Electronic Supplementary Information (ESI)

Assessment of van der Waals inclusive density functional theory methods for adsorption and selective dehydrogenation of formic acid on Pt(111) surface

Dingwang Yuan*, Heting Liao, and Wangyu Hu

College of Materials Science and Engineering, Hunan University, Changsha 410082, China

*Corresponding authors. E-mail: dwyuan@hnu.edu.cn

Table S1 Adsorption energy of HCOOH and HCOO with PBE+D3 method for different adsorption configurations at 1/4 monolayer (ML) coverage.

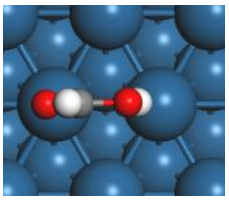
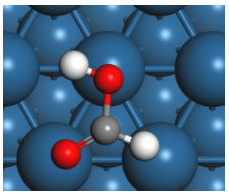
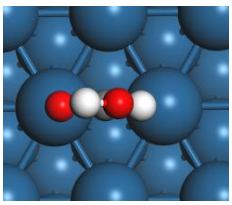
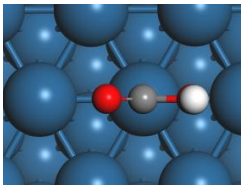
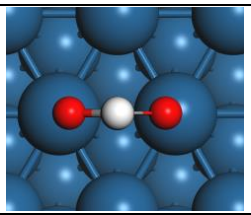
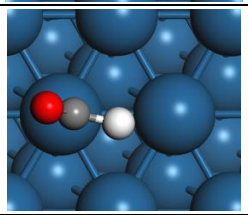
adsorbate	structure	adsorption energy(eV)
HCOOH (O/OH-down)		-0.73
HCOOH(flat)		-0.46
HCOOH (O/CH-down)		-0.46
HCOOH (CH-down)		-0.39
HCOO (bidentate)		-2.69
HCOO (monodenate)		-1.67

Table S2 Adsorption energy of HCOOH on Pt(111) surface with GGA functionals (PBE and RPBE) and 14 vdW inclusive density functional theory methods at 1/4, 1/9, and 1/16 monolayer (ML) coverage.

	1/4 ML	1/9 ML	1/16 ML
PBE	-0.29	-0.33	-0.31
RPBE	-0.04	-0.04	-0.03
PBE+D2	-0.99	-0.99	-0.99
PBE+D3	-0.73	-0.75	-0.73
PBE+D3-BJ	-0.70	-0.72	-0.71
PBE+TS	-0.67	-0.68	-0.68
PBE+TS-SCS	-0.60	-0.66	-0.66
PBE+TS-IH	-0.67	-0.69	-0.69
PBE+MBD@rsSCS	-0.62	-0.64	-0.64
PBE+dDsC	-0.59	-0.59	-0.59
revPBE-vdW	-0.44	-0.42	-0.42
optPBE-vdW	-0.62	-0.62	-0.62
optB88-vdW	-0.68	-0.69	-0.70
optB86b-vdW	-0.73	-0.74	-0.74
rPW86-vdW	-0.47	-0.47	-0.44
BEEF-vdW	-0.39	-0.37	-0.36

Table S3 Adsorption energy of HCOO on Pt(111) surface with GGA functionals (PBE and RPBE) and 14 vdW inclusive density functional theory methods at 1/4, 1/9, and 1/16 monolayer (ML) coverage.

	1/4 ML	1/9 ML	1/16 ML
PBE	-2.28	-2.30	-2.32
RPBE	-1.87	-1.89	-1.91
PBE+D2	-2.91	-2.92	-2.90
PBE+D3	-2.69	-2.69	-2.69
PBE+D3-BJ	-2.67	-2.67	-2.68
PBE+TS	-2.60	-2.60	-2.61
PBE+TS-SCS	-2.51	-2.57	-2.58
PBE+TS-IH	-2.58	-2.59	-2.60
PBE+MBD@rsSCS	-2.56	-2.56	-2.57
PBE+dDsC	-2.49	-2.52	-2.52
revPBE-vdW	-2.34	-2.34	-2.36
optPBE-vdW	-2.65	-2.63	-2.65
optB88-vdW	-2.76	-2.74	-2.77
optB86b-vdW	-2.84	-2.82	-2.83
rPW86-vdW	-2.39	-2.42	-2.43
BEEF-vdW	-2.29	-2.29	-2.31

Table S4 Lattice constants of fcc Pt bulk with GGA functionals (PBE and RPBE) and 14 vdW inclusive density functional theory methods. The relative error is calculated compared with experimental results[1].

	Lattice constant	Relatvie error
PBE	3.966	1.168
RPBE	3.990	1.742
PBE+D2	3.839	-2.110
PBE+D3	3.919	-0.031
PBE+D3-BJ	3.925	0.139
PBE+TS	3.934	0.347
PBE+TS-SCS	3.944	0.602
PBE+TS-IH	3.934	0.364
PBE+MBD@rsSCS	3.926	0.162
PBE+dDsC	3.944	0.606
revPBE-vdW	4.032	2.780
optPBE-vdW	3.990	1.747
optB88-vdW	3.975	1.385
optB86b-vdW	3.948	0.721
rPW86-vdW	4.110	4.633
BEEF-vdW	3.993	1.838

Table S5 Geometries of transition states in O-H and C-H breaking reations for HCOOH dehydrogenation on Pt(111) with PBE functionals and 10 vdW inclusive density functional theory methods.

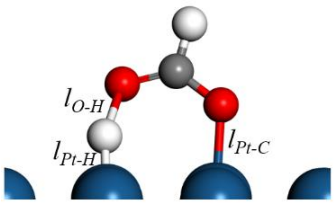
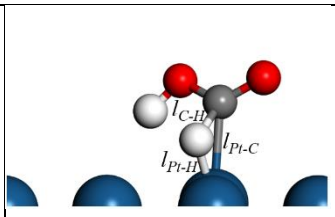
	 TS1 in HCOOH→ HCOO+H			 TS2 in HCOOH→ COOH+H		
	l_{O-H}	l_{Pt-H}	l_{Pt-C}	l_{C-H}	l_{Pt-H}	l_{Pt-C}
PBE	1.732	1.595	2.099	1.346	1.708	2.340
PBE+D3	1.772	1.581	2.093	1.353	1.726	2.386
PBE+D3-BJ	1.696	1.598	2.092	1.353	1.716	2.374
PBE+TS	1.766	1.584	2.091	1.367	1.697	2.334
PBE+TS-SCS	1.750	1.666	2.090	1.340	1.709	2.318
PBE+TS-IH	1.792	1.582	2.091	1.346	1.711	2.323
PBE+MBD@rsSCS	1.720	1.593	2.093	1.348	1.707	2.349
PBE+dDsC	1.785	1.580	2.084	1.353	1.703	2.324
optPBE-vdW	1.709	1.597	2.104	1.360	1.724	2.292
optB88-vdW	1.740	1.595	2.086	1.358	1.714	2.328
optB86b-vdW	1.741	1.594	2.082	1.330	1.730	2.311

Table S6 The vibrational energies (in THz) were calculated by PBE+dDsC and optPBE-vdw methods for the 9 internal modes and 6 external modes of adsorbed HCOOH.

modes	vibration in initial state (THz)	
	PBE+dDsC	optPBE-vdW
internal modes	90.598	90.380
	77.904	82.767
	47.949	47.484
	40.461	41.040
	39.223	38.699
	34.530	34.372
	29.522	29.788
	22.468	21.946
	19.715	19.417
external modes	7.768	7.463
	6.908	6.6087
	4.492	3.893
	2.754	2.736
	2.300	1.823
	0.945	1.511

Table S7 The vibrational energies (in THz) were calculated by PBE+dDsC and optPBE-vdw methods for the vibrational modes of transition states in O-H and C-H bond breaking reactions.

vibration in transition state (THz)			
$HCOOH \rightarrow HCOO + H$		$HCOOH \rightarrow COOH + H$	
PBE+dDsC	optPBE-vdW	PBE+dDsC	optPBE-vdW
87.560	87.134	92.142	98.661
60.439	56.094	54.016	52.865
45.816	43.961	48.045	46.945
38.604	39.098	37.046	37.093
36.902	36.501	32.144	31.265
28.613	28.691	25.639	23.593
21.880	21.885	23.409	22.338
15.864	16.860	19.010	18.478
10.431	9.993	17.690	17.192
8.9749	8.683	8.282	7.194
5.542	6.293	6.869	6.698
3.862	3.918	2.490	2.492
2.998	2.774	1.595	1.692
1.143	1.510	1.3530	1.195

Table S8 Comparison between PBE+vdW and HSE+vdW methods for adsorption energy (E_{ad}, in eV) of HCOOH on Pt(111) surface and barriers (E_a^{O-H} and E_a^{C-H}, in eV) of O-H and C-H bond breaking at 1/9 monolayer (ML) coverage. For HSE+vdW methods, we utilized the optimized geometries of adsorption configurations and transition states obtained with PBE+vdW methods for single point energy calculations, and 3x3x1 k-points mesh was employed.

vdW methods	E_{ad}		E_a^{O-H}	E_a^{C-H}
	5x5x1	3x3x1		
PBE+D3	-0.75	-0.76	0.543	0.663
HSE+D3		-0.84	0.582	0.713
PBE+dDsC	-0.59	-0.60	0.581	0.687
HSE+dDsC		-0.71	0.598	0.725
PBE+TS	-0.68	-0.68	0.616	0.677
HSE+TS		-0.71	0.612	0.694

References:

1, C. Kittel, Introduction to Solid State Physics, 7th ed.; John Wiley& Sons: New York, 1996.