

Sulfidation of Metal Oxide Crystallites: An Ex-Situ TEM Study

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The concentration of sulfur in diesel is becoming regulated to increasingly lower levels.¹⁻³ Thus, new catalytic systems are necessary to effectively address this challenge. To effectively develop these new materials, it is important to better understand the complex nanostructures existing in the current hydrodesulfurization (HDS) catalysts.⁴⁻¹¹ This study looks into that issue by using ex-situ TEM time-temperature-transformation (T-T-T) data to follow the development of the active phase in a Ni-promoted Mo-rich HDS catalyst.

Oxide particles were first crushed into fines using an agate mortar and pestle. The fines were dusted onto standard, 200 mesh, holey-carbon-coated TEM grids. The grids were transferred into a Philips CM200F where the oxide particles were imaged in the bright field TEM mode at an accelerating voltage of 200 kV. The locations of the oxide particles on the grid were “mapped” during the TEM examination so that those same particles could be re-located and re-examined with subsequent thermal treatments. A fixed bed reactor designed specifically for ex-situ TEM studies¹² was used to treat the grid.

Examination of the fresh oxide agglomerates revealed numerous structures (Figure 1a). The metal oxide crystallites are represented by the darker phase, while a binder phase is presented by the light gray, mottled structure. The TEM grid holding the oxide crystallites was then treated at 200 °C for 8 h under a 10% H₂S/H₂ environment. An examination of the same crystallites revealed a significant difference in the material. While the binder phase did not change, newly formed particles were apparent (Figure 1b). Elemental analysis of these particles indicated that they were enriched in Ni and S. This provided visual evidence of the low temperature Ni phase partitioning that can occur during the sulfidation process and is thus consistent with open literature studies discussing the formation of detrital Ni and Co sulfide particles during the sulfidation of Mo-based catalysts.^{4,5,7,9,10}

The grid was given a final sulfidation treatment at 375 °C for 4 h under a 10% H₂S / H₂ environment and then returned to the TEM for re-examination. Significant changes were again evident within the agglomerate (Figure 1c). First, the Ni sulfide particles observed in Figure 2b continued to growth with time and temperature. Second, distinct layered structures became evident. The presence of the layered features clearly indicated the Mo-rich sulfide particles had formed within the system. It is well known that the Mo-rich sulfide particles must be decorated with the promoter atoms to be fully active.¹³ Thus, these data indicate the importance of an overabundance of Ni in the oxide in order to have sufficient Ni remaining to coat the exterior of the Mo-rich sulfide particles and allow catalysis to occur.

References:

1. K.G. Knudsen et. al. “Catalyst and Process Technologies for Ultra Low Sulfur Diesel” *Applied Catal. A: General* (1999) **189** 205-215.

2. C. Song “An Overview of New Approaches to Deep Desulfurization for Ultra-Clean Gasoline, Diesel Fuel, and Jet Fuel” *Catalysis Today* (2003) **86** 211-263.
3. M.C. Kerby et. al. “Advanced Catalyst technology and Applications for High Quality Fuels and Lubricants” *Catalysis Today* (2005) **104** 55-63.
4. R. Candia et. al. “Effect of Sulfiding Temperature on Activity and Structures of Co-Mo/Al₂O₃ Catalysts II” *Bull. Soc. Chim. Belg.* (1984) **93** 763-773.
5. R. Prada Silvy et. al. “Influence of the Activation Temperature on the Degree of Sulfidation, Dispersion, and Catalytic Activity of Co-Mo/Al₂O₃ Catalysts” *Indian Journal of Technology* (1987) **25** 627-638.
6. E. Prayen et. al. “Morphology Study of MoS₂- and WS₂-Based Hydrotreating Catalysts by High-Resolution Electron Microscopy” *J. Catal.* (1994) **147** 123-132.
7. S. Eijsbouts “On the Flexibility of the Active Phase in Hydrotreating Catalysts” *Appl. Catal.* **158** (1997) 53-92.
8. L.S. Byskov et. al. “Sulfur Bonding in MoS₂ and Co-Mo-S Structures” *Catal. Lett.* **47** (1997) 177-182.
9. S. Eijsbouts et. al. “Changes of MoS₂ Morphology and the Degree of Co Segregation during the Sulfidation and Deactivation of Commercial Co-Mo/Al₂O₃ Hydroprocessing Catalysts” *Ind. Eng. Chem. Res.* **46** (2007) 3945-3954.
10. S.D. Kelly et. al. “Structural Characterization of Ni-W Hydrocracking Catalysts Using In-Situ EXAFS and HRTEM” *J. Catal.* (2009) **263** 16-33.
11. Y. Okamoto et. al. “Effect of Sulfidation Atmosphere on the Hydrodesulfurization Activity of SiO₂-supported Co-Mo Sulfide Catalysts: Local Structure and Intrinsic Activity of the Active Sites” *J. Catal.* (2009) **268** 49-59.
12. C.E. Klierer et. al. “Ex-Situ Transmission Electron Microscopy: A Fixed Bed Reactor Approach” *Microscopy and Microanalysis* (2006) **12** (2) 135-144.
13. M. Daage and R.R. Chianelli, “Structure-Function Relations in Molybdenum Sulfide Catalysts: The “Rim-Edge” Model” *J. Catal.* **149** (1994) 414-427.

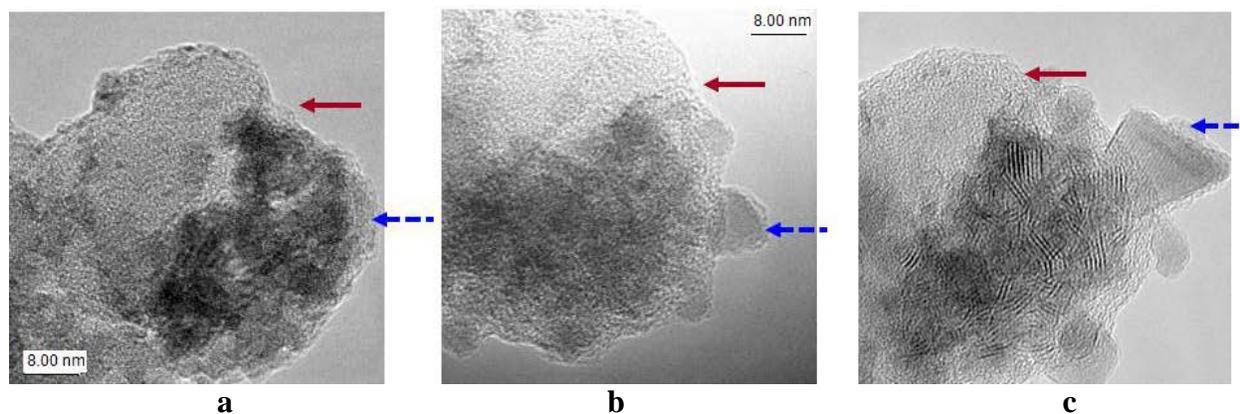


Figure 1: BF TEM image showing: (a) oxide crystallites (dark phase) and binder (lighter gray phase with mottled texture), (b) original crystallites after a 200 °C, 8 h treatment in a 10% H₂S / H₂ environment, and (c) original crystallites after a 375 °C, 4 h treatment in a 10% H₂S / H₂ environment. Arrows indicate the same region in each image. Solid arrow shows region of binder that does not change with sulfidation, while broken arrow presents region of significant phase partitioning with sulfidation.