Supporting Information

Rationalization of Nonlinear Adsorption Energy-Strain Relations and Brønsted–Evans–Polanyi and Transition State Scaling Relationships under Strain

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Computational methods

Generalized-gradient approximation (GGA) DFT calculations were performed using the Vienna *ab initio* simulation package (VASP)[1-5]. The projection augmented plane wave method (PAW)[6-7] was used for the electron ion interaction and the PBE functional of generalized gradient approximation (GGA) [8-9] was used for calculations of exchange correlation energy. A kinetic energy cutoff of 400eV was used for all calculations. Dispersion correction (DFT-D3 method with Becke-Jonson damping[10-11]) and Z-direction dipole correction were considered for all the surface reactions. The effect of spin polarization was considered for systems containing Ni. The ground state crystal structures of Cu, Ni, Ag, Pd and Pt belong to FCC structures. The strain was applied uniformly to the PBE functional optimized equilibrium bulk lattice parameters from +5% to -5% with an interval of 1%. Strain ε is defined as $(a_s - a_0)/a_0$. Here a_0 and a_s are the lattice parameters of the DFT optimized bulk and the scaled bulk respectively. Five-layer periodically repeated slabs were constructed by cleaving the (111) surfaces from respective bulk structures. The adsorbate and the top three layers of metal atoms were allowed to be relaxed till the force on each relaxed atom is smaller than 0.02eV/Å, and the remaining two layers were fixed. A (2 × 2) unit cell was used for all the calculations. A vacuum spacing 10 Å was used to eliminate the interaction between neighboring slabs. The nudged elastic band (NEB) method was used to locate the transition state structures, which were verified by vibrational analyses that show no imaginary frequencies for local minima and one and only one proper imaginary frequency for transition states. K-points used in calculations are listed in Table S1.

Table S1. K-points used in the calculations.

Slab	K-points
Pt(111)	7 7 1
Cu(111)	8 8 1
Pd(111)	7 7 1
Ag(111)	7 7 1
Ni(111)	8 8 1

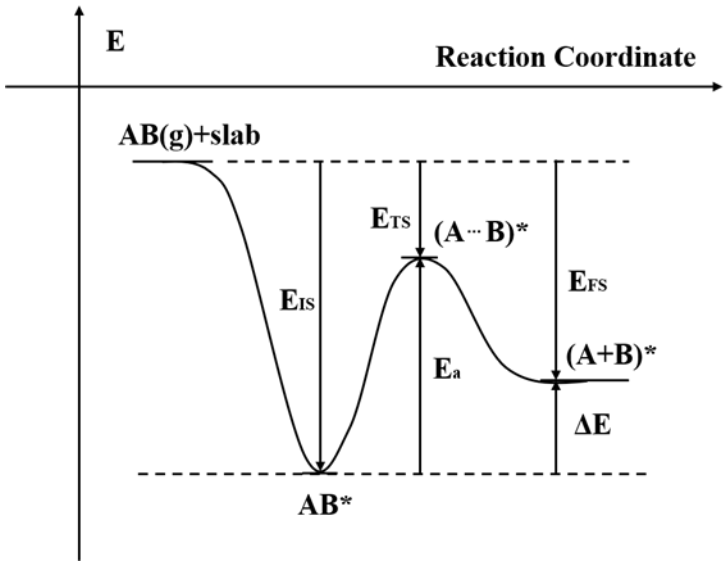

Figure S1. Energy diagram for diatomic species dissociation on metal surfaces.

Energies and structural parameters under no strain

Table S2. Dissociation energies ΔE and energy barriers E_a of BH, CH, NH, CO and NO on unstrained (111) surfaces of FCC crystals. All the energies are ZPVE-corrected.*

Species	Surfaces	ΔE(eV)		E_a (eV)	
BH	Pd(111)	0.21	-	0.71	-
	Pt(111)	0.49	-	0.67	-
	Ag(111)	1.52	-	1.66	-
	Cu(111)	1.25	-	1.30	-
	Ni(111)	0.47	-	0.70	-
CH	Pd(111)	0.40	0.61[12], 0.42[13]	1.17	1.44[12], 1.38[13]
	Pt(111)	0.76	1.03[12], 0.67[13]	1.11	1.46[12], 1.87[13]
	Ag(111)	1.97	2.20[12], 1.95[13]	2.20	2.43[12], 2.57[13]
	Cu(111)	1.58	1.68[12], 1.49[13]	1.76	1.91[12], 2.21[13]
	Ni(111)	0.45	0.59[13]	1.14	1.39[13]
NH	Pd(111)	0.40	0.42[13]	1.36	1.45[13]
	Pt(111)	0.54	0.49[13]	1.09	4.1[13]
	Ag(111)	2.09	1.94[13]	2.45	2.75[13]
	Cu(111)	1.56	1.32[13]	1.93	2.28[13]
	Ni(111)	0.33	0.43[13]	1.20	1.44[13]
CO	Pd(111)	3.19	3.34[14]	3.73	4.01[14]
	Pt(111)	2.77	3.13[14]	3.71	4.08[14]
	Ag(111)	5.19	5.46[14]	5.31	5.55[14]
	Cu(111)	3.86	3.94[14]	3.90	4.05[14]
	Ni(111)	2.41	2.24[14], 1.27[15]	2.86	3.63[14], 2.96[15]
NO	Pd(111)	1.31	1.38[16]	2.26	2.36[16]
	Pt(111)	0.67		2.13	
	Ag(111)	2.63		3.04	
	Cu(111)	1.19	0.591[17]	1.67	1.953[17]
	Ni(111)	0.19	0.04[18]	1.35	

*: Superscripted numbers denote the reference.

Table S3. Adsorption and dissociation sites of five adsorbates on unstrained metal surface (H is the HCP hole site; F is the FCC hole site; T is the top site; B is the bridge site).

Diatomic species(AB)	Surface	Adsorption site of initial state	Adsorption site of final state A(A=B, C, N)	Adsorption site of final state B(B=H, O)	Adsorption site of transition state A (A=B, C, N)	Adsorption site of transition state B(B=H, O)
BH	Pd(111)	H	H	F	H	T
	Pt(111)	H	H	F	H	T
	Ag(111)	F	F	F	F	B
	Cu(111)	F	F	F	F	B
	Ni(111)	H	H	H	H	B
CH	Pd(111)	H	H	F	H	T
	Pt(111)	F	F	H	F	T
	Ag(111)	F	F	F	F	B
	Cu(111)	F	F	F	F	B
	Ni(111)	H	H	F	H	T
NH	Pd(111)	F	F	H	F	T
	Pt(111)	F	F	H	F	T
	Ag(111)	F	F	F	F	B
	Cu(111)	F	F	F	F	B
	Ni(111)	F	F	H	F	T
CO	Pd(111)	H	H	H	H	B
	Pt(111)	B	F	F	F	B
	Ag(111)	F	F	F	F	B
	Cu(111)	F	F	F	F	B
	Ni(111)	H	H	H	H	B
NO	Pd(111)	H	H	H	H	B
	Pt(111)	F	F	F	F	B
	Ag(111)	F	F	F	F	B
	Cu(111)	F	F	F	F	B
	Ni(111)	H	H	H	H	B

Table S4. Bond length data of five adsorbates on unstrained metal surface.

Diatomic species (AB)	Surface	Bond length of initial state AB(Å)	Bond length of final state AB(Å)	Bond length of transition state AB(Å)
BH	Pd(111)	1.209	3.229	2.061
	Pt(111)	1.202	3.239	1.861
	Ag(111)	1.203	2.972	2.227
	Cu(111)	1.201	2.586	1.938
	Ni(111)	1.204	2.499	1.700
CH	Pd(111)	1.104	3.229	1.763
	Pt(111)	1.098	3.236	1.641
	Ag(111)	1.101	2.967	2.138
	Cu(111)	1.098	2.577	1.860
	Ni(111)	1.102	2.870	1.740
NH	Pd(111)	1.029	3.233	1.616
	Pt(111)	1.025	3.240	1.516
	Ag(111)	1.026	2.974	1.988
	Cu(111)	1.024	2.579	1.722
	Ni(111)	1.026	2.872	1.614
CO	Pd(111)	1.193	2.808	2.063
	Pt(111)	1.183	2.814	1.925
	Ag(111)	1.172	2.947	2.321
	Cu(111)	1.183	2.569	2.153
	Ni(111)	1.193	2.488	1.821
NO	Pd(111)	1.211	2.801	1.815
	Pt(111)	1.215	2.806	1.823
	Ag(111)	1.207	2.944	2.087
	Cu(111)	1.222	2.564	1.846
	Ni(111)	1.222	2.488	1.689

Table S5. Adsorption energies of five adsorbates on unstrained metal surfaces. All energies are ZPVE-corrected.

Diatomic species (AB)	Surface	Adsorption energy(eV)
BH	Pd(111)	-5.81
	Pt(111)	-6.19
	Ag(111)	-3.40
	Cu(111)	-4.23
	Ni(111)	-5.34
CH	Pd(111)	-6.36
	Pt(111)	-6.68
	Ag(111)	-3.90
	Cu(111)	-5.08
	Ni(111)	-6.38
NH	Pd(111)	-3.84
	Pt(111)	-3.90
	Ag(111)	-2.45
	Cu(111)	-3.64
	Ni(111)	-4.40
CO	Pd(111)	-2.06
	Pt(111)	-1.85
	Ag(111)	-0.29
	Cu(111)	-0.97
	Ni(111)	-1.94
NO	Pd(111)	-2.41
	Pt(111)	-2.00
	Ag(111)	-0.57
	Cu(111)	-1.33
	Ni(111)	-2.59

Table S6. Adsorption energies of single atoms. All energies are ZPVE-corrected.

Atom	Surface	Adsorption energy(eV)
B	Pd(111)	-6.70
	Pt(111)	-6.93
	Ag(111)	-3.76
	Cu(111)	-4.54
	Ni(111)	-5.99
C	Pd(111)	-7.24
	Pt(111)	-7.32
	Ag(111)	-3.91
	Cu(111)	-5.21
	Ni(111)	-7.02
N	Pd(111)	-4.92
	Pt(111)	-4.96
	Ag(111)	-2.55
	Cu(111)	-4.01
	Ni(111)	-5.40
H	Pd(111)	-2.78
	Pt(111)	-2.69
	Ag(111)	-2.06
	Cu(111)	-2.44
	Ni(111)	-2.72
O	Pd(111)	-4.86
	Pt(111)	-4.68
	Ag(111)	-4.02
	Cu(111)	-5.18
	Ni(111)	-5.80

Derivation of equations

According to the theory of continuum mechanics and Green formula[19], the stress tensor element σ_{ij} is

$$\sigma_{ij} = \frac{\partial W(\varepsilon_{ij})}{\partial \varepsilon_{ij}} \qquad (i,j = 1,2,3) \tag{1}$$

ε_{ij} is the strain tensor element of the strain tensor matrix [ε_{ij}] , and $W(\varepsilon_{ij})$ is the energy density. For three-dimensional elastic deformation[19-20], the energy density $W(\varepsilon_{ij})$ can be expressed in the form of a Taylor expansion.

$$W(\varepsilon_{ij}) = C_0 + C_{ij}\varepsilon_{ij} + \frac{1}{2}C_{ijkl}\varepsilon_{ij}\varepsilon_{kl} + o(\varepsilon^3) \qquad (i,j,k,l = 1,2,3)$$

$$= W_0 + \sigma_{ij}^0\varepsilon_{ij} + \frac{1}{2}\sigma_{ij}\varepsilon_{ij} + o(\varepsilon^3) \tag{2}$$

In (2) $W_0 = C_0 = W|_{\varepsilon_{ij}=0}$ is the energy density at $\varepsilon_{ij} = 0$. In our work the energy density of strained and unstrained clean slabs are expressed as W_ε^{clean} and W_0^{clean} respectively, and the energy density of strained and unstrained slabs with adsorbates on them are denoted by W_ε^{AB} and W_0^{AB} respectively. $C_{ij} = \left.\frac{\partial W}{\partial \varepsilon_{ij}}\right|_{\varepsilon_{ij=0}} = \sigma_{ij}^0$ is the initial stress tensor element, and σ_{ij} is the elastic stress tensor element. The initial stress tensor element of the slab with adsorbates on it is σ_{ij}^{ads} [21], which is regarded to be triaxial and independent of strain in our work. The "ads" in the whole paper refers to the states, i.e. IS (initial state), TS (transition state) or FS (final state). Similar meaning applies to other notations like Δv_{ads}, K_{ads} and σ_{ij}^{ads} below. The elastic modulus tensor element C_{ijkl} is: $C_{ijkl} = \frac{\partial^2 W}{\partial \varepsilon_{ij}\partial \varepsilon_{kl}} = \frac{\partial \sigma_{kl}}{\partial \varepsilon_{ij}}$.

The constitutive relation (generalized Hooke law[22]) of isotropic and linear elastic material is

$$\sigma_{ij} = 2G\varepsilon_{ij} + \lambda\varepsilon_{kk}\delta_{ij} \tag{3}$$

$$\delta_{ij} = \begin{cases} 1 & (i = j) \\ 0 & (i \neq j) \end{cases} \qquad (i,j,k = 1,2,3)$$

For the problems we study here, G and λ in (3) are two lamé constants of the slab. Strain tensor matrix $[\varepsilon_{ij}]$ is a diagonal matrix. For small strain the higher-order terms $o(\varepsilon^3)$ in (2) can be neglected. Substituting (3) into (2), we get

$$W_\varepsilon^{AB} = W_0^{AB} + \sigma_{ij}^{\text{ads}}\varepsilon_{ij} + \frac{1}{2}\left(2G\varepsilon_{ij} + \lambda\varepsilon_{kk}\delta_{ij}\right)\varepsilon_{ij} = W_0^{AB} + \sigma_{ij}^{\text{ads}}\varepsilon_{ij} + \frac{1}{2}\lambda\varepsilon_{kk}\varepsilon_{jj} + G\varepsilon_{ij}\varepsilon_{ij} = W_0^{AB} + \sigma_{ij}^{\text{ads}}\varepsilon_{ij} + \frac{1}{2}\lambda\varepsilon_{ii}\varepsilon_{jj} + G\varepsilon_{ij}\varepsilon_{ij} \quad (4)$$

For a strained clean slab there is no initial stress induced by adsorbates, $\sigma_{ij}^{\text{ads}} = 0$, energy density W_ε^{clean} from (4) is

$$W_\varepsilon^{clean} = W_0^{clean} + \frac{1}{2}\lambda\varepsilon_{ii}\varepsilon_{jj} + G\varepsilon_{ij}\varepsilon_{ij} \quad (5)$$

Although strain is applied on a slab in three directions uniformly, atoms of the slab can be changed freely along Z direction (direction normal to the slab surface) due to the existence of vacuum spacing during the structure optimization. Thus the strain tensors of a slab without adsorbates, $\left[\varepsilon_{ij}^{clean}\right]$, and with adsorbates on the slab, $[\varepsilon_{ij}^{AB}]$, are

$$[\varepsilon_{ij}^{clean}] = \begin{bmatrix} \varepsilon & 0 & 0 \\ 0 & \varepsilon & 0 \\ 0 & 0 & -v\varepsilon \end{bmatrix} \quad (6a)$$

$$[\varepsilon_{ij}^{AB}] = \begin{bmatrix} \varepsilon & 0 & 0 \\ 0 & \varepsilon & 0 \\ 0 & 0 & -(v + \Delta v_{\text{ads}})\varepsilon \end{bmatrix} \quad (6b)$$

v is the ratio of -(L-L_0)/L_0 with respect to the applied strain ε (-5% to 5% in our case). L is the inter-layer distance between the 1st(top) and 4th layer of the strained and relaxed clean slab without adsorbates on it and L_0 refers to the inter-layer distance between the 1st(top) and 4th layer of the unstrained and relaxed clean slab without adsorbates on it. Δv_{ads} is the ratio of -(L'-L)/L (which can be approximated as -(L'-L)/L_0) with respect to the applied strain ε. L' is the inter-layer distance between the 1st and 4th layer of the relaxed and strained slab with adsorbates on it. $-v\varepsilon$ is the strain in the Z direction without adsorbates on the slab, and $-\Delta v_{\text{ads}}\,\varepsilon$ is the strain in the Z direction due to adsorption. $-\Delta v_{\text{ads}}$ depends on the substrate, adsorbates and the states (i.e., initial state, transition state and final state) and is listed in Table S13.

The triaxial stress tensor diagonal matrix in the presence of adsorbates, $[\sigma_{ij}^{\text{ads}}]$, is

$$[\sigma_{ij}^{\text{ads}}] = \begin{bmatrix} \sigma_{11}^{\text{ads}} & \sigma_{12}^{\text{ads}} & \sigma_{13}^{\text{ads}} \\ \sigma_{21}^{\text{ads}} & \sigma_{22}^{\text{ads}} & \sigma_{23}^{\text{ads}} \\ \sigma_{31}^{\text{ads}} & \sigma_{32}^{\text{ads}} & \sigma_{33}^{\text{ads}} \end{bmatrix} = \begin{bmatrix} \sigma_{11}^{\text{ads}} & 0 & 0 \\ 0 & \sigma_{22}^{\text{ads}} & 0 \\ 0 & 0 & \sigma_{33}^{\text{ads}} \end{bmatrix} \quad (7)$$

Substituting (6b) and (7) into (4), the elastic energy density of the strained slab with adsorbates on it, W_ε^{AB}, can be expressed as follow,

$$W_\varepsilon^{AB} = W_0^{AB} + (\sigma_{11}^{\text{ads}} + \sigma_{22}^{\text{ads}} - (v + \Delta v_{\text{ads}})\sigma_{33}^{\text{ads}})\varepsilon + \left[\frac{1}{2}\lambda(2 - v - \Delta v_{\text{ads}})^2 + G(2 + (v + \Delta v_{\text{ads}})^2)\right]\varepsilon^2 \tag{8}$$

Substituting (6a) into (5), the elastic energy density of a strained slab without adsorbates,W_ε^{clean}, is:

$$W_\varepsilon^{clean} = W_0^{clean} + \left[\frac{1}{2}\lambda(2 - v)^2 + G(2 + v^2)\right]\varepsilon^2 \tag{9}$$

The adsorption energies on an unstrained slab, E_{ads}^0(E_{ads}^0 represents E_{IS}^0, E_{FS}^0 or E_{TS}^0 which refers to the adsorption energy in initial state, final state and transition state respectively), is defined as

$$E_{\text{ads}}^0 = E_{\text{AB/slab}}^0 - E_{\text{slab}}^0 - E_{\text{AB}} \tag{10}$$

$$E_{\text{slab}}^0 = V_0 W_0^{clean} \tag{11}$$

$$E_{\text{AB/slab}}^0 = V_0 W_0^{AB} \tag{12}$$

$E_{\text{AB/slab}}^0$, E_{slab}^0 and E_{AB} are total energies of the unstrained slab with adsorbates on it, the total energies of the unstrained clean slab and the total energies of the isolated adsorbates, respectively. The adsorption energies on a strained slab, $E_{\text{ads}}^\varepsilon$($E_{\text{ads}}^\varepsilon$ represents $E_{\text{IS}}^\varepsilon$, $E_{\text{FS}}^\varepsilon$ and $E_{\text{TS}}^\varepsilon$) is:

$$E_{\text{ads}}^\varepsilon = E_{\text{AB/slab}}^\varepsilon - E_{\text{slab}}^\varepsilon - E_{\text{AB}} \tag{13}$$

$$E_{\text{slab}}^\varepsilon = V_\varepsilon W_\varepsilon^{clean} \tag{14}$$

$$E_{\text{AB/slab}}^\varepsilon = V_\varepsilon W_\varepsilon^{AB} \tag{15}$$

$E_{\text{AB/slab}}^\varepsilon$ and $E_{\text{slab}}^\varepsilon$ are total energies of the strained slab with adsorbates on it and the total energies of the strained clean slab. V_0 is the clean slab volume (enclosed by the upper 4 layers in our case) under no strain. V_ε is the volume of the clean slab (enclosed by the upper 4 layers) under strain and can be written as

$$\begin{aligned} V_\varepsilon &= V_0(1 + \varepsilon)(1 + \varepsilon)(1 - v\varepsilon) \\ &= V_0[1 + (2 - v)\varepsilon + (1 - 2v)\varepsilon^2 - v\varepsilon^3] \\ &\approx V_0[1 + (2 - v)\varepsilon] \end{aligned} \tag{16}$$

When the 2nd order and 3rd order terms are dropped, V_ε is a linear function of strain, which is consistent with the phenomenon observed in our case.

The relation between $E_{\text{ads}}^\varepsilon$ and E_{ads}^0can be obtained from (8) to (16):

$$E_{\text{ads}}^{\varepsilon} = V_{\varepsilon}[W_{\varepsilon}^{AB} - W_{\varepsilon}^{clean}] - E_{\text{AB}}$$

$$= V_{\varepsilon}\left(W_0^{AB} - W_0^{clean}\right) - E_{\text{AB}} + V_{\varepsilon}\left\{\left[\sigma_{11}^{\text{ads}} + \sigma_{22}^{\text{ads}} - (v + \Delta v_{\text{ads}})\sigma_{33}^{\text{ads}}\right]\varepsilon + \left[\frac{1}{2}\lambda(-4 + 2v + \Delta v_{\text{ads}}) + G(2v + \Delta v_{\text{ads}})\right]\Delta v_{\text{ads}}\varepsilon^2\right\}$$

$$=(V_0 + (2 - v)\varepsilon V_0)\left(W_0^{AB} - W_0^{clean}\right) - E_{\text{AB}} + [V_0 + (2 - v)\varepsilon V_0](K_{\text{ads}}^{w}\varepsilon + B_{\text{ads}}\varepsilon^2)$$

$$=\left[V_0\left(W_0^{AB} - W_0^{clean}\right) - E_{\text{AB}}\right] + \left[(2 - v)\varepsilon V_0\left(W_0^{AB} - W_0^{clean}\right)\right] + [V_0 + (2 - v)\varepsilon V_0](K_{\text{ads}}^{w}\varepsilon + B_{\text{ads}}\varepsilon^2)$$

$$=E_{\text{ads}}^{0} + (2 - v)(E_{\text{ads}}^{0} + E_{\text{AB}})\,\varepsilon + [V_0 + (2 - v)\varepsilon V_0](K_{\text{ads}}^{w}\varepsilon + B_{\text{ads}}\varepsilon^2)$$

$$=E_{\text{ads}}^{0} + V_0[K_{\text{ads}}^{w} + (2 - v)(E_{\text{ads}}^{0} + E_{\text{AB}})/V_0]\varepsilon + [V_0 B_{\text{ads}} + (2 - v)V_0 K_{\text{ads}}^{w}]\varepsilon^2 + (2 - v)V_0 B_{\text{ads}}\varepsilon^3$$

$$=E_{\text{ads}}^{0} + V_0 K_{\text{ads}}\varepsilon + [V_0 B_{\text{ads}} + (2 - v)V_0 K_{\text{ads}}^{w}]\varepsilon^2 + (2 - v)V_0 B_{\text{ads}}\varepsilon^3 \quad (17)$$

where

$$K_{\text{ads}} = K_{\text{ads}}^{w} + \frac{(2-v)\left(E_{\text{ads}}^{0} + E_{\text{AB}}\right)}{V_0} \quad (18)$$

$$K_{\text{ads}}^{w} = \sigma_{11}^{\text{ads}} + \sigma_{22}^{\text{ads}} - (v + \Delta v_{\text{ads}})\sigma_{33}^{\text{ads}} \quad (19)$$

$$B_{\text{ads}} = \left[\frac{1}{2}\lambda(-4 + 2v + \Delta v_{\text{ads}}) + G(2v + \Delta v_{\text{ads}})\right]\Delta v_{\text{ads}} \quad (20)$$

As ε ranges from -0.05 to 0.05, $(2 - v)V_0 B_{\text{ads}}\varepsilon^3$ can be neglected. Then we have

$$E_{\text{ads}}^{\varepsilon} = E_{\text{ads}}^{0} + V_0 K_{\text{ads}}\varepsilon + [V_0 B_{\text{ads}} + (2 - v)V_0 K_{\text{ads}}^{w}]\varepsilon^2 \quad (21)$$

Thus, the adsorption energies of the initial state (IS) on the strained slab, $E_{\text{IS}}^{\varepsilon}$ is:

$$E_{\text{IS}}^{\varepsilon} = E_{\text{IS}}^{0} + V_0 K_{\text{IS}}\varepsilon + [V_0 B_{\text{IS}} + (2 - v)V_0 K_{\text{IS}}^{w}]\varepsilon^2 \quad (22)$$

$$K_{\text{IS}} = K_{\text{IS}}^{w} + (2 - v)(E_{\text{IS}}^{0} + E_{\text{AB}})/V_0 = \sigma_{11}^{\text{IS}} + \sigma_{22}^{\text{IS}} - (v + \Delta v_{\text{IS}})\sigma_{33}^{\text{IS}} + (2 - v)(E_{\text{IS}}^{0} + E_{\text{AB}})/V_0 \quad (23)$$

$$B_{\text{IS}} = \left[\frac{1}{2}\lambda(-4 + 2v + \Delta v_{\text{IS}}) + G(2v + \Delta v_{\text{IS}})\right]\Delta v_{\text{IS}} \quad (24)$$

Similarly, the adsorption energies for the transition state (25) and the final state (26) are

$$E_{\text{TS}}^{\varepsilon} = E_{\text{TS}}^{0} + V_0 K_{\text{TS}}\varepsilon + [V_0 B_{\text{TS}} + (2 - v)V_0 K_{\text{TS}}^{\text{w}}]\varepsilon^2 \quad (25)$$

$$E_{\text{FS}}^{\varepsilon} = E_{\text{FS}}^{0} + V_0 K_{\text{FS}}\varepsilon + [V_0 B_{\text{FS}} + (2 - v)V_0 K_{\text{FS}}^{\text{w}}]\varepsilon^2 \quad (26)$$

$$K_{\text{FS}} = K_{\text{FS}}^{w} + (2 - v)(E_{\text{FS}}^{0} + E_{\text{AB}})/V_0 = \sigma_{11}^{\text{FS}} + \sigma_{22}^{\text{FS}} - (v + \Delta v_{\text{FS}})\sigma_{33}^{\text{FS}} + (2 - v)(E_{\text{FS}}^{0} + E_{\text{AB}})/V_0 \quad (27)$$

$$K_{\text{TS}} = K_{\text{TS}}^{w} + (2 - v)(E_{\text{TS}}^{0} + E_{\text{AB}})/V_0 = \sigma_{11}^{\text{TS}} + \sigma_{22}^{\text{TS}} - (v + \Delta v_{\text{TS}})\sigma_{33}^{\text{TS}} + (2 - v)(E_{\text{TS}}^{0} + E_{\text{AB}})/V_0 \quad (28)$$

$$B_{\mathrm{FS}} = \left[\frac{1}{2}\lambda(-4 + 2v + \Delta v_{\mathrm{FS}}) + G(2v + \Delta v_{\mathrm{FS}})\right]\Delta v_{\mathrm{FS}} \quad (29)$$

$$B_{\mathrm{TS}} = \left[\frac{1}{2}\lambda(-4 + 2v + \Delta v_{\mathrm{TS}}) + G(2v + \Delta v_{\mathrm{TS}})\right]\Delta v_{\mathrm{TS}} \quad (30)$$

(22), (25) and (26) show that $E_{\mathrm{IS}}^{\varepsilon}$, $E_{\mathrm{TS}}^{\varepsilon}$ and $E_{\mathrm{FS}}^{\varepsilon}$ are quadratic with respect to strain ε if the strain is small so that the 3rd order term in (17) is neglected. In our study, quadratic terms can be observed when the absolute value of $V_0 B_{\mathrm{ads}}$ is much larger than that of $(2 - v)V_0 K_{\mathrm{ads}}^{w}$ (see Table S11). For some metals the absorption-induced strains are small, then B_{ads} is very small, leading to the small value of $V_0 B_{\mathrm{ads}}$+$(2 - v)V_0 K_{\mathrm{ads}}^{w}$. In this case, $E_{\mathrm{IS}}^{\varepsilon}$, $E_{\mathrm{TS}}^{\varepsilon}$ and $E_{\mathrm{FS}}^{\varepsilon}$ are linear with respect to strain ε.

The relationship between reaction heat and strain, (31), and the relationship between energy barrier and strain, (32), are:

$$\Delta E^{\varepsilon} = E_{\mathrm{FS}}^{\varepsilon} - E_{\mathrm{IS}}^{\varepsilon} = E_{\mathrm{FS}}^{0} - E_{\mathrm{IS}}^{0} + V_0 K_{\mathrm{FS/IS}}\varepsilon + \left[V_0 B_{\mathrm{FS/IS}} + (2 - v)V_0 K_{\mathrm{FS/IS}}^{w}\right]\varepsilon^2 \quad (31)$$

$$E_{\mathrm{a}}^{\varepsilon} = E_{\mathrm{TS}}^{\varepsilon} - E_{\mathrm{IS}}^{\varepsilon} = E_{\mathrm{TS}}^{0} - E_{\mathrm{IS}}^{0} + V_0 K_{\mathrm{TS/IS}}\varepsilon + \left[V_0 B_{\mathrm{TS/IS}} + (2 - v)V_0 K_{\mathrm{TS/IS}}^{w}\right]\varepsilon^2 \quad (32)$$

where

$$K_{\mathrm{FS/IS}}^{w} = K_{\mathrm{FS}}^{w} - K_{\mathrm{IS}}^{w} \quad (33)$$

$$K_{\mathrm{TS/IS}}^{w} = K_{\mathrm{TS}}^{w} - K_{\mathrm{IS}}^{w} \quad (34)$$

$$K_{\mathrm{FS/IS}} = K_{\mathrm{FS}} - K_{\mathrm{IS}} \quad (35)$$

$$K_{\mathrm{TS/IS}} = K_{\mathrm{TS}} - K_{\mathrm{IS}} \quad (36)$$

$$B_{\mathrm{FS/IS}} = \mathrm{B}_{\mathrm{FS}} - \mathrm{B}_{\mathrm{IS}} \quad (37)$$

$$B_{\mathrm{TS/IS}} = \mathrm{B}_{\mathrm{TS}} - \mathrm{B}_{\mathrm{IS}} \quad (38)$$

Since $\sigma_{ij}^{\mathrm{ads}}$, v, λ, G and Δv_{ads} are independent of strain, $K_{\mathrm{TS/IS}}$, $K_{\mathrm{FS/IS}}$, $B_{\mathrm{FS/IS}}$ and $B_{\mathrm{TS/IS}}$ are independent of strain. We can see that there are still quadratic terms in ΔE^{ε} and $E_{\mathrm{a}}^{\varepsilon}$, depending on the value of $\left[V_0 B_{\mathrm{FS/IS}} + (2 - v)V_0 K_{\mathrm{FS/IS}}^{w}\right]$ and $\left[V_0 B_{\mathrm{TS/IS}} + (2 - v)V_0 K_{\mathrm{TS/IS}}^{w}\right]$.

The variation of the BEP relation with respect to strain (39) can be derived from (31) and (32). (39) shows that BEP relationship under strain can be a quadratic function.

$$E_{\mathrm{a}}^{\varepsilon} = (E_{\mathrm{TS}}^{0} - E_{\mathrm{FS}}^{0}) + \Delta E^{\varepsilon} + V_0\left(K_{\mathrm{TS/IS}} - K_{\mathrm{FS/IS}}\right)\varepsilon + V_0\left[B_{\mathrm{TS/IS}} - B_{\mathrm{FS/IS}} + (2 - v)(K_{\mathrm{TS/IS}}^{w} - K_{\mathrm{FS/IS}}^{w})\right]\varepsilon^2$$

(39)

Another form that does not contain strain ε explicitly is 39' which was used to draw the curves in Figure 2c and Figure S16. The relevant parameters are listed in Tables 3 and Table S14.

$$E_{\mathrm{a}}^{\varepsilon} = \frac{K_{\mathrm{TS/IS}}}{K_{\mathrm{FS/IS}}}\Delta E^{\varepsilon} + \left[(E_{\mathrm{TS}}^{0} - E_{\mathrm{IS}}^{0}) - \frac{K_{\mathrm{TS/IS}}}{K_{\mathrm{FS/IS}}}(E_{\mathrm{FS}}^{0} - E_{\mathrm{IS}}^{0})\right] +$$

$$\frac{\left\{(E_{\mathrm{a}}^{\varepsilon} - C_{\mathrm{BEP}}\Delta E^{\varepsilon}) - \left[(E_{\mathrm{TS}}^{0} - E_{\mathrm{IS}}^{0}) - C_{\mathrm{BEP}}(E_{\mathrm{FS}}^{0} - E_{\mathrm{IS}}^{0})\right]\right\}^{2}}{V_0(C_{\mathrm{BEP}}K_{\mathrm{FS/IS}} - K_{\mathrm{TS/IS}})C_{\mathrm{BEP}}K_{\mathrm{FS/IS}}}\left[B_{\mathrm{TS/IS}} + (2-v)K_{\mathrm{TS/IS}}^{w}\right] \quad (39')$$

$$C_{\mathrm{BEP}} = \frac{V_0 B_{\mathrm{TS/IS}} + (2-v)V_0 K_{\mathrm{TS/IS}}^{w}}{V_0 B_{\mathrm{FS/IS}} + (2-v)V_0 K_{\mathrm{FS/IS}}^{w}} = \frac{B_{\mathrm{TS/IS}} + (2-v)K_{\mathrm{TS/IS}}^{w}}{B_{\mathrm{FS/IS}} + (2-v)K_{\mathrm{FS/IS}}^{w}}$$

(39') can be simplified as:

$$E_{\mathrm{a}}^{\varepsilon} = \frac{K_{\mathrm{TS/IS}}}{K_{\mathrm{FS/IS}}}\Delta E^{\varepsilon} + \left[(E_{\mathrm{TS}}^{0} - E_{\mathrm{IS}}^{0}) - \frac{K_{\mathrm{TS/IS}}}{K_{\mathrm{FS/IS}}}(E_{\mathrm{FS}}^{0} - E_{\mathrm{IS}}^{0})\right] \quad (39'')$$

In this form, $E_{\mathrm{a}}^{\varepsilon}$ is a function of ΔE^{ε} and itself, and can be written as $E_{\mathrm{a}}^{\varepsilon}(\Delta E^{\varepsilon}, E_{\mathrm{a}}^{\varepsilon})$. TSS relation under strain can be derived from (25) and (26):

$$E_{\mathrm{TS}}^{\varepsilon} = E_{\mathrm{FS}}^{\varepsilon} + (E_{\mathrm{TS}}^{0} - E_{\mathrm{FS}}^{0}) + V_0(K_{\mathrm{TS}} - K_{\mathrm{FS}})\varepsilon + V_0[B_{\mathrm{TS}} - B_{\mathrm{FS}} + (2-v)(K_{\mathrm{TS}}^{w} - K_{\mathrm{FS}}^{w})]\varepsilon^2 \quad (40)$$

$$E_{\mathrm{TS}}^{\varepsilon} = \frac{K_{\mathrm{TS}}}{K_{\mathrm{FS}}}E_{\mathrm{FS}}^{\varepsilon} + \left[E_{\mathrm{TS}}^{0} - \frac{K_{\mathrm{TS}}}{K_{\mathrm{FS}}}E_{\mathrm{FS}}^{0}\right] + \frac{\left[(E_{\mathrm{TS}}^{\varepsilon} - C_{\mathrm{TSS}}E_{\mathrm{FS}}^{\varepsilon}) - (E_{\mathrm{TS}}^{0} - C_{\mathrm{TSS}}E_{\mathrm{FS}}^{0})\right]^{2}}{V_0(C_{\mathrm{TSS}}K_{\mathrm{FS}} - K_{\mathrm{TS}})C_{\mathrm{TSS}}K_{\mathrm{FS}}}[B_{\mathrm{TS}} + (2-v)K_{\mathrm{TS}}^{w}] \quad (40')$$

$$C_{\mathrm{TSS}} = \frac{V_0 B_{\mathrm{TS}} + (2-v)V_0 K_{\mathrm{TS}}^{w}}{V_0 B_{\mathrm{FS}} + (2-v)V_0 K_{\mathrm{FS}}^{w}} = \frac{B_{\mathrm{TS}} + (2-v)K_{\mathrm{TS}}^{w}}{B_{\mathrm{FS}} + (2-v)K_{\mathrm{FS}}^{w}}$$

(40') can be simplified as:

$$E_{\mathrm{TS}}^{\varepsilon} = \frac{K_{\mathrm{TS}}}{K_{\mathrm{FS}}}E_{\mathrm{FS}}^{\varepsilon} + \left[E_{\mathrm{TS}}^{0} - \frac{K_{\mathrm{TS}}}{K_{\mathrm{FS}}}E_{\mathrm{FS}}^{0}\right] \quad (40'')$$

In equation (40') $E_{\mathrm{TS}}^{\varepsilon}$ is a function of $E_{\mathrm{FS}}^{\varepsilon}$ and itself, and can be written as $E_{\mathrm{TS}}^{\varepsilon}(E_{\mathrm{FS}}^{\varepsilon}, E_{\mathrm{TS}}^{\varepsilon})$.

Curves in Figures S12a, S13a, S14a and S15a were drawn using eq (39'') and those in Figure 2b, Figures S12b, S13b, S14b and S15b were plotted with eq (40'').

Adsorption energies under strain and corresponding parameters

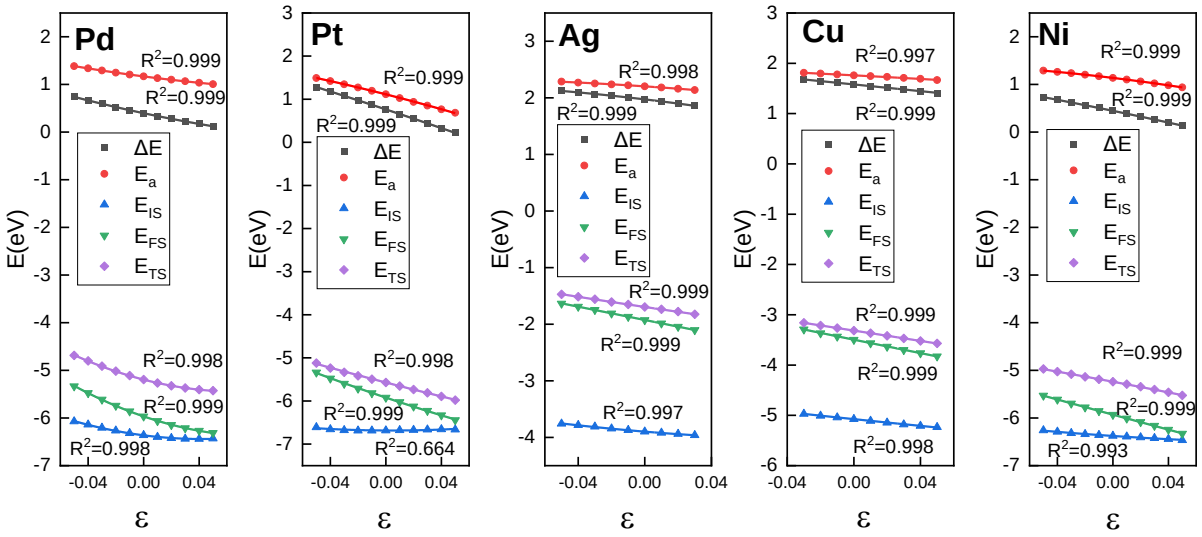

Figure S2. Variation of ΔE, E_a, E_{IS}, E_{FS} and E_{TS} of CH dissociation with respect to strain on the FCC structure. Note the quadratic (linear) relationship between adsorption energies (energy barriers and reaction energy) and strain. ε is the strain (-0.05~0.05). For E_{IS}~ε on Pt(111), fitting with cubic polynomial like Eq. (17) in Derivation of equations gives much better result with $R^2 = 0.986$.

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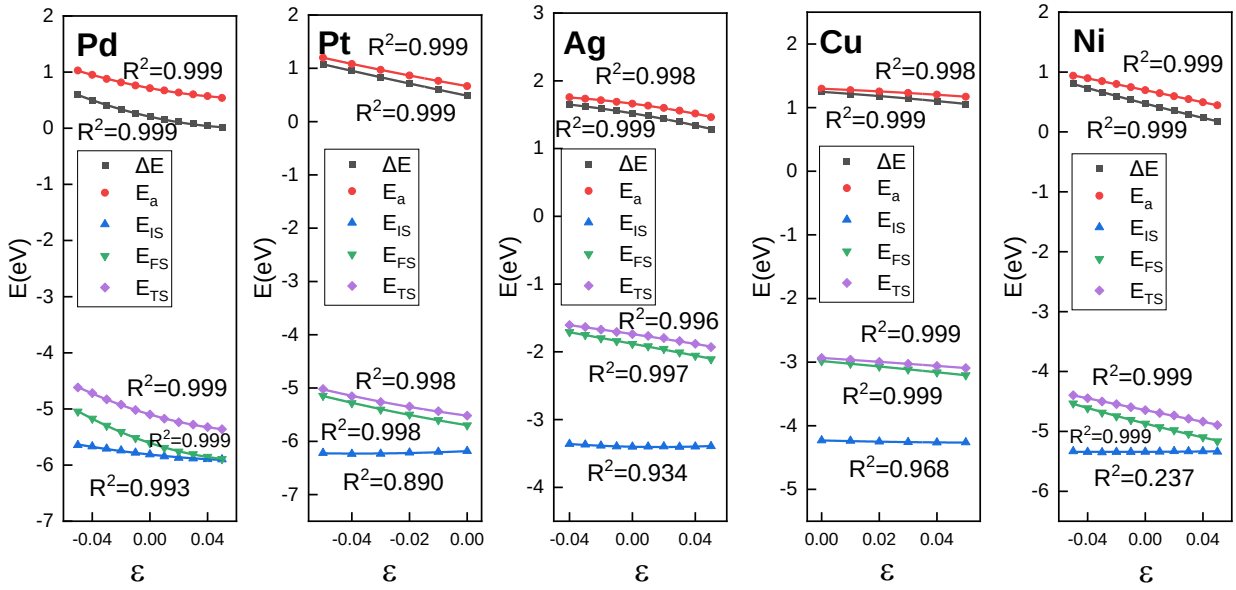

Figure S3. Variation of ΔE, E_a, E_{IS}, E_{FS} and E_{TS} of BH dissociation with respect to strain on the FCC structure. Note the quadratic (linear) relationship between adsorption energies (energy barriers and reaction energy) and strain. ε is the strain (-0.05~0.05). For E_{IS} ~ε on Ni(111), fitting with cubic polynomial like Eq. (17) in Derivation of equations gives much better result with $R^2 = 0.885$.

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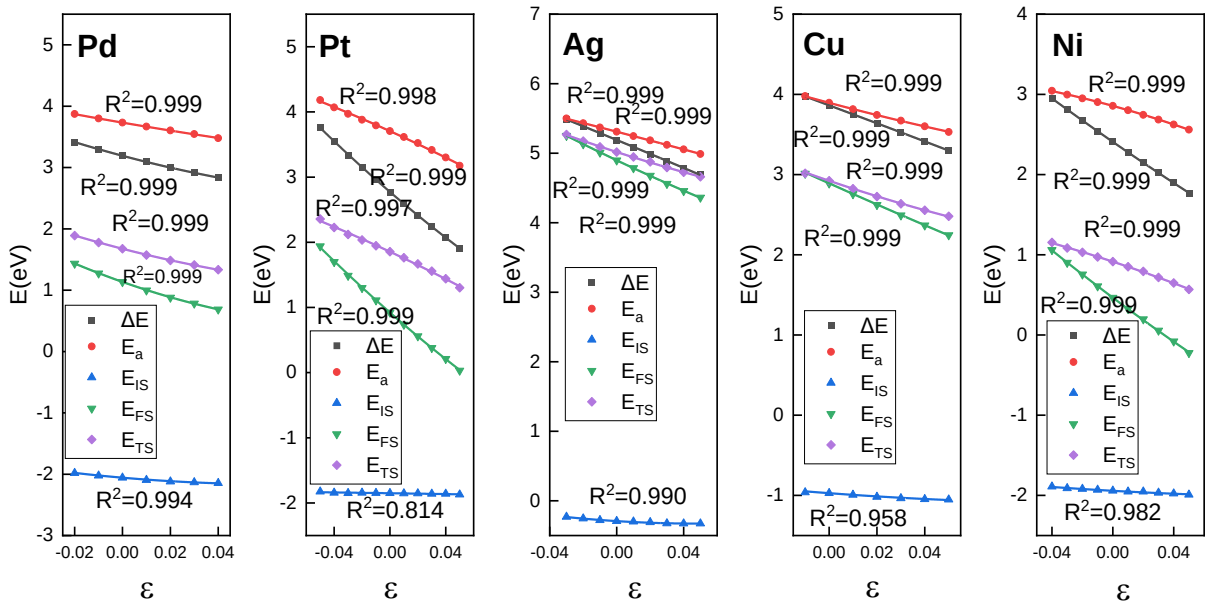

Figure S4. Variation of ΔE, E_a, E_{IS}, E_{FS} and E_{TS} of CO dissociation with respect to strain on the FCC structure. Note the quadratic (linear) relationship between adsorption energies (energy barriers and reaction energy) and strain. ε is the strain (-0.05~0.05).

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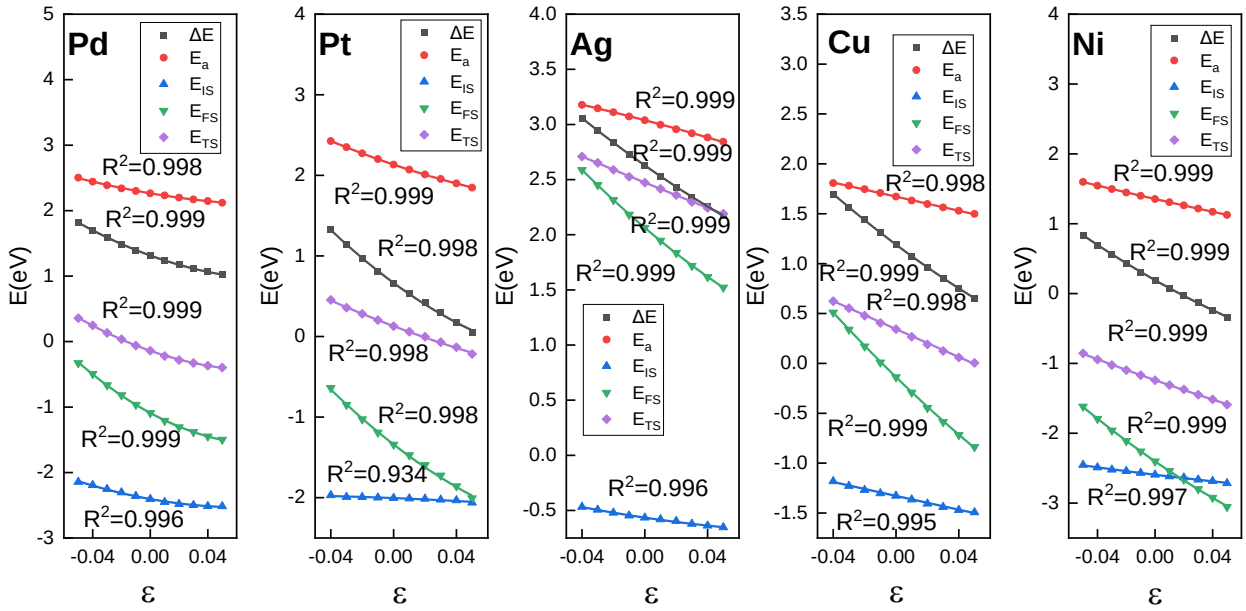

Figure S5. Variation of ΔE, E_a, E_{IS}, E_{FS} and E_{TS} of NO dissociation with respect to strain on the FCC structure. Note the quadratic (linear) relationship between adsorption energies (energy barriers and reaction energy) and strain. ε is the strain (-0.05~0.05).

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Table S7. The volume of slab (top 4 layers) of five metals under no strain.

Metal	V_0(Å^3)
Pd	179.6
Pt	182.5
Ag	207.5
Cu	139.2
Ni	128.0

The slab volume under strain is a linear function of strain as:

$$V_\varepsilon = V_0(1+\boldsymbol{\varepsilon})(1+\boldsymbol{\varepsilon})(1-v\boldsymbol{\varepsilon})$$
$$= V_0\left[1+(2-v)\boldsymbol{\varepsilon}+(\mathbf{1}-\mathbf{2}v)\boldsymbol{\varepsilon^2}-v\boldsymbol{\varepsilon^3}\right]$$
$$\approx V_0[1+(2-v)\boldsymbol{\varepsilon}]$$

which is consistent with the phenomenon observed in our data.

Table S8. The value of v of the five metals.

Metal	v
Pd	1.094
Pt	1.297
Ag	0.8202
Cu	0.7335
Ni	0.6386

Table S9. The fitting parameters (in eV) of CH, NH, BH, CO and NO dissociation for equations (13) to (15) in the text.

Diatomic species	Metal	E_{IS}^{0} (eV)	V_0K_{IS} (eV)	$[V_0B_{\mathrm{IS}}+(2-v)V_0K_{\mathrm{IS}}^{w}]$ (eV)	E_{FS}^{0} (eV)	V_0K_{FS} (eV)	$[V_0B_{\mathrm{FS}}+(2-v)V_0K_{\mathrm{FS}}^{w}]$ (eV)	E_{TS}^{0} (eV)	V_0K_{TS} (eV)	$[V_0B_{\mathrm{TS}}+(2-v)V_0K_{\mathrm{TS}}^{w}]$ (eV)
CH	Pd	-6.363	-3.724	44.77	-5.966	-9.894	58.34	-5.194	-7.504	55.78
	Pt	-6.684	-0.1614	17.83	-5.921	-10.78	12.30	-5.571	-8.321	6.226
	Ag	-3.899	-2.407	9.862	-1.926	-5.896	-0.2461	-1.695	-4.358	3.291
	Cu	-5.075	-3.415	1.756	-3.495	-6.729	1.315	-3.314	-5.132	-0.1162
	Ni	-6.377	-1.928	5.756	-5.929	-7.903	1.071	-5.239	-5.447	-3.666
NH	Pd	-3.836	-4.473	56.43	-3.435	-7.070	47.65	-2.477	-5.322	53.85
	Pt	-3.901	-4.811	37.43	-3.360	-7.097	7.847	-2.810	-5.345	15.14
	Ag	-2.453	-4.700	14.75	-0.3662	-6.018	22.02	-0.006535	-4.738	12.54
	Cu	-3.641	-5.784	10.46	-2.077	-7.818	13.95	-1.716	-5.767	2.259
	Ni	-4.401	-3.922	14.73	-4.073	-6.625	9.096	-3.198	-4.254	8.380
BH	Pd	-5.812	-2.755	16.691	-5.606	-8.499	56.708	-5.098	-7.510	45.539
	Pt	-6.185	2.385	31.412	-5.698	-8.802	43.549	-5.519	-7.102	55.106
	Ag	-3.401	-0.468	13.593	-1.881	-4.312	-1.718	-1.738	-3.467	-4.366
	Cu	-4.230	-1.169	9.873	-2.983	-4.181	-5.518	-2.934	-2.994	-3.654
	Ni	-5.341	0.083	1.749	-4.869	-6.139	8.456	-4.645	-4.902	0.650
CO	Pd	-2.057	-3.361	26.671	1.135	-13.738	64.091	1.675	-10.051	37.795
	Pt	-1.851	-0.317	-0.262	0.922	-18.806	23.262	1.855	-10.020	-11.700
	Ag	-0.292	-1.489	15.534	4.898	-11.419	12.585	5.017	-7.770	13.324
	Cu	-0.972	-2.197	9.681	2.891	-13.316	6.588	2.923	-10.143	24.097
	Ni	-1.942	-1.053	3.643	0.466	-14.230	12.901	0.915	-6.257	-11.240
NO	Pd	-2.405	-3.928	30.360	-1.090	-11.864	72.640	-0.140	-7.645	48.548
	Pt	-2.004	-0.765	-3.584	-1.339	-15.126	48.152	0.129	-7.359	14.743
	Ag	-0.565	-2.097	7.327	2.063	-12.118	25.272	2.473	-5.814	2.259
	Cu	-1.328	-3.471	0.500	-0.137	-15.296	22.113	0.344	-7.003	0.272
	Ni	-2.594	-2.508	3.810	-2.402	-14.184	27.420	-1.240	-7.203	6.678

Table S10. The parameters (in eV) of CH, NH, BH, CO and NO dissociation for equations (16) to (17) in the text.

Diatomic species	Metal	E^0_{FS}-E^0_{IS} (eV)	$V_0K_{FS/IS}$ (eV)	$[V_0B_{FS/IS} + (2-v)V_0K^w_{FS/IS}]$ (eV)	E^0_{TS}-E^0_{IS} (eV)	$V_0K_{TS/IS}$ (eV)	$[V_0B_{TS/IS} + (2-v)V_0K^w_{TS/IS}]$ (eV)
CH	Pd	0.3974	-6.170	13.57	1.169	-3.781	11.01
	Pt	0.7636	-10.62	-5.536	1.114	-8.159	-11.61
	Ag	1.973	-3.490	-10.11	2.204	-1.951	-6.572
	Cu	1.580	-3.314	-0.4417	1.760	-1.717	-1.873
	Ni	0.4471	-5.975	-4.685	1.138	-3.519	-9.422
NH	Pd	0.4007	-2.597	-8.775	1.359	-0.8488	-2.583
	Pt	0.5414	-2.285	-29.58	1.091	-0.5342	-22.29
	Ag	2.087	-1.318	7.272	2.447	-0.03750	-2.212
	Cu	1.564	-2.033	3.489	1.925	0.01753	-8.203
	Ni	0.3278	-2.703	-5.630	1.204	-0.3324	-6.346
BH	Pd	0.2060	-5.7442	40.0170	0.7140	-4.7551	28.8481
	Pt	0.4862	-11.1872	12.1367	0.6660	-9.4874	23.6938
	Ag	1.5202	-3.8440	-15.3113	1.6627	-2.9991	-17.9594
	Cu	1.2476	-3.0121	-15.3910	1.2967	-1.8249	-13.5266
	Ni	0.4729	-6.2220	6.7068	0.6966	-4.9856	-1.1000
CO	Pd	3.1916	-10.3775	37.4199	3.7321	-6.6900	11.1239
	Pt	2.7731	-18.4887	23.5249	3.7057	-9.7028	-11.4380
	Ag	5.1904	-9.9302	-2.9484	5.3096	-6.2814	-2.2095
	Cu	3.8633	-11.1189	-3.0932	3.8952	-7.9460	14.4160
	Ni	2.4080	-13.1765	9.2587	2.8568	-5.2038	-14.8825
NO	Pd	1.3146	-7.9360	42.2793	2.2648	-3.7173	18.1874
	Pt	0.6655	-14.3605	51.7362	2.1337	-6.5940	18.3268
	Ag	2.6285	-10.0208	17.9454	3.0387	-3.7165	-5.0681
	Cu	1.1909	-11.8256	21.6129	1.6718	-3.5328	-0.2283
	Ni	0.1919	-11.6764	23.6102	1.3543	-4.6953	2.8686

Table S11. The value of the parameters in CH, NH, BH, CO and NO dissociation.

Diatomic species	Metal	V_0B_{IS} (eV)	V_0B_{FS} (eV)	V_0B_{TS} (eV)	$(2-v)V_0K_{IS}^w$ (eV)	$(2-v)V_0K_{FS}^w$ (eV)	$(2-v)V_0K_{TS}^w$ (eV)
CH	Pd	37.94	57.42	53.34	6.83	0.91	2.44
	Pt	11.64	13.95	6.32	6.19	-1.66	-0.10
	Ag	-1.17	-4.41	-2.37	11.03	4.17	5.66
	Cu	-11.79	-5.50	-8.66	13.55	6.82	8.55
	Ni	-14.68	-10.40	-17.20	20.44	11.47	13.54
NH	Pd	50.69	44.60	49.99	5.74	3.06	3.86
	Pt	34.88	7.18	13.51	2.55	0.67	1.63
	Ag	5.62	17.35	6.85	9.14	4.68	5.69
	Cu	-1.04	7.54	-6.17	11.50	6.41	8.43
	Ni	-3.09	-4.44	-6.76	17.82	13.53	15.14
BH	Pd	10.24	55.63	43.98	6.45	1.08	1.56
	Pt	24.16	44.41	54.86	7.25	-0.86	0.25
	Ag	2.33	-6.33	-9.78	11.27	4.61	5.41
	Cu	-3.60	-13.18	-12.74	13.48	7.66	9.09
	Ni	-17.70	-1.64	-10.72	19.45	10.10	11.37
CO	Pd	15.87	65.31	36.12	10.80	-1.22	1.68
	Pt	-8.27	29.62	-11.06	8.01	-6.36	-0.64
	Ag	-3.73	12.26	8.86	19.26	0.32	4.46
	Cu	-12.86	4.33	17.87	22.54	2.26	6.23
	Ni	-25.97	5.69	-28.47	29.61	7.21	17.23
NO	Pd	21.87	72.42	45.29	8.49	0.22	3.26
	Pt	-10.10	52.06	13.92	6.52	-3.91	0.83
	Ag	-8.06	25.36	-4.52	15.39	-0.09	6.78
	Cu	-16.92	21.58	-10.00	17.42	0.54	10.27
	Ni	-20.32	19.54	-8.55	24.13	7.88	15.23

Table S12. The value of K_{ads}^{w} and B_{ads} of CH, NH, BH, CO and NO dissociation.

Diatomic species	Metal	IS		FS		TS	
		K_{IS}^{w} (eV/Å^3)	B_{IS} (eV/Å^3)	K_{FS}^{w} (eV/Å^3)	B_{FS} (eV/Å^3)	K_{TS}^{w} (eV/Å^3)	B_{TS} (eV/Å^3)
CH	Pd	0.0420	0.2113	0.0056	0.3197	0.0150	0.2970
	Pt	0.0482	0.0638	-0.0129	0.0765	-0.0008	0.0347
	Ag	0.0451	-0.0056	0.0170	-0.0213	0.0231	-0.0114
	Cu	0.0768	-0.0847	0.0387	-0.0395	0.0485	-0.0622
	Ni	0.1173	-0.1147	0.0658	-0.0813	0.0777	-0.1344
NH	Pd	0.0353	0.2822	0.0188	0.2483	0.0237	0.2783
	Pt	0.0198	0.1911	0.0052	0.0393	0.0127	0.0740
	Ag	0.0373	0.0271	0.0191	0.0836	0.0232	0.0330
	Cu	0.0652	-0.0074	0.0364	0.0541	0.0478	-0.0443
	Ni	0.1023	-0.0242	0.0777	-0.0347	0.0869	-0.0528
BH	Pd	0.0397	0.0570	0.0066	0.3097	0.0096	0.2449
	Pt	0.0565	0.1324	-0.0067	0.2433	0.0019	0.3006
	Ag	0.0460	0.0112	0.0188	-0.0305	0.0221	-0.0471
	Cu	0.0764	-0.0259	0.0435	-0.0947	0.0515	-0.0915
	Ni	0.1116	-0.1382	0.0579	-0.0128	0.0652	-0.0837
CO	Pd	0.0664	0.0884	-0.0075	0.3636	0.0103	0.2011
	Pt	0.0624	-0.0453	-0.0496	0.1623	-0.0050	-0.0606
	Ag	0.0787	-0.0180	0.0013	0.0591	0.0182	0.0427
	Cu	0.1278	-0.0924	0.0128	0.0311	0.0353	0.1284
	Ni	0.1699	-0.2029	0.0414	0.0445	0.0989	-0.2225
NO	Pd	0.0522	0.1218	0.0013	0.4032	0.0200	0.2521
	Pt	0.0508	-0.0553	-0.0305	0.2853	0.0064	0.0763
	Ag	0.0629	-0.0389	-0.0004	0.1222	0.0277	-0.0218
	Cu	0.0988	-0.1216	0.0030	0.1550	0.0582	-0.0718
	Ni	0.1385	-0.1588	0.0452	0.1526	0.0874	-0.0668

Table S13. The value of $-\Delta v_{\mathrm{ads}}$ of CH, NH, BH, CO and NO dissociation on five metals.

Diatomic species	Metal	$-\Delta v_{\mathrm{IS}}$	$-\Delta v_{\mathrm{FS}}$	$-\Delta v_{\mathrm{TS}}$
CH	Pd	0.1055	0.1159	0.1648
	Pt	0.0395	0.0610	0.0944
	Ag	-0.0282	-0.0055	0.0318
	Cu	0.0190	0.0568	0.0591
	Ni	-0.0063	-0.0027	0.0160
NH	Pd	0.1280	0.1536	0.1423
	Pt	0.0557	0.0664	0.0565
	Ag	0.0322	0.0001	0.0163
	Cu	0.0475	0.0533	0.0554
	Ni	0.0089	0.0397	0.0363
BH	Pd	0.0673	0.1095	0.1093
	Pt	0.0407	0.0230	0.1028
	Ag	-0.0069	0.0073	0.0157
	Cu	0.0418	0.0232	0.0471
	Ni	-0.0115	0.0035	-0.0123
CO	Pd	0.0808	0.1808	0.1512
	Pt	-0.0045	0.1154	0.0582
	Ag	0.0238	0.0625	0.0367
	Cu	0.0204	0.1124	0.0936
	Ni	0.0065	0.0512	-0.0951
NO	Pd	0.0726	0.1224	0.1153
	Pt	0.0169	0.1238	0.0666
	Ag	0.0301	0.0376	-0.0665
	Cu	0.0304	0.0950	-0.0322
	Ni	0.0002	0.0302	0.0276

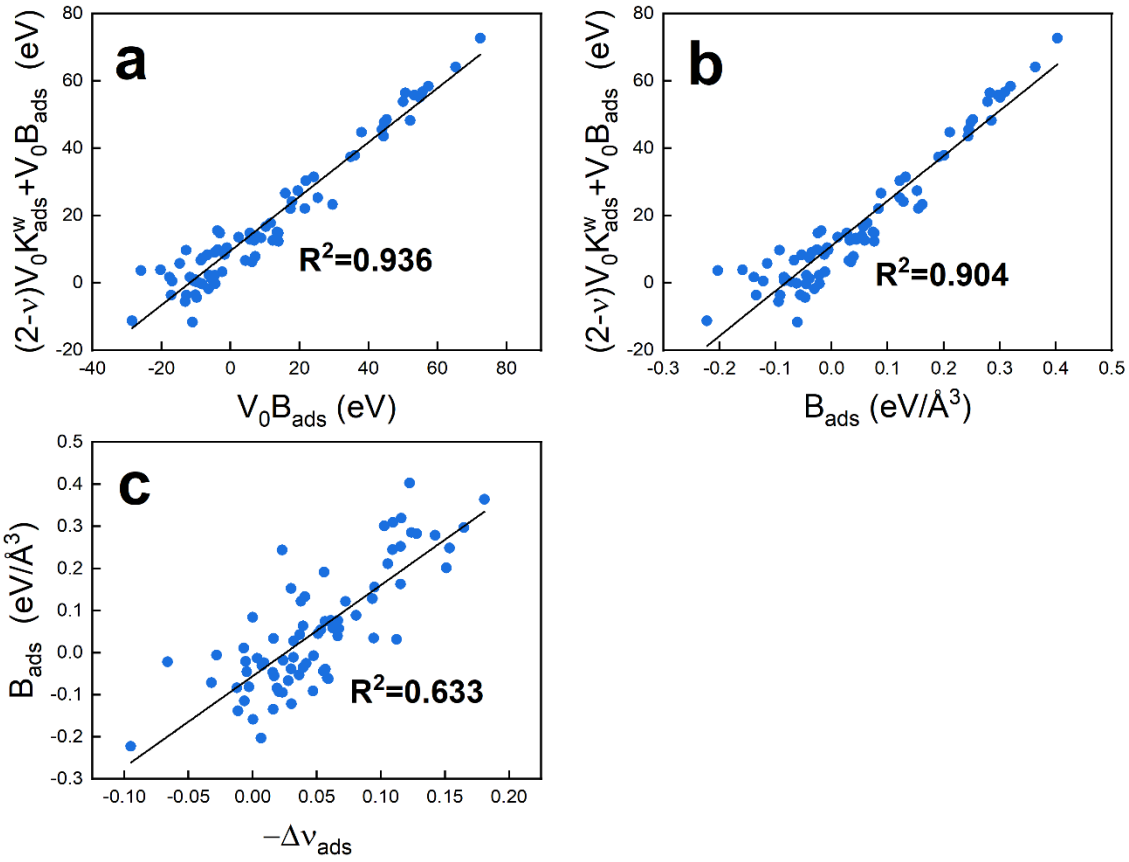

Figure S6. (a) $[V_0B_{\mathrm{ads}} + (2-v)V_0K_{\mathrm{ads}}^{w}]$ vs. V_0B_{ads}; (b) $[V_0B_{\mathrm{ads}} + (2-v)V_0K_{\mathrm{ads}}^{w}]$ vs. B_{ads}; (c) B_{ads} vs. $-\Delta v_{\mathrm{ads}}$

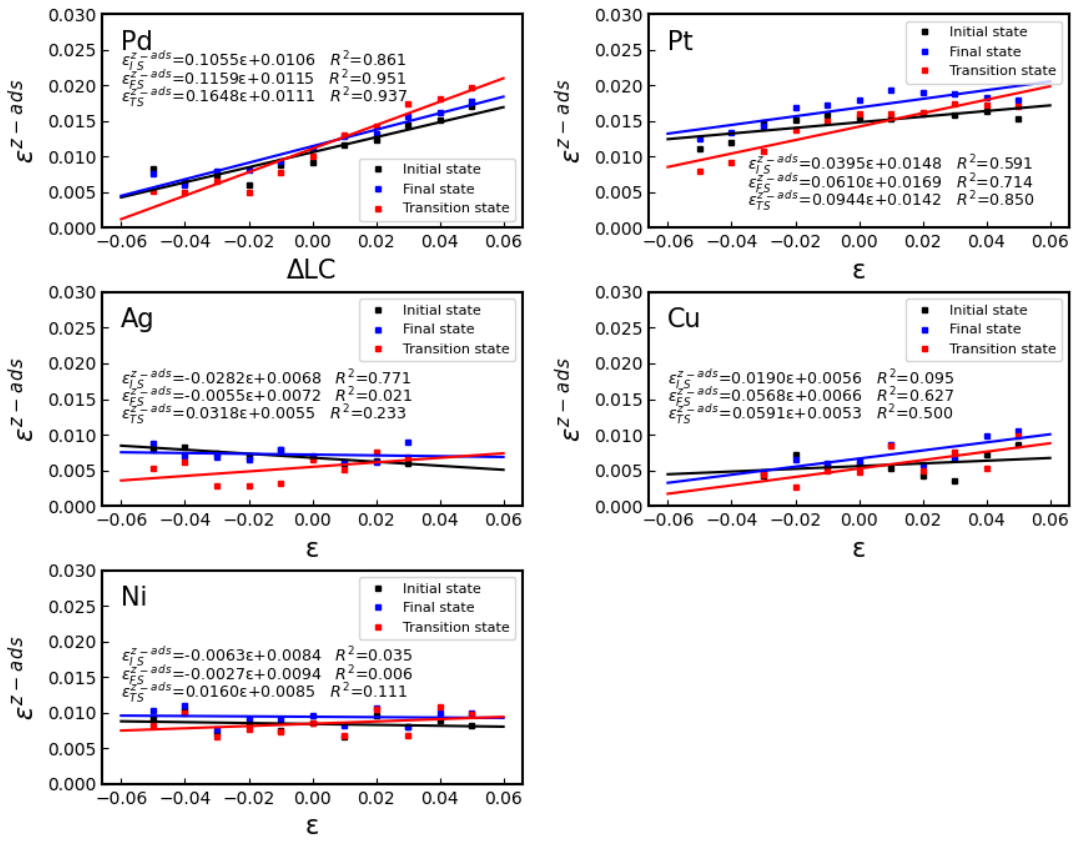

Figure S7. The plots of Z-direction strain of slab caused by adsorption (ε^{z-ads}) against applied strain ε in CH dissociation. ε is the strain (-0.05~0.05). The slopes of the curves in this figure are the value of $-\Delta v_{ads}$ of CH dissociation on five metals.

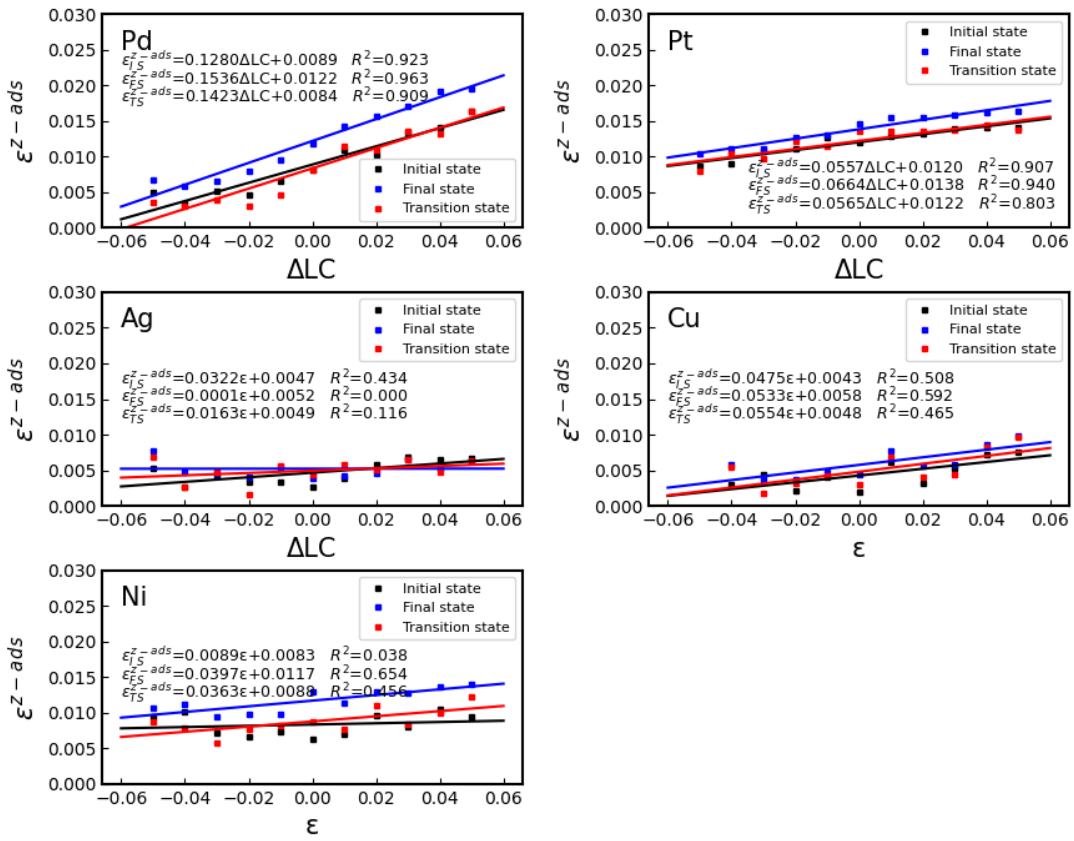

Figure S8. The plots of Z-direction strain of slab caused by adsorption (ε^{z-ads}) against applied strain ε in NH dissociation. ε is the strain (-0.05~0.05). The slopes of the curves in this figure are the value of $-\Delta v_{ads}$ of NH dissociation on five metals.

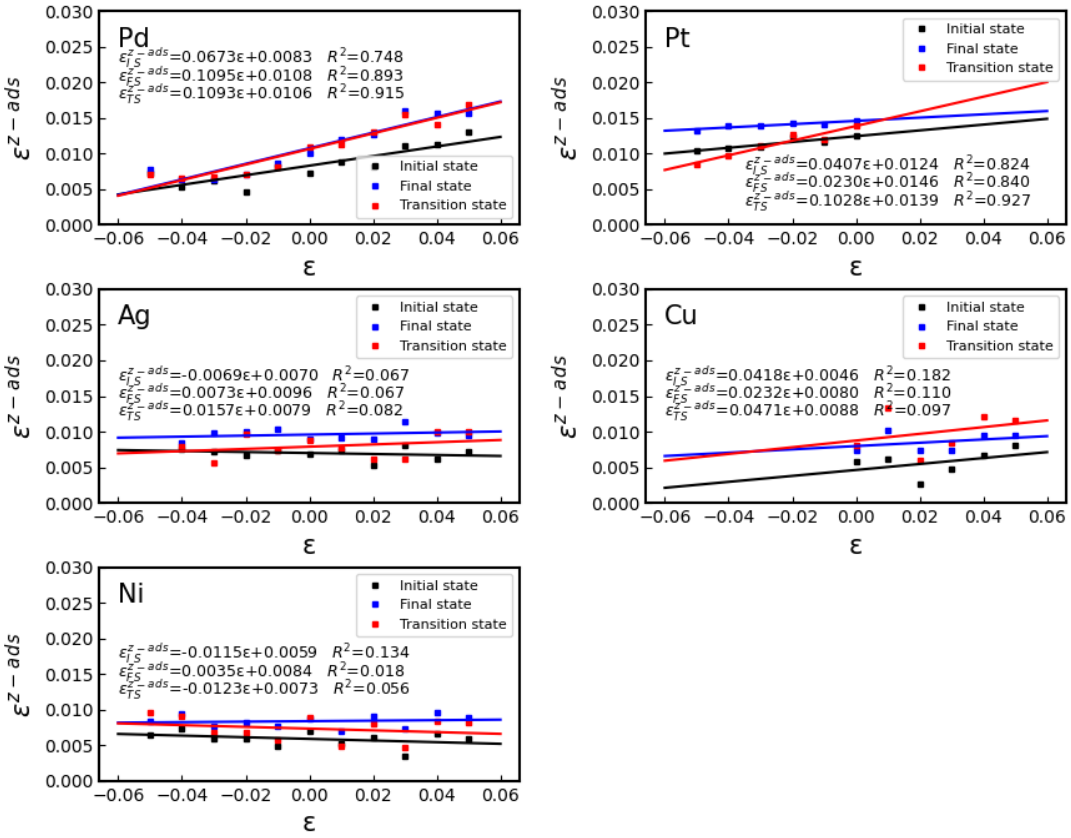

Figure S9. The plots of Z-direction strain of slab caused by adsorption (ε^{z-ads}) against applied strain ε in BH dissociation. ε is the strain (-0.05~0.05). The slopes of the curves in this figure are the value of $-\Delta v_{ads}$ of BH dissociation on five metals.

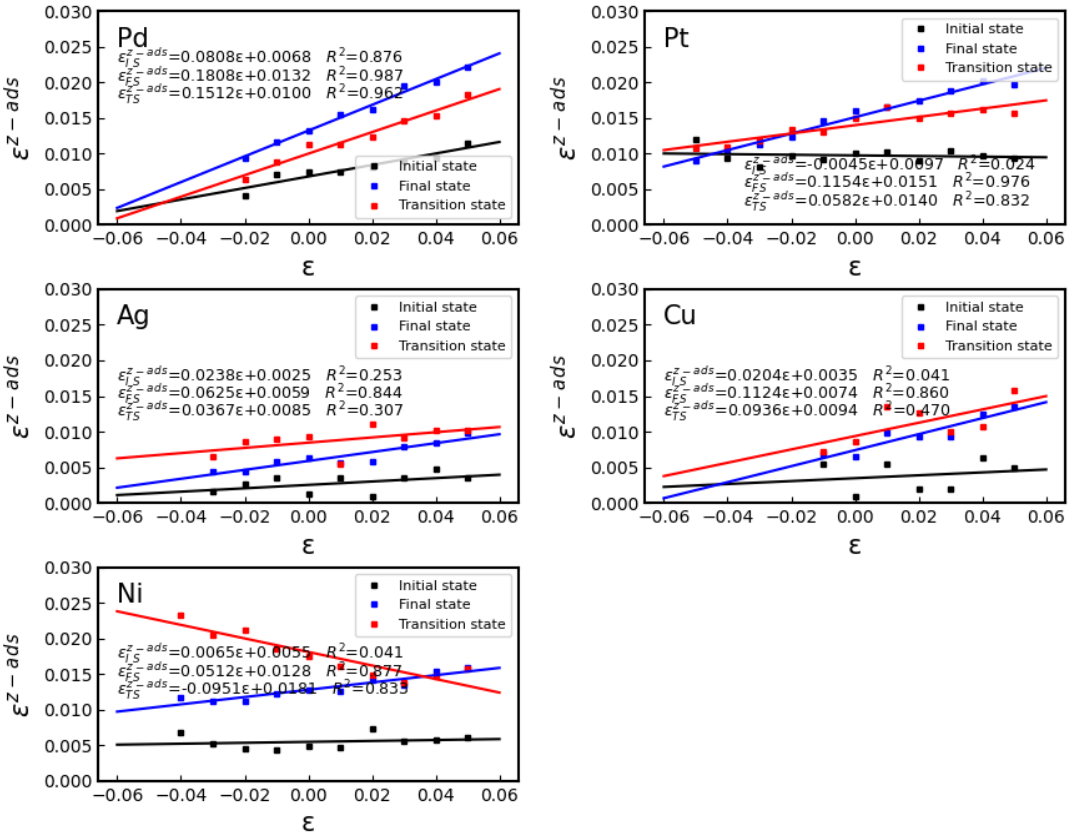

Figure S10. The plots of Z-direction strain of slab caused by adsorption ($\varepsilon^{\mathrm{z-ads}}$) against applied strain ε in CO dissociation. ε is the strain (-0.05~0.05). The slopes of the curves in this figure are the value of $-\Delta v_{\mathrm{ads}}$ of CO dissociation on five metals.

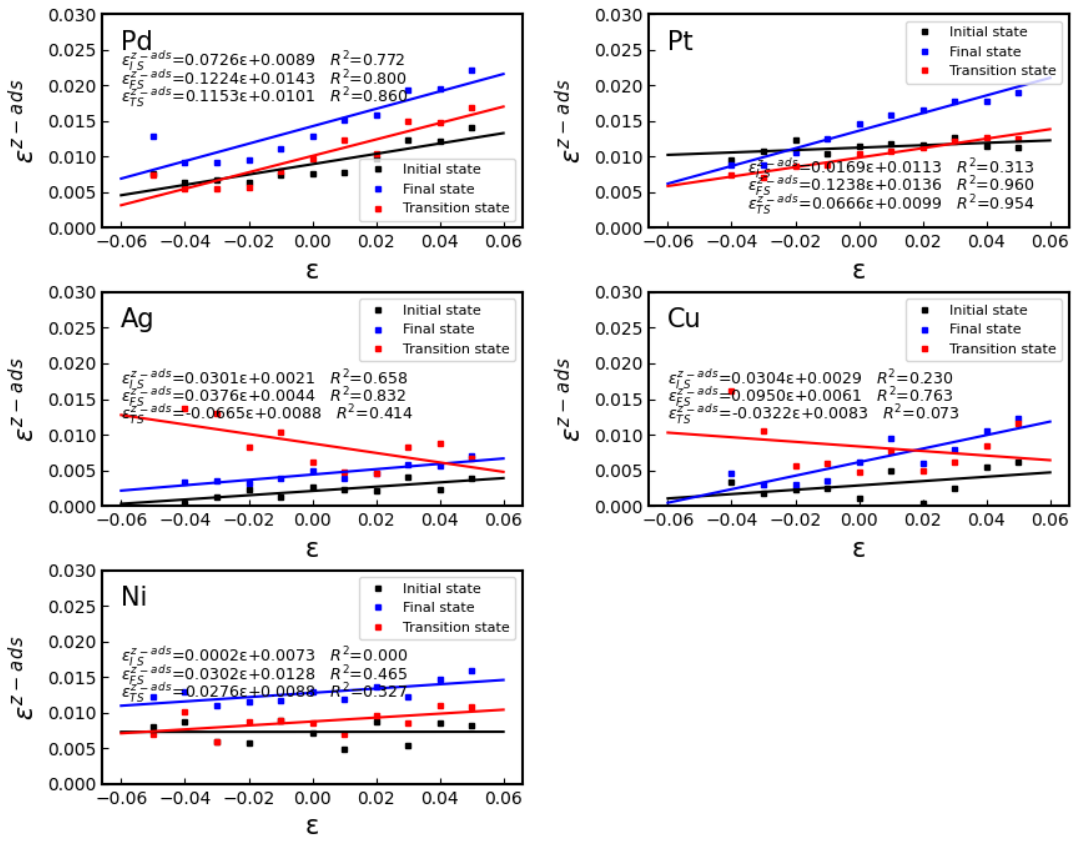

Figure S11. The plots of Z-direction strain of slab caused by adsorption ($\varepsilon^{\mathrm{z-ads}}$) against applied strain ε in NO dissociation. ε is the strain (-0.05~0.05). The slopes of the curves in this figure are the value of $-\Delta v_{\mathrm{ads}}$ of NO dissociation on five metals.

BEP and TSS relations under strain and corresponding parameters

Table S14. Coefficients of TSS and BEP relations in CH, NH, BH, CO and NO dissociation under strain in Eqs. (18a) and (19a) in the text.

Diatomic species	Metal	$E_{\mathrm{TS}}^{0}-\frac{K_{\mathrm{TS}}}{K_{\mathrm{FS}}}E_{\mathrm{FS}}^{0}$ (eV)	$\frac{K_{\mathrm{TS}}}{K_{\mathrm{FS}}}$	$\left[(E_{\mathrm{TS}}^{0}-E_{\mathrm{IS}}^{0})-\frac{K_{\mathrm{TS/IS}}}{K_{\mathrm{FS/IS}}}(E_{\mathrm{FS}}^{0}-E_{\mathrm{IS}}^{0})\right]$ (eV)	$\frac{K_{\mathrm{TS/IS}}}{K_{\mathrm{FS/IS}}}$
CH	Pd	-0.669	0.759	0.925	0.613
	Pt	-1.00	0.772	0.527	0.768
	Ag	-0.272	0.739	1.10	0.559
	Cu	-0.649	0.763	0.942	0.518
	Ni	-1.15	0.689	0.875	0.589
NH	Pd	0.109	0.753	1.23	0.327
	Pt	-0.280	0.753	0.964	0.234
	Ag	0.282	0.787	2.39	0.0285
	Cu	-0.184	0.738	1.94	-0.00862
	Ni	-0.582	0.642	1.16	0.123
BH	Pd	-0.144	0.884	0.543	0.828
	Pt	-0.921	0.807	0.254	0.848
	Ag	-0.226	0.804	0.477	0.780
	Cu	-0.798	0.716	0.541	0.606
	Ni	-0.757	0.799	0.318	0.801
CO	Pd	0.845	0.732	1.675	0.645
	Pt	1.364	0.533	2.250	0.525
	Ag	1.684	0.680	2.026	0.633
	Cu	0.721	0.762	1.134	0.715
	Ni	0.710	0.440	1.906	0.395
NO	Pd	0.562	0.644	1.649	0.468
	Pt	0.781	0.487	1.828	0.459
	Ag	1.484	0.480	2.064	0.371
	Cu	0.407	0.458	1.316	0.299
	Ni	-0.020	0.508	1.277	0.402

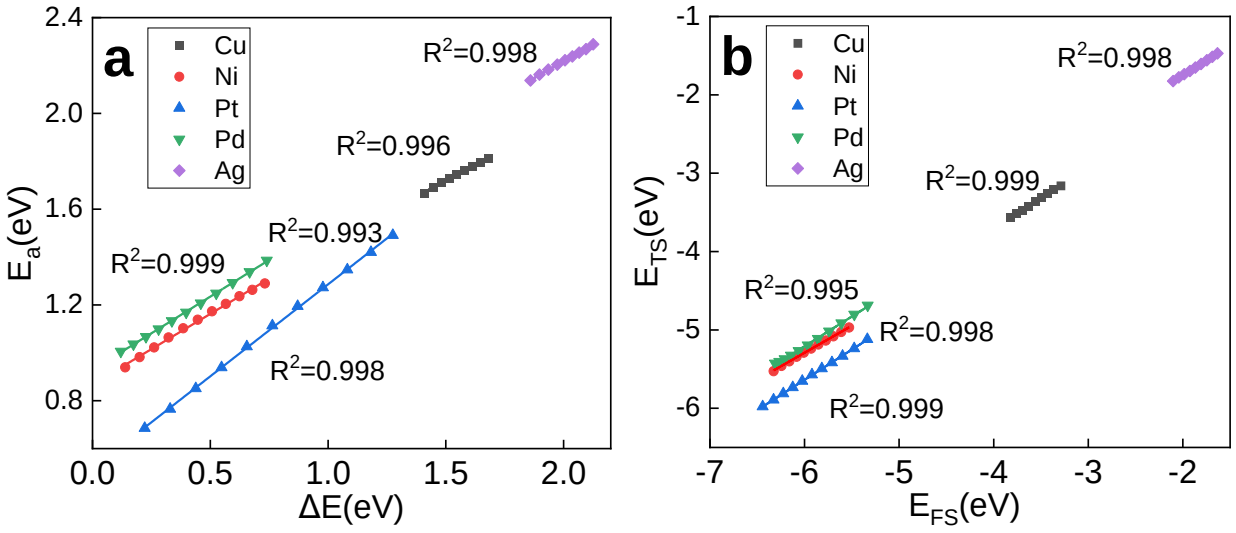

Figure S12. BEP (a) and TSS (b) relations of CH dissociation on the five (111) surfaces under strain; the points are the results calculated by DFT. And the curves are drawn according to Eqs. (18a) and (19a) in the text.

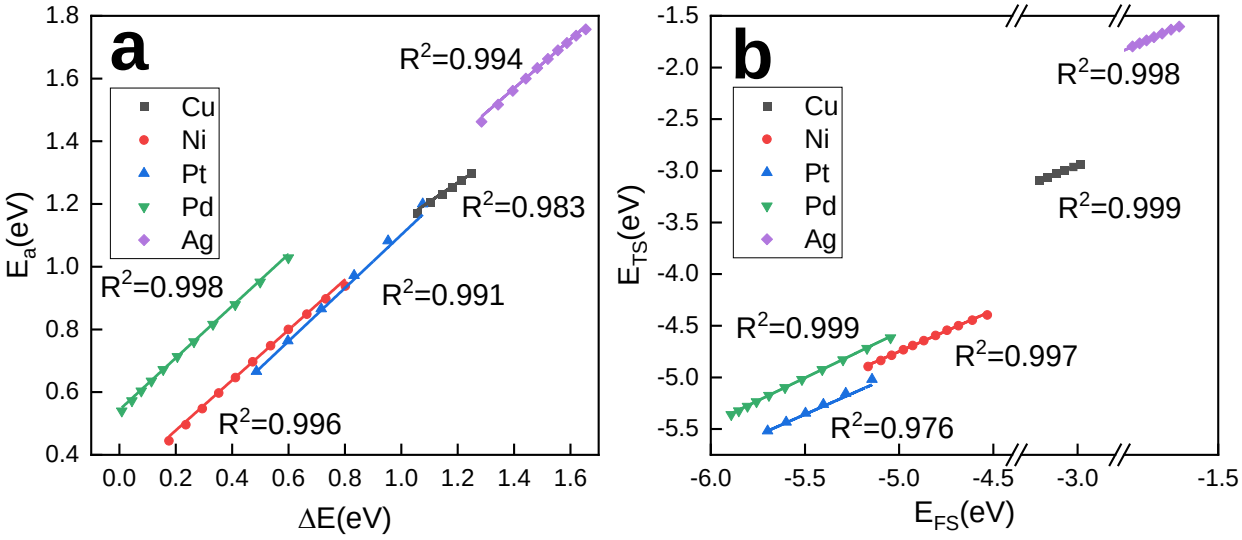

Figure S13. BEP (a) and TSS (b) relations of BH dissociation on the five (111) surfaces under strain; the points are the results calculated by DFT. And the curves are drawn according to Eqs. (18a) and (19a) in the text.

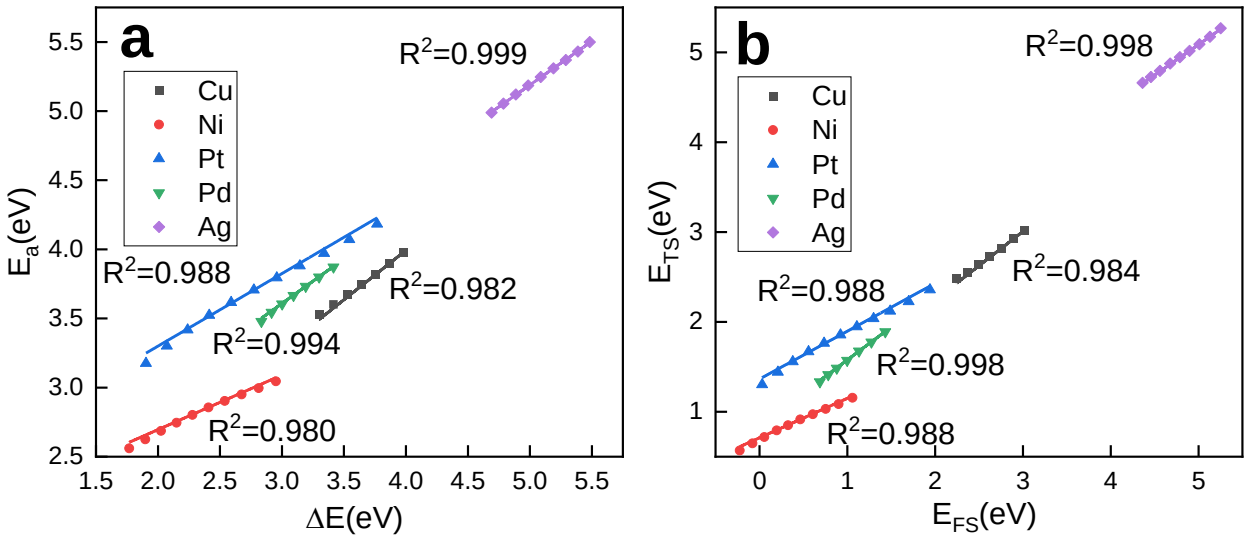

Figure S14. BEP (a) and TSS (b) relations of CO dissociation on the five (111) surfaces under strain; the points are the results calculated by DFT. And the curves are drawn according to Eqs. (18a) and (19a) in the text.

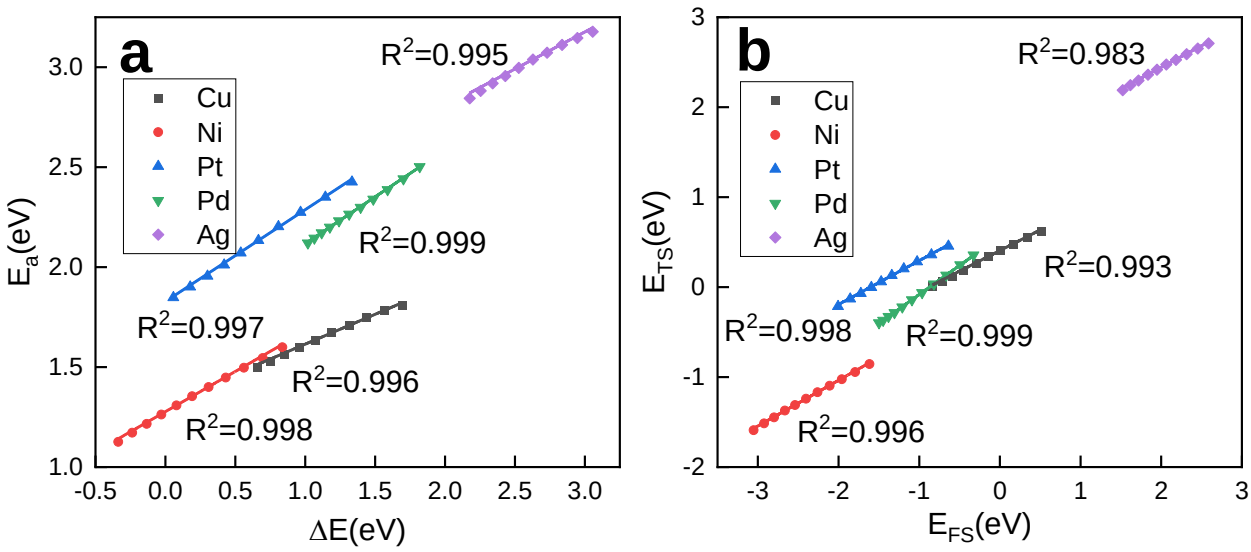

Figure S15. BEP (a) and TSS (b) relations of NO dissociation on the five (111) surfaces under strain; the points are the results calculated by DFT. And the curves are drawn according to Eqs. (18a) and (19a) in the text.

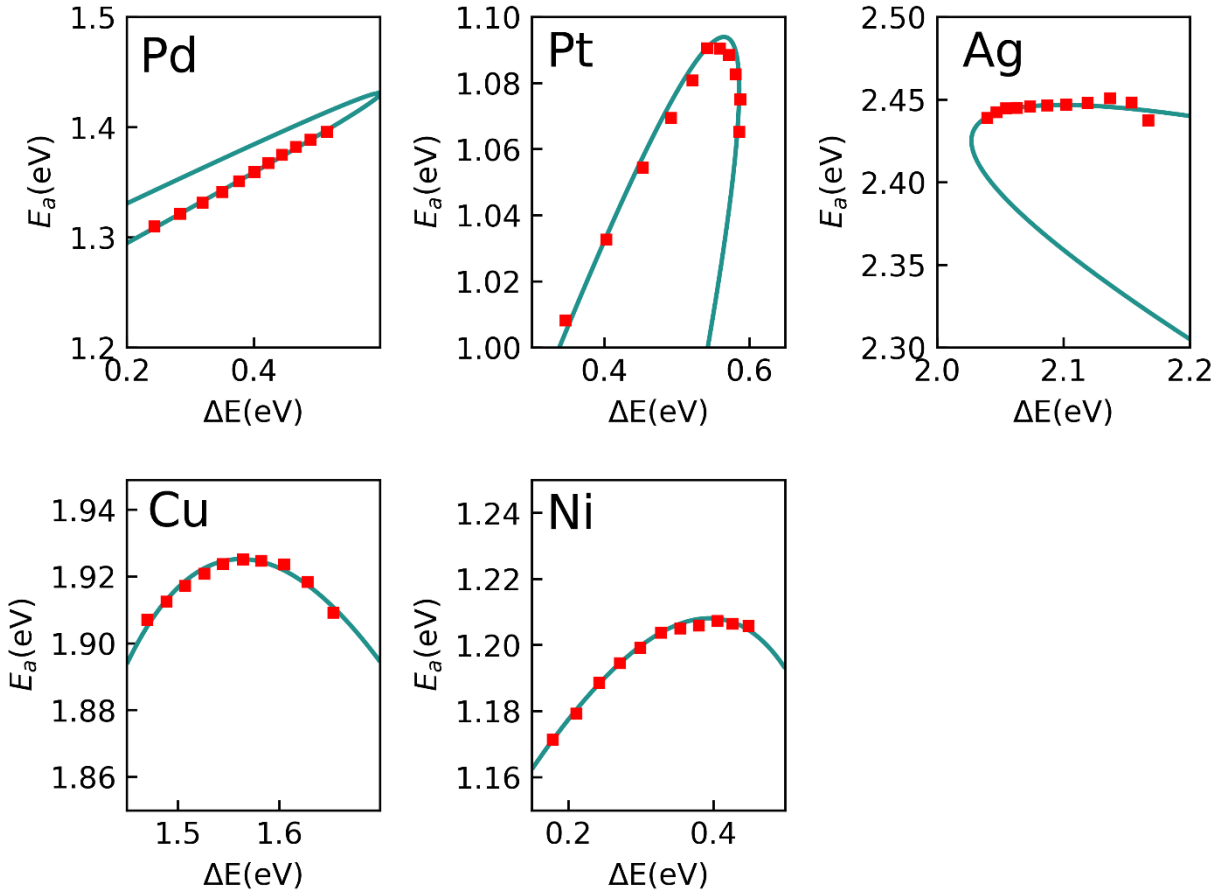

Figure S16. BEP relations of NH dissociation on the five (111) surfaces under strain. The points are the results calculated by DFT. And the curves are drawn according to Eqs. (18) in the text.

Proposed index characterizing the nonlinearity

Table S15. Proposed index (F_{nL}) characterizing the nonlinearity*

Metal	atomic distance(Å)	V_{ad}^2	f	ε_d	V_{dd}	V_{ss}	V_{sd}	coefficent	$F_{nL}(eV^{-3})$
Pd	2.795	2.78	0.9	-1.78	-0.601	-1.37	-0.601	47.7	0.544
Pt	2.802	3.90	0.9	-2.42	-0.804	-1.36	-0.693	21.9	0.488
Ag	2.942	2.26	1.0	-4.04	-0.395	-1.23	-0.463	10.4	0.296
Ni	2.485	1.16	0.9	-1.59	-0.466	-1.73	-0.595	7.9	0.185
Cu	2.561	1.00	1.0	-2.46	-0.337	-1.63	-0.492	7.4	0.135

*: $F_{nL}= -V_{ad}^2*f/\varepsilon_d/(V_{ss}^2+V_{sd}^2+V_{dd}^2)$. V_{ss}, V_{sd} and V_{dd} are s-s, s-d and d-d coupling matrix elements of metals (in eV)[23] . Both V_{ad}^2, the coupling matrix element between an adsorbate and the metal d-states, and ε_d (in eV), the first moment are taken from ref.[24]. d-band filling is from ref. [25] Coefficent refers to the averaged absolute values of $[V_0 B_{\mathrm{ads}} + (2-v)V_0 K_{\mathrm{ads}}^w]$ for the 25 systems studied here.

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