Supporting Information

Kinetic Monte Carlo Simulations of Methanol Synthesis from Carbon Dioxide and Hydrogen on Cu(111) Catalysts: Statistical Uncertainty Study

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Table S1: Gas and surface species energetics and properties

ID	Species	Zacros mapped formation energy [eV]	Moments of intertia I (I_a, I_b, I_c) [amu Å^2]	Symmetry number σ
1	H_2(gas)	0.0^a	0.28	2.0
2	CO_2(gas)	0.0^a	43.024	2.0
3	H_2O(gas)	0.0^a	$(0.613, 1.175, 1.788)$	2.0
4	CO(gas)	0.96	8.685	1.0
5	CH_3OH(gas)	-0.99	$(3.924, 20.453, 21.178)$	1.0
6	H^*	-0.15		
7	OH^*	0.94		
8	CO^*	0.24		
9	H_2O^*	-0.18		
10	HCO^*	0.78		
11	$HOCO^*$	0.24		
12	H_2CO^*	0.18		
13	$HCOO^*$	-0.31		
14	H_2COO^*	0.24		
15	H_3CO^*	-1.05		
16	CH_3OH^*	-1.26		

[a] Reference species.

Table S2: Elementary reaction steps included in our simulations

ID	Reaction	E_a [eV][a]	ΔE [eV][b]	Pre-exponential factor
1	$H_2(gas) + 2^* \rightarrow H^* + H^*$	0.54[c]	−0.3	Eq. (2)
2-fwd	$H^* + CO_2(gas) \rightarrow HOCO^*$	1.41[c]	0.39	Eq. (2)
2-rev	$HOCO^* \rightarrow H^* + CO_2(gas)$	1.02	−0.39	Eq. (3)
3-fwd	$HOCO^* + ^* \rightarrow CO^* + OH^*$	0.59	−0.02	Eq. (1)
3-rev	$CO^* + OH^* \rightarrow HOCO^* + ^*$	0.61	0.02	Eq. (1)
4-fwd	$CO^* \rightarrow CO(gas) + ^*$	0.72	0.72	Eq. (8)
4-rev	$CO(gas) + ^* \rightarrow CO^*$	0.0	−0.72	Eq. (7)
5-fwd	$CO^* + H^* \rightarrow HCO^* + ^*$	1.0	0.69	Eq. (1)
5-rev	$HCO^* + ^* \rightarrow CO^* + H^*$	0.31	−0.69	Eq. (1)
6-fwd	$HCO^* + H^* \rightarrow H_2CO^* + ^*$	0.46	−0.45	Eq. (1)
7-fwd	$H^* + CO_2(gas) \rightarrow HCOO^*$	1.22	−0.16	Eq. (2)
7-rev	$HCOO^* \rightarrow H^* + CO_2(gas)$	1.38	0.16	Eq. (3)
8-fwd	$HCOO^* + H^* \rightarrow H_2COO^* + ^*$	1.2	0.7	Eq. (1)
8-rev	$H_2COO^* + ^* \rightarrow HCOO^* + H^*$	0.5	−0.7	Eq. (1)
9-fwd	$H_2COO^* + H^* \rightarrow H_2CO^* + OH^*$	1.64	−0.1	Eq. (1)
9-rev	$H_2CO^* + OH^* \rightarrow H_2COO^* + H^*$	1.74	0.1	Eq. (1)
10-fwd	$H_2CO^* + H^* \rightarrow H_3CO^* + ^*$	0.77	−1.08	Eq. (1)
11-fwd	$H_3CO^* + H^* \rightarrow CH_3OH^* + ^*$	1.25	−0.06	Eq. (1)
11-rev	$CH_3OH^* + ^* \rightarrow H_3CO^* + H^*$	1.31	0.06	Eq. (1)
12-fwd	$CH_3OH^* \rightarrow CH_3OH(gas) + ^*$	0.27	0.27	Eq. (8)
12-rev	$CH_3OH(gas) + ^* \rightarrow CH_3OH^*$	0.0	−0.27	Eq. (7)
13-fwd	$H^* + OH^* \rightarrow H_2O^* + ^*$	1.35	−0.01	Eq. (1)
13-rev	$H_2O^* + ^* \rightarrow H^* + OH^*$	1.36	0.01	Eq. (1)
14-fwd	$H_2O^* \rightarrow H_2O(gas) + ^*$	0.18	0.18	Eq. (8)
14-rev	$H_2O(gas) + ^* \rightarrow H_2O^*$	0.0	−0.18	Eq. (7)

[a]Activation energy from Yang *et al.* (2012),[1] except where stated otherwise; [b]Reaction energy from Yang *et al.* (2012);[1] [c]From Gokhale *et al.* (2008).[2]

References

(1) Yang, Y.; White, M. G.; Liu, P. Theoretical Study of Methanol Synthesis from CO2 Hydrogenation on Metal-Doped Cu(111) Surfaces. *J. Phys. Chem. C* **2012**, *116*, 248–256.

(2) Gokhale, A. A.; Dumesic, J. A.; Mavrikakis, M. On the Mechanism of Low-Temperature Water Gas Shift Reaction on Copper. *J. Am. Chem. Soc.* **2008**, *130*, 1402–1414.