Supporting Information for

Computational Studies of Electrochemical CO_2 Reduction on Subnanometer Transition Metal Clusters

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S1. Computational Details

All the Gibbs free energies were calculated in gas phase at 298.15K, in which all the gaseous molecules (CO_2, CO, H_2 and CH_4) and all the metal cluster containing systems were calculated at 101325Pa, while the liquid phase molecules (H_2O, HCOOH and CH_3OH) were calculated under their corresponding vapor fugacity, which comes from their vapor-liquid equilibrium with water and corresponds to a liquid mole fraction of 0.01.

Table S1. Structures of tetra-atomic metal clusters calculated by this work and previous studies

Cluster	This Work		Previous Studies			
	Ground-state Multiplicity	Geometry	Method	Ground-state Multiplicity	Geometry	Ref.
Fe_4	9	Tetrahedral	PBE/DZP	-	Tetrahedral	[1]
Co_4	11	Rhombus	PW91/DNP	11	Rhombus	[2]
Ni_4	5	Tetrahedral	BP/ [6s5p3d]	5	Tetrahedral	[3]
Cu_4	3	Rhombus	PW91/DNP	-	Rhombus	[4]
Rh_4	7	Tetrahedral	PW91	1	Tetrahedral	[5]
Pd_4	3	Tetrahedral	MRSDCI and MRSDCI+Q	3	Tetrahedral	[6]
Ag_4	1	Rhombus	PBE/ DZP	-	Rhombus	[7]
Ir_4	9	Square-planar	BP/[8s,7p,5d,3f]	9	Square-planar	[8]
Pt_4	3	Tetrahedral	MRSDCI and MRSDCI+Q	3	Tetrahedral	[6]
Au_4	1	Triangle C_{2V}	B3LYP/LANL2DZ	-	Triangle C_{2V}	[9]

Various computational studies have been carried out to predict the ground state electronic structures of tetra-atomic metal clusters[1-9]. In this study, ten tetra-atomic clusters (Fe_4, Co_4, Ni_4, Cu_4, Ir_4, Pd_4, Ag_4, Rh_4, Pt_4 and Au_4) were calculated using the B3LYP functional. The 6-31G* basis set was applied to all the main group elements. An improved 6-31G* basis set, m6-31G*, was utilized for all the 3d metals, and the LANL2DZ basis set was used for all the 4d and 5d metals. To assess the reliability of the B3LYP functional, the B3LYP results were compared with previous computational studies, shown in Table S1. In general, the structures of the clusters calculated in the present work have good agreement with previous studies[1-9].

Table S2. Adsorption free energies of CO_2 to tetra-atomic metal clusters calculated at B3LYP (without empirical corrections to CO_2 molecule), M06, PBE0 and CCSD(T) levels of theory (eV)

Cluster	ΔG B3LYP	ΔG M06	ΔG PBE0	ΔG CCSD(T)
Fe_4	-0.73	-3.04	-1.14	
Co_4	-0.56	-0.72	-0.68	
Ni_4	-1.05	-1.36	-1.50	
Cu_4	0.09	0.11	-0.07	0.13
Rh_4	-0.05	-0.11	0.14	
Pd_4	0.09	0.02	0.07	
Ag_4	0.12	0.07	0.11	0.05
Ir_4	0.20	0.12	0.17	
Pt_4	0.24	0.28	-0.10	
Au_4	0.10	0.08	0.07	-0.01

In addition to B3LYP, the adsorption free energies of CO_2 to the ten clusters were calculated using the M06, PBE0 and CCSD(T) methods (only Cu, Ag and Au clusters were calculated using CCSD(T) method) , based on the B3LYP geometries and thermal correction. As shown in Table S2, the more negative the adsorption free energies are, the stronger CO_2 binds to the cluster. The B3LYP binding energies showed the same signs (positive or negative values) with the M06 values, while PBE0 values showed opposite signs with the other two methods for the Cu_4, Rh_4 and Pt_4 systems. Generally, all three DFT functionals suggested that Fe_4, Co_4 and Ni_4 have much stronger binding with CO_2, compared to the other metal clusters. Compared to the CCSD(T) results for Cu, Ag and Au systems, M06 gave the smallest deviation (MAD=0.04eV) among the three functionals. However, the M06 energy of Fe system is extremely low (-3.04eV), which

does not agree with the other two functionals. This implies the M06 value of Fe system may not be reliable. On the other hand, the B3LYP binding energies showed smaller deviations (MAD=0.07eV) than the PBE0 values (MAD=0.11eV) compared to the CCSD(T) results, and the adsorption free energies of Fe_4, Co_4, Ni_4 and Cu_4 showed the same trend (Ni < Fe < Co < Cu) with both B3LYP and PBE0 functionals. Since this work is focused on the comparisons and tendency of the metal clusters for the electrocatalysis of CO_2, the B3LYP functional was selected to study the reaction energetics based on its reliability and acceptable accuracy.

Table S3. Atomization energies of selected molecules and radicals (eV)

	Expt.[10]	B3LYP/6-31G*	Error/Empirical correction
H_2	4.488	4.484	-0.004
H_2O	9.509	8.887	-0.622
CO	11.109	10.816	-0.293
CO2	16.560	16.375	-0.184
CH_4	17.019	17.028	0.009
CH_3OH	20.848	20.542	-0.306
HCOOH	20.835	20.501	-0.334
COOH	17.128	16.240	-0.887
OH	4.393	4.197	-0.195
HCO	11.721	11.698	-0.023
H_2CO	15.493	15.406	-0.087
H_3CO	16.367	16.521	0.154
C_2H_4	23.064	22.926	-0.138

Table S4. Reaction enthalpies of selected reactions (eV) (ΔH_{ref} values were calculated from the enthalpies of formation[10])

	Reaction	ΔH_{ref}	B3LYP/6-31G*	Error	Error after correction
1	$CO_2 + H_2 \rightarrow CO + H_2O$	0.43	1.16	0.73	0.00
2	$4\ H_2 + CO_2 \rightarrow CH_4 + 2\ H_2O$	-1.71	-0.63	1.08	0.04
3	$3\ H_2 + CO \rightarrow CH_4 + H_2O$	-2.14	-1.80	0.34	0.03
4	$CO_2 + H_2 \rightarrow HCOOH$	0.15	0.28	0.13	-0.02
5	$CO + H_2O \rightarrow HCOOH$	-0.27	-0.88	-0.61	-0.03
6	$3\ H_2 + CO_2 \rightarrow CH_3OH + H_2O$	-0.55	0.25	0.80	0.07
7	$2\ H_2 + CO \rightarrow CH_3OH$	-0.98	-0.91	0.07	0.06
8	$3\ H_2 + CO_2 \rightarrow 1/2\ C_2H_4 + 2\ H_2O$	-0.66	0.48	1.14	0.03
9	$2\ H_2 + CO \rightarrow 1/2\ C_2H_4 + H_2O$	-1.09	-0.68	0.41	0.02

Since the B3LYP/6-31G* method is used to calculate the reaction energies we have carried out calculations of the B3LYP/6-31G* atomization energies of small molecules and radicals related to the present work and compared with experiment. The results are given in Table S3. The errors of the atomization energies of H_2O, CO, CH_3OH, HCOOH and COOH are significant, while those of the other systems are less than 0.2 eV. These errors may affect the energies of certain reactions, such as the water-gas shift reaction. Therefore, the reaction enthalpies of 9 reactions were analyzed, and corrections were added to the total energies for each molecule based on the errors of the atomization energies against experiment (Table S3). Shown in Table S4, before correction, B3LYP/6-31G* yields large errors for some of the analyzed reactions, especially reactions 2 and 8. The small errors shown for reactions 3 and 7 are mainly due to error cancellation. After the empirical corrections were added to each molecule, the errors were reduced to no more than 0.07 eV. In the present work, corresponding empirical corrections (Table S3) were added to the total energies of related small molecules and radicals calculated by B3LYP/6-31G* to obtain more accurate reaction free energies. For the PBE/plane wave calculations, the same corrections as that Peterson et al.[11] suggested for PBE calculations were used.

S2. Reaction Network of the Electrochemical Reduction of CO_2 to Fuels

A reaction network containing 38 intermediates was studied for the electrochemical reduction of CO_2 to HCOOH, CO, CH_4, CH_3OH and C_2H_4 (Figure S1). In general, the reaction pathways in the network are initiated by three major reactions:

$$CO_2 + * \rightarrow CO_2* \quad (1)$$

$$CO_2 + H^+ + e^- + * \rightarrow COOH* \quad (2)$$

$$CO_2 + H^+ + e^- + * \rightarrow HCOO* \quad (3)$$

Eqn. 1 is the chemisorption of CO_2, Eqn. 2 and 3 are the electrochemical adsorption of CO_2 with the proton transferred to an oxygen atom and the carbon atom, respectively. The reaction free energies of all elementary steps were calculated. The highlighted reaction pathway in Figure S1 was identified to be the thermodynamically most favorable pathway for all five considered clusters (Fe_4, Co_4, Ni_4, Cu_4 and Pt_4). This pathway is initiated by Eqn. 2. On the other hand, the reaction pathways initiated by Eqn. 3 are not thermodynamically favorable. The reaction pathways gave either highly endergonic or highly exergonic reactions, engendering thermodynamic sinks. Thus this pathway was eliminated in the beginning. The CO_2

chemisorption is endergonic for Cu_4 and Pt_4, and the C-O cleavage barriers of CO_2 are extremely high for these two metal clusters, therefore the pathways initiated by Eqn. 1 are not thermodynamically favorable for Cu_4 and Pt_4 clusters. However, chemisorption of CO_2 and C-O cleavage of CO_2 are spontaneous for Fe_4, Co_4 and Ni_4 clusters, and the barriers of C-O cleavage are below 1 eV. Therefore, as in the main text, the thermodynamically most favorable pathway was presented for all five clusters, and the CO_2 chemisorption initiated pathway was also considered for Fe_4, Co_4 and Ni_4 clusters.

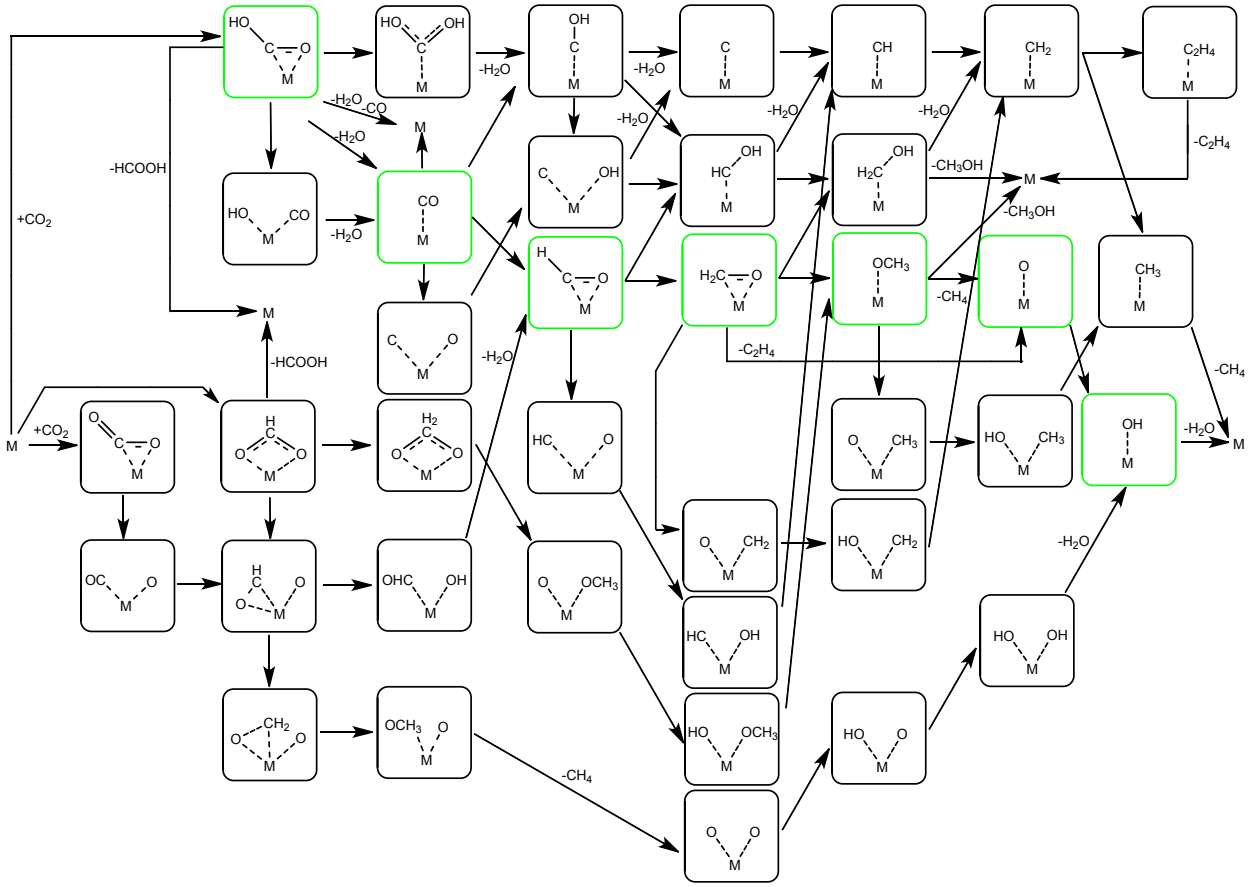

Figure S1. Reaction network of the electrochemical reduction of CO_2 to fuels (M represents the tetra-atomic metal cluster)

S3. Ground State Multiplicities and Relative Energies

All possible multiplicities of all species were taken into account. The ground state multiplicities and relative free energies of the species in the discussed pathways (pathways 1 and 2 in the main text) are listed in Table S3, where the index numbers correspond to the indices of intermediates in Figures 2-6 in the main text. The energies of all the states relative to the initial state, * + CO_2, were calculated using Eqn. 4:

$$G_{rel} = G_{state} - G_{int} - nG_{(H+ + e-)} \quad (4),$$

where G_{state} is the calculated free energy of the considered state, G_{int} is the calculated free energy of the initial state, $G_{(H+ + e-)}$ is the calculated free energy of a (proton + electron) pair, which equals to a half of the free energy of a H_2 molecule, and n is the total number of (proton + electron) pairs transferred to form the corresponding state from the initial state. For example, the relative free energy of state 4 (CHO*) is calculated as:

$$G_{rel}\,(4) = G_{(CHO*)} - (G_{(*)} + G_{(CO2)}) - 3(1/2G_{(H2)})$$

Table S3. Multiplicities and relative free energies of the states (eV)

Cluster		Fe_4		Co_4		Ni_4		Cu_4		Pt_4	
Index	State	Spin State	Relative Free Energy	Spin State	Relative Free Energy	Spin State	Relative Free Energy	Spin State	Relative Free Energy	Spin State	Relative Free Energy
1	* + CO_2	9	0	11	0	5	0	3	0	3	0
2	COOH*	8	0.008	10	-0.083	6	-0.668	2	0.498	4	0.221
3	CO* + H_2O	9	-0.712	9	-0.772	7	-1.115	1	-0.447	3	-1.418
4	CHO*	8	-0.328	10	-0.02	6	-0.688	2	0.603	2	-0.098
5	CH_2O*	9	-0.642	9	-0.3	5	-0.894	1	0.168	3	-0.074
6	CH_3O*	8	-1.274	10	-0.957	6	-1.334	2	-0.264	2	0.053
7	O* + CH_4	9	-2.482	11	-1.697	5	-2.078	1	-0.141	5	0.254
8	OH*	8	-2.055	10	-1.964	6	-2.341	2	-1.347	4	-1.088
9	* + H_2O	9	-1.335	11	-1.335	5	-1.335	1	-1.335	3	-1.335
2b	CO_2*	7	-0.549	9	-0.371	5	-0.865				
3b	TS-CO_2*	7	0.071	11	0.507	7	0.008				
4b	CO* + O*	7	-2.051	11	-0.813	3	-1.797				
5b	CHO* + O*	8	-1.558	10	-1.044	6	-1.355				
6b	CH_2O* + O*	7	-2.193	11	-1.018	5	-1.219				
7b	CH_3O* + O*	8	-2.228	10	-2.018	2	-1.986				
8b	O* + O* + CH_4	9	-3.240	11	-2.587	7	-2.520				
9b	OH* + O*	8	-3.928	10	-3.040	6	-2.454				
10b	OH* + OH*	9	-3.224	9	-2.999	3	-3.867				
11b	OH* + H_2O	8	-2.054	10	-1.966	6	-2.338				

S4. Cu_4 vs. Supported Cu_4

Table S4. Bader Charge Distribution in Cu_4 Cluster in Different Cu materials

Atom	Cu1	Cu2	Cu3	Cu4	Cu_4 cluster
Cu_4	-0.1436	0.1772	0.1099	-0.1435	0
Cu_4/Graphene	-0.1481	0.0815	0.2992	-0.1492	0.0834
Cu_4/Defective graphene	0.0177	0.4935	-0.0172	0.2377	0.7317

References

1. S. Yuan, Y. Kong, F. Wen and F. Li, *J. Phys.: Condens. Matter*, 2007, 19, 466203.
2. W. F. Hu, H. K. Yuan, H. Chen, G. Z. Wang and G. L. Zhang, *Phys. Lett. A*, 2014, 378, 198-206.
3. P. St. Petkov, G. N. Vayssilov, S. Krüger and N. Rösch, *Phys. Chem. Chem. Phys.*, 2006, 8, 1282.
4. X.-J. Kuang, X.-Q. Wang and G.-B. Liu, *Journal of Chemical Sciences*, 2011, 123, 743-754.
5. T. Futschek, M. Marsman and J. Hafner, *J. Phys.: Condens. Matter*, 2005, 17, 5927-5963.
6. D. Dai and K. Balasubramanian, *J. Chem. Phys.*, 1995, 103, 648.
7. R. Fournier, *J. Chem. Phys.*, 2001, 115, 2165.
8. C. Bussai, S. Krüger, G. N. Vayssilov and N. Rösch, *Phys. Chem. Chem. Phys.*, 2005, 7, 2656.
9. G. Zanti and D. Peeters, *Theor. Chem. Acc.*, 2012, 132.
10. National Institute of Standards and Technology (U.S.), in *NIST standard reference database 69*, National Institute of Standards and Technology., Washington, D.C., June 2005 release. edn.
11. A. A. Peterson, F. Abild-Pedersen, F. Studt, J. Rossmeisl and J. K. Nørskov, *Energy Environ. Sci.*, 2010, 3, 1311.