Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information

Table S1. Interaction Energy ($E_{int.} = E_{abs.} - E_{relax.} - E_{dist.}$) of C_2H_6, C_3H_8 and C_4H_{10} on DI-Rh_{19} and DI-Ni_{19} Clusters on $Rh_{13}L_s$, $Rh_{13}L_s$/UGO and $Rh_{13}L_s/TiO_2$.

	Rh_{13}-L_s			
Alkanes	$E_{dist.}$/eV	$E_{relax.}$/eV	$E_{ads.}$/eV	$E_{int.}$/eV
C_2H_6	0.066	0.035	-0.33	-0.431
C_3H_8	0.090	0.043	-0.36	-0.493
C_4H_{10}	0.108	0.027	-0.42	-0.555
	Rh_{13}-L_s/UGO			
Alkanes	$E_{dist.}$/eV	$E_{relax.}$/eV	$E_{ads.}$/eV	$E_{int.}$/eV
C_2H_6	0.069	0.033	-0.38	-0.482
C_3H_8	0.098	0.038	-0.43	-0.566
C_4H_{10}	0.101	0.023	-0.49	-0.614
	Rh_{13}-L_s/TiO_2			
Alkanes	$E_{dist.}$/eV	$E_{relax.}$/eV	$E_{ads.}$/eV	$E_{int.}$/eV
C_2H_6	0.059	0.033	-0.49	-0.582
C_3H_8	0.085	0.042	-0.52	-0.647
C_4H_{10}	0.098	0.021	-0.50	-0.619

Table S2. Calculated Activation Energies (E_a) of 1_{st} alkanes dehydrogenation, and Difference of Integrated Overlap Areas (ΔA) between Initial State and Transition State of the Local Density of States (LDOS) between the top Rh atoms (d state) and alkanes (s and p states) on $Rh_{13}L_s$, $Rh_{13}L_s$/UGO and $Rh_{13}L_s/TiO_2$, respectively.

	$C_2H_6 \rightarrow C_2H_5 + H$			
Substrates	A(IS) /arb. units	A(TS) /arb. units	ΔA/ arb. units	E_a/eV
Rh_{13}-L_s	0.75	2.43	1.68	0.25
Rh_{13}-L_s/UGO	0.80	2.33	1.53	0.21
Rh_{13}-L_s/TiO_2	0.86	2.57	1.71	0.29
	$C_3H_8 \rightarrow C_3H_7 + H$			
Substrates	A(IS) /arb. units	A(TS) /arb. units	ΔA/ arb. units	E_a/eV
Rh_{13}-L_s	0.85	2.59	1.74	0.28
Rh_{13}-L_s/UGO	0.93	2.48	1.55	0.22
Rh_{13}-L_s/TiO_2	0.95	2.74	1.79	0.32
	$C_4H_{10} \rightarrow C_4H_9 + H$			
Substrates	A(IS) /arb. units	A(TS) /arb. units	ΔA/ arb. units	E_a/eV
Rh_{13}-L_s	0.88	2.58	1.70	0.26
Rh_{13}-L_s/UGO	1.04	2.27	1.23	0.16
Rh_{13}-L_s/TiO_2	1.01	2.83	1.82	0.35

Table S3. Calculated Activation Energies (E_a) and Gibbs Free Energies (ΔG) of $C_nH_{2n+2(a)} \rightarrow C_nH_{2n+1(a)} + H_{(a)}$ and $C_nH_{2n+1(a)} \rightarrow C_nH_{2n\ (a)} + H_{(a)}$ on $Rh_{13}L_s$, $Rh_{13}L_s$/UGO and $Rh_{13}L_s/TiO_2$ in 1073K.

	$C_2H_{6(a)} \rightarrow C_2H_{5(a)} + H_{(a)}$		$C_2H_{5(a)} + H_{(a)} \rightarrow C_2H_{4(a)} + 2H_{(a)}$	
Substrates	E_a(1073K)/eV	ΔG(1073K)/eV	E_a(1073K) /eV	ΔG(1073K)/eV
Rh_{13}-L_s	0.17	-0.69	0.15	- 0.09
Rh_{13}-L_s/UGO	015	- 0.62	0.14	- 0.37
Rh_{13}-L_s/TiO_2	0.23	- 0.36	0.15	- 0.08

	$C_3H_{8(a)} \rightarrow C_3H_{7(a)} + H_{(a)}$		$C_3H_{7(a)} + H_{(a)} \rightarrow C_3H_{6(a)} + 2H_{(a)}$	
Substrates	E_a(1073K)/eV	ΔG(1073K)	E_a(1073K)/eV	ΔG(1073K)
Rh_{13}-L_s	0.23	- 0.67	0.19	- 0.12
Rh_{13}-L_s/UGO	0.17	- 0.57	0.15	- 0.39
Rh_{13}-L_s/TiO_2	0.32	- 0.41	0.19	- 0.09

	$C_4H_{10(a)} \rightarrow C_4H_{9(a)} + H_{(a)}$		$C_4H_{9(a)} + H_{(a)} \rightarrow C_4H_{8(a)} + 2H_{(a)}$	
Substrates	E_a(1073K)/eV	ΔG(1073K)	E_a(1073K)/eV	ΔG(1073K)
Rh_{13}-L_s	0.25	- 0.43	0.20	- 0.23
Rh_{13}-L_s/UGO	0.14	-0.56	0.06	-0.36
Rh_{13}-L_s/TiO_2	0.27	- 0.41	0.19	- 0.12

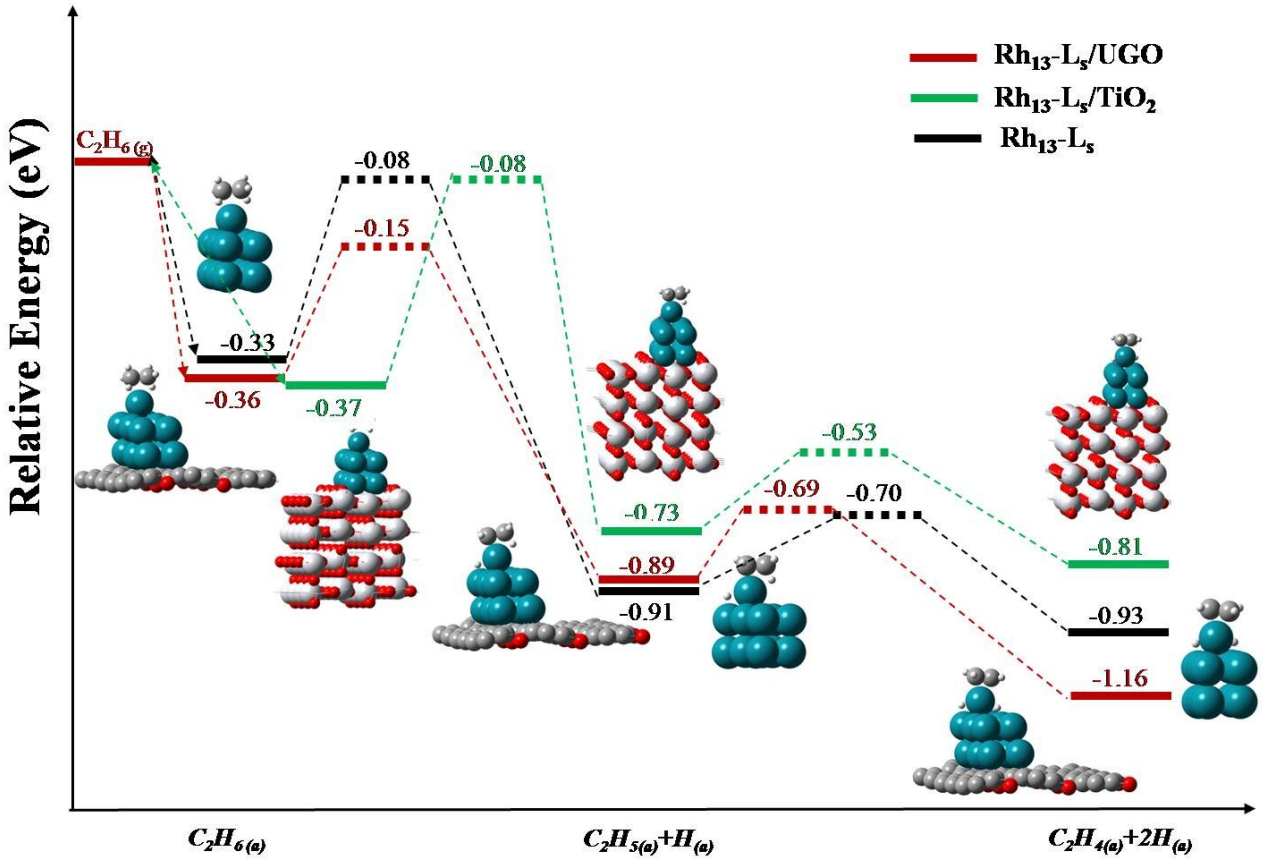

Figure S1. Profiles of the potential-energy surface for the dehydrogenation of ethane on Rh_{13}-L_s, Rh_{13}-L_s/UGO and Rh_{13}-L_s/TiO_2.

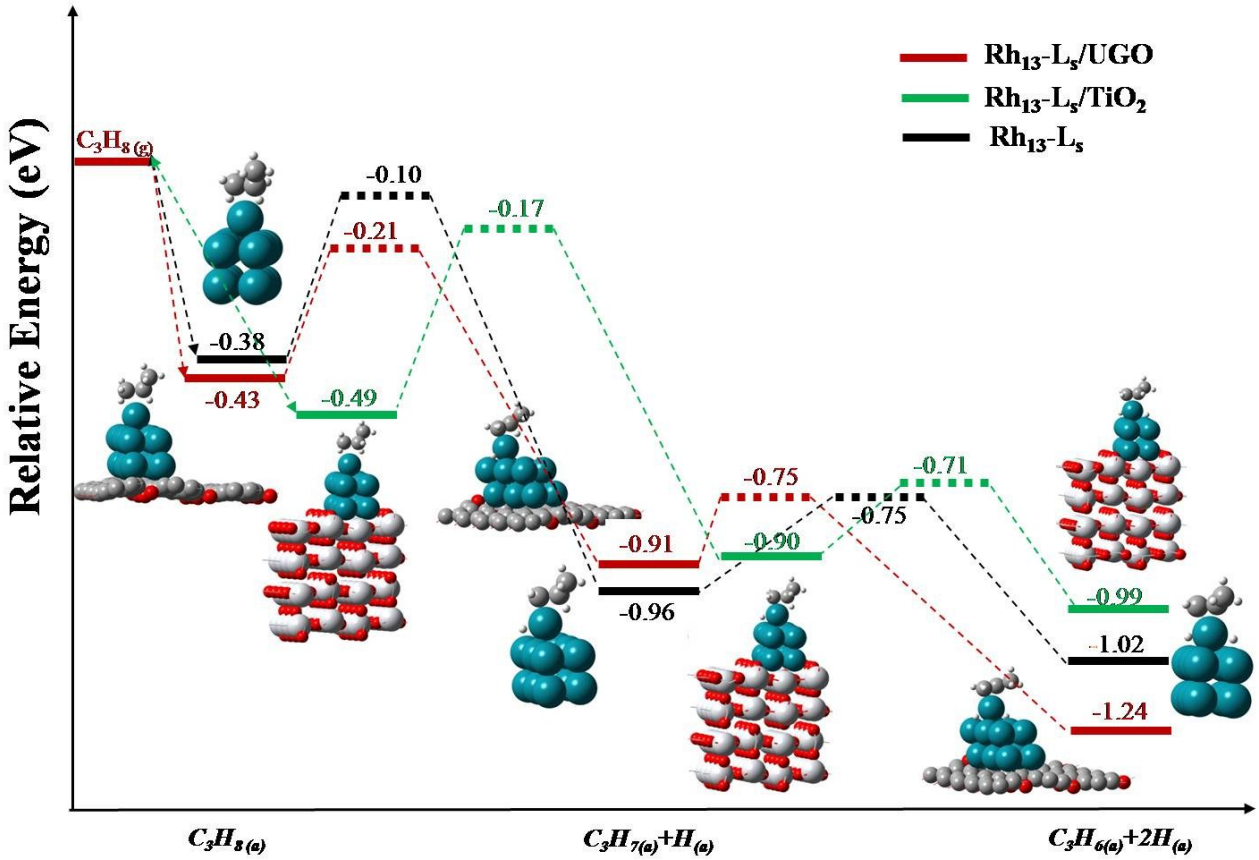

Figure S2. Profiles of the potential-energy surface for the dehydrogenation of propane on Rh_{13}-L_s, Rh_{13}-L_s/UGO and Rh_{13}-L_s/TiO_2.

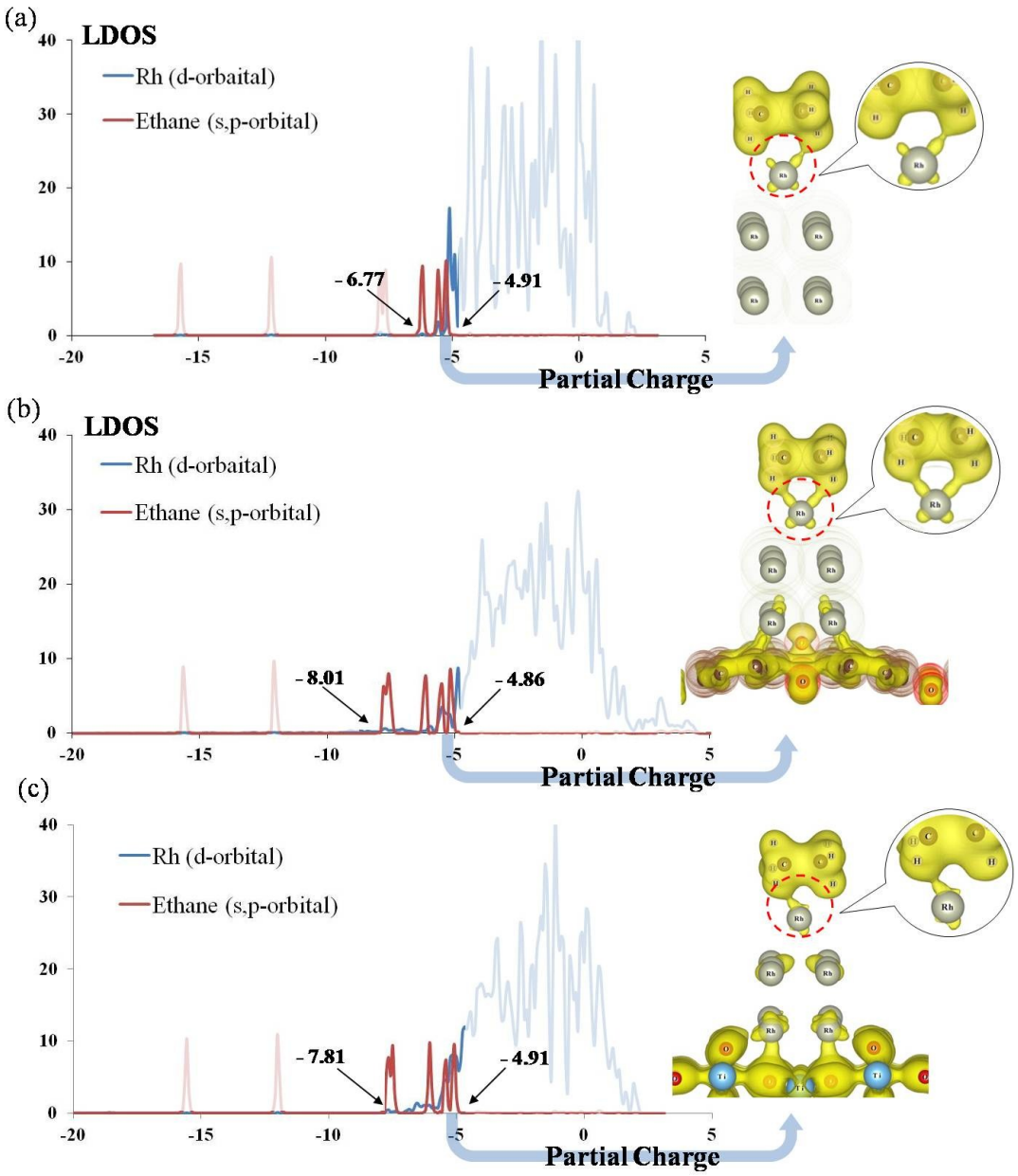

Figure S3. Local density of states (LDOS) and partial charge between rhodium atoms (*d* state) and ethane (*s* and *p* states) on (a) Rh_{13}-L_s cluster; (b) Rh_{13}-L_s/UGO; (c) Rh_{13}-L_s/TiO_2.

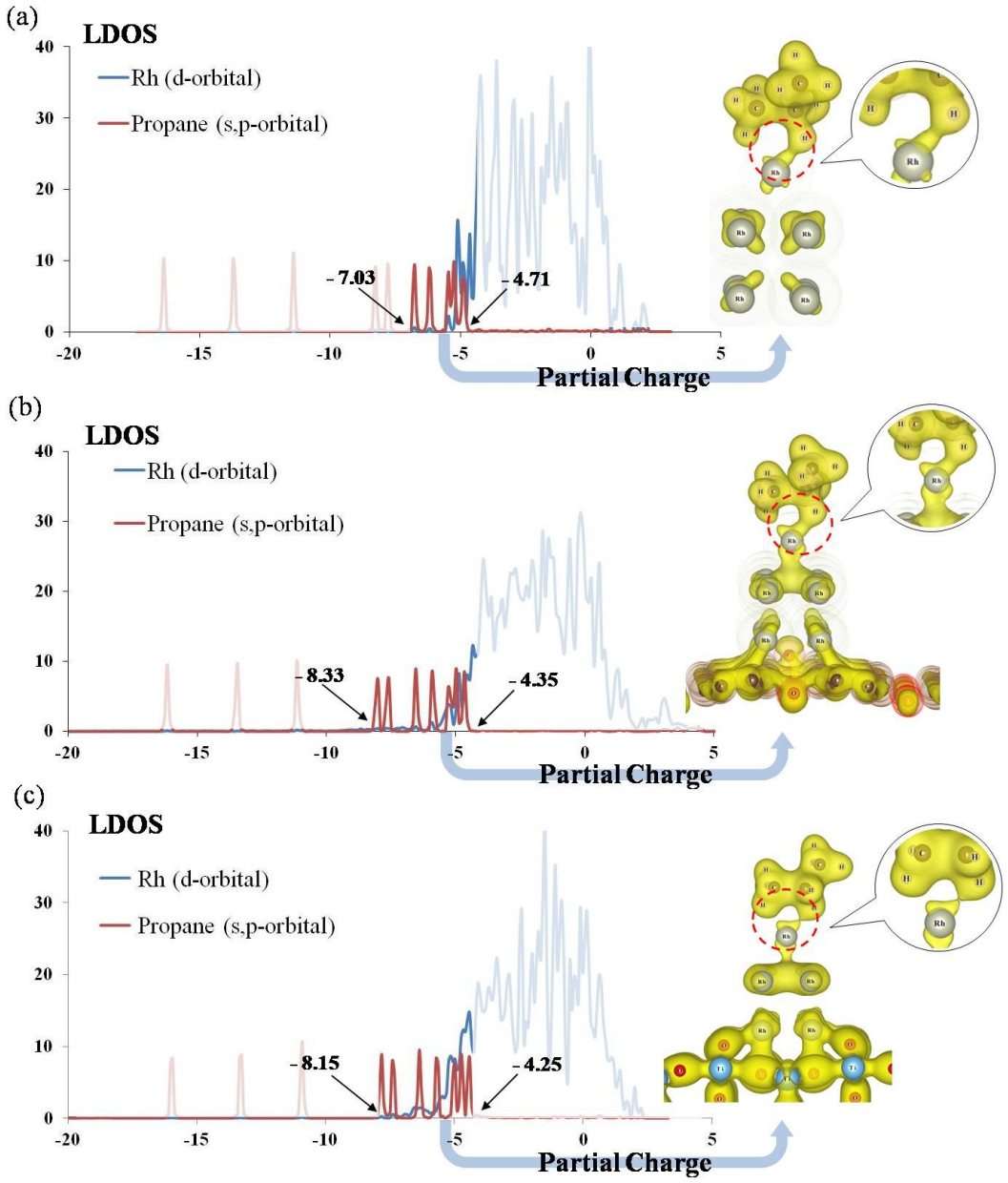

Figure S4. Local density of states (LDOS) and partial charge between rhodium atoms (*d* state) and propane (*s* and *p* states) on (a) Rh_{13}-L_s cluster; (b) Rh_{13}-L_s/UGO; (c) Rh_{13}-L_s/TiO_2.

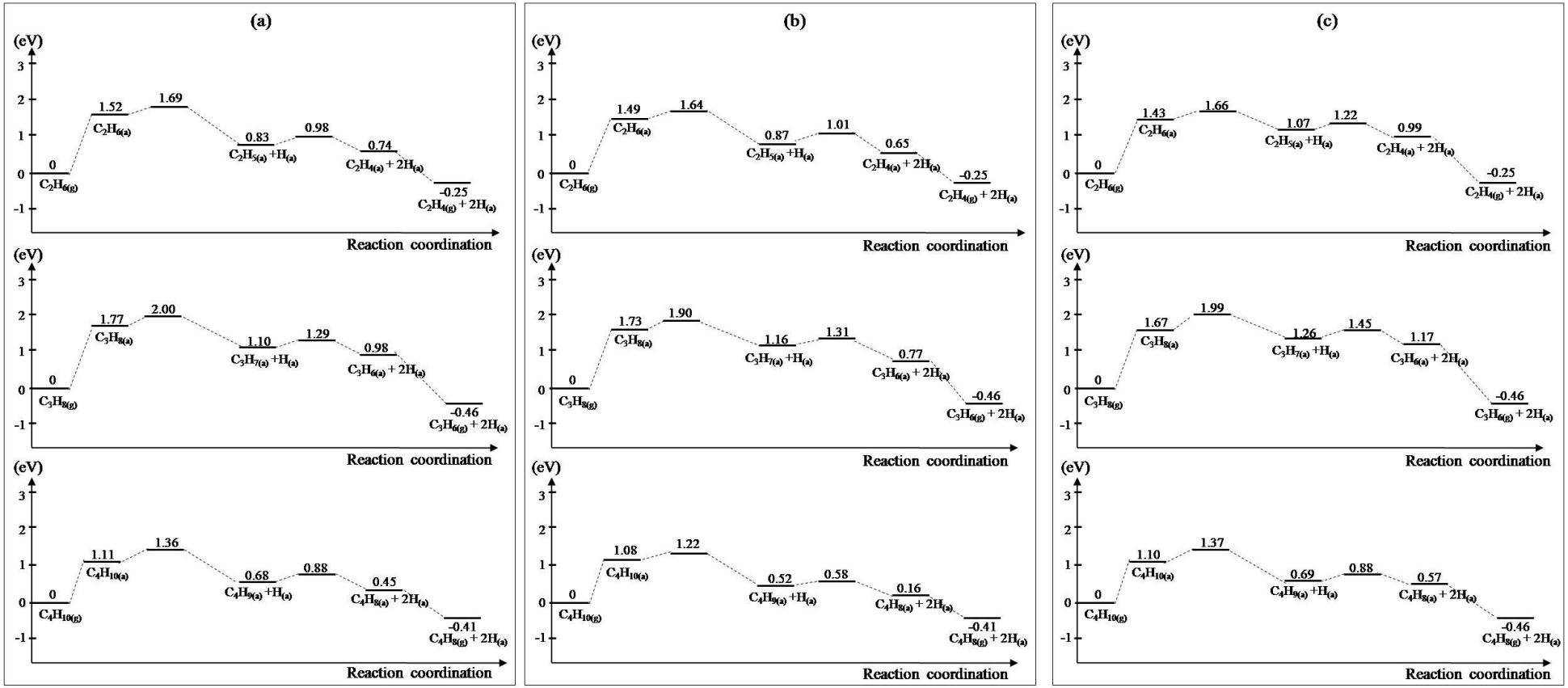

Figure S5. Calculated energetics of Gibbs free energy for alkanes (C_2H_6, C_3H_8 and C_4H_{10}) dehydrogenation on (a)Rh_{13}-L_s; (b)Rh_{13}-L_s/UGO and (c)Rh_{13}-L_s/TiO_2 at 1073K.