Density Functional Theory Study on Catalytic Activation and Dissociation of CO_2 on Bimetallic Alloy Surfaces

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Supplementary Information

S1. Scaling relations of adsorption energies on pure metals and bimetallic alloys.

We investigated that the scaling relation in adsorption energies of reaction intermediates is valid on not only pure metals but also bimetallic alloys. In order to check this relationship in bimetallic alloy systems, several pairs of alloys were selected in these calculations. Figure S1 and Table S1 show that it works quite well on both systems.

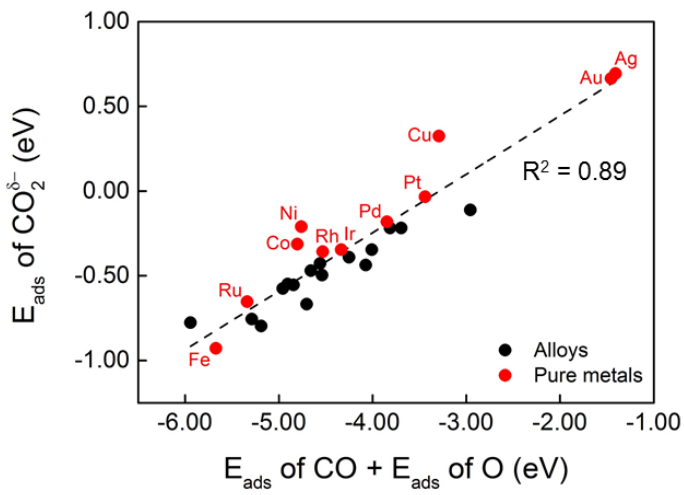

Figure S1: The scaling relations between E_{ads}(CO) + E_{ads}(O) and $E_{ads}(CO_2^{\delta-})$ on pure metals and bimetallic alloys (in eV).

Surface	E_{ads}(CO)	E_{ads}(O)	E_{ads}(CO) + E_{ads}(O)	$E_{ads}(CO_2^{\delta-})$
Ni/Ru	–2.29	–2.90	–2.90	–0.80
Fe/Ru	–2.14	–3.14	–3.14	–0.76

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Cu/Ru	–2.27	–2.43	–2.43	–0.67
Co/Ru	–2.58	–3.36	–3.36	–0.78
Ir/Ru	–2.06	–2.48	–2.48	–0.50
Pt/Ru	–2.11	–2.55	–2.55	–0.47
Pd/Ru	–2.21	–2.63	–2.63	–0.55
Rh/Ru	–2.20	–2.75	–2.75	–0.58
Au/Ru	–2.06	–1.63	–1.63	–0.22
Ag/Ru	–2.23	–2.67	–2.67	–0.55
Ni/Rh	–2.25	–2.31	–2.31	–0.43
Cu/Rh	–2.12	–1.96	–1.96	–0.44
Pt/Rh	–2.07	–1.74	–1.74	–0.22
Pd/Rh	–2.17	–1.83	–1.83	–0.35
Au/Rh	–1.81	–1.15	–1.15	–0.11
Ag/Rh	–2.23	–2.02	–2.02	–0.39
Fe	–2.16	–3.51	–3.51	–0.93
Ir	–2.35	–1.99	–1.99	–0.35
Ru	–2.28	–3.06	–3.06	–0.65
Pd	–2.35	–1.50	–1.50	–0.18
Rh	–2.33	–2.20	–2.20	–0.36
Ni	–2.26	–2.50	–2.50	–0.21
Pt	–2.09	–1.35	–1.35	–0.03
Co	–2.06	–2.74	–2.74	–0.31
Cu	–1.30	–1.99	–1.99	0.32[a]
Ag	–0.62	–0.79	–0.79	0.69[a]
Au	–0.88	–0.57	–0.57	0.66[a]

[a] Structural parameters of $CO_2^{\delta-}$ adsorbed on Pt(111) were employed for these calculations.

Table S1: The scaling relations between the sum of E_{ads}(CO) and E_{ads}(O), and $E_{ads}(CO_2^{\delta-})$ on pure metals and bimetallic alloys (in eV).

S2. Reaction energies, activation energies, actual reaction energies, and actual activation energies on pure metal surfaces.

Table S2 shows that DFT-calculated reaction energies (ΔE), activation energies (E_a), actual reaction energies (ΔE^{act}), and actual activation energies (E_a^{act}) for CO_2 dissociation on pure metal surfaces. The definition of actual reaction and activation energies is specified in Chapter 4 of the manuscript.

	ΔE (eV)	E_a (eV)	ΔE^{act} (eV)	E_a^{act} (eV)
Fe(110)	–1.46	0.11	–1.46	0.11
Co(0001)	–1.21	0.11	–1.21	0.11
Ni(111)	–1.25	0.42	–1.31	0.48
Cu(111)[a]	–0.31	0.59	–0.87	1.15
Ru(0001)	–1.32	0.66	–1.32	0.66
Rh(111)	–0.85	0.56	–0.85	0.56
Pd(111)	–0.34	1.25	–0.49	1.40
Ag(111)[a]	1.17	1.33	0.22	2.29
Ir(111)	–0.78	0.79	–0.78	0.79
Pt(111)	–0.01	0.93	–0.20	1.12
Au(111)[a]	1.27	1.96	0.31	2.92

[a] Structural parameters of $CO_2^{\delta-}$ adsorbed on Pt(111) were employed for these calculations.

Table S2: DFT calculation results of reaction energies (ΔE), activation energies (E_a), actual reaction energies (ΔE^{act}) and actual activation energies (E_a^{act}) for CO_2 dissociation on pure metal surfaces (in eV).

S3. Prediction of kinetic parameters for CO_2 dissociation on pure metal and bimetallic surfaces.

By combining BEP relation, scaling relation and surface mixing rule, we rapidly predicted the kinetic parameters (E_{ads}(CO), E_{ads}(O), $E_{ads}(CO_2)$, $E_{ads}(CO_2^{\delta-})$, ΔE, E_a, ΔE^{act}, E_a^{act}) for CO_2 dissociation on pure metal and bimetallic surfaces. These results are summarized in Table S3.

	[a]E_{ads}(CO)	[a]E_{ads}(O)	[b]$E_{ads}(CO_2)$	[c]$E_{ads}(CO_2^{\delta-})$	[d]ΔE	[e]E_a	ΔE^{act}	E_a^{act}
Co/Fe	–2.12	–3.26	–0.28	–0.63	–1.45	0.28	–1.45	0.28
Ni/Fe	–2.19	–3.18	–0.28	–0.63	–1.44	0.29	–1.44	0.29
Cu/Fe	–1.87	–3.01	–0.28	–0.46	–1.11	0.46	–1.11	0.46
Ru/Fe	–2.20	–3.36	–0.28	–0.70	–1.57	0.22	–1.57	0.22
Rh/Fe	–2.21	–3.08	–0.28	–0.60	–1.39	0.31	–1.39	0.31

Pd/Fe	–2.22	–2.84	–0.28	–0.52	–1.24	0.39	–1.24	0.39
Ag/Fe	–1.64	–2.61	–0.28	–0.24	–0.70	0.67	–0.73	0.71
Ir/Fe	–2.22	–3.00	–0.28	–0.58	–1.34	0.34	–1.34	0.34
Pt/Fe	–2.13	–2.79	–0.28	–0.48	–1.15	0.44	–1.15	0.44
Au/Fe	–1.73	–2.53	–0.28	–0.25	–0.71	0.67	–0.74	0.70
Ni/Co	–2.13	–2.64	–0.28	–0.42	–1.04	0.49	–1.04	0.49
Cu/Co	–1.81	–2.47	–0.28	–0.25	–0.71	0.66	–0.74	0.69
Rh/Co	–2.15	–2.54	–0.28	–0.40	–0.99	0.52	–0.99	0.52
Pd/Co	–2.15	–2.31	–0.28	–0.32	–0.84	0.60	–0.84	0.60
Ag/Co	–1.58	–2.07	–0.28	–0.04	–0.30	0.88	–0.54	1.12
Ir/Co	–2.15	–2.47	–0.28	–0.37	–0.94	0.54	–0.94	0.54
Pt/Co	–2.07	–2.25	–0.28	–0.27	–0.75	0.65	–0.76	0.66
Au/Co	–1.67	–2.00	–0.28	–0.04	–0.31	0.87	–0.55	1.11
Cu/Ni	–1.94	–2.33	–0.28	–0.25	–0.71	0.66	–0.74	0.69
Rh/Ni	–2.28	–2.40	–0.28	–0.39	–0.99	0.52	–0.99	0.52
Pd/Ni	–2.29	–2.17	–0.28	–0.31	–0.83	0.60	–0.83	0.60
Ag/Ni	–1.71	–1.93	–0.28	–0.03	–0.29	0.88	–0.54	1.13
Pt/Ni	–2.20	–2.11	–0.28	–0.27	–0.74	0.65	–0.76	0.66
Au/Ni	–1.80	–1.86	–0.28	–0.04	–0.30	0.87	–0.54	1.11
Pd/Cu	–1.65	–1.83	–0.28	0.02	–0.18	0.94	–0.49	1.24
Ag/Cu	–1.07	–1.59	–0.28	0.30	0.36	1.21	–0.23	1.80
Au/Cu	–1.16	–1.52	–0.28	0.30	0.35	1.21	–0.23	1.79
Fe/Ru	–2.24	–3.21	–0.28	–0.66	–1.49	0.26	–1.49	0.26
Co/Ru	–2.21	–2.95	–0.28	–0.56	–1.30	0.36	–1.30	0.36
Ni/Ru	–2.27	–2.87	–0.28	–0.55	–1.29	0.36	–1.29	0.36
Cu/Ru	–1.95	–2.70	–0.28	–0.38	–0.97	0.53	–0.97	0.53
Rh/Ru	–2.30	–2.77	–0.28	–0.53	–1.24	0.39	–1.24	0.39
Pd/Ru	–2.30	–2.54	–0.28	–0.45	–1.09	0.47	–1.09	0.47
Ag/Ru	–1.73	–2.30	–0.28	–0.17	–0.55	0.75	–0.66	0.86
Ir/Ru	–2.30	–2.70	–0.28	–0.50	–1.20	0.41	–1.20	0.41
Pt/Ru	–2.22	–2.49	–0.28	–0.40	–1.00	0.51	–1.00	0.51
Au/Ru	–1.81	–2.23	–0.28	–0.17	–0.56	0.74	–0.67	0.85
Ni/Rh	–2.31	–2.30	–0.28	–0.37	–0.93	0.55	–0.93	0.55
Cu/Rh	–1.99	–2.13	–0.28	–0.20	–0.61	0.72	–0.69	0.80
Pd/Rh	–2.33	–1.97	–0.28	–0.26	–0.73	0.65	–0.75	0.67
Ag/Rh	–1.76	–1.73	–0.28	0.02	–0.19	0.93	–0.49	1.23
Pt/Rh	–2.25	–1.92	–0.28	–0.22	–0.64	0.70	–0.71	0.76
Au/Rh	–1.85	–1.66	–0.28	0.01	–0.20	0.93	–0.50	1.22
Ag/Pd	–1.77	–1.26	–0.28	0.18	0.11	1.09	–0.35	1.54
Au/Pd	–1.86	–1.19	–0.28	0.17	0.10	1.08	–0.35	1.53

Cu/Ir	–2.00	–1.99	–0.28	–0.15	–0.52	0.76	–0.65	0.89
Rh/Ir	–2.34	–2.06	–0.28	–0.30	–0.80	0.62	–0.80	0.62
Pd/Ir	–2.35	–1.82	–0.28	–0.22	–0.64	0.70	–0.71	0.76
Ag/Ir	–1.77	–1.59	–0.28	0.06	–0.10	0.98	–0.45	1.32
Pt/Ir	–2.26	–1.77	–0.28	–0.17	–0.55	0.74	–0.66	0.85
Au/Ir	–1.86	–1.51	–0.28	0.06	–0.12	0.97	–0.45	1.31
Ag/Pt	–1.60	–1.16	–0.28	0.27	0.29	1.18	–0.26	1.73
Au/Pt	–1.69	–1.09	–0.28	0.26	0.28	1.18	–0.26	1.72
Fe	–2.16	–3.51	–0.28	–0.73	–1.64	0.18	–1.64	0.18
Co	–2.06	–2.74	–0.28	–0.43	–1.06	0.48	–1.06	0.48
Ni	–2.26	–2.50	–0.28	–0.42	–1.04	0.50	–1.04	0.50
Cu	–1.30	–1.99	–0.28	0.09	–0.06	1.00	–0.43	1.37
Ru	–2.28	–3.06	–0.28	–0.62	–1.42	0.30	–1.42	0.30
Rh	–2.33	–2.20	–0.28	–0.34	–0.88	0.57	–0.88	0.57
Pd	–2.35	–1.50	–0.28	–0.10	–0.43	0.81	–0.60	0.98
Ag	–0.62	–0.79	–0.28	0.74	1.19	1.65	0.17	2.66
Ir	–2.35	–1.99	–0.28	–0.27	–0.75	0.64	–0.76	0.65
Pt	–2.09	–1.35	–0.28	0.04	–0.16	0.95	–0.47	1.27
Au	–0.88	–0.57	–0.28	0.72	1.16	1.63	0.16	2.63

[a] The adsorption energies were estimated by surface mixing rule.
[b] The adsorption energies of CO_2 were assumed constant value of –0.28 eV.
[c~e] The adsorption energies of $CO_2^{\delta-}$ ($E_{ads}(CO_2^{\delta-})$), reaction energies (ΔE) and activation energies (E_a) were scaled by Eq. (2), (3) and (1) respectively. Eq. (1) ~ (3) are specified in Section 4.1 of our manuscript.

Table S3: The predicted kinetic parameters ($E_{ads}(CO)$, $E_{ads}(O)$, $E_{ads}(CO_2)$, $E_{ads}(CO_2^{\delta-})$, ΔE, E_a, ΔE^{act}, E_a^{act}) for CO_2 dissociation on pure metal and bimetallic surfaces (in eV).