

Characterization of Cobalt Sulfide Catalysts

Steven Rozeveld¹, Wen-Sheng Lee¹ and Paolo Longo²

¹Dow Chemical Co., Midland, Michigan, United States, ²Gatan Inc, Pleasanton, California, United States

Transition metal sulfides are an important class of materials known for their structural variety along with technologically significant electronic and catalytic properties [1]. Cobalt sulfides have been investigated as oxygen-reduction catalyst and have the highest activity among all chalcogenides of nonprecious metals [2-3]. However, the phase diagram of cobalt sulfide is relatively complex containing several phases including Co₄S₃, Co₉S₈, CoS, Co₃S₄, Co₂S₃, and CoS₂ phases making analysis of samples with mixed cobalt sulfides phases challenging [1].

A commercial cobalt-sulfide catalyst was investigated in this study using scanning transmission electron microscopy (STEM) and energy dispersive x-ray spectroscopy (EDS) techniques to understand the material structure. The scanning-TEM image in Figure 1a shows the as-received nanoparticle CoS₂ catalyst with a size ranging from 50-300nm. The EDS map showed a partial oxide surface coverage of the cobalt-sulfide particles (Figure 1b). EDS maps were collected at 80keV to improve the EDS signal and reduce beam damage.

Elemental mapping by EDS is less sensitive to variations in the sample thickness compared to electron energy loss (EELS) methods but the time required for data collection can be significant for EDS analysis of light elements. Improvements in the large detector solid angle in the Titan ChemiSTEM provides a significant improvement in this respect over conventional FEG-TEM instruments.

The catalyst uniformity was also studied using a dedicated PEELS system (Gatan Enfinium). Spectrum-Image (SI) data sets were collected in a few minutes, similar to the EDS data collection time, but with a reduced probe current of ~100pA vs ~500pA for EDS. Using Dual-PEELS, low-loss and core-loss SI data were collected simultaneously from the catalyst regions (Figure 2a). Low loss SI map, shown in Figure 2b, indicated a relatively thickness range of 0-3.0 for this region. Multiple linear least squares (MLLS) fitting was used to identify the oxide phase distribution after deconvolution to remove plural scattering from the core-loss SI data (Figure 2c) [4]. PEELS analysis of the oxide phase (Figure 2d) showed that it contained sulfur with S-L_{2,3} near-edge features consistent with sulfate coordination [5]. The near-edge fine structure of S-L_{2,3} edge was found to be useful as a fingerprint for identification of the sulfide and sulfate phase distribution.

Experimental: The TEM analysis was conducted at Dow Chemical using a ThermoScientific Titan Themis G2 80-300kV aberration probe corrected S/TEM which was equipped with ChemiSTEM EDS detectors and a Gatan Enfinium PEELS. Samples were prepared from a mixture of catalyst and methanol which was dispersed onto a standard lacey-carbon supported Cu TEM grid.

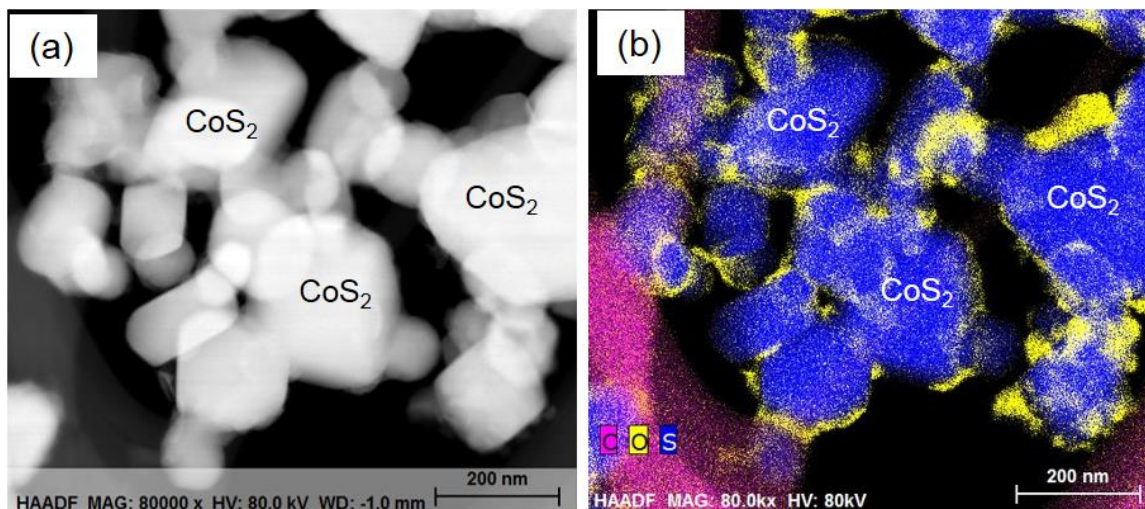


Figure 1. (a) Scanning TEM image 80keV (b) EDS map showing elemental distribution of cobalt , oxygen, and sulfur. STEM Magnification 80kx, accelerating voltage 80keV, probe current ~500pA, 2nm / pixel, 512x512, 13μsec dwell time/ pixel/frame, 750 seconds total collection time.

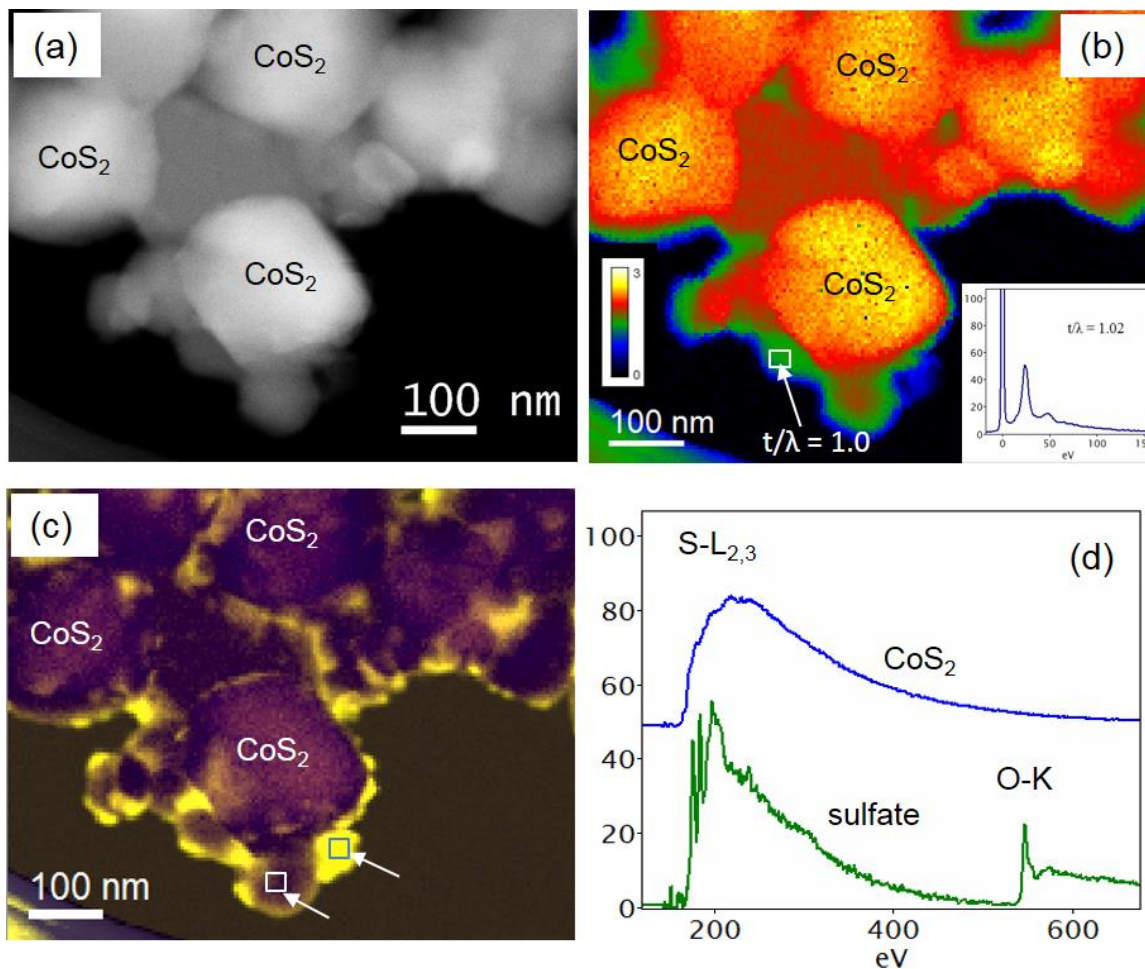


Figure 2. (a) scanning-TEM of CoS₂ catalyst (b) relative thickness determined from low-loss SI (c) core-loss SI showing oxide phase distribution (d) overlay of background subtracted PEELS spectra from oxide

and sulfide phases. SI 80keV, 4.5nm /pixel, probe current ~100pA, 168x134 pixels, low loss ~100µsec/pixel, core-loss ~30msec/ pixel, 0.4 eV/ channel, bin = [2x ,26x].

References

1. Kumar, N. Raman, and A. Sundaresan, “Synthesis and Properties of Cobalt Sulfide Phases: CoS₂ and Co₉S₈” *Z. Anorg. Allg. Chem.* 2014, *640*, (6), 1069–1074
2. Wang, Y.Liang, Y. Li, and H. Dai, “ Co_{1-x} S–Graphene Hybrid: A High-Performance Metal Chalcogenide Electrocatalyst for Oxygen Reduction” **Angew. Chem. Int. Ed.** 2011, *50*, 10969 –10972
3. Ganesan, M. Prabu, J. Sanetuntikul, and S. Shanmugam, “Cobalt Sulfide Nanoparticles Grown on Nitrogen and Sulfur Codoped Graphene Oxide: An Efficient Electrocatalyst for Oxygen Reduction and Evolution Reactions” **ACS Catal.** 2015, *5*, 3625–3637
4. Bobynko, I. MacLaren , A. J. Craven “Spectrum imaging of complex nanostructures using DualEELS: I. digital extraction replicas” **Ultramicroscopy** 149 (2015) 9–20 Analytical TEM
5. Hofer and P. Golob, “New Examples for Near-Edge Fine Structures in Electron Energy Loss Spectroscopy” **Ultramicroscopy** 21 (1987) 379-384 379