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Investigation of the structure of the copper sites in Cu_xO/γ-Al_2O_3 catalysts for the upgrading of ethanol to C4 chemicals

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Initially, the goal of this beam time was to evaluate the copper oxidation state and coordination in the course of ethanol transformation into butanol-1 and butadiene. Unfortunately, the samples provided by our Italian colleagues showed the activity and selectivity insufficient for the XAS measurements. Therefore, during the planning the beam time and discussion with local scientist we decided to study the oxidative transformation of ethanol into acetaldehyde and COx, over the copper-based catalysts which have already showed the excellent activity and were characterized by the pool of the phyciso-chemical techniques as well as catalytic tests.

Within this plan the beam time was successful allowing to observe in situ the changes in copper oxidation state and geometry during the activation and reaction with ethanol or oxygen. Three types of distinct experiments were performed: temperature-programmed reduction of the samples in a flow of ethanol vapours in helium, temperature-programmed reaction in the stoichiometric mixture of ethanol and oxygen, and fast switching experiments using 6-port valve from oxygen to ethanol feed. For all these experiments we collected fast XANEX spectra at Cu K-edge. Technical opportunities of BM31 allowed us to achieve great quality of the spectra for the measurements within 8900-9200 eV for 20 seconds giving excellent time resolution. Possibility to switch the 6-port valve remotely, using equipment installed at BM31, allowed the collection of series of XANES spectra in switch experiments without interruption and losing the data. The composition of the products at the reactor exit was continuously monitored by on-line mass spectrometer, which is available at BM31. That enables the correlation of time-resolved XANES spectra with the real composition of the feed at the outlet of the reactor.

Also, at the key temperatures, where the dramatic changes in the catalyst activity and selectivity happen, the EXAFS spectra were taken to deeply study the changes in copper coordination.

In terms of the provision of the X-Rays, the BM31 must be considered as an unqualified success on the bases of these results, though only time will tell what structural details may be obtained through modelling and fitting of this data.

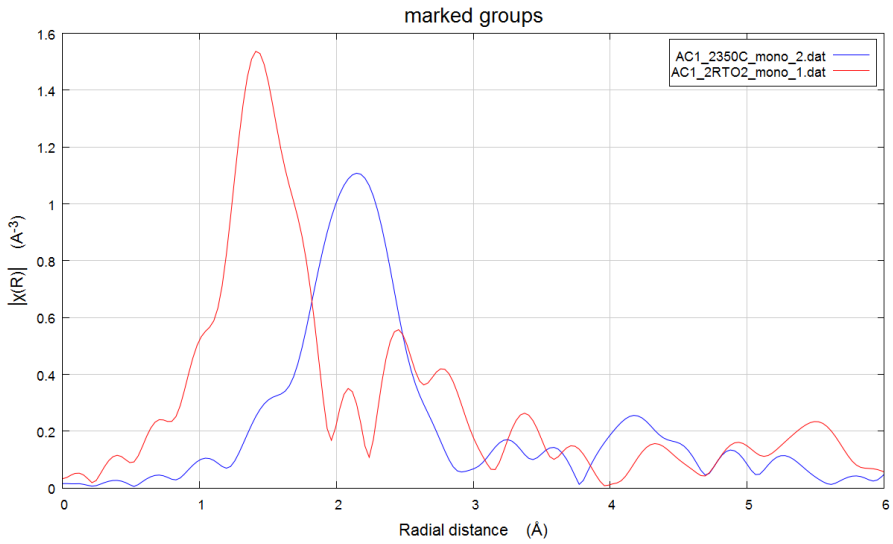

Fig. 1. FT-EXAFS spectra for the CuOx/Al_2O_3 before and after the reaction with ethanol/oxygen mixture, obtained by Fourier transforming the $k^2\chi(k)$ curves in the 3.0–14.0 $Å^{-1}$ range.

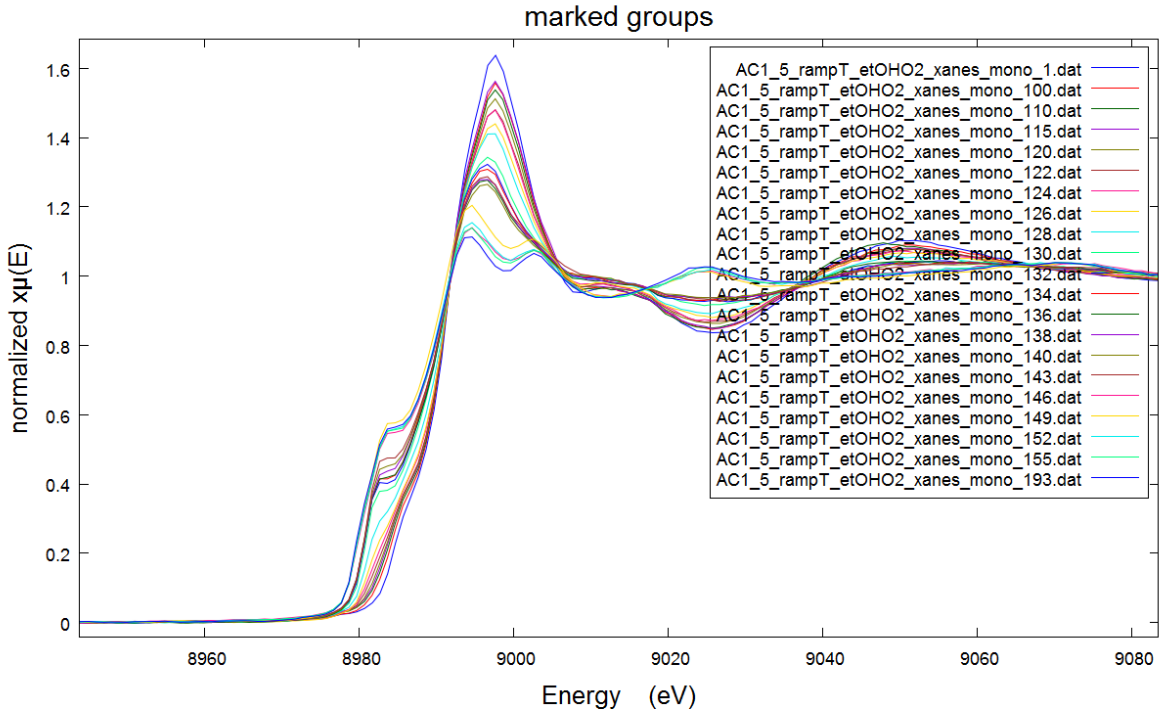

Fig. 2. The XANES spectra obtained during temperature programmed reaction of ethanol with oxygen in the range of 25-350C. The development of the peak at 8981 eV indicates the reduction of Cu(II) into Cu(0). This behavior correlates with the catalytic data showing the dramatic change in the selectivity towards acetaldehyde within the temperature range of Cu(0) species formation.