Supporting Information:

Efficient CO_2 Reduction to Methane on Ru_2-based Adjacent-Vacant Graphene Catalysts: Insights into Bimetallic Synergies, Thermodynamics, and Kinetics

by

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Table 1. Relative energies ($^{\Delta E_{Rel}}$) of surface bound species on 2MV-Ru_2 electrode in various spin multiplicities (SM).

S. No.	Species	SM	ΔE_{Rel} (eV)	S. No.	Species	SM	ΔE_{Rel} (eV)
1	2MV-Ru_2	1	0.00	**11**	CHO*	2	0.00
		3	0.70			4	1.49
		5	1.68			6	2.23
		7	4.20			8	5.02
		9	6.52			10	7.16
2	C*	1	0.00	**12**	CHOH*	1	0.00
		3	0.56			3	0.53
		5	1.48			5	1.95
		7	2.75			7	3.50
		9	4.78			9	6.11
3	CH*	2	0.00	**13**	CO*	1	0.00
		4	1.27			3	0.79
		6	2.83			5	2.35
		8	4.75			7	4.57
		10	7.29			9	7.24
4	CH_2*	1	0.00	**14**	CO_2*	1	0.00
		3	0.91			3	1.12
		5	2.13			5	2.41
		7	3.51			7	3.88
		9	6.36			9	6.60
5	CH_2O*	1	0.00	**15**	COH*	2	0.00
		3	0.51			4	1.56
		5	1.76			6	2.52
		7	3.74			8	4.78
		9	6.42			10	7.37
6	CH_2OH*	2	0.00	**16**	COOH*	2	0.00
		4	0.98			4	1.36
		6	2.79			6	2.16
		8	5.46			8	4.94
		10	8.44			10	8.10
7	CH_3*	2	0.00	**17**	HCOO*	2	0.00
		4	0.99			4	1.12
		6	2.72			6	2.33

		8	5.41			8	5.03
		10	8.19			10	8.36
8	CH_3O*	2	0.00	**18**	HCOOH*	1	0.00
		4	0.91			3	0.56
		6	2.15			5	1.70
		8	4.99			7	3.70
		10	8.65			9	6.57
9	CH_3OH*	1	0.00	**19**	H*	2	0.00
		3	0.69			4	1.25
		5	1.67			6	2.02
		7	4.21			8	4.81
		9	6.53			10	7.79
10	CH_4*	1	0.00	**20**	H_2*	1	0.00
		3	0.54			3	0.53
		5	1.70			5	1.78
		7	4.04			7	3.67
		9	6.65			9	6.74

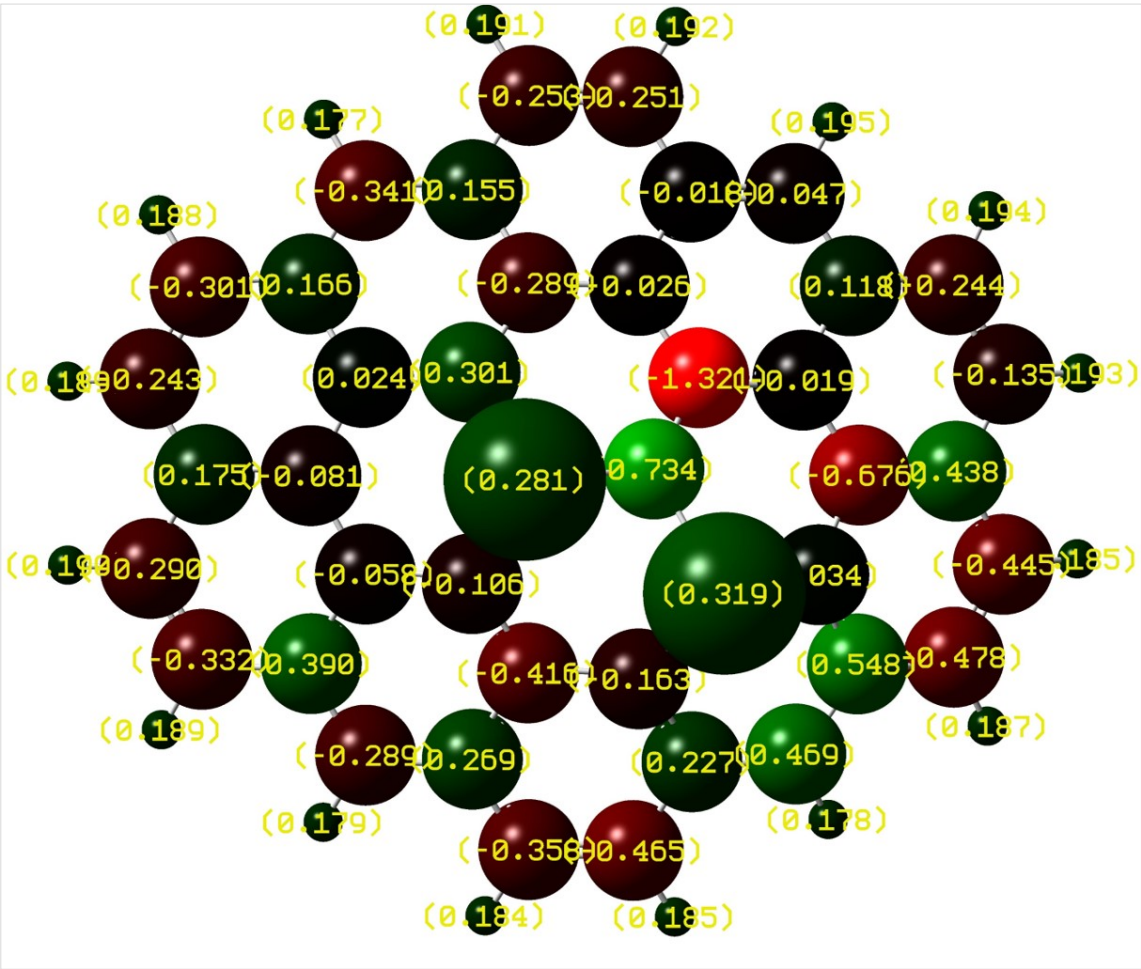

Figure S1. Atomic charge distribution, derived from Mulliken analysis, of 2MV-Ru_2 electrode. Biggest and shortest atomic radii atoms represent ruthenium and hydrogen atoms, respectively, while all other atoms represent carbon atoms.

Table 2. Reaction energy (ΔE), reaction enthalpy (ΔH), and reaction free energy (ΔG) of all adsorption and desorption reactions on 2MV-Ru_2 electrode. ΔE includes the contributions of zero-point energies (ZPE).

S. No.	Adsorption/desorption steps	ΔE (eV)	ΔH (eV)	ΔG (eV)
1	CO_2 (aq) + * = CO_2*	-0.25	-0.27	0.24
2	CO* = CO (aq) + *	0.94	0.98	0.48
3	CH_2O* = CH_2O (aq) + *	0.24	0.25	-0.25
4	CH_3OH* = CH_3OH(aq) + *	0.24	0.22	-0.20
5	CH_4* = CH_4 (aq) + *	0.12	0.13	-0.23
6	HCOOH* = HCOOH (aq) + *	0.11	0.11	-0.39
7	H_2* = H_2 (aq) + *	0.09	0.15	-0.21

Table 3. Reaction energy (ΔE), reaction enthalpy (ΔH), and reaction free energy (ΔG) of all surface reactions on 2MV-Ru_2 electrode. ΔE includes the contributions of zero-point energies (ZPE).

S. No.	Surface reactions	ΔE (eV)	ΔH (eV)	ΔG (eV)
1	CO_2* + H^+ + e^- = COOH*	0.07	0.05	0.16
2	COOH* + H^+ + e^- = CO* + H_2O	-0.55	-0.54	-0.79
3	CO* + H^+ + e^- = CHO*	0.77	0.75	0.88
4	CHO* + H^+ + e^- = CHOH*	0.31	0.26	0.48
5	CHOH* + H^+ + e^- = CH_2OH*	-1.14	-1.16	-1.04
6	CH_2OH* + H^+ + e^- = CH_3OH*	-0.97	-1.00	-0.86
7	CH_3OH* + H^+ + e^- = CH_3* + H_2O	-0.31	-0.30	-0.54
8	CH_3* + H^+ + e^- = CH_4*	-0.89	-0.91	-0.76
9	CO_2* + H^+ + e^- = HCOO*	-1.07	-1.08	-1.02
10	HCOO* + H^+ + e^- = HCOOH*	0.82	0.78	1.01
11	COOH* + H^+ + e^- = HCOOH*	-0.32	-0.35	-0.18
12	HCOOH* + H^+ + e^- = CHO* + H_2O	0.54	0.56	0.27
13	CHO* + H^+ + e^- = CH_2O*	-0.64	-0.67	-0.47
14	CH_2O* + H^+ + e^- = CH_3O*	-1.07	-1.11	-0.93
15	CH_2O* + H^+ + e^- = CH_2OH*	-0.20	-0.23	-0.09
16	CH_3O* + H^+ + e^- = CH_3OH*	-0.10	-0.11	-0.02
17	CO* + H^+ + e^- = COH*	2.24	2.23	2.34
18	COH* + H^+ + e^- = CHOH*	-1.17	-1.21	-0.97
19	CHOH* + H^+ + e^- = CH* + H_2O	0.96	0.99	0.65
20	CH* + H^+ + e^- = CH_2*	-2.05	-2.11	-1.84
21	CH_2OH* + H^+ + e^- = CH_2* + H_2O	0.06	0.04	-0.14
22	CH_2* + H^+ + e^- = CH_3*	-1.34	-1.34	-1.26
23	COH* + H^+ + e^- = C* + H_2O	1.06	1.07	0.83
24	C* + H^+ + e^- = CH*	-1.26	-1.29	-1.14
25	* + H^+ + e^- = H*	0.22	0.18	0.36
26	H* + H^+ + e^- = * + H_2 (aq)	-0.22	-0.18	-0.36
27	H* + H^+ + e^- = H_2*	-0.30	-0.32	-0.14
28	H* + H* = H_2 (aq) + 2*	-0.43	-0.35	-0.71

Table 4. Relative energies ($^{\Delta E_{Rel}}$) of surface bound species on all bifunctional electrodes in various spin multiplicities (SM).

S. No.	Electrodes	CO		CHO		Catalyst	
		SM	ΔE_{Rel} (eV)	SM	ΔE_{Rel} (eV)	SM	ΔE_{Rel} (eV)
1	2MV-RuAg	2	0.00	1	0.00	2	0.00
		4	0.70	3	0.16	4	-0.51
		6	3.77	5	1.95	6	1.64
		8	4.98	7	4.09	8	3.32
		10	7.86	9	6.31	10	6.50
2	2MV-RuAu	2	0.00	1	0.00	2	0.00
		4	0.65	3	0.33	4	0.79
		6	1.89	5	2.08	6	2.70
		8	4.33	7	4.23	8	5.25
		10	7.53	9	6.78	10	7.52
3	2MV-RuCu	2	0.00	1	0.00	2	0.00
		4	0.96	3	0.30	4	0.45
		6	2.07	5	2.01	6	1.53
		8	4.55	7	3.50	8	4.06
		10	7.42	9	6.02	10	6.92
4	2MV-RuIr	2	0.00	1	0.00	2	0.00
		4	1.92	3	1.01	4	0.56
		6	3.29	5	2.27	6	3.22
		8	5.29	7	4.63	8	5.20
		10	8.33	9	7.52	10	8.24
5	2MV-RuOs	1	0.00	2	0.00	1	0.00
		3	0.75	4	1.25	3	0.74
		5	3.10	6	2.20	5	1.81
		7	4.34	8	4.86	7	3.65
		9	6.68	10	7.43	9	5.84
6	2MV-RuPd	1	0.00	2	0.00	1	0.00
		3	0.71	4	0.91	3	-0.01
		5	1.56	6	2.77	5	1.40
		7	3.63	8	4.89	7	3.83
		9	5.76	10	7.22	9	5.90
7	2MV-RuPt	1	0.00	2	0.00	1	0.00
		3	0.93	4	0.89	3	0.27

		5	1.90	6	2.89	5	1.73
		7	4.07	8	5.12	7	4.25
		9	6.26	10	8.26	9	6.28
8	2MV-RuRh	2	0.00	1	0.00	2	0.00
		4	2.62	3	0.93	4	0.63
		6	3.35	5	2.32	6	3.44
		8	5.37	7	4.82	8	5.46
		10	8.42	9	6.73	10	8.44

Table 5. Structural details of CO* and CHO* on all bifunctional electrodes along with their adsorption energies (ΔE_{Ads} in eV). The limiting potential shown as U_L (vs. SHE) refers to the PDS, i.e., CO* → CHO* reaction step. ΔE_{Ads} includes the contributions of zero-point energies (ZPE).

S. No.	2MV-RuM	U_L	CHO*				CO*		
			Bond lengths (Å)			ΔE_{Ads}	Bond lengths (Å)		ΔE_{Ads}
			C-M	C=O	C-H		C-M	C=O	
1	2MV-RuAg	-2.96	2.13	1.23	1.12	0.87	2.15	1.13	-2.08
2	2MV-RuAu	-0.21	2.10	1.23	1.12	0.24	1.95	1.15	0.03
3	2MV-RuCu	-0.77	1.98	1.23	1.12	0.30	1.96	1.14	-0.47
4	2MV-RuIr	-0.52	2.14	1.25	1.12	0.10	1.91	1.16	-0.43
5	2MV-RuOs	-0.68	2.11	1.25	1.13	-0.35	1.90	1.17	-1.03
6	2MV-RuPd	-0.13	2.14	1.24	1.12	0.32	2.04	1.15	0.19
7	2MV-RuPt	-0.23	2.13	1.24	1.12	-0.29	1.94	1.16	-0.52
8	2MV-RuRh	-0.64	2.16	1.25	1.13	0.47	1.99	1.14	-0.17
9	2MV-Ru_2	-0.88	2.12	1.24	1.13	0.40	1.93	1.16	-0.48

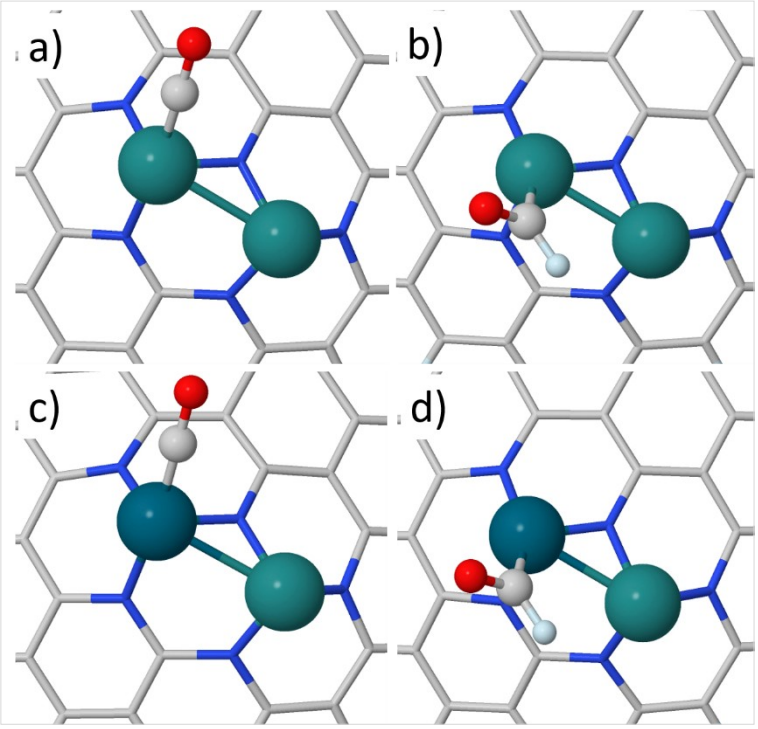

Figure S2. a) and b) Bindings of CO and CHO on nitrogen coordinated 2MV-N_5-Ru_2 electrode, respectively, c) and d) bindings of CO and CHO on nitrogen coordinated 2MV-N_5-RuPd electrode, respectively.

Table 6. Formation energy ($^{\Delta E_{form}}$), formation enthalpy ($^{\Delta H_{form}}$), and formation free energy ($^{\Delta G_{form}}$) of all bifunctional electrodes. $^{\Delta E_{form}}$ includes the contributions of zero-point energies (ZPE).

S. No.	Electrodes	ΔE_{form} (eV)	ΔH_{form} (eV)	ΔG_{form} (eV)
1	2MV-RuAg	-1.37	-1.38	-0.92
2	2MV-RuAu	-1.40	-1.44	-0.91
3	2MV-RuCu	-1.89	-1.92	-1.43
4	2MV-RuIr	-3.44	-3.47	-2.95
5	2MV-RuOs	-2.48	-2.51	-1.97
6	2MV-RuPd	-2.16	-2.19	-1.71
7	2MV-RuPt	-2.21	-2.25	-1.72
8	2MV-RuRh	-2.95	-2.99	-2.48
9	2MV-Ru_2	-3.13	-3.17	-2.63

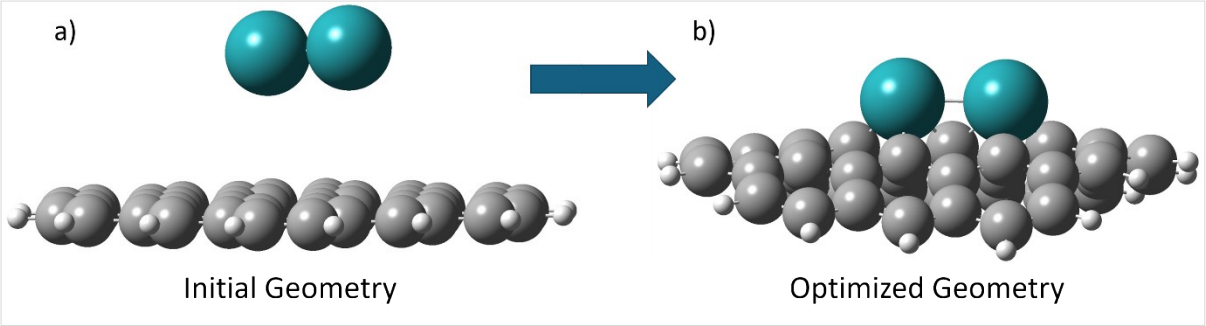

Figure S3: a) Initial input geometry of two Ru atoms in a dimer form placed far above the dual-vacant graphene sheet, and b) optimized geometry based on the initial input geometry.

Electrochemical formation free energies

The electrochemical stability of Ru_2-doped graphene sheet, i.e., 2MV-Ru_2, is only influenced by the electrode potential. Since the reduction of Ru^{2+} to Ru does not involve the transfer of protons, there is no need to consider the pH dependence in this model. Therefore, only the applied electrode potential will govern the thermodynamic feasibility of the reduction process. The free energy of metal species in an electrochemical environment shifts due to electron transfer at the electrode interface.

The reaction describing the incorporation of two Ru^{2+} ions into adjacent-vacant graphene sheet can be written as:

$$Graphene + 2Ru^{2+} + 4e^- \rightarrow Ru_2\text{-}Graphene \qquad \text{(S1)}$$

where *Graphene* is two monovacant (adjacent-vacant) pristine graphene sheet, Ru^{2+} are the *Ru* ions in solution, $4e^-$ accounts for the reduction of two Ru^{2+} ions, and Ru_2-*Graphene* is Ru_2-doped graphene sheet, i.e., 2MV-Ru_2.

The reaction S1 represents the reduction process required to stabilize two Ru atoms within the graphene vacancies. In this regard, the electrochemical formation free energies of 2MV-Ru_2 with respect to potential (U) are computed based on the following equation:

$$\Delta G_{elec-form} = \Delta G_{form} + neU \qquad \text{(S2)}$$

where $\Delta G_{elec-form}$ and ΔG_{form} are the electrochemical and thermochemical formation free energy, respectively. And, *n, e,* and *U* are the number of electrons transfer (4), elementary charge (~1.7), and applied potential, respectively. Elementary charges on Ru atoms are computed based on the charge distribution.

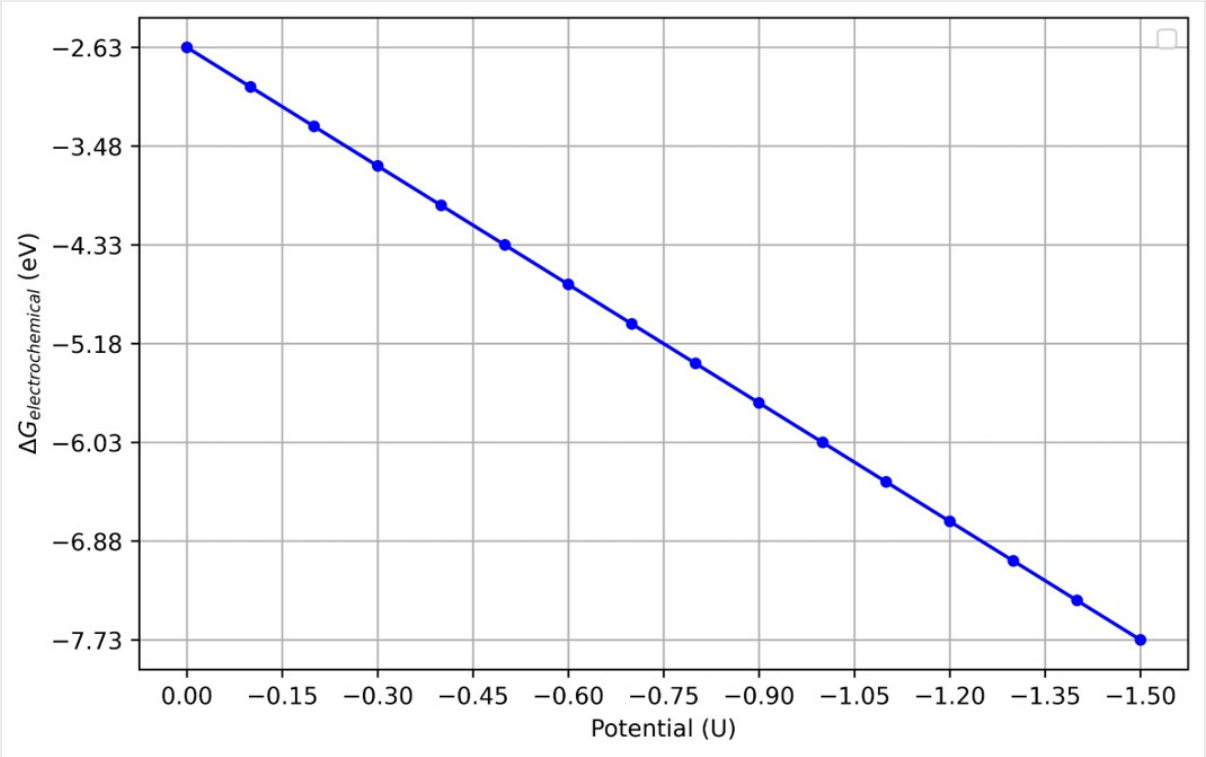

Figure S4: Electrochemical formation free energies of 2MV-Ru_2 electrode with respect to potential (*U*).