

Structural Insights Into the Poisoning of Metal Sulfide Hydrotreating Catalysts Through the Use of Electron Tomography

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Introduction

In refinery hydroprocessing, catalysts deactivate through several mechanisms including coking and poisoning with metals. Poisons can enter the hydroprocessing unit with the feed either from the crude oil, through additives from upstream processes, or through consequences of an upset. Different poisons have different effects on the hydroprocessing catalyst. Some poisons have large effects on catalyst activity during use whereas others only affect catalyst activity upon regeneration to remove hydrocarbons.

New insights into the structure of industrial hydroprocessing catalysts have been made through the use of electron tomography.[1] Though transmission electron microscopy (TEM) is an incredibly useful tool to image hydroprocessing catalyst active sites, it suffers because the 3D catalyst image must be projected onto a two dimensional plane. Electron tomography combines multiple images at different tilt angles to collect sufficient data to recreate a 3D image of the catalyst. Albemarle and Utrecht University have been able to use electron tomography to study an industrial NiMo/ γ -Al₂O₃ catalyst.[2] This new understanding of the active site structure of the hydroprocessing catalyst will be applied to known poisoning mechanisms.

Materials and Methods

A extrudate-shaped commercial “type II” NiMo catalyst was sulfided in the gas phase with a mixture of H₂S and H₂. It was run in typical hydrocracking pretreat operations in a pilot plant reactor for 8 days. At the end of the run it was discharged, washed with toluene to remove residual hydrocarbon and crushed. The powder was embedded in epoxy resin and sliced into ultra-thin sections. Bright-field TEM tilt series were recorded at 200kV with a Tecnai20 Twin FEG. Catalyst poisoning information was taken from a database of historical operation at commercial refineries with Albemarle catalysts in a variety of services.

Results and Discussion

Poisons of commercial hydroprocessing catalysts include metallic and organometallic species such as arsenic, lead, mercury, nickel, phosphorus, silicon, sodium and vanadium.[3] Catalyst poisons can be deposited on the catalyst, decreasing activity, but can also break through the catalyst bed and damage downstream processes as well. Metal poisoned catalyst can also be difficult to regenerate. Poisoning during use typically occurs either by chemical destruction of active sites or by blocking access to active sites. To properly address this blocked access, it is important to have a proper image of the active site distribution of an industrial catalyst.

Two dimensional pictures as well as 3D renderings of MoS₂ in hydrotreating catalysts are available from TEM / electron tomography. On first examination, it is apparent that most MoS₂ crystal planes are bent and appear “peeled off” the alumina support. A signature of the newer, type II catalysts is thought to be the lack of interaction of the metal sulfide with the support surface. The 3D renderings show that most of the MoS₂ slabs are interconnected in space forming complex three dimensional networks. It is apparent that MoS₂ particles in industrial catalysts cannot be described as simple triangles or truncated hexagons as indicated from studies of model systems.[4]

It is easy to envision the effects of catalyst poisons that act through pore mouth plugging on a system as pictured from the tomography results. Pores of hydroprocessing catalysts are not simple cylinders but have complex shapes. Thus, pore mouth plugging will not necessarily result in zero residual activity, but can drastically reduce available active site, as corroborated by commercial poisoning data.

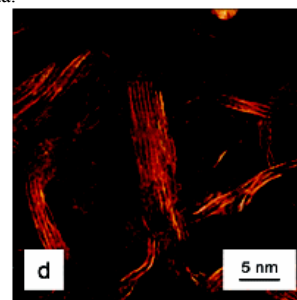


Figure 1. MoS₂ particles within a 44x44x32 nm³ volume visualized without alumina support

Significance

Hydrotreating catalyst poisons can and do significantly shorten the life of commercial hydrotreaters. Deactivation can occur through deposition of contaminant metals at the active site or through pore mouth plugging. Recent insights into catalyst structure through electron tomography show how pore mouth plugging might be thought to take place. Though in early stages, these experiments demonstrate “proof of principle” that electron tomography can provide fundamental insights into the structure of industrial hydroprocessing catalysts.

References

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