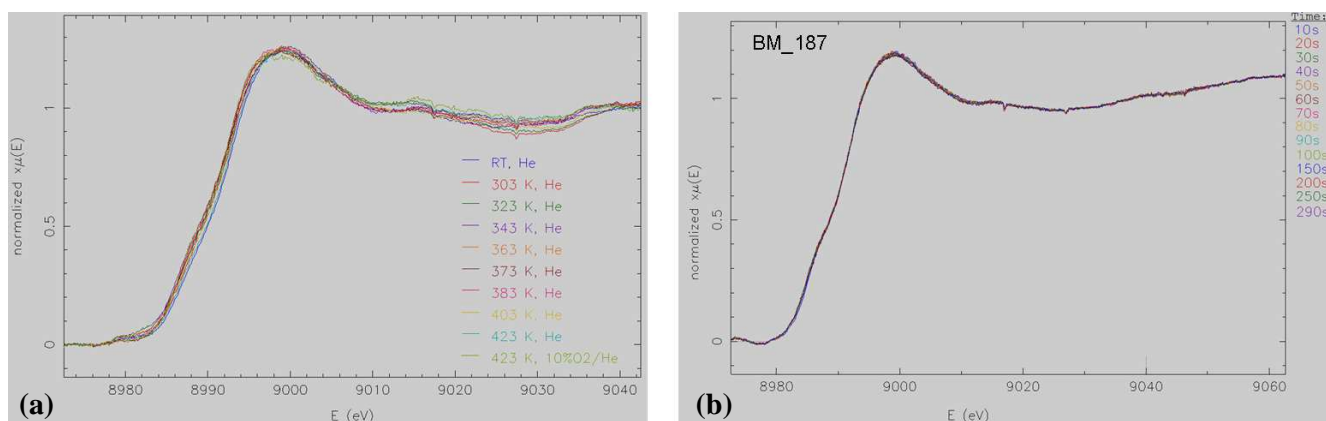


Figure 2. XANES spectra of the $\text{CuO-CeO}_2/\text{Al}_2\text{O}_3$ catalyst; (a) while heating with He and after pretreatment with 10% O_2/He ; (b) under total oxidation reaction conditions at 723 K, $\text{He} \rightarrow \{1\% \text{C}_3\text{H}_8-5\% \text{O}_2\}/\text{He}$ step-response experiment: BM_187

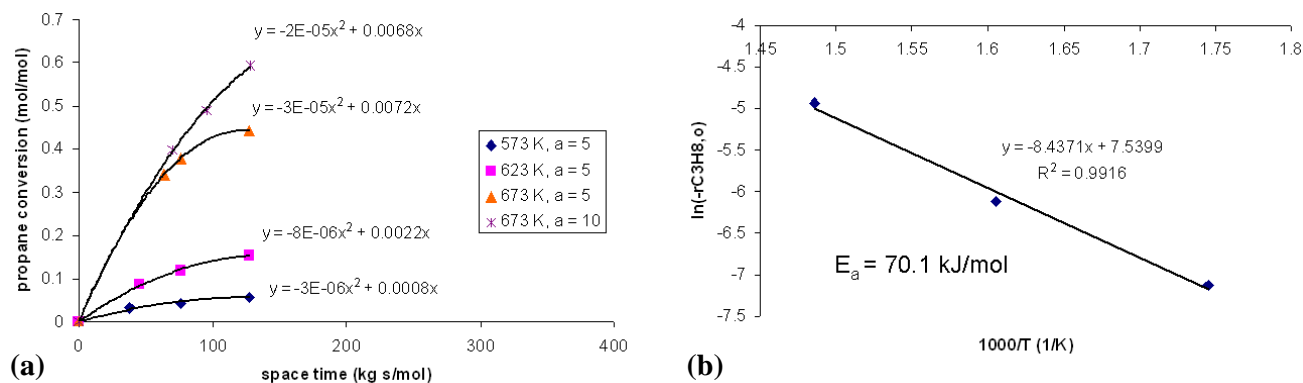


Figure 3. (a) Propane conversion versus space time at different temperatures with $p_{\text{C}_3\text{H}_{8,0}} = 1.013 \cdot 10^3 \text{ Pa}$ and $a = p_{\text{O}_2,0} / p_{\text{C}_3\text{H}_{8,0}}$; (b) Initial reaction rate versus temperature at $p_{\text{C}_3\text{H}_{8,0}} = 1.013 \cdot 10^3 \text{ Pa}$ and $p_{\text{O}_2,0} = 5.066 \cdot 10^3 \text{ Pa}$

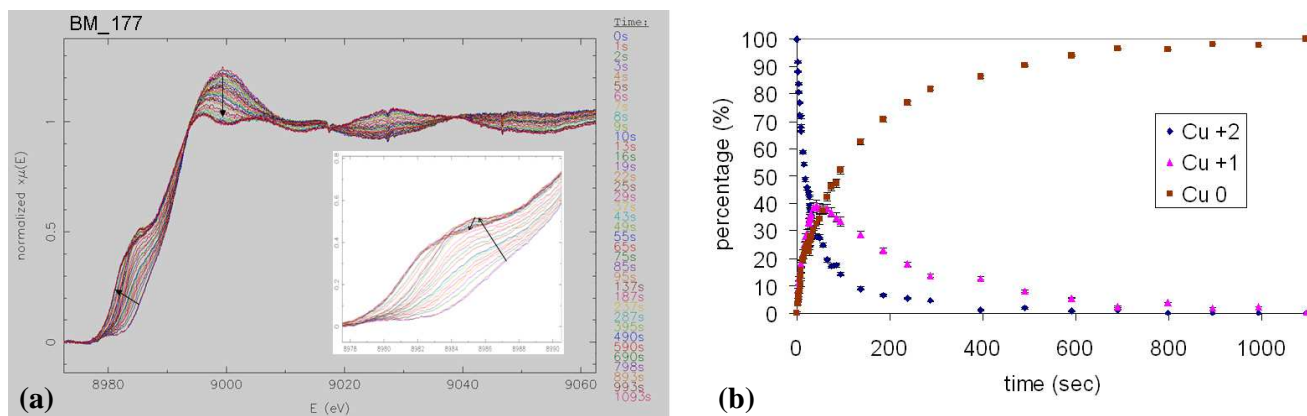


Figure 4. $\text{He} | \rightarrow 2\% \text{C}_3\text{H}_8 / \text{He}$ step-response experiment at 723 K: BM_177; (a) Evolution of XANES spectra of the $\text{CuO-CeO}_2/\text{Al}_2\text{O}_3$ catalyst (inset: evolution of the pre-edge feature); (b) Evolution of the composition of the $\text{CuO-CeO}_2/\text{Al}_2\text{O}_3$ catalyst as obtained from the LCF

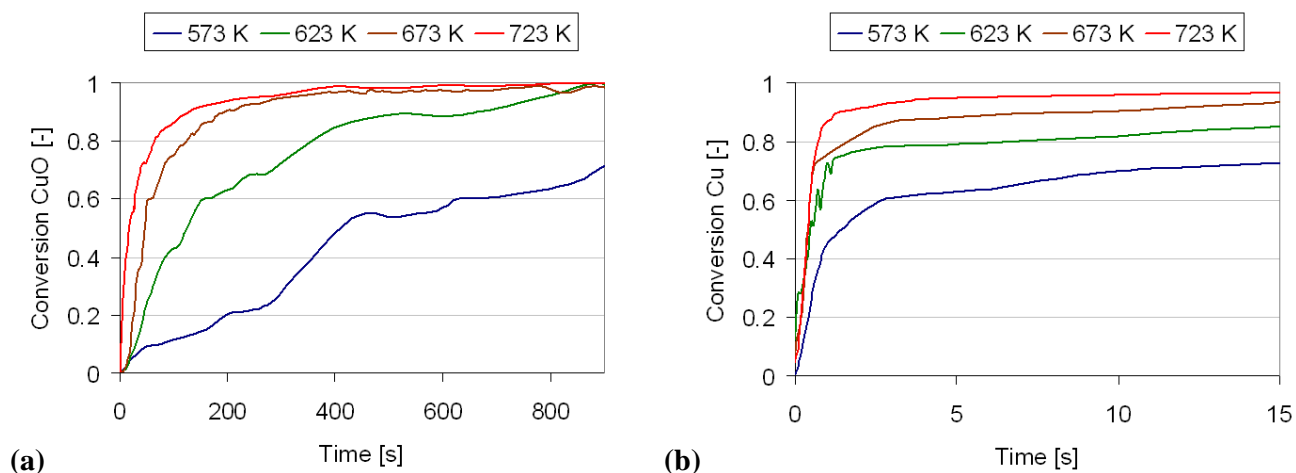


Figure 5. (a) Conversion of the CuO -phase during reduction of the $\text{CuO-CeO}_2/\text{Al}_2\text{O}_3$ catalyst with $2\% \text{C}_3\text{H}_8/\text{He}$ at different temperatures; (b) Conversion of the Cu -phase during re-oxidation of the $\text{CuO-CeO}_2/\text{Al}_2\text{O}_3$ catalyst with $10\% \text{O}_2/\text{He}$ at different temperatures

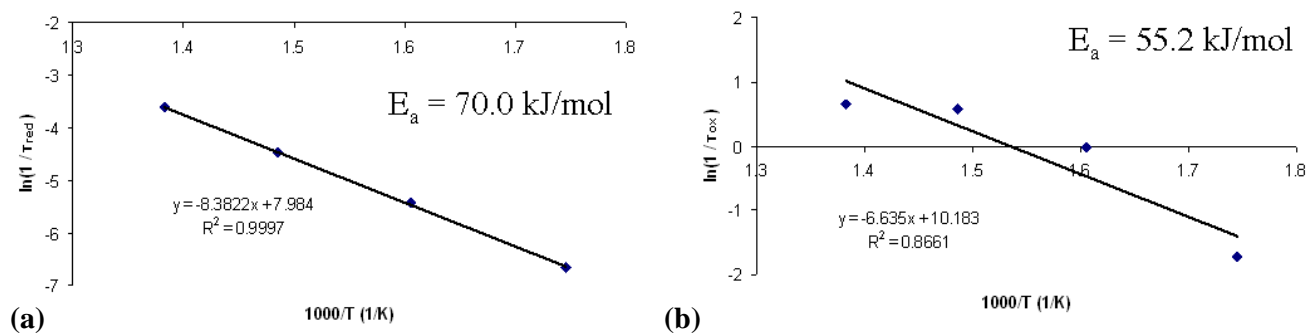


Figure 6. (a) Time constants for catalytic reduction under $2\% \text{C}_3\text{H}_8/\text{He}$ versus temperature; (b) Time constants for catalytic oxidation under $10\% \text{O}_2/\text{He}$ versus temperature