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In situ XAS study on the Cu and Ce local structural changes in a CuO-CeO₂/Al₂O₃ catalyst under propane reduction and re-oxidation

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Abstract

The redox behaviour of a CuO-CeO₂/Al₂O₃ catalyst is studied under propane reduction and re-oxidation. The evolution of the local Cu and Ce structure is studied with in-situ transmission X-ray absorption spectroscopy (XAS) at the Cu K and Ce L₃ absorption edges.

CuO and CeO₂ structures are present in the catalyst as such. No structural effect on the local Cu structure is observed upon heating in He up to 873 K or after pre-oxidation at 423 K.

Exposure to propane at reaction temperature (600-763 K) fully reduces the Cu²⁺ cations towards metallic Cu⁰. Quick EXAFS spectra taken during reduction show a small amount of intermediate Cu¹⁺ species. Parallel to the CuO reduction, CeO₂ is also reduced in the same temperature range. About 25 % of the Ce⁴⁺ reduces rapidly to Ce³⁺ in the 610-640 K temperature interval, while beyond 640 K a further slower reduction of Ce⁴⁺ to Ce³⁺ occurs. At 763 K, Ce reduction is still incomplete with 32 % of Ce³⁺.

Re-oxidation of Cu and Ce is fast and brings back the original oxides. The propane reduction of the CuO-CeO₂/Al₂O₃ catalyst involves both CuO and CeO₂ reduction at similar temperatures, which is ascribed to an interaction between the two compounds.

Keywords: A. oxides, C. XAFS (EXAFS and XANES), D. electronic structure, D. microstructure

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1. Introduction

Transition metal based catalysts are frequently applied as substitute for the more expensive noble metal catalysts. Supported copper oxide has received considerable attention in this respect, as it is one of the most active and selective catalysts for various reactions: steam reforming of methanol [1], water gas shift reaction [2], reduction of NO_x and SO₂ [3]. Furthermore, supported CuO has been successfully applied in CO and CH₄ oxidation reactions, making it a candidate for VOC (volatile organic compound) emission control [4]. The properties of supported CuO catalysts can be enhanced by addition of yet another oxide to the support. For this purpose, the properties of CeO₂ are to be noted because of its enhancement of CuO activity and stabilising effect against sintering [5-7].

In view of application as total oxidation catalyst for elimination of light alkanes, the structural changes of a CuO-CeO₂/Al₂O₃ commercial catalyst under propane reduction and reoxidation have been studied in the temperature range 600-763 K. Reduction of CuO can either follow a one-step Cu²⁺ → Cu⁰ mechanism or rather proceed through an intermediate Cu¹⁺ state. The presence of an intermediate Cu¹⁺ state depends on the conditions of reduction such as gas flow rate and temperature ramping speed [8-9]. In studies on supported copper oxide, Cu₂O has equally been observed as an intermediate phase, e.g. with ex situ XRD [10] or through analysis of XAFS data identifying Cu¹⁺ during reduction [9-13]. In literature, the addition of CeO₂ to the catalyst is held responsible for an enhanced reducibility of CuO [6-7, 14]. Hence, for a complete picture of the catalyst's redox properties, a study of structural changes under redox conditions must include both CuO and CeO₂ compounds. In this way, the specific contribution of each compound to the reaction can be separated and evaluated. In situ XAS presents the ideal tool for this purpose, as it is element specific and applicable under reaction conditions.

In this work, the redox properties of the CuO-CeO₂/Al₂O₃ catalyst were investigated using quick X-ray absorption spectroscopy (Q-XANES and Q-EXAFS). With appropriate choice of redox conditions, this technique allows following the catalyst under reaction, yielding the structural and electronic properties of Cu and Ce during in-situ propane reduction and re-oxidation. After a preliminary analysis of the Cu environment in the CuO-CeO₂/Al₂O₃ catalyst [15], a detailed XAS analysis of the changes at both the Cu K and Ce L₃ edge is now presented. In this way, intermediate

states and contribution of each specific compound to the structural changes of the catalyst are identified.

2. Experimental

2.1. Catalyst characterisation

The CuO-CeO₂/Al₂O₃ catalyst was synthesized via impregnation of γ -Al₂O₃ with Cu(NO₃)₂ and Ce(NO₃)₄ precursors, pressed into extrudates, dried and calcined above 723 K. The latter material was crushed to fine powder (< 20 μ m) for XAS experiments and characterisation.

X-ray diffraction (XRD) measurements were performed with a Siemens Diffractometer Kristalloflex D5000, using Cu K α radiation. The catalyst material as received presented broad lines from ceria and alumina, and narrow diffraction peaks for CuO (Figure 1, A). The XRD pattern of a sample used in a XAS propane reduction showed very sharp Cu diffraction lines instead of the original CuO lines (Figure 1, B). Estimates of the crystallite size of the different particles for both samples were obtained from the width of the diffraction peaks using Scherrer's equation [16]. In the fresh sample, CuO is mainly present as large crystallites, whereas both the alumina and ceria are smaller sized crystallites, a few nm large (Table 1). Within experimental error, no significant difference could be found between different peaks from one compound. Hence, it is concluded that the crystallites are essentially isotropic. The sharp CuO and Cu diffraction lines point towards crystallites of some 100 nm in size, i.e. an order of magnitude larger than the alumina and ceria. As the width of these CuO and Cu peaks lies close to the instrumental width, small differences in FWHM can lead to large variation in resulting size and hence, accurate crystallite size determination is impossible. Therefore, an order of magnitude is indicated in table 1 for CuO and Cu crystallite sizes, while for the other compounds, values averaged over different diffraction lines are given.

HRTEM (High Resolution Transmission Electron Microscopy) analysis of the catalyst was performed with a JEM-2200FS instrument (JEOL, 200 keV with scanning unit and EDX). Figure 2 shows the STEM images and corresponding elemental mappings for Cu K, Ce L and Al K fluorescence radiation on the CuO-CeO₂/Al₂O₃ catalyst. The left image (Figure 2, A) presents a large CuO feature in an Al₂O₃ matrix, and no Ce intensity. The CuO entity displays sharp edges and measures at least 100 nm

square. In the right image (Figure 2, B), a cluster of ceria particles about 100 nm wide is visible within the alumina matrix. No Cu intensity was registered in this image. Similar images were observed throughout the catalyst sample. Performing selective area diffraction (SAD) upon this sample, the crystallinity of the different compounds was determined (Figure 3). The alumina matrix of the catalyst gives rise to rings of diffraction in the SAD pattern (Figure 3, A), indicating randomly oriented nanoparticles. The distances between the rings correspond with gamma-alumina. Focussing on a ceria cluster, rings from the alumina matrix are accompanied by ring fragments arising from ceria nanoparticles (Figure 3, B). The distances agree with crystalline CeO₂. As the rings from ceria are not complete, it seems that there is a partial preferential orientation, aligning the particles within about 20° around the <110> direction in this case. Finally, SAD on a CuO entity yields sharp diffraction spots, corresponding to a large single crystal particle. Hence, the XRD findings are largely confirmed by the present TEM results: the CuO-CeO₂/Al₂O₃ catalyst consists mainly of large CuO blocks and clustered CeO₂ nanoparticles embedded in a matrix of nanocrystalline Al₂O₃.

Table 2 contains general characteristics of the CuO-CeO₂/Al₂O₃ catalyst. The specific surface area of the catalyst was determined with a Micromeritics ASAP 2010 instrument with N₂ adsorption at 77 K. Full elemental composition of the catalyst was obtained using inductively coupled plasma (ICP-MS) analysis (IRIS Advantage system, Thermo Jarrell Ash) by fusion in NaO and NaOH. All samples were dried at 378 K before mineralization. The catalyst contains 9.3 wt% Cu and 5.2 wt% Ce, corresponding to 9.17 μmol Cu/m² and 2.35 μmol Ce/m² respectively. Larsson et al. have investigated a series of CuO catalysts supported on ceria modified alumina [5]. They found CuO diffraction peaks for catalysts containing at least 6 μmol Cu/m². Hence, the given loading of 9.17 μmol Cu/m² is high enough to give rise to bulk CuO and thus also to CuO crystallites.

Surface atomic concentrations were obtained by means of XPS using a Perkin Elmer PHI ESCA 5500 system equipped with a monochromatic 450 Watt Al Kα source. The crushed CuO-CeO₂/Al₂O₃ catalyst gave rise to a Cu/Al XPS intensity ratio of 0.12 (see Table 2). The overall Ce 3d signal was very weak and allowed no further analysis (not shown). The Cu 2p photoline displayed a satellite feature at higher binding energy, characteristic for Cu²⁺, with a Cu_{sat}/Cu_{main} ratio of 0.28 (not shown; see Table 2). As Cu¹⁺ is known not to exhibit such feature, the Cu_{sat}/Cu_{main} intensity ratio can be used to

149 evaluate the presence of reduced copper. The value found here is lower than the
150 literature values of ~0.5 for bulk CuO [4, 6, 12]. Hence, this could point towards the
151 presence of some reduced copper, possibly caused by photoreduction of CuO in the
152 process of the XPS measurement.

155 2.2. X-ray absorption measurements

156 The copper K-edge and cerium L₃-edge X-ray absorption spectra were recorded in
157 transmission mode at the DUBBLE beamline (Dutch-Belgian beamline, BM26A) [17]
158 of the 6 GeV ESRF synchrotron (Grenoble, France) during a uniform filling mode,
159 giving a typical storage ring current of 200 down to 160 mA within one synchrotron
160 run. The synchrotron radiation emitted by the bending magnet (magnetic field strength:
161 0.4 Tesla) was monochromatized with a double crystal Si(111) monochromator. The
162 higher harmonics of the primary energy that are also being transmitted by the
163 monochromator were suppressed with the mirror after the monochromator. Ionisation
164 chambers filled with Ar/He mixtures at atmospheric pressure were used to measure the
165 intensity of the incoming, I_0 , and transmitted, I_t , X-ray beam. A reference sample placed
166 between the second and the third ionisation chamber is used for energy scale correction,
167 especially during the QEXAFS mode.

168 The samples were pressed into self-supporting pellets in the rectangular shaped hole
169 of a stainless steel sample holder. The pellet thickness was chosen to give an absorption
170 jump of about 1.0 over the Cu K or Ce L₃ absorption edges. In a typical sample
171 preparation, 43 mg of catalyst powder was mixed and pressed with about 12 mg of BN,
172 an inert and weakly absorbing binder, for the Cu K-edge spectra while 50 mg of pure
173 catalyst powder was used for the Ce L₃-edge spectra.

174 The in-situ X-ray absorption spectroscopy (XAS) measurements were performed in a
175 stainless steel XAS chemical reactor cell (volume ~ 1.75 l) designed and built at the
176 department of Solid State Sciences at the Ghent University. Kapton foils (25 µm
177 thickness) were used as X-ray transparent windows. The cell has a double wall design,
178 allowing a cooling water flow and preventing the heating of the Kapton windows. The
179 sample holder with pressed pellet was mounted inside the reactor in an inconel block
180 with thermocoax wiring for resistive heating allowing a maximum sample holder
181 temperature of 973 K. The sample holder temperature was controlled with an Eurotherm

PID temperature control. A gas flow through the reactor was established using mass flow controllers. The design resembles that of a pellet cell with gas flow streaming on both sides of the pellet [18].

Reduction treatments were performed with propane gas flows diluted in He (2.2 or 10% propane in He), and re-oxidation treatments with O₂ flows in He (50%) at atmospheric pressure. Specific temperatures and gas flow rates are given below. The catalyst reduction was followed in-situ by recording full EXAFS scans in 1 minute in a quick scanning EXAFS mode (Q-EXAFS). The fast scans resulted in high quality Cu K EXAFS spectra. Although good Ce L₃ XANES spectra were obtained in the quick scanning mode, the data quality did not allow to extract acceptable Ce L₃ EXAFS signals.

The XAS spectra of Cu foil, Cu₂O, CuO, Ce, CeF₃ and CeO₂ powders were recorded in transmission mode at ambient temperature and pressure as references. The energy scale for the Cu K-edge absorption spectra was calibrated to the first maximum of the first derivative spectrum of a metallic Cu foil measured simultaneously with the samples by using the second and third ionisation chamber at ambient conditions. For the Ce L₃ spectra there was insufficient flux left to measure a reference spectrum in between the second and third ionisation chamber. Therefore a glitch in the I_0 signal around 5987.46 eV was used to correct the energy scale during the Q-EXAFS scanning mode.

2.3. EXAFS data analysis and fit parameter errors

The EXAFS data reduction and analysis were performed with the XDAP software [19]. The pre-edge background was subtracted using a modified Victoreen curve [20] and the atomic background, μ_0 , was subtracted with a cubic spline routine [21]. The pre-edge background subtracted spectra were normalised to the edge jump, which was taken to the value of the atomic background at 50 eV above the edge position. The fit parameters were determined by multiple shell fitting in R-space, by applying the difference file technique using Fourier Transformations [22]. The agreement between model and fit in R or k -space is expressed by a variance, which gives the relative deviation between model and experiment in percentages [20]. Phase shift and backscattering amplitude functions used to calculate the Cu-Cu and Cu-O contribution

in an EXAFS spectrum were obtained with FEFF 8.0 calculations [23] on fcc Cu metal and Cu₂O spherical clusters with a radius of 8.0 Å and 8.2 Å respectively.

In order to quantify the error upon the EXAFS analysis and fits, both systematic and statistical errors should be taken into account. As recommended in the report of the International Workshop on Standards and Criteria in X-ray Absorption Spectroscopy [24] by the International X-Ray Society, an estimate of the systematic errors in the EXAFS analysis and data reduction can be obtained by using the calculated Cu-Cu and Cu-O phase and amplitude functions to fit the experimental spectra of different references with known structure and treating them as 'unknown' samples. The differences between the fit results and the crystal structures serve as an estimate of the systematic errors. Four reference measurements were available for the systematic errors evaluation: Cu metal foil and Cu₂O powder measured at 12 K and at ambient conditions. The following procedure was used to estimate these systematic errors.

As a first step, the first shell in Cu foil (Cu-Cu) and Cu₂O (Cu-O) are fitted with the calculated phase shift and backscattering amplitude functions. The S_0^2 factor for the Cu-Cu and Cu-O contribution was tuned to have agreement with the co-ordination number of the first Cu-Cu shell in Cu metal ($R = 2.556$ Å, $N = 12$) and the first Cu-O shell in Cu₂O ($R = 1.849$ Å, $N = 2$) [25], both for the spectra taken at 12 K and under ambient conditions. The resulting S_0^2 values for the Cu metal and the Cu₂O spectrum taken at 12 K were 0.89 and 0.73 respectively, comparable with the values reported in [25] for the same structures measured at 83 K. The resulting S_0^2 factors for the spectra taken at ambient conditions were 0.86 and 0.80 for the Cu-Cu and Cu-O contributions respectively.

As a second step, new fits using up to 3 shells for the Cu foil and 2 shells for the Cu₂O structures (both spectra recorded at 12 K and ambient conditions) were performed in order to treat these reference spectra as 'unknown' samples. The Debye-Waller factors over Cu shells in the Cu foil fit were constrained to one optimised value. The maximum absolute differences between the crystal structure and the fit values over different k -weightings (k^1 , k^2 and k^3) and over the four spectra are taken as systematic error values and are summarized in Table 3. For the systematic error on the Debye-Waller factor (σ^2) we take 10%, a typical value found for the amplitude factors from theoretical references [25]. The errors calculated from the statistical error in the data were smaller than 10% of the systematic errors and can therefore be neglected.

The nearest neighbours for Cu in CuO are two O shells at bond distances of 1.951 and 1.961 Å, both with a co-ordination number of 2. Using the optimized theoretical Cu-Cu and Cu-O amplitude and phase functions, a fit of the CuO EXAFS spectrum taken at ambient conditions with the crystallographic co-ordination numbers was possible, but large absolute ΔE_0 values were needed for the Cu-O shells compared to the Cu₂O fits. A fit with acceptable ΔE_0 values was possible by combining the two nearest Cu-O shells into one single Cu-O shell with a co-ordination number of 4, using a S_0^2 of 0.63.

An EXAFS fit can be considered to be proper if it yields a good result in different k -weightings (k^1 , k^2 and k^3). Therefore, EXAFS fits were performed with a k^1 , k^2 and k^3 weighting and the reported fit parameters are the average values. The standard deviation over the values is added to the systematic errors to obtain the total error: $Err_{tot} = Err_{systematic} + \sigma_{kweightings}$. The k^1 weighted fits on Cu₂O and Cu metal taken at ambient conditions resulted in co-ordination numbers for the first Cu shell in the Cu₂O and the higher shells in Cu metal that were considerably larger than the crystal structure values (up to 40 %), while the corresponding co-ordination numbers obtained from the k^2 and k^3 weighted fits only deviated by maximum 10%. Reported co-ordination numbers for these Cu contributions are therefore the average over the k^2 and k^3 weighted fits only.

3. Results and discussion

3.1. Local Cu structure

3.1.1. Local Cu structure at ambient conditions

The Cu K XANES spectrum for the as prepared catalyst recorded in He at ambient temperature is compared in Figure 4 with the spectra of Cu metal, Cu₂O and CuO references taken at ambient conditions. The good resemblance with the CuO XANES indicates that at ambient temperature the local structure in the catalyst is as in CuO. However, the catalyst has a more intense white line (first peak after the absorption edge), indicating a higher 4p_o density of states compared to the bulk 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 the CuO reference as shown in Figure 5. The intensity in the k^2 -weighted Fourier Transform for the Cu-O shell (0.0-2.0 Å) is more intense for

the catalyst than for the CuO reference, while the intensity for the Cu-Cu shells (2.0-3.0 Å) is lower. An EXAFS fit with the parameters from the CuO structure as starting values was possible, see Figure 6 and Table 4 for the optimised parameters. Compared to the CuO crystal structure, similar bond distances are obtained, but a higher total Cu-O co-ordination number is found, 5.8 (± 0.4) instead of 4, and a lower total Cu-Cu co-ordination number, 3.3 (±1.5) instead of 8.

For CuO/Al₂O₃, different species are reported depending on copper loading and calcination temperature [4, 26]. If the calcination temperature is high enough (> 973 K), bulk CuAl₂O₄ can form through solid-solid interaction between CuO and Al₂O₃ [27]. For lower calcination temperatures and low loadings of Cu, < 8-10 wt%, well-dispersed isolated Cu²⁺ has been observed, as well as a copper surface spinel [4, 26]. The latter is a defective CuAl₂O₄-like species, with Cu²⁺ occupying a distorted octahedral geometry in the alumina surface [28]. With increasing copper loading, > 8-10 wt%, bulk CuO starts to appear, giving rise to XRD diffraction peaks [4, 26, 29]. If ceria is added to the alumina, the threshold between well-dispersed and bulk CuO still holds for low ceria loadings [5, 29]. At very high ceria loadings, ~ 25 wt%, CuO is no longer found in crystalline form but rather appears surface dispersed on both alumina and ceria, even for high Cu loadings [29].

For the present system, XRD gives no indication of bulk copper aluminate being formed, the calcination temperature being too low. The diffraction peaks for CuO as well as the TEM images clearly show that the Cu loading in this CuO-CeO₂/Al₂O₃ catalyst gives rise to bulk CuO crystallites (see Table 1, Figure 2, A and Figure 3, C). The good EXAFS fit obtained starting from the CuO structure is in accordance with the CuO species identification for this catalyst. Further, the Cu-Cu contributions around 3 Å show that the copper oxide has indeed neighbouring CuO in the catalyst. Moreover, the satisfactory fit leaves no indication of a significant amount of Cu₂O present in the catalyst sample in ambient conditions. Hence, the lower Cu_{sat}/Cu_{main} ratio of 0.28 as found with XPS (§ 2.1) can be ascribed to photoreduction during the XPS measurements rather than to the intrinsic presence of reduced copper oxide.

3.1.2. Local Cu structure after drying, pre-oxidation and C₃H₈ adsorption

The local structure of a catalyst may be altered by pre-treatments given to it like drying, pre-oxidation, adsorption of reactants below reaction temperature, ... No

changes could be observed in the Cu K XANES spectra for the catalyst after drying up to 423 K in a He flow of 7.4×10^{-5} mol/s (at standard temperature and pressure), after a pre-oxidation at 423 K in a O₂ flow of 3.7×10^{-5} mol/s in 3.7×10^{-5} mol/s He and after pre-adsorption with C₃H₈ at 473 K in a C₃H₈ flow of 7.4×10^{-6} mol/s in 6.7×10^{-5} mol/s He. Moreover the EXAFS analysis for these pre-treatment spectra resulted in fit parameters similar to the values for the catalyst recorded at ambient temperature in He. Hence, the above mentioned pre-treatments do not influence the local Cu structure. Further drying under He flow of the as prepared catalyst up to 873 K does not alter the XAS spectra either (spectra not shown).

3.1.3. Local Cu structure after reduction with C₃H₈

The XANES, $k^2 \chi(k)$ and $\text{FT}[k^2 \chi(k)]$ spectra for the catalyst after reduction with propane at a reaction temperature of 723 K in a propane flow of 7.4×10^{-6} mol/s in 6.7×10^{-5} mol/s He at ambient pressure are given in Figure 7. A clear metallic Cu spectrum is present, indicating that complete reduction took place. The Cu K EXAFS fit result is given in Figure 8 and Table 5, the nearest Cu-Cu bond distance is somewhat smaller than the bond distance for the crystal structure of metallic fcc Cu.

3.1.4. Reversibility of the reduction/oxidation process

After an initial drying period of 2 hours in a He flow of 1×10^{-3} mol/s at 423 K, four propane reductions and three intermediate re-oxidations were performed consecutively on the CuO-CeO₂/Al₂O₃ catalyst. The reduction and re-oxidation treatments were carried out at 698 K in respectively a propane flow of 7.4×10^{-6} mol/s in 6.7×10^{-5} mol/s He and an O₂ flow of 3.7×10^{-5} mol/s in 3.7×10^{-5} mol/s He. A metallic Cu structure develops after each reduction and each re-oxidation restores the CuO structure as is present at ambient conditions, indicating a reversible local Cu structure in the catalyst (spectra not shown).

3.1.5. Evolution of the local Cu structure during isothermal C₃H₈ reduction

The evolution of the local Cu structure in the CuO-CeO₂/Al₂O₃ catalyst during reduction with propane was followed by recording full XAS spectra in a measuring time of 1 minute. The reduction was performed at a reaction temperature of 623 K in a propane flow of 7.4×10^{-6} mol/s in 3.4×10^{-4} mol/s He at ambient pressure. The catalyst was pre-treated by flushing with C₃H₈/He for 15 minutes at 424 K, followed by a fast heating to the reaction temperature of 623 K. The acquisition of the XAS spectra was already started during the heating and reaction temperature was reached after 3 minutes. The corresponding Cu K-edge QXANES spectra are given in Figure 9. Effect of the reduction on the XANES spectra can already be seen from the very beginning of the heating, before the reaction temperature was reached, as appears from the decreasing intensity in the 4p_σ transition just after the edge. Although the post-edge structure can be seen as a linear combination of the first (Cu²⁺O) and last (Cu⁰) spectrum, the edge structure cannot. During the reduction process, a shoulder appears on the lower half of the absorption edge which moves to lower energy values. A small pre-edge peak starts to develop from this shoulder, but then this pre-edge peak evolution stops and disappears again, see the inset in Figure 9. This implies that the XANES spectra cannot solely be regarded as a linear combination of the first (Cu²⁺O) and last (Cu⁰) spectrum. As the Cu₂O structure has a large pre-edge peak, see Figure 4, the observed pre-edge development can be ascribed to the presence of some Cu₂O during the propane reduction process.

The corresponding QEXAFS spectra are also given in Figure 9. Following the evolution of the XANES spectra, a linear combination fit with three base components (one for each Cu oxidation state) was performed on this QEXAFS spectrum series. As Cu²⁺ component in the linear combination fit, a fully oxidized spectrum (i.e. at the beginning of the reduction series) was used, a fully reduced spectrum (i.e. at the series' end) was taken as Cu⁰ component and the Cu₂O reference spectrum was chosen as Cu¹⁺ component. The resulting percentages of each component as a function of time in the reduction process are given in Figure 10. The exact fit percentages are dependent on the amplitude of the base spectra. As the reference Cu₂O spectrum was taken at ambient temperature from a Cu₂O reference powder, presenting a different disorder than present in the catalyst, the scaling factor for the Cu₂O contribution is not known. Hence, the reported concentrations are only qualitative and not quantitative. The Cu₂O spectrum is

found as a minor intermediate component, which has a maximum after about 6 minutes reduction time.

The evolution of the XANES and EXAFS spectra (Figure 9) clearly shows the presence of an intermediate Cu¹⁺ phase upon propane reduction at 623 K over the CuO-CeO₂/Al₂O₃ catalyst. Caballero et al. investigated a CuO/ZrO₂ catalyst under C₃H₈ diluted in He at 773 K [12]. Under these conditions, reduction of the catalyst was incomplete and factor analysis of the XANES spectra identified three components: CuO, Cu₂O and Cu. In methanol steam reforming over CuO/ZrO₂, Cu₂O was obtained as post-reaction oxidation state for certain Cu loadings and water/methanol ratios [10]. H₂ reduction of the same catalyst confirmed the presence of the Cu⁺, now as intermediate towards metallic Cu [10]. In H₂ reduction or oxidative methanol reforming over CuO/ZnO₂ [30-31] and in CO-CO₂-H₂/Ar reduction of a CuO/ZnO₂/Al₂O₃ catalyst, Cu₂O was equally identified as an intermediate copper phase preceding the formation of metallic Cu [11]. But the presence of Cu₂O as intermediate during reduction of CuO is not general: CuO in ZSM5 was found to reduce in H₂-TPR via Cu₂O in small CuO particles only, while the larger ones exhibited a direct Cu²⁺ → Cu⁰ transition [13]. For unsupported CuO, it was found that the presence of an intermediate Cu₂O phase upon CO or H₂ reduction strongly depends on the reduction conditions and the reduction can follow either a direct or a two-step transition [8-9]. The sequential pathway is observed when either a limited feed or fast temperature ramping conditions are applied, i.e. a more 'mild' reduction, where Cu₂O can appear.

Hence, the presence of Cu¹⁺ in present CuO-CeO₂/Al₂O₃ catalyst during the propane reduction process is not surprising but related to the CuO particle structure and conditions of reduction. Under a flow of 7.4×10⁻⁶ mol/s propane in 3.4×10⁻⁴ mol/s He at ambient pressure and 623 K, the large CuO crystallites of the catalyst are reduced through a Cu¹⁺ intermediate state. These conditions are hence 'mild' enough to allow the Cu₂O intermediate state to occur during reduction.

3.2. Local Ce structure

3.2.1. Local Ce structure at ambient conditions

The Ce L₃ XANES spectra for Ce³⁺ compounds have a strong absorption line at the absorption edge (white line: WL) due to a 2p_{3/2} → (4f^l)5d* electronic transition (d*

denotes an excited electron in the d orbital). Ce⁴⁺ compounds however present a double white line. These two peaks correspond to the $2p_{3/2} \rightarrow (4f^L)5d^*$ and $2p_{3/2} \rightarrow (4f^0)5d^*$ transitions (L denotes that an electron from an O2p orbital is transferred to a Ce4f orbital) [32-35]. The Ce L₃ spectra for CeO₂, CeF₃ and Ce powder are given in Figure 11 as references, while more spectra of Ce³⁺ and Ce⁴⁺ compounds can be found in for example [36].

The Ce L₃ XANES spectrum for the CuO-CeO₂/Al₂O₃ catalyst at ambient conditions is compared with the references in Figure 11. A local CeO₂ structure can be concluded for the CuO-CeO₂/Al₂O₃ catalyst at ambient conditions, with Ce⁴⁺ oxidation state.

When ceria is supported on alumina, up to 3 different Ce species have been identified in literature [37]: Ce species in Al₂O₃ cation vacancies (named a CeAlO₃ precursor phase, with Ce³⁺ oxidation state), well-dispersed small CeO₂ particles, too small to be detected in XRD, and bulk-like CeO₂. In the present CuO-CeO₂/Al₂O₃ catalyst, the ceria loading of 2.35 $\mu\text{mol Ce/m}^2$ was in the XRD analysis identified as ceria particles of size around 6 nm (see Table 1), while TEM showed them to be clustered within the alumina matrix (Figure 2B). At ambient conditions the observed Ce oxidation state is 4+ (Figure 11). Hence, it is concluded that Ce is present as CeO₂ particles only and not as CeAlO₃ precursor state, which bears a Ce³⁺ state.

3.2.2. Local Ce structure after C₃H₈ reduction and re-oxidation

Two subsequent reductions (RED1 and RED2) were performed on the CuO-CeO₂/Al₂O₃ catalyst, with a re-oxidation in between. The sample was heated from 600 to 763 K (723 K for RED2) in steps of 8 K in a propane flow of 7.4×10^{-6} mol/s in 3.4×10^{-4} mol/s He at ambient pressure. The final Ce L₃ spectra for each reduction and the intermediate re-oxidation (performed at 763 K, in an O₂ flow of 7.4×10^{-6} mol/s in 3.4×10^{-4} mol/s He at ambient pressure) are shown in Figure 12. The two reductions yield a similar spectrum. The re-oxidation brings back the CeO₂ structure. Compared to the oxidized spectrum, the main edges in the spectra for the reduction treatments are shifted to lower X-ray energy values and there is a different ratio in the intensity of the two white lines. As two white lines can still be noticed after reduction, Ce⁴⁺ cations are still present. In order to quantify the amount of Ce³⁺ in the spectra upon the reduction

treatments, a fit of the Ce L₃ XANES was performed with the CeO₂ XANES spectrum as model for the Ce⁴⁺ oxidation state and the CeF₃ spectrum for the Ce³⁺ oxidation state. The fit procedure used is explained below.

Ce L₃ XANES spectra are commonly analysed by fitting procedures in which the white line transitions are approximated with Lorentzian curves and the absorption step by an arctangent function [32, 35-36, 38]. The resulting fits on the CeF₃ and CeO₂ references are given in Figure 13. For the CeF₃ reference compound spectrum for example, the fit function was $\frac{a}{\pi} * (\arctan(E - b) + \pi / 2) + c * \left(1 + (2 * (E - d) / e)^2\right)^{-1}$, with E the X-ray energy value. The first term represents an arctangent with a and b the height and position of its inflection point respectively, while the second term is a Lorentzian function with c , d and e its height, position and width at half maximum respectively. For the CeO₂, three Lorentzians are needed, one for each WL and an extra component at the rising edge. This third component is in literature often ascribed to some Ce³⁺ present in the CeO₂ [35], but more recently attributed to many-body final states of the 2p→5d transition [34]. According to this last reference, we have considered this third component as an intrinsic feature of the CeO₂ XANES spectra.

Relative constraints on the height, position and width for the arctangents and Lorentzians were determined from fits on the Ce L₃ XANES spectra for the CeO₂ and CeF₃ references and on the catalyst taken at ambient conditions. These constraints were then applied to all further fits on the spectra for the reduced catalyst. In this way, from the 16 parameters (4 Lorentzians and 2 arctangents) needed to fit an unknown spectrum only 7 remained as free parameters. The fits on the XANES spectra for the reductions RED1 and RED2 from Figure 12 are given in Figure 14, with indication of the resulting percentages Ce³⁺ and Ce⁴⁺. A contribution of about 30% Ce³⁺ is found after each reduction. The absolute error on this concentration determination is estimated to amount to 2-3 percent.

3.2.3. Ce⁴⁺/Ce³⁺ evolution during temperature programmed C₃H₈ reduction

The heating of the catalyst from 600 to 763 K in temperature intervals of 8 K (1°/min) in a propane flow of 7.4×10⁻⁶ mol/s in 3.4×10⁻⁴ mol/s He at ambient pressure was followed in-situ by taking Ce L₃ spectra with a measuring time of 1 min. For each temperature interval the Ce L₃ XANES spectrum was fitted to obtain the relative Ce³⁺

and Ce⁴⁺ concentrations. The amount of Ce³⁺ in the spectra as function of the treatment time and temperature is given in Figure 15. A transition from 0 to about 25% Ce³⁺ in the fit occurs in the 610-640 K temperature interval. After this transition, a further increase in the Ce³⁺ fit percentage as function of time of about 1.3 %/hour can be noticed. Hence, the CuO-CeO₂/Al₂O₃ catalyst presents a clear reduction of the CeO₂ particles during temperature programmed C₃H₈ reduction. This means that not only CuO is reduced by C₃H₈ in this temperature interval, but also CeO₂ to a certain extent.

A clear two-step propane reduction of ceria in the CuO-CeO₂/Al₂O₃ catalyst appears from Figure 15. This two-step process reminds of the bimodal H₂-reduction curve that is characteristic of high surface area ceria [39]. Moreover, a XAS investigation of the H₂-redox properties of ceria in the temperature range of 573 to 773 K has yielded similar observations: for high surface area ceria kept at 673 K, a fast initial H₂-reduction up to about 20% Ce³⁺ was found, followed by a slower reduction [40]. This sequential process for pure ceria was thought to consist of first a fast surface reduction (of outermost Ce⁴⁺ layers or small particles), followed by slower bulk reduction. The two-step profile is then governed by a balance between reduction kinetics and morphological changes (sintering of ceria into larger particles) [39-40]. For low surface area ceria, only the bulk reduction step is observed [39]. When ceria is supported on alumina, quite different results are being reported regarding H₂-reduction: no reduction below 773 K [5], two reduction peaks at 873 and 1073 K [37] or a single H₂-reduction temperature of 623K has been reported [41].

Even though C₃H₈ and H₂ reduction can only be linked to a certain extent [42], similarities can help identifying the processes that occur. The first transition in the C₃H₈-reduction of Figure 15 occurs in the temperature range 610-640 K. This temperature region can be related to surface reduction of the ceria nanoparticles. The second transition sets off at 640 K and continues with a lower rate up to 763 K. The different slope of both transitions indicates the reduction is dominated by a different mechanism. Given the XRD detection of 7 nm particles, this transition could be related to ceria bulk reduction, which follows a first faster surface reduction. At 763 K the reduction has reached about 32%, but from the constant slope at the end of the temperature range in Figure 15, it can be expected that this reduction process is still incomplete.

The onset of C₃H₈ reduction of ceria in the present catalyst, ~610 K, occurs at quite low temperature, which is similar to the starting reduction of CuO, <623 K (see § 3.1.5).

For CuO-CeO₂/Al₂O₃ catalysts, the presence of CeO₂ is reported to enhance the reducibility of CuO, but most often, H₂-TPR reduction peaks up to 773 K are identified as CuO related only [5, 7, 41]. On the other hand, interaction between CuO and CeO₂ is sometimes believed to enhance the reducibility of both compounds [43]. Such mutual promotion between copper oxide and ceria is then responsible not only for lowering the CuO reduction temperature, but also for inducing a higher ceria reducibility than expected [43]. In the present CuO-CeO₂/Al₂O₃ catalyst system, temperature programmed C₃H₈ reduction induces at first a fast reduction of some 25 % of the Ce⁴⁺ to Ce³⁺ followed by a slower proceeding reduction. The combined presence of CuO and CeO₂ lowers C₃H₈ reduction temperatures for ceria, so that both compounds start reducing in the same temperature range (≥ 600 K).

4. Conclusions

X-ray absorption spectroscopy was used to follow the C₃H₈ reduction and re-oxidation behaviour of a CuO-CeO₂/Al₂O₃ catalyst, by measuring in-situ both Cu K and Ce L₃ transmission XAS spectra. A detailed analysis including error estimation of the XAS data was performed. The starting material displayed fully oxidized Ce⁴⁺ and Cu²⁺ and these states were preserved upon pre-treatment (heating to 873 K in He or pre-oxidation at 423 K). From the combined XAS, XRD, XPS and TEM characterisation, it follows that in this CuO-CeO₂/Al₂O₃ catalyst, CuO is present as large single crystallites, while CeO₂ and Al₂O₃ occur as nanoparticles.

Upon reduction with C₃H₈ in the temperature range 600-763 K, Cu²⁺ reduced fully towards metallic Cu⁰. QEXAFS was applied to follow this reduction in detail. Analysis of the XANES edge region and a linear combination fit to the EXAFS spectra allowed to identify the presence of some Cu¹⁺ during the first stage of the reduction, indicating a two-step reduction process.

In XANES temperature programmed C₃H₈ reduction, Ce was found to partially reduce to Ce³⁺ in two steps: a fast initial reduction up to 25% at low temperature, followed by a slower transition, which continued beyond the investigated temperature range (32% Ce³⁺ at 763 K). The first transition was ascribed to surface reduction of the ceria nanoparticles. The onset temperature of 610 K is similar to the one for the Cu reduction. The second slower reduction is related to bulk reduction of the CeO₂

544 particles. Both processes occur at far lower temperature than expected for bulk ceria,
545 which can only be accounted for by interaction between CuO and CeO₂.

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Figure Captions

Figure 1: XRD pattern for the CuO-CeO₂/Al₂O₃ catalyst: A) as received, B) after reduction under propane/He.

Figure 2: STEM images and element mappings of the CuO-CeO₂/Al₂O₃ catalyst, CuO entity in alumina matrix (A); cluster of CeO₂ particles in alumina matrix (B).

Figure 3: Inverted Selective Area Diffractions (SAD) for the CuO-CeO₂/Al₂O₃ catalyst, centred on alumina matrix (A), cluster of CeO₂ particles (B) and CuO entity (C).

Figure 4: Cu K XANES spectra for Cu metal, Cu₂O, CuO and the CuO-CeO₂/Al₂O₃ catalyst taken at ambient temperature.

Figure 5: k^2 -weighted EXAFS signals and Fourier Transforms for the CuO-CeO₂/Al₂O₃ catalyst at room temperature and the CuO reference (Catalyst: $\Delta k = 3.47$ -14.09 Å⁻¹; CuO: $\Delta k = 3.55$ -9.96 Å⁻¹).

Figure 6: $k^2 \cdot \chi(k)$ and $FT[k^2 \cdot \chi(k)]$ spectra for the experimental Cu K EXAFS signal of the CuO-CeO₂/Al₂O₃ catalyst at room temperature and the fit ($\Delta k = 3.47$ -14.09 Å⁻¹, $\Delta R = 0.6$ -3.3 Å, k^2 variances : 0.66 (Imaginary part) and 0.27 (Absolute part)).

Figure 7: Cu K XANES (left), $k^2 \cdot \chi(k)$ and $FT[k^2 \cdot \chi(k)]$ (right) spectra for the CuO-CeO₂/Al₂O₃ catalyst taken at 723 K, after reduction with C₃H₈/He and for Cu foil at RT in air (Catalyst: $\Delta k = 1.34$ -12.40 Å⁻¹; Cu foil: $\Delta k = 2.07$ -17.40 Å⁻¹).

Figure 8: Fit and experimental $k^3 \cdot \chi(k)$ (left) and $FT[k^3 \cdot \chi(k)]$ (right) spectra for the CuO-CeO₂/Al₂O₃ catalyst after full reduction ($\Delta k = 3.29$ -10.40 Å⁻¹, $\Delta R = 1.00$ -5.0 Å, k^3 variances: 0.92 (Imaginary part) and 0.39 (Absolute part)).

Figure 9: Cu K QXANES (left) and QEXAFS (right) spectra for the CuO-CeO₂/Al₂O₃ catalyst during propane reduction, 1 minute measuring time per XAS spectrum. The inset shows a detail of the edge structure.

Figure 10: Percentages of Cu²⁺, Cu¹⁺ and Cu⁰ contributions to the Cu K QEXAFS spectra of Figure 9 as function of propane reduction time. During the first 3 minutes, the temperature was increased from 423 to 623 K. The error bars represent the 99% confidence intervals from the fitting procedure.

Figure 11: Ce L₃ XANES spectra for the CuO-CeO₂/Al₂O₃ catalyst at ambient conditions and the CeO₂, CeF₃ and Ce powder reference compounds.

Figure 12: Ce L₃ XANES spectra for the CuO-CeO₂/Al₂O₃ catalyst in a cycle of two subsequent propane reductions with a re-oxidation in between.

Figure 13: Ce L₃ XANES spectra and fits for the CeF₃ (left) and CeO₂ (right) references.

Figure 14: Ce L₃ XANES spectra and fits for the spectra RED1 (left) and RED2 (right) from Figure 12.

Figure 15: Percentage of the CeF₃ spectrum (Ce³⁺ contribution) in the CuO-CeO₂/Al₂O₃ Ce L₃ XANES fit as function of reduction time. The temperature increase per step was about 8 K (1 K/min), after an initial heating from 423 to 600 K.

Tables

Table 1: Crystallite sizes determined from XRD in the crushed CuO-CeO₂/Al₂O₃ catalyst as received and after reduction under C₃H₈/He flow at 770 K. An order of magnitude is given for CuO and Cu; averaged values over several diffraction peaks for CeO₂ and Al₂O₃.

crystallite size (nm)	CuO/Cu	CeO ₂	Al ₂ O ₃
as received	~ 100	6	4
reduced	~ 100	8	5

Table 2: Specific surface area, nominal ratio Cu/Al and Cu/Ce (from ICP), surface Cu/Al and Cu/Ce ratio and Cu satellite/main peak ratio (from XPS) for the crushed CuO-CeO₂/Al₂O₃ catalyst.

	S _{BET} (m ² /g)	Nominal Cu/Al	Nominal Cu/Ce	Surface Cu/Al	Surface Cu/Ce	Cu _{sat} /Cu _{main}
CuO-CeO ₂ /Al ₂ O ₃	156	0.10	3.9	0.12	27	0.28

Table 3: Estimated systematic errors in the EXAFS analysis. Error on the Debye-Waller factor (σ^2): 10%.

Absorber – scatterer	systematic error		
	$ \Delta R $ (Å)	$ \Delta N/N $ (%)	$ \Delta E_d $ (eV)
Cu-Cu (1 st shell) in Cu metal	<0.018	6	1
Cu-Cu (1 st shell) in oxides <i>N</i> values from <i>k</i> ² and <i>k</i> ³ weighted fits only	<0.018	14	<3
Cu-Cu (higher shells)	<0.022	20-30	<3
Cu-O (1 st shell)	<0.013	5	1

Table 4: Bond distances, R , co-ordination numbers, N , for the EXAFS fit on the experimental Cu K EXAFS spectrum for the CuO-CeO₂/Al₂O₃ catalyst at room temperature compared to the CuO reference structure values ($\Delta k = 3.47$ -14.09 Å⁻¹, $\Delta R = 0.6$ -3.3 Å, k^2 variances: 0.53 (Imaginary part) and 0.23 (Absolute part)).

Absorber - scatter	Crystal structure		EXAFS fit values			
	R (Å)	N	R (Å)	N	σ^2 (Å ²)	ΔE_0 (eV)
Cu-O	1.955	2+2	1.938 (±0.022)	6.1 (±1.3)	0.0064 (±0.001)	-0.4 (±1.5)
Cu-O	2.784	2	2.822 (±0.030)	1.0 (±0.5)	0.0064 (±0.001)	-0.2 (±2.4)
Cu-Cu	2.901	4	2.970 (±0.032)	1.6 (±0.3)	0.0029 (±0.001)	-2.7 (±3.6)
Cu-Cu	3.083	4	3.094 (±0.020)	1.5 (±0.3)	0.0029 (±0.001)	-4.6 (±3.2)

Table 5: Comparison between the bond distances R , co-ordination numbers N , for the Cu K EXAFS fit result on CuO-CeO₂/Al₂O₃ catalyst after full reduction and the fcc Cu crystal structure values ($\Delta k = 3.29$ -10.40 Å⁻¹, $\Delta R = 1.00$ -5.0 Å, k^3 variances: 0.92 (Imaginary part) and 0.39 (Real part)).

Absorber - scatterer	Cu fcc crystal structure		EXAFS fit values for CuO-CeO ₂ /Al ₂ O ₃ catalyst				difference	
	R _{Cu} (Å)	N _{Cu}	R (Å)	N	σ^2 (Å ²)	ΔE_0 (eV)	ΔR (Å)	N/N _{Cu}
Cu-Cu	2.556	12	2.483 (±0.019)	7.42 (±1.0)	0.019 (±0.003)	5.78 (±1.2)	0.073	0.62
Cu-Cu	3.615	6	3.488 (±0.024)	3.58 (±1.03)	0.019 (±0.003)	10.0 (±3.)	0.127	0.60
Cu-Cu	3.427	24	4.498 (±0.025)	8.02 (±1.7)	0.019 (±0.003)	3.58 (±3.0)	0.071	0.33

Figure02