

Supplementary information for:

Grafting metal complexes onto amorphous supports: from elementary steps to catalyst site populations via kernel regression

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S1. Parameters in model of grafting barriers and lattice displacements

S1.1. Grafting temperature and dimensionless precursor concentration (m)

The grafting temperature was chosen to be 298.15 K (room temperature). The ratio of the ML_2 concentration in the gas phase to the reference concentration (\hat{V}_0^{-1}), $m = [\text{ML}_2]/\hat{V}_0^{-1}$, was set to the ratio of CrO_2Cl_2 vapor pressure at 298.15 K (20 Torr) to atmospheric pressure (760 Torr), giving $m = 0.026$.

S1.2. DFT computational details

$D_{\text{M-O}}$, $D_{\text{M}\dots\text{O}}$, $a_{\text{M-O}}$, $a_{\text{M}\dots\text{O}}$, and $\Delta G^\ddagger_{\text{ref}}$ were set using density functional theory (DFT) calculations. All DFT calculations were performed with the $\omega\text{B97X-D}$ functional.¹ The def-2TZVP basis set² was used for chromium and the TZVP basis set^{3,4} was used for all other atoms. The Berny algorithm, as implemented in Gaussian 16, was used to find minima and transition states.⁵ The RMS and maximum forces were required to be less than 3.00×10^{-4} Hartrees/Bohr and 4.50×10^{-4} Hartrees/Bohr, respectively, while the RMS and maximum displacements were required to be less than 1.20×10^{-3} Bohr and 1.80×10^{-3} Bohr respectively. Transition states were required to have one imaginary frequency.

To make a reference site for DFT calculations, the bis(silanolato)chromium(II) cluster was optimized and its peripheral atom positions were held fixed for all subsequent computations to mimic a rigid support, Fig. S1.

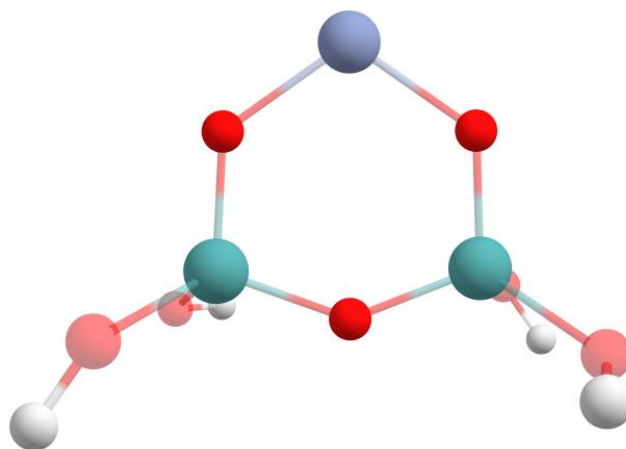


Fig. S1 The optimized bis(silanolato)chromium(II) cluster. Color scheme: oxygen (red), hydrogen (white), silicon (blue), and chromium (purple). Peripheral atoms (fixed) are transparent.⁶

S.1.3. Morse potential parameters

The M-O bond strength (D_{M-O}) was calculated by removing the Cr atom from the bis(silanolato) chromium(II) and performing a single-point energy calculation, Fig. S2. D_{M-O} was calculated using

$$D_{M-O} = E_{II} + E_{Cr} - E_I. \quad (S1)$$

Here E_{II} is the electronic energy of structure II, E_{Cr} is the electronic energy of a Cr atom, and E_I is the electronic energy of the bis(silanolato)chromium(II) cluster (structure I). We get $D_{M-O} = 524.4$ kJ/mol.

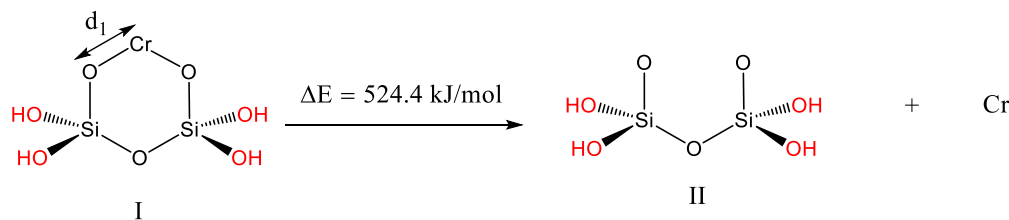


Fig. S2 Calculation of the M-O bond strength. Electronic energies of the optimized Cr(II) cluster (left) and cluster with dissociated Cr (right). Peripheral atoms (fixed) are red. d_1 is used as the displacement variable in a Morse potential model (below).

The Morse potential width (a) can be related to the force constant by a second-order Taylor expansion of $V(r)$ around the equilibrium bond length (r_{eq}):

$$V(r) \approx \frac{d^2V}{dr^2} \frac{(r - r_{eq})^2}{2!} = k \frac{(r - r_{eq})^2}{2} = Da^2 (r - r_{eq})^2. \quad (S2)$$

Here, k is the force constant. The zeroth-order term of the Taylor expansion evaluates to 0 by construction, while the first derivative evaluates to 0 because r_{eq} corresponds to the minimum of the potential energy surface. Thus, $a = [k/2D]^{1/2}$. The force constant was computed using DFT by calculating the second derivative of the potential energy with respect to the Cr-O bond length (d_1). We obtain $k_{M-O} = 0.2063$ Ha/Bohr and $a_{M-O} = 1$. Here a_{M-O} was non-dimensionalized by d_1 .

The non-dimensionalized equilibrium bond distance for the M-O bond ($r_{M-O,eq}$) was set to 1.

To calculate the $M\cdots O$ bond strength ($D_{M\cdots O}$), a water molecule was adsorbed on the bare Cr cluster, and the cluster was reoptimized while keeping the positions of the peripheral atoms fixed, Fig. S3. The bond strength of the $Cr\cdots OH_2$ bond was calculated using

$$D_{M\cdots O} = E_I + E_{H_2O} - E_{III}. \quad (S3)$$

Here E_I is the electronic energy of structure I, E_{H_2O} is the electronic energy of the optimized water molecule, and E_{III} is the electronic energy of structure III. We get $D_{M\cdots O} = 117$ kJ/mol.

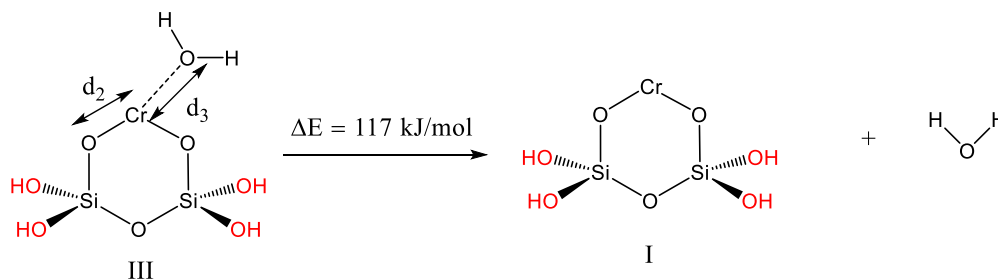


Fig. S3 Calculation of the $M\cdots O$ bond strength. Electronic energies of the Cr cluster with H_2O adsorbed (left) and the bare Cr cluster and H_2O in the gas phase (right). Peripheral atoms (fixed) are red. d_2/d_3 was used to compute $r_{M\cdots O,eq}$ and d_3 was used as a displacement variable in the Morse potential model for $M\cdots O$.

$k_{M\cdots O}$ was computed as the second derivative of the energy of structure III with respect to the $Cr\cdots O$ bond length (d_3). We get $k_{M\cdots O} = 0.054$ Ha/Bohr and $a_{M\cdots O} = 2.3$ (Eq. (S2)). Here $a_{M\cdots O}$ was non-dimensionalized by d_3 (Fig. S3).

The non-dimensionalized equilibrium $M\cdots O$ bond length ($r_{M\cdots O,eq}$) was set to d_3/d_2 . This yields $r_{M\cdots O,eq} = 1.16$.

S1.4. Lattice displacements

The lattice points were displaced by drawing displacements according to a bivariate Gaussian distribution using the `numpy.random.multivariate_normal` function in python:⁷

$$p(\mathbf{x}, \boldsymbol{\mu}, \Sigma) = \frac{1}{2\pi |\Sigma|^{\frac{1}{2}}} \exp\left(-\frac{1}{2}(\mathbf{x} - \boldsymbol{\mu})^T \Sigma^{-1}(\mathbf{x} - \boldsymbol{\mu})\right). \quad (\text{S4})$$

Here Σ is a 2x2 dimensional covariance matrix, $\boldsymbol{\mu} \in \mathbf{R}^2$ is the mean, and $\mathbf{x} \in \mathbf{R}^2$ is a 2D random variable representing displacement of lattice points. The covariance matrix was set equal to a scalar diagonal matrix

$$\Sigma = \sigma_{\text{lattice}}^2 I. \quad (\text{S5})$$

Here I is the 2x2 identity matrix. The value of $\sigma_{\text{lattice}}^2$ was set to 0.00022 and the value of $\boldsymbol{\mu}$ was set to (0,0).

S1.5. ε_{HL} , V^* , ΔPV , and ΔS° to compute grafting free energy

From Eq. (4), it follows that the grafting energy for a site on the unperturbed lattice is given by

$$\Delta E_{\text{unperturbed}} = 2\varepsilon_{\text{HL}} - (V_* + 2\varepsilon_{\text{ML}}) + V_{\mathbf{M}^*}(\mathbf{x}_{\text{unperturbed}}). \quad (\text{S6})$$

Here $V_{\mathbf{M}^*}$ is obtained by optimizing the metal position in a site on an unperturbed lattice. Similarly, from Eq. (8) it follows that the grafting free energy on an unperturbed site is given by

$$\Delta G_{\text{unperturbed}}^\circ = 2\varepsilon_{\text{HL}} - (V_* + 2\varepsilon_{\text{ML}}) + V_{\mathbf{M}^*}(\mathbf{x}_{\text{unperturbed}}) + \Delta PV - T\Delta S^\circ. \quad (\text{S7})$$

Rearranging Eq. (S7), we get

$$2\varepsilon_{\text{HL}} - (V_* + 2\varepsilon_{\text{ML}}) + \Delta PV - T\Delta S^\circ = \Delta G_{\text{unperturbed}}^\circ - V_{\mathbf{M}^*}(\mathbf{x}_{\text{unperturbed}}). \quad (\text{S8})$$

Using Morse potential parameters from Section 1.3, we obtain $V_{\mathbf{M}^*}(\mathbf{x}_{\text{unperturbed}}) = -1259.57$ kJ/mol. To make grafting favorable for a reference site, $\Delta G_{\text{unperturbed}}^\circ$ was set equal to -30 kJ/mol. This yields $2\varepsilon_{\text{HL}} - (V_* + 2\varepsilon_{\text{ML}}) + \Delta PV - T\Delta S^\circ = 1229.56$ kJ/mol. ε_{HL} , V_* , ε_{ML} , ΔPV , and ΔS° always occur together in the combination on the LHS of Eq. (S8), therefore they do not need to be determined separately.

S1.6. Reference free energy barrier and linear free energy relation ($\Delta G_{\text{ref}}^\ddagger$)

The LFER for an unperturbed site is given by

$$\Delta G_{\text{unperturbed}}^\ddagger(\mathbf{r}) = \Delta G_{\text{ref}}^\ddagger + \alpha \Delta G_{\text{unperturbed}}^\circ(\mathbf{r}). \quad (\text{S9})$$

$\Delta G_{\text{unperturbed}}^\ddagger(\mathbf{r})$ was set equal to the DFT-computed activation barrier for CrO_2Cl_2 grafting to a vicinal disilanol model site at 1 atm pressure of CrO_2Cl_2 (Fig. S4).

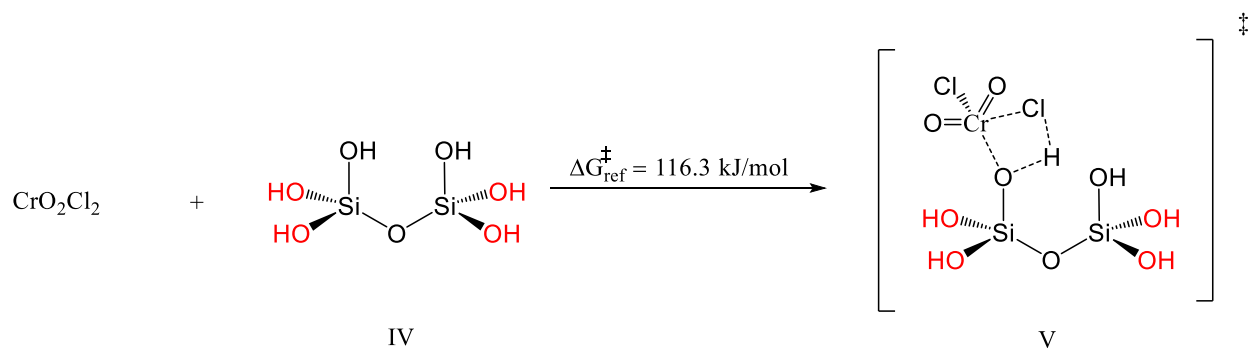


Fig. S4 Calculation of the reference free energy barrier. Free energies of CrO_2Cl_2 in the gas phase with the vicinal silanol site (left) and the transition state for CrO_2Cl_2 grafting to the vicinal silanol site (right). Free energies are at 1 atm CrO_2Cl_2 and 298.15 K. Peripheral atoms (fixed) are red.

Using $\Delta G_{\text{unperturbed}}^{\circ} = -30 \text{ kJ/mol}$ (Section 1.5) and solving for $\Delta G_{\text{ref}}^{\ddagger}$ we get

$$\Delta G_{\text{ref}}^{\ddagger} = 131.3 \text{ kJ/mol} . \tag{S10}$$

S2. Effect of training set size on test set error

100 sites were chosen for training because it is the minimum training set size with a test set error < 0.5 kJ/mol. $2\sigma < 1$ kJ/mol implies a 95 % confidence in predictions within chemical accuracy (1kJ/mol). Figure S5.

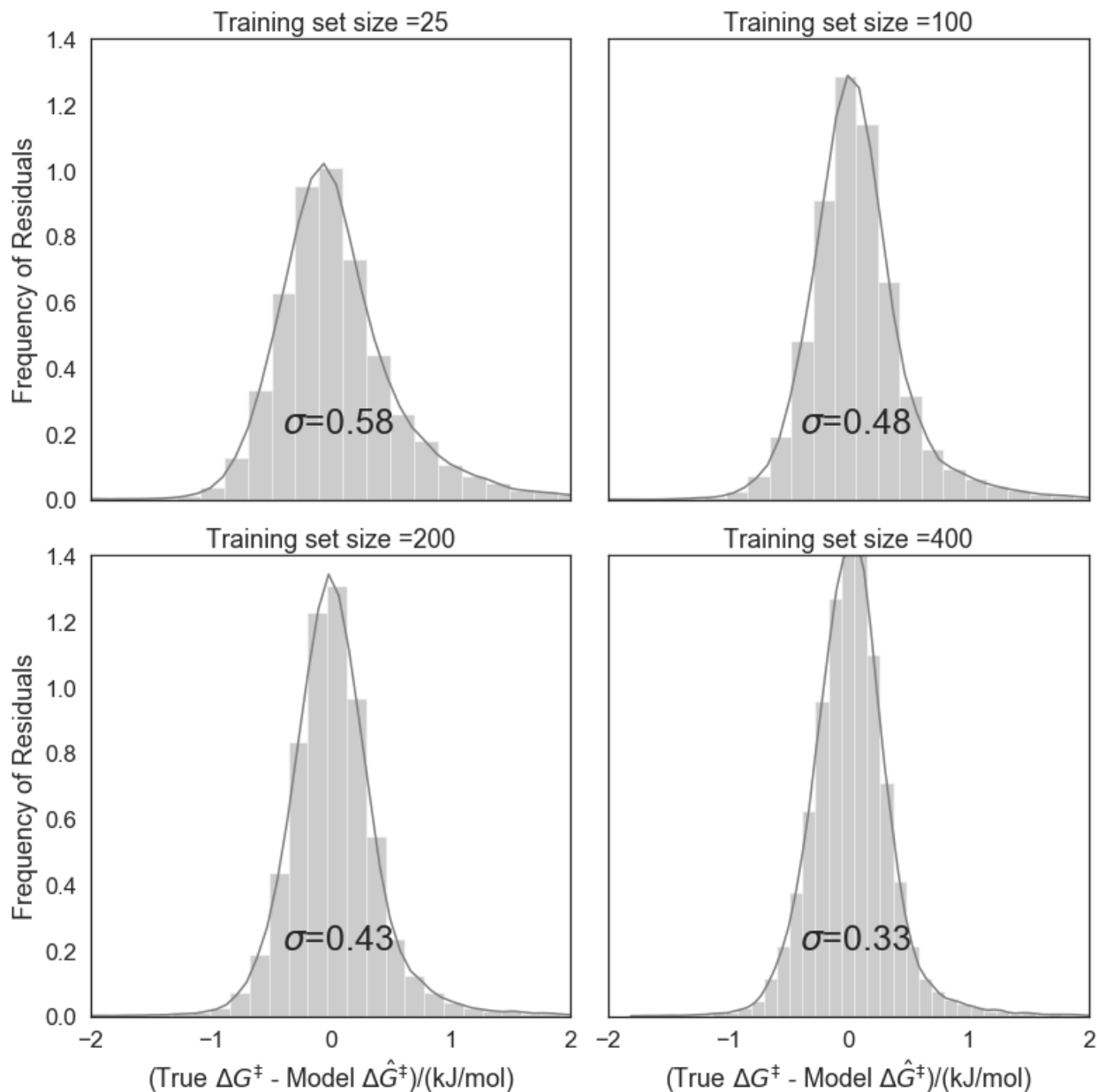


Fig. S5 Residual distributions for predicted grafting barriers as a function of training set size for all ~ 20,000 sites. As expected, the width of the residual distribution decreases on increasing the training set size.

S3. Optimized Cartesian coordinates

I				Si	0.326075	2.970978	0.018794
O	1.528811	1.824313	-0.017388	H	1.148930	6.972860	2.668851
O	0.329378	3.677175	-1.481621	O	1.081087	6.020796	2.752306
O	-3.798259	2.422246	0.623913	H	1.518486	5.602420	1.984661
O	-2.438002	0.962699	2.368112	H	2.801681	-1.777950	-1.369223
H	1.471909	1.112917	0.626314	H₂O			
H	0.721158	3.163281	-2.193268	H	-4.608746	5.621161	3.576918
H	-3.813749	2.949384	-0.179589	O	-4.583973	5.230285	4.450516
H	-3.058546	0.287885	2.079326	H	-4.630806	5.969246	5.057441
Cr	-0.581114	4.653929	2.451205	CrO₂Cl₂			
O	0.574657	4.129092	1.143994	Cr	-0.813596	0.931968	-0.026679
O	-2.075437	3.611653	2.410588	O	-1.929832	1.847660	-0.541532
O	-1.118168	2.236282	0.338845	O	0.532336	1.454304	-0.541523
Si	-2.359099	2.327446	1.438932	Cl	-1.126960	-1.029644	-0.761437
Si	0.334619	2.972583	0.013179	Cl	-0.808773	0.962166	2.091171
II				IV			
O	-1.479020	1.063597	-0.171917	O	1.528811	1.824313	-0.017388
O	1.479919	1.062495	0.169382	O	0.329378	3.677175	-1.481621
O	-0.000064	-1.152570	-0.010169	O	-3.798259	2.422246	0.623913
Si	1.549993	-0.562218	0.019959	O	-2.438002	0.962699	2.368112
Si	-1.549694	-0.561184	-0.022650	H	1.471909	1.112917	0.626314
O	-2.373190	-1.327126	-1.234709	H	0.721158	3.163281	-2.193268
O	-2.338964	-0.932841	1.376401	H	-3.813749	2.949384	-0.179589
O	2.357723	-1.330005	1.241761	H	-3.058546	0.287885	2.079326
O	2.354669	-0.932487	-1.370478	O	0.452818	4.100190	1.148729
H	-1.862034	-1.546446	-2.012360	O	-2.079978	3.617865	2.397352
H	-2.799779	-1.770818	1.373882	O	-1.125250	2.209046	0.338162
H	1.832745	-1.558780	2.007440	Si	-2.366906	2.321508	1.441114
H	2.801681	-1.777950	-1.369223	Si	0.297459	2.926241	-0.015455
III				H	1.131843	4.762355	1.026301
O	1.528715	1.824430	-0.017273	H	-1.227754	4.046968	2.262093
O	0.329040	3.677023	-1.481622	V			
O	-3.798037	2.422373	0.623959	O	1.528811	1.824313	-0.017388
O	-2.437772	0.962573	2.367903	O	0.329378	3.677175	-1.481621
H	1.471874	1.112840	0.626215	O	-3.798259	2.422246	0.623913
H	0.721382	3.163392	-2.193211	O	-2.438002	0.962699	2.368112
H	-3.813726	2.949265	-0.179675	H	1.471909	1.112917	0.626314
H	-3.058776	0.288005	2.079504	H	0.721158	3.163281	-2.193268
Cr	-0.583821	4.714397	2.500341	H	-3.813749	2.949384	-0.179589
O	0.579509	4.129526	1.136052	H	-3.058546	0.287885	2.079326
O	-2.065920	3.613509	2.402040	O	0.532837	4.159347	1.128393
O	-1.121537	2.226881	0.331971	O	-2.188510	3.614718	2.443646
Si	-2.356280	2.335183	1.444016	O	-1.098231	2.277343	0.398604
				Si	-2.367921	2.298347	1.428234

Si	0.342124	2.973369	0.006307	Cl	-3.077539	6.049800	2.962288
Cr	-1.133593	4.244207	3.873462	Cl	0.122137	2.506696	4.047915
O	-0.168197	5.426249	3.758314	H	-2.839503	4.669098	2.418243
O	-1.837495	4.321604	5.228652	H	1.181758	4.843077	0.968990

S4. Additional references

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