Supporting Information

Density Functional Study of Ethanol Decomposition on Rh(111)

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Figure S1

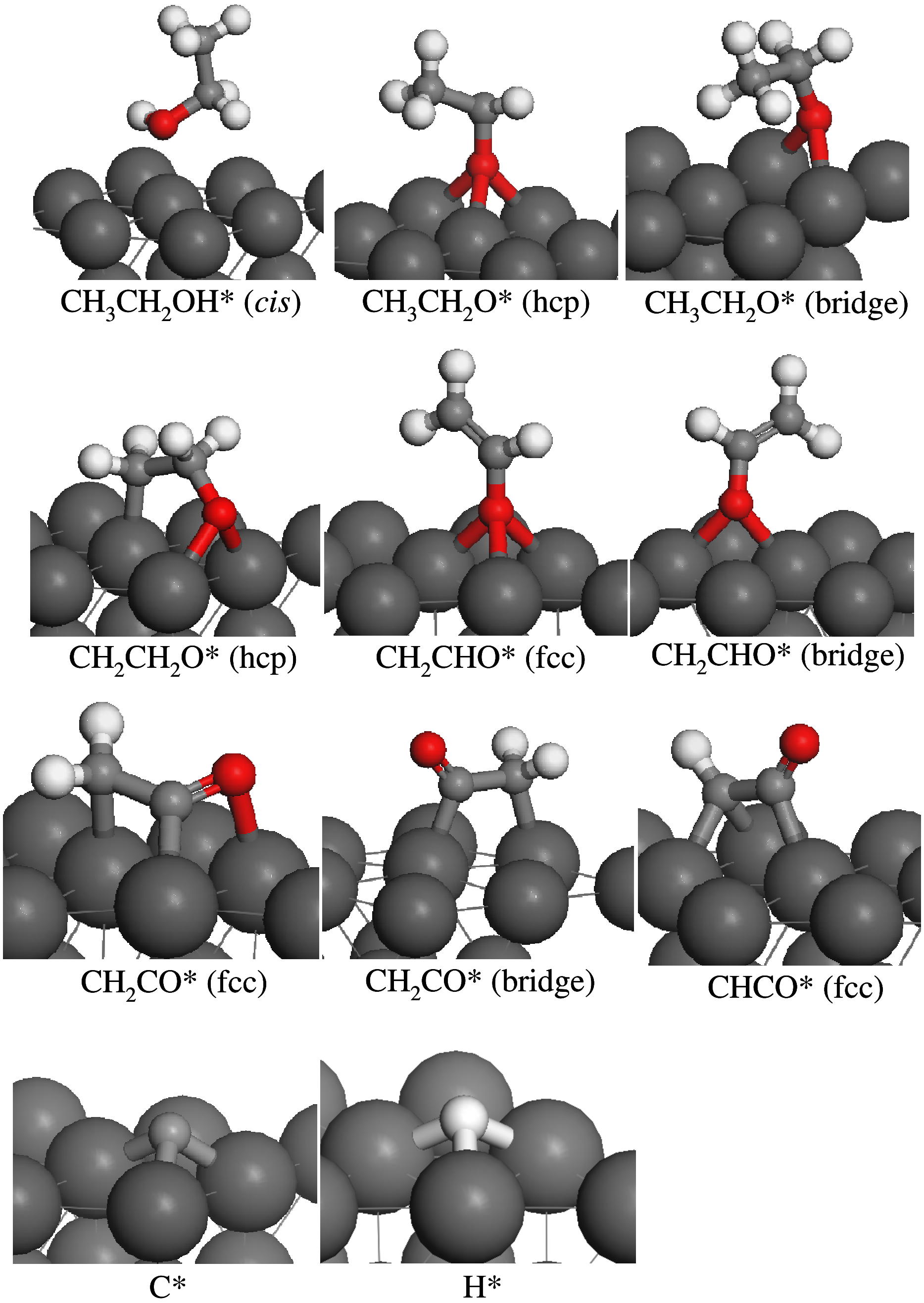


Figure S1. Optimized adsorption geometries for the other stable configurations of the intermediates included in the reaction pathway

Figure S2

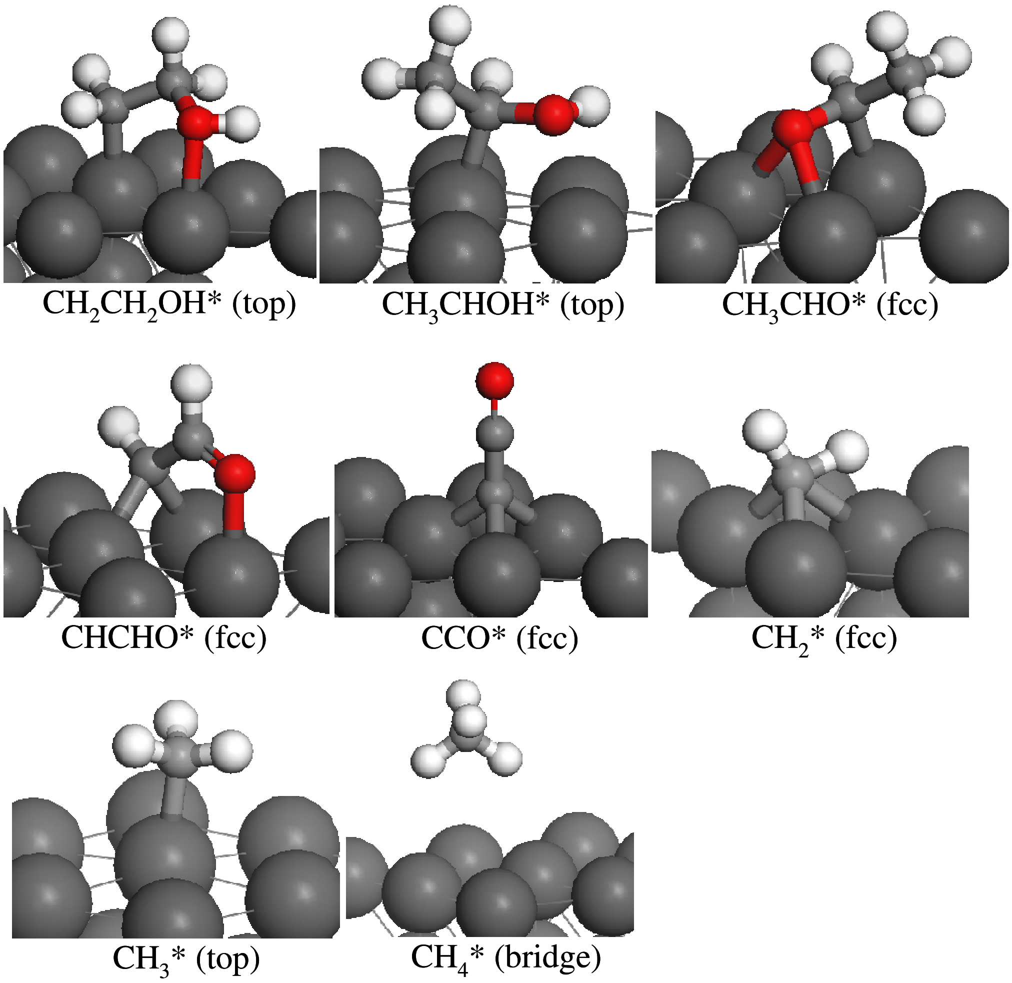
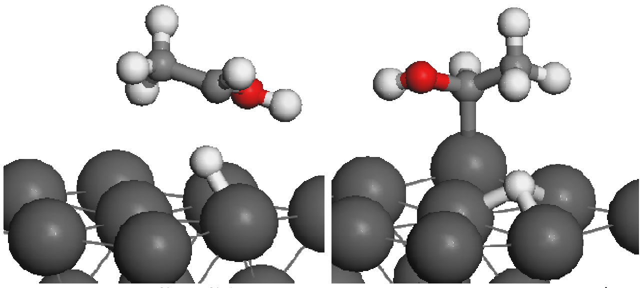


Figure S2. Optimized adsorption geometries for species involved in the excluded steps of ethanol decomposition on Rh(111)

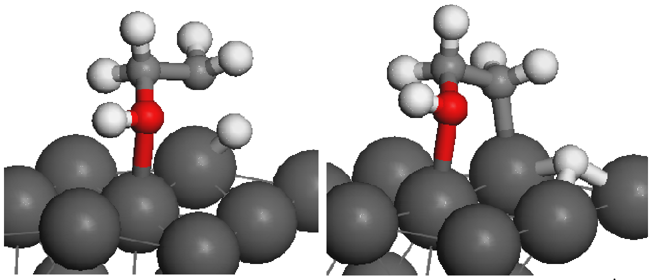
Figure S3

(a) $CH_3CH_2OH \rightarrow CH_3CHOH + H$



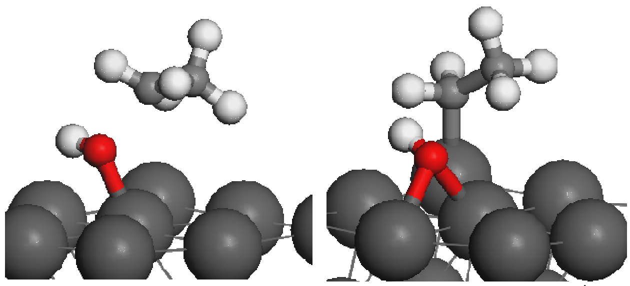
S-TS1 [$CH_3CHOH + H$]*

(b) $CH_3CH_2OH \rightarrow CH_2CH_2OH + H$



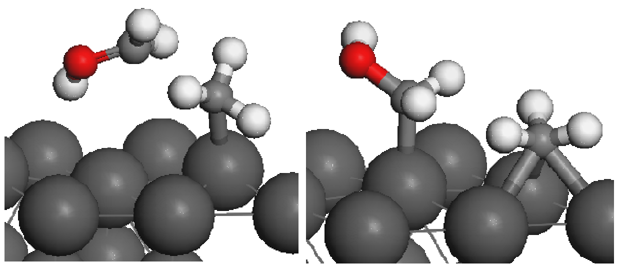
S-TS2 [$CH_2CH_2OH + H$]*

(c) $CH_3CH_2OH \rightarrow CH_3CH_2 + OH$



S-TS3 [$CH_3CH_2 + OH$]*

(d) $CH_3CH_2OH \rightarrow CH_3 + CH_2OH$



S-TS4 [$CH_3 + CH_2OH$]*

Figure S3. TS and FS structures for the excluded steps relevant to ethanol decomposition on Rh(111)

Figure S4

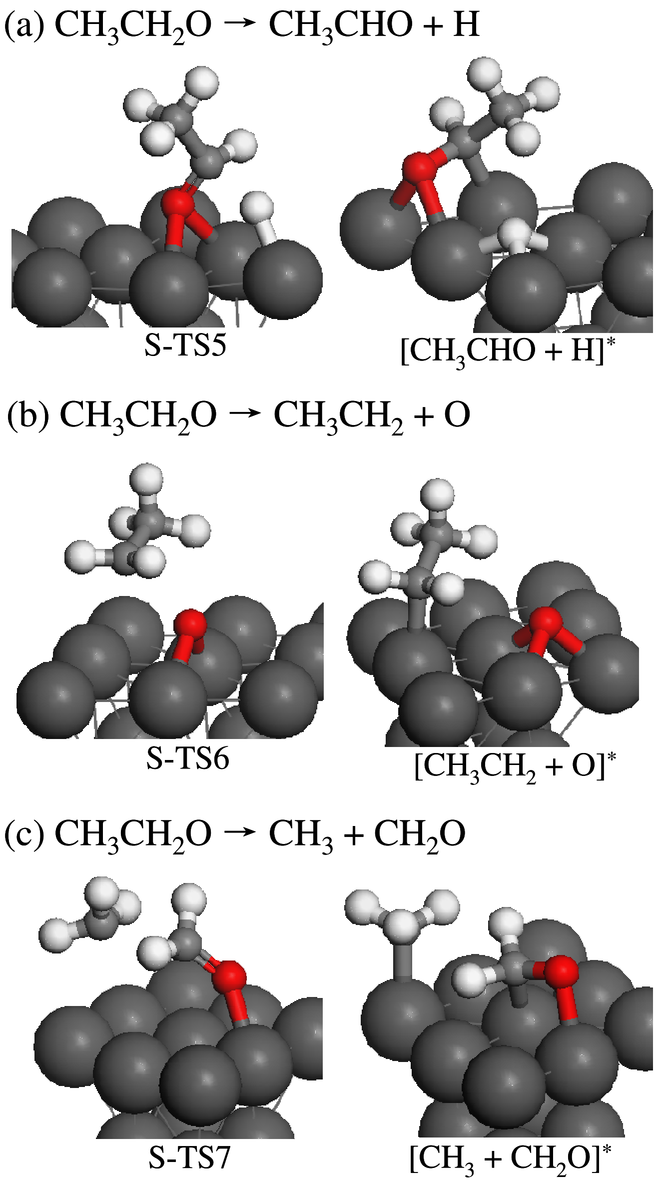
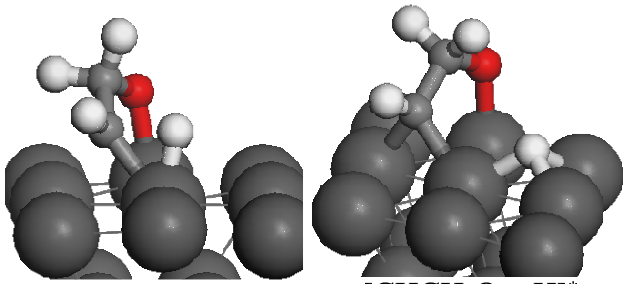


Figure S4. TS and FS structures for the excluded steps relevant to CH_3CH_2O decomposition on Rh(111)

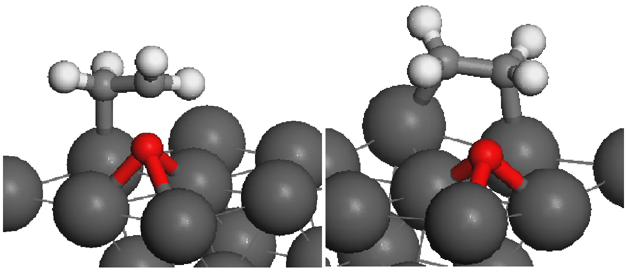
Figure S5

(a) $CH_2CH_2O \rightarrow CHCH_2O + H$



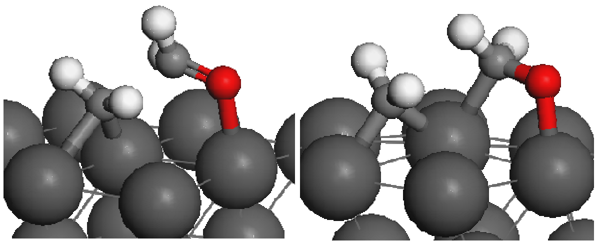
S-TS8 [$CHCH_2O + H]^*$

(b) $CH_2CH_2O \rightarrow CH_2CH_2 + O$



S-TS9 [$CH_2CH_2 + O]^*$

(c) $CH_2CH_2O \rightarrow CH_2 + CH_2O$

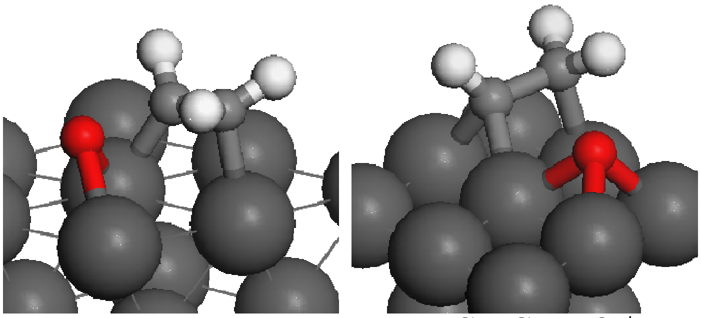


S-TS10 [$CH_2 + CH_2O]^*$

Figure S5. TS and FS structures for the excluded steps relevant to CH_2CH_2O decomposition on Rh(111)

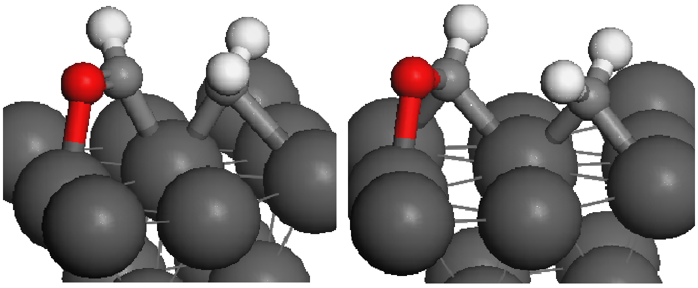
Figure S6

(a) $CH_2CHO \rightarrow CH_2CH + O$



S-TS10 $[CH_2CH + O]^*$

(b) $CH_2CHO \rightarrow CH_2 + CHO$

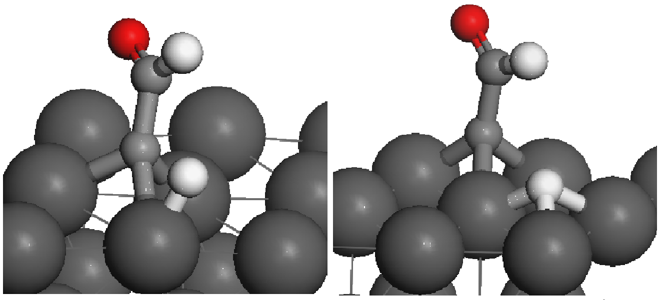


S-TS11 $[CH_2 + CHO]^*$

Figure S6. TS and FS structures for the excluded steps relevant to CH_2CHO decomposition on Rh(111)

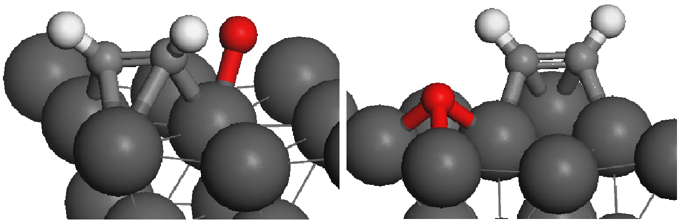
Figure S7

(a) CHCHO → CCHO + H



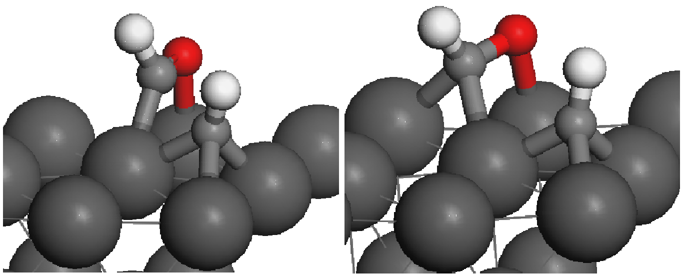
S-TS12 [CCHO + H]*

(b) CHCHO → CHCH + O



S-TS13 [CHCH + O]*

(c) CHCHO → CH + CHO

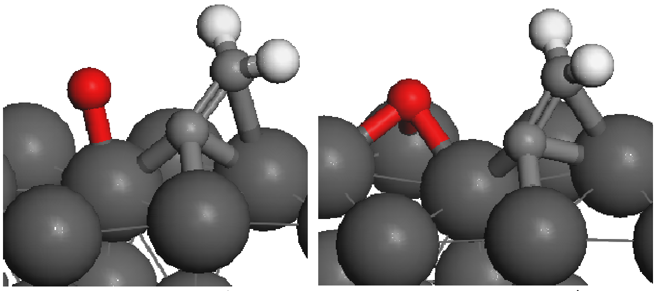


S-TS14 [CH + CHO]*

Figure S7. TS and FS structures for the excluded steps relevant to CHCHO decomposition on Rh(111)

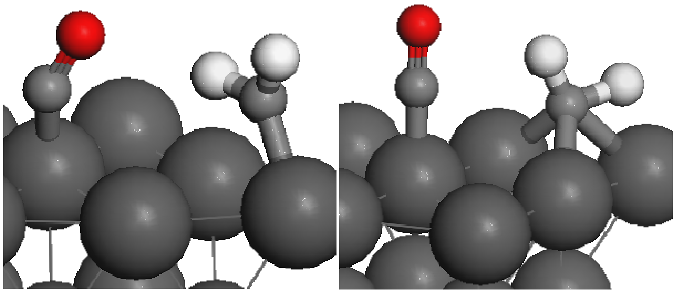
Figure S8

(a) $CH_2CO \rightarrow CH_2C + O$



S-TS15 $[CH_2C + O]^*$

(b) $CH_2CO \rightarrow CH_2 + CO$

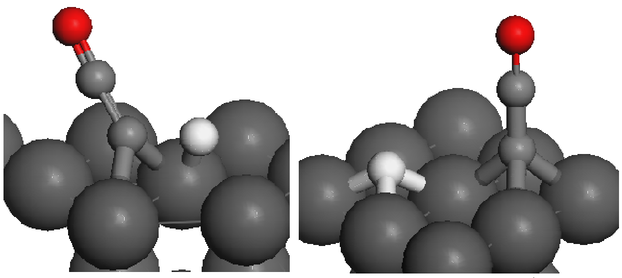


S-TS16 $[CH_2 + CO]^*$

Figure S8. TS and FS structures for the excluded steps relevant to CH_2CO decomposition on Rh(111)

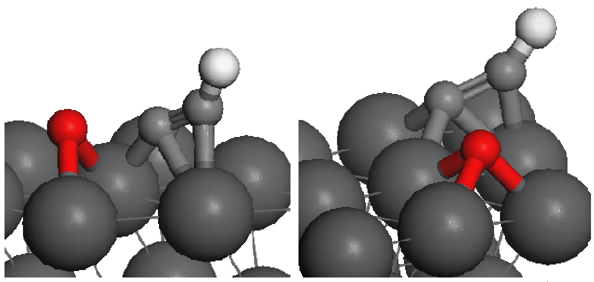
Figure S9

(a) CHCO → CCO + H



S-TS17 [CCO + H]*

(b) CHCO → CCH + O



S-TS18 [CCH + O]*

Figure S9. TS and FS structures for the excluded steps relevant to CHCO decomposition on Rh(111)

Figure S10

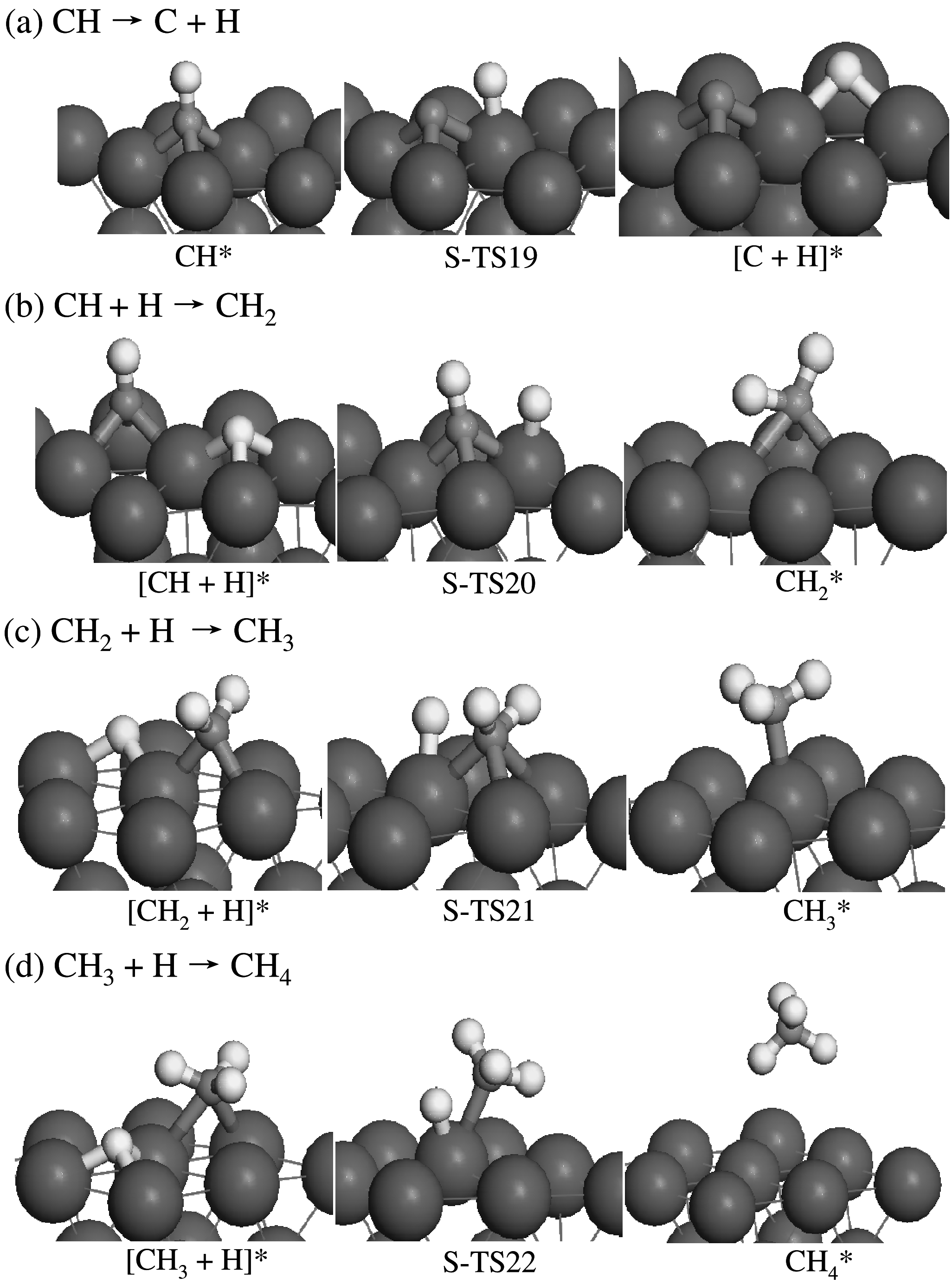


Figure S10. The reaction processes of CH_x (x = 1-3) on Rh(111)

Figure S11

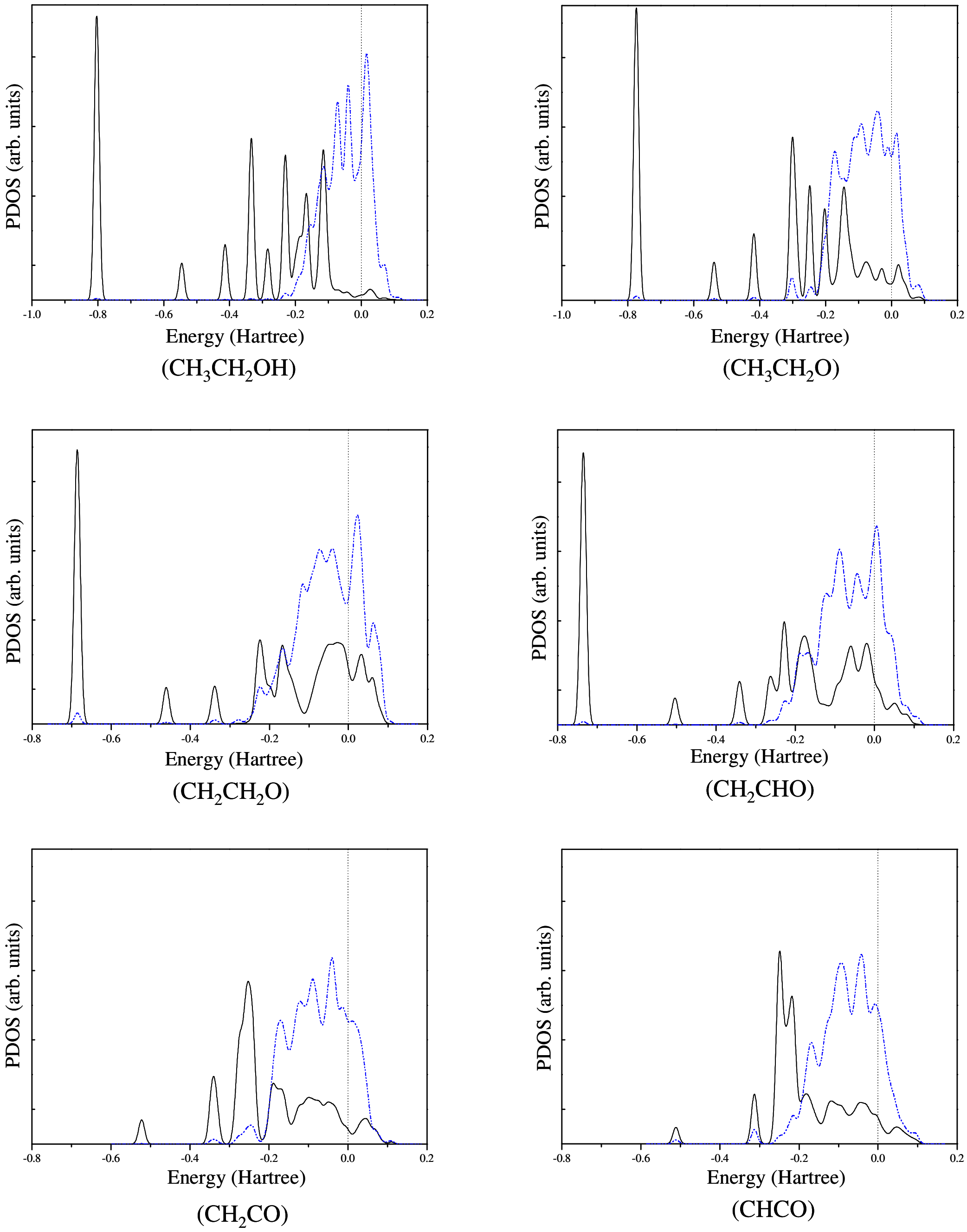


Figure S11. Projected density of states for the O atom and its nearest Rh atom for intermediates relevant to ethanol decomposition on Rh(111). Vertical dotted line denotes the Fermi level. The solid and dash lines represent the PDOS of the O and its nearest Rh.

Figure S12

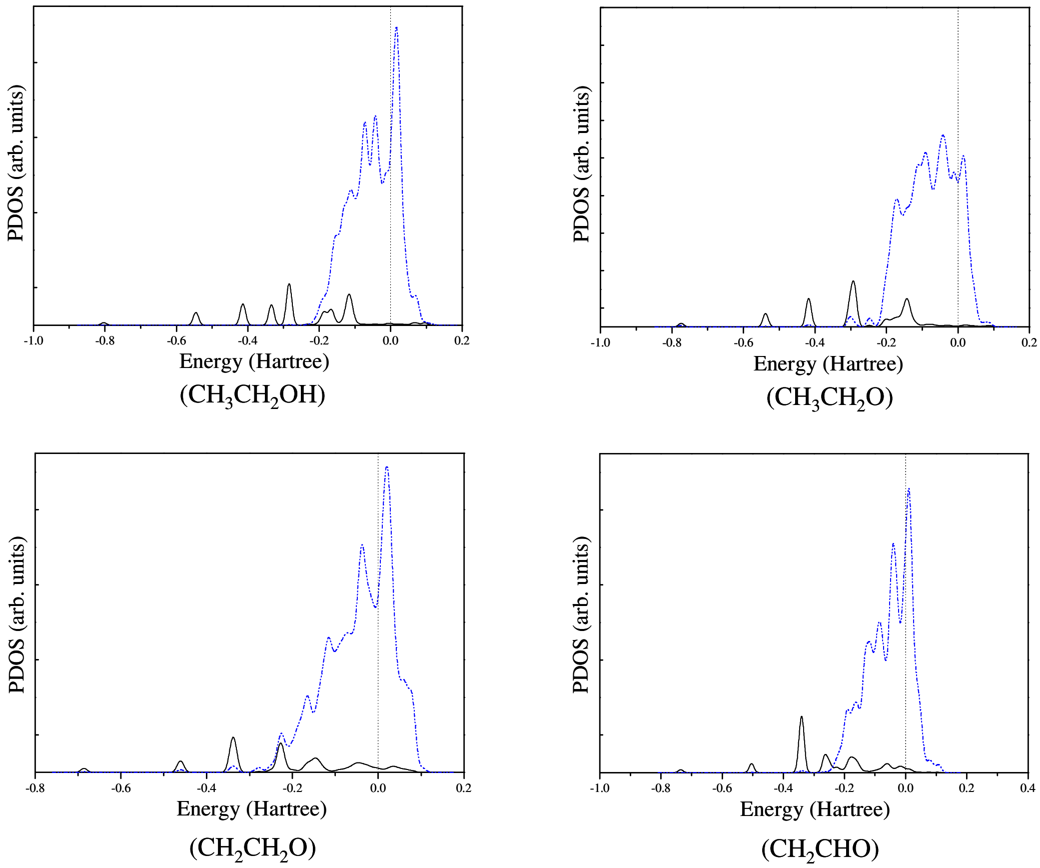


Figure S12. Projected density of states for the H^{α} atom and its nearest Rh atom for intermediates relevant to ethanol decomposition on Rh(111). Vertical dotted line denotes the Fermi level. The solid and dash lines represent the PDOS of the H and its nearest Rh.

TABLE S1. Adsorption Sites, Adsorption Energies (in kcal/mol), and Structural Parameters (in Å and °) for Intermediates Involved in Ethanol Dissociation over Rh(111).

species	site	configuration	ΔE [a]	$d_{C^{\alpha}/CRh}$	$d_{C^{\beta}Rh}$	d_{ORh}	angles [b]
$CH_3CH_2OH^*$	top	*trans*	10.7 (11.8)			2.37	55
	top	*cis*	10.9 (12.1)			2.32	58
$CH_3CH_2O^*$	fcc	η^1(O)	49.9 (53.0)			2.18, 2.18, 2.19	4
	bridge	η^2(O)	47.7 (50.8)			2.13, 2.14	23
	hcp	η^1(O)	46.3 (50.0)			2.18, 2.19, 2.21	3
$CH_2CH_2OH^*$	bridge	$\eta^1(C^{\beta})$	46.6 (49.8)	2.08	2.30	69	
CH_3CHOH^*	top	$\eta^1(C^{\alpha})$	42.3 (44.0)	2.06		86	
$CH_2CH_2O^*$	fcc	$\eta^1(C^{\beta})$-η^1(O)	29.3 (29.8)		2.08	2.02	76
	hcp	$\eta^1(C^{\beta})$-η^1(O)	29.6 (29.9)		2.08	2.01	76
	fcc	$\eta^1(C^{\beta})$-η^2(O)	31.7 (30.2)		2.08	2.13, 2.16	48
	hcp	$\eta^1(C^{\beta})$-η^2(O)	32.4 (30.2)		2.09	2.13, 2.13	46
CH_3CHO^*	fcc	$\eta^1(C^{\alpha})$-η^2(O)	13.0 (14.4)	2.08	2.18, 2.25	79	
	hcp	$\eta^1(C^{\alpha})$-η^2(O)	12.8 (14.2)	2.08	2.16, 2.24	79	
CH_2CHO^*	bridge	$\eta^1(C^{\beta})$-η^1(O)	51.3 (53.7)		2.16	2.08	86
	fcc	η^3(O)	31.6 (34.1)			2.19, 2.21, 2.23	0
	bridge	η^2(O)	28.9 (31.1)			2.14, 2.18	17

$CHCH_2O^*$	hcp	$\eta^2(C^\beta)$-$\eta^1(O)$	69.7 (70.5)	2.05, 2.05	1.99	68	
	fcc	$\eta^2(C^\beta)$-$\eta^1(O)$	68.4 (69.1)	2.05, 2.05	1.99	68	
CH_2CO^*	hcp	$\eta^1(C^\beta)$-$\eta^1(C^\alpha)$-$\eta^1(O)$	30.4 (32.4)	2.04	2.17	2.14	74
	fcc	$\eta^1(C^\beta)$-$\eta^1(C^\alpha)$-$\eta^1(O)$	30.4 (32.4)	2.03	2.16	2.17	73
	bridge	$\eta^1(C^\beta)$-$\eta^1(C^\alpha)$	29.7 (31.4)	2.00	2.09		40
$CHCHO^*$	hcp	$\eta^2(C^\beta)$-$\eta^1(O)$	103.3 (107.0)		2.07, 2.11	2.10	73
	fcc	$\eta^2(C^\beta)$-$\eta^1(O)$	102.0 (105.5)		2.10, 2.10	2.11	74
$CHCO^*$	hcp	$\eta^2(C^\beta)$-$\eta^1(C^\alpha)$	74.1 (76.6)	2.06	2.04, 2.06		34
	fcc	$\eta^2(C^\beta)$-$\eta^1(C^\alpha)$	72.2 (74.7)	2.06	2.05, 2.08		73
CCO	fcc	$\eta^3(C^\beta)$	119.3 (122.6)		2.02, 2.02, 2.05		0
	hcp	$\eta^3(C^\beta)$	119.2 (122.6)		2.01, 2.01, 2.03		0
CO^*	top		42.5 (44.5)	1.83			
	hcp		40.6 (41.9)	2.06, 2.11, 2.11			
	fcc		39.1 (40.3)	2.05, 2.14, 2.14			
H^*	fcc		64.3 (64.4)				
	hcp		63.7 (63.7)				
	bridge		63.2 (62.6)				
	top		58.8 (59.2)				
C^*	hcp		156.9 (156.8)	1.89, 1.90, 1.90			
	fcc		151.6 (151.4)	1.89, 1.91, 1.91			

	top	115.7 (116.2)	1.67
CH^*	hcp	146.6 (151.1)	1.97, 1.98, 1.98
	fcc	144.0 (148.4)	1.97, 1.99, 1.99
CH_2^*	fcc	92.5 (95.8)	2.01, 2.04, 2.33
	hcp	91.8 (95.3)	2.01, 2.04, 2.24
	top	75.1 (79.0)	1.85
CH_3^*	top	42.4 (45.8)	2.06
	fcc	42.1 (44.1)	2.26, 2.35, 2.36
CH_4^*	top	2.5 (2.7)	3.38
	bridge	2.5 (2.8)	3.86, 3.91
	fcc	2.0 (2.6)	4.02, 4.04, 4.06
	hcp	2.0 (2.5)	3.97, 3.97, 4.05

[a] Parameters in parentheses are adsorption energies without ZPE corrections. [b] Values are angles between the surface normal and the C−O axis in the corresponding species.

TABLE S2. The Most Stable Adsorption Sites, Adsorption Configuration and Adsorption Energies (in kcal/mol) for Intermediates Involved in Ethanol Decomposition on Pd(111) and Rh(111)

species	Rh(111)			Pd(111)		
	site	configuration	ΔE [a]	site	configuration	ΔE [a]
$CH_3CH_2OH^*$	top		10.7	top		10.7
$CH_3CH_2O^*$	fcc	η^3(O)	49.9	fcc	η^3(O)	39.3
CH_3CHOH^*	top	$\eta^1(C^\alpha)$	42.3	top	$\eta^1(C^\alpha)$	40.8
CH_2CH_2OH	bridge	$\eta^2(C^\beta)$	46.6	top	$\eta^1(C^\beta)$	41.0
CH_3CHO^*	fcc	$\eta^1(C^\alpha)$-η^2(O)	13.0	bridge		8.0
CH_2CHO	bridge	$\eta^1(C^\beta)$-η^1(O)	51.3	bridge	$\eta^1(C^\beta)$-η^1(O)	41.3
CH_2CO	hcp	$\eta^1(C^\beta)$-$\eta^1(C^\alpha)$-η^1(O)	30.4	bridge	$\eta^1(C^\beta)$-$\eta^1(C^\alpha)$	24.8
CHCO	hcp	$\eta^2(C^\beta)$-$\eta^1(C^\alpha)$	74.1	hcp	$\eta^2(C^\beta)$-$\eta^1(C^\alpha)$	66.2
CCO	fcc	$\eta^3(C^\beta)$	119.3	fcc	$\eta^3(C^\beta)$	106.7
CH	hcp		146.6	fcc		133.4
CH_2	fcc		92.5	bridge		83.3
CH_3	top		42.4	top		39.5