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 (C_{2-5}). Transition metal sulfides have been shown recently[1] 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. As a consequence, these catalysts are stable in the presence of H_2S 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 CO_2 and H_2S – on transition metal (in particular, molybdenum) sulfide catalyst (MoS_2) to evaluate the potential of using this material in upgrading acidic shale/natural gas.

MoS_2 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. *Our contribution* so far is to develop 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 MoS_2) using periodic DFT. The model we used is a 50% S covered Mo-edge. The choice of Mo-edge is motivated by its likely involvement in hydrodesulfurization[2] while the 50% coverage of S is based on a phase diagram analysis that identified this decoration as the most thermodynamically feasible one under typical catalyst pre-treatment conditions (given in [1]).
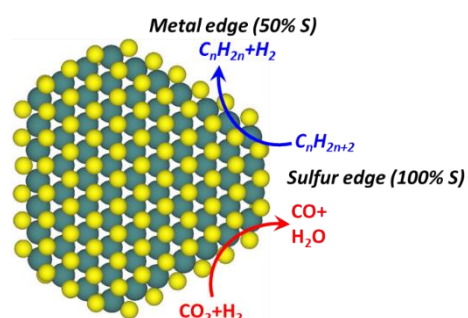

Figure 1: Schematic of MoS_2 catalyzed dehydrogenation and reverse water gas shift reactions
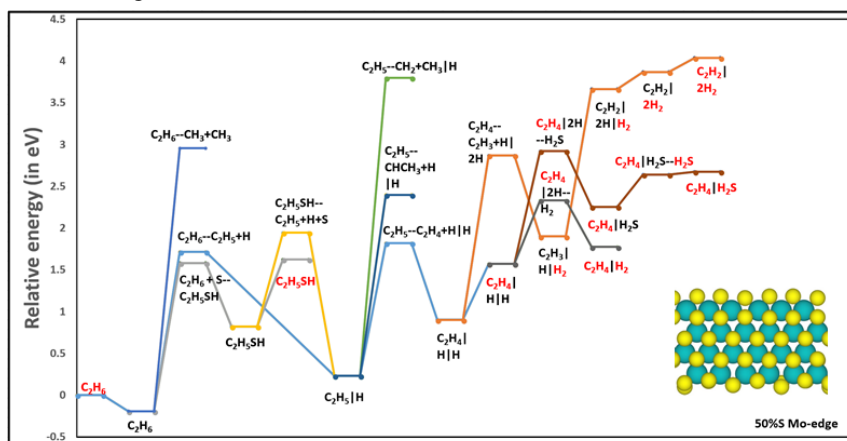

Figure 2: The potential energy diagram for the alkane dehydrogenation reaction network on the 50%S Mo-edge. 1eV is 100 kJ/mol. States identified by a reaction (set of species) indicate transitions or intermediates. The vertical bar "|" indicates infinite separation. Species in red are gaseous.

Figure 2, shows the energetics of ethane dehydrogenation on 50%S covered Mo-edge (1 S for each Mo on the edge, shown in Figure 1). The catalyst model comprises of a single layer slab with four (4) rows of six (6) metal atoms each. The blue line in Figure 2 represents the main pathway which leads to the formation of the main dehydrogenated product (ethylene). The silver line represents the pathway which leads to the formation of ethyl thiol. The dark blue and green lines represent the pathway for the formation of cracked products. The yellow line is the dissociation of ethyl thiol. The orange line represents the over dehydrogenation of adsorbed ethylene. The brown line represents the formation of hydrogen sulfide and the gray line represents the

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

[2] Raybaud, P. *Catal. Today*, **2007**, 322, 76-91

formation of hydrogen. The species represented in red are gas phase species and the ones in black are adsorbed species. All the species energies are referenced with respect to the gas phase ethane energy and the clean 50%S Mo-edge. From Figure 2, it can be observed that alkane dehydrogenation is endothermic. Further, the sequence of steps which lead to the formation of product (viz. ethylene), is competing with several side reactions, namely the cracking reaction, the over dehydrogenation steps and the formation of sulfur compounds (like ethyl thiol and H_2S). It is observed that the barrier for removal of the edge sulfur as ethyl thiol (a side product) is lesser as compared to the barrier for formation of ethyl intermediate by 0.13 eV. This suggests the possibility of formation of a coordinative unsaturated site or CUS site on the edge via the abstraction of sulfur during the initial stages of the dehydrogenation reaction. Therefore, this dehydrogenation pathway needs to be reworked again on a model containing a CUS site. We are currently pursuing this new catalyst site model.
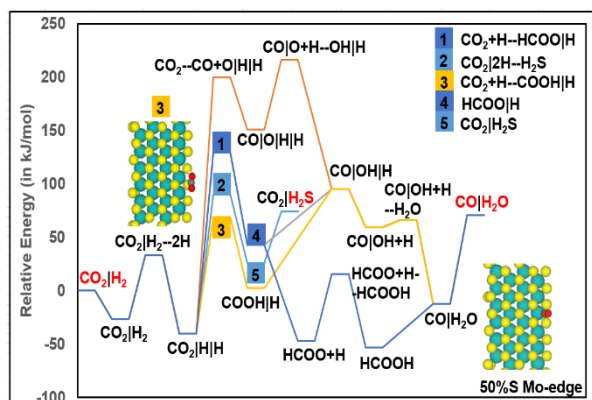

Figure 3: The energy diagram for the reverse water gas shift reaction network on the 50%S Mo-edge. The species represented in red are gas phase species and the ones in black are adsorbed species. All the species energies are referenced with respect to the gas phase CO_2 and H_2 energy and the clean 50%S Mo-edge.

In addition, we also explored the mechanism of reverse water gas shift reaction to consume the generated hydrogen. Figure 3 shows the corresponding potential energy diagram. The orange line represents the redox pathway which leads to the formation of CO* and O* species. The golden and silver line represents the associative pathway which leads to the formation of COOH* and HCOO* species. The blue line represents the formation of hydrogen sulfide. The dark blue line represents the formation of formic acid via the HCOO* species. It is observed that the associative pathway, (via the formation of COOH* intermediate) is more kinetically feasible as compared to the redox pathway or the other pathway involving the formation of the HCOO intermediate. However, once the COOH intermediate is formed, breaking it into CO and OH intermediate incurs a thermodynamic barrier equivalent in value to the kinetic barrier for the formation of H_2S, i.e. via plucking a sulfur atom from the 50%S Mo-edge (thereby introducing a CUS site). Therefore, if product formation is possible on the 50%S Mo-edge, other mechanism needs to be explored such as formation of germinal diol via H addition to COOH or the formic acid mechanism formed via H addition to COOH, and the eventual decomposition of the two complex adsorbates to form CO and H_2O. We are currently pursuing this pathway. In addition, as in the case of ethane dehydrogenation, we are also assessing the role of CUS sites for this chemistry.

Summary and Future work: DFT analysis of the Mo-edge suggests that the formation of CUS sites is energetically competitive compared to both dehydrogenation and reverse water gas shift chemistry. However, these calculations do not consider temperature effects carefully; we are currently incorporating temperature and entropic effects into our analysis. In the remaining funding period, we will: (1) complete our analysis of the role of CUS sites on both chemistries, (2) incorporate H_2S-mediated steps, (3) incorporate temperature effects, and (4) explore the other (sulfur) edge of MoS_2. We anticipate that at the end of these steps, we will have a comprehensive mechanistic picture of ethane and acid gas conversion on MoS_2 catalysts.

Impact on Students and the PI: This grant provided the PI a path to recruit his first graduate student at Lehigh University. It also enabled the PI to establish collaborations at Lehigh and seek additional funding. In particular, in collaboration with Jonas Baltrusaitis at Lehigh, the PI has established an experimental-computational program to study the mechanism and site requirements of alkane dehydrogenation in the presence of acid gases on transition metal sulfides and successfully obtained a seed grant (from a DOE EFRC based out of Georgia Tech, known as UNCAGE-ME) that supported one graduate student to carry out experimental reaction kinetic studies to complement the DFT calculations during this funding period. The PI now has sufficient preliminary results to publish two papers and submit multiple NSF proposals by the end of 2018. The graduate student passed his qualifying exam in Jan 2018 based on some of the results presented above and will co-author two publications this year. This will allow him to defend his research proposal, which is the penultimate step to his graduation.