**Supplementary Information for:**

# "A DFT Study of Chlorine Coverage over Late Transition Metals and Its Implication on 1,2-Dichloroethane Hydrodechlorination"

| | | |
|---|---|---|
| *Ethylene Path* | 1. | $ClCH_2CH_2Cl(g) + * \rightarrow ClCH_2CH_2Cl*$ |
| | 2. | $H_2(g) + 2* \rightarrow 2H*$ |
| | 3. | $ClCH_2CH_2Cl* + * \rightarrow ClCH_2CH_2* + Cl*$ |
| | 4. | $ClCH_2CH_2* + * \rightarrow CH_2CH_2* + Cl*$ |
| | 5. | $H* + Cl* \rightarrow HCl(g) + 2*$ |
| | 6. | $CH_2CH_2* \rightarrow CH_2CH_2(g) + *$ |
| *Ethane Path* | 1. | $ClCH_2CH_2Cl(g) + * \rightarrow ClCH_2CH_2Cl*$ |
| | 2. | $H_2(g) + 2* \rightarrow 2H*$ |
| | 3. | $ClCH_2CH_2Cl* + * \rightarrow ClCH_2CH_2* + Cl*$ |
| | 4. | $ClCH_2CH_2* + * \rightarrow CH_2CH_2* + Cl*$ |
| | 5. | $CH_2CH_2* + H* \rightarrow CH_3CH_2* + *$ |
| | 6. | $CH_3CH_2* + H* \rightarrow CH_3CH_3* + *$ |
| | 7. | $H* + Cl* \rightarrow HCl(g) + 2*$ |
| | 8. | $CH_3CH_3* \rightarrow CH_3CH_3(g) + *$ |

**Scheme S1:** Elementary steps in 1,2-DCA hydrodechlorination mechanism

**Table S1:** Comparison between calculated lattice parameters used in this work and experimental values

| | **Lattice constant (Å)** | |
|---|---|---|
| **Metal** | DFT (PW91) | Experiment [1] |
| Pt (fcc) | $a = 3.986$ | $a = 3.924$ |
| Co (hcp) | $a = 2.499$ | $a = 2.507$ |
| | $c = 4.031$ | $c = 4.069$ |
| Ni (fcc) | $a = 3.527$ | $a = 3.524$ |
| Cu (fcc) | $a = 3.638$ | $a = 3.615$ |
| Ru (hcp) | $a = 2.728$ | $a = 2.706$ |
| | $c = 4.305$ | $c = 4.282$ |
| Rh (fcc) | $a = 3.844$ | $a = 3.803$ |
| Pd (fcc) | $a = 3.957$ | $a = 3.890$ |
| Ag (fcc) | $a = 4.163$ | $a = 4.086$ |
| Ir (fcc) | $a = 3.880$ | $a = 3.839$ |
| Au (fcc) | $a = 4.176$ | $a = 4.078$ |

**Table S2:** Calculated binding energy of atomic hydrogen, minimum energy structure, at 1/9 ML

| Surface | $BE_H$ (eV)[a] |
|---|---|
| Pt(111) | -2.81 (top) |
| Co(0001) | -2.83 (fcc) |
| Ni(111) | -2.78 (fcc) |
| Cu(111) | -2.57 (fcc) |
| Ru(0001) | -2.79 (fcc) |
| Rh(111) | -2.79 (fcc) |
| Pd(111) | -2.90 (fcc) |
| Ag(111) | -2.14 (fcc) |
| Ir(111) | -2.72 (top) |
| Au(111) | -2.18 (fcc) |

[a]Preferred binding sites are listed in parentheses.

**Table S3:** Calculated d band center ($\varepsilon_d$) of surface metal atoms on clean and 1/3 ML Cl-covered surfaces (all values in eV).

| Surface | $\varepsilon_d$ (clean) | $\varepsilon_d$ (covered) | shift[a] |
|---|---|---|---|
| Pt(111) | -1.90 | -2.09 | -0.19 |
| Co(0001) | -0.95 | -1.06 | -0.19 |
| Ni(111) | -1.11 | -1.25 | -0.14 |
| Cu(111) | -2.24 | -2.40 | -0.16 |
| Ru(0001) | -2.02 | -2.08 | -0.06 |
| Rh(111) | -1.82 | -1.97 | -0.15 |
| Pd(111) | -1.48 | -1.72 | -0.24 |
| Ag(111) | -3.74 | -3.76 | -0.02 |
| Ir(111) | -2.33 | -2.56 | -0.23 |
| Au(111) | -2.99 | -3.22 | -0.23 |

[a]shift = $\varepsilon_d$ (covered) – $\varepsilon_d$ (clean)

**Table S4:** Comparison between destabilization in binding of 1,2-DCA hydrodechlorination intermediates induced by 1/3 ML Cl and Cl displacement energies ($\Delta E_{3Cl}$) associated with the adsorption on Pt(111) (all values in eV).

| Species | BE (clean) | BE (1/3 ML Cl) | Destabilization[a] | $\Delta E_{3Cl}$[b] |
|---|---|---|---|---|
| $CH_3CH_3$ | -0.05 | -0.04 | 0.01 | 0.01 |
| $CH_3CH_2Cl$ | -0.26 | -0.03 | 0.23 | 0.00 |
| $ClCH_2CH_2Cl$ | -0.22 | -0.05 | 0.17 | 0.01 |
| $CH_3CH_2$ | -2.08 | -1.85 | 0.23 | 0.35 |
| $ClCH_2CH_2$ | -2.16 | -1.78 | 0.38 | 0.35 |
| $CH_2CH_2$ | -1.36 | -1.12 | 0.24 | 0.32 |
| H | -2.81 | -2.62 | 0.19 | 0.20 |
| Cl | -2.83 | -2.41 | 0.42 | 0.31 |

[a]Destabilization = BE (1/3 ML Cl) – BE (clean)

[b]$\Delta E_{3Cl} = E_{3Cl+slab}$ (adsorbate) – $E_{3Cl+slab}$ (opt), where $E_{3Cl+slab}$ (adsorbate) is the total energy obtained using a single-point calculation with the three Cl spectators and the slab Pt atoms fixed at their corresponding positions in the preferred adsorption geometry of the respective adsorbate on 1/3 ML Cl-covered Pt(111)

and the adsorbate atoms themselves removed, and $E_{3Cl+slab}$ (opt) is the total energy of three Cl atoms adsorbed at their most stable $(\sqrt{3}\times\sqrt{3})R60°$ superstructure on Pt(111).

**Table S5:** Summary of average binding energy per chlorine atom at all chlorine surface coverages studied.

| Coverage | Average BE per chlorine atom (eV) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Pt(111) | Co(0001) | Ni(111) | Cu(111) | Ru(0001) | Rh(111) | Pd(111) | Ag(111) | Ir(111) | Au(111) |
| 1/9 ML | -2.83 | -3.63 | -3.49 | -3.41 | -3.77 | -3.51 | -3.25 | -3.04 | -3.16 | -2.36 |
| 2/9 ML | -2.75 | -3.60 | -3.48 | -3.35 | -3.78 | -3.47 | -3.19 | -3.03 | -3.12 | -2.35 |
| 1/4 ML | -2.72 | -3.59 | -3.48 | -3.32 | -3.81 | -3.49 | -3.17 | -3.00 | -3.08 | -2.30 |
| 1/3 ML | -2.75 | -3.59 | -3.48 | -3.32 | -3.75 | -3.45 | -3.14 | -2.98 | -3.09 | -2.33 |
| 4/9 ML | -2.66 | -3.38 | -3.21 | -3.15 | -3.57 | -3.22 | -2.91 | -2.89 | -3.03 | -2.28 |
| 1/2 ML | -2.58 | -2.86 | -2.75 | -2.66 | -3.38 | -3.04 | -2.71 | -2.64 | -2.94 | -2.15 |
| 5/9 ML | -2.51 | -2.93 | -2.72 | -2.69 | -3.28 | -2.93 | -2.63 | -2.67 | -2.83 | -2.13 |
| 2/3 ML | -2.34 | -2.53 | -2.37 | -2.25 | -2.97 | -2.66 | -2.41 | -2.38 | -2.67 | -1.95 |
| 3/4 ML | -2.21 | -2.45 | -2.21 | -2.16 | -2.97 | -2.62 | -2.31 | -2.28 | -2.52 | -1.89 |
| 7/9 ML | -2.18 | -2.13 | -1.95 | -1.77 | -2.76 | -2.44 | -2.18 | -2.20 | -2.45 | -1.83 |
| 8/9 ML | -1.87 | -1.94 | -1.78 | -1.21 | -2.51 | -2.24 | -1.79 | -1.80 | -2.20 | -1.48 |
| 1 ML | -1.76 | -0.88 | -0.82 | -1.00 | -2.02 | -1.86 | -1.68 | -1.67 | -2.04 | -1.42 |

**Table S6:** Binding energies of 1,2-DCA hydrodechlorination intermediates on clean and 1/3 ML Cl-covered surfaces.

| | BE (eV) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | **Pt(111)** | | **Co(0001)** | | **Ni(111)** | | **Cu(111)** | |
| Species | clean | covered | clean | covered | clean | covered | clean | covered |
| $CH_3CH_3$ | -0.05 | -0.04 | -0.04 | 0.01 | -0.05 | -0.04 | -0.05 | -0.04 |
| $CH_3CH_2Cl$ | -0.26 | -0.03 | -0.18 | 0.03 | -0.18 | -0.02 | -0.12 | -0.04 |
| $ClCH_2CH_2Cl$ | -0.22 | -0.05 | -0.17 | -0.01 | -0.18 | -0.02 | -0.11 | -0.06 |
| $CH_3CH_2$ | -2.08 | -1.85 | -1.62 | -0.55 | -1.51 | -0.75 | -1.17 | -0.78 |
| $ClCH_2CH_2$ | -2.16 | -1.78 | -1.63 | -0.64 | -1.52 | -0.73 | -1.20 | -0.76 |
| $CH_2CH_2$ | -1.36 | -1.12 | -0.81 | -0.03 | -0.70 | -0.03 | -0.21 | -0.04 |
| H | -2.81 | -2.62 | -2.83 | -2.51 | -2.77 | -2.44 | -2.57 | -2.26 |
| Cl | -2.83 | -2.41 | -3.63 | -2.75 | -3.49 | -2.41 | -3.41 | -2.67 |
| | **Ru(0001)** | | **Rh(111)** | | **Pd(111)** | | **Ir(111)** | |
| Species | clean | covered | clean | covered | clean | covered | clean | covered |
| $CH_3CH_3$ | -0.05 | -0.02 | -0.05 | -0.04 | -0.06 | -0.04 | -0.04 | -0.03 |
| $CH_3CH_2Cl$ | -0.31 | -0.05 | -0.31 | -0.07 | -0.31 | -0.08 | -0.25 | -0.06 |
| $ClCH_2CH_2Cl$ | -0.29 | -0.08 | -0.29 | -0.07 | -0.29 | -0.09 | -0.22 | -0.03 |
| $CH_3CH_2$ | -1.70 | -1.07 | -1.69 | -1.16 | -1.77 | -1.39 | -1.84 | -1.49 |
| $ClCH_2CH_2$ | -1.73 | -1.08 | -1.70 | -1.17 | -1.76 | -1.33 | -1.84 | -1.49 |
| $CH_2CH_2$ | -0.90 | -0.37 | -0.92 | -0.35 | -1.05 | -0.46 | -0.96 | -0.65 |
| H | -2.79 | -2.39 | -2.79 | -2.46 | -2.90 | -2.59 | -2.72 | -2.33 |
| Cl | -3.77 | -2.77 | -3.51 | -2.50 | -3.25 | -2.26 | -3.16 | -2.67 |

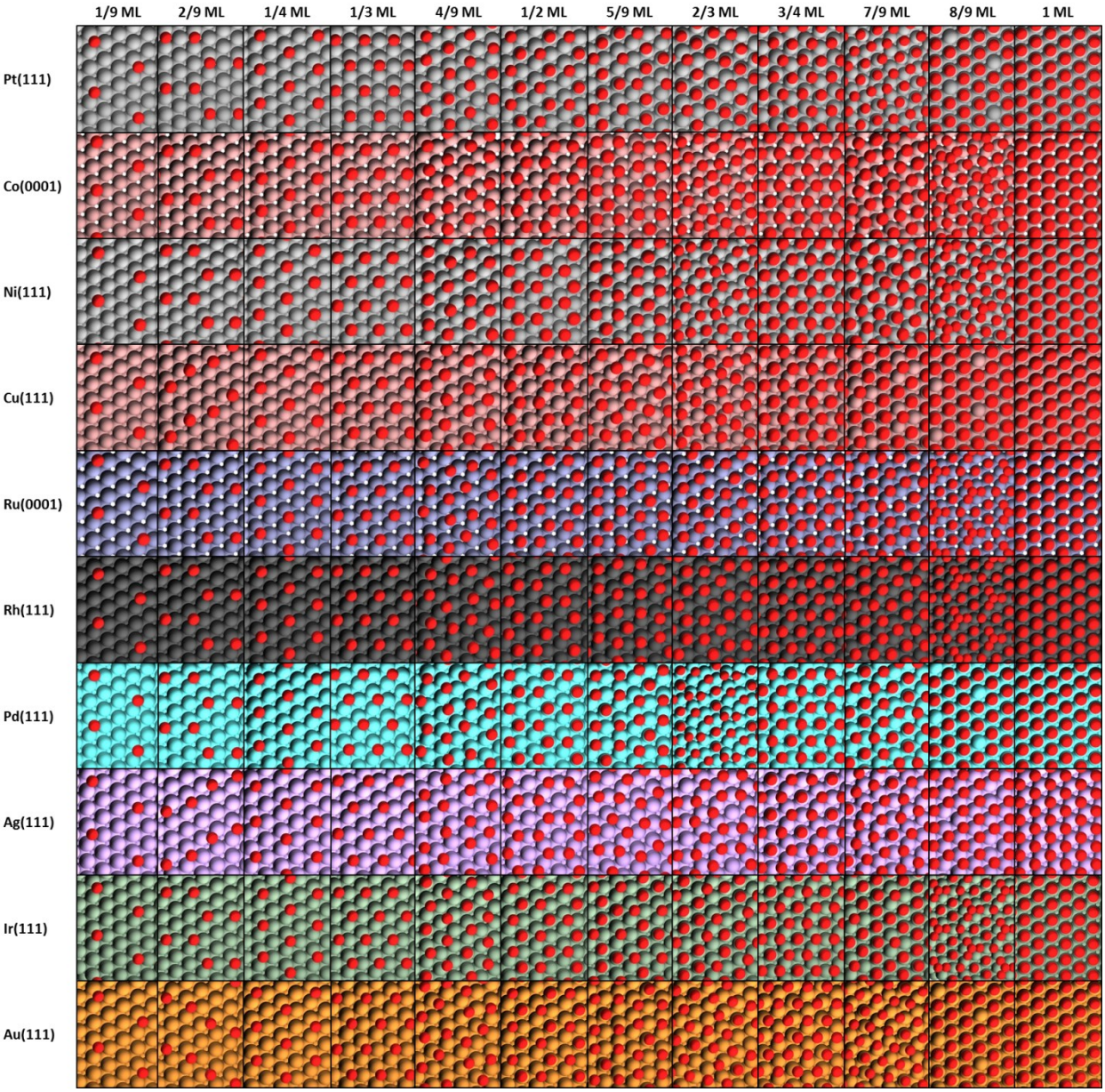


**Figure S1:** Optimized lowest-energy structures at all chlorine surface coverages studied. Red spheres indicate Cl atoms.

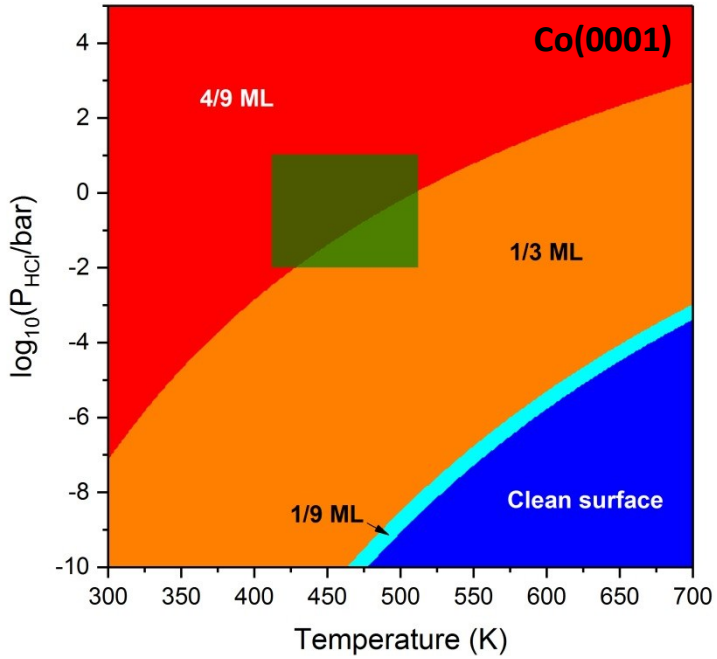


**Figure S2:** Pressure-Temperature phase diagram of atomic chlorine adsorption over Co(0001). The dark green rectangle indicates the typical reaction conditions of 1,2-DCA hydrodechlorination ($T$ = 423–523 K, $P_{HCl} = 10^{-2}$–$10^{1}$ bar).

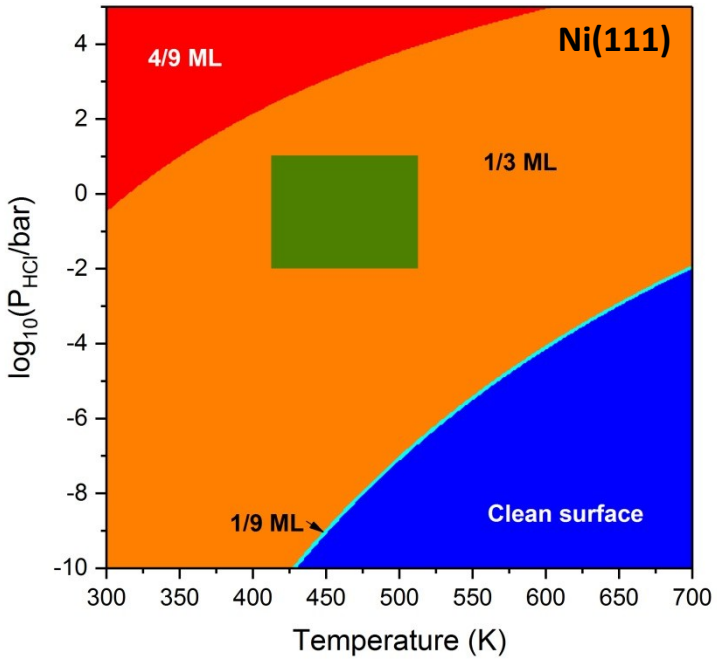


**Figure S3:** Pressure-Temperature phase diagram of atomic chlorine adsorption over Ni(111). The dark green rectangle indicates the typical reaction conditions of 1,2-DCA hydrodechlorination ($T$ = 423–523 K, $P_{HCl} = 10^{-2}$–$10^{1}$ bar).

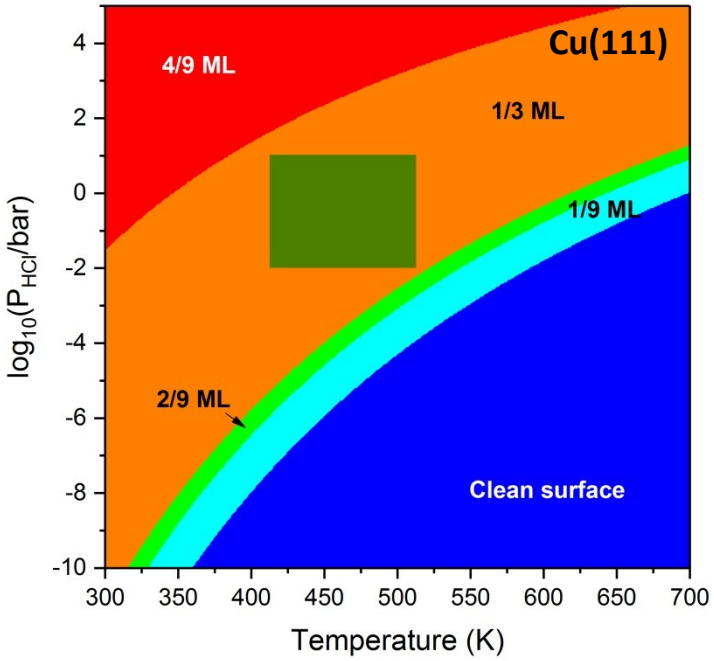


**Figure S4:** Pressure-Temperature phase diagram of atomic chlorine adsorption over Cu(111). The dark green rectangle indicates the typical reaction conditions of 1,2-DCA hydrodechlorination ($T$ = 423–523 K, $P_{HCl} = 10^{-2}$–$10^{1}$ bar).

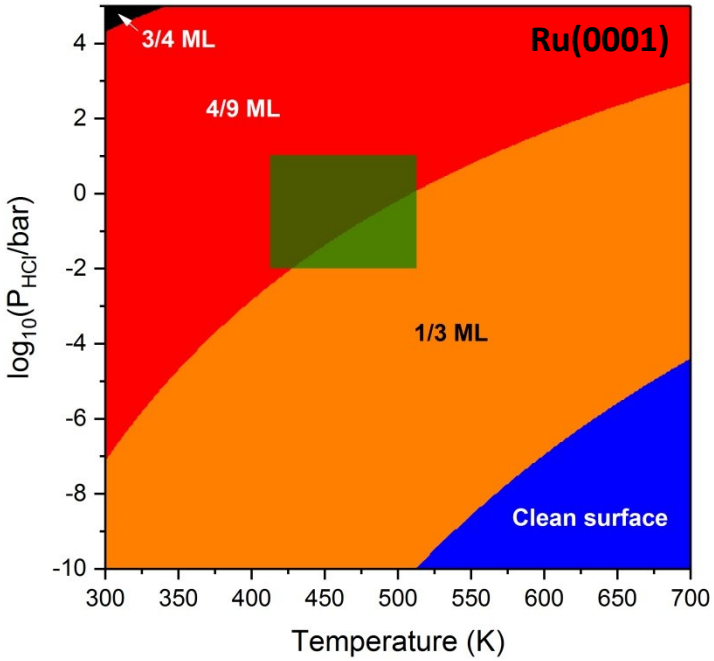


**Figure S5:** Pressure-Temperature phase diagram of atomic chlorine adsorption over Ru(0001). The dark green rectangle indicates the typical reaction conditions of 1,2-DCA hydrodechlorination ($T$ = 423–523 K, $P_{HCl} = 10^{-2}$–$10^{1}$ bar).

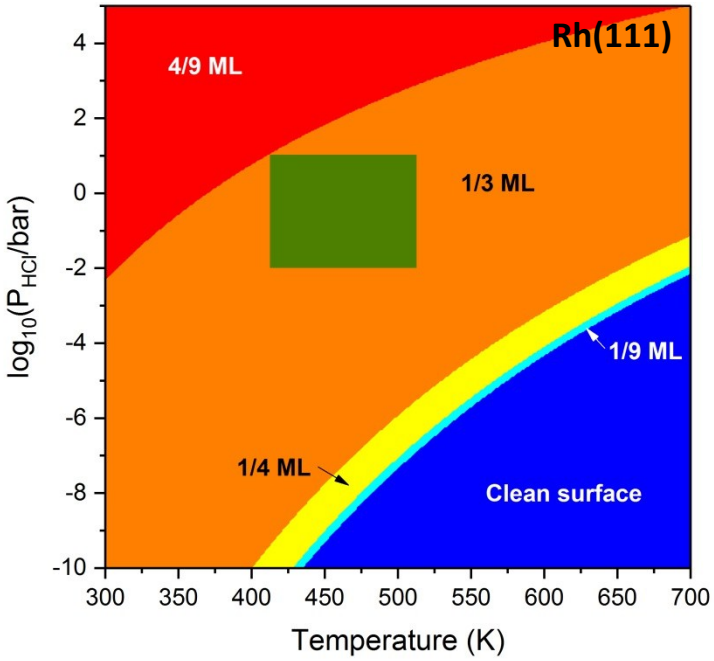


**Figure S6:** Pressure-Temperature phase diagram of atomic chlorine adsorption over Rh(111). The dark green rectangle indicates the typical reaction conditions of 1,2-DCA hydrodechlorination ($T$ = 423–523 K, $P_{HCl} = 10^{-2}$–$10^{1}$ bar).

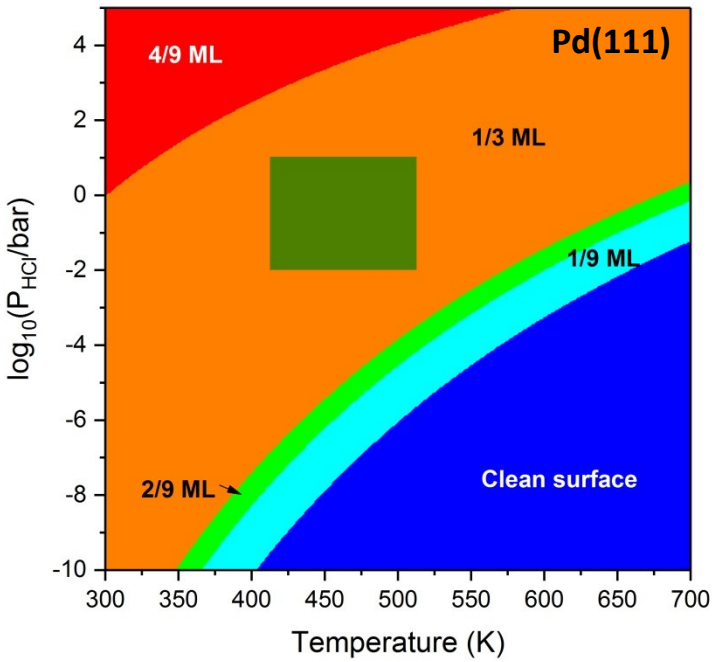


**Figure S7:** Pressure-Temperature phase diagram of atomic chlorine adsorption over Pd(111). The dark green rectangle indicates the typical reaction conditions of 1,2-DCA hydrodechlorination ($T$ = 423–523 K, $P_{HCl} = 10^{-2}$–$10^{1}$ bar).

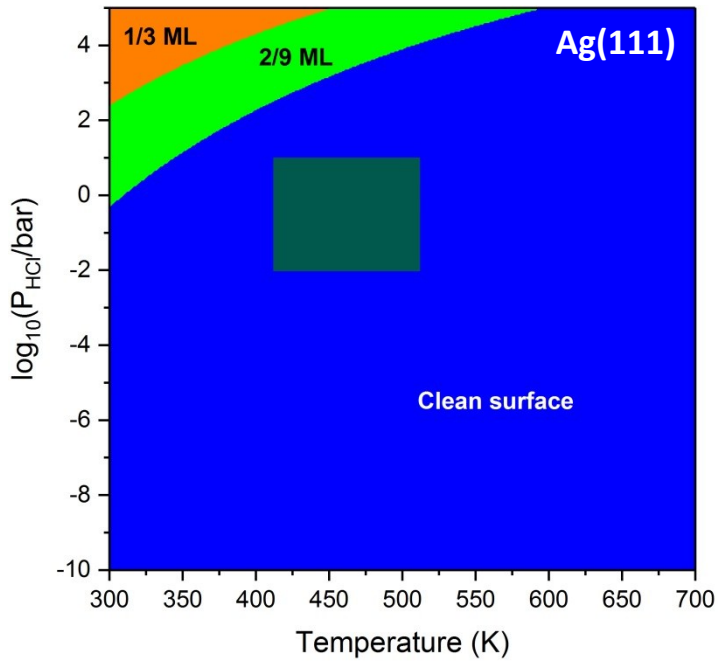


**Figure S8:** Pressure-Temperature phase diagram of atomic chlorine adsorption over Ag(111). The dark green rectangle indicates the typical reaction conditions of 1,2-DCA hydrodechlorination ($T$ = 423–523 K, $P_{HCl}$ = $10^{-2}$–$10^{1}$ bar).

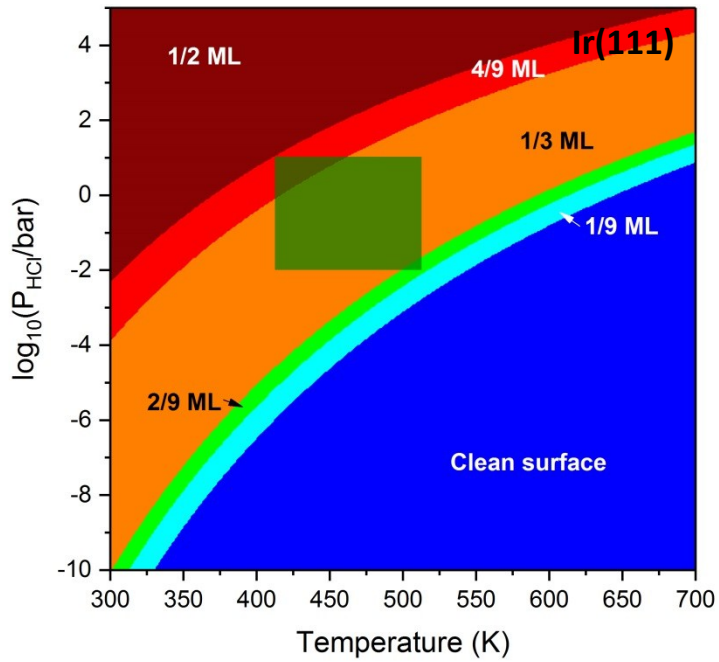


**Figure S9:** Pressure-Temperature phase diagram of atomic chlorine adsorption over Ir(111). The dark green rectangle indicates the typical reaction conditions of 1,2-DCA hydrodechlorination ($T$ = 423–523 K, $P_{HCl}$ = $10^{-2}$–$10^{1}$ bar).

## Reference

[1] V. Milman, B. Winkler, J. A. White, C. J. Pickard, M. C. Payne, E. V. Akhmatskaya, R. H. Nobes, *Int. J. Quantum Chem.* **2000**, *77*, 895–910.