Supporting information

Differentiation of C-O and C-C bond Scission Mechanism of 1-Hexadecanol on Pt(111) and Ru(0001): A First Principles Analysis

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Table S1. Partition Functions Applied in the Micro-kinetic Model of ethanol reactions

type	Partition function
Translation	$q^T = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}$
Rotational (linear)	$q^R_{linear} = \frac{1}{\sigma}\frac{k_B T}{hB}$
Rotational (non-linear)	$q^R_{non-linear} = \frac{1}{\sigma}\left(\frac{k_B T}{hB}\right)^{3/2}\sqrt{\frac{\pi}{ABC}}$
Vibration	$q^v = \prod_i^{DF}\left(\frac{1}{1-e^{-\frac{hv_i}{k_B T}}}\right)$
Electronic	$q^E = (2S+1)e^{-\frac{E_a}{k_B T}}$
Total	$q = q^T q^R q^V q^E$

Note: h, V and σ refer to Plank's constant, the volume of the system and the symmetry factor, respectively. A, B and C are rotational constants, V_i is denoted as the vibrational frequency of the ith mode, DF refers to the degree of freedoms, S is the total spin angular momentum, E_g is the electronic energy from the ground state.

Table S2. Elementary reaction steps and kinetic parameters for Hexadecanol decomposition Reaction on Ru (0001) in this work [a]

Reaction		E_a/ eV	A	E_a^{-1}/ eV	A^{-1}
M1	RCH_2CH_2OH (g)+*→RCH_2CH_2OH*	0.00	6.15e2	1.66(1.78)	5.69e19
M2	RCH_2CH_2OH*+*→RCH_2CH_2O*+H*	0.57(0.72)	1.95e13	1.02(1.02)	2.75e13
M3	RCH_2CH_2O*+*→RCH_2CHO*+H*	0.21(0.36)	1.79e13	0.49(0.50)	1.81e13
M4	RCH_2CHO*+*→RCH_2CO*+H*	0.00(0.09)	1.73e13	0.80(0.83)	1.81e13

M5	$RCH_2CO^*+^*\rightarrow RCHCO^*+H^*$	0.75(0.89)	1.55e13	1.01(1.07)	1.73e13
M6	$RCHCO^*+^*\rightarrow RCH^*+CO^*$	0.47(0.54)	2.19e13	1.35(1.36)	1.52e13
M7	$CO^*\rightarrow CO(g)+^*$	1.86(1.97)	5.85e17	0.00	1.81e3
M8	$RCHCO^*+^*\rightarrow RCHC^*+O^*$	0.85(0.85)	1.16e13	2.42(2.42)	2.28e13
M9	$RCH^*+H^*\rightarrow RCH_2^*+^*$	0.87(0.83)	1.73e13	0.16(0.29)	1.97e13
M10	$RCH_2^*+H^*\rightarrow RCH_3^*+^*$	0.85(0.85)	2.07e13	0.80(0.96)	2.16e13
M11	$RCH_3^*\rightarrow RCH_3(g)+^*$	0.70(0.71)	4.52e19	0.00	6.57e2
M12	$RCHC^*+H^*\rightarrow RCHCH^*+^*$	0.43(0.45)	1.68e13	0.00(0.15)	1.66e13
M13	$RCHCH^*+H^*\rightarrow RCH_2CH^*+^*$	0.34(0.38)	1.66e13	0.00(0.11)	1.72e13
M14	$RCH_2CH^*+H^*\rightarrow RCH_2CH_2^*+^*$	0.43(0.43)	1.60e13	0.12(0.26)	1.65e13
M15	$RCH_2CH_2^*+H^*\rightarrow RCH_2CH_3^*+^*$	1.03(1.03)	1.66e13	0.74(0.91)	1.73e13
M16	$RCH_2CH_3^*\rightarrow RCH_2CH_3(g)+^*$	1.15(1.15)	5.11e19	0.00	6.37e2
M17	$CO^*+H^*\rightarrow HCO^*+^*$	1.32(1.32)	2.32e13	0.27(0.34)	2.53e13
M18	$HCO^*+H^*\rightarrow H_2CO^*+^*$	0.50(0.50)	2.11e13	0.13(0.21)	2.48e13
M19	$H_2CO^*+^*\rightarrow CH_2^*+O^*$	1.10(1.14)	2.19e13	1.46(1.46)	2.86e13
M20	$CH_2^*+H^*\rightarrow CH_3^*+^*$	0.55(0.55)	1.84e13	0.38(0.49)	1.13e13
M21	$CH_3^*+H^*\rightarrow CH_4^*+^*$	0.72(0.72)	3.08e13	0.75(0.90)	4.98e12
M22	$CH_4^*\rightarrow CH_4(g)+^*$	0.38(0.42)	1.01e16	0.00	2.39e3
M23	$2H^*\rightarrow H_2^*+^*$	0.61(0.64)	3.25e13	0.00(0.02)	2.06e13
M24	$H_2^*\rightarrow H_2(g)+^*$	0.82(0.96)	6.54e14	0.00	6.77e3
M25	$O^*+H^*\rightarrow OH^*+^*$	1.30(1.35)	2.38e13	0.65(0.84)	1.87e13
M26	$OH^*+H^*\rightarrow H_2O^*+^*$	0.94(0.99)	2.24e13	0.77(0.96)	1.34e13
M27	$H_2O^*\rightarrow H_2O(g)+^*$	0.56(0.64)	1.00e13	0.00	2.93e8

Note: The magnitude of pre-exponential factors (A) was estimated at 473 K and 1.00 MPa. [a] Entries in parentheses are the energies before ZPE correction.

Table S3. Elementary reaction steps and kinetic parameters for Hexadecanol decomposition Reaction on Pt(111) in this work [a]

Reaction	E_a/ eV	A	E_a^{-1}/ eV	A^{-1}

M1	RCH_2CH_2OH (g)+*→RCH_2CH_2OH*	0.00	6.15e2	1.34(1.45)	5.69e19
M2	RCH_2CH_2OH*+*→RCH_2CHOH*+H*	0.34(0.46)	2.03e13	0.68(0.68)	2.12e13
M3	RCH_2CHOH*+*→RCH_2COH*+H*	0.42(0.66)	1.53e13	0.33(0.40)	1.38e13
M4	RCH_2COH*+*→RCH_2C*+OH*	0.70(0.72)	1.72e13	0.91(0.91)	1.54e13
M5	RCH_2COH *+*→RCH_2CO*+H*	0.18(0.40)	1.35e13	0.75(0.79)	1.35e13
M6	RCH_2CO *+*→ RCHCO*+H*	1.36(1.47)	1.75e13	0.48(0.62)	2.06e13
M7	RCHCO*+*→RCH*+CO*	0.98(1.01)	3.95e13	0.81(0.82)	1.34e13
M8	RCH_2C*+H*→ RCH_2CH*+*	0.91(0.91)	1.61e13	0.25(0.39)	1.85e13
M9	RCH_2CH*+H*→ RCH_2CH_2*+*	0.45(0.51)	1.16e13	0.96(1.17)	1.78e13
M10	RCH_2CH_2*+H*→RCH_2CH_3*+*	0.89(0.93)	1.16e13	0.70(0.87)	1.89e13
M11	RCH*+H*→RCH_2*+*	0.70(0.70)	1.57e13	0.98(1.14)	1.96e13
M12	RCH_2*+H*→RCH_3*+*	0.72(0.74)	2.51e13	0.60(0.78)	1.77e13
M13	RCH_2CH_3*→ RCH_2CH_3(g) +*	0.98(0.98)	5.11e19	0.00	6.37e2
M14	RCH_3*→ RCH_3(g)+ *	1.49(1.49)	4.52e19	0.00	6.57e2
M15	2H*→H_2*+*	1.12(1.12)	2.28e13	0.30(0.33)	5.11e12
M16	H_2*→H_2(g)+*	0.11(0.11)	6.54e14	0.00	6.77e3

Note: The magnitude of pre-exponential factors (A) was estimated at 473 K and 1.00 MPa. [a] Entries in parentheses are the energies before ZPE correction.

Table S4. The calculated binding energies and the predicted binding energies of 1-Hexadecanol and its dehydrogenated intermediates in Figure 2 on Pt (111)

species	binding energy (eV)	
	Pt(111), DFT[a]	Pt(111), Scaling[b]
RCH_2CH_2OH	-0.25	-0.25
RCH_2CH_2O	0.88	0.88
RCH_2CHOH	0.03	0.03
$RCHCH_2OH$	0.22	0.22
RCH_2CHO	0.77	0.77
$RCHCH_2O$	1.08	1.41
RCHCHOH	0.45	0.50
$RCCH_2OH$	1.14	0.68

RCH_2COH	0.65	0.31
RCHCHO	1.30	1.30
RCH_2CO	0.45	0.66
$RCCH_2O$	1.89	1.94
RCCHOH	0.61	0.96
RCHCOH	0.90	0.78
RCCOH	1.00	1.24
RCHCO	1.36	1.19
RCCHO	1.74	1.83

Note: [a] refers to the calculated binding energies of the 1-Hexadecanol and its dehydrogenated intermediates in Figure 2 on Pt (111); [b] refers to the predicted binding energies of the 1-Hexadecanol and its dehydrogenated intermediates in Figure 2 on Pt (111)

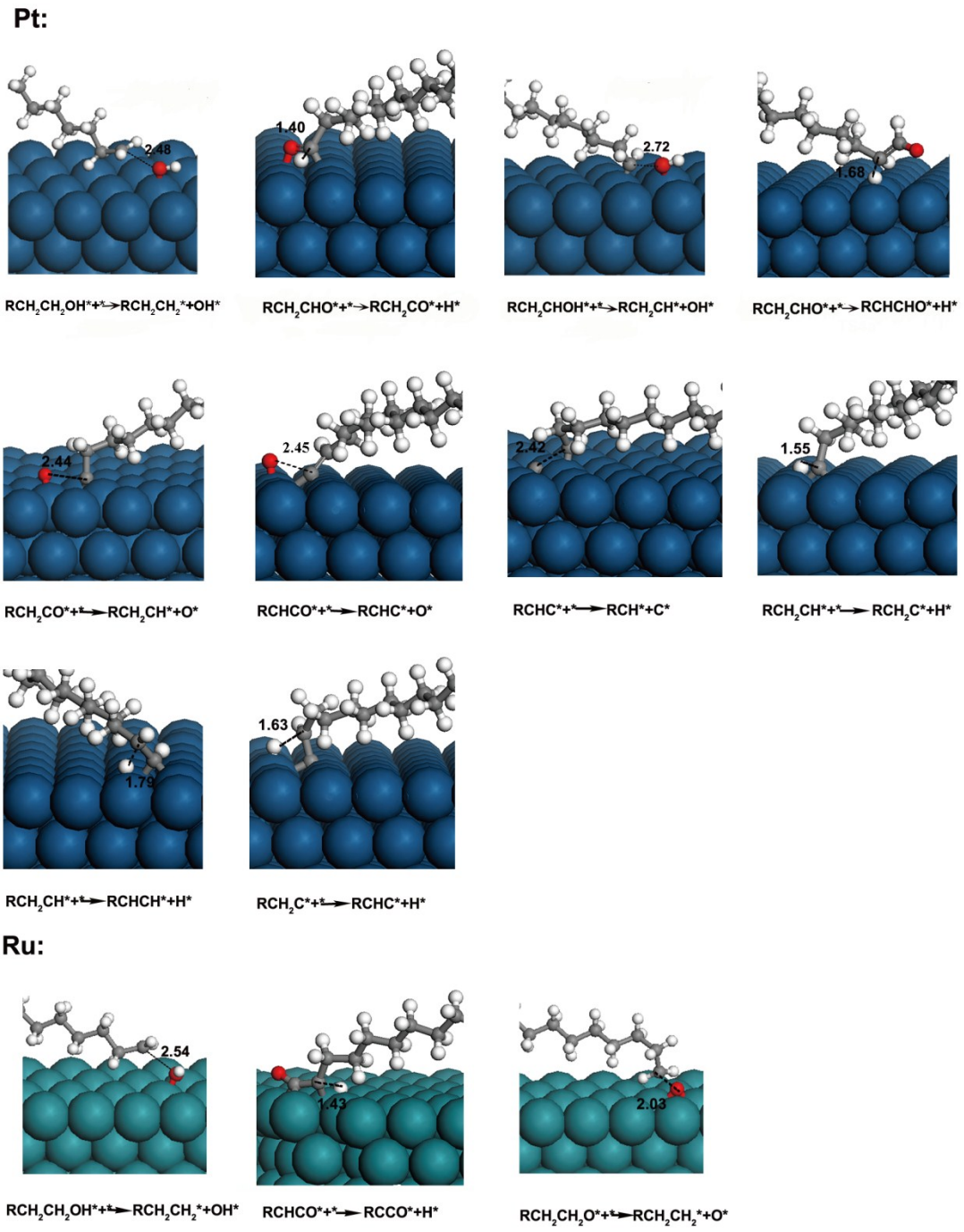

Figure S1. Optimized configurations for the TSs involved in the side reaction on Pt (111) and Ru (0001).

Here R=$C_{14}H_{29}$.