

Supporting Information

Optimizing Binding Energies of Key Intermediates for CO₂ Hydrogenation to Methanol over Oxide-Supported Copper

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The KMC simulations were performed at experimental conditions: ratio of partial pressure of H₂ and CO₂ (P_{H2}/P_{CO2}) = 3:1 and temperature (T) = 220 °C. The P_{H2}/P_{CO2} ratio in our KMC simulations is adjusted by the rate of dissociative adsorption of H₂ and adsorption of molecular CO₂. The elementary steps included in the KMC simulation are summarized in Table S1 in Supporting Information, where the corresponding reaction rates were computed based on calculated reaction barriers using the Arrhenius equation given by $\nu \exp(-E_a/k_B T)$. ν is the prefactor. For all the surface reactions, a prefactor of $1.0 \times 10^{13} \text{ s}^{-1}$ was used. E_a is the activation energy of the corresponding reaction obtained from DFT calculations, k_B is the Boltzmann constant and T is the temperature of the KMC simulations. For the reactions involving molecules in the gas-phase, the contribution from the entropy was taken from the NIST database [1] and was included in the KMC simulations. The adsorption coefficient was calculated according to $P A_{\text{site}} \sigma / \sqrt{2 \pi m k_B T}$ [2], where P, A_{site} , σ and m represent the pressure of the adsorbed gas, the area of a single site, the sticking coefficient and the mass of adsorption gas, respectively.

Table S1. DFT calculated energetics and corresponding rates for the elementary steps included in the KMC simulations at 220 °C for CO₂ hydrogenation to methanol.

Reactions	TiO ₂ /Cu			ZrO ₂ /Cu		
	E _a (eV)	ΔE (eV)	Rate (s ⁻¹ site ⁻¹)	E _a (eV)	ΔE (eV)	Rate (s ⁻¹ site ⁻¹)
*H + *CO ₂ → *HOCO + *	0.89	0.07	7.96×10 ³	0.76	0.18	1.70×10 ⁵
*HOCO + * → *CO + *OH	0.68	-0.20	1.12×10 ⁶	0.72	-0.99	4.36×10 ⁵
*CO → CO(g) + *	1.21	1.21	4.26	1.86	1.86	9.64×10 ⁻⁷
*H + *OH → *H ₂ O + *	0.61	-0.12	5.80×10 ⁶	1.36	1.03	1.25×10 ⁻¹
*H ₂ O → H ₂ O(g) + *	0.83	0.83	3.27×10 ⁴	0.99	0.99	7.56×10 ²
*H + *CO → *HCO + *	0.73	0.47	3.44×10 ⁵	0.88	0.39	1.01×10 ⁴
*H + *HCO → *H ₂ CO + *	0.54	-0.23	3.02×10 ⁷	0.44	-0.69	3.17×10 ⁸
*H + *H ₂ CO → *H ₃ CO + *	0.14	-0.86	3.70×10 ¹¹	0.43	-1.10	4.02×10 ⁸
*H + *H ₃ CO → *CH ₃ OH + *	0.77	-0.08	1.34×10 ⁵	1.11	1.07	4.49×10 ¹
*CH ₃ OH → CH ₃ OH(g) + *	0.88	0.88	1.01×10 ⁴	1.10	1.10	5.68×10 ¹
*H + *CO ₂ → *HCOO + *	0.46	-0.63	1.98×10 ⁸	0.14	-0.58	3.70×10 ¹¹
*H + *HCOO → *HCOOH + *	0.85	0.30	2.04×10 ⁴	0.80	0.70	6.63×10 ⁴
*H + *HCOOH → *H ₂ COOH + *	0.67	0.01	1.41×10 ⁶	0.28	-0.98	1.37×10 ¹⁰
*H ₂ COOH + * → *H ₂ CO + *OH	0.79	0.57	8.38×10 ⁴	1.32	0.67	3.20×10 ⁻¹

E_a = activation energy, ΔE = reaction energy

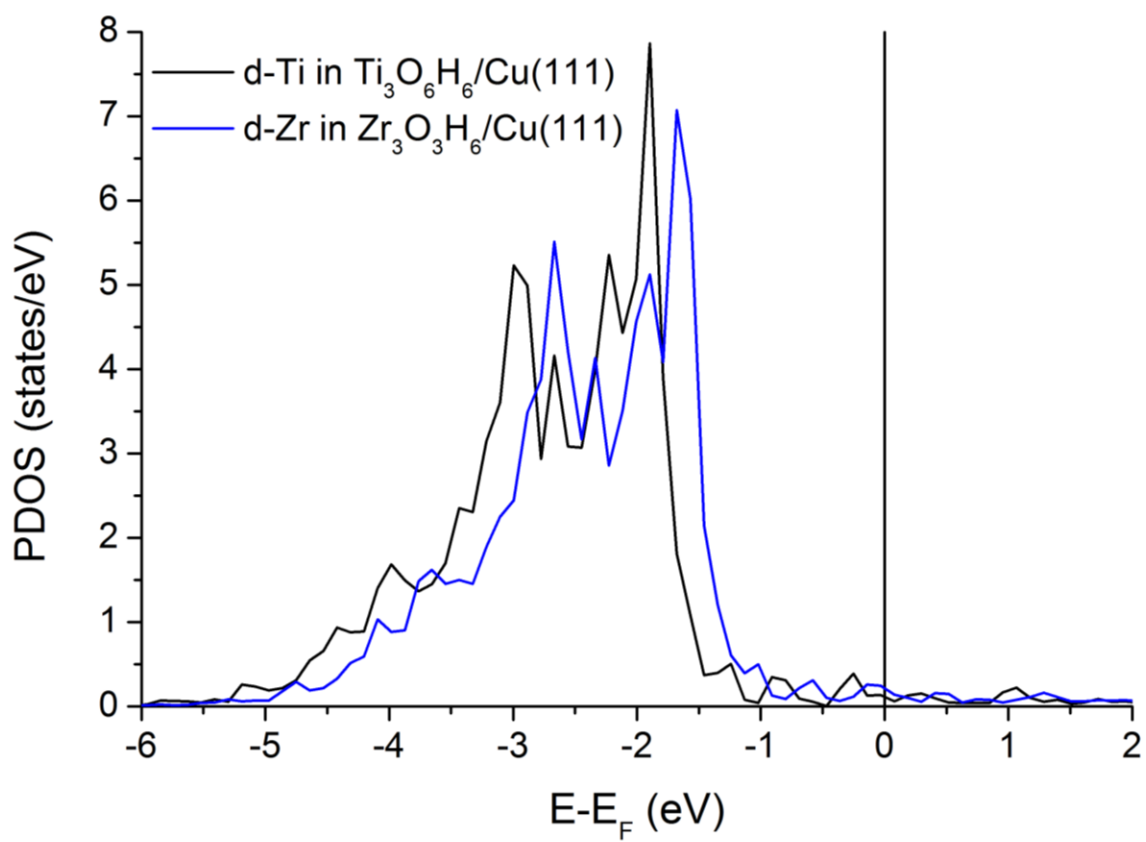


Figure S1. Partial density of states (PDOS) of Ti and Zr d-states in $\text{Ti}_3\text{O}_6\text{H}_6/\text{Cu}(111)$ and $\text{Zr}_3\text{O}_6\text{H}_6/\text{Cu}(111)$, respectively.

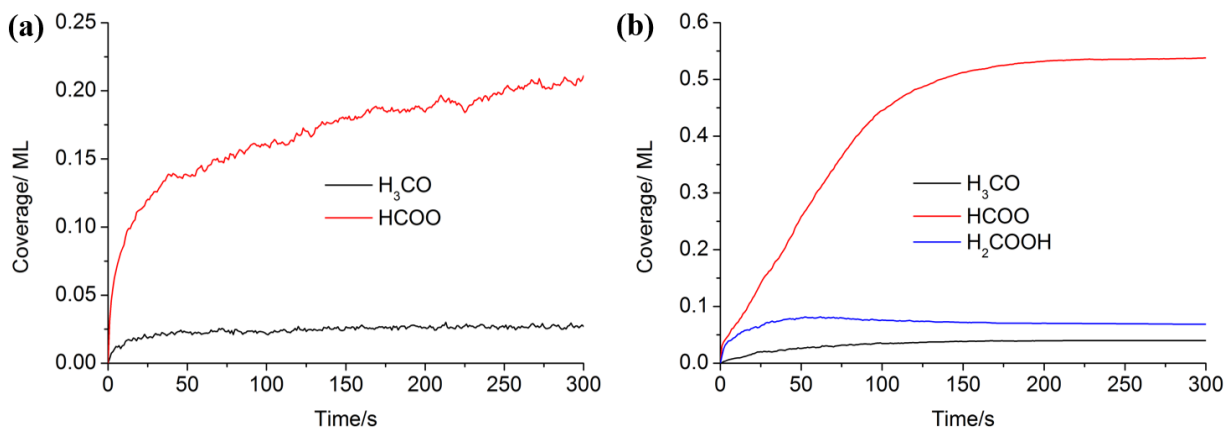


Figure S2. KMC(simulation time = 300 s)-simulated coverage of surface formate-like species over Cu/TiO₂ (a) and Cu/ZrO₂ (b) catalysts during the CO₂ hydrogenation reaction at T = 220 °C.

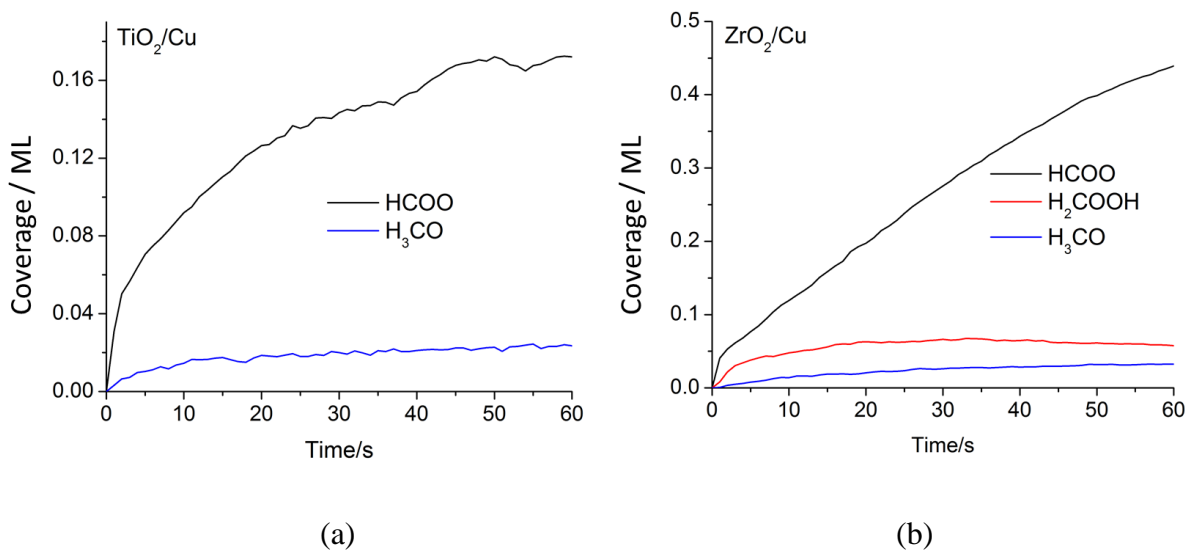


Figure S3. KMC(simulation time = 60 s)-simulated coverage of surface formate-like species over Cu/TiO₂ (a) and Cu/ZrO₂ (b) catalysts during the CO₂ hydrogenation reaction at T = 220 °C.

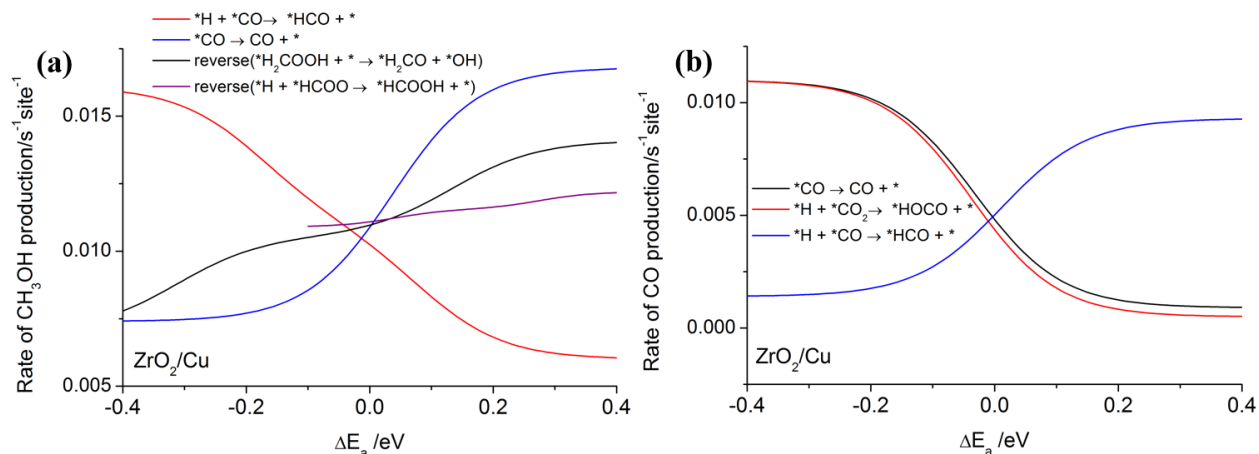


Figure S4. Sensitivity analysis based on KMC simulations on the controlling-steps for CH_3OH production (a) and CO production (b) during the CO_2 hydrogenation reaction on Cu/TiO_2 at $T = 220^\circ\text{C}$.

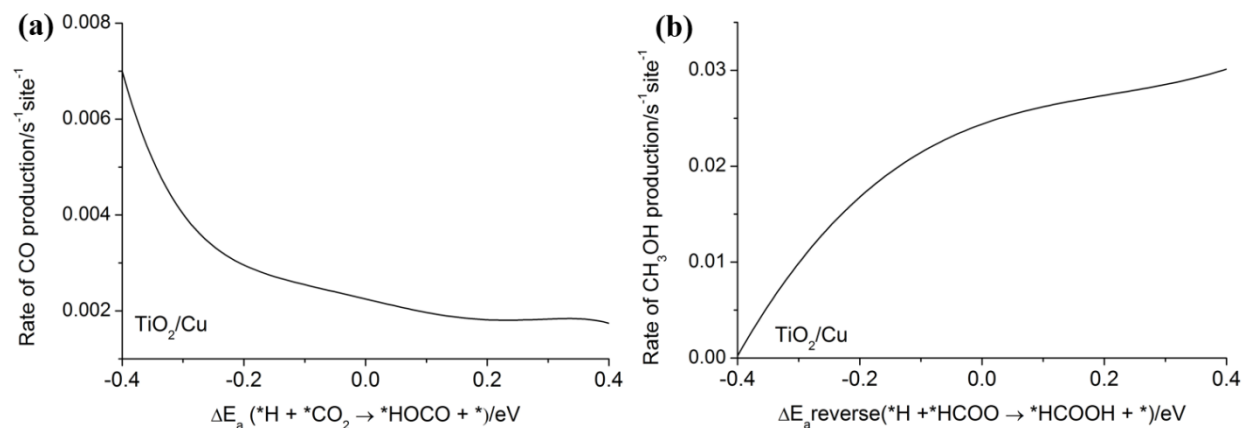


Figure S5. Sensitivity analysis based on KMC simulations on the controlling-steps for CH_3OH production (a) and CO production (b) during the CO_2 hydrogenation reaction on Cu/ZrO_2 at $T = 220^\circ\text{C}$.

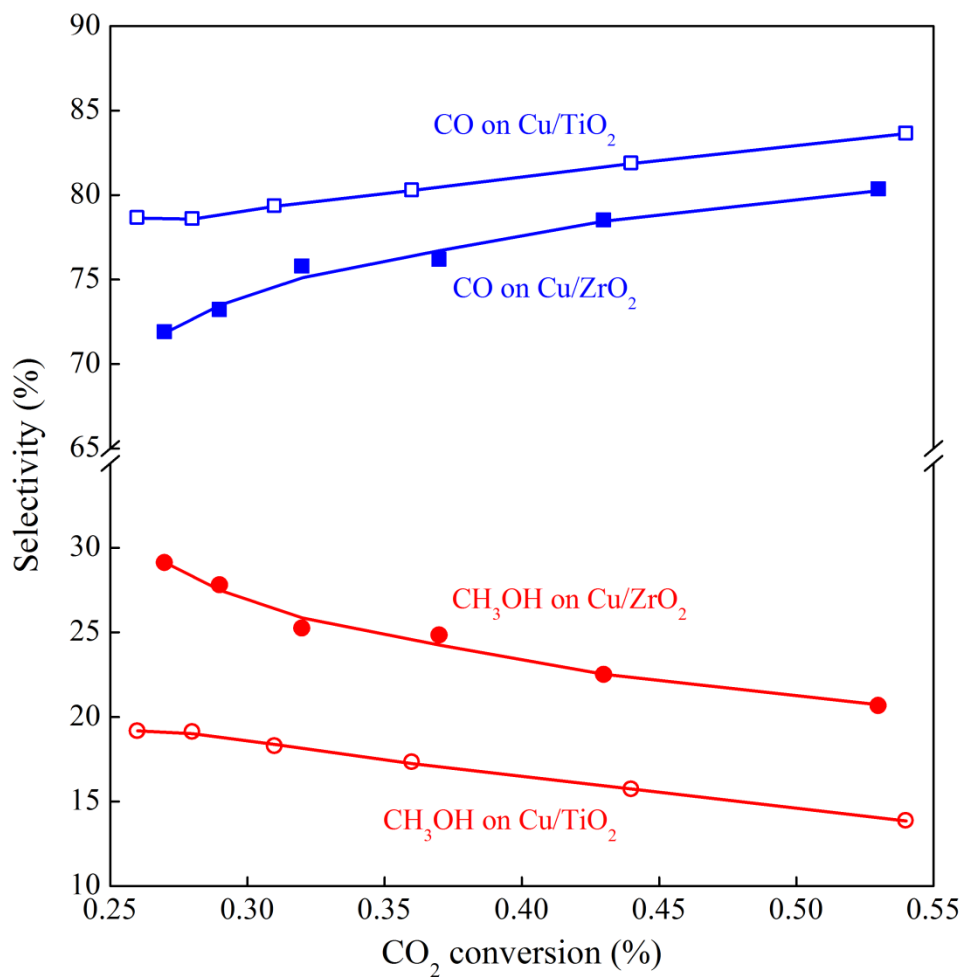


Figure S6. Selectivity to CH₃OH and CO of Cu/ZrO₂ and Cu/TiO₂ catalysts at different CO₂ conversions by varying the total flow rate of the reactants (reaction conditions: 220 °C, CO₂:H₂:N₂ = 1:3:1, 30 mg Cu/ZrO₂, 400 mg Cu/TiO₂)

References

1. <http://cccbdb.nist.gov>
2. A.P.J. Jansen, "An introduction to Monte Carlo simulations of surface reactions", .
[http://arxiv.org/abs/cond-mat/0303028/\(2003\)](http://arxiv.org/abs/cond-mat/0303028/(2003)) and <http://www.catalysis.nl/~chembond/kMC/>.