Confined catalysis under two-dimensional materials

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Computational details

Theoretical calculations were performed using Vienna *ab* initio simulation packages (VASP)[1] with the projector-augmented wave (PAW) scheme[2]. We used the Perdew-Burke-Ernzerhof (PBE)[3] functional at the level of the Generalized Gradient Approximation (GGA) for electronic exchange-correlation interactions. The plane wave cutoff was set to 400 eV. In addition, the weak van der Waals (vdW) interactions were corrected in the form of C^6/R^6 pair potentials (PBE-D), where C^6 and the vdW radius, R^0, were set as shown in the table below:

Element	Pt	C	H	N	O	S	Li
C^6 ($J \cdot nm^6 \cdot mol^{-1}$)	24.67	1.75	0.14	1.23	0.70	5.57	1.61
R^0 (Å)	1.75	1.452	1.001	1.397	1.342	1.683	0.825
Element	Na	K	Rb	Cs	B	Zn	
C^6 ($J \cdot nm^6 \cdot mol^{-1}$)	5.71	10.80	24.67	24.67	3.13	10.80	
R^0 (Å)	1.144	1.485	1.628	1.628	1.485	1.562	

The Brillouin zone was sampled by a 6×6×1 *k*-point grid for the calculations of charge density and local potential, and a 2×2×1 Monkhorst-Pack[4] *k*-point grid for structural optimizations. The convergence of energy and forces were set to 1×10^{-5} eV and 0.05 $eV \cdot Å^{-1}$.

For graphene/Pt(100) surface, A 3×3 Pt(111) supercell with $3\times2\sqrt{3}$ graphene

overlayer was used as a simplified model for calculations. For graphene/Pt(110) surface, A 2×3 Pt(110) supercell with 3×2√3 graphene overlayer was used for calculations.

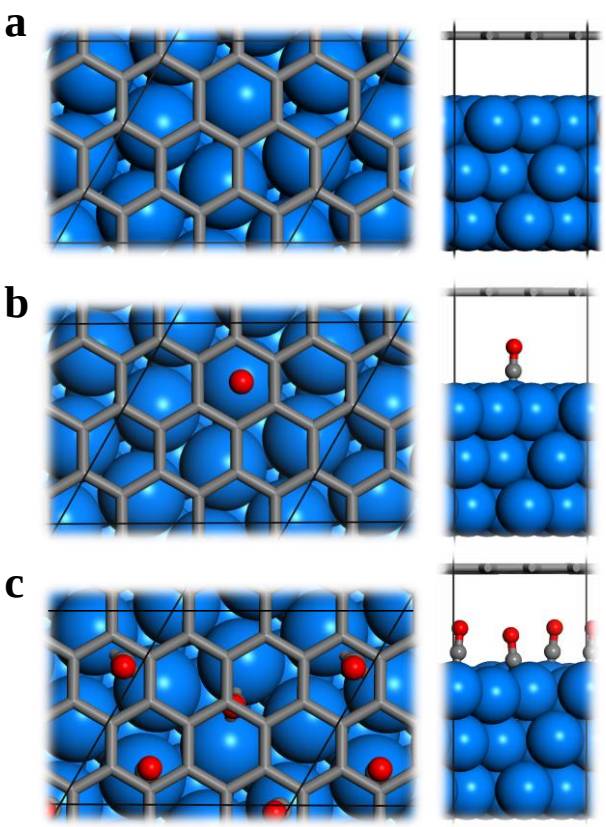

Figure S1. Atomic structure diagrams of the calculation models used in this work. a) Graphene (Gr) covered Pt(111). b-c) CO adsorption at the interface of Gr/Pt(111) at the coverage of 1/7 ML (b) and 3/7 ML (c).

Table S1. Comparison of different vdW correction methods, as well as without vdW corrections, for the Gr/CO/Pt(111) system.

Method	E_{ad}(CO) (bare surface)	E_{ad}(CO) (with graphene)	E_{con}	Gr-Pt distance	Gr-CO-Pt distance
vdW-D2[5]	-2.02 eV	-0.61 eV	1.41 eV	3.2 Å	5.7 Å
vdW-D3[6]	-2.06 eV	-0.57 eV	1.49 eV	3.2 Å	5.7 Å
vdW-DF opt-B88[7,8,9,10]	-1.95 eV	-0.88 eV	1.07 eV	3.3 Å	5.7 Å
w/o vdW	-1.75 eV	-1.63 eV	0.12 eV	4.2 Å	5.9 Å

Table S2. The adsorption energies of CO at the interface of Gr/Pt(100) and Gr/Pt(110), as well as the adsorption energy difference.

Adsorption surface	**Adsorption site**	**Adsorption energy (eV)**			**Coverage (ML)**	**Gr-height (Å)**	
		Bare surface	With Gr	Δ		Gr/Pt	Gr/CO/Pt
Gr/Pt(100)	Top	-1.88	-0.04	1.84	1/9	3.18	5.65
Gr/Pt(110)	Top	-2.46	1.29	3.75	1/6	2.25	5.49

Table S3. The adsorption energies of CO at the interface of Gr/Pt(111) with different adsorption sites at 1/7 ML coverage.

Adsorption site	**Adsorption energy (eV)**			**Gr-height (Å)**	
	Bare surface	With Gr	Δ	Gr/Pt	Gr/CO/Pt
Top	-2.02	-0.61	1.41	3.27	5.73
Bridge	-2.15	-0.82	1.33	3.27	5.61
Hollow (FCC)	-2.22	-0.94	1.28	3.27	5.51

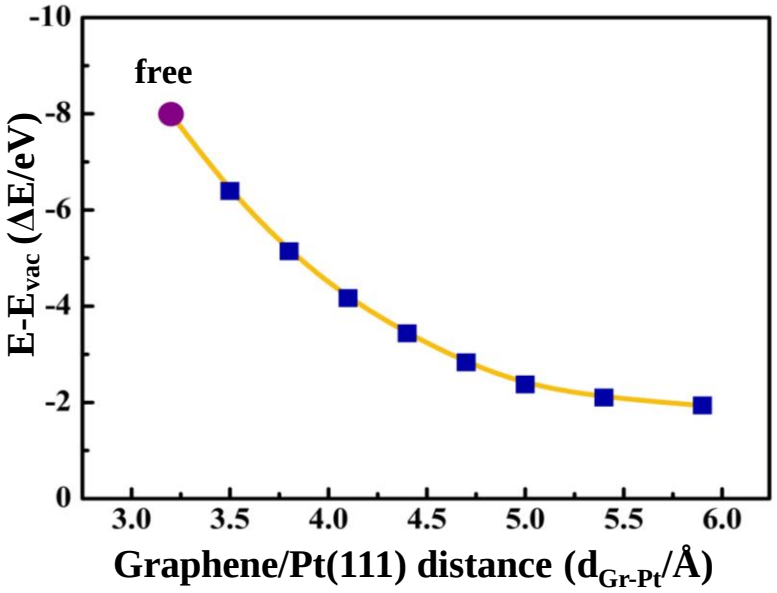

Figure S2. The maximum potential energy between Gr and Pt(111) (corresponding to the energies at the positions marked by orange dots in Fig. 3a) as a function of d_{Gr-Pt}.

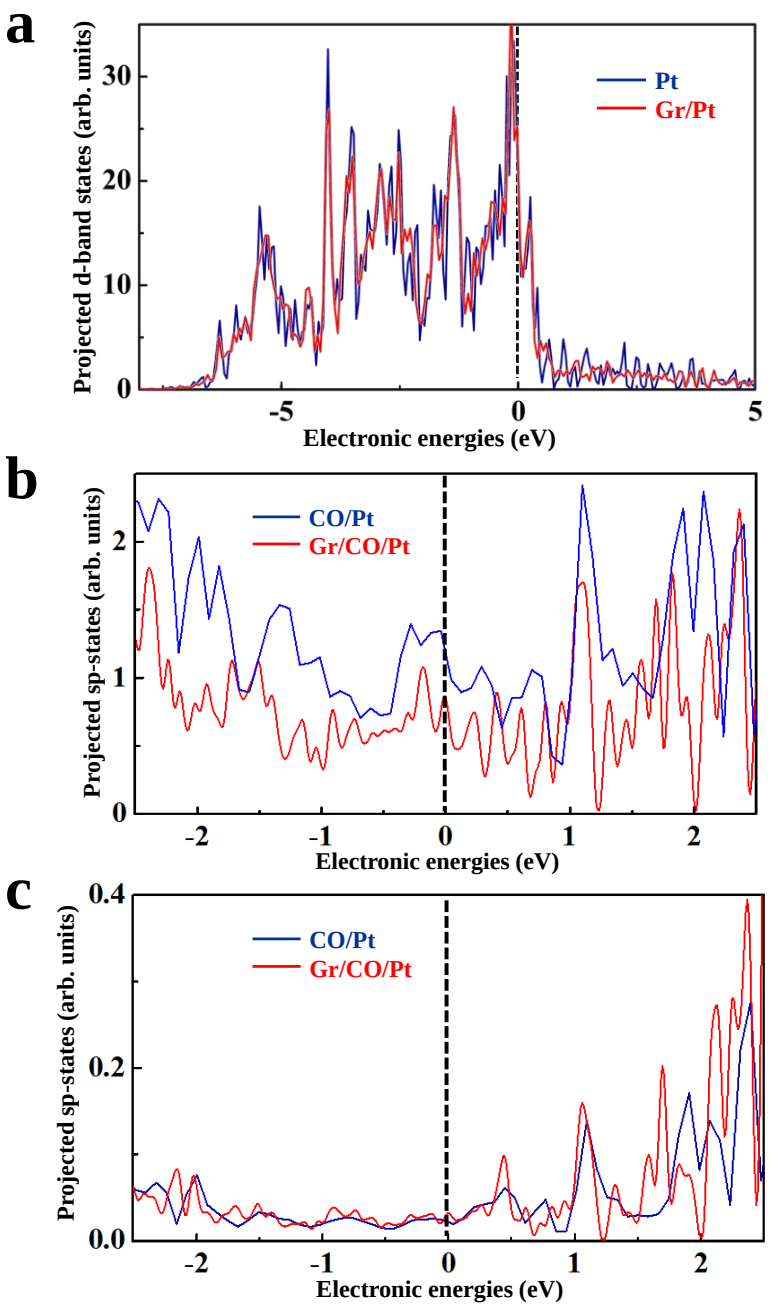

Figure S3. a) Projected d-band states of Pt atoms of bare Pt(111) surface (blue) and Gr/Pt(111) interface (red). b) Projected sp-states of Pt atoms of CO/Pt(111) (blue) and Gr/CO/Pt(111) (red) structures. c) Projected sp-states of CO molecules of CO/Pt(111) (blue) and Gr/CO/Pt(111) (red) structures. The Fermi level is set to 0 eV as shown in dashed line.

Table S4. The adsorption sites and adsorption energies of different adsorbates (non-metal atoms, molecules, alkali metal atoms) on bare Pt(111) surface and Gr/Pt(111) surface at 1/7 ML coverage, as well as the adsorption energy difference, the Gr height of the Gr/Pt(111) surface at full relaxation, the bind length of atoms or molecules with Pt(111) and the bond length of the adsorbed molecules.

	Adsorption site		Adsorption energy (eV)			Gr-height	Bind length (Å)	
Adsorbate	Pt	Gr/Pt	Pt	Gr/Pt	Δ	(Å)	Pt	Gr/Pt
H atom	Top	Fcc	-0.58	-0.49	0.09	3.26	1.56	1.80
C atom	Fcc	Fcc	-7.59	-7.35	0.24	3.40	1.90	1.90
N atom	Fcc	Fcc	-0.00	0.30	0.30	3.38	1.95	1.93
O atom	Fcc	Fcc	-1.43	-1.08	0.35	3.45	2.04	2.02
S atom	Fcc	Fcc	-2.13	-1.18	0.95	4.18	2.26	2.24
CO	Top	Top	-2.02	-0.61	1.41	5.73	1.84	1.83
NO	Fcc	Fcc	-2.29	-1.00	1.28	5.12	2.07	2.09
H_2O	Top	Top	-0.52	0.59	1.11	4.97	2.32	2.23
NH_3	Top	Top	-1.37	-0.19	1.18	5.56	2.10	2.10
Li atom	Fcc	Fcc	-1.90	-2.06	0.16	3.69	---	---
Na atom	Fcc	Fcc	-1.37	-2.09	0.72	4.50	---	---
K atom	Fcc	Fcc	-1.34	-2.47	1.13	5.45	---	---
Rb atom	Fcc	Fcc	-1.52	-2.66	1.13	5.85	---	---
Cs atom	Fcc	Fcc	-1.61	-2.88	1.26	6.10	---	---

Table S5. The adsorption sites and adsorption energies of different adsorbates (non-metal atoms, molecules, alkali metal atoms) on bare Pt(111) surface and Gr/Pt(111) surface at 3/7 ML coverage, as well as the adsorption energy difference, the Gr height of the Gr/Pt(111) surface at full relaxation, the bind length of atoms or molecules with Pt(111) and the bond length of the adsorbed molecules. (a: two molecules at Bridge site and one molecule at Fcc site in one unit cell; b: one molecule at Bridge site and two molecules at Fcc site in one unit cell)

	Adsorption site		Adsorption energy (eV)			Gr-height	Bind length (Å)	
Adsorbate	Pt	Gr/Pt	Pt	Gr/Pt	Δ	(Å)	Pt	Gr/Pt
H atom	Fcc	Fcc	-0.56	-0.48	0.08	3.40	1.56	1.85
C atom	Fcc	Fcc	-7.02	-6.78	0.16	3.86	1.92	1.92
N atom	Fcc	Fcc	0.64	0.82	0.18	3.85	1.97	1.97
O atom	Fcc	Fcc	-1.04	-0.84	0.20	3.88	2.05	2.04
S atom	Fcc	Fcc	-1.09	-0.77	0.32	4.73	2.31	2.31
CO	2B1F[a]	1B2F[b]	-1.94	-1.50	0.44	5.89	2.06	2.10
NO	Fcc	Fcc	-1.87	-1.47	0.40	5.39	2.10	2.09
Li atom	Fcc	Fcc	-1.86	-1.72	-0.14	4.04	---	---
Na atom	Fcc	~Fcc	-1.61	-1.63	0.02	4.90	---	---
K atom	Fcc	Fcc	-1.63	-1.67	0.04	5.63	---	---
Rb atom	Fcc	Fcc	-1.79	-1.81	0.02	5.88	---	---
Cs atom	Fcc	Fcc	-1.77	-1.93	0.16	6.18	---	---

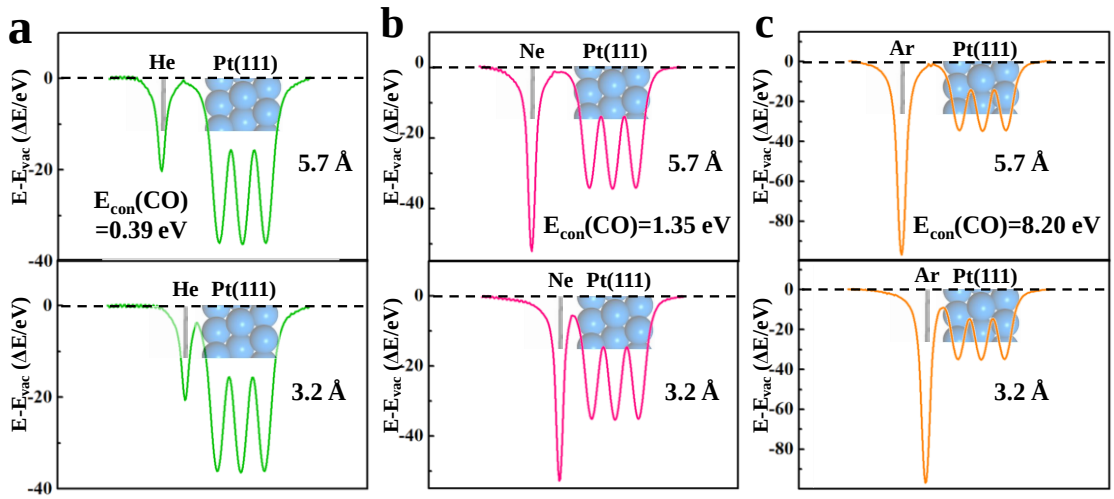

Figure S4. One-dimensional local potential energies of a) He/Pt(111), b) Ne/Pt(111), and c) Ar/Pt(111) interfaces with the overlayer-surface distance at 5.7 Å (above) and 3.2 Å (below), respectively. The corresponding schematic atomic structures in the real space are shown as the semitransparent insets.

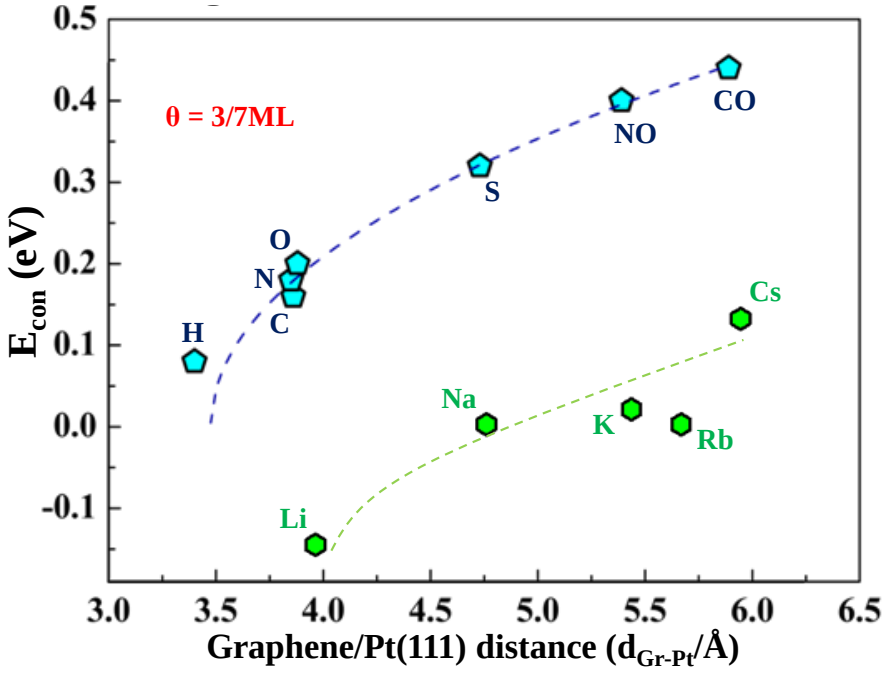

Figure S5. Confinement energies of a series of non-metal atoms and small molecules (blue dots) together with alkali metal atoms (green dots) at 3/7 ML coverage, and their relationship with the Gr/Pt(111) distance at full optimal relaxation. The blue dots and green dots are fitted in blue and green dashed lines, respectively, which is just 1/3 of the pink dashed line in Fig. 4a. The blue dots fit the curve well with a little lower than the curve, which is supposed to be due to the slight charge transfer between intercalation species and the Gr layer.

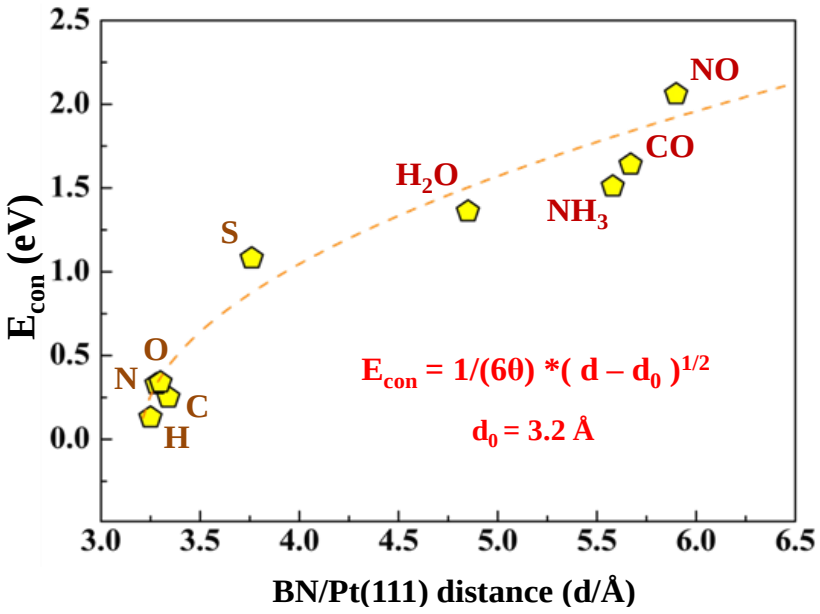

Figure S6. Confinement energies of a series of non-metal atoms and small molecules at 1/7 ML coverage, and their relationship with the h-BN/Pt(111) distance at full optimal relaxation. The curve plotted using an exponential function (in red) is shown as the yellow dashed line.

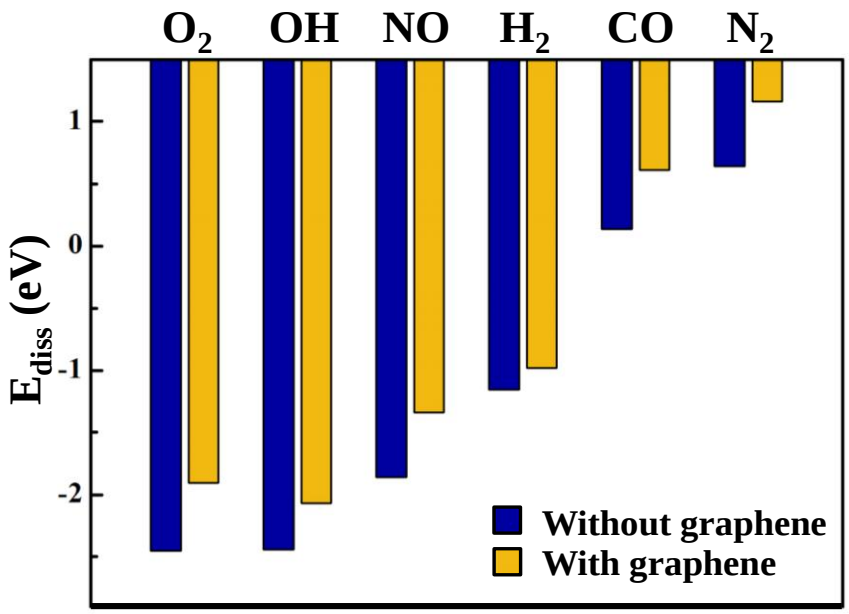

Figure S7. Dissociative binding energies of O_2, OH, NO, H_2, CO, and N_2 molecules on Gr/Pt(111) (yellow) in comparison to those on bare Pt(111) surface (blue).

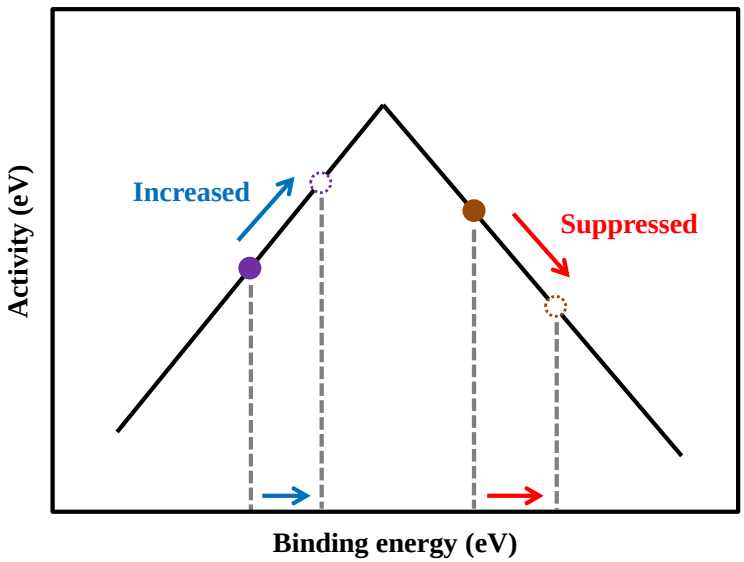

Figure S8. Schematic diagram of a volcano curve for catalytic reactions. The catalytic activity can be increased or suppressed when the binding energy of adsorbates on a catalyst surface is modulated.

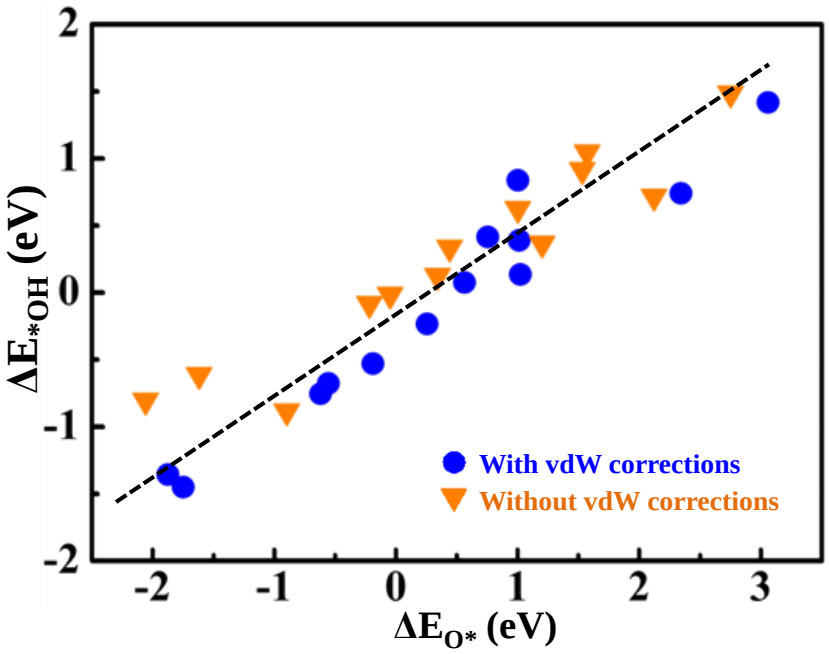

Figure S9. Linear relation between the binding energy of O* (ΔE_{O*}) and *OH (ΔE_{*OH}) on different metals with or without vdW corrections (over the most close packed surface, at 1/4 ML coverage). The corresponding metals and values of each point are listed in Table S6. The data without vdW corrections are cited from the literature by Nørskov et al.[11]

Table S6. Corresponding metals and values of each point in Fig. S9. The data without vdW corrections are cited from the literature by Norskov et al.[11]

Metal	ΔE_{O*} (with vdW)	ΔE_{*OH} (with vdW)	ΔE_{O*} (without vdW)	ΔE_{*OH} (without vdW)
Ag	0.72	2.12	0.74	2.34
Au	1.49	2.75	1.41	3.06
Co	-0.08	-0.22	-0.76	-0.62
Cu	0.37	1.20	0.13	1.02
Fe	-0.88	-0.90	-0.68	-0.55
Ir	0.63	1.00	0.41	0.75
Mo	-0.61	-1.62	-0.45	-1.75
Ni	0.13	0.34	-0.53	-0.19
Pd	0.92	1.53	0.38	1.01
Pt	1.05	1.57	0.83	1.00
Rh	0.34	0.44	0.07	0.56
Ru	-0.01	-0.05	-0.24	0.26
W	-0.80	-2.06	-1.36	-1.87

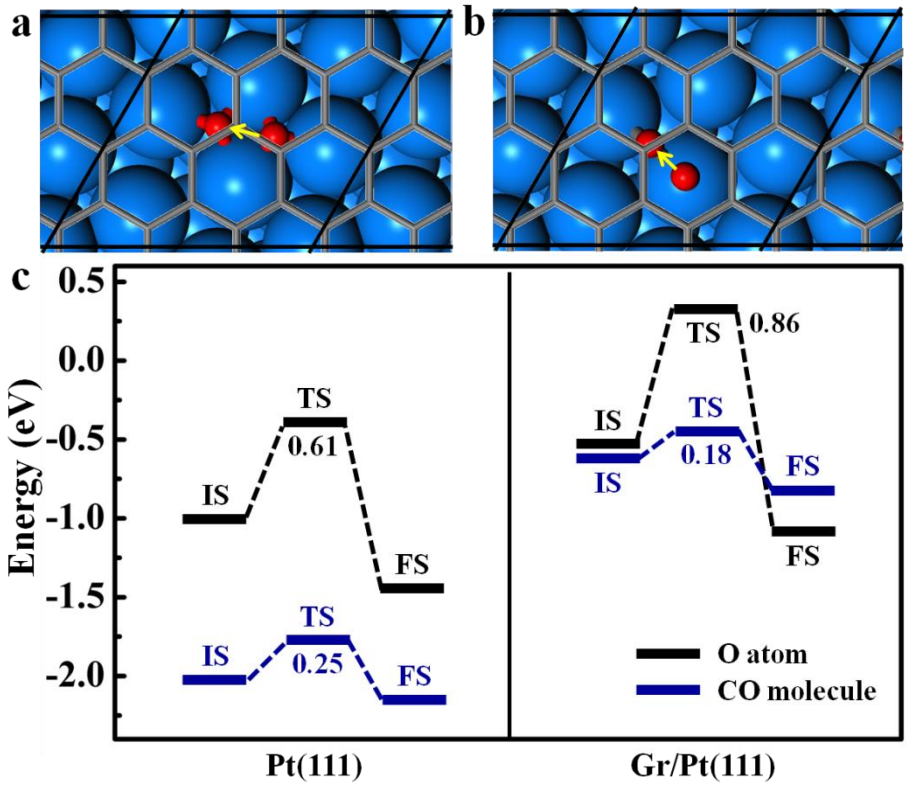

Figure S10. (a-b) Schematic diffusion process of adsorbed species at the interface of Gr/Pt(111): (a) O atom (from fcc site to hcp site); (b) CO molecule (from top site to bridge site). Pt: light blue balls; C: grey sticks or balls; O: red balls. The diffusion steps of initial states (IS) to final states (FS) are shown in yellow arrows. (c) Diffusion barriers of the process on Pt(111) (left side) and Gr/Pt(111) (right side). Black lines: O atom; blue lines: CO molecule.

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