

PRF#57946-DNI5: Computational investigation of alkane dehydrogenation chemistry on transition metal sulfides for olefin production from shale gas derived alkanes

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Shale gas and natural gas sources contain a significant quantity of lower alkanes (C₂₋₅). Transition metal sulfides have been shown recently¹ to catalyze the dehydrogenation of these alkanes; indeed, they have been shown to perform better than commercial catalyst (based on Platinum and Chromium) in terms of activity, cost, and toxicity; however, they deactivate rapidly due to loss of sulfur. Therefore, these catalysts are stable in the presence of H₂S in the cofeed (while catalysts such as platinum get severely poisoned). These catalysts are also known to catalyze reverse water gas shift reactions. The main goal of this proposal, therefore, is to employ density functional theory (DFT) to study the dehydrogenation of alkanes (ethane in particular), in the presence of acidic gases – especially CO₂ and H₂S – on transition metal (in particular, molybdenum) sulfide catalyst (MoS₂) to evaluate the potential of using this material in upgrading acidic shale/natural gas.

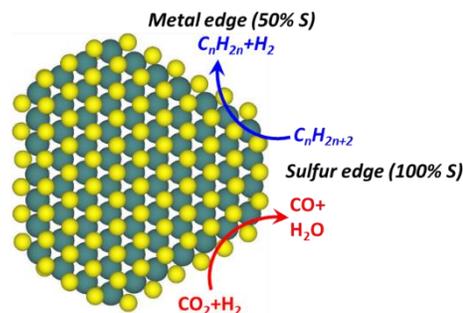


Figure 1: Schematic of MoS₂ catalyzed dehydrogenation and reverse water gas shift reactions

MoS₂ catalysts contain a variety of potential sites, including metallic, Brønsted acidic, and Lewis acidic sites, however in prior literature there is no theoretical understanding behind the sites responsible for the high dehydrogenation activity of these class of catalyst. In previous year's report, we discussed *our contribution* in developing a detailed understanding of the energetics associated with dehydrogenation of ethane and reverse water gas shift reaction on one likely active site (metal edge of MoS₂) using periodic DFT. In year 2018-19, we collaborated with Prof. Jonas Baltusaitis of Lehigh University to understand experimentally and computationally if reverse water gas shift reaction can happen on this catalyst under the same conditions as a first step to see if the alkane dehydrogenation chemistry could be coupled with CO₂ hydrogenation. Such coupling can potentially shift the direction of equilibrium and provide an alternative conduit for hydrogen to be consumed without "leaching" the sulfur out as hydrogen sulfide. Furthermore, since acidic shale gas and natural gas also contain H₂S, we wished to study its effect on the reverse water gas shift reaction.

Their experimental results showed an unintuitive trend for CO₂ hydrogenation at different cofeeds of H₂S. Specifically, MoS₂ selectively converts CO₂ to CO (i.e. reverse water gas shift reaction) under most conditions in the absence of H₂S in the feed. Interestingly, however, the co-feeding of H₂S has results in a non-monotonic behavior. At low cofeeds (< 60 ppm), H₂S inhibits hydrogenation; a higher co-feed (>200 ppm), though, the rate of hydrogenation increases (see Fig 2). **We studied** the effect of low cofeed of H₂S on the catalyst and the chemistry in more detail using DFT. MoS₂ particles, as shown in Figure 1, has two different types of edges (three of each kind makes the hexagon), namely the Mo-edge and the sulfur-edge. Under reaction conditions where there is a finite chemical potential of hydrogen and sulfur in the gas phase, the edges of the catalyst, where the active sites are located (because the basal plane or the terrace is fully coordinated and therefore unreactive), are further decorated by S and H atoms. We found via ab initio thermodynamics that there is a collection of these decorations (that is, there is no one type of decoration

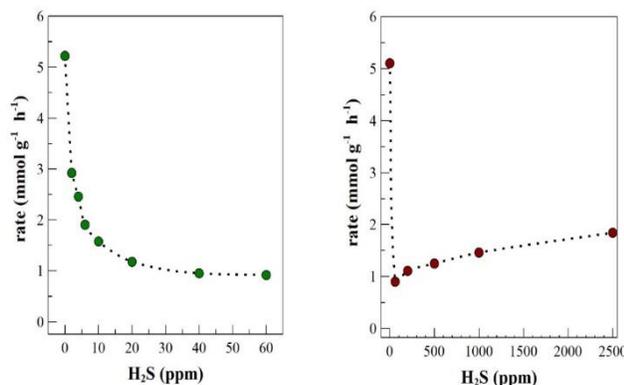


Figure 2: The rate of CO₂ hydrogenation to CO on unsupported MoS₂ catalyst. The feed contained 2% H₂, 2% CO₂, and H₂S as indicated above, with the balance being N₂ and the reaction temperature of 600 C. The dashed lines

¹ Wang, G.; Li, C.; Shan, H. *ACS Catalysis*, 2014, 4(4), 1139–1143

alone at all conditions) whose relative concentrations (populations) vary as a function of H₂S co-feed. See Fig. 3 for a Boltzmann distribution of the edge decorations at different H₂S co-feeds. The plot shows that the edges are more sulfided as H₂S co-feed increases to 60 ppm and, correspondingly, there is a drop in the population of sulfur-deficient sites (often referred to as the coordinative unsaturated sites). This drop correlates well with the drop in the activity of the catalyst (also plotted). A similar observation was also made for the sulfur edge (not shown) where the drop in the rate was proportional to the drop in the sulfur-deficient sites although the correlation was better for the case of the Mo-edge.

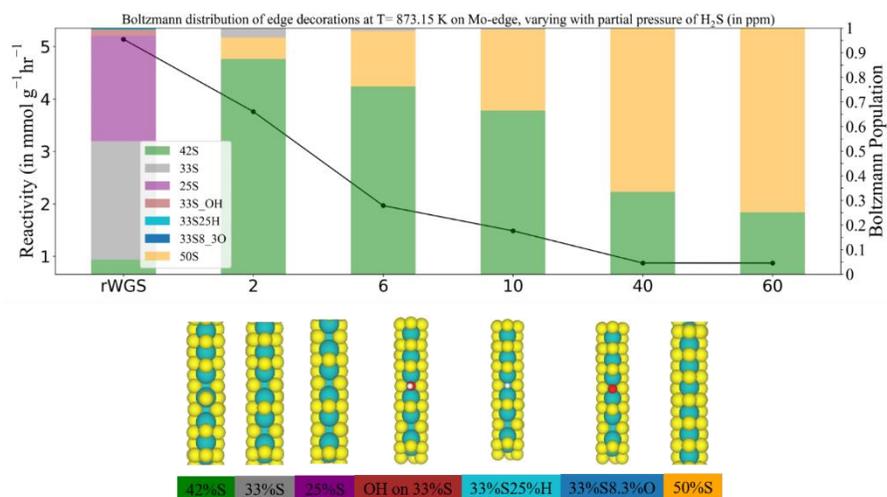


Figure 3: A Boltzmann distribution plot of different edge decorations on Mo-edge at $T = 873.15\text{ K}$, for the experimental condition undertaken in the study (assumed 10% conversion towards H₂O formation under reaction condition). 'rWGS' - rWGS condition (having (1:1) CO₂ and H₂ in the inlet stream, assuming 0.01 ppm of H₂S); '2' - '60' correspond to rWGS conditions with 2 - 60 ppm co-feed of H₂S.

Next, using DFT, we explored the reaction mechanism for the reverse water gas shift chemistry for the three major edge decoration as observed in the Figure 3, namely the 33%S, 42%S and 50%S decorated Mo-edge. To understand which pathway dominates, we have employed the maximum rate analysis approach² which offers an approximate way of calculating the reaction rate without the need for a full-fledged microkinetic model. This approach allows us to identify the rate limiting step within each route (redox, carboxyl, and formate pathways) and further elucidate which reaction mechanism may be dominant for this chemistry. Figure 4 illustrates the redox catalytic cycle on the 42%S Mo-edge (an edge decoration consisting of one site with a sulfur vacancy) which had the largest rate for CO₂ hydrogenation.

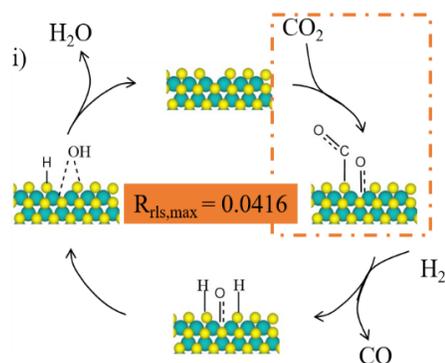


Figure 4: Schematic of the redox pathway, the dominant route for RWGS

2019-2020: During the one-year project extension, we will be exploring the other regimes of H₂S co-feed using DFT and compiling the dehydrogenation and CO₂ hydrogenation networks to develop a more complete understanding of whether alkanes and CO₂ can be co-processed in the absence and presence of H₂S on molybdenum sulfide.

Impact of ACS-PRF funding: This DNI support has substantially contributed to developing the early career of this PI. First, this support allowed the PI to recruit his first graduate student at Lehigh and collect substantive DFT data on this project. Second, it allowed the PI to establish a complementary experimental collaboration with Prof. Jonas Baltrusaitis to explore the same reaction system. This has already led to one joint publication in *ACS Catalysis* (Just Accepted)³ and one more in preparation. In addition, this work has also contributed concepts and data that has led to at least two more invited manuscripts (one in preparation and one in review). Finally, this funding has enabled the PI to collect enough preliminary data to allow him to write collaborative proposals to the NSF on this topic.

²Motagamwala, A.H.; Dumesic, J.; *PNAS*, **2016**, *113* (21), 2879-2888

³Sharma, L.; Upadhyay, R.; Rangarajan, S.; Baltrusaitis, J. *ACS Catalysis*, Just Accepted Article [10.1021/acscatal.9b02986](https://doi.org/10.1021/acscatal.9b02986)