Área: _TEO_____
(Inserir a sigla da seção científica para qual o resumo será submetido. Ex: ORG, BEA, CAT)

Ab initio Study of Catalytic Properties of 2D CuS_x Nanolayer, with x = 0.5, 1.0, and 1.5, in CO_2 Reduction

Henrique A. B. Fonseca (PG),[1] Lucas G. Verga,[1] Juarez L. F. Da Silva.[1]

henrique.alves.fonseca@usp.br; juarez_dasilva@iqsc.usp.br

[1] São Carlos Institute of Chemistry, University of São Paulo. P.O. Box 780, 13560-970 São Carlos, SP, Brazil

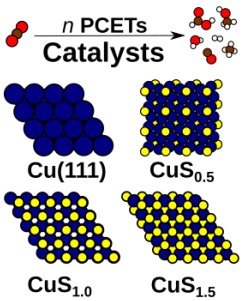
Palavras Chave: Two-dimensional, CuS, Chalcogenide, CO_2RR, CHE model.

Highlights

We explored the adsorption of several CO_2RR-related intermediates on 2D CuS_x using the CHE model. CuS_1 and $CuS_{1.5}$ were favorable to the CO and HCOOH formation. For $CuS_{1.5}$ we investigated beyond CO.

Resumo/Abstract

Global warming problems are becoming increasingly alarming nowadays and are mainly caused by anthropogenic activities such as the burning fossil fuels that increase greenhouse gas emissions, for example, the CO_2. This atmospheric CO_2 is an inexpensive C1 resource that we can use to transform into products with aggregate values, such as CO, HCOOH, and CH_4, which are very useful chemicals. So, one of the potential solutions that have received a lot of interest is CO_2 reduction reaction (CO_2RR) via an electrochemical pathway, owing to the possibility of being carried out under normal temperature and pressure conditions, as well as being associated with a source of clean energy like solar energy or wind energy.[1] But for this, we need catalysts. Copper has gained a lot of attention because it reduces CO_2 to several products, despite its low selectivity. Copper sulfide, for example, is an environment-friendly and abundant material and has also attracted extensive attention for the production of formate in CO_2 electroreduction.[2] In the same way, the 2D transition-metal dichalcogenides materials have many implications, mainly because of their different structures, active sites, defects, and so on. So, in this work, we performed DFT calculations using the Vienna Ab initio Simulation Package (VASP), with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional and van der Waals correction D3, to study the effect of Cu/S ratio of the CuS_x layers on the CO_2RR reaction pathways toward C1 produtcs. We used the Computational Hydrogen Electrode model[3] and observed that the reaction step CO_2 → *COOH was the potential determinant step (PDS) for CO formation on all materials. Meanwile, for HCOOH formation the PDS depends on the considered substrate. As compared to the results for Cu(111), the $CuS_{0.5}$ system has a high onset potential, while the CuS and $CuS_{1.5}$ systems have small onset potential values for CO and HCOOH. Additionally, we also investigate the possibility of CH_4 formation for $CuS_{1.5}$.



[1] Sonali Das, Javier Pérez-Ramírez, Jinlong Gong, Nikita Dewangan, Kus Hidajat, Bruce C. Gates, and Sibudjing Kawi. Coreshell structured catalysts for thermocatalytic, photocatalytic, and electrocatalytic conversion of CO2. Chem. Soc. Rev., 49:2937–3004, 2020.

[2] Yun Huang, Yilin Deng, Albertus D. Handoko, Gregory K. L. Goh, and Boon Siang Yeo. Rational design of sulfur-doped copper catalysts for the selective electroreduction of carbon dioxide to formate. ChemSusChem, 11(1):320–326, 2018.

[3] J. K. Nørskov, J. Rossmeisl, A. Logadottir, L. Lindqvist, J. R. Kitchin, T. Bligaard, and H. Jónsson. Origin of the overpotential for oxygen reduction at a fuel-cell cathode. J. Phys. Chem. B, 108:17886–17892, 2004.

Agradecimentos/Acknowledgments

Grant nº 2021/05728-9, São Paulo Research Foundation (FAPESP). The opinions, hypotheses and conclusions or recommendations expressed in this material are the responsibility of the author(s) and do not necessarily reflect the views of FAPESP.