

## Supporting information

# A new insight into the initial step in the Fischer-Tropsch synthesis: CO dissociation on Ru surfaces

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Table S1. The calculated adsorption energies on the stepped Ru(0001) and Ru(11 $\bar{2}$ 1) surfaces <sup>a</sup>

	Stepped Ru(0001)		Ru(11 $\bar{2}$ 1)	
C	7.61	(4F, 1-2-3-4)	7.39	(4F, 1-2-3-4)
O	5.94	(3F, 1-2-10)	6.01	(bri, 5-6)
H	2.89	(3F, 5-6-7)	2.88	(3F, 1-2-10)
HCO	3.06	(B5 site)	2.50	(6F, 1-2-3-4-5-6)
CH	6.94	(4F, 1-2-3-4)	6.68	(4F, 1-2-3-4)
CO	2.04	(B5 site)	1.75	(6F, 1-2-3-4-5-6)

<sup>a</sup> Energies are in eV. The adsorption sites are given in the corresponding parentheses.

Table S2. Selected bonding distances before and after co-adsorption of O\* on the Ru(11 $\bar{2}$ 1) surface. Unit: Å.

	No co-adsorbate	O* co-adsorbed
H*+CO*	C-Ru1: 2.178	C-Ru1: 2.082
	C-Ru2: 2.179	C-Ru2: 1.987
	C-Ru3: 2.204	C-Ru3: 2.821
	C-Ru4: 2.225	C-Ru4: 3.102
	C-O: 1.302	C-O: 1.238
	O-Ru5: 2.166	O-Ru5: 2.251
	O-Ru6:2.840	O-Ru6:3.160
H*+C*+O*	C-Ru1: 1.925	C-Ru1: 1.954
	C-Ru2: 2.027	C-Ru2: 1.967
	C-Ru3: 2.118	C-Ru3: 2.010
	C-Ru4: 1.996	C-Ru4: 2.062
	O-Ru5: 1.885	O-Ru5: 1.887
	O-Ru6:1.949	O-Ru6:1.945
HCO*	C-Ru1: 2.369	C-Ru1: 2.755
	C-Ru2: 2.379	C-Ru2: 2.489
	C-Ru3: 2.171	C-Ru3: 2.083
	C-Ru4: 2.143	C-Ru4: 2.133
	C-O: 1.372	C-O: 1.365
	O-Ru5: 2.151	O-Ru5: 2.116
	O-Ru6:2.278	O-Ru6:2.237
CH*+O*	C-Ru1: 2.035	C-Ru1: 2.085
	C-Ru2: 2.110	C-Ru2: 2.046
	C-Ru3: 2.199	C-Ru3: 2.133
	C-Ru4: 2.130	C-Ru4: 2.214
	O-Ru5: 1.887	O-Ru5: 1.892
	O-Ru6:1.965	O-Ru6:1.959
TS1	C...H: 1.350	C...H: 1.363
TS2	C...O: 1.835	C...O: 1.827
TS3	C...O: 1.922	C...O: 1.991
TS4	C...H: 1.500	C...H: 1.487

Table S3. Selected bonding distances before and after co-adsorption of O\* on the stepped Ru(0001) surface. Unit: Å.

	No co-adsorbate	O* co-adsorbed
H*+CO*	C-Ru3: 2.072	C-Ru3: 2.083
	C-Ru4: 2.071	C-Ru4: 2.079
	C-Ru5: 2.069	C-Ru5: 2.069
	C-O: 1.305	C-O: 1.297
	O-Ru1: 2.317	O-Ru1: 2.348
	O-Ru2:2.302	O-Ru2:2.348
H*+C*+O*	C-Ru1: 2.082	C-Ru1: 2.091
	C-Ru2: 2.098	C-Ru2: 2.071
	C-Ru3: 1.993	C-Ru3: 1.995
	C-Ru4: 1.986	C-Ru4: 1.982
	O-Ru1: 2.060	O-Ru1: 2.039
	O-Ru2:2.034	O-Ru2:2.029
HCO*	O-Ru10:2.060	O-Ru10:2.026
	C-Ru3: 2.100	C-Ru3: 2.107
	C-Ru4: 2.104	C-Ru4: 2.106
	C-Ru5: 2.269	C-Ru5: 2.253
	C-O: 1.372	C-O: 1.355
	O-Ru1: 2.168	O-Ru1: 2.218
CH*+O*	O-Ru2:2.182	O-Ru2:2.214
	C-Ru1: 2.295	C-Ru1: 2.233
	C-Ru2: 2.279	C-Ru2: 2.238
	C-Ru3: 2.084	C-Ru3: 2.096
	C-Ru4: 2.087	C-Ru4: 2.093
	O-Ru1: 2.054	O-Ru1: 2.032
TS	O-Ru2:2.028	O-Ru2:2.028
	O-Ru10:2.065	O-Ru10:2.066
	C...H: 1.544	C...H: 1.514
	C...O: 1.816	C...O: 1.866
TS3	C...O: 1.942	C...O: 2.026
TS4	C...H: 1.442	C...H: 1.445