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Electrochemical Reduction of CO2 using Cu-Pd clusters on Graphene

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ELECTROCHEMICAL REDUCTION OF CO_2 USING Cu-Pd CLUSTERS ON GRAPHENE

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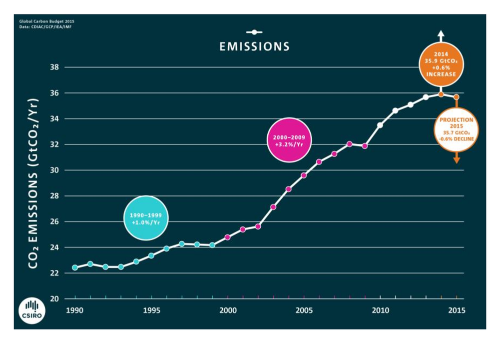
Motivation

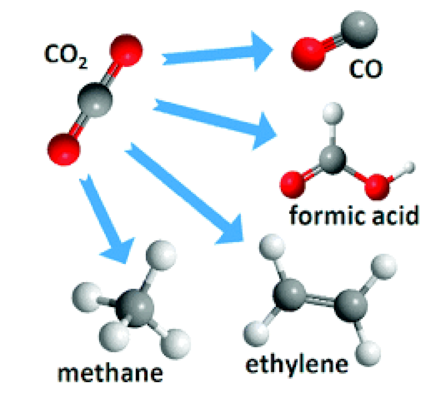
Over the past decade, the amount of CO_2 in the atmosphere has increased drastically, creating adverse climate effects. We must ensure that the level of CO_2 in the atmosphere doesn't increase further.



One way of preventing this increase, is to convert CO_2 into useful hydrocarbons such as methane. Current catalysts for this conversion are not efficient, and as such our group is screening for potential new catalysts for this conversion.

Computational Method

Five Cu-Pd alloy clusters were screened for the electrochemical CO_2 reduction based on density functional theory (DFT)



- Vienna Ab-initio Simulation Package (VASP)
- PBE exchange–correlation functional
- van der Waals (vdW) interaction (D2 method)
- Projector augmented wave (PAW) potentials and plane waves
- Free energies were calculated based on the computational hydrogen electrode model

Optimizing Clusters

First, the cluster geometry in gas phase was optimized to find the stable state.

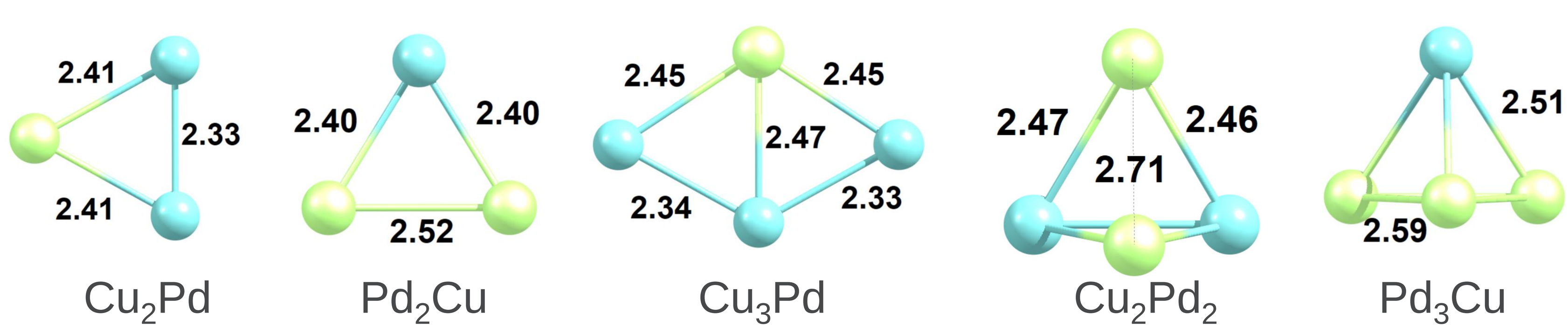


Figure 1: The ground-state configurations of Cu-Pd alloy clusters (blue: Cu, green: Pd).

The clusters were then placed on a single vacancy graphene support. Different binding sites and orientations were tested.

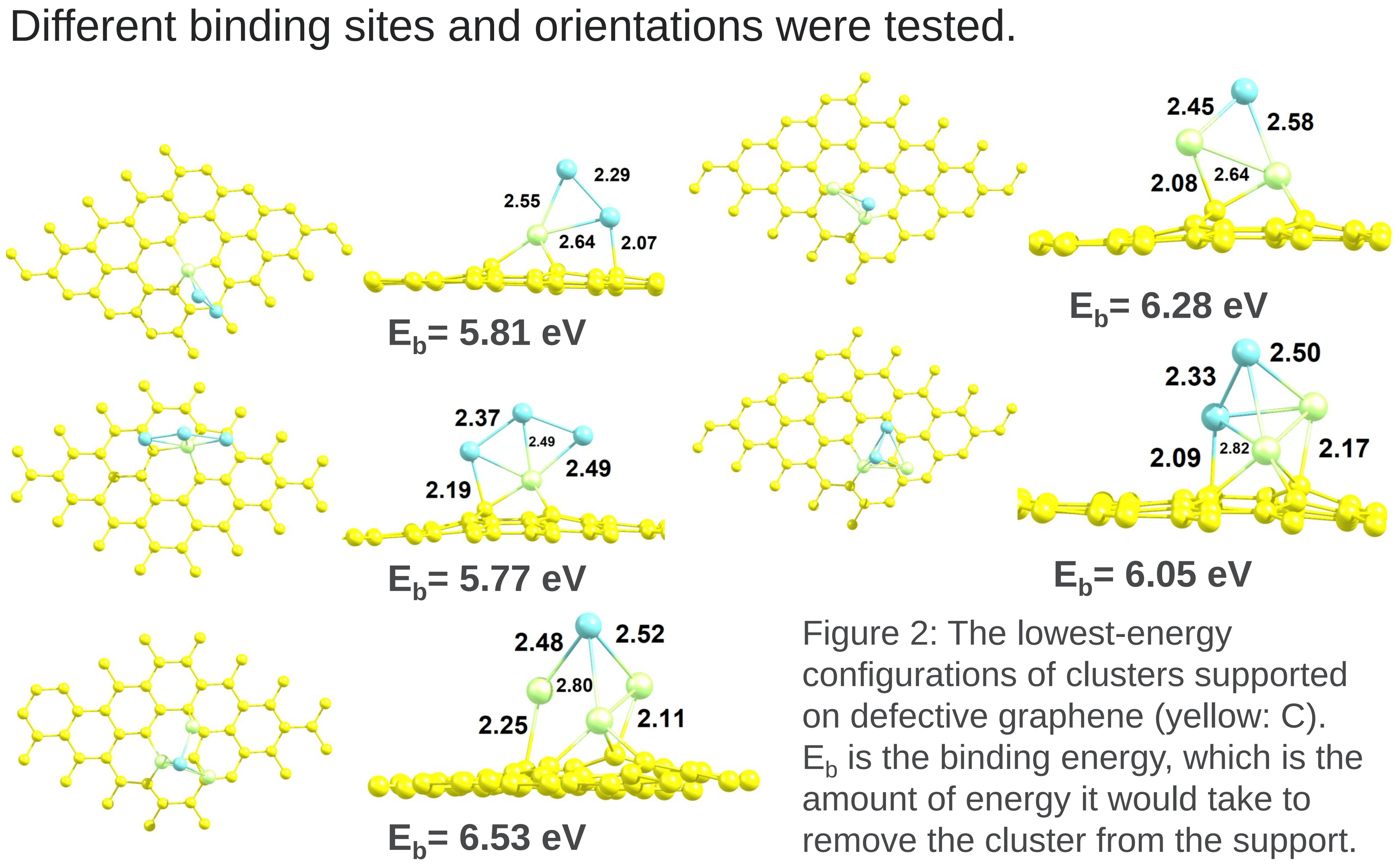


Figure 2: The lowest-energy configurations of clusters supported on defective graphene (yellow: C). E_b is the binding energy, which is the amount of energy it would take to remove the cluster from the support.

All the clusters are found to bind strongly to the vacancy site and are very unlikely to move and aggregate.

Screening

Free energies of the first hydrogenation steps of competing reactions was compared.

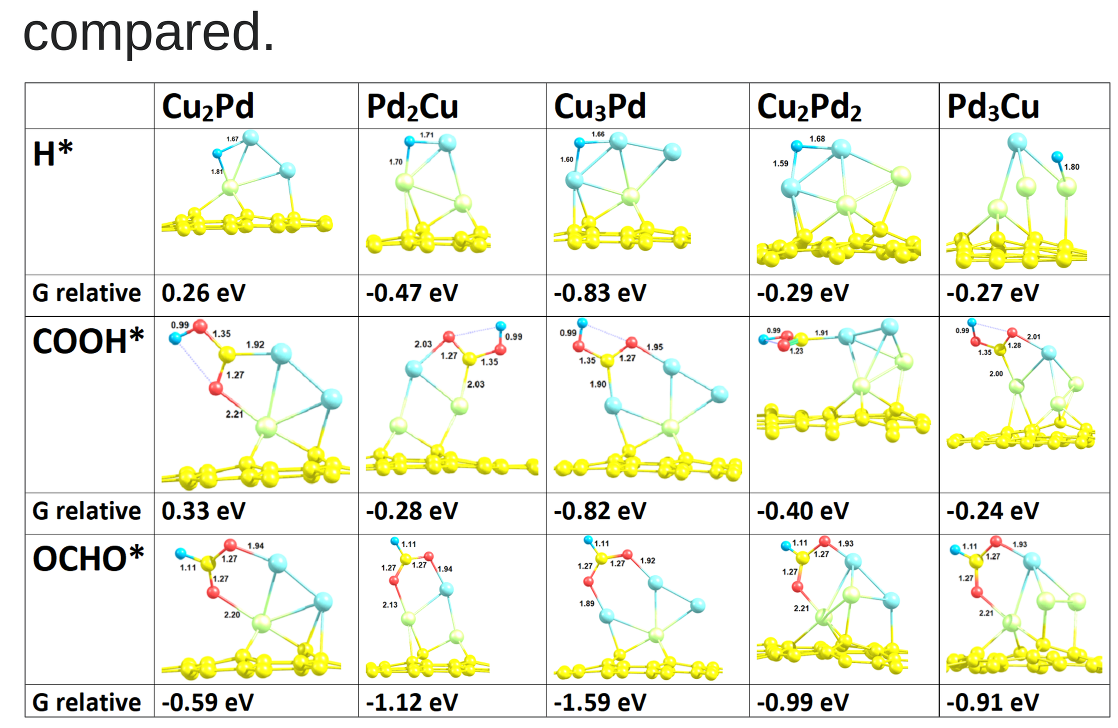


Figure 3: The optimized configurations of the first hydrogenation for the reduction of CO_2 and the production of H_2 (red: O, small blue: H). The relative energy associated with each of the configuration is the free energy of the configuration with respect to the sum of energies of reactants.

- In all cases the formation of OCHO* is preferred to the formation of H*
- CO_2 reduction is more favorable than production of hydrogen gas

Most probable rate limiting steps to CH_4

OH*: $$OH^* + H^+ + e^- \rightarrow H_2O$$

CHO*:
$$CO_2 + H^+ + e^- \rightarrow OCHO^*$$
$$OCHO^* + H^+ + e^- \rightarrow HCOOH^*$$
$$HCOOH^* \rightarrow CHO^* + H_2O$$

The optimal binding configuration for all of the intermediates for possible rate limiting steps were found.

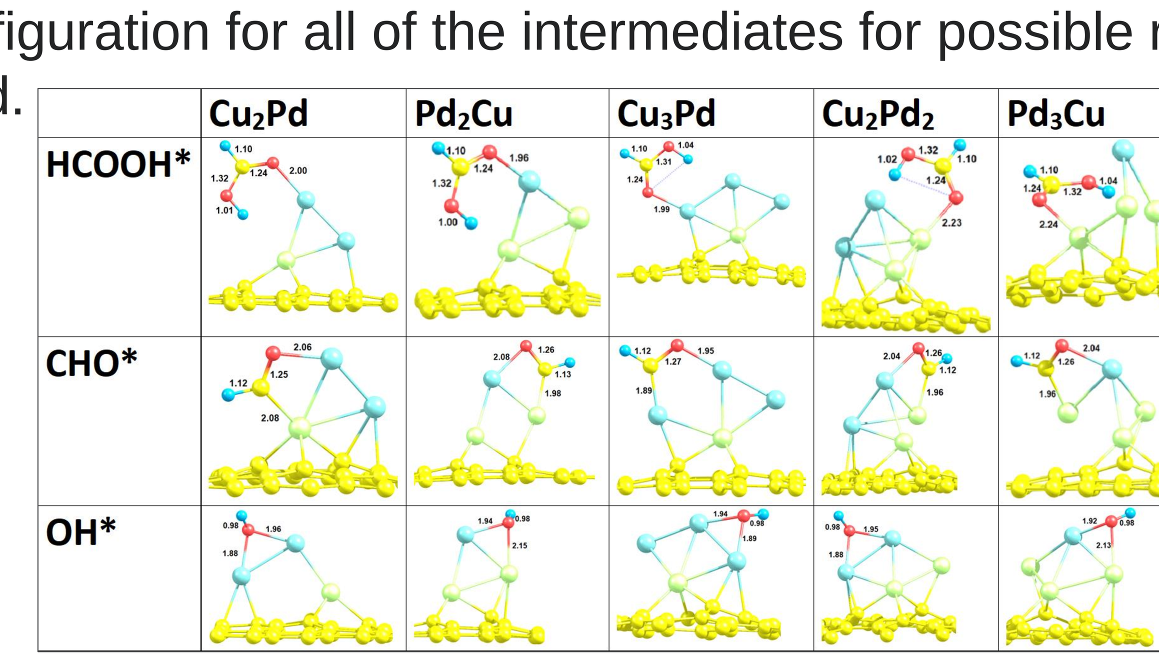


Figure 4: The optimized configurations for the possible rate limiting steps of the reduction of CO_2.

- Carbon prefers to bond to Pd, and oxygen prefers to bond to Cu
- The bonding of C and O also depends on an atom's coordination number

Results and Discussion

Elementary limiting potentials and overpotentials (in V)

	Cu_2Pd	Pd_2Cu	Cu_3Pd	Cu_2Pd_2	Pd_3Cu
$-U_L$ [OH*]	0.30	0.75	1.53	0.95	0.98
$-U_L$ [CHO*]	0.76	0.92	1.29	0.64	0.58
Overpotential	0.93	1.09	1.70	1.12	1.15

- Rate limiting step: CHO* formation for triatomic clusters
  OH* desorption for other clusters
- The cluster that appears to make the best catalyst is Cu_2Pd

Future Direction

- The electronic structure of the Cu_2Pd cluster on graphene will be analyzed to better understand the bonding that occurs during the reaction
- More clusters doped on graphene will be screened to determine if they could be good catalysts for the electrochemical reduction of CO_2

References

- **"Rapid growth in carbon dioxide emissions breaks in 2015." CSIRO. https://www.csiro.au/en/News/News-releases/2015/Rapid-growth-in-carbon-dioxide-emissions-breaks-in-2015.**

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