

Supporting Information

Unveiling the Mechanism of CO₂ Electroreduction to CO over ZIF-8, ZIF-67, and ZIF-90: A DFT Perspective

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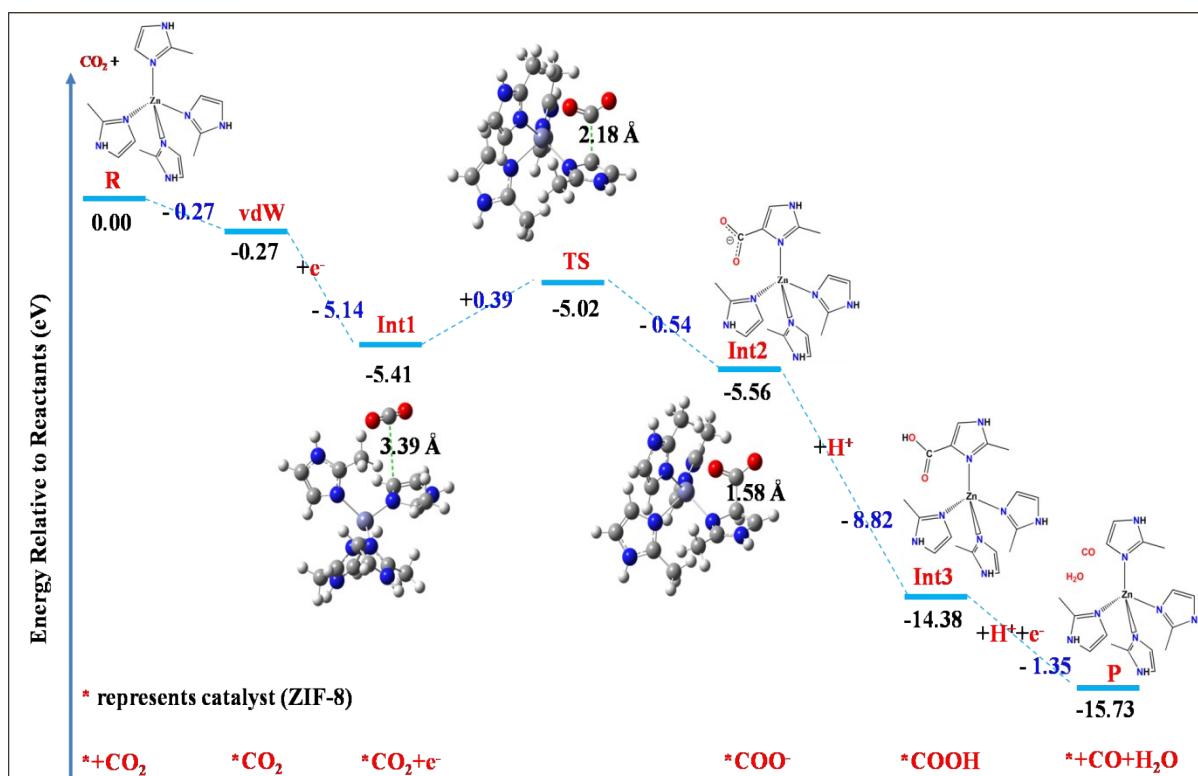


Figure S1: Energy Diagram of CO_2RR by ZIF-8.

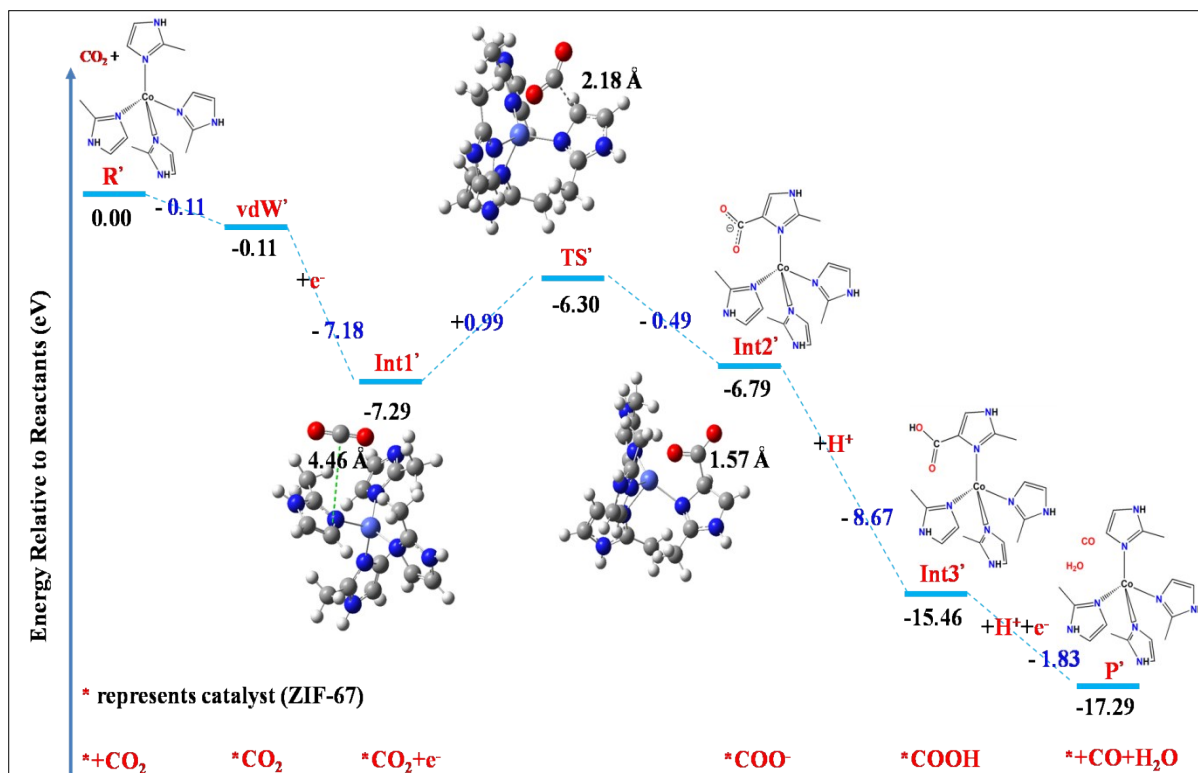


Figure S2: Energy Diagram of CO_2RR by ZIF-67.

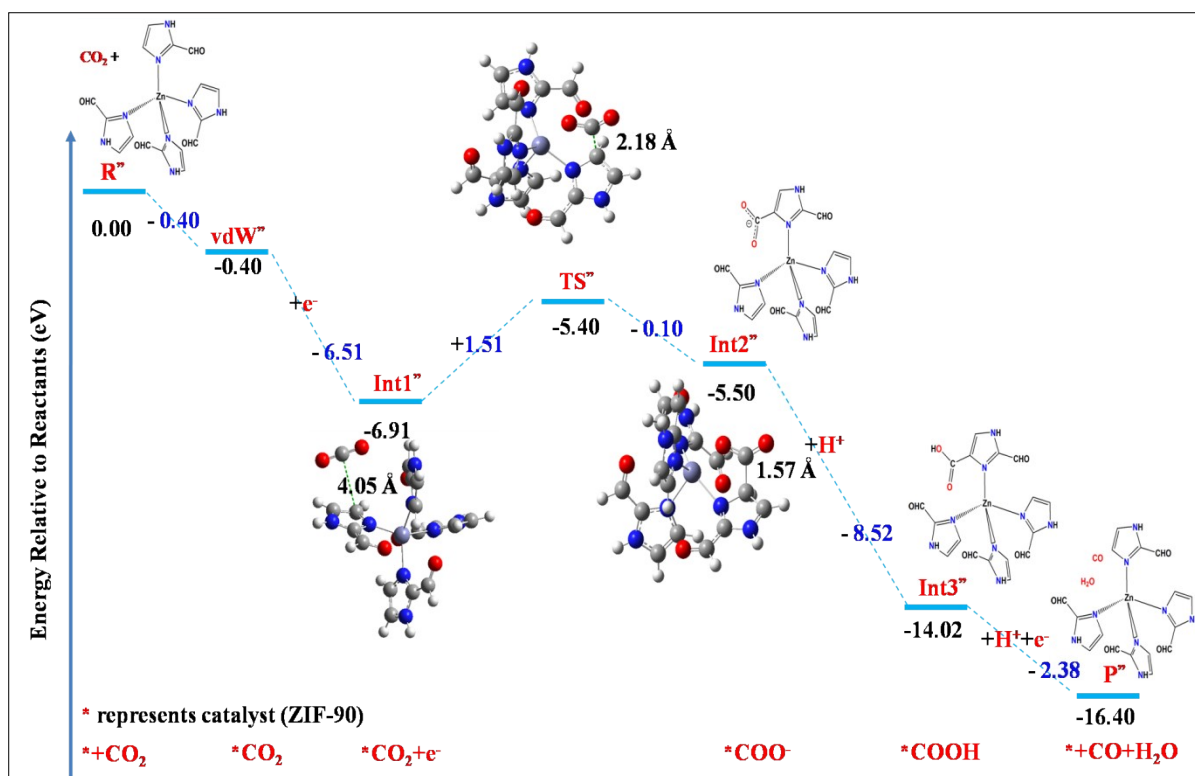


Figure S3: Energy Diagram of CO₂RR by ZIF-90.

Table S1. Computed Total and Relative Spin-State Energies (in eV) for ZIF-Based Catalysts

Catalyst	Metal Center	Spin Multiplicity (2S + 1)	Total Energy (eV)	ΔE (eV)	Relative Stability
ZIF-8	Zn ²⁺ (d ¹⁰)	Singlet (S = 0)	-30679.95	0.00	Ground state
		Triplet (S = 1)	-30676.33	+3.62	Unstable
ZIF-90	Zn ²⁺ (d ¹⁰)	Singlet (S = 0)	-38734.38	0.00	Ground state
		Triplet (S = 1)	-38731.62	+2.76	Unstable
ZIF-67	Co ²⁺ (d ⁷)	Quartet (S = 3/2)	-32842.80	0.00	Ground state
		Sextet (S = 5/2)	-32839.21	+3.59	Unstable

Table S2: Summary of energy (eV) values for HOMO, LUMO, and HOMO-LUMO gap, along with overall NBO charge on the catalyst and the central metal for ZIF-8, ZIF-67, and ZIF-90 at the B3LYP/6-31G(d,p) (H, C, N, and O) and SDD (Zn and Co) levels of theory.

Catalyst	HOMO eV	LUMO eV	$\Delta E_{(H-L)}$ eV	NBO Charge	
				<i>Overall on Catalyst</i>	<i>On Central Metal</i>
ZIF-8	-12.22	-5.71	6.50	2	1.341
ZIF-67	-12.25	-5.69	6.56	2	1.18
ZIF-90	-12.62	-7.85	4.77	2	1.315

Table S3: Summary of gas phase energies for adsorption (E_{ads}) and activation (E_a) of CO₂, and energy of reaction (E_r) for reduction of CO₂ to CO by ZIF-8, ZIF-67, and ZIF-90.

Catalyst	E_{ads} (eV)	E_a (eV)	E_r (eV)
ZIF-8	-0.27	0.48	-15.72
ZIF-67	-0.11	1.30	-16.23
ZIF-90	-0.40	1.51	-16.39

Table S4. Computed CO₂ Vibrational Frequencies (cm⁻¹) on Different Catalysts

Catalyst	Intermediate	Asymmetric Stretch (ν_3)	Symmetric Stretch (ν_1)	Shift from Gas Phase ($\Delta\nu_3, \Delta\nu_1$)
Gas-phase CO ₂	–	2436	1372	–
ZIF-8	Int1	1788	1233	–648 / –139
	TS	1873	1233	–563 / –139
	Int2	1805	1305	–631 / –67
ZIF-90	Int1	2433	1371	–3 / –1
	TS	1999	1263	–437 / –109
	Int2	1829	1305	–607 / –67
ZIF-67	Int1	2427	1368	–9 / –4
	TS	1996	1215	–440 / –157
	Int2	1788	1309	–607 / –63

Table S5: Summary table of non-bonding interaction of Int1 and TS for ZIF-8, ZIF-67, and ZIF-90 via QTAIM analysis

ZIF-8									
	BCP	Atoms	P	$\nabla^2\rho$	H	G	V	-(V/G)	$E_{int}=V/2$
			a.u.	a.u.	a.u.	a.u.	a.u.	a.u.	kcal/mol
Int1	BCP 67	O52 C15	0.003	0.014	0.001	0.003	-0.002	0.667	-0.628
	BCP 84	O51 C14	0.004	0.015	0.001	0.003	-0.002	0.667	-0.628
	BCP 106	O51 H38	0.004	0.018	0.001	0.004	-0.003	0.750	-0.941
TS	BCP 67	C50 C14	0.062	0.066	-0.017	0.033	-0.050	1.515	-15.688
	BCP 71	O51 H40	0.017	0.072	0.000	0.018	-0.018	1.000	-5.648
	BCP 82	O52 H36	0.006	0.027	0.001	0.006	-0.004	0.667	-1.255
	BCP 86	O51 Zn32	0.055	0.319	-0.014	0.094	-0.108	1.149	-33.885
	BCP 92	O51 C33	0.008	0.035	0.001	0.008	-0.006	0.750	-1.883
ZIF-67									
Int1	BCP 91	O51 N31	0.004	0.017	0.000	0.004	-0.003	0.750	-0.941
	BCP 93	O50 H34	0.003	0.015	0.001	0.003	-0.002	0.667	-0.628
	BCP 108	O51 H45	0.004	0.016	0.001	0.003	-0.002	0.667	-0.628
	BCP 115	O50 H39	0.004	0.016	0.001	0.003	-0.002	0.667	-0.628
TS	BCP 61	O50 H39	0.015	0.061	0.000	0.015	-0.015	1.000	-4.706
	BCP 68	C49 C14	0.052	0.033	-0.014	0.022	-0.036	1.636	-11.295
	BCP 77	O51 H35	0.005	0.022	0.001	0.005	-0.004	0.800	-1.255
	BCP 87	O50 C32	0.006	0.319	0.001	0.006	-0.005	0.833	-1.569
	BCP 88	O50 Co52	0.038	0.262	-0.004	0.008	-0.074	9.250	-23.218
ZIF-90									
Int1	BCP 70	O48 N7	0.004	0.017	0.000	0.004	-0.003	0.750	-0.941
	BCP 113	O47 N29	0.004	0.016	0.001	0.003	-0.003	1.000	-0.941
	BCP 120	O47 C30	0.004	0.019	0.001	0.004	-0.003	0.750	-0.941
TS	BCP 98	O47 O33	0.007	0.029	0.000	0.007	-0.007	1.000	-2.196
	BCP 102	O47 Zn1	0.038	0.231	-0.003	0.061	-0.064	1.049	-20.080
	BCP 111	O47 O44	0.006	0.020	0.000	0.005	-0.006	1.200	-1.883
	BCP 120	C46 C3	0.022	0.168	-0.004	0.046	-0.050	1.087	-15.688

Table S6: Summary table of NBO charge analysis of Int1, TS, and Int2 for ZIF-8, ZIF-67, and ZIF-90

Surface	Charge on	Int1	TS	Int2
ZIF-8	Catalyst	1.003	1.612	1.643
	Analyte	-0.003	-0.612	-0.643
	Overall	1	1	1
ZIF-67	Catalyst	0.994	1.387	1.611
	Analyte	0.006	-0.387	-0.611
	Overall	1	1	1
ZIF-90	Catalyst	0.997	1.354	1.569
	Analyte	0.003	-0.354	-0.569
	Overall	1	1	1