

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

Duchstein, Linus Daniel Leonhard; Wu, Qiongxiao; Christensen, Jakob Munkholt; Elkjær, Christian Fink; Sharafutdinov, Irek; Wagner, Jakob Birkedal; Hansen, Thomas Willum; Dunin-Borkowski, Rafal E.

Published in:
MC 2011 Kiel

Publication date:
2011

[Link back to DTU Orbit](#)

Citation (APA):

Duchstein, L. D. L., Wu, Q., Christensen, J. M., Elkjær, C. F., Sharafutdinov, I., Wagner, J. B., ... Dunin-Borkowski, R. E. (2011). Dynamic studies of catalysts for biofuel synthesis in an Environmental Transmission Electron Microscope. In MC 2011 Kiel: Microscopy Conference 2011 (pp. M3-336). DGE – German Society for Electron Microscopy.

DTU Library

Technical Information Center of Denmark

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

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

L.D.L. Duchstein¹, Q. Wu², J.M. Christensen², C.F. Elkjær³, I. Sharafutdinov³, J.B. Wagner¹, T.W. Hansen¹ 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 observations 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/MoS₂ catalyst during treatment in 1.5 mbar H₂ at 600K. The Co phase is seen to segregate from MoS₂. The EDX scans in Figure 2 b) and c) indicate this segregation.

1. J. J. Spivey, A. Egbeki, 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

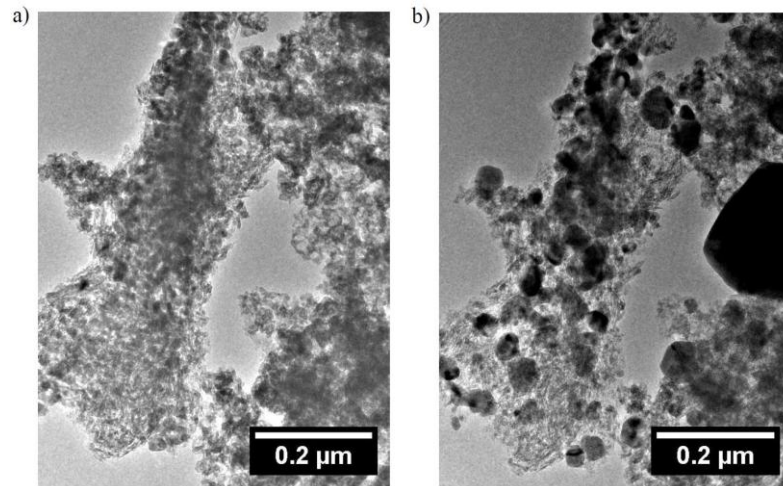


Figure 1. Representative bright-field TEM images of a CuSn catalyst supported on Al_2O_3 for higher alcohol synthesis, acquired a) in high vacuum at room temperature and b) in 1.2 mbar H_2 at 600K after about 1 hour of exposure. CuSn particles sinter reducing the activity of the catalyst.

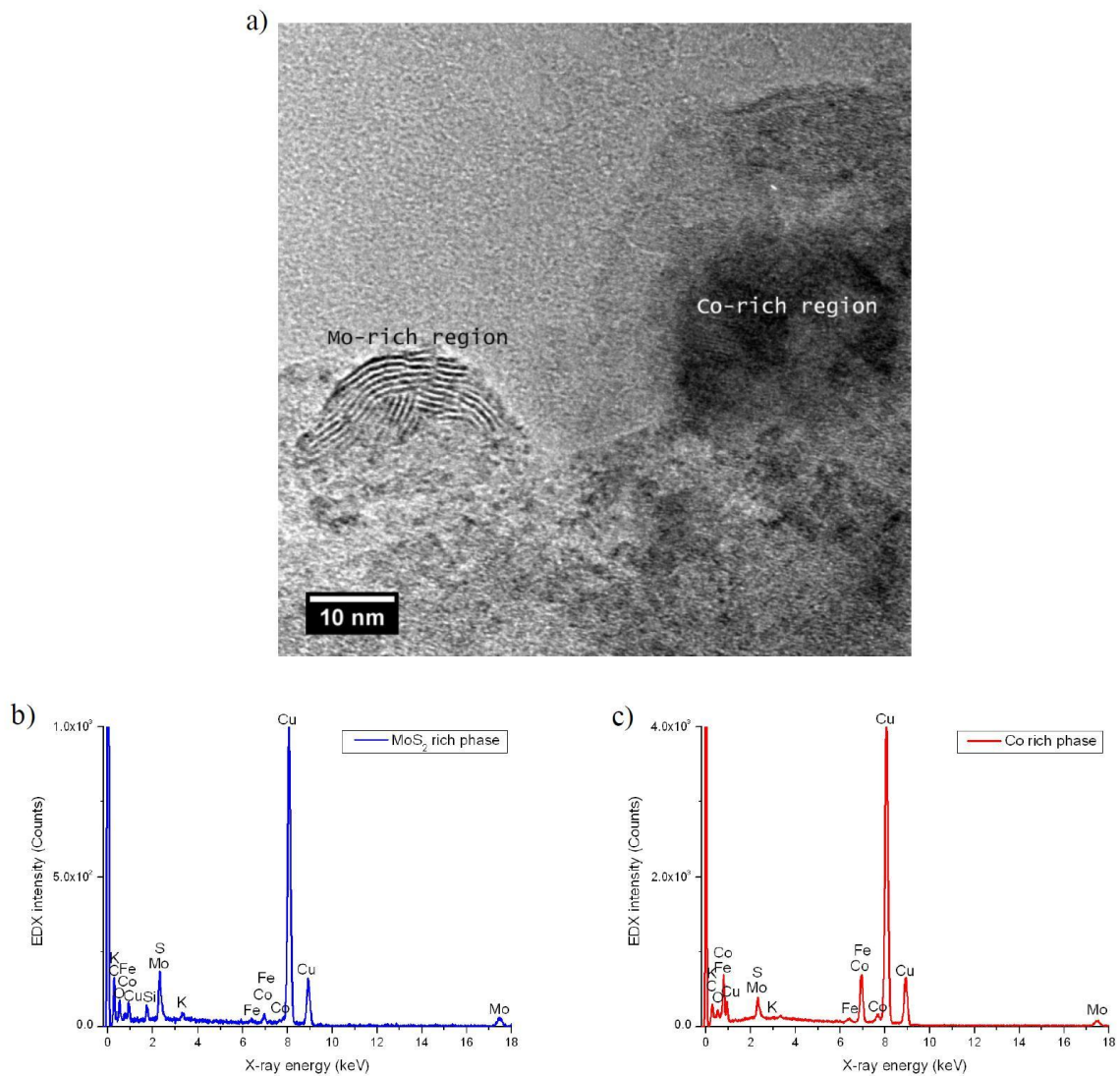


Figure 2. a) Image of a K promoted Co/MoS₂ catalyst for higher alcohol synthesis after *in situ* reduction in 1.5mbar H_2 atmosphere at 630K. The phases were identified with EELS during the reduction and EDX post reduction. Figure 2b) shows the EDX scan on the Mo rich region and Figure 2c) the scan of the Co rich region, indicating the segregation.