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

Supporting Information

Reaction-driven Selective CO_2 Hydrogenation to Formic Acid on Pd(111)

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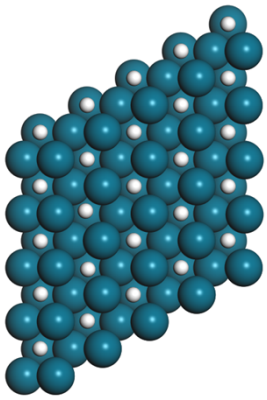
Figure S1. Optimized $*H_{1ML}$/Pd(111) slab with top and side views. [Blue: Pt. White: H]



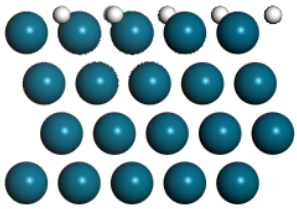


Figure S2. KMC-simulated surface. [Blue: Pt; White: H]

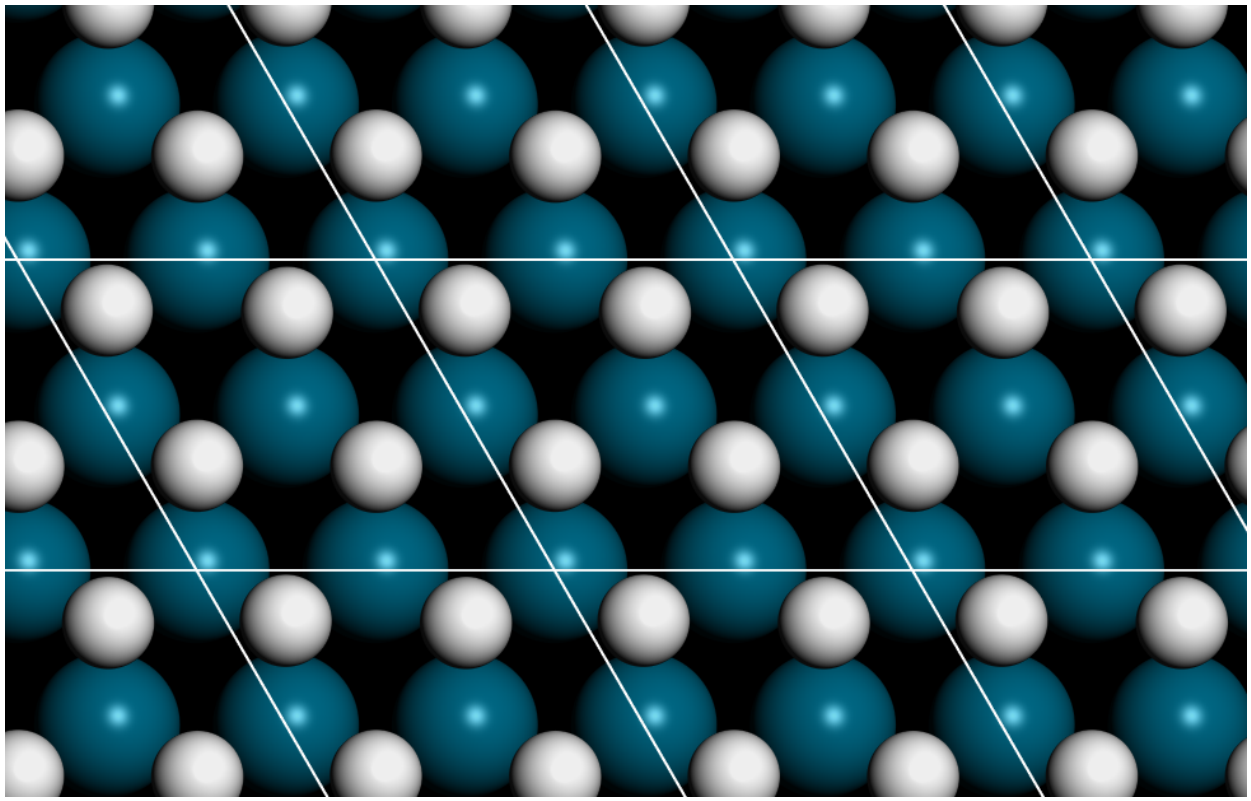
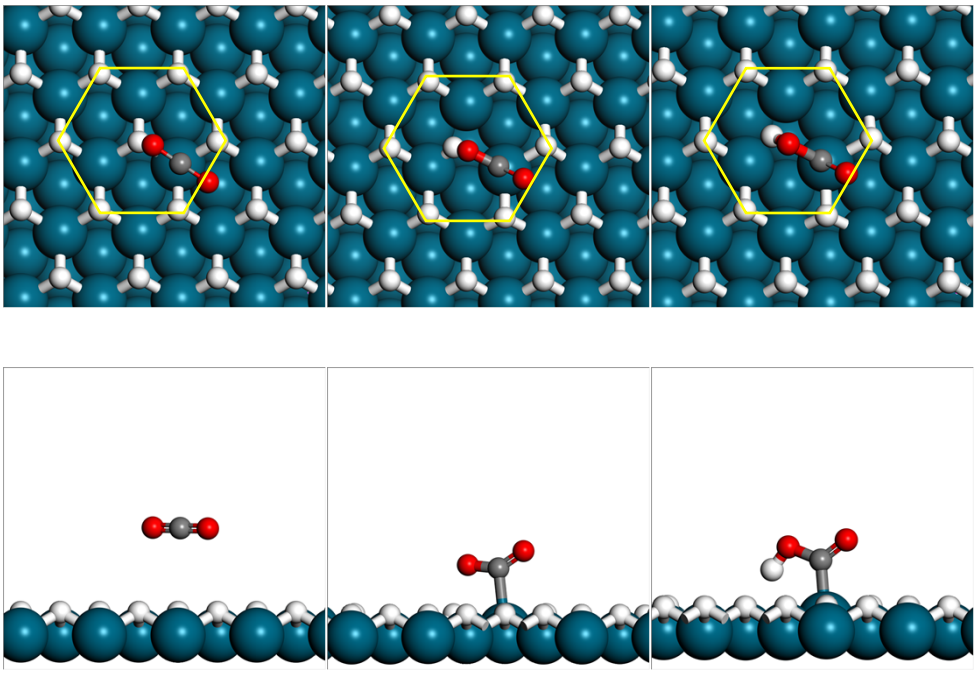
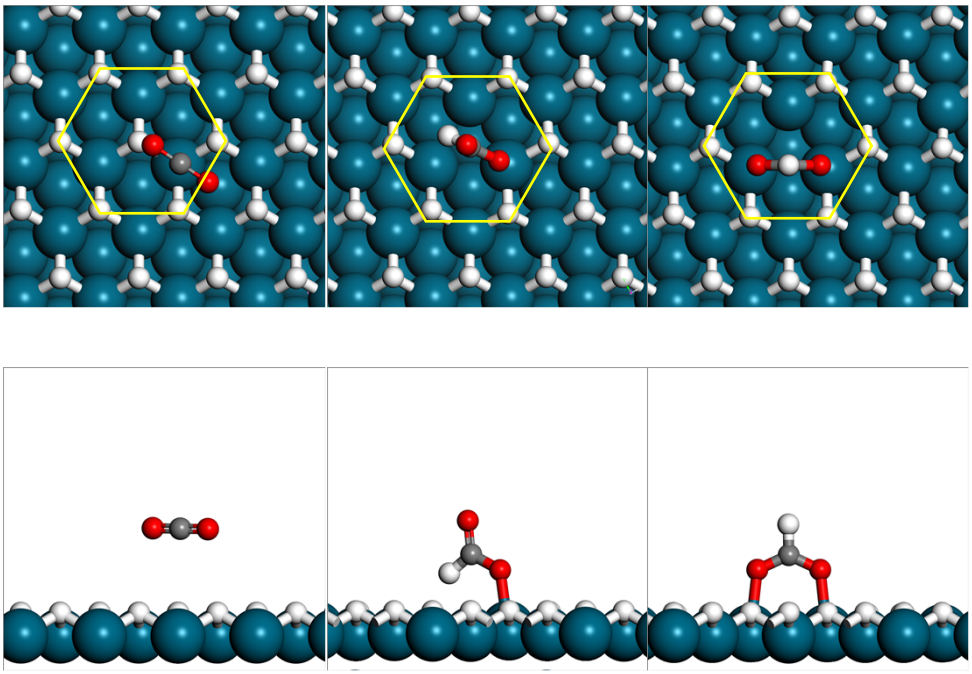


Figure S3. DFT-optimized binding geometry (top and side views) of initial (left), transition (middle) and final (right) states involved in the elementary steps for CO_2 hydrogenation on $*H_{ML}$/Pd(111). The confined hydrogen vacancy space is highlighted in dashed lines. The corresponding reaction energy and activation barrier were also included [Blue: Pt; White: H; Grey: C; Red: O]

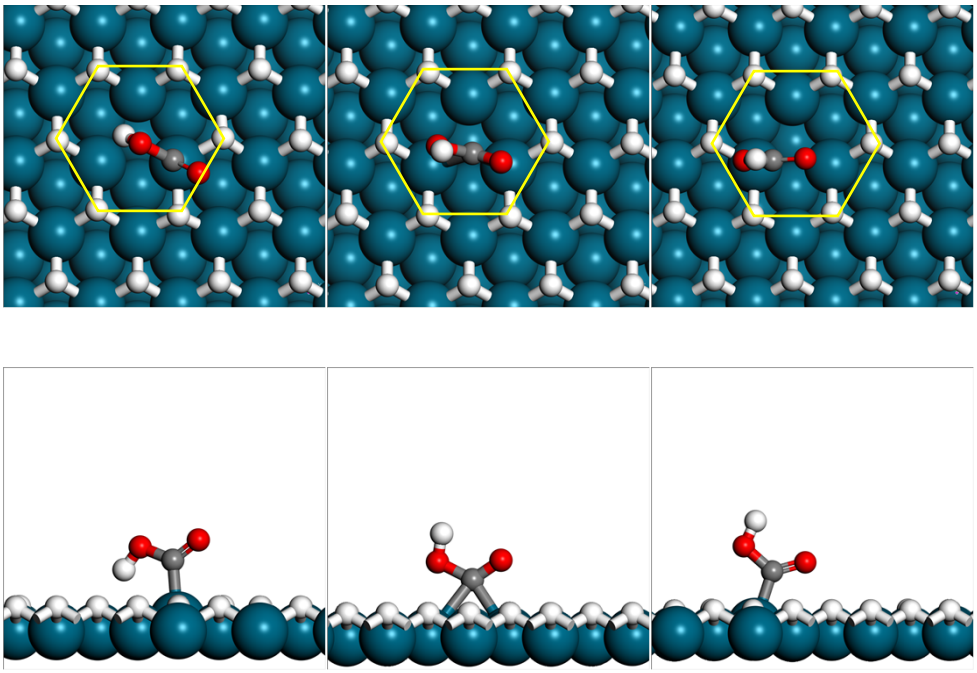
a. $CO_2 + *H \rightarrow *HOCO_{trans}$ ($\Delta E = 0.78eV$, $E_a = 1.40eV$)



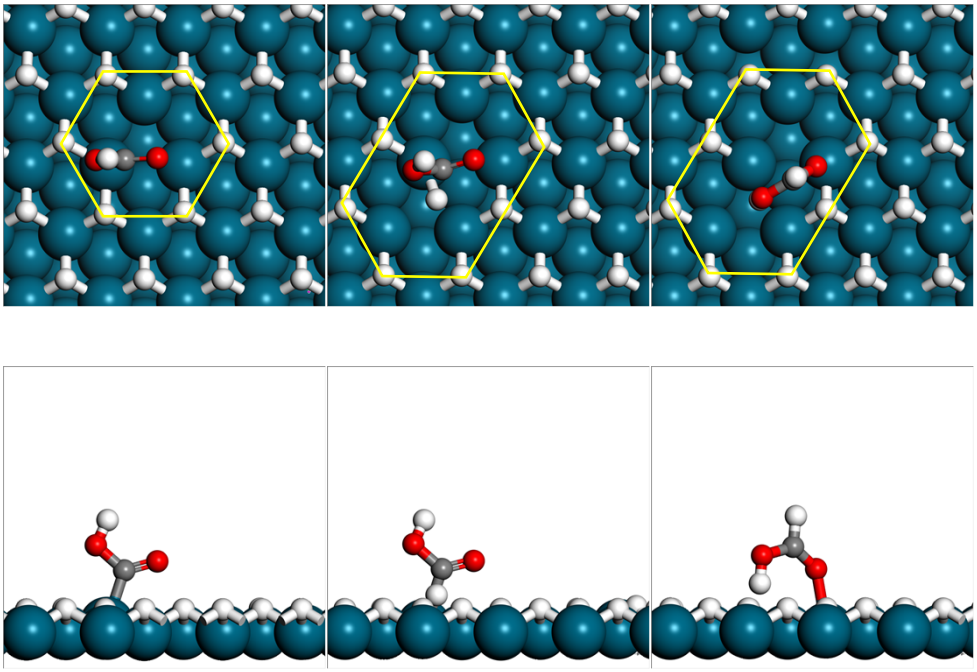
b. CO_2 + *H → *HCOO (ΔE = 1.12eV, E_a = 1.83eV)



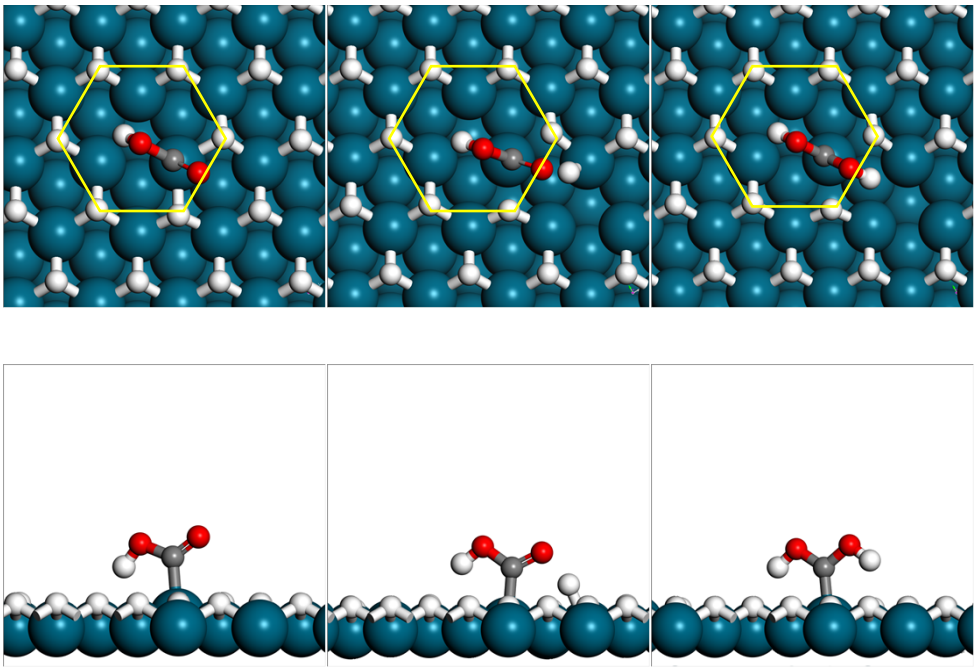
c. $*HOCO_{trans}$ → $*HOCO_{cis}$ (ΔE = 0.13eV, E_a = 0.78eV)



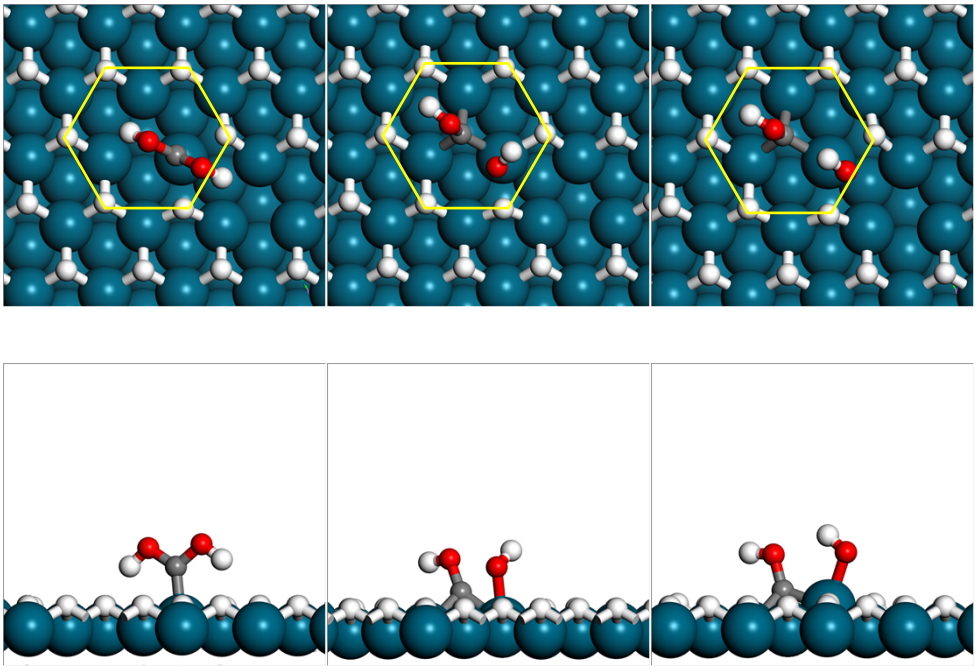
d. *$HOCO_{cis}$ + *H → *HCOOH (ΔE = -0.34eV, E_a = 0.53eV)



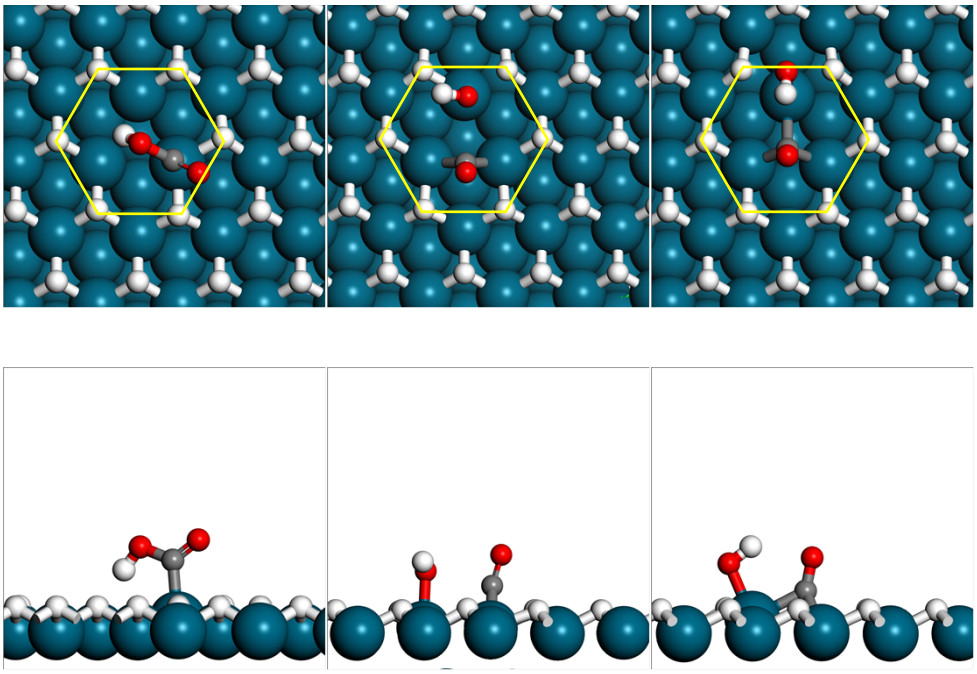
e. *$HOCO_{trans}$ + *H → *HOCOH (ΔE = 0. 30eV, E_a = 0.96eV)



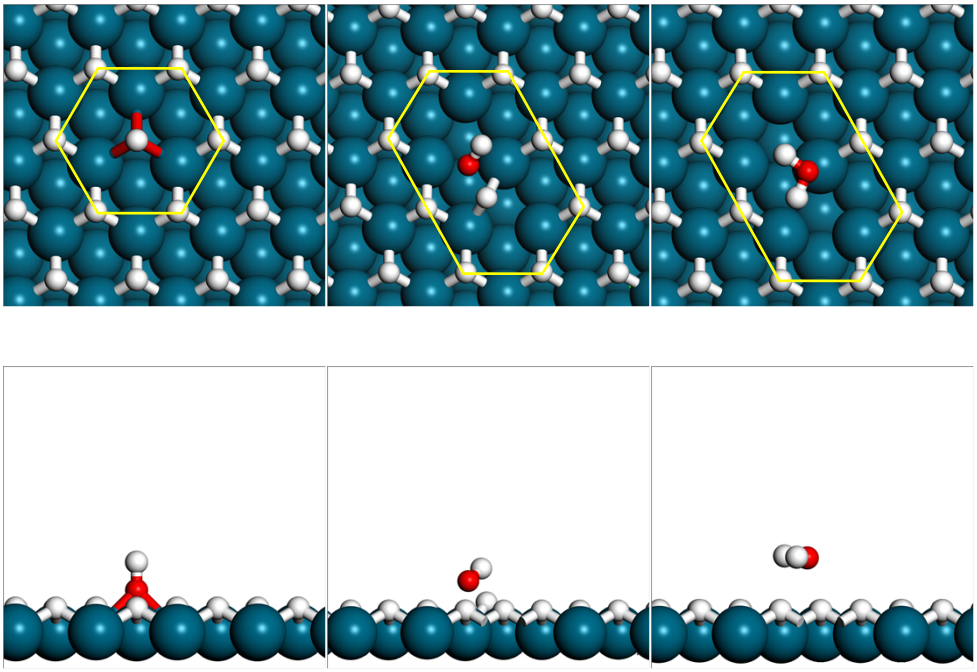
f. *HOCOH → *OH + *COH (ΔE = 1.65eV, E_a = 2.02eV)



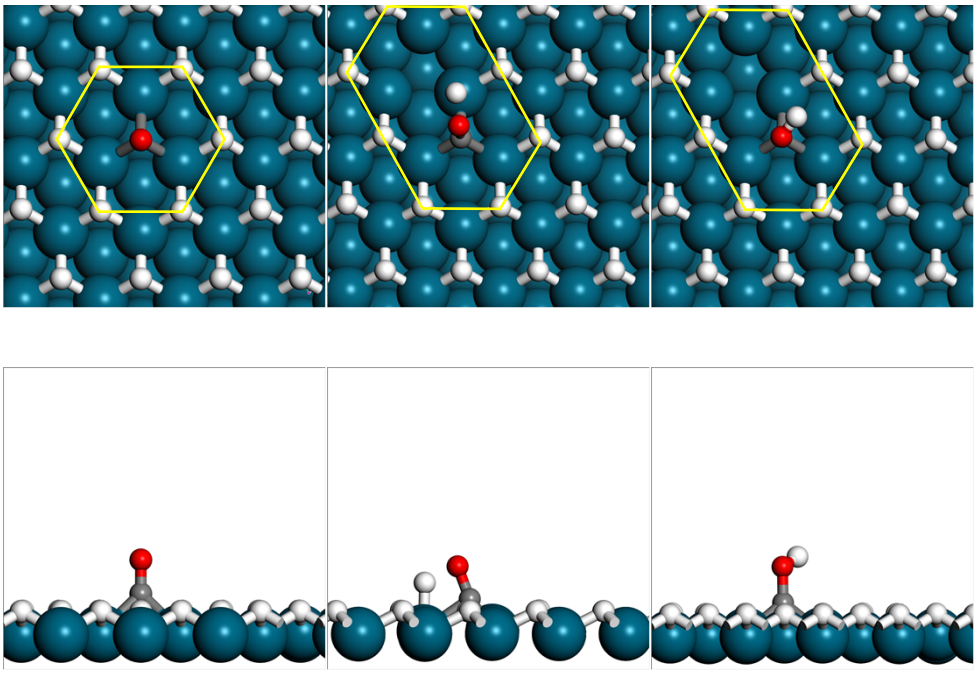
g. *$HOCO_{trans}$ → *OH + *CO (ΔE = 0.96eV, E_a = 1.19eV)



h. *OH + *H → H_2O (ΔE = -0.94eV, E_a = 0.63eV)



i. *CO + *H → *COH (ΔE = 0.99eV, E_a = 1.56eV)



j. *CO + *H → *HCO ($\Delta E = 1.27eV$, $E_a = 1.84eV$)

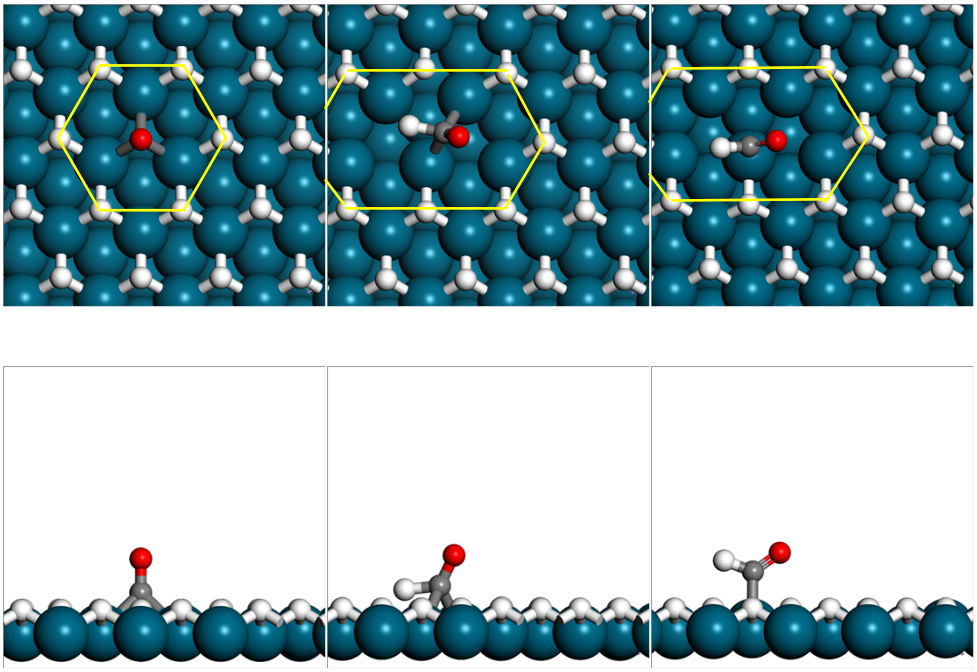
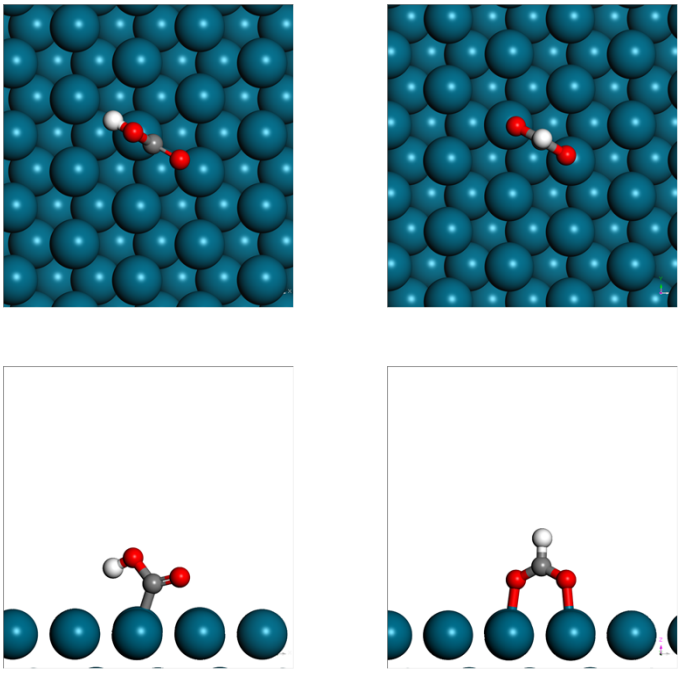


Figure S4. DFT-optimized binding geometry (top and side views) of (a) *HOCO and (b) *HCOO on Pd(111).



(a) (b)

Table S1. Gas molecules chemical potential contributions (eV)

	E_0 0K	**ZPE 0K[a]**	**ΔH 300K[b]**	**ΔH 500K[b]**	**ΔH 700K[b]**	**TS 300K[a]**	**TS 500K[a]**	**TS 700K[a]**
CO_2	-22.97	0.301	0.098	0.183	0.281	0.669	1.226	1.833
H_2	-6.75	0.266	0.088	0.149	0.210	0.406	0.754	1.127
CO	-14.79	0.130	0.090	0.151	0.214	0.616	1.104	1.620
H_2O	-14.22	0.554	0.103	0.174	0.250	0.589	1.072	1.588
HCOOH	0.775	0.871	0.139	0.237	0.332	0.775	1.432	2.168

a. Computational Chemistry Comparison and Benchmark DataBase. *National Institute of Standards and Technology*.

b. NIST-JANAF Thermochemical Tables, 4th Edition. *American Institute of Physics* **1998**

Table S2. KMC calculated turn-over-frequency TOF of all elementary steps (Unit: molecules·s^{-1}·site^{-1})

	500K 1bar	**500K 10bar**	**700K 1bar**	**700K 10bar**
CO_2(g) + *H → *HOCO	3.5	34.7	104178	1040338
*HOCO → CO_2(g) + *H	3.4	33.7	97077	969331
*HOCO + *H → *HCOOH	0.1	0.9	7099	71008
*HCOOH → *HOCO +*H	0	0	0	0
***HCOOH → HCOOH(g)**	**0.1**	**0.9**	**7099**	**71008**
*HOCO → *CO + *OH	0	0.1	106	1063
*CO + *OH → *HOCO	0	0.1	104	1044
***CO → CO(g)**	**0**	**0**	**2**	**19**
*OH + *H → *H_2O	0	0	2	19
*H_2O → *OH +*H	0	0	0	0

***H_2O → H_2O(g)**	**0**	**0**	**2**	**19**
*HOCO + *H → *HOCOH	0	0.1	1691	16843
*HOCOH → *HOCO + *H	0	0.1	1691	16843
*HOCOH → *COH + *OH	0	0	0	0
*COH + *OH → *HOCOH	0	0	0	0