

## Computational design of MoS<sub>2</sub>-based catalysts for methanol synthesis from syngas

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Catalytic conversion of syngas (CO+H<sub>2</sub>) into useful compounds such as alcohol is of great importance in industrial processes, and potential applications in hydrogen storage. It demands the design of cheap and efficient catalyst materials and a prudent way to achieve this goal is through predictive modeling employing modern quantum mechanical methods and powerful computational techniques. One such material of interest for a variety of reasons is single-layer molybdenum disulphide (MoS<sub>2</sub>). Because of the inertness of the basal plane, however, it is necessary to discover ways that make it catalytically active. Herein, by employing density functional theory including van der Waals interaction, we provide a general strategy to make single-layer MoS<sub>2</sub> active by creation of S vacancies and to functionalize it through either a metallic support or through the deposition of nanoparticles on it. Here, we show first that the presence of S vacancies (patch) by itself facilitates methanol synthesis from syngas on MoS<sub>2</sub> [1]. On the other hand, S vacancy-rows, naturally present in samples are less reactive compared to vacancy patches [1] because the narrow size of the row restricts adsorption, diffusion, and formation of reaction intermediates. We next show that when defect-laden single-layer MoS<sub>2</sub> is supported on Cu(111), strong interactions with the support reduce the surface corrugation of MoS<sub>2</sub>, resulting in a larger area of active sites (exposed Mo) to the reactants and their intermediates. In addition, charge transfer and other electronic structural changes help shift the position of the frontier orbitals (d orbitals of the exposed Mo atoms) towards the Fermi level. These factors have positive influence on the activity of MoS<sub>2</sub>. The potential energy profile, indeed, indicates that the Cu(111) substrate promotes methanol synthesis on MoS<sub>2</sub>. In the second part, in a reverse construct, we show that the MoS<sub>2</sub> support substantially alters both geometric and electronic structure of sub-nanometer sized gold nanoparticles. The electronic interaction and charge transfer between MoS<sub>2</sub> and Au nanoparticles now helps shift frontier orbitals, which are localized in Au atoms away from the interface, closer to the Fermi level. Such modified electronic structure remarkably enhances the chemical activity of the Au-MoS<sub>2</sub> towards methanol synthesis from syngas – a very different activity from that of the Au-TiO<sub>2</sub> nanocatalyst which promotes methanol decomposition [2].

[1] D. Le, T. B. Rawal, and T. S. Rahman, *J. Phys. Chem. C*, **118**, 5346 (2014).

[2] S. Hong and T. S. Rahman, *JACS*, **135**, 7629 (2013)

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