SELECTIVE DEHYDROGENATION OF FORMIC ACID CATALYZED BY Mo_3S_4 CLUSTERS: CATALYTIC PERFORMANCE AND MECHANISTIC INSIGHTS

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Hydrogen storage methods are emerging as a sustainable alternative to deal with the environmental impact of fossil fuels.[1] In this context, formic acid (FA) is an attractive storage medium due to its chemical properties such as high volumetric capacity and energy density, low toxicity, and its recyclability via CO_2 hydrogenation [2]

Homogenous CO-free catalysts based on molybdenum are limited to a few examples.[3,4] Recently, our group has reported that diphosphino Mo_3S_4 hydrido clusters are active for FA dehydrogenation.[5] In this work we have extended the investigation to other Mo_3S_4 clusters containing aminophosphines and imidazolyl amino ligands. Optimum activities have been obtained with the aminophosphine $[Mo_3S_4Cl_3(ed^ip_rp)_3]^+$ complex. Based on mechanistic experiments combined with DFT calculations we propose the reaction mechanism depicted in Figure 1.

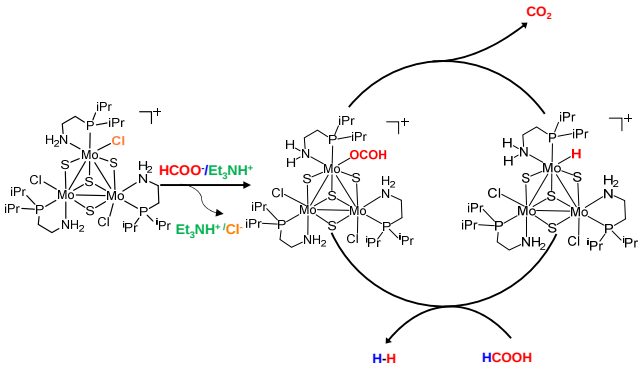

Figure 1. Proposed mechanism for the FADH.

Results on the catalytic optimization will be presented. Experiments and theoretical calculations directed towards the mechanistic elucidation will be also discussed.

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