

Visualizing single-atom promotion of ultra-deep hydrodesulfurization catalysts (Pt-Co-Mo-S)

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Background incl. aims

The shift towards environmentally friendly fuels has led to stricter regulations on transportation fuel purity, necessitating more efficient catalysts for high-quality, low-sulfur diesel from both fossil and renewable sources. Co-Mo catalysts, supported on alumina, are used to remove sulfur from organosulfur molecules in mineral oil in industrial processes conducted under high hydrogen pressure. However, a significant challenge remains in extracting sulfur atoms from certain sulfur compounds, such as 4,6-dimethyldibenzothiophene (4,6-DMDBT), due to steric hindrance in the molecular reaction pathway.

Over the last four decades, our understanding of Co-Mo catalysts has greatly improved, largely thanks to the Co-Mo-S model introduced by Dr. Henrik Topsøe and his team [1]. According to this model, the active phase of the catalyst is MoS₂ nanocrystals with Co atoms attached at the edges [1,2]. Similar detailed atomic-level imaging of industrial catalysts has remained a challenge since the catalysts are prepared by incipient wetness methods on high-surface area (oxide) supports. However, recent advancements in aberration-corrected electron microscopy, which now allow for single atom detection, have extended this understanding to industrial-grade catalysts supported on high-surface area (conducting) materials, such as graphite, by imaging atom-by-atom the Co-Mo-S structure, even in 3D [3,4]. This has been available due to a combination of ultra-thin supports for single atom contrast optimization and low-voltage (60kV) and low-dose imaging schemes to suppress beam damage.

These breakthroughs provide a powerful set of tools for designing and characterize new active edge and corner structures in hydrotreating catalysts. Here, we present such an approach to enhance a commercial alumina-supported Co-Mo catalyst with small amounts of Pt [5]. This has significantly increased the catalyst's hydrodesulfurization (HDS) activity, boosting the process of removing sulfur from diesel distillates, including 4,6-DMDBT molecules, by +46% in a pilot test unit under industrial conditions. The tested catalysts are analyzed using atomically resolved scanning transmission electron microscopy (STEM) to precisely pinpoint the location of the Pt promoter atoms. These findings are compared to DFT studies based on the well-established Co-Mo-S model. Furthermore, the desulfurization process of 4,6-DMDBT molecules will be modeled to shed light on the catalytic role of Pt.

Methods

The Pt-Co-Mo catalysts were synthesized by incipient wetness impregnation on a mesoporous shaped alumina carrier, resulting in catalysts with metal loads of 16 wt% Mo, 3.5 wt% Co, and between 0 and 1.9 wt% Pt [5]. The catalysts were tested for their HDS activity in a pilot unit using a diesel oil feed containing 1.22 wt% sulfur. After the HDS process, the catalysts were cleaned with the solvent dichloromethane to remove any remaining oil residues. The catalysts were then characterized by scanning transmission electron microscopy (STEM) using two different microscopes; a FEI Talos F200X for element mapping (EDX), and a probe-corrected JEOL ARM-200F for high resolution imaging, operated at 200kV with a probe size of ~1Å for single-atom detection. The interpretation of these results was

aided by STEM image simulations conducted in QSTEM, and density functional theory (DFT) calculations of Pt and Co-Mo-S interactions to visualize edge motifs of the Pt-Co-Mo-S catalyst. The nature of Pt was further justified by Pt L-edge X-ray absorption near edge structure (XANES).

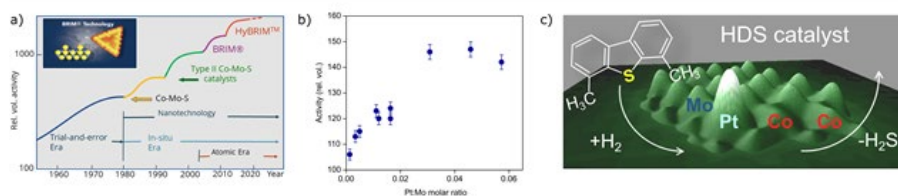
Results

Here we present the synthesis of platinum-cobalt-molybdenum (Pt-Co-Mo) catalysts and their application in the hydrodesulfurization (HDS) process. The resulting catalysts showed a significant increase of +46% in HDS activity when tested in a pilot unit under industrial conditions. Surface science studies using scanning tunneling microscopy (STM) and density functional theory (DFT) have provided a detailed understanding of the catalysts' edge-motifs in Co-Mo-S structures at the atomic level [2]. These model studies, prepared on planar Au substrates under ultra-high vacuum levels, suggest that the cobalt atoms act to increase the concentration of sulfur vacancies on the MoS₂ edges and that corner sites provide favorable geometries for adsorption of specifically the sterically hindered 4,6-DMDBT molecules. Therefore, we focus on characterizing the Pt-Co-Mo catalysts at the atomic level using Pt L-edge XANES and high-resolution STEM. The results revealed a tertiary transition metal sulfide nanostructure, Pt-Co-Mo-S, with Pt attached to edges and corner sites of the Co-Mo-S structure. The study also utilize DFT calculations to further understand the catalytic working principle and the promotional role of Pt in ultra-deep hydrodesulfurization, especially the desulfurization of refractory 4,6-DMDBT molecules.

Conclusion

This study reveals that a Pt-Co-Mo-S nanostructure, with Pt strategically positioned at the edges and corners of the Co-Mo-S structure, significantly enhances the desulfurization process, particularly for bulky 4,6-DMDBT molecules. The introduction of Pt in these tertiary structures appears to break the conventional scaling relations, modifying the behavior of corner and edge sites in the Co-Mo-S catalyst. These single-atom level insights into complex edge motifs in industrial catalysts elucidate the role of promoter elements and provide a new perspective on how to tailor nanostructures for more efficient catalysts in the future.

Graphic:



Keywords:

HDS catalyst, single-atom promotion, HRSTEM

Reference:

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