In situ investigations of gas-solid interactions of nanocrystals by high resolution TEM

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The size, shape, and structure of a nanomaterial affect its catalytic, optical, and electronic properties in ways that are difficult to predict [1-4]. TEM is a powerful technique for characterization of such nanomaterials, but is mostly performed ex situ. As gas-solid interactions have influence on the characteristics of the structure at atomic range in situ studies of the nanomaterial in controlled gaseous environments are necessary in particular for catalyst materials. The in situ TEM (Philips CM300 FEG) located at Haldor Topsøe A/S in Lyngby, Denmark is equipped with an environment cell pumped differentially by molecular drag and -turbo pumps. The design of the environmental cell is adopted from Boyes and Gai at DuPont [5] and constructed by Philips in collaboration with Haldor Topsøe A/S. The resolution of the microscope at temperatures up to 900ºC and pressures up to 20 mbar is better than 0.16 nm, which is sufficient for atomic resolution of most metals used in catalysts.

The morphology and faceting of Cu nanocrystals supported on ZnO are studied in situ under different gas environments at elevated temperatures in the TEM. This system is used as a model system for methanol synthesis catalysts. The gas components are chosen to model the environment of the methanol synthesis under reaction conditions. Significant changes are observed as a function of the reduction potential of the surrounding gas atmosphere, see Figure 1 [6]. These changes can be attributed to adsorbate induced changes (H/H_2O) and changes induced by reduction of the ZnO support (H/CO).

The microscope is furthermore equipped with a Gatan Image Filter allowing acquisition of in situ EEL spectra. The fine structure of the Cu $L_{2,3}$ ionisation edges are used to study the metal-support interaction in respect to strain and Cu/Zn alloying under different gas atmospheres. The experimental data (Figure 2) are supported by calculated fine structures of the Cu L_3 ionisation edge of strained and alloyed models [7].

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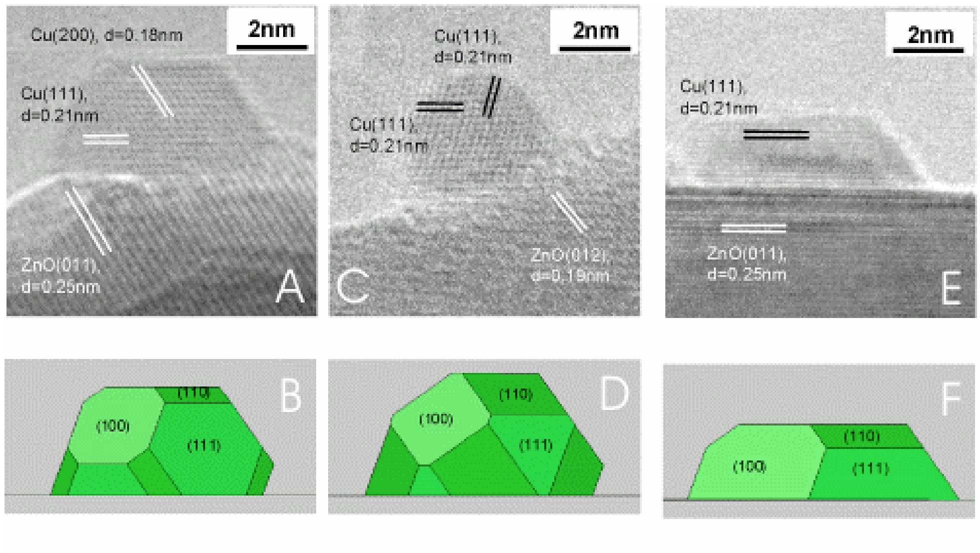

Figure 1. In situ TEM images (A, C, and E) of a Cu/ZnO catalyst in various gas environments together with the corresponding Wulff constructions of the Cu nanocrystals (B, D, and F). (A) The image was recorded at a pressure of 1.5 mbar of H_2 at 220ºC. The electron beam is parallel to the [011] zone axis of copper. (C) Obtained in a gas mixture of H_2 and H_2O, $H_2 : H_2O = 3 : 1$ at a total pressure of 1.5 mbar at 220ºC. (E) Obtained in a gas mixture of H_2 (95%) and CO (5%) at a total pressure of 5 mbar at 220ºC.

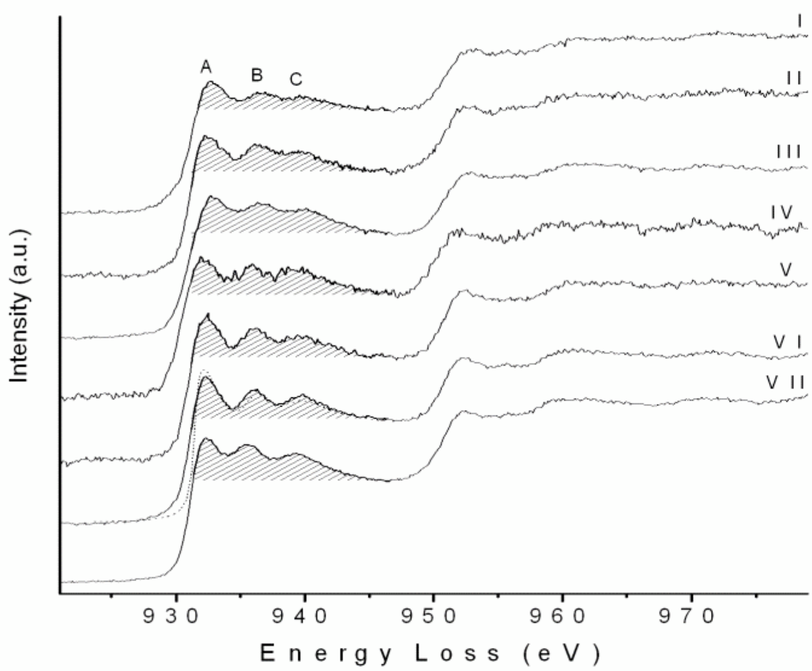

Figure 2. In situ ELNES spectra at the Cu $L_{2,3}$ edges of Cu in its metallic state and brass. (I): Cu/ZnO (1.5 mbar H_2 at 220ºC), (II): Cu/ZnO (1.5 mbar CO/H_2 at 275ºC), (III): Cu/ZnO (1.5 mbar CO/H_2 at 450ºC), (IV): Cu/SiO_2 (1.5 mbar H_2 at 220ºC), (V): Cu/SiO_2 (1.5 mbar CO/H_2 at 275ºC), (VI): Cu foil (1.5 mbar H_2 at 220ºC), (VII): Brass foil (1.5 mbar H_2 at 220ºC). The hatched areas are used as a measure for the differences in the fine-structure.