

First-principles study of single-layer MoS₂-based catalysts for alcohol synthesis from syngas

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Abstract

Rational designing of cheap and efficient catalyst material for alcohol synthesis from syngas is in great demand because of diminishing supply of the current state-of-the-art catalysts. One material of interest is single-layer molybdenum disulphide (MoS₂) owing to its low cost, abundance, and catalytic applications. Because of the inertness of its basal plane, however, it is essential to find ways that make it catalytically active. Herein, by means of density functional theory based calculations of reaction pathways and activation energy barriers, we show that a general strategy to make MoS₂ active is by the creation of S vacancies [1]. Further enhancement of chemical activity and selectivity may be achieved by interfacing the MoS₂ layer either with a metallic support or with adsorbed nanoparticles [2]. More concretely, we show that MoS₂ with S vacancies by itself facilitates methanol synthesis from syngas, the effect being more promising for a S vacancy-patch than a vacancy-row structure. When defect-laden MoS₂ is grown on Cu(111) there is an increase in the active region (surface area of active sites) of MoS₂. Moreover, charge transfer from Cu to MoS₂ and strong electronic interaction between them results in shift of the frontier states toward the Fermi level, making it more amenable for chemical activity. On complementing our calculations of reaction energetic with kinetic Monte Carlo simulations we conclude that the Cu(111) substrate promotes ethanol synthesis on MoS₂, rather than the formation of methane. In the second part, we show that the Au/MoS₂ composite could serve as a catalyst for methanol synthesis – a very different activity from that of the Au/TiO₂ composite which promotes methanol decomposition [3]. We trace the differences in the role of the two supports to the unique local electronic structural environments that they create at the active sites.

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

[2] T. B. Rawal, D. Le, and T. S. Rahman, *J. Phys. Chem. C*, **121**, 7282 (2017).

[3] S. Hong and T. S. Rahman, *J. Am. Chem. Soc.*, **135**, 7629 (2013).

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