Supporting Information:

Theoretical insight into the deoxygenation molecular mechanism of butyric acid catalyzed by $Ni_{12}P_6$ cluster

Shuai Fu[a], Zhao-Meng Wang[a], Li-Juan Liu[a], Ting-Hao Liu[a], Dan Li[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 85464466; Telephone: 86 28 85464466

Catalysis Science & Technology

content

i. **NOTES:** Evaluation of rate constants……..…..S1

ii. **Figure S1:** Arrhenius plots of rate constants for the crucial reaction step of $Ni_{12}P_6$ + C_3H_7COOH → 2-TS2 in the reaction of C_3H_7COOH → C_3H_8 + CO_2 (RP-CO_2) catalyzed over $Ni_{12}P_6$ cluster. S2

iii. **Figure S2:** Arrhenius plots of rate constants for the crucial reaction step of 3-IM2 + C_3H_7COOH → 3-TS3 in the reaction of C_3H_7COOH + H_2 → C_3H_8 + H_2O + CO (RP-CO-hyde) catalyzed over $Ni_{12}P_6$ cluster. S3

iv. **Figure S3:** Arrhenius plots of rate constants for the crucial reaction step of $Ni_{12}P_6$ + C_3H_7COOH → 7-TS3 + CO + H_2O in the reaction of C_3H_7COOH + H_2 → C_3H_8 + CO + H_2O (RP-CO-ene) catalyzed over $Ni_{12}P_6$ cluster. S4

v. **Figure S4:** Arrhenius plots of rate constants for the crucial reaction step of 4-IM5 + CO → 4-TS1 in the reaction of C_3H_7CHO → C_3H_8 + CO catalyzed over $Ni_{12}P_6$ cluster. S5

vi. **Figure S5:** Arrhenius plots of rate constants for the crucial reaction step of 3-IM2 + C_3H_7CHO → 8-TS2 in the reaction of C_3H_7CHO + H_2 → $C_3H_7CH_2OH$ catalyzed over $Ni_{12}P_6$ cluster. S6

vii. **Figure S6:** Arrhenius plots of rate constants for the crucial reaction step of 3-IM2 + $C_3H_7CH_2OH$ → 9-TS2 in the reaction of $C_3H_7CH_2OH$ +H_2 → C_4H_8 + H_2O catalyzed over $Ni_{12}P_6$ cluster. S7

viii. **Figure S7:** Arrhenius plots of rate constants for the crucial reaction step of 10-IM4 + H_2O → 10-TS1 in the reaction of $C_3H_7CH_2OH$ → $CH_3CH_2CH{=}CH_2$ + H_2O catalyzed over $Ni_{12}P_6$ cluster. S8

ix. **Table S1:** Sum of electronic energies (E_t, hartree), free energy (G_0, hartree), relative energies (G_r, kJ mol^{-1}) and relative energies considering 10^{-5} atm pressure of CO_2 ［G_r(CO_2↑), kJ mol^{-1}] of various species with respect to the reactants for the reaction of $CH_3CH_2CH_2COOH$ → $CH_3CH_2CH_3$ + CO_2 catalyzed over $Ni_{12}P_6$ at GGA-PBE/DNP, DSPP. S9

x. **Table S2:** Sum of electronic energies (E_t, hartree), free energy (G_0, hartree) and relative energies (G_r, kJ mol^{-1}) of various species with respect to the reactants for the reaction of $CH_3CH_2CH_2COOH$ + H_2 → $CH_3CH_2CH_2CHO$ + H_2O catalyzed over $Ni_{12}P_6$ at GGA-PBE/DNP, DSPP. S10

xi. **Table S3:** Sum of electronic energies (E_t, hartree), free energy (G_0, hartree), relative energies (G_r, kJ mol^{-1}) and relative energies considering 10^{-5} atm pressure of CO ［G_r(CO↑), kJ mol^{-1}] of various species with respect to the reactants for the reaction of $CH_3CH_2CH_2CHO$ → $CH_3CH_2CH_3$ + CO catalyzed over $Ni_{12}P_6$ at GGA-PBE/DNP, DSPP. S12

xii. **Table S4:** Sum of electronic energies (E_t, hartree), free energy (G_0, hartree), relative energies (G_r, kJ mol^{-1}) and relative energies considering 10^{-5} atm pressure of CO (G_r (CO↑), kJ mol^{-1}) of various species with respect to the reactants for the reaction of $CH_3CH_2CH_2COOH$ → $CH_3CH_2CH_2OH$ + CO catalyzed over $Ni_{12}P_6$ at GGA-PBE/DNP, DSPP. S13

xiii. **Table S5:** Sum of electronic energies (E_t, hartree), free energy (G_0, hartree), relative energies (G_r, kJ mol^{-1}) and relative energies considering 10^{-5} atm pressure of CO (G_r (CO↑), kJ mol^{-1}) of various species with respect to the reactants for the reaction of $CH_3CH_2CH_2COOH$ → $CH_3CH_2CH_3$ + CO + H_2O catalyzed over $Ni_{12}P_6$ at GGA-PBE/DNP, DSPP. S14

xiv. **Table S6:** Sum of electronic energies (E_t, hartree), free energy (G_0, hartree), relative energies (G_r, kJ mol^{-1}) and relative energies considering 10^{-5} atm pressure of CO (G_r (CO↑), kJ mol^{-1}) of various species with respect to the reactants for the reaction of $CH_3CH_2CH_2OH$ + H_2 → $CH_3CH_2CH_3$ + H_2O catalyzed over $Ni_{12}P_6$ at GGA-PBE/DNP, DSPP. S15

xv. **Table S7:** Sum of electronic energies (E_t, hartree), free energy (G_0, hartree), relative energies (G_r, kJ mol^{-1}) and relative energies considering 10^{-5} atm pressure of CO (G_r (CO↑), kJ mol^{-1}) of various species with respect to the reactants for the reaction of $CH_3CH_2CH_2OH$ → $CH_3CH{=}CH_2$ + H_2O catalyzed over $Ni_{12}P_6$ at GGA-

PBE/DNP, DSPP. S16

xvi. **Table S8:** Sum of electronic energies (E_t, hartree), free energy (G_0, hartree), relative energies (G_r, kJ mol^{-1}) and relative energies considering 10^{-5} atm pressure of CO (G_r (CO↑), kJ mol^{-1}) of various species with respect to the reactants for the reaction of $CH_3CH_2CH_2OH \rightarrow CH_3CH{=}CH_2 + H_2O$ catalyzed over $Ni_{12}P_6$ at GGA-PBE/DNP, DSPP. S17

xvii. **Table S9:** Sum of electronic energies (E_t, hartree), free energy (G_0, hartree), relative energies (G_r, kJ mol^{-1}) and relative energies considering 10^{-5} atm pressure of CO (G_r (CO↑), kJ mol^{-1}) of various species with respect to the reactants for the reaction of $CH_3CH{=}CH_2 + H_2 \rightarrow CH_3CH_2CH_3$ catalyzed over $Ni_{12}P_6$ at GGA-PBE/DNP, DSPP. S18

xviii. **Table S10:** Sum of electronic energies (E_t, hartree), free energy (G_0, hartree) and relative energies (G_r, kJ mol^{-1}) of various species with respect to the reactants for the reaction of $CH_3CH_2CH_2CHO + H_2 \rightarrow CH_3CH_2CH_2CH_2OH$ catalyzed over $Ni_{12}P_6$ at GGA-PBE/DNP, DSPP. S19

xix. **Table S11:** Sum of electronic energies (E_t, hartree), free energy (G_0, hartree) and relative energies (G_r, kJ mol^{-1}) of various species with respect to the reactants for the reaction of $CH_3CH_2CH_2CH_2OH + H_2 \rightarrow CH_3CH_2CH_2CH_3 + H_2O$ catalyzed over $Ni_{12}P_6$ at GGA-PBE/DNP, DSPP. S20

xx. **Table S12:** Sum of electronic energies (E_t, hartree), free energy (G_0, hartree) and relative energies (G_r, kJ mol^{-1}) of various species with respect to the reactants for the reaction of $CH_3CH_2CH_2CH_2OH \rightarrow CH_3CH_2CH{=}CH_2 + H_2O$ catalyzed over $Ni_{12}P_6$ at GGA-PBE/DNP, DSPP. S21

xxi. **Table S13:** Sum of electronic energies (E_t, hartree), free energy (G_0, hartree) and relative energies (G_r, kJ mol^{-1}) of various species with respect to the reactants for the reaction of $CH_3CH_2CH{=}CH_2 + H_2 \rightarrow CH_3CH_2CH_2CH_3$ catalyzed over $Ni_{12}P_6$ at GGA-PBE/DNP, DSPP. S22

NOTES: Evaluation of rate constants:

The rate constants k(T) were evaluated according to conventional transition state theory k'(T), including the tunneling correction κ(T) based on Wigner's formulation as follows:[1,2]

$$k' = \frac{k_B T}{hc^0} \bullet e^{\frac{-\Delta G^{\neq}}{RT}} \qquad (i)$$

$$\kappa\ (T) = 1 + \frac{1}{24}\left|\frac{w^{\neq} h}{k_B T}\right|^2$$

$$k = \kappa\ (T) \times k' \qquad (iii)$$

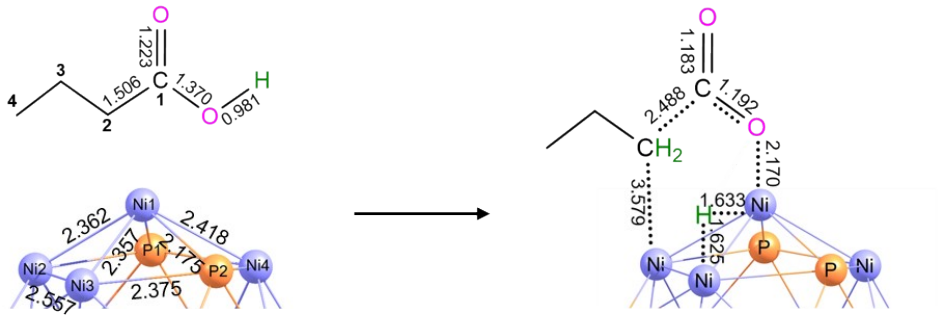
$$\ln k = -\frac{E_a}{RT} + \ln A \qquad (iv)$$

$$k = A \bullet e^{\frac{-E_a}{RT}} \qquad (v)$$

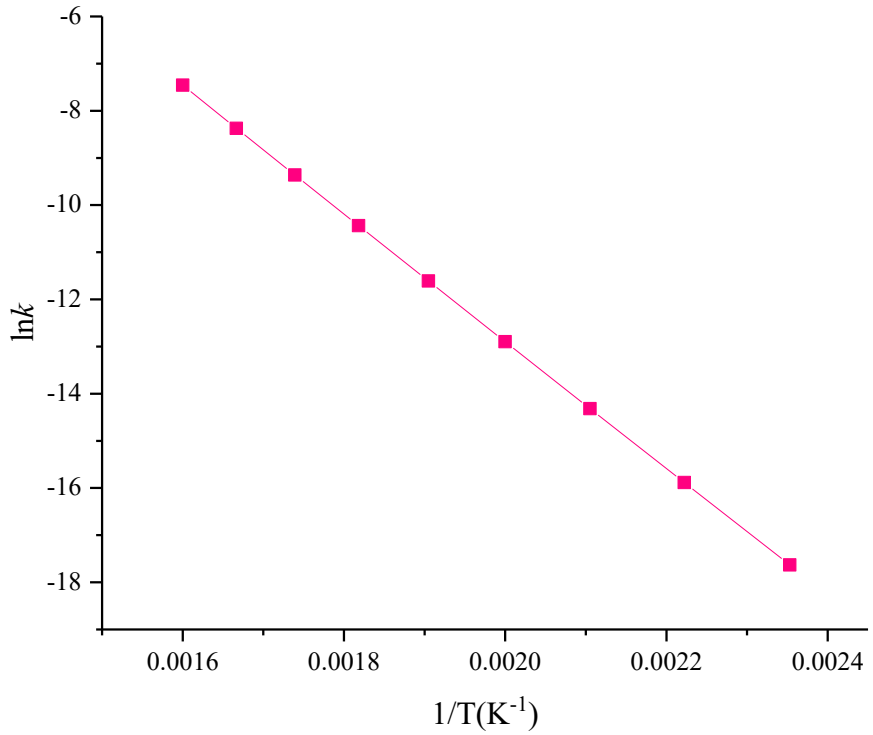
where k_B is Boltzmann's constant, T is the absolute temperature, h is Planck's constant, c^0 is the standard concentration (1 mol dm^{-3}), $\Delta G^{\neq}$ is the activation Gibbs free energy barrier and $\omega^{\neq}$ is the imaginary frequency of the T_S.

References:

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

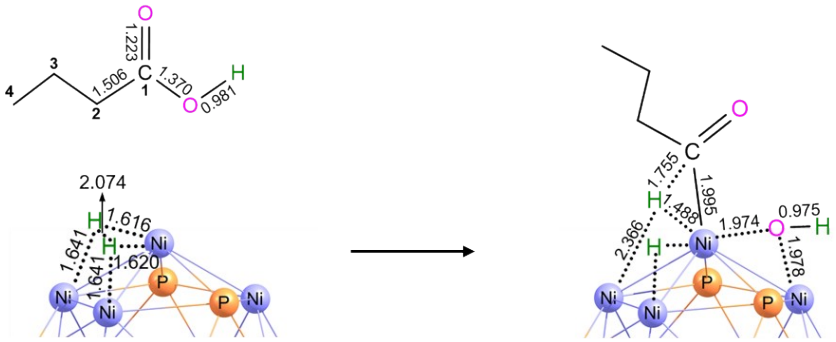


$Ni_{12}P_6 + C_3H_7COOH$ 2-TS2

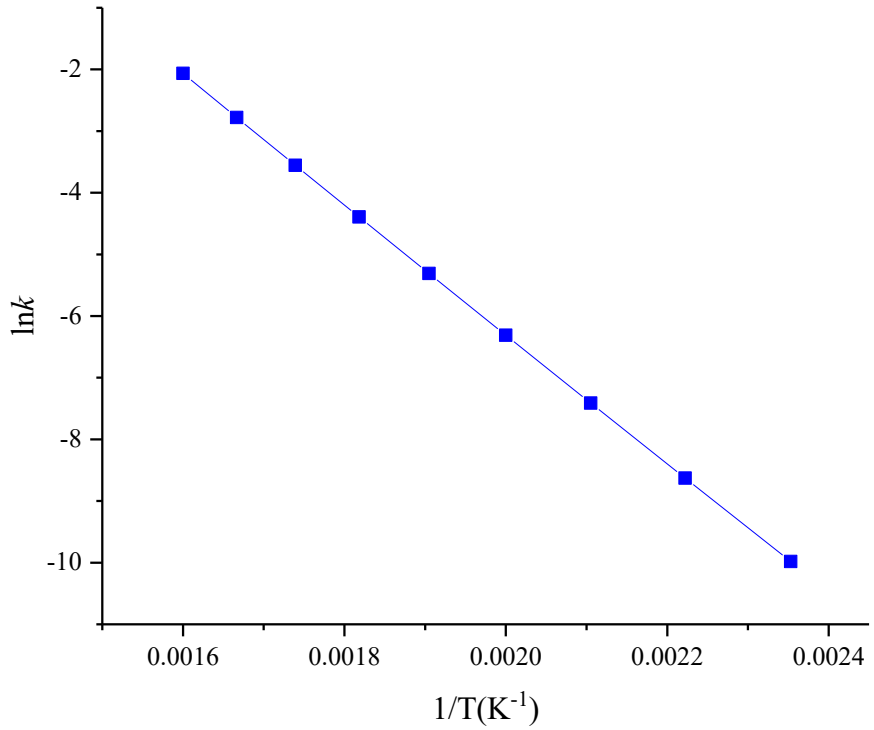


$$k = 1.39 \times 10^{6} \exp(- 112347/RT)$$

Figure S1: Arrhenius plots of rate constants for the crucial reaction step of $Ni_{12}P_6$ + C_3H_7COOH → 2-TS2 in the reaction of C_3H_7COOH → C_3H_8 + CO_2 (RP-CO_2) catalyzed over $Ni_{12}P_6$ cluster.

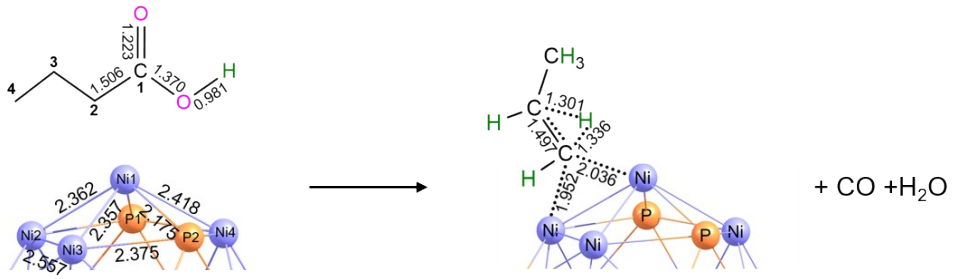


3-IM2 + C_3H_7COOH 3-TS3

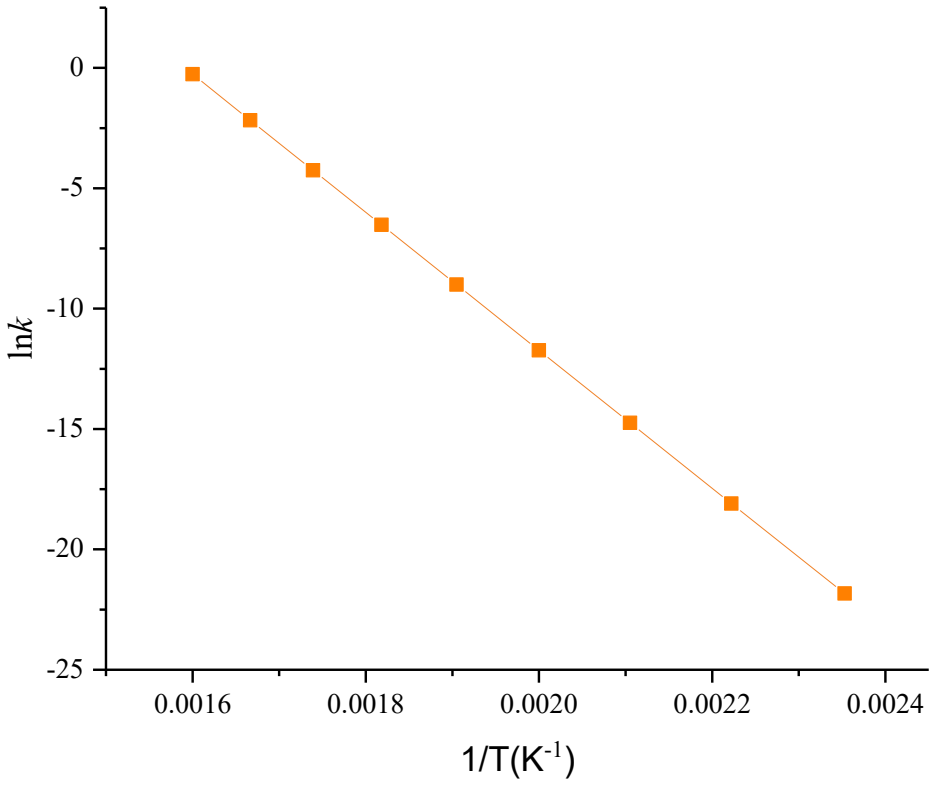


$$k = 2.52 \times 10^{6} \exp(- 87438/RT)$$

Figure S2: Arrhenius plots of rate constants for the crucial reaction step of 3-IM2 + C_3H_7COOH → 3-TS3 in the reaction of $C_3H_7COOH + H_2 \rightarrow C_3H_8 + H_2O + CO$ (RP-CO-hyde) catalyzed over $Ni_{12}P_6$ cluster.

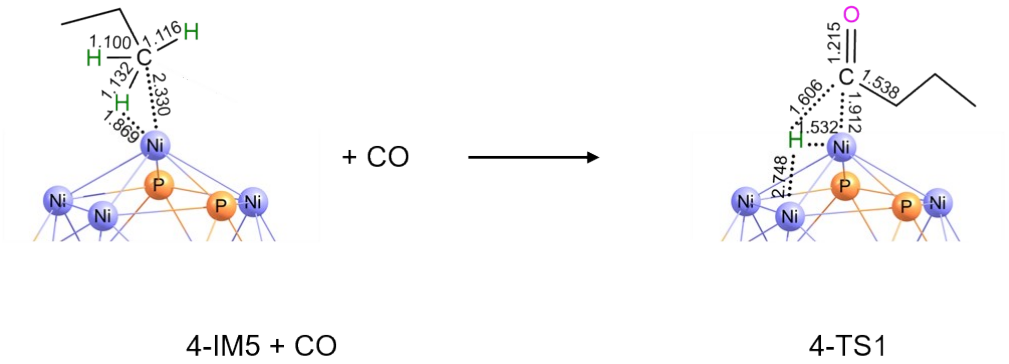


$Ni_{12}P_6 + C_3H_7COOH$ $\qquad$ 2-TS2 + CO + H_2O

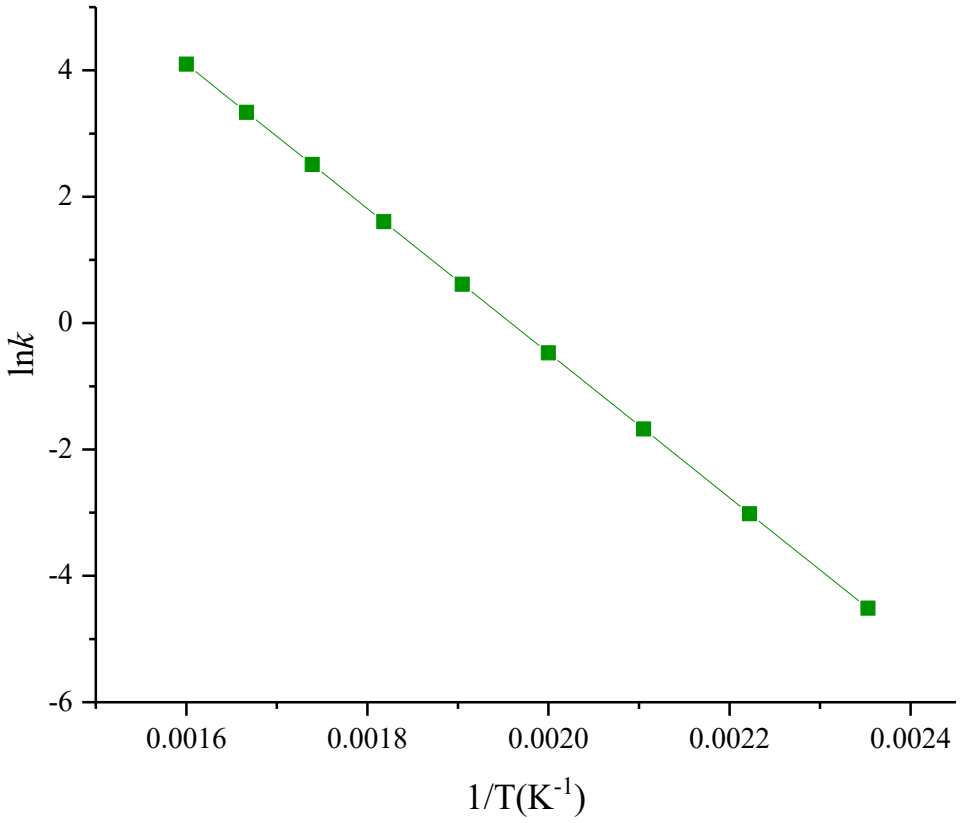


$$k = 6.15 \times 10^{19} \exp\left(-238171/RT\right)$$

Figure S3: Arrhenius plots of rate constants for the crucial reaction step of $Ni_{12}P_6 + C_3H_7COOH \rightarrow$ 7-TS3 + CO + H_2O in the reaction of $C_3H_7COOH + H_2 \rightarrow C_3H_8 + CO + H_2O$ (RP-CO-ene) catalyzed over $Ni_{12}P_6$ cluster.

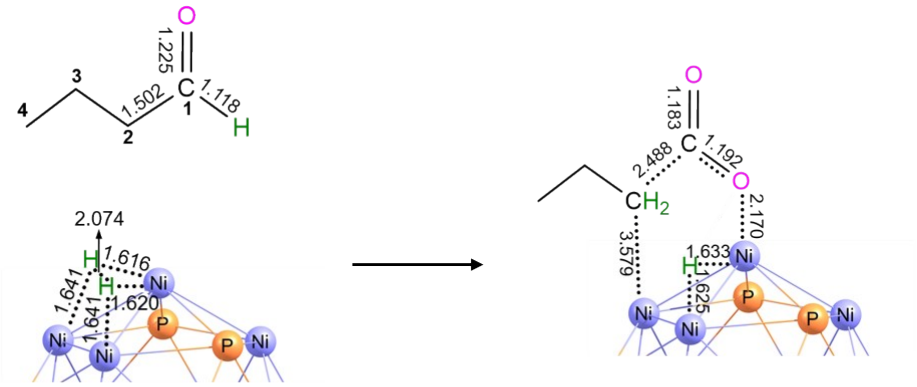


4-IM5 + CO 4-TS1

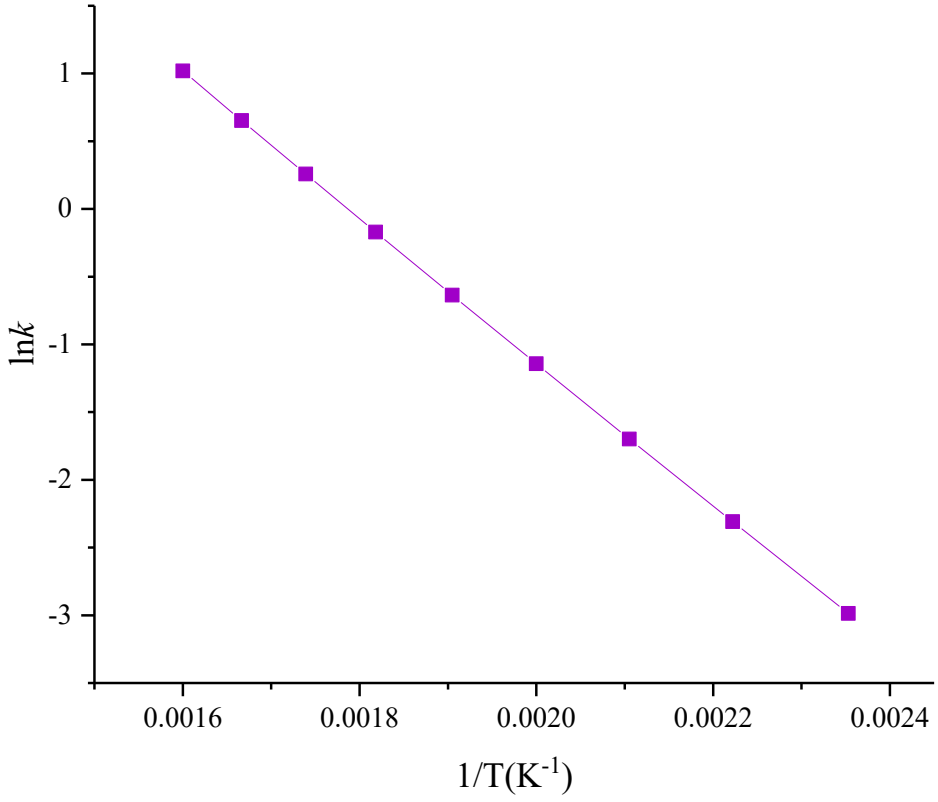


$$k = 5.32 \times 10^{9} \exp\left(-95071/RT\right)$$

Figure S4: Arrhenius plots of rate constants for the crucial reaction step of 4-IM5 + CO → 4-TS1 in the reaction of $C_3H_7CHO \rightarrow C_3H_8 + CO$ catalyzed over $Ni_{12}P_6$ cluster.

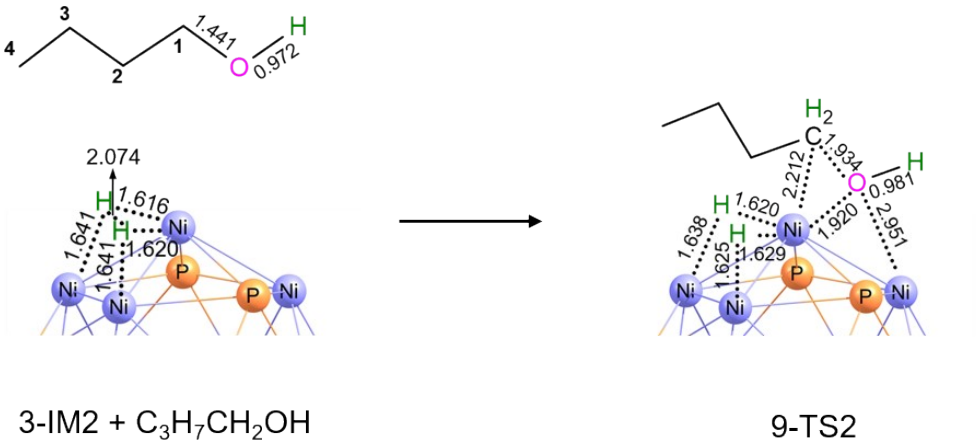


3-IM2 + C_3H_7CHO 2-TS2

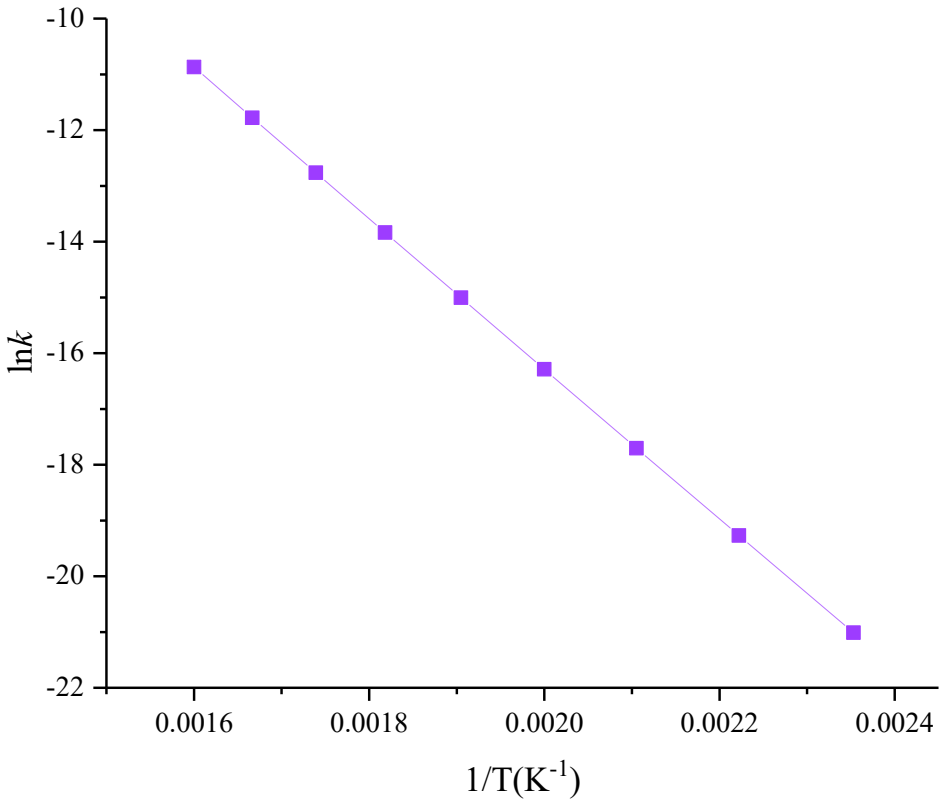


$k = 1.36 \times 10^4 \exp(-44246/RT)$

Figure S5: Arrhenius plots of rate constants for the crucial reaction step of 3-IM2 + C_3H_7CHO → 8-TS2 in the reaction of $C_3H_7CHO + H_2 \rightarrow C_3H_7CH_2OH$ catalyzed over $Ni_{12}P_6$ cluster.

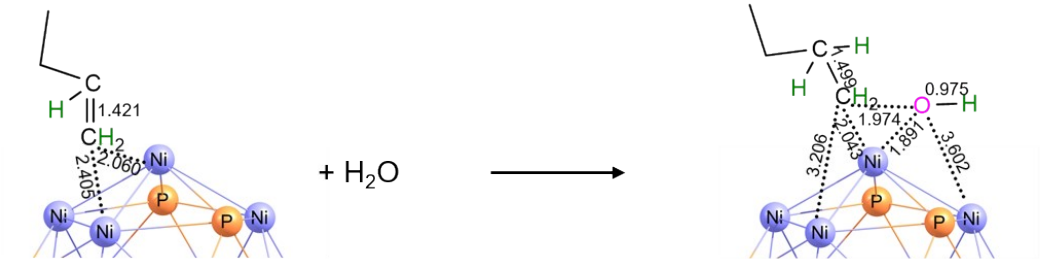


3-IM2 + $C_3H_7CH_2OH$ 9-TS2

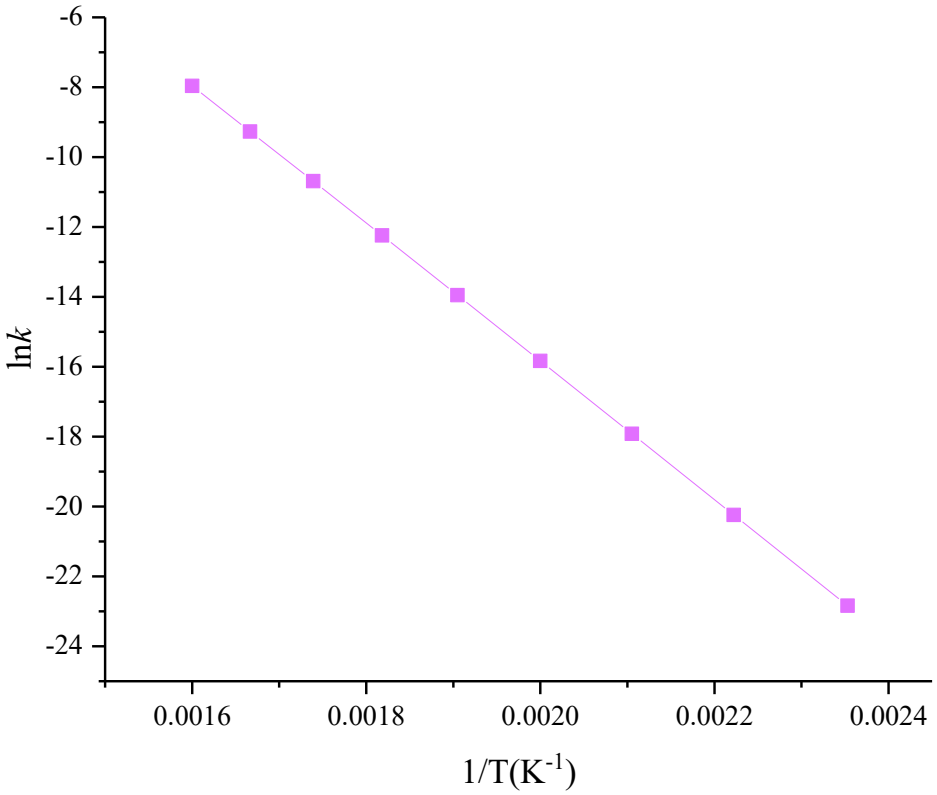


$k = 4.30 \times 10^4 \exp(-112014/RT)$

Figure S6: Arrhenius plots of rate constants for the crucial reaction step of 3-IM2 + $C_3H_7CH_2OH$ → 9-TS2 in the reaction of $C_3H_7CH_2OH$ +H_2 → C_4H_8 + H_2O catalyzed over $Ni_{12}P_6$ cluster.



10-IM5 + H_2O 10-TS1



$$k = 1.91 \times 10^{10} \exp(-164284/RT)$$

Figure S7: Arrhenius plots of rate constants for the crucial reaction step of 10-IM4 + H_2O → 10-TS1 in the reaction of $C_3H_7CH_2OH$ → $CH_3CH_2CH{=}CH_2$ + H_2O catalyzed over $Ni_{12}P_6$ cluster.

Table S1: Sum of electronic energies (E_t, hartree), free energy (G_0, hartree), relative energies (G_r, kJ mol^{-1}) and relative energies ($G_r(CO_2\uparrow)$, kJ mol^{-1}, under the experimental condition of 10^{-5} atm pressure of CO_2) of various species with respect to the reactants for the reaction of $CH_3CH_2CH_2COOH \rightarrow CH_3CH_2CH_3 + CO_2$ catalyzed over $Ni_{12}P_6$ at GGA-PBE/DNP, DSPP.

Species	E_t	G_0	G_r	$G_r(CO_2\uparrow)$
acid+Ni12P6（0.0）	-4677.35823	-0.05644	0.0	0.0
2-IM1	-4677.37807	-0.01963	44.6	44.6
2-TS1	-4677.34798	-0.02397	112.2	112.2
2-IM2	-4677.36261	-0.02855	61.7	61.7
2-TS2	-4677.30799	-0.03744	181.8	181.8
2-IM3	-4677.39099	-0.03746	-36.2	61.7
2-IM5	-4488.89620	-0.03350		
2-IM5 + CO_2	-4677.37455	-0.06099	-54.8	-103.9
2-TS3	-4488.87013	-0.03179		
2-TS3 + CO_2	-4677.34848	-0.05929	18.1	-31.0
2-IM6	-4488.89375	-0.03176		
2-IM6 + CO_2	-4677.37210	-0.05925	-43.8	-92.9
$Ni_{12}P_6$	-4369.88077	-0.10951		
$Ni_{12}P_6$ + CO_2 + $CH_3CH_2CH_3$	-4677.36344	-0.08831	-97.4	-146.5

Table S2: Sum of electronic energies (E_t, hartree), free energy (G_0, hartree) and relative energies (G_r, kJ mol^{-1}) of various species with respect to the reactants for the reaction of $CH_3CH_2CH_2COOH + H_2 \rightarrow CH_3CH_2CH_2CHO + H_2O$ catalyzed over $Ni_{12}P_6$ at GGA-PBE/DNP, DSPP.

Species	E_t	G_0	G_r
$H_2 + Ni_{12}P_6$	-4371.04508	-0.12425	0.0
3-IM1	-4371.06842	-0.10124	-0.9
3-TS1	-4371.06348	-0.10041	14.3
3-IM2	-4371.07765	-0.09631	-12.2
3-IM3	-4678.56975	-0.00872	
3-IM3 - $CH_3CH_2CH_2COOH$	-4371.09229	-0.06178	40.1
3-TS2	-4678.52363	-0.01622	
3-TS2 - $CH_3CH_2CH_2COOH$	-4371.04616	-0.06928	141.5
3-IM4	-4678.54441	-0.01386	
3-IM4 - $CH_3CH_2CH_2COOH$	-4371.06695	-0.06693	93.1
3-TS3	-4678.52135	-0.01813	
3-TS3 - $CH_3CH_2CH_2COOH$	-4371.04388	-0.07119	142.4
3-IM5	-4678.55256	-0.01163	
3-IM5 - $CH_3CH_2CH_2COOH$	-4371.07510	-0.06470	77.5
3-IM6	-4446.29111	-0.09408	
3-IM6 - $CH_3CH_2CH_2COOH$ + $CH_3CH_2CH_2CHO$	-4371.06621	-0.09747	14.9
3-TS4	-4446.26116	-0.09901	
3-TS4 - $CH_3CH_2CH_2COOH$ + $CH_3CH_2CH_2CHO$	-4371.03626	-0.10240	80.5
3-IM7	-4446.29250	-0.09598	
3-IM7 - $CH_3CH_2CH_2COOH$ + $CH_3CH_2CH_2CHO$	-4371.06759	-0.09937	6.2
$Ni_{12}P_6$	-4369.88077	-0.10951	
$Ni_{12}P_6$ - $CH_3CH_2CH_2COOH$ + $CH_3CH_2CH_2CHO$ + H_2O	-4371.03865	-0.12425	6.6

Table S3: Sum of electronic energies (E_t, hartree), free energy (G_0, hartree), relative energies (G_r, kJ mol^{-1}) and relative energies (G_r(CO↑), kJ mol^{-1}, under the experimental condition of 10^{-5} atm pressure of CO) of various species with respect to the reactants for the reaction of $CH_3CH_2CH_2CHO \rightarrow CH_3CH_2CH_3 + CO$ catalyzed over $Ni_{12}P_6$ at GGA-PBE/DNP, DSPP.

Species	E_t	G_0	G_r	G_r(CO↑)
$Ni_{12}P_6$ - C_3H_7COOH + C_3H_7CHO +H_2O	-4371.03865	-0.12816	6.6	6.6
4-IM1	-4602.17007	-0.02171		
4-IM1- $CH_3CH_2CH_2COOH$ +H_2O	-4371.07539	-0.09004	10.2	10.2
4-ITS1	-4602.14617	-0.02507		
4-TS1- $CH_3CH_2CH_2COOH$ +H_2O	-4371.05149	-0.09341	64.2	64.2
4-IM2	-4602.17221	-0.02679		
4-IM2- $CH_3CH_2CH_2COOH$ +H_2O	-4371.07753	-0.09513	-8.7	-8.7
4-TS2	-4602.15757	-0.03139		
4-TS2- $CH_3CH_2CH_2COOH$ +H_2O	-4371.06288	-0.09972	17.7	17.7
4-IM3	-4602.16919	-0.02850		
4-IM3- $CH_3CH_2CH_2COOH$ +H_2O	-4371.07450	-0.09683	-5.3	-5.3
4-TS3	-4602.16036	-0.02788		
4-TS3- $CH_3CH_2CH_2COOH$ +H_2O	-4371.06568	-0.09621	55.0	5.9
4-IM4	-4602.17761	-0.03001		
4-IM4- $CH_3CH_2CH_2COOH$ +H_2O	-4371.08293	-0.09834	68.7	19.6
4-IM5	-4483.16872	-0.11253		
4-IM5- $CH_3CH_2CH_2COOH$ +H_2O	-4371.07836	-0.13217	-4.9	-54.0
$Ni_{12}P_6$	-4369.88077	-0.10951		
$Ni_{12}P_6$ - $CH_3CH_2CH_2COOH$ +H_2O + CO+$CH_3CH_2CH_3$	-4371.0	-0.16139	-36.9	-86.0

Table S4: Sum of electronic energies (E_t, hartree), free energy (G_0, hartree), relative energies (G_r, kJ mol^{-1}) and relative energies (G_r(CO↑), kJ mol^{-1}, under the experimental condition of 10^{-5} atm pressure of CO) of various species with respect to the reactants for the reaction of $CH_3CH_2CH_2COOH \rightarrow CH_3CH_2CH_2OH + CO$ catalyzed over $Ni_{12}P_6$ at GGA-PBE/DNP, DSPP.

Species	E_t	G_0	G_r	G_r(CO↑)
$CH_3CH_2CH_2COOH + Ni_{12}P_6$	-4677.35823	-0.05644	0.0	0.0
5-IM1	-4677.37807	-0.01963	44.6	44.6
5-TS1	-4677.34090	-0.02965	115.8	115.8
5-IM2	-4677.36451	-0.02613	63.1	63.1
5-TS2	-4677.35277	-0.02606	94.1	94.1
5-IM3	-4677.37922	-0.02662	23.2	23.2
5-IM4	-4564.09277	-0.02803		
5-IM4 + CO	-4677.32433	-0.06027	78.9	29.8
5-TS3	-4564.04376	-0.03257		
5-TS3 + CO	-4677.27532	-0.06481	195.7	146.6
5-IM5	-4564.08543	-0.02767		
5-IM5 + CO	-4677.31699	-0.05991	99.1	50.0
$Ni_{12}P_6$	-4369.88077	-0.10951		
$Ni_{12}P_6 + CO + CH_3CH_2HC_2OH$	-4677.29544	-0.09411	66.0	16.9

Table S5: Sum of electronic energies (E_t, hartree), free energy (G_0, hartree), relative energies (G_r, kJ mol^{-1}) and relative energies (G_r(CO↑), kJ mol^{-1}, under the experimental condition of 10^{-5} atm pressure of CO) of various species with respect to the reactants for the reaction of $CH_3CH_2CH_2COOH \rightarrow CH_3CH_2CH_3 + CO + H_2O$ catalyzed over $Ni_{12}P_6$ at GGA-PBE/DNP, DSPP.

Species	E_t	G_0	G_r	G_r(CO↑)
$CH_3CH_2CH_2COOH + Ni_{12}P_6$	-4677.35823	-0.05644	0.0	0.0
5-IM1	-4677.37807	-0.01963	44.6	44.6
5-TS1	-4677.34090	-0.02965	115.8	115.8
5-IM2	-4677.36451	-0.02613	63.1	63.1
5-TS2	-4677.35277	-0.02606	94.1	94.1
5-IM3	-4677.37922	-0.02662	23.2	23.2
5-IM4	-4564.09277	-0.02803		
5-IM4 + CO	-4677.32433	-0.06027	78.9	29.8
5-TS3a	-4564.05612	-0.03315		
5-TS3a + CO	-4677.28768	-0.06540	161.7	112.6
5-IM5a	-4564.08846	-0.03032		
5-IM5a + CO	-4677.32002	-0.06256	84.2	35.1
5-IM6a	-4487.68254	-0.04520		
5-IM6a + CO + H_2O	-4677.29688	-0.09272	65.8	16.7
5-TS4a	-4487.63904	-0.04831		
5-TS4a + CO + H_2O	-4677.25338	-0.09583	171.9	122.8
5-IM7a	-4487.71039	-0.04416		
5-IM7a + CO + H_2O	-4677.32474	-0.09167	-4.6	-53.7
$Ni_{12}P_6$	-4369.88077	-0.10951		
$Ni_{12}P_6$ + CO + H_2O + $CH_3CH{=}CH_2$	-4677.27324	-0.13014	29.6	-19.5

Table S6: Sum of electronic energies (E_t, hartree), free energy (G_0, hartree), relative energies (G_r, kJ mol^{-1}) and relative energies (G_r(CO↑), kJ mol^{-1}, under the experimental condition of 10^{-5} atm pressure of CO) of various species with respect to the reactants for the reaction of $CH_3CH_2CH_2OH + H_2 \rightarrow CH_3CH_2CH_3 + H_2O$ catalyzed over $Ni_{12}P_6$ at GGA-PBE/DNP, DSPP.

Species	E_t	G_0	G_r	G_r(CO↑)
$Ni_{12}P_6$ + CO + $CH_3CH_2HC_2OH$	-4677.29544	-0.09411	66.0	16.9
6-IM1	-4371.06842	-0.10124		
6-IM1 + CO + $CH_3CH_2CH_2OH$ - H_2	-4677.31877	-0.07111	65.1	16.0
6-TS1	-4371.06348	-0.10041		
6-TS1 + CO + $CH_3CH_2CH_2OH$ - H_2	-4677.31383	-0.07027	80.2	31.1
6-IM2	-4371.07765	-0.09631		
6-TS1 + CO + $CH_3CH_2CH_2OH$ - H_2	-4677.32801	-0.06617	53.8	4.7
6-IM3	-4565.28440	-0.01278		
6-IM3 +CO - H_2	-4677.35165	-0.03029	85.9	36.8
6-TS2	-4565.21988	-0.01661		
6-TS2 +CO - H_2	-4677.28713	-0.03411	245.3	196.2
6-IM4	-4565.26058	-0.01418		
6-IM4 +CO - H_2	-4677.32783	-0.03168	144.8	95.7
6-TS3	-4565.25423	-0.01314		
6-TS3 +CO - H_2	-4677.32147	-0.03064	164.2	115.1
6-IM5	-4565.30110	-0.00953		
6-IM5 +CO - H_2	-4677.36835	-0.02703	50.6	1.5
6-IM6	-4446.29111	-0.09408		
6-IM6 + CO - H_2 +$CH_3CH_2CH_3$	-4677.36269	-0.06289	-28.6	-77.7
6-TS4	-4446.26116	-0.09901		
6-TS4 + CO - H_2 +$CH_3CH_2CH_3$	-4677.33274	-0.06782	37.0	-12.1
6-IM7	-4446.29250	-0.09598		
6-IM7 + CO - H_2 +$CH_3CH_2CH_3$	-4677.36407	-0.06479	-37.3	-86.4
$Ni_{12}P_6$	-4369.88077	-0.10951		
$Ni_{12}P_6$ + CO - H_2 +$CH_3CH_2CH_3$ + H_2O	-4677.33513	-0.09358	-36.9	-86.0

Table S7: Sum of electronic energies (E_t, hartree), free energy (G_0, hartree), relative energies (G_r, kJ mol^{-1}) and relative energies (G_r(CO↑), kJ mol^{-1}, under the experimental condition of 10^{-5} atm pressure of CO) of various species with respect to the reactants for the reaction of $CH_3CH_2CH_2OH \rightarrow CH_3CH{=}CH_2 + H_2O$ catalyzed over $Ni_{12}P_6$ at GGA-PBE/DNP, DSPP.

Species	E_t	G_0	G_r	G_r(CO↑)
$Ni_{12}P_6$ + CO + $CH_3CH_2HC_2OH$	-4677.29544	-0.09411	66.0	16.9
7-IM1	-4564.08543	-0.02767		
7-IM1 + CO	-4677.31699	-0.05991	99.1	50.0
6-TS1	-4564.04300	-0.03006		
7-TS1 + CO	-4677.27456	-0.06230	204.3	155.2
7-IM2	-4564.09277	-0.02803		
7-IM2 + CO	-4677.32433	-0.06027	78.9	29.8
7-TS2	-4564.05612	-0.03315		
7-TS2 + CO	-4677.28768	-0.06540	161.7	112.6
7-IM3	-4564.08846	-0.03032		
7-IM3 + CO	-4677.32002	-0.06256	84.2	35.1
7-IM4	-4487.68254	-0.04520		
7-IM4 + CO + H_2O	-4677.29688	-0.09272	65.8	16.7
7-TS3	-4487.63904	-0.04831		
7-TS3 + CO + H_2O	-4677.25338	-0.09583	171.9	122.8
7-IM5	-4487.71039	-0.04416		
7-IM5 + CO + H_2O	-4677.32474	-0.09167	-4.6	-53.7
$Ni_{12}P_6$	-4369.88077	-0.10951		
$Ni_{12}P_6$ + CO + H_2O + $CH_3CH{=}CH_2$	-4677.27324	-0.13014	29.6	-19.5

Table S8: Sum of electronic energies (E_t, hartree), free energy (G_0, hartree), relative energies (G_r, kJ mol^{-1}) and relative energies (G_r(CO↑), kJ mol^{-1}, under the experimental condition of 10^{-5} atm pressure of CO) of various species with respect to the reactants for the reaction of $CH_3CH_2CH_2OH \rightarrow CH_3CH{=}CH_2 + H_2O$ catalyzed over $Ni_{12}P_6$ at GGA-PBE/DNP, DSPP.

Species	E_t	G_0	G_r	G_r(CO↑)
$Ni_{12}P_6$ + CO + $CH_3CH_2HC_2OH$	-4677.29544	-0.09411	66.0	16.9
7-IM1	-4564.08543	-0.02767		
7-IM1 + CO	-4677.31699	-0.05991	99.1	50.0
7-TS1	-4564.04300	-0.03006		
7-TS1 + CO	-4677.27456	-0.06230	204.3	155.2
7-IM2	-4564.09277	-0.02803		
7-IM2 + CO	-4677.32433	-0.06027	78.9	29.8
7-TS2	-4564.03928	-0.03187		
7-TS2 + CO	-4677.27084	-0.06411	209.3	160.2
7-IM3	-4564.08820	0.01502		
7-IM3 + CO	-4677.31976	-0.01723	204.0	154.9
7-IM4	-4487.70842	-0.04871		
7-IM4 + CO + H_2O	-4677.32276	-0.09623	-11.3	-60.4
$Ni_{12}P_6$	-4369.88077	-0.10951		
$Ni_{12}P_6$ + CO + H_2O + $CH_3CH{=}CH_2$	-4677.27324	-0.13014	29.6	-19.5

Table S9: Sum of electronic energies (E_t, hartree), free energy (G_0, hartree), relative energies (G_r, kJ mol^{-1}) and relative energies (G_r(CO↑), kJ mol^{-1}, under the experimental condition of 10^{-5} atm pressure of CO) of various species with respect to the reactants for the reaction of $CH_3CH{=}CH_2 + H_2 \rightarrow CH_3CH_2CH_3$ catalyzed over $Ni_{12}P_6$ at GGA-PBE/DNP, DSPP.

Species	E_t	G_0	G_r	G_r(CO↑)
$Ni_{12}P_6$ + CO + H_2O + $CH_3CH{=}CH_2$	-4677.27324	-0.13014	29.6	-19.5
7-IM5	-4371.06842	-0.10124		
7-IM5 + CO + H_2O + $CH_3CH{=}CH_2$ -H_2	-4677.29657	-0.10714	28.8	-20.3
7-TS3	-4371.06348	-0.10041		
7-TS3 + CO + H_2O + $CH_3CH{=}CH_2$ -H_2	-4677.29163	-0.10631	43.9	-5.2
7-IM6	-4371.07765	-0.09631		
7-IM6 + CO + H_2O + $CH_3CH{=}CH_2$ -H_2	-4677.30581	-0.10220	17.5	-31.6
7-IM7	-4488.89423	-0.03043		
7-IM7 + CO + H_2O -H_2	-4677.34426	-0.06321	18.9	-30.2
7-TS4	-4488.87817	-0.02952		
7-TS4 + CO + H_2O -H_2	-4677.32821	-0.06229	63.5	14.4
7-IM8	-4488.89804	-0.02904		
7-IM + CO + H_2O -H_2	-4677.34808	-0.06182	12.5	-36.6
7-TS5	-4488.89183	-0.03217		
7-IM + CO + H_2O -H_2	-4677.34186	-0.06494	20.7	-28.4
7-IM9	-4488.89796	-0.03024		
7-IM + CO + H_2O -H_2	-4677.34799	-0.06301	9.6	-39.5
$Ni_{12}P_6$	-4369.88077	-0.10951		
$Ni_{12}P_6$ + CO + H_2O -H_2 + $CH_3CH_2CH_3$	-4677.33513	-0.09358	-36.9	-86.0

Table S10: Sum of electronic energies (E_t, hartree), free energy (G_0, hartree) and relative energies (G_r, kJ mol^{-1}) of various species with respect to the reactants for the reaction of $CH_3CH_2CH_2CHO + H_2 \rightarrow CH_3CH_2CH_2CH_2OH$ catalyzed over $Ni_{12}P_6$ at GGA-PBE/DNP, DSPP.

Species	E_t	G_0	G_r
$Ni_{12}P_6$ - $CH_3CH_2CH_2COOH$ + $CH_3CH_2CH_2CHO$ + H_2O	-4371.03865	-0.12816	6.6
8-IM1	-4371.06842	-0.10124	
8-IM1 + H_2O + $CH_3CH_2CH_2CHO$ - $CH_3CH_2CH_2COOH$ - H_2	-4371.06198	-0.10515	5.8
8-TS1	-4371.06348	-0.10041	
8-TS1 + H_2O + $CH_3CH_2CH_2CHO$ - $CH_3CH_2CH_2COOH$ - H_2	-4371.05704	-0.10432	20.9
8-IM2	-4371.07765	-0.09631	
8-IM2 + H_2O + $CH_3CH_2CH_2CHO$ - $CH_3CH_2CH_2COOH$ - H_2	-4371.07122	-0.10022	-5.5
8-IM3	-4603.35103	-0.01070	
8-IM2 + H_2O - $CH_3CH_2CH_2COOH$ - H_2	-4371.09203	-0.06429	34.2
8-TS2	-4603.31290	-0.01250	
8-IM2 + H_2O - $CH_3CH_2CH_2COOH$ - H_2	-4371.05391	-0.06609	129.5
8-IM4	-4603.35695	-0.00182	
8-IM2 + H_2O - $CH_3CH_2CH_2COOH$ - H_2	-4371.09795	-0.05541	41.9
8-TS3	-4603.33826	-0.01080	
8-IM2 + H_2O - $CH_3CH_2CH_2COOH$ -H_2	-4371.07926	-0.06439	67.4
8-IM5	-4603.35100	-0.00933	
8-IM2 + H_2O - $CH_3CH_2CH_2COOH$ - H_2	-4371.09201	-0.06292	37.8
$Ni_{12}P_6$	-4369.88077	-0.10951	
$Ni_{12}P_6$ + H_2O - $CH_3CH_2CH_2COOH$ - H_2 +$CH_3HC_2CH_2CH_2OH$	-4371.07567	-0.09258	2.8

Table S11: Sum of electronic energies (E_t, hartree), free energy (G_0, hartree) and relative energies (G_r, kJ mol^{-1}) of various species with respect to the reactants for the reaction of $CH_3CH_2CH_2CH_2OH + H_2 \rightarrow CH_3CH_2CH_2CH_3 + H_2O$ catalyzed over $Ni_{12}P_6$ at GGA-PBE/DNP, DSPP.

Species	E_t	G_0	G_r
$Ni_{12}P_6 + H_2O$ - $CH_3CH_2CH_2COOH$ - H_2 $+CH_3HC_2CH_2CH_2OH$	-4371.07567	-0.09258	2.8
9IM1	-4371.06842	-0.10124	
9-IM1 + H_2O - $CH_3CH_2CH_2COOH$ - H_2 $+CH_3HC_2CH_2CH_2OH$-H_2	-4371.09900	-0.06957	2.0
9-TS1	-4371.06348	-0.10041	
9-TS1 + H_2O - $CH_3CH_2CH_2COOH$ - H_2 $+CH_3HC_2CH_2CH_2OH$-H_2	-4371.09406	-0.06874	17.1
9-IM2	-4371.07765	-0.09631	
9-IM2 + H_2O - $CH_3CH_2CH_2COOH$ - H_2 $+CH_3HC_2CH_2CH_2OH$-H_2	-4371.10824	-0.06464	-9.3
9-IM3	-4604.55624	0.01298	
9-IM3 + H_2O - $CH_3CH_2CH_2COOH$ - H_2 -H_2	-4371.13293	-0.02588	27.6
9-TS2	-4604.48946	0.00711	
9-TS2 + H_2O - $CH_3CH_2CH_2COOH$ - H_2 -H_2	-4371.06615	-0.03174	187.6
9-IM4	-4604.53634	0.00750	
9-IM4 + H_2O - $CH_3CH_2CH_2COOH$ - H_2 -H_2	-4371.11303	-0.03135	65.5
9-TS3	-4604.52806	0.00861	
9-TS3 + H_2O - $CH_3CH_2CH_2COOH$ - H_2 -H_2	-4371.10475	-0.03024	90.1
9-IM5	-4604.57325	0.01295	
9-IM5 + H_2O - $CH_3CH_2CH_2COOH$ - H_2 -H_2	-4371.14994	-0.02591	-17.1
9-IM6	-4446.29111	-0.09408	
9-IM6 + H_2O - $CH_3CH_2CH_2COOH$ - H_2 -H_2 $+CH_3CH_2CH_2CH_3$	-4371.14318	-0.06203	-94.2
9-TS4	-4446.26116	-0.09901	
9-TS4 + H_2O - $CH_3CH_2CH_2COOH$ - H_2 -H_2 $+CH_3CH_2CH_2CH_3$	-4371.11323	-0.06696	-28.5
9-IM7	-4446.29250	-0.09598	
9-IM7 + H_2O - $CH_3CH_2CH_2COOH$ - H_2 -H_2 $+CH_3CH_2CH_2CH_3$	-4371.14456	-0.06393	-102.8
$Ni_{12}P_6$	-4369.88077	-0.10951	
$Ni_{12}P_6 + H_2O$ - $CH_3CH_2CH_2COOH$ - H_2 -H_2 $+CH_3CH_2CH_2CH_3 + H_2O$	-4371.11562	-0.09272	-102.4

Table S12: Sum of electronic energies (E_t, hartree), free energy (G_0, hartree) and relative energies (G_r, kJ mol^{-1}) of various species with respect to the reactants for the reaction of $CH_3CH_2CH_2CH_2OH \rightarrow CH_3CH_2CH{=}CH_2 + H_2O$ catalyzed over $Ni_{12}P_6$ at GGA-PBE/DNP, DSPP.

Species	E_t	G_0	G_r
$Ni_{12}P_6 + H_2O$ - $CH_3CH_2CH_2COOH$ - H_2 +$CH_3HC_2CH_2CH_2OH$	-4371.07567	-0.09258	2.8
10-IM1	-4603.36776	0.00071	
10-IM1+ H_2O - $CH_3CH_2CH_2COOH$ - H_2	-4371.10876	-0.05289	20.2
10-TS1	-4603.31446	-0.00016	
10-TS1+ H_2O - $CH_3CH_2CH_2COOH$ - H_2	-4371.05547	-0.05376	157.8
10-IM2	-4603.36303	-0.00855	
10-IM2+ H_2O - $CH_3CH_2CH_2COOH$ - H_2	-4371.10404	-0.06215	8.3
10-TS2	-4603.33050	-0.01234	
10-TS2+ H_2O - $CH_3CH_2CH_2COOH$ - H_2	-4371.07151	-0.06594	83.7
10-IM3	-4603.38017	-0.00721	
10-IM3+ H_2O - $CH_3CH_2CH_2COOH$ - H_2	-4371.12117	-0.06080	-33.2
10-IM4	-4526.98041	-0.02454	
10-IM4+ H_2O - $CH_3CH_2CH_2COOH$ - H_2 + H_2O	-4371.10420	-0.09340	-74.2
$Ni_{12}P_6$	-4369.88077	-0.10951	
$Ni_{12}P_6$+ H_2O - $CH_3CH_2CH_2COOH$ - H_2 +H_2O	-4371.05320	-0.12857	-32.6

Table S13: Sum of electronic energies (E_t, hartree), free energy (G_0, hartree) and relative energies (G_r, kJ mol^{-1}) of various species with respect to the reactants for the reaction of $CH_3CH_2CH{=}CH_2 + H_2 \rightarrow CH_3CH_2CH_2CH_3$ catalyzed over $Ni_{12}P_6$ at GGA-PBE/DNP, DSPP.

Species	E_t	G_0	G_r
$Ni_{12}P_6$+ H_2O - $CH_3CH_2CH_2COOH$ - H_2 +H_2O + $CH_3CH_2CH{=}CH_2$	-4371.05320	-0.12857	-32.6
10-IM5	-4371.06842	-0.10124	
10-IM5 + H_2O - $CH_3CH_2CH_2COOH$ - H_2 +H_2O + $CH_3CH_2CH{=}CH_2$ - H_2	-4371.07654	-0.10556	-33.5
10-TS3	-4371.06348	-0.10041	
10-TS3 + H_2O - $CH_3CH_2CH_2COOH$ - H_2 +H_2O + $CH_3CH_2CH{=}CH_2$ - H_2	-4371.07160	-0.10473	-18.4
10-IM6	-4371.07765	-0.09631	
10-IM6 + H_2O - $CH_3CH_2CH_2COOH$ - H_2 +H_2O + $CH_3CH_2CH{=}CH_2$ - H_2	-4371.08577	-0.10062	-44.8
10-IM7	-4528.166207	-0.00747	
10-IM6 + H_2O - $CH_3CH_2CH_2COOH$ - H_2 +H_2O - H_2	-4371.12568	-0.06159	-47.1
10-TS4	-4528.150216	-0.00940	
10-TS4 + H_2O - $CH_3CH_2CH_2COOH$ - H_2 +H_2O - H_2	-4371.10969	-0.06351	-10.2
10-IM8	-4528.163071	-0.00695	
10-IM8 + H_2O - $CH_3CH_2CH_2COOH$ - H_2 +H_2O - H_2	-4371.12255	-0.06107	-37.5
10-TS5	-4528.155571	-0.00734	
10-TS5 + H_2O - $CH_3CH_2CH_2COOH$ - H_2 +H_2O - H_2	-4371.11505	-0.06146	-18.8
10-IM9	-4528.169048	-0.00501	
10-IM9 + H_2O - $CH_3CH_2CH_2COOH$ - H_2 +H_2O - H_2	-4371.12852	-0.05913	-48.1
$Ni_{12}P_6$	-4369.88077	-0.10951	
$Ni_{12}P_6$ + H_2O - $CH_3CH_2CH_2COOH$ - H_2 +H_2O - H_2 + $CH_3CH_2CH_2CH_3$	-4371.11562	-0.09272	-102.4