Supplementary Material for

Investigation on the Mechanism of Methanol Electrooxidation: A Potential-Dependent DFT Study

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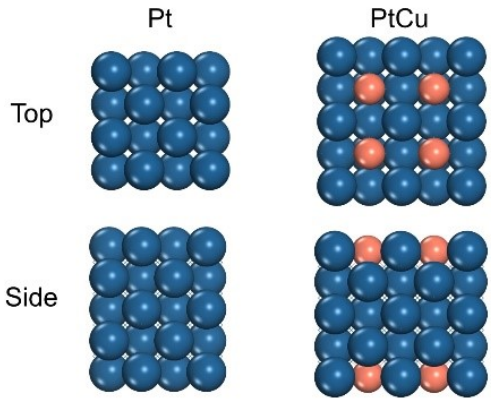

Figure s1. The geometric structures of Pt(100), PtCu and PtCu_np (top and side views). Blue, orange, grey and yellow spheres represent Pt, Cu, C and S atoms, respectively.

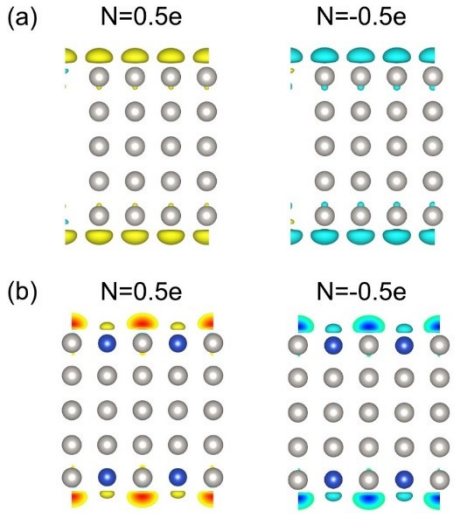

Figure s2. The differential charge density distribution for charge-defect catalysts (Pt, PtCu, PtCu_np). Isosurface value is equal to 0.0004. White, blue, grey and yellow spheres represent Pt, Cu, C and S atoms, respectively.

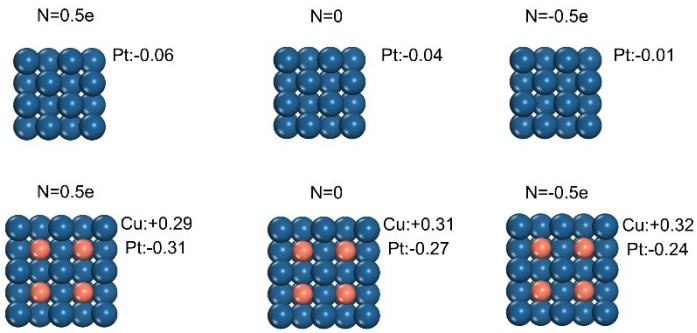

Figure s3. Bader charge analysis for pristine and charge-defect catalysts includes Pt, PtCu and PtCu_np.

Table s1. The predicted relative free energy of the methanol electro-oxidation reactants or products on Pt surface using charge-variable method.

Pt	Electrons	-1.00	-0.75	-0.50	-0.25	0.00	0.25	0.50	0.75	1.00
	U	2.27	2.02	1.76	1.49	1.21	0.91	0.61	0.29	-0.03
	G	-0.29	-0.17	-0.07	-0.02	0.00	-0.02	-0.09	-0.20	-0.36
	Fitting	G=-0.25*(U-1.207)^2					G=-0.237*(U-1.207)^2			
CH3OH@Pt	Electrons	-1.00	-0.75	-0.50	-0.25	0.00	0.25	0.50	0.75	1.00
	U	1.67	1.42	1.15	0.88	0.59	0.29	-0.01	-0.31	-0.60
	G	-0.30	-0.17	-0.08	-0.02	0.00	-0.02	-0.09	-0.20	-0.34
	Fitting	G=-0.255*(U-0.592)^2-0.001					G=-0.239*(U-0.592)^2-0.001			
CH2OH@Pt	Electrons	-1.00	-0.75	-0.50	-0.25	0.00	0.25	0.50	0.75	1.00
	U	1.76	1.57	1.33	1.11	0.87	0.59	0.31	0.03	-0.25
	G	-2.34	-2.04	-1.71	-1.44	-1.18	-0.92	-0.69	-0.51	-0.37
	Fitting	G=-0.326*(U-0.865)^2-0.31-U					G=-0.25*(U-0.865)^2-0.31-U			
CH3O@Pt	Electrons	-1.00	-0.75	-0.50	-0.25	0.00	0.25	0.50	0.75	1.00
	U	2.00	1.75	1.48	1.20	0.92	0.62	0.32	0.01	-0.30
	G	-2.21	-1.82	-1.46	-1.12	-0.81	-0.54	-0.30	-0.10	0.06
	Fitting	G=-0.263*(U-0.917)^2+0.105-U					G=-0.232*(U-0.917)^2+0.105-U			
CHOH@Pt	Electrons	-1.00	-0.75	-0.50	-0.25	0.00	0.25	0.50	0.75	1.00
	U	1.80	1.54	1.28	1.01	0.73	0.44	0.14	-0.15	-0.45
	G	-4.40	-3.76	-3.14	-2.53	-1.95	-1.39	-0.86	-0.37	0.09
	Fitting	G=-0.266*(U-0.726)^2-0.495-2U					G=-0.233*(U-0.726)^2-0.495-2U			
CH2O@Pt	Electrons	-1.00	-0.75	-0.50	-0.25	0.00	0.25	0.50	0.75	1.00
	U	2.14	1.89	1.64	1.38	1.11	0.82	0.54	0.24	-0.06
	G	-4.49	-3.88	-3.29	-2.71	-2.14	-1.60	-1.08	-0.59	-0.14
	Fitting	G=-0.271*(U-1.107)^2+0.071-2U					G=-0.241*(U-1.107)^2+0.071-2U			
COH@Pt	Electrons	-1.00	-0.75	-0.50	-0.25	0.00	0.25	0.50	0.75	1.00
	U	1.82	1.58	1.32	1.06	0.79	0.51	0.23	-0.06	-0.35
	G	-6.45	-5.60	-4.74	-3.89	-3.07	-2.25	-1.45	-0.69	0.04
	Fitting	G=-0.278*(U-0.793)^2-0.689-3U					G=-0.244*(U-0.793)^2-0.689-3U			
HCO@Pt	Electrons	-1.00	-0.75	-0.50	-0.25	0.00	0.25	0.50	0.75	1.00
	U	2.12	1.87	1.61	1.34	1.05	0.76	0.47	0.16	-0.15
	G	-7.07	-6.19	-5.32	-4.45	-3.58	-2.73	-1.90	-1.09	-0.32
	Fitting	G=-0.265*(U-1.054)^2-0.422-3U					G=-0.238*(U-1.054)^2-0.422-3U			
CO@Pt	Electrons	-1.00	-0.75	-0.50	-0.25	0.00	0.25	0.50	0.75	1.00
	U	2.34	2.10	1.85	1.59	1.32	1.04	0.75	0.46	0.16
	G	-10.86	-9.79	-8.70	-7.60	-6.50	-5.41	-4.31	-3.23	-2.17
	Fitting	G=-0.277*(U-1.321)^2-1.219-4U					G=-0.241*(U-1.321)^2-1.219-4U			
COOH@Pt	Electrons	-1.00	-0.75	-0.50	-0.25	0.00	0.25	0.50	0.75	1.00
	U	1.97	1.72	1.46	1.20	0.92	0.64	0.35	0.05	-0.25
	G	-10.51	-9.15	-7.75	-6.38	-4.97	-3.57	-2.21	-0.81	0.53
	Fitting	G=-0.269*(U-0.919)^2-0.373-5U					G=-0.243*(U-0.919)^2-0.373-5U			

CO2(g)	Electrons	-1.00	-0.75	-0.50	-0.25	0.00	0.25	0.50	0.75	1.00
	U	2.30	2.04	1.77	1.49	1.19	0.89	0.57	0.25	-0.07
	G	-13.96	-12.28	-10.57	-8.81	-7.01	-5.20	-3.37	-1.57	0.20
	Fitting	G=-0.236*(U-1.192)^2+0.14-6U					G=-0.229*(U-1.192)^2+0.14-6U			

Table s2. The predicted relative free energy of the methanol electro-oxidation reactants or products on PtCu surface using charge-variable method.

PtCu	Electrons	-1.00	-0.75	-0.50	-0.25	0.00	0.25	0.50	0.75	1.00
	U	1.72	1.49	1.24	0.97	0.67	0.38	0.07	-0.24	-0.56
	G	-0.30	-0.18	-0.09	-0.02	0.00	-0.02	-0.08	-0.19	-0.35
	Fitting	G=-0.274*(U-0.671)^2					G=-0.232*(U-0.671)^2			
CH3OH@PtCu	Electrons	-1.00	-0.75	-0.50	-0.25	0.00	0.25	0.50	0.75	1.00
	U	1.31	1.05	0.80	0.52	0.24	-0.05	-0.32	-0.62	-0.85
	G	-0.51	-0.37	-0.28	-0.22	-0.20	-0.22	-0.28	-0.38	-0.50
	Fitting	G=-0.275*(U-0.241)^2-0.201					G=-0.252*(U-0.241)^2-0.201			
CH2OH@PtCu	Electrons	-1.00	-0.75	-0.50	-0.25	0.00	0.25	0.50	0.75	1.00
	U	1.37	1.16	1.00	0.76	0.50	0.22	-0.07	-0.36	-0.66
	G	-2.04	-1.71	-1.49	-1.19	-0.91	-0.64	-0.42	-0.23	-0.07
	Fitting	G=-0.332*(U-0.501)^2-0.409-U					G=-0.243*(U-0.501)^2-0.409-U			
CH3O@PtCu	Electrons	-1.00	-0.75	-0.50	-0.25	0.00	0.25	0.50	0.75	1.00
	U	1.57	1.33	1.07	0.80	0.52	0.22	-0.06	-0.38	-0.69
	G	-1.87	-1.50	-1.15	-0.82	-0.52	-0.25	-0.04	0.13	0.30
	Fitting	G=-0.266*(U-0.518)^2-0.003-U					G=-0.274*(U-0.518)^2-0.003-U			
CHOH@PtCu	Electrons	-1.00	-0.75	-0.50	-0.25	0.00	0.25	0.50	0.75	1.00
	U	1.10	0.84	0.58	0.30	0.02	-0.27	-0.56	-0.86	
	G	-2.61	-1.96	-1.34	-0.73	-0.14	0.42	0.93	1.44	
	Fitting	G=-0.27*(U-0.021)^2-0.102-2U					G=-0.239*(U-0.021)^2-0.102-2U			
CH2O@PtCu	Electrons	-1.00	-0.75	-0.50	-0.25	0.00	0.25	0.50	0.75	1.00
	U	1.60	1.36	1.11	0.84	0.57	0.28	-0.01	-0.31	-0.62
	G	-3.70	-3.10	-2.51	-1.92	-1.35	-0.80	-0.27	0.22	0.70
	Fitting	G=-0.276*(U-0.569)^2-0.209-2U					G=-0.244*(U-0.569)^2-0.209-2U			
COH@PtCu	Electrons	-1.00	-0.75	-0.50	-0.25	0.00	0.25	0.50	0.75	1.00
	U	1.05	0.81	0.55	0.29	0.08	-0.18	-0.44	-0.70	
	G	-3.01	-2.17	-1.31	-0.46	0.21	0.98	1.71	2.39	
	Fitting	G=-0.334*(U-0.08)^2+0.454-3U					G=-0.265*(U-0.08)^2+0.454-3U			
HCO@PtCu	Electrons	-1.00	-0.75	-0.50	-0.25	0.00	0.25	0.50	0.75	1.00
	U	1.62	1.38	1.13	0.87	0.59	0.31	0.01	-0.29	-0.60
	G	-5.76	-4.92	-4.08	-3.23	-2.38	-1.55	-0.73	0.07	0.84
	Fitting	G=-0.275*(U-0.591)^2-0.611-3U					G=-0.241*(U-0.591)^2-0.611-3U			
CO@PtCu	Electrons	-1.00	-0.75	-0.50	-0.25	0.00	0.25	0.50	0.75	1.00
	U	1.75	1.52	1.28	1.03	0.76	0.48	0.19	-0.11	-0.41

	G	-8.54	-7.50	-6.44	-5.36	-4.27	-3.18	-2.09	-1.01	0.04
	Fitting	G=-0.285*(U-0.757)^2-1.244-4U					G=-0.249*(U-0.757)^2-1.244-4U			
COOH@PtCu	Electrons	-1.00	-0.75	-0.50	-0.25	0.00	0.25	0.50	0.75	1.00
	U	1.59	1.36	1.10	0.84	0.57	0.29	0.02	-0.29	-0.59
	G	-8.82	-7.52	-6.17	-4.81	-3.43	-2.03	-0.76	0.69	2.04
	Fitting	G=-0.273*(U-0.57)^2-0.576-5U					G=-0.249*(U-0.57)^2-0.576-5U			
CO2(g)	Electrons	-1.00	-0.75	-0.50	-0.25	0.00	0.25	0.50	0.75	1.00
	U	1.77	1.52	1.25	0.97	0.68	0.38	0.07	-0.25	-0.57
	G	-10.81	-9.15	-7.45	-5.71	-3.93	-2.13	-0.34	1.45	3.18
	Fitting	G=-0.259*(U-0.677)^2+0.137-6U					G=-0.223*(U-0.677)^2+0.137-6U			

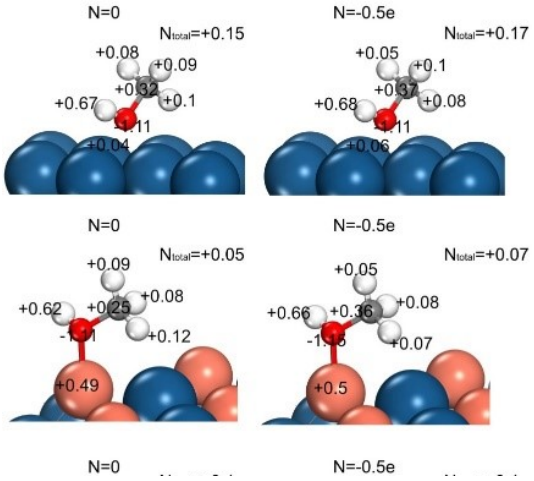

Figure s4. Bader charge analysis for methanol adsorption over pristine and charge-defect catalysts includes Pt (top), PtCu (middle) and PtCu_np (bottom). N_{total} represents the number of electrons transformed from methanol molecules to catalysts.

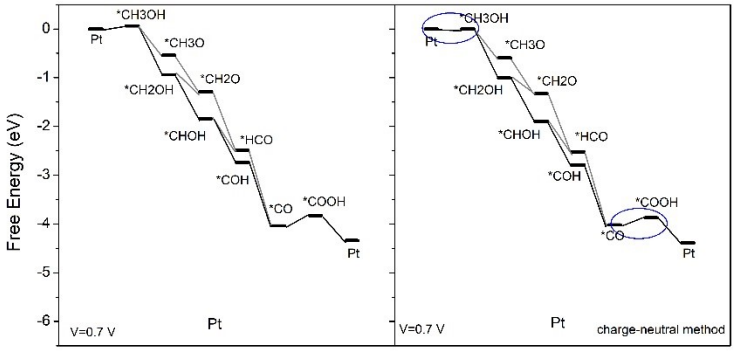

Figure s5. Comparison of reaction free energies of MER on Pt surface at U= 0.7 V by using charge-variable method (left) and charge-neutral method (right).

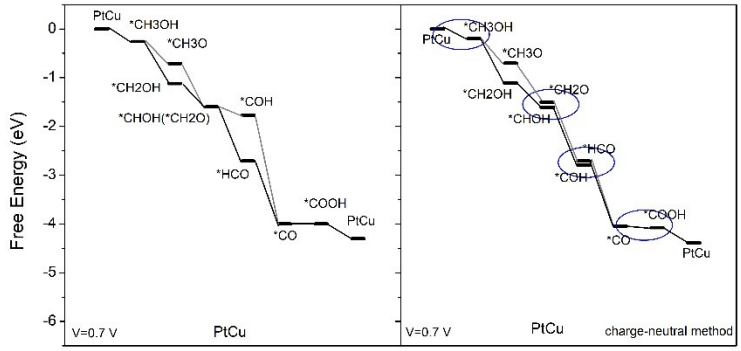

Figure s6. Comparison of reaction free energies of MER on PtCu surface at U= 0.7 V by using charge-variable method (left) and charge-neutral method (right).