Electronic Supplementary Information

Ethanol decomposition on Pd(110) surface: A density functional theory investigation

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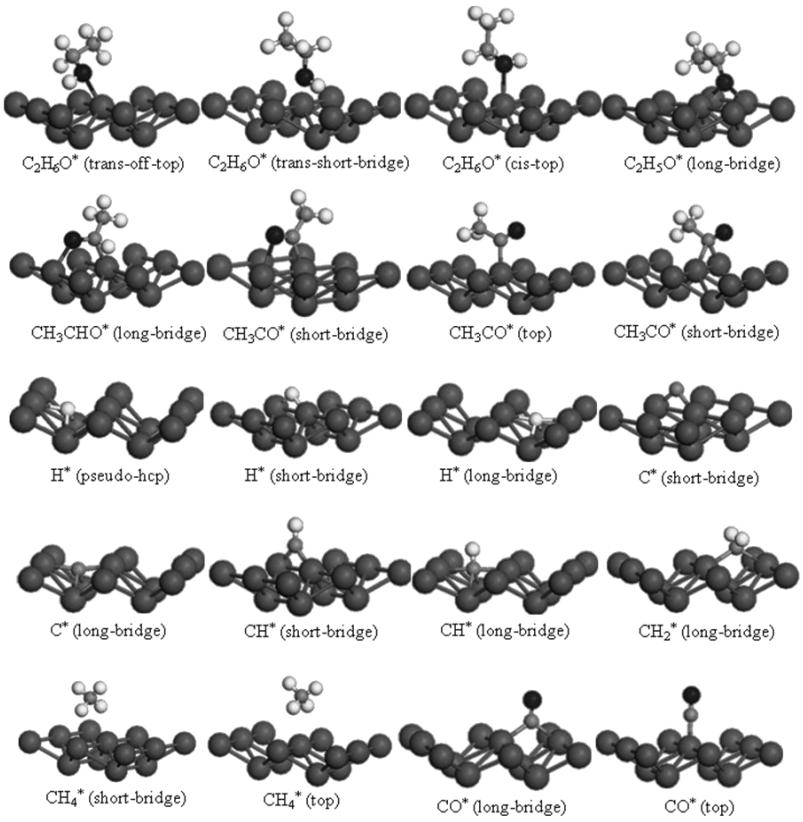

Fig. S1 Optimized adsorption geometries of the metastable configurations for the intermediates involved in the decomposition of ethanol over Pd(110)

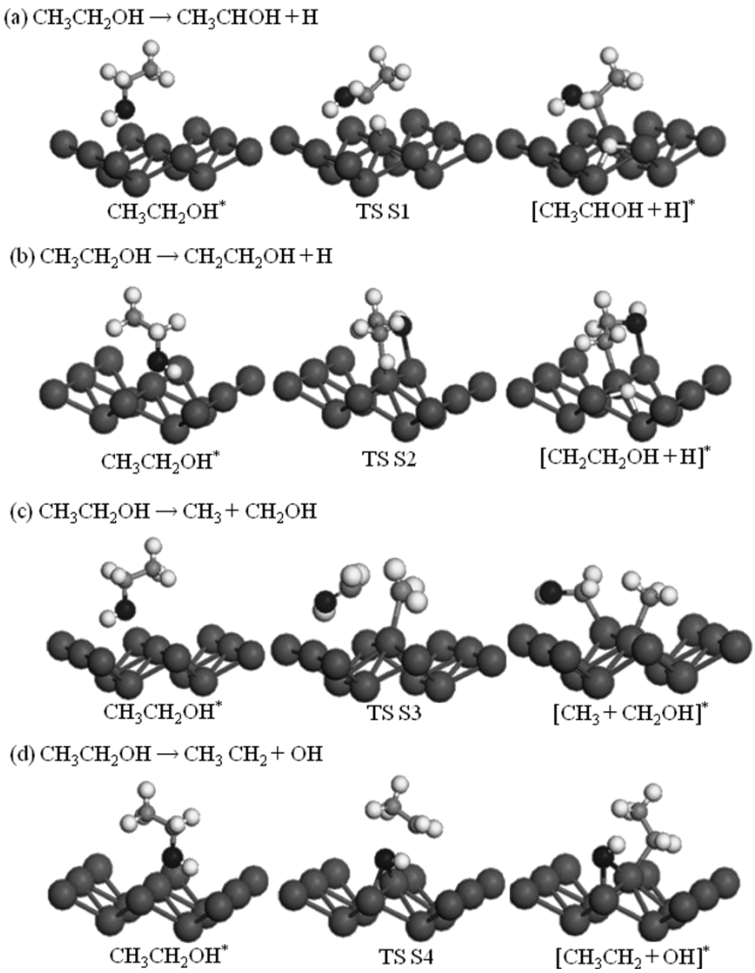

Fig. S2 Reaction processes for the excluded steps relevant to short-bridge adsorbed *trans*-ethanol decomposition on Pd(110).

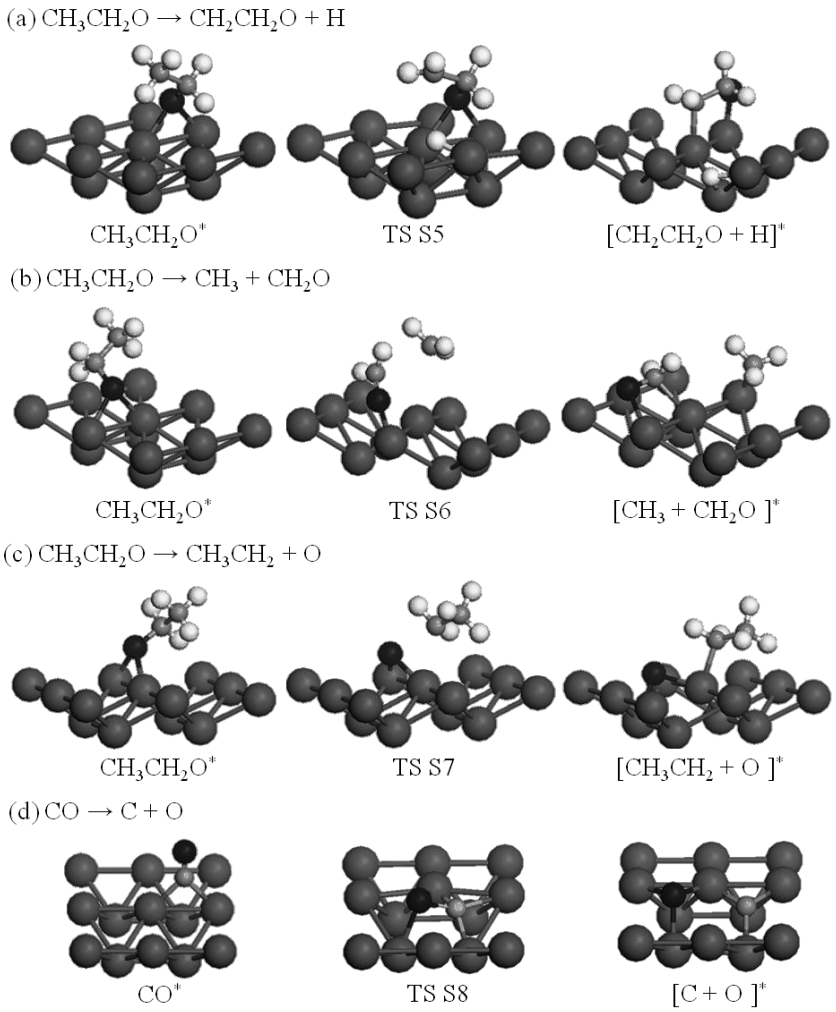

Fig. S3 Reaction processes for the excluded steps relevant to CH_3CH_2O decomposition and CO dissociation on Pd(110).

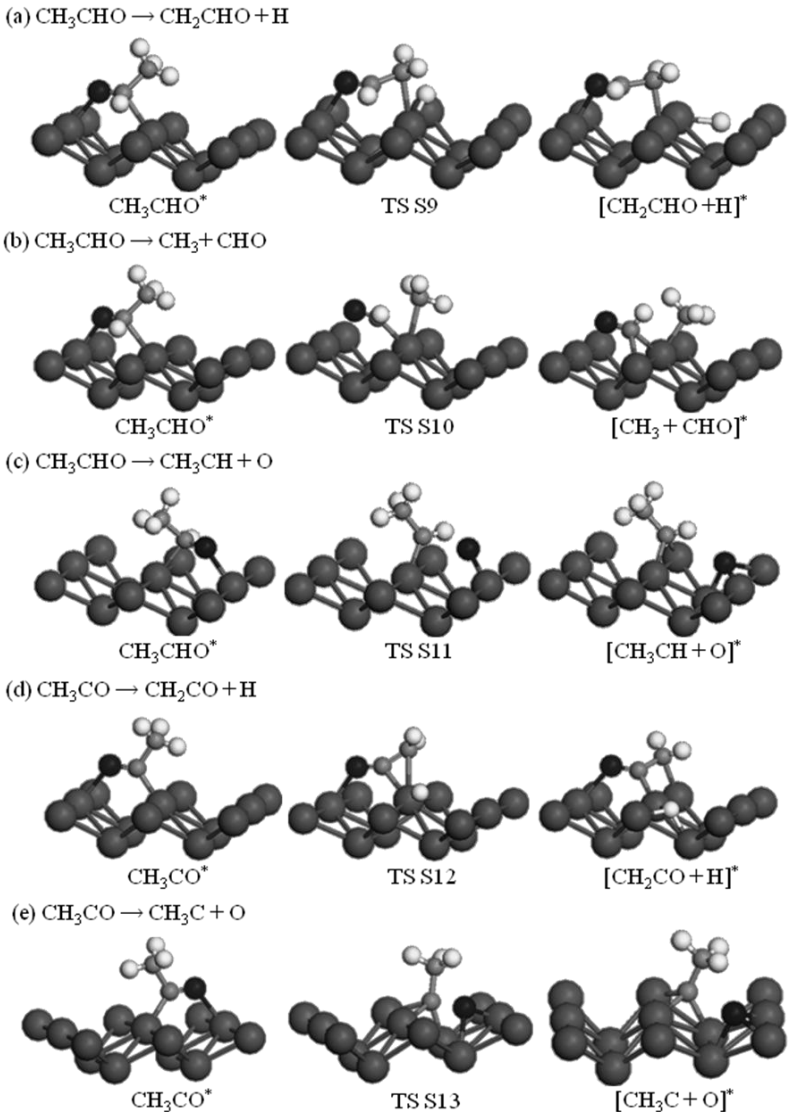

Fig. S4 Reaction processes for the excluded steps relevant to decomposition of CH_3CHO and CH_3CO on Pd(110).

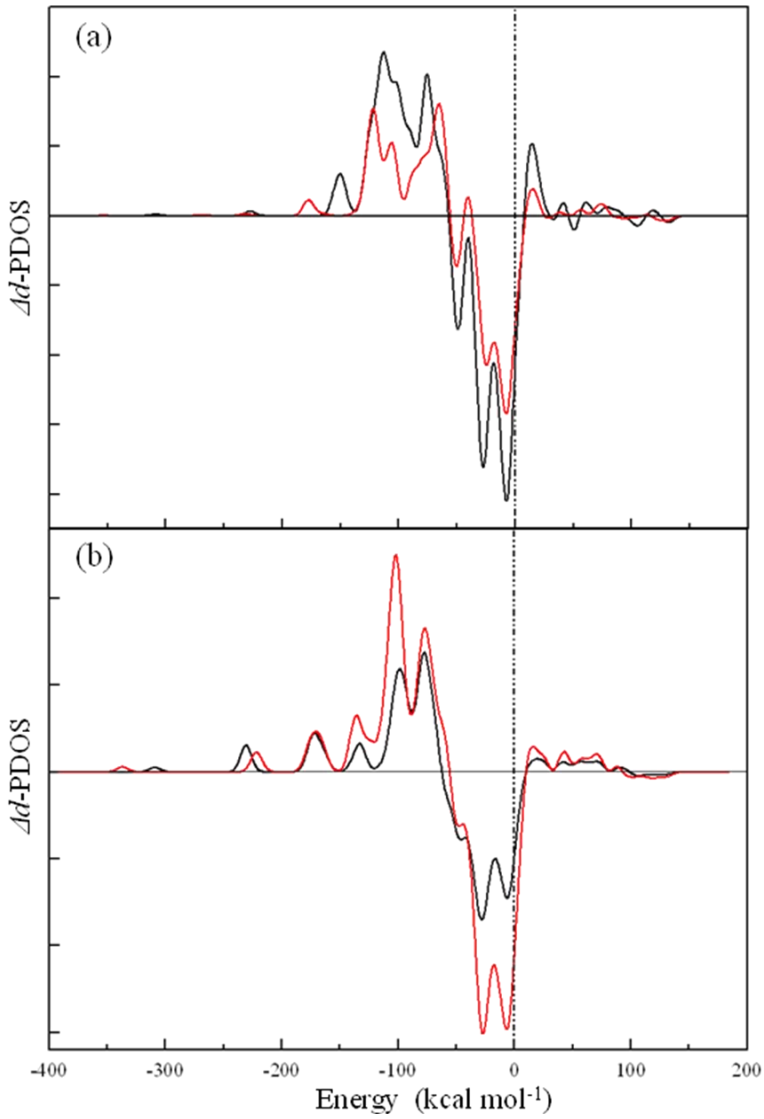

Fig. S5 Variations of the *d*-projected density of states of surface Pd atoms due to bonding with TS complex in the competitive bond scission of CH_3CH_2OH and CH_3CO on Pd(111). (a) The black and red lines represent the O–H and C^{α}–H bond scission of ethanol. (b) The black and red lines represent the C–C and C–H bond scission of CH_3CO.

Table S1 Adsorption sites, adsorption energies ΔE_{ads} (in kcal mol^{-1}), and geometric parameters (in angstroms and degrees) for intermediates involved in ethanol decomposition on Pd(110).

species	configuration	ΔE[a]	$d_{C/H-Pd}$	d_{O-Pd}	*angles*[b]
$CH_3CH_2OH^*$	*trans*-off-top	11.7 (12.8)		2.31	33
	trans-short-bridge	9.0 (10.3)		2.53, 2.55	3
	cis-top	8.9 (9.8)		2.32	64
	cis-off-top	11.9 (12.3)		2.37	66
$CH_3CH_2O^*$	short-bridge, η^1(O)	44.1 (47.5)		2.12, 2.12	55
	long-bridge, η^1(O)	41.6 (44.3)		2.18, 2.18	28
CH_3CHO^*	short-bridge, $\eta^1(C^\alpha)$-η^1(O)	13.4 (14.3)	2.20	2.11	86
	long-bridge, $\eta^1(C^\alpha)$-η^1(O)	10.7 (11.0)	2.21	2.15	87
CH_3CO^*	short-bridge, $\eta^1(C^\alpha)$-η^1(O)	50.9 (53.4)	1.94	2.28	79
	long-bridge, $\eta^1(C^\alpha)$-η^1(O)	51.2 (53.3)	1.94	2.29	85
	top, $\eta^1(C^\alpha)$	49.8 (51.9)	1.96		60
	short-bridge, $\eta^2(C^\alpha)$	49.9 (51.7)	2.11, 2.11		62
H^*	pseudo-fcc(111)	63.5 (63.3)	1.78, 1.78, 1.79		
	pseudo-hcp (111)	62.7 (61.5)	1.79, 1.86, 1.86		
	short-bridge	62.3 (62.5)	1.68, 1.68		
	long-bridge	63.8 (61.7)	1.88, 1.94		
CO^*	short-bridge	36.2 (41.0)	2.00, 2.00		0
	long-bridge	30.4 (35.1)	2.01, 2.01		0
	top	32.6 (34.1)	1.86		0
C^*	pseudo-fcc(111)	143.2 (143.2)	1.86, 1.87, 1.87		
	short-bridge	127.5 (127.3)	1.81, 1.82		
	long-bridge	158.9 (158.9)	1.93, 1.93		
CH^*	pseudo-fcc(111)	128.6 (133.2)	1.95, 1.95, 1.96		
	short-bridge	113.7 (117.7)	1.87, 1.87		
	long-bridge	131.4 (135.0)	2.03, 2.03		
CH_2^*	short-bridge	84.8 (89.2)	1.99, 1.99		
	long-bridge	81.4 (86.2)	2.03, 2.03		
CH_3^*	top	39.4 (42.7)	2.03		
CH_4^*	short-bridge	1.4 (1.1)	3.19, 3.25		
	long-bridge	1.9 (1.8)	3.34, 3.35		
	top	1.3 (1.7)	2.97		

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

Table S2 Thermodynamic and kinetic parameters (in kcal mol^{-1} and s^{-1}) for the elementary reactions of ethanol decomposition from different adsorption geometries on Pd(110)[a].

adsorption mode	reaction[b]	ΔE[c]	E_a
trans-top	$CH_3CH_2OH^* \rightarrow [CH_3CH_2O + H]^*$	11.3	29.8
	$CH_3CH_2OH^* \rightarrow [CH_2CH_2OH + H]^*$	12.4	29.9
	$CH_3CH_2OH^* \rightarrow [CH_3CHOH + H]^*$	5.7	45.1
	$CH_3CH_2OH^* \rightarrow [CH_3CH_2 + OH]^*$	14.2	44.9
	$CH_3CH_2OH^* \rightarrow [CH_3 + CH_2OH]^*$	20.9	67.6
trans-short bridge	$CH_3CH_2OH^* \rightarrow [CH_3CH_2O + H]^*$	7.9	23.7
	$CH_3CH_2OH^* \rightarrow [CH_2CH_2OH + H]^*$	10.8	37.8
	$CH_3CH_2OH^* \rightarrow [CH_3CHOH + H]^*$	2.5	29.0
	$CH_3CH_2OH^* \rightarrow [CH_3CH_2 + OH]^*$	16.1	49.9
	$CH_3CH_2OH^* \rightarrow [CH_3 + CH_2OH]^*$	18.0	72.3
cis-top	$CH_3CH_2OH^* \rightarrow [CH_3CH_2O + H]^*$	6.1	32.5
	$CH_3CH_2OH^* \rightarrow [CH_2CH_2OH + H]^*$	9.5	33.2
	$CH_3CH_2OH^* \rightarrow [CH_3CHOH + H]^*$	5.1	44.7
	$CH_3CH_2OH^* \rightarrow [CH_3CH_2 + OH]^*$	10.5	52.6
	$CH_3CH_2OH^* \rightarrow [CH_3 + CH_2OH]^*$	15.6	63.9
cis-off top	$CH_3CH_2OH^* \rightarrow [CH_3CH_2O + H]^*$	7.6	29.6
	$CH_3CH_2OH^* \rightarrow [CH_2CH_2OH + H]^*$	9.8	28.7
	$CH_3CH_2OH^* \rightarrow [CH_3CHOH + H]^*$	4.3	41.9
	$CH_3CH_2OH^* \rightarrow [CH_3CH_2 + OH]^*$	9.4	53.8
	$CH_3CH_2OH^* \rightarrow [CH_3 + CH_2OH]^*$	13.1	64.5

[a] Values are without ZPEC. [b] [A+B]* denotes the coadsorbed A and B speices. [c] Reaction energies of the reactions are calculated as $\Delta E = E_{FS} - E_{IS}$, where E_{FS} and E_{IS} are the energies of FS and IS without ZPEC, respectively.

Table S3 Changes (in kcal mol^{-1}) of energy barriers and contribution factors for the common reactions steps involved in ethanol decomposition when switching from Pd(111) to Pd(110)[a]

Reactions[b]	ΔE_a	ΔE_{AB}^{IS}	ΔE_{AB}^{TS}	$\Delta E_{\text{int}}^{TS}$	ΔE_{A}^{TS}	ΔE_{B}^{TS}
$CH_3CH_2OH^* \rightarrow [CH_3CH_2O^* + H^*]$	-14.5	-1.4	13.1	-7.6	4.5	1.0
$CH_3CHO^* \rightarrow [CH_3CO^* + H^*]$	-2.4	2.0	4.5	-3.6	0.3	0.6
$CH_3CO^* \rightarrow [CH_3^* + CO^*]$	-16.4	2.6	19	-15	7.2	-3.2

[a] Values without ZPEC. [b] [A + B] denotes the coadsorbed A and B species.

Table S4 Energy barriers and contribution factors (in kcal mol^{-1}) for the C–C bond scission reactions involved in ethanol decomposition on Pd surfaces[a]

reactions on Pd(110)	ΔE_{AB}^{g}	E_{AB}^{IS}	E_{int}^{TS}	E_{A}^{TS}	E_{B}^{TS}	E_{a}
$CH_3CH_2OH^* \rightarrow CH_3^* + CH_2OH^*$	91.8	10.3	-11.8	12.9	5.1	72.3
$CH_3CH_2O^* \rightarrow CH_3^* + CH_2O^*$	26.4	47.5	-5.9	4.3	-8.5	72.2
$CH_3CHO^* \rightarrow CH_3^* + CHO^*$	91.5	11.0	-1.4	29.0	44.3	27.8
$CH_3CO^* \rightarrow CH_3^* + CO^*$	25.0	53.3	-8.4	24.3	28.5	17.1
reactions on Pd(111)	ΔE_{AB}^{g}	E_{AB}^{IS}	E_{int}^{TS}	E_{A}^{TS}	E_{B}^{TS}	E_{a}
$CH_3CH_2OH^* \rightarrow CH_3^* + CH_2OH^*$	91.8	11.7	-2.1	6.3	12.6	82.5
$CH_3CHOH^* \rightarrow CH_3^* + CHOH^*$	65.9	42.5	-0.1	8.0	33.3	67.0
$CH_3CHO^* \rightarrow CH_3^* + CHO^*$	91.5	9.0	4.8	27.4	42.1	35.8
$CH_3CO^* \rightarrow CH_3^* + CO^*$	25.0	50.7	7.5	25.1	24.6	33.5
$CH_2CO^* \rightarrow CH_2^* + CO^*$	95.2	26.6	13.0	76.4	27.6	30.8
$CHCO^* \rightarrow CH^* + CO^*$	96.8	68.6	7.5	123.9	26.5	22.5

[a] Values without ZPEC.