

MoS₂ Catalyst for Bioethanol Synthesis from Syngas

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Introduction

The Fischer-Tropsch process offers the potential to produce high-value transportation fuels or petrochemicals from biomass. The process begins with the production of syngas, which is then reacted over a suitable catalyst to yield a wide range of products containing mainly n-alkanes and n-alkenes, as well as oxygenates including alcohols. Murchison et al. [1] of Dow Chemical Corporation discovered that alkali-doping of MoS₂ would shift the selectivity of CO hydrogenation production from hydrocarbons to alcohols on undoped MoS₂. Further addition of promoters on alkali-doped MoS₂ surface such as Ni or Co would increase the selectivity of the reaction towards ethanol and higher alcohols [1-5]. These reactions are complicated as they may involve many complex elementary reaction steps such as dissociative and non dissociative adsorption of H₂ and CO, C-C bond formation, C-H bond formation, O-H bond formation, and CO insertion into the surface alkyls on MoS₂ surface. The reaction mechanisms are very likely to be diverse, and it is generally assumed that not a single reaction pathway exists, but a number of parallel reaction pathways instead. Identifying the key mechanisms of controlling the CO hydrogenation reactions leading to CH₄, CH₃OH, C₂H₅OH, and higher alcohols and hydrocarbons theoretically would be greatly useful for improving the activity of catalysts by means of modifying catalysts or finding new potential catalysts in experiments. In this study, we will perform a systematical Density Functional Theory (DFT) study on the CO hydrogenation reactions on pure MoS₂ surface.

Methodology

The calculations were performed by using the Quantum-ESPRESSO/PWSCF computer package, and with the generalized gradient corrected PW91 approximation and ultrasoft pseudopotentials. The cutoff energy used is 30Ry. The Monkhorst-Pack k-point meshes of 4x4x1 were employed. Energy barriers and transition states for reactions were calculated with the nudged elastic band (NEB) method.

The (100) surface of MoS₂ was predicted to be most stable and was modeled with tetragonal (4x1) supercell slabs consisting of 8 atomic layers with lattice parameters of a=b=3.18Å and c=12.6 Å, and a vacuum thickness of 12.0Å. The CO, H₂ molecules and reactants were adsorbed on one side of the supercell and the coordinates of the atoms in the upper four layers of the slab (containing the adsorbates) were relaxed while the rest of the atoms in the lower half of the slab were fixed at their bulk positions.

Results and Discussions

CO molecule was found to chemisorb on MoS₂ surface with adsorption energy ranging from 0.79 eV to 2.24 eV. The most stable configuration is a tilted one at Bridge Mo site with CO bond length of 1.223Å. The dissociation of CO on MoS₂ surface was calculated to be difficult with high barrier energy of 2.61 eV. H₂ was found to spontaneously dissociate on

(100) MoS₂ surface forming H-Mo bonds. Hence, in the Fischer-Tropsch process on MoS₂ surface from syngas, molecular hydrogen will supply atomic H.

The adsorbed CO was predicted to be unlikely dissociated on MoS₂ surface as described above, the adsorbed CO molecules would react with the spontaneously dissociated hydrogen atoms in the Fischer-Tropsch reaction to yield the products. We found that the CO dissociation mediated by H is much easier than pure CO dissociation, as shown in Figure 1, which shows the reaction in individual steps of CO hydrogenation. The most possible intermediate species of the hydrogenation reaction from syngas on pure MoS₂ catalyst surface are CH₃ and O, which can be further converted to CH₄ and CO₂ by atomic H and CO on surface respectively. These results are in agreement with the previous in situ diffuse reflectance infrared Fourier transform (DRIFT) study on sulfide Mo/γ-Al₂O₃ catalysts, which showed the main products of CO hydrogenation are CO₂ and CH₄ [2]. Doped with alkali and other promoters, the formate species for reaction from syngas on MoS₂ catalyst converted to methanol and higher alcohols and hydrocarbons. Hence, the effects of the promoters and the chain growth will be the future research topics.

Acknowledgment. This research is supported by Nanostellar Inc.

Significance

MoS₂ and Rh are well known catalysts for ethanol synthesis from syngas. However, these two catalyst systems have problems of selectivity (methanol production from MoS₂ catalyst) and supply limitation (Rh catalyst). It is highly desirable to develop new potential catalyst systems or improve the activity of catalysts by means of modifying catalysts in experiments. Our systematic study of fundamental structure-property relationship of catalyst surface will provide the necessary understanding on the reaction mechanisms and facilitate the development of ethanol synthesis catalyst systems.

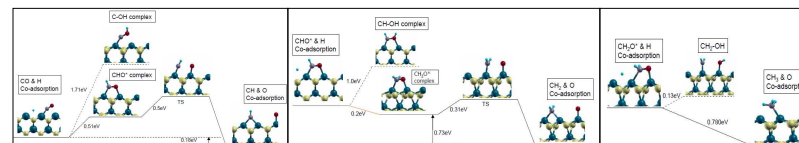


Figure 1. Energy diagram for sequential hydrogenation of CO by H atoms on MoS₂ surface. The blue, yellow, gray, red and light blue (small) spheres represent Mo, S, C, O and H atoms, respectively.

References

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