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Applications of Environmental TEM for Catalysis Research

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In the quest for a better understanding of the dynamics of heterogeneous catalysts under working conditions, *in situ* characterization plays a key role. Catalyst efficiency and sustainability are strongly linked to the dynamic morphology and atomic arrangements of the active entities of these complex materials. Here, we provide examples of how environmental transmission electron microscopy (ETEM) can be applied in catalysis research.

ETEM is a unique tool combining imaging and spectroscopy capabilities with a spatial resolution approaching 1Å at elevated temperatures and controlled gaseous environments. As with any other characterization technique, ETEM has drawbacks. Limitations in sample geometry and field of view call for use of complementary *in situ* characterization techniques. Such techniques could be *in situ* X-ray based techniques such as XRD, XAS and EXAFS. The combination of techniques will paint a more complete picture of the sample under a reactive environment.

In order to take full advantage of the complementary *in situ* techniques, transfer under reaction conditions is essential. Here we introduce the in *situ* transfer concept by use of a dedicated TEM transfer holder capable of enclosing the sample in a gaseous environment at temperatures up to approx. 900°C. The holder is compatible with other *in situ* technique set-ups [1].

Figure 1 shows the concept of the transfer holder. In this experiment, cuprous oxide has been initially characterized in the ETEM at room temperature in vacuum, then transferred to an *in situ* XRD set-up, reduced in hydrogen, and finally transferred back to the microscope in 10^5 Pa of H_2 at 220°C.

In general, the catalytic behaviour of nanoparticle systems can be greatly influenced by the synthesis procedure used. The different stages of the formation process such as drying, calcination, and reduction can all be optimized by tweaking parameters such as temperature, time of treatment and gaseous environment. Following the process of identified volume subsets of the catalyst material by means of electron beam based characterization at the different stages of synthesis gives insight in the formation mechanisms of individual nanoparticles from precursor to active catalyst.

Converting solar energy into chemical bonds and thereby increase the storage capability of light energy harvesting requires the use of photocatalysts. In order to characterize and study such catalysts under relevant conditions we have developed a TEM holder capable of exposing a sample to visible light inside the microscope. This way photo induced reactions and phenomena such as Cu_2O degradation (Figure 2) are studied in situ under different gaseous environments [2].

[1] C. D. Damsgaard, H. Zandbergen, T. W. Hansen, I. Chorkendorff, J. B. Wagner, Microsc. and Microanal. 20 1038 (2014).

[2] F. Cavalca, A. B. Laursen, J. B. Wagner, C. D. Damsgaard, I. Chorkendorff, T. W. Hansen, ChemCatChem 5, 2667 (2013).

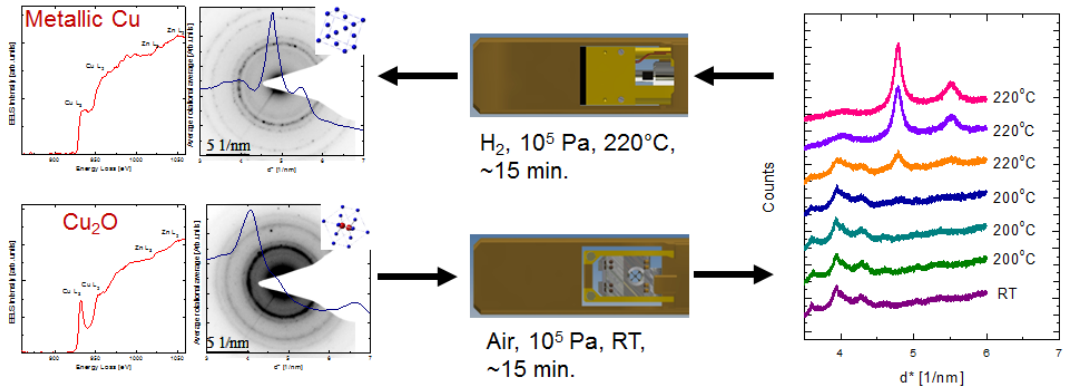

Figure 1: In situ transfer of copper containing nanoparticles between ETEM and in situ XRD setup. The cuprous oxide particles are reduced in the XRD and transferred under elevated temperature in hydrogen to the ETEM keeping the copper metallic.

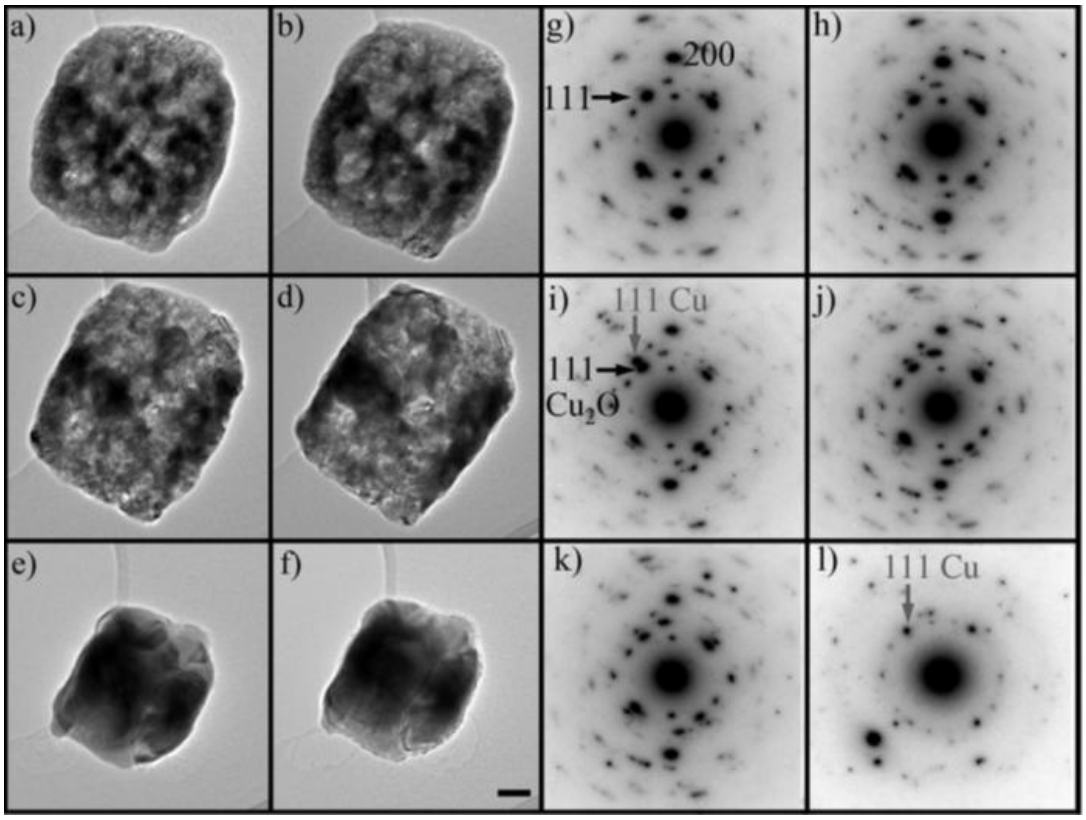

Figure 2: Dynamic study of degradation of Cu2O to metallic Cu in 500 Pa H2O under irradiation of visible light in situ in the ETEM. a)-f) TEM imaging. Scale bar 50nm. g)-l) corresponding SAD. Each frame separated by 15 min.