



	Experiment title: Total oxidation of propane over CeO ₂ /Al ₂ O ₃ and CuO-CeO ₂ /Al ₂ O ₃ catalysts : Structural-kinetic characterization by operando X-ray absorption spectroscopy coupled with XRD and Mass spectrometry. (submission for SNBL (BM01B) through DUBBLE (BM26))’.	Experiment number: 26-01-876
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Shifts: 12	Local contact(s): Olga Safonova	

Names and affiliations of applicants:

Prof. dr. ir. **MARIN Guy B.** Phone +32 9 264 4517, Email : Guy.Marin@UGent.be
Dr. **POELMAN Hilde** Phone +32 9 264 45 23, Email: hilde.poelman@UGent.be
Dr. **GALVITA Vladimir**, Phone +32 9 264 45 21, Email: Vladimir.Galvita@UGent.be
Ir. **ALEXOPOULOS Konstantinos** Phone +32 9 264 56 83, Email : Konstantinos.Alexopoulos@UGent.be
All from **Dept. Chemical Engineering, Laboratory for Chemical Technology**, Krijgslaan 281, S5, 9000 Ghent Belgium, Fax +32 (0)9 264 499

Dr **CRISTOL Sylvain** Phone +33 3 20 43 69 85 Fax +33 3 20 33 65 61 Email sylvain.cristol@univ-lille1.fr
CNRS UMR 8181 - **USTL Unité de Catalyse & de Chimie du Solide** Bât C3 59655 Villeneuve D'Ascq, France

Report: (max. 2 pages)

Introduction

The aim of the proposed experiment was to investigate the oxidation states and crystal structure of CeO₂ in CeO₂/Al₂O₃ and CuO-CeO₂/Al₂O₃ catalysts in redox and isothermal oxygen/propane reactions by an *in-situ* method, which combines X-ray absorption spectroscopy (XAS) at the Ce K edge (~40 keV) with X-ray diffraction (XRD) and mass spectrometry (MS) and possibly Raman vibrational spectroscopy. By comparison of the two samples, the behaviour of ceria with and without CuO in the catalyst can be assessed.

Experiments performed

In view of optimal XAS signal, a sample of 20 to 40 mg was loaded between with 2 quartz wool plugs into a 3 mm quartz capillary, which fits into the capillary frame setup of SNBL, allowing in situ XAS, XRD and Raman measurements. Figure 1 shows an example of Raman measurements at RT over both samples.

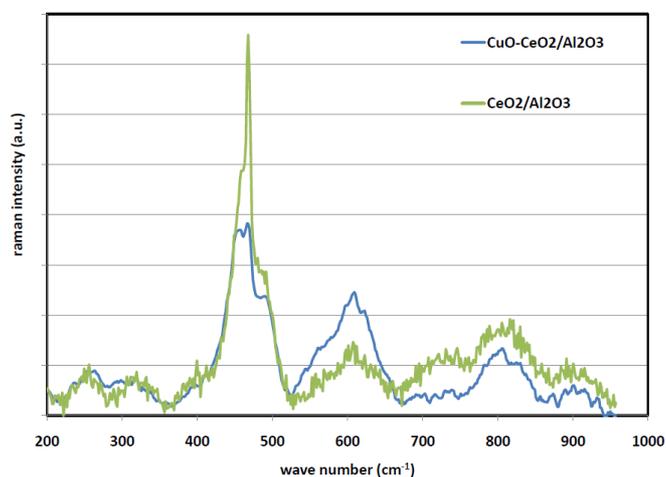


Fig. 1: averaged Raman scans over CuO-CeO₂/Al₂O₃ and CeO₂/Al₂O₃ at ambient conditions.

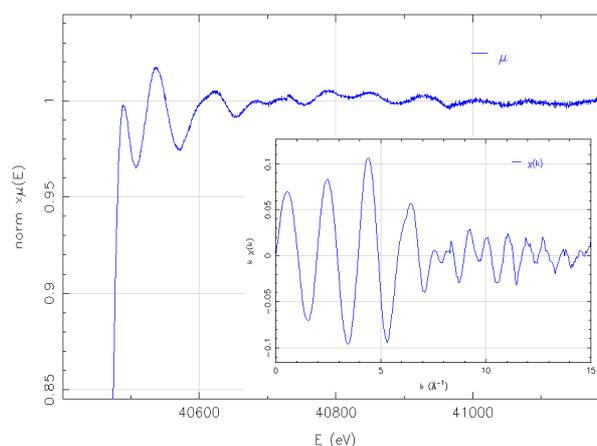


Fig. 2: zoom on Ce K edge XAS spectrum of CuO-CeO₂/Al₂O₃ catalyst at ambient conditions; inset: full EXAFS signal $k\chi(k)$

Good quality XAS spectra were obtained with Ce K edge EXAFS measurements up to $k = 15 \text{ \AA}^{-1}$ at room temperature (see Fig. 2). Gas-phase compositions were obtained, using a calibrated MS (OmnistarTM). Typically, the reaction temperature varied between RT and 1000 K, with total flow rates of 40 ml/min. Powder reference materials CeO₂, CeCl₃ and CeF₃ were measured in pellet form and in capillary with reference : BN dilution of 1 : 9. Thermal reduction as well as hydrogen and propane reduction experiments were performed on both samples at various temperatures. For the re-oxidation experiments, both O₂ and CO₂ were used as oxidant. Finally, isothermal reactions with O₂:C₃H₈ ratios of 5, 2 and 1 were followed.

Example experiments: reduction

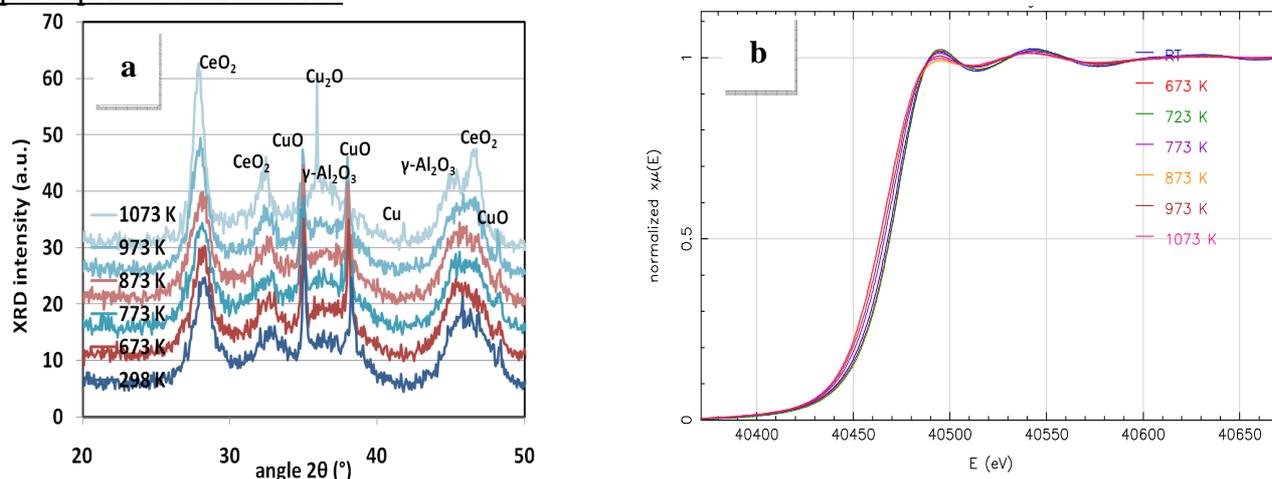


Fig. 3: CuO-CeO₂/Al₂O₃ sample during thermal reduction (40 ml/min He flow); **a:** zoomed XRD pattern (calibrated to Cu K α X-rays); **b:** Ce K edge XANES spectra after alignment of the reference measurements.

When heating the sample CuO-CeO₂/Al₂O₃ under He flow, distinct changes occur in the XRD pattern at the highest temperature, 1073 K: the characteristic peaks from CuO diffraction (35 and 38°) have been replaced by an intense line from Cu₂O, while an onset of the Cu diffraction already appears (Fig. 2a). The diffractions associated with CeO₂ (28 and 32°) display an increase in intensity as well as a small shift towards lower angle with increasing T. In the Ce K XANES spectra, also some small changes occur (Fig. 2b).

In propane reduction, the XRD pattern for the same sample shows changes from T = 673 K on, i.e. before thermal reduction is at play (Fig. 4). On the other hand, propane reduction of CeO₂/Al₂O₃ shows no noticeable changes in XRD pattern up to 1073 K (not shown), indicating the reduction affects mainly CuO.

In H₂ reduction, XANES spectra from both samples show evidence of some reduction (Fig. 5). Analysis of the data will allow to assess to which extent CeO₂ has suffered oxygen loss during reduction in both samples.

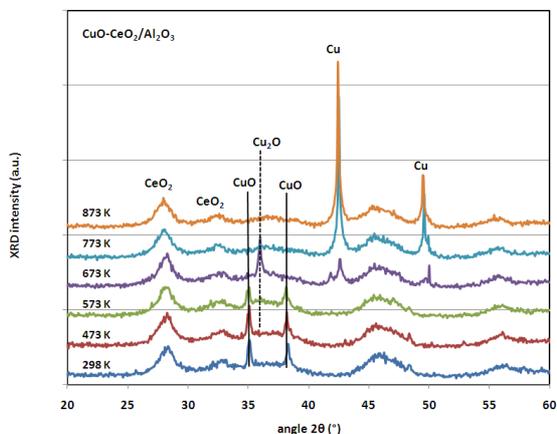


Fig. 4: XRD patterns from CuO-CeO₂/Al₂O₃ under isothermal propane reduction (2.4% C₃H₈ in He, 41 ml/min).

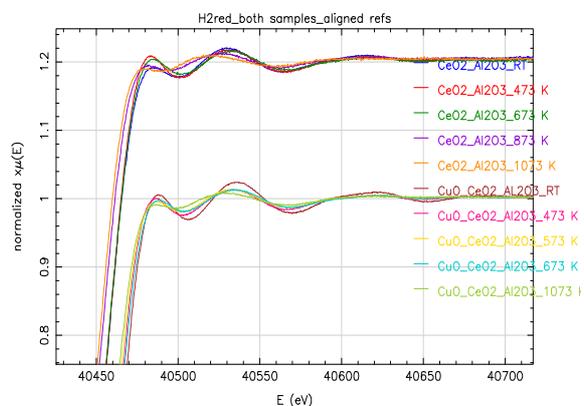


Fig. 5: zoom on XANES spectra from CuO-CeO₂/Al₂O₃ (lower set) and CeO₂/Al₂O₃ (upper set) under isothermal H₂ reduction (3% H₂ in He, 40 ml/min).