Supplementary materials

M-Single Atoms Embedded in the Surface of Pt Nanocatalysts: the Effect of Temperature and Hydrogen Pressure

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I. Evolution of hydrogen coverage and interface tension on Pt surfaces

Under 0.1 bar (10^4 Pa) of hydrogen pressure (**Figure S1**), the coverage of hydrogen on the three facets is almost equal until temperature of 600K. Above this temperature, the coverage of hydrogen over (111) facets highly decrease while 0.9 ML of hydrogen covers the (100) and the (110) facets for temperature as high as 1000K. The fraction of (110) facets is found dominate for the studied temperature range.

(a) (b)

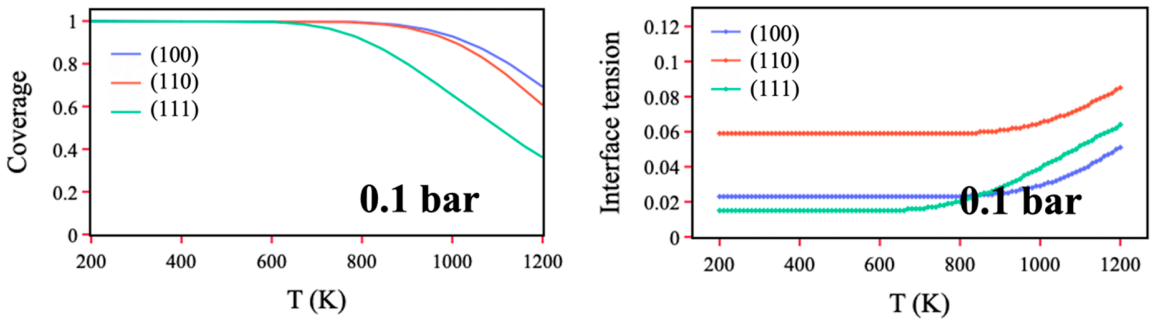


Figure S1. (a) evolution of hydrogen coverage as a function of temperature at pressure of 0.1 bar on (111), (110) and (100). (b) Pt interface tension evolution profiles of (111), (110) and (100) surface of Pt-NP constructed by MSR model as functions of temperature under 0.1 bar of hydrogen pressure.

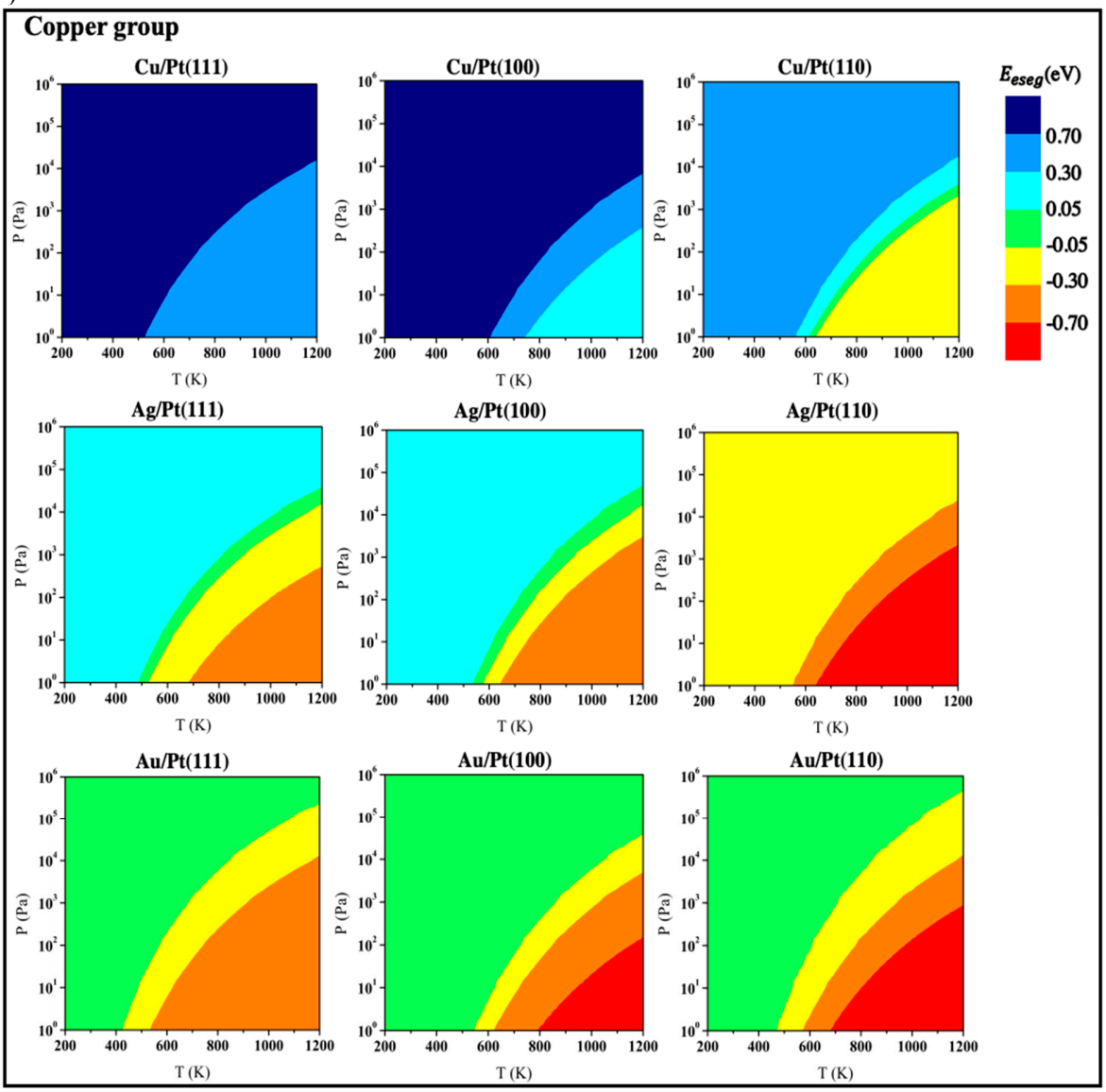
II. Mapped environmental segregation energies E_{eseg} of single-atoms M embedded in Pt(111), Pt(100) and Pt(110) host surfaces as function of temperature and H_2 pressure

The segregation trend of 8 M-promoted Pt systems (with M: Cu, Ag, Au, Ni, Pd, Co, Rh and Ir) under hydrogen reaction condition were evaluated under the temperature range covering [200 K - 1200 K] and the pressure range [1 Pa -10^6 Pa]. The counter plots of environmental segregation energy E_{eseg} in the three main facets of (111), (100) and (110) Pt surfaces are reported in **Figure S2**. The results are reported for each M transition metal group: M-single atom from coinage group (i.e. Cu, Ag, Au), Figure S2A, from nickel group (Ni, Pd), Figure S2B, and from the cobalt group (Co, Rh, Ir), Figure S2C.

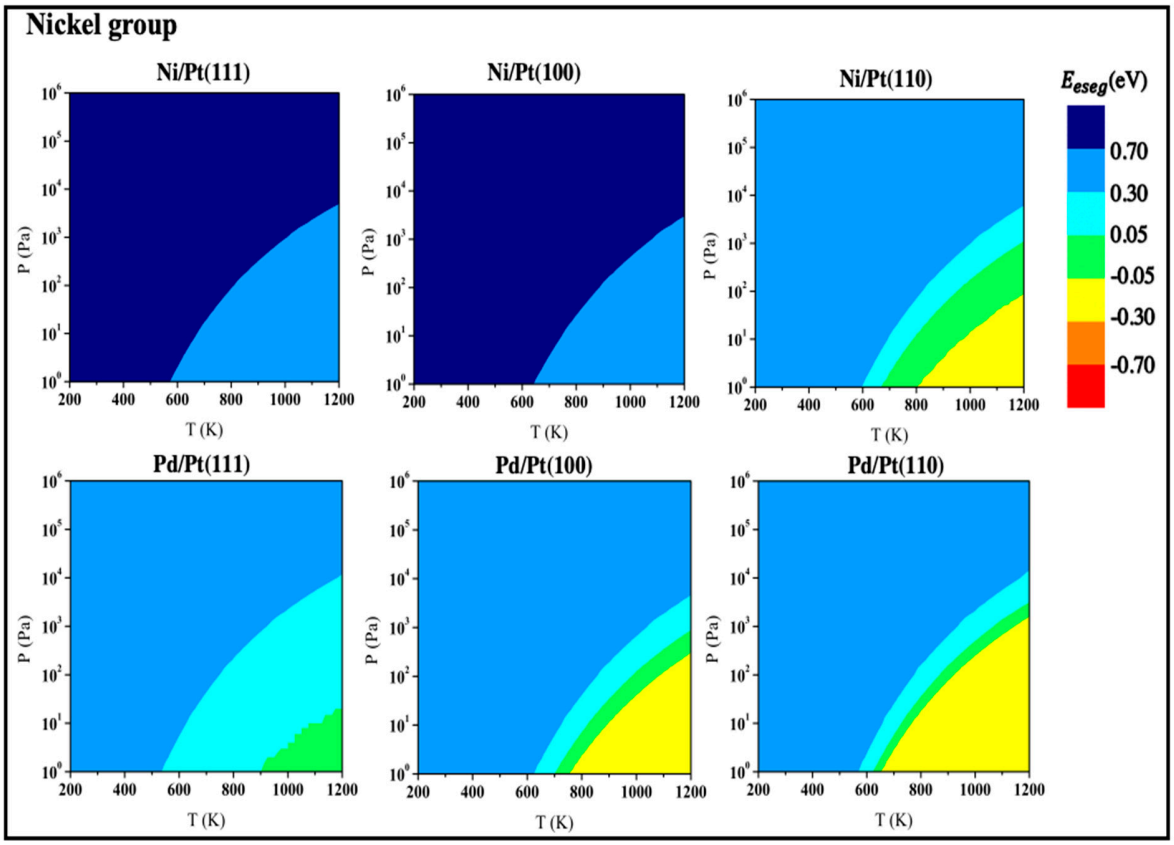
The color code of the counter plots is defined as follows: positive values of E_{eseg} superior to +0.7eV (dark blue), between +0.7eV and +0.3eV (light blue) and between +0.3eV and +0.05eV (aqua) represent the 'very strong', 'strong' and 'weak' bulk segregation of single-atom M, respectively. The negative values of E_{eseg} inferior to -0.7 eV (red), between -0.3eV and -0.7 eV (orange) and between -0.05 eV and -0.3 eV (yellow) represent the 'very strong', 'strong' and 'weak' surface segregation of M-single atom, respectively. When E_{eseg} is between -0.05eV and +0.05eV

(light green), single-atom M is considered as stable on the surface as in the bulk (no segregation preference).

A)



B)


Nickel group
Ni/Pt(111)
Ni/Pt(100)
Ni/Pt(110)
Pd/Pt(111)
Pd/Pt(100)
Pd/Pt(110)
P (Pa)
T (K)
E_{eseg}(eV)
0.70
0.30
0.05
-0.05
-0.30
-0.70

C)

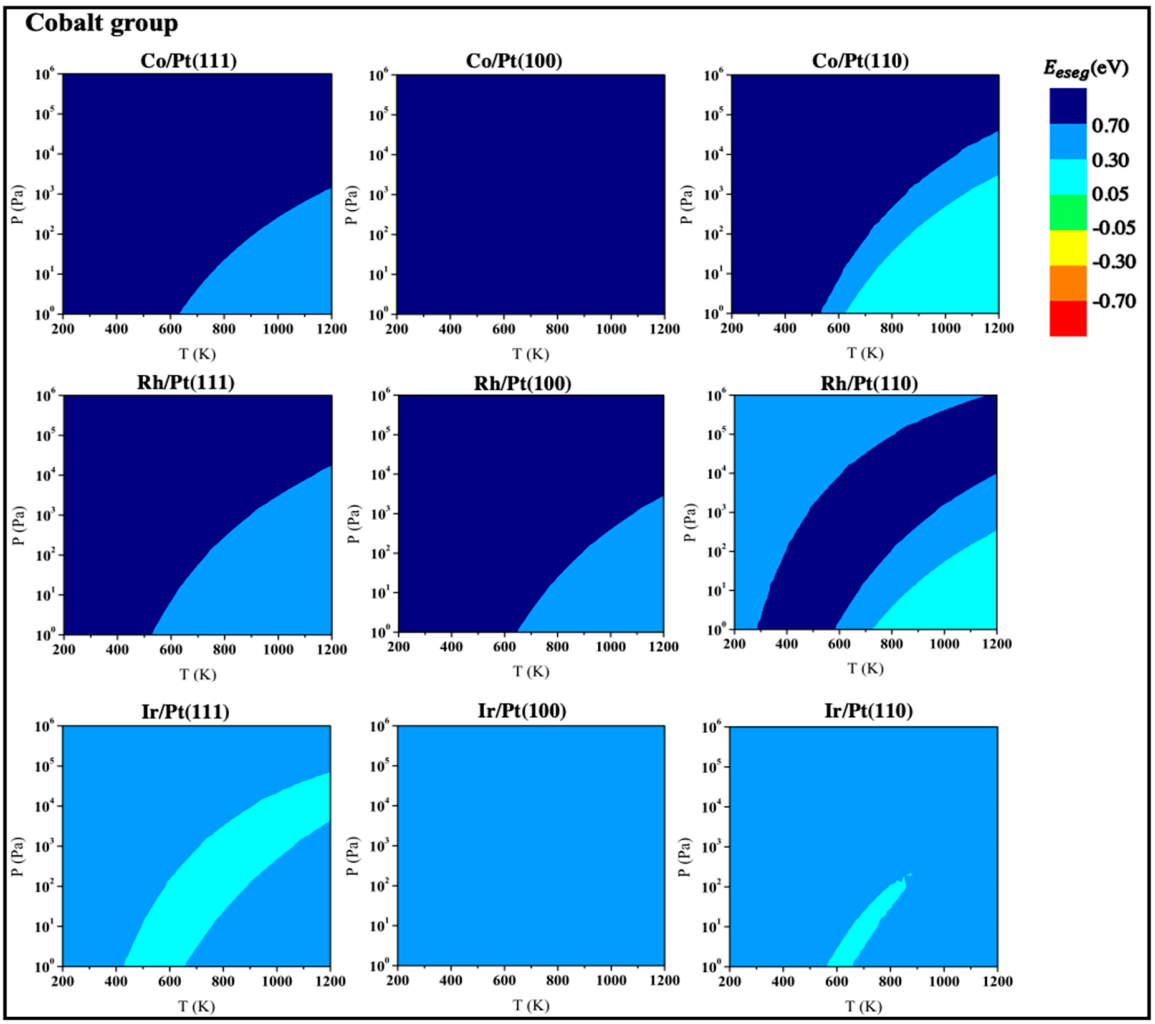


Figure S2: **Mapped environmental E_{eseg} of single-atoms M embedded in Pt(111), Pt(100) and Pt(110) host surfaces as function of temperature (T) and H_2 pressure (P).** (A) copper group: M = Cu, Ni, Co. (B) Nickel group: M = Ni, Pd. (C) Cobalt group: M = Co, Rh, Ir.

III. All DFT calculated pre-requisite parameters for the calculation of environmental segregation energies of M-single atoms embedded in Pt host surfaces

Table S1. Segregation energy in vacuum E_{seg}, binding energy between adsorbed H and M-single atom BE_{SA}, binding energy between adsorbed H and the host Pt surface BE_{host}, the lateral interaction between H zw, on (111), (100) and (110) surfaces representing the main facets of Pt NPs. All data are used to calculate the E_{eseg} evolution as a function of temperature and hydrogen pressure.

SA/Host	E_{seg}(eV)	BE_{sol}(eV)	BE_{host}(eV)	zw(eV)
		M/Pt(111)		
Cu/Pt	0.42	0	-0.70	-0.13
Ag/Pt	-0.33	0	-0.70	-0.13
Au/Pt	-0.56	0	-0.70	-0.13
Ni/Pt	0.53	-0.070	-0.70	-0.13
Pd/Pt	0.049	-0.16	-0.70	-0.13
Co/Pt	0.63	0	-0.70	-0.13
Rh/Pt	0.43	-0.43	-0.70	-0.13
Ir/Pt	0.47	-0.79	-0.70	-0.13
		M/Pt (100)		
Cu/Pt	0.21	0	-0.84	-0.063
Ag/Pt	-0.66	0	-0.84	-0.063
Au/Pt	-0.74	0	-0.84	-0.063
Ni/Pt	0.35	-0.049	-0.84	-0.063
Pd/Pt	-0.12	-0.078	-0.84	-0.063
Co/Pt	1.011	-0.49	-0.84	-0.063
Rh/Pt	0.36	-0.37	-0.84	-0.063
Ir/Pt	0.51	-0.81	-0.84	-0.063
		M/Pt (110)		
Cu/Pt	-0.24	0	-0.76	-0.0051

Ag/Pt	-0.89	0	-0.76	-0.0051
Au/Pt	-0.79	-0.013	-0.76	-0.0051
Ni/Pt	-0.060	-0.021	-0.76	-0.0051
Pd/Pt	-0.20	-0.13	-0.76	-0.0051
Co/Pt	0.058	0	-0.76	-0.0051
Rh/Pt	0.26	-0.38	-0.76	-0.0051
Ir/Pt	0.51	-0.83	-0.76	-0.0051

IV. Binding hydrogen energies

Table S2. Hydrogen binding energy comparison between M-single atoms embedded in Pt-host surfaces Pt(1 0 0) and neighboring Pt-sites (free from hydrogen). Pure Pt-host surfaces are added as reference. Unfavorable (endothermic) binding energies are fixed to 0 and reported in red color to facilitate the comparisons.

		adsorption energies of H in (eV)	
Pt(100)		-0.84	
M- Single atom		**ads. on M-single atom**	**ads on Pt neigbourg**
Coinage group	**Cu**	0	-0.65
	Ag	0	-0.65
	Au	0.	-0.62
Nickel group	**Ni**	-0.05	-0.63
	Pd	-0.08	-0.64
Cobalt group	**Co**	-0.49	-0.63
	Rh	-0.37	-0.72

	Ir	-0.81	-0.64

Table S3. Hydrogen binding energy comparison between M-single atoms embedded in Pt-host surfaces Pt(1 1 0) and neighboring Pt-sites (free from hydrogen). Pure Pt-host surfaces are added as reference.

		Adsorption energies of H atom in (eV)	
Pt(1 1 0)		-0.76	
M-single atom in Pt(110)		**ads. on M-single atom**	**ads on neighbor Pt**
Coinage group	**Cu**	0	-0.80
	Ag	0	-0.82
	Au	-0.01	-0.79
Nickel group	**Ni**	-0.02	-0.78
	Pd	-0.13	-0.78
Cobalt group	**Co**	0	-0.77
	Rh	-0.38	-0.83
	Ir	-0.83	-0.71

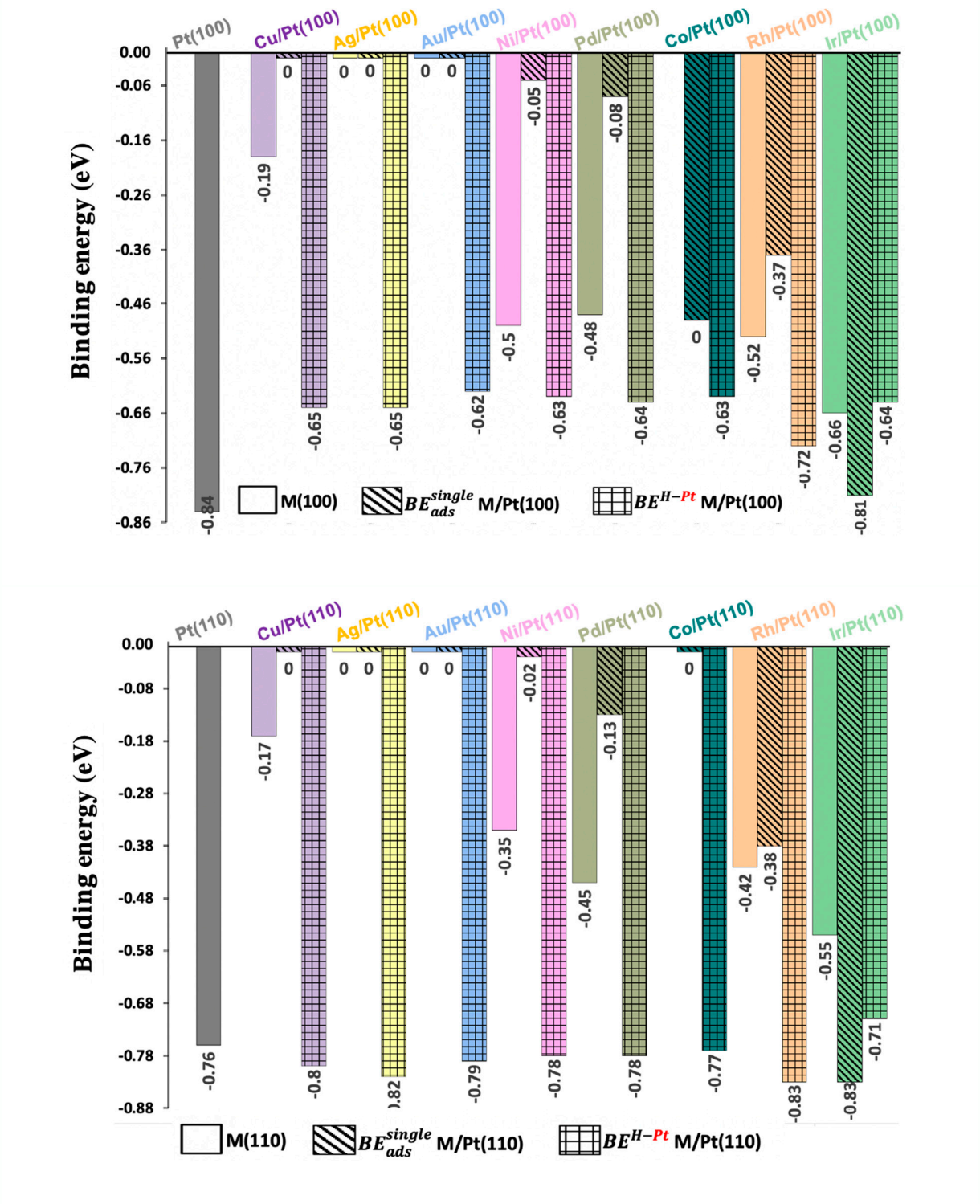


Figure S3. Hydrogen binding energy on M-single atoms embedded in Pt-host surfaces (A) for (100) and (B) for (110) surfaces. (BE_{ads}^{SA}, histograms filled with diagonal lines) and on

the neighboring Pt-site of M (with M free of hydrogen) (BE^{H-Pt}, histograms filled in cubic-grills). The binding energy of hydrogen atom on Pure Pt(1 0 0), Pt(110), M(1 0 0) and M(110) surfaces are added for comparison. Unfavorable (endothermic) biding energy values are fixed at 0 eV.