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Geert Silversmit, Hilde Poelman, Veerle Balcaen, Philippe M. Heynderickx, Maria Olea, et al.. In situ XAS study on the Cu and Ce local structural changes in a CuO–CeO/AlO catalyst under propane reduction and re-oxidation. Journal of Physics and Chemistry of Solids, 2009, 70 (9), pp.1274. 10.1016/j.jpcs.2009.07.008 . hal-00570130

HAL Id: hal-00570130 https://hal.science/hal-00570130

Submitted on 27 Feb 2011

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Author's Accepted Manuscript

In situ XAS study on the Cu and Ce local structural changes in a $CuO-CeO_2/Al_2O_3$ catalyst under propane reduction and re-oxidation

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PII: DOI: Reference: S0022-3697(09)00171-1 doi:10.1016/j.jpcs.2009.07.008 PCS 5898

To appear in:

Journal of Physics and Chemistry of Solids

Received date:17 March 2009Revised date:28 May 2009Accepted date:8 July 2009

Cite this article as: Geert Silversmit, Hilde Poelman, Veerle Balcaen, Philippe M. Heynderickx, Maria Olea, Sergey Nikitenko, Wim Bras, Philippe F. Smet, Dirk Poelman, Roger De Gryse, Marie-Françoise Reniers and Guy B. Marin, In situ XAS study on the Cu and Ce local structural changes in a CuO–CeO₂/Al₂O₃ catalyst under propane reduction and re-oxidation, *Journal of Physics and Chemistry of Solids*, doi:10.1016/j.jpcs.2009.07.008

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3	$C_{\rm H}O_{\rm T}C_{\rm H}O_{\rm T}$ catalyst under propane reduction and re-oxidation
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15	
16	Abstract
17	The redox behaviour of a CuO-CeO ₂ /Al ₂ O ₂ catalyst is studied under
18	propane reduction and re-oxidation. The evolution of the local Cu and
19	Ce structure is studied with in-situ transmission X-ray absorption
20	spectroscopy (XAS) at the Cu K and Ce L_3 absorption edges.
21	CuO and CeO_2 structures are present in the catalyst as such. No
22	structural effect on the local Cu structure is observed upon heating in
23	He up to 873 K or after pre-oxidation at 423 K.
24	Exposure to propane at reaction temperature (600-763 K) fully
25	reduces the Cu ²⁺ cations towards metallic Cu ⁰ . Quick EXAFS spectra
26	taken during reduction show a small amount of intermediate Cu
27	species. Parallel to the CuO reduction, CeO ₂ is also reduced in the
28	same temperature range. About 25 % of the Ce reduces rapidly to Co^{3+} in the 610 640 K temperature interval while beyond 640 K a
29 30	further slower reduction of Ce^{4+} to Ce^{3+} occurs. At 763 K Ce
31	reduction is still incomplete with 32 % of Ce^{3+}
32	Re-oxidation of Cu and Ce is fast and brings back the original oxides.
33	The propane reduction of the CuO-CeO ₂ /Al ₂ O ₃ catalyst involves both
34	CuO and CeO_2 reduction at similar temperatures, which is ascribed to
35	an interaction between the two compounds.
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39	Keywords: A. oxides, C. XAFS (EXAFS and XANES), D. electronic structure, D.
40	microstructure
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48 **1. Introduction**

49 Transition metal based catalysts are frequently applied as substitute for the more 50 expensive noble metal catalysts. Supported copper oxide has received considerable 51 attention in this respect, as it is one of the most active and selective catalysts for various 52 reactions: steam reforming of methanol [1], water gas shift reaction [2], reduction of 53 NO_x and SO_2 [3]. Furthermore, supported CuO has been successfully applied in CO and 54 CH₄ oxidation reactions, making it a candidate for VOC (volatile organic compound) 55 emission control [4]. The properties of supported CuO catalysts can be enhanced by 56 addition of yet another oxide to the support. For this purpose, the properties of CeO_2 are 57 to be noted because of its enhancement of CuO activity and stabilising effect against 58 sintering [5-7].

In view of application as total oxidation catalyst for elimination of light alkanes, the 59 60 structural changes of a CuO-CeO₂/Al₂O₃ commercial catalyst under propane reduction 61 and reoxidation have been studied in the temperature range 600-763 K. Reduction of CuO can either follow a one-step $Cu^{2+} \rightarrow Cu^{0}$ mechanism or rather proceed through an 62 intermediate Cu¹⁺ state. The presence of an intermediate Cu¹⁺ state depends on the 63 64 conditions of reduction such as gas flow rate and temperature ramping speed [8-9]. In 65 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⁺ 66 67 during reduction [9-13]. In literature, the addition of CeO_2 to the catalyst is held 68 responsible for an enhanced reducibility of CuO [6-7, 14]. Hence, for a complete picture 69 of the catalyst's redox properties, a study of structural changes under redox conditions 70 must include both CuO and CeO_2 compounds. In this way, the specific contribution of 71 each compound to the reaction can be separated and evaluated. In situ XAS presents the 72 ideal tool for this purpose, as it is element specific and applicable under reaction 73 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 insitu 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

Cu K and Ce L3 on CuO-CeO2/Al2O3

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

83 84

85 **2. Experimental**

86 2.1. Catalyst characterisation

87 The CuO-CeO₂/Al₂O₃ catalyst was synthesized via impregnation of γ -Al₂O₃ with 88 Cu(NO₃)₂ and Ce(NO₃)₄ precursors, pressed into extrudates, dried and calcined above 89 723 K. The latter material was crushed to fine powder (< 20 µm) for XAS experiments 90 and characterisation.

91 X-ray diffraction (XRD) measurements were performed with a Siemens 92 Diffractometer Kristalloflex D5000, using Cu Ka radiation. The catalyst material as 93 received presented broad lines from ceria and alumina, and narrow diffraction peaks for 94 CuO (Figure 1, A). The XRD pattern of a sample used in a XAS propane reduction 95 showed very sharp Cu diffraction lines instead of the original CuO lines (Figure 1, B). 96 Estimates of the crystallite size of the different particles for both samples were obtained 97 from the width of the diffraction peaks using Scherrer's equation [16]. In the fresh 98 sample, CuO is mainly present as large crystallites, whereas both the alumina and ceria 99 are smaller sized crystallites, a few nm large (Table 1). Within experimental error, no 100 significant difference could be found between different peaks from one compound. 101 Hence, it is concluded that the crystallites are essentially isotropic. The sharp CuO and 102 Cu diffraction lines point towards crystallites of some 100 nm in size, i.e. an order of 103 magnitude larger than the alumina and ceria. As the width of these CuO and Cu peaks 104 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 105 106 impossible. Therefore, an order of magnitude is indicated in table 1 for CuO and Cu 107 crystallite sizes, while for the other compounds, values averaged over different 108 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

Cu K and Ce L_3 on CuO-CeO₂/Al₂O₃

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115 square. In the right image (Figure 2, B), a cluster of ceria particles about 100 nm wide is 116 visible within the alumina matrix. No Cu intensity was registered in this image. Similar 117 images were observed throughout the catalyst sample. Performing selective area 118 diffraction (SAD) upon this sample, the crystallinity of the different compounds was 119 determined (Figure 3). The alumina matrix of the catalyst gives rise to rings of 120 diffraction in the SAD pattern (Figure 3, A), indicating randomly oriented nanoparticles. The distances between the rings correspond with gamma-alumina. 121 122 Focussing on a ceria cluster, rings from the alumina matrix are accompanied by ring 123 fragments arising from ceria nanoparticles (Figure 3, B). The distances agree with 124 crystalline CeO₂. As the rings from ceria are not complete, it seems that there is a partial 125 preferential orientation, aligning the particles within about 20° around the <110> 126 direction in this case. Finally, SAD on a CuO entity yields sharp diffraction spots, 127 corresponding to a large single crystal particle. Hence, the XRD findings are largely 128 confirmed by the present TEM results: the CuO-CeO₂/Al₂O₃ catalyst consists mainly of 129 large CuO blocks and clustered CeO₂ nanoparticles embedded in a matrix of 130 nanocrystalline Al₂O₃.

131 Table 2 contains general characteristics of the CuO-CeO₂/Al₂O₃ catalyst. The 132 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 133 134 obtained using inductively coupled plasma (ICP-MS) analysis (IRIS Advantage system, 135 Thermo Jarrell Ash) by fusion in NaO and NaOH. All samples were dried at 378 K 136 before mineralization. The catalyst contains 9.3 wt% Cu and 5.2 wt% Ce, corresponding to 9.17 μ mol Cu/m² and 2.35 μ mol Ce/m² respectively. Larsson et al. have investigated 137 138 a series of CuO catalysts supported on ceria modified alumina [5]. They found CuO diffraction peaks for catalysts containing at least 6 umol Cu/m². Hence, the given 139 loading of 9.17 μ mol Cu/m² is high enough to give rise to bulk CuO and thus also to 140 141 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 K α 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

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

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155 **2.2.** X-ray absorption measurements

156 The copper K-edge and cerium L_3 -edge X-ray absorption spectra were recorded in transmission mode at the DUBBLE beamline (Dutch-Belgian beamline, BM26A) [17] 157 of the 6 GeV ESRF synchrotron (Grenoble, France) during a uniform filling mode, 158 159 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.

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 jump of about 1.0 over the Cu K or Ce L₃ absorption edges. In a typical sample preparation, 43 mg of catalyst powder was mixed and pressed with about 12 mg of BN, an inert and weakly absorbing binder, for the Cu K-edge spectra while 50 mg of pure 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

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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].

185 Reduction treatments were performed with propane gas flows diluted in He (2.2 or 10% propane in He), and re-oxidation treatments with O_2 flows in He (50%) at 186 187 atmospheric pressure. Specific temperatures and gas flow rates are given below. The 188 catalyst reduction was followed in-situ by recording full EXAFS scans in 1 minute in a 189 quick scanning EXAFS mode (Q-EXAFS). The fast scans resulted in high quality Cu K 190 EXAFS spectra. Although good Ce L_3 XANES spectra were obtained in the quick scanning mode, the data quality did not allow to extract acceptable Ce L₃ EXAFS 191 192 signals.

The XAS spectra of Cu foil, Cu₂O, CuO, Ce, CeF₃ and CeO₂ powders were recorded 193 194 in transmission mode at ambient temperature and pressure as references. The energy 195 scale for the Cu K-edge absorption spectra was calibrated to the first maximum of the 196 first derivative spectrum of a metallic Cu foil measured simultaneously with the 197 samples by using the second and third ionisation chamber at ambient conditions. For the 198 Ce L₃ spectra there was insufficient flux left to measure a reference spectrum in 199 between the second and third ionisation chamber. Therefore a glitch in the I_0 signal 200 around 5987.46 eV was used to correct the energy scale during the Q-EXAFS scanning 201 mode.

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204 2.3. EXAFS data analysis and fit parameter errors

205 The EXAFS data reduction and analysis were performed with the XDAP software 206 [19]. The pre-edge background was subtracted using a modified Victoreen curve [20] 207 and the atomic background, μ_0 , was subtracted with a cubic spline routine [21]. The pre-208 edge background subtracted spectra were normalised to the edge jump, which was taken 209 to the value of the atomic background at 50 eV above the edge position. The fit 210 parameters were determined by multiple shell fitting in R-space, by applying the 211 difference file technique using Fourier Transformations [22]. The agreement between 212 model and fit in R or k-space is expressed by a variance, which gives the relative 213 deviation between model and experiment in percentages [20]. Phase shift and 214 backscattering amplitude functions used to calculate the Cu-Cu and Cu-O contribution

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in an EXAFS spectrum were obtained with FEFF 8.0 calculations [23] on fcc Cu metal

and Cu_2O spherical clusters with a radius of 8.0 Å and 8.2 Å respectively.

217 In order to quantify the error upon the EXAFS analysis and fits, both systematic and 218 statistical errors should be taken into account. As recommended in the report of the 219 International Workshop on Standards and Criteria in X-ray Absorption Spectroscopy 220 [24] by the International X-Ray Society, an estimate of the systematic errors in the 221 EXAFS analysis and data reduction can be obtained by using the calculated Cu-Cu and 222 Cu-O phase and amplitude functions to fit the experimental spectra of different 223 references with known structure and treating them as 'unknown' samples. The 224 differences between the fit results and the crystal structures serve as an estimate of the 225 systematic errors. Four reference measurements were available for the systematic errors 226 evaluation: Cu metal foil and Cu₂O powder measured at 12 K and at ambient 227 conditions. The following procedure was used to estimate these systematic errors.

228 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-229 230 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 231 Cu_2O (R = 1.849 Å, N = 2) [25], both for the spectra taken at 12 K and under ambient 232 conditions. The resulting S_0^2 values for the Cu metal and the Cu₂O spectrum taken at 233 234 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 235 ambient conditions were 0.86 and 0.80 for the Cu-Cu and Cu-O contributions 236 237 respectively.

238 As a second step, new fits using up to 3 shells for the Cu foil and 2 shells for the 239 Cu₂O structures (both spectra recorded at 12 K and ambient conditions) were performed 240 in order to treat these reference spectra as 'unknown' samples. The Debye-Waller factors 241 over Cu shells in the Cu foil fit were constrained to one optimised value. The maximum 242 absolute differences between the crystal structure and the fit values over different kweightings $(k^1, k^2 \text{ and } k^3)$ and over the four spectra are taken as systematic error values 243 244 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 245 246 references [25]. The errors calculated from the statistical error in the data were smaller 247 than 10% of the systematic errors and can therefore be neglected.

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248 The nearest neighbours for Cu in CuO are two O shells at bond distances of 1.951 249 and 1.961 Å, both with a co-ordination number of 2. Using the optimized theoretical 250 Cu-Cu and Cu-O amplitude and phase functions, a fit of the CuO EXAFS spectrum 251 taken at ambient conditions with the crystallographic co-ordination numbers was 252 possible, but large absolute ΔE_0 values were needed for the Cu-O shells compared to the 253 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 254 255 0.63.

256 An EXAFS fit can be considered to be proper if it yields a good result in different kweightings $(k^1, k^2 \text{ and } k^3)$. Therefore, EXAFS fits were performed with a k^1, k^2 and k^3 257 weighting and the reported fit parameters are the average values. The standard deviation 258 259 over the values is added to the systematic errors to obtain the total error: $Err_{tot} =$ $Err_{systematic} + \sigma_{kweightings}$. The k¹ weighted fits on Cu₂O and Cu metal taken at ambient 260 conditions resulted in co-ordination numbers for the first Cu shell in the Cu₂O and the 261 higher shells in Cu metal that were considerably larger than the crystal structure values 262 (up to 40 %), while the corresponding co-ordination numbers obtained from the k^2 and 263 k^3 weighted fits only deviated by maximum 10%. Reported co-ordination numbers for 264 these Cu contributions are therefore the average over the k^2 and k^3 weighted fits only. 265

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- 268 **3. Results and discussion**
- 269 3.1. Local Cu structure
- 270 3.1.1. Local Cu structure at ambient conditions

271 The Cu K XANES spectrum for the as prepared catalyst recorded in He at ambient 272 temperature is compared in Figure 4 with the spectra of Cu metal, Cu₂O and CuO 273 references taken at ambient conditions. The good resemblance with the CuO XANES 274 indicates that at ambient temperature the local structure in the catalyst is as in CuO. 275 However, the catalyst has a more intense white line (first peak after the absorption edge), indicating a higher $4p_{\sigma}$ density of states compared to the bulk CuO crystal 276 277 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 278 279 Transforms for the catalyst and the CuO reference as shown in Figure 5. The intensity 280 in the k^2 -weighted Fourier Transform for the Cu-O shell (0.0-2.0 Å) is more intense for

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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 (\pm 0.4) instead of 4, and a lower total Cu-Cu coordination number, 3.3 (\pm 1.5) instead of 8.

287 For CuO/Al₂O₃, different species are reported depending on copper loading and 288 calcination temperature [4, 26]. If the calcination temperature is high enough (> 973 K), 289 bulk CuAl₂O₄ can form through solid-solid interaction between CuO and Al₂O₃ [27]. 290 For lower calcination temperatures and low loadings of $Cu_{s} < 8-10$ wt%, well-dispersed isolated Cu^{2+} has been observed, as well as a copper surface spinel [4, 26]. The latter is 291 a defective CuAl₂O₄-like species, with Cu^{2+} occupying a distorted octahedral geometry 292 293 in the alumina surface [28]. With increasing copper loading, > 8-10 wt%, bulk CuO 294 starts to appear, giving rise to XRD diffraction peaks [4, 26, 29]. If ceria is added to the 295 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 296 297 crystalline form but rather appears surface dispersed on both alumina and ceria, even for 298 high Cu loadings [29].

For the present system, XRD gives no indication of bulk copper aluminate being 299 300 formed, the calcination temperature being too low. The diffraction peaks for CuO as 301 well as the TEM images clearly show that the Cu loading in this CuO-CeO₂/Al₂O₃ 302 catalyst gives rise to bulk CuO crystallites (see Table 1, Figure 2, A and Figure 3, C). 303 The good EXAFS fit obtained starting from the CuO structure is in accordance with the 304 CuO species identification for this catalyst. Further, the Cu-Cu contributions around 3 Å 305 show that the copper oxide has indeed neighbouring CuO in the catalyst. Moreover, the 306 satisfactory fit leaves no indication of a significant amount of Cu₂O present in the 307 catalyst sample in ambient conditions. Hence, the lower Cu_{sat}/Cu_{main} ratio of 0.28 as 308 found with XPS (§ 2.1) can be ascribed to photoreduction during the XPS 309 measurements rather than to the intrinsic presence of reduced copper oxide.

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311 *3.1.2. Local Cu structure after drying, pre-oxidation and C*₃*H*₈ *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

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changes could be observed in the Cu K XANES spectra for the catalyst after drying up 314 to 423 K in a He flow of 7.4×10^{-5} mol/s (at standard temperature and pressure), after a 315 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 316 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 317 318 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. 319 320 Hence, the above mentioned pre-treatments do not influence the local Cu structure. 321 Further drying under He flow of the as prepared catalyst up to 873 K does not alter the 322 XAS spectra either (spectra not shown).

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326 3.1.3. Local Cu structure after reduction with C_3H_8

The XANES, $k^2 * \chi(k)$ and $FT[k^2 * \chi(k)]$ 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.

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335 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 336 337 propane reductions and three intermediate re-oxidations were performed consecutively on the CuO-CeO₂/Al₂O₃ catalyst. The reduction and re-oxidation treatments were 338 carried out at 698 K in respectively a propane flow of 7.4×10^{-6} mol/s in 6.7×10^{-5} mol/s 339 He and an O_2 flow of 3.7×10^{-5} mol/s in 3.7×10^{-5} mol/s He. A metallic Cu structure 340 develops after each reduction and each re-oxidation restores the CuO structure as is 341 342 present at ambient conditions, indicating a reversible local Cu structure in the catalyst 343 (spectra not shown).

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346 3.1.5. Evolution of the local Cu structure during isothermal C₃H₈ reduction

347 The evolution of the local Cu structure in the CuO-CeO₂/Al₂O₃ catalyst during 348 reduction with propane was followed by recording full XAS spectra in a measuring time 349 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 350 351 was pre-treated by flushing with C_3H_8/He for 15 minutes at 424 K, followed by a fast 352 heating to the reaction temperature of 623 K. The acquisition of the XAS spectra was 353 already started during the heating and reaction temperature was reached after 3 minutes. 354 The corresponding Cu K-edge QXANES spectra are given in Figure 9. Effect of the 355 reduction on the XANES spectra can already be seen from the very beginning of the 356 heating, before the reaction temperature was reached, as appears from the decreasing intensity in the $4p_{\sigma}$ transition just after the edge. Although the post-edge structure can 357 be seen as a linear combination of the first $(Cu^{2+}O)$ and last (Cu^{0}) spectrum, the edge 358 structure cannot. During the reduction process, a shoulder appears on the lower half of 359 360 the absorption edge which moves to lower energy values. A small pre-edge peak starts 361 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 362 solely be regarded as a linear combination of the first $(Cu^{2+}O)$ and last (Cu^{0}) spectrum. 363 364 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 365 366 reduction process.

367 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 368 (one for each Cu oxidation state) was performed on this QEXAFS spectrum series. As 369 Cu^{2+} component in the linear combination fit, a fully oxidized spectrum (i.e. at the 370 371 beginning of the reduction series) was used, a fully reduced spectrum (i.e. at the series' end) was taken as Cu^0 component and the Cu_2O reference spectrum was chosen as Cu^{1+} 372 component. The resulting percentages of each component as a function of time in the 373 374 reduction process are given in Figure 10. The exact fit percentages are dependent on the 375 amplitude of the base spectra. As the reference Cu_2O spectrum was taken at ambient 376 temperature from a Cu₂O reference powder, presenting a different disorder than present 377 in the catalyst, the scaling factor for the Cu₂O contribution is not known. Hence, the 378 reported concentrations are only qualitative and not quantitative. The Cu₂O spectrum is

Cu K and Ce L3 on CuO-CeO₂/Al₂O₃

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

381 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-382 CeO₂/Al₂O₃ catalyst. Caballero et al. investigated a CuO/ZrO₂ catalyst under C₃H₈ 383 384 diluted in He at 773 K [12]. Under these conditions, reduction of the catalyst was 385 incomplete and factor analysis of the XANES spectra identified three components: 386 CuO, Cu₂O and Cu. In methanol steam reforming over CuO/ZrO₂, Cu₂O was obtained 387 as post-reaction oxidation state for certain Cu loadings and water/methanol ratios [10]. H_2 reduction of the same catalyst confirmed the presence of the Cu⁺, now as 388 intermediate towards metallic Cu [10]. In H₂ reduction or oxidative methanol reforming 389 390 over CuO/ZnO₂ [30-31] and in CO-CO₂-H₂/Ar reduction of a CuO/ZnO₂/Al₂O₃ catalyst, 391 Cu₂O was equally identified as an intermediate copper phase preceding the formation of 392 metallic Cu [11]. But the presence of Cu₂O as intermediate during reduction of CuO is 393 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 $Cu^{2+} \rightarrow Cu^0$ transition [13]. For 394 unsupported CuO, it was found that the presence of an intermediate Cu₂O phase upon 395 CO or H₂ reduction strongly depends on the reduction conditions and the reduction can 396 397 follow either a direct or a two-step transition [8-9]. The sequential pathway is observed 398 when either a limited feed or fast temperature ramping conditions are applied, i.e. a more 'mild' reduction, where Cu₂O can appear. 399

400 Hence, the presence of Cu^{1+} in present CuO-CeO₂/Al₂O₃ catalyst during the propane 401 reduction process is not surprising but related to the CuO particle structure and 402 conditions of reduction. Under a flow of 7.4×10⁻⁶ mol/s propane in 3.4×10⁻⁴ mol/s He at 403 ambient pressure and 623 K, the large CuO crystallites of the catalyst are reduced 404 through a Cu¹⁺ intermediate state. These conditions are hence 'mild' enough to allow 405 the Cu₂O intermediate state to occur during reduction.

406 407

- 408 3.2. Local Ce structure
- 409 *3.2.1. Local Ce structure at ambient conditions*

410 The Ce L₃ XANES spectra for Ce³⁺ compounds have a strong absorption line at the 411 absorption edge (white line: WL) due to a $2p_{3/2} \rightarrow (4f^l)5d^*$ electronic transition (d^{*}

Cu K and Ce L_3 on CuO-CeO₂/Al₂O₃

412 denotes an excited electron in the d orbital). Ce^{4+} compounds however present a double 413 white line. These two peaks correspond to the $2p_{3/2} \rightarrow (4f^{1}L)5d^{*}$ and $2p_{3/2} \rightarrow (4f^{0})5d^{*}$ 414 transitions (*L* denotes that an electron from an O2p orbital is transferred to a Ce4f 415 orbital) [32-35]. The Ce L₃ spectra for CeO₂, CeF₃ and Ce powder are given in 416 Figure 11 as references, while more spectra of Ce³⁺ and Ce⁴⁺ compounds can be found 417 in for example [36].

418 The Ce L₃ XANES spectrum for the CuO-CeO₂/Al₂O₃ catalyst at ambient 419 conditions is compared with the references in Figure 11. A local CeO₂ structure can be 420 concluded for the CuO-CeO₂/Al₂O₃ catalyst at ambient conditions, with Ce⁴⁺ oxidation 421 state.

422 When ceria is supported on alumina, up to 3 different Ce species have been 423 identified in literature [37]: Ce species in Al_2O_3 cation vacancies (named a CeAlO₃) precursor phase, with Ce³⁺ oxidation state), well-dispersed small CeO₂ particles, too 424 small to be detected in XRD, and bulk-like CeO₂. In the present CuO-CeO₂/Al₂O₃ 425 catalyst, the ceria loading of 2.35 µmol Ce/m² was in the XRD analysis identified as 426 427 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 428 oxidation state is 4+ (Figure 11). Hence, it is concluded that Ce is present as CeO₂ 429 particles only and not as CeAlO₃ precursor state, which bears a Ce^{3+} state. 430

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433 3.2.2. Local Ce structure after C_3H_8 reduction and re-oxidation

Two subsequent reductions (RED1 and RED2) were performed on the CuO-434 435 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 436 3.4×10^{-4} mol/s He at ambient pressure. The final Ce L₃ spectra for each reduction and 437 the intermediate re-oxidation (performed at 763 K, in an O_2 flow of 7.4×10⁻⁶ mol/s in 438 3.4×10^{-4} mol/s He at ambient pressure) are shown in Figure 12. The two reductions 439 yield a similar spectrum. The re-oxidation brings back the CeO₂ structure. Compared to 440 441 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 442 two white lines. As two white lines can still be noticed after reduction, Ce⁴⁺ cations are 443 still present. In order to quantify the amount of Ce^{3+} in the spectra upon the reduction 444

Cu K and Ce L_3 on CuO-CeO₂/Al₂O₃

treatments, a fit of the Ce L_3 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.

448 Ce L₃ XANES spectra are commonly analysed by fitting procedures in which the 449 white line transitions are approximated with Lorentzian curves and the absorption step 450 by an arctangent function [32, 35-36, 38]. The resulting fits on the CeF₃ and CeO₂ 451 references are given in Figure 13. For the CeF₃ reference compound spectrum for

452 example, the fit function was
$$\frac{a}{\pi} * (\arctan(E-b) + \pi/2) + c * (1 + (2*(E-d)/e)^2)^{-1}$$
, with

453 E the X-ray energy value. The first term represents an arctangent with a and b the height 454 and position of its inflection point respectively, while the second term is a Lorentzian 455 function with c, d and e its height, position and width at half maximum respectively. For 456 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 457 the CeO₂ [35], but more recently attributed to many-body final states of the $2p\rightarrow 5d$ 458 459 transition [34]. According to this last reference, we have considered this third 460 component as an intrinsic feature of the CeO₂ XANES spectra.

461 Relative constraints on the height, position and width for the arctangents and 462 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 463 464 then applied to all further fits on the spectra for the reduced catalyst. In this way, from 465 the 16 parameters (4 Lorentzians and 2 arctangents) needed to fit an unknown spectrum 466 only 7 remained as free parameters. The fits on the XANES spectra for the reductions 467 RED1 and RED2 from Figure 12 are given in Figure 14, with indication of the resulting percentages Ce^{3+} and Ce^{4+} . A contribution of about 30% Ce^{3+} is found after each 468 469 reduction. The absolute error on this concentration determination is estimated to amount to 2-3 percent. 470

471

472 3.2.3. Ce^{4+}/Ce^{3+} evolution during temperature programmed C_3H_8 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⁺

Cu K and Ce L3 on CuO-CeO₂/Al₂O₃

477 and Ce^{4+} concentrations. The amount of Ce^{3+} in the spectra as function of the treatment 478 time and temperature is given in Figure 15. A transition from 0 to about 25% Ce^{3+} in the 479 fit occurs in the 610-640 K temperature interval. After this transition, a further increase 480 in the Ce^{3+} fit percentage as function of time of about 1.3 %/hour can be noticed. Hence, 481 the CuO-CeO₂/Al₂O₃ catalyst presents a clear reduction of the CeO₂ particles during 482 temperature programmed C₃H₈ reduction. This means that not only CuO is reduced by 483 C₃H₈ in this temperature interval, but also CeO₂ to a certain extent.

484 A clear two-step propane reduction of ceria in the CuO-CeO₂/Al₂O₃ catalyst appears 485 from Figure 15. This two-step process reminds of the bimodal H_2 -reduction curve that is 486 characteristic of high surface area ceria [39]. Moreover, a XAS investigation of the H₂-487 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 488 about 20% Ce^{3+} was found, followed by a slower reduction [40]. This sequential 489 490 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-491 492 step profile is then governed by a balance between reduction kinetics and morphological 493 changes (sintering of ceria into larger particles) [39-40]. For low surface area ceria, only 494 the bulk reduction step is observed [39]. When ceria is supported on alumina, quite 495 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 496 497 623K has been reported [41].

498 Even though C_3H_8 and H_2 reduction can only be linked to a certain extent [42], 499 similarities can help identifying the processes that occur. The first transition in the 500 $C_{3}H_{8}$ -reduction of Figure 15 occurs in the temperature range 610-640 K. This 501 temperature region can be related to surface reduction of the ceria nanoparticles. The 502 second transition sets off at 640 K and continues with a lower rate up to 763 K. The 503 different slope of both transitions indicates the reduction is dominated by a different 504 mechanism. Given the XRD detection of 7 nm particles, this transition could be related 505 to ceria bulk reduction, which follows a first faster surface reduction. At 763 K the 506 reduction has reached about 32%, but from the constant slope at the end of the 507 temperature range in Figure 15, it can be expected that this reduction process is still 508 incomplete.

509 The onset of C_3H_8 reduction of ceria in the present catalyst, ~610 K, occurs at quite 510 low temperature, which is similar to the starting reduction of CuO, <623 K (see § 3.1.5). 511 For CuO-CeO₂/Al₂O₃ catalysts, the presence of CeO₂ is reported to enhance the 512 reducibility of CuO, but most often, H₂-TPR reduction peaks up to 773 K are identified 513 as CuO related only [5, 7, 41]. On the other hand, interaction between CuO and CeO₂ is 514 sometimes believed to enhance the reducibility of both compounds [43]. Such mutual 515 promotion between copper oxide and ceria is then responsible not only for lowering the 516 CuO reduction temperature, but also for inducing a higher ceria reducibility than 517 expected [43]. In the present CuO-CeO₂/Al₂O₃ catalyst system, temperature programmed C_3H_8 reduction induces at first a fast reduction of some 25 % of the Ce⁴⁺ to 518 Ce^{3+} followed by a slower proceeding reduction. The combined presence of CuO and 519 CeO_2 lowers C_3H_8 reduction temperatures for ceria, so that both compounds start 520 521 reducing in the same temperature range (≥ 600 K).

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524 **4.** Conclusions

X-ray absorption spectroscopy was used to follow the C₃H₈ reduction and re-525 oxidation behaviour of a CuO-CeO₂/Al₂O₃ catalyst, by measuring in-situ both Cu K and 526 527 Ce L₃ transmission XAS spectra. A detailed analysis including error estimation of the XAS data was performed. The starting material displayed fully oxidized Ce^{4+} and Cu^{2+} 528 529 and these states were preserved upon pre-treatment (heating to 873 K in He or preoxidation at 423 K). From the combined XAS, XRD, XPS and TEM characterisation, it 530 531 follows that in this CuO-CeO₂/Al₂O₃ catalyst, CuO is present as large single crystallites, 532 while CeO₂ and Al₂O₃ occur as nanoparticles.

533 Upon reduction with C_3H_8 in the temperature range 600-763 K, Cu^{2+} reduced fully 534 towards metallic Cu^0 . QEXAFS was applied to follow this reduction in detail. Analysis 535 of the XANES edge region and a linear combination fit to the EXAFS spectra allowed 536 to identify the presence of some Cu^{1+} during the first stage of the reduction, indicating a 537 two-step reduction process.

In XANES temperature programmed C_3H_8 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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- 547

548 Acknowledgements

Geert Silversmit is a Postdoctoral Fellow of the Fund for Scientific Research – Flanders
(FWO-Vlaanderen). The authors thank the FWO-Vlaanderen for the access to the
DUBBLE beam line and financial support. Part of this work was performed in the
framework of the Belgian Programme on Interuniversity Poles of Attraction (IUAP V3) initiated by the Belgian State, Prime Minister's Office, Science Policy Programming.
The scientific responsibility is assumed by its authors.

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687 688	Figure Captions
689 690 691 692 693	<i>Figure 1:</i> XRD pattern for the CuO-CeO ₂ /Al ₂ O ₃ catalyst: A) as received, B) after reduction under propane/He.
694 695 696 697 698	<i>Figure 2:</i> STEM images and element mappings of the CuO-CeO ₂ /Al ₂ O ₃ catalyst, CuO entity in alumina matrix (A); cluster of CeO ₂ particles in alumina matrix (B).
699 700 701 702 703 704 705 706	<i>Figure 3:</i> Inverted Selective Area Diffractions (SAD) for the CuO-CeO ₂ /Al ₂ O ₃ catalyst, centred on alumina matrix (A), cluster of CeO ₂ particles (B) and CuO entity (C).
707 708 709 710 711	<i>Figure 4:</i> Cu K XANES spectra for Cu metal, Cu ₂ O, CuO and the CuO-CeO ₂ /Al ₂ O ₃ catalyst taken at ambient temperature.
712 713 714 715 716 717	<i>Figure 5:</i> k^2 -weighted EXAFS signals and Fourier Transforms for the CuO-CeO ₂ /Al ₂ O ₃ 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).
718 719 720 721 722 723 724	Figure 6: $k^{2}*\chi(k)$ and $FT[k^{2}*\chi(k)]$ spectra for the experimental Cu K EXAFS signal of the CuO-CeO ₂ /Al ₂ O ₃ 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)).
725 726 727 728 729 730	Figure 7: Cu K XANES (left), $k^{2*}\chi(k)$ and $FT[k^{2*}\chi(k)]$ (right) spectra for the CuO-CeO ₂ /Al ₂ O ₃ catalyst taken at 723 K, after reduction with C ₃ H ₈ /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).
731 732 733 734 735 736	Figure 8: Fit and experimental $k^3 * \chi(k)$ (left) and $FT[k^3 * \chi(k)]$ (right) spectra for the CuO-CeO ₂ /Al ₂ O ₃ 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)).

Cu K and Ce L_3 on CuO-CeO₂/Al₂O₃

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<i>Figure 9:</i> Cu K QXANES (left) and QEXAFS (right) spectra for the CuO-CeO ₂ /Al ₂ O ₃ catalyst during propane reduction, 1 minute measuring time per XAS spectrum. The inset shows a detail of the edge structure.
<i>Figure 10:</i> Percentages of Cu^{2+} , Cu^{1+} and Cu^{0} 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 L ₃ XANES spectra for the CuO-CeO ₂ /Al ₂ O ₃ catalyst at ambient conditions and the CeO ₂ CeE ₂ and Ce powder reference
compounds.
<i>Figure 12:</i> Ce L ₃ XANES spectra for the CuO-CeO ₂ /Al ₂ O ₃ catalyst in a cycle of two subsequent propane reductions with a re-oxidation in between.
<i>Figure 13:</i> Ce L ₃ XANES spectra and fits for the CeF ₃ (left) and CeO ₂ (right) references.
<i>Figure 14:</i> Ce L_3 XANES spectra and fits for the spectra RED1 (left) and RED2 (right) from Figure 12.
<i>Figure 15:</i> Percentage of the CeF ₃ spectrum (Ce ³⁺ contribution) in the CuO-CeO ₂ /Al ₂ O ₃ Ce L ₃ 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.

781 Tables

Table 1: Crystallite sizes determined from XRD in the crushed CuO-CeO₂/Al₂O₃ catalyst as received and after reduction under C_3H_8 /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		
788						
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790						
791						
792 793 794	<i>Table 2:</i> 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-CeO ₂ /Al ₂ O ₃ catalyst.					

		${S_{BET} \over (m^2/g)}$	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
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Table 3: Estimated systematic errors in the EXAFS analysis. Error on the 801 Debye-Waller factor (σ^2): 10%.

		sys	r	
	Absorber – scatterer	$ \Delta R $ (Å)	Δ <i>N/N</i> (%)	$ \Delta E_0 $ (eV)
C	u-Cu (1 st shell) in Cu metal	< 0.018	6	1
C N fi	u-Cu (1 st shell) in oxides values from k ² and k ³ weighted ts only	<0.018	14	<3
C	u-Cu (higher shells)	< 0.022	20-30	<3
С	u-O (1 st shell)	< 0.013	5	1
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Cu K and Ce L_3 on CuO-CeO₂/ Al_2O_3

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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 (Δk = 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)).

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	Crystal structure		EXAFS fit values				
Absorber - scatter	R (Å)	Ν	R (Å)	Ν	σ^2 (Å ²)	$\frac{\Delta E_0}{(eV)}$	
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)	
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816	Table 5: Comparison between the bond distances R, co-ordination numbers
817	N, for the Cu K EXAFS fit result on CuO-CeO ₂ /Al ₂ O ₃ catalyst after full
818	reduction and the fcc Cu crystal structure values ($\Delta k = 3.29-10.40 \text{ Å}^{-1}$, $\Delta R =$
819	1.00-5.0 Å, k^3 variances: 0.92 (Imaginary part) and 0.39 (Real part)).

	Cu fcc struc	crystal cture	EXAFS fit values for CuO-CeO ₂ /Al ₂ O ₃ catalyst				differ	rence
Absorber - scatterer	R _{Cu} (Å)	N_{Cu}	R (Å)	N	$\overset{\sigma^2}{(\text{\AA}^2)}$	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

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