Supporting Information

Si(111)−(7×7) surface as a natural substrate for identical clusters catalysts

Yu Guo,[a] Yanyan Zhao,[a] Wei Pei,[b] Si Zhou,[*,a] Jijun Zhao[*,a]

[a]*State Key Laboratory of Structural Analysis for Industrial Equipment, Dalian University of Technology, Dalian, 116024, China*

[b]*College of Physics Science and Technology, Yangzhou University, Jiangsu 225009, China*

[*]Corresponding authors. Email: sizhou@dlut.edu.cn; zhaojj@dlut.edu.cn

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S1. Electronic structures of Si(111)−(7×7) system

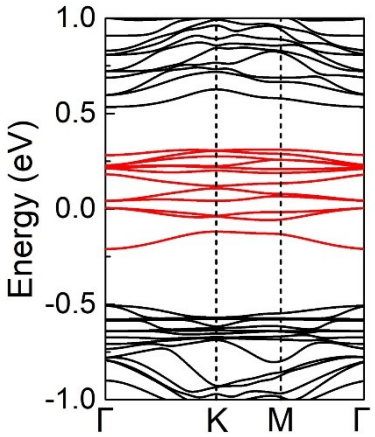

Fig. S1. The calculated band structure of the Si(111)−(7×7) surface. Here, the bands originating from adatoms are shown with red colors. The energy zero represents the Fermi level.

S2. Electronic structures of identical metal clusters on Si(111)−(7×7) surface

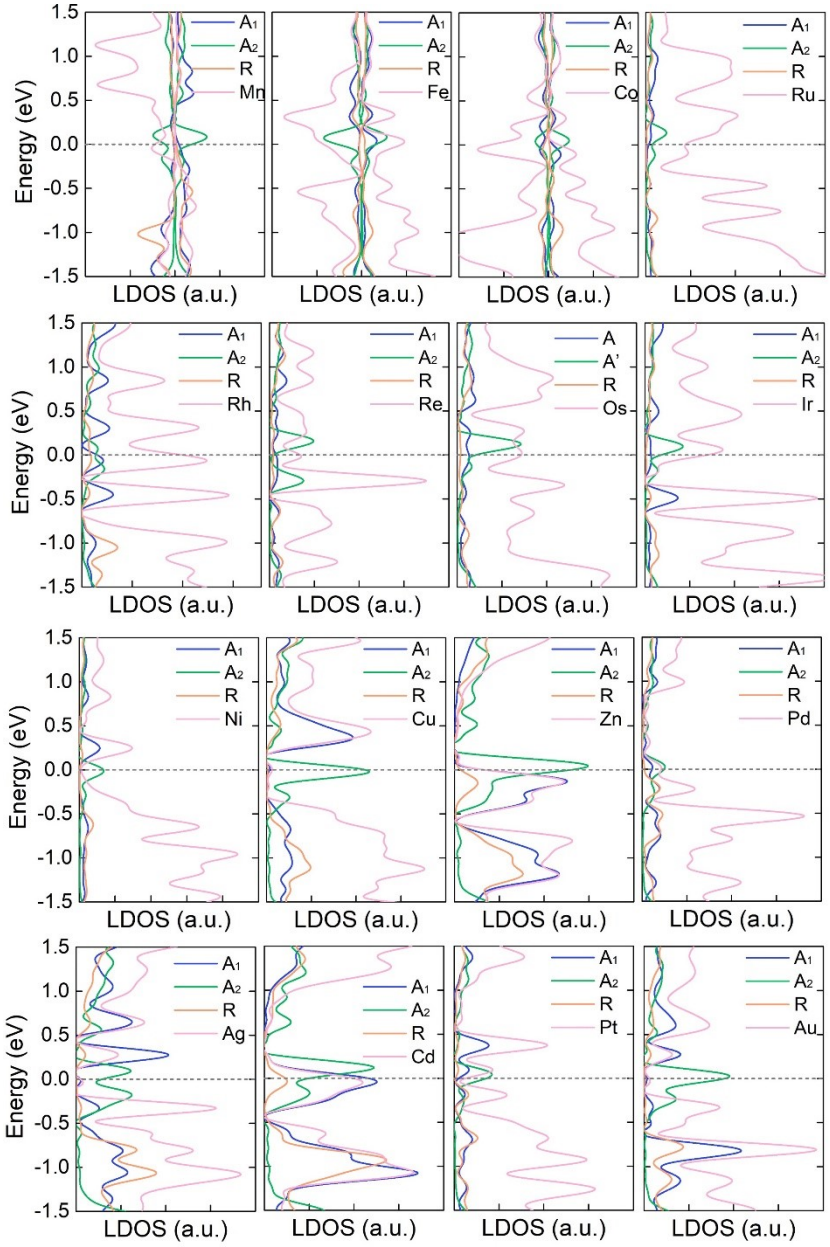

Fig. S2. The local density of states (LDOS) for identical metal clusters on Si(111)−(7×7) surface.

S3. Binding energy and charge transfer between metal cluster and Si(111)–(7×7)

Table S1. Binding energy (E_b) and charge transfer (CT) between metal cluster and Si(111)–(7×7) template

Cluster	E_b (eV/atom)	CT (*e*)
Mn	–0.51	0.51
Re	–1.58	0.62
Fe	–0.32	0.51
Ru	–1.94	0.69
Os	–3.08	1.11
Co	0.58	0.27
Rh	–2.18	0.76
Ir	–3.12	1.21
Ni	0.22	0.33
Pd	–1.21	0.58
Pt	–2.48	1.08
Cu	1.34	0.01
Ag	1.17	0.05
Au	1.43	0.01
Zn	0.61	0.24
Cd	0.71	0.23

S4. *d* orbital center (ε_d) of the supported clusters

Table S2. *d* orbital center (ε_d) of the supported clusters.

Cluster	ε_d (eV)
Ni	–2.85
Pd	–2.73
Pt	–1.59
Cu	–2.38
Ag	–3.91
Au	–3.53
Zn	–6.74
Cd	–8.34

S5. Free energy calculation

Table S3. Zero–point energy (ZPE) and entropic correction (*TS*) at T =298.15 K for the molecules and intermediate species involved in CO_2 reduction to C_1 products. The ZPE and *TS* values of reaction intermediates adsorbed on Pd_6@Si(111)−(7×7) are presented and used throughout our calculations.

Species	ZPE (eV)	*TS* (eV)	ZPE–*TS* (eV)
CO_2*	0.30	0.12	0.18
COOH*	0.62	0.20	0.43
HCOOH*	0.91	0.15	0.76
CO*	0.19	0.05	0.14
HCO*	0.45	0.16	0.29
HCOH*	0.79	0.10	0.69
H_2COH*	1.09	0.25	0.84
CH_3OH*	1.37	0.21	1.16
CH_2*	0.65	0.09	0.56
CH_3*	0.93	0.13	0.80
CH_4*	1.20	0.20	0.99
CH_2O*	0.71	0.17	0.53

Table S4. Zero–point energy (ZPE) and entropic correction (*TS*) at *T* =298.15 K for the molecules and intermediate species involved in CO_2 reduction to C_2 products. The ZPE and *TS* values of reaction intermediates adsorbed on Pd_6@Si(111)−(7×7) are presented and used throughout our calculations.

Species	ZPE (eV)	*TS* (eV)	ZPE–*TS* (eV)
$CO_2.CO_2$*	0.60	0.24	0.36
CHO–CHO*	0.92	0.26	0.66
CHO–CHOH*	1.31	0.25	1.06
CHO–CH*	0.93	0.17	0.76
CHO–CH_2*	1.19	0.13	1.06
CHOH–CH_2*	1.53	0.18	1.35
CH–CH_2*	1.07	0.17	0.90
C_2H_4*	1.37	0.22	1.15
CHO–CH_3*	1.49	0.28	1.22
CH_2O–CH_3*	1.79	0.19	1.60
C_2H_5OH*	2.15	0.33	1.81

Table S5. Zero–point energy (ZPE) and entropic correction (*TS*) at *T* =298.15 K for the molecules and intermediate species involved in CO_2 reduction to C_3 products. The ZPE and *TS* values of reaction intermediates adsorbed on Pd_6@Si(111)−(7×7) are presented and used throughout our calculations.

Species	ZPE (eV)	*TS* (eV)	ZPE–*TS* (eV)
CHO–CH–CHO*	1.44	0.25	1.20
CHO–CH–CHOH*	1.78	0.27	1.52
CHO–CH–CH*	1.35	0.22	1.13
CHO–CH–CH_2*	1.64	0.18	1.47
CHOH–CH–CH_2*	1.99	0.32	1.67
CHOH–CH_2–CH_2*	2.25	0.27	1.99
CHOH–CH_2–CH_3*	2.58	0.24	2.33
CH_2OH–CH_2–CH_3*	2.87	0.38	2.49
CH–CH–CH_2*	1.55	0.22	1.33
CH_2–CH–CH_2*	1.85	0.17	1.68
CH_2–CH–CH_3*	2.14	0.23	1.92

Table S6. Zero–point energy (ZPE) and entropic correction (*TS*) at *T* =298.15 K for the molecules and intermediate species involved in CO_2 reduction to C_4 products. The ZPE and *TS* values of reaction intermediates adsorbed on Pd_6@Si(111)−(7×7) are presented and used throughout our calculations.

Species	ZPE (eV)	*TS* (eV)	ZPE–*TS* (eV)
CHO–CH–CH–CHO*	1.89	0.34	1.55
CHO–CH–CH–CHOH*	2.22	0.31	1.91
CHO–CH–CH–CH*	1.77	0.26	1.51
CHO–CH–CH–CH_2*	2.10	0.27	1.84
CHOH–CH–CH–CH_2*	2.43	0.32	2.10
CH–CH–CH–CH_2*	1.96	0.25	1.72
CH_2–CH–CH–CH_2*	2.28	0.27	2.01
CH_2–CH–CH–CH_3*	2.39	0.32	2.07
CH_2–CH–CH_2–CH_3*	2.91	0.33	2.57
CHOH–CH–CH–CH_3*	2.72	0.39	2.33
CH_2OH–CH–CH–CH_3*	3.01	0.32	2.69
CH_2OH–CH–CH_2–CH_3*	3.29	0.26	3.03
CH_2OH–CH_2–CH_2–CH_3*	3.63	0.42	3.21

S6. Schematic illustration for CO_2 reduction reaction

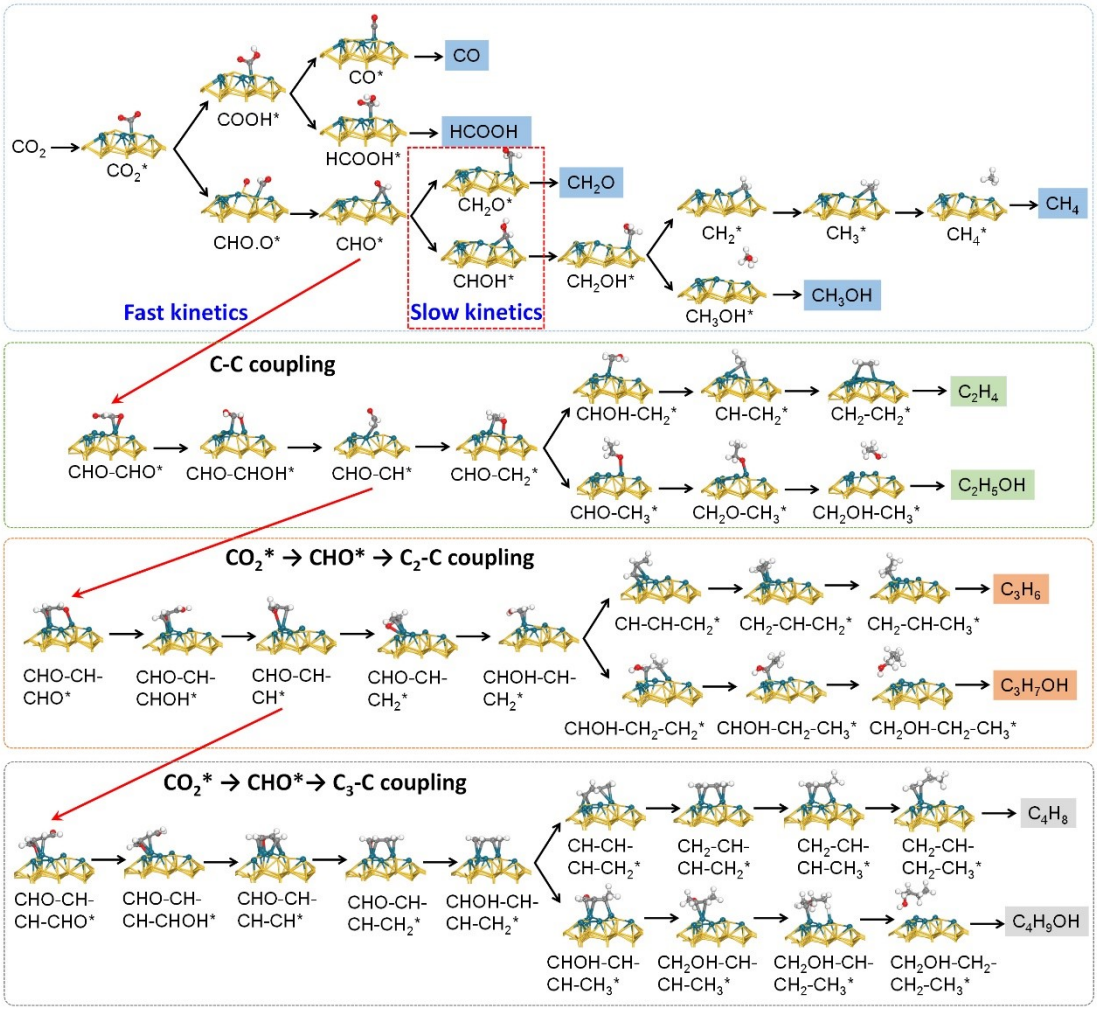

Fig. S3. Schematic illustration of the most efficient pathways for CO_2 reduction toward C_1–C_4 products on Pd_6@Si(111)−(7×7). The asterisk (*) indicates chemisorption of reaction intermediates on the catalyst. The Si, Pd, H, C and O atoms are shown in yellow, green, white, gray and red colors, respectively.

S7. Free energy diagrams of CO_2 reduction

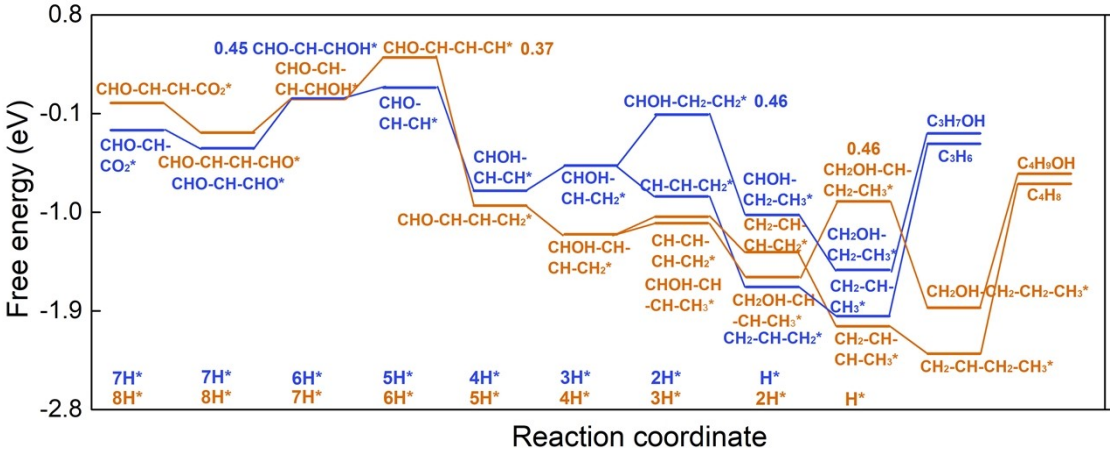

Fig. S4. Free energy diagrams of CO_2 reduction to yield C_3–C_4 products on Pd_6@Si(111)−(7×7). The blue and orange numbers indicate the Gibbs free energy of formation for C_3 and C_4 products at the rate-determining step. 0.45, 0.46, 0.37 and 0.46 are the ΔG_{RDS} for C_3H_6, C_3H_7OH, C_4H_8 and C_4H_9OH, respectively.

S8. CO_2 reduction of Pt_6 clusters on Si(111)−(7×7) surface

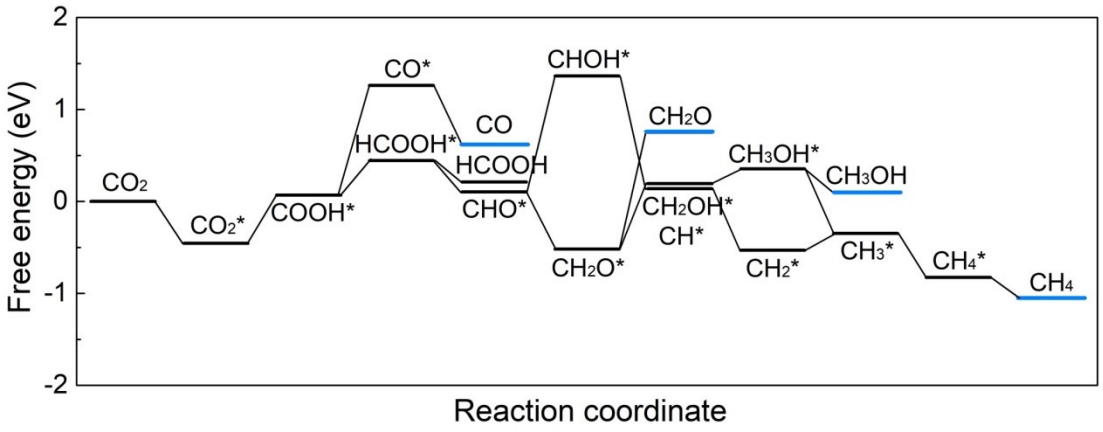

Fig. S5. Free energy diagrams of CO_2 reduction to yield C_1 products for Pt_6 clusters on Si(111)−(7×7) surface, respectively.

S9. Kinetic process of reaction channels on Pd_6@Si(111)−(7×7)

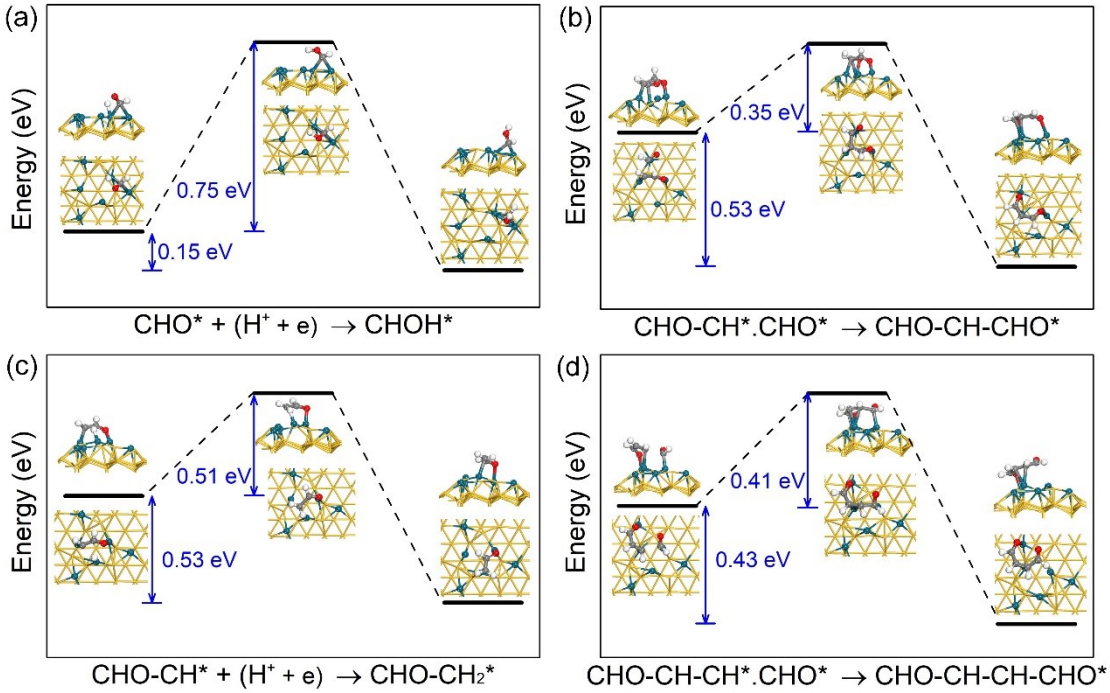

Fig. S6. Kinetic process of reaction channels toward C_1, C_2, C_3 and C_4 products on Pd_6@Si(111)−(7×7), respectively. The insets display the side- and top-view structures of initial state (left), transition state (middle) and final state (right). The numbers indicate reaction heat (left) and kinetic barrier (middle). The Si, Pd, H, C and O atoms are shown in yellow, green, white, gray and red colors, respectively.

S10. H_2O decomposition on Pd_6@Si(111)–(7×7) surface

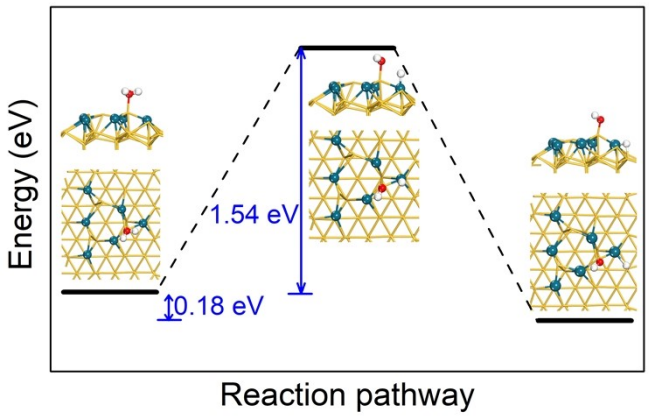

Fig. S7. The reaction pathway of H_2O decomposition on Pd_6@Si(111)–(7×7) surface.

S11. Gibbs free energy of formation for C_1 products

Table S7. Gibbs free energy of formation (ΔG) for each elementary step of CO_2 reduction to C_1 products on Pd_6@Si(111)−(7×7). Related to Fig. 5.

Reaction	ΔG (eV)
$CO_2 \rightarrow CO_2^*$	–0.02
$CO_2^* + H \rightarrow COOH^*$	0.47
$COOH^* + H^* \rightarrow CO^* + H_2O$	0.16
$CO_2^* + H^* \rightarrow CHO.O^*$	–0.01
$CHO.O + H^* \rightarrow CHO.OH^*$	–0.68
$CHO.OH^* + H^* \rightarrow CHO^* + H_2O$	0.42
$COOH^* + H^* \rightarrow HCOOH^*$	–0.11
$CHO^* + H^* \rightarrow CH_2O^*$	1.02
$CHO^* + H^* \rightarrow HCOH^*$	–0.05
$HCOH^* + H^* \rightarrow CH_2OH^*$	–0.08
$CH_2 + H^* \rightarrow CH_3^*$	–0.34
$CH_3 + H^* \rightarrow CH_4^*$	–0.71
$CH_2OH + H^* \rightarrow CH_3OH^*$	–0.14

S12. Gibbs free energy of formation for C_2 products

Table S8. Gibbs free energy of formation (ΔG) for each elementary step of CO_2 reduction to C_2 products on Pd_6@Si(111)−(7×7). Related to Fig. 5.

Reaction	ΔG (eV)
$2CO_2 \rightarrow CO_2.CO_2$*	–0.13
$CO_2.CO_2$* + 2H* → CHO.O–CHO.O*	–0.12
CHO.O–CHO.O* + 2H* → CHO.OH–CHO.OH*	–0.55
CHO.OH–CHO.OH* + 2H* → CHO–CHO*+$2H_2O$	0.41
CHO–CHO* + H* → CHO–CHOH*	–0.01
CHO–CHOH* + H* → CHO–CH* + H_2O	0.26
CHO–CH* +H* → CHO–CH_2*	–0.21
CHO–CH_2* + H* → CHO–CH_3*	–0.35
CHO–CH_2* + H* → CHOH–CH_2*	–0.20
CHOH–CH_2* + H* → CH–CH_2* + H_2O	0.22
CHO–CH_3* + H* → CH_2O–CH_3*	0.56
CH_2O–CH_3* + H* → CH_2OH–CH_3*	–0.97
CH–CH_2* + H* → C_2H_4*	–0.94

S13. Gibbs free energy of formation for C_3 products

Table S9. Gibbs free energy of formation (ΔG) for each elementary step of CO_2 reduction to C_3 products on Pd_6@Si(111)−(7×7). Related to Fig. S4.

Reaction	ΔG (eV)
CHO–CH* + CHO* → CHO–CH–CHO*	–0.16
CHO–CH–CHO* + H* → CHO–CH–CHOH*	0.45
CHO–CH–CHOH* + H* → CHO–CH–CH* + H_2O	0.10
CHO–CH–CH* + H* → CHO–CH–CH_2*	–0.94
CHO–CH–CH_2* + H* → CHOH–CH–CH_2*	0.23
CHOH–CH–CH_2* + H* → CHOH–CH_2–CH_2*	0.46
CHOH–CH–CH_2* + H* → CH–CH–CH_2* + H_2O	–0.28
CHOH–CH_2–CH_2* + H* → CHOH–CH_2–CH_3*	–0.91
CH–CH–CH_2* + H* → CH_2–CH–CH_2*	–0.83
CHOH–CH_2–CH_3* + H* → CH_2OH–CH_2–CH_3*	–0.50
CH_2–CH–CH_2* + H* → CH_2–CH–CH_3*	–0.26

S14. Gibbs free energy of formation for C_4 products

Table S10. Gibbs free energy of formation (ΔG) for each elementary step of CO_2 reduction to C_4 products on Pd_6@Si(111)−(7×7). Related to Fig. S4.

Reaction	ΔG (eV)
CHO–CH–CH* + CHO* → CHO–CH–CH–CHO*	–0.27
CHO–CH–CH–CHO* + H* → CHO–CH–CH–CHOH*	0.31
CHO–CH–CH–CHOH* + H* → CHO–CH–CH–CH* + H_2O	0.38
CHO–CH–CH–CH* + H* → CHO–CH–CH–CH_2*	–1.35
CHO–CH–CH–CH_2* + H* → CHOH–CH–CH–CH_2*	–0.26
CHOH–CH–CH–CH_2* + H* → CH–CH–CH–CH_2 *+ H_2O	0.16
CHOH–CH–CH–CH_2* + H* → CHOH–CH–CH–CH_3*	0.10
CH–CH–CH–CH_2 + H* → CH_2–CH–CH–CH_2*	–0.55
CHOH–CH–CH–CH_3* + H* → CH_2OH–CH–CH–CH_3*	–0.26
CH_2–CH–CH–CH_2* + H* → CH_2–CH–CH–CH_3*	–0.45
CH_2OH–CH–CH–CH_3* + H* → CH_2OH–CH–CH_2–CH_3*	0.46
CH_2–CH–CH–CH_3* + H* → CH_2–CH–CH_2–CH_3*	–0.25
CH_2OH–CH–CH_2–CH_3* + H* → CH_2OH–CH_2–CH_2–CH_3*	–0.97