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Catalytic hydrogenation of CO_2 to ethanol over high entropy alloys

Aim

Computational screening of high entropy alloy (HEA) catalysts for the selective hydrogenation of CO_2 to ethanol reaction via density functional theory (DFT) calculations combined with machine learning algorithms.

Justification

Catalytic conversion of CO_2 with green H_2 not only mitigates CO_2 emissions but also produces valuable products, such as ethanol, and therefore nicely fits with the objectives of the European Green Deal, to make Europe the first climate-neutral continent by 2050.

Much efforts has been devoted to discovering selective catalysts for CO_2 hydrogenation to ethanol. Such catalysts need to be active both for C-O activation and C-C coupling. Cu-based multimetallic catalysts have shown a reasonable selectivity towards ethanol (CuZnAl (35%)[1], $CuZnFe_{0.5}K_{0.15}$ (37%)[2]), CuPd (92%, but at low CO_2 conversion)[3], and Cu@Na-Beta (100%, but at less than 7.9% of CO_2 conversion)[4]). It is clear there is room to significantly improve both the selectivity and activity of such catalysts. High entropy alloys include five or more elements and form a single solid-solution phase. They are promising new class of materials for catalysis. Instead of 1 or 2 types of active sites, HEAs provide a tuneable distribution of active sites with a near-continuum distribution of adsorption energies. Within this distribution, it is expected that optimal active sites for both C-O activation and C-C copling can be found [5].

In this master's thesis project, Cu-based HEA (CuPdPtNiRh) structures with random compositions will be modeled. Furthermore, adsorption energies of relevanmt intermediates for the CO_2 hydrogenation to ethanol on those HEAs will be calculated via DFT calculations. To model the reaction kinetics on those surfaces, we will use a machine-learning model (**Figure 1**). Importantly, this type of HEAs has recently been successfully synthesized[6], providing a roadmap to experimentally validate the model predictions.

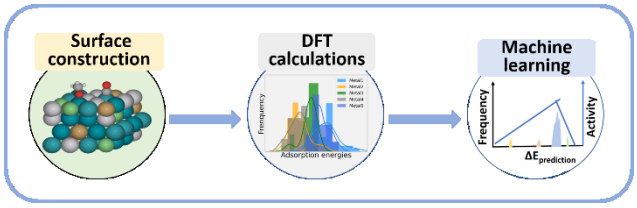

Figure 1 Workflow for finding active HEA catalysts for the CO_2 hydrogenation towards ethanol production

Program

1. Literature survey about typical catalysts and reaction mechanisms for CO_2 hydrogenation to ethanol.
2. Model CuPdPtNiRh fcc(111) surfaces with random compositions, screen stable HEAs, and calculate binding energies of intermediates.
3. Build machine learning models to predict the activity and selectivity of CuPdPtNiRh HEAs with specific atomic configurations.

References

[1] Y. Wang, K. Z. Wang, et al., *Acs Catal.*, **2021**, 11, 11742-11753; [2] S. G. Li, H. J. Guo, et al., *Catal. Lett.*, **2013**, 143, 345-355; [3] S. X. Bai, Q. Shao, et al., *J. Am. Chem. Soc.*, **2017**, 139, 6827-6830.; [4] L. P. Ding, T. T. Shi, et al., *Chem*, **2020**, 6, 2673-2689.; [5] Y. Yao, Q. Dong, et al., *Science*, **2022**, 376, 3103.; [6] S. L. A. Bueno, A. Leonardi, et al., *ACS Nano*, **2022**, 16, 11, 18873–18885.

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