Electronic Supplementary Information

Molecular Mechanism Comparison of Decarbonylation with Deoxygenation and Hydrogenation of 5-Hydroxymethylfurfural Catalyzed by Palladium Acetate

Hong Xie[a], Ting Qi[a], Ya-Jing Lyu[b], Jin-Feng Zhang[a], Zhen-Bin Si[a], Li-Juan Liu[a], Liang-Fang Zhu[b], Hua-Qing Yang[a]*, Chang-Wei Hu[b]

[a]*College of Chemical Engineering, Sichuan University, Chengdu, Sichuan, 610065, P.R. China*

[b]*Key Laboratory of Green Chemistry and Technology, Ministry of Education, College of Chemistry, Sichuan University, Chengdu, Sichuan, 610064, P.R. China*

*Correspondence to:

H.-Q. Yang; e-mail: huaqingyang@scu.edu.cn;

Fax: 86 28 85415608;

Telephone: 86 28 85415608

Catalog

Table S1. Some typical energy data for some experimentally available species calculated at the M06/aug-cc-pvtz, SDD*, M06-L/aug-cc-pvtz, SDD*, and M06-L/6-311++G (d, p), SDD* levels.

Item	Calculated values (kJ mol^{-1})			Experimental values (kJ mol^{-1})	References
	M06/aug-cc-pvtz, SDD*	M06-L/aug-cc-pvtz, SDD*	M06-L/6-311++G(d,p), SDD*		
Energy difference between Pd(^{1}S) and Pd(^{3}D)	141.7	98.4	98.4	91.6	[1]
Bond strength of PdO($^3\Sigma$)	196.1	274.8	277.1	277.0	[1]
Ionization energy of Pd(^{1}S)	876.1	812.5	812.5	804.4	[2]
Ionization energy of PdO($^3\Sigma$)	957.4	898.6	905.2	878.0; 941.7	[3,4]
Electron affinity of PdO($^3\Sigma$)	169.7	143.1	143.0	151.5; 161.3	[5,6]
Electron affinity of PdCN($^2\Sigma$)	261.7	230.1	232.5	245.4	[7]
Reaction enthalpy (Δ_rH^0) of $Pd^-(^2D) + H^+ = HPd(^2\Sigma)$	1448.2	1501.2	1496.0	1492.0±25	[8]

Notes: As shown in Table S1, firstly, at the M06/aug-cc-pvtz, SDD* level, the calculated data for the electron affinity of PdO($^3\Sigma$) and PdCN($^2\Sigma$), the reaction enthalpy (Δ_rH^0) of $Pd^-(^2D) + H^+ = HPd(^2\Sigma)$, and the ionization energy of PdO($^3\Sigma$), are in good agreement with the corresponding experimental observations [3-8], whereas the calculated data for the energy difference between Pd(^{1}S) and Pd(^{3}D), the bond strength of PdO($^3\Sigma$), and the ionization energy of Pd(^{1}S), are far away from the corresponding experimental observations [1,2]. Secondly, at the M06-L/aug-cc-pvtz, SDD* level, the calculated energy data for the energy difference between Pd(^{1}S) and Pd(^{3}D), the bond strength of PdO($^3\Sigma$), the ionization energy of Pd(^{1}S) and PdO($^3\Sigma$), electron affinity of PdO($^3\Sigma$) and PdCN($^2\Sigma$), and the reaction enthalpy (Δ_rH^0) of $Pd^-(^2D) + H^+ = HPd(^2\Sigma)$, are in good agreement with the corresponding experimental observations [1-8]. Thirdly, at the M06-L/6-311++G (d, p), SDD* level, the calculated energy data for the energy difference between Pd(^{1}S) and Pd(^{3}D), the bond strength of PdO($^3\Sigma$), the ionization energy of Pd(^{1}S) and PdO($^3\Sigma$), electron affinity of PdO($^3\Sigma$) and PdCN($^2\Sigma$), and the reaction enthalpy (Δ_rH^0) of $Pd^-(^2D) + H^+ = HPd(^2\Sigma)$, are also in good agreement with the corresponding experimental observations [1-8]. To save computational time, the M06-L/6-311++G (d, p), SDD* level is preferred in the present study.

References:

[1] D.-Y. Hwang, A. M. Mebel, *J. Phys. Chem. A* **2002**, *106*, 12072–12083.

[2] C. L. Callender, P. A. Hackett, D. M. Rayner, *J. Opt. Soc. Am. B* **1988**, *5*, 614–618.

[3] J. H. Norman, H. G. Staley, W. E. Bell, *J. Phys. Chem.* **1964**, *68*, 662–663.

[4] Y.-M. Chen, P. B. Armentrout, *J. Chem. Phys.* **1995**, *103*, 618–625.

[5] T. M. Ramond, G.E. Davico, F. Hellberg, F. Svedberg, P. Sale´n, P.So. derqvist, W.C. Lineberger, *J. Mol. Spectrosc.* **2002**, *216*, 1–14.

[6] S. A. Klopcic, V. D. Moravec, C. C. Jarrold, *J. Chem. Phys.* **1999**, *110*, 10216–10217.

[7] S. A. Klopcic, V. D. Moravec, C. C. Jarrold, *J. Chem. Phys*. **1999**, *110*, 8986–8991.

[8] M. Scheer, C. A. Brodie, R. C. Bilodeau, H. K. Haugen, *Phys. Rev. A* **1998**, *58*, 2051–2062.

Table S2. Zero-point energies (*ZPE*, hartree), thermal correction to Gibbs free energy (G_0, hartree), total energies (E_c, hartree) corrected by *ZPE*, sum of electronic and thermal free energies (G_c, hartree) with *ZPE* and thermal corrections, and relative energies (E_r, kJ mol^{-1}) and relative Gibbs free energies (G_r, kJ mol^{-1}) of eight conformers of HMF at M06L/6-311++G(d,p),SDD* level in 1,4-dioxane solution under the temperature of 423K and the pressure of 5.0 atm.

Species	*ZPE*	E_c	G_0	G_c	E_r	G_r
HMF-1	0.11154	-457.84963	0.06049	-457.90068	-1.2	-2.4
HMF-2	0.11238	-457.84918	0.06182	-457.89974	0.0	0.0
HMF-3	0.11201	-457.84782	0.06112	-457.89871	3.6	2.7
HMF-4	0.11180	-457.84904	0.05957	-457.90126	0.4	-4.0
HMF-5	0.11206	-457.84769	0.06134	-457.89840	3.9	3.5
HMF-6	0.11207	-457.84940	0.06197	-457.89950	-0.6	0.7
HMF-7	0.11124	-457.84923	0.06222	-457.89825	-0.1	3.9
HMF-8	0.11190	-457.84898	0.06142	-457.89945	0.5	0.8

Table S3. Zero-point energies (*ZPE*, hartree), thermal correction to Gibbs free energy (G_0, hartree), total energies (E_c, hartree) corrected by *ZPE*, sum of electronic and thermal free energies (G_c, hartree) with *ZPE* and thermal corrections, and relative energies (E_r, kJ mol^{-1}) and relative Gibbs free energies (G_r, kJ mol^{-1}) of various species with respect to the reactants for the uncatalyzed reaction of HMF-to-FFA isomerization (HMF-4 → FFA + CO) at M06L/6-311++G(d,p), SDD* level in 1,4-dioxane solution under the temperature of 423K and the pressure of 5.0 atm.

Species	*ZPE*	E_c	G_0	G_c	E_r	G_r
CO	0.00503	-113.32041	-0.02159	-113.34703		
CO ↑	-0.01039	-113.33583	-0.03701	-113.36245		
HMF-4	0.11180	-457.84904	0.05957	-457.90126	0.0	0.0
u1-TS1	0.10612	-457.70801	0.05210	-457.76204	370.3	365.5
u1-IM1	0.10906	-457.82908	0.05260	-457.88554	52.4	41.3
FFA + CO	0.10787	-457.82507	0.03585	-457.89756	62.9	9.7
FFA + CO ↑	0.09245	-457.84050	0.02043	-457.91298	22.4	-30.8

Table S4. Zero-point energies (*ZPE*, hartree), thermal correction to Gibbs free energy (G_0, hartree), total energies (E_c, hartree) corrected by *ZPE*, Sum of electronic and thermal free energies (G_c, hartree) with *ZPE* and thermal corrections, and relative energies (E_r, kJ mol^{-1}) and relative Gibbs free energies (G_r, kJ mol^{-1}) of various species with respect to the reactants for the uncatalyzed reaction of HMF-to-5-MF isomerization (HMF-4 + HCOOH → 5-MF + H_2O + CO_2) at M06L/6-311++G(d,p), SDD* level in 1,4-dioxane solution under the temperature of 423K and the pressure of 5.0 atm.

Species	*ZPE*	E_c	G_0	G_c	E_r	G_r
HMF-4	0.11180	-457.84904	0.05957	-457.90126		
H_2O	0.02130	-76.43296	0.00365	-76.45061		
HCOOH	0.03386	-189.76929	-0.00028	-189.80342		
CO_2	0.01180	-188.62050	-0.01725	-188.64955		
CO_2 ↑	-0.00362	-188.63592	-0.03267	-188.66497		
HMF-4 + HCOOH	0.14566	-647.61832	0.05929	-647.70468	0.0	0.0
u2-IM1	0.14821	-647.62585	0.08540	-647.68866	-19.8	42.1
u2-TS1	0.14324	-647.57448	0.08210	-647.63562	115.1	181.3
u2-IM2	0.14544	-647.62030	0.07970	-647.68604	-5.2	49.0
u2-IM3	0.12159	-571.19314	0.06482	-571.24991		
u2-IM3 + H_2O	0.14289	-647.62610	0.06847	-647.70052	-20.4	10.9
u2-TS2	0.11679	-571.13261	0.06071	-571.18870		
u2-TS2 + H_2O	0.13809	-647.56558	0.06436	-647.63931	138.5	171.6
u2-IM4	0.11987	-571.25408	0.06008	-571.31387		
u2-IM4 + H_2O	0.14117	-647.68705	0.06373	-647.76449	-180.4	-157.0
5-MF	0.10700	-382.62987	0.05997	-382.67690		
5-MF + H_2O + CO_2	0.14011	-647.68333	0.04638	-647.77707	-170.7	-190.0
5-MF + H_2O + CO_2↑	0.12469	-647.69876	0.03095	-647.79249	-211.2	-230.5

Table S5. Zero-point energies (*ZPE*, hartree), thermal correction to Gibbs free energy (G_0, hartree), total energies (E_c, hartree) corrected by *ZPE*, sum of electronic and thermal free energies (G_c, hartree) with *ZPE* and thermal corrections, and relative energies (E_r, kJ mol^{-1}) and relative Gibbs free energies (G_r, kJ mol^{-1}) of various species with respect to the reactants for the uncatalyzed reaction of HMF-to-5-MF (HMF-4 + HCOOH → DHMF + CO_2) at M06L/6-311++G(d,p), SDD* level in 1,4-dioxane solution under the temperature of 423K and the pressure of 5.0 atm.

Species	*ZPE*	E_c	G_0	G_c	E_r	G_r
HMF-4	0.11180	-457.84904	0.05957	-457.90126		
HCOOH	0.03386	-189.76929	-0.00028	-189.80342		
CO_2	0.01180	-188.62050	-0.01725	-188.64955		
CO_2 ↑	-0.00362	-188.63592	-0.03267	-188.66497		
HMF-4 + HCOOH	0.14566	-647.61832	0.05929	-647.70468	0.0	0.0
u3-IM1	0.14757	-647.62521	0.08173	-647.69105	-18.1	35.8
u3-TS1	0.14472	-647.58512	0.08369	-647.64615	87.2	153.7
u3-IM2	0.14840	-647.64564	0.08111	-647.71294	-71.7	-21.7
DHMF	0.13576	-459.02485	0.08333	-459.07727		
DHMF + CO_2	0.14757	-647.64534	0.06609	-647.72682	-70.9	-58.1
DHMF + CO_2↑	0.13214	-647.66077	0.05066	-647.74224	-111.4	-98.6

Table S6. Zero-point energies (*ZPE*, hartree), thermal correction to Gibbs free energy (G_0, hartree), total energies (E_c, hartree) corrected by *ZPE*, sum of electronic and thermal free energies (G_c, hartree) with *ZPE* and thermal corrections, and relative energies (E_r, kJ mol^{-1}) and relative Gibbs free energies (G_r, kJ mol^{-1}) of various species with respect to the reactants for the whole reaction of HMF-to-FFA (HMF-4 → FFA) catalyzed by $Pd(OAc)_2$ at M06L/6-311++G(d,p), SDD* level in 1,4-dioxane solution under the temperature of 423K and the pressure of 5.0 atm.

Species	*ZPE*	E_c	G_0	G_c	E_r	G_r
HAc	0.06177	-229.07394	0.02183	-229.11388		
CO	0.00503	-113.32041	-0.02159	-113.34703		
CO ↑	-0.01040	-113.33583	-0.03701	-113.36245		
HMF-4	0.11180	-457.84904	0.05957	-457.90126		
$Pd(OAc)_2$	0.10346	-584.96785	0.04685	-585.02446		
HMF-4 + $Pd(OAc)_2$	0.21527	-1042.81688	0.10642	-1042.92572	0.0	0.0
1a-IM1	0.21649	-1042.82709	0.13115	-1042.91243	-26.8	34.9
1a-TS1	0.21574	-1042.80829	0.12965	-1042.89439	22.5	82.3
1a-IM2	0.21689	-1042.82233	0.13050	-1042.90872	-14.3	44.6
1a-TS2	0.21194	-1042.80499	0.13225	-1042.88467	31.2	107.8
1a-IM3	0.21771	-1042.84121	0.13432	-1042.92460	-63.9	3.0
1a-IM4	0.15383	-813.74467	0.08391	-813.81459		
1a-IM4 + HAc	0.21560	-1042.81860	0.10574	-1042.92847	-4.5	-7.2
1a-IM5	0.15284	-813.75140	0.08387	-813.82038		
1a-IM5 + HAc	0.21462	-1042.82534	0.10569	-1042.93426	-22.2	-22.4
1a-TS3	0.15118	-813.74253	0.08177	-813.81194		
1a-TS3 + HAc	0.21295	-1042.81647	0.10360	-1042.92582	1.1	-0.3
1a-IM6	0.15174	-813.75213	0.08002	-813.82384		
1a-IM6 + HAc	0.21351	-1042.82606	0.10185	-1042.93773	-24.1	-31.5
1a-IM7	0.21535	-1042.83557	0.12790	-1042.92302	-49.1	7.1
1a-IM8	0.20758	-929.47653	0.12916	-929.55495		
1a-IM8 + CO	0.21260	-1042.79694	0.10757	-1042.90198	52.4	62.3
1a-IM8 + CO↑	0.19718	-1042.81236	0.09215	-1042.91740	11.9	21.9
1a-TS4	0.20224	-929.46595	0.12646	-929.54173		
1a-TS4 + CO	0.20727	-1042.78635	0.10486	-1042.88876	80.2	97.0
1a-TS4 + CO ↑	0.19185	-1042.80177	0.08944	-1042.90418	39.7	56.6
1a-IM9	0.20748	-929.49203	0.12983	-929.56968		
1a-IM9 + CO	0.21251	-1042.81243	0.10823	-1042.91670	11.7	23.7
1a-IM9 + CO ↑	0.19708	-1042.82785	0.09281	-1042.93213	-28.8	-16.8

Continued from **Table S6**

Species	*ZPE*	E_c	G_0	G_c	E_r	G_r
1a-IM10	0.20818	-929.48333	0.13121	-929.56030		
1a-IM10 + CO	0.21321	-1042.80374	0.10962	-1042.90733	34.5	48.3
1a-IM10 + CO↑	0.19779	-1042.81916	0.09420	-1042.92275	-6.0	7.8
1b-TS1	0.21541	-1042.80925	0.13526	-1042.88940	20.0	95.4
1b-IM2	0.21558	-1042.82253	0.13221	-1042.90591	-14.8	52.0
1b-TS2	0.21302	-1042.78501	0.12996	-1042.86807	83.7	151.4
1b-IM3	0.21428	-1042.78948	0.13163	-1042.87214	71.9	140.7
1b-TS3	0.20973	-1042.78881	0.12668	-1042.87185	73.7	141.4
1b-IM4	0.21443	-1042.80548	0.12846	-1042.89146	29.9	90.0
FFA	0.10284	-344.50467	0.05745	-344.55053		
FFA + CO + $Pd(OAc)_2$	0.21133	-1042.79292	0.08270	-1042.92202	62.9	9.7
FFA + CO↑ + $Pd(OAc)_2$	0.19591	-1042.80834	0.06728	-1042.93744	22.4	-30.8

Table S7. Zero-point energies (*ZPE*, hartree), thermal correction to Gibbs free energy (G_0, hartree), total energies (E_c, hartree) corrected by *ZPE*, Sum of electronic and thermal free energies (G_c, hartree) with *ZPE* and thermal corrections, and relative energies (E_r, kJ mol^{-1}) and relative Gibbs free energies (G_r, kJ mol^{-1}) of various species with respect to the reactants for the whole reaction of HMF-to-5-MF (HMF-4 → 5-MF) catalyzed by $Pd(OAc)_2$ at M06L/6-311++G(d,p), SDD* level in 1,4-dioxane solution under the temperature of 423K and the pressure of 5.0 atm.

Species	*ZPE*	E_c	G_0	G_c	E_r	G_r
HAc	0.06177	-229.07394	0.02183	-229.11388		
H_2O	0.02130	-76.43296	0.00365	-76.45061		
CO_2	0.01180	-188.62050	-0.01725	-188.64955		
CO_2↑	-0.00362	-188.63592	-0.03267	-188.66497		
HCOOH	0.03386	-189.76929	-0.00028	-189.80343		
$Pd(OAc)_2$	0.10346	-584.96785	0.04685	-585.02446		
HMF-4	0.11180	-457.84904	0.05957	-457.90126		
HMF + HCOOH + $Pd(OAc)_2$	0.24913	-1232.58617	0.10614	-1232.72915	0.0	0.0
2-IM1	0.13849	-774.74038	0.06608	-774.81280		
2-IM1 + HMF	0.25029	-1232.58942	0.12565	-1232.71406	-8.5	39.6
2-TS1	0.13755	-774.72699	0.06754	-774.79701		
2-TS1 + HMF	0.24935	-1232.57603	0.12711	-1232.69827	26.6	81.1
2-IM2	0.13791	-774.75371	0.06798	-774.82364		
2-IM2 + HMF	0.24971	-1232.60275	0.12755	-1232.72491	-43.5	11.1
2-TS2	0.13501	-774.75628	0.06877	-774.82252		
2-TS2 + HMF	0.24682	-1232.60532	0.12835	-1232.72379	-50.3	14.1
2-IM3	0.13845	-774.75697	0.06974	-774.82568		
2-IM3 + HMF	0.25025	-1232.60601	0.12931	-1232.72694	-52.1	5.8
2-IM4	0.18914	-1003.52807	0.10556	-1003.61164		
2-IM4 + HAc	0.25091	-1232.60200	0.12739	-1232.72552	-41.6	9.5
2-TS3	0.18676	-1003.47759	0.10539	-1003.55897		
2-TS3 + HAc	0.24854	-1232.55153	0.12721	-1232.67285	90.9	147.8
2-IM5	0.18671	-1003.52778	0.10328	-1003.61121		
2-IM5 + HAc	0.24849	-1232.60172	0.12511	-1232.72510	-40.8	10.6
2-IM6	0.17338	-814.90189	0.09955	-814.97572		
2-IM6 + CO_2 + HAc	0.24695	-1232.59633	0.10413	-1232.73915	-26.7	-26.3
2-IM6 + CO_2↑ + HAc	0.23153	-1232.61175	0.08871	-1232.75457	-67.2	-66.8
2-TS4	0.16757	-814.82766	0.09052	-814.90471		
2-TS4 + CO_2 + HOAc	0.24114	-1232.52209	0.09510	-1232.66814	168.2	160.2

Continued from **Table S7**

Species	*ZPE*	E_c	G_0	G_c	E_r	G_r
2-TS4 + CO_2↑ + HAc	0.22572	-1232.53751	0.07968	-1232.68356	127.7	119.7
2-IM7	0.17358	-814.94469	0.10227	-815.01600		
2-IM7 + CO_2 + HAc	0.24716	-1232.63913	0.10685	-1232.77943	-139.0	-132.0
2-IM7 + CO_2↑ + HAc	0.23173	-1232.65455	0.09143	-1232.79486	-179.5	-172.5
2-IM8	0.21174	-967.60338	0.13205	-967.68307		
2-IM8 + CO_2 + H_2O	0.24484	-1232.65684	0.11845	-1232.78324	-185.6	-142.0
2-IM8 + CO_2↑ + H_2O	0.22942	-1232.67227	0.10303	-1232.79866	-226.0	-182.5
2-TS5	0.20602	-967.56748	0.12681	-967.64669		
2-TS5 + CO_2 + H_2O	0.23912	-1232.62094	0.11321	-1232.74685	-91.3	-46.5
2-TS5 + CO_2↑ + H_2O	0.22370	-1232.63636	0.09779	-1232.76227	-131.8	-87.0
2-IM9	0.21066	-967.57870	0.12951	-967.65985		
2-IM9 + H_2O + CO_2	0.24376	-1232.63216	0.11591	-1232.76001	-120.8	-81.0
2-IM9 + H_2O + CO_2↑	0.22834	-1232.64758	0.10049	-1232.77543	-161.2	-121.5
2-IM10	0.21077	-967.60082	0.12294	-967.68865		
2-IM10 + H_2O + CO_2	0.24387	-1232.65428	0.10934	-1232.78881	-178.8	-156.6
2-IM10 + H_2O + CO_2↑	0.22845	-1232.66970	0.09392	-1232.80423	-219.3	-197.1
5-MF	0.10700	-382.62987	0.05997	-382.67690		
5-MF + $Pd(OAc)_2$ + CO_2 + H_2O	0.24357	-1232.65118	0.09323	-1232.80153	-170.7	-190.0
5-MF + $Pd(OAc)_2$ + CO_2↑ + H_2O	0.22815	-1232.66660	0.07780	-1232.81695	-211.2	-230.5

Table S8. Zero-point energies (*ZPE*, hartree), thermal correction to Gibbs free energy (G_0, hartree), total energies (E_c, hartree) corrected by *ZPE*, sum of electronic and thermal free energies (G_c, hartree) with *ZPE* and thermal corrections, and relative energies (E_r, kJ mol^{-1}) and relative Gibbs free energies (G_r, kJ mol^{-1}) of various species with respect to the reactants for the whole reaction of HMF-to-DHMF (HMF-4 → DHMF) catalyzed by $Pd(OAc)_2$ at M06L/6-311++G(d,p), SDD* level in 1,4-dioxane solution under the temperature of 423K and the pressure of 5.0 atm.

Species	*ZPE*	E_c	G_0	G_c	E_r	G_r
HAc	0.06177	-229.07394	0.02183	-229.11388		
CO_2	0.01180	-188.62050	-0.01725	-188.64955		
CO_2↑	-0.00362	-188.63592	-0.03267	-188.66497		
HCOOH	0.03386	-189.76929	-0.00028	-189.80343		
$Pd(OAc)_2$	0.10346	-584.96785	0.04685	-585.02446		
HMF-4	0.11180	-457.84904	0.05957	-457.90126		
HMF + HCOOH + $Pd(OAc)_2$	0.24913	-1232.58617	0.10614	-1232.72915	0.0	0.0
2-IM1	0.13849	-774.74038	0.06608	-774.81280		
2-IM1 + HMF	0.25029	-1232.58942	0.12565	-1232.71406	-8.5	39.6
2-TS1	0.13755	-774.72699	0.06754	-774.79701		
2-TS1 + HMF	0.24935	-1232.57603	0.12711	-1232.69827	26.6	81.1
2-IM2	0.13791	-774.75371	0.06798	-774.82364		
2-IM2 + HMF	0.24971	-1232.60275	0.12755	-1232.72491	-43.5	11.1
2-TS2	0.13501	-774.75628	0.06877	-774.82252		
2-TS2+HMF	0.24682	-1232.60532	0.12835	-1232.72379	-50.3	14.1
2-IM3	0.13845	-774.75697	0.06974	-774.82568		
2-IM3 + HMF	0.25025	-1232.60601	0.12931	-1232.72694	-52.1	5.8
3-IM1	0.18901	-1003.52203	0.10717	-1003.60387		
3-IM1 + HAc	0.25078	-1232.59596	0.12900	-1232.71775	-25.7	29.9
3-TS1	0.18617	-1003.47761	0.10424	-1003.55954		
3-TS1 + HAc	0.24794	-1232.55155	0.12606	-1232.67343	90.9	146.3
3-IM2	0.18568	-1003.53251	0.09824	-1003.61996		
3-IM2 + HAc	0.24745	-1232.60645	0.12006	-1232.73384	-53.2	-12.3
3-IM3	0.17278	-814.90818	0.09788	-814.98309		
3-IM3 + HAc + CO_2	0.24636	-1232.60261	0.10246	-1232.74652	-43.2	-45.6
3-IM3 + HAc + CO_2↑	0.23094	-1232.61804	0.08703	-1232.76194	-83.7	-86.1
3-TS2	0.17184	-814.89539	0.10108	-814.96616		
3-TS2 + CO_2 + HAc	0.24542	-1232.58983	0.10566	-1232.72959	-9.6	-1.1
3-TS2 + CO_2 + Hac	0.23000	-1232.60525	0.09024	-1232.74501	-50.1	-41.6
3-IM4	0.17443	-814.89539	0.10301	-814.96681		
3-IM4 + CO_2 + HAc	0.24801	-1232.58982	0.10759	-1232.73024	-9.6	-2.9
3-IM4 + CO_2↑ + HAc	0.23259	-1232.60524	0.09217	-1232.74566	-50.1	-43.4

Continued from **Table S8**

Species	*ZPE*	E_c	G_0	G_c	E_r	G_r
3-IM5	0.23994	-1044.00697	0.15374	-1044.09317		
3-IM5 + CO_2	0.25174	-1232.62747	0.13649	-1232.74272	-108.4	-35.6
3-IM5 + CO_2↑	0.23632	-1232.64289	0.12107	-1232.75814	-148.9	-76.1
3-TS3	0.23702	-1044.00639	0.15069	-1044.09272		
3-TS3 + CO_2	0.24883	-1232.62688	0.13344	-1232.74227	-106.9	-34.4
3-TS3 + CO_2↑	0.23340	-1232.64231	0.11802	-1232.75769	-147.4	-74.9
3-IM6	0.24029	-1044.00951	0.15381	-1044.09599		
3-IM6 + CO_2	0.25209	-1232.63001	0.13656	-1232.74554	-115.1	-43.0
3-IM6 + CO_2↑	0.23667	-1232.64543	0.12114	-1232.76096	-155.6	-83.5
3-IM7	0.24077	-1044.00675	0.16321	-1044.08431		
3-IM7 + CO_2	0.25257	-1232.62725	0.14596	-1232.73386	-107.9	-12.4
3-IM7 + CO_2↑	0.23715	-1232.64267	0.13054	-1232.74928	-148.3	-52.9
DHMF	0.13576	-459.02485	0.08333	-459.07727		
DHMF + $Pd(OAc)_2$ +CO_2	0.25103	-1232.61319	0.11294	-1232.75128	-70.9	-58.1
DHMF+ $Pd(OAc)_2$ +CO_2↑	0.23561	-1232.62861	0.09751	-1232.76670	-111.4	-98.6

Table S9. Relative Gibbs free energies of the $Pd(OAc)_2$ molecular in 1,4-dioxane solution.

	ΔE/kJ mol^{-1}	ΔG /kJ mol^{-1}
$Pd(OAc)_2$ (^{1}A)	0.0	0.0
$Pd(OAc)_2$ (^{3}A)	86.4	78.0

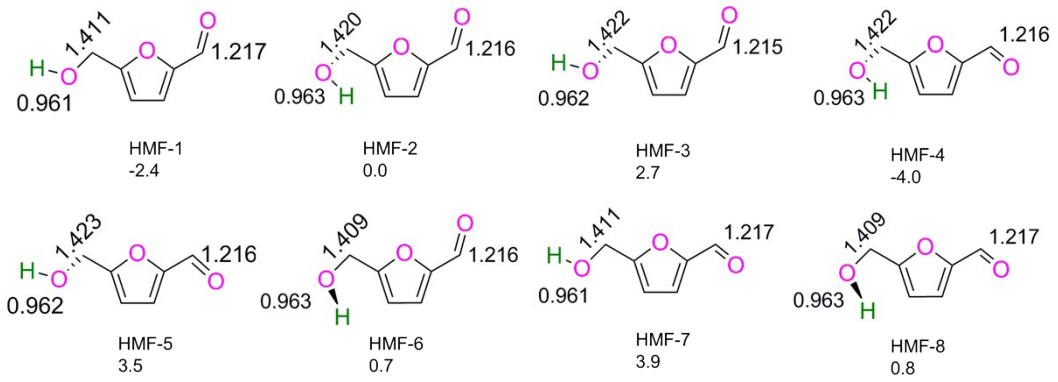


Figure S1. The geometric structures and the relative Gibbs free energy (G_r, kJ mol^{-1}) relative to HMF-2 for eight conformers of HMF in 1,4-dioxane solution. For clarity, hydrogen atoms on carbon are not shown. Bond lengths are reported in Å.

Notes: As both the formyl (–CHO) and hydroxymethyl (–CH2OH) groups in HMF can rotate around the C–C single bond, there may exist eight conformers in 1,4-dioxane solution. The geometric structures and relative Gibbs free energy for eight conformers of HMF in 1,4-dioxane solution are depicted in Figure S1. As shown in Figure S1, for the eight conformers of HMF, the relative Gibbs free energies increase as HMF–4 < HMF–1 < HMF–2 < HMF–6 < HMF–8 < HMF–3 < HMF–5 < HMF–7 in 1,4-dioxane solution. It is indicated that the HMF-4 is the thermodynamically most stable in 1,4-dioxane solution. Therefore, the HMF–4 conformer is preferred to be representative of HMF in the present study.

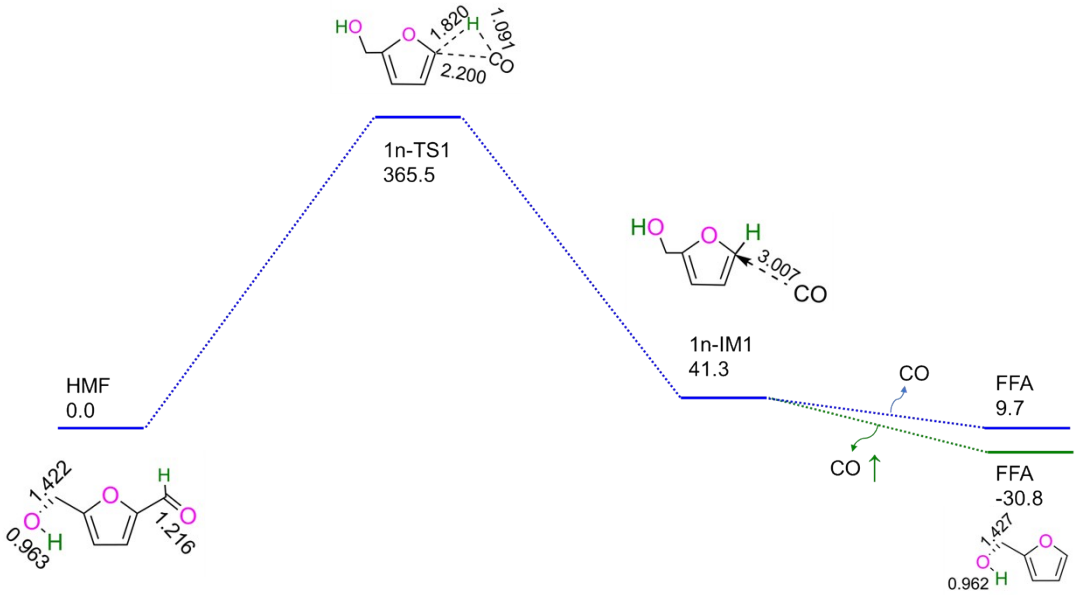


Figure S2. The geometric structures and the schematic energy diagrams with the relative Gibbs free energy (G_r, kJ mol^{-1}) for the uncatalyzed reaction of HMF → FFA + CO. For clarity, hydrogen atoms on carbon are not shown. Bond lengths are reported in Å.

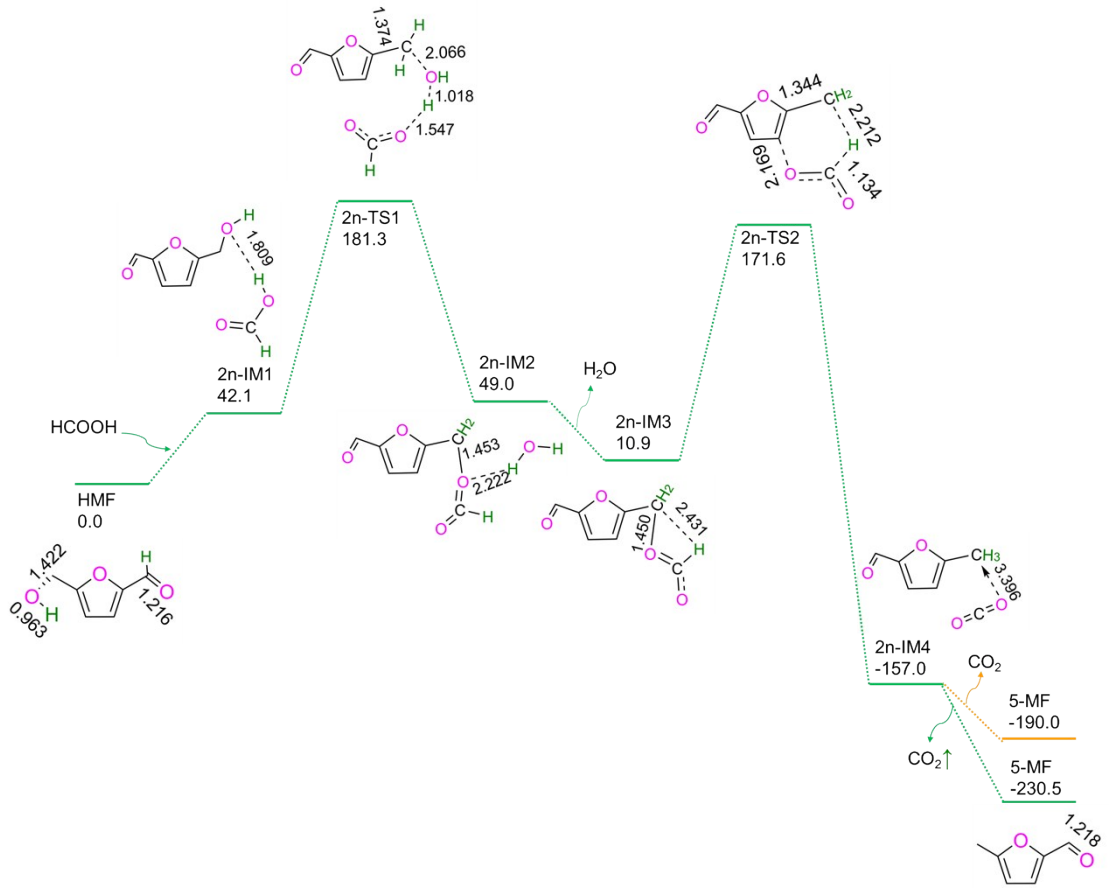


Figure S3. The geometric structures and the schematic energy diagrams with the relative Gibbs free energy (G_r, kJ mol^{-1}) for the uncatalyzed reaction of HMF + HCOOH → 5-MF + H_2O + CO_2. For clarity, hydrogen atoms on carbon are not shown. Bond lengths are reported in Å.

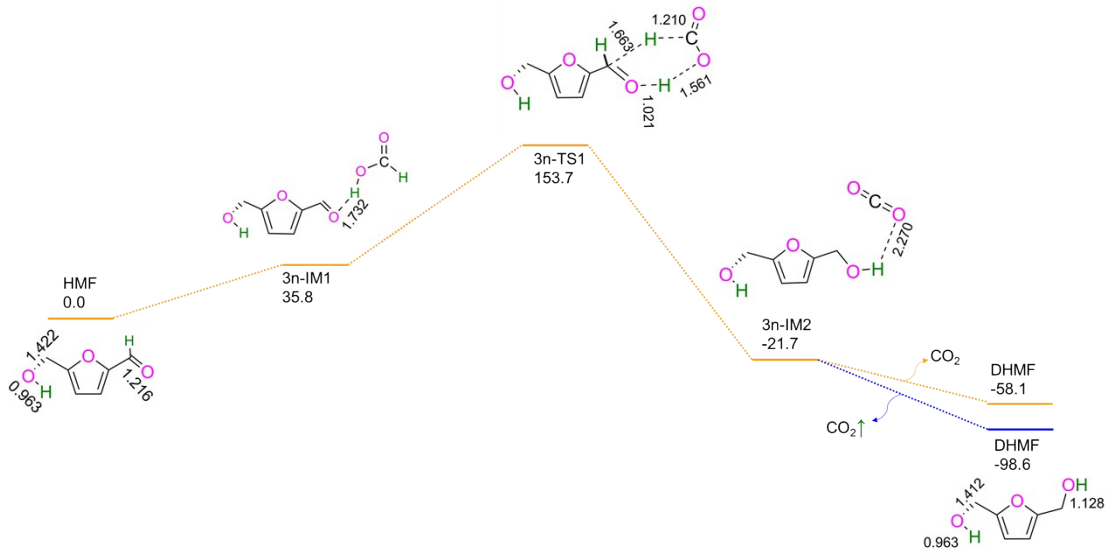
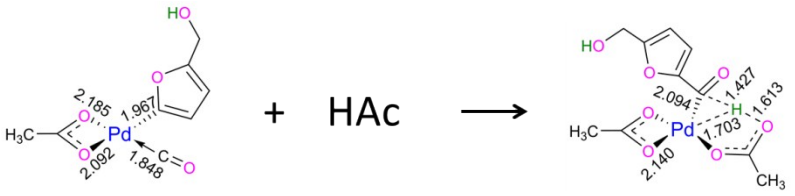
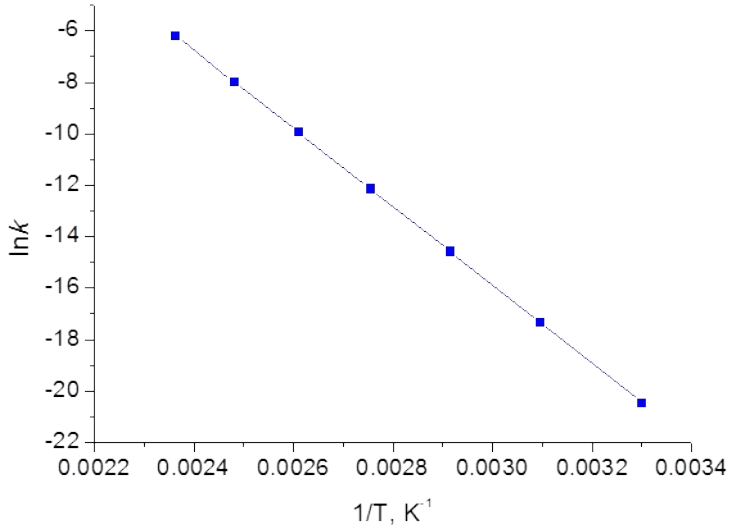


Figure S4. The geometric structures and the schematic energy diagrams with the relative Gibbs free energy (G_r, kJ mol^{-1}) for the uncatalyzed reaction of HMF + HCOOH → 2,5-DHMF + CO_2. For clarity, hydrogen atoms on carbon are not shown. Bond lengths are reported in Å.

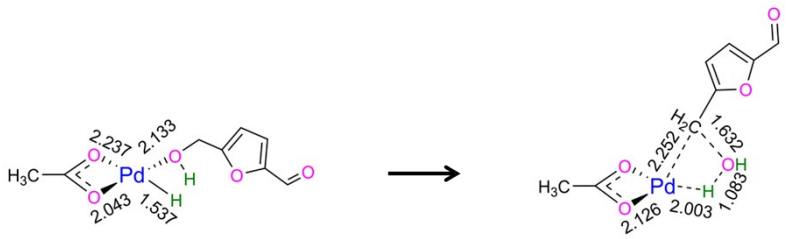


1a-IM6 1a-TS2

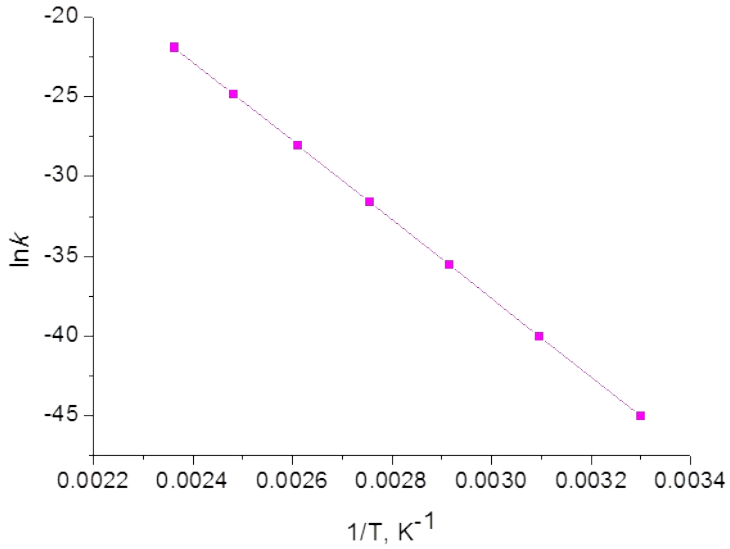


$$k_{\text{D-CO}}(T) = 8.740 \times 10^{12} \exp(-126,613 / RT) \ \text{(s}^{-1}\ \text{mol}^{-1}\ \text{dm}^3\text{)}$$

Figure S5. Arrhenius plots of rate constants for the crucial reaction step 1a-IM6 + HAc → 1a-TS2 for the reaction HMF-4 → FFA + CO catalyzed by $Pd(OAc)_2$ in 1,4-dioaxne rolution.

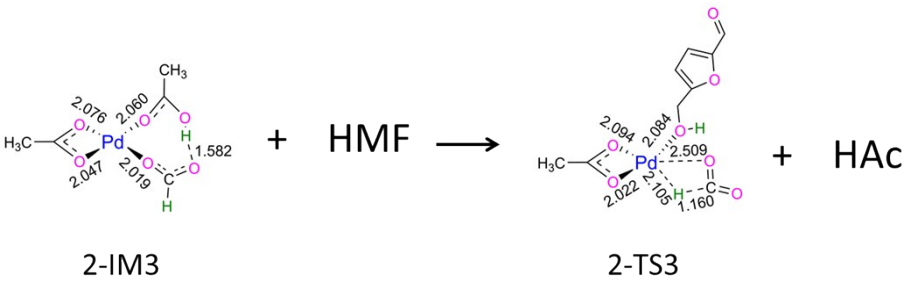


2-IM6 2-TS4

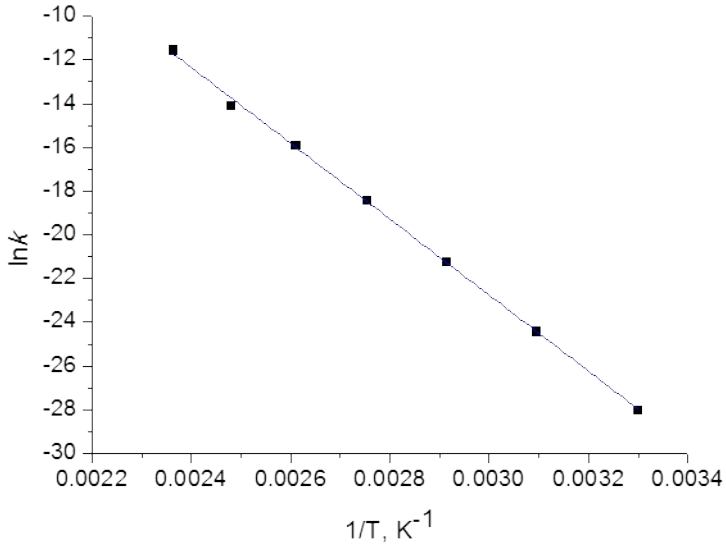


$$k_{\text{D-O}}(T) = 7.324\times10^{15}\exp(-205,605/RT)\ \ (\text{s}^{-1})$$

Figure S6. Arrhenius plots of rate constants for the crucial reaction step 2-IM6 → 2-TS4 for the reaction HMF + HCOOH → 5-MF + H_2O + CO_2 catalyzed by $Pd(OAc)_2$ in 1,4-dioxane solution.

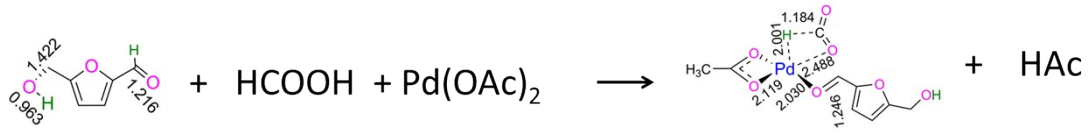


2-IM3 2-TS3



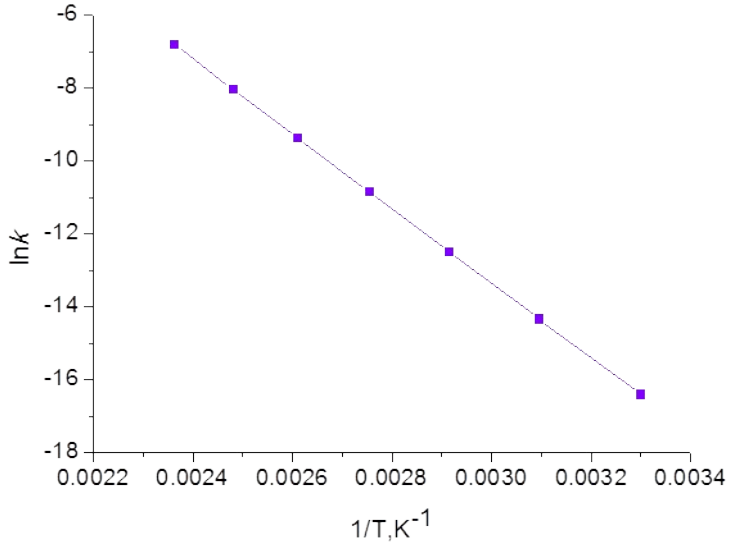
$$k_{\text{S-O}}(T) = 5.567 \times 10^{12} \exp(-144,455 / RT) \ \ (\text{s}^{-1}\ \text{mol}^{-1}\ \text{dm}^3)$$

Figure S7. Arrhenius plots of rate constants for the selective reaction step 2-IM3 + HMF → 2-TS4 + HAc for the reaction HMF + HCOOH → 5-MF + H_2O + CO_2 catalyzed by $Pd(OAc)_2$ in 1,4-dioxane solution.



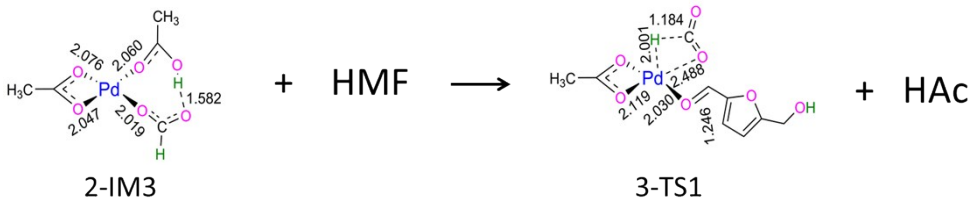
HMF

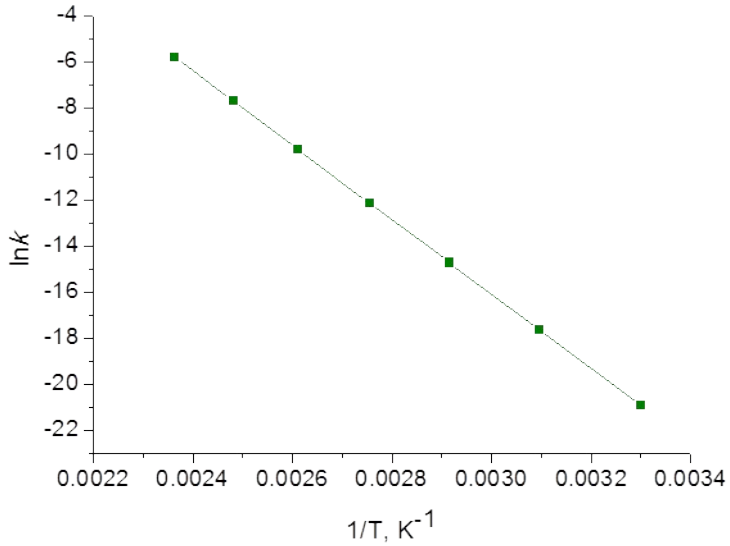
3-TS1



$$k_{\mathrm{H}}(T) = 3.59\times10^{7}\ \exp(-85,260\,/\,RT)\ \ (\mathrm{s^{-1}\ mol^{-2}\ dm^{6}})$$

Figure S8. Arrhenius plots of rate constants for the selective reaction step HMF + HCOOH + $Pd(OAc)_2$ → 3-TS1 for the reaction HMF + HCOOH → DHMF + CO_2 catalyzed by $Pd(OAc)_2$ in 1,4-dioxane solution.





$$k_{\text{S-H}}(T) = 1.205 \times 10^{14} \exp(-134,420 / RT) \quad (\text{s}^{-1}\ \text{mol}^{-1}\ \text{dm}^3)$$

Figure S9. Arrhenius plots of rate constants for the crucial reaction step 2-IM3 + HMF → 3-TS1 + HAc for the reaction HMF + HCOOH → DHMF + CO_2 catalyzed by $Pd(OAc)_2$ in 1,4-dioxane solution.

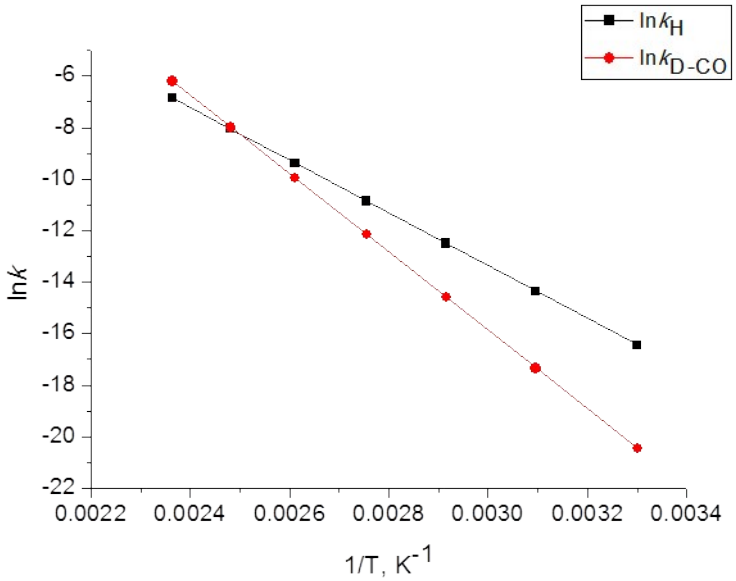
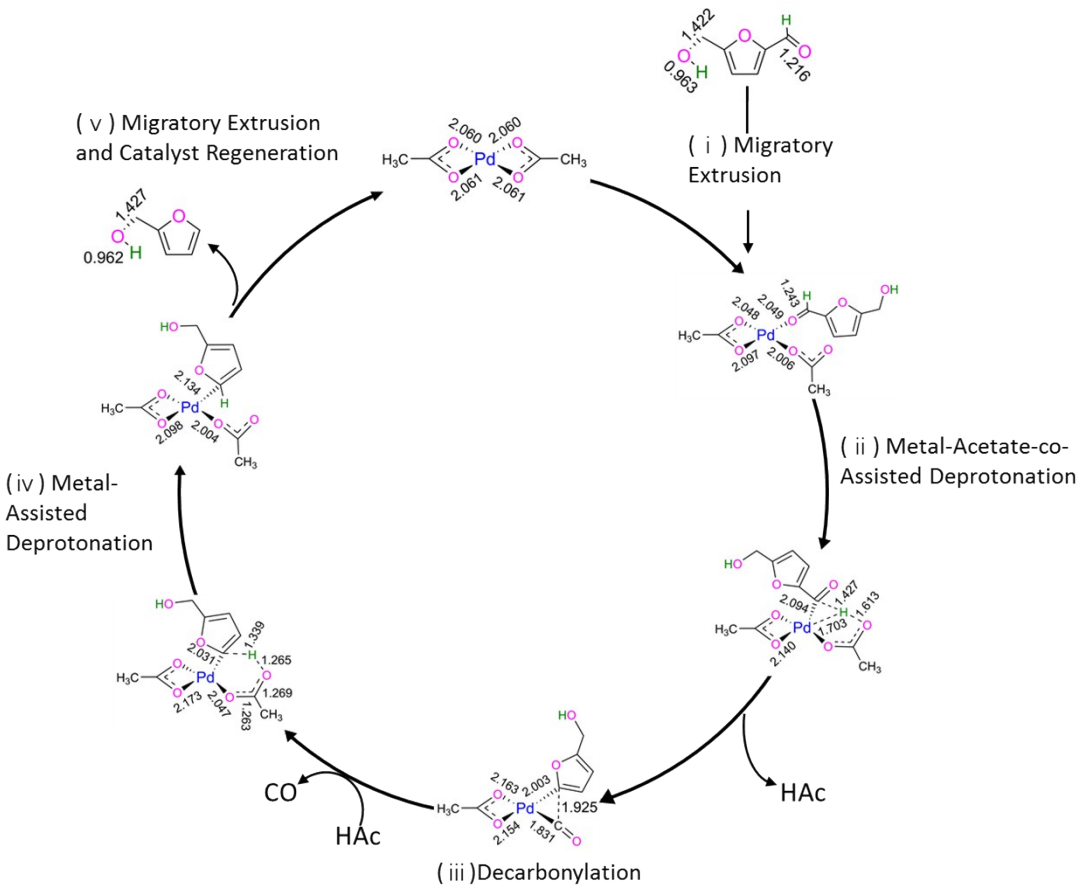
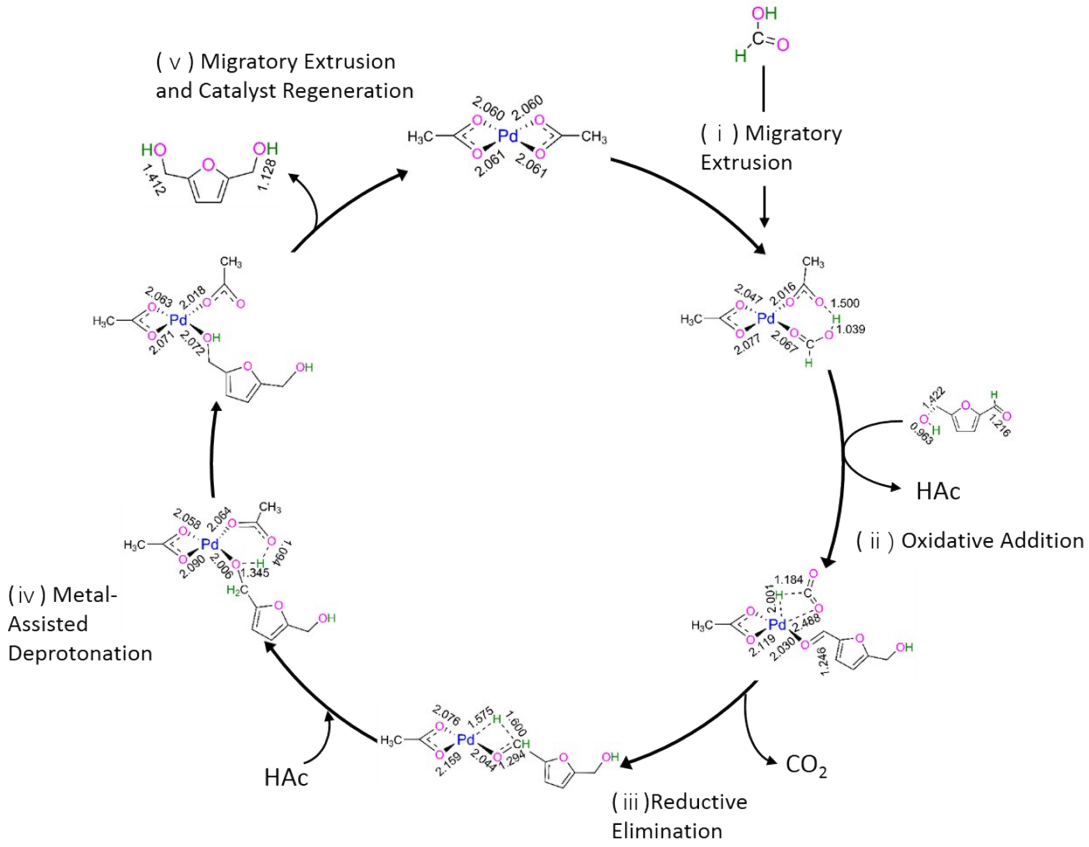


Figure S10. The comparison of $k_{D\text{-}CO}$ and k_H .The black represent arrhenius plots of rate constants for the selective reaction step HMF + HCOOH + $Pd(OAc)_2$ → 3-TS1 for the reaction HMF + HCOOH → DHMF + CO_2 in 1,4-dioxane solution and the red represent arrhenius plots of rate constants for the crucial reaction step 1a-IM6 + HAc → 1a-TS2 for the reaction HMF-4 → FFA + CO in 1,4-dioxane solution.

Notes: The temperature at the intersection point is about 401.5 K.



Scheme S1. The reaction mechanism for the decarbonylation of HMF to FFA catalyzed by $Pd(OAc)_2$.



Scheme S2. The reaction mechanism for the hydrogenation of HMF to DHMF catalyzed by $Pd(OAc)_2$.