Supporting Information

Promising Ru-based cathode catalysts of Li-CO_2 batteries via single-atom alloying

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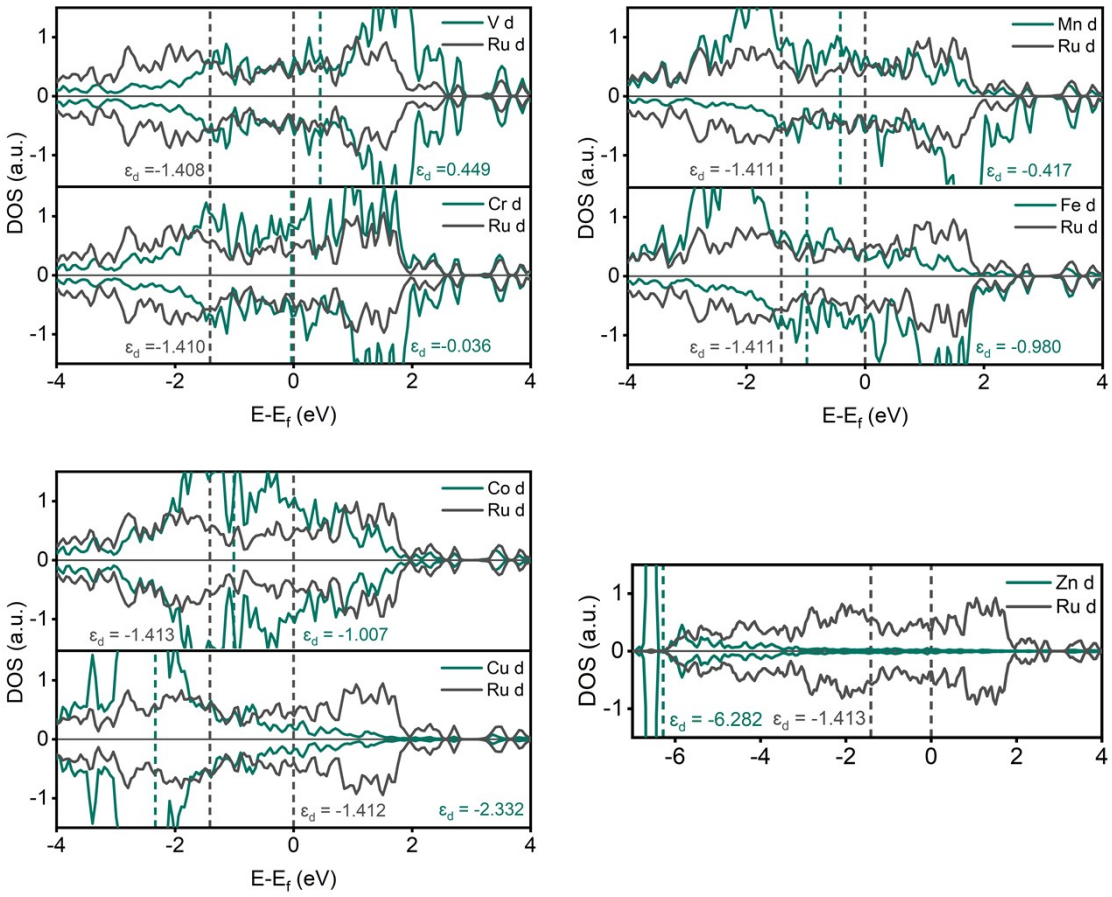

Figure S1. The DOS of VRu, CrRu, MnRu, FeRu, CoRu, CuRu and ZnRu.

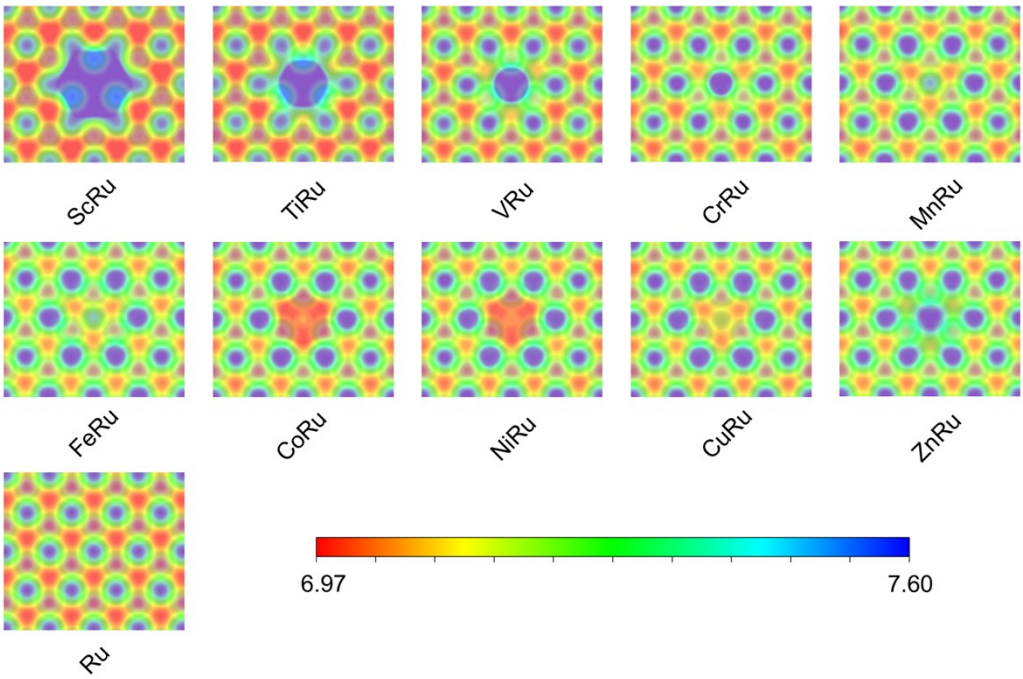

Figure S2. The surface electrostatic potential of MRu and Ru.

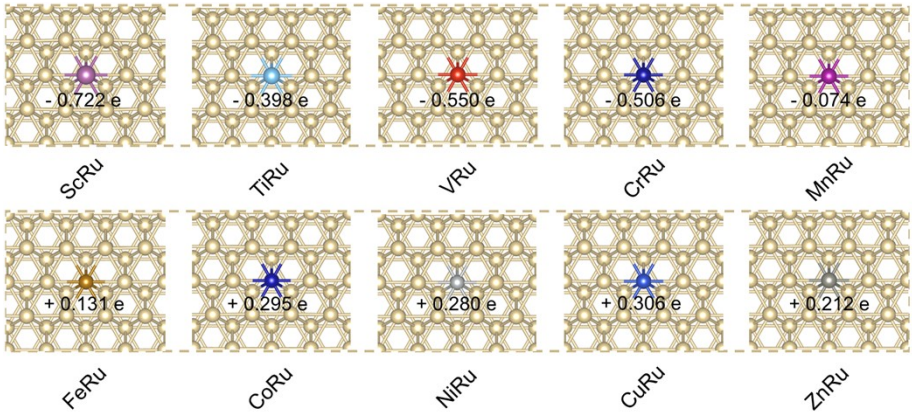

Figure S3. The Bader charge of 10 MRu, - and + represent the loss and gain of electrons by M, respectively.

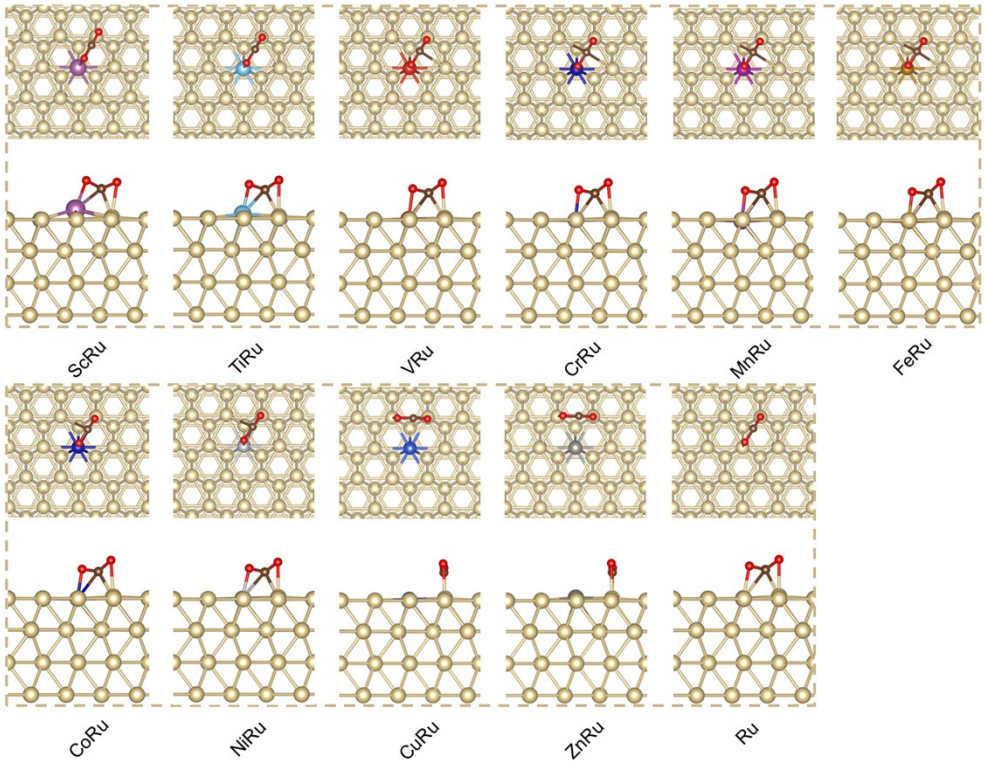

Figure S4. The optimized structures of CO_2 adsorption on M and Ru sites.

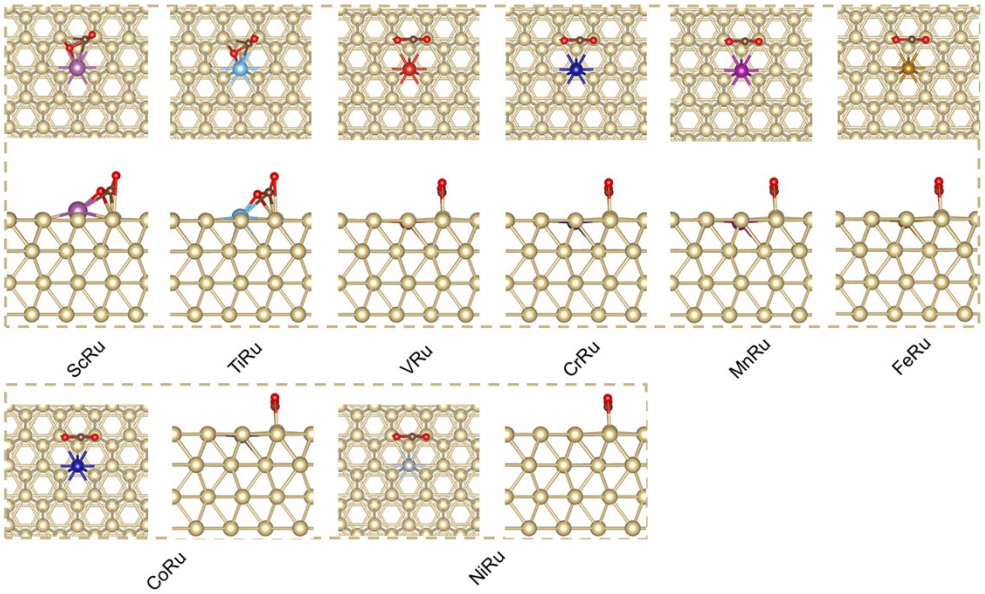

Figure S5. The optimized structures of CO_2 adsorption on two Ru sites.

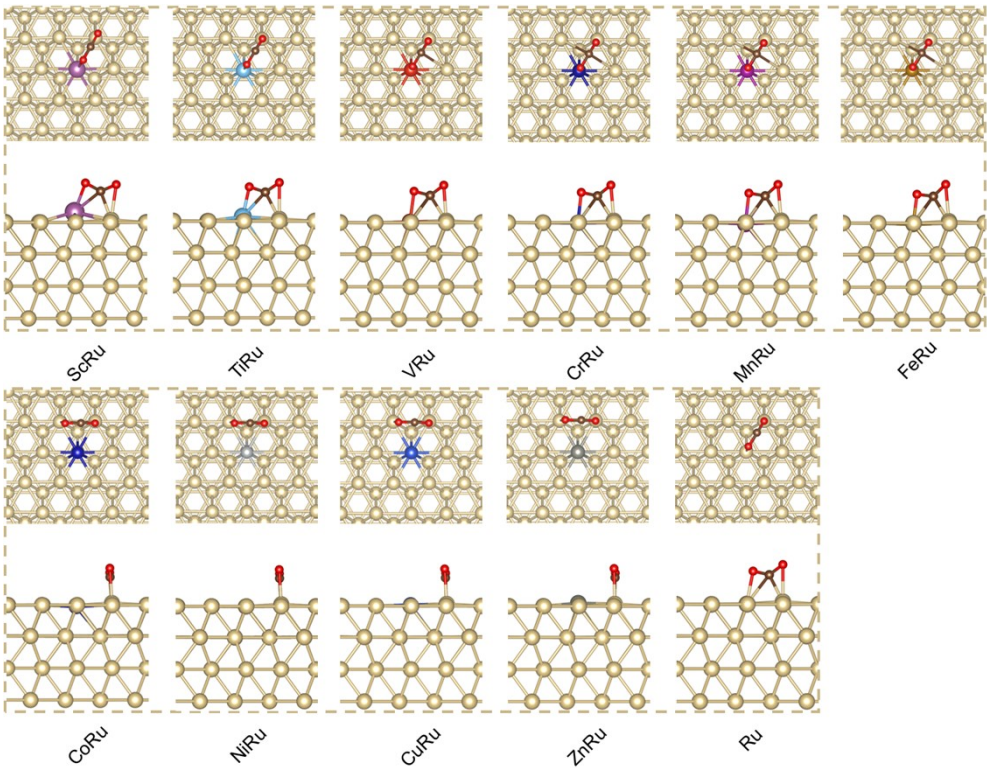

Figure S6. The best structures of CO_2 adsorbed on MRu and Ru.

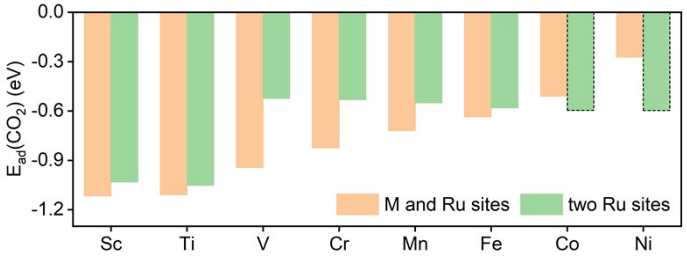

Figure S7. The $E_{ad}(CO_2)$ on M and Ru sites, and two Ru sites, respectively.

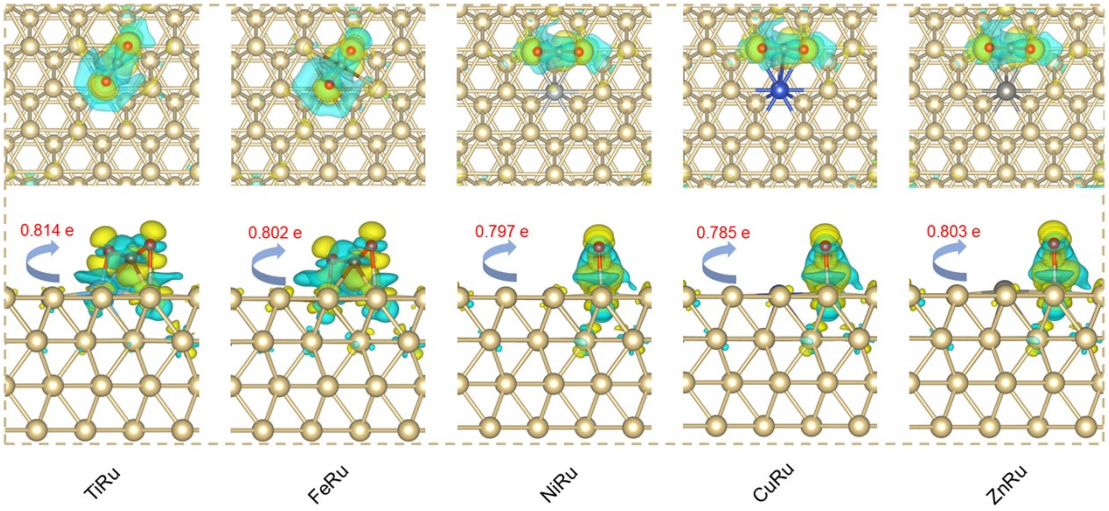

Figure S8. The charge density difference and Bader charge for CO_2 on TiRu, FeRu, NiRu, CuRu and ZnRu.

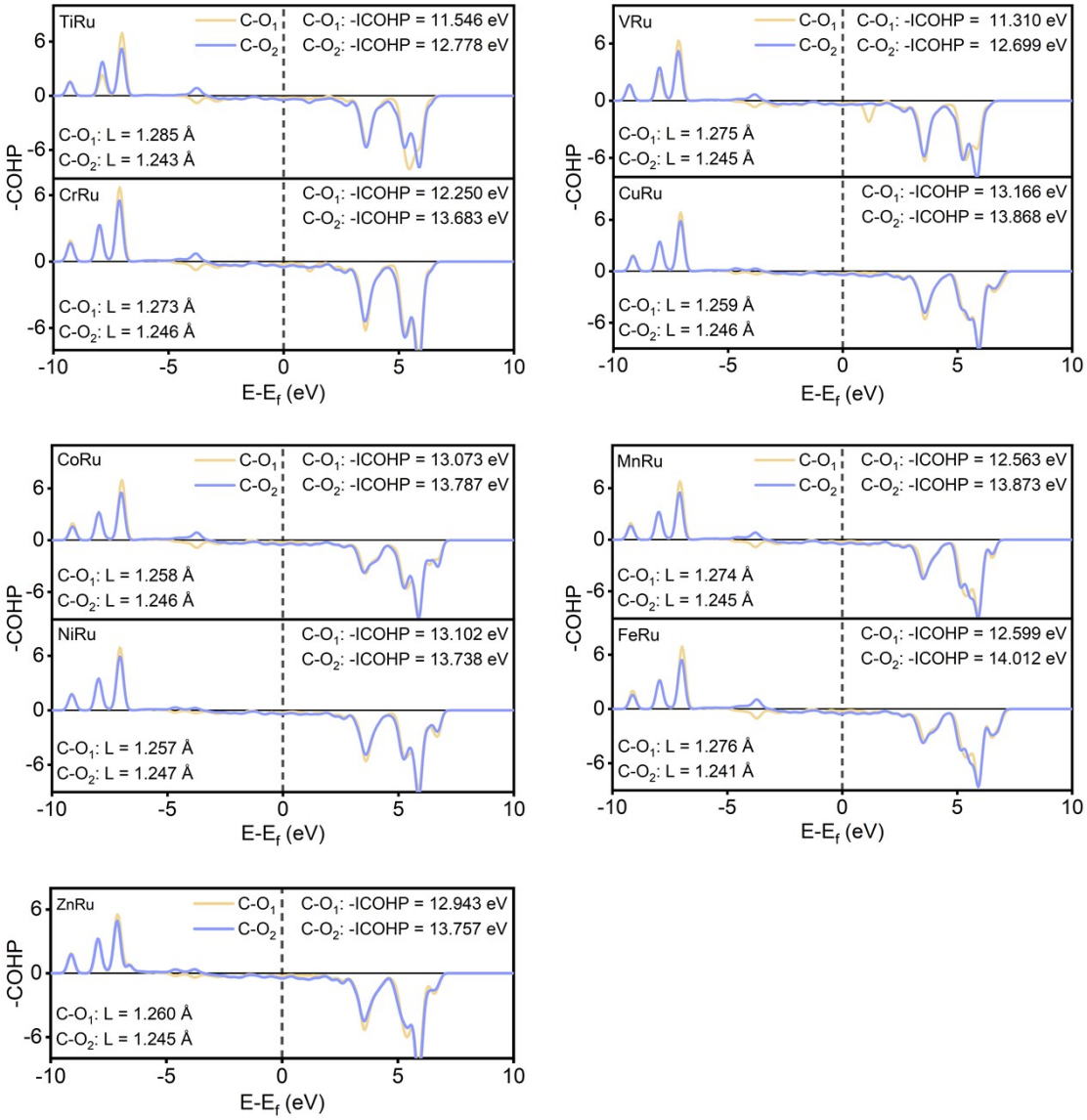

Figure S9. The -COHP of TiRu, CrRu, VRu, CuRu CoRu, NiRu, MnRu, FeRu and ZnRu for C-O bond of CO_2.

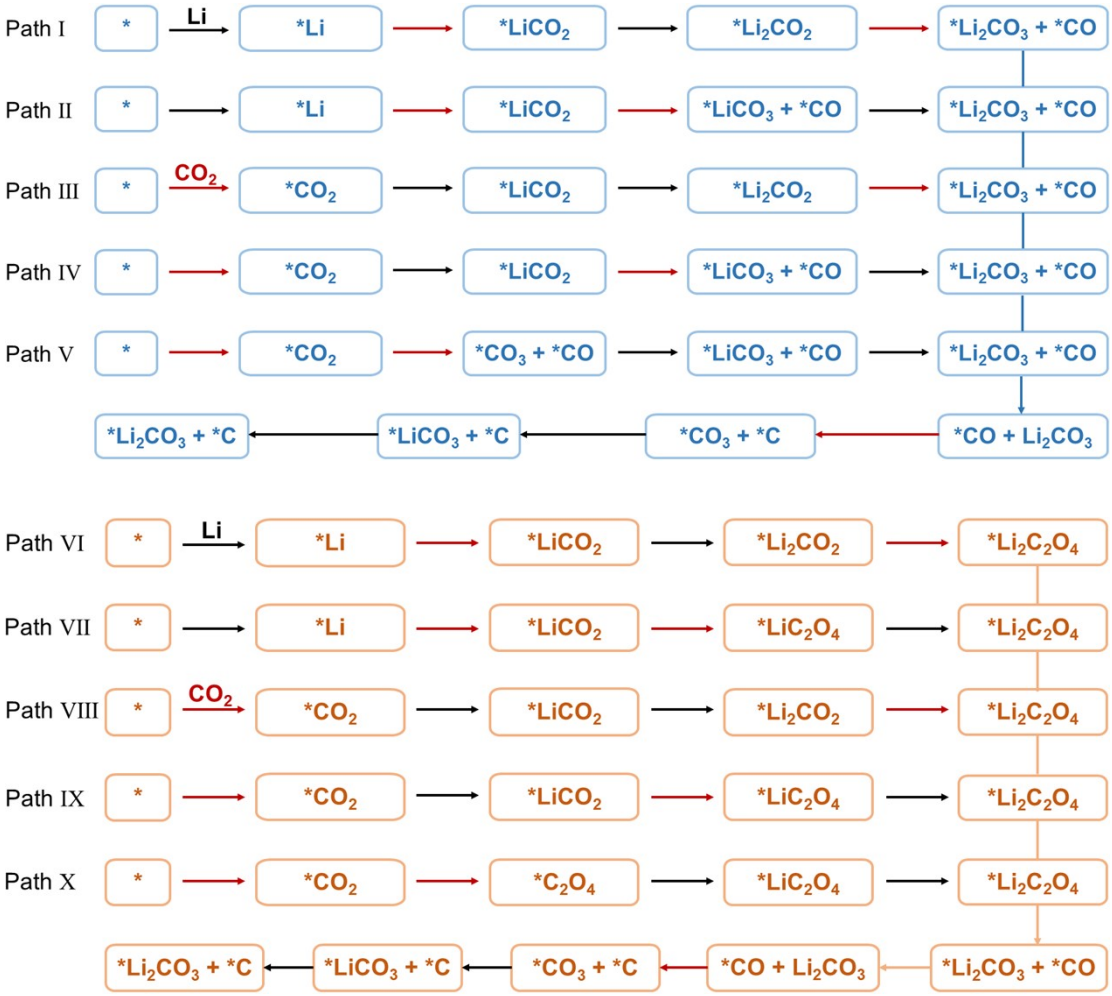

Figure S10. The conventional reaction pathway A of Li_2CO_3 + C, the reaction pathway B involving formation and decomposition of $Li_2C_2O_4$. (The black and red arrows represented the participation of Li and CO_2 in the reaction, respectively.)

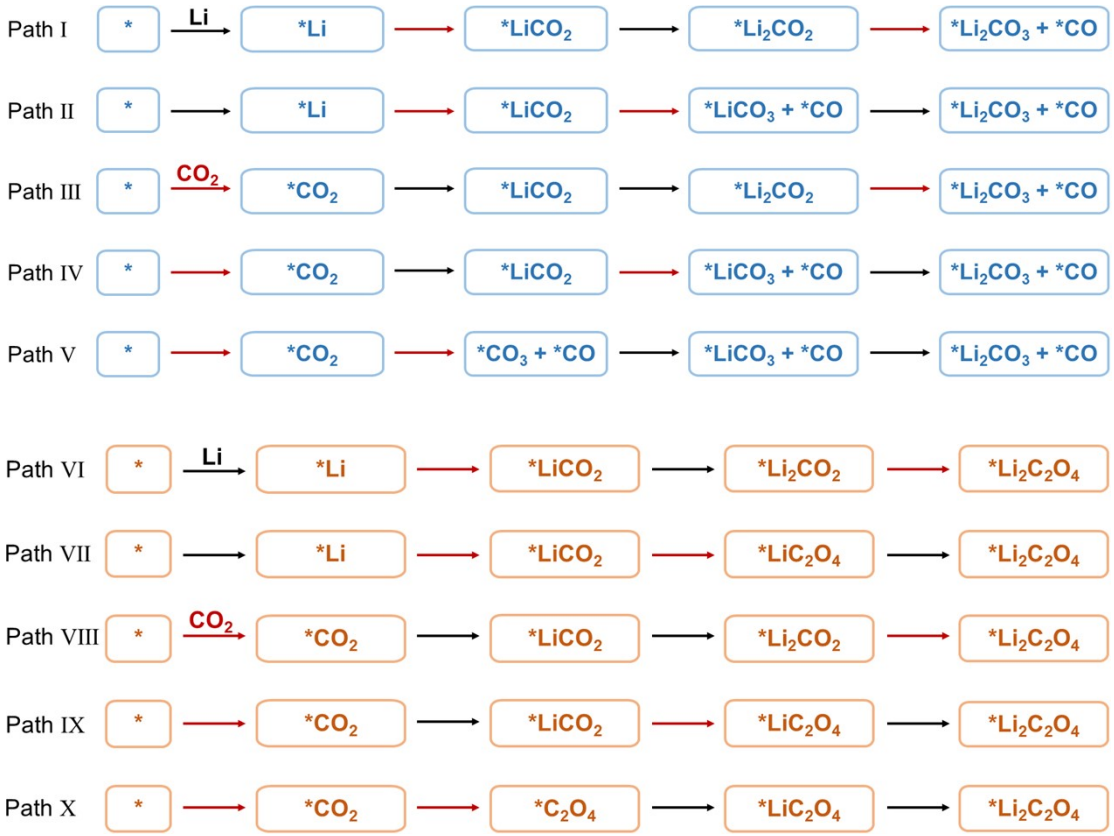

Figure S11. The reaction pathways of Li_2CO_3+CO and $Li_2C_2O_4$.

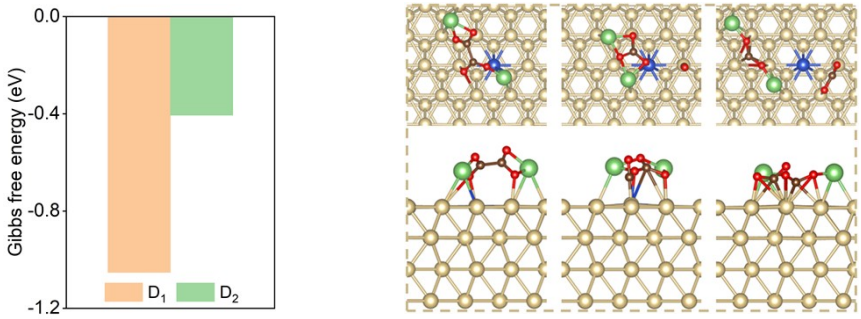

Figure S12. The Gibbs free energy change and structures of decomposition pathways (D_1 and D_2) of $Li_2C_2O_4$ on the CuRu.

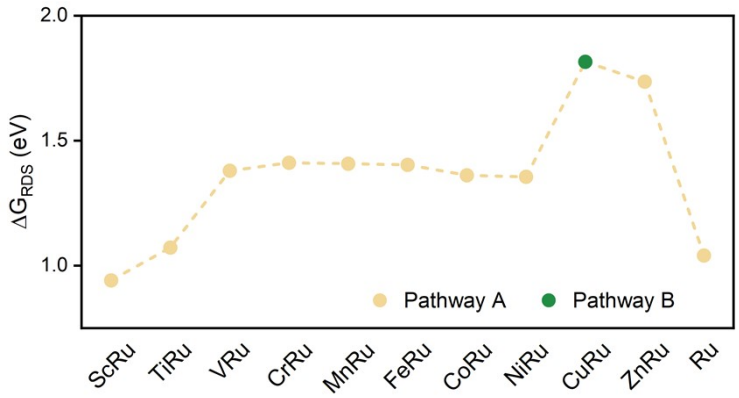

Figure S13. The Gibbs free energy change of the more favorable reaction pathways A or B during Li_2CO_3 formation at U = U_0 = 2.85 V on 11 catalysts.

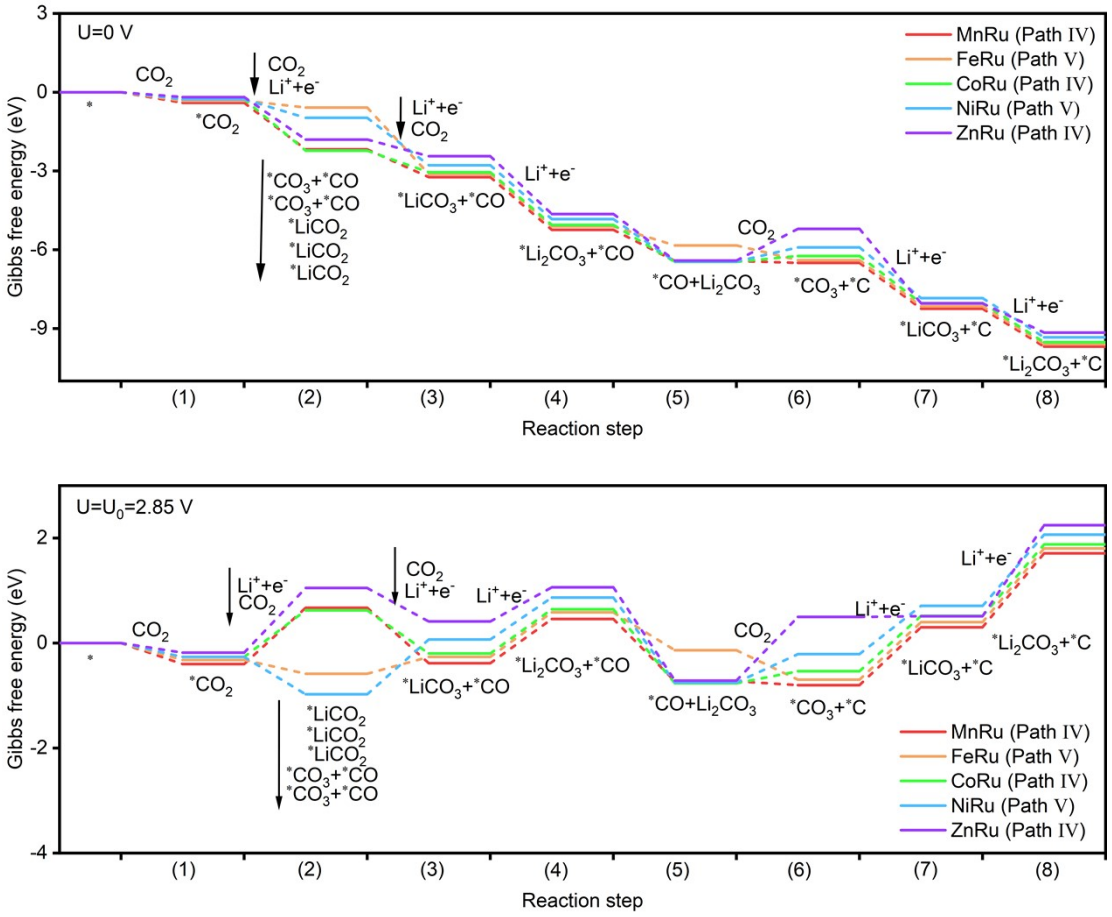

Figure S14. The Gibbs free energy change of the more favorable reaction pathway A during Li_2CO_3 formation at U = 0 and U = U_0 = 2.85V on MnRu, Feru, CoRu, NiRu and ZnRu.

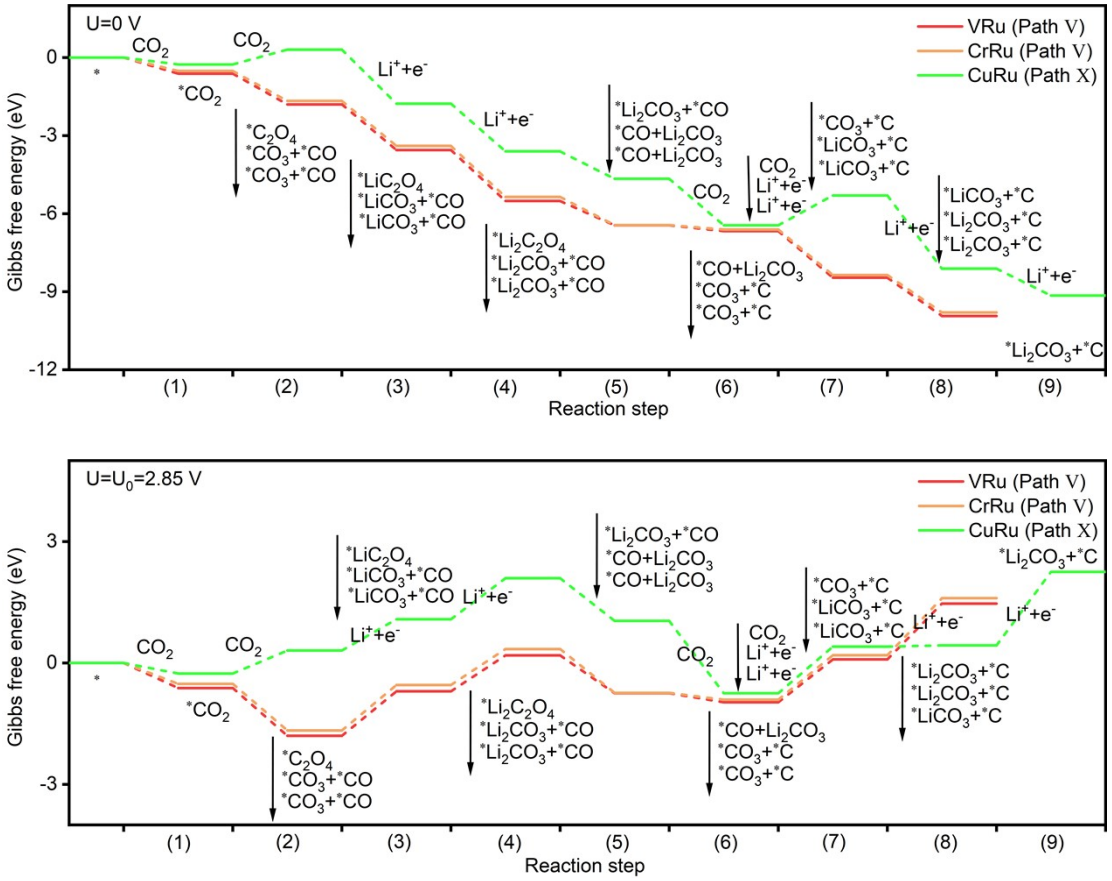

Figure S15. The Gibbs free energy change of the more favorable reaction pathway A or B during Li_2CO_3 formation at U = 0 and U = U_0 = 2.85 V on VRu, CrRu and CuRu.

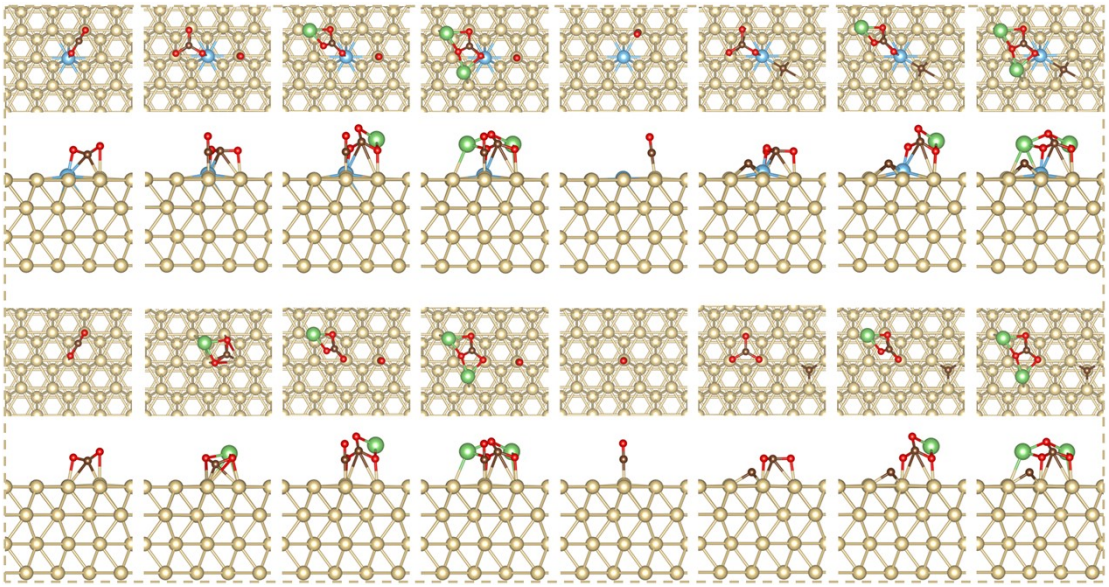

Figure S16. The structures of the more favorable reaction pathway A on TiRu and Ru.

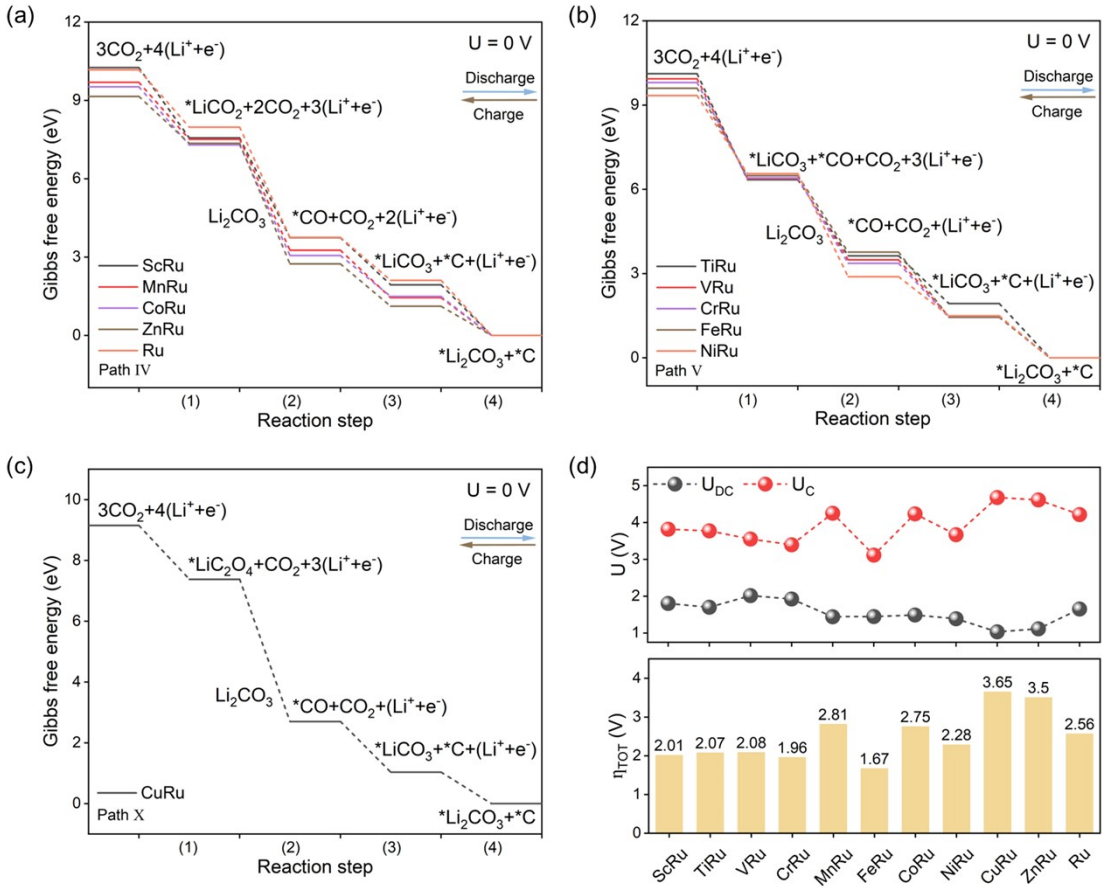

Figure S17. The Gibbs free energy change of the reaction pathway A during Li_2CO_3 formation at U = 0 V on 11 catalysts((a), (b) and (c)), (d) the U_{DC}, U_C and η_{TOT} on 11 catalysts.

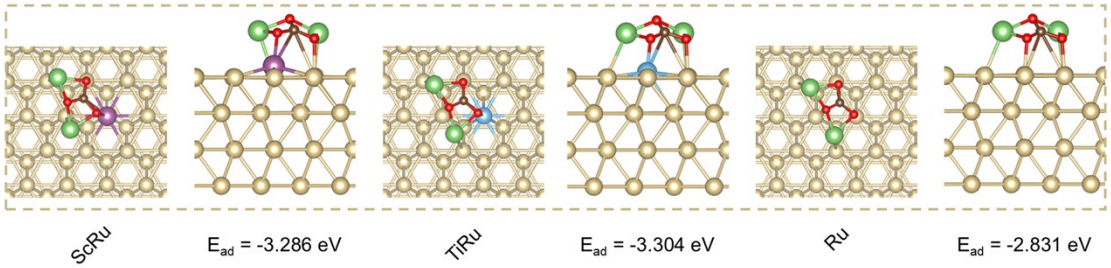

Figure S18. The optimized structures of Li_2CO_3 adsorbed on ScRu, TiRu and Ru.

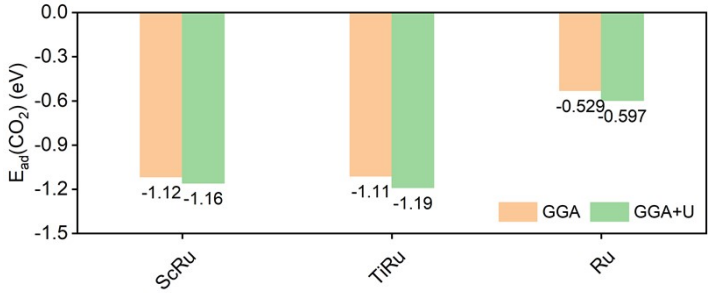

Figure S19. The $E_{ad}(CO_2)$ on ScRu, TiRu and Ru by adopting GGA and GGA+U calculations.

Table S1. The Gibbs free energy of reaction pathway A on the ScRu.

Reaction Step on ScRu	I	II	III	IV	V
(1) (U=0 V), ΔG (eV)	-1.169	-1.169	-0.770	-0.770	-0.770
(2) (U=0 V), ΔG (eV)	-1.522	-1.522	-1.921	-1.921	-1.118
(3) (U=0 V), ΔG (eV)	-1.590	-1.054	-1.590	-1.054	-1.857
(4) (U=0 V), ΔG (eV)	-1.448	-1.983	-1.448	-1.983	-1.983
(5) (U=0 V), ΔG (eV)	-0.780	-0.780	-0.780	-0.780	-0.780
(6) (U=0 V), ΔG (eV)	0.104	0.104	0.104	0.104	0.104
(7) (U=0 V), ΔG (eV)	-1.909	-1.909	-1.909	-1.909	-1.909
(8) (U=0 V), ΔG (eV)	-1.939	-1.939	-1.939	-1.939	-1.939
(1) (U=U_0 =2.85 V), ΔG (eV)	1.681	1.681	-0.770	-0.770	-0.770
(2) (U=U_0 =2.85 V), ΔG (eV)	-1.522	-1.522	0.929	**0.929**	-1.118
(3) (U=U_0 =2.85 V), ΔG (eV)	1.260	-1.054	1.260	-1.054	0.993
(4) (U=U_0 =2.85 V), ΔG (eV)	-1.448	0.867	-1.448	0.867	0.867
(5) (U=U_0 =2.85 V), ΔG (eV)	-0.780	-0.780	-0.780	-0.780	-0.780
(6) (U=U_0 =2.85 V), ΔG (eV)	0.104	0.104	0.104	0.104	0.104
(7) (U=U_0 =2.85V), ΔG (eV)	0.941	0.941	0.941	**0.941**	0.941
(8) (U=U_0 =2.85 V), ΔG (eV)	0.911	0.911	0.911	0.911	0.911

Table S2. The Gibbs free energy of reaction pathway A on the TiRu.

Reaction Step on TiRu	I	II	III	IV	V
(1) (U=0 V), ΔG (eV)	-1.182	-1.182	-0.774	-0.774	-0.774
(2) (U=0 V), ΔG (eV)	-0.578	-0.578	-0.987	-0.987	-1.221
(3) (U=0 V), ΔG (eV)	-2.400	-2.013	-2.400	-2.013	-1.778
(4) (U=0 V), ΔG (eV)	-1.564	-1.951	-1.564	-1.951	-1.951
(5) (U=0 V), ΔG (eV)	-0.759	-0.759	-0.759	-0.759	-0.759
(6) (U=0 V), ΔG (eV)	0.126	0.126	0.126	0.126	0.126
(7) (U=0 V), ΔG (eV)	-1.824	-1.824	-1.824	-1.824	-1.824
(8) (U=0 V), ΔG (eV)	-1.931	-1.931	-1.931	-1.931	-1.931
(1) (U=U_0 =2.85 V), ΔG (eV)	1.668	1.668	-0.774	-0.774	-0.774
(2) (U=U_0 =2.85 V), ΔG (eV)	-0.578	-0.578	1.863	1.863	-1.221
(3) (U=U_0 =2.85 V), ΔG (eV)	0.450	-2.013	0.450	-2.013	**1.072**
(4) (U=U_0 =2.85 V), ΔG (eV)	-1.564	0.899	-1.564	0.899	0.899
(5) (U=U_0 =2.85 V), ΔG (eV)	-0.759	-0.759	-0.759	-0.759	-0.759
(6) (U=U_0 =2.85 V), ΔG (eV)	0.126	0.126	0.126	0.126	0.126
(7) (U=U_0 =2.85V), ΔG (eV)	1.026	1.026	1.026	1.026	1.026
(8) (U=U_0 =2.85 V), ΔG (eV)	0.919	0.919	0.919	0.919	0.919

Table S3. The Gibbs free energy of reaction pathway A on the VRu.

Reaction Step on VRu	I	II	III	IV	V
(1) (U=0 V), ΔG (eV)	-1.025	-1.025	-0.619	-0.619	-0.619
(2) (U=0 V), ΔG (eV)	-0.899	-0.899	-1.305	-1.305	-1.181
(3) (U=0 V), ΔG (eV)	-2.070	-1.628	-2.070	-1.628	-1.752
(4) (U=0 V), ΔG (eV)	-1.519	-1.961	-1.519	-1.961	-1.961
(5) (U=0 V), ΔG (eV)	-0.935	-0.935	-0.935	-0.935	-0.935
(6) (U=0 V), ΔG (eV)	-0.223	-0.223	-0.223	-0.223	-0.223
(7) (U=0 V), ΔG (eV)	-1.792	-1.792	-1.792	-1.792	-1.792
(8) (U=0 V), ΔG (eV)	-1.470	-1.470	-1.470	-1.470	-1.470
(1) (U=U_0 =2.85 V), ΔG (eV)	1.825	1.825	-0.619	-0.619	-0.619
(2) (U=U_0 =2.85 V), ΔG (eV)	-0.899	-0.899	1.545	1.545	-1.181
(3) (U=U_0 =2.85 V), ΔG (eV)	0.780	-1.628	0.780	-1.628	**1.098**
(4) (U=U_0 =2.85 V), ΔG (eV)	-1.519	0.889	-1.519	0.889	0.889
(5) (U=U_0 =2.85 V), ΔG (eV)	-0.935	-0.935	-0.935	-0.935	-0.935
(6) (U=U_0 =2.85 V), ΔG (eV)	-0.223	-0.223	-0.223	-0.223	-0.223
(7) (U=U_0 =2.85V), ΔG (eV)	1.058	1.058	1.058	1.058	1.058
(8) (U=U_0 =2.85 V), ΔG (eV)	1.380	1.380	1.380	1.380	**1.380**

Table S4. The Gibbs free energy of reaction pathway A on the CrRu.

Reaction Step on CrRu	I	II	III	IV	V
(1) (U=0 V), ΔG (eV)	-1.086	-1.086	-0.515	-0.515	-0.515
(2) (U=0 V), ΔG (eV)	-0.991	-0.991	-1.563	-1.563	-1.153
(3) (U=0 V), ΔG (eV)	-1.895	-1.316	-1.895	-1.316	-1.726
(4) (U=0 V), ΔG (eV)	-1.383	-1.962	-1.383	-1.962	-1.962
(5) (U=0 V), ΔG (eV)	-1.081	-1.081	-1.081	-1.081	-1.081
(6) (U=0 V), ΔG (eV)	-0.171	-0.171	-0.171	-0.171	-0.171
(7) (U=0 V), ΔG (eV)	-1.751	-1.751	-1.751	-1.751	-1.751
(8) (U=0 V), ΔG (eV)	-1.439	-1.439	-1.439	-1.439	-1.439
(1) (U=U_0 =2.85 V), ΔG (eV)	1.764	1.764	-0.515	-0.515	-0.515
(2) (U=U_0 =2.85 V), ΔG (eV)	-0.991	-0.991	1.287	1.287	-1.153
(3) (U=U_0 =2.85 V), ΔG (eV)	0.955	-1.316	0.955	-1.316	**1.124**
(4) (U=U_0 =2.85 V), ΔG (eV)	-1.383	0.888	-1.383	0.888	0.888
(5) (U=U_0 =2.85 V), ΔG (eV)	-1.081	-1.081	-1.081	-1.081	-1.081
(6) (U=U_0 =2.85 V), ΔG (eV)	-0.171	-0.171	-0.171	-0.171	-0.171
(7) (U=U_0 =2.85V), ΔG (eV)	1.099	1.099	1.099	1.099	1.099
(8) (U=U_0 =2.85 V), ΔG (eV)	1.411	1.411	1.411	1.411	**1.411**

Table S5. The Gibbs free energy of reaction pathway A on the MnRu.

Reaction Step on MnRu	I	II	III	IV	V
(1) (U=0 V), ΔG (eV)	-1.177	-1.177	-0.401	-0.401	-0.401
(2) (U=0 V), ΔG (eV)	-1.000	-1.000	-1.776	-1.776	-1.117
(3) (U=0 V), ΔG (eV)	-1.883	-1.057	-1.883	-1.057	-1.716
(4) (U=0 V), ΔG (eV)	-1.182	-2.008	-1.182	-2.008	-2.008
(5) (U=0 V), ΔG (eV)	-1.187	-1.187	-1.187	-1.187	-1.187
(6) (U=0 V), ΔG (eV)	-0.071	-0.071	-0.071	-0.071	-0.071
(7) (U=0 V), ΔG (eV)	-1.748	-1.748	-1.748	-1.748	-1.748
(8) (U=0 V), ΔG (eV)	-1.442	-1.442	-1.442	-1.442	-1.442
(1) (U=U_0 =2.85 V), ΔG (eV)	1.673	1.673	-0.401	-0.401	-0.401
(2) (U=U_0 =2.85 V), ΔG (eV)	-1.000	-1.000	1.074	**1.074**	-1.117
(3) (U=U_0 =2.85 V), ΔG (eV)	0.967	-1.057	0.967	-1.057	1.134
(4) (U=U_0 =2.85 V), ΔG (eV)	-1.182	0.842	-1.182	0.842	0.842
(5) (U=U_0 =2.85 V), ΔG (eV)	-1.187	-1.187	-1.187	-1.187	-1.187
(6) (U=U_0 =2.85 V), ΔG (eV)	-0.071	-0.071	-0.071	-0.071	-0.071
(7) (U=U_0 =2.85V), ΔG (eV)	1.102	1.102	1.102	1.102	1.102
(8) (U=U_0 =2.85 V), ΔG (eV)	1.408	1.408	1.408	**1.408**	1.408

Table S6. The Gibbs free energy of reaction pathway A on the FeRu.

Reaction Step on FeRu	I	II	III	IV	V
(1) (U=0 V), ΔG (eV)	-1.231	-1.231	-0.322	-0.322	-0.322
(2) (U=0 V), ΔG (eV)	-1.004	-1.004	-1.914	-1.914	-0.263
(3) (U=0 V), ΔG (eV)	-1.832	-0.879	-1.832	-0.879	-2.530
(4) (U=0 V), ΔG (eV)	-1.047	-2.000	-1.047	-2.000	-2.000
(5) (U=0 V), ΔG (eV)	-0.722	-0.722	-0.722	-0.722	-0.722
(6) (U=0 V), ΔG (eV)	-0.560	-0.560	-0.560	-0.560	-0.560
(7) (U=0 V), ΔG (eV)	-1.755	-1.755	-1.755	-1.755	-1.755
(8) (U=0 V), ΔG (eV)	-1.447	-1.447	-1.447	-1.447	-1.447
(1) (U=U_0 =2.85 V), ΔG (eV)	1.619	1.619	-0.322	-0.322	-0.322
(2) (U=U_0 =2.85 V), ΔG (eV)	-1.004	-1.004	0.936	0.936	-0.263
(3) (U=U_0 =2.85 V), ΔG (eV)	1.018	-0.879	1.018	-0.879	0.320
(4) (U=U_0 =2.85 V), ΔG (eV)	-1.047	0.850	-1.047	0.850	**0.850**
(5) (U=U_0 =2.85 V), ΔG (eV)	-0.722	-0.722	-0.722	-0.722	-0.722
(6) (U=U_0 =2.85 V), ΔG (eV)	-0.560	-0.560	-0.560	-0.560	-0.560
(7) (U=U_0 =2.85V), ΔG (eV)	1.095	1.095	1.095	1.095	1.095
(8) (U=U_0 =2.85 V), ΔG (eV)	1.403	1.403	1.403	1.403	**1.403**

Table S7. The Gibbs free energy of reaction pathway A on the CoRu.

Reaction Step on CoRu	I	II	III	IV	V
(1) (U=0 V), ΔG (eV)	-1.281	-1.281	-0.264	-0.264	-0.264
(2) (U=0 V), ΔG (eV)	-0.946	-0.946	-1.963	-1.963	-0.991
(3) (U=0 V), ΔG (eV)	-1.655	-0.820	-1.655	-0.820	-1.792
(4) (U=0 V), ΔG (eV)	-1.174	-2.010	-1.174	-2.010	-2.010
(5) (U=0 V), ΔG (eV)	-1.408	-1.408	-1.408	-1.408	-1.408
(6) (U=0 V), ΔG (eV)	0.228	0.228	0.228	0.228	0.228
(7) (U=0 V), ΔG (eV)	-1.796	-1.796	-1.796	-1.796	-1.796
(8) (U=0 V), ΔG (eV)	-1.489	-1.489	-1.489	-1.489	-1.489
(1) (U=U_0 =2.85 V), ΔG (eV)	1.569	1.569	-0.264	-0.264	-0.264
(2) (U=U_0 =2.85 V), ΔG (eV)	-0.946	-0.946	0.887	**0.887**	-0.991
(3) (U=U_0 =2.85 V), ΔG (eV)	1.195	-0.820	1.195	-0.820	1.058
(4) (U=U_0 =2.85 V), ΔG (eV)	-1.174	0.840	-1.174	0.840	0.840
(5) (U=U_0 =2.85 V), ΔG (eV)	-1.408	-1.408	-1.408	-1.408	-1.408
(6) (U=U_0 =2.85 V), ΔG (eV)	0.228	0.228	0.228	0.228	0.228
(7) (U=U_0 =2.85V), ΔG (eV)	1.054	1.054	1.054	1.054	1.054
(8) (U=U_0 =2.85 V), ΔG (eV)	1.361	1.361	1.361	**1.361**	1.361

Table S8. The Gibbs free energy of reaction pathway A on the NiRu.

Reaction Step on NiRu	I	II	III	IV	V
(1) (U=0 V), ΔG (eV)	-1.253	-1.253	-0.264	-0.264	-0.264
(2) (U=0 V), ΔG (eV)	-0.775	-0.775	-1.765	-1.765	-0.711
(3) (U=0 V), ΔG (eV)	-1.639	-0.752	-1.639	-0.752	-1.806
(4) (U=0 V), ΔG (eV)	-1.166	-2.053	-1.166	-2.053	-2.053
(5) (U=0 V), ΔG (eV)	-1.618	-1.618	-1.618	-1.618	-1.618
(6) (U=0 V), ΔG (eV)	0.541	0.541	0.541	0.541	0.541
(7) (U=0 V), ΔG (eV)	-1.930	-1.930	-1.930	-1.930	-1.930
(8) (U=0 V), ΔG (eV)	-1.495	-1.495	-1.495	-1.495	-1.495
(1) ($U=U_0$ =2.85 V), ΔG (eV)	1.597	1.597	-0.264	-0.264	-0.264
(2) ($U=U_0$ =2.85 V), ΔG (eV)	-0.775	-0.775	1.085	1.085	-0.711
(3) ($U=U_0$ =2.85 V), ΔG (eV)	1.211	-0.752	1.211	-0.752	**1.044**
(4) ($U=U_0$ =2.85 V), ΔG (eV)	-1.166	0.797	-1.166	0.797	0.797
(5) ($U=U_0$ =2.85 V), ΔG (eV)	-1.618	-1.618	-1.618	-1.618	-1.618
(6) ($U=U_0$ =2.85 V), ΔG (eV)	0.541	0.541	0.541	0.541	0.541
(7) ($U=U_0$ =2.85V), ΔG (eV)	0.920	0.920	0.920	0.920	0.920
(8) ($U=U_0$ =2.85 V), ΔG (eV)	1.355	1.355	1.355	1.355	**1.355**

Table S9. The Gibbs free energy of reaction pathway A on the CuRu.

Reaction Step on CuRu	I	II	III	IV	V
(1) (U=0 V), ΔG (eV)	-1.142	-1.142	-0.261	-0.261	-0.261
(2) (U=0 V), ΔG (eV)	-0.678	-0.678	-1.559	-1.559	-0.699
(3) (U=0 V), ΔG (eV)	-1.589	-1.324	-1.589	-1.324	-2.184
(4) (U=0 V), ΔG (eV)	-1.250	-1.515	-1.250	-1.515	-1.515
(5) (U=0 V), ΔG (eV)	-1.790	-1.790	-1.790	-1.790	-1.790
(6) (U=0 V), ΔG (eV)	1.151	1.151	1.151	1.151	1.151
(7) (U=0 V), ΔG (eV)	-2.817	-2.817	-2.817	-2.817	-2.817
(8) (U=0 V), ΔG (eV)	-1.034	-1.034	-1.034	-1.034	-1.034
(1) ($U=U_0$ =2.85 V), ΔG (eV)	1.708	1.708	-0.261	-0.261	-0.261
(2) ($U=U_0$ =2.85 V), ΔG (eV)	-0.678	-0.678	**1.291**	1.291	-0.699
(3) ($U=U_0$ =2.85 V), ΔG (eV)	1.261	-1.324	1.261	-1.324	0.666
(4) ($U=U_0$ =2.85 V), ΔG (eV)	-1.250	1.335	-1.250	1.335	1.335
(5) ($U=U_0$ =2.85 V), ΔG (eV)	-1.790	-1.790	-1.790	-1.790	-1.790
(6) ($U=U_0$ =2.85 V), ΔG (eV)	1.151	1.151	1.151	1.151	1.151
(7) ($U=U_0$ =2.85V), ΔG (eV)	0.033	0.033	0.033	0.033	0.033
(8) ($U=U_0$ =2.85 V), ΔG (eV)	1.816	1.816	1.816	1.816	**1.816**

Table S10. The Gibbs free energy of reaction pathway A on the ZnRu.

Reaction Step on ZnRu	I	II	III	IV	V
(1) (U=0 V), ΔG (eV)	-1.007	-1.007	-0.184	-0.184	-0.184
(2) (U=0 V), ΔG (eV)	-0.794	-0.794	-1.617	-1.617	-0.682
(3) (U=0 V), ΔG (eV)	-1.508	-0.637	-1.508	-0.637	-1.572
(4) (U=0 V), ΔG (eV)	-1.328	-2.199	-1.328	-2.199	-2.199
(5) (U=0 V), ΔG (eV)	-1.778	-1.778	-1.778	-1.778	-1.778
(6) (U=0 V), ΔG (eV)	1.212	1.212	1.212	1.212	1.212
(7) (U=0 V), ΔG (eV)	-2.836	-2.836	-2.836	-2.836	-2.836
(8) (U=0 V), ΔG (eV)	-1.114	-1.114	-1.114	-1.114	-1.114
(1) (U=U_0 =2.85 V), ΔG (eV)	1.843	1.843	-0.184	-0.184	-0.184
(2) (U=U_0 =2.85 V), ΔG (eV)	-0.794	-0.794	1.233	**1.233**	-0.682
(3) (U=U_0 =2.85 V), ΔG (eV)	1.342	-0.637	1.342	-0.637	1.278
(4) (U=U_0 =2.85 V), ΔG (eV)	-1.328	0.651	-1.328	0.651	0.651
(5) (U=U_0 =2.85 V), ΔG (eV)	-1.778	-1.778	-1.778	-1.778	-1.778
(6) (U=U_0 =2.85 V), ΔG (eV)	1.212	1.212	1.212	1.212	1.212
(7) (U=U_0 =2.85V), ΔG (eV)	0.014	0.014	0.014	0.014	0.014
(8) (U=U_0 =2.85 V), ΔG (eV)	1.736	1.736	1.736	**1.736**	1.736

Table S11. The Gibbs free energy of reaction pathway A on the Ru.

Reaction Step on Ru	I	II	III	IV	V
(1) (U=0 V), ΔG (eV)	-1.147	-1.147	-0.200	-0.200	-0.200
(2) (U=0 V), ΔG (eV)	-1.050	-1.050	-1.998	-1.998	-1.112
(3) (U=0 V), ΔG (eV)	-1.750	-0.909	-1.750	-0.909	-1.795
(4) (U=0 V), ΔG (eV)	-1.223	-2.064	-1.223	-2.064	-2.064
(5) (U=0 V), ΔG (eV)	-1.243	-1.243	-1.243	-1.243	-1.243
(6) (U=0 V), ΔG (eV)	0.158	0.158	0.158	0.158	0.158
(7) (U=0 V), ΔG (eV)	-1.809	-1.809	-1.809	-1.809	-1.809
(8) (U=0 V), ΔG (eV)	-2.106	-2.106	-2.106	-2.106	-2.106
(1) (U=U_0 =2.85 V), ΔG (eV)	1.703	1.703	-0.200	-0.200	-0.200
(2) (U=U_0 =2.85 V), ΔG (eV)	-1.050	-1.050	0.852	**0.852**	-1.112
(3) (U=U_0 =2.85 V), ΔG (eV)	1.100	-0.909	1.100	-0.909	1.055
(4) (U=U_0 =2.85 V), ΔG (eV)	-1.223	0.786	-1.223	0.786	0.786
(5) (U=U_0 =2.85 V), ΔG (eV)	-1.243	-1.243	-1.243	-1.243	-1.243
(6) (U=U_0 =2.85 V), ΔG (eV)	0.158	0.158	0.158	0.158	0.158
(7) (U=U_0 =2.85V), ΔG (eV)	1.041	1.041	1.041	**1.041**	1.041
(8) (U=U_0 =2.85 V), ΔG (eV)	0.744	0.744	0.744	0.744	0.744

Table S12. The Gibbs free energy of reaction pathway of $Li_2C_2O_4$ on the ScRu, TiRu and VRu.

Reaction Step on ScRu	VI	VII	VIII	IX	X
(1) (U=0 V), ΔG (eV)	-1.169	-1.169	-0.770	-0.770	-0.770
(2) (U=0 V), ΔG (eV)	-1.522	-1.522	-1.921	-1.921	0.234
(3) (U=0 V), ΔG (eV)	-1.590	0.084	-1.590	0.084	-2.070
(4) (U=0 V), ΔG (eV)	-0.070	-1.744	-0.070	-1.744	-1.744
(1) (U=U_0 =3.01 V), ΔG (eV)	1.841	1.841	-0.770	-0.770	-0.770
(2) (U=U_0 =3.01 V), ΔG (eV)	-1.522	-1.522	1.089	1.089	0.234
(3) (U=U_0 =3.01 V), ΔG (eV)	1.420	0.084	1.420	0.084	0.940
(4) (U=U_0 =3.01 V), ΔG (eV)	-0.070	1.266	-0.070	**1.266**	1.266
Reaction Step on TiRu	VI	VII	VIII	IX	X
(1) (U=0 V), ΔG (eV)	-1.182	-1.182	-0.774	-0.774	-0.774
(2) (U=0 V), ΔG (eV)	-0.578	-0.578	-0.987	-0.987	0.195
(3) (U=0 V), ΔG (eV)	-2.400	-0.697	-2.400	-0.697	-1.880
(4) (U=0 V), ΔG (eV)	0.133	-1.569	0.133	-1.569	-1.569
(1) (U=U_0 =3.01 V), ΔG (eV)	1.828	1.828	-0.774	-0.774	-0.774
(2) (U=U_0 =3.01 V), ΔG (eV)	-0.578	-0.578	2.023	2.023	0.195
(3) (U=U_0 =3.01 V), ΔG (eV)	0.610	-0.697	0.610	-0.697	1.130
(4) (U=U_0 =3.01 V), ΔG (eV)	0.133	1.441	0.133	1.441	**1.441**
Reaction Step on VRu	VI	VII	VIII	IX	X
(1) (U=0 V), ΔG (eV)	-1.025	-1.025	-0.619	-0.619	-0.619
(2) (U=0 V), ΔG (eV)	-0.899	-0.899	-1.305	-1.305	0.427
(3) (U=0 V), ΔG (eV)	-2.070	-0.105	-2.070	-0.105	-1.837
(4) (U=0 V), ΔG (eV)	0.157	-1.807	0.157	-1.807	-1.807
(1) (U=U_0 =3.01 V), ΔG (eV)	1.985	1.985	-0.619	-0.619	-0.619
(2) (U=U_0 =3.01 V), ΔG (eV)	-0.899	-0.899	1.705	1.705	0.427
(3) (U=U_0 =3.01 V), ΔG (eV)	0.940	-0.105	0.940	-0.105	1.173
(4) (U=U_0 =3.01 V), ΔG (eV)	0.157	1.203	0.157	1.203	**1.203**

Table S13. The Gibbs free energy of reaction pathway of $Li_2C_2O_4$ on the CrRu, MnRu and FeRu.

Reaction Step on CrRu	VI	VII	VIII	IX	X
(1) (U=0 V), ΔG (eV)	-1.086	-1.086	-0.515	-0.515	-0.515
(2) (U=0 V), ΔG (eV)	-0.991	-0.991	-1.563	-1.563	0.603
(3) (U=0 V), ΔG (eV)	-1.895	0.326	-1.895	0.326	-1.841
(4) (U=0 V), ΔG (eV)	0.254	-1.966	0.254	-1.966	-1.966
(1) ($U=U_0$ =3.01 V), ΔG (eV)	1.924	1.924	-0.515	-0.515	-0.515
(2) ($U=U_0$ =3.01 V), ΔG (eV)	-0.991	-0.991	1.447	1.447	0.603
(3) ($U=U_0$ =3.01 V), ΔG (eV)	1.115	0.326	1.115	0.326	**1.169**
(4) ($U=U_0$ =3.01 V), ΔG (eV)	0.254	1.044	0.254	1.044	1.044
Reaction Step on MnRu	VI	VII	VIII	IX	X
(1) (U=0 V), ΔG (eV)	-1.177	-1.177	-0.401	-0.401	-0.401
(2) (U=0 V), ΔG (eV)	-1.000	-1.000	-1.776	-1.776	1.005
(3) (U=0 V), ΔG (eV)	-1.883	-0.034	-1.883	-0.034	-2.814
(4) (U=0 V), ΔG (eV)	0.458	-1.391	0.458	-1.391	-1.391
(1) ($U=U_0$ =3.01 V), ΔG (eV)	1.833	1.833	-0.401	-0.401	-0.401
(2) ($U=U_0$ =3.01 V), ΔG (eV)	-1.000	-1.000	**1.234**	1.234	1.005
(3) ($U=U_0$ =3.01 V), ΔG (eV)	1.127	-0.034	1.127	-0.034	0.196
(4) ($U=U_0$ =3.01 V), ΔG (eV)	0.458	1.619	0.458	1.619	1.619
Reaction Step on FeRu	VI	VII	VIII	IX	X
(1) (U=0 V), ΔG (eV)	-1.231	-1.231	-0.322	-0.322	-0.322
(2) (U=0 V), ΔG (eV)	-1.004	-1.004	-1.914	-1.914	0.362
(3) (U=0 V), ΔG (eV)	-1.832	0.249	-1.832	0.249	-2.028
(4) (U=0 V), ΔG (eV)	0.569	-1.511	0.569	-1.511	-1.511
(1) ($U=U_0$ =3.01 V), ΔG (eV)	1.779	1.779	-0.322	-0.322	-0.322
(2) ($U=U_0$ =3.01 V), ΔG (eV)	-1.004	-1.004	1.096	1.096	0.362
(3) ($U=U_0$ =3.01 V), ΔG (eV)	1.178	0.249	**1.178**	0.249	0.982
(4) ($U=U_0$ =3.01 V), ΔG (eV)	0.569	1.499	0.569	1.499	1.499

Table S14. The Gibbs free energy of reaction pathway of $Li_2C_2O_4$ on the CoRu, NiRu and CuRu.

Reaction Step on CoRu	VI	VII	VIII	IX	X
(1) (U=0 V), ΔG (eV)	-1.281	-1.281	-0.264	-0.264	-0.264
(2) (U=0 V), ΔG (eV)	-0.946	-0.946	-1.963	-1.963	0.370
(3) (U=0 V), ΔG (eV)	-1.655	0.373	-1.655	0.373	-1.960
(4) (U=0 V), ΔG (eV)	1.102	-0.926	1.102	-0.926	-0.926
(1) (U=U_0 =3.01 V), ΔG (eV)	1.729	1.729	-0.264	-0.264	-0.264
(2) (U=U_0 =3.01 V), ΔG (eV)	-0.946	-0.946	1.047	1.047	0.370
(3) (U=U_0 =3.01 V), ΔG (eV)	1.355	0.373	**1.355**	0.373	1.050
(4) (U=U_0 =3.01 V), ΔG (eV)	1.102	2.084	1.102	2.084	2.084
Reaction Step on NiRu	VI	VII	VIII	IX	X
(1) (U=0 V), ΔG (eV)	-1.253	-1.253	-0.264	-0.264	-0.264
(2) (U=0 V), ΔG (eV)	-0.775	-0.775	-1.765	-1.765	0.499
(3) (U=0 V), ΔG (eV)	-1.639	0.244	-1.639	0.244	-2.019
(4) (U=0 V), ΔG (eV)	-0.042	-1.925	-0.042	-1.925	-1.925
(1) (U=U_0 =3.01 V), ΔG (eV)	1.757	1.757	-0.264	-0.264	-0.264
(2) (U=U_0 =3.01 V), ΔG (eV)	-0.775	-0.775	1.245	1.245	0.499
(3) (U=U_0 =3.01 V), ΔG (eV)	1.371	0.244	1.371	0.244	0.991
(4) (U=U_0 =3.01 V), ΔG (eV)	-0.042	1.085	-0.042	1.085	**1.085**
Reaction Step on CuRu	VI	VII	VIII	IX	X
(1) (U=0 V), ΔG (eV)	-1.142	-1.142	-0.261	-0.261	-0.261
(2) (U=0 V), ΔG (eV)	-0.678	-0.678	-1.559	-1.559	0.569
(3) (U=0 V), ΔG (eV)	-1.589	0.051	-1.589	0.051	-2.077
(4) (U=0 V), ΔG (eV)	-0.197	-1.837	-0.197	-1.837	-1.837
(1) (U=U_0 =3.01 V), ΔG (eV)	1.868	1.868	-0.261	-0.261	-0.261
(2) (U=U_0 =3.01 V), ΔG (eV)	-0.678	-0.678	1.451	1.451	0.569
(3) (U=U_0 =3.01 V), ΔG (eV)	1.421	0.051	1.421	0.051	0.933
(4) (U=U_0 =3.01 V), ΔG (eV)	-0.197	1.173	-0.197	1.173	**1.173**

Table S15. The Gibbs free energy of reaction pathway of $Li_2C_2O_4$ on the ZnRu, Ru and CuRu.

Reaction Step on ZnRu	VI	VII	VIII	IX	X
(1) (U=0 V), ΔG (eV)	-1.007	-1.007	-0.184	-0.184	-0.184
(2) (U=0 V), ΔG (eV)	-0.794	-0.794	-1.617	-1.617	0.154
(3) (U=0 V), ΔG (eV)	-1.508	-0.213	-1.508	-0.213	-1.984
(4) (U=0 V), ΔG (eV)	0.429	-0.865	0.429	-0.865	-0.865
(1) (U=U_0 =3.01 V), ΔG (eV)	2.003	2.003	-0.184	-0.184	-0.184
(2) (U=U_0 =3.01 V), ΔG (eV)	-0.794	-0.794	1.393	1.393	0.154
(3) (U=U_0 =3.01 V), ΔG (eV)	1.502	-0.213	**1.502**	-0.213	1.026
(4) (U=U_0 =3.01 V), ΔG (eV)	0.429	2.145	0.429	2.145	2.145
Reaction Step on Ru	VI	VII	VIII	IX	X
(1) (U=0 V), ΔG (eV)	-1.147	-1.147	-0.200	-0.200	-0.200
(2) (U=0 V), ΔG (eV)	-1.050	-1.050	-1.998	-1.998	0.241
(3) (U=0 V), ΔG (eV)	-1.750	0.381	-1.750	0.381	-1.858
(4) (U=0 V), ΔG (eV)	0.434	-1.697	0.434	-1.697	-1.697
(1) (U=U_0 =3.01 V), ΔG (eV)	1.863	1.863	-0.200	-0.200	-0.200
(2) (U=U_0 =3.01 V), ΔG (eV)	-1.050	-1.050	1.012	1.012	0.241
(3) (U=U_0 =3.01 V), ΔG (eV)	1.260	0.381	**1.260**	0.381	1.152
(4) (U=U_0 =3.01 V), ΔG (eV)	0.434	1.313	0.434	1.313	1.313
Reaction Step on CuRu	VI	VII	VIII	IX	X
(1) (U=0 V), ΔG (eV)	-1.142	-1.142	-0.261	-0.261	-0.261
(2) (U=0 V), ΔG (eV)	-0.678	-0.678	-1.559	-1.559	0.569
(3) (U=0 V), ΔG (eV)	-1.589	0.051	-1.589	0.051	-2.077
(4) (U=0 V), ΔG (eV)	-0.197	-1.837	-0.197	-1.837	-1.837
(1) (U=U_0 =2.85 V), ΔG (eV)	1.708	1.708	-0.261	-0.261	-0.261
(2) (U=U_0 =2.85 V), ΔG (eV)	-0.678	-0.678	1.291	1.291	0.569
(3) (U=U_0 =2.85 V), ΔG (eV)	1.261	0.051	1.261	0.051	0.773
(4) (U=U_0 =2.85 V), ΔG (eV)	-0.197	1.013	-0.197	1.013	**1.013**

Table S16. The Gibbs free energy of reaction pathway A on the 11 catalysts.

Path IV (U=0 V), ΔG (eV)	ScRu	MnRu	CoRu	ZnRu	Ru
step (1)	-2.691	-2.177	-2.227	-1.801	-2.197
step (2)	**-3.818**	**-4.252**	**-4.237**	**-4.613**	**-4.216**
step (3)	**-1.805**	-1.818	-1.568	-1.624	**-1.651**
step (4)	-1.939	**-1.442**	**-1.489**	**-1.114**	-2.106
Path V (U=0 V), ΔG (eV)	TiRu	VRu	CrRu	FeRu	NiRu
step (1)	**-3.773**	**-3.551**	**-3.394**	**-3.115**	-2.781
step (2)	-2.710	-2.896	-3.043	-2.722	**-3.671**
step (3)	**-1.699**	-2.015	-1.923	-2.314	**-1.389**
step (4)	-1.931	**-1.470**	**-1.439**	**-1.447**	-1.495
Path X (U=0 V), ΔG (eV)	CuRu				
step (1)	-1.769				
step (2)	**-4.680**				
step (3)	-1.666				
step (4)	**-1.034**				

Table S17. The image, decomposition and energy barrier on the ScRu, TiRu and Ru during the decomposition of Li_2CO_3.

Image	Decomposition(Å)	Energy barrier(eV)	Catalyst
0	0	0	ScRu
1	0.7845	0.2647	
2	1.5670	0.5796	
3	2.3497	0.6752	
4	3.1316	**0.7167**	
5	3.7662	0.7131	
0	0	0	TiRu
1	0.7674	0.1111	
2	1.5383	0.5566	
3	2.3167	0.6837	
4	3.1032	0.7061	
5	3.8966	**0.7542**	
6	4.5946	0.7489	
0	0	0	Ru
1	0.7404	0.1870	
2	1.4811	0.6855	
3	2.2247	0.8240	
4	2.9708	0.8408	
5	3.7205	**0.8893**	
6	4.3941	0.8882	

Table S18. The ε_d and r of M, $E_{ad}(CO_2)$ and ΔG_{RDS} of 11 catalysts.

	ε_d	r	$E_{ad}(CO_2)$	ΔG_{RDS}
Sc	2.007	184	-1.116	0.941
Ti	1.155	176	-1.109	1.072
V	0.451	171	-0.943	1.380
Cr	-0.098	166	-0.823	1.411
Mn	-0.460	161	-0.719	1.408
Fe	-1.030	156	-0.635	1.403
Co	-1.047	152	-0.597	1.361
Ni	-1.387	149	-0.598	1.355
Cu	-2.336	145	-0.591	1.816
Zn	-6.291	142	-0.516	1.736
Ru	-1.099	178	-0.529	1.041