Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Support Information

CO Oxidation Catalyzed By A Single Gold Atom

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Table of Contents:

S1 Binding energies of Au-CO calculated at the SBS and MBS basis sets in kcal/mol.

Method	SBS	MBS
BLYP	-15.69	-15.70
BP86	-21.11	-21.31
PW91	-22.70	-22.92
PBE	-22.37	-22.66
HCTH93	-12.42	-12.58
HCTH147	-15.51	-15.66
HCTH407	-13.93	-14.09
tHCTH	-16.79	-16.39
TPSS	-20.03	-20.18
M06-L	-16.57	-16.58
BHandHLYP	-3.87	-4.10
B3LYP	-11.01	-11.13
mPW3PBE	-15.25	-15.53
B3P86	-15.73	-15.99
B3PW91	-13.86	-14.13
B97-1	-13.01	-13.28
VSXC	-15.06	-15.25
PBE0	-14.69	-15.09
B97-2	-11.30	-11.49
O3LYP	-10.29	-10.65
HSE2PBE	-11.27	-11.41
X3LYP	-14.69	-15.02
HSEh1PBE	-14.75	-15.10
tHCTHhyb	-16.08	-16.16
TPSSh	-16.99	-17.20
BMK	-11.65	-12.06
M06	-9.80	-9.66
M06-2X	-3.31	-3.84
LC-BLYP	-11.96	-12.36
LC-BP86	-18.06	-18.73
LC-PW91	-16.59	-17.26
LC-PBE	-16.96	-17.67
LC-HCTH407	-4.77	-4.95
LC-tHCTH	-11.74	-11.69
LC-TPSS	-14.53	-15.22
LC-wPBE	-10.69	-11.30
CAM-B3LYP	-9.89	-10.12
LC-M06-L	-16.83	-17.39
wB97	-8.59	-9.02

wB97X	-8.76	-9.10
mPW2PLYP	-11.65	-11.88
B2PLYP	-12.29	-12.51
CCSD	-8.24	-7.84
CCSD(T)	-12.41	-12.37

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S2 (A) The relative energies calculated by other DFT functionals not presented in the text and (B) their performance.

(A) The relative energies calculated by other DFT functionals not presented in the text.

Method	Au+2CO +O_2	Au-CO +CO+O_2	*I1* +CO	*TS1* +CO	*I2* +CO	*TS2* +CO	*I3* +CO	AuO+CO +CO_2	Au-O_2 +CO+O_2	*TS3* +CO	*I4* +CO	*I5* +CO	*TS4* +CO	*I6* +CO_2	*TS5* +CO_2	*I7* +CO_2	*TS6* +CO_2	*I8* CO_2	Au +2CO_2
BP86	0.00	-21.31	N/A	N/A	-9.42	11.58	-58.70	10.66	-12.08	72.74	-70.59	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
HCTH93	0.00	-12.58	N/A	N/A	-1.12	16.12	-64.23	4.29	-2.83	80.97	-68.29	0.43	2.02	-0.20	2.49	N/A	N/A	-88.98	0.01
HCTH147	0.00	-15.66	N/A	N/A	-4.54	15.14	-63.24	7.14	-6.23	79.31	-68.26	-0.59	0.79	-0.33	0.40	N/A	N/A	-85.06	0.22
HCTH407	0.00	-14.09	-1.47	0.33	-1.93	16.33	-64.47	6.29	-3.77	81.82	-66.66	-1.10	0.52	-0.91	1.21	N/A	N/A	-89.91	0.87
tHCTH	0.00	-16.39	N/A	N/A	-5.79	14.71	-62.24	8.00	-6.59	79.00	-66.44	-2.51	3.03	N/A	N/A	N/A	N/A	N/A	N/A
TPSS	0.00	-20.18	N/A	N/A	-8.20	10.43	-60.40	11.06	-11.19	69.01	-69.77	0.91	-1.43	N/A	N/A	N/A	N/A	N/A	N/A
M06-L	0.00	-16.58	N/A	N/A	-7.65	11.88	-70.78	12.14	-8.99	74.04	-64.55	-1.33	-0.42	-2.22	0.18	N/A	N/A	-85.94	1.32
BHandHLYP	0.00	-4.10	-0.12	9.98	-11.23	25.83	-85.43	12.33	-0.03	95.72	-76.21	-0.45	27.81	-0.84	4.11	-27.72	0.16	-59.61	0.01
mPW3PBE	0.00	-15.53	-0.20	1.11	-7.71	18.57	-69.24	11.74	-2.19	72.19	-53.99	-0.38	1.76	-0.55	0.50	N/A	N/A	-86.22	0.10
B3P86	0.00	-15.99	-0.27	0.30	-8.19	18.02	-69.07	12.53	-3.37	72.50	-62.72	7.41	1.23	-0.58	0.10	N/A	N/A	-85.88	0.00
B3PW91	0.00	-14.13	0.00	2.08	-7.20	18.49	-69.86	10.63	-1.06	71.88	-53.28	-8.63	10.86	-0.15	0.98	N/A	N/A	-86.84	0.00
B97-1	0.00	-13.28	-1.13	0.82	-7.04	19.07	-69.94	11.17	-3.03	71.04	-52.72	-0.83	2.52	-1.24	0.98	N/A	N/A	-82.30	0.46
VSXC	0.00	-15.25	-6.87	N/A	N/A	14.31	-70.55	13.60	-7.96	66.66	-62.77	-3.55	8.97	-4.21	2.98	N/A	N/A	-80.66	3.95
O3LYP	0.00	-10.65	-0.13	3.53	-4.28	26.34	-75.45	5.82	-0.10	78.22	-62.68	-0.25	9.52	-0.36	3.13	N/A	N/A	-90.33	0.09
HSE2PBE	0.00	-15.02	-0.66	1.54	-8.26	19.98	-70.49	11.64	-1.65	78.87	-55.84	-0.71	-11.31	-1.06	0.39	N/A	N/A	-86.69	0.29
HSEh1PBE	0.00	-15.10	-0.60	1.67	-8.10	8.10	-59.59	12.85	-1.54	78.84	-67.64	-0.66	12.70	-1.01	0.41	N/A	N/A	-86.50	0.26
tHCTHhyb	0.00	-16.16	N/A	N/A	-7.44	17.03	-67.71	11.56	-5.50	71.30	-57.61	-6.54	7.82	N/A	N/A	N/A	N/A	N/A	N/A
TPSSh	0.00	-17.20	N/A	N/A	-6.71	14.01	-65.65	11.52	-5.86	65.57	-63.41	-0.41	7.41	-0.54	0.34	N/A	N/A	-77.85	0.12
BMK	0.00	-12.06	-0.12	3.60	-10.75	27.56	-87.64	14.81	-1.26	65.77	-62.93	-0.45	16.15	-0.56	2.92	-27.60	0.62	-55.68	-0.33
LC-BP86	0.00	-18.73	-0.80	6.28	-7.50	18.39	-83.42	21.81	-1.03	88.97	-81.98	-1.69	19.02	-2.07	0.36	-39.29	0.55	-47.77	0.77
LC-HCTH407	0.00	-4.95	-4.04	11.42	-10.24	27.72	-91.44	17.34	-3.21	103.11	-80.67	-3.71	28.02	-4.09	4.32	-31.52	0.97	-57.14	3.56
LC-tHCTH	0.00	-11.69	-7.77	5.55	-8.21	24.94	-90.11	25.31	-6.91	93.23	-82.42	-6.31	24.88	-6.64	0.96	-27.41	0.91	-51.10	6.74
LC-TPSS	0.00	-15.22	-0.14	8.34	-5.94	17.35	-84.79	18.80	-0.06	89.74	-82.18	-0.59	22.19	-0.84	1.08	-37.46	0.67	-48.40	0.07

LC-M06-L	0.00	-17.39	-9.48	3.11	-10.95	24.45	-87.26	29.58	-8.24	92.68	-82.36	-7.22	22.39	-10.29	2.17	N/A	N/A	-84.48	9.23

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(B) Energy Barrier and Mean Absolute Error (MAE) on the Relative Energies Calculated at Different Levels of Theory without ZPE Correction. All Units are kcal/mol. The Performance of All DFT Methods are Listed: (A) Large Error on Au-CO Geometry; (B) Large Error on the Binding Energy of Au-CO; (C) Wrong Au-O_2 Geometry; (D) Large Error on the Binding Energy of Au-O_2; (E) Not All the Intermediates and Transition States Can be Optimized; (F) Wrong Sign of ΔE_1; (G) Wrong Sign of ΔE_2.

Method	ΔE_1 [a]	ΔE_2 [b]	MAE	defects						
				A	B	C	D	E	F	G
BP86	-19.15		17.97		B	C	D	E	F	
HCTH93	2.42	2.30	2.72			C		E		
HCTH147	-5.06	0.07	2.83		B	C	D	E	F	
HCTH407	-0.83	0.30	0.61		B	C	D	E	F	
tHCTH	-7.47		2.69		B	C	D	E	F	
TPSS	-17.96		12.05		B	C	D	E	F	
M06-L	-12.34	-2.04	10.80		B	C	D	E	F	G
BHandHLYP	20.36	3.28	10.70		B	C			F	
mPW3PBE	-3.76	-0.06	1.37		B	C	D	E	F	G
B3P86	-6.13	-0.48	3.38		B	C	D	E	F	G
B3PW91	-0.76	0.84	0.04		B	C		E	F	
B97-1	-1.56	-0.27	0.34			C	D	E	F	G
VSXC	-7.80	-1.22	8.00		B	C	D	E	F	G
O3LYP	14.82	2.76	5.40			C		E	F	
HSE2PBE	-2.43	-0.68	0.78		B	C		E	F	G
HSEh1PBE	-14.04	-0.60	2.02		B	C		E	F	G
tHCTHhyb	-6.58		3.27		B	C	D	E	F	
TPSSh	-9.90	-0.20	6.39		B	C	D	E	F	G
BMK	8.23	2.37	2.98			C				
LC-BP86	-2.35	-1.71	5.61	A	B				F	G
LC-HCTH407	19.90	0.24	7.53		B		D		F	
LC-tHCTH	2.82	-5.68	4.00				D			G
LC-TPSS	4.40	0.25	1.17	A	B					
LC-M06-L	-10.25	-8.11	10.53		B	C	D	E	F	G

[a] $\Delta E_1 = E_{TS2} - (E_{Au} + E_{O2} + E_{CO})$.

[b] $\Delta E_2 = E_{TS5} - (E_{AuO} + E_{CO})$.