

Supporting Information

Synergistic promotion of oxygen vacancy and Lewis acidity of Nb₂O₅ on the preferential hydroxymethyl hydrogenolysis of 5-hydroxymethylfurfural catalyzed by single atom Pt

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Evaluation of rate constants:

The rate constants $k(T)$ was evaluated according to conventional transition state theory $k'(T)$, including the tunneling correction $\kappa(T)$ based on Wigner's formulation as follows:¹

$$k'(T) = \frac{k_B T}{hc^0} \cdot e^{-\frac{\Delta G^\ddagger}{RT}} \quad (\text{i})$$

$$\kappa(T) = 1 + \frac{1}{24} \left| \frac{\omega^\ddagger h}{k_B T} \right|^2 \quad (\text{ii})$$

$$k(T) = \kappa(T) \times k'(T) \quad (\text{iii})$$

$$\ln k(T) = -\frac{E_a}{RT} + \ln A \quad (\text{iv})$$

$$k(T) = A \cdot e^{-\frac{E_a}{RT}} \quad (\text{v})$$

where k_B is Boltzmann's constant, T is the absolute temperature, h is Planck's constant, c^0 is the standard concentration (1 mol dm^{-3}), ΔG^\ddagger is the activation Gibbs free energy barrier and ω^\ddagger is the imaginary frequency of the TS, A is preexponential factor.

References:

1. E. Wigner, *J. Chem. Phys.* **1937**, *5*, 720-723.

The equations for calculating TOF according to the energetic span model:

The efficiency of catalyst can be determined by the turnover frequency (TOF) of the catalytic cycle. Based on the transition state theory (TST), the TOF can be calculated by Eqs. (i) and (ii) proposed by Kozuch et al., in which δE (the energetic span) is defined as the energy difference between the summit and trough of the catalytic cycle.²⁻⁷

$$\text{TOF} = \frac{k_B T}{h} e^{-\delta E/RT}$$

$$\delta E = \begin{cases} G_{\text{TDTs}} - G_{\text{TDI}} & \text{if TDTs appears after TDI} \\ G_{\text{TDTs}} - G_{\text{TDI}} + \Delta G_r & \text{if TDTs appears before TDI} \end{cases}$$

where k_B is the Boltzmann constant, T is the absolute temperature, and h is the Planck constant. G_{TDTs} and G_{TDI} are the Gibbs free energies of the TOF determining transition state (TDTs) and the TOF determining intermediate (TDI), and ΔG_r is the global free energy of the whole cycle.

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2. C. Amatore and A. Jutand, *J. Organomet. Chem.*, 1999, **576**, 254-278.
3. S. Kozuch and S. Shaik, *J. Am. Chem. Soc.*, 2006, **128**, 3355-3365.
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The relative Gibbs free energies of two oxygen defective Nb₂O₅ (010) models are computed by the following equation, eq(S1):

$$G_r = G_{\text{Nb}_2\text{O}_5\text{-ovx}} + \frac{1}{2}G_{\text{O}_2} - G_{\text{Nb}_2\text{O}_5} \dots\dots\dots\text{eq(S1)}$$

G_r is the relative Gibbs free energy of the formation of oxygen vacancies on Nb₂O₅ (010), $G_{\text{Nb}_2\text{O}_5\text{-ovx}}$, $G_{\text{Nb}_2\text{O}_5}$ and G_{O_2} are the Gibbs free energies of Nb₂O₅ (010) with oxygen vacancies, Nb₂O₅ (010) and the ground-state Oxygen molecule, respectively, x is equal to 1 and 2.

Description of the calculation method for the stability of Pt₁/Nb₂O₅-Ov1 and Pt₁/Nb₂O₅-Ov2:

Two types of oxygen defective Nb₂O₅ (010) model supported platinum catalyser models were built in this work, which are named Pt₁/Nb₂O₅-Ov1 and Pt₁/Nb₂O₅-Ov2, respectively. First, one O1 or one O2 atom was removed from the Nb₂O₅ (010) model to obtain Nb₂O₅-Ov1 and Nb₂O₅-Ov2, respectively. Then, a platinum atom was placed at the surface of oxygen defective Nb₂O₅ (010) model, coordinating with an oxygen atom and a niobium atom, as shown in Fig. S3.

The relative Gibbs free energies of Pt₁/Nb₂O₅-Ov1 and Pt₁/Nb₂O₅-Ov2 models (G_r) are computed by the following reaction equation, eq(S2):



The relative Gibbs free energies of H₂ adsorption over Pt₁/Nb₂O₅-Ovx are computed by the following equation, eq(S3):

$$G_r = G_{\text{H}_2\text{-Pt}_1/\text{Nb}_2\text{O}_5\text{-Ovx}} - G_{\text{H}_2} - G_{\text{Pt}_1/\text{Nb}_2\text{O}_5\text{-Ovx}} \dots\dots\dots\text{eq(S3)}$$

In eq(S2), the structures and energies of ground-state Pt metal atom, Nb₂O₅-Ovx and Pt₁/Nb₂O₅-Ovx are calculated, x = the type of O atoms in the outermost atomic layer of Nb₂O₅ (010), x is equal to 1 and 2. In eq(S3), G_r is the relative Gibbs free energy of H₂ adsorption on Pt₁/Nb₂O₅-Ovx, $G_{\text{H}_2\text{-Pt}_1/\text{Nb}_2\text{O}_5\text{-Ovx}}$, G_{H_2} and $G_{\text{Pt}_1/\text{Nb}_2\text{O}_5\text{-Ovx}}$ are the Gibbs free energies of H₂-Pt₁/Nb₂O₅-Ovx, H₂ and Pt₁/Nb₂O₅-Ovx, respectively.

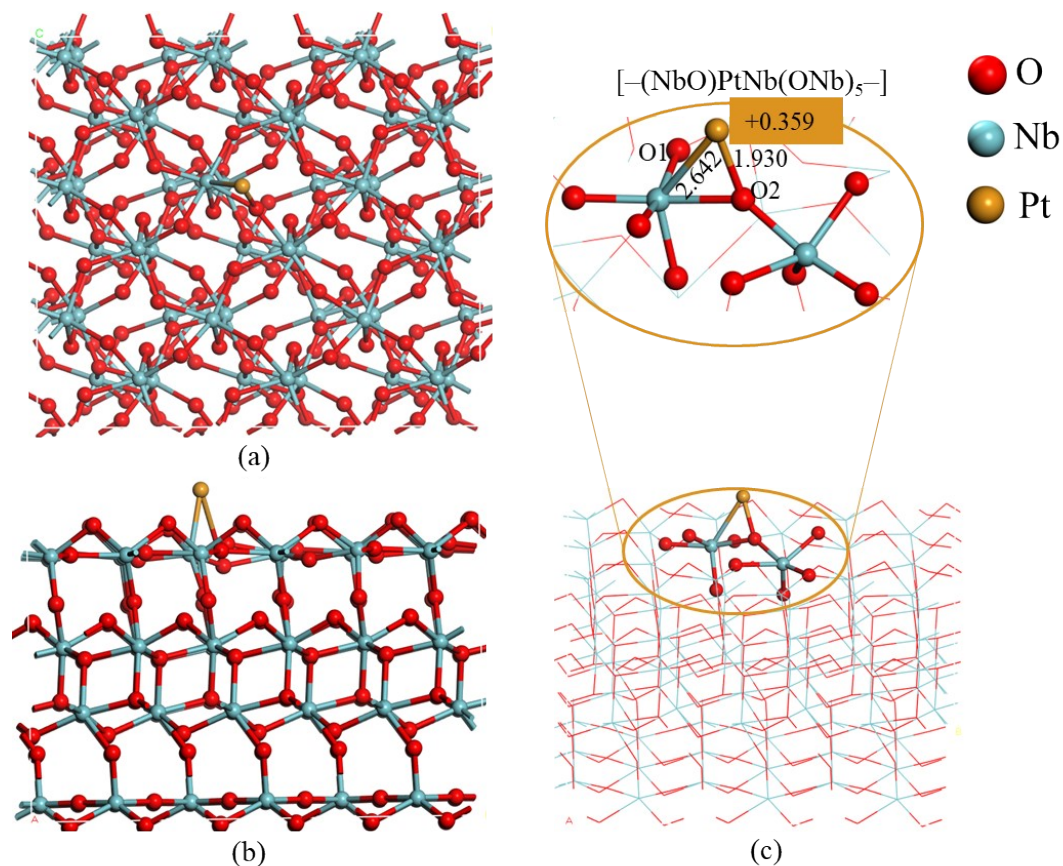


Fig. S1. $\text{Pt}_1/\text{Nb}_2\text{O}_5$ model; atoms shown in red, blue, and orange represent O, Nb, and Pt atoms, respectively. (a) Top view. (b) Side view. (c) $\text{Pt}_1/\text{Nb}_2\text{O}_5(010)$ surface QM/MM model. Spherical atoms are QM atoms, others are MM atoms. On $\text{Nb}_2\text{O}_5(010)$ surface, there is only one kind of catalytically active site, i.e., $[-(\text{NbO})_5\text{Nb}]$, denoted as $[\text{Nb}]$. Then, the Pt-containing active site was constructed by placing a platinum atom on $[\text{Nb}]$ active site, resulting in Pt-supported $\text{Nb}_2\text{O}_5(010)$ model ($\text{Pt}_1/\text{Nb}_2\text{O}_5$) including $\text{O}180\text{Nb}72\text{Pt}1$. On $\text{Pt}_1/\text{Nb}_2\text{O}_5$, there is only a type of Pt-containing catalytically active site i.e., $[-(\text{NbO})\text{PtNb}(\text{ONb})_5-]$ ($[\text{OPtNb}]$). Hirshfeld charge of Pt atom is shown in orange. The Mayer bond orders of Pt–Nb (0.726), being symbolic of semi-single-bond, and Pt–O2 (0.972), being typical of single-bond.

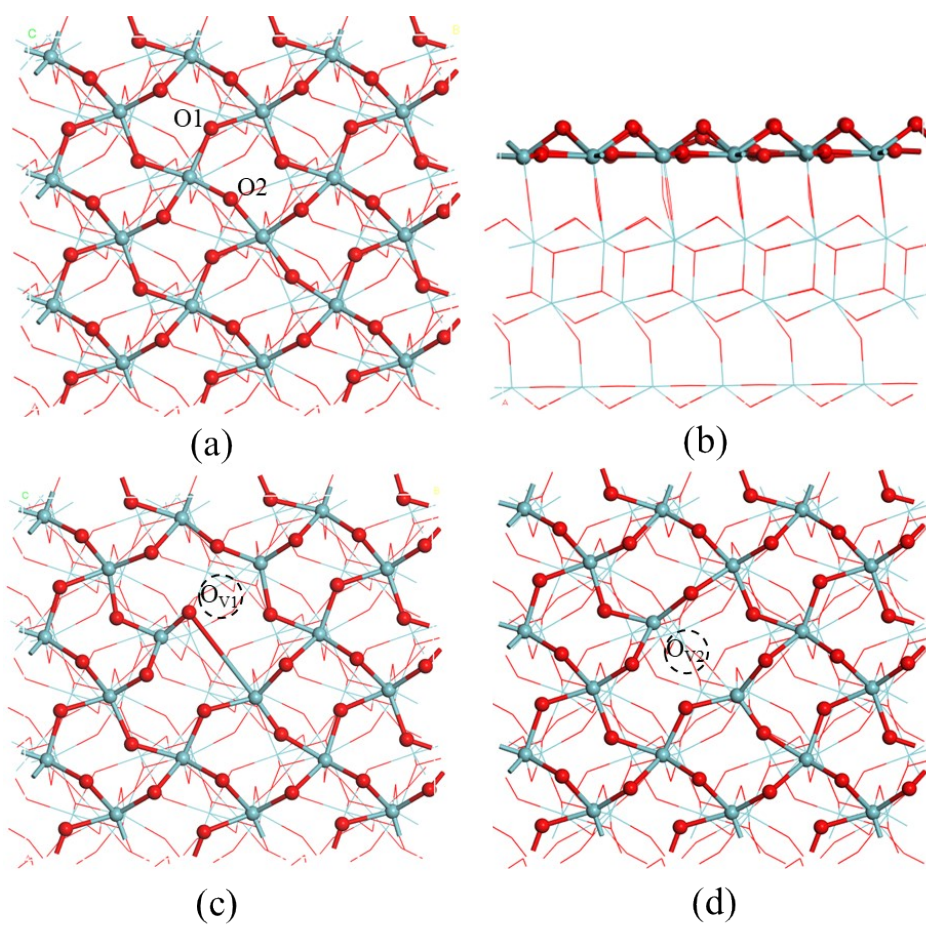


Fig. S2. Nb₂O₅(010) model; atoms shown in red and blue represent O and Nb atoms, respectively, (a) Top view. (b) Side view. (c) and (d) two different O vacancies Nb₂O₅(010) models on Nb₂O₅(010) named Nb₂O₅-Ov1 and Nb₂O₅-Ov2, respectively. The dotted circles label the missing oxygens (vacancies).

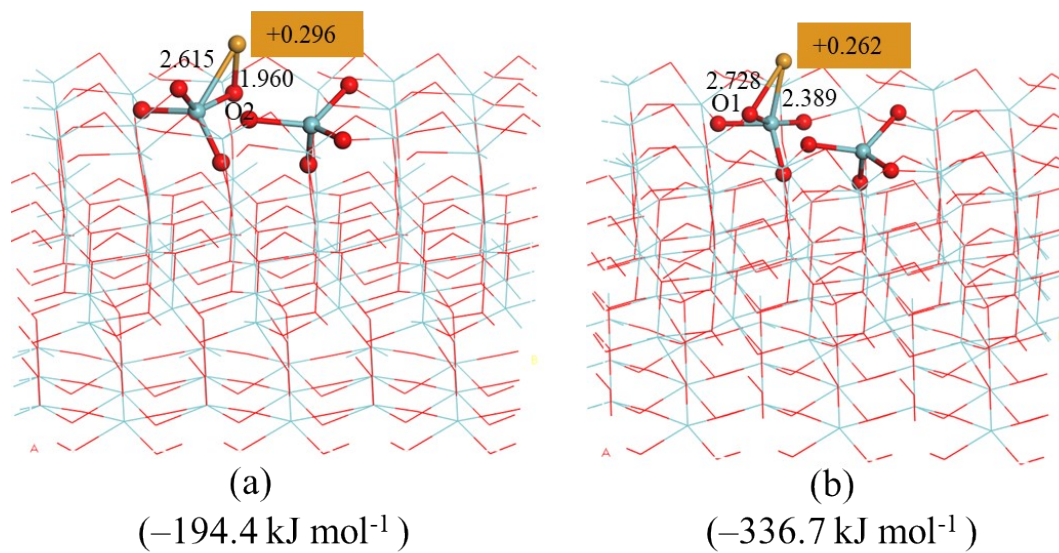


Fig. S3. (a) Pt₁/Nb₂O₅-Ov1 and (b) Pt₁/Nb₂O₅-Ov2 are the two types of oxygen defective Nb₂O₅(010) model supported platinum single-atom catalysts, respectively. Bond lengths are reported in Å. Hirshfeld charge of Pt atom is shown in orange. The relative Gibbs free energies (G_r , kJ mol⁻¹) shown in brackets.

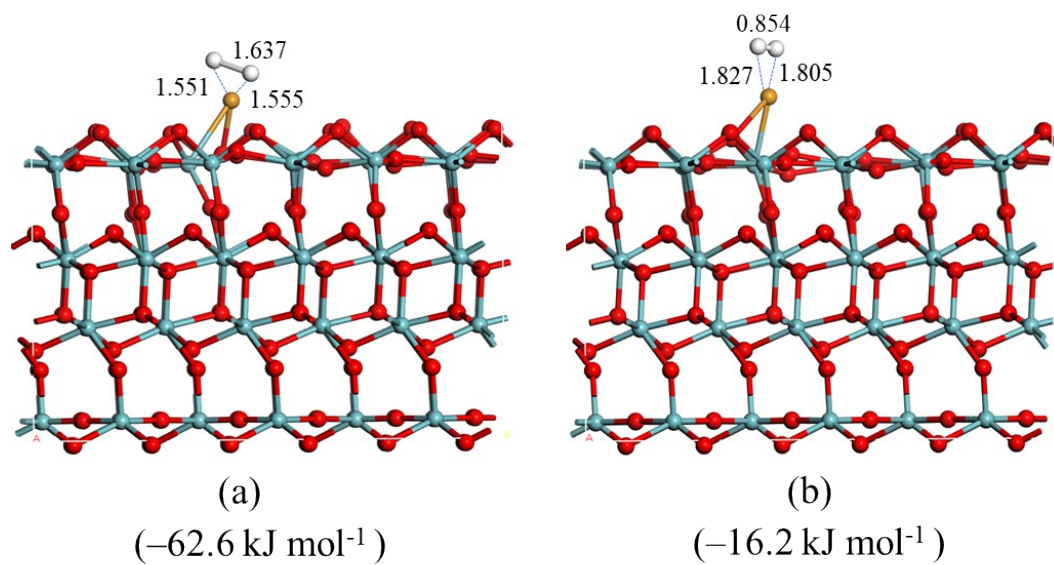


Fig. S4. (a) $\text{H}_2\text{-Pt}_1/\text{Nb}_2\text{O}_5\text{-Ov1}$ (1-v-IM1) and (b) $\text{H}_2\text{-Pt}_1/\text{Nb}_2\text{O}_5\text{-Ov2}$ are the optimized geometric structures of H_2 adsorption over $\text{Pt}_1/\text{Nb}_2\text{O}_5\text{-Ov1}$ and $\text{Pt}_1/\text{Nb}_2\text{O}_5\text{-Ov2}$, respectively, Bond lengths are reported in Å. Hirshfeld charge of Pt atom is shown in orange. The relative Gibbs free energies (G_r , kJ mol^{-1}) to the dissociated reactant and catalyst are shown in brackets.

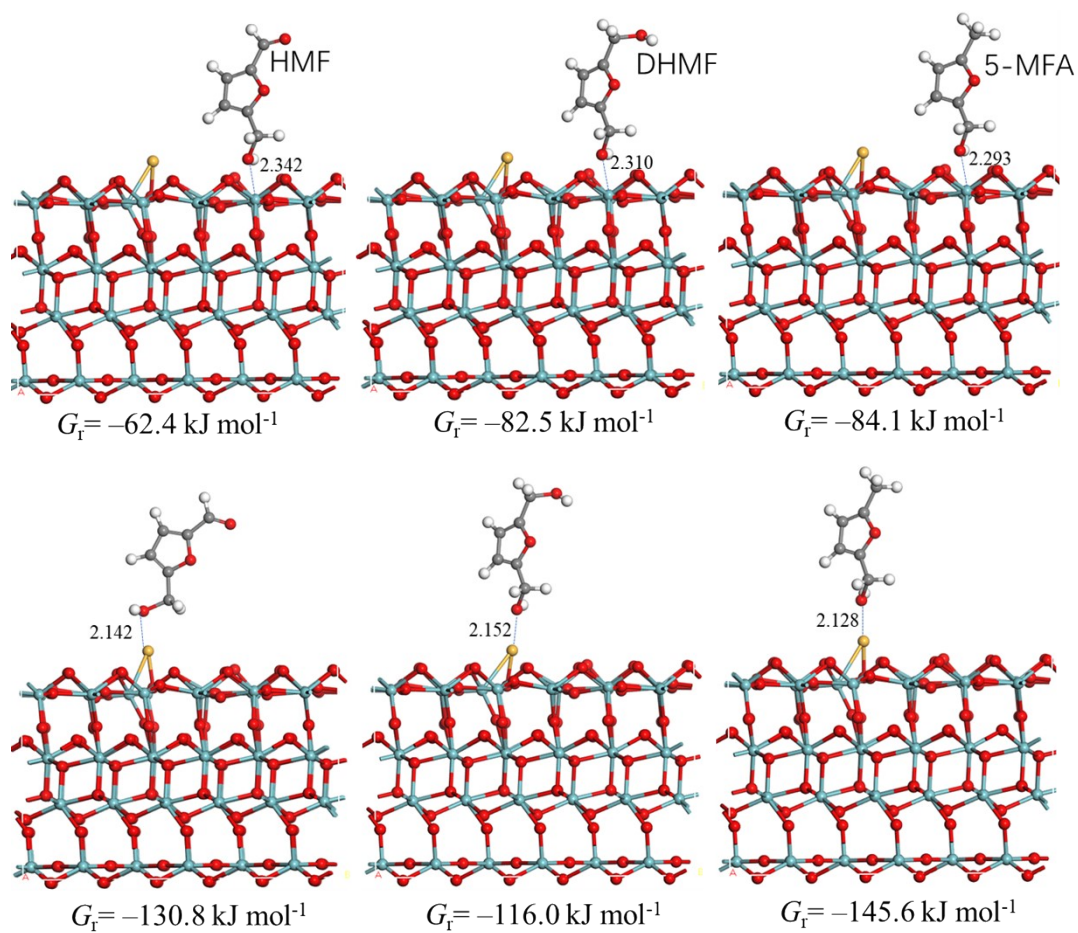


Fig. S5. The adsorption modes for HMF, DHMF, and 5-MFA over Nb-site of $\text{Pt}_1/\text{Nb}_2\text{O}_5\text{-OV}$ (upper row) and over Pt-site of $\text{Pt}_1/\text{Nb}_2\text{O}_5\text{-OV}$ (bottom row), respectively, Bond lengths are reported in Å. The relative Gibbs free energies (G_r , kJ mol^{-1}) are shown.

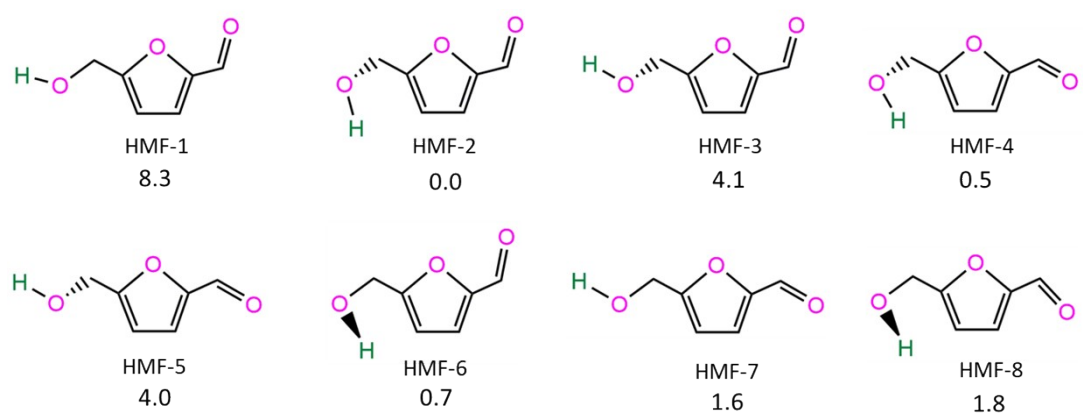
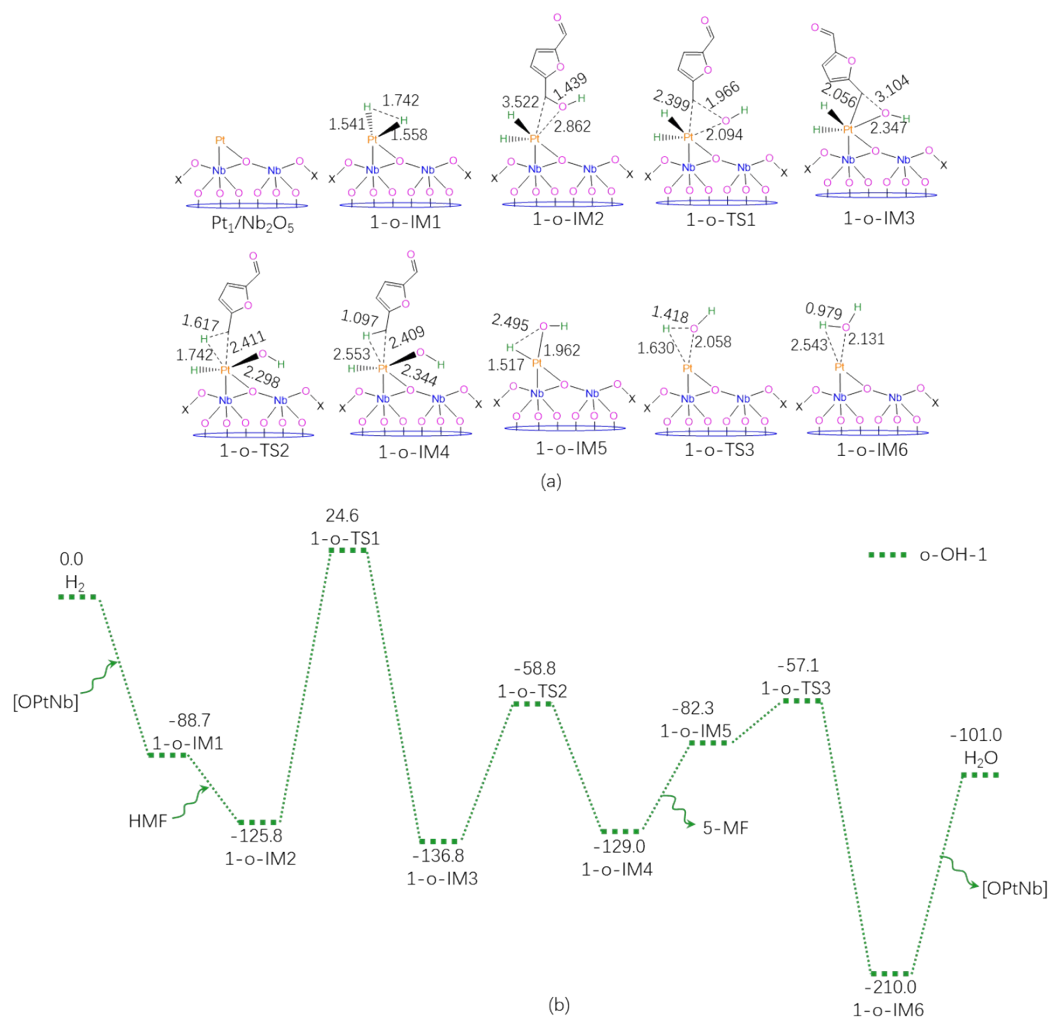


Fig. S6. The geometric structures and the relative Gibbs free energy (G_r , kJ mol⁻¹) relative to HMF-2 for eighth conformers of HMF in THF solution at the G4 level. For clarity, hydrogen atoms on carbon are not shown. Bond lengths are reported in Å.



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g. S7. The optimized geometric structures (a) and the schematic energy diagrams (b) with the Gibbs free energy (G_r , kJ mol⁻¹) relative to the reactants for catalytic hydrogenolysis of HMF to 5-MF over [OPtNb]. Bond lengths are reported in Å.

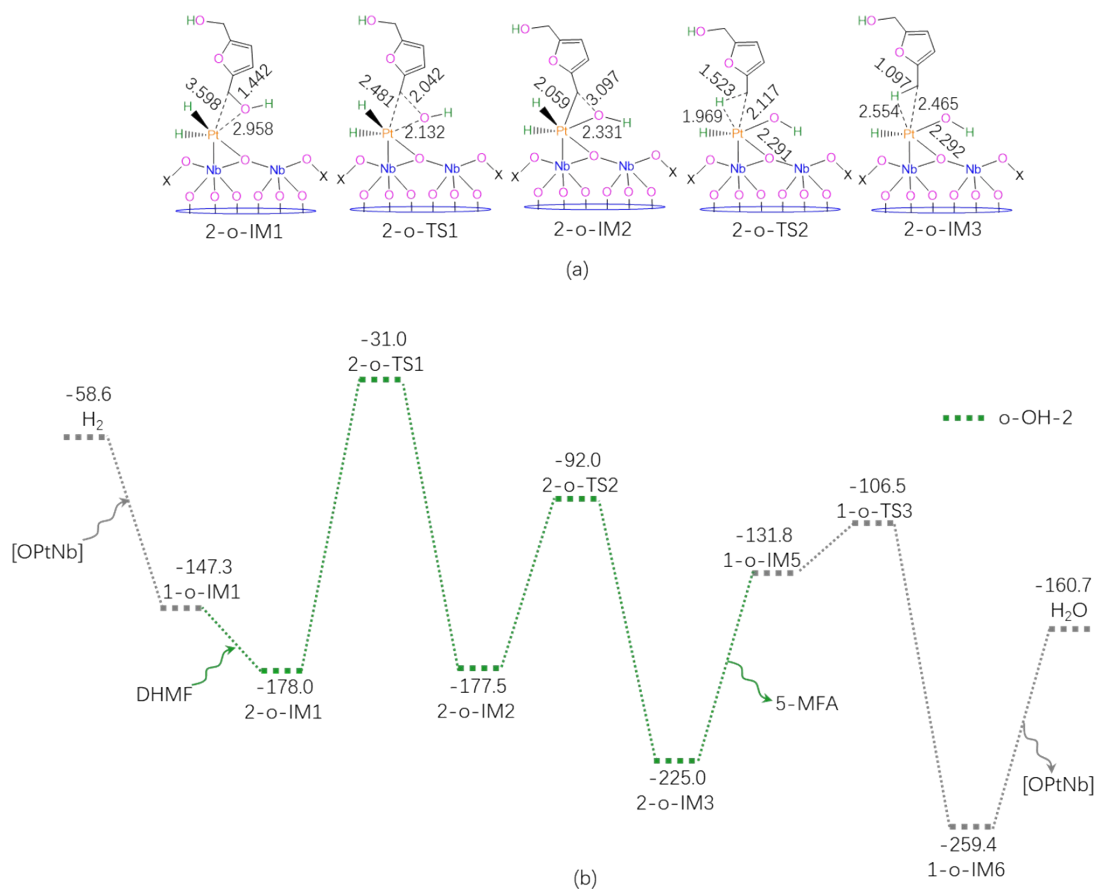


Fig. S8. The optimized geometric structures (a) and the schematic energy diagrams (b) with the Gibbs free energy (G_r , kJ mol⁻¹) relative to the reactants for catalytic hydrogenolysis of DHMF to 5-MFA over [OPtNb]. Bond lengths are reported in Å.

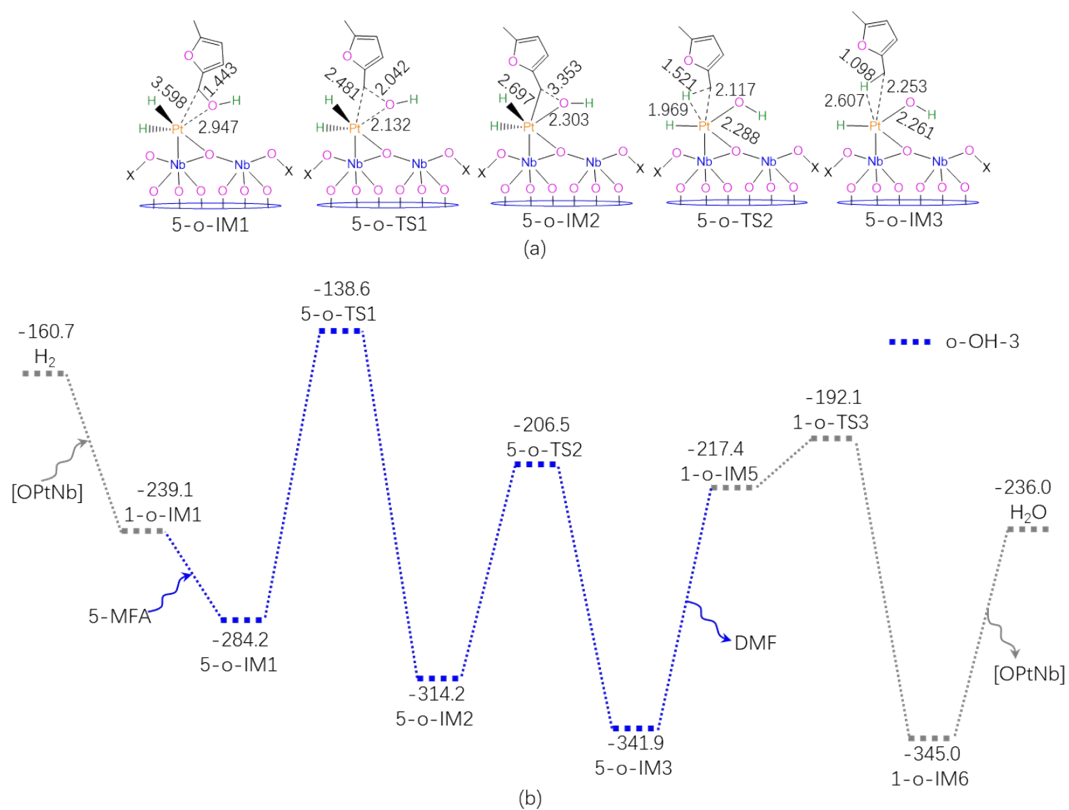


Fig. S9. The optimized geometric structures (a) and the schematic energy diagrams (b) with the Gibbs free energy (G_r , kJ mol⁻¹) relative to the reactants for catalytic hydrogenolysis of 5-MFA to DMF over [OPtNb]. Bond lengths are reported in Å.

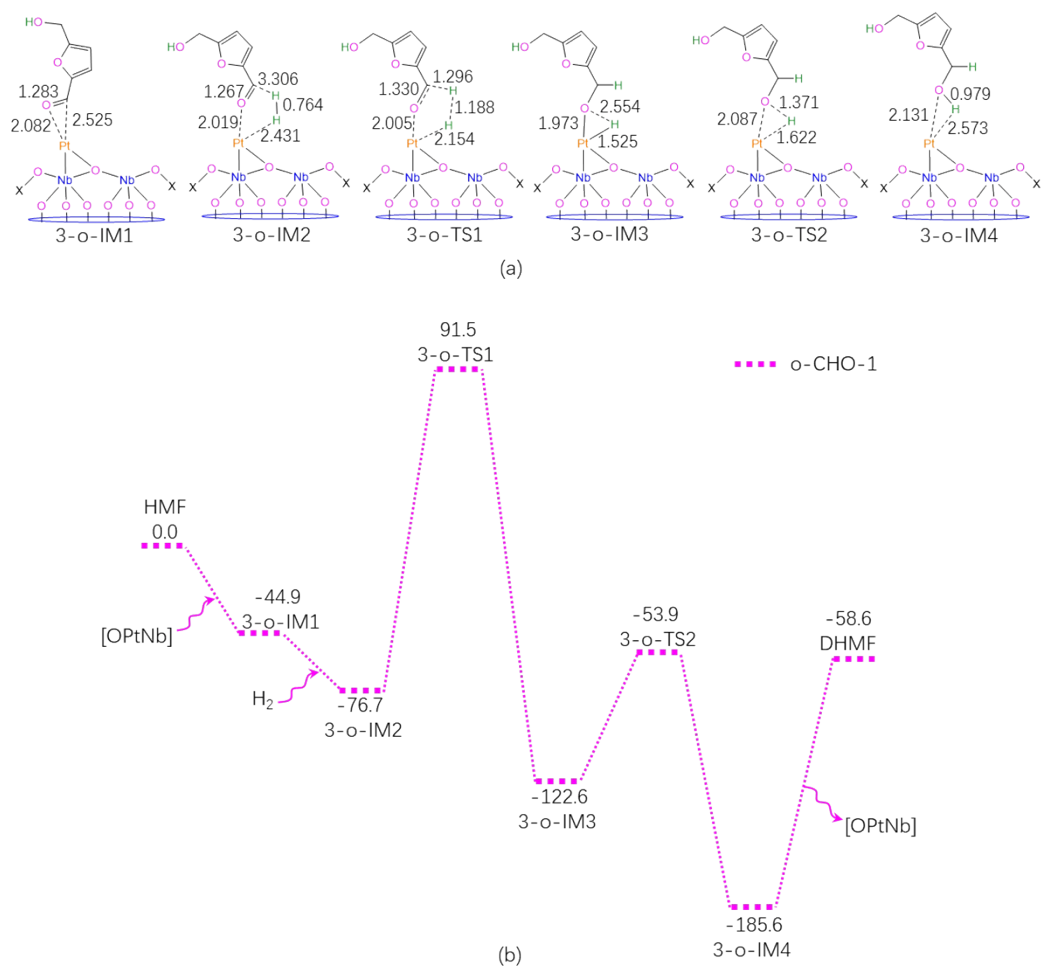


Fig. S10. The optimized geometric structures (a) and the schematic energy diagrams (b) with the Gibbs free energy (G_r , kJ mol⁻¹) relative to the reactants for catalytic hydrogenation of HMF to DHMF over [OPtNb]. Bond lengths are reported in Å.

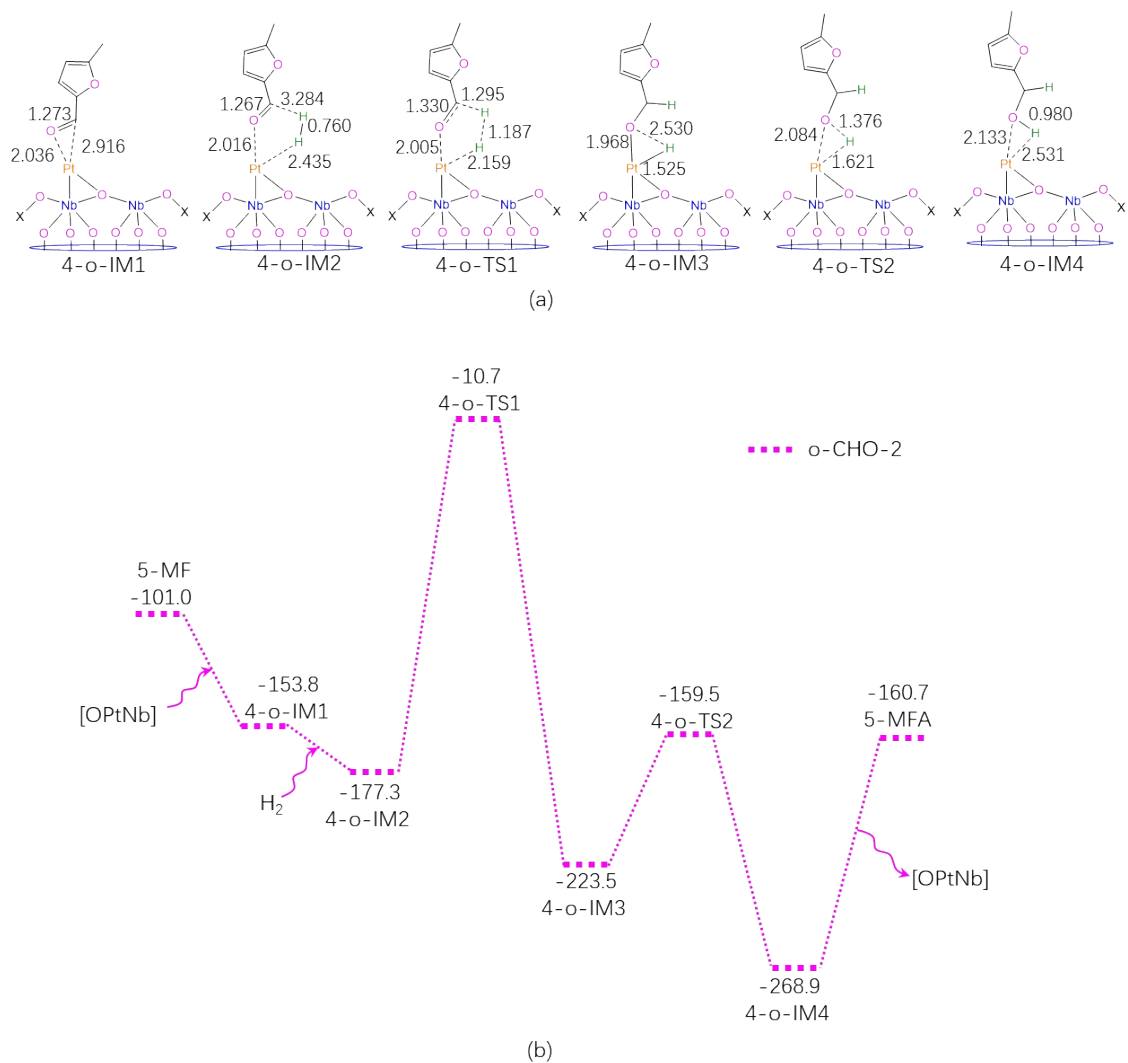


Fig. S11. The optimized geometric structures (a) and the schematic energy diagrams (b) with the Gibbs free energy (G_r , kJ mol⁻¹) relative to the reactants for catalytic hydrogenation of 5-MF to MFA over [OPtNb]. Bond lengths are reported in Å.

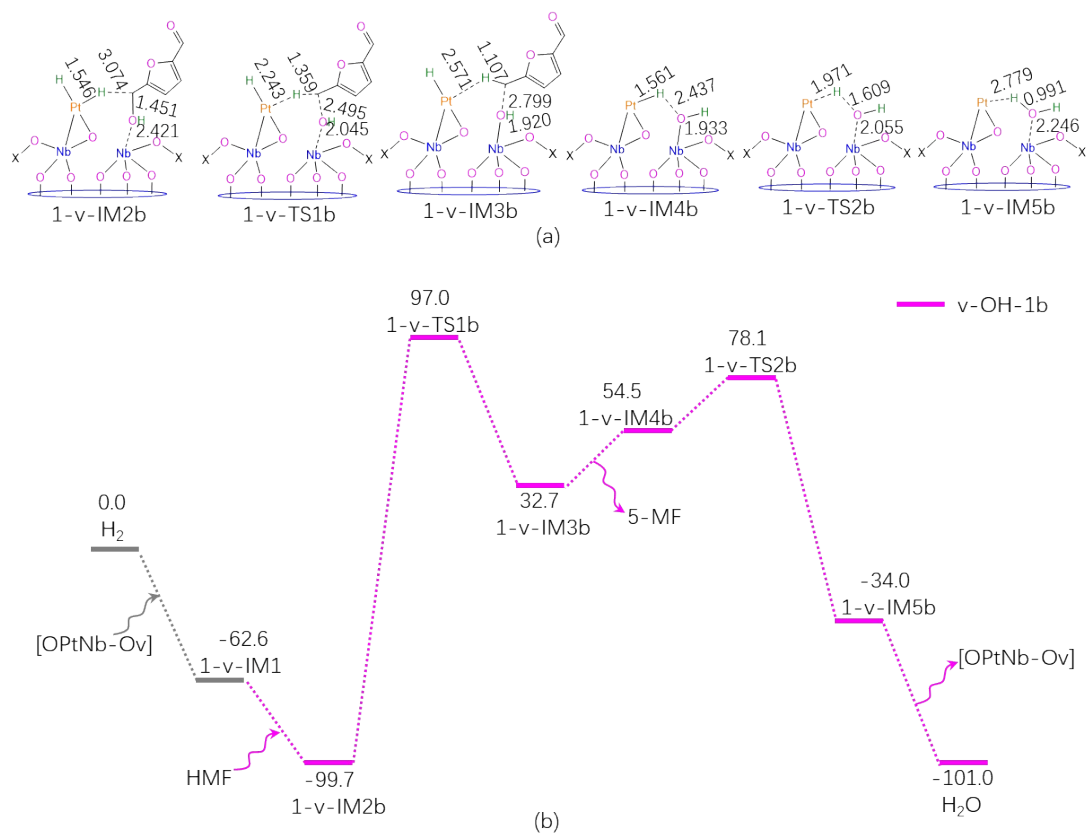


Fig. S12. The optimized geometric structures (a) and the schematic energy diagrams (b) with the Gibbs free energy (G_r , kJ mol⁻¹) relative to the reactants for catalytic hydrogenolysis of HMF to 5-MF over [OPtNb-Ov]. Bond lengths are reported in Å.

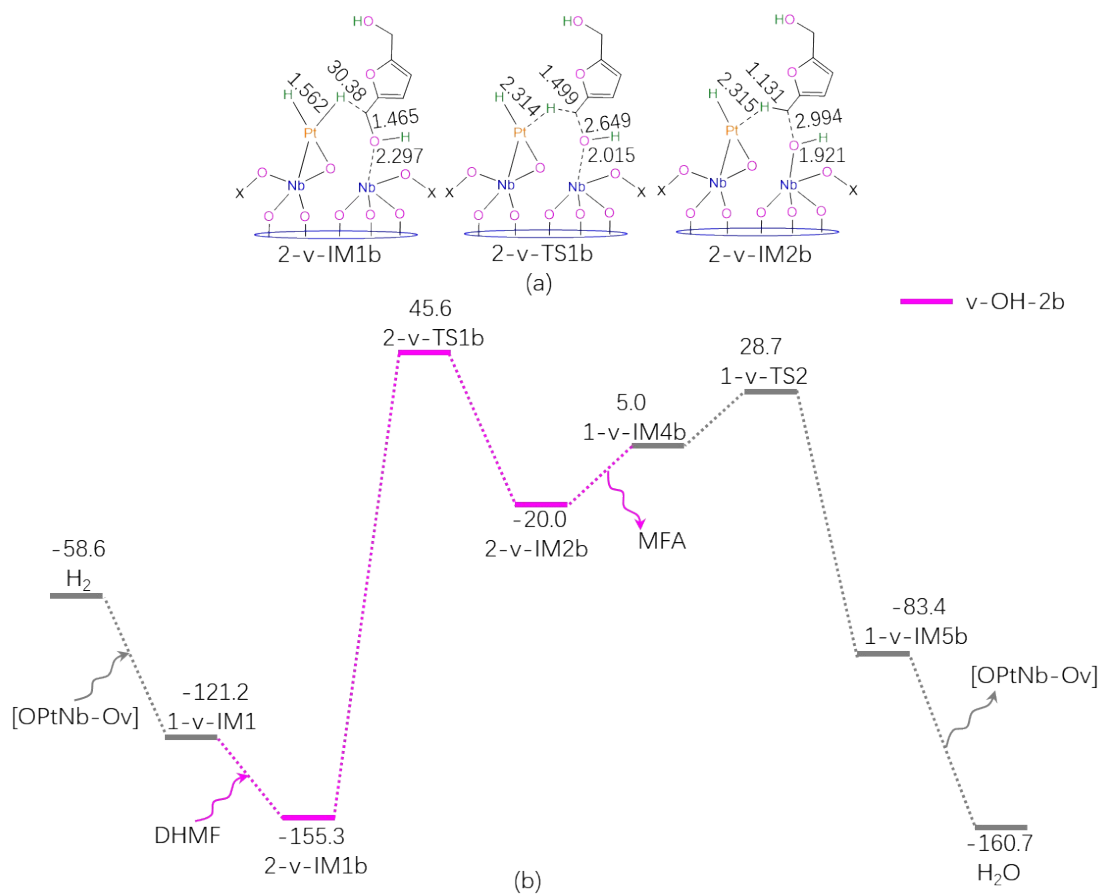


Fig. S13. The optimized geometric structures (a) and the schematic energy diagrams (b) with the Gibbs free energy (G_r , kJ mol⁻¹) relative to the reactants for catalytic hydrogenolysis of DHMF to 5-MFA over [OPtNb-Ov]. Bond lengths are reported in Å.

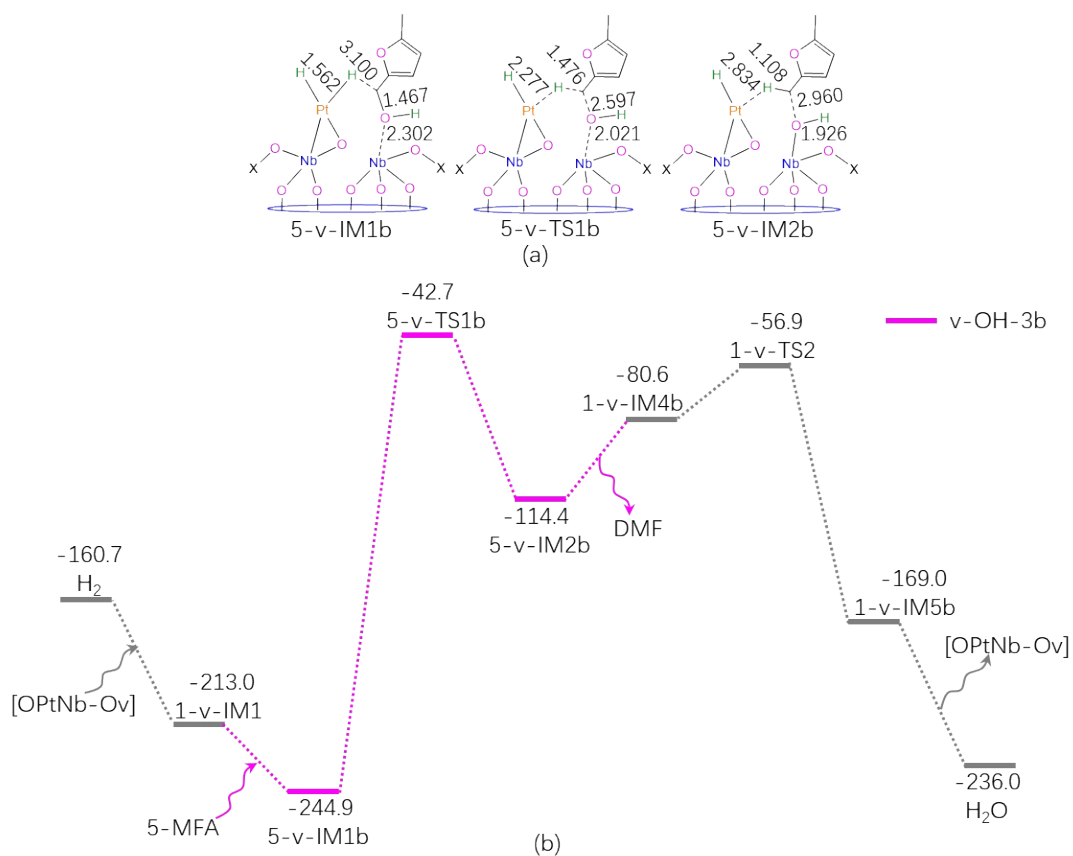
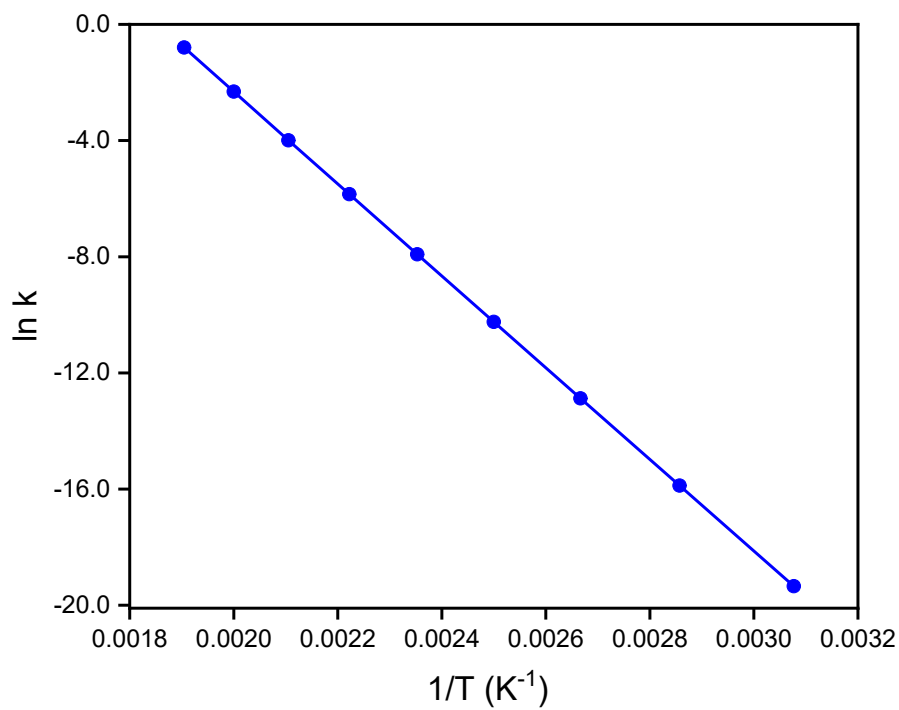
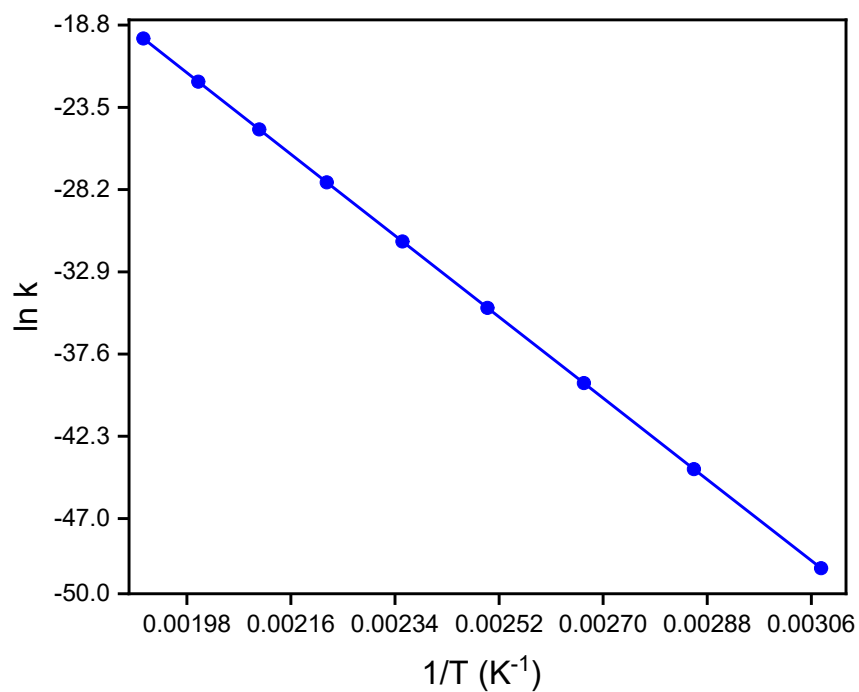


Fig. S14. The optimized geometric structures (a) and the schematic energy diagrams (b) with the Gibbs free energy (G_r , kJ mol⁻¹) relative to the reactants for catalytic hydrogenolysis of 5-MFA to DMF over [OPtNb-Ov]. Bond lengths are reported in Å.



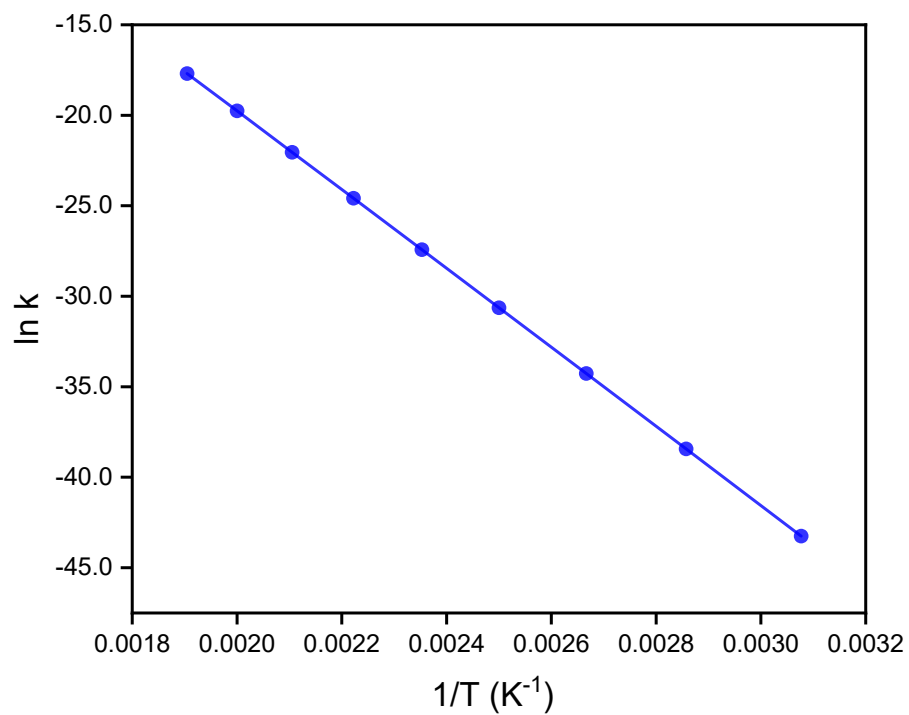
$$k_{\text{o-OH-1}} = 1.09 \times 10^{12} \exp(-142693 / RT)$$

Fig. S15. Arrhenius plots of rate constants for the crucial reaction step of 1-o-IM2 → 1-o-TS1 in the reaction of HMF-to-5-MF hydrogenolysis catalyzed by Pt₁/Nb₂O₅ in THF solution.



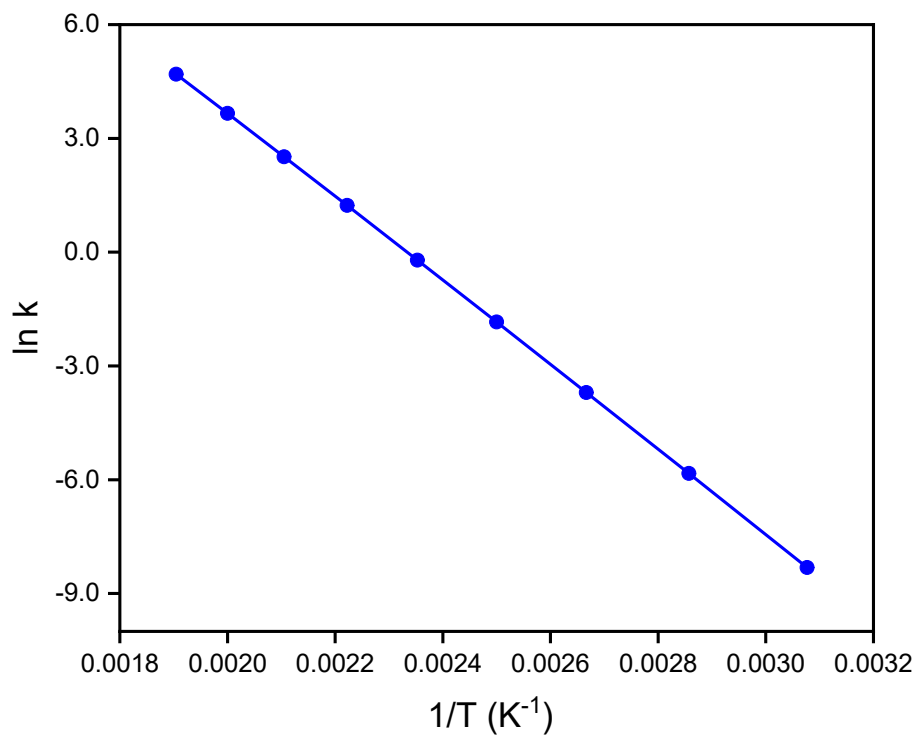
$$k_{\text{o-CHO-1}} = 7.29 \times 10^{12} \exp(-214742 / RT)$$

Fig. S16. Arrhenius plots of rate constants for the crucial reaction step of 3-o-IM4 → 3-o-TS1(before) in the reaction of HMF-to-DHMF hydrogenation catalyzed by Pt₁/Nb₂O₅ in THF solution.



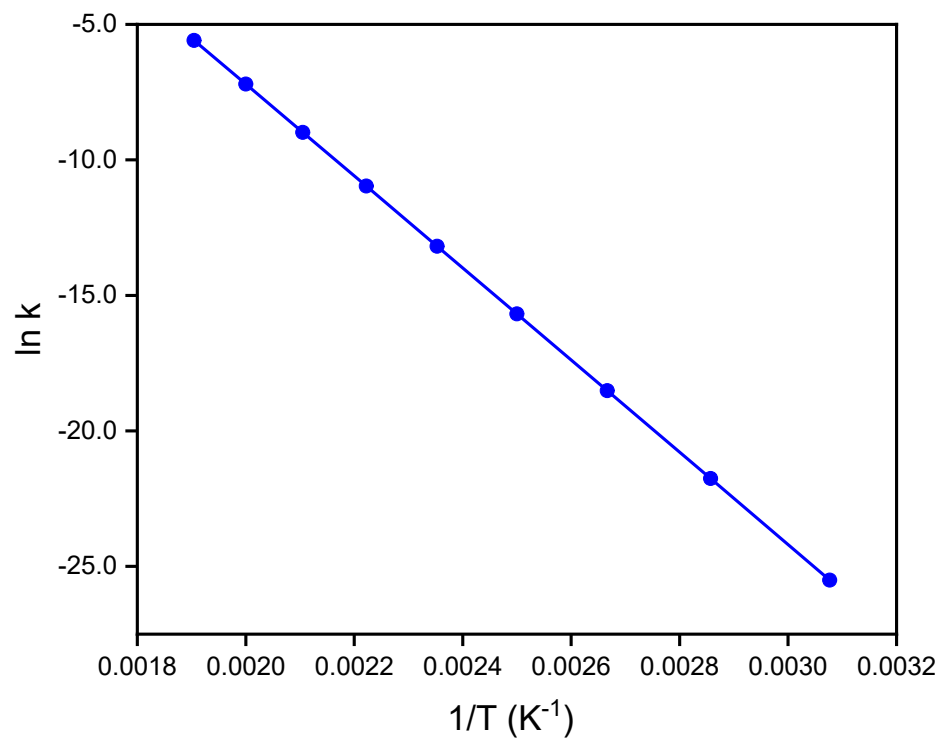
$$k_{o-6/7} = 1.31 \times 10^{12} \exp(-189518 / RT)$$

Fig. S17. Arrhenius plots of rate constants for the crucial reaction step of 1-o-IM6 + H₂ + 5-MF → 4-o-TS1 + H₂O in the reaction of HMF-to-DMF hydrogenation catalyzed by Pt₁/Nb₂O₅ in THF solution.



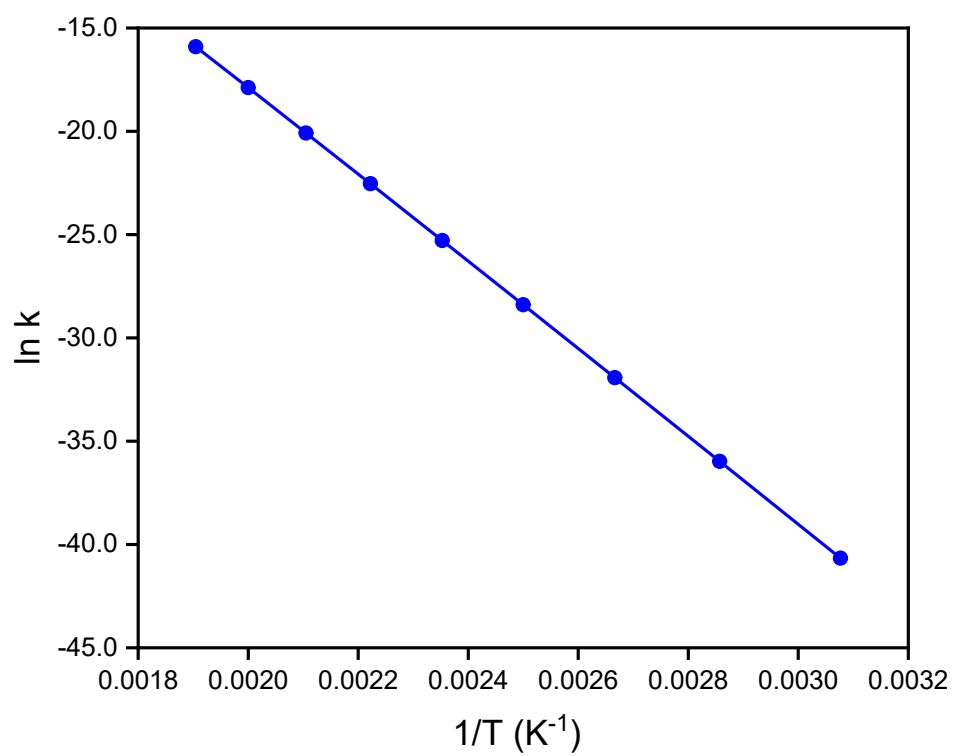
$$k_{v\text{-OH-1}} = 1.72 \times 10^{11} \exp(-92252 / RT)$$

Fig. S18. Arrhenius plots of rate constants for the crucial reaction step of 1-v-IM4 → 1-v-TS1 (before) in the reaction of HMF-to-5-MF hydrogenolysis catalyzed by Pt₁/Nb₂O₅-Ov in THF solution.



$$k_{v\text{-CHO-1}} = 4.25 \times 10^{11} \exp(-141229 / RT)$$

Fig. S19. Arrhenius plots of rate constants for the crucial reaction step of 3-v-IM2 → 3-v-TS1 in the reaction of HMF-to-DHMF hydrogenation catalyzed by Pt₁/Nb₂O₅-Ov in THF solution.



$$k_{v-6/7} = 3.85 \times 10^{10} \exp(-175608 / RT)$$

Fig. S20. Arrhenius plots of rate constants for the crucial reaction step of 1-v-IM4 + H₂ → 4-v-TS1 + H₂O in the reaction of HMF-to-DMF hydrogenation catalyzed by Pt₁/Nb₂O₅-Ov in THF solution.

Table S1. Over the 325 ~ 525 K temperature range, the rate constant ratios of $k_{v-OH-1}/k_{v-CHO-1}$, $k_{v-OH-1}/k_{v-6/7}$, $k_{o-OH-1}/k_{o-CHO-1}$, k_{v-OH-1}/k_{o-OH-1} , and $k_{v-CHO-1}/k_{o-CHO-1}$, as a function of temperature T .

T/K	$k_{v-OH-1}/k_{v-CHO-1}$	$k_{v-OH-1}/k_{v-6/7}$	$k_{o-OH-1}/k_{o-CHO-1}$	k_{v-OH-1}/k_{o-OH-1}	$k_{v-CHO-1}/k_{o-CHO-1}$	^a S_{v-OH-1}
325	3.01×10^7	1.12×10^{14}	5.69×10^{10}	2.02×10^7	3.81×10^{10}	100.00%
350	8.26×10^6	1.23×10^{13}	8.47×10^9	5.32×10^6	5.46×10^9	100.00%
375	2.69×10^6	1.83×10^{12}	1.63×10^9	1.68×10^6	1.01×10^9	100.00%
400	1.01×10^6	3.43×10^{11}	3.83×10^8	6.10×10^5	2.32×10^8	100.00%
425	4.24×10^5	7.86×10^{10}	1.07×10^8	2.50×10^5	6.33×10^7	100.00%
450	1.96×10^5	2.12×10^{10}	3.45×10^7	1.13×10^5	1.99×10^7	100.00%
475	9.85×10^4	6.56×10^9	1.25×10^7	5.56×10^4	7.08×10^6	100.00%
500	5.30×10^4	2.28×10^9	5.03×10^6	2.94×10^4	2.79×10^6	100.00%
525	3.02×10^4	8.79×10^8	2.21×10^6	1.65×10^4	1.20×10^6	100.00%

Notes:

S_{v-OH-1} represents the selectivity of the hydrogenolysis of HMF-to-5-MF, catalyzed by Pt₁/Nb₂O₅-Ov.

$$^a S_{v-OH-1} = \frac{k_{v-OH-1}}{k_{v-OH-1} + k_{v-CHO-1}} \times 100\%$$

Table S2. Zero-point vibrational energies (*ZPVE*, hartree), sum of electronic energies in the gas phase ($E_{t, g}$, hartree), thermal correction to Gibbs free energies (G_0 , hartree), sum of electronic energies in aqueous solution ($E_{t, l}$, hartree), sum of electronic and thermal Gibbs free energies (G_c , hartree) and relative Gibbs free energies ($G_{r, l}$, kJ mol⁻¹) of various species with respect to the reactants for the reaction of HMF-to-5-MF over Pt₁/Nb₂O₅.

Species	<i>ZPVE</i>	$E_{t, g}$	G_0	$E_{t, l}$	G_c	$G_{r, l}$
Pt ₁ /Nb ₂ O ₅	0.13282	-1428.02665	0.04171	-19700.54552	-19700.50381	
H ₂	0.01026	-1.16417	0.00885	-1.16444	-1.15559	
HMF	0.10966	-457.54293	0.09384	-457.55733	-457.46349	
H ₂ O	0.02089	-76.37869	0.02089	-76.38734	-76.36645	
DHMF	0.13286	-458.74163	0.11343	-458.75485	-458.64141	
5-MF	0.10505	-382.37249	0.09172	-382.38281	-382.29108	
MFA	0.12845	-383.56738	0.11075	-383.57626	-383.46551	
DMF	0.12311	-308.39298	0.11028	-308.39752	-308.28724	
[OPtNb] + H ₂ + HMF	0.25086	-1886.74011	0.12125	-20159.27913	-20159.15787	0.0
1-o-IM1	0.14717	-1429.27272	0.05569	-19701.78384	-19701.72815	
1-o-IM1 + HMF	0.25683	-1886.81566	0.14953	-20159.34117	-20159.19164	-88.7
1-o-IM2	0.25792	-1886.82083	0.14217	-20159.34797	-20159.20580	-125.8
1-o-TS1	0.25573	-1886.76801	0.14333	-20159.29182	-20159.14850	24.6
1-o-IM3	0.26029	-1886.84552	0.14872	-20159.35871	-20159.20999	-136.8
1-o-TS2	0.25507	-1886.80117	0.14271	-20159.32297	-20159.18026	-58.8
1-o-IM4	0.25703	-1886.81558	0.14435	-20159.35135	-20159.20700	-129.0
1-o-IM5	0.15297	-1504.45521	0.05969	-19776.95783	-19776.89814	
1-o-IM5 + 5-MF	0.25802	-1886.82771	0.15141	-20159.34063	-20159.18923	-82.3
1-o-TS3	0.15073	-1504.43680	0.05772	-19776.94624	-19776.88852	
1-o-TS3 + 5-MF	0.25579	-1886.80929	0.14944	-20159.32905	-20159.17960	-57.1
1-o-IM6	0.15677	-1504.46024	0.06088	-19777.00763	-19776.94675	
1-o-IM6 + 5-MF	0.26182	-1886.83273	0.15260	-20159.39043	-20159.23784	-210.0

Table S3. Zero-point vibrational energies (*ZPVE*, hartree), sum of electronic energies in the gas phase ($E_{t, g}$, hartree), thermal correction to Gibbs free energies (G_0 , hartree), sum of electronic energies in aqueous solution ($E_{t, l}$, hartree), sum of electronic and thermal Gibbs free energies (G_c , hartree) and relative Gibbs free energies ($G_{r, l}$, kJ mol⁻¹) of various species with respect to the reactants for the reaction of DHMF-to-5-MFA over Pt₁/N₂O₅.

Species	<i>ZPVE</i>	$E_{t, g}$	G_0	$E_{t, l}$	G_c	$G_{r, l}$
1-o-IM1	0.14717	-1429.27272	0.05569	-19701.78384	-19701.72815	
1-o-IM1 + DHMF - H ₂	0.26977	-1886.85019	0.16027	-20159.37425	-20159.21398	-147.3
2-o-IM1	0.28054	-1888.02013	0.17249	-20160.55374	-20160.38125	
2-o-IM1 - H ₂	0.27028	-1886.85596	0.16364	-20159.38930	-20159.22566	-178.0
2-o-TS1	0.27846	-1887.96855	0.18280	-20160.50806	-20160.32526	
2-o-TS1 - H ₂	0.26820	-1886.80438	0.17395	-20159.34362	-20159.16967	-31.0
2-o-IM2	0.28103	-1888.04840	0.17144	-20160.55252	-20160.38107	
2-o-IM2 - H ₂	0.27076	-1886.88423	0.16259	-20159.38808	-20159.22548	-177.5
2-o-TS2	0.27843	-1887.99467	0.16823	-20160.51674	-20160.34850	
2-o-TS2 - H ₂	0.26817	-1886.83050	0.15938	-20159.35229	-20159.19291	-92.0
2-o-IM3	0.28304	-1888.03733	0.16507	-20160.56424	-20160.39917	
2-o-IM3 - H ₂	0.27278	-1886.87316	0.15622	-20159.39980	-20159.24358	-225.0
1-o-IM5	0.15297	-1504.45521	0.05969	-19776.95783	-19776.89814	
1-o-IM5 - H ₂ + 5-MFA	0.27116	-1886.85842	0.16159	-20159.36965	-20159.20806	-131.8
1-o-TS3	0.15073	-1504.43680	0.05772	-19776.94624	-19776.88852	
1-o-TS3 - H ₂ + 5-MFA	0.26892	-1886.84001	0.15962	-20159.35806	-20159.19844	-106.5
1-o-IM6	0.15677	-1504.46024	0.06088	-19777.00763	-19776.94675	
1-o-IM6 - H ₂ + 5-MFA	0.27496	-1886.86345	0.16278	-20159.41945	-20159.25667	-259.4

Table S4. Zero-point vibrational energies (*ZPVE*, hartree), sum of electronic energies in the gas phase ($E_{t, g}$, hartree), thermal correction to Gibbs free energies (G_0 , hartree), sum of electronic energies in aqueous solution ($E_{t, l}$, hartree), sum of electronic and thermal Gibbs free energies (G_c , hartree) and relative Gibbs free energies ($G_{r, l}$, kJ mol⁻¹) of various species with respect to the reactants for the reaction of 5-MFA-to-DMF over Pt₁/N₂O₅.

Species	<i>ZPVE</i>	$E_{t, g}$	G_0	$E_{t, l}$	G_c	$G_{r, l}$
1-o-IM1	0.14717	-1429.27272	0.05569	-19701.78384	-19701.72815	
1-o-IM1 + MFA - 2H ₂ + H ₂ O	0.27598	-1886.89046	0.16962	-20159.41855	-20159.24893	-239.1
5-o-IM1	0.27506	-1812.84456	0.16854	-20085.37937	-20085.21083	
5-o-IM1 - 2H ₂ + H ₂ O	0.27543	-1886.89492	0.17173	-20159.43783	-20159.26610	-284.2
5-o-TS1	0.27305	-1812.79530	0.18065	-20085.33603	-20085.15539	
5-o-TS1 - 2H ₂ + H ₂ O	0.27342	-1886.84565	0.18383	-20159.39449	-20159.21066	-138.6
5-o-IM2	0.27653	-1812.87061	0.16778	-20085.39008	-20085.22229	
5-o-IM2 - 2H ₂ + H ₂ O	0.27690	-1886.92096	0.17097	-20159.44853	-20159.27756	-314.2
5-o-TS2	0.27359	-1812.81994	0.16228	-20085.34352	-20085.18124	
5-o-TS2 - 2H ₂ + H ₂ O	0.27396	-1886.87029	0.16547	-20159.40197	-20159.23650	-206.5
5-o-IM3	0.27829	-1812.86787	0.16474	-20085.39756	-20085.23282	
5-o-IM3 - 2H ₂ + H ₂ O	0.27866	-1886.91822	0.16793	-20159.45601	-20159.28808	-341.9
1-o-IM5	0.15297	-1504.45521	0.05969	-19776.95783	-19776.89814	
1-o-IM5 - 2H ₂ + H ₂ O + DMF	0.27645	-1886.89854	0.17315	-20159.41381	-20159.24065	-217.4
1-o-TS3	0.15073	-1504.43680	0.05772	-19776.94624	-19776.88852	
1-o-TS3 - 2H ₂ + H ₂ O + DMF	0.27421	-1886.88013	0.17119	-20159.40222	-20159.23103	-192.1
1-o-IM6	0.15677	-1504.46024	0.06088	-19777.00763	-19776.94675	
1-o-IM6 - 2H ₂ + H ₂ O + DMF	0.28025	-1886.90357	0.17434	-20159.46361	-20159.28926	-345.0

Table S5. Zero-point vibrational energies (*ZPVE*, hartree), sum of electronic energies in the gas phase ($E_{t, g}$, hartree), thermal correction to Gibbs free energies (G_0 , hartree), sum of electronic energies in aqueous solution ($E_{t, l}$, hartree), sum of electronic and thermal Gibbs free energies (G_c , hartree) and relative Gibbs free energies ($G_{r, l}$, kJ/mol) of various species with respect to the reactants for the reaction of HMF-to-DHMF over Pt₁/N₂O₅.

Species	<i>ZPVE</i>	$E_{t, g}$	G_0	$E_{t, l}$	G_c	$G_{r, l}$
3-o-IM1	0.24283	-1885.60945	0.14391	-20158.16332	-20158.01940	
3-o-IM1 + H ₂	0.25310	-1886.77362	0.15277	-20159.32776	-20159.17499	-44.9
3-o-IM2	0.25449	-1886.79198	0.12720	-20159.31429	-20159.18708	-76.7
3-o-TS1	0.25435	-1886.73793	0.14096	-20159.26397	-20159.12301	91.5
3-o-IM3	0.26276	-1886.81990	0.15027	-20159.35483	-20159.20456	-122.6
3-o-TS2	0.25964	-1886.78632	0.14759	-20159.32599	-20159.17840	-53.9
3-o-IM4	0.26570	-1886.81137	0.14999	-20159.37856	-20159.22857	-185.6

Table S6. Zero-point vibrational energies (*ZPVE*, hartree), sum of electronic energies in the gas phase ($E_{t, g}$, hartree), thermal correction to Gibbs free energies (G_0 , hartree), sum of electronic energies in aqueous solution ($E_{t, l}$, hartree), sum of electronic and thermal Gibbs free energies (G_c , hartree) and relative Gibbs free energies ($G_{r, l}$, kJ mol⁻¹) of various species with respect to the reactants for the reaction of 5-MF-to-5-MFA over Pt₁/N₂O₅.

Species	<i>ZPVE</i>	$E_{t, g}$	G_0	$E_{t, l}$	G_c	$G_{r, l}$
4-o-IM1	0.23838	-1810.44885	0.12315	-20082.97315	-20082.85000	
4-o-IM1 + H ₂ O	0.25927	-1886.82754	0.14404	-20159.36048	-20159.21644	-153.8
4-o-IM2	0.25004	-1811.62109	0.12772	-20084.14228	-20084.01456	
4-o-IM2 + H ₂ O	0.26067	-1886.83561	0.13975	-20159.36517	-20159.22542	-177.3
- H ₂						
4-o-TS1	0.24967	-1811.56505	0.14030	-20084.09138	-20083.95107	
4-o-TS1 + H ₂ O	0.26030	-1886.77957	0.15234	-20159.31427	-20159.16193	-10.7
- H ₂						
4-o-IM3	0.25912	-1811.64596	0.14972	-20084.18186	-20084.03215	
4-o-IM3 + H ₂ O	0.26975	-1886.86049	0.16175	-20159.40476	-20159.24301	-223.5
- H ₂						
4-o-TS2	0.25568	-1811.61347	0.14365	-20084.15139	-20084.00775	
4-o-TS2 + H ₂ O	0.26631	-1886.82800	0.15568	-20159.37429	-20159.21861	-159.5
- H ₂						
4-o-IM4	0.26114	-1811.64516	0.14333	-20084.19275	-20084.04942	
4-o-IM4 + H ₂ O	0.27177	-1886.85969	0.15537	-20159.41565	-20159.26028	-268.9
- H ₂						

Table S7. Zero-point vibrational energies (*ZPVE*, hartree), sum of electronic energies in the gas phase ($E_{t, g}$, hartree), thermal correction to Gibbs free energies (G_0 , hartree), sum of electronic energies in aqueous solution ($E_{t, l}$, hartree), sum of electronic and thermal Gibbs free energies (G_c , hartree) and relative Gibbs free energies ($G_{r, l}$, kJ mol⁻¹) of various species with respect to the reactants for the reaction of HMF-to-5-MF over Pt₁/Nb₂O₅-Ov.

Species	<i>ZPVE</i>	$E_{t, g}$	G_0	$E_{t, l}$	G_c	$G_{r, l}$
Pt ₁ /Nb ₂ O ₅ -Ov	0.23998	-1810.96430	0.11932	-20084.18067	-20084.06135	0.0
1-v-IM1	0.13710	-1353.48996	0.04777	-19626.66946	-19626.62169	
1-v-IM1 + HMF	0.24677	-1811.03289	0.14161	-20084.22679	-20084.08517	-62.6
1-v-IM2	0.24991	-1811.04142	0.13783	-20084.23334	-20084.09551	-89.7
1-v-TS1	0.24696	-1810.98391	0.13594	-20084.19400	-20084.05806	8.6
1-v-IM3	0.24656	-1811.02943	0.13655	-20084.20813	-20084.07158	-26.9
1-v-TS2	0.24373	-1811.01351	0.13477	-20084.20316	-20084.06840	-18.5
1-v-IM4	0.24931	-1811.07206	0.13911	-20084.27606	-20084.13695	-198.5
1-v-IM5	0.22396	-1734.66715	0.11374	-20007.86176	-20007.74802	
1-v-IM5 + H ₂ O	0.24486	-1811.04584	0.13462	-20084.24910	-20084.11447	-139.5
1-v-TS3	0.22254	-1734.64661	0.11333	-20007.84750	-20007.73417	
1-v-TS3 + H ₂ O	0.24344	-1811.02530	0.13422	-20084.23484	-20084.10062	-103.1
1-v-IM6	0.22654	-1734.63159	0.09796	-20007.83556	-20007.73760	
1-v-IM6 + H ₂ O	0.24743	-1811.01028	0.11885	-20084.22290	-20084.10405	-112.1

Table S8. Zero-point vibrational energies (*ZPVE*, hartree), sum of electronic energies in the gas phase ($E_{t, g}$, hartree), thermal correction to Gibbs free energies (G_0 , hartree), sum of electronic energies in aqueous solution ($E_{t, l}$, hartree), sum of electronic and thermal Gibbs free energies (G_c , hartree) and relative Gibbs free energies ($G_{r, l}$, kJ mol⁻¹) of various species with respect to the reactants for the reaction of DHMF-to-5-MFA over Pt₁/N₂O₅-Ov.

Species	<i>ZPVE</i>	$E_{t, g}$	G_0	$E_{t, l}$	G_c	$G_{r, l}$
1-v-IM1	0.13710	-1353.48996	0.04777	-19626.66946	-19626.62169	
1-v-IM1+ DHMF - H ₂	0.25970	-1811.06743	0.15235	-20084.25986	-20084.10751	-121.2
2-v-IM1	0.27221	-1812.24062	0.17053	-20085.43976	-20085.26922	
2-v-IM1 - H ₂	0.26194	-1811.07645	0.16168	-20084.27531	-20084.11363	-137.3
2-v-TS1	0.27035	-1812.20044	0.16310	-20085.39707	-20085.23397	
2-v-TS1 - H ₂	0.26009	-1811.03628	0.15424	-20084.23263	-20084.07838	-44.7
2-v-IM2	0.26970	-1812.22648	0.15542	-20085.41689	-20085.26148	
2-v-IM2 - H ₂	0.25943	-1811.06232	0.14656	-20084.25245	-20084.10589	-116.9
2-v-TS2	0.26633	-1812.20389	0.15303	-20085.40207	-20085.24904	
2-v-TS2 - H ₂	0.25607	-1811.03972	0.14418	-20084.23763	-20084.09345	-84.3
2-v-IM3	0.27136	-1812.26755	0.14664	-20085.45933	-20085.31269	
2-v-IM3 - H ₂	0.26110	-1811.10338	0.13779	-20084.29489	-20084.15710	-251.4
2-v-IM4	0.24657	-1735.85981	0.13609	-20009.06346	-20008.92737	
2-v-IM4 - H ₂ + H ₂ O	0.25720	-1811.07433	0.14812	-20084.28635	-20084.13823	-201.8
2-v-TS3	0.24502	-1735.84192	0.14311	-20009.05560	-20008.91250	
2-v-TS3 - H ₂ + H ₂ O	0.25565	-1811.05644	0.15514	-20084.27850	-20084.12335	-162.8
2-v-IM5	0.24894	-1735.82748	0.11840	-20009.03775	-20008.91934	
2-v-IM5 - H ₂ + H ₂ O	0.25957	-1811.04200	0.13044	-20084.26054	-20084.13020	-180.8

Table S9. Zero-point vibrational energies (*ZPVE*, hartree), sum of electronic energies in the gas phase ($E_{t, g}$, hartree), thermal correction to Gibbs free energies (G_0 , hartree), sum of electronic energies in aqueous solution ($E_{t, l}$, hartree), sum of electronic and thermal Gibbs free energies (G_c , hartree) and relative Gibbs free energies ($G_{r, l}$, kJ mol⁻¹) of various species with respect to the reactants for the reaction of 5-MFA-to-DMF over Pt₁/N₂O₅-Ov.

Species	<i>ZPVE</i>	$E_{t, g}$	G_0	$E_{t, l}$	G_c	$G_{r, l}$
1-v-IM1	0.13710	-1353.48996	0.04777	-19626.66946	-19626.62169	
1-v-IM1 + MFA - 2H ₂ + H ₂ O	0.26592	-1811.10769	0.16171	-20084.30417	-20084.14246	-213.0
5-v-IM1	0.26786	-1737.06550	0.16308	-20010.26165	-20010.09857	
5-v-IM1 - 2H ₂ + H ₂ O	0.26822	-1811.11585	0.16627	-20084.32010	-20084.15383	-242.8
5-v-TS1	0.26352	-1737.00802	0.14025	-20010.20472	-20010.06447	
5-v-TS1 - 2H ₂ + H ₂ O	0.26389	-1811.05838	0.14343	-20084.26317	-20084.11974	-153.3
5-v-IM2	0.26504	-1737.06214	0.15689	-20010.24015	-20010.08326	
5-v-IM2 - 2H ₂ + H ₂ O	0.26540	-1811.11249	0.16008	-20084.29860	-20084.13853	-202.6
5-v-TS2	0.26211	-1737.03566	0.16227	-20010.23449	-20010.07223	
5-v-TS2 - 2H ₂ + H ₂ O	0.26247	-1811.08602	0.16545	-20084.29295	-20084.12750	-173.7
5-v-IM3	0.26708	-1737.09194	0.15746	-20010.29991	-20010.14245	
5-v-IM3 - 2H ₂ + H ₂ O	0.26744	-1811.14230	0.16064	-20084.35836	-20084.19772	-358.0
5-v-IM4	0.24109	-1660.68036	0.13346	-19933.87855	-19933.74510	
5-v-IM4 - 2H ₂ + 2H ₂ O	0.26234	-1811.10940	0.15753	-20084.32434	-20084.16682	-276.9
5-v-TS3	0.24061	-1660.66094	0.13840	-19933.87314	-19933.73474	
5-v-TS3 - 2H ₂ + 2H ₂ O	0.26186	-1811.08998	0.16247	-20084.31893	-20084.15646	-249.7
5-v-IM5	0.24441	-1660.65716	0.12977	-19933.86685	-19933.73708	
5-v-IM5 - 2H ₂ + 2H ₂ O	0.26566	-1811.08620	0.15384	-20084.31264	-20084.15880	-255.9

Table S10. Zero-point vibrational energies (*ZPVE*, hartree), sum of electronic energies in the gas phase ($E_{t, g}$, hartree), thermal correction to Gibbs free energies (G_0 , hartree), sum of electronic energies in aqueous solution ($E_{t, 1}$, hartree), sum of electronic and thermal Gibbs free energies (G_c , hartree) and relative Gibbs free energies ($G_{r, 1}$, kJ mol⁻¹) of various species with respect to the reactants for the reaction of HMF-to-DHMF over Pt₁/N₂O₃-Ov.

Species	<i>ZPVE</i>	$E_{t, g}$	G_0	$E_{t, 1}$	G_c	$G_{r, 1}$
3-v-IM1	0.23209	-1809.84329	0.11863	-20083.04042	-20082.92179	
3-v-IM1 + H ₂	0.24235	-1811.00745	0.12748	-20084.20486	-20084.07738	-42.1
3-v-IM2	0.24584	-1811.01400	0.13276	-20084.21468	-20084.08192	-54.0
3-v-TS1	0.24155	-1810.95068	0.13302	-20084.15652	-20084.02349	99.4
3-v-IM3	0.25112	-1811.02937	0.13891	-20084.22636	-20084.08745	-68.5
3-v-TS2	0.25107	-1811.00885	0.14334	-20084.20369	-20084.06035	2.6
3-v-IM4	0.25580	-1811.03453	0.14606	-20084.24276	-20084.09671	-92.8

Table S11. Zero-point vibrational energies (*ZPVE*, hartree), sum of electronic energies in the gas phase ($E_{t, g}$, hartree), thermal correction to Gibbs free energies (G_0 , hartree), sum of electronic energies in aqueous solution ($E_{t, l}$, hartree), sum of electronic and thermal Gibbs free energies (G_c , hartree) and relative Gibbs free energies ($G_{r, l}$, kJ mol^{-1}) of various species with respect to the reactants for the reaction of 5-MF-to-5-MFA over $\text{Pt}_1/\text{N}_2\text{O}_5\text{-Ov}$.

Species	<i>ZPVE</i>	$E_{t, g}$	G_0	$E_{t, l}$	G_c	$G_{r, l}$
4-v-IM1	0.22749	-1734.66938	0.11909	-20007.86522	-20007.74613	
4-v-IM1 + H ₂ O	0.24838	-1811.04807	0.13998	-20084.25256	-20084.11258	-134.5
4-v-IM2	0.24019	-1735.84043	0.13165	-20009.03840	-20008.90675	
4-v-IM2 + H ₂ O	0.25082	-1811.05495	0.14369	-20084.26129	-20084.11760	-147.7
- H ₂						
4-v-TS1	0.23934	-1735.78709	0.13210	-20008.98376	-20008.85165	
4-v-TS1 + H ₂ O	0.24997	-1811.00162	0.14414	-20084.20665	-20084.06251	-3.1
- H ₂						
4-v-IM3	0.24716	-1735.85665	0.13974	-20009.04529	-20008.90555	
4-v-IM3 + H ₂ O	0.25779	-1811.07117	0.15178	-20084.26818	-20084.11640	-144.5
- H ₂						
4-v-TS2	0.24501	-1735.83663	0.13836	-20009.02952	-20008.89116	
4-v-TS2 + H ₂ O	0.25564	-1811.05115	0.15039	-20084.25241	-20084.10202	-106.8
- H ₂						
4-v-IM4	0.25075	-1735.86105	0.14596	-20009.07080	-20008.92483	
4-v-IM4 + H ₂ O	0.26138	-1811.07557	0.15800	-20084.29369	-20084.13569	-195.2
- H ₂						