Supporting Information:

Mechanism insight into catalytic performance of $Ni_{12}P_5$ over Ni_2P toward the catalytic deoxygenation of butyric acid

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Catalysts

content

NOTES: Evaluation of rate constants:

The energetic span was employed to acquire the determining intermediate (DI) and determining transition state (DTS) through the whole catalytic cycle [1-6]. Based on transition state theory (TST), the *k′* can be evaluated by equations (i) and (ii). Together with tunnelling correction κ (iii) [7], the rate constants *k* can be evaluated by equation (iv).

$$k' = \frac{k_B T}{hc^0} \times e^{\frac{-\Delta G^{\neq}}{RT}} \tag{i}$$

$$-\Delta G^{\neq} = \begin{pmatrix} G_{\mathrm{DTS}} - G_{\mathrm{DI}} & \text{if DTS appears after DI} \\ G_{\mathrm{DTS}} - G_{\mathrm{DI}} + \Delta G_{\mathrm{r}} & \text{if DTS appears before DI} \end{pmatrix} \tag{ii}$$

$$\kappa = 1 + \frac{1}{24}\left|\frac{\omega^{\neq} h}{k_B T}\right|^2 \tag{iii}$$

$$k = \kappa \times k' \tag{iv}$$

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

Refs:

1. Amatore, C.; Jutand, A. *J. Organomet. Chem.*, **1999**, 576, 254-278.
2. Kozuch, S.; Shalk, S. *J. Am. Chem. Soc.*, **2006**, 128, 3355–3365.
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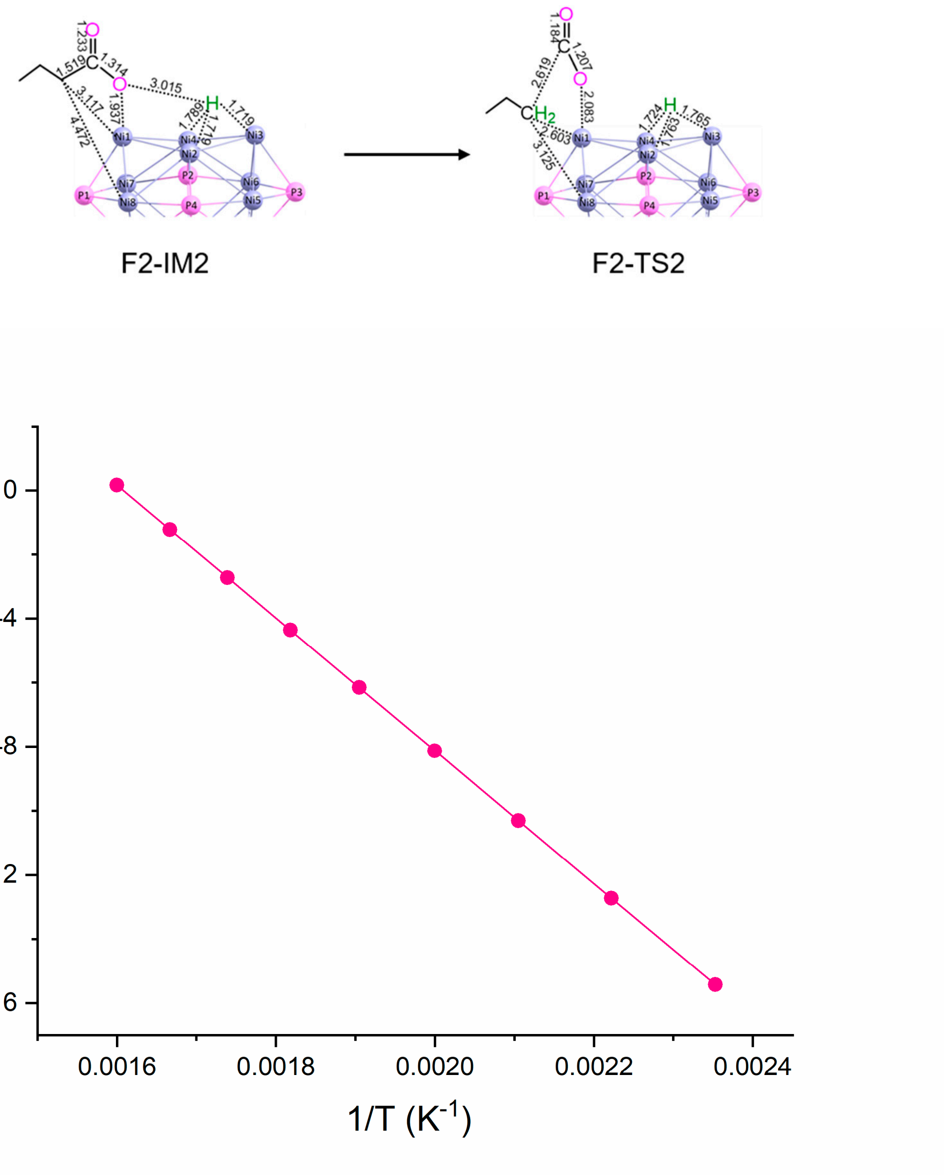
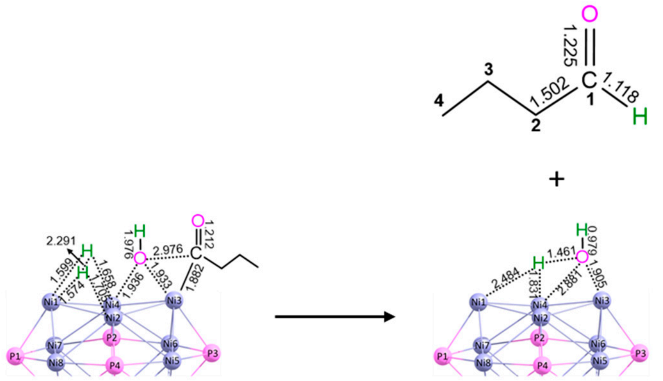
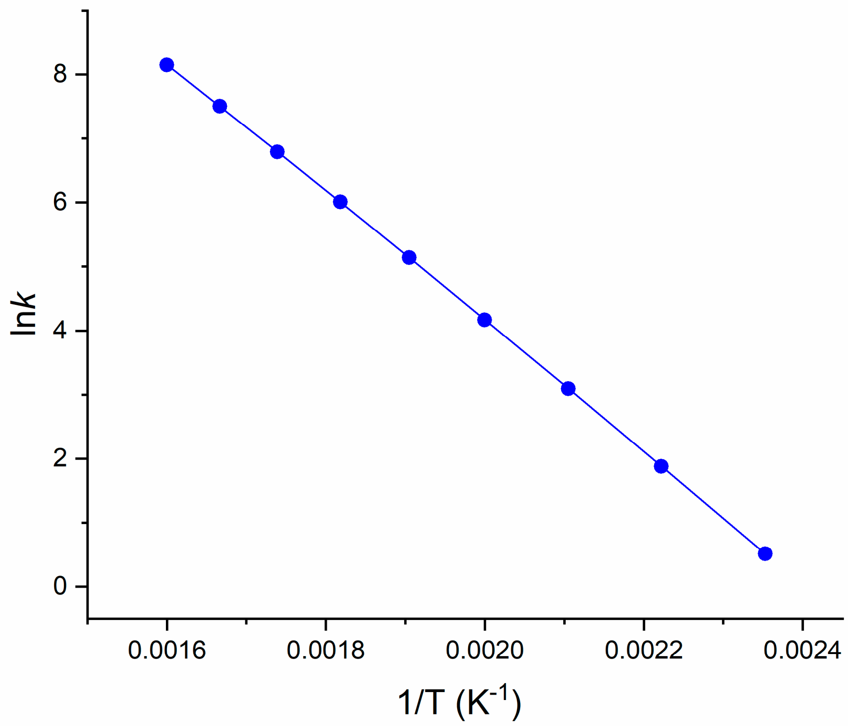
4. Uhe, A.; Kozuch, S.; Shaik, S. *J. Comput. Chem.*, **2011**, 32, 978-985.
5. Kozuch, S.; Shalk, S. *Acc. Chem. Res.*, **2011**, 44, 101-110.
6. Kozuch, S. *ACS Catal.*, **2015**, 5, 5242-5255.
7. Wigner, E. J. Chem. Phys. **1937**, 5, 720-725.



$$k_{S2} = 2.88 \times 10^{14} \exp(-172166 / RT)$$

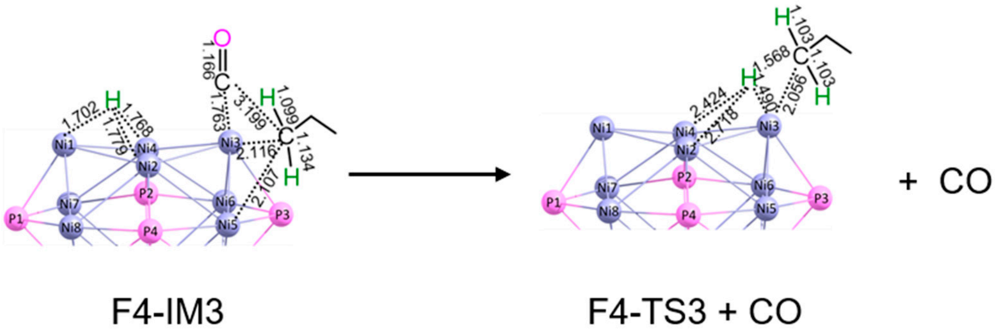
Figure S1: Arrhenius plots of rate constants for the crucial reaction step (F2-IM2 → F2-TS2) in the reaction stage C_3H_7COOH → C_3H_8 + CO_2 (S2) catalyzed $Ni_{12}P_5$ cluster.

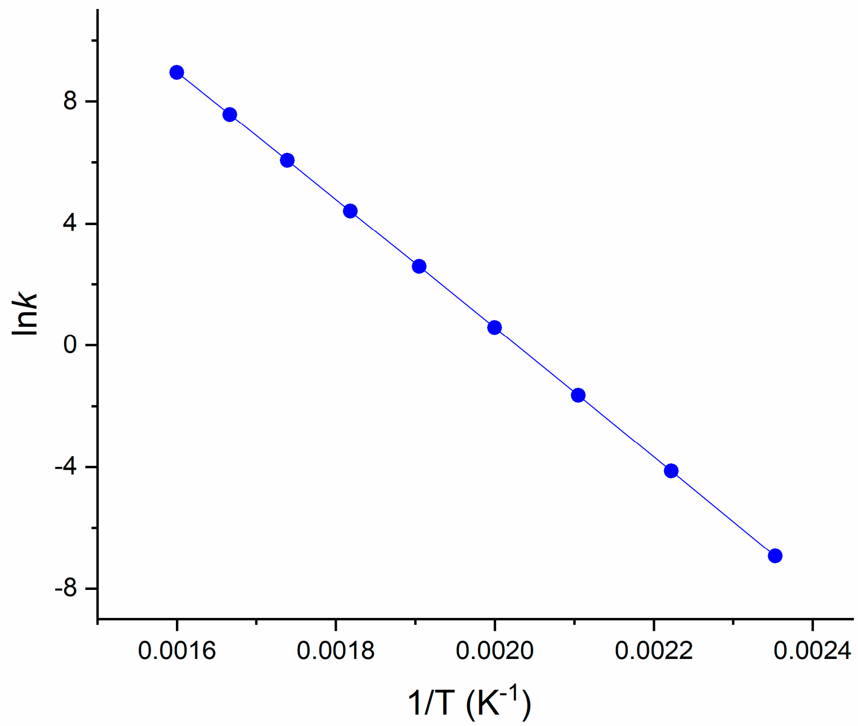




$$k_{S3} = 1.79\times10^{20}\exp(-174054/RT)$$

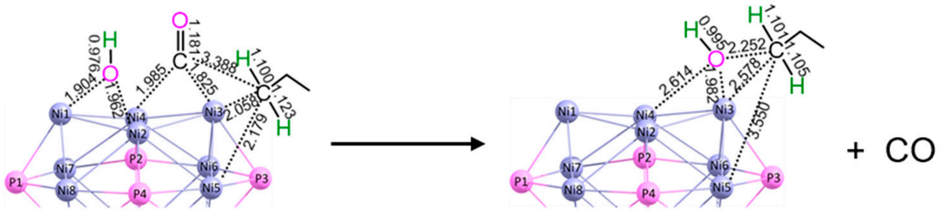
Figure S2: Arrhenius plots of rate constants for the crucial reaction step (F3-IM4 → F3-TS4 + C_3H_7CHO) in the reaction stage $C_3H_7COOH + H_2 \rightarrow C_3H_7CHO + H_2O$ (S3) catalyzed by $Ni_{12}P_5$ cluster.



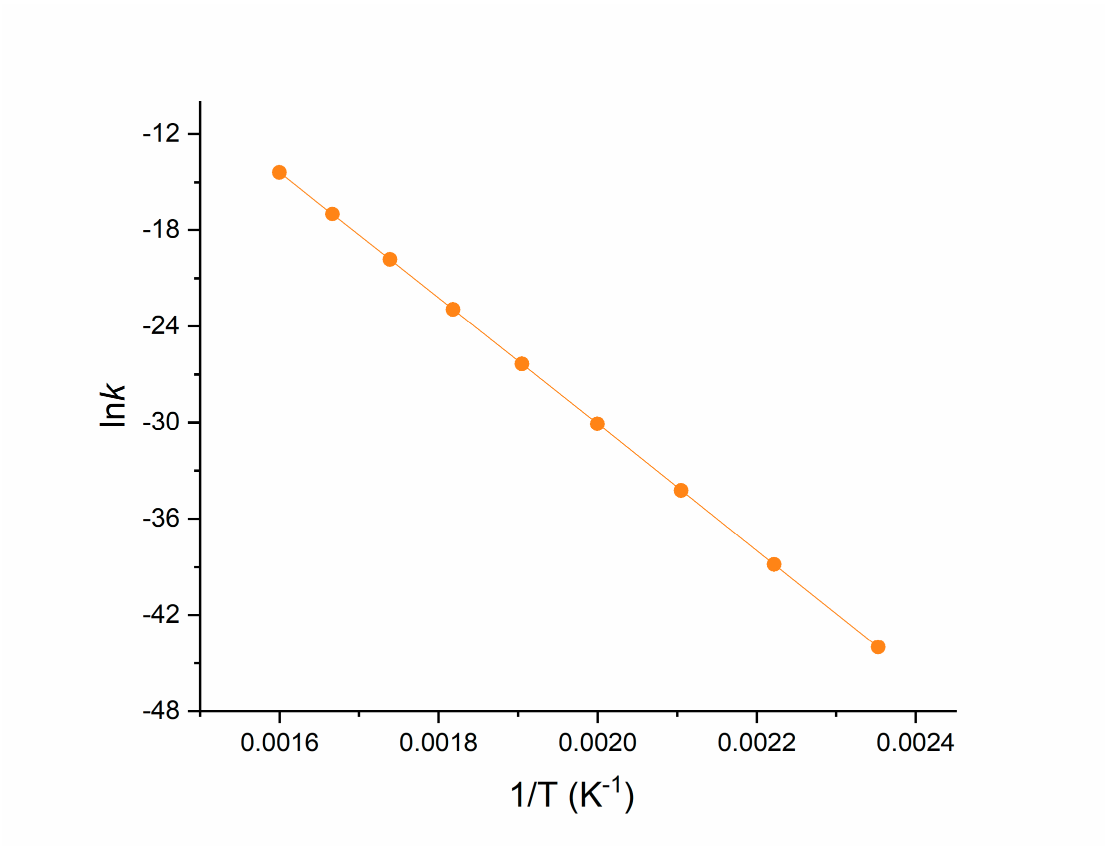


$$k_{S4} = 3.65\times10^{18}\exp(-175375/RT)$$

Figure S3: Arrhenius plots of rate constants for the crucial reaction step (F4-IM3 → F4-TS3 + CO) in the reaction stage C_3H_7CHO → C_3H_8 + CO (S4) catalyzed by $Ni_{12}P_5$ cluster.

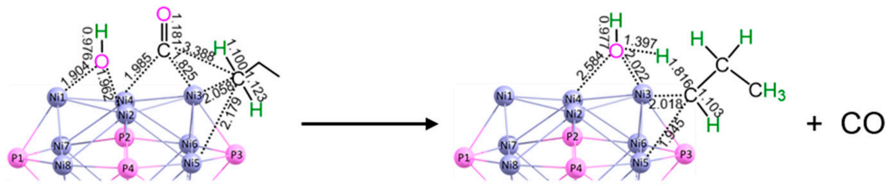


F5-IM4 F5-TS3 + CO

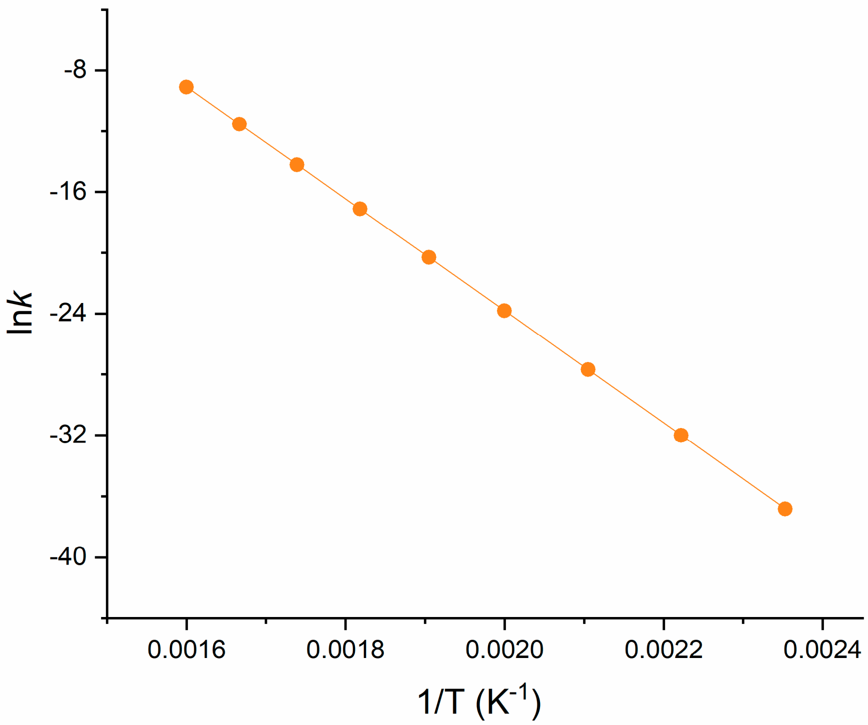


$$k_{S5} = 1.23\times10^{21} \exp(-327015 / RT)$$

Figure S4: Arrhenius plots of rate constants for the crucial reaction step (F5-IM4 → F5-TS3 + CO) in the reaction stage C_3H_7COOH → $C_2H_5CH_2OH$+ CO (S5) catalyzed by $Ni_{12}P_5$ cluster.

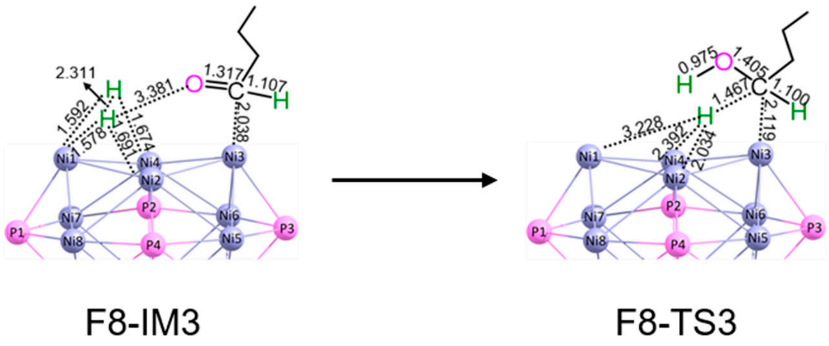


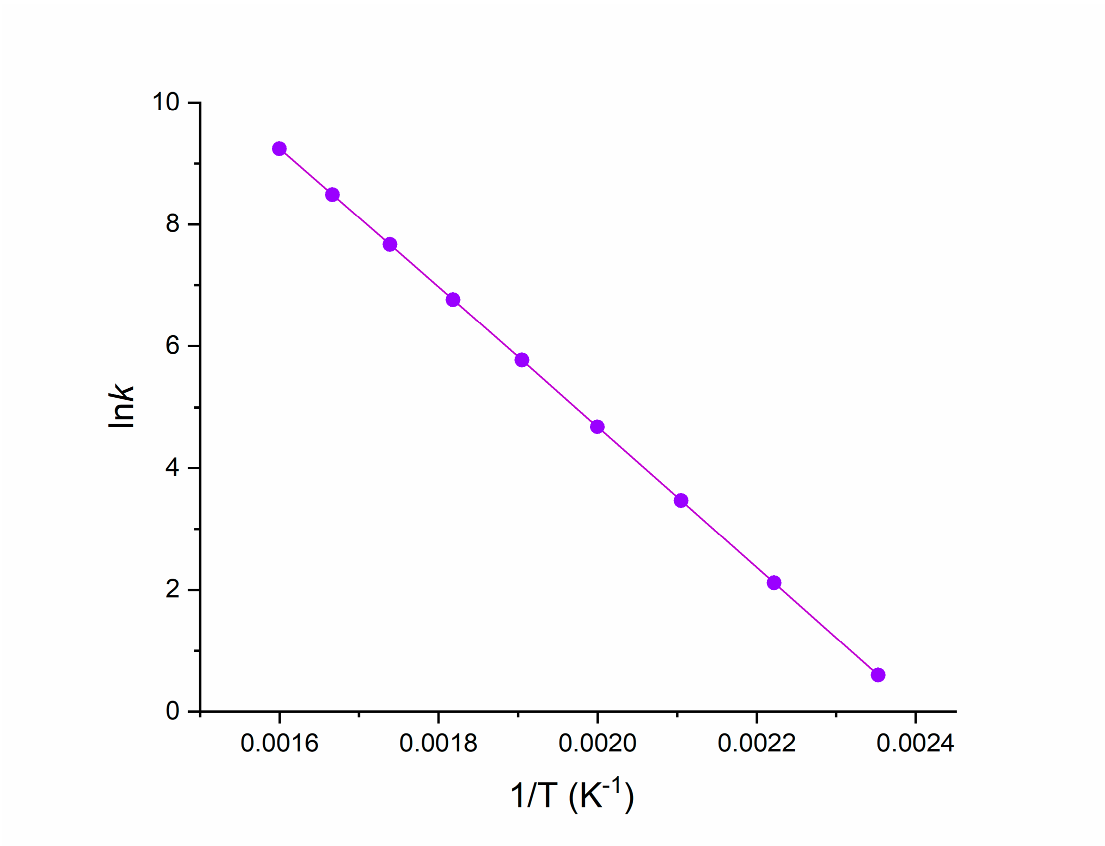
F5-IM4 F7-TS2 + CO



$$k_{S(5/7a)} = 4.45\times10^{21}\exp(-306230/RT)$$

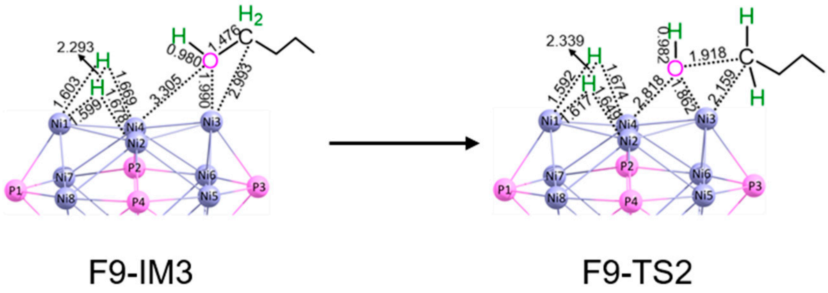
Figure S5: Arrhenius plots of rate constants for the crucial reaction step (F5-IM4 → F7-TS2 + CO) in the reaction stage C_3H_7COOH → $CH_3CH{=}CH_2$ + H_2O + CO (S5/7a) catalyzed by $Ni_{12}P_5$ cluster.

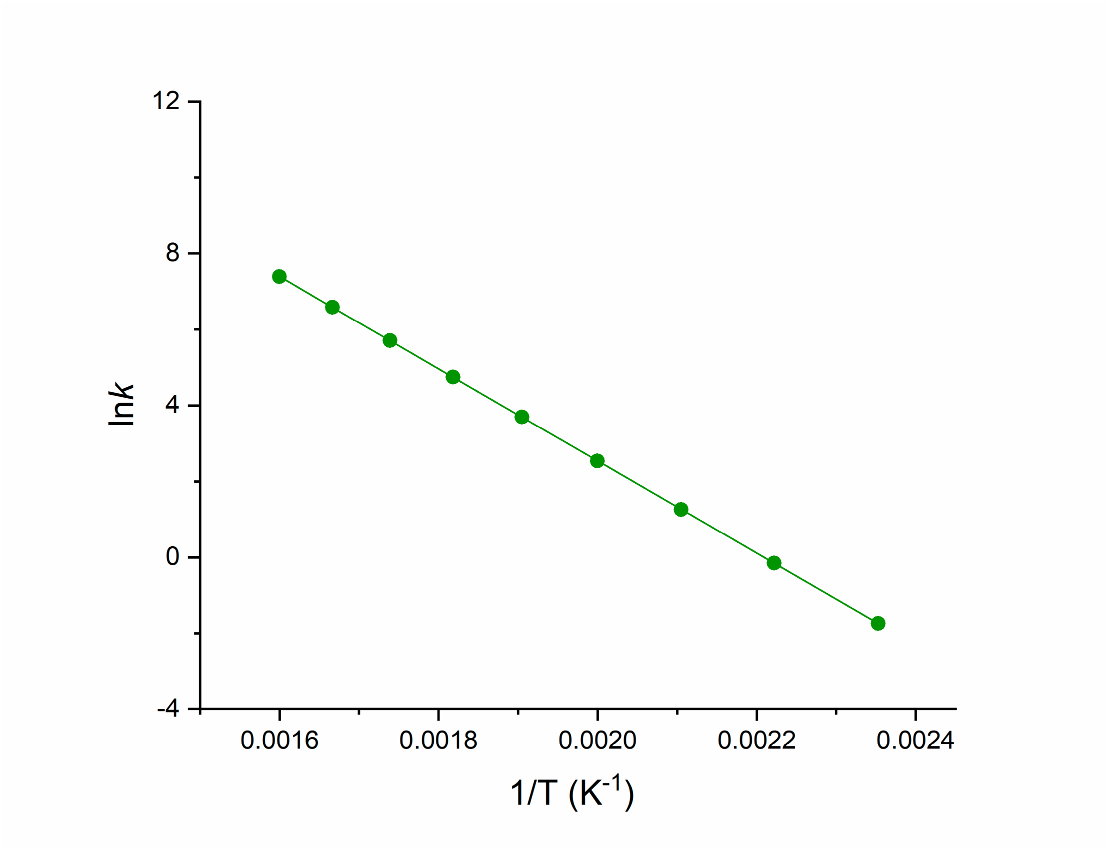




$$k_{S8} = 1.00 \times 10^{12} \exp(-95469 / RT)$$

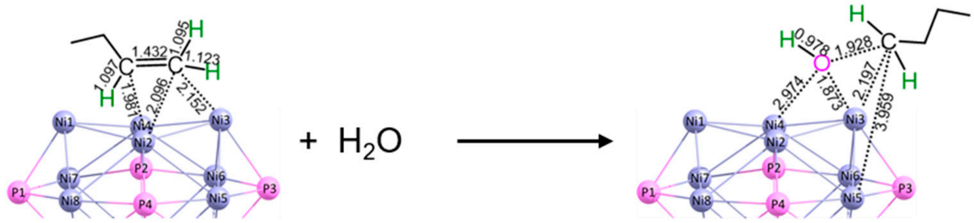
Figure S6: Arrhenius plots of rate constants for the crucial reaction step (F8-IM3 → F8-TS3) in the reaction stage $C_3H_7CHO + H_2 \rightarrow C_3H_7CH_2OH$ catalyzed by $Ni_{12}P_5$ cluster.





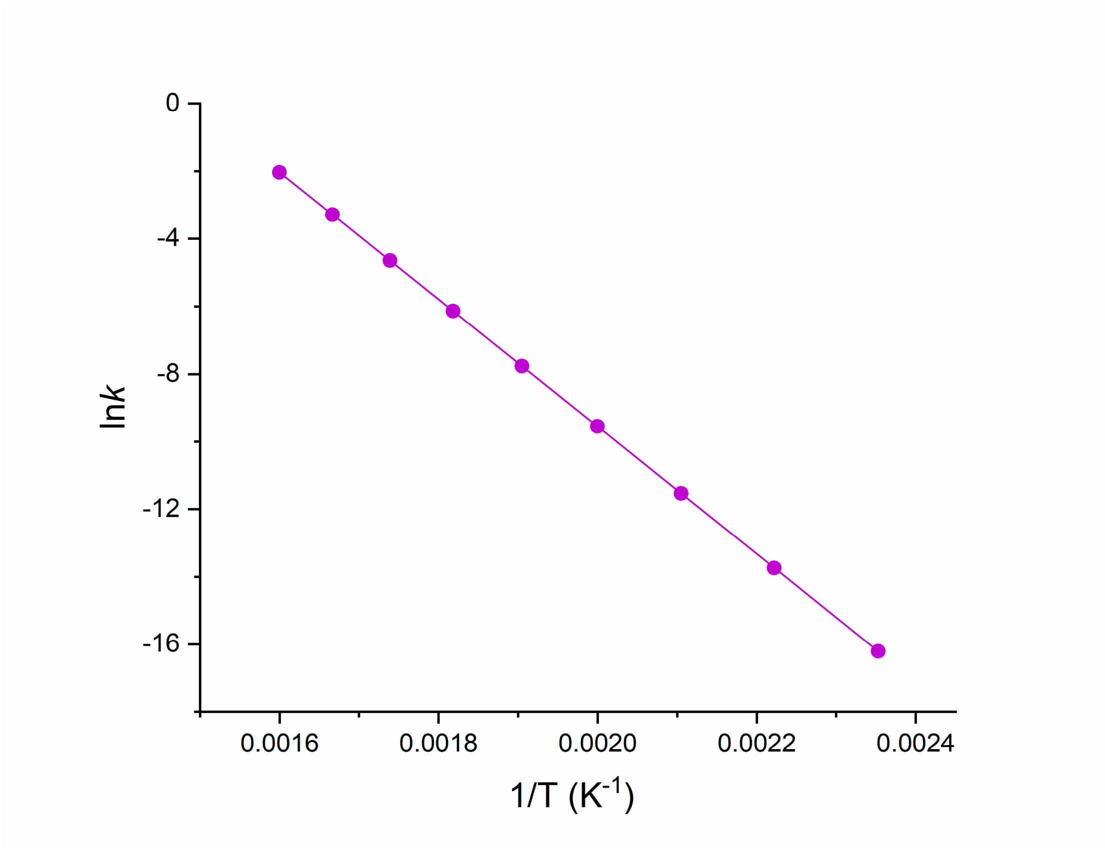
$$k_{S9} = 4.32\times10^{11}\exp(-100816/RT)$$

Figure S7: Arrhenius plots of rate constants for the crucial reaction step (F9-IM3 → F9-TS2) in the reaction stage $C_3H_7CH_2OH + H_2 \rightarrow C_4H_{10} + H_2O$ catalyzed by $Ni_{12}P_5$ cluster.



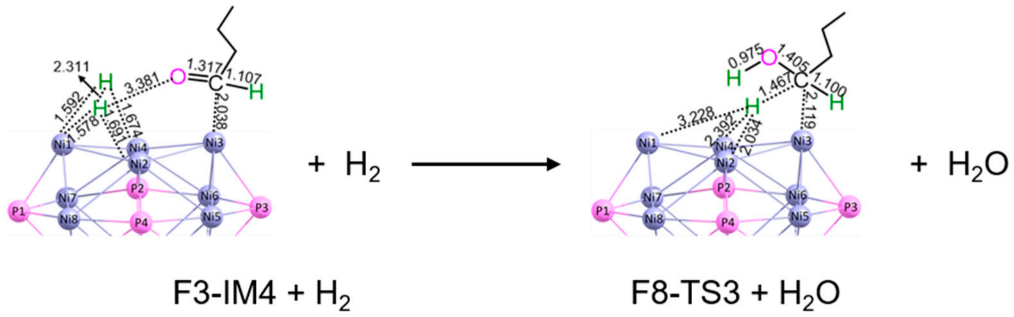
F10-IM5 + H_2O

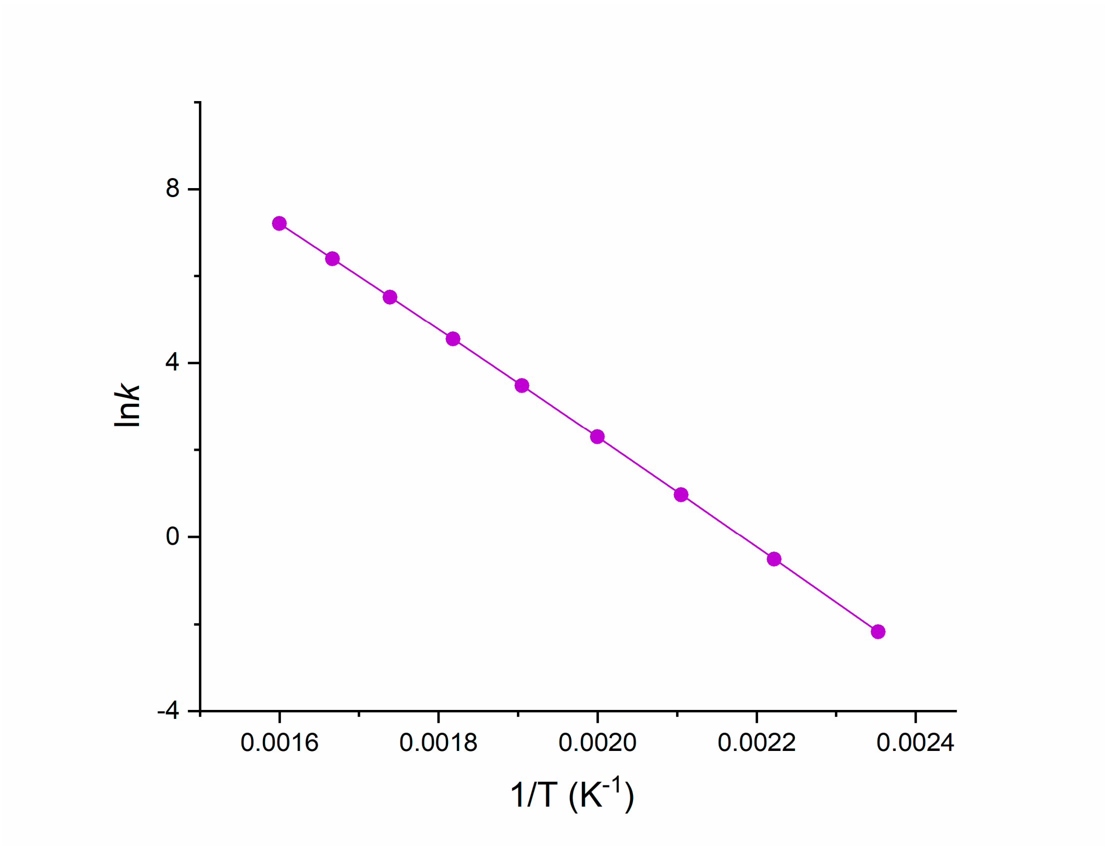
F10-TS1



$$k_{S10} = 1.55\times 10^{12}\exp(-156411/RT)$$

Figure S8: Arrhenius plots of rate constants for the crucial reaction step (F10-IM5 + H_2O → F10-TS1) in the reaction stage $C_3H_7CH_2OH$ + H_2 → C_4H_{10} + H_2O (S10a + S10b) catalyzed by $Ni_{12}P_5$ cluster.





$$k_{C_4H_{10}} = 6.26\times10^{11}\exp(-103468/RT)$$

Figure S9: Arrhenius plots of rate constants for the crucial reaction step (F3-IM4 + H_2 → F8-TS3 + H_2O) in the reaction stage C_3H_7COOH + $3H_2$ → C_4H_{10} + $2H_2O$ (S3 + S8 + S9) catalyzed by $Ni_{12}P_5$ cluster.

Table S1: Sum of electronic energies (E_t, hartree), free energies (G_0, hartree), sum of electronic and free energies (G_c, 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 $C_3H_7COOH \rightarrow C_3H_8 + CO_2$ catalyzed by $Ni_{12}P_5$ cluster at GGA-PBE/DNP, DSPP level.

Species	E_t	G_0	G_c	G_r	$G_r(CO_2\uparrow)$
$C_3H_7COOH + Ni_{12}P_5$	-4336.00003	-0.05954	-4336.05957	0.0	0.0
F2-IM1	-4336.02356	-0.03277	-4336.05633	8.5	8.5
F2-TS1	-4335.99038	-0.03776	-4336.02814	82.5	82.5
F2-IM2	-4336.03597	-0.02437	-4336.06034	-2.0	-2.0
F2-TS2	-4335.96595	-0.03421	-4336.00016	156.0	156.0
F2-IM3	-4336.02470	-0.04138	-4336.06608	-17.1	-17.1
F2-IM4	-4147.54755	-0.03086	-4147.57842		
F2-IM4 + CO_2	-4336.02590	-0.05836	-4336.08426	-64.8	-113.9
F2-TS3	-4147.52561	-0.03377	-4147.55938		
F2-TS3 + CO_2	-4336.00396	-0.06126	-4336.06522	-14.8	-63.9
F2-IM5	-4147.54142	-0.02771	-4147.56913		
F2-IM5 + CO_2	-4336.01977	-0.05520	-4336.07497	-40.4	-89.6
$Ni_{12}P_5$	-4028.52257	-0.11260	-4028.63517		
$Ni_{12}P_5 + CO_2 + C_3H_8$	-4336.00525	-0.09140	-4336.09665	-97.4	-146.5

Table S2: Sum of electronic energies (E_t, hartree), free energies (G_0, hartree), sum of electronic and free energies (G_c, hartree) and relative energies (G_r, kJ mol^{-1}) of various species with respect to the reactants for the reaction of $C_3H_7COOH + H_2 \rightarrow C_3H_7CHO + H_2O$ catalyzed by $Ni_{12}P_5$ at GGA-PBE/DNP, DSPP level.

Species	E_t	G_0	G_c	G_r
$H_2 + Ni_{12}P_5$	-4029.68688	-0.12734	-4029.81423	0.0
F3-IM1	-4029.71450	-0.10315	-4029.81765	-9.0
F3-TS1	-4029.71220	-0.10121	-4029.81341	2.1
F3-IM2	-4029.73086	-0.09956	-4029.83042	-42.5
F3-IM3	-4337.23107	-0.00538	-4337.23645	
F3-IM3 - C_3H_7COOH	-4029.75361	-0.05845	-4029.81206	5.7
F3-TS2	-4337.21041	-0.00844	-4337.21885	
F3-TS2 - C_3H_7COOH	-4029.73295	-0.06151	-4029.79446	51.9
F3-IM4	-4337.23771	-0.02003	-4337.25774	
F3-IM4 - C_3H_7COOH	-4029.76024	-0.07310	-4029.83335	-50.2
F3-IM5	-4337.22910	-0.01378	-4337.24288	
F3-IM5 - C_3H_7COOH	-4029.75164	-0.06684	-4029.81848	-11.2
F3-TS3	-4337.21262	-0.01607	-4337.22869	
F3-TS3 - C_3H_7COOH	-4029.73516	-0.06913	-4029.80429	26.1
F3-IM6	-4337.21767	-0.01481	-4337.23247	
3-IM6 - C_3H_7COOH	-4029.74020	-0.06788	-4029.80808	16.2
F3-IM7	-4104.95550	-0.09667	-4105.05217	
F3-IM7 - $C_3H_7COOH + C_3H_7CHO$	-4029.73060	-0.10005	-4029.83065	-43.1
3-TS4	-4104.91349	-0.10246	-4105.01595	
F3-TS4 - $C_3H_7COOH + C_3H_7CHO$	-4029.68858	-0.10585	-4029.79443	52.0
3-IM8	-4104.93598	-0.09718	-4105.03316	
F3-IM8 - $C_3H_7COOH + C_3H_7CHO$	-4029.71108	-0.10056	-4029.81164	6.8
$Ni_{12}P_5$	-4028.52257	-0.11260	-4028.63517	
$Ni_{12}P_5$ - $C_3H_7COOH + C_3H_7CHO + H_2O$	-4029.68044	-0.13126	-4029.81170	6.6

Table S3: Sum of electronic energies (E_t, hartree), free energies (G_0, hartree), sum of electronic and free energies (G_c, 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 $C_3H_7CHO \rightarrow C_3H_8 + CO$ catalyzed by $Ni_{12}P_5$ cluster at GGA-PBE/DNP, DSPP level.

Species	E_t	G_0	G_C	G_r	G_r(CO↑)
$Ni_{12}P_5$ - C_3H_7COOH + C_3H_7CHO +H_2O	-4029.68044	-0.13126	-4029.81170	6.6	6.6
F4-IM1	-4260.82409	-0.02045	-4260.84454		
F4-IM1 - C_3H_7COOH + H_2O	-4029.729406	-0.08878	-4029.81819	-10.4	-10.4
F4-ITS1	-4260.79641	-0.02784	-4260.82425		
F4-TS1 - C_3H_7COOH + H_2O	-4029.70172	-0.09618	-4029.79790	42.9	42.9
F4-IM2	-4260.83218	-0.02638	-4260.85856		
F4-IM2 - C_3H_7COOH + H_2O	-4029.73750	-0.09471	-4029.83221	-47.2	-47.2
F4-TS2	-4260.81529	-0.03433	-4260.84962		
F4-TS2 - C_3H_7COOH + H_2O	-4029.72060	-0.10266	-4029.82327	-23.7	-23.7
F4-IM3	-4260.83511	-0.03682	-4260.87193		
F4-IM3 - C_3H_7COOH + H_2O	-4029.74043	-0.10515	-4029.84558	-82.3	-82.3
F4-IM4	-4147.54424	-0.03472	-4147.57897		
F4-IM4 - C_3H_7COOH + H_2O + CO	-4029.68112	-0.13530	-4029.81642	-5.8	-54.9
F4-TS3	-4147.52727	-0.03326	-4147.56053		
F4-TS3 - C_3H_7COOH + H_2O + CO	-4029.66414	-0.13384	-4029.79798	42.7	-6.4
F4-IM5	-4147.53590	-0.03040	-4147.56630		
F4-IM5 - C_3H_7COOH + H_2O + CO	-4029.67278	-0.13098	-4029.80376	27.5	-21.6
$Ni_{12}P_5$	-4028.52257	-0.11260	-4028.63517		
$Ni_{12}P_5$ - C_3H_7COOH +H_2O + CO + C_3H_8	-4029.66377	-0.16449	-4029.82826	-36.8	-85.9

Table S4: Sum of electronic energies (E_t, hartree), free energies (G_0, hartree), sum of electronic and free energies (G_c, 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 C_3H_7COOH → $C_2H_5CH_2OH$ + CO catalyzed by $Ni_{12}P_5$ cluster at GGA-PBE/DNP, DSPP level.

Species	E_t	G_0	G_C	G_r	G_r**(CO↑)**
$C_3H_7COOH + Ni_{12}P_5$	-4336.00003	-0.05954	-4336.05957	0.0	0.0
F5-IM1	-4336.02356	-0.03277	-4336.05633	8.5	8.5
F5-TS1	-4335.98031	-0.02971	-4336.01002	130.1	130.1
F5-IM2	-4336.03381	-0.02430	-4336.05811	3.8	3.8
F5-IM3	-4336.04538	-0.01939	-4336.06477	-13.6	-13.6
F5-TS2	-4336.00541	-0.03395	-4336.03935	53.1	53.1
F5-IM4	-4336.05753	-0.02749	-4336.08503	-66.8	-66.8
F5-IM5	-4222.74875	-0.03151	-4222.78026		
F5-IM5+ CO	-4335.98031	-0.06375	-4336.04407	40.7	-8.4
F5-TS3	-4222.69690	-0.03049	-4222.72740		
F5-TS3 + CO	-4335.92846	-0.06274	-4335.99120	179.5	130.4
F5-IM6	-4222.73881	-0.02243	-4222.76124		
F5-IM6 + CO	-4335.97037	-0.05467	-4336.02505	90.6	41.5
$Ni_{12}P_5$	-4028.52257	-0.11260	-4028.63517		
$Ni_{12}P_5$ + CO + $C_2H_5HC_2OH$	-4335.93724	-0.09721	-4336.03445	66.0	16.9

Table S5: Sum of electronic energies (E_t, hartree), free energies (G_0, hartree), sum of electronic and free energies (G_c, 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 $C_2H_5CH_2OH$ + H_2 → C_3H_8 + H_2O catalyzed by $Ni_{12}P_5$ cluster at GGA-PBE/DNP, DSPP level.

Species	E_t	G_0	G_c	G_r	G_r (CO↑)
$Ni_{12}P_5$ + CO + $C_2H_5CH_2OH$	-4335.93724	-0.09721	-4336.03445	66.0	16.9
F6-IM1	-4029.71450	-0.10315	-4029.81765		
F6-IM1 + CO + $C_2H_5CH_2OH$ - H_2	-4335.96486	-0.07301	-4336.03787	57.0	7.9
F6-TS1	-4029.71220	-0.10121	-4029.81341		
F6-TS1 + CO + $C_2H_5CH_2OH$ - H_2	-4335.96255	-0.07108	-4336.03363	68.1	19.0
F6-IM2	-4029.73086	-0.09956	-4029.83042		
F6-IM2 + CO + $C_2H_5CH_2OH$ - H_2	-4335.98121	-0.06943	-4336.05064	23.5	-25.7
F6-IM3	-4223.94962	-0.01151	-4223.96113		
F6-IM3 +CO - H_2	-4336.01687	-0.02901	-4336.04588	35.9	-13.2
F6-TS2	-4223.90600	-0.01588	-4223.92188		
F6-TS2 +CO - H_2	-4335.97325	-0.03339	-4336.00664	139.0	89.9
F6-IM4	-4223.95841	-0.01804	-4223.97644		
F6-IM4 +CO - H_2	-4336.02566	-0.03554	-4336.06120	-4.3	-53.4
F6-TS3	-4223.90811	-0.02192	-4223.93003		
F6-TS3 +CO - H_2	-4335.97536	-0.03942	-4336.01478	117.6	68.5
F6-IM5	-4223.95305	-0.01400	-4223.96705		
F6-IM5 +CO - H_2	-4336.02030	-0.03150	-4336.05180	20.4	-28.7
F6-IM6	-4147.54432	-0.03517	-4147.57949		
F6-IM6 + CO - H_2 + H_2O	-4335.99435	-0.06794	-4336.06229	-7.1	-56.2
F6-TS4	-4147.52768	-0.03657	-4147.56425		
F6-TS4 + CO - H_2 + H_2O	-4335.97771	-0.06934	-4336.04705	32.9	-16.2
F6-IM7	-4147.53751	-0.03431	-4147.57183		
F6-IM7 + CO - H_2 + H_2O	-4335.98755	-0.06708	-4336.05463	13.0	-36.1
$Ni_{12}P_5$	-4028.52257	-0.11260	-4028.63517		
$Ni_{12}P_5$ + CO - H_2 + C_3H_8 + H_2O	-4335.97693	-0.09668	-4336.07361	-36.9	-86.0

Table S6: Sum of electronic energies (E_t, hartree), free energies (G_0, hartree), sum of electronic and free energies (G_c, 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 $C_2H_5CH_2OH$ → $CH_3CH{=}CH_2$ + H_2O catalyzed by $Ni_{12}P_5$ cluster at GGA-PBE/DNP, DSPP level.

Species	E_t	G_0	G_c	G_r	G_r(CO↑)
$Ni_{12}P_5$ + CO + $C_2H_5CH_2OH$	-4335.93724	-0.09721	-4336.03445	66.0	16.9
F7-IM1	-4222.73881	-0.02243	-4222.76124		
F7-IM1 + CO	-4335.97037	-0.05467	-4336.02505	90.6	41.5
F7-TS1	-4222.69682	-0.03049	-4222.72731		
F7-TS1 + CO	-4335.92838	-0.06274	-4335.99111	179.7	130.6
F7-IM2	-4222.74875	-0.03151	-4222.78026		
F7-IM2 + CO	-4335.98031	-0.06375	-4336.04407	40.7	-8.4
F7-TS2	-4222.69632	-0.03881	-4222.73513		
F7-TS2 + CO	-4335.92788	-0.07106	-4335.99893	159.2	110.1
F7-IM3	-4222.72951	-0.02883	-4222.75834		
F7-IM3 + CO	-4335.96107	-0.06107	-4336.02215	98.3	49.2
F7-IM4	-4146.33129	-0.04709	-4146.37838		
F7-IM4 + CO + H_2O	-4335.94563	-0.09460	-4336.04023	50.8	1.7
F7-TS3	-4146.29242	-0.04955	-4146.34197		
F7-TS3 + CO + H_2O	-4335.90676	-0.09706	-4336.00383	146.4	97.2
F7-IM5	-4146.35640	-0.04777	-4146.40417		
F7-IM5 + CO + H_2O	-4335.97074	-0.09528	-4336.06602	-16.9	-66.0
$Ni_{12}P_5$	-4028.52257	-0.11260	-4028.63517		
$Ni_{12}P_5$ + CO + H_2O + $CH_3CH{=}CH_2$	-4335.91504	-0.13324	-4336.04828	29.6	-19.5

Table S7: Sum of electronic energies (E_t, hartree), free energies (G_0, hartree), sum of electronic and free energies (G_c, 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 → C_3H_8 catalyzed by $Ni_{12}P_5$ cluster at GGA-PBE/DNP, DSPP level.

Species	E_t	G_0	G_c	G_r	G_r (CO↑)
$Ni_{12}P_5$ + CO + H_2O + $CH_3CH=CH_2$	-4335.91504	-0.13324	-4336.04828	29.6	-19.5
F3-IM1	-4029.71450	-0.10315	-4029.81765		
F3-IM1 + CO + H_2O + $CH_3CH=CH_2$ - H_2	-4335.94266	-0.10905	-4336.05171	20.6	-28.5
F3-TS1	-4029.71220	-0.10121	-4029.81341		
F3-TS1 + CO + H_2O + $CH_3CH=CH_2$ - H_2	-4335.94035	-0.10711	-4336.04747	31.8	-17.3
F3-IM2	-4029.73086	-0.09956	-4029.83042		
F3-IM2 + CO + H_2O + $CH_3CH=CH_2$ - H_2	-4335.95901	-0.10546	-4336.06447	-12.9	-62.0
F7-IM6	-4147.55887	-0.03395	-4147.59281		
F7-IM6 + CO + H_2O - H_2	-4336.00890	-0.06672	-4336.07562	-42.1	-91.2
F7-TS4	-4147.53352	-0.03684	-4147.57035		
F7-TS4 + CO + H_2O - H_2	-4335.98355	-0.06961	-4336.05315	16.8	-32.3
F7-IM7	-4147.54681	-0.03149	-4147.57830		
F7-IM7 + CO + H_2O - H_2	-4335.99684	-0.06426	-4336.06110	-4.0	-53.1
F7-TS5	-4147.52812	-0.03627	-4147.56438		
F7-TS5 + CO + H_2O - H_2	-4335.97815	-0.06904	-4336.04719	32.5	-16.6
F7-IM8	-4147.54279	-0.03035	-4147.57313		
F7-IM8 + CO + H_2O - H_2	-4335.99282	-0.06312	-4336.05594	9.5	-39.6
$Ni_{12}P_5$	-4028.52257	-0.11260	-4028.63517		
$Ni_{12}P_5$ + CO + H_2O -H_2 + C_3H_8	-4335.97693	-0.09668	-4336.07361	-36.9	-86.0

Table S8: Sum of electronic energies (E_t, hartree), free energies (G_0, hartree), sum of electronic and free energies (G_c, hartree) and relative energies (G_r, kJ mol^{-1}) of various species with respect to the reactants for the reaction of $C_3H_7CHO + H_2 \rightarrow C_3H_7CH_2OH$ catalyzed by $Ni_{12}P_5$ cluster at GGA-PBE/DNP, DSPP level.

Species	E_t	G_0	G_c	G_r
$Ni_{12}P_5$ - C_3H_7COOH + C_3H_7CHO + H_2O	-4029.68044	-0.13126	-4029.81170	6.6
F3-IM1	-4029.71450	-0.10315	-4029.81765	
F3-IM1 - C_3H_7COOH + C_3H_7CHO + H_2O - H_2	-4029.70807	-0.10706	-4029.81513	-2.4
F3-TS1	-4029.71220	-0.10121	-4029.81341	
F3-TS1 - C_3H_7COOH + C_3H_7CHO + H_2O - H_2	-4029.70576	-0.10513	-4029.81089	8.8
F3-IM2	-4029.73086	-0.09956	-4029.83042	
F3-IM2 - C_3H_7COOH + C_3H_7CHO + H_2O - H_2	-4029.72442	-0.10347	-4029.82789	-35.9
F8-IM3	-4262.02168	-0.01326	-4262.03494	
F8-IM3 + H_2O - C_3H_7COOH - H_2	-4029.76269	-0.06685	-4029.82954	-40.2
F8-TS2	-4261.99075	-0.01603	-4262.00678	
F8-TS2 + H_2O - C_3H_7COOH - H_2	-4029.73176	-0.06962	-4029.80138	33.7
F8-IM4	-4262.01172	-0.00328	-4262.01499	
F8-IM4 + H_2O - C_3H_7COOH - H_2	-4029.75272	-0.05687	-4029.80959	12.2
F8-TS3	-4261.97891	-0.00838	-4261.98729	
F8-TS3 + H_2O - C_3H_7COOH - H_2	-4029.71991	-0.06198	-4029.78189	84.9
F8-IM5	-4261.99110	-0.00016	-4261.99126	
F8-IM5 + H_2O - C_3H_7COOH - H_2	-4029.73211	-0.05375	-4029.78586	74.5
$Ni_{12}P_5$	-4028.52257	-0.11260	-4028.63517	
$Ni_{12}P_5$ + H_2O - C_3H_7COOH - H_2 + $C_3H_7CH_2OH$	-4029.71747	-0.09568	-4029.81315	2.8

Table S9: Sum of electronic energies (E_t, hartree), free energies (G_0, hartree), sum of electronic and free energies (G_c, hartree) and relative energies (G_r, kJ mol^{-1}) of various species with respect to the reactants for the reaction of $C_3H_7CH_2OH + H_2 \rightarrow C_4H_{10} + H_2O$ catalyzed by $Ni_{12}P_5$ cluster at GGA-PBE/DNP, DSPP level.

Species	E_t	G_0	G_c	G_r
$Ni_{12}P_5 + H_2O - C_3H_7COOH - H_2 + C_3H_7CH_2OH$	-4029.71747	-0.09568	-4029.81315	2.8
F3-IM1	-4029.71450	-0.10315	-4029.81765	
F3-IM1 + $H_2O - C_3H_7COOH - 2H_2 + C_3H_7CH_2OH$	-4029.74509	-0.07148	-4029.81657	-6.2
F3-TS1	-4029.71220	-0.10121	-4029.81341	
F3-TS1 + $H_2O - C_3H_7COOH - 2H_2 + C_3H_7CH_2OH$	-4029.74278	-0.06955	-4029.81233	5.0
F3-IM2	-4029.73086	-0.09956	-4029.83042	
F3-IM2 + $H_2O - C_3H_7COOH - 2H_2 + C_3H_7CH_2OH$	-4029.76144	-0.06789	-4029.82934	-39.7
F9-IM3	-4263.22161	0.00937	-4263.21224	
F9-IM3 + $H_2O - C_3H_7COOH - 2H_2$	-4029.79830	-0.02948	-4029.82779	-35.6
F9-TS2	-4263.17838	0.01002	-4263.16837	
F9-TS2 + $H_2O - C_3H_7COOH - 2H_2$	-4029.75508	-0.02884	-4029.78391	79.6
F9-IM4	-4263.23383	0.00835	-4263.22548	
F9-IM4 + $H_2O - C_3H_7COOH - 2H_2$	-4029.81052	-0.03050	-4029.84102	-70.3
F9-TS3	-4263.17957	-0.00299	-4263.18257	
F9-TS3 + $H_2O - C_3H_7COOH - 2H_2$	-4029.75627	-0.04185	-4029.79811	42.3
F9-IM5	-4263.22532	0.00811	-4263.21721	
F9-IM5 + $H_2O - C_3H_7COOH - 2H_2$	-4029.80202	-0.03074	-4029.83276	-48.6
F9-IM6	-4186.81653	-0.00572	-4186.82225	
F9-IM6 + $2H_2O - C_3H_7COOH - 2H_2$	-4029.77601	-0.05983	-4029.83584	-56.7
F9-TS4	-4186.86917	-0.01187	-4186.88104	
F9-TS4 + $2H_2O - C_3H_7COOH - 2H_2$	-4029.82864	0.02018	-4029.80847	15.1
F9-IM7	-4186.80856	0.00396	-4186.80460	
F9-IM7 + $2H_2O- C_3H_7COOH - 2H_2$	-4029.76804	-0.05016	-4029.81820	-10.4
$Ni_{12}P_6$	-4028.52257	-0.11260	-4028.63517	
$Ni_{12}P_5 + 2H_2O - C_3H_7COOH - 2H_2 + C_4H_{10}$	-4029.75742	-0.09582	-4029.85324	-102.4

Table S10: Sum of electronic energies (E_t, hartree), free energies (G_0, hartree), sum of electronic and free energies (G_c, hartree) and relative energies (G_r, kJ mol^{-1}) of various species with respect to the reactants for the reaction of $C_3H_7CH_2OH \rightarrow CH_3CH_2CH=CH_2 + H_2O$ catalyzed over $Ni_{12}P_5$ cluster at GGA-PBE/DNP, DSPP level.

Species	E_t	G_0	G_c	G_r
$Ni_{12}P_5 + H_2O - C_3H_7COOH - H_2 + C_3H_7CH_2OH$	-4029.71747	-0.09568	-4029.81315	2.8
F10-IM1	-4262.01293	-0.00466	-4262.01758	
F10-IM1+ $H_2O - C_3H_7COOH - H_2$	-4029.75393	-0.05825	-4029.81218	5.4
F10-TS1	-4261.97090	-0.00720	-4261.97810	
F10-TS1+ $H_2O - C_3H_7COOH - H_2$	-4029.71190	-0.06080	-4029.77270	109.0
F10-IM2	-4262.02099	-0.00803	-4262.02902	
F10-IM2+ $H_2O - C_3H_7COOH - H_2$	-4029.76200	-0.06162	-4029.82362	-24.7
F10-TS2	-4261.97062	-0.01553	-4261.98615	
F10-TS2+ $H_2O - C_3H_7COOH - H_2$	-4029.71163	-0.06912	-4029.78075	87.9
F10-IM3	-4262.00179	-0.01170	-4262.01349	
F10-IM3+ $H_2O - C_3H_7COOH - H_2$	-4029.74280	-0.06529	-4029.80809	16.1
F10-IM4	-4185.60329	-0.02465	-4185.62794	
F10-IM4 - $C_3H_7COOH - H_2 + 2H_2O$	-4029.72708	-0.09351	-4029.82059	-16.7
F10-TS3	-4185.56470	-0.02943	-4185.59413	
F10-TS3 - $C_3H_7COOH - H_2 + 2H_2O$	-4029.68848	-0.09829	-4029.78677	72.1
F10-IM4	-4185.62859	-0.02733	-4185.65592	
F10-IM4 - $C_3H_7COOH - H_2 + 2H_2O$	-4029.75237	-0.09619	-4029.84857	-90.1
$Ni_{12}P_5$	-4028.52257	-0.11260	-4028.63517	
$Ni_{12}P_5 - C_3H_7COOH - H_2 + 2H_2O + CH_3CH_2CH=CH_2$	-4029.69500	-0.13166	-4029.82666	-32.6

Table S11: Sum of electronic energies (E_t, hartree), free energies (G_0, hartree), sum of electronic and free energies (G_c, hartree) and relative energies (G_r, kJ mol^{-1}) of various species with respect to the reactants for the reaction of $CH_3CH_2CH{=}CH_2 + H_2 \rightarrow C_4H_{10}$ catalyzed by $Ni_{12}P_5$ cluster at GGA-PBE/DNP, DSPP level.

Species	E_t	G_0	G_c	G_r
$Ni_{12}P_5$+ $2H_2O$ - C_3H_7COOH - H_2 + $CH_3CH_2CH{=}CH_2$	-4029.69500	-0.13166	-4029.82666	-32.6
F3-IM1	-4029.71450	-0.10315	-4029.81765	
F3-IM1 + $2H_2O$ - C_3H_7COOH - $2H_2$ + $CH_3CH_2CH{=}CH_2$	-4029.72262	-0.10747	-4029.83009	-41.6
F3-TS1	-4029.71220	-0.10121	-4029.81341	
F3-TS1 + $2H_2O$ - C_3H_7COOH - $2H_2$ + $CH_3CH_2CH{=}CH_2$	-4029.72032	-0.10553	-4029.82585	-30.5
F3-IM2	-4029.73086	-0.09956	-4029.83042	
F3-IM2 + $2H_2O$ - C_3H_7COOH - $2H_2$ + $CH_3CH_2CH{=}CH_2$	-4029.73898	-0.10388	-4029.84285	-75.2
F10-IM6	-4186.827522	-0.01624	-4186.84376	
F10-IM6 + $2H_2O$ - C_3H_7COOH - $2H_2$	-4029.78700	-0.07036	-4029.85735	-113.2
F10-TS4	-4186.798328	-0.01376	-4186.81209	
F10-TS4 + $2H_2O$ - C_3H_7COOH - $2H_2$	-4029.75780	-0.06788	-4029.82569	-30.1
F10-IM8	-4186.817812	-0.00985	-4186.82766	
F10-IM7 + $2H_2O$ - C_3H_7COOH - $2H_2$	-4029.77729	-0.06397	-4029.84125	-70.9
F10-TS5	-4186.789665	-0.01258	-4186.80225	
F10-TS5 + $2H_2O$ - C_3H_7COOH - $2H_2$	-4029.74914	-0.06670	-4029.81584	-4.2
F10-IM9	-4186.810419	-0.00408	-4186.81450	
F10-IM9 + $2H_2O$ - C_3H_7COOH - $2H_2$	-4029.76989	-0.05820	-4029.82810	-36.4
$Ni_{12}P_5$	-4028.52257	-0.11260	-4028.63517	
$Ni_{12}P_5$ + $2H_2O$ - C_3H_7COOH - $2H_2$ + C_4H_{10}	-4029.75742	-0.09582	-4029.85324	-102.4