

Supplementary Information

Reexamination of formic acid decomposition on thePt(111) surface both in the absence and in the presence of water, from periodic DFT calculations

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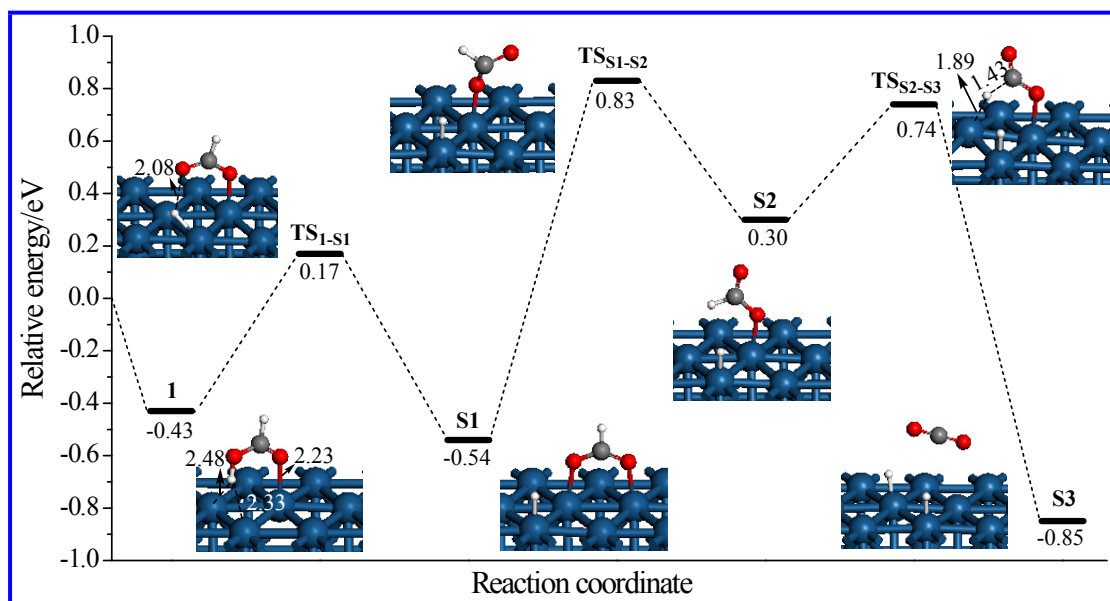


Fig. S1 Relative energy profile and geometries of key intermediates and transition states identified for the decomposition of monomeric formic acid to CO₂ along with the formate pathway in the gas phase on Pt(111). The sum energy of *trans*-HCOOH and the clean Pt(111) surface is taken as the zero energy reference. The C, H, O and Pt atoms are shown in gray, white, red and dark blue, respectively. The distances are in Å.

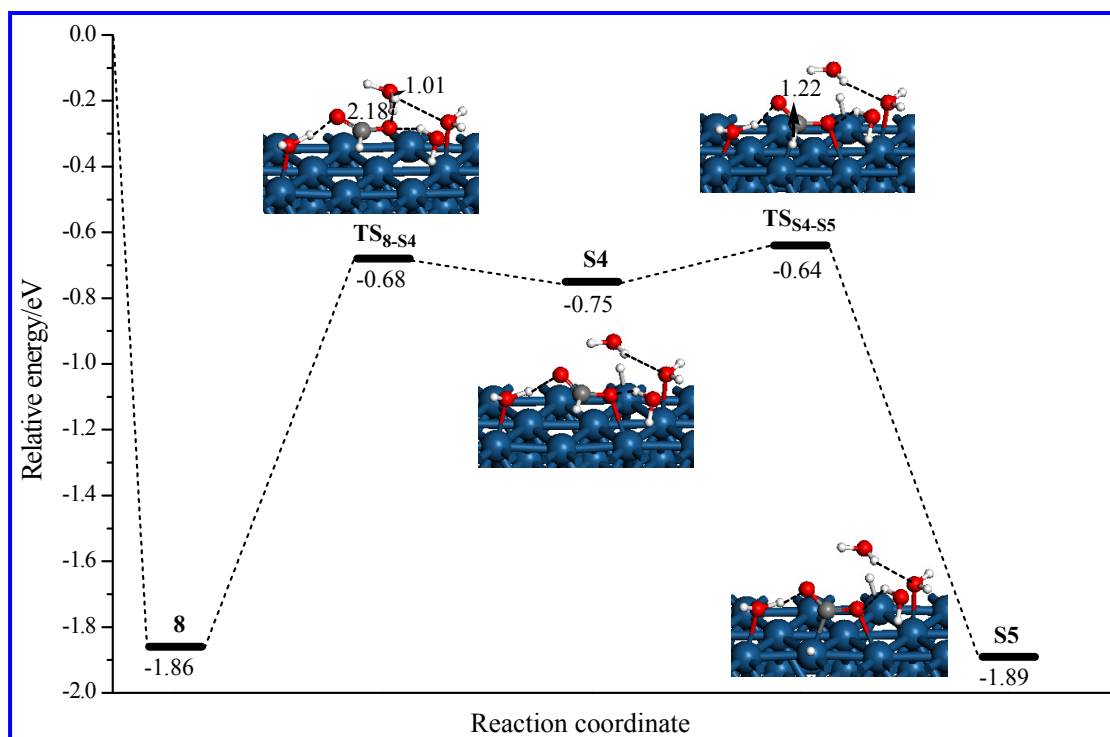


Fig. S2 Relative energy profile and geometries of key intermediates and transition states identified for the decomposition of monomeric formic acid to CO₂ along with the formate pathway with the presence of water on Pt(111). The sum energy of *trans*-HCOOH, four water molecules and the clean Pt(111) surface is taken as the zero energy reference. The C, H, O and Pt atoms are shown in gray, white, red and dark blue, respectively. The distances are in Å.

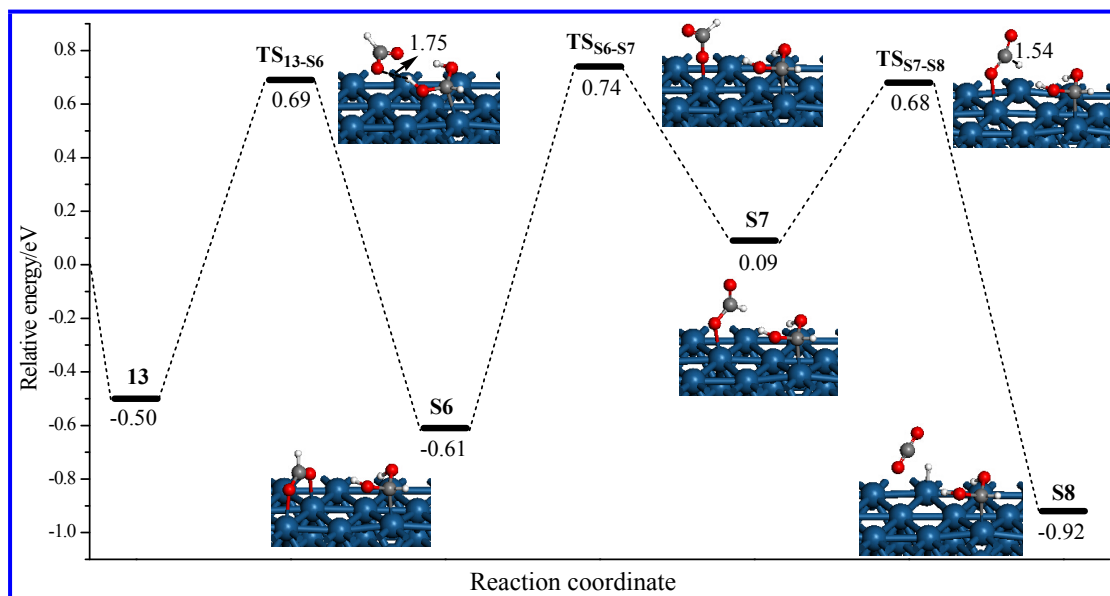


Fig. S3 Relative energy profile and geometries of key intermediates and transition states identified for the decomposition of dimeric formic acid to CO₂ along with the formate pathway in the gas phase on Pt(111). The sum energy of two *trans*-HCOOH molecules and the clean Pt(111) surface is taken as the zero energy reference. The C, H, O and Pt atoms are shown in gray, white, red and dark blue, respectively. The distances are in Å.

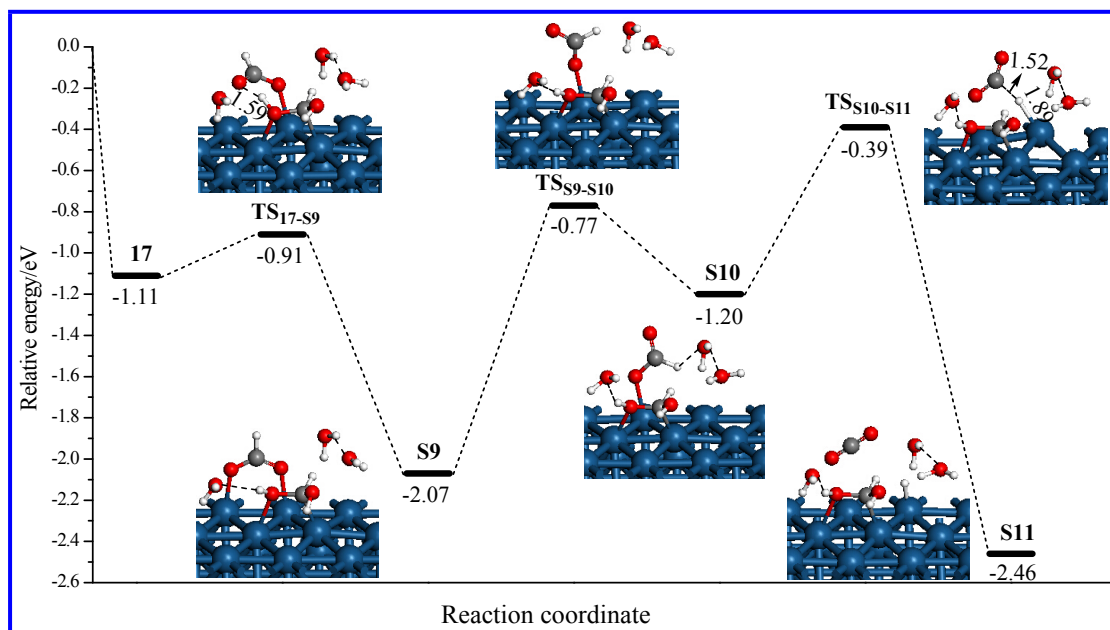


Fig. S4 Relative energy profile and geometries of key intermediates and transition states identified for the decomposition of dimeric formic acid to CO₂ along with the formate pathway with the presence of water on Pt(111). The sum energy of *trans*-HCOOH, three water molecules and the clean Pt(111) surface is taken as the zero energy reference. The C, H, O and Pt atoms are shown in gray, white, red and dark blue, respectively. The distances are in Å.

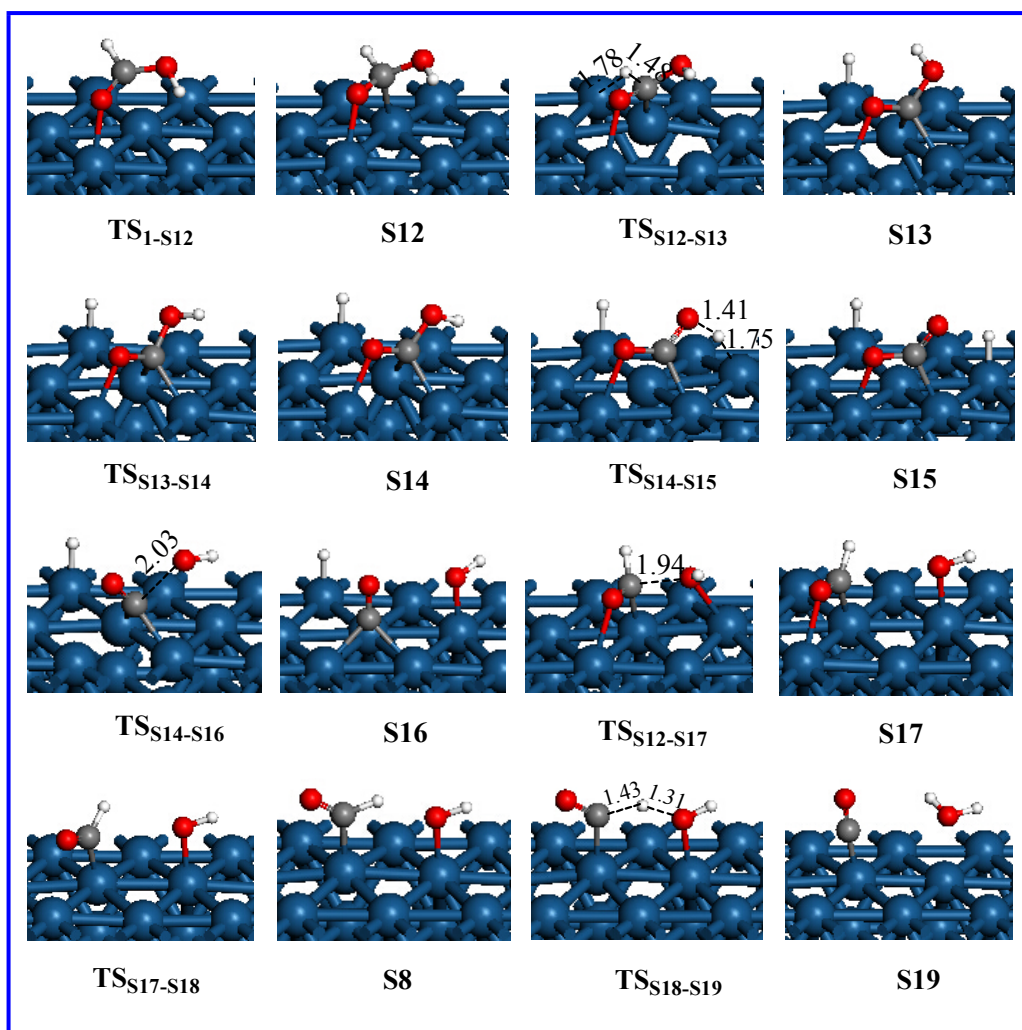


Fig. S5 Geometries of key intermediates and transition states identified for the decomposition of monomer of *trans*-formic acid in the gas phase on Pt(111). The C, H, O and Pt atoms are shown in gray, white, red and dark blue, respectively. The distances are in Å.

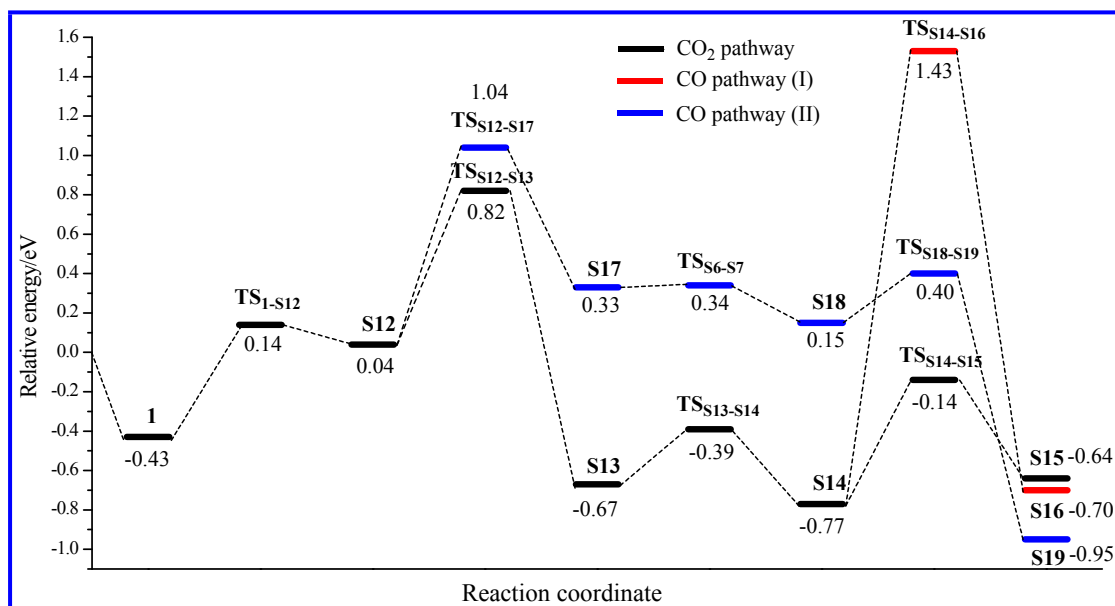


Fig. S6 Relative energy profiles for the decomposition of monomeric *trans*-HCOOH to CO₂ and CO in the gas phase. The sum energy of *trans*-HCOOH and the clean Pt(111) surface is taken as the zero energy reference. CO pathway (I) donates the pathway that involving the COOH intermediate, and CO pathway (II) donates the pathway that involving the HCO intermediate.

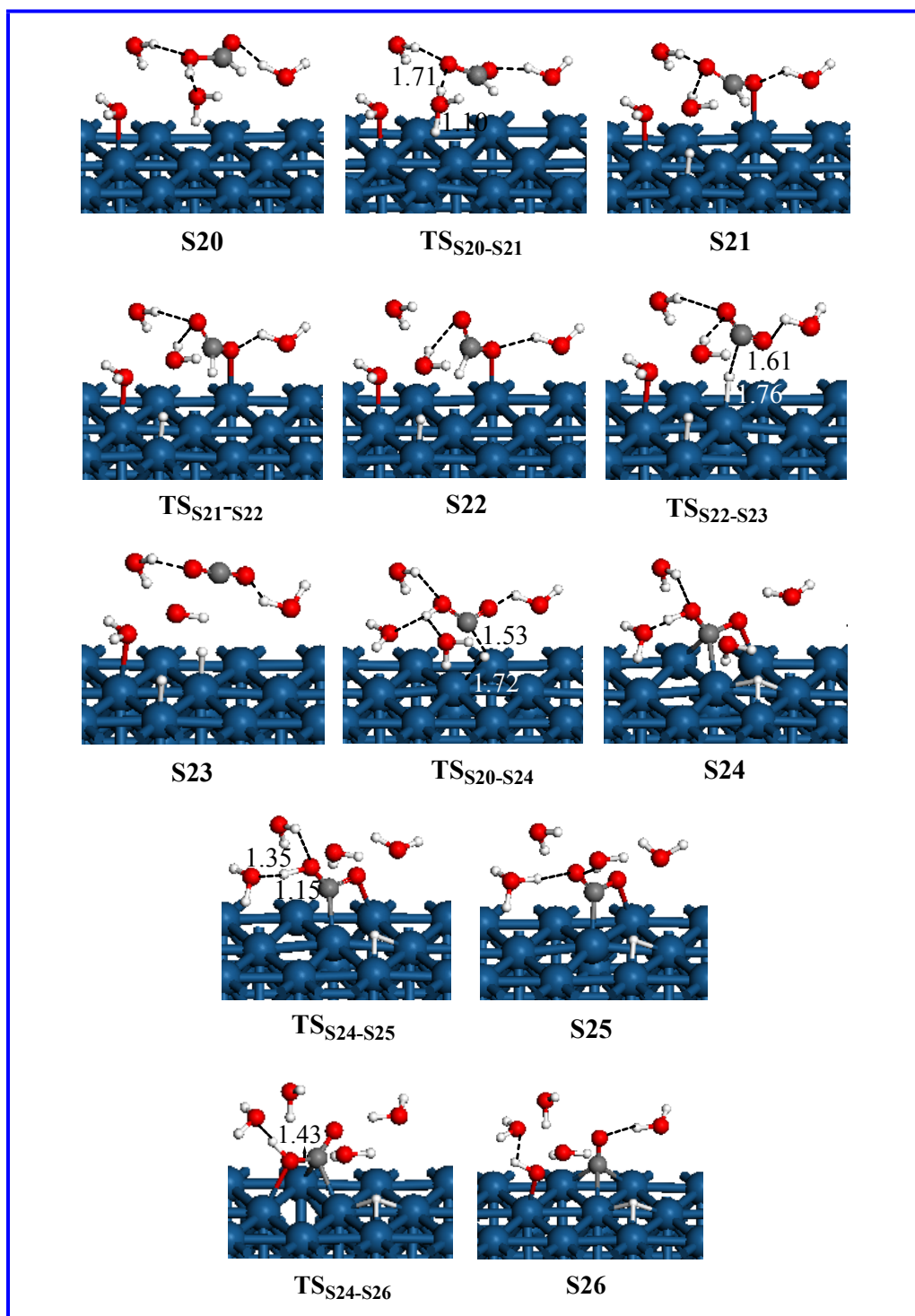


Fig. S7 Geometries of key intermediates and transition states identified for the decomposition of monomeric *cis*-formic acid with the presence of water on Pt(111). The C, H, O and Pt atoms are shown in gray, white, red and dark blue, respectively. The distances are in Å.

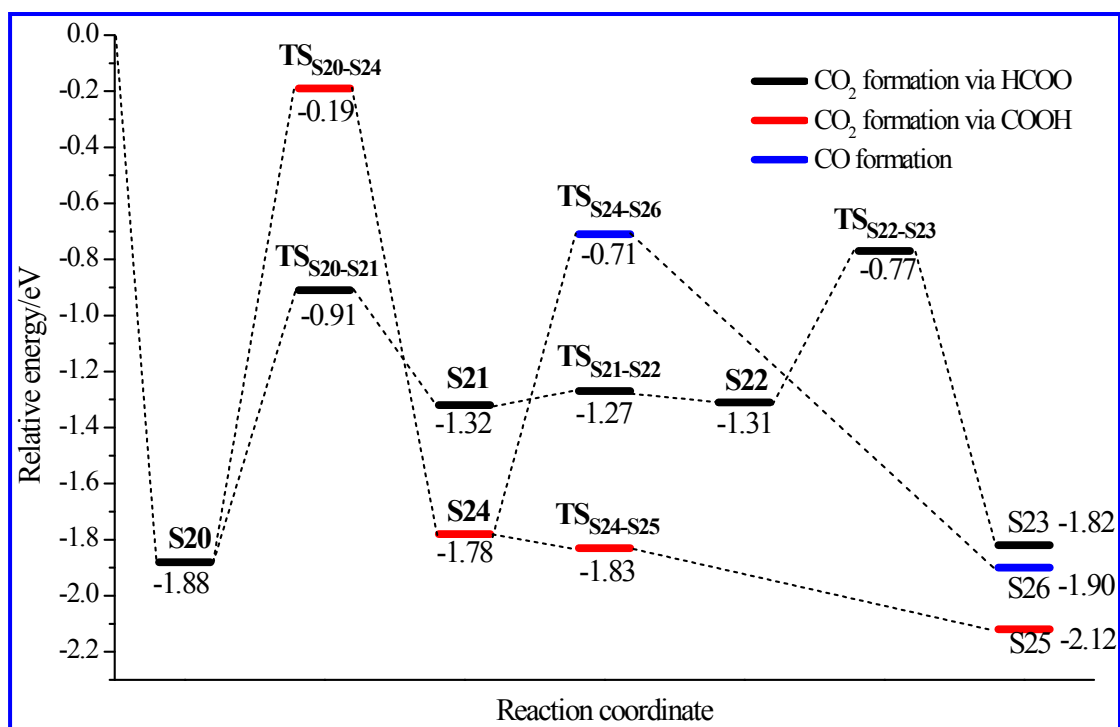


Fig. S8 Relative energy profiles for the decomposition of monomeric *cis*-HCOOH to CO₂ and CO with the presence of water on Pt(111). The sum energy of *cis*-HCOOH, four water molecules and the clean Pt(111) surface is taken as the zero energy reference.

Table S1 Calculated activation barriers (ΔE) and reaction energies (ΔH) (in eV) of the decomposition of formic acid via the COOH intermediate from the present and previous works

Adsorbates		C-H bond cleavage				O-H bond cleavage				C-OH bond cleavage			
		Our work		Literatures		Our work		Literatures		Our work		Literatures	
		ΔE	ΔH	ΔE	ΔH	ΔE	ΔH	ΔE	ΔH	ΔE	ΔH	ΔE	ΔH
<i>cis</i> -HCOOH	CO ₂ path	0.50 ^a	-0.84 ^a	0.50 ³²	-	0.73 ^a	0.16 ^a	1.02 ⁴⁸	-	-	-	-	-
	CO path	0.14 ^a	1.11 ^a	-	-	-	-	-	-	0.88 ^a	0.20 ^a	over 1.00 ³²	-
<i>trans</i> -HCOOH	CO ₂ path	0.78 ^b	0.71 ^b	1.58 ²⁰ 1.83 ²⁰ 1.97 ³⁶	-0.33 ²⁰ -0.23 ²⁰ - 0.36 ³⁶	0.63 ^b	0.13 ^b	0.90 ²⁰ -0.02 ²⁰ 0.94 ²⁰ 0.02 ²⁰	-	-	-	-	-
	CO path	0.25 ^b	-1.10 ^b	1.58 ²⁰ 1.83 ²⁰ 1.97 ³⁶	-0.33 ²⁰ -0.23 ²⁰ - 0.36 ³⁶	-	-	-	-	1.00 ^b 0.29 ^b 2.20 ^b 0.07 ^b	1.53 ²⁰	-0.22 ²⁰	
<i>cis</i> -HCOOH +4H ₂ O	CO ₂ path	1.69 ^c	0.10 ^c	-	-	-0.05 ^c	-0.34 ^c	0.48 ⁷	-0.25 ⁷	-	-	-	-
	CO path	1.69 ^c	0.10 ^c	-	-	-	-	-	-	0.57 ^c	-0.12 ^c	-	-
<i>trans</i> -HCOOH +4H ₂ O	CO ₂ path	0.26 ^d	-1.01 ^d	1.67 ²⁰ 0.45 ¹⁹	-0.32 ⁷	0.35 ^d	-0.32 ^d	1.05 ⁷ 0.00 ⁷ - 2.46 ²⁰ 0.20 ²⁰	-	-	-	-	-
	CO path	0.26 ^d	-1.01 ^d	1.67 ²⁰ 0.45 ¹⁹	-0.32 ⁷	-	-	-	-	0.19 ^d -0.50 ^d	1.80 ⁷ 3.20 ²⁰ ^g -0.73 ⁷ -1.05 ²⁰ - 1.39 ²⁰ 2.74 ²⁰ 0.58 ²⁰ -0.53 ²⁰	-	
2HCOOH	CO ₂ path	0.26 ^e	-0.51 ^e	-	-	0.69 ^e	-0.76 ^e	-	-	-	-	-	-
	CO path	0.26 ^e	-0.51 ^e	-	-	-	-	-	-	0.45 ^e	0.18 ^e	-	-
2HCOOH +3H ₂ O	CO ₂ path	0.42 ^f	-1.05 ^f	-	-	0.15 ^f	-0.17 ^f	-	-	-	-	-	-
	CO path	0.42 ^f	-1.05 ^f	-	-	-	-	-	-	0.11 ^f	-0.33 ^f	0.66 ²⁷ ^h	0.51 ²⁷

^{a, b, c, d, e, f}The activation energies and reaction energies obtained from Figs. 2, S6, S8, 4, 6, and 8, respectively. ^gThe barrier involved in a synergetic process with the simultaneous cleavage of C-H and C-OH bond. ^hThe barrier involved in a synergetic process with the simultaneous formation of CO₂ and CO.

Table S2 Calculated activation barriers (E_{act}) and reaction energies (ΔH) (in eV) of the decomposition of formic acid initiated from the O-H scission

Adsorbates	O-H bond cleavage		Formate adjustment ^a				C-H bond cleavage			
	Our work		Our work		Literatures		Our work		Literatures	
	ΔE	ΔH	ΔE	ΔH	ΔE	ΔH	ΔE	ΔH	ΔE	ΔH
<i>trans</i> -HCOOH	0.60 ^b	-0.11 ^b	1.37 ^b	0.84 ^b	1.16 ²⁰	0.55 ²⁰	0.44 ^b	-1.15 ^b	-	-
<i>trans</i> -HCOOH + 4H ₂ O	1.18 ^c	1.11 ^c	-	-	1.27 ²⁰	0.85 ²⁰	0.11 ^c	-1.14 ^c	0.58 ²⁰ 0.92 ²⁰	-0.59 ²⁰ -0.68 ²⁰
<i>cis</i> -HCOOH + 4H ₂ O	0.97 ^d	0.56 ^d	0.05 ^d	0.01 ^d	-	-	0.54 ^d	-0.51 ^d	-	-
2HCOOH	1.19 ^e	-0.11 ^e	1.35 ^e	0.70 ^e	-	-	0.59 ^e	-1.01 ^e	-	-
2HCOOH + 3H ₂ O	0.42 ^f	-1.05 ^f	0.15 ^f	-0.17 ^f	-	-	0.81 ^f	-1.26 ^f	-	-

^aRotation or transformation of formate from bidentate form to monodentate one. ^{b, c, d, e, f}The activation barriers and reaction energies obtained from Figs. S1, S2, S8, S3, and S4, respectively.