Electronic Supplementary Information

Electronic structure and catalytic activity of exsolved Ni on Pd core-shell nanoparticles

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To rigorously show that three layers for the core is sufficient, we calculated the adsorption energy (E_{ads}) of an O atom at the fcc site on 2x2 surface unit cells of Ni(111) as well as Ni-1ML/Pd(111) with different number of core layers. For Ni(111) the total number of layers was varied from three to five. For Ni-1ML/Pd(111) structures with Ni in the top layer, the number of Pd layers in the core was varied from three to five. As seen in **Table S0** the E_{ads} for O was within ±0.01 eV for all the slabs for both Ni(111) as well as Ni/Pd(111). This demonstrates that increasing the number of layers beyond three beneath the surface layer has a negligible influence on adsorbate binding energy or the electronic structure of the surface.

Slab	Lattice constant, a (Å)	Total # of layers	E_{ads} (eV)
Ni(111)	3.58	3	-1.89
		4	-1.88
		5	-1.90
Ni-1ML/Pd(111)	3.88	4	-2.30
		5	-2.31
		6	-2.31

Table S0. E_{ads} (eV) for atomic oxygen (Θ=0.25 ML) adsorption on Ni(111) and Ni-1ML/Pd(111) core-shell structure with different number of layers.

Slab	xy-plane		z-direction	
	d_{Ni-Ni} (Å)	strain (%)	d_{Ni-X} (Å)	strain (%)
Ni(111)	2.52	---	2.50	---
Ni-1ML/Pd(111)	2.74	8.73	2.62	5.22
Ni-2ML/Pd(111)	2.74	8.73	2.46	-1.20
Ni-3ML/Pd(111)	2.74	8.73	2.48	0

Table S1. Ni-Ni and Ni-X bond lengths parallel to the surface and between the top layer and the second layer respectively in Pd-Ni core-shell catalyst. X is Pd for Ni-1ML/Pd(111) and Ni for Ni-2ML/Pd(111) and Ni-3ML/Pd(111).
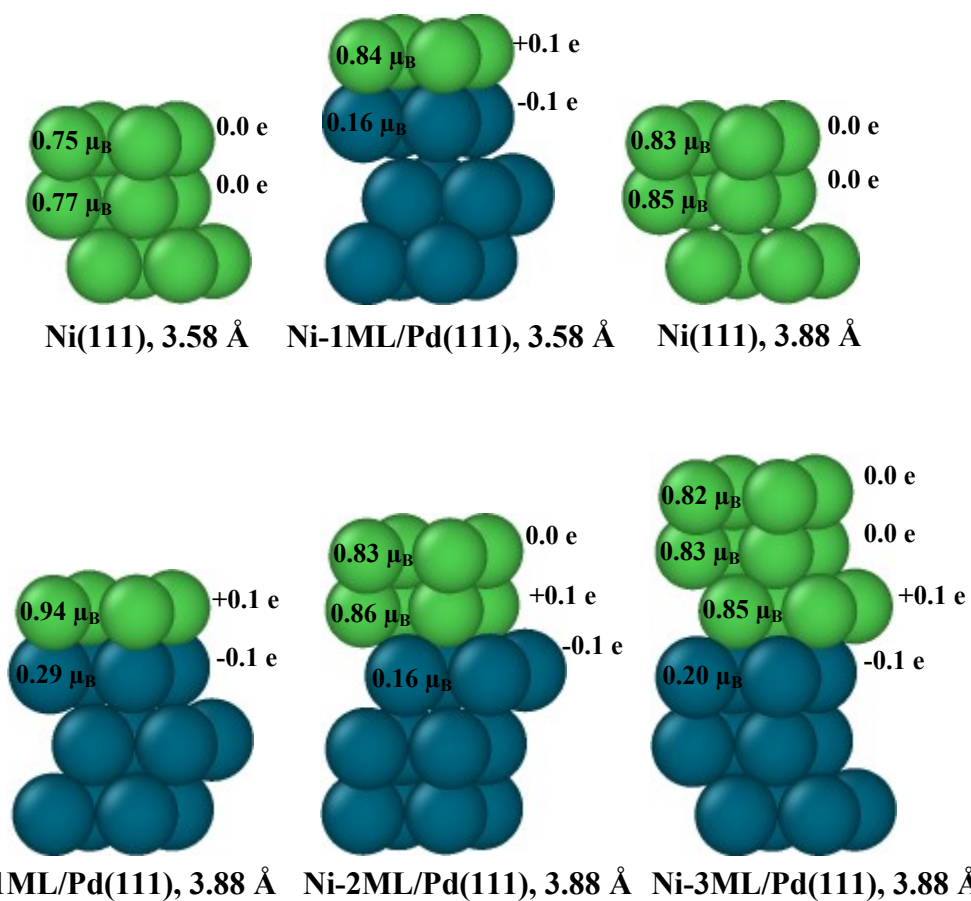

Figure S1. Charge (e/atom) and magnetic moment (μ_B/atom) at the surface and Ni-Pd interface of Ni/Pd(111) core-shell as well as on Ni(111) catalysts.
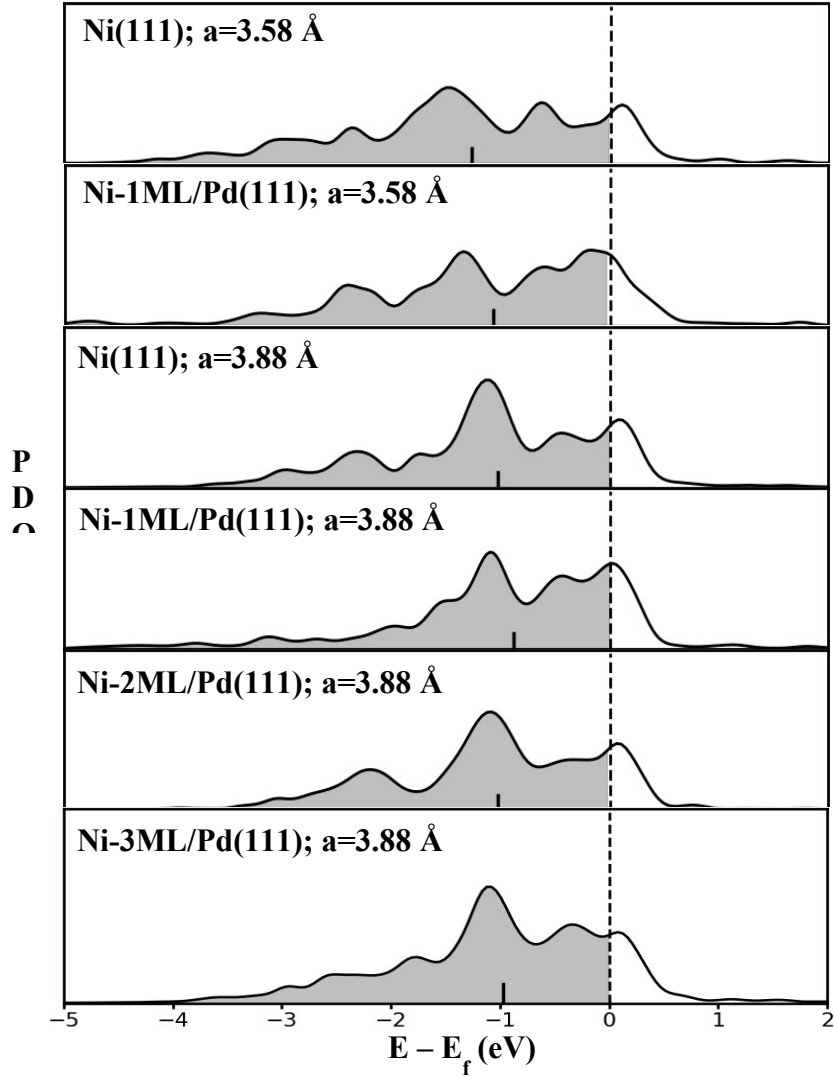
Figure S2. Projected density of states for *d*-bands of unstrained Ni(111), a=3.58 Å; Ni-1ML/Pd(111), a=3.58 Å; strained Ni(111), Ni-1ML/Pd(111), Ni-2ML/Pd(111), and Ni-3ML/Pd(111) slabs with a = 3.88 Å. The vertical solid black line and black dash line shows the position of *d*-band center and *Fermi* level respectively.

The mathematical expressions used to calculate *d*-band center (ε_d) and *d*-band width (w_d) are given below

$$\varepsilon d = \frac{\int\limits_{-\infty}^{\infty} nd(\varepsilon)\varepsilon \, d\varepsilon}{\int\limits_{-\infty}^{\infty} nd(\varepsilon)d\varepsilon}$$

$$w_d^{(2)} = \frac{\int\limits_{-\infty}^{\infty} nd(\varepsilon)(\varepsilon - \varepsilon d)2 \, d\varepsilon}{\int\limits_{-\infty}^{\infty} nd(\varepsilon)d\varepsilon}$$

In the above equations n_d and ε represent the *d*-DOS and corresponding eigenvalue respectively.

Lattice constant, *a* (Å)	Interlayer distance, d_{12} (Å)			
	Ni(111)	Ni-1ML/Pd(111)	Ni-2ML/Pd(111)	Ni-3ML/Pd(111)
3.53	2.05			
3.58	2.03	2.24	2.01	2.03
3.63	2.01			
3.68	1.99			
3.73	1.97			
3.78	1.95			
3.83	1.93			
3.88	1.92	2.08	1.89	1.91
3.93	1.88			

Table S2. The values of interlayer distance d_{12} (Å) as a function of lattice constant, *a* (Å) for Ni(111), Ni-1ML/Pd(111), Ni-2ML/Pd(111), and Ni-3ML/Pd(111).
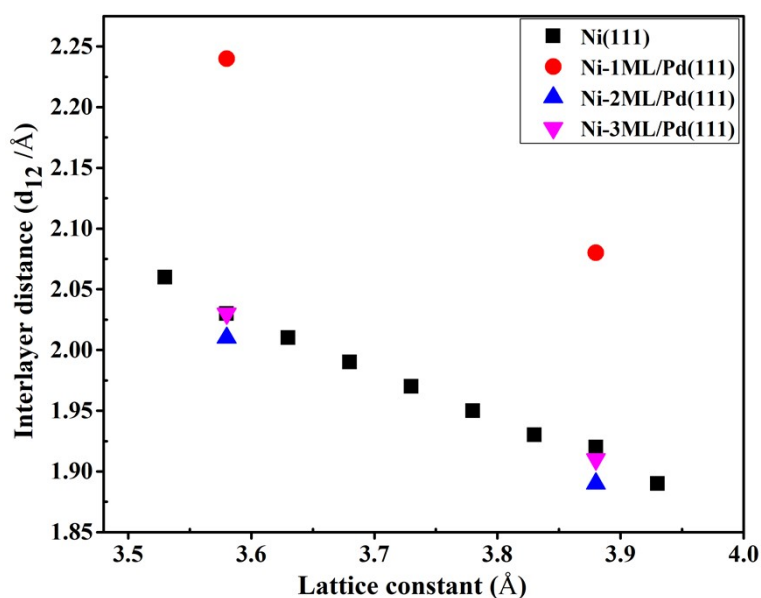

Figure S3. Variation in the interlayer distances d_{12} (Å) as a function of lattice constant *a* for Ni(111) as well as Ni/Pd(111) surfaces. The subscript "12" gives the layer index numbers – so this is the distance between the surface and first subsurface layers.

The main observations from **Figure S3** and **Table S2** are:

1. For Ni(111), there is a clear linear relationship between the interlayer distance (d_{12}) and lattice constant (*a*) with a slope of ~1/2. We observed a decrease of ~0.2 Å in the value of d_{12} as we move from 3.53 Å to 3.93 Å. This shows that the interlayer spacing decreases as the tensile strain at the surface increases. This can be explained as the slab trying to counter the forced stretching at the surface by bringing the surface atoms closer to the Ni atoms in the first subsurface.

2. For the same lattice constant, either 3.58 Å or 3.88 Å, we observed an increase of ~0.2 Å in the d_{12} of Ni-1ML/Pd(111) in comparison to the d_{12} of Ni(111). This increase in the value of d_{12} of Ni-1ML/Pd(111) is anticipated because of different spatial extent of *d*-orbitals of Ni and Pd. The spatial extent of the *d*-orbital of the Pd is 3.38 Å whereas for Ni atoms it is 2.46 Å. The topmost Ni layer in Ni-1ML/Pd(111) encounters a repulsion because of the larger *d*-orbitals of the Pd atoms underneath, which results in a larger value of d_{12} than that when both layers are Ni.

For a given lattice constant, the d_{12} is within ~0.03 Å for Ni(111), Ni-2ML/Pd(111), and Ni-3ML/Pd(111). This is easily explained by noting that in all these structures, the surface as well as first subsurface layers are both Ni. Thus for Ni layers > 1 on a Pd core, d_{12} is essentially the same as that for a pure Ni surface.

Lattice constant, a (Å)	*d*-band center (eV)			
	Ni(111)	Ni-1ML/Pd(111)	Ni-2ML/Pd(111)	Ni-3ML/Pd(111)
3.53	-1.30			
3.58	-1.27	-1.07	-1.26	-1.25
3.63	-1.18			
3.68	-1.13			
3.73	-1.08			
3.78	-1.04			
3.83	-1.00			
3.88	-1.03	-0.88	-1.02	-0.99
3.93	-0.93			

Table S3. The values of *d*-band center as function of lattice constant, a (Å) on Ni(111), Ni-1ML/Pd(111), Ni-2ML/Pd(111), and Ni-3ML/Pd(111).

Lattice constant, a (Å)	E$_{ads}$/eV (O atom)			
	Ni(111)	Ni-1ML/Pd(111)	Ni-2ML/Pd(111)	Ni-3ML/Pd(111)
3.53	-1.81			
3.58	-1.89	-2.10	-1.90	-1.89
3.63	-1.94			
3.68	-1.99			
3.73	-2.05			
3.78	-2.09			
3.83	-2.14			
3.88	-2.18	-2.30	-2.13	-2.17
3.93	-2.21			

Table S4. Adsorption energies (E$_{ads}$/eV) of atomic O as function of lattice constant, a (Å) on Ni(111), Ni-1ML/Pd(111), Ni-2ML/Pd(111), and Ni-3ML/Pd(111).

Lattice constant, a (Å)	E$_{ads}$/eV (CO molecule)			
	Ni(111)	Ni-1ML/Pd(111)	Ni-2ML/Pd(111)	Ni-3ML/Pd(111)
3.53	-1.38			
3.58	-1.39	-1.62	-1.40	-1.39
3.63	-1.41			
3.68	-1.42			
3.73	-1.44			
3.78	-1.45			
3.83	-1.46			
3.88	-1.48	-1.65	-1.49	-1.48
3.93	-1.49			

Table S5. Adsorption energies (E$_{ads}$/eV) of molecular CO as function of lattice constant, a (Å) on Ni(111), Ni-1ML/Pd(111), Ni-2ML/Pd(111), and Ni-3ML/Pd(111).

Figure S4 shows the variation in E$_{ads}$ as a function of the *d*-band center. It can be seen that there is a linear relationship between adsorption energy and the surface *d*-band center; the

adsorption energies increase (becomes more negative) as the surface d-band center becomes less negative. For CO adsorption, the computed E_{ads} for Ni-1ML/Pd(111) at different lattice constants do not fall on the same line as the other surfaces. This is perhaps because the ligand effect is stronger than the strain effect for CO on Ni-1ML/Pd(111) as discussed in the manuscript. Our findings on E_{ads} vs d-band centre for O and CO adsorption on Ni(111) and Ni/Pd(111) surfaces are consistent with the results of previous studies on transition metals, overlayers, and surface alloys.[1,2]
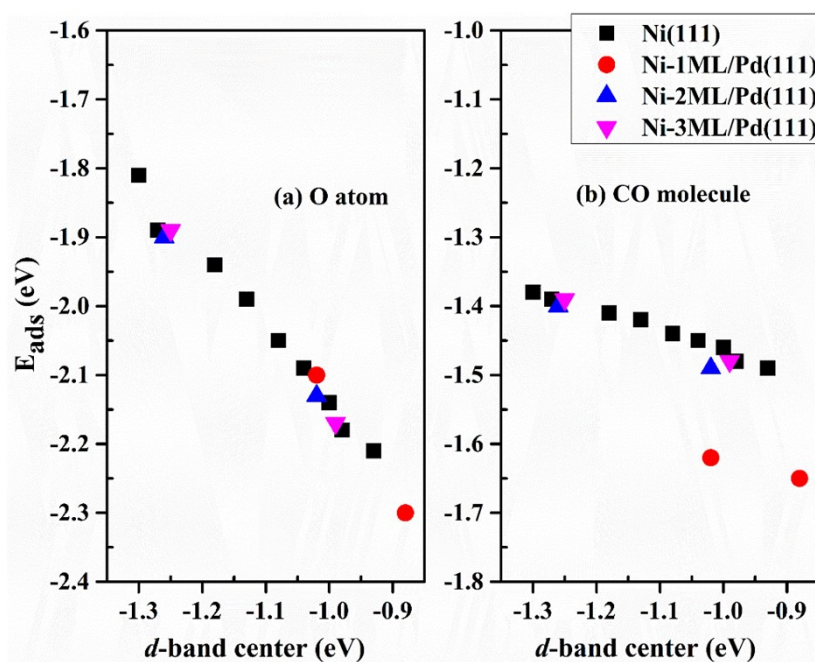

Figure S4. Variation in adsorption energy (E_{ads}/eV) for (a) O atom and (b) CO molecule on (111) surfaces of Ni/Pd and Ni *vs* d-band center.

Adsorption sites	Surface	E_{ads} (eV/O_2)	$q(O_2)$	d_{O-O} (Å)	d_{Ni-Ni} (Å)
	Ni(111)	-0.65	-0.63	1.35	2.55
	Ni-1ML/Pd(111)	-1.10	-0.65	1.35	2.85
	Ni-2ML/Pd(111)	-0.95	-0.66	1.35	2.80
t-b-t	Ni-3ML/Pd(111)	-0.91	-0.66	1.35	2.85
	Ni(111)	-0.75	-0.81	1.41	2.56
	Ni-1ML/Pd(111)	-1.28	-0.85	1.41	2.87
	Ni-2ML/Pd(111)	-1.05	-0.85	1.42	2.84
t-f-b	Ni-3ML/Pd(111)	-1.03	-0.84	1.42	2.84
	Ni(111)	-0.77	-0.81	1.41	2.53
	Ni-1ML/Pd(111)	-1.31	-0.86	1.41	2.79
	Ni-2ML/Pd(111)	-1.09	-0.86	1.42	2.76
t-h-b	Ni-3ML/Pd(111)	-1.08	-0.86	1.43	2.76

Table S6. Adsorption energy (E_{ads}), O-O bond length (d_{O-O}), Ni-Ni bond length (d_{Ni-Ni}) and charge on adsorbed O_2 (q) on (111) surfaces Pd-Ni core-shell and Ni at top-bridge-top (t-b-t), top-fcc-bridge (t-f-b), and top-hcp-bridge (t-h-b) sites.

Figure S5 gives O *p*-projected DOS in the gas phase as well as in the adsorbed state on Ni(111) and Ni/Pd(111) surfaces in blue. The surface Ni 3*d* PDOS is shown in red. Comparing the O *p* PDOS brings out how the antibonding orbital of adsorbed O_2 broadens out due to interactions with the metal atom *d* band. The relative population of these flattened bands does not vary much between the surfaces studied here.
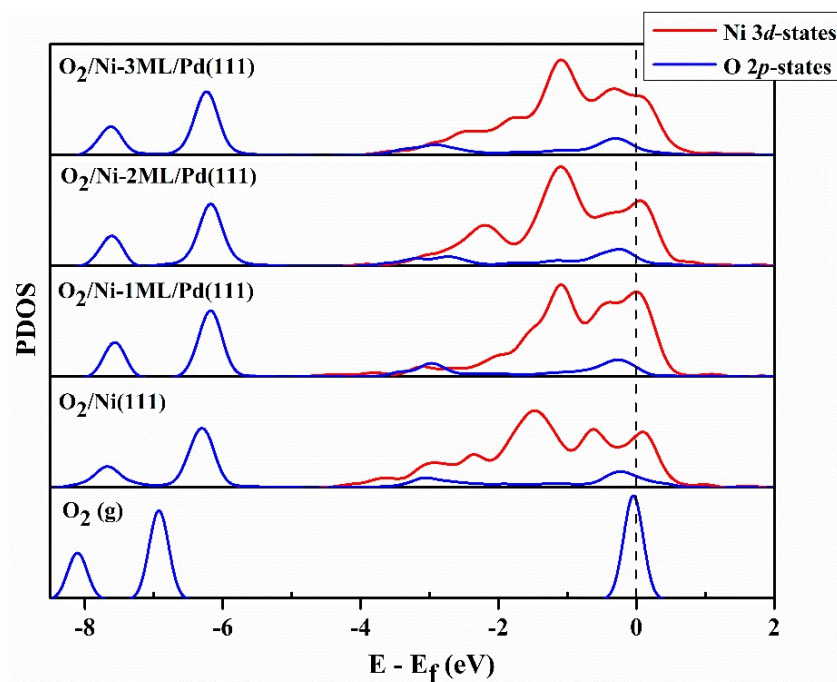

Figure S5. PDOS for an O_2 molecule in the gas phase and adsorbed state. The blue lines show *p*-projected DOS for O_2 and the red lines represent *d*-projected DOS for top layer of Ni/Pd(111) core-shell and Ni(111) surfaces.

Surface	E_a (meV)	ΔE (eV)
Ni(111)	138	-1.98
Ni-1ML/Pd(111)	0	-2.79
Ni-2ML/Pd(111)	21	-2.62
Ni-3ML/Pd(111)	22	-2.65

Table S7. The reaction enthalpy (ΔE/eV) and energy barrier (E_a/meV) for O_2 dissociation on Ni/Pd(111) core-shell and Ni(111) surfaces.

Co-adsorbed states	surface	E_{ads} (eV)	d_{C-O1} (Å)	d_{C-O2} (Å)	d_{Ni-C} (Å)	d_{Ni-O1} (Å)
CO_{top}-O_{fcc}	Ni(111)	-2.87	2.91	1.16	1.81	1.89
	Ni-1ML/Pd(111)	-3.57	3.31	1.16	1.79	1.88
	Ni-2ML/Pd(111)	-3.29	3.32	1.16	1.80	1.89
	Ni-3ML/Pd(111)	-3.31	3.31	1.16	1.80	1.88
CO_{fcc}-O_{fcc}	Ni(111)	-2.50	2.57	1.18	2.01	1.87
	Ni-1ML/Pd(111)	-3.45	2.77	1.19	1.98	1.87
	Ni-2ML/Pd(111)	-3.09	2.78	1.19	2.02	1.88
	Ni-3ML/Pd(111)	-3.11	2.78	1.19	1.99	1.88
CO_{hcp}-O_{hcp}	Ni(111)	-2.37	2.51	1.18	1.99	1.87
	Ni-1ML/Pd(111)	-3.28	2.76	1.19	1.98	1.88
	Ni-2ML/Pd(111)	-2.96	2.77	1.19	1.99	1.88
	Ni-3ML/Pd(111)	-2.98	2.78	1.19	1.99	1.89

Table S8. Adsorption energies (E_{ads}/eV) and the geometrical parameters (d_{C-O1}: distance between CO and atomic O, d_{C-O2}: C-O bond length in CO, and d_{Ni-C}: Ni-C bond length, and d_{Ni-O1}: bond length of Ni and atomic O) for all possible CO+O co-adsorbed states on Ni(111) and Ni/Pd core-shell surfaces.

Slab	E_a (eV)	ΔE (eV)	d_{C-O1} (Å)	d_{C-O2} (Å)	∠O1CO2 (º)
Ni(111)	1.11	-0.13	1.79	1.17	114.4
Ni-1ML/Pd(111)	1.30	0.65	1.73	1.18	116.2
Ni-2ML/Pd(111)	1.23	0.37	1.76	1.17	115.6
Ni-3ML/Pd(111)	1.24	0.36	1.74	1.18	116.1

Table S9. Energy barrier (E_a) and reaction energy (ΔE) for CO oxidation process on (111) surface of Ni and Pd-Ni core-shell catalysts. d_{C-O1} and d_{C-O2} represent the bond lengths and ∠O1CO2 is the bond angle of the transition state. O1 denotes an atomic O at fcc of (111) surface of Pd-Ni and O2 represents the oxygen atom of CO molecule.

References

1   M. Mavrikakis, B. Hammer and J. K. Nørskov, Effect of strain on the reactivity of metal surfaces, *Phys. Rev. Lett.*, 1998, **81**, 2819–2822. DOI: 10.1103/PhysRevLett.81.2819

2   T. Bligaard and J. K. Nørskov, Ligand effects in heterogeneous catalysis and electrochemistry, *Electrochim. Acta*, 2007, **52**, 5512–5516. DOI: 10.1016/j.electacta.2007.02.041