Dynamic studies of catalysts for biofuel synthesis in an Environmental Transmission Electron Microscope

L.D.L. Duchstein[1], Q. Wu[2], J.M. Christensen[2], C.F. Elkjær[3], I. Sharafutdinov[3], J.B. Wagner[1], T.W. Hansen[1] and R.E. Dunin-Borkowski[1,4]

1. Center for Electron Nanoscopy, Technical University of Denmark, Fysikvej, Building 307, DK-2800 Kgs. Lyngby, Denmark
2. Department of Chemical and Biochemical Engineering, Technical University of Denmark, Soeltofts Plads, Building 229, DK-2800 Kgs. Lyngby, Denmark
3. Department of Physics, Technical University of Denmark, Fysikvej, Building 307, DK-2800 Kgs. Lyngby, Denmark
4. Institute for Microstructure Research, Research Centre Juelich, D-52425 Juelich, Germany

ldld@cen.dtu.dk
Keywords: Biofuel, catalysis, environmental TEM

The development of transportation fuels from sustainable resources requires new and better production paths. One approach involves the use of biogas to synthesize alcohols, such as methanol or higher alcohols for fuel. For the production of methanol a reduction of processing temperature and pressure to lower the process cost and make the product more competitive is desired. Higher alcohols are in general favourable over methanol due to their high energy density and ease of use in current internal combustion engines. However, the yield of higher alcohols in present production routes is poor prompting for the development of better catalysts [1].

The Catalysis for Sustainable Energy Project (CASE) at the Technical University of Denmark aims at discovering new and improved catalysts based on density functional theory and on testing the chemical reactivity of the most promising candidates experimentally. Transmission electron microscopy (TEM) is used for microstructural characterization and provides feedback for both theory and synthesis.

TEM is a powerful tool for characterizing of catalysts. However, conventional TEM does not provide dynamic information about catalysts in their working state. We have recently installed an environmental transmission electron microscope (ETEM) equipped with a differential pumping system to confine a controlled flow of gas around the specimen, allowing observation in a gaseous environment (FEI Titan E-cell, monochromated, objective lens aberration corrector, Gatan imaging filter). In combination with a heating holder, this microscope allows catalysts to be studied using a variety of TEM techniques *in situ* in a reactive environment approaching the working conditions of the catalysts [2,3].

Here, we present recent ETEM studies of newly synthesized catalysts for alcohol synthesis. Using High-Resolution TEM, electron diffraction, energy electron-loss spectroscopy (EELS), Energy Dispersive X-ray spectroscopy (EDX) and High-Angle Annular Dark Field (HAADF) investigations we have studied the structural changes of these catalysts. Complementary obeservations have been done using Extended X-ray Absorption Fine Structure (EXAFS). The experimental findings have been correlated with the observed changes in the chemical activity of the catalysts. Systematic studies involving variation in temperature, gas pressure and composition were performed and related to structural changes in the specimen.

Representative TEM images of a CuSn based catalyst for synthesis of higher alcohols are shown in Figure 1. The CuSn particles are observed to sinter during the reduction leading to a decreased activity of the catalyst. Figure 2 shows the distribution of Co and Mo in a Co/MoS_2 catalyst during treatment in 1.5 mbar H_2 at 600K. The Co phase is seen to segregate from MoS_2. The EDX scans in Figure 2 b) and c) indicate this segregation.

1. J. J. Spivey, A. Egbebi, Chemical Society Reviews, 36 (2007), 1514 - 1528
2. A. K. Datye, Journal of Catalysis, 2003, 216 (2003), 144 - 154
3. T. W. Hansen et al., Science, 294, (5546) (2001), 1508 - 1510

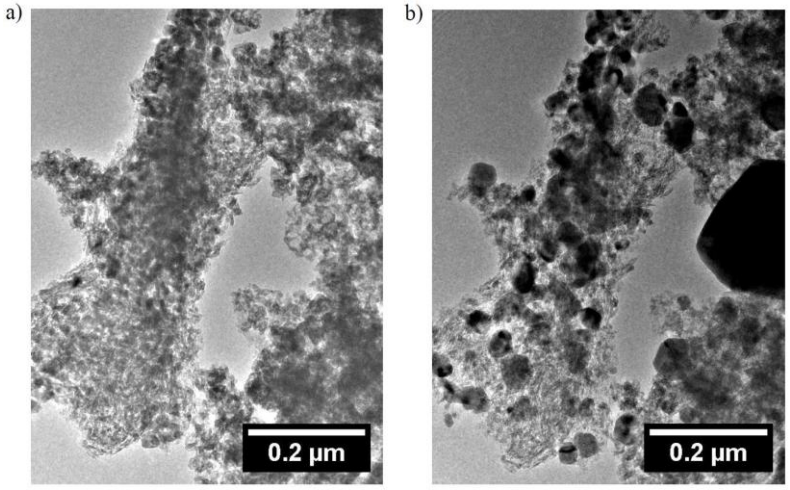

Figure 1. Representative bright-field TEM images of a CuSn catalyst supported on Al_2O_3 for higher alcohol synthesis, acquired a) in high vacuum at room temperature and b) in 1.2 mbar H_2 at 600K after about 1 hour of exposure. CuSn particles sinter reducing the activity of the catalyst.

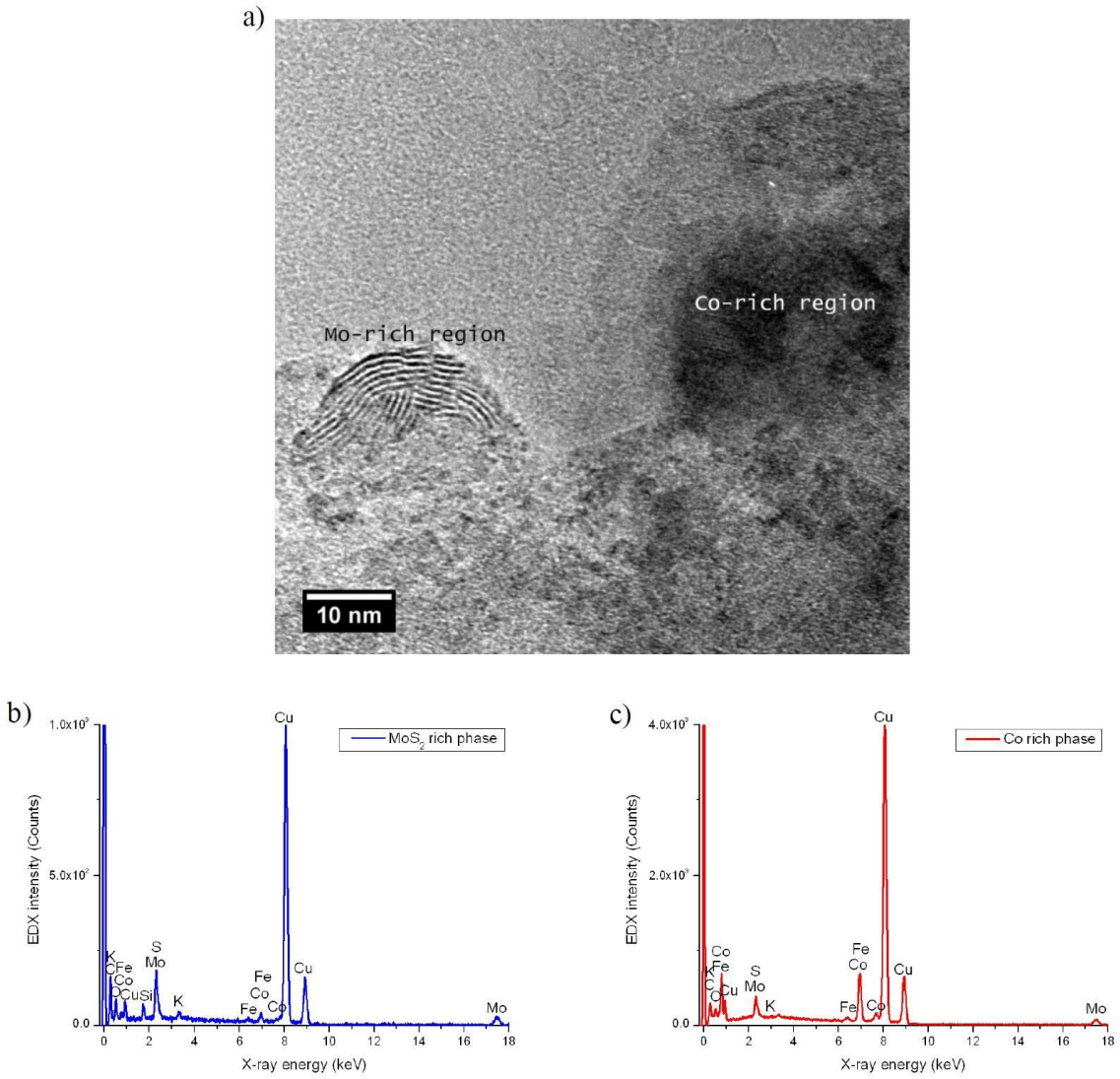

Figure 2. a) Image of a K promoted Co/MoS_2 catalyst for higher alcohol synthesis after *in situ* reduction in 1.5mbar H_2 atmosphere at 630K. The phases were identified with EELS during the reduction and EDX post reduction. Figure 2b) shows the EDX scan on the Mo rich region and Figure 2c) the scan of the Co rich region, indicating the segregation.