Electronic Supplementary Information for:

Density functional investigation of methanol dehydrogenation on Pd(100)

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Table S1 Calculated vibrational frequencies (in cm^{-1}) and zero-point energies (in kcal mol^{-1}) of all adsorbates on Pd(100) and Pd(111) surfaces

Species	surface	frequencies	ZPE
CH_3OH*	Pd(111)	3700, 3218, 3146, 3067, 1504, 1494, 1477, 1353, 1180, 1084, 997, 489, 242, 146, 110, 89, 48, 33	32.6
	Pd(100)	3732, 3218, 3142, 3064, 1489, 1478, 1463, 1343, 1158, 1076, 994, 474, 211, 135, 121, 69, 50, 32	33.2
CH_3O*	Pd(111)	3155, 3136, 3066, 1488, 1469, 1434, 1150, 1109, 1046, 295, 263, 242, 102, 53, 23	25.8
	Pd(100)	3143, 3101, 3002, 1485, 1472, 1453, 1160, 1152, 1015, 355, 335, 239, 207, 117, 63	26.2
CH_2OH*	Pd(111)	3694, 3212, 3098, 1457, 1370, 1189, 1107, 1038, 700, 504, 460, 234, 91, 76, 63	26.2
	Pd(100)	3600, 3224, 3124, 1444, 1356, 1155, 1092, 981, 686, 535, 496, 245, 117, 83, 69	26.0
CH_2O	Pd(111)	3113, 3014, 1495, 1294, 1177, 956, 510, 403, 264, 166, 162, 54	18.0
	Pd(100)	3092, 3005, 1477, 1279, 1149, 951, 493, 442, 340, 181, 99, 67	18.0
CHOH	Pd(111)	3496, 3120, 1386, 1196, 1167, 875, 506, 469, 404, 257, 158, 76	18.7
	Pd(100)	3426, 3163, 1413, 1207, 1174, 848, 485, 478, 376, 281, 160, 83	18.7
CHO	Pd(111)	3045, 1430, 1158, 759, 497, 310, 307, 196, 188	11.3
	Pd(100)	3027, 1617, 1194, 726, 555, 315, 169, 137, 73	11.2
COH	Pd(111)	3763, 1296, 1134, 525, 486, 389, 187, 173, 27	11.4
	Pd(100)	3753, 1189, 1110, 401, 387, 299, 179, 174, 63	10.8
CO	Pd(111)	1889, 346, 327, 305, 164, 154	4.6
	Pd(100)	1951, 396, 360, 354, 195, 71	4.8
H	Pd(111)	1012, 851, 817	3.8
	Pd(100)	1253, 1208, 388	4.1

Table S2 Calculated vibrational frequencies (in cm^{-1}) and zero-point energies (in kcal mol^{-1}) of the TSs on Pd(100) and Pd(111) surfaces

Species	surface	frequencies	ZPE
$CH_3OH \rightarrow CH_3O + H$	Pd(111)	3092, 3022, 2924, 1589, 1496, 1483, 1475, 1163, 1129, 1020, 854, 252, 195, 64, 44, 35, 24, *i*572	28.4
	Pd(100)	3085, 3047, 2929, 1478, 1471, 1448, 1170, 1134, 1024, 719, 634, 448, 310, 269, 206, 125, 62, *i*496	28.0
$CH_3O \rightarrow CH_2O + H$	Pd(111)	3049, 2964, 1986, 1526, 1279, 1234, 1053, 780, 402, 205, 189, 78, 31, 20, *i*959	21.2
	Pd(100)	3069, 2980, 1626, 1464, 1388, 1221, 1027, 839, 319, 252, 164, 123, 82, 49, *i*681	20.9
$CH_2O \rightarrow CHO + H$	Pd(111)	3116, 1548, 1506, 1221, 751, 693, 493, 245, 170, 153, 106, *i*978	14.3
	Pd(100)	2981, 1507, 1325, 1253, 851, 743, 528, 307, 213, 175, 52, *i*1032	14.2
$CHO \rightarrow CO + H$	Pd(111)	1882, 1789, 581, 384, 304, 227, 115, 73, *i*633	7.7
	Pd(100)	1861, 1770, 559, 367, 312, 248, 135, 68, *i*754	7.6
$CH_3OH \rightarrow CH_2OH + H$	Pd(111)	3752, 3247, 3126, 2095, 1491, 1371, 1290, 1125, 973, 846, 506, 332, 280, 106, 70, 33, 15, *i*988	29.6
	Pd(100)	3756, 3266, 3193, 1485, 1403, 1317, 1194, 1080, 1034, 755, 700, 412, 370, 220, 129, 116, 81, *i*1086	29.3
$CH_2OH \rightarrow CHOH + H$	Pd(111)	3343, 3228, 1481, 1445, 1242, 1220, 946, 639, 536, 488, 215, 119, 85, 36, *i*1145	21.5
	Pd(100)	3252, 3201, 1824, 1431, 1224, 1143, 1001, 728, 636, 477, 276, 252, 142, 97, *i*831	22.4
$CH_2OH \rightarrow CH_2O + H$	Pd(111)	3253, 3098, 1499, 1305, 1184, 934, 910, 566, 537, 349, 222, 190, 101, 49, *i*1206	20.3
	Pd(100)	3117, 3017, 1983, 1461, 1252, 1141, 880, 451, 435, 303, 237, 139, 59, 38, *i*424	20.8
$CHOH \rightarrow COH + H$	Pd(111)	3377, 1916, 1251, 1213, 531, 526, 374, 362, 305, 168, 99, *i*850	14.5
	Pd(100)	3646, 1377, 1269, 1062, 567, 442, 374, 195, 139, 50, 17, *i*1197	13.1
$CHOH \rightarrow CHO + H$	Pd(111)	2839, 1701, 1439, 1186, 727, 569, 492, 344, 263, 152, 118, *i*892	14.1
	Pd(100)	3053, 1431, 1176, 992, 683, 553, 499, 361, 357, 209, 194, *i*1116	13.6
$COH \rightarrow CO + H$	Pd(111)	1579, 1357, 544, 422, 359, 323, 243, 161, *i*1506	7.1
	Pd(100)	1486, 1419, 583, 433, 328, 248, 232, 142, *i*1500	7.0

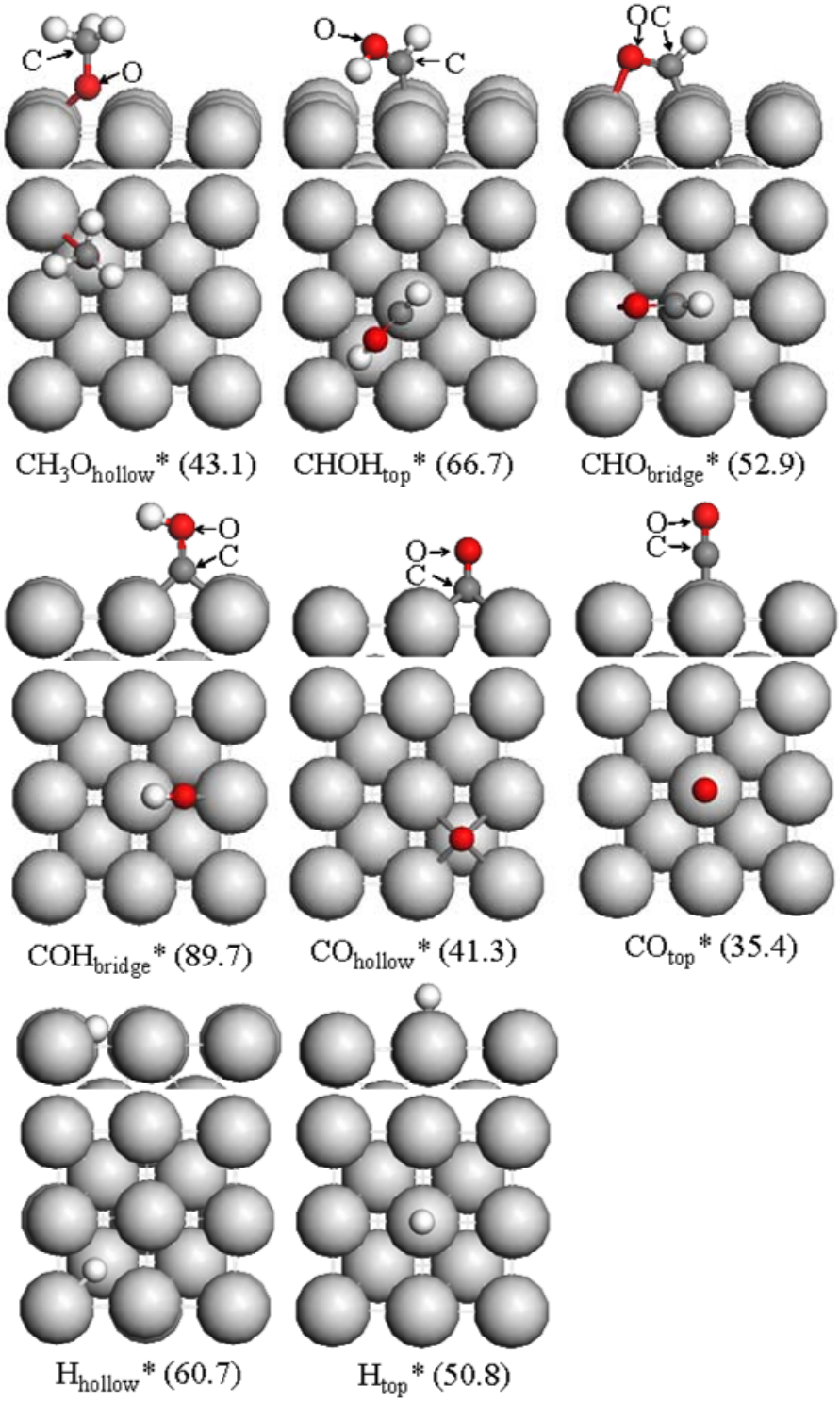


Fig. S1 Metastable adsorption configurations of intermediates involved in methanol dehydrogenation on Pd(100). Values (in kcal mol^{-1}) in parentheses are adsorption energies with ZPE correction.

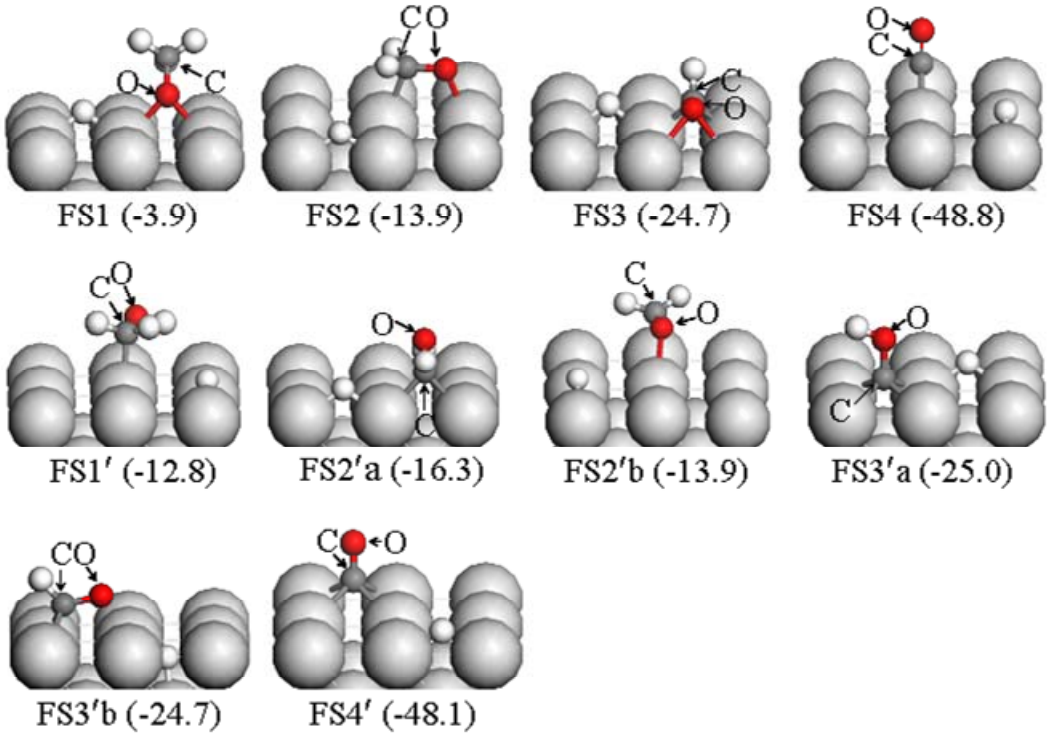


Fig. S2 Final states (FS) involved in methanol dehydrogenation on Pd(100). Values (in kcal mol^{-1}) in parentheses are the energies of FS with respect to gas-phase methanol plus the clean slab (with ZPE corrections).

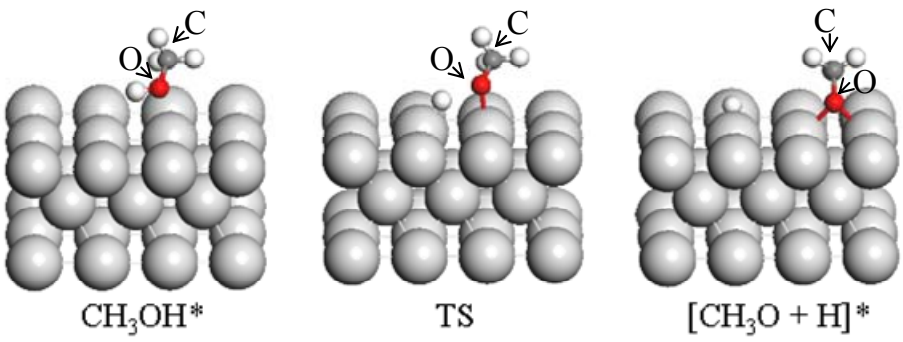


Fig. S3 Structures involved in O–H bond scission of methanol on (2 × 3) slab Pd(100) model.

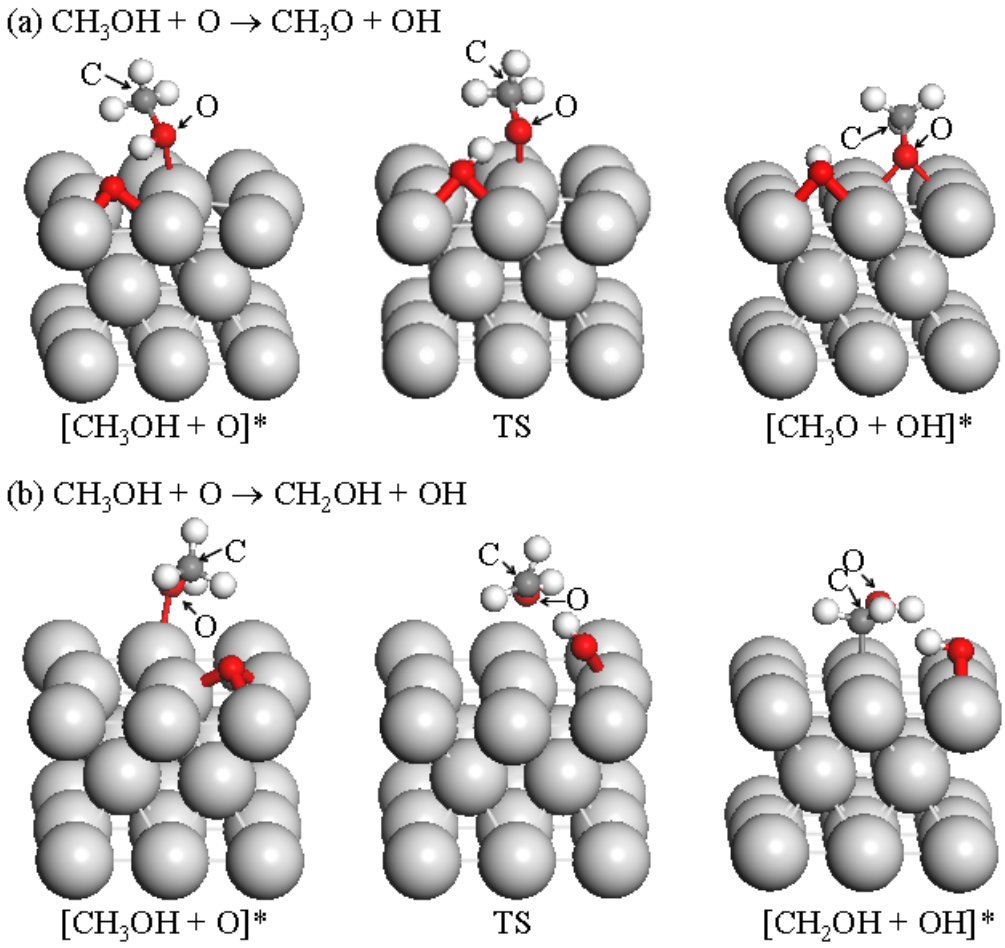
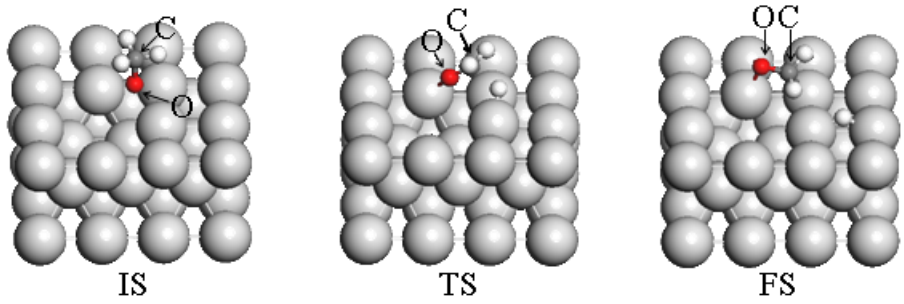
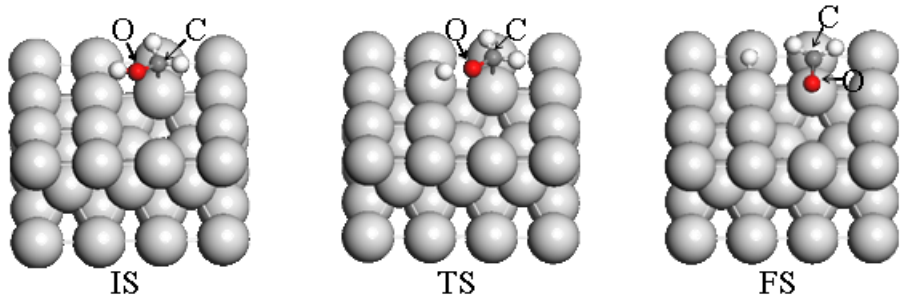


Fig. S4 Structures involved in methanol dehydrogenation on pre-adsorbed oxygen Pd(100).

(a) Dehydrogenation of methoxy adsorbed at defect site



(b) O−H bond scission of CH_2OH adsorbed at defect site



(c) C−H bond scission of CH_2OH adsorbed at defect site

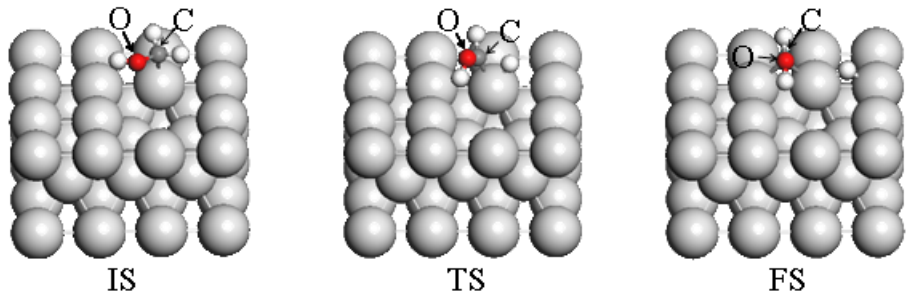


Fig. S5 Structures involved in dehydrogenation of methoxy and hydroxymethyl adsorbed at defect sites on Pd(100).