Electronic Supplementary Information

Origin of CO_2 as the Main Carbon Source in Syngas-to-Methanol Process over Cu: Theoretical Evidence from a Combined DFT and Microkinetic Modeling Study

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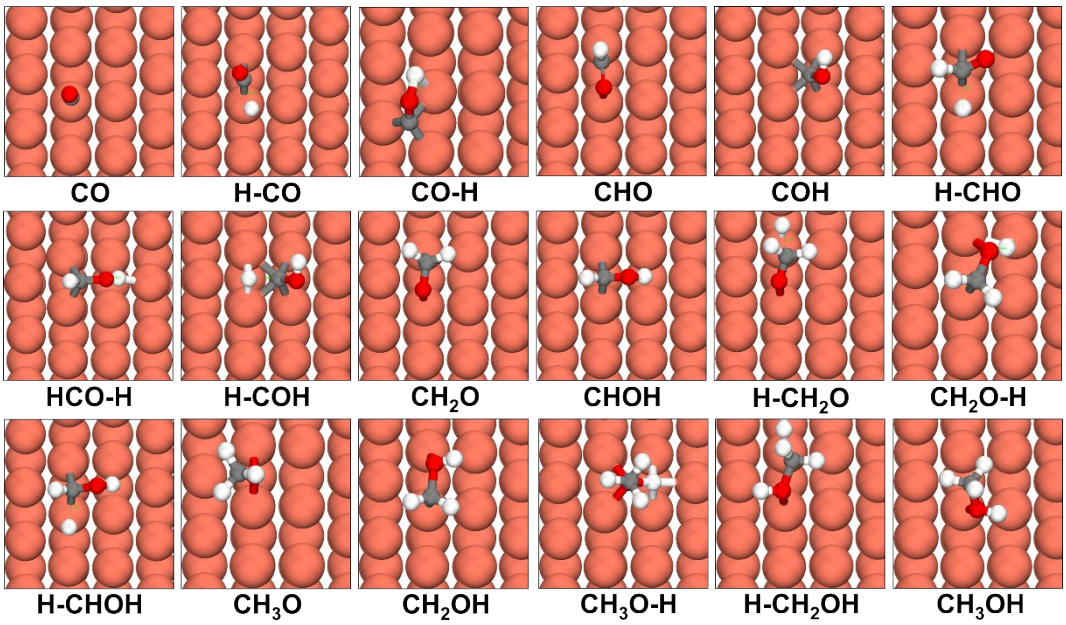

Figure S1. Configurations of the adsorption and transition states in the pathway of CO hydrogenation to methanol over clean Cu(211). In this figure and those hereafter, the Cu, C, H, and O atoms are colored orange, gray, white, and red, respectively.

Table S1. Activation energies (E_a) and reaction energies (ΔE) (both in eV) of the elementary reactions of methanol synthesis from CO_2 hydrogenation over the Cu(211) surface with no HCOO (0HCOO), one HCOO (1HCOO) and two HCOO (2HCOO) pre-covered. The values were obtained from our previous work (Wu and Yang, *ACS Catal.* 2017, 7, 10, 7187-7195).

Elementary reactions	0HCOO		1HCOO		2HCOO	
	E_a	ΔE	E_a	ΔE	E_a	ΔE
$CO_2(g)+H^*\rightarrow HCOO^*$	0.20	-1.27	0.23	-0.99	0.29	-0.71
$HCOO^*+H^*\rightarrow HCOOH^*+^*$	1.27	0.55	1.02	0.17	0.88	0.04
$HCOOH^*+H^*\rightarrow CH_2OOH^*+^*$	0.76	-0.11	0.79	0.03	0.82	0.05
$CH_2OOH^*+^*\rightarrow CH_2O^*+OH^*$	0.42	0.35	0.49	0.34	0.30	0.31
$CH_2O^*+H^*\rightarrow CH_3O^*+^*$	0.11	-1.09	0.21	-0.91	0.61	-0.53
$CH_3O^*+H^*\rightarrow CH_3OH(g)+2^*$	0.89	0.37	0.72	0.29	0.59	0.02
$H^*+OH^*\rightarrow H_2O(g)+2^*$	1.01	0.32	0.87	0.20	0.83	-0.05

Table S2. Coverage (in ML) of surface HCOO at steady state obtained from microkinetic modeling at different ratios between gaseous CO and CO_2 at 573 K and 14.24 bar of gaseous reactant. The coverage of pre-covered HCOO on Cu(211) are also listed in the brackets for comparison.

$CO/(CO+CO_2)$	**Clean (0 ML)**	**1HCOO (0.083 ML)**	**2HCOO (0.167 ML)**
0.8	0.595	0.088	0.167
0.6	0.746	0.092	0.167
0.4	0.815	0.097	0.167
0.2	0.855	0.102	0.167
0	0.880	0.107	0.167