Methanol is one of the most important petrochemical molecules. It is considered as a prospective sustainable synthetic fuel obtained by the catalytic hydrogenation of CO2.[1] Industrial relevant catalysts are mainly composed of Cu (>50 mol%)/ZnO in combination with a structural promoter, such as Al2O3 (<10 %).[2] The presence of ZnO drastically increases the intrinsic activity of Cu-based catalysts. This Cu-ZnO synergy can be explained by the appearance of strong metal support interaction (SMSI) upon reduction in hydrogen.[3] The nature of the SMSI effect is versatile and can be expressed by electronic or morphological changes. In the former case an electron transfer from the support to the metal can occur, whereas for the latter situation a migration of the partially reduced oxide over the metal particle arises.

For model systems this migration has already been proposed in one of the early studies of Cu-ZnO synergy[4] and has recently been identified as metastable graphitic ZnO by IR measurements.[5]

Here we present experimental evidence for the presence of this metastable graphitic ZnO overlayer on Cu nanoparticles in an industrially relevant Cu/ZnO/Al2O3 catalyst for methanol synthesis. Direct structural imaging and elemental mapping in the transmission electron microscope show the formation of a layered ZnO overgrowth during reduction (Fig 1). The results demonstrate a step further towards a complete understanding of the synergistic effects in Cu-ZnO based catalyst for methanol synthesis.

References
Fig. 1: A) Representative TEM micrograph of the reduced catalyst that shows the graphitic overlayer. B) The corresponding energy filtered TEM map of the O K edge indicates a core-shell structure. C) Scanning TEM image of Cu/ZnO/Al2O3. The inset denotes electron energy loss spectra of the Cu L2,3 and Zn L2,3 edge of one single Cu nanoparticle (see ROI).