

Supporting information

Microkinetic Study of CO₂ Hydrogenation to Methanol on Pd₁- Cu(111) and Pd₁-Ag(111) Catalysts: A DFT Analysis

1. Transition states structure and frequency

Table S1: All imaginary frequencies of the corresponding transition states.

No.	elementary reaction	Cu(111)	Pd ₁ -Cu(111)	Pd ₁ -Ag(111)
		(cm ⁻¹)	(cm ⁻¹)	(cm ⁻¹)
R2	CO ₂ * + * → CO* + O*	-346.25	-323.69	-208.84
R3	CO ₂ * + H* → HCOO*	-643.44	-596.55	-593.94
R4	CO ₂ * + H* → COOH*	-1,460.34	-1,414.75	-1,340.03
R5	HCOO* + H* → HCOOH*	-754.28	-293.50	-530.01
R6	HCOO* + H* → H ₂ COO*	-911.61	-891.47	-657.23
R7	COOH*+H* → COHOH*	-1,154.49	-1,258.58	-1,140.37
R8	COOH* → CO* + OH*	-267.14	-286.92	-262.27
R9	HCOOH*+H* → H ₂ COOH*	-865.28	-953.72	-913.24
R10	HCOOH*+* → HCO*+OH*	-277.06	-221.66	-240.69
R11	H ₂ COO* + H* → H ₂ COOH*	-1,184.83	-850.74	-773.08
R12	H ₂ COO* + * → CH ₂ O* + O*	-188.40	-159.11	-169.66
R13	H ₂ COOH* + * → CH ₂ O* + OH*	-72.67	-111.27	-131.66
R14	CO* + H* → HCO*	-697.88	-830.69	-869.32
R15	CO* + H* → COH*	-1,692.11	-1,640.54	-1,678.26
R16	COHOH* + * → COH* + OH*	-259.06	-269.92	-283.85
R17	COH* + H* → HCOH*	-808.41	-812.40	-817.16
R18	HCO*+H* → CH ₂ O*	-917.23	-895.70	-828.33
R19	HCOH* + H* → CH ₂ OH*	-846.74	-771.37	-826.45
R20	CH ₂ O* + H* → CH ₂ OH*	-1,379.61	-1,231.59	-1,166.35
R21	CH ₂ O* + H* → CH ₃ O*	-317.43	-872.86	-735.82
R22	CH ₂ OH* + H* → CH ₃ OH*	-934.69	-889.68	-775.28
R23	CH ₃ O* + H* → CH ₃ OH*	-1,184.10	-929.72	-224.81

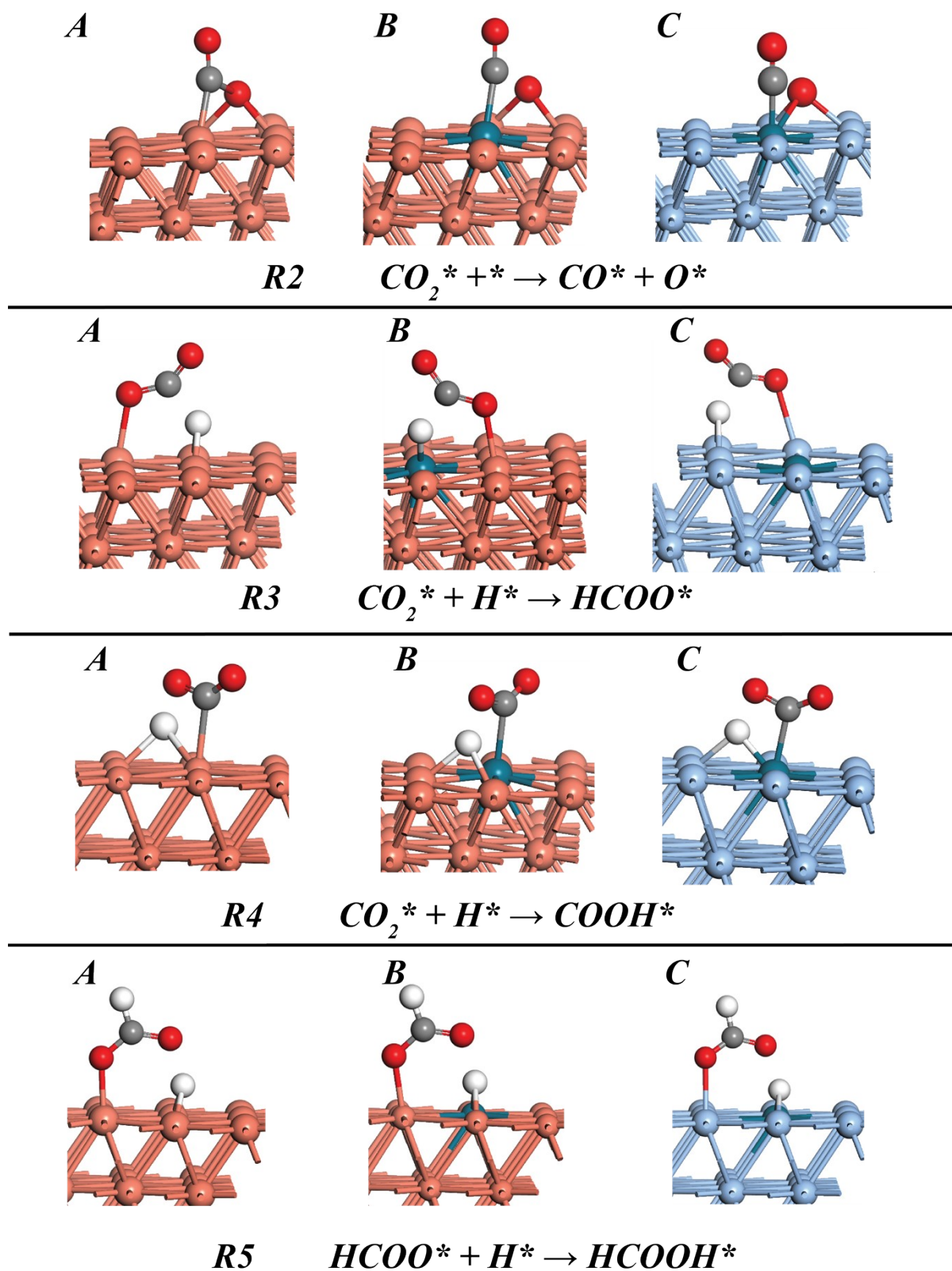


Figure S1: Transition state structure for reaction step (A = Cu(111) surface, B = Pd₁-Cu(111) surface, C = Pd₁-Ag(111) surface).

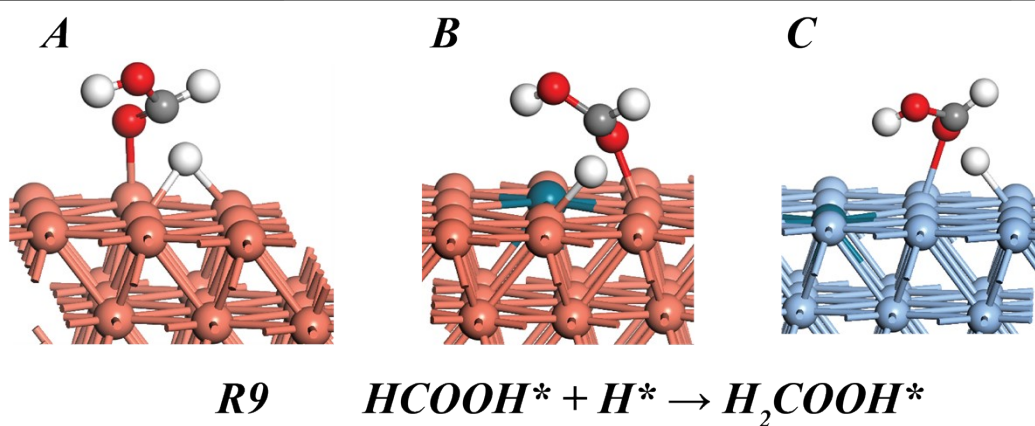
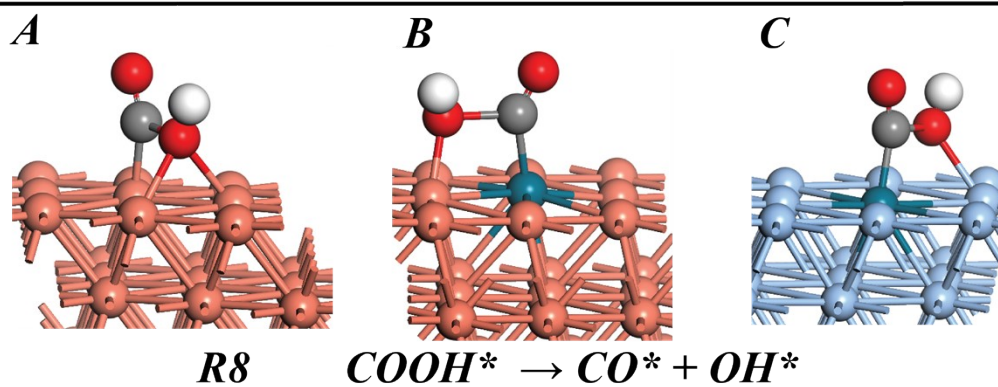
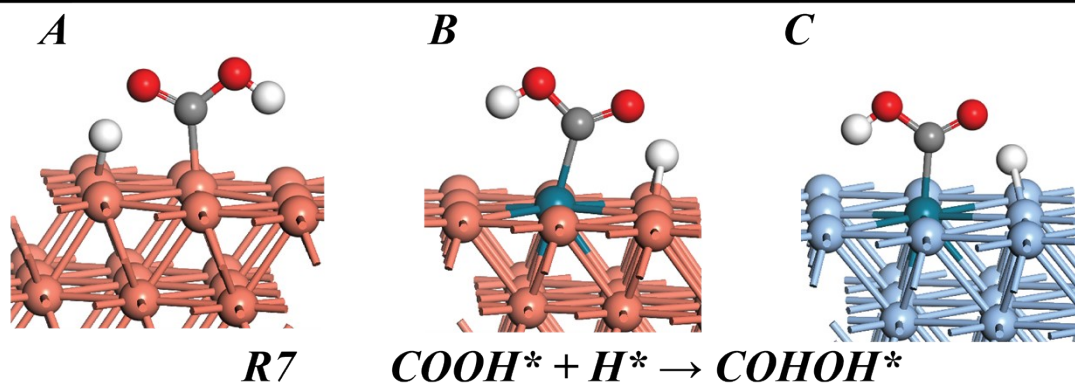
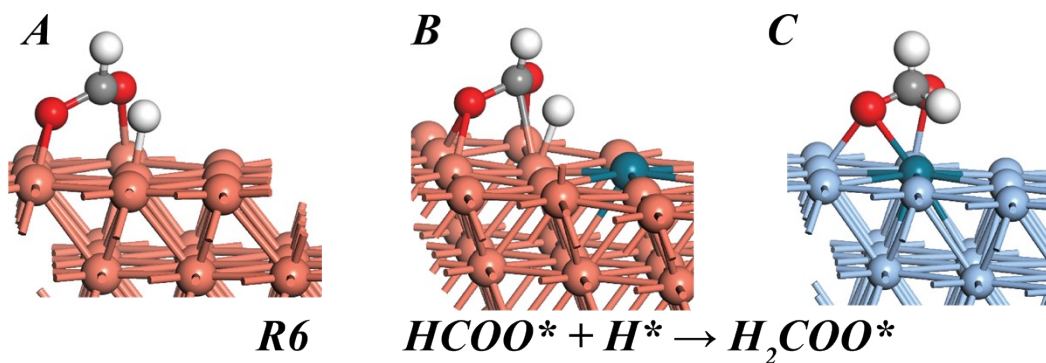


Figure S1 cont'd

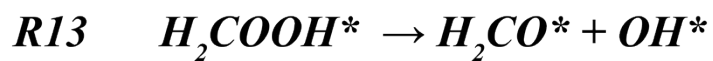
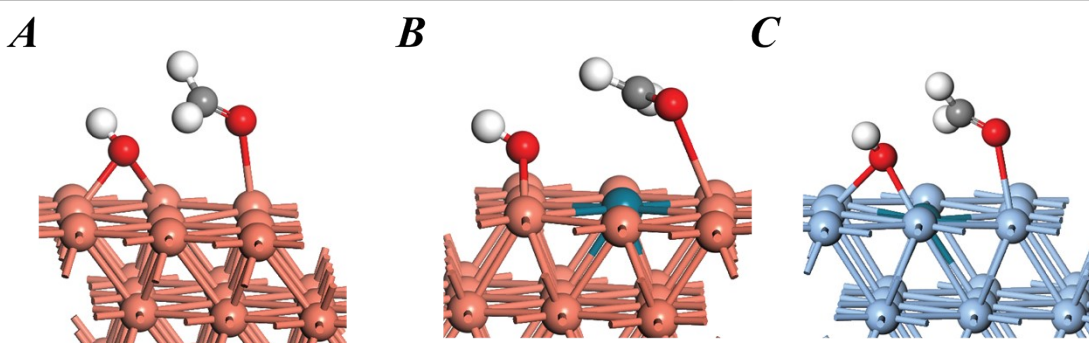
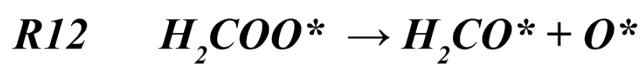
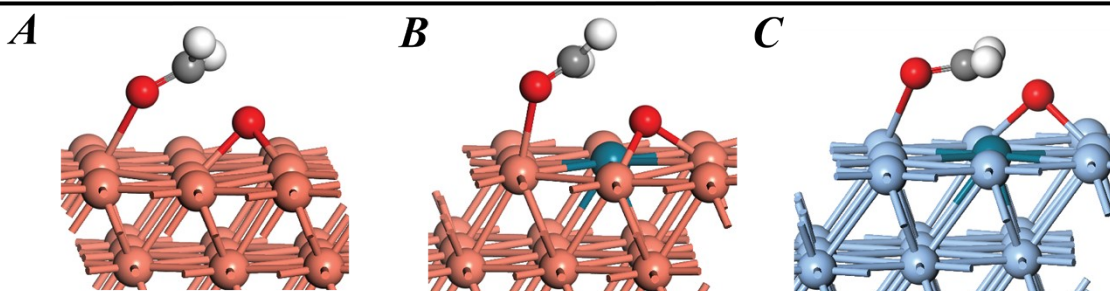
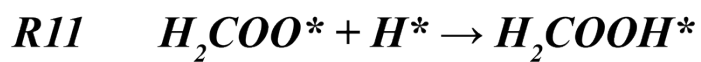
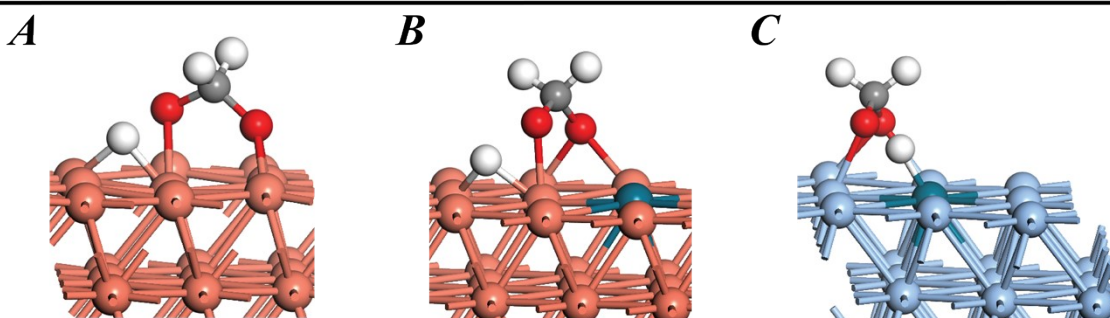
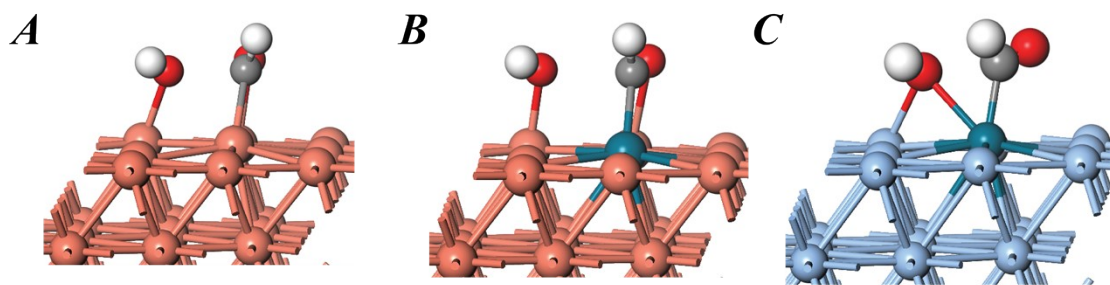


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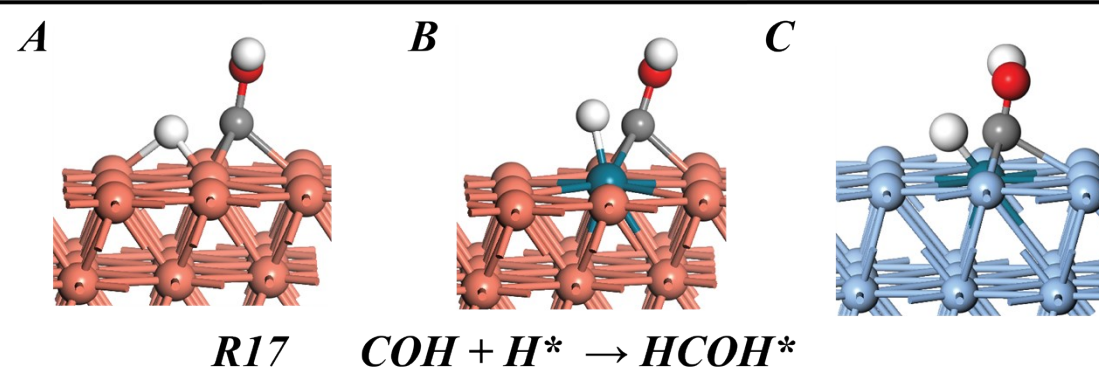
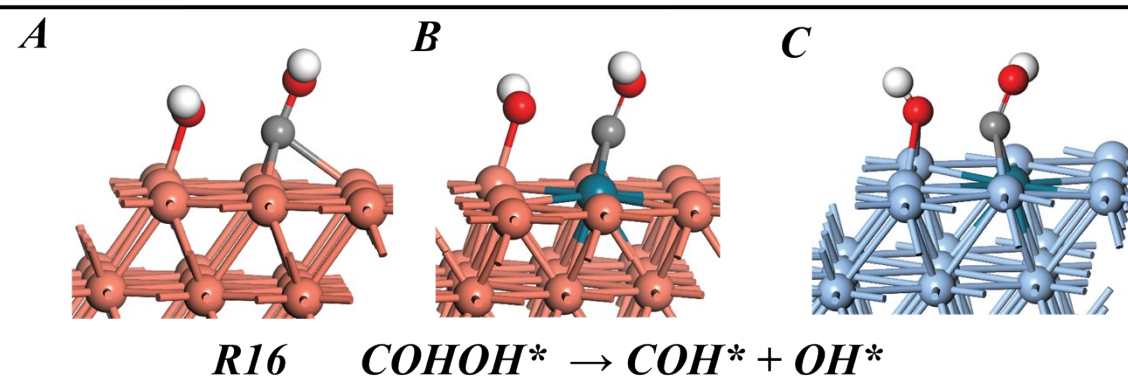
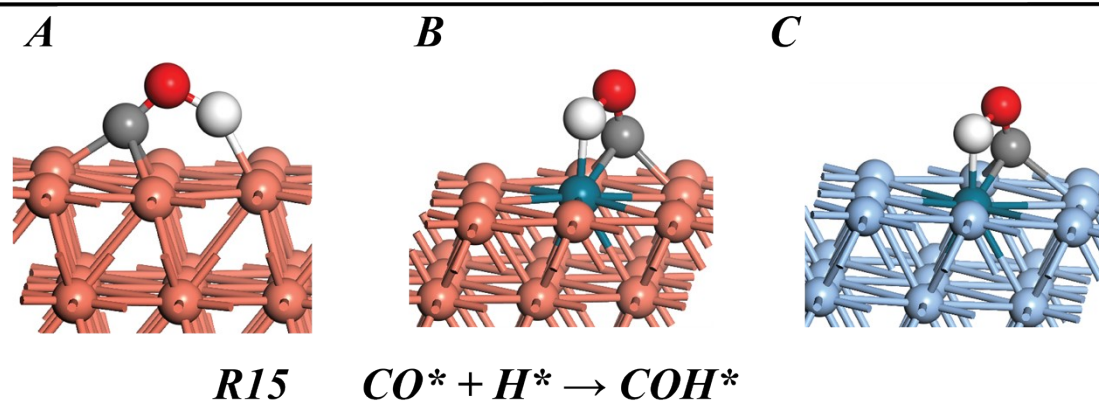
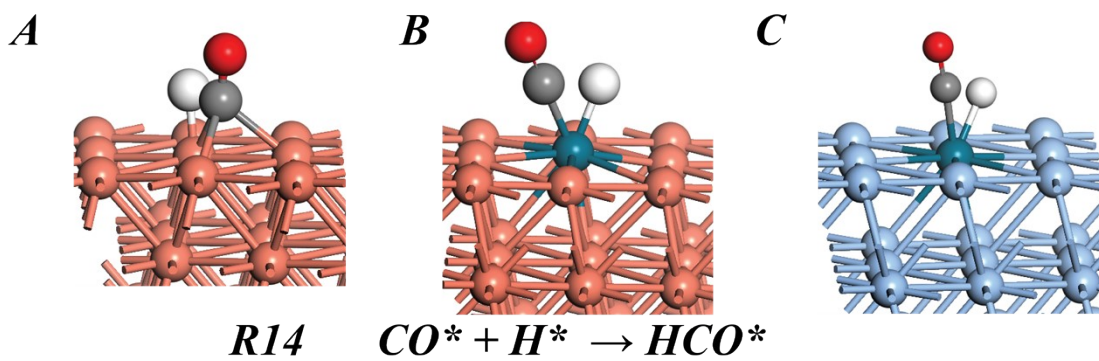


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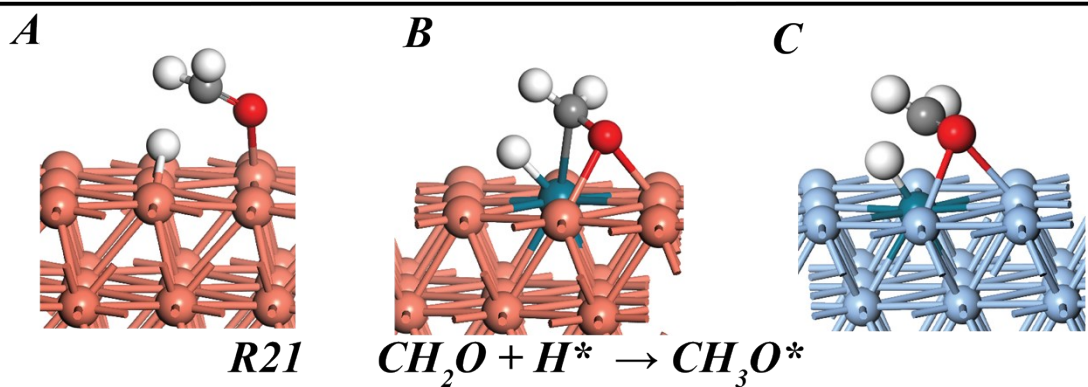
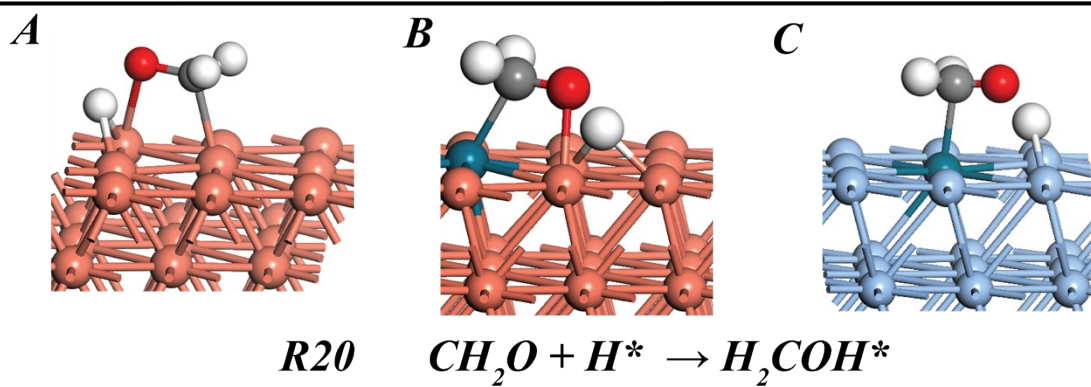
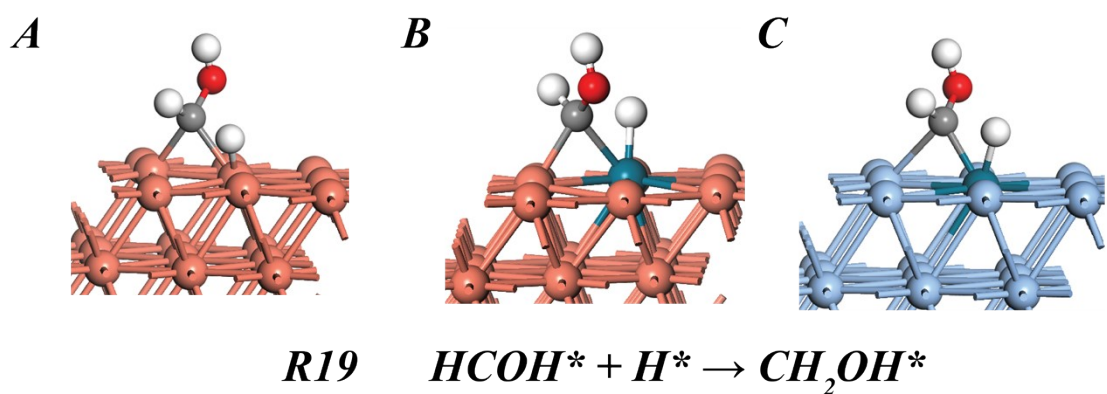
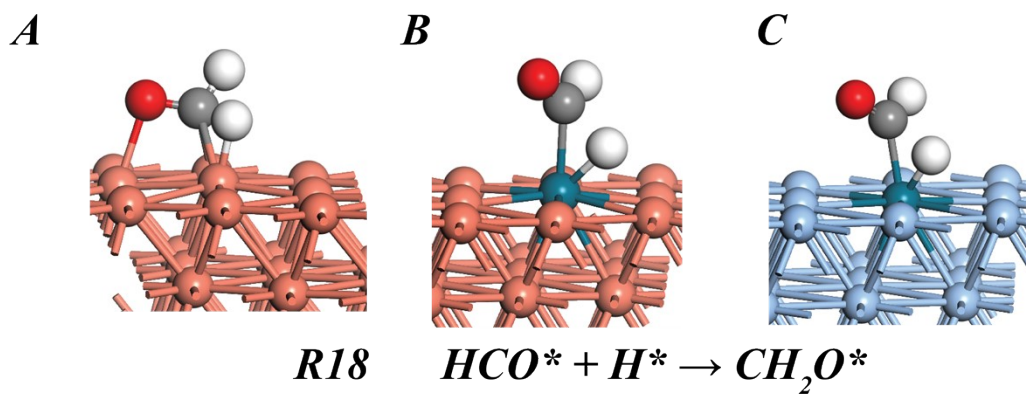


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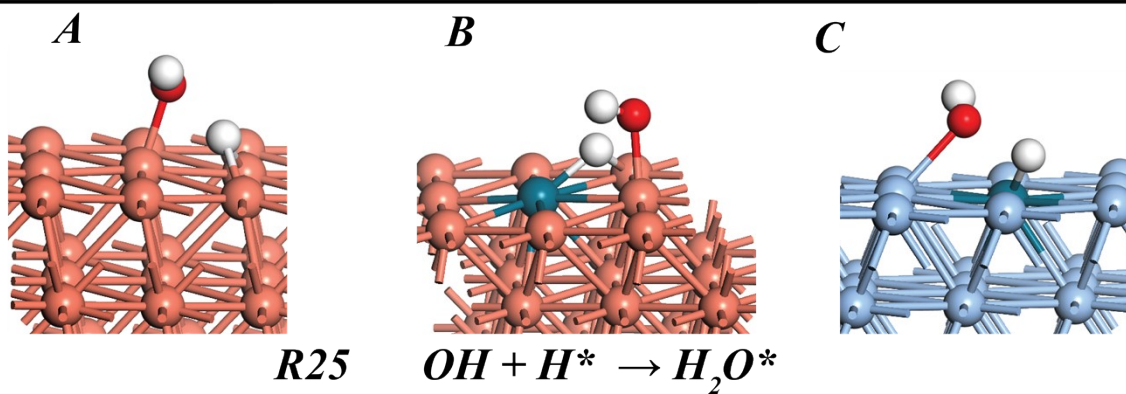
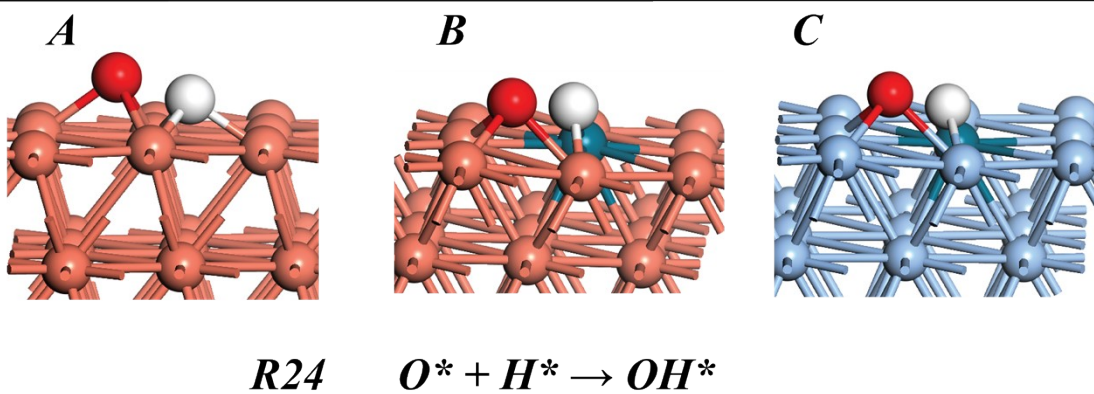
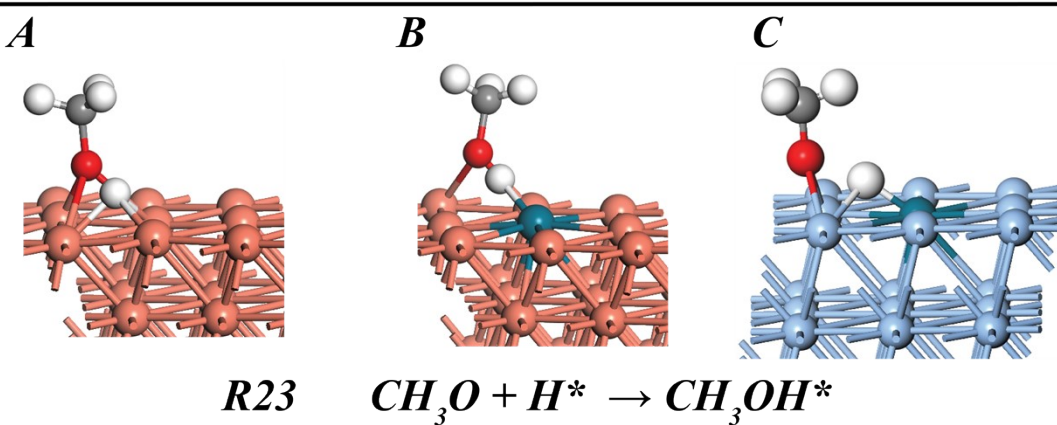
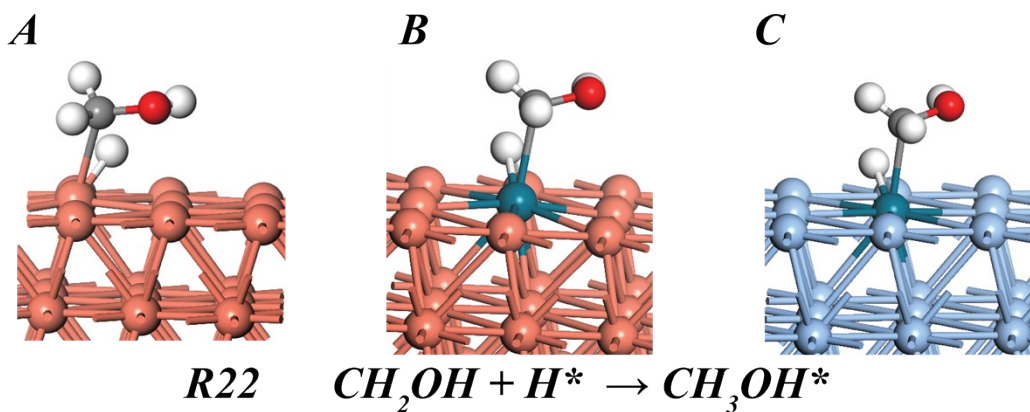


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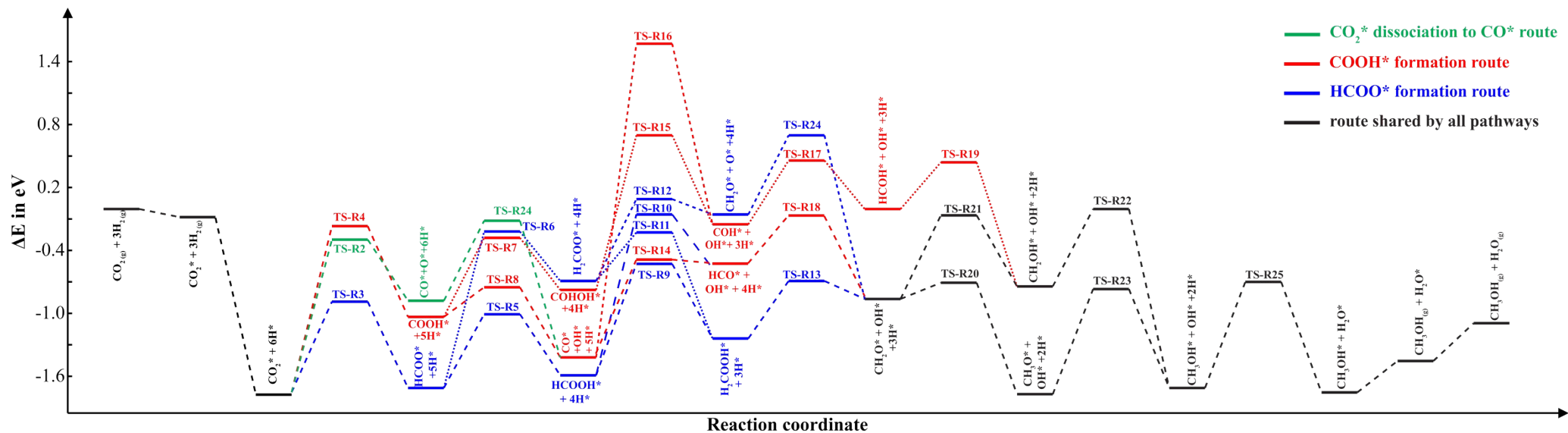


Figure S2: The energy profile diagram depicting possible reaction paths of CO₂ hydrogenation to CH₃OH on the Cu(111) surface

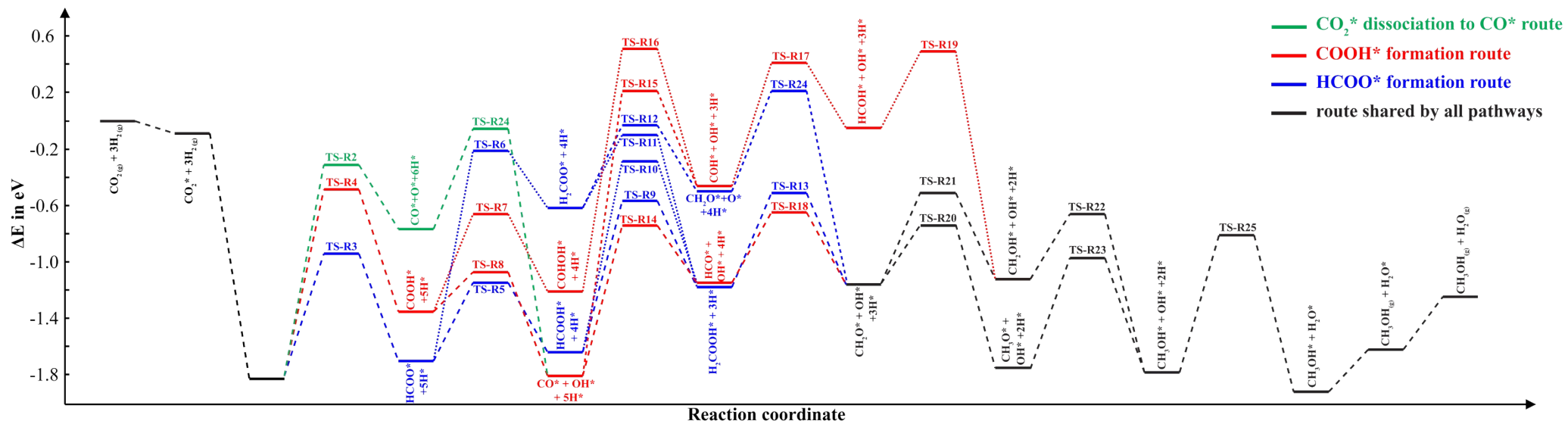


Figure S3: The energy profile diagram depicting possible reaction paths of CO₂ hydrogenation to CH₃OH on the Pd₁-Cu(111) SAA surface.

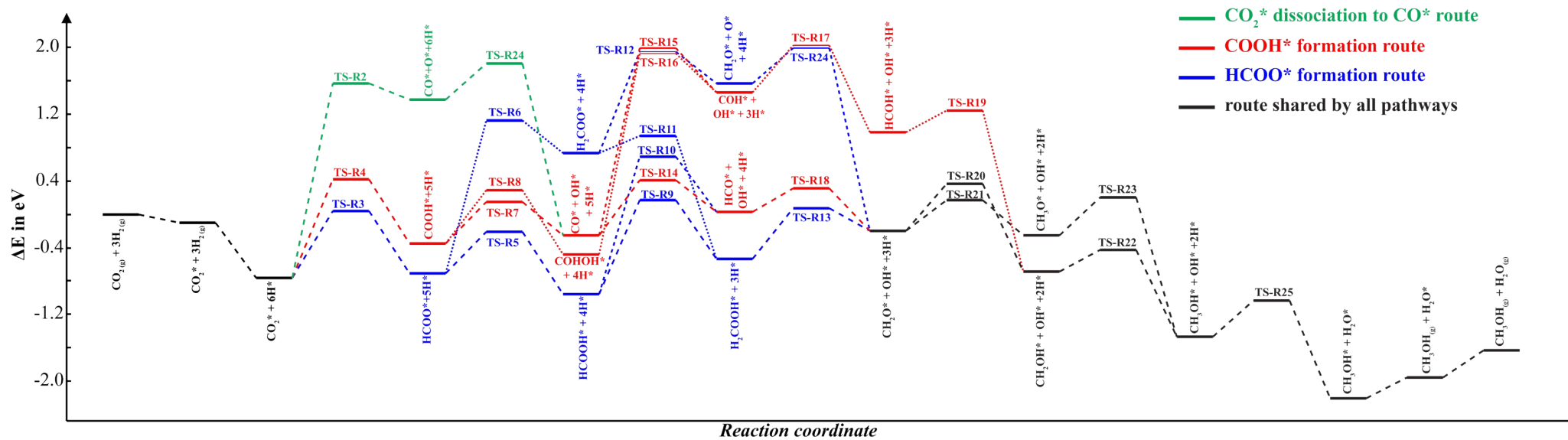


Figure S4: The energy profile diagram depicting possible reaction paths of CO_2 hydrogenation to CH_3OH on the $\text{Pd}_1\text{-Ag}(111)$ SAA surface.