Selective Electrochemical Reduction of CO_2 to High Value Chemicals

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Deliverable Report

D2.2 Report on DFT prediction of selected benchmark Catalysts

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Workpackage	2
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Lead Beneficiary	DTU
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Dissemination Level

PU	*Public*	***X***
PP	*Restricted to other programme participants (including the Commission Services)*	
RE	*Restricted to a group specified by the consortium (including the Commission Services)*	
CO	*Confidential, only for members of the consortium (including the Commission Services)*	

Nature of the Deliverable

R	*Report*	***X***
P	*Prototype*	
D	*Demonstrator*	
O	*Other*	

SUMMARY	
Keywords	*single-site catalysts in nitrogen-doped graphene, CO, computational screening, DFT*
Abstract	This deliverable reports on density functional theory (DFT) predictions of the activity and stability of single atom metal catalysts supported on nitrogen-doped graphene for CO_2 reduction to CO. We find several candidates beyond Fe- and Ni- single site catalysts with promising activity. These efforts are part of the objective for SELECTCO2 to design electrolyzers with with 90% selectivity for CO_2R to CO at high current densities. Promising candidates will be tested by the Strasser group at TU Berlin (WP2 leader).
Public abstract for confidential deliverables	

REVISIONS			
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1 INTRODUCTION AND SCOPE

Single site catalysts embedded in 2D materials have recently emerged as potential earth-abundant catalysts for several electrochemical processes. In particular, metal- and nitrogen-doped graphene has shown promising activity and selectivity towards CO_2 reduction (CO_2R) to CO. This deliverable reports on progress in WP2 towards the computation-guided design of efficient single-site catalysts in nitrogen-doped graphene for the SELECTCO2 project, which has the objective of designing CO_2R electrolyzers with high conversion efficiency and selectivity towards high value products. In particular, SELECTCO2 has the objective of achieving electrolyzers with with 90% selectivity for CO_2R to CO. The reported candidates will be synthesized by the Strasser group in TUB (WP2 leader) for experimental testing.

The recent theoretical literature has generally explored single metal atoms in porphyrin-like M-N_4 site motifs at the level of workhorse, GGA-level functionals, and using standard thermodynamic descriptors (scaling of *COOH vs. *CO binding energies, as well as *H as a descriptor toward hydrogen evolution)[1,2]. These studies have found that that site motifs usually bind *H more weakly than transition metals, such that CO_2R to CO has a high selectivity over hydrogen evolution.

However, we have recently shown that self-interaction errors in these systems necessitate the use of hybrid level functionals. Fig. 1 shows a benchmark study of CO binding on various Fe site motifs with both GGA (RPBE) and hybrid (HSE06) functionals, overlaid with the CO adsorption energy estimated from temperature-programmed desorption (TPD) experiments (blue band)[3]. Both the hybrid functional and TPD energies suggest that the RPBE completely overbinds *CO such that all Fe sites would be poisoned with *CO and never evolve $CO_{(g)}$ off its surface. The corresponding *CO coverage, θ_{CO}, as determined by a kinetic model is indicated in the plot in green shading; RPBE adsorption energies suggest the saturation of the sites at θ_{CO}=1.

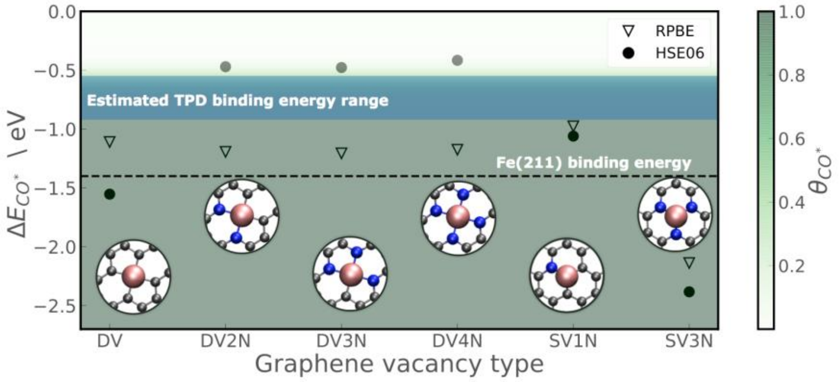

Fig. 1: Benchmark study of CO binding on various Fe-N_x-C site motifs from Ref. [3], comparing a hybrid (HSE06) and GGA (RPBE)-level functional and TPD binding energies from Ref. [4]. Both HSE06 calculations and TPD CO binding energies suggest that the RPBE functional completely overbinds *CO on these materials, such that all Fe sites would be poisoned with *CO and never evolve CO off its surface

In addition the adsorption energy of *CO_2, its dipole moment has been suggested to be a critical determinant for activity in FeNC catalysts, beyond the traditional thermodynamic thermodynamic descriptors.

Here, we show results from a comprehensive stability and activity screening study of M-N_x-C catalysts applying these recent theoretical insights. We map out the energetics in activity volcanoes as a function of CO_2 and COOH binding energies. On the basis of this initial screening, we propose several candidates for experimental testing.

2 DISCUSSION

2.1 Stability of metal in graphene under different sites

We evaluated the stability of transition metals in a wide range of site motifs (see Fig. 2). Generally, we find it energetically favorable to form many of the site-motifs considered and we screened them for high activity.

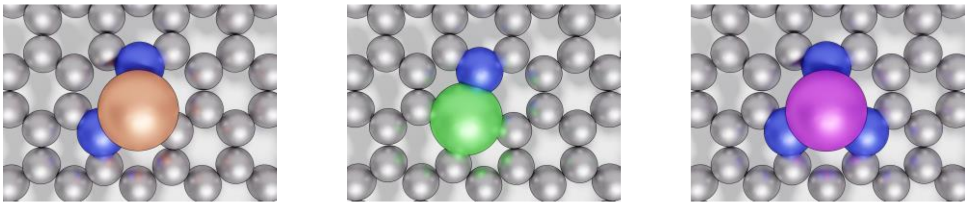

Fig. 2: Schematic of a few site motifs considered

2.2 Kinetics of CO2R to CO and scaling of CO_2 and COOH

Fig. 3 shows the contour plot corresponding to the turnover frequencies (TOFs) from kinetic modelling as a function of the adsorption energies of *COOH and *CO_2 (ΔE(COOH) and ΔE(CO_2), respectively).

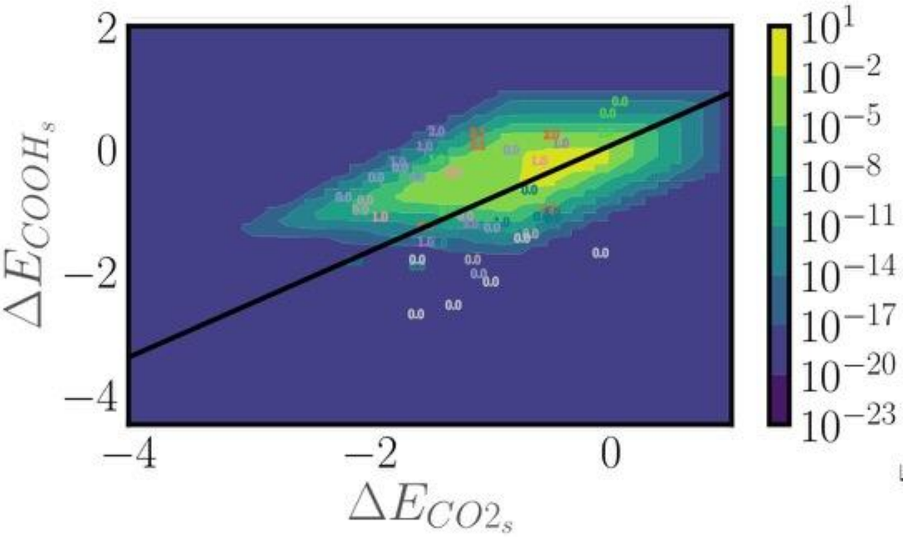

Fig. 3: Simulated kinetic volcano scaling showing the dependence of CO2R to CO activity on ΔE(COOH) and ΔE(CO_2)) at U=-0.5V vs. SHE, pH 1. The shaded colours indicate the TOF [s^{-1}] as evaluated through the kinetic model. Numbers indicate spins and their position the binding energies of considered candidates. Colours correspond to metal identity (not indicated – information is in confidential deliverable)

In general, (ΔE(COOH) and ΔE(CO_2) do not scale and can arise from spins or binding orientations. Beyond Fe- and Ni- catalysts, we find about 7 candidates to be potentially active for CO_2R to CO in the present study (not indicated).

3 CONCLUSIONS AND FUTURE WORK

From our computational screening study thus far, we have three takeaways:

1. In modelling these single-site catalysts, we need to go beyond our standard protocols for transition metal catalysts to consider $\Delta E(CO_2)$ adsorption energies and hybrid functionals
2. Optimal activity for CO_2R to CO occurs with intermediate binding for *COOH and $*CO_2$.
3. Several candidates beyond Fe- and Ni- single atom catalysts have emerged with promising theoretical activities, which are potential candidates for experimental testing in the Strasser group.

Future work will focus on selectivity, potential-dependence of stability, and the establishment of a deeper fundamental understanding of the scaling behaviour on these materials.

4 REFERENCES

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