

Rational Design of Bimetallic Alloys for Effective Hydrodechlorination of 4-Chlorophenol

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Table 1. The d-band centers of Pd and Pd-based alloys

Surface	d-band center
Pd (111)	-1.67 eV
Pd ₃ Cu (111)	-1.12 eV
Pd ₃ Ag (111)	-1.73 eV
Pd ₃ Au (111)	-1.77 eV

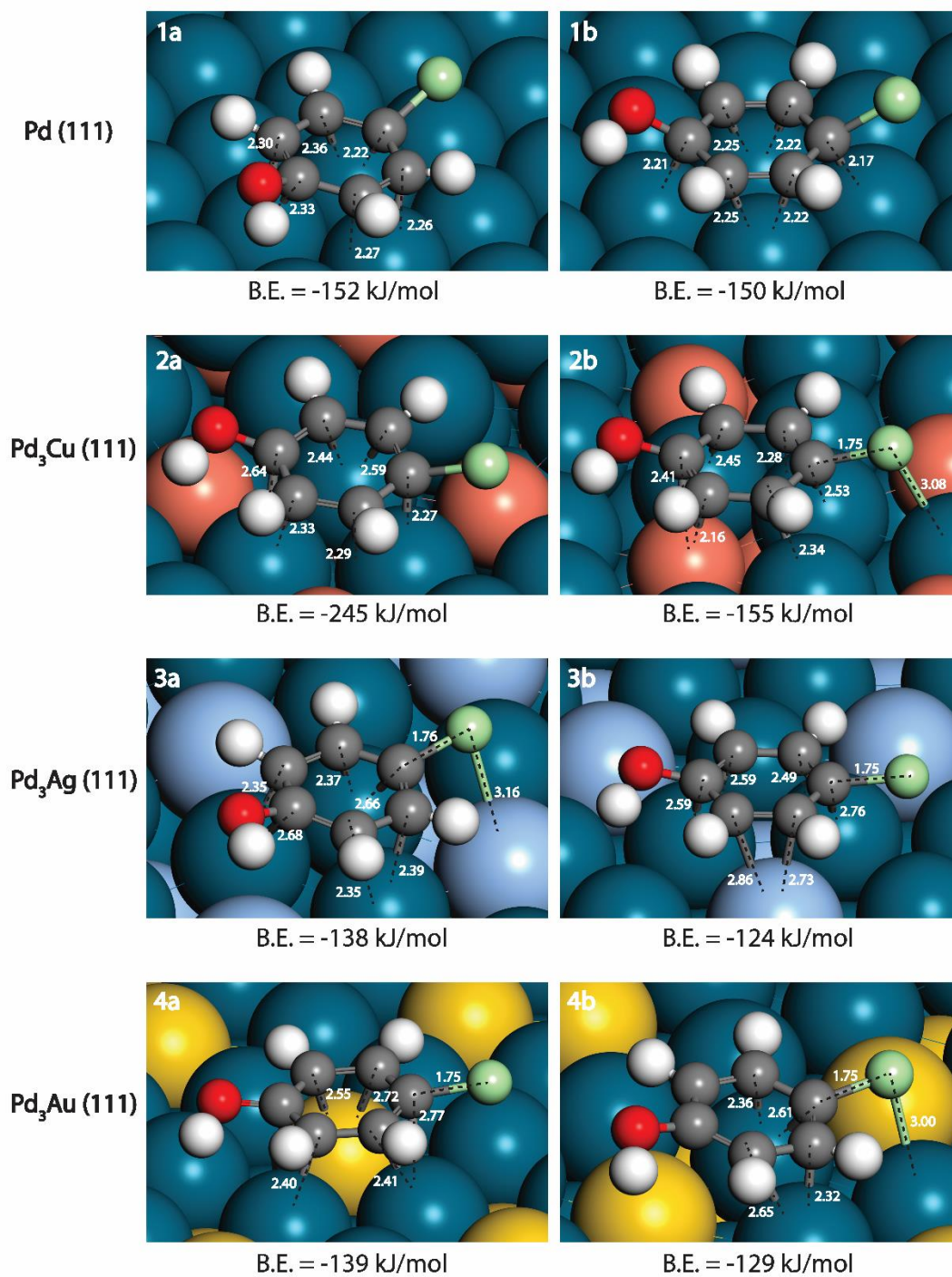


Figure S1(A). Various Binding Modes of 4-CP on (1) Pd (111), (2) Pd₃Cu (111), (3) Pd₃Ag (111) and (4) Pd₃Au (111) surfaces.

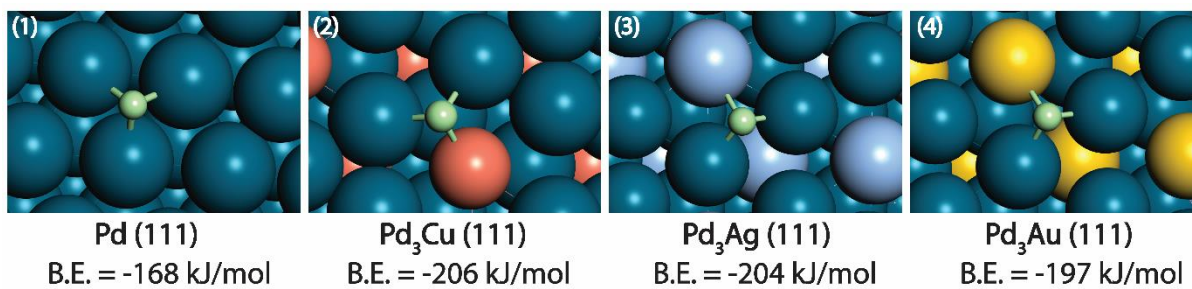


Figure S1(B). The Most Stable Binding Modes of Cl on (1) Pd (111), (2) Pd₃Cu (111), (3) Pd₃Ag (111) and (4) Pd₃Au (111) surfaces.

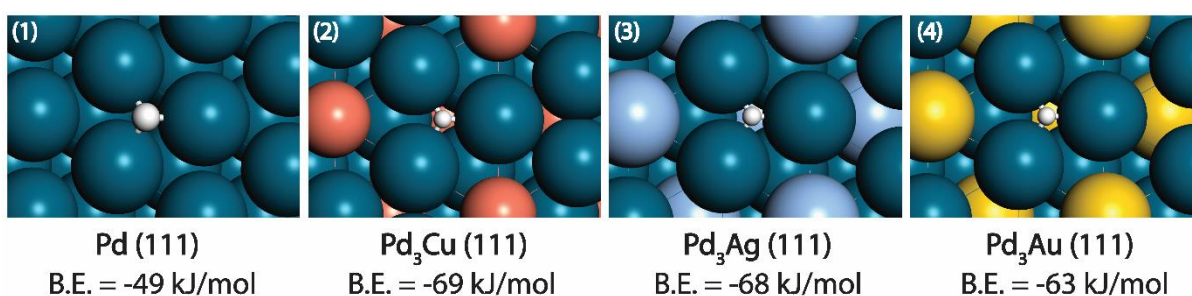


Figure S1(C). The Most Stable Binding Modes of H on (1) Pd (111), (2) Pd₃Cu (111), (3) Pd₃Ag (111) and (4) Pd₃Au (111) surfaces.

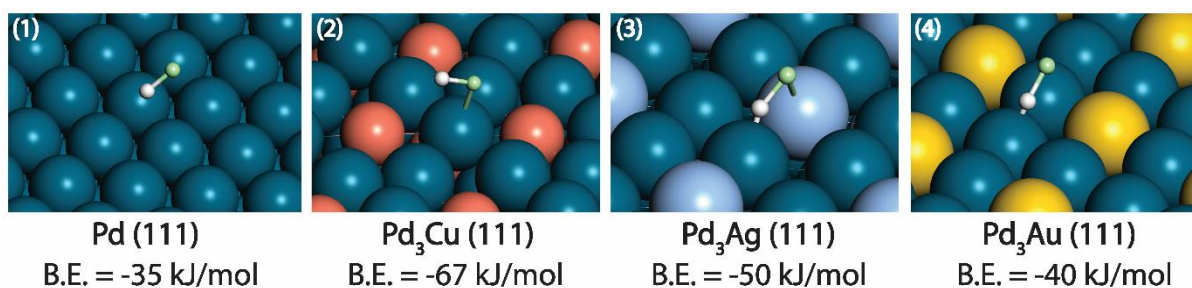


Figure S1(D). The Most Stable Binding Modes of HCl on (1) Pd (111), (2) Pd₃Cu (111), (3) Pd₃Ag (111) and (4) Pd₃Au (111) surfaces.

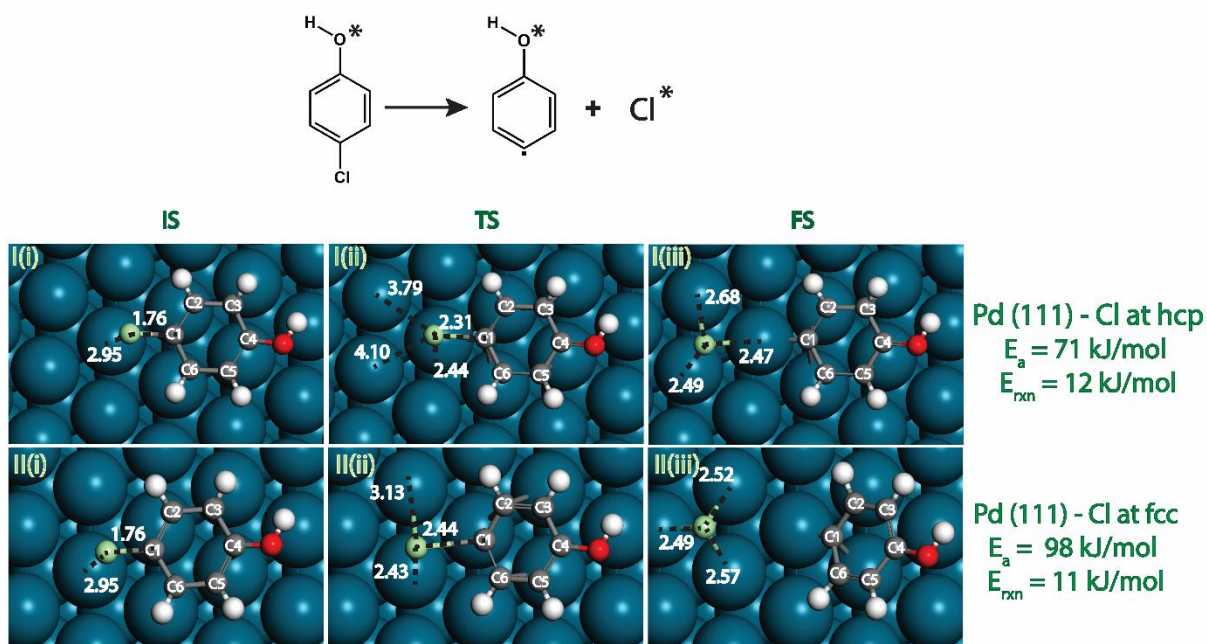
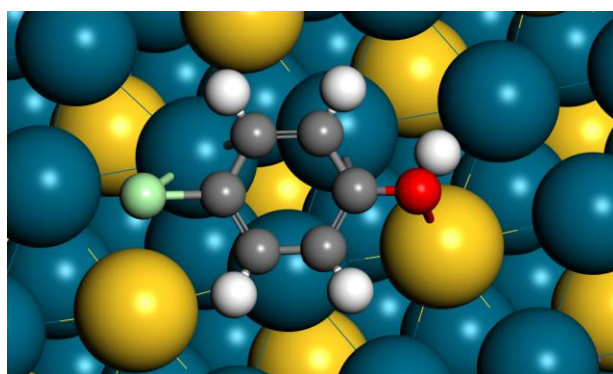


Figure S2. Transition state structures on the Pd (111) surface for the C-Cl bond dissociation step with Cl at the hcp site (I) and Cl at the fcc site (II).



B.E = -128 kJ/mol

Figure S3. Binding Energy of 4-CP over the fcc site on the Pd₃Au (111) surface.

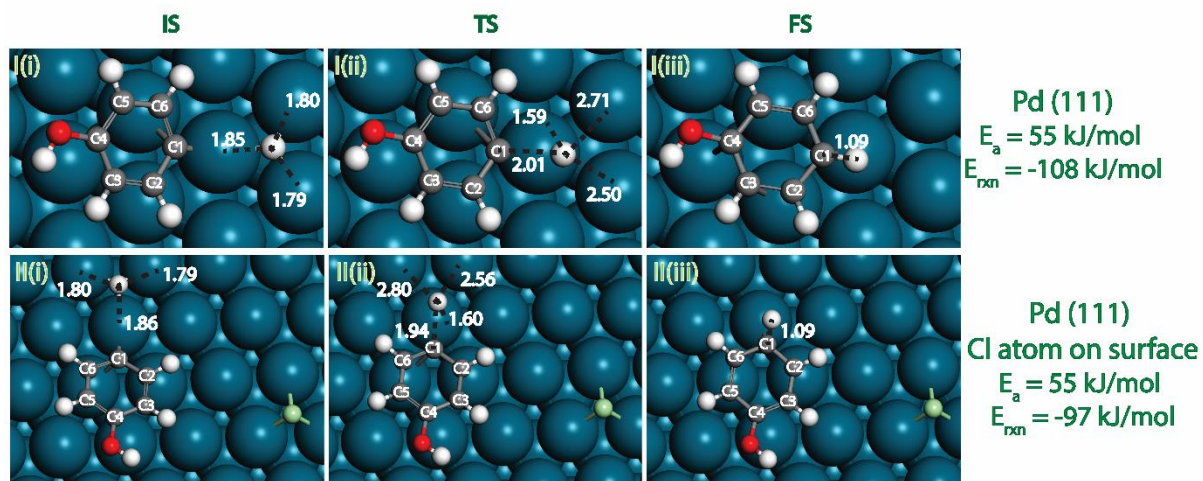
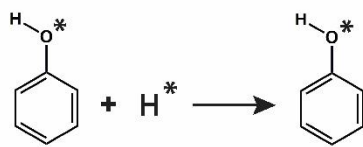


Figure S4. Transition state structures for the hydrogenation step to form phenol without Cl on the surface (I) and with Cl at the fcc site (II).

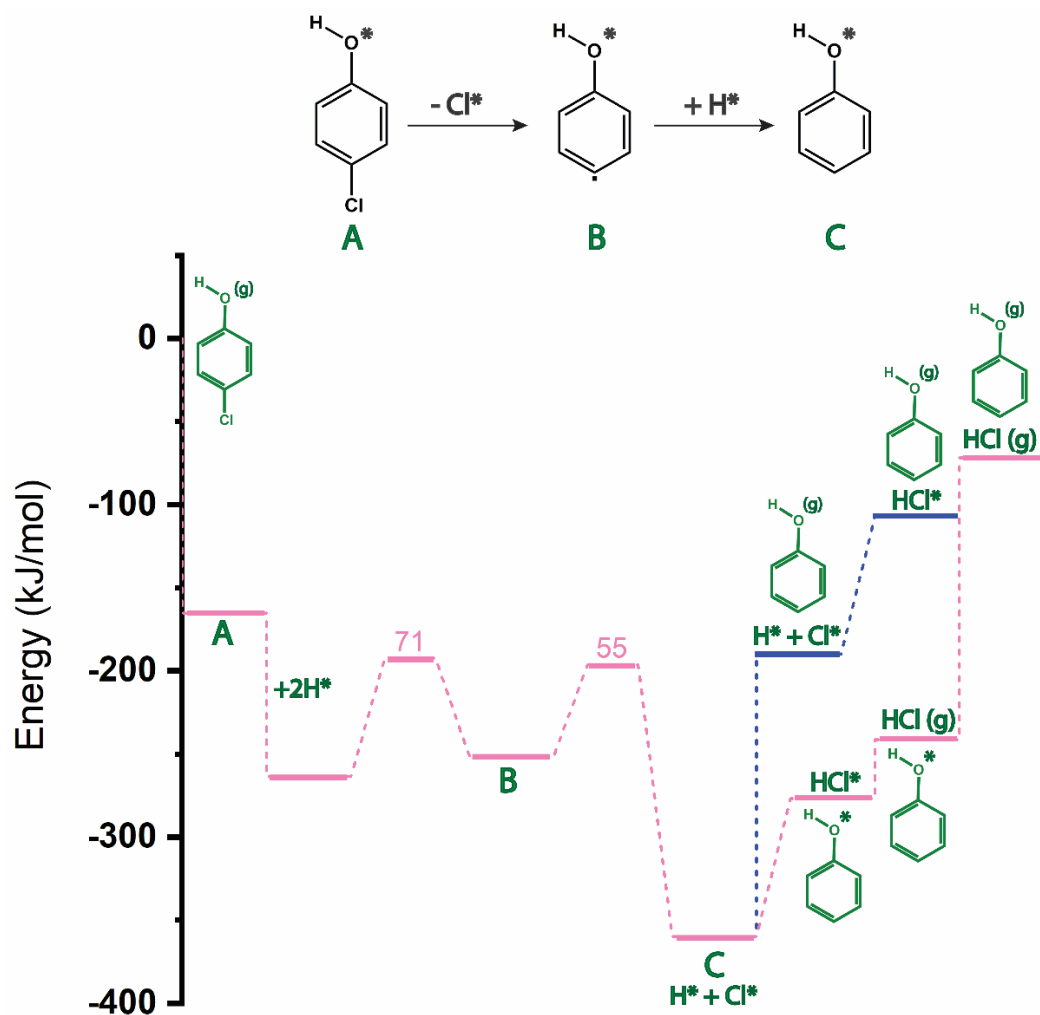
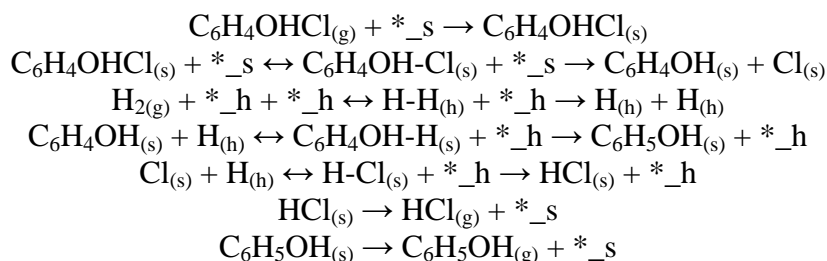


Figure S5. Energy Diagram for the HDC of 4-CP over the Pd (111) surface (the pathway for phenol desorption followed by HCl desorption is displayed in blue and the pathway for HCl desorption followed by phenol desorption is displayed in pink).

In order to understand the HDC of 4-CP over the different surfaces (Pd (111), Pd₃Cu (111), Pd₃Ag (111) and Pd₃Au (111)), a set of elementary steps are solved simultaneously as described in the Methodology Section. The elementary steps are given below:



where,

*_s denotes free surface site

*_h denotes free hydrogen site

Subscripts (g), (s) and (h) denotes gas phase species, surface species and hydrogen occupied surface site

→ denotes the product species formation step

↔ denotes the transition state species formation

Due to the small size of the hydrogen atom, a separate reservoir is assigned for hydrogen, denoted by (h), as it would not compete with other intermediates for adsorption sites, denoted by (s). The hydrogen reservoir model has been used by Prof. Norskov and co-workers¹ and in our previous publications².

Table 2. Formation Energies of the Species used to Construct the MKM (Reference states considered are CH₄, H₂, H₂O and Cl₂)

Species	Facet	Surface	Formation Energy (eV)
CH ₄	Gas	None	0.0
H ₂	Gas	None	0.0
H ₂ O	Gas	None	0.0
Cl ₂	Gas	None	0.0
C ₆ H ₄ OHCl	Gas	None	7.34
C ₆ H ₅ OH	Gas	None	7.53
HCl	Gas	None	-0.93
C ₆ H ₄ OHCl	111	Pd	5.63
C ₆ H ₄ OHCl	111	Pd ₃ Cu	4.68
C ₆ H ₄ OHCl	111	Pd ₃ Ag	5.78
C ₆ H ₄ OHCl	111	Pd ₃ Au	5.77

C ₆ H ₄ OH	111	Pd	7.41
C ₆ H ₄ OH	111	Pd ₃ Cu	6.46
C ₆ H ₄ OH	111	Pd ₃ Ag	7.37
C ₆ H ₄ OH	111	Pd ₃ Au	7.23
C ₆ H ₅ OH	111	Pd	5.77
C ₆ H ₅ OH	111	Pd ₃ Cu	5.82
C ₆ H ₅ OH	111	Pd ₃ Ag	6.16
C ₆ H ₅ OH	111	Pd ₃ Au	6.11
H	111	Pd	-0.51
H	111	Pd ₃ Cu	-0.71
H	111	Pd ₃ Ag	-0.69
H	111	Pd ₃ Au	-0.66
Cl	111	Pd	-1.65
Cl	111	Pd ₃ Cu	-2.14
Cl	111	Pd ₃ Ag	-2.12
Cl	111	Pd ₃ Au	-2.04
HCl	111	Pd	-1.34
HCl	111	Pd ₃ Cu	-2.66
HCl	111	Pd ₃ Ag	-1.45
HCl	111	Pd ₃ Au	-1.35
C ₆ H ₄ OH-Cl	111	Pd	6.37
C ₆ H ₄ OH-Cl	111	Pd ₃ Cu	5.47
C ₆ H ₄ OH-Cl	111	Pd ₃ Ag	6.24
C ₆ H ₄ OH-Cl	111	Pd ₃ Au	6.46
C ₆ H ₄ OH-H	111	Pd	7.56
C ₆ H ₄ OH-H	111	Pd ₃ Cu	6.56
C ₆ H ₄ OH-H	111	Pd ₃ Ag	7.44
C ₆ H ₄ OH-H	111	Pd ₃ Au	7.72
H-H	111	Pd	0.12
H-H	111	Pd ₃ Cu	-0.43
H-H	111	Pd ₃ Ag	0.02
H-H	111	Pd ₃ Au	-0.27
H-Cl	111	Pd	-1.21
H-Cl	111	Pd ₃ Cu	-2.66
H-Cl	111	Pd ₃ Ag	-1.39
H-Cl	111	Pd ₃ Au	-1.31

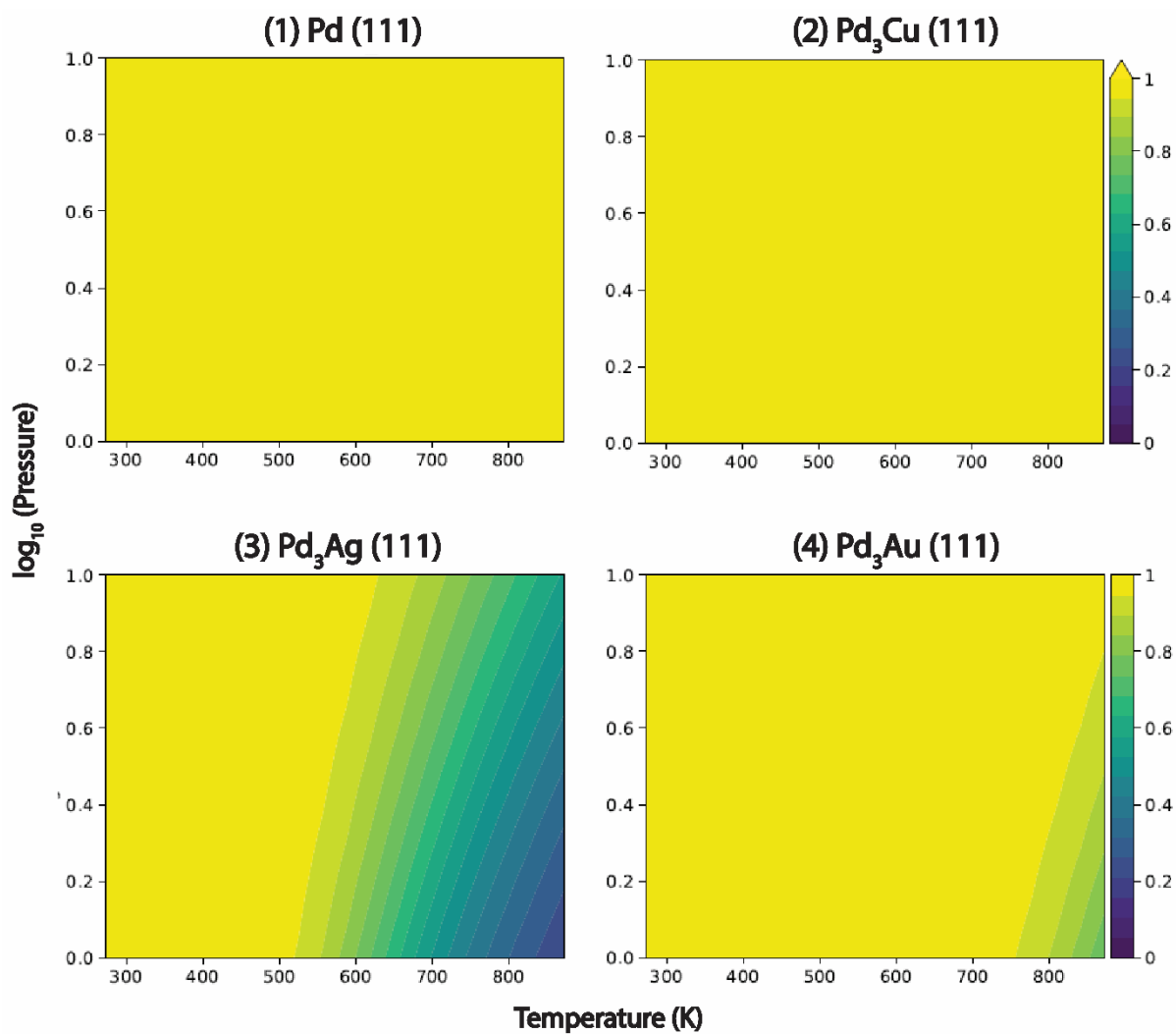


Figure S6. Surface coverage of $\text{C}_6\text{H}_4\text{OHCl}$ with varying temperatures and pressures over different surfaces ((1) Pd (111), (2) Pd₃Cu (111), (3) Pd₃Ag (111) and (4) Pd₃Au (111))

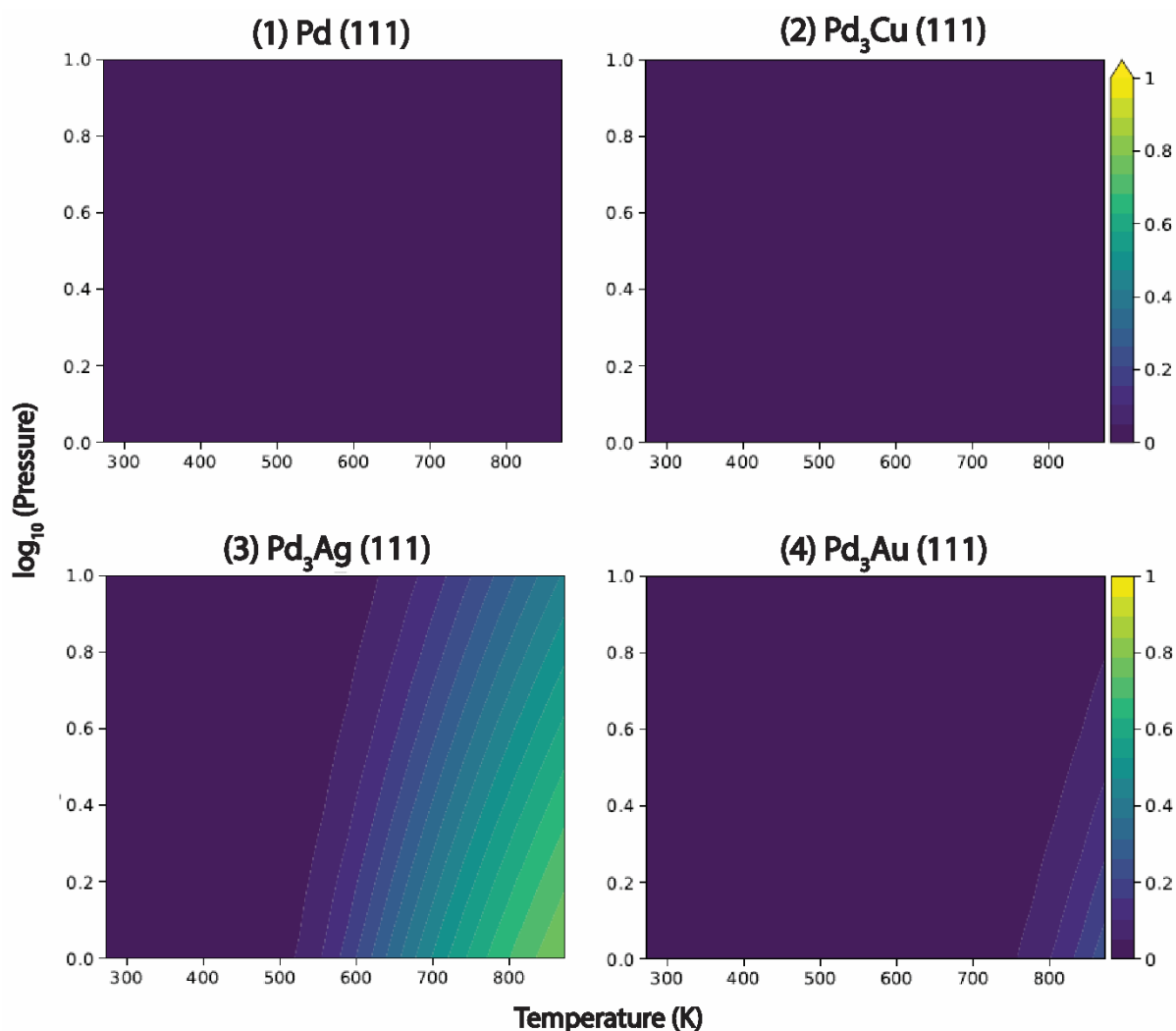


Figure S7. Surface coverage of Cl with varying temperatures and pressures over different surfaces ((1) Pd (111), (2) Pd₃Cu (111), (3) Pd₃Ag (111) and (4) Pd₃Au (111))

References:

- (1) Medford, A. J.; Lausche, A. C.; Abild-Pedersen, F.; Temel, B.; Schjødt, N. C.; Nørskov, J. K.; Studt, F. Activity and Selectivity Trends in Synthesis Gas Conversion to Higher Alcohols. *Top. Catal.* **2014**, *57* (1–4), 135–142. <https://doi.org/10.1007/s11244-013-0169-0>.
- (2) Jalid, F.; Khan, T. S.; Haider, M. A. CO₂ Reduction and Ethane Dehydrogenation on Transition Metal Catalysts: Mechanistic Insights, Reactivity Trends and Rational Design of Bimetallic Alloys. *Catal. Sci. Technol.* **2021**, *11*, 97–115. <https://doi.org/10.1039/d0cy01290d>.