Supporting Information

Circumventing Scaling Relationship on Bimetallic Monolayer Electrocatalysts for Selective CO$_2$ Reduction

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COMPUTATIONAL DETAILS

a. Free energy, limiting potential, overpotential, and reaction pathways for CO$_2$RR

The reaction free energy of the intermediates is derived from the binding energy ($E_B$) at 18.5 °C by including the zero-point energy (ZPE), heat capacity ($C_p$) and entropy (-TS) corrections:

$$G = E_B + ZPE + \int C_p dT - TS$$ (1)

All the free energy corrections are calculated based on the molecular vibration analysis and assuming that the changes in the vibrations of the surface caused by the intermediate are minimal. We applied approximate solvation corrections to the reaction intermediates proposed by Peterson et al.$^2$ The binding energy of an intermediate is calculated as:

$$E_B[C_{x}H_{y}O_{z}] = E[C_{x}H_{y}O_{z}] - E_{\text{slab}} - xE_C - yE_H - zE_O$$ (2)

Where $E[C_{x}H_{y}O_{z}]$ and $E_{\text{slab}}$ denote the total energy of the system with and without the intermediate, respectively. $E_C$, $E_H$, and $E_O$ are the total energy of one atom in grapheme, gaseous hydrogen, and the difference between H$_2$O and H$_2$, respectively.

According to the computational hydrogen electrode (CHE) model, the limiting potential ($U_L$) for the reaction step, for example, CO$_2$ → *HCOO, is defined as the change of the free energies between *HCOO and CO$_2$, in addition to the chemical potential of a proton-electron pair $\mu(H^+ + e^-)$, calculated as half of the free energy of gas-phase H$_2$ at zero applied voltage:

$$U_L = -\frac{G[\text{HCOO}] - G[\text{CO}_2] - \frac{1}{2}G[\text{H}_2\text{g}](U = 0\text{V}_{\text{RHE}})}{e}$$ (3)

The free energies of non-adsorbed species such as CO$_2$ and HCOOH are taken from previous work.$^2$ Note that to correct the inconsistency between the theoretical and experimental gas-phase reaction enthalpies, +0.45 eV is added to the energy of CO$_2$ and HCOOH, as also proposed in previous work.$^2$

The following reaction pathways for CO$_2$ hydrogenation have been considered in this work:

As discussed in the main paper, the reduction of CO$_2$ into *COOH is disfavored on the proposed BMEs and CO$_2$ is only expected to be reduced into *HCOO. Thus, the reactions after *COOH
are excluded. In addition, *CO cannot be reduced from *HCOO because the reduction requires breaking of a C-O bond and a C-H bond in *HCOO, which is energetically unfavorable. Thus, the reduction of *HCOO to *CO and other intermediates after *CO is also excluded. Furthermore, because the desorption of *HCOOH is exothermic on the proposed BMEs, *HCOOH cannot be reduced further and is the final product. Hence, no products other than HCOOH can be produced on the proposed BMEs. Based on the two-step reaction (CO$_2$ → *HCOO → HCOOH), the more negative U_L among the two steps is defined as the reaction overpotential U_OP in this work.

b. Activation barrier calculations

The activation barrier for the hydrogenation reaction is calculated based on the model proposed by Nie et al.\textsuperscript{3-4} In the model, the activation barrier for an elementary electrochemical reaction (A* + H$^+$ + e$^-$ → AH*) is derived from analogous surface hydrogenation reaction (A* + H* → AH*). The activation barrier as a function of the electrode potential U is calculated as:

$$E_{act}(U) = E_{act0} + \beta' (U - U^0)$$

(3)

where $E_{act0}$ is the reaction barrier calculated from DFT plus the ZPE correction. $U^0$ is set so that the chemical potential of the adsorbed H* is equal to that of a proton-electron pair. $\beta'$ is an effective symmetry factor calculated by:

$$\beta' = 0.5 + (\mu_{TS} - \mu_{reactant})/3$$

(4)

where $\mu_{TS} - \mu_{reactant}$ represents the variation in the surface dipole moments between the reactant and the transition state.

c. Water-Assisted reaction model

In the activation barrier calculations, we considered the presence of one water molecule below the H-down ice-like water bilayer to assist the hydrogenation reactions. More specifically, water can assist the reaction in two manners: (1) the surface proton is transferred directly to the adsorbate, assisted by the hydrogen bond between the water molecule and the adsorbate; (2) the surface proton is transferred to the water molecule, which concurrently shuttles another proton to the adsorbate, analogous to the Grothuss mechanism.

We note that the above water-assisted activation barrier calculation model was able to reproduce experimentally identified CO$_2$RR species on Cu, and also predicted a correct methanol product for CH$_3$O reduction on Cu.\textsuperscript{3-4} Besides, the model was also used to examine C$_2$ product selectivity on Cu(100) for CO$_2$RR,\textsuperscript{5} to predict Cu monolayer catalysts and bimetallic alloys for
CO$_2$RR$^{6-7}$ to study binary metal catalyst for electrochemical nitrogen reduction reaction$^8$, to design Au$_{22}$(L$^8$)$_6$ nano-clusters for oxygen reduction reaction,$^9$ and to predict bimetallenes for selective CO$_2$RR to HCOOH.$^{10}$
Table S1. The calculated formation energy ($E_f$) and segregation energy ($E_{seg}$) of the stable BMEs. Negative $E_f$ and positive $E_{seg}$ values indicate that the catalyst is stable.

|          | $E_f$  | $E_{seg}$ |          | $E_f$  | $E_{seg}$ |          | $E_f$  | $E_{seg}$ |
|----------|--------|-----------|----------|--------|-----------|----------|--------|-----------|
| ML/hcp(0001) |        |           | ML/fcc(111) |        |           | ML/bcc(110) |        |           |
| Ag/Ti    | -0.351 | 0.951     | Ag/Rh     | -0.349 | 1.198     | Ag/V      | -0.195 | 0.255     |
| Cu/Ti    | -0.489 | 0.645     | Au/Rh     | -0.317 | 0.605     | Cu/V      | -0.327 | 0.826     |
| Pd/Ti    | -0.731 | 0.199     | Cu/Rh     | -0.451 | 0.448     | Pd/V      | -0.525 | 0.717     |
| Ag/Zr    | -0.424 | 1.201     | Pd/Rh     | -0.489 | 0.570     | Ag/Nb     | -0.245 | 1.963     |
| Au/Zr    | -0.579 | 0.420     | Pt/Rh     | -0.496 | 0.421     | Au/Nb     | -0.312 | 0.830     |
| Cu/Zr    | -0.570 | 0.081     | Ag/Pd     | -0.534 | 0.141     | Cu/Nb     | -0.388 | 0.770     |
| Ag/Ru    | -0.194 | 2.381     | Pt/Ag     | -0.787 | 0.046     | Pd/Nb     | -0.623 | 1.141     |
| Au/Ru    | -0.174 | 1.702     | Ag/Ir     | -0.288 | 1.771     | Ag/Mo     | -0.096 | 1.902     |
| Cu/Ru    | -0.307 | 1.264     | Au/Ir     | -0.248 | 1.272     | Au/Mo     | -0.106 | 1.055     |
| Pd/Ru    | -0.390 | 1.344     | Cu/Ir     | -0.421 | 0.775     | Cu/Mo     | -0.247 | 1.093     |
| Pt/Ru    | -0.403 | 0.879     | Pd/Ir     | -0.472 | 0.767     | Pd/Mo     | -0.374 | 0.950     |
| Ag/Hf    | -0.332 | 1.497     | Pt/Ir     | -0.472 | 0.620     | Ag/Ta     | -0.148 | 1.900     |
| Au/Hf    | -0.487 | 0.686     | Ag/Pt     | -0.522 | 0.668     | Au/Ta     | -0.226 | 0.843     |
| Cu/Hf    | -0.489 | 0.543     | Au/Pt     | -0.466 | 0.534     | Cu/Ta     | -0.312 | 0.888     |
| Ag/Re    | -0.001 | 2.200     | Pd/Ta     | -0.574 | 1.207     | Au/W      | -0.000 | 1.708     |
| Cu/Re    | -0.135 | 0.709     |          |        |           | Au/W      | -0.000 | 1.708     |
| Pd/Re    | -0.265 | 0.697     |          |        |           | Cu/W      | -0.162 | 1.682     |
| Ag/Os    | -0.118 | 3.371     |          |        |           | Pd/W      | -0.302 | 1.558     |
| Au/Os    | -0.091 | 2.747     |          |        |           | Pt/W      | -0.357 | 0.306     |
| Cu/Os    | -0.252 | 1.997     |          |        |           |           |        |           |
| Pd/Os    | -0.334 | 1.623     |          |        |           |           |        |           |
| Pt/Os    | -0.347 | 1.159     |          |        |           |           |        |           |
Table S2. Standard dissolution potential $U_{\text{diss}}$(bulk) of the bulk metal of the MLs, formation energy $E_f$ of the BMEs, number of transferred electrons during the dissolution ($N_e$), and the dissolution potential $U_{\text{diss}}$ of the proposed BMEs. The proposed catalysts with a positive $U_{\text{diss}}$ (V vs SHE) are regarded as electrochemically stable under acidic conditions.

| ML/substrate     | $U_{\text{diss}}$(bulk) (V) | $E_f$ (eV) | $N_e$ | $U_{\text{diss}}$ (V) |
|------------------|-------------------------------|------------|-------|-----------------------|
| Ag/Ti(0001)      | 0.80                          | 0.264      | 1     | 0.536                 |
| Ag/Zr(0001)      | 0.80                          | 0.191      | 1     | 0.609                 |
| Au/Zr(0001)      | 1.50                          | 0.037      | 3     | 1.488                 |
| Ag/Hf(0001)      | 0.80                          | 0.283      | 1     | 0.517                 |
| Au/Hf(0001)      | 1.50                          | 0.129      | 3     | 1.457                 |
| Pd/V(110)        | 0.95                          | 0.090      | 2     | 0.905                 |
| Ag/Nb(110)       | 0.80                          | 0.370      | 1     | 0.430                 |
| Au/Nb(110)       | 1.50                          | 0.304      | 3     | 1.399                 |
| Ag/Mo(110)       | 0.80                          | 0.520      | 1     | 0.280                 |
| Au/Ta(110)       | 1.50                          | 0.390      | 3     | 1.370                 |
| Pd/Ta(110)       | 0.95                          | 0.042      | 2     | 0.929                 |
Table S3. Free energy changes for the formation of *H, the reduction of CO$_2$ to *HCOO and *COOH, the reduction of *HCOO to HCOOH*, and desorption of *HCOOH on the proposed BMEs.

| ML/substrate | *H  | CO$_2$ → *H | CO$_2$ → *HCOO | *HCOO → HCOOH | *HCOOH → HCOOH |
|--------------|-----|-------------|----------------|---------------|---------------|
| Ag/Ti(0001)  | 0.662 | 0.051 | 0.787 | 0.290 | -0.061 |
| Cu/Ti(0001)  | 0.385 | -0.409 | 0.478 | 0.675 | 0.014 |
| Ag/Zr(0001)  | 0.705 | -0.082 | 0.701 | 0.435 | -0.073 |
| Au/Zr(0001)  | 0.905 | 0.225 | 0.827 | 0.148 | -0.093 |
| Cu/Ru(0001)  | 0.077 | -0.045 | 0.481 | 0.364 | -0.039 |
| Ag/Hf(0001)  | 0.825 | 0.035 | 0.824 | 0.318 | -0.073 |
| Au/Hf(0001)  | 0.990 | 0.296 | 0.930 | 0.078 | -0.094 |
| Cu/Re(0001)  | -0.221 | -0.440 | 0.070 | 0.552 | 0.168 |
| Cu/Os(0001)  | 0.113 | 0.014 | 0.521 | 0.259 | 0.007 |
| Cu/Ir(111)   | 0.067 | 0.002 | 0.453 | 0.274 | 0.004 |
| Cu/V(110)    | 0.021 | -0.436 | 0.210 | 0.647 | 0.069 |
| Pd/V(110)    | 0.373 | 0.355 | 0.787 | -0.149 | 0.074 |
| Ag/Nb(110)   | 0.334 | -0.042 | 0.632 | 0.365 | -0.043 |
| Au/Nb(110)   | 0.492 | 0.243 | 0.655 | 0.110 | -0.073 |
| Cu/Nb(110)   | 0.006 | -0.712 | -0.004 | 0.865 | 0.127 |
| Ag/Mo(110)   | 0.408 | 0.354 | 0.963 | 0.015 | -0.089 |
| Cu/Mo(110)   | 0.040 | -0.276 | 0.312 | 0.472 | 0.084 |
| Ag/Ta(110)   | 0.285 | -0.150 | 0.526 | 0.442 | -0.012 |
| Au/Ta(110)   | 0.498 | 0.063 | 0.561 | 0.273 | -0.056 |
| Cu/Ta(110)   | 0.004 | -0.752 | -0.026 | 0.914 | 0.118 |
| Pd/Ta(110)   | 0.379 | 0.259 | 0.807 | 0.010 | 0.011 |
| Cu/W(110)    | -0.072 | -0.342 | 0.225 | 0.472 | 0.150 |
| Pd/W(110)    | -0.406 | -0.500 | -0.094 | 0.203 | 0.577 |
Table S4. The adsorption distance of *COOH and Bader charge transfer from the substrate to the surface Ag atoms on pure Ag (111) surface and selected Ag based BMEs. The Ag-O distance is reduced on the BMEs compared with that on Ag(111) surface. In contrast, the Ag-C distance is either the same or slightly longer than that on Ag(111).

| Catalysts | Ag-C distance (Å) | Ag-O distance (Å) | Charge transfer/Ag atom |
|-----------|------------------|------------------|------------------------|
| Ag (111)  | 2.176            | 2.551            | none                   |
| Ag/Ti(0001) | 2.183          | 2.471            | 0.327e                 |
| Ag/Zr(0001) | 2.173          | 2.493            | 0.388e                 |
| Ag/Hf(0001) | 2.213          | 2.449            | 0.393e                 |
| Ag/Nb(110)  | 2.199           | 2.520            | 0.266e                 |
| Ag/Mo(110)  | 2.210           | 2.458            | 0.140e                 |
Figure S1 Radial distribution function and crystal structure of the selected BMEs at 300 K in the presence of HCOO* on the surface after a 4 ps MD simulation. The vertical lines indicate the equilibrium nearest-neighbor (NN) distance at 0 K. The proposed BMEs are found to be stable because of the negligible changes in the NN distance between 0 K and 300 K.
Figure S2 The adsorption structure and differential charge density isosurfaces for *H on Ag\textsuperscript{ML}/Hf and pure Ag surfaces. Cyan and yellow isosurfaces correspond to the charge density contour of -0.01 and +0.01 e Å\textsuperscript{3}. Light gray, blue gray, and white spheres represent Hf, Ag, and H atoms, respectively.
Figure S3 Projected crystal orbital Hamilton population (pCOHP) for the subsurface Hf - H interaction on Ag^{ML}/Hf surface calculated with (red) and without (black) the Hf $d$ orbitals. Bonding and antibonding states are shown on the right and left, respectively. The horizontal dashed lines indicate the Fermi level.
Figure S4 The adsorption structures and projected crystal orbital Hamilton population (COHP) for *H-substrate and O-substrate (in *HCOO) interactions in the three BMEs. The contributions of s, p, and d orbitals are included. The antibonding and bonding states are shown on the left and the right of the vertical zero line. The horizontal dashed line indicates the Fermi level.
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