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Reduction and re-oxidation of Cu/Al₂O₃ catalysts investigated with quick-scanning XANES and EXAFS

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Abstract. In the present study the structure of copper catalysts on alumina support were investigated *in situ* and time resolved during reduction and re-oxidation at different temperatures with the quick-scanning EXAFS (QEXAFS) technique. Different impregnation times (2 min and 90 min) were chosen for the preparation which resulted in different copper species that show a strong variation in the reduction/re-oxidation behaviour. These dynamic changes as well as possible intermediate phases during the gas atmospheres changes were followed with up to 20 EXAFS spectra per second at the copper K-edge covering an energy range of 450 eV. The high time resolution provided new insights into the dynamics of the catalysts e.g. revealing Cu(I) as intermediate state during re-oxidation. Latest advances in the data acquisition hardware are leading to an improved data quality of spectra collected at the SuperXAS beamline. Thus, not only accurate analysis of the catalysts via XANES but also by EXAFS was possible. This is also due to the recent upgrade to monitor the Bragg angle directly with an encoder during the experiments.

1. Introduction

Quick-scanning EXAFS (QEXAFS) is an invaluable tool to investigate rapid structural transformations of systems of scientific and industrial interest such as heterogeneously catalysed reactions. In analogy to other EXAFS-techniques one of the most striking advantages is the sensitivity to the short range order of materials which allows studying not only periodic crystal structures but also amorphous, liquid and gaseous materials in a fraction of a second. Considering nano-sized particles it is even possible to measure surface structures in absorption mode under conditions where other surface sensitive methods cannot be applied since they require a vacuum and/or a flat surface. Thus the application of QEXAFS in catalysis is most interesting due to the possibility of studying the dynamic changes of a catalyst *in situ* under realistic conditions [1–5]. Since the setup of a QEXAFS experiment is equal to conventional EXAFS setups and thus nowadays rather simple, it provides an easy access to such experiments and has recently attracted more and more attention. The time resolution of a QEXAFS system depends on the monochromator mechanics due to the requirement of

a quick oscillating crystal. Different setups in the past have shown that a high time resolution is achievable with QEXAFS using piezo tilt tables [6] and more recently cam-driven mechanics [7]. However, so far most reports about the limits of new QEXAFS instrumentation concentrated on reference samples e.g. metal foils, which provide high cross sections and low parasitical absorption. With the piezo-QEXAFS technique spectra were taken on catalysts with a time resolution of 17 ms/spectrum [3], but only the XANES region was monitored. More recently, full EXAFS data were taken with a cam-driven mechanical system with 1 Hz [8] and 2 Hz [4]. Here we demonstrate that for the acquisition of full EXAFS scans the time resolution can be significantly enhanced. For this purpose industrially relevant Cu/Al₂O₃ catalysts were investigated. With one full EXAFS spectrum every 50 ms the capabilities of current QEXAFS setups at bending magnet beamlines (located at third generation light sources) will be demonstrated. With energy-dispersive EXAFS (DEXAFS) an even higher time resolution down to microseconds can be achieved. However, due to the more complex setup the application of DEXAFS is limited by the homogeneity of the sample and the data quality by uncompensated instabilities [9,10] which do not exist in QEXAFS, where the incident beam intensity can be measured simultaneously to the transmitted beam intensity. Thus, down to about 10 ms (dependent on the energy range) QEXAFS gives a more convenient access to time-resolved measurements in catalysis.

Copper catalysts are widely used in catalysis, e.g. methanol synthesis, steam reforming and for gas phase oxychlorination. QEXAFS studies on Cu/ZnO systems have been reported in detail previously and indicate that Cu(I) species are very short-living intermediates in many reactions [2,3]. In other cases Cu(I) is much more stable, especially if spinels can be formed [11,12]. Interestingly the reduction behaviour of copper catalysts prepared with different impregnation times varies tremendously [13]. Thus, the dynamic behaviour of copper on alumina prepared with different impregnation times was studied here and compared to the results on Cu/ZnO in literature [2,3]. For this purpose, the Cu/Al₂O₃ catalysts were reduced at 350°C and the gas atmosphere was periodically switched between oxidizing and reducing conditions using 21%O₂/He and 5%H₂/He, respectively. The periodic change of gas atmosphere provided the possibility to average over several cycles corresponding to modulation excitation spectroscopy (MES), a useful technique in time-resolved spectroscopy to improve signal-to-noise ratios without losing resolution in time or energy [14].

2. Experimental

The QEXAFS data were acquired at the SuperXAS beamline at the Swiss Light Source (SLS, Villigen, Switzerland), where a cam-driven QEXAFS monochromator is permanently installed [15], the storage ring is operated in top-up mode and the current amounted to about 400 mA during the experiments. The superbend magnet with a magnetic field of 2.9 T and a critical energy of 11.9 keV was used as polychromatic source. The X-ray beam is vertically collimated on the water-cooled Si(111) channel-cut crystal while a second toroidal mirror behind the monochromator focused the beam on the sample. This resulted in a beam spot of about 100 μm x 100 μm with a flux of about 10¹² photons/s. With an excenter disk of 0.30° an energy range between about 8960 eV and 9440 eV was covered providing the possibility to study the EXAFS region at the Cu K-edge. The Bragg angle was acquired simultaneously to the signal of the three air-filled ionisation chambers using a recently installed angular encoder [16]. A copper metal foil placed between the second and third chamber was used for accurate energy calibration.

The catalysts were prepared by different impregnation times with CuCl₂ solution of alumina pellets with cylindrical shape (3.2 x 3.6 mm, Engelhard, cf. ref. [13]). Whereas the sample impregnated for 120 seconds had a sharp impregnation profile (later called “shell-impregnated catalyst”) and is not fully impregnated, the second sample with an impregnation time of 90 min was fully impregnated (denoted as “fully impregnated catalyst”). The samples were dried and crushed into ca. 100 μm large particles. The reduction/re-oxidation was conducted in a quartz glass capillary (Markröhrchen, Hilgenberg GmbH, 1.0 mm in diameter) functioning as microreactor [17]. The capillary was heated from below by a mass flow controlled air jet (Brooks mass flow controller) with a home-built oven.

The sample temperature was measured just below the microreactor. The reduction was performed in 5% H_2/He , the re-oxidation in 21% O_2/He and the evolving products during the reduction and re-oxidation were monitored by a quadrupole mass spectrometer (Balzers Thermostar).

3. Results and discussion

First, the fully impregnated $\text{Cu}/\text{Al}_2\text{O}_3$ system (impregnated for 90 min) was investigated and heated in 5% H_2/He to 350°C. Thereby the catalyst was reduced and the dynamic oxidation and reduction behaviour was studied by switching the sample gas atmosphere between O_2 and H_2 with a period of 120 seconds. The evolving or disappearing $\text{Cu}(0)$, $\text{Cu}(\text{I})$ and $\text{Cu}(\text{II})$ species were recorded by QEXAFS using a crystal oscillation frequency of 10 Hz. This resulted in one spectrum each 50 milliseconds. Data of three full gas atmosphere change cycles were obtained leading to more than

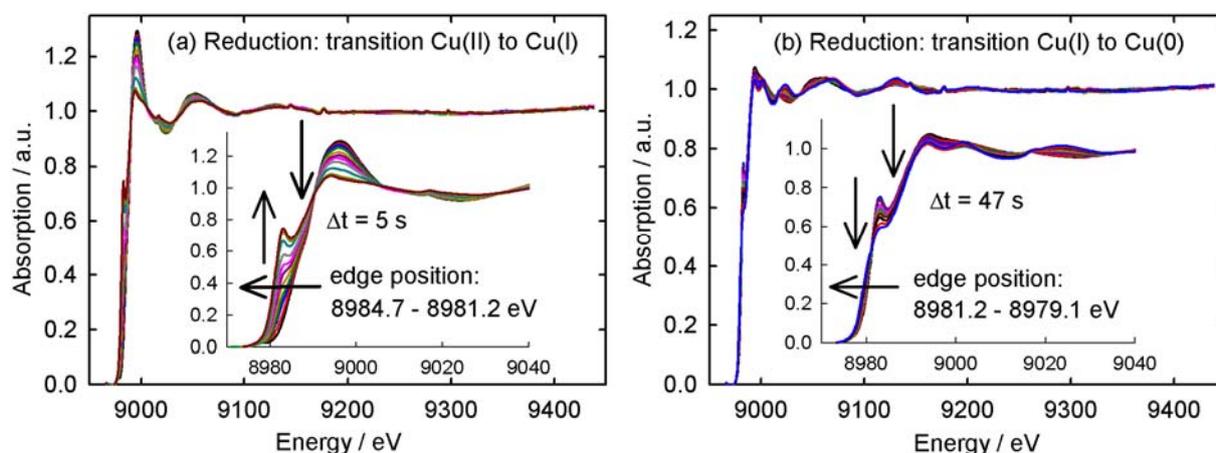


Figure 1: Reduction of fully impregnated $\text{Cu}/\text{Al}_2\text{O}_3$ at 350°C in 5% H_2/He occurring in two steps. The XANES region is shown enlarged as inset.

7200 spectra only for this first measurement.

Figure 1 shows some normalized spectra during the first reduction process. The reduction proceeds much slower than the re-oxidation. For the reduction process it is thus possible to average over 5 spectra to cancel out some of the statistical noise and still remaining below one second in time resolution. The reduction process can be separated into two parts as can be easily observed in the edge structure. According to a shift of 3.5 eV in edge position and the increased pre-edge feature for the intermediate state [12], the two steps can be assigned to a reduction of $\text{Cu}(\text{II})$ to $\text{Cu}(\text{I})$ and from $\text{Cu}(\text{I})$ to $\text{Cu}(0)$. The first and second transitions are shown in figures 1a and 1b – both with an enlargement of the near edge structure as inset. The first striking observation is the outstanding data quality of these spectra combined with the high resolution in energy and time. Even small changes can be analyzed very accurately and with the chosen energy range EXAFS analysis is possible. Due to high sampling rates combined with well shielded data acquisition hardware even in the enlarged edge the structures are very smooth and reproducible. Regarding the time scales, the first transition from $\text{Cu}(\text{II})$ to $\text{Cu}(\text{I})$ takes only five seconds and the changes in whiteline intensity and edge position, marked by the arrows in figure 1a, are easy to detect and to quantify as has exemplarily been done for the edge positions of the first and the last spectra. The edge positions were determined from the maximum of the consistently smoothed first derivatives and the resulting values are also displayed in the graphs. Compared to the first transition the second transition proceeds much slower as can be seen in figure 1b where spectra of an overall time interval $\Delta t = 47$ s are shown (only selected spectra, not equidistant in time). This reduction in two steps is much more pronounced than on Cu/ZnO catalysts [2,3] and cannot be traced back to mass transfer limitations [17] but rather the stabilization of copper in the alumina matrix.

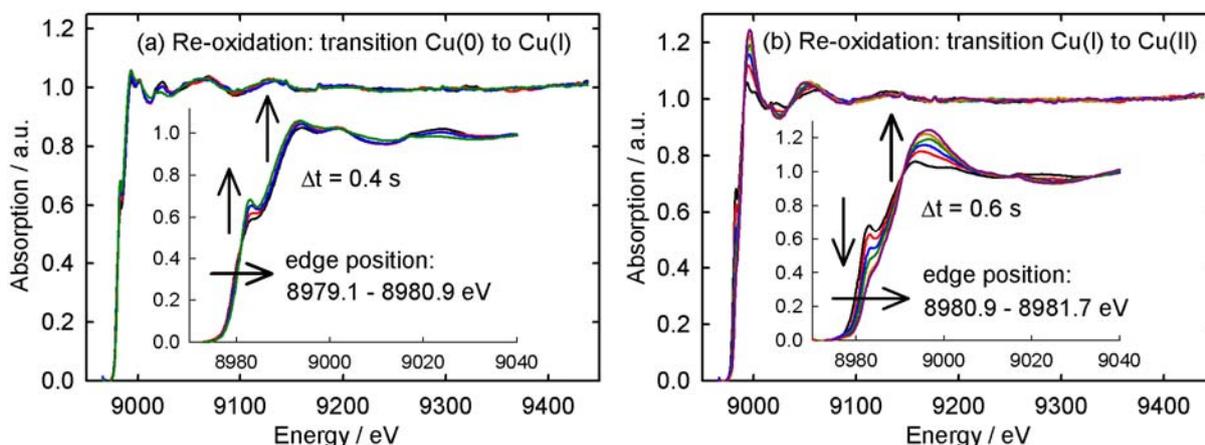


Figure 2: Re-oxidation of fully impregnated Cu/A₂O₃ at 350°C in 21%O₂/He separated in two transition steps with the XANES region enlarged as inset.

In figure 2 the spectra of the re-oxidation are shown similarly as in figure 1. However, no averaging was performed here so that each of the depicted spectra was acquired in only 50 milliseconds. Only one direction of the crystal oscillation was investigated resulting in 10 spectra each second contributing to these diagrams. Two important results can be directly extracted. Firstly, there is also an intermediate during re-oxidation which was not observed on Cu/ZnO catalysts. Secondly, the formation of the intermediate (*cf.* figure 2a) only takes 0.4 seconds and a further transformation mostly occurs in the next 0.6 seconds (*cf.* figure 2b). Hence, the high time resolution is really required in this case. Despite the higher noise level, it is still possible to follow changes in the edge structure and even in the EXAFS region. Note that data of three full gas atmosphere change cycles were collected, which will allow significant improvements in the data quality, as we have shown in a recent study during the catalytic partial oxidation of methane (J. Stötzel et al., in these conference proceedings). This requires that the reduction and re-oxidation of the catalyst is reproducible during several cycles.

More quantitative results about the dynamic behaviour of the three copper species were achieved using linear combination fit analysis (LCA). While for this experiment it is easy to isolate the fully oxidized state as the first reference, the two other ones have to be chosen in a proper manner. It is not known whether there is a situation where all the copper is in the Cu(I) state during the performed experiments. Since in the present study nano-sized copper particles are present, bulk Cu₂O and CuO cannot be used (different geometry, particle size dependence in the XANES). Hence, the intermediate species detected during the reduction in figure 1 was used as Cu(I) reference for all further LCA investigations presented. Since 350°C was the highest temperature and the amount of the intermediate is lower at lower temperatures, as will be shown later, this choice appears reasonable. Accordingly, the reference of the fully reduced Cu(0) was chosen from the data at 350°C after a long reduction procedure. Figure 3a displays the used references and figure 3b the Fourier transformations of the k³-weighted separated EXAFS. It can be seen in 3b that the reference of Cu(0) still shows a first shell oxygen backscattering peak. This as well as the edge position of 8979.1 eV ahead of re-oxidation (*cf.* figure 2a) evidence that some of the copper is still oxidized. Thus, for further results it has to be kept in mind that the fractions of Cu(I) and Cu(0) are related to the fractions of Cu(I) and Cu(0) obtained at 350°C. In figure 4 the results of LCA for all three reductions (a) and re-oxidations (b) measured at 350°C are shown. The curves were shifted in time to make them comparable. For the reductions as well as for the re-oxidations every cycle leads to the same result. Hence, the system is reproducible during several cycles. However, averaging over several cycles is not straightforward as can be seen by the maximum of Cu(I) during the re-oxidation. For the second run a peak of one spectrum was detected while for the two other runs this peak is located between two other spectra. Averaging would lead to a loss of information in this case caused by the fast dynamics or the distance between two data

points. Concerning the dynamics, the amount of Cu(I) during re-oxidation (*cf.* figure 4b) reaches only about 80% of the value reached during reduction. After half a second this amount is rapidly reduced to about 30% and further reduction proceeds much slower.

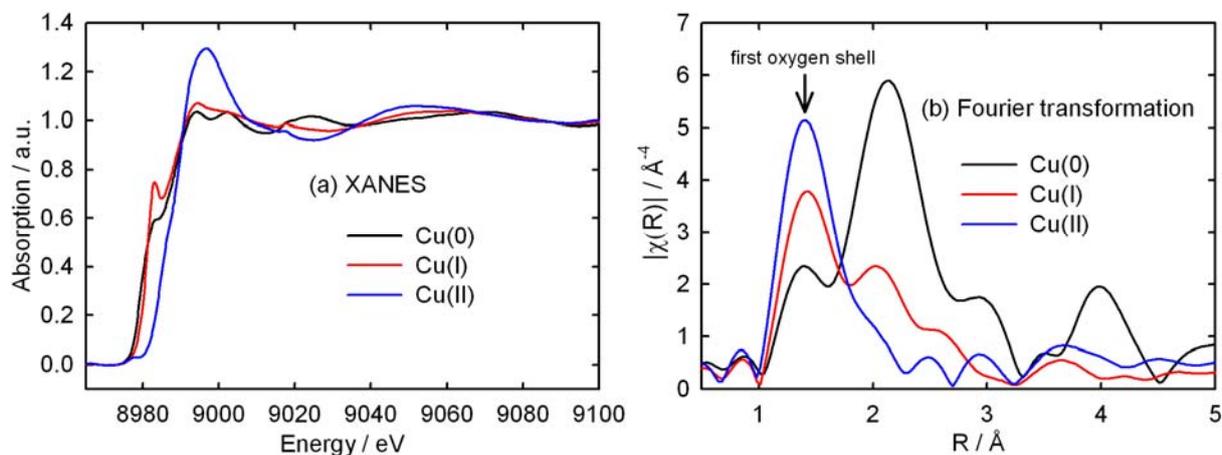


Figure 3: (a) XANES spectra and (b) Fourier transformations of copper references in different oxidation states used for further investigations with LCA

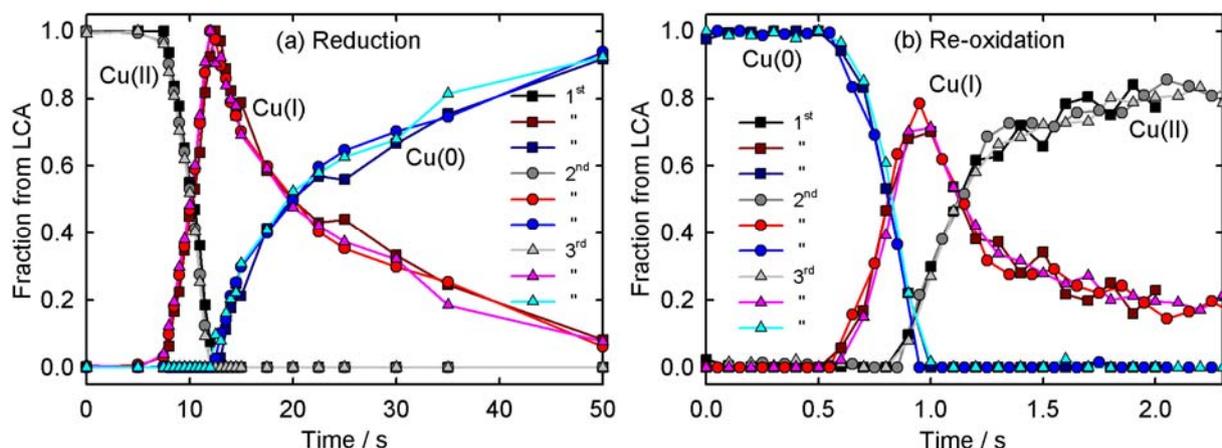


Figure 4: LCA of all three (a) extinctions and (b) ignitions of Cu/Al₂O₃ at 350°C.

In a next step the reduction and re-oxidation processes at lower temperatures were investigated. Again LCA was applied with the references shown in figure 3a. The results for 322°C and 293°C are shown in figure 5. At lower temperatures it becomes more difficult to fully reduce the catalyst as can be observed by the consistent amount of Cu(I) ahead of the re-oxidation. In addition, the transitions proceed much slower at lower temperatures. Note that the maximum amount of Cu(I) decreases at lower temperatures during reduction but is more or less the same during the re-oxidations.

The same experiments were performed with the shell-impregnated catalyst (impregnation time of 2 min). In figure 6 spectra of reduction and re-oxidation at 341°C are shown. Although the amount of copper is much lower it is still possible to properly analyze the spectra. There are several striking differences to the fully impregnated samples. Only one transition can be observed which corresponds to Cu(II) to Cu(I) for reduction and Cu(I) to Cu(II) for re-oxidation. No reduction to Cu(0) occurs due to the lower amount of copper and probably due to its stabilization in the alumina matrix. The height of the peak in the edge is an indicator for the amount and geometry of Cu(I) and evolves to a higher value than for the fully impregnated copper catalysts. This shows that either another Cu(I) species is formed or the Cu(I) species formed during the reduction of the fully impregnated catalyst at 350°C is

already accompanied by metallic copper species. Therefore, a more detailed analysis of the spectra is currently carried out to find the best fitting references leading to optimized results using LCA analysis.

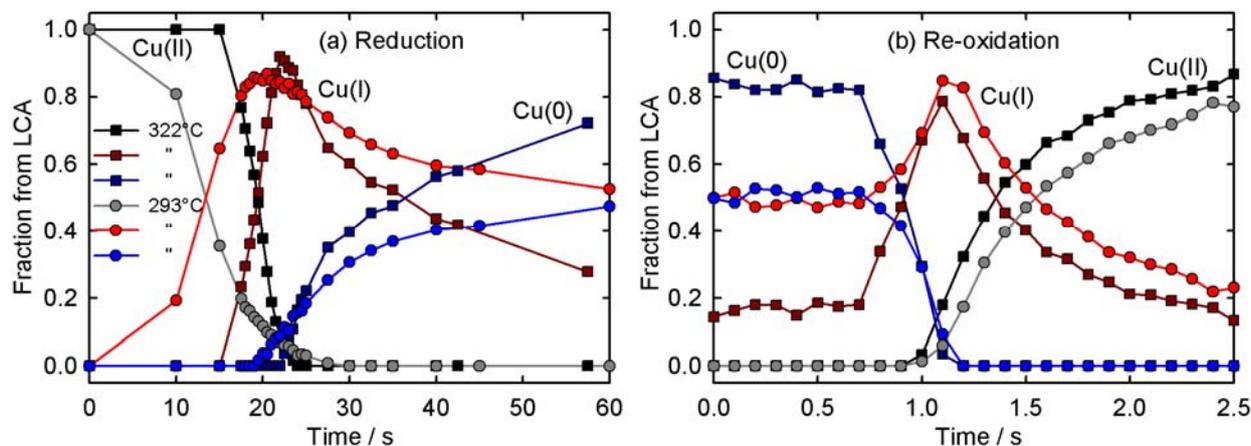


Figure 5: LCA results of Cu/Al₂O₃ during (a) extinction and (b) ignition at 322°C and 293°C

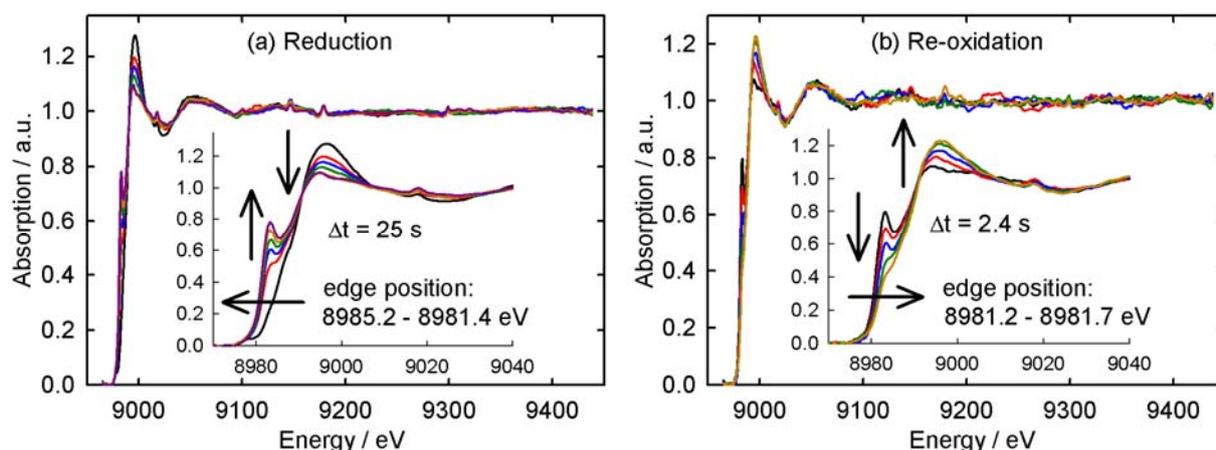


Figure 6: Spectra of Cu/Al₂O₃ prepared with an impregnation time of two minutes during (a) extinction and (b) ignition at 341°C. The enlarged XANES region is shown as inset.

4. Conclusions

The present study shows that the dynamics of the reduction of copper on alumina is significantly different to Cu/ZnO and depends on the copper loading. Interestingly, not only during reduction but also during the faster re-oxidation Cu(I) was detected as an intermediate. In addition, the study demonstrates that not only XANES but also full EXAFS data can be obtained with the new QEXAFS setup at the SLS where it is installed on a bending magnet beamline. Here a full EXAFS spectrum was recorded with a time resolution of 50 ms providing new insights in the fast dynamics of the investigated processes. The measurements at different temperatures revealed a decreasing amount of Cu(0) and different kinetics at lower temperatures. The maximum amount of Cu(I) decreased during reduction at lower temperatures while it was constant during re-oxidation evidencing different dynamic processes. A shorter impregnation time led to significantly different dynamics since no transition to Cu(0) could be observed while the spectra evidenced a higher amount of Cu(I) than for longer impregnation times at comparable temperatures. This confirms that two different species with different reduction behaviour are present on fully impregnated Cu/Al₂O₃ that might lead to a better understanding of the catalytic reactions over these Cu/Al₂O₃ catalysts.

5. Acknowledgements

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