

# An In-Situ XAS Study of the Structural Changes in a CuO-CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> Catalyst during Total Oxidation of Propane

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**Abstract.** A CuO<sub>x</sub>-CeO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst was studied with in-situ transmission Cu K XAS for the total oxidation of propane as model reaction for the catalytic elimination of volatile organic compounds. The local Cu structure was determined for the catalyst as such, after pre-oxidation and after reduction with propane. The catalyst as such has a local CuO structure. No structural effect was observed upon heating in He up to 600°C or after pre-oxidation at 150°C. A full reduction of the Cu<sup>2+</sup> towards metallic Cu<sup>0</sup> occurred, when propane was fed to the catalyst. The change in local Cu structure during propane reduction was followed with a time resolution of 1 min. The  $\chi(k)$  scans appeared as linear combinations of start and end spectra, CuO and Cu structure, respectively. However, careful examination of the XANES edge spectra indicates the presence of a small amount of additional Cu<sup>1+</sup> species.

**Keywords:** CuO-CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, propane reduction, Cu K XAS.

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## INTRODUCTION

Volatile organic compounds (VOCs), are organic compounds with a high vapour pressure at ambient temperature and pressure and they are important contributors to air pollution. Two processes can be applied to destroy large volumes and high concentration of VOCs: thermal and catalytic incineration. For the thermal incineration, temperatures above 750°C are needed, while catalytic incineration can be performed at temperatures between 200-500°C, thus providing a more energy efficient process. Supported noble metal catalysts, Pt or Pd, are established as efficient catalysts for VOCs combustion. However, metal oxide catalysts can also be applied and are cheaper than the noble metal catalysts, allowing a higher catalyst load. Although the noble metal catalysts are more active, the higher catalyst loadings for the metal oxide catalysts allow a higher active surface area in the catalyst bed, which increases the overall activity of the metal oxide based catalyst systems and hence makes them competitive with the noble metal catalysts. The metal oxide based catalysts are therefore of increasing interest [1,2].

## EXPERIMENTAL

The transmission Copper K-edge X-ray absorption spectroscopy (XAS) measurements were recorded at the DUBBLE beamline (BM26A) of the ESRF synchrotron. This beamline is equipped with a Si(111) double crystal monochromator and ionisation chambers filled with Ar/He mixtures. The higher harmonics of the primary energy that are also being transmitted by the monochromator were suppressed with the vertical focussing mirror after the monochromator.

The samples were pressed into self-supporting pellets in the rectangular shaped hole of a stainless steel sample holder. The pellet thickness was chosen to give an absorption ( $\mu x = \ln(I_0/I_t)$ ) of 2.5 at the Cu K absorption edge in which  $I_0$  is the intensity of the direct X-ray beam and  $I_t$  of the transmitted beam. In a typical sample preparation, 43 mg of catalyst powder was pressed with about 12 mg of BN, an inert and weakly absorbing binder. The XAS spectra of Cu foil, CuO and Cu<sub>2</sub>O were recorded at ambient temperature and pressure for reference. The energy scale for each absorption spectrum was calibrated to the first maximum of the derivative spectrum of a metallic Cu foil measured simultaneously with the samples by

using the second and third ionisation chamber at ambient conditions.

The EXAFS data reduction was performed with the XDAP software [3]. The pre-edge background was subtracted using a modified Victoreen curve [4] whilst the atomic background,  $\mu_0$ , was subtracted using a cubic spline routine [5]. The spectra were normalised by division of the absorption data by the value of the edge step at 50 eV above the edge position.

The *in-situ* measurements were performed in a stainless steel XAS chemical cell designed and built at the department of Solid State Sciences at the Ghent University. Kapton foils (25  $\mu\text{m}$  thickness) were used as X-ray transparent windows. Reduction treatments were performed with propane gas flows diluted in He, specific temperatures and gas flow are given below.

## RESULTS AND DISCUSSION

### Local Cu Structure in $\text{CuO}_x\text{-CeO}_x/\text{Al}_2\text{O}_3$

#### *Cu Structure as Prepared*

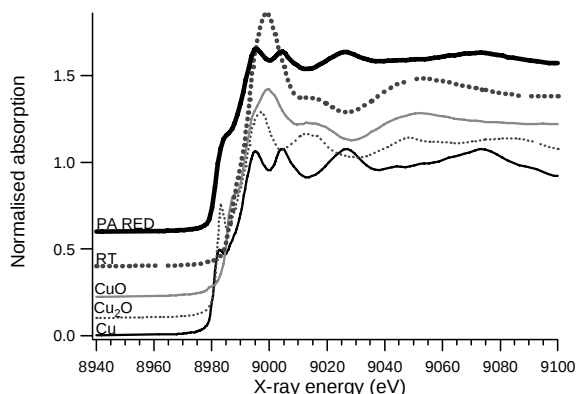
Figure 1 shows the Cu K XANES spectra for the  $\text{CuO}_x\text{-CeO}_x/\text{Al}_2\text{O}_3$  catalyst measured at ambient temperature in a He atmosphere, compared with the Cu,  $\text{Cu}_2\text{O}$  and CuO references. The good resemblance with the CuO XANES indicates that at room temperature, the local structure in the catalyst is as in CuO. However, the catalyst has a more intense white line, indicating a higher  $4p_\sigma$  density of states compared to the CuO crystal structure. The local CuO structure in the catalyst is further supported by the good agreement between the  $k^2$ -weighted EXAFS signals and corresponding Fourier Transforms for the catalyst and CuO given in Figure 2.

#### *Cu Structure after Propane Reduction*

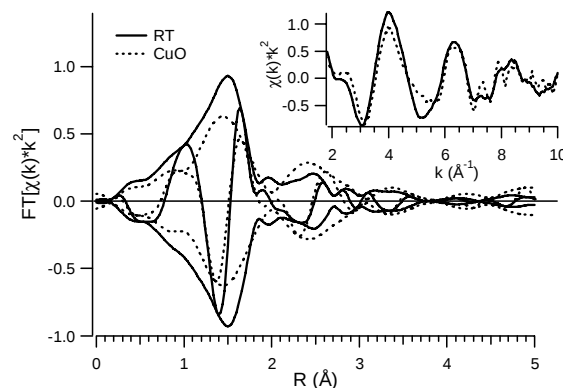
Drying the catalyst up to 873 K in He and pre-oxidizing at 323 K in a  $\text{O}_2$  flow of  $3.7 \times 10^{-5} \text{ mol/s}$  (at standard temperature and pressure) in  $3.7 \times 10^{-5} \text{ mol/s}$  He have no influence on the local Cu structure.

The XANES spectrum for the catalyst after full reduction with propane at a reaction temperature of 723 K in a propane flow of  $7.4 \times 10^{-6} \text{ mol/s}$  in  $6.7 \times 10^{-5} \text{ mol/s}$  He at ambient pressure is given in Figure 1. A clear metallic Cu spectrum is present after full reduction. Two differences appear, the pre-edge peak is not separated from the absorption edge and the  $4p_\sigma$  absorption peak is again more intense compared with the Cu reference. The  $k^2$ -weighted EXAFS signals and corresponding Fourier Transforms for this sample are

much less intense than for metallic Cu, see Figure 3. A high Debye-Waller factor due to the high measuring temperature of 723 K and structural disorder in the Cu cluster size account for this low signal intensity.



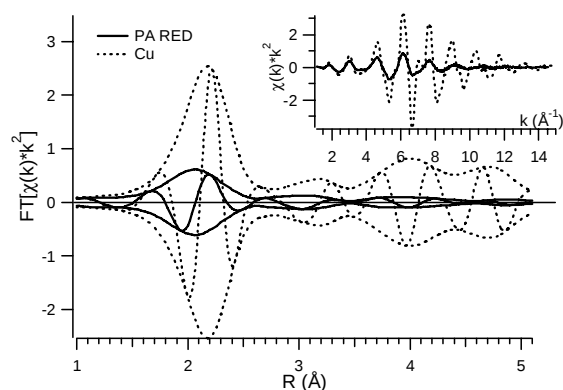
**FIGURE 1.** Cu K-edge XANES spectra for the  $\text{CuO}_x\text{-CeO}_x/\text{Al}_2\text{O}_3$  catalyst at room temperature (RT) and after reduction with propane (PA RED), together with the CuO,  $\text{Cu}_2\text{O}$  and Cu references.



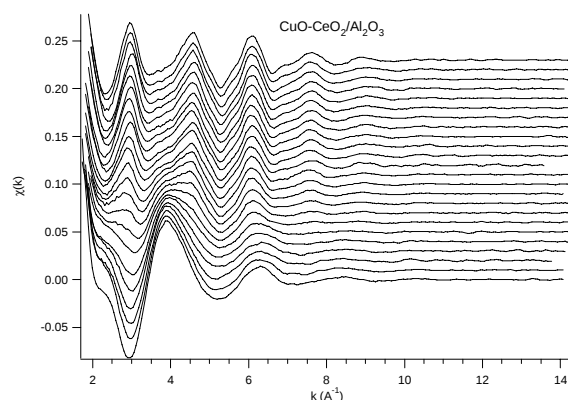
**FIGURE 2.**  $k^2$ -weighted EXAFS signals and Fourier Transforms for the  $\text{CuO}_x\text{-CeO}_x/\text{Al}_2\text{O}_3$  catalyst at room temperature (RT) and the CuO reference (Catalyst:  $\Delta k = 2.11\text{-}14.09 \text{ Å}^{-1}$ ; CuO:  $\Delta k = 2.64\text{-}9.96 \text{ Å}^{-1}$ ).

#### *Local Cu Structure in $\text{CuO}_x\text{-CeO}_x/\text{Al}_2\text{O}_3$ during Propane Reduction*

The evolution of the local Cu structure in the  $\text{CuO}_x\text{-CeO}_x/\text{Al}_2\text{O}_3$  during reduction with propane was followed by recording full XAS spectra in 1 minute, the corresponding EXAFS spectra are given in Figure 4. The reduction was performed at a reaction temperature of 623 K in a propane flow of  $7.4 \times 10^{-6} \text{ mol/s}$  in  $3.4 \times 10^{-4} \text{ mol/s}$  He at ambient pressure. The intermediate spectra can be seen as a linear combination of the first (CuO structure) and last (metallic Cu) spectrum.



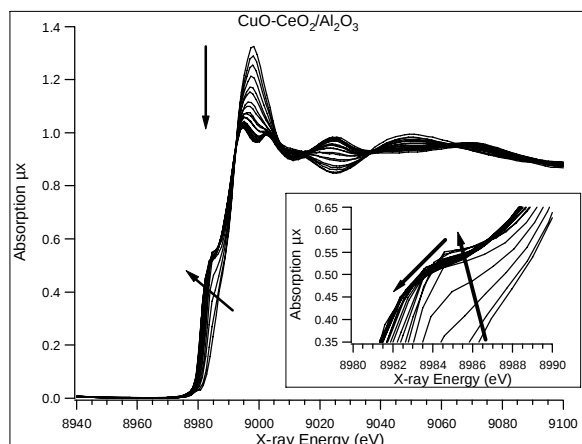
**FIGURE 3.**  $k^2$ -weighted EXAFS signals and Fourier Transforms for the  $\text{CuO}_x\text{-CeO}_x/\text{Al}_2\text{O}_3$  catalyst after propane reduction (RED) and the Cu reference (Catalyst:  $\Delta k = 3.29\text{-}12.40 \text{ \AA}^{-1}$ ; Cu:  $\Delta k = 3.27\text{-}17.17 \text{ \AA}^{-1}$ ).



**FIGURE 4.** EXAFS spectra for the  $\text{CuO}_x\text{-CeO}_x/\text{Al}_2\text{O}_3$  catalyst during propane reduction, 1 minute measuring time per spectrum.

The corresponding Cu K-edge XANES spectra are given in Figure 5. Although the post-edge structure can be seen as a linear combination of the first ( $\text{Cu}^{2+}\text{O}$ ) and last ( $\text{Cu}^0$ ) spectrum, the edge structure cannot. During the reduction process, a shoulder develops on the lower half of the absorption edge and this shoulder moves to lower energy values. A small pre-edge peak starts to develop, but then this pre-edge peak evolution stops and disappears again, see the inset in Figure 5. This implies that the XANES cannot fully be seen as a linear combination of the first ( $\text{Cu}^{2+}\text{O}$ ) and last ( $\text{Cu}^0$ ) spectrum. As the  $\text{Cu}_2\text{O}$  structure has a large pre-edge peak, see Figure 1, the observed pre-edge development can be ascribed to the presence of some  $\text{Cu}_2\text{O}$  during the propane reduction process.

The reduction of  $\text{CuO}$  towards metallic Cu and the presence of  $\text{Cu}^{1+}$  intermediate species is also found in literature on  $\text{CuO}/\text{ZnO}$  [6] and  $\text{CuO}/\text{Al}_2\text{O}_3$  systems [7].



**FIGURE 5.** XANES spectra for the  $\text{CuO}_x\text{-CeO}_x/\text{Al}_2\text{O}_3$  catalyst during propane reduction, 1 minute measuring time per spectrum. The inset shows a detail around the edge structure.

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