	Experiment title: Total oxidation of propane over CuO-CeO2/Al2O3 catalyst : Structure-activity relationship of metal oxides using XAFS coupled with mass spectrometry	**Experiment number**: 26-01-860
Beamline**:** BM26A	Date(s) of experiment : 4-9/11/2009	**Date of report**: 15/12/2009
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Report: (max. 2 pages)

Introduction

The aim of the proposed experiment was to investigate the structure-activity relationship of a CuO-CeO_2/Al_2O_3 catalyst in propane total oxidation by an *in-situ* method, combining X-ray absorption spectroscopy (XAS) at the Cu K and Ce L_3 edge and on-line catalytic measurements using mass spectrometry (MS). A new *in-situ/operando* XAS cell/plug-flow micro-reactor was developed at the Laboratory for Chemical Technology of Ghent University for this purpose.

Experiments performed

The reactor setup was successfully installed at the BM26A sample stage. With undiluted catalyst loaded into a reactor capillary of 0.8 mm outer diameter, good quality XAS spectra were obtained: for Ce LIII edge, XANES was measured up to k = ~ 4 $Å^{-1}$, while for Cu K edge EXAFS was recorded to k = ~ 8 $Å^{-1}$. Gas-phase compositions were obtained, using a calibrated MS (Omnistar^{TM}). Typically, the reaction temperature was varied between RT and 723 K, with total flow rates in the range 3.5-10.5 ml/min. Powder reference materials for Cu (CuO, Cu_2O and Cu) and Ce (CeO_2 and CeF_3) were measured in capillary and in pellet form. For both Cu and Ce, isothermal experiments were performed consisting of catalytic red/ox cycles with propane/He and oxygen/He respectively. Further, total oxidation reactions were carried out under simultaneous flow of propane and oxygen with ratio 1:10 for 3 space times at 3 temperatures. Finally, temperature programmed reduction (TPR) experiments using 5%H_2/He were equally performed.

Isothermal red/ox experiments

Isothermal reduction/oxidation cycles were performed with 5% C_3H_8/He and 20% O_2/He respectively, up to 673K (400°C). The Ce edge started showing effect of the propane reduction at the highest temperature 673 K, while for Cu, changes were already obvious at 623 K on (Fig. 1, oval indications).

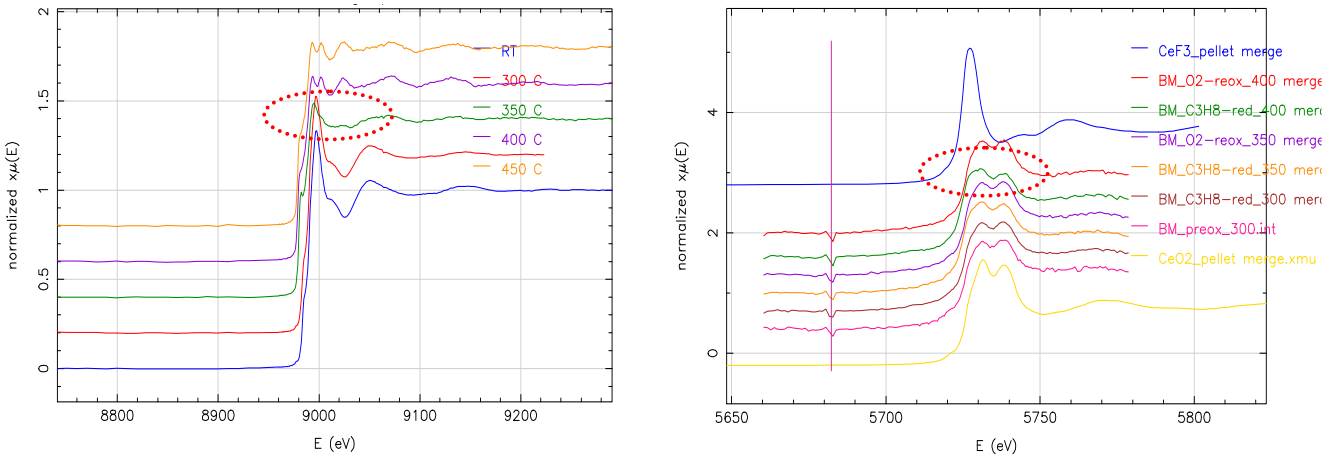

***Fig. 1**: Cu K (left) and Ce LIII XANES (right) for isothermal red/ox cycles (5% C_3H_8/He and 20% O_2/He, resp.);*

Total oxidation experiments

As expected, the XAS measurements during total oxidation showed no changes. From the MS measurements, the conversion of propane could be obtained as function of space time. From these results, an Arrhenius plot was made yielding an apparent activation energy of 68.74 KJ/mol (see Fig. 2).

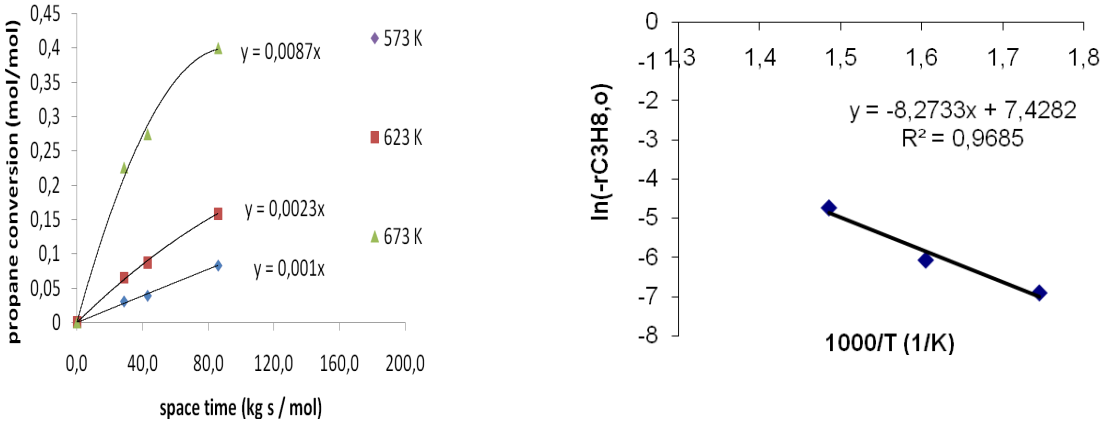

***Fig. 2.** Propane conversion at total oxidation reaction conditions (left) and related Arrhenius plot (right).*

H_2-TPR experiments

The stepwise TPR measurements with 5% H_2/He showed reduction of the catalyst from T = 473-523K (200-250°C) on. This was evident not only in the Cu K XANES, but also in the Ce LIII XANES, indicating that in this mixed oxide catalyst, the CeO_2 compound is equally reduced at low temperature (see Fig. 3; arrow indicates evolution upon reduction).

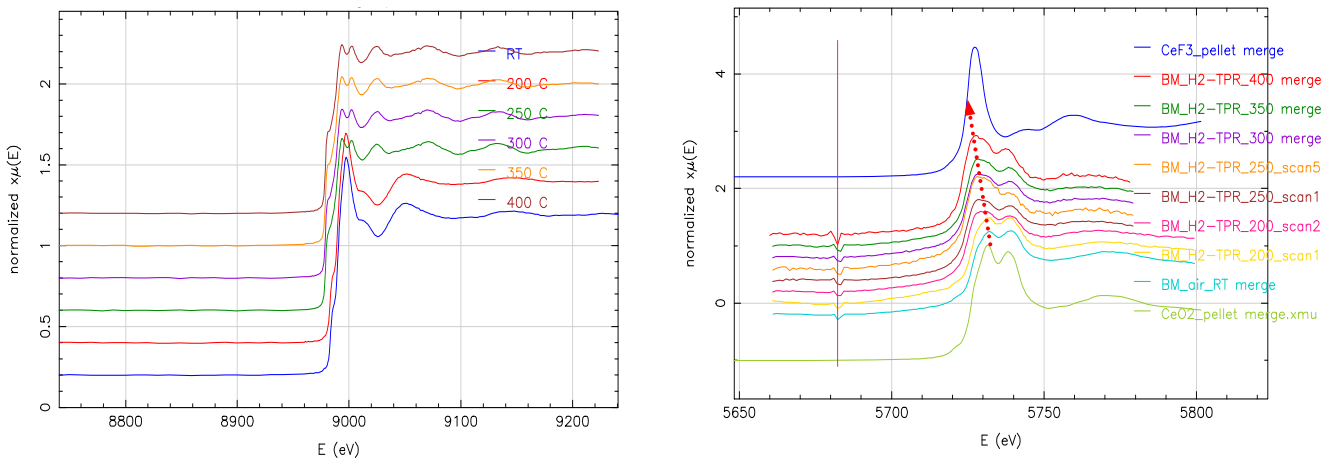

***Fig. 3:** XANES results of BM catalyst at Cu-K edge (left) and Ce-LIII edge (right) during stepwise H_2-TPR measurements.*