Computational Study on the Catalytic Performance of Single-Atom Catalysts Anchored on g-CN for Electrochemical Oxidation of Formic Acid

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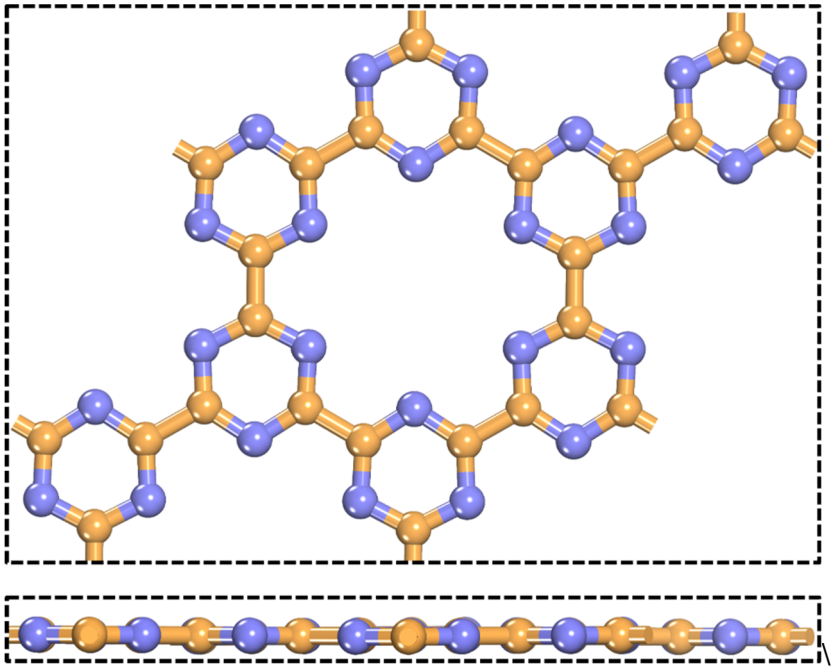
g-CN



g-CN
1.0
14.223100 0.000000 0.000000
-7.111550 12.317566 0.000000
0.000000 0.000000 20.000000
C N
24 24
Direct
0.219300 0.438470 0.499170
0.060860 0.280060 0.498660
0.219280 0.280020 0.499310
0.280310 0.060520 0.500490
0.438740 0.218940 0.500040
0.280300 0.218950 0.499630
0.719220 0.438450 0.499820
0.560830 0.280000 0.499880
0.719280 0.280050 0.499190
0.780340 0.060580 0.498510
0.938760 0.219010 0.498390
0.780320 0.218990 0.498640
0.219250 0.938430 0.500740
0.060820 0.780000 0.500780
0.219260 0.780000 0.500430
0.280340 0.560550 0.499470
0.438770 0.719000 0.499540

0.280310 0.718960 0.500130
0.719290 0.938480 0.498840
0.560850 0.780060 0.499310
0.719290 0.780050 0.499440
0.780260 0.560530 0.500010
0.938720 0.718950 0.500530
0.780310 0.718980 0.499760
0.388910 0.277710 0.499570
0.221470 0.110330 0.499920
0.388960 0.110330 0.500730
0.110680 0.221280 0.499010
0.278120 0.388640 0.499470
0.110660 0.388680 0.498650
0.388920 0.777750 0.500010
0.221490 0.610340 0.499950
0.388990 0.610380 0.499160
0.110660 0.721240 0.500520
0.278100 0.888630 0.500390
0.110600 0.888620 0.501070
0.888920 0.277770 0.498520
0.721500 0.110380 0.498680
0.888990 0.110390 0.498330
0.610670 0.221250 0.499390
0.778080 0.388660 0.499300
0.610580 0.388630 0.500130
0.888910 0.777740 0.500100
0.721440 0.610360 0.499610
0.888900 0.610330 0.500670
0.610690 0.721290 0.499510
0.778130 0.888670 0.499160
0.610650 0.888680 0.498890

Figure S1. The top and side view of the optimized g-CN and the corresponding coordination information.

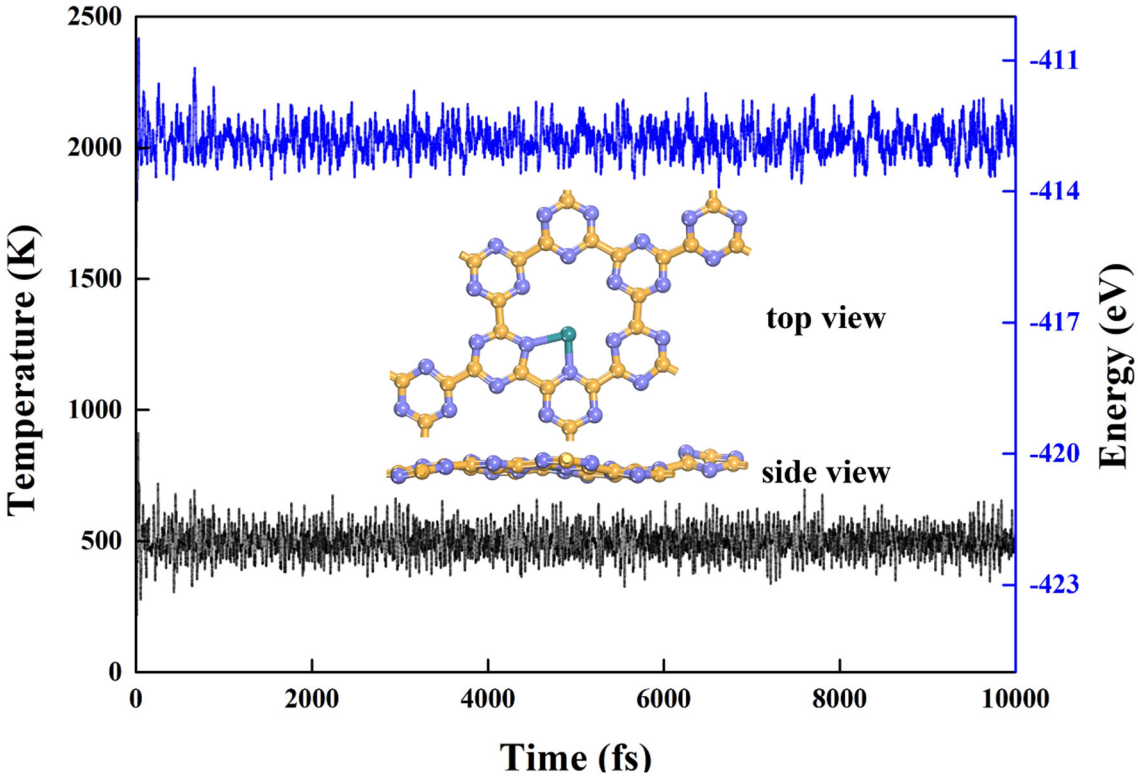
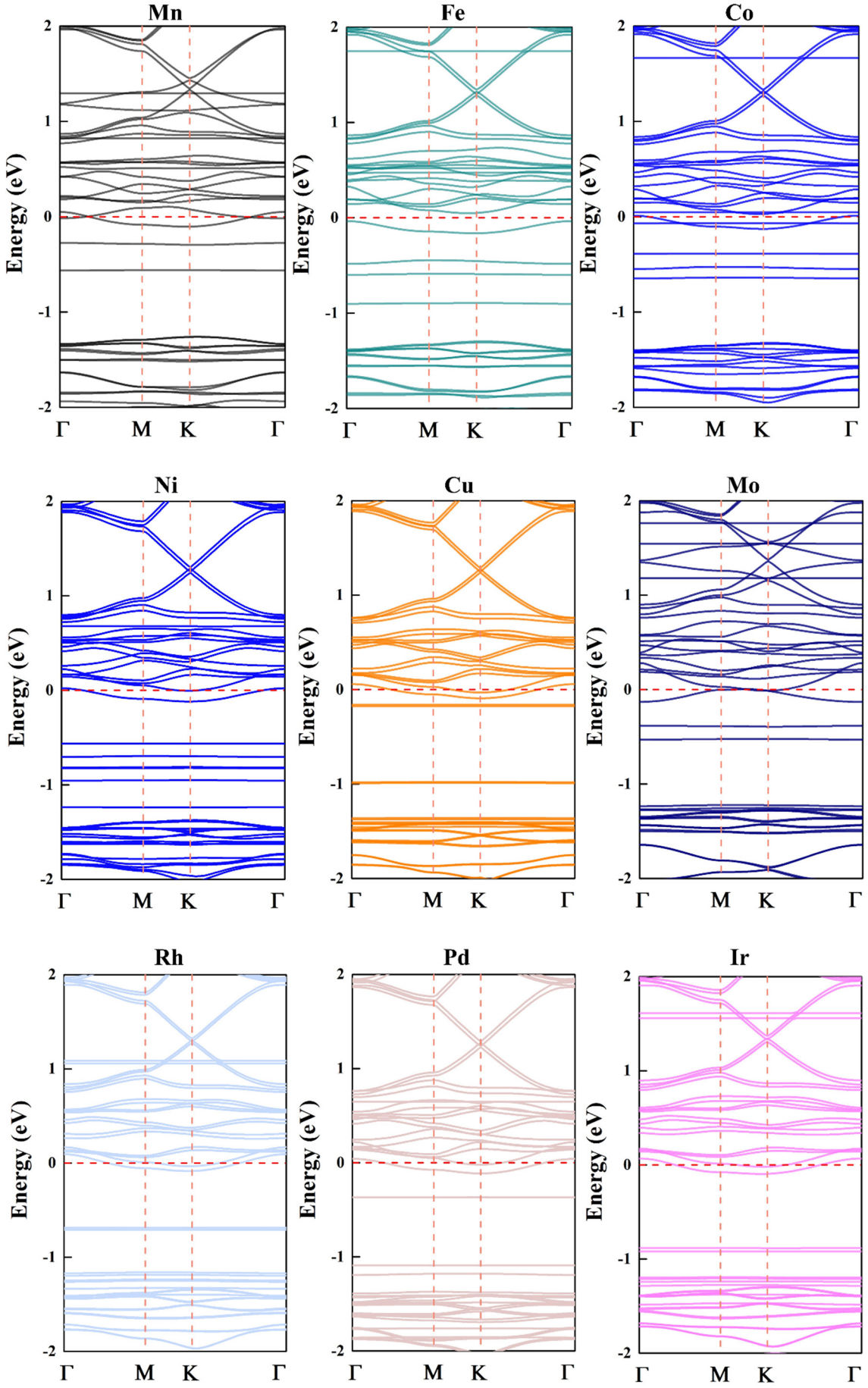


Figure S2. Variations of temperature and energy as a function of the time for AIMD simulations of Ru/g-CN; insert is top view of the snapshot of atomic configuration. The simulation is run under 500 K for 10 ps with a time step of 1 fs. Gray, blue and dark green spheres represent the C, N and Ru atoms, respectively.


Mn
Fe
Co
Ni
Cu
Mo
Rh
Pd
Ir
Energy (eV)
2
1
0
-1
-2
Γ
M
K
Γ

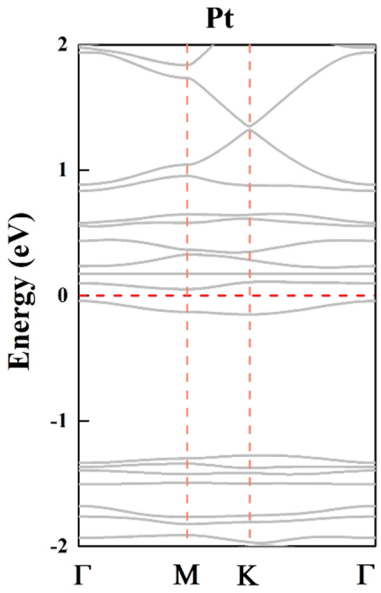


Figure S3. The band structure of all TM/g-CN which we considered.

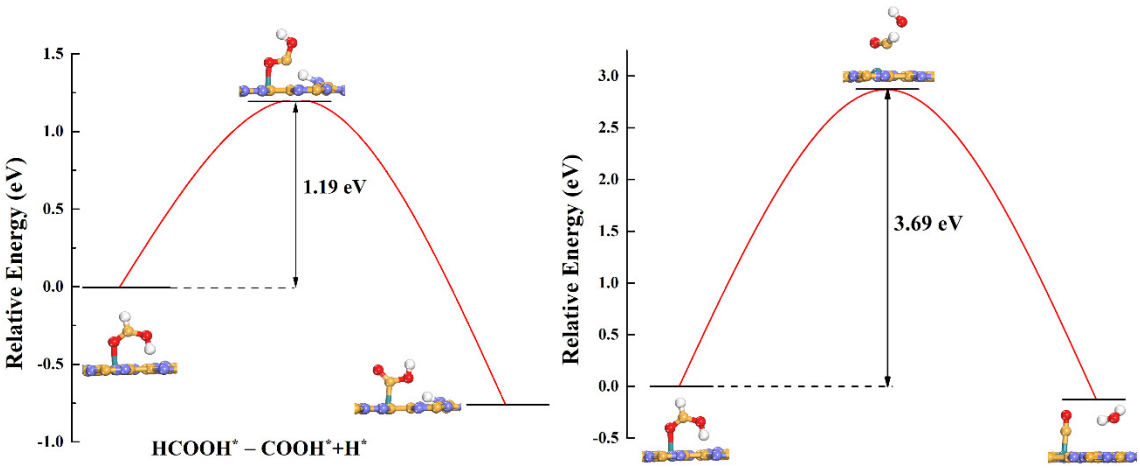


Figure S4. Energy barrier profiles for $HCOOH^{*}$– $COOH^{*}$ and $HCOOH^{*}$– $CO_2{}^{*}$ + H_2O on the Ru/g-CN.

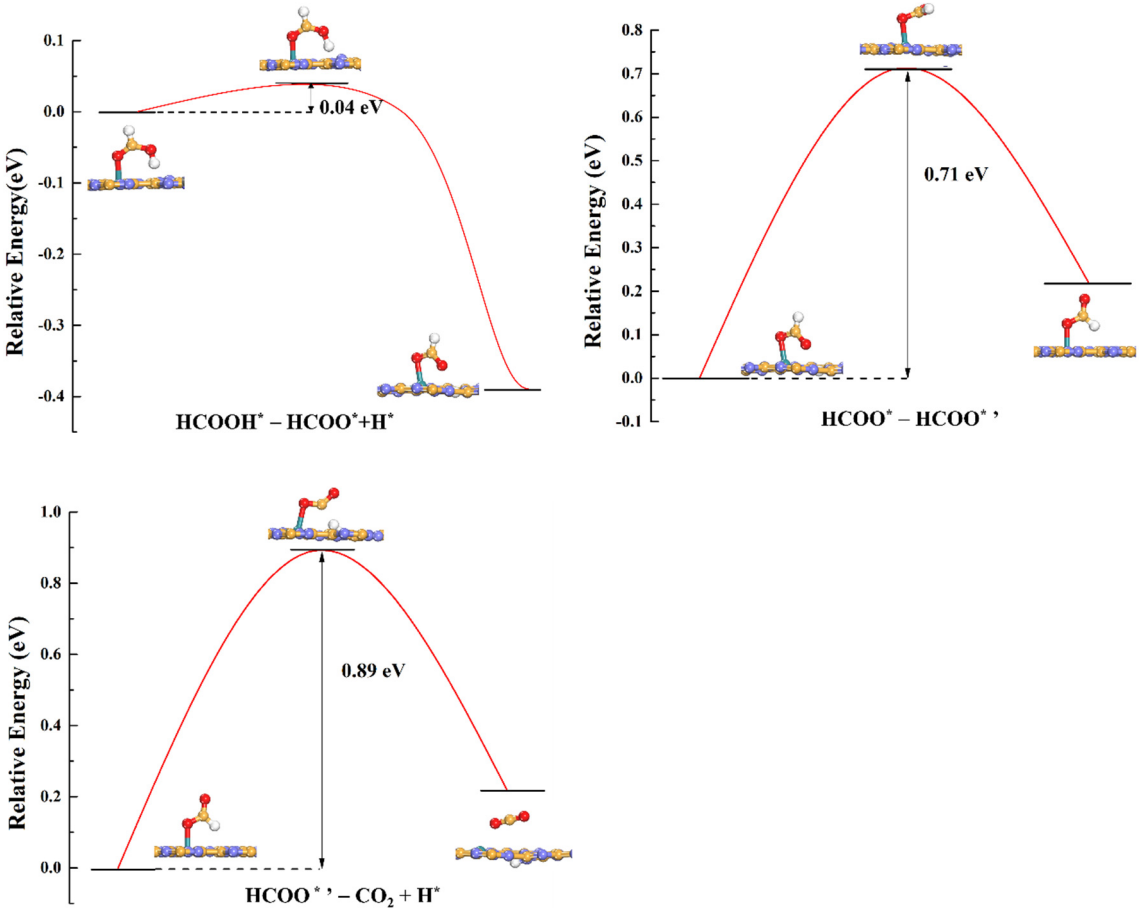
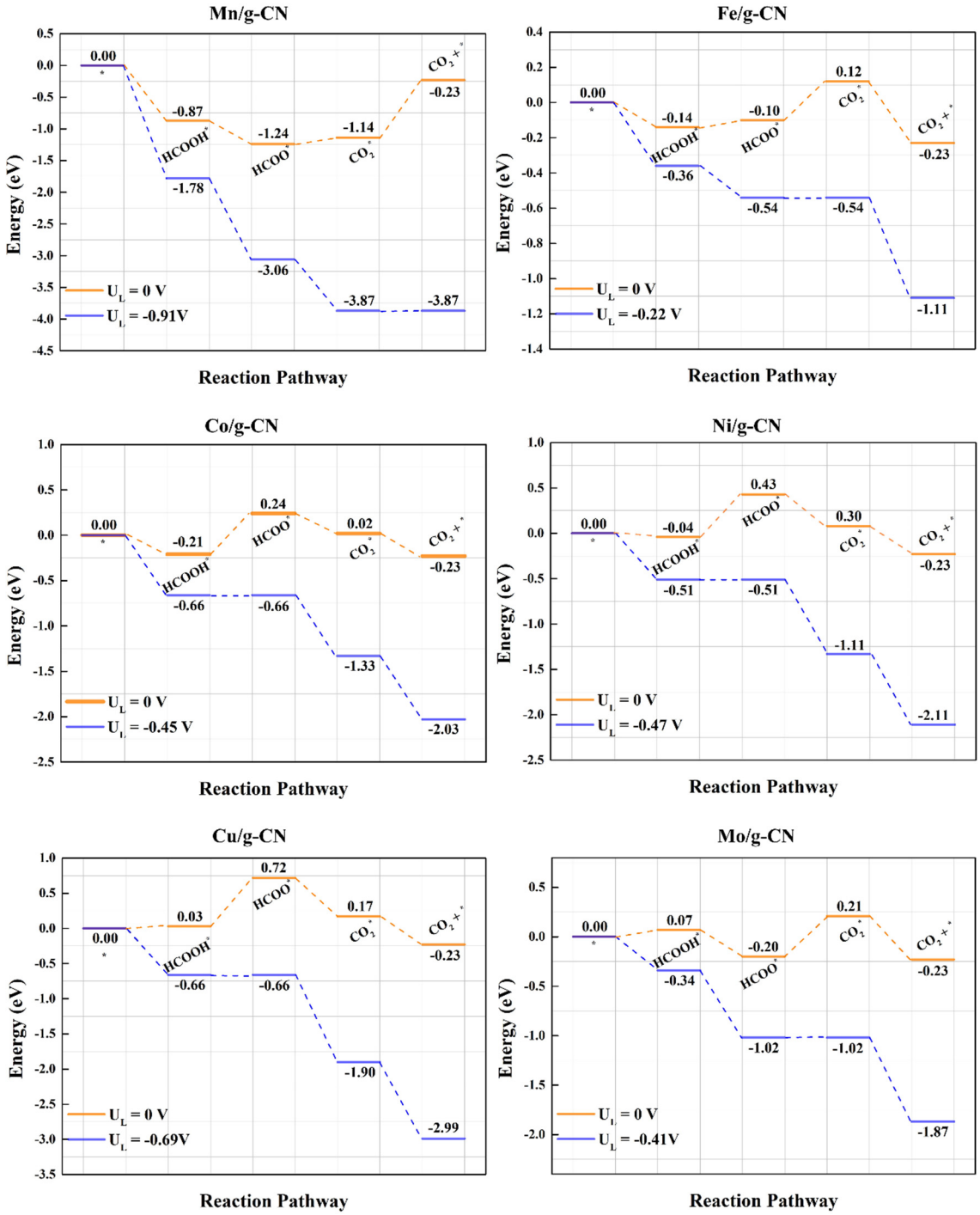


Figure S5. Energy barrier profiles for HCOOH decomposition on the Ru/g-CN.


Mn/g-CN
Energy (eV)
Reaction Pathway
0.00
-0.87
-1.24
-1.14
-0.23
-1.78
-3.06
-3.87
-3.87
HCOOH*
HCOO*
CO2*
CO2+*
U_L = 0 V
U_L = -0.91V
Fe/g-CN
Energy (eV)
Reaction Pathway
0.00
-0.14
-0.10
0.12
-0.23
-0.36
-0.54
-0.54
-1.11
HCOOH*
HCOO*
CO2*
CO2+*
U_L = 0 V
U_L = -0.22 V
Co/g-CN
Energy (eV)
Reaction Pathway
0.00
-0.21
0.24
0.02
-0.23
-0.66
-0.66
-1.33
-2.03
HCOOH*
HCOO*
CO2*
CO2+*
U_L = 0 V
U_L = -0.45 V
Ni/g-CN
Energy (eV)
Reaction Pathway
0.00
-0.04
0.43
0.30
-0.23
-0.51
-0.51
-1.11
-2.11
HCOOH*
HCOO*
CO2*
CO2+*
U_L = 0 V
U_L = -0.47 V
Cu/g-CN
Energy (eV)
Reaction Pathway
0.00
0.03
0.72
0.17
-0.23
-0.66
-0.66
-1.90
-2.99
HCOOH*
HCOO*
CO2*
CO2+*
U_L = 0 V
U_L = -0.69V
Mo/g-CN
Energy (eV)
Reaction Pathway
0.00
0.07
-0.20
0.21
-0.23
-0.34
-1.02
-1.02
-1.87
HCOOH*
HCOO*
CO2*
CO2+*
U_L = 0 V
U_L = -0.41V

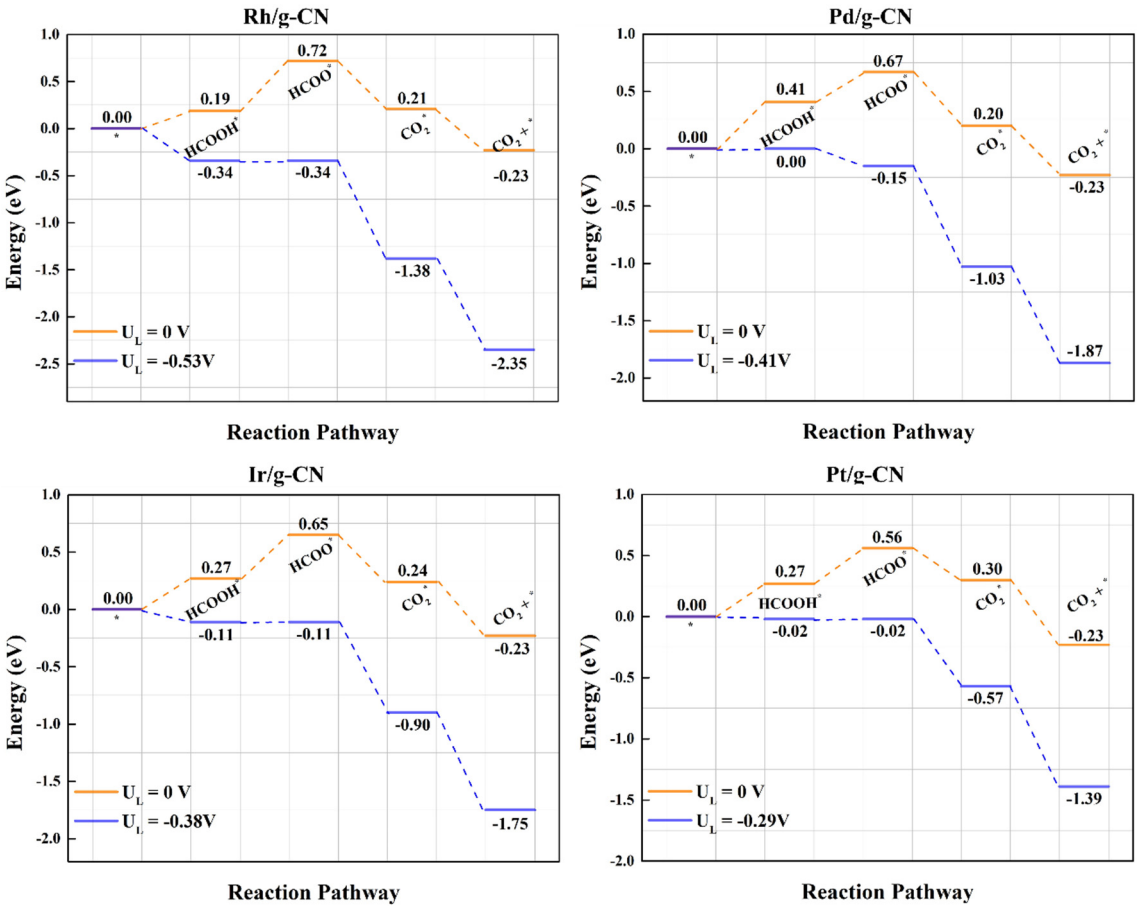


Figure S6. The free energy diagram of FAOR on TM/g-CN along direct pathway.