

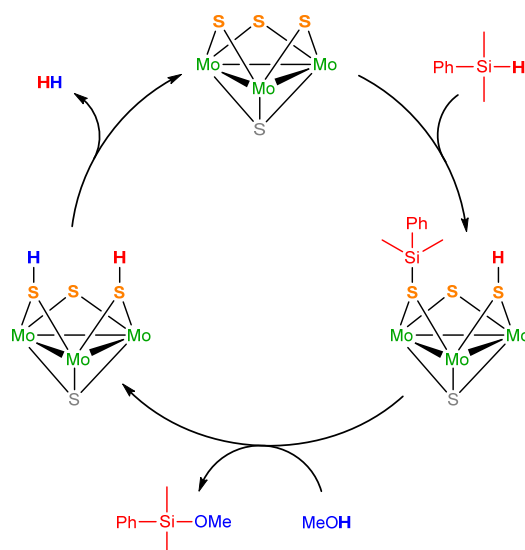
THEORETICAL STUDY OF THE DEHYDROGENATIVE COUPLING OF SILANES AND ALCOHOLS CATALYZED BY MOLYBDENUM CLUSTERS SULFIDES

Mónica Oliva, Juanjo Mateu-Campos, Vicent S. Safont and Rosa Llusar

Universitat Jaume I, Castelló, Spain

Molybdenum cluster sulfides are active catalysts for the transfer hydrogenation and direct hydrogenation of organic substrates such as azocompounds and alkynes. Previous studies on the semihydrogenation of alkynes and on the hydrogenation of azobenzene suggest that the sulfur atoms of the cuboidal Mo_3S_4 clusters are the active centers of these catalysts [1,2].

Herein, we report a DFT-based theoretical study on the dehydrogenative coupling of silanes and alcohols catalyzed by the $[\text{Mo}_3\text{S}_4\text{Cl}_3(\text{dmen})_3]^+$ and $[\text{Mo}_3\text{S}_4\text{Cl}_3(\text{ImNH}_2)_3]^+$ clusters. The proposed catalytic cycle is shown in the next scheme.



Both theoretical results and experimental data suggest that the silane activation occurs at the bridging sulfur atoms.

[1] Algarra, A.G., Guillamón, E., Andrés, J., Fernández-Trujillo, M. J., Pedrajas, E., Pino-Chamorro, J. A., Llusar, R., Basallote, M. G. *ACS Catalysis* 2018, **8**, 7346-7350

[2] Guillamón, E., Oliva, M., Andrés, J., Llusar, R., Pedrajas, E., Safont, V. S., Algarra, A. G., Basallote, M. G. *ACS Catalysis* 2021, **11**, 608-614