

EXAFS determined sulfidation pathway of hydrotreating catalysts

Shelly D. Kelly¹, S. Basu², Meghan E. Charochak¹, Tom Mezza¹, Sergio I. Sanchez¹, Colleen Costello¹, and Wharton Sinker¹

¹Honeywell UOP, 25 E. Algonquin Rd., Des Plaines, IL 60017-5017, USA

²Honeywell India Technology Centre (HITC), Gurgaon, Haryana, INDIA -122004

Shelly.Kelly@Honeywell.com

Refiners use hydrotreating processes to remove contaminants from crude oil. These contaminants such as sulfur, nitrogen and metals can be detrimental to refinery equipment, catalysts, and the environment. Stricter government regulations are tightening the specifications on sulfur in fuels requiring even better performing hydrotreating catalysts.

The catalytically active phase in supported hydrotreating catalysts are molybdenum disulfide (MoS₂) clusters dispersed on high surface area aluminas. The edge sites of the MoS₂ clusters are widely accepted as the catalytically active sites for hydrogenation and contaminant removal. In addition, sulfided metals such as Ni and Co have been found to promote the activity of these catalysts, presumably through incorporation in the MoS₂ structures. The sulfidation conditions for the catalyst must be severe enough to produce fully sulfided Mo and promoters to maximize the performance of the catalyst.

Understanding the sulfidation process has led to valuable insights into the performance and mobility of the metals on the alumina support. In some cases, simultaneous sulfidation of the metals (Mo and promoters) increases the incorporation of the promoters into MoS₂ clusters leading to enhanced activity, but there are other cases where this is not the case.

One common deactivation mechanism of hydrotreating catalysts is through the movement of metals on the support resulting in separation of the promoter from the sulfided metal and/or metal agglomeration resulting in few catalytically active edge sites. By tuning the metal to support interaction, the catalyst can be readily sulfided and also effectively anchored to the support.

A number of studies have used XANES to follow the rates of metals sulfiding during the sulfidation process. A few others have done in depth EXAFS studies to determine the specific mechanism of sulfidation from the oxide precursors to the fully functional sulfided catalyst. In addition to the rates and extent of sulfidation, the interaction of the metals with the support is key to catalyst performance.

In-situ temperature programmed sulfidation (TPS) using gas effluent monitoring and synchrotron-based sulfiding systems and ex-situ aberration corrected STEM were performed on three catalyst systems to study the effect of Mo concentration and support interaction as affected by a modifier. Mo K-edge XAFS spectra of these catalysts were collected at beamline 10ID at the Advanced Photon Source (APS), Argonne National Laboratory.

The combination of ex-situ AC-STEM and in-situ Mo EXAFS sheds light on the gas phases evolving from the samples as observed by TPS. The TPS plots show the expected consumption of H₂S and evolution of H₂O at low temperature. At higher temperatures ~250C, there is an initially unexpected sharp evolution of H₂S and H₂. Beyond this temperature region, there is further consumption of H₂S and evolution of H₂O as sulfidation appears to continue in the temperature regime above ~350C. These results will be presented.