

CO₂ reduction on solid state surface

Study of CO₂ adsorption, dissociation and reduction on pentlandite mineral

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In Short

- Pentlandite exhibits remarkable properties as electrode material for hydrogen evolution and CO₂ reduction
- This study aims to elucidate the reaction mechanism of CO₂ reduction on a molecular level to allow for a systematic improvement of the material
- Periodic density functional theory is utilized to identify most favorable binding sites, intermediates and transition states

As CO₂ is one of the most prominent green-house gases its reduction towards other, environmentally more benign compounds is of high social and economic relevance.[1] In this context the transformation of CO₂ into synthetically valuable products like formic acid, CO or methane has gained a lot of attraction in the field of chemistry in the last years for its obvious benefits.[2] A particularly attractive approach to this goal is represented by electrocatalytic setups that utilize electricity from renewable sources like wind or photovoltaics. Hence, considerable efforts have been made to identify and optimize electrode materials that are able to reduce CO₂ with a high faradaic efficiency and selectivity at a low overpotential.[3]

Recently, Apfel and coworkers introduced pentlandite (Fe_{4.5}Ni_{4.5}S₈, see Figure 1) electrodes as viable materials for the evolution of dihydrogen and the reduction of CO₂ with remarkable properties in terms of overpotentials, efficiencies and durability.[4–6] However, at this point a systematic improvement

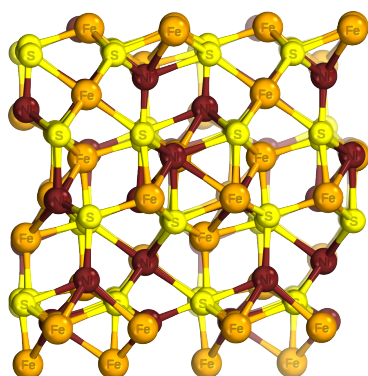


Figure 1: Structure of the pentlandite (111) surface.[7]

of the pentlandite material is impeded by a lack of mechanistic insight. While the selectivity towards CO₂ reduction can to a certain extent be controlled by the chemical environment, i.e. the availability of protons as well as the solubility of CO₂ and its corresponding reduction products,[6] other factors that contribute to the selectivity and – perhaps more importantly – the activity are elusive.

This project aims at identifying possible active sites for CO₂ reduction as well as elucidating the most probable reaction mechanism for the former by means of state-of-the-art quantum chemical calculations. Such insight on a molecular level is a prerequisite for a systematic improvement of the pentlandite catalyst in terms of activity and/or selectivity. More precisely, we will utilize periodic density functional theory to model possible reaction intermediates and transition states to identify a minimum energy pathway on multiple different pentlandite surfaces. The present work will provide the groundworks for a subsequent set of periodically embedded calculations that employ highly correlated *ab initio* electronic structure methods.

WWW

<https://www.chemie.hu-berlin.de/en/forschung-en/theoretical-chemistry/research>

More Information

- [1] K. Ricke, L. Drouet, K. Caldeira, M. Tavoni, *Nat. Clim. Change*, **8**, 895 (2018).
- [2] R. Francke, B. Schille, M. Roemelt, *Chem. Rev.*, **118**, 4631–4701 (2018)
- [3] S. Nitopi, E. Bertheussen, Soren B. Scott, X. Liu, Albert K. Engstfeld, S. Horch, B. Seger, I. E. L. Stephens, K. Chan, C. Hahn, J. K. Nørskov, Thomas F. Jaramillo, I. Chorkendorff, *Chem. Rev.*, **119** 7610–7672, (2019)
- [4] B. Konkena, K. Junge Puring, I. Sinev, S. Piontek, O. Khavryuchenko, J. P. Dürholt, R. Schmid, H. Tüysüz, M. Muhler, W. Schuhmann and U.P. Apfel *Nat. Com.* **7**, 12269 (2016).
- [5] I. Zegkinoglou, A. Zendegani, I. Sinev, S. Kunze, H. Mistry, H. S. Jeon, J. Zhao, M. Y. Hu, E. E. Alp, S. Piontek, M. Smialkowski, U.-P. Apfel, F. Körmann, J. Neugebauer, T. Hickel, B. Roldan Cuenya, *J. Am. Chem. Soc.*, **139**, 14360–14363 (2017)

- [6] S. Piontek, K. Junge Puring, D. Siegmund, M. Smialkowski, I. Sinev, D. Tetzlaff, B. Roldan Cuenya, and U.-P. Apfel, *Chem. Sci.* **10**, 1075–1081 (2019).
- [7] L. Linguo, Y. Shansheng, and T. Hongwei, *J. Colloid Interface Sci.*, **607**, 645–654 (2022).

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