Supporting Information

Graphene Supported Monometallic and Bimetallic Dimers for Electrochemical CO_2 Reduction

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Table S1 Negative of the calculated elementary limiting potentials $-U_L$ (in V) required for three critical steps in the production of CH_4 for the homonuclear dimers supported on defective graphene. The rate-limiting step is the more negative of the three. And the overpotentials (in V) are calculated from the rate limiting potential and the equilibrium potential (+0.17 V) for CO_2 electroreduction to CH_4.

	Ni_2	Pd_2	Pt_2	Cu_2	Ag_2	Au_2
OCHO*→HCOOH*	0.80	0.35	0.14	0.74	-0.02	-0.68
HCOOH*→CHO*	0.39	0.52	0.20	0.69	1.04	1.03
OH*→*+H_2O	1.10	0.21	-0.29	0.80	0.02	-0.04
Overpotential	1.27	0.69	0.37	0.97	1.21	1.20

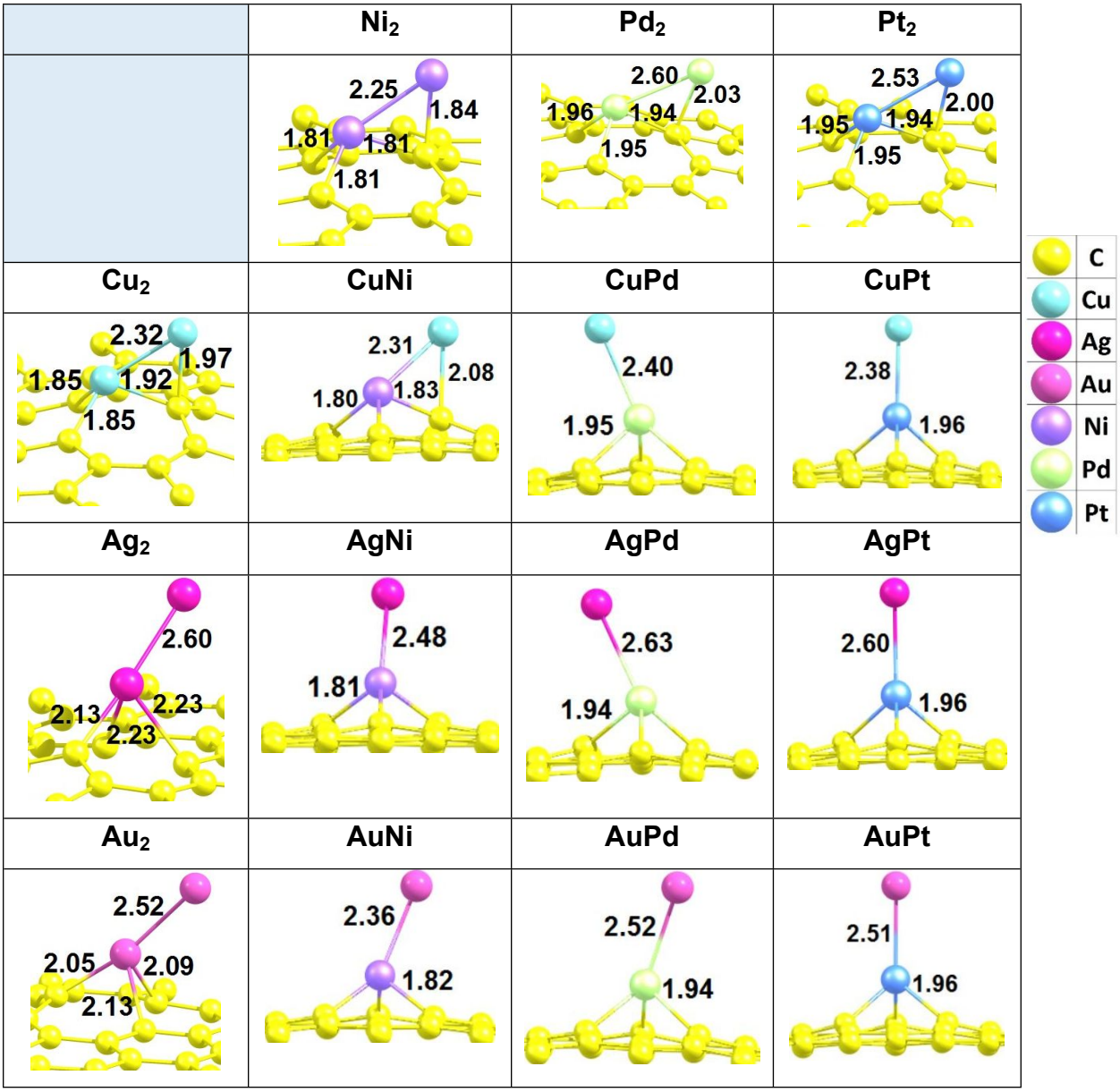


Figure S1 The most stable binding configurations of M_2/MN dimers supported on the single-vacancy site of graphene. Atomic symbols are listed on the right.

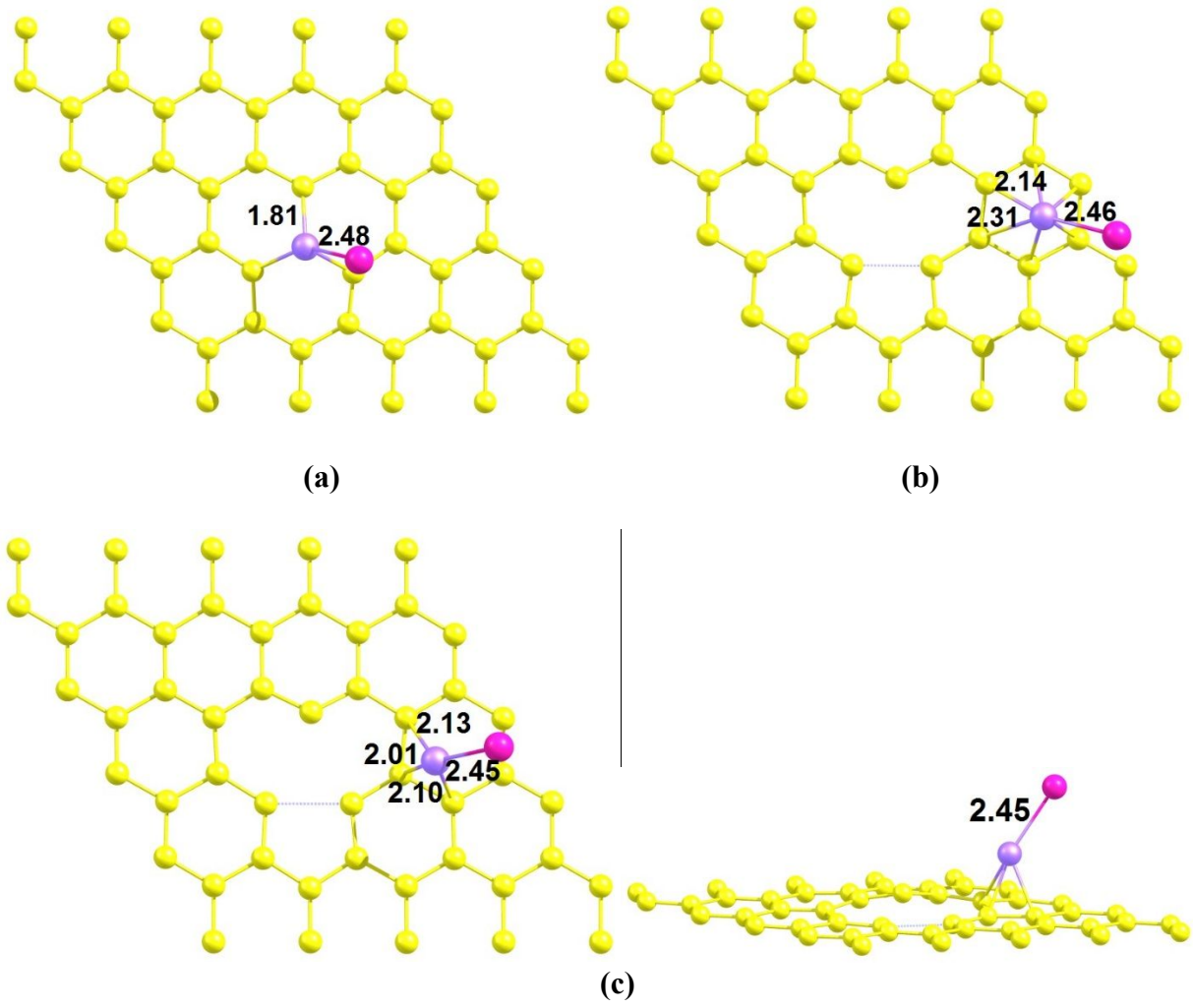


Figure S2 The supported AgNi dimer on graphene at: (a) the most stable binding site (single C vacancy); (b) the nearest meta-stable binding site; (c) the transition state for migrating from (a) to (b) with side and top views. C: yellow, Ag: pink, Ni: purple.

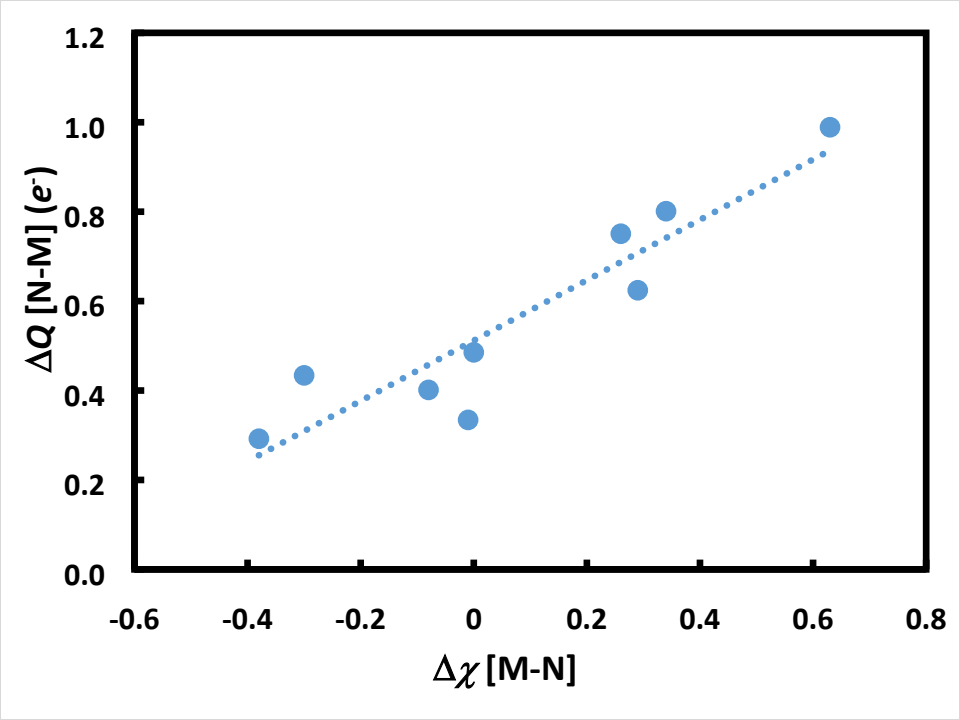


Figure S3 Correlation of the charge difference between N and M (ΔQ [N–M]) (M=Cu, Ag, Au; N=Ni, Pd, Pt) with the difference in their electronegativity for defective graphene supported heteronuclear metal dimers MN. The Pauling scale is adopted for the electronegativity. Note an electronegativity value of 2.2 in the Pauling scale is taken for Ag, instead of the reported value of 1.93, in observing the similarity in performance of Ag containing systems to Pd containing systems, which results in better correlation.

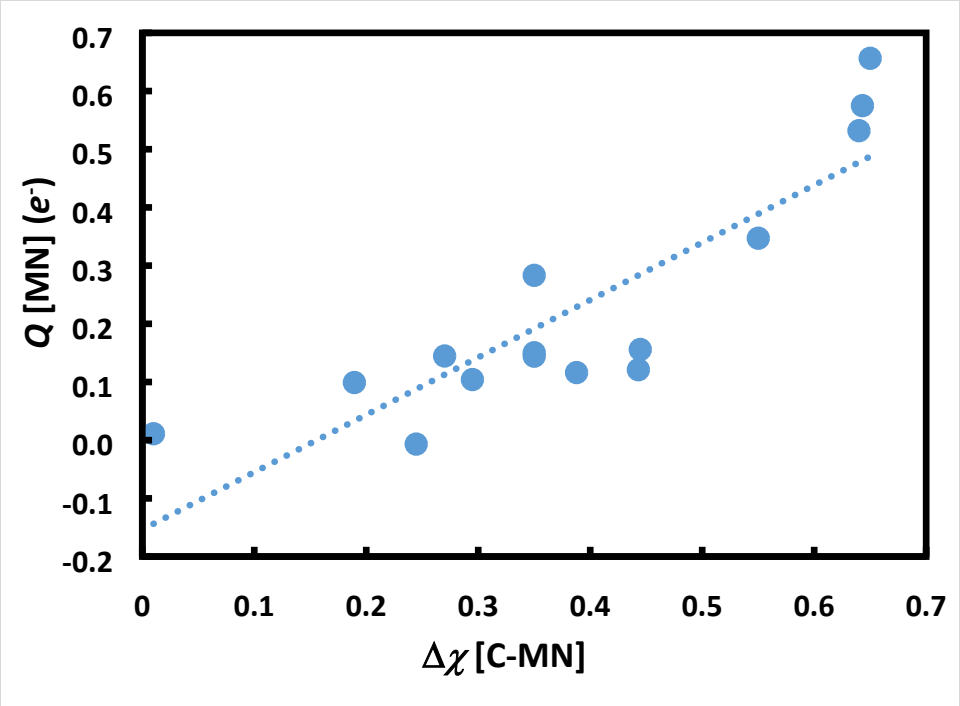


Figure S4 Correlation of the charge on the metal dimer *Q* [MN] with the difference in the electronegativity of C and the weighted value of the MN dimer for defective graphene supported metal dimers MN. The Pauling scale is adopted for the electronegativity. Note an electronegativity value of 2.2 in the Pauling scale is taken for Ag, instead of the reported value of 1.93, in observing the similarity in performance of Ag containing systems to Pd containing systems, which results in better correlation.

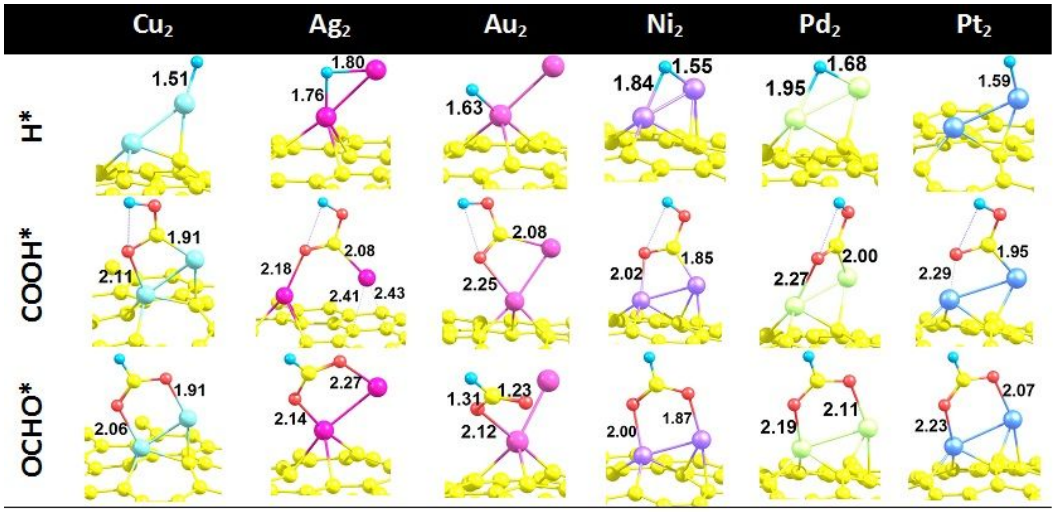


Figure S5 Lowest energy structures of the first hydrogenation species on monometallic dimers M_2 (M=Cu, Ag, Au, Ni, Pd, Pt) supported on defective graphene. Atomic symbols are the same as in Figure S1. In addition, H is in blue (small) and O in red.

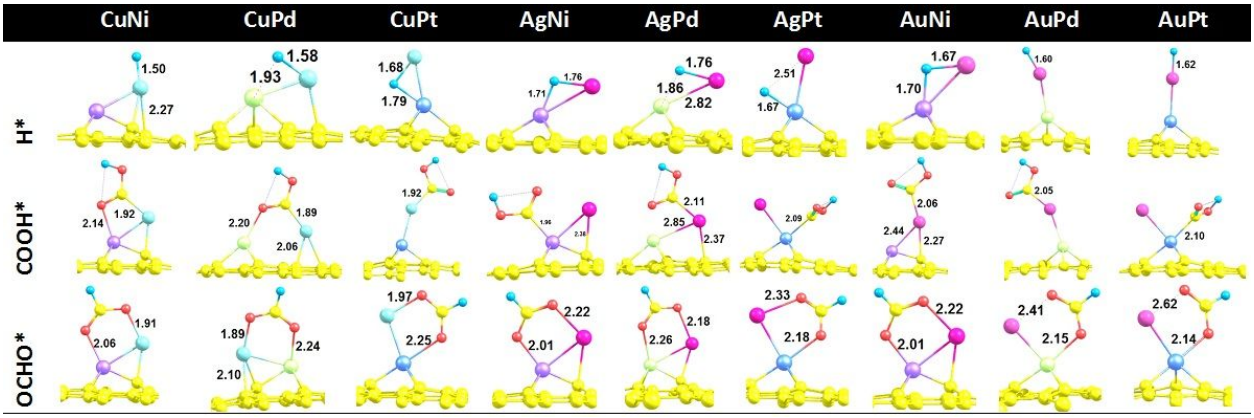
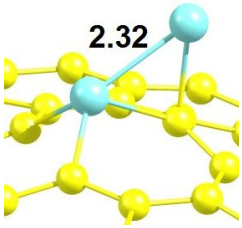
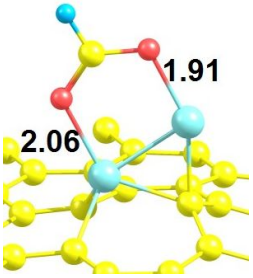
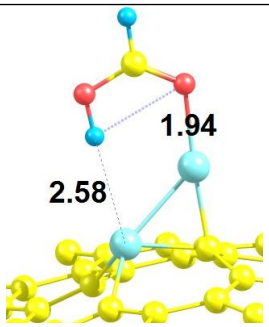


Figure S6 Lowest energy structures of the first hydrogenation species on bimetallic dimers MN (M=Cu, Ag, Au; N=Ni, Pd, Pt) supported on defective graphene. Atomic symbols are the same as in Figure S1. In addition, H is in blue (small) and O in red.

Cu_2			
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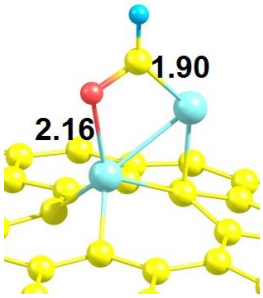
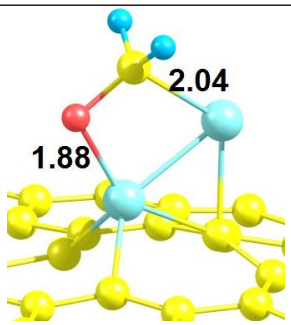
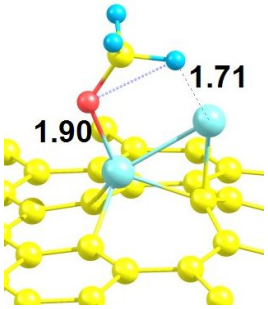
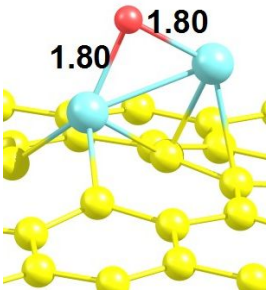
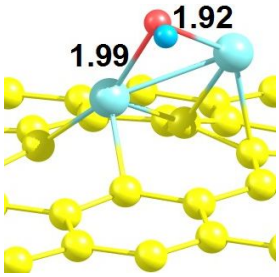
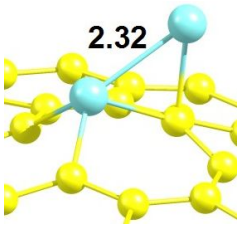
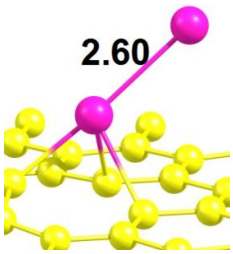
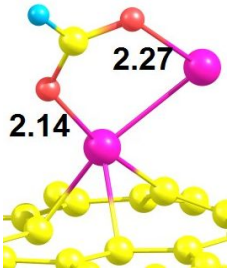
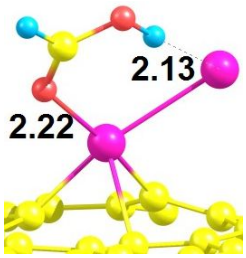
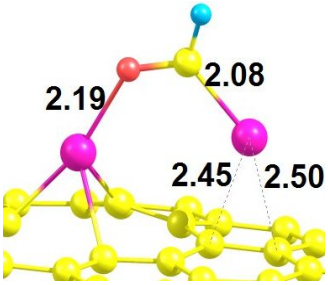
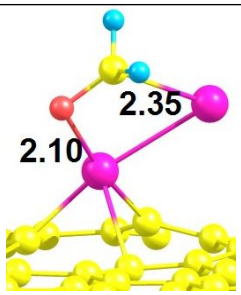
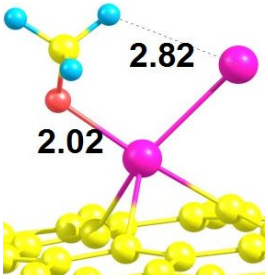
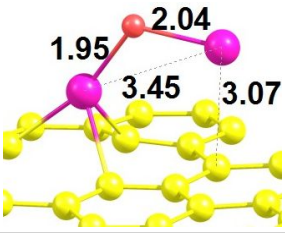
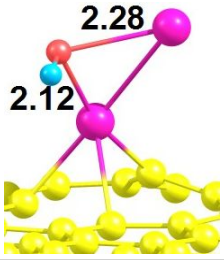
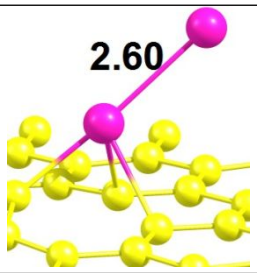
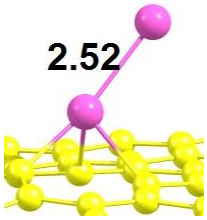
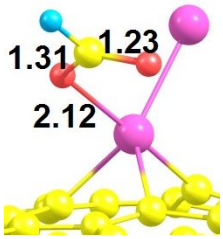
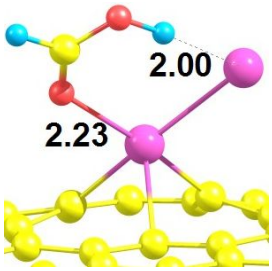
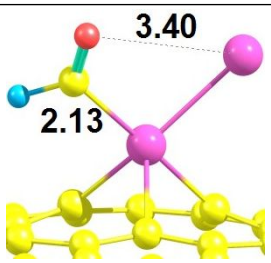
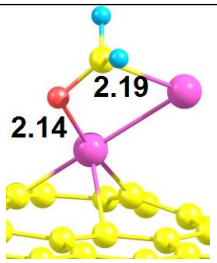
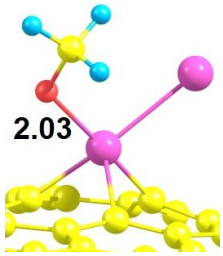
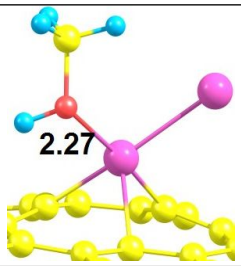
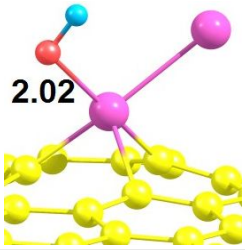
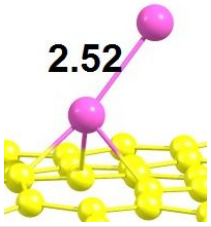
			
	C H O *	C H $_2$ O *	C H $_3$ O *
			
	O * + C H $_4$	O H *	* + H $_2$ O

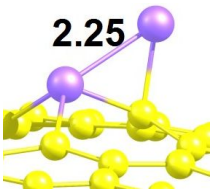
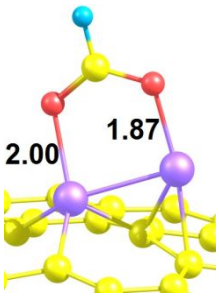
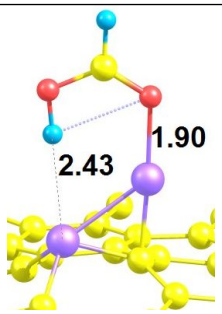
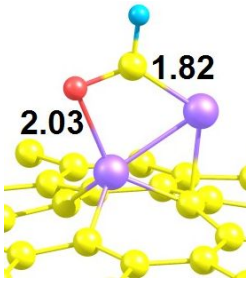
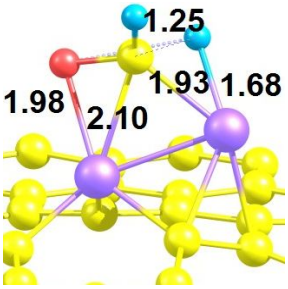
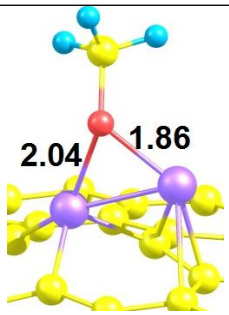
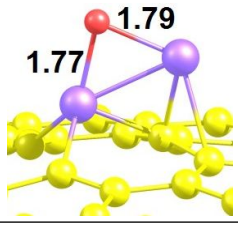
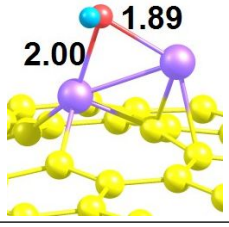
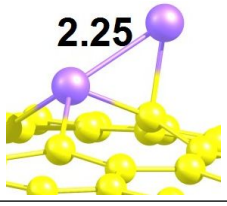
(a)

Ag_2			
	* + C O 2	O C H O *	H C O O H *
			
	C H O *	C H 2 O *	C H 3 O *
			
	O * + C H 4	O H *	* + H 2 O

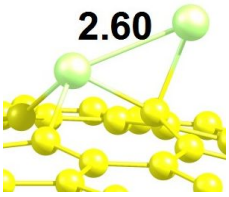
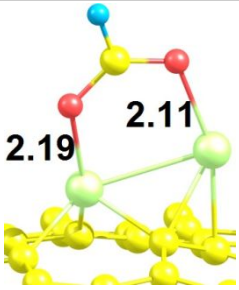
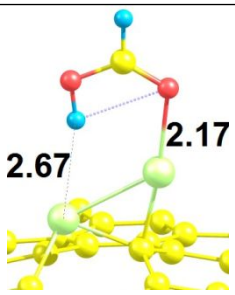
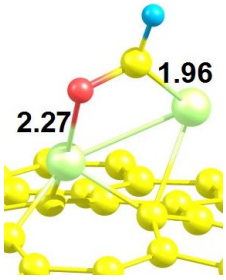
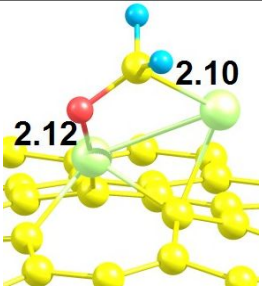
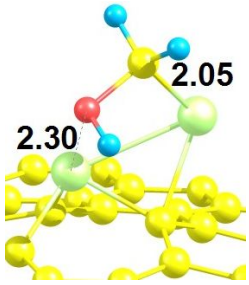
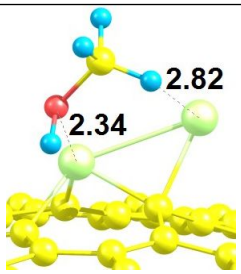
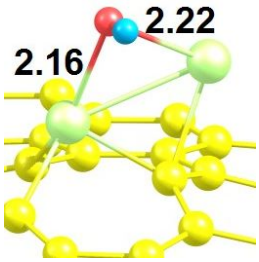
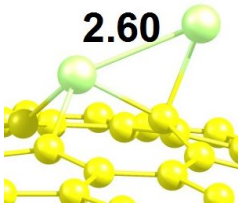
(b)

Au_2			
	* + C O $_2$	O C H O *	H C O O H *
			
	C H O *	C H $_2$ O *	C H $_3$ O *
			
	CH_3OH*	OH*+CH_4	* + H $_2$ O

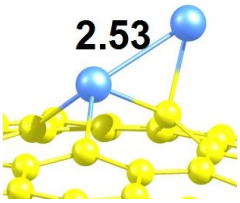
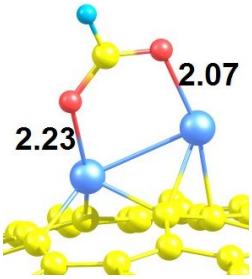
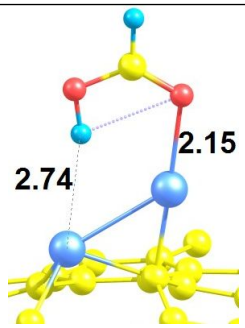
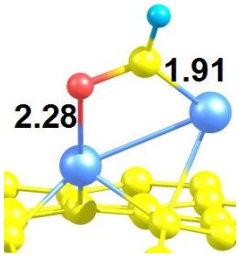
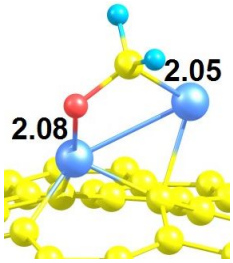
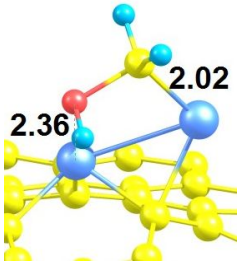
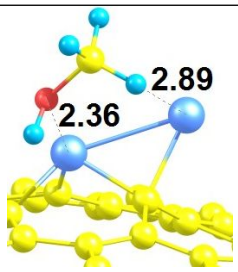
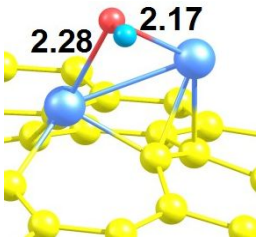
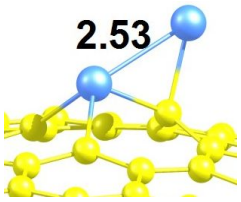
(c)

Ni_2			
	* + C O $_2$	O C H O *	H C O O H *
			
	C H O *	C H $_2$ O *	C H $_3$ O *
			
	O * + C H $_4$	O H *	* + H $_2$ O

(d)

Pd_2			
	* + C O $_2$	O C H O *	H C O O H *
			
	C H O *	C H $_2$ O *	C H $_2$ O H *
			
	C H $_3$ O H *	OH*+CH_4	* + H $_2$ O

(e)

Pt_2			
	* + CO_2	O C H O *	H C O O H *
			
	C H O *	CH_2O *	CH_2OH *
			
	CH_3OH *	OH*+CH_4	* + H_2O

(f)

Figure S7 Structures of surface species along the lowest energy reaction pathways for electrochemical reduction of CO_2 to CH_4 on a homonuclear metal dimer M_2 (M=Cu, Ag, Au, Ni, Pd, Pt) supported on graphene. Atomic symbols: Cu in light blue, Ag in pink, Au in light pink, Ni in purple, Pd in green, Pt in dark blue, C in yellow, O in red, H in blue (small).