Supplementary Information

Towards rational catalyst design: Boosting rapid prediction of transition-

metal activity by improved scaling relations

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Part S1 UBI-QEP method

The UBI-QEP method was proposed and developed by Shustorovich and coworkers^{1, 2}, based on three principle assumptions. The first is that all forces depend only on interbody distance in a many-body system; Secondly, Morse potential (MP) is taken to describe each two-center (A-B) interaction; Thirdly, the total bond index (X) is conserved at unity in a many-body system.

$$E(x(r)) = a(x^{2}(r) - 2x(r))$$
(S1)

$$x(r) = \exp\{-(r - r_0)/b\}$$
 (S2)

$$X = \sum_{i} x_{i} = 1 \tag{S3}$$

Where x(r) is bond index, which is exponential related to bond distance r; r_0 is A-B bond equilibrium distance; b is distance scaling constant; a is A-B bond energy at r_0 (equilibrium distance). The total bond energy of a many-body system is then estimated by sum of all A-B two-center interactions:

$$E(X) = \sum_{i} a_i \left(x_i^2 - 2x_i \right) \tag{S4}$$

Constrained minimization of the UBI-QEP energy (Eq. S4) leads to the solved x_i , with which we can obtain respective equations for calculation of adsorption heats towards different adsorption cases, shown as Table S1^{2–6}. On the basis of UBI-QEP category, an adsorbed species can be strongly, weakly or intermediate binding to the metal surface via one or two atoms. The radicals such as CH, CH₂, OH and COH are strongly bounded adsorbates, which have unpaired electrons. The weakly bounded species usually have a closed electronic shell (e.g., H₂, CO, CH₄ and H₂O) or strongly delocalized unpaired electrons (O₂ or NO). For intermediate bounded adsorbates like CH₃ and CH₃CH₂, the adsorption heats are determined by interpolation between strongly and weakly cases.

Eq. no.	Case	Equation
(S5) ^a	Atomic chemisorption M _n -A binding	$Q_A = (2 - \frac{1}{n})Q_{0A}$
(S6) ^b	Strong M _n -AB binding via A	$Q_{AB} = \frac{Q_A^2}{Q_A + D_{AB}}$
(S7) ^b	Weak M _n -AB binding via A	$Q_{AB} \approx \frac{Q_{0A}^2}{(Q_{0A}/n) + D_{AB}} for D_{AB} > \frac{n-1}{n} Q_{0A}$
(S8) ^b	Intermediate M _n -AB binding via A	$Q_{AB} = \frac{1}{2} \left(\frac{Q_A^2}{Q_A + D_{AB}} + \frac{Q_{0A}^2}{(Q_{0A}/n) + D_{AB}} \right)$
(S9)°	M _n -AB binding via both A and B	$Q_{AB} = \frac{ab(a+b) + D_{AB}(a-b)^{2}}{ab + D_{AB}(a+b)}$
	$(\eta^2 \mu_n \text{ coordination})$	$a = Q_{0A}^{2} \frac{(Q_{0A} + 2Q_{0B})}{(Q_{0A} + Q_{0B})^{2}}; \ b = Q_{0B}^{2} \frac{(Q_{0B} + 2Q_{0A})}{(Q_{0A} + Q_{0B})^{2}}$
(S10)°	Symmetric molecules (CO ₂ , H ₂)	$Q_{AB} = \frac{9Q_{0A}^2}{6Q_{0A} + 16D_{AB}}$
	Polyatomic molecules $(AX_m - BY_m)$	$Q_{AB} = \frac{ab(a+b) + D_{AB}(a-b)^{2}}{ab + D_{AB}(a+b)}$
(S11)°	$(\eta^2 \mu_n \text{ coordination})$	$a = Q_{0A} \left(1 - \left(\frac{mQ_{0X}}{mQ_{0A} + Q_{0X}} \right)^2 \right)$
	a, b apply to both $m > 0$ and $m' > 0$	
	or one of them (m and m') is 0	$b = Q_{0B} \left(1 - \left(\frac{m' Q_{0Y}}{m' Q_{0B} + Q_{0Y}} \right)^2 \right)$

 Table S1 Standard UBI-QEP equations for calculation of adsorption heats towards different metal-adsorbate binding

 cases²⁻⁶.

^c AB binds to a metal surface via both A and B ($\eta^2 \mu_n$ coordination), D_{AB} is the total gas-phase bond energy of AB.

^a Q_A is the M_n-A binding energy (one A atom binds to *n* metal atoms), which is estimated from experiments or DFT calculations; Q_{0A} is M-A two-center bond energy at equilibrium distance; *n* is coordination number, namely the total number of metal atoms with which A binds.

^b AB binds to a metal surface via only one atom A ($\eta^1 \mu_n$ coordination), D_{AB} is the total bond energy between A and the rest of molecule AB in gas-phase.



Figure S1 DFT calculated total gas-phase bond energy (D, Blue) and bond energy for calculating adsorption heat (D_{AB} , black) against suggested UBI-QEP values in literature⁴.

Adsorption configurations over Co(0001) surface based on DFT calculations

(1) Atomic chemisorption:



(2) Weak binding ($\eta^1 \mu_n$ coordination):



(3) Strong binding ($\eta^1 \mu_n$ coordination):







(4) Intermediate binding ($\eta^1 \mu_n$ coordination):



(5) Symmetric molecules ($\eta^2 \mu_n$ coordination):





(6) Non-symmetric molecules ($\eta^2 \mu_n$ coordination):



To better understand the UBI-QEP method, an example is given here to illustrate how to calculate D_{AB} , n, Q_A , Q_{0A} and Q_{AB} values. For example, COH adsorbs over Co(0001) surface, shown as Figure S2. In the configuration, only one carbon atom binds to the metal surface, therefore A stands for carbon here, B stands for -OH group. The carbon atom binds with 3 Co atoms, so the coordination number (n) is 3. The physical meaning of coordination number is the total number of metal atoms with which A binds. Q_A is M_n-A binding energy, namely atomic binding energy, C-Co binding energy here, which is estimated from DFT calculations in this work. Q_{0A} is M-A two-center bond energy at equilibrium distance, namely the bond energy between the carbon atom and one Co atom, which is calculated from Q_A based on Eq. (S5).



Figure S2 COH adsorbs over Co(0001) surface. Towards COH species, gray ball means C atom; red ball means O atom; white ball means H atom.

 D_{AB} is AB bond dissociation energy in the gas-phase. For COH, D_{AB} represents for bond dissociation of C-OH in the gas-phase. At first, the total gas-phase bond energies (*D*) of COH, C and OH are calculated by DFT. The detailed calculaton is given in Eq. (2) of the main text. Then D_{AB} is estimated by $D_{COH} - D_C - D_{OH}$. Scince the D_{AB} , n, Q_A , and Q_{0A} values have already obtained, Q_{AB} can be easily determined. Due to having unpaired electrons, COH is a strongly bounded adsorbate. We can use Eq. (S6) to calculate the adsorption heat (Q_{AB}) of COH over Co(0001) surface.

Species	Values in litera	ature (kcal/mol)	DFT calculated values (kcal/mol)			
Species	D	D_{AB}	D	D_{AB} (previous)	D_{AB} (new)	
С	0	/	0	/	/	
Н	0	/	0	/	/	
0	0	/	0	/	/	
СО	257	257	259	259	259	
H_2	104	104	111	111	111	
OH	102	102	108	108	108	
СН	81	81	91	91	91	
CH_2	183	183	198	198	198	
CH ₃	293	293	313	313	313	
CH ₄	397	397	422	422	422	
CH ₃ CH ₃	674	674	715	715	402	
CH ₂ CH ₂	538	538	568	568	370	
CH ₃ CH ₂	576	283	611	298	298	
CH ₃ CH	466	173	500	187	187	
CH ₂ CH	421	157	455	166	364, 257	
CHCH	392	392	410	410	319	
CCH ₃	376	114	406	133	133	
CCH	259	161	273	182	182, 273	
$\rm CCH_2$	348	155	367	169	169, 367	
H_2O	220	220	233	233	233	
CO ₂	385	385	394	394	394	
НСО	274	274	287	287	287	
CH ₂ O	361	361	380	380	182	
CH ₃ O	383	90	411	98	98	
CH ₃ OH	487	194	517	204	204	
НСОН			328	220	220	
СОН			247	139	139	
СООН			407	299	299	
CH ₂ OH			417	309	309	

Table S2 DFT calculated total gas-phase bond energies (*D*) and bond energies for calculating adsorption heats (D_{AB}) with respect to suggested UBI-QEP values in literature⁴.

Species	Co(0001)	Ru(0001)	Fe(110)	Ni(111)	Cu(111)	Rh(111)	Pd(111)	Pt(111)
С	6.42	7.27	7.54	6.35	4.39	6.99	6.52	6.81
Н	2.72	2.81	2.93	2.72	2.40	2.73	2.74	2.64
0	5.49	5.81	6.32	5.20	4.54	5.02	4.21	4.13
СО	0.98	1.22	1.30	0.96	0.50	1.14	1.01	1.09
H_2	0.28	0.29	0.32	0.28	0.22	0.28	0.28	0.26
OH	2.96	3.22	3.63	2.74	2.23	2.60	1.99	1.94
СН	3.98	4.71	4.95	3.92	2.31	4.47	4.06	4.31
CH_2	2.75	3.33	3.53	2.70	1.49	3.14	2.81	3.01
CH ₃	1.53	1.90	2.02	1.50	0.78	1.78	1.57	1.70
CH ₄	0.67	0.84	0.90	0.66	0.33	0.78	0.69	0.75
CH ₃ CH ₃	0.34	0.45	0.48	0.33	0.13	0.42	0.35	0.40
$\mathrm{CH}_2\mathrm{CH}_2$	0.43	0.57	0.61	0.42	0.18	0.53	0.45	0.50
CH ₃ CH ₂	1.59	1.97	2.10	1.56	0.81	1.84	1.63	1.76
CH ₃ CH	2.84	3.44	3.63	2.79	1.54	3.24	2.91	3.11
CH ₂ CH	1.33	1.71	1.82	1.30	0.60	1.59	1.37	1.52
CHCH	0.63	0.82	0.88	0.62	0.28	0.76	0.65	0.72
$\rm CCH_3$	3.38	4.05	4.27	3.33	1.90	3.83	3.46	3.69
CCH	1.40	1.77	1.89	1.37	0.68	1.65	1.44	1.57
CCH_2	1.45	1.83	1.95	1.42	0.71	1.71	1.49	1.63
H_2O	0.81	0.89	1.03	0.74	0.58	0.69	0.51	0.49
CO_2	0.33	0.37	0.44	0.30	0.23	0.28	0.20	0.19
HCO	1.63	2.02	2.16	1.60	0.83	1.89	1.68	1.81
CH ₂ O	0.96	1.06	1.23	0.87	0.68	0.82	0.60	0.58
CH ₃ O	3.09	3.36	3.78	2.86	2.34	2.72	2.09	2.04
CH ₃ OH	0.89	0.99	1.14	0.81	0.64	0.76	0.56	0.54
НСОН	2.58	3.14	3.33	2.54	1.38	2.96	2.65	2.84
СОН	3.31	3.97	4.19	3.26	1.85	3.75	3.39	3.61
СООН	2.13	2.61	2.77	2.09	1.11	2.45	2.18	2.34
CH ₂ OH	1.47	1.81	1.93	1.44	0.76	1.70	1.51	1.62

Table S3 Standard UBI-QEP estimated binding energies (eV) over 8 transition metal surfaces. Q_A , n and D_{AB} are obtained from DFT calculations.

Species	Co(0001)	Ru(0001)	Fe(110)	Ni(111)	Cu(111)	Rh(111)	Pd(111)	Pt(111)
С	6.42	7.27	7.54	6.35	4.39	6.99	6.52	6.81
Н	2.72	2.81	2.93	2.72	2.40	2.73	2.74	2.64
Ο	5.49	5.81	6.32	5.20	4.54	5.02	4.21	4.13
СО	1.19	1.50	1.61	1.16	0.57	1.39	1.22	1.33
H_2	0.28	0.29	0.32	0.28	0.22	0.28	0.28	0.26
OH	3.42	3.70	4.14	3.17	2.61	3.01	2.34	2.28
СН	5.49	6.37	6.65	5.42	3.41	6.08	5.59	5.89
CH_2	3.27	3.93	4.15	3.22	1.81	3.71	3.35	3.57
CH ₃	1.53	1.90	2.02	1.50	0.78	1.78	1.57	1.70
CH ₄	0.17	0.21	0.22	0.16	0.08	0.20	0.17	0.19
CH ₃ CH ₃	0.19	0.25	0.26	0.19	0.09	0.23	0.20	0.22
$\mathrm{CH}_2\mathrm{CH}_2$	0.63	0.79	0.85	0.62	0.31	0.74	0.65	0.70
CH ₃ CH ₂	1.51	1.86	1.98	1.48	0.78	1.74	1.55	1.67
CH ₃ CH	3.36	4.04	4.26	3.31	1.88	3.82	3.44	3.67
CH ₂ CH	2.53	3.13	3.34	2.48	1.29	2.93	2.59	2.80
CHCH	2.14	2.69	2.88	2.10	1.05	2.51	2.20	2.39
$\rm CCH_3$	4.98	5.85	6.12	4.91	2.97	5.56	5.08	5.38
CCH	4.57	5.58	5.92	4.49	2.44	5.24	4.69	5.03
CCH_2	3.75	4.56	4.82	3.68	2.02	4.29	3.84	4.11
H_2O	0.40	0.45	0.52	0.37	0.29	0.35	0.25	0.24
CO_2	0.33	0.37	0.44	0.30	0.23	0.28	0.20	0.19
HCO	2.18	2.68	2.84	2.15	1.14	2.51	2.24	2.41
CH ₂ O	0.97	1.07	1.23	0.88	0.70	0.83	0.61	0.59
CH ₃ O	3.09	3.36	3.78	2.86	2.34	2.72	2.09	2.04
CH ₃ OH	0.45	0.49	0.57	0.41	0.32	0.38	0.28	0.27
НСОН	2.58	3.14	3.33	2.54	1.38	2.96	2.65	2.84
СОН	3.85	4.57	4.81	3.79	2.21	4.33	3.93	4.18
СООН	2.13	2.61	2.77	2.09	1.11	2.45	2.18	2.34
CH ₂ OH	1.47	1.81	1.93	1.44	0.76	1.70	1.51	1.62

Table S4 Modified UBI-QEP estimated binding energies (eV) over 8 transition metal surfaces. Q_A , n and D_{AB} are obtained from DFT calculations.



Table S5 Standard UBI-QEP equations for calculation of activation energies towards dissociation reactions²⁻⁶.



Figure S3 a, Standard UBI-QEP estimated activation energies (in combination with DFT calculated adsorption heats) versus DFT values towards C-H, C-C bond cleavage and CO dissociation on the most close-packed surfaces of Co, Ru, Fe, Ni, Cu, Rh, Pd and Pt; b, Standard UBI-QEP estimated activation energies (in combination with improved UBI-QEP calculated adsorption heats) versus DFT values towards C-H, C-C bond cleavage and CO dissociation on the most close-packed surfaces of Co, Ru, Fe, Ni, Cu, Rh, Pd and Pt; b, Standard UBI-QEP estimated activation energies (in combination with improved UBI-QEP calculated adsorption heats) versus DFT values towards C-H, C-C bond cleavage and CO dissociation on the most close-packed surfaces of Co, Ru, Fe, Ni, Cu, Rh, Pd and Pt.

Part S2 Detailed classification of BEP relationships

Type 1: C-H bond cleavage. Reactions of this class correspond to bond breaking of C-H in fragments like C_xH_y, H_xCO, and H_xCOH, with the BEP relationship identified as:

$$E_a = 0.89\Delta H + 0.75$$
 (S14)

The relationship is generated based on more than 20 elementary steps over 8 transition metal flat surfaces, shown as Figure S4a, thus universality is proved. The slope is 0.89, signifying a product-like transition state, which is in good agreement with the work of Michaelides et al.⁷, 0.92 ± 0.05 for dehydrogenation. The constant term 0.75 is also similar to the work of Michaelides et al.⁷, 0.87 ± 0.05 . H₂ dissociation (H_{2(g)} \rightarrow 2H*) was considered separately herein, because of not belonging to any of the 4 key classes, while the obtained scaling is close to that of C-H bond cleavage, expressed as:

$$E_a = 0.98\Delta H + 0.91$$
(S15)

The reason might be that removing one H atom occurred in both reactions, which can be confirmed by the phenomenon that the BEP relationship of H₂ dissociation is also in the range of Michaelides' result for dehydrogenation⁷. Here we do not put C-H bond cleavage and H₂ dissociation in the same category like dehydrogenation because dehydrogenation includes more reactions such as O-H bond cleavage in OH, H₂O and so on, which exhibits a totally different scaling (Type 4). In addition, there is still some difference between Eq. (S14) and Eq. (S15). The parameter 0.98 in Eq. (S15) stands for a total 'late' transition state, indicating that the transition state configuration of H₂ dissociation is mostly dependent on adsorbed H atoms.



Figure S4 DFT calculated activation energies against reaction heats over Co(0001), Ru(0001), Fe(110), Ni(111), Cu(111), Rh(111), Pd(111), Pt(111), Ag (111) and Au(111) surfaces for a, C-H bond cleavage; b, C-O bond cleavage; c, C-C bond cleavage (original data); d, C-C bond cleavage with adjusted activation barrier, $E_{adjust} = E_a - 0.25n_0$; e, O-H bond recombination; f, H₂ dissociation; g, CO dissociation; h, CO* + OH* \rightarrow COOH*; i, CH₃* + OH* \rightarrow CH₃OH*; j, CH₃* + CH₃* \rightarrow CH₃CH₃*.

Type 2: C-O bond cleavage. Into this type fall C-O bond breaking in CO₂, COOH, COH,

H_xCOH and H_xCO. The general BEP relationship that we determine for this type of reaction is

$$E_a = 0.65\Delta H + 1.21$$
 (S16)

Where 0.65 presents a slightly 'late' transition state. Most C-O bond cleavage reactions follow this relationship very well, shown as Figure S4b. However, there are several exceptions, namely CO dissociation (CO* \rightarrow C* + O*), CO* + OH* \rightarrow COOH* and CH₃* + OH* \rightarrow CH₃OH*, plotted as Figure S4g, h, i, respectively. The BEP relationship for CO dissociation is described as:

$$E_a = 0.69\Delta H + 1.99 \tag{S17}$$

Which has a similar slope to that of general C-O cleavage reactions, while their intercepts have a large difference, 1.99 and 1.21, respectively. The analogous slopes indicate that their transition state structures towards C-O bond positions are very close. A higher intercept for CO dissociation demonstrates that it is more difficult to break the C-O bond in CO molecule rather than the other species such as CO₂, COH, HCOH, and COOH, due to stronger electron donation from C atom to O atom in the CO molecule. For COH and HCOH species, O atom gains electrons not only from the C atom but also from the connected H atom, resulting in a weaker C-O bond strength compared to the CO molecule. The calculated C-O bond distances of adsorbed CO, COH and HCOH over Co hcp (0001) surface are 1.212 Å, 1.357 Å and 1.390 Å, respectively, which certifies the speculation. For CO₂ and COOH, C atom donates electrons to two connected O atoms, weakening each C-O bond strength versus that in CO molecule. Therefore, different scaling relationships for CO dissociation and general C-O bond cleavage are existed.



Figure S5 Configurations of (a) reactant, (b) transition state and (c) product for COOH* \rightarrow CO* + OH* on Ni (111) surface.

 $COOH^* \rightarrow CO^* + OH^*$ is another special case that can't be classified in the general C-O bond cleavage reactions, because the transition state structure of this reaction is more like the structure of COOH (see Figure S5a). According to Hammond postulate^{8, 9}, for reactions with product-like transition states, the forward activation energies should correlate to the forward reaction heats. For reactions with reactant-like transition states, the reverse activation energies should correlate with corresponding reaction heats. In consequence, the BEP relationship should be applied to the reverse reaction, namely $CO^* + OH^* \rightarrow COOH^*$, which is characterized by

$$E_a = 0.83\Delta H + 0.52$$
 (S18)

Figure S4h displays a very good linear relationship regarding this elementary step. The other exception of C-O bond cleavage is $CH_3^* + OH^* \rightarrow CH_3OH^*$, which also behaves a BEP relationship for recombination, shown as Figure S4i:

$$E_a = 0.81 \Delta H + 1.85$$
 (S19)

Even though slopes of above two BEP relationships towards recombination are approximate, their intercepts have a huge difference, 0.52 and 1.85, respectively. That is to say, the activation energy of CO + OH reaction is much lower than that of CH_3 + OH, with the average difference around 1.0 eV. The energy barrier difference is mainly caused by different stability of products,

owing to product-like transition states occurred in both reactions. DFT calculations illustrate that product COOH is more stable than CH₃OH about 1.9 eV, while reactants CO and CH₃ have similar stability. Therefore, it is indeed that different stability of COOH and CH₃OH leads to the difference in activation barrier. The more stable the product, the lower the activation barrier.

Type 3: C-C bond cleavage. This class comprises C-C bond breaking in hydrocarbon and radicals that including 2 or more than 2 carbon atoms. In Figure S4c, the fitted BEP relationships are divided into three parts: Pt; Ru, Rh, Pd; and Fe, Co, Ni, Cu, respectively, due to the non-uniform linear relationship for all metals together. From which, we can see that slopes of the three scaling relations are similar, while their intercepts have certain difference. Interestingly, the intercepts (φ) are related to period numbers (n_0) of these metals, which is found in this work. The period number of Pt is 6, corresponds to the highest intercept, 1.58; Ru, Rh, Pd has intercept of 1.23, with 5 as period number; Fe, Co, Ni, Cu has the lowest intercept, 0.95, and the period number is 4. As a result, an average value of φ/n_0 , 0.25, is achieved from these data. We guess that using 0.25 n_0 as the intercept for BEP relationship of C-C bond cleavage might be a good choice. To test and verify that, adjusted activation barriers: E_a - 0.25*6 for Pt; E_a - 0.25*5 for Ru, Rh, Pd; and E_a - 0.25*4 for Fe, Co, Ni, Cu, are applied to generate the new scaling, shown as Figure S4d, which exhibits a much better relationship than Figure S4c. The new slope is around 0.67, and the new intercept is about 0, proving the guess. Therefore, this type of reactions could be determined by:

$$E_a = 0.67\Delta H + 0.25n_0 \tag{S20}$$

Where 0.67 is obtained from the fitting slope in Figure S4d; n_0 is period number of metal. The phenomenon that period number influences activation energy may be related to the d-band center of different period metals. Figure S6 gives the average d-band center (ε_d) of VIIIB metals as a function of period number (n_0). The VIIIB metals are choosed because of the similar property and most used herein, of which the d-band center could be utilized to characterize the general metal feature in this work. The energies of d-band center for these metals are obtained from the work of Hammer and Norskov¹⁰, calculated based on fcc(111), hcp(0001) and bcc(110) surfaces, same with this study. Ni, Co and Fe are elements in period 4, which have the least negative ε_{d} ; Ir and Pt are located in period 6, with the most negative ε_{d} ; Pd, Rh and Ru are in the middle of them. In consequence, we can conclude that the larger the period number, the more negative the d-band center, the higher the activation barrier, which is in agreement with the result reported by Hammer and Norskov's result¹⁰, namely activation energy is inversely proportional to metal d-band center for dissociation reactions.



Figure S6 Average d-band center (ε_d) of VIIIB metals as a function of period number (n_0), where the most closepacked metal surfaces were used.

 $CH_3^* + CH_3^* \rightarrow CH_3CH_3^*$ is one exception, which has the BEP relationship:

$$E_a = 0.68\Delta H + 2.49$$
 (S21)

The high activation barrier of this elementary could be explained by weak stability of CH₃CH₃, similar to the reason for CH₃OH formation in previous part.

Type 4: O-H bond recombination. H₂O, OH, COH, H_xCOH and COOH formation via O-H bond association belongs to reactions of this class, with BEP relation shown as Figure S4e:

$$E_a = 0.89\Delta H + 0.98$$
 (S22)

The slope is 0.89, indicating a product-like transition state. From the microscopic reversibility principle¹¹, the relationship of forward activation energies (E_f), reverse activation energies (E_r) and reaction heat (ΔH) can be described as $E_f = E_r + \Delta H$. Thus, 0.11 is predicted as the slope for the reverse reactions, namely O-H bond cleavage. Fajín et al.¹² researched BEP relationship for water splitting over several transition metal surfaces, with 0.29 as slope, revealing a H₂O-like transition state. Even though there is some difference between 0.11 and 0.29, both values illustrate reactant-like transition state for O-H bond cleavage.

Above BEP relationships were obtained based on the most close-packed surfaces. To check whether other metal surfaces such as steps (211) and square-packed (100) surfaces follow the same BEP relationships, we summarized new BEP relationships of three types reactions on M(100), M(211), M(111), M(0001) and M(110) surfaces, shown as Figure S7. After taking into account different metal surfaces together, the new BEP relations are found similar to previous ones. Consequently, we can assume that different metal surfaces follow the same BEP relationships, which will be applied in the fast prediction of activation energies, further aid in rational catalyst design.



Figure S7 DFT calculated activation energies against reaction heats for a, C-H bond cleavage; b, C-O bond cleavage; c, O-H bond recombination; d, CO dissociation on M(100), M(211), M(111), M(0001) and M(110) surfaces. M represents for Co, Fe, Pt, Pd, Ru, Rh, Ni, Cu, Ag and Au.

Part S3 TSS correlations

Besides BEP relationship, TSS is also among the commonly used approach to estimate activation energy, which directly correlates the transition state energy (E_{TS}) with finial state energy (E_{FS}) or initial state energy (E_{IS}), described as:

$$E_{TS} = \alpha_1 E_{FS} + \beta_1 \tag{S23}$$

$$E_{\rm TS} = \alpha_2 E_{\rm TS} + \beta_2 \tag{S24}$$

Figure S8 and Figure S9 give the two TSS correlations, respectively. We can see that for C-H, C-C and C-O bond cleavage, E_{TS} estimated from E_{FS} displays much better scaling than that from E_{IS} . While for O-H bond cleavage, the E_{TS} is related to E_{IS} more than E_{FS} . Therefore, C-H, C-C and C-O bond cleavage and O-H bond recombination are considered for BEP relationships. The mean absolute error (MAE) of the two TSS correlations are 0.18 eV and 0.41 eV, respectively, which are both higher than that of BEP relationship (0.13 eV). Consequently, BEP relationships exhibit better error performance than the TSS correlations. Moreover, due to its straightforward identification of homologous series by means of statistical tests, the BEP relationship is selected to estimate activation energies in this work.



Figure S8 DFT calculated transition state energy against finial state energy for C-H, C-O, C-C and O-H bond cleavage over Co(0001), Ru(0001), Fe(110), Ni(111), Cu(111), Rh(111), Pd(111) and Pt(111) surfaces.



Figure S9 DFT calculated transition state energy against initial state energy for C-H, C-O, C-C and O-H bond cleavage over Co(0001), Ru(0001), Fe(110), Ni(111), Cu(111), Rh(111), Pd(111) and Pt(111) surfaces.

Part S4 Microkinetic modeling method

All elementary steps involved in the microkinetic model for steam methane reforming are shown as following, which include CO formation via several possible pathways, direct C* and O* combination pathway and hydrogen insertion involving CHO*, COH* and HCOH* intermediates pathways. In addition, the model simulates CO₂ formation via COOH* intermediate.

$CH_{4(g)} \neq CH_3^* + H^*,$	(ES1)
$CH_3^* \neq CH_2^* + H^*,$	(ES2)
CH ₂ * <i>₹</i> CH* + H*,	(ES3)
CH* <i>₹</i> C* + H*,	(ES4)
$H_2O_{(g)} \neq H_2O^*,$	(ES5)
H_2O^* ≈ $H^* + OH^*$,	(ES6)
OH* <i>₹</i> O* + H*,	(ES7)
C* + OH* ≈ COH*,	(ES8)
COH* <i>₹</i> CO* + H*,	(ES9)
$C^* + O^* \neq CO^*,$	(ES10)
CH* + O* <i>₹</i> HCO*,	(ES11)
$HCO^* \neq CO^* + H^*,$	(ES12)
HCO* + H* <i>≥</i> HCOH*,	(ES13)
$CH^* + OH^* \neq HCOH^*,$	(ES14)
HCOH* <i>₹</i> H* + COH*,	(ES15)
$\mathrm{CO}^* \neq \mathrm{CO}_{(\mathrm{g})},$	(ES16)
2H* <i>≥</i> H _{2(g)} ,	(ES17)

$$COH^* + O^* \neq COOH^*,$$
 (ES18)

$$CO^* + OH^* \neq COOH^*$$
, (ES19)

$$COOH^* \neq CO_{2(g)} + H^*.$$
(ES20)

The microkinetic model is conducted on CatMAP, which generates reaction rates of the system by solving a mean-field model to steady state¹³. Improved UBI-QEP calculated adsorption energies and BEP estimated activation energies are performed as input parameters of the microkinetic model. Zero point energies are ignored for both gas-phase and adsorbed species, integrated heat capacity and entropy are neglected for adsorbates, and shomate equations are used to calculate gas-phase thermochemistry. The reaction temperature is 773 K, total pressure is 1 bar, with gas composition of 18.2% CH₄, 63.6% H₂O and 18.2% H₂.

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