Lateral adsorbate interactions inhibit $HCOO^-$ while promoting CO production for CO_2 electrocatalysis on Ag

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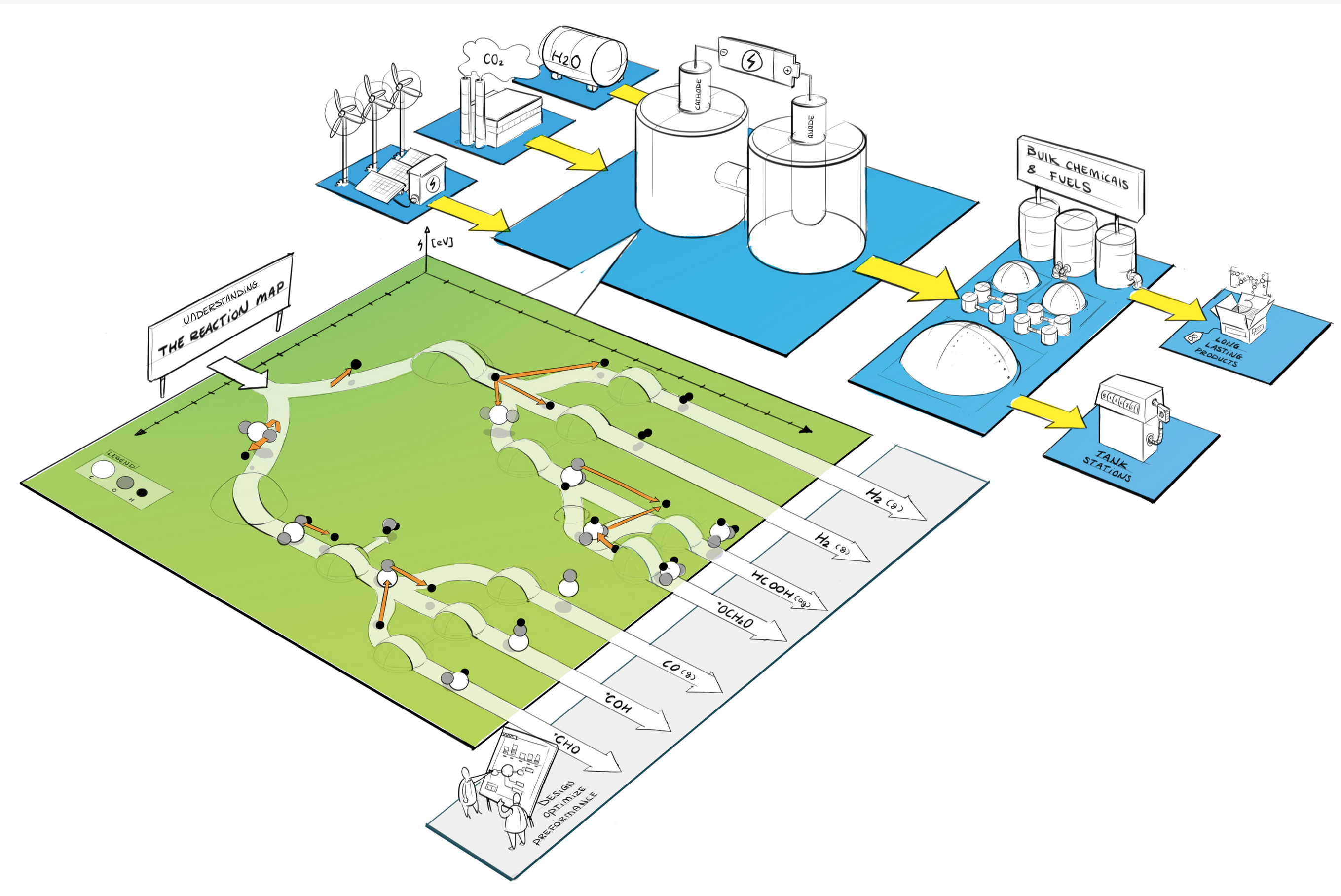
Introduction

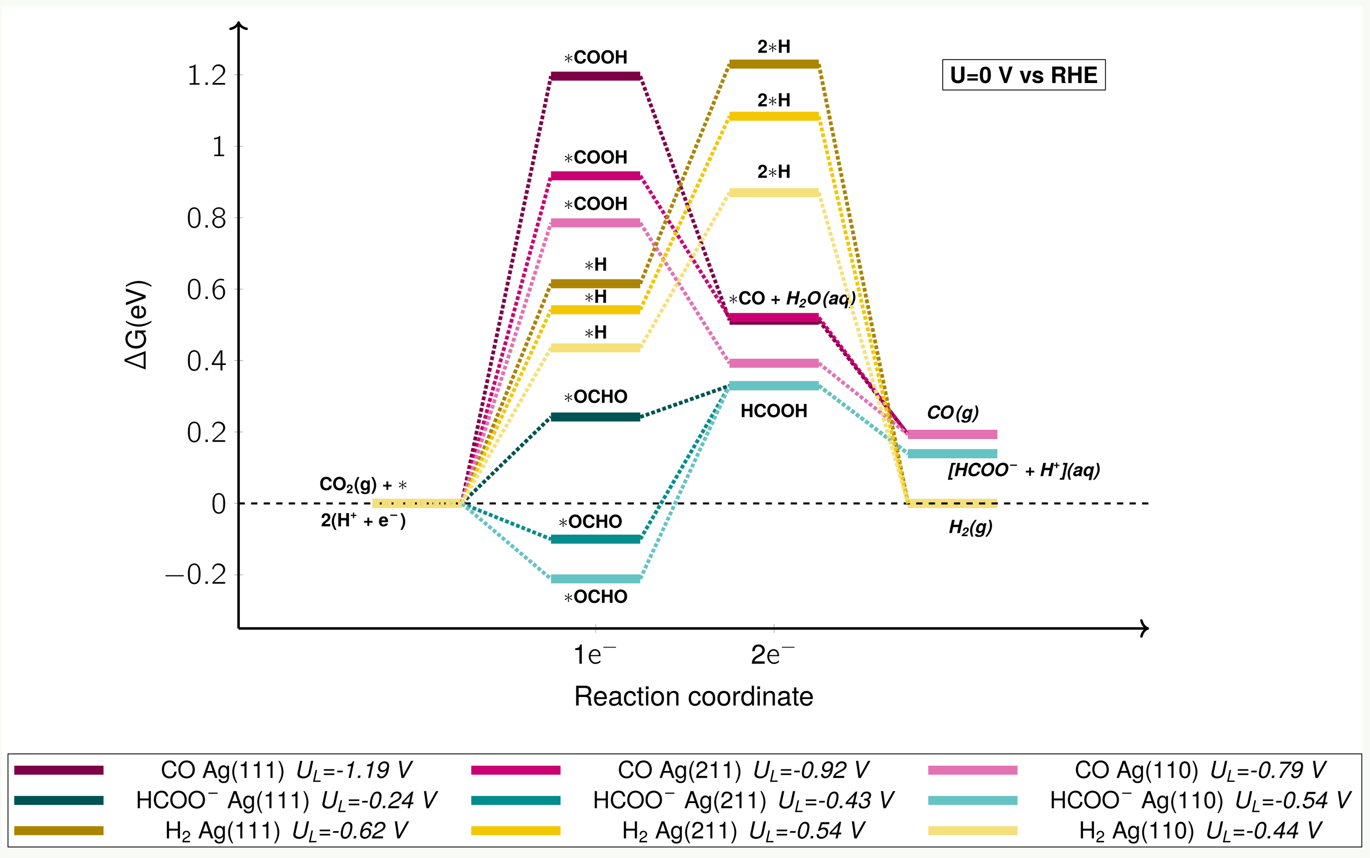
Electrocatalytic reduction of carbon dioxide (CO_2ER): manage intermittent renewable electricity, produce valuable molecules, recycle climate change-inducing CO_2.

$$\mathbf{nCO_2 + m(H^+ + e^-) \rightleftharpoons Products + xH_2O}$$



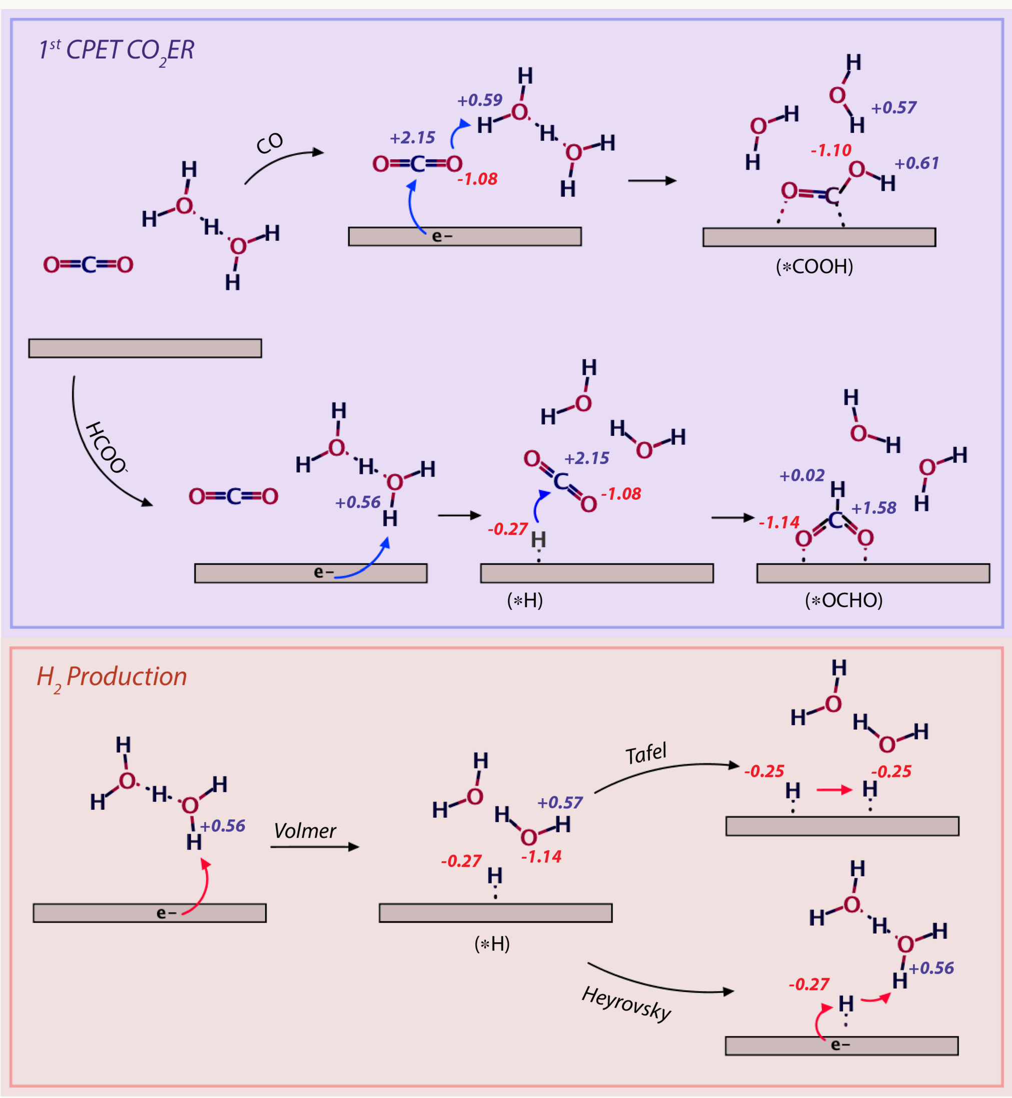
CO and $HCOO^-$: 2 CPET products with relatively low overpotentials, high faradaic efficiencies.

Ag catalysts: balance of performance with low cost electrodes.

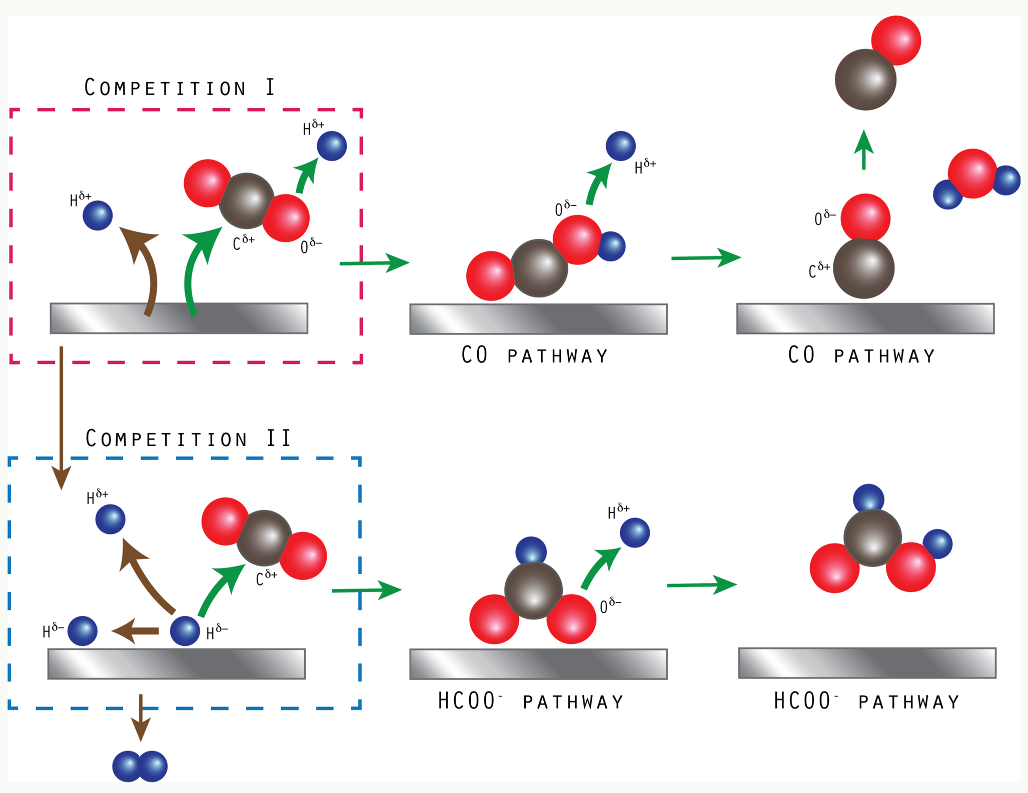


Experimental observation: CO(g) > H_2(g) >> $HCOO^-$(aq)

Reaction Pathways



- LUMO of a bent CO_2: highly localized at the C.
- HOMO: highly localized at the O.
- *COOH: nucleophile and electrophile interaction combination.
- *OCHO: $*H^{\delta-}$ acts as nucleophile for $C^{\delta+}$ of CO_2.
- Volmer-Heyrovsky and Volmer-Tafel for H_2: $*H^{\delta-}$ is 1^{st} CPET.



Competition I (bare catalyst site): *COOH vs. *H

Competition II (post *H): *OCHO vs. H_2

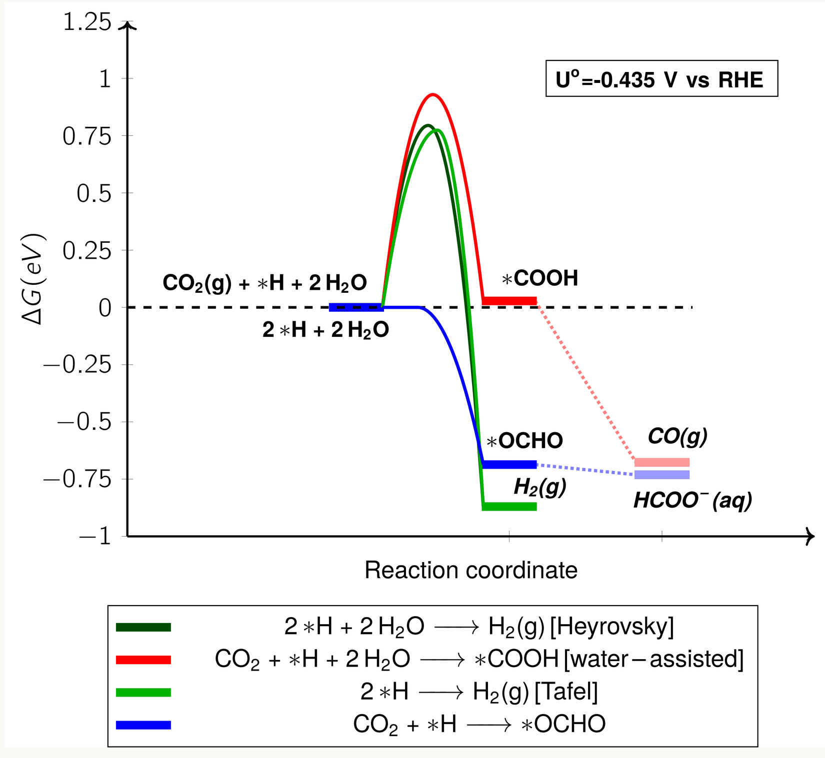
$HCOO^-$ vs. H_2 inherently more challenging than CO vs. H_2.

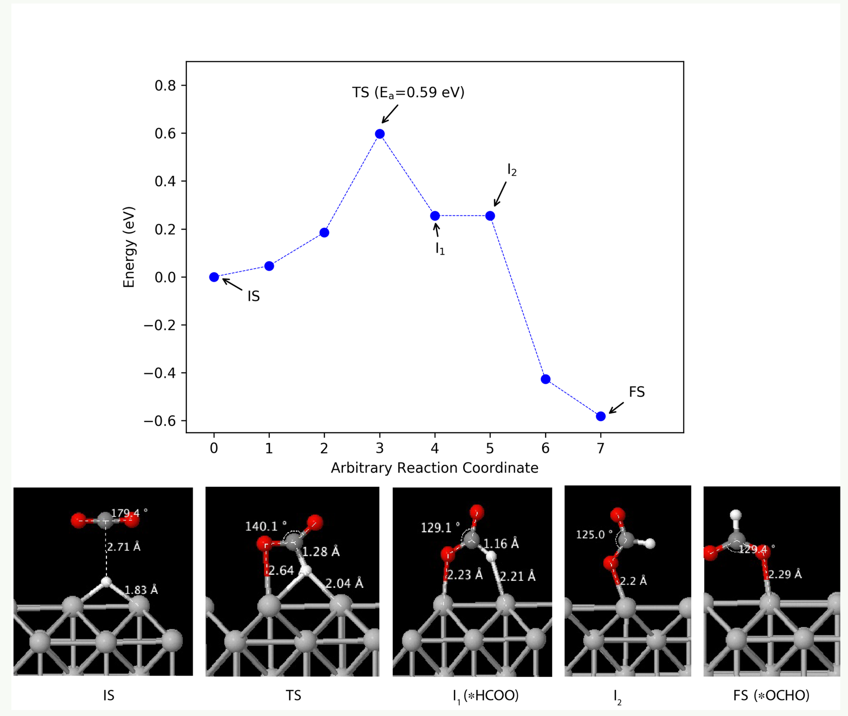
Reaction Barriers

*COOH and H_2 via Heyrovsky and Tafel steps: 0.93 eV, 0.79 eV and 0.77 eV respectively.

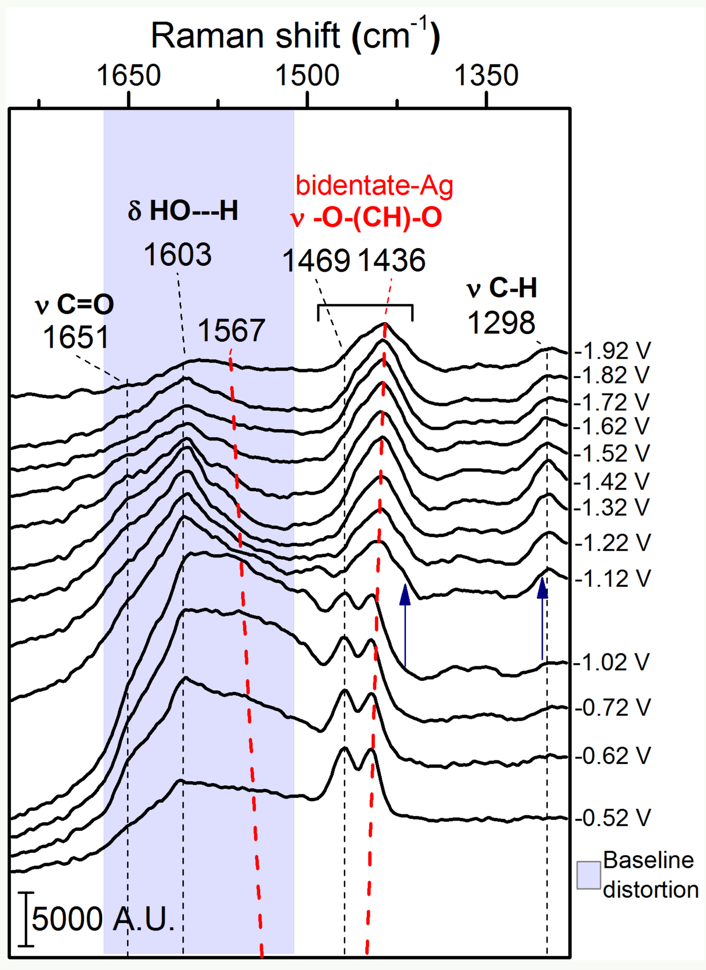
H_2 is the most thermodynamically favorable product.

No kinetic barrier for *OCHO: high solvation energy of the TS relative to the IS.





In-situ surface-enhanced Raman Spectroscopy (SERS)



Polycrystalline Ag, during CO_2ER, in 0.05 M $Li_2B_4O_7$ saturated with CO_2, bulk pH of 6.1.

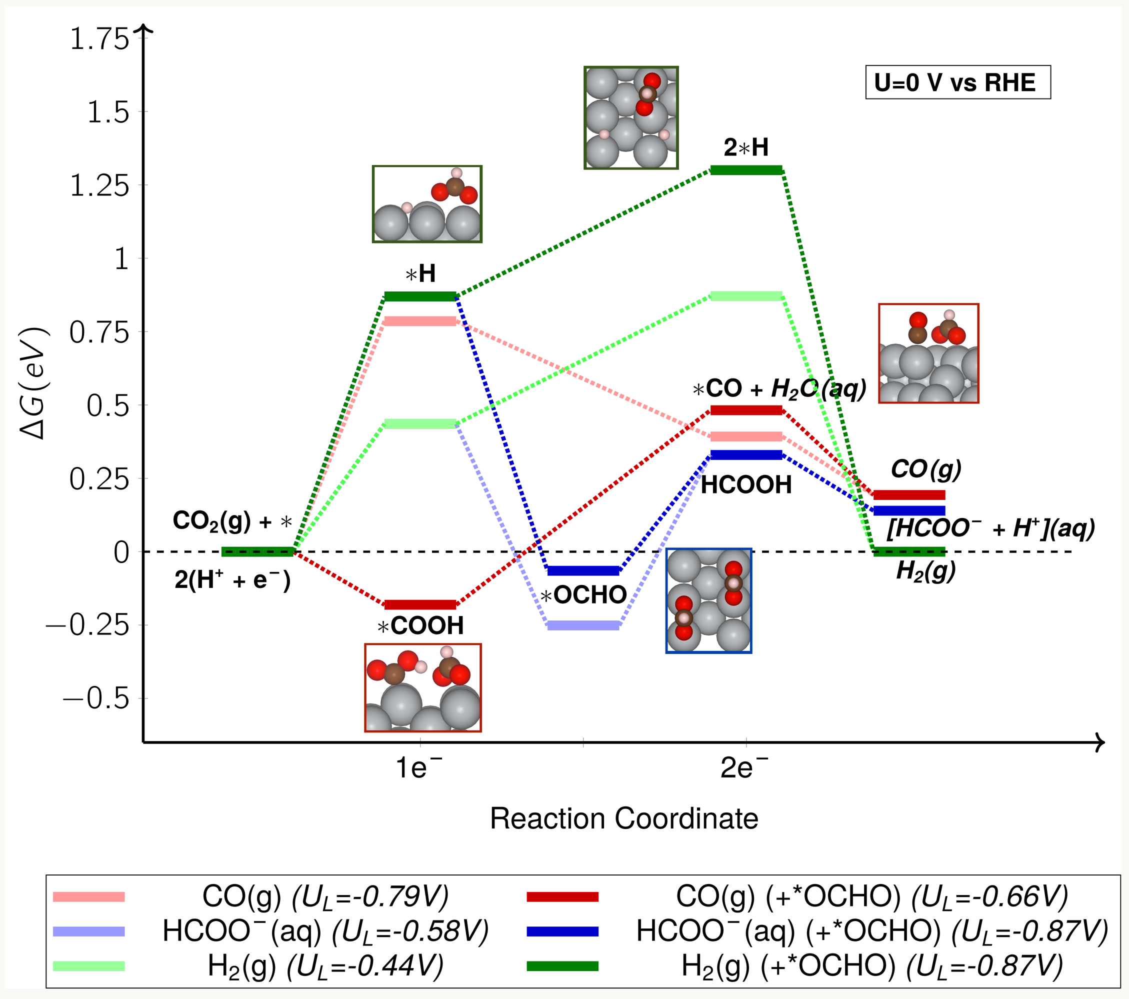
Bands at 1436 and 1469 cm^{-1} assigned to O-bound bidentate intermediate *OCHO.

Absence of νAg−O bands rule out surface oxides and hydroxides.

>-1.12 V vs. RHE:
Bidentate signal merges into a broader band.
A δC−H vibration band forms at 1298 cm^{-1}.

Interactions of O-bound species appear at low overpotentials.

Lateral Adsorbate Interactions



- *OCHO:
  Weakens *H binding
  Strengthens *COOH binding: H-bonding.
- U_L for CO ↓
  U_L for both H_2 and $HCOO^-$ ↑.
- *OCHO inhibits its own population by adversely affecting θ_{*H}.

Lateral adsorbate interactions can resolve the inconsistency between theoretical and experimental results for Ag catalysts.

Conclusions

- The fundamentally different nature of an $H^{\delta+}$ in solution and an $H^{\delta-}$ adsorbed on a catalyst surface has implications for catalyst selectivity.
- Solvation by surrounding water molecules and lateral adsorbate interactions have a significant effect on the energy landscape of CO_2ER reaction pathways.
- There is strong evidence of the presence of O-bound bidentate species on Ag during CO_2ER at low overpotentials, thereby altering our understanding of the catalyst surface at operational steady-state.

References

1. J. T. Feaster, *et al.* *ACS Catalysis* **7**, 4822 (2017).
2. S. Kai, W. Chaozhi, X. Guangzhi, *Spectrochimica Acta Part A: Molecular Spectroscopy* **45**, 1029 (1989).

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