Cuboidal Mo_3S_4 clusters as hydrogenation catalysts – Substrate dependent mechanisms

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Cuboidal Mo(IV) sulfide clusters, whereby the metals adopt a triangular arrangement, are well-known for their material science applications, having also been studied as models of their heterogeneous MoS_2 counterparts. The latter have been traditionally employed in industry for the hydrodesulfurization (HDS) of fossil fuels, and more recently they have also emerged as an alternative to noble metals for the hydrogen evolution reaction (HER) and the hydrogenation of organic substrates.

By combining experimental and computational methods, in the last few years we have studied the performance of cuboidal Mo_3S_4 clusters as catalysts for the semihydrogenation of alkynes[1] and the hydrogenation of azobenzene into aniline.[2] Notably, our results not only show that such clusters catalyze both processes, but also that the reactions occur without direct participation of the Mo centers. In fact, in all cases the bond cleavage and formation events take place at the bridging (μ-S) ligands of the clusters. Important mechanistic differences are nonetheless observed in both processes, and these will be the focus of this communication.

References

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