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SUPPLEMENTARY INFORMATION

Lattice mismatch as the descriptor of segregation, stability and reactivity of supported thin catalyst films

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1. Lattice constants of investigated bimetallic systems

Table S1. Calculated lattice parameters of investigated A_3B bimetallic systems

A_3B	a_0 / Å
Pt_3Cu	3.923
Pt_3Ag	4.020
Pt_3Au	4.034
Pd_3Cu	3.910
Pd_3Ag	4.019
Pd_3Au	4.027

2. Strain dependence of the segregation energies for the case of pure $A_3B(111)$ surfaces

Table S2. Dependence of surface segregation (in eV) energies of A (Pt, Pd) and B (Cu, Ag, Au) on the lateral surface strain in $A_3B(111)$ surfaces. At the end parameter of the polynomial fit of E_{seg} *vs*. strain (S, in %) are given.

		strain / %				
	segregates	**6**	**3**	**0**	**−3**	**−6**
Pd_3Cu	**A**	−0.07	−0.07	−0.06	−0.04	−0.13
	B	0.15	0.20	0.25	0.29	0.34
Pd_3Ag	**A**	0.30	0.27	0.22	0.18	0.17
	B	−0.30	−0.27	−0.24	−0.23	−0.22
Pd_3Au	**A**	0.32	0.34	0.35	0.37	0.41
	B	−0.21	−0.22	−0.22	−0.22	−0.22
Pt_3Cu	**A**	−0.07	−0.13	−0.18	−0.23	−0.28
	B	0.28	0.40	0.50	0.55	0.57
Pt_3Ag	**A**	0.40	0.29	0.14	0.01	−0.07
	B	−0.51	−0.44	−0.39	−0.39	−0.48
Pt_3Au	**A**	0.35	0.31	0.26	0.21	0.22
	B	−0.56	−0.53	−0.51	−0.50	−0.56
				fit*		
	segregates	**A0**	**B1**	**B2**	**B3**	**B4**
Pd_3Cu	**A**	−5.86E−02	−7.85E−03	1.20E−03	3.38E−04	−6.59E−05
	B	2.47E−01	−1.57E−02	−4.56E−05	4.35E−07	2.07E−06
Pd_3Ag	**A**	2.25E−01	1.59E−02	−2.78E−05	−1.47E−04	1.14E−05
	B	−2.44E−01	−6.64E−03	−5.95E−04	−3.16E−06	3.49E−06
Pd_3Au	**A**	3.52E−01	−4.96E−03	2.75E−04	−8.20E−05	3.63E−06
	B	−2.23E−01	2.20E−04	3.33E−04	1.83E−05	−3.52E−06
Pt_3Cu	**A**	−1.81E−01	1.62E−02	1.53E−04	4.00E−05	−1.10E−06
	B	5.00E−01	−2.73E−02	−2.96E−03	8.30E−05	2.60E−05
Pt_3Ag	**A**	1.43E−01	5.08E−02	5.61E−04	−3.24E−04	4.59E−06
	B	−3.92E−01	−1.01E−02	−1.72E−03	2.08E−04	−3.41E−05
Pt_3Au	**A**	2.58E−01	1.95E−02	4.28E−04	−2.30E−04	1.08E−05
	B	−5.07E−01	−6.76E−03	−1.22E−03	1.99E−04	−5.98E−06

*$E_{seg} = A0 + B1\times S + B2\times S^2 + B3\times S^3 + B4\times S^4$

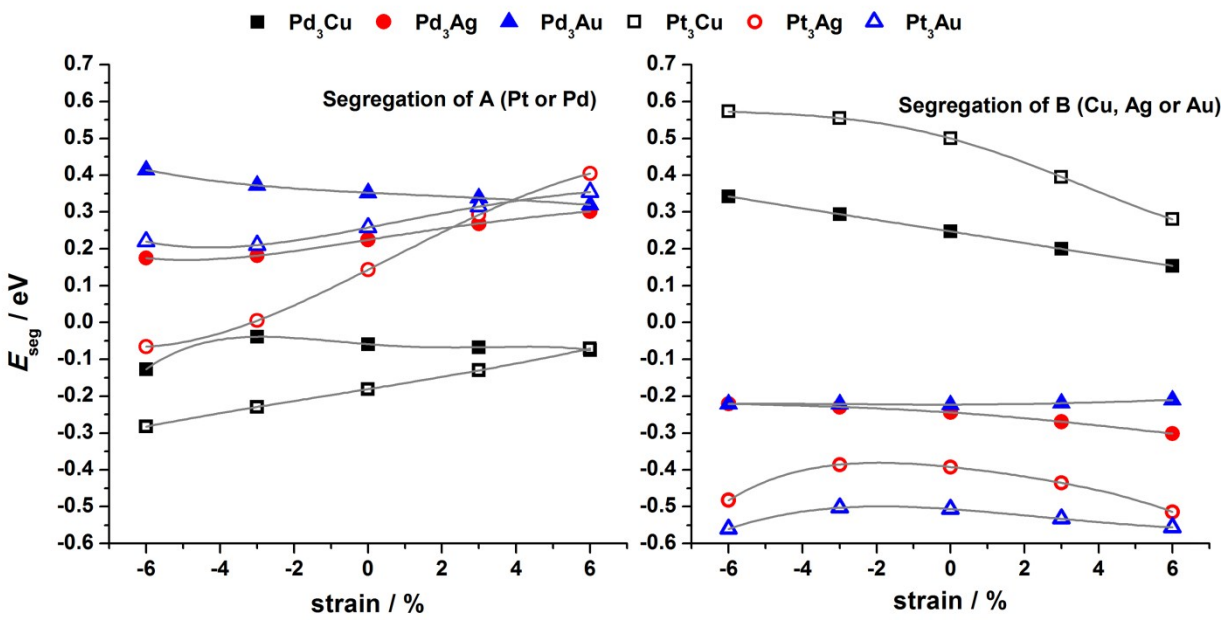

Figure S1. Strain dependence of A (Pt or Pd; left) and B (Cu, Ag or Au; right) segregation energies.

3. Strain dependence of the dissolution energies for the case of pure segregated $A_3B(111)$ surfaces

Table S3. Dependence of dissolution energies (in eV) of given atoms (defined by rows) on the lateral surface strain in segregated $A_3B(111)$ surfaces. At the end parameter of the polynomial fit of E_{diss} *vs*. strain (S, in %) are given.

		strain / %				
	dissolves	**6**	**3**	**0**	**−3**	**−6**
Pd_3Cu (Pd segregated)	**Pd**	−0.79	−0.87	−0.87	−0.73	−0.39
Pd_3Ag (Ag segregated)	**Ag**	−1.07	−1.09	−1.03	−0.85	−0.52
	Pd	−0.49	−0.58	−0.61	−0.56	−0.39
Pd_3Au (Au segregated)	**Au**	−1.12	−1.16	−1.11	−0.92	−0.55
	Pd	−0.59	−0.65	−0.62	−0.47	−0.17
Pt_3Cu (Pt segregated)	**Pt**	−0.91	−1.09	−1.14	−1.02	−0.64
Pt_3Ag (Ag segregated)	**Ag**	−0.97	−1.02	−0.94	−0.74	−0.46
	Pt	−0.41	−0.54	−0.59	−0.55	−0.15
Pt_3Au (Au segregated)	**Au**	−0.87	−0.93	−0.86	−0.67	−0.35
	Pt	−0.47	−0.52	−0.48	−0.30	−0.03
				fit*		
	dissolves	**A0**	**B1**	**B2**	**B3**	**B4**
Pd_3Cu (Pd segregated)	**Pd**	−8.67E−01	−2.02E−02	7.62E−03	−3.64E−04	−4.56E−07
Pd_3Ag (Ag segregated)	**Ag**	−1.03E+00	−3.99E−02	6.41E−03	−1.64E−04	−7.67E−07
	Pd	−6.13E−01	−2.86E−03	4.96E−03	−1.56E−04	−1.96E−06
Pd_3Au (Au segregated)	**Au**	−1.11E+00	−3.72E−02	7.48E−03	−2.70E−04	3.63E−06
	Pd	−6.20E−01	−2.71E−02	6.82E−03	−2.22E−04	−1.95E−06
Pt_3Cu (Pt segregated)	**Pt**	−1.14E+00	−6.52E−03	9.06E−03	−4.37E−04	3.00E−05
Pt_3Ag (Ag segregated)	**Ag**	−9.38E−01	−4.85E−02	6.92E−03	1.50E−04	−1.99E−05
	Pt	−5.92E−01	9.77E−03	3.89E−03	−8.77E−04	1.31E−04
Pt_3Au (Au segregated)	**Au**	−8.58E−01	−4.34E−02	6.87E−03	−2.85E−06	2.20E−06
	Pt	−4.83E−01	−3.56E−02	8.46E−03	−3.38E−05	−5.40E−05

*$E_{diss} = A0 + B1\times S + B2\times S^2 + B3\times S^3 + B4\times S^4$

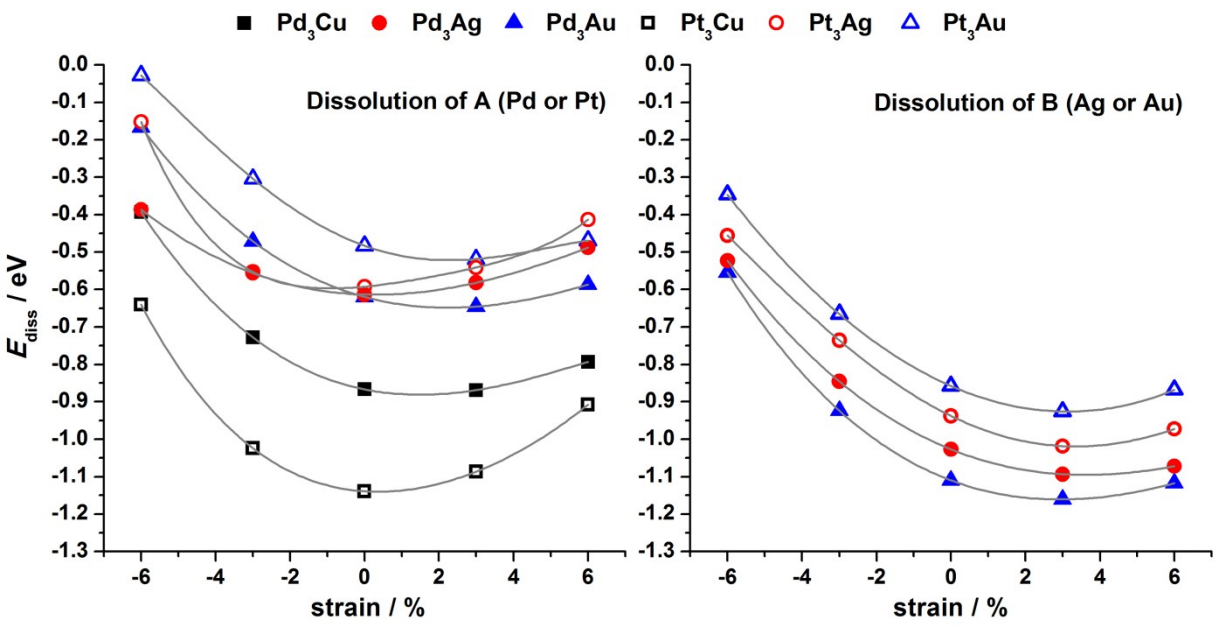

Figure S2. Strain dependence of E_{diss} of A (Pt or Pd; left) and B (Ag or Au; right) in the most stable segregated surfaces.

4. Strain dependence of the d-band centers for the case of pure segregated $A_3B(111)$ surfaces

Table S4. Dependence of the *d*-band centers (in eV) of given atoms (defined by rows) on the lateral surface strain in segregated $A_3B(111)$ surfaces. At the end parameter of the polynomial fit of $E_{\text{d-band}}$ *vs*. strain (S, in %) are given.

		strain / %				
	***d*-band**	**6**	**3**	**0**	**−3**	**−6**
Pd_3Cu (Pd segregated)	**Pd**	−1.77	−1.90	−2.05	−2.23	−2.32
Pd_3Ag (Ag segregated)	**Ag**	−3.25	−3.32	−3.43	−3.57	−3.69
	Pd	−1.58	−1.68	−1.80	−1.95	−2.15
Pd_3Au (Au segregated)	**Au**	−2.83	−2.93	−3.08	−3.27	−3.45
	Pd	−1.61	−1.70	−1.85	−2.03	−2.27
Pt_3Cu (Pt segregated)	**Pt**	−2.28	−2.45	−2.65	−2.89	−3.13
Pt_3Ag (Ag segregated)	**Ag**	−3.35	−3.39	−3.48	−3.57	−3.55
	Pt	−2.07	−2.18	−2.32	−2.49	−2.62
Pt_3Au (Au segregated)	**Au**	−3.05	−3.12	−3.22	−3.34	−3.32
	Pt	−2.10	−2.23	−2.39	−2.59	−2.77
				fit*		
	***d*-band**	**A0**	**B1**	**B2**	**B3**	**B4**
Pd_3Cu (Pd segregated)	**Pd**	−1.93E+00	4.32E−02	2.94E−03	−2.78E−05	−8.72E−05
Pd_3Ag (Ag segregated)	**Ag**	−3.43E+00	4.31E−02	−1.73E−03	−1.76E−04	1.77E−05
	Pd	−1.80E+00	4.43E−02	−1.63E−03	7.88E−05	−8.08E−06
Pd_3Au (Au segregated)	**Au**	−3.08E+00	5.91E−02	−2.31E−03	−1.96E−04	1.71E−05
	Pd	−1.85E+00	5.47E−02	−2.37E−03	5.55E−06	−7.89E−06
Pt_3Cu (Pt segregated)	**Pt**	−2.65E+00	7.42E−02	−2.37E−03	−1.03E−04	1.84E−05
Pt_3Ag (Ag segregated)	**Ag**	−3.48E+00	3.35E−02	−7.71E−04	−4.57E−04	4.16E−05
	Pt	−2.32E+00	5.44E−02	−1.59E−03	−2.24E−04	2.57E−05
Pt_3Au (Au segregated)	**Au**	−3.22E+00	4.02E−02	−1.45E−03	−4.86E−04	6.50E−05
	Pt	−2.39E+00	6.05E−02	−2.75E−03	−1.22E−04	4.27E−05

*$E_{\text{d-band}} = A0 + B1\times S + B2\times S^2 + B3\times S^3 + B4\times S^4$

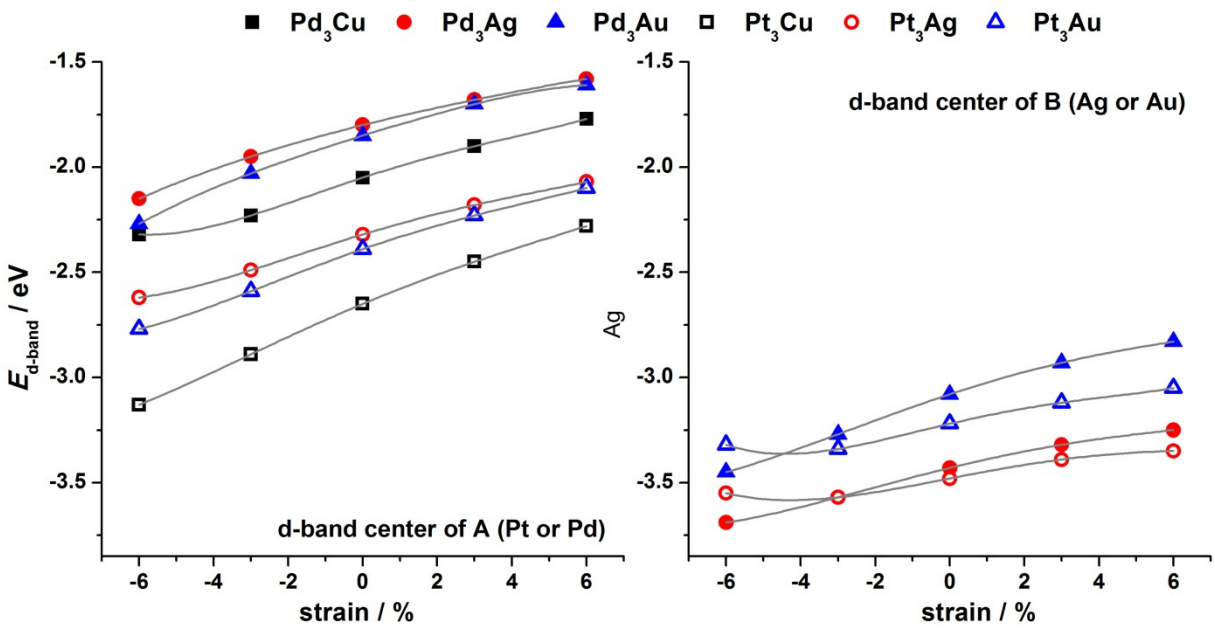

Figure S3. Strain dependence of $E_{\text{d-band}}$ of A (Pt or Pd; left) and B (Ag or Au; right) in the most stable segregated surfaces.

5. Strain dependence of CO adsorption energies and surface segregation energies in the presence of CO for pure strained $A_3B(111)$ surfaces

Table S5. Dependence of the CO adsorption energies ($E_{ads,CO}$, in eV) and the surface segregation energies in the presence of CO ($E_{seg,CO}$, in eV) on the lateral surface strain in $Pd_3Au(111)$ surfaces.

		strain / %				
	surface termination	**6**	**3**	**0**	**−3**	**−6**
$E_{ads,CO}$ / eV	**Pd-segregated**	−2.18	−2.12	−2.02	−1.90	−1.75
	stoichiometric	−2.17	−2.10	−2.00	−1.86	−1.67
	Au-segregated	−1.73	−1.66	−1.58	−1.47	−1.32
	segregates					
$E_{seg,CO}$ / eV	**Au**	0.23	0.22	0.19	0.17	0.13
	Pt	0.31	0.32	0.33	0.34	0.33