Electrochemical Reduction of CO_2 by Single Atom Catalyst TM−TCNQ Monolayers

Supplemental Information

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Table. S1 Lattice constant a and b of TM−TCNQ in Å, where TM are the metal atoms of the first transition metal series.

TM−TCNQ	Lattice (a)	Lattice (b)
Sc−TCNQ	7.2383	11.6652
Ti−TCNQ	7.1576	11.5513
V−TCNQ	7.1767	11.4626
Cr−TCNQ	7.1495	11.4075
Mn−TCNQ	6.9973	11.3408
Fe−TCNQ	7.1285	11.2672
Co−TCNQ	6.9116	11.1595
Ni−TCNQ	7.1073	11.2714
Cu−TCNQ	6.8897	11.1371
Zn−TCNQ	7.0104	11.2765

Table. S2 E_c is the cohesive energy of the bulk TM, E_b is the binding energy between the TM and the TM–TCNQ, and E_f is the formation energy of TM–TCNQ, where TM are the metal atoms of the first transition metal series.

TM−TCNQ	E_b / eV	E_c / eV	E_f / eV
Sc	−9.194	−4.518	−3.148
Ti	−8.596	−5.282	−2.523
V	−8.317	−5.632	−2.117
Cr	−6.907	−4.547	−0.848
Mn	−6.741	−4.247	−0.630
Fe	−6.815	−5.283	−1.013
Co	−7.463	−5.633	−1.320
Ni	−6.312	−4.645	0.023
Cu	−5.088	−3.857	0.859
Zn	−3.665	−1.402	2.461

[1]E_b is binding energy of metal atoms on the TCNQ, which is calculated by: $E_b = E_{TM-TCNQ} - E_{TM} - E_{TCNQ}$, where the $E_{TM-TCNQ}$, E_{TM} and E_{TCNQ} are the energies of TM−TCNQ, TCNQ and metal atoms.

[2]E_c is the cohesive energy of metals, which is calculated by $E_c = (E_{M(bulk)} - nE_M) / n$, where the $E_{M(bulk)}$ is the energy of metal crystal, E_M is the energy of single metal atoms and n is the number of metal atoms in the crystal.

[3]E_f is the formation energy of TM−TCNQ, which is calculated by $E_f = E_{TM-TCNQ} - n_{TM}\mu_{TM} - nC\mu_C - n_N\mu_N - n_H\mu_H$, where the $E_{TM-TCNQ}$ are the energies of TM−TCNQ, n_{TM}, n_C, n_N and n_H are the number of TM, C, N and H, respectively. μ_{TM}, μ_C, μ_N and μ_H are the chemical potential of TM, C, N and H, respectively.

Table S3 Adsorption Energy (E_{ads}/**eV**) of different CO_2 reduction products and the bond length between metal atom and the carbon or oxygen atom ($R_{M\text{-}C/M\text{-}O}$/**Å**).

TM–TCNQ		CO	HCOOH	HCHO	CH_3OH	CH_4
Sc–TCNQ	$R_{Sc\text{-}C/Sc\text{-}O}$ / Å	2.296	2.121	2.011	2.161	2.561
	E_{ads} / eV	−0.731	−1.002	−1.171	−1.141	−0.306
Ti–TCNQ	$R_{Ti\text{-}C/Ti\text{-}O}$ / Å	2.066	2.017	1.916	2.089	2.571
	E_{ads} / eV	−1.397	−1.181	−1.466	−1.291	−0.408
V–TCNQ	$R_{V\text{-}C/V\text{-}O}$ / Å	1.923	2.026	1.816	2.066	3.126
	E_{ads} / eV	−1.165	−0.481	−0.615	−0.582	−0.161
Cr–TCNQ	$R_{Cr\text{-}C/Cr\text{-}O}$ / Å	1.817	2.325	1.906	2.044	3.185
	E_{ads} / eV	−0.824	−0.336	0.029	0.147	−0.175
Mn–TCNQ	$R_{Mn\text{-}C/Mn\text{-}O}$ / Å	1.747	1.982	1.894	2.029	3.111
	E_{ads} / eV	−1.204	0.172	0.155	0.060	−0.200
Fe–TCNQ	$R_{Fe\text{-}C/Fe\text{-}O}$ / Å	1.736	2.083	1.969	2.249	3.086
	E_{ads} / eV	−1.259	−0.053	−0.172	−0.552	−0.197
Co–TCNQ	$R_{Co\text{-}C/Co\text{-}O}$ / Å	1.796	2.182	2.154	2.180	3.345
	E_{ads} / eV	−0.716	−0.205	−0.254	−0.346	−0.153
Ni–TCNQ	$R_{Ni\text{-}C/Ni\text{-}O}$ / Å	1.844	2.345	2.296	2.219	3.199
	E_{ads} / eV	−0.701	−0.034	−0.044	−0.390	−0.265
Cu–TCNQ	$R_{Cu\text{-}C/Cu\text{-}O}$ / Å	1.845	3.012	2.413	2.315	3.218
	E_{ads} / eV	−0.674	−0.418	−0.263	−0.492	−0.148
Zn–TCNQ	$R_{Zn\text{-}C/Zn\text{-}O}$ / Å	2.229	2.128	2.188	2.126	3.251
	E_{ads} / eV	−0.398	−0.589	−0.723	−0.876	−0.466

Table S4 Gibbs free energy change (ΔG/eV) of the first protonation step in the CO_2 reduction reaction (CRR) and H_2 evolution reaction (HER) on the TM–TCNQ

M–TCNQ	ΔG_H	ΔG_{C^*OOH}	ΔG_{O^*CHO}
Sc–TCNQ	0.074	−0.662	−1.745
Ti–TCNQ	−0.383	−0.711	−1.848
V–TCNQ	0.319	−0.043	−0.657
Cr–TCNQ	0.982	0.694	−0.138
Mn–TCNQ	0.594	0.260	0.373
Fe–TCNQ	0.196	−0.133	0.284
Co–TCNQ	0.465	0.203	0.630
Ni–TCNQ	1.233	0.673	0.452
Cu–TCNQ	1.239	0.812	0.520
Zn–TCNQ	0.640	0.501	−0.226

Table S5. The calculated free energy corrections (G_c) for adsorbates. The temperature of the reaction is 298.15 K.

Sc-TCNQ	E_{ZPE} (kcal/mol)	C_v (cal/mol·k)	S (cal/mol·k)	H (kcal/mol)	G_c (kcal/mol)
C*OOH	95.012	67.159	82.663	106.358	81.712
O*CHO	93.307	63.730	77.835	104.067	80.861
C*O	82.834	60.512	67.753	92.840	72.639
O*CHOH	99.777	67.981	88.448	111.406	85.035
O*CH	88.157	60.400	64.537	98.013	78.771
C*OH	89.022	60.396	71.725	98.896	77.511
C*HO	91.066	61.861	72.603	101.303	79.656
O*CH_2	96.242	61.033	64.620	106.139	86.873
O*CH_3	104.853	60.964	68.092	114.889	94.587
O*HCH_2	105.645	66.893	73.019	116.653	94.883
CH_3O*H	112.077	66.799	78.273	123.065	99.728
O*	81.309	57.304	66.144	90.805	71.084
O*H	86.008	57.735	74.513	95.516	73.300

Ti-TCNQ	E_{ZPE} (kcal/mol)	C_v (cal/mol·k)	S (cal/mol·k)	H (kcal/mol)	G_c (kcal/mol)
C*OOH	90.367	61.177	62.787	100.130	81.410
O*CHO	93.533	65.108	73.922	104.348	82.308
C*O	83.448	61.596	72.328	93.509	71.945
O*CHOH	100.125	75.017	65.713	110.918	88.552
O*CH	88.786	65.723	77.425	99.777	76.693
C*OH	90.367	61.177	62.787	100.130	81.410
C*HO	88.856	61.489	75.666	99.094	76.534
O*CH_2	96.383	64.916	71.147	107.022	85.809
O*CH_3	105.123	64.391	69.231	115.616	94.975
O*HCH_2	105.758	64.170	60.985	115.655	97.472
CH_3O*H	111.800	66.904	77.823	122.778	99.575
O*	81.231	57.303	68.903	90.630	70.086
O*H	86.755	60.720	62.527	96.499	77.857

V-TCNQ	E_{ZPE} (kcal/mol)	C_v (cal/mol·k)	S (cal/mol·k)	H (kcal/mol)	G_c (kcal/mol)
C*OOH	93.637	65.571	69.870	104.084	83.252
O*CHO	94.191	64.228	63.902	104.316	85.264
C*O	84.521	60.218	58.360	93.852	76.452
O*CHOH	101.098	66.501	69.221	111.712	91.074
O*CH	90.172	62.287	61.091	99.943	81.729
C*OH	90.912	60.364	57.834	100.232	82.989
C*HO	90.191	61.992	62.508	99.961	81.324
O*CH_2	97.013	61.860	60.557	106.644	88.588
O*CH_3	106.563	64.869	63.476	116.772	97.847
O*HCH_2	104.461	67.899	73.868	115.275	93.251
CH_3O*H	112.985	67.668	71.232	123.859	102.621
O*	81.937	56.058	52.112	90.495	74.957
O*H	87.668	59.232	59.898	96.801	78.942

Cr-TCNQ	E_{ZPE} (kcal/mol)	C_v (cal/mol·k)	S (cal/mol·k)	H (kcal/mol)	G_c (kcal/mol)
C*OOH	94.103	62.405	56.745	103.390	86.472
O*CHO	93.785	64.667	67.153	104.142	84.121
C*O	85.115	60.845	58.981	94.461	76.875
O*CHOH	100.687	67.161	84.439	111.976	86.800
O*CH	89.497	62.017	59.128	99.049	81.420
C*OH	90.697	61.947	63.239	100.380	81.525
C*HO	90.651	60.909	55.599	99.869	83.292
O*CH_2	97.997	64.306	62.956	107.955	89.185
O*CH_3	104.988	63.340	58.901	114.644	97.082
O*HCH_2	104.170	67.553	68.644	114.767	94.301
CH_3O*H	112.759	67.010	66.686	123.231	103.349
O*	81.540	57.858	55.921	90.476	73.803
O*H	87.237	57.734	54.465	96.077	79.838

Mn-TCNQ	E_{ZPE} (kcal/mol)	C_v (cal/mol·k)	S (cal/mol·k)	H (kcal/mol)	G_c (kcal/mol)
C*OOH	94.553	65.746	64.537	104.628	85.386
O*CHO	94.304	65.417	66.121	104.572	84.858
C*O	85.553	60.237	55.114	94.610	78.178
O*CHOH	102.230	66.944	64.281	112.553	93.387
O*CH	90.381	62.969	58.699	99.968	82.467
C*OH	91.763	62.702	59.628	101.404	83.626
C*HO	91.097	62.089	58.038	100.517	83.213
O*CH_2	98.677	63.629	58.542	108.306	90.852
O*CH_3	105.209	64.950	61.626	115.186	96.812
O*HCH_2	103.776	65.792	64.477	113.970	94.746
CH_3O*H	113.673	66.140	61.609	123.767	105.398
O*	81.823	57.622	51.987	90.515	75.016
O*H	87.436	58.906	53.730	96.328	80.308

Fe-TCNQ	E_{ZPE} (kcal/mol)	C_v (cal/mol·k)	S (cal/mol·k)	H (kcal/mol)	G_c (kcal/mol)
C*OOH	94.452	64.177	59.742	104.080	86.268
O*CHO	91.742	64.217	56.472	101.306	84.469
C*O	84.933	59.339	52.859	93.805	78.045
O*CHOH	101.154	63.939	62.874	110.913	92.167
O*CH	90.314	63.401	59.598	100.015	82.246
C*OH	90.335	59.908	54.599	99.295	83.016
C*HO	91.019	60.542	53.345	99.994	84.089
O*CH_2	97.835	62.937	57.124	107.370	90.339
O*CH_3	105.610	64.744	63.114	115.577	96.759
O*HCH_2	103.047	67.178	69.916	113.828	92.983
CH_3O*H	112.481	65.557	65.944	122.705	103.044
O*	81.247	54.307	47.751	89.335	75.098
O*H	87.520	56.932	48.843	95.865	81.303

Co-TCNQ	E_{ZPE} (kcal/mol)	C_v (cal/mol·k)	S (cal/mol·k)	H (kcal/mol)	G_c (kcal/mol)
C*OOH	94.517	65.011	64.671	104.678	85.397
O*CHO	93.977	64.920	63.530	104.187	85.246
C*O	85.140	62.080	61.440	94.955	76.637
O*CHOH	101.016	67.373	70.805	111.931	90.820
O*CH	89.363	63.238	62.435	99.307	80.692
C*OH	90.911	64.063	65.844	101.133	81.502
C*HO	91.096	61.701	59.308	100.670	82.987
O*CH_2	97.648	75.542	66.234	108.491	85.968
O*CH_3	105.149	65.819	68.838	115.688	95.164
O*HCH_2	104.054	63.721	73.897	114.311	92.279
CH_3O*H	113.195	67.985	71.276	124.197	102.946
O*	81.473	59.231	66.730	91.230	71.334
O*H	88.360	61.020	67.973	97.985	77.719

Ni-TCNQ	E_{ZPE} (kcal/mol)	C_v (cal/mol·k)	S (cal/mol·k)	H (kcal/mol)	G_c (kcal/mol)
C*OOH	93.835	65.973	74.408	104.609	82.424
O*CHO	94.057	65.557	74.086	104.856	82.767
C*O	84.753	63.115	70.325	95.213	74.245
O*CHOH	100.592	61.990	64.156	110.587	91.459
O*CH	88.676	64.205	73.445	99.370	77.473
C*OH	89.626	63.620	78.525	100.233	76.821
C*HO	90.656	60.443	64.869	100.365	81.024
O*CH_2	95.725	58.228	66.901	105.128	85.181
O*CH_3	104.635	63.063	66.914	114.823	94.873
O*HCH_2	104.625	66.325	78.214	115.779	92.460
CH_3O*H	112.331	67.061	84.552	123.616	98.407
O*	80.893	60.064	71.612	91.043	69.692
O*H	87.288	56.744	55.525	96.181	79.627

Cu-TCNQ	E_{ZPE} (kcal/mol)	C_v (cal/mol·k)	S (cal/mol·k)	H (kcal/mol)	G_c (kcal/mol)
C*OOH	93.120	65.348	79.912	104.247	80.421
O*CHO	93.183	66.367	81.747	104.653	80.280
C*O	83.337	60.643	76.609	93.663	70.822
O*CHOH	100.381	65.851	74.829	111.477	89.167
O*CH	87.286	54.159	56.428	96.093	79.269
C*OH	88.759	62.705	79.735	99.459	75.686
C*HO	89.153	59.787	72.039	99.141	77.663
O*CH_2	97.034	59.563	68.791	106.982	86.472
O*CH_3	104.225	67.329	78.029	115.740	92.475
O*HCH_2	103.925	64.649	72.819	114.816	93.105
CH_3O*H	111.502	63.682	71.610	122.177	100.827
O*	79.797	54.980	68.151	89.093	68.774
O*H	86.514	59.617	68.068	96.503	76.208

Zn-TCNQ	E_{ZPE} (kcal/mol)	C_v (cal/mol·k)	S (cal/mol·k)	H (kcal/mol)	G_c (kcal/mol)
C*OOH	93.607	62.877	71.504	103.916	82.597
O*CHO	94.190	63.783	79.125	104.956	81.365
C*O	84.691	57.984	62.890	94.231	75.481
O*CHOH	100.865	60.002	71.461	110.636	89.330
O*CH	88.681	64.520	75.193	99.692	77.273
C*OH	90.408	61.709	72.345	100.715	79.146
C*HO	89.751	61.300	72.053	100.006	78.524
O*CH_2	98.015	64.230	77.397	108.882	85.806
O*CH_3	105.041	64.743	73.954	115.960	93.911
O*HCH_2	103.396	65.954	72.684	114.420	92.749
CH_3O*H	113.534	68.190	87.387	125.153	99.099
O*	80.666	58.606	73.992	90.680	68.619
O*H	87.409	57.059	66.524	96.742	76.907