Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information for

Mechanism of Methanol Synthesis on Ni(110)

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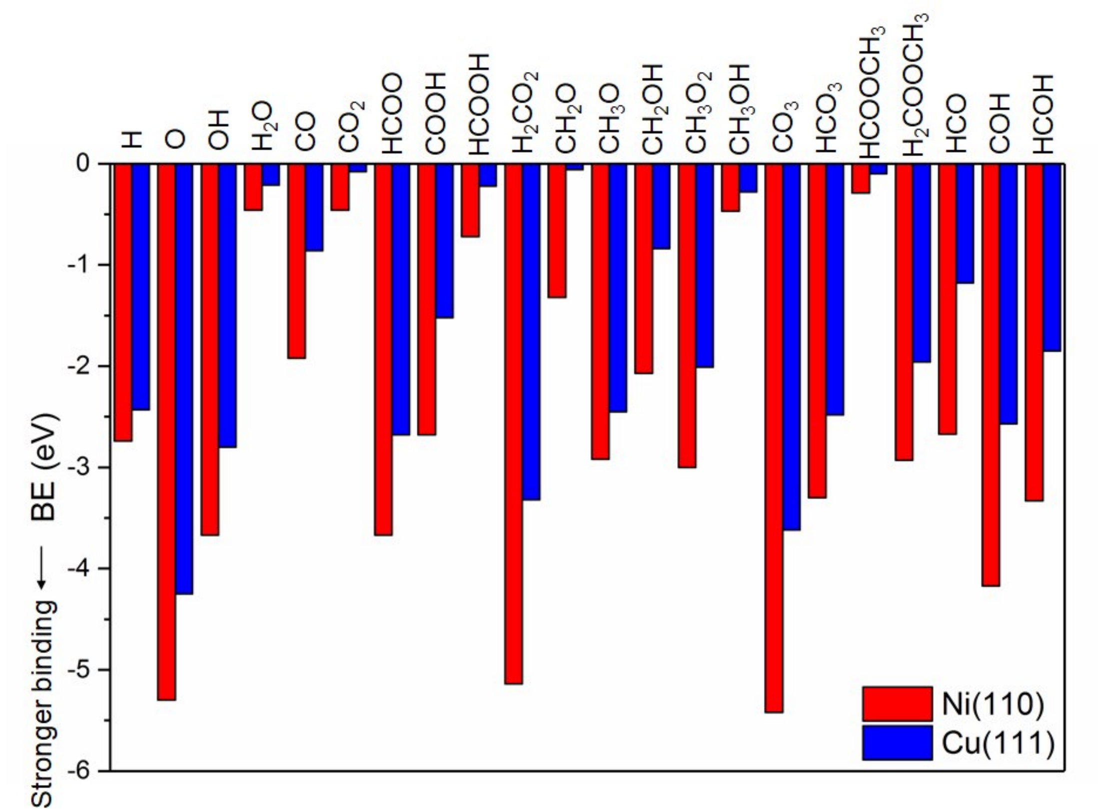

Figure S1. Comparison of calculated binding energies (BE) for adsorbed species on Ni(110) (red bars) and Cu(111) (blue bars). The Cu(111) values were taken from Ref. 1. Values on Cu(111) were obtained using a different software package (DACAPO),[1-3] and therefore small discrepancies should be expected.

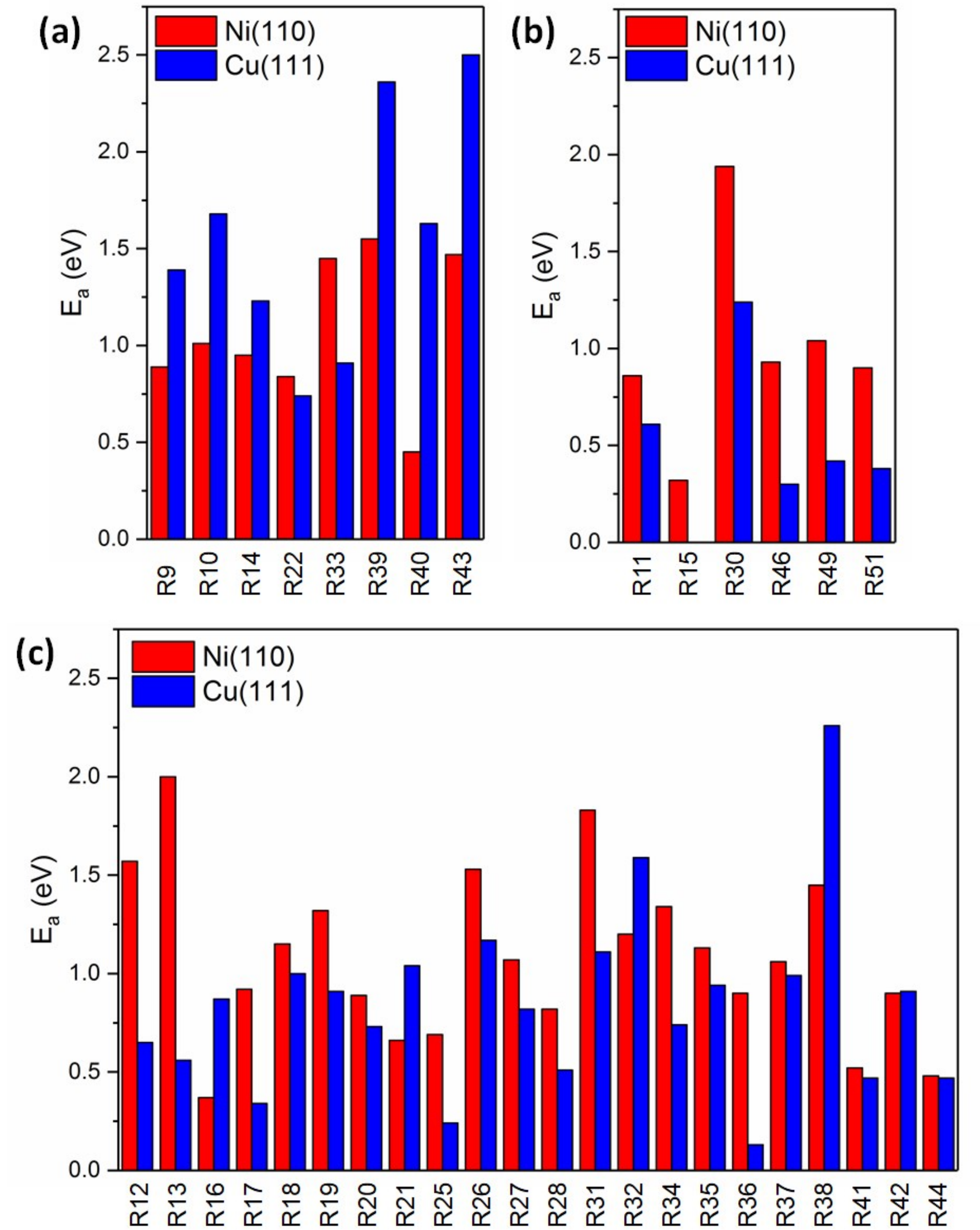

Figure S2. Comparison of calculated activation energy barriers (E_a) for (a) bond-breaking, (b) disproportionation, and (c) bond-making elementary steps in the methanol synthesis reaction network on Ni(110) (red bars) and Cu(111) (blue bars). The reactions are numbered according to Table 2. The Cu(111) values were taken from Ref. 1. In (b), R15 ($COOH^* + OH^* \rightarrow CO_2^* + H_2O^*$) is a spontaneous reaction ($E_a = 0$) on Cu(111). Values on Cu(111) were obtained using a different software package (DACAPO),[1-3] and therefore small discrepancies should be expected.

Table S1. Calculated vibrational frequencies of gas-phase species and adsorbed species at their preferred adsorption sites on Ni(110). Notation on binding sites: PT for pseudo three-fold, SB for short bridge, and t for top.

Species	**Binding site**	**Frequencies (1/cm)**
H_2	Gas phase	4315
CO	Gas phase	2127
CO_2	Gas phase	2367, 1322, 633, 632
H_2O	Gas phase	3773, 3671, 1489
CH_2O	Gas phase	2861, 2809, 1762, 1484, 1224, 1148
HCOOH	Gas phase	3611, 2989, 1759, 1355, 1256, 1075, 1006, 678, 602
CH_3OH	Gas phase	3740, 3060, 2980, 1462, 1449, 1428, 1329, 1134, 1056, 1010, 286
$HCOOCH_3$	Gas phase	3111, 3074, 3001, 2870, 1740, 1449, 1435, 1414, 1343, 1182, 1136, 1130, 989, 906, 748, 357, 296, 83
H*	PT	1123, 945, 695
O*	PT	464, 409, 303
OH*	SB (tilted)	3660, 674, 599, 437, 290, 147
H_2O*	Top	3689, 3545, 1543, 532, 461, 239, 152, 75, 53
CO*	SB	1853, 380, 347, 293, 157
CO_2*	V-shape	1405, 1115, 704, 408, 317, 302, 204, 151, 112
HCOO*	t-t (ridge)	2984, 1516, 1339, 1310, 978, 743, 343, 328, 325, 136, 115, 65
COOH*	SB (trans)	3610, 1475, 1200, 1114, 697, 596, 442, 338, 217, 167, 99, 44
HCOOH*	Top	3052, 2850, 1614, 1351, 1295, 1137, 953, 689, 650, 282, 249, 136, 107
H_2CO_2*	SB-SB (trench)	2992, 2937, 1433, 1359, 1238, 1073, 999, 841, 533, 365, 351, 340, 335, 171, 149
CH_2O*	SB-SB (trench)	2708, 2656, 1279, 1131, 1112, 851, 370, 363, 305, 304, 253, 224
CH_3O*	SB	3017, 2971, 2836, 1431, 1423, 1401, 1128, 1110, 992, 365, 324, 198, 119, 84, 36
CH_2OH*	t-t (ridge)	3603, 3077, 2992, 1398, 1285, 1095, 1052, 822, 576, 523, 456, 314, 163, 152,101
CH_3O_2*	SB-t (trench)	3441, 3003, 2946, 1439, 1354, 1295, 1195, 1049, 1002, 831, 553, 448, 317, 256, 252, 147, 139, 60
CH_3OH*	top	3573, 3085, 3035, 2958, 1148, 1444, 1420, 1294, 1133, 1044, 971, 494, 269, 164, 143, 71, 48, 29
CO_3*	t-t-SB	1356, 1198, 959, 737, 640, 625, 337, 315, 304, 181, 136, 131
HCO_3*	t-SB	3669, 1517, 1366, 1188, 1010, 737, 632, 623, 566, 254, 225, 133, 116, 101, 56
$HCOOCH_3$*	top	3109, 3037, 3019, 2964, 1677, 1432, 1428, 1408, 1354, 1199, 1142, 1115, 940, 883, 734, 345, 265, 197, 135, 107, 75, 51, 38, 30
H_2COOCH_3*	SB-SB (trench)	3087, 3038, 2963, 2962, 2909, 1449, 1445, 1440, 1417, 1357, 1238, 1192, 1137, 1127, 1068, 964, 642, 465, 348, 319, 267, 228, 185, 137, 132, 118, 55
HCO*	SB-SB	2832, 1165, 1032, 509, 402, 330, 287, 222, 186
COH*	PT	3559, 1214, 1078, 485, 426, 364, 170, 148, 138
HCOH*	SB	3312, 2974, 1343, 1159, 1104, 821, 476, 460, 334, 246, 140, 80

References

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