Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Modeling the Effect of Surface CO Coverage on the Electrocatalytic Reduction of CO_2 to CO on Pd Surfaces

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Table S1 Differential adsorption energies obtained with force convergence criteria of 0.05 eV/ Å and 0.01 eV/ Å.

criteria / θ_{CO}	111		100		110		211	
	0.05	0.01	0.05	0.01	0.05	0.01	0.05	0.01
0.25-CO	-1.714	-1.713	-1.688	-1.684	-1.616	-1.621	-1.705	-1.698
0.5-CO	-1.223	-1.224	-1.193	-1.192	-1.568	-1.567	-1.665	-1.667
0.75-CO	-0.688	-0.687	-1.090	-1.096	-1.366	-1.366	-1.478	-1.489
1-CO	0.805	0.803	-0.507	-0.511	-1.313	-1.317	-1.255	-1.249
0.25-COOH	-0.213	-0.219	-0.625	-0.626	-0.697	-0.697	-0.628	-0.630
0.5-COOH	0.542	0.541	-0.128	-0.128	-0.387	-0.387	-0.522	-0.523
0.75-COOH	1.718	1.725	1.395	1.395	0.393	0.370	-0.252	-0.252

Table S2 Slope (*a*) and intercept (*b*) of the linear relations obtained from Eq. 3 in the main text. Unit in eV.

	CO		COOH	
	a	*b*	*a*	*b*
111	3.24	-2.73	3.67	-1.19
100	1.46	-2.03	4.04	-1.81
110	0.51	-1.80	2.18	-1.32
211	0.82	-2.08	0.75	-0.84

Table S3 The steady-state coverage of CO, θ_{CO}, while assuming step ES1 or ES3 as the rate-determining step. Values in bold represent the CO coverage at the real rate-determining step under the reaction conditions.

θ_{CO}/ML	Pd(111)		Pd(100)		Pd(110)		Pd(211)	
U/V	ES1	ES3	ES1	ES3	ES1	ES3	ES1	ES3
-0.6	**0.601**	0.984	**0.810**	0.990	**0.990**	0.990	0.990	**0.990**
-0.7	**0.601**	0.990	**0.810**	0.990	**0.990**	0.990	0.990	**0.990**
-0.8	**0.601**	0.990	**0.810**	0.990	0.990	**0.990**	0.990	**0.990**
-0.9	**0.601**	0.990	**0.810**	0.990	0.990	**0.990**	0.990	**0.990**
-1	**0.601**	0.990	**0.810**	0.990	0.990	**0.990**	0.990	**0.990**
-1.1	**0.601**	0.990	**0.810**	0.990	0.990	**0.990**	0.990	**0.990**
-1.2	**0.601**	0.990	**0.810**	0.990	0.990	**0.990**	0.990	**0.990**

Table S4 Free energy corrections (in eV) to the reaction energies at θ_{CO} = 0.25 ML and U = 0 V vs RHE.

Pd(111)	E_{ZPE}	TS	$\int C_p dT$	Total
$CO_2(g) + * + ½\ H_2 \rightarrow COOH*$	0.17	-0.56	-0.03	0.70
$COOH* + ½\ H_2 \rightarrow CO* + H_2O(l)$	0.01	0.21	0.01	-0.18
$CO* \rightarrow * + CO(g)$	-0.05	0.49	0.02	-0.52

Pd(100)	E_{ZPE}	TS	$\int C_p dT$	Total
$CO_2(g) + * + ½\ H_2 \rightarrow COOH*$	0.16	-0.66	-0.04	0.78
$COOH* + ½\ H_2 \rightarrow CO* + H_2O(l)$	0.03	0.26	0.00	-0.22
$CO* \rightarrow * + CO(g)$	-0.06	0.54	0.04	-0.56

Pd(110)	E_{ZPE}	TS	$\int C_p dT$	Total
$CO_2(g) + * + ½\ H_2 \rightarrow COOH*$	0.17	-0.71	-0.06	0.82
$COOH* + ½\ H_2 \rightarrow CO* + H_2O(l)$	0.01	0.37	0.05	-0.31
$CO* \rightarrow * + CO(g)$	-0.06	0.47	0.02	-0.51

Pd(211)	E_{ZPE}	TS	$\int C_p dT$	Total
$CO_2(g) + * + ½\ H_2 \rightarrow COOH*$	0.18	-0.65	-0.04	0.79
$COOH* + ½\ H_2 \rightarrow CO* + H_2O(l)$	0.00	0.30	0.02	-0.27
$CO* \rightarrow * + CO(g)$	-0.05	0.49	0.02	-0.52

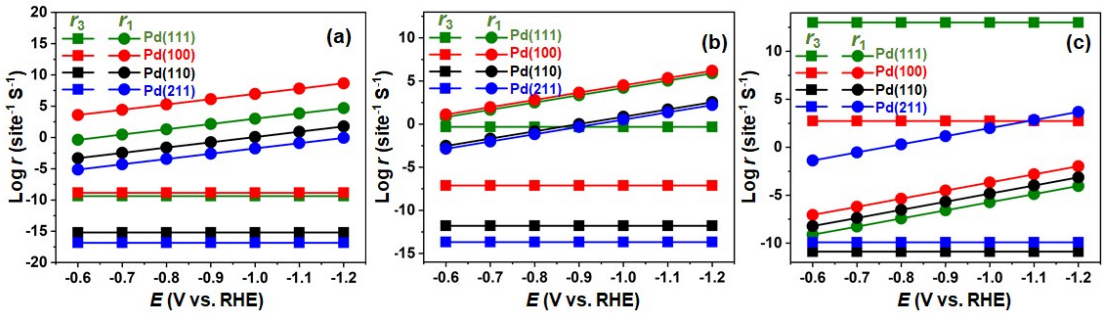


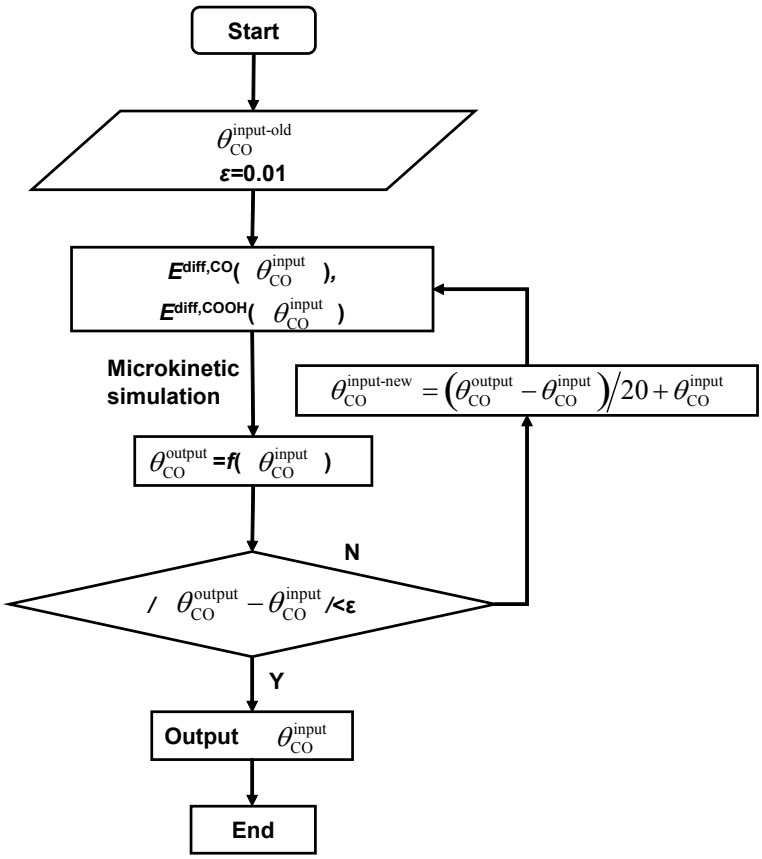
Figure S1 Calculated lg r (s^{-1} $site^{-1}$) over all the Pd surfaces with pre-adsorbed CO coverage of (a) 0.25, (b) 0.5 and (c) 0.75 ML.

Self-consistent iterative equation:

For accuracy and efficiency, we iterate with the following equation:

$$\theta_{CO}^{\text{input-new}} = \left(\theta_{CO}^{\text{output}} - \theta_{CO}^{\text{input}}\right)/20 + \theta_{CO}^{\text{input}} \quad \text{(S1)}$$

where $\theta_{CO}^{\text{input}}$ is the input coverage of CO, $\theta_{CO}^{\text{output}}$ is the coverage of CO obtained from the microkinetic modeling, and $\theta_{CO}^{\text{input-new}}$ is the coverage of CO used for the next iteration. For example: if the input value ($\theta_{CO}^{\text{input}}$) is 0.25 ML, and the output value ($\theta_{CO}^{\text{output}}$) from microkinetic modeling is 1.000 ML, in this case, the tolerance (0.01 ML) is not satisfied. Hence, we need to derived the new input value through iteration using Eq. S1, and the new input value is therefore changed to $(1.000 - 0.25)/20 + 0.25 = 0.2875$ ML. Subsequently, we need to run these iterations until the desired tolerance is achieved. The flow chart showing the process of self-consistent iterative microkinetic modeling can be found in Scheme S1.



Scheme S1 Flow chart showing the process of self-consistent iterative microkinetic modeling.