

CATALYTIC HYDROGENATION AND DEHYDROGENATION REACTION MECHANISMS MEDIATED BY MOLYBDENUM SULFIDE CLUSTERS

Rosa Llusar^a, Eva Guillamón^a, María Gutiérrez-Blanco^a, Juanjo Mateu-Campos^a,
Mónica Oliva^a, Elena Pedrajas^a, V. Sixte Safont^a, Andrés G. Algarra^b,
Manuel G. Basallote^b, M. Jesús Fernández-Trujillo^b

^aDepartament de Química Física i Analítica, Universitat Jaume I, Av. Sos Baynat s/n,
12071 Castelló, Spain

^bDepartamento de Ciencia de los Materiales e Ingeniería Metalúrgica y Química
Inorgánica, Universidad de Cádiz, Apartado 40, Puerto Real, 11510 Cádiz, Spain

MoS₂-based materials, both crystalline and amorphous, have become a research hotspot in catalysis.[1] The inherent difficulties to obtain mechanistic information from heterogeneous catalysts have led to the design of molecular clusters capable of emulating the reactivity of these solid materials. Given the structural similarities, cuboidal Mo₃(μ₃-S)(μ-S)₃ clusters can be considered as models of the basal planes of MoS₂, as illustrated in Figure 1.

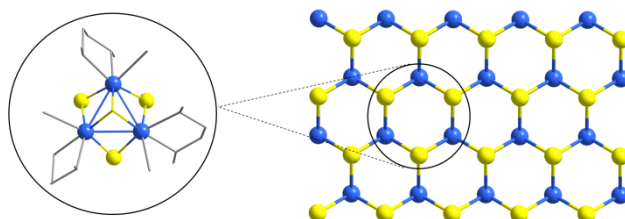


Figure 1. Topological relationship between Mo₃S₄ clusters and the MoS₂ basal planes.

Diamino and imidazolyl amino Mo₃S₄ clusters catalyze the semihydrogenation of alkynes as well as the hydrogenation of azo- and nitroarenes to afford aniline.[2-3] Interestingly, hydrogen activation in both reactions occurs without direct participation of the metal. Diphosphino Mo₃S₄ cluster hydrides and imidazolyl amino Mo₃S₄ clusters are active catalyst for the dehydrogenation of formic acid. In this last case, the catalytic activity is centered on the metal.[4]

In this presentation, we will discuss the catalytic protocols developed in our group for the semihydrogenation of alkynes and for the hydrogenation of azo- and nitrocompounds using Mo₃S₄ clusters. Dehydrogenation of formic acid catalyzed by these cluster complexes will be also discussed. Special emphasis will be placed on their reaction mechanisms.

Acknowledgements: Financial support from Generalitat Valenciana (CIAICO/2021/122), Spanish Ministerio de Ciencia e Innovación (TED2021-132328B-I00) and Universitat Jaume I (UJI-B2021-29) is gratefully acknowledged.

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