

Supplementary Information for

Factors Controlling Oxophilicity and Carbophilicity of Transition Metals and Main Group Metals

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1 Electronegativity as a descriptor

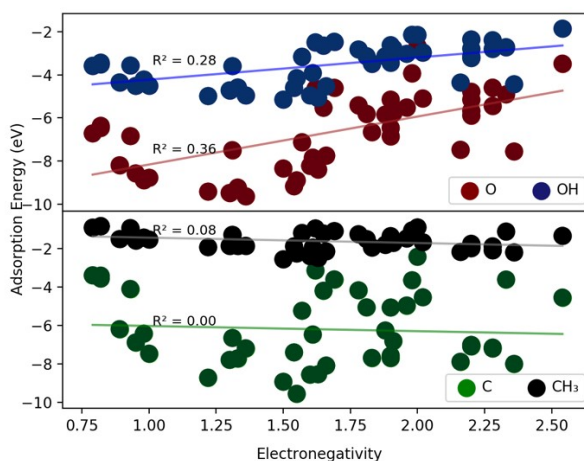


Figure S1 Correlation plot between the adsorption energies of different chemical species on pure metal and their electronegativity. This plot clearly shows the limitations of electronegativity in capturing oxophilic and carbophilic trends.

Electronegativity has been suggested to explain trends in oxophilicity across metals.^{1,2} However, it performs poorly when considering metals from different regions of the periodic table as shown in Figure S1. It does, however, fairly correlate well with oxophilicity when considering transition metals alone with an R^2 of 0.57.

2 Uniformly scaled periodic tables of energies

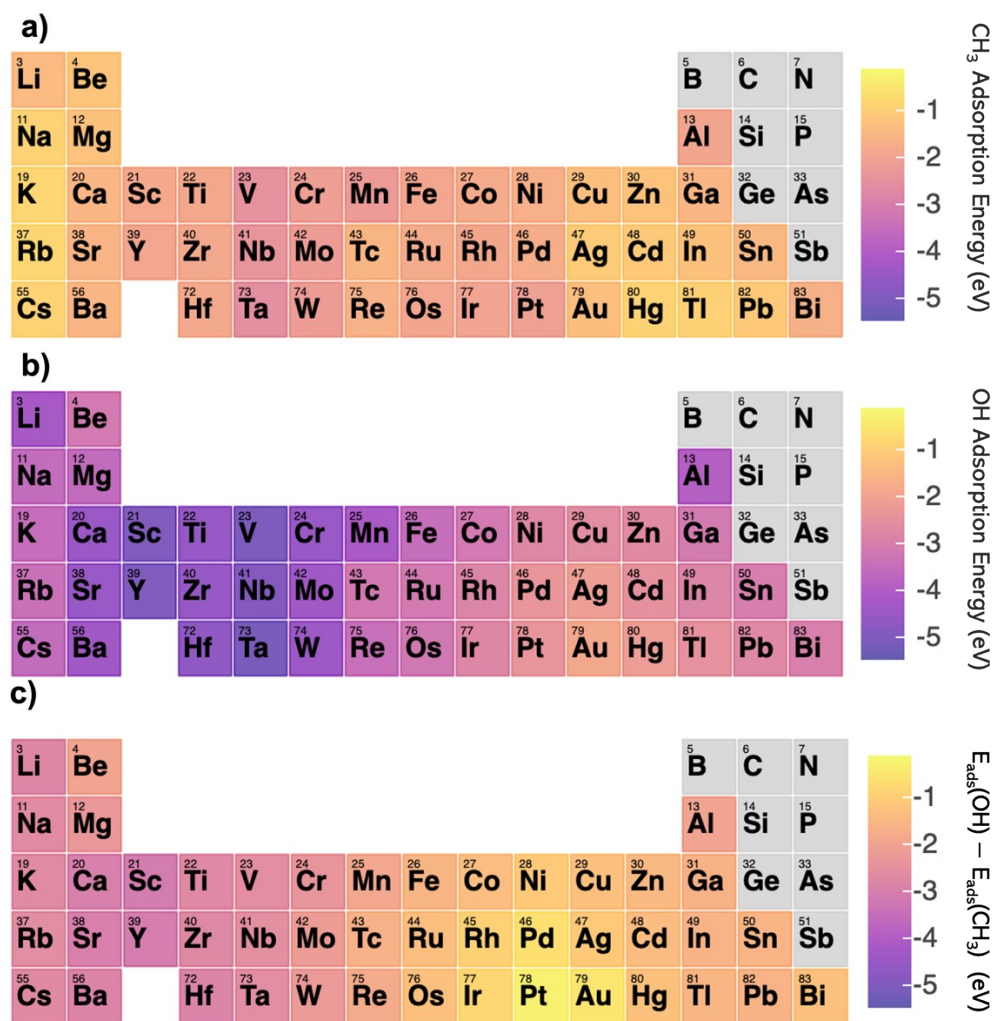


Figure S2 A uniformly scaled version of the periodic table of the DFT-calculated, OH and CH₃ adsorption energies and their quantitative difference for all metals considered in this work.

3 Surface properties

The full set of surface properties tested in this work together with their description is listed in Table S1. Most of these properties were either calculated with DFT or taken from literature.

Table S1: Full list of all the surface properties tested in this work.

Term	Description
ε_d	d band center
V_{as}^2	adsorbate-surface <i>s</i> coupling matrix
$V_{as}^2 f$	adsorbate-surface <i>s</i> coupling matrix × Idealized band filling
V_{ad}^2	adsorbate-surface <i>d</i> coupling matrix
$V_{ad}^2 f$	adsorbate-surface <i>d</i> coupling matrix × Idealized band filling
$R_p f$	reduction potential × Idealized band filling
R_p	reduction potential
ε_p	p band center
ε_s	s band center
ε_{sp}	sp band center
n_p	number of p electrons
n_s	number of s electrons
n_d	number of d electrons
n_{sp}	number of s electrons × number of p electrons
n_{sd}	number of s electrons × number of d electrons
n_{pd}	number of p electrons × number of d electrons

Table S1: Full list of all the surface properties tested in this work.

Term	Description
<i>average s and d band center</i>	(s band center + d band center)/2
<i>average p and d band center</i>	(p band center + d band center)/2
V_{as}^4	$(V_{as}^2)^2$
V_{ad}^4	$(V_{ad}^2)^2$
$V_{as}^2 V_{ad}^2$	$V_{as}^2 \times V_{ad}^2$
$V_{as}^2 V_{ad}^2 f$	$V_{as}^2 \times V_{ad}^2 f$
X_p	Pauli's electronegativity
$X_p f$	$X_p \times f$
$V_{as}^2 X_p$	$V_{as}^2 \times X_p$
$V_{ad}^2 X_p$	$V_{ad}^2 \times X_p$
X_m	Mulliken's electronegativity
$X_m f$	$X_p \times f$
$V_{as}^2 X_m$	$V_{as}^2 \times X_p$
$V_{ad}^2 X_m$	$V_{ad}^2 \times X_p$
$V_{ad}^2 R_p$	$V_{ad}^2 \times R_p$
$V_{as}^2 R_p$	$V_{as}^2 \times R_p$
G	metal's group
P	metal's period
W_f	work function
E	$\varepsilon = \varepsilon_d$ (for metals within the d block) $\varepsilon = \varepsilon_s$ (for metals within the s block) $\varepsilon = \varepsilon_p$ (for metals within the p block)
<i>average number of s and p electrons</i>	(number of s electrons + number of p electrons)/2
<i>average number of s and d electrons</i>	(number of s electrons + number of d electrons)/2
<i>average number of p and d electrons</i>	(number of p electrons + number of d electrons)/2

<i>average s and p band center</i>	$(s \text{ band center} + p \text{ band center})/2$
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3 Final model terms

All of the properties used as inputs for our final model together with their physical justification are the listed in Table S2 below.

Table S2: Terms in our linear model for adsorption/formation energies and their physical justification.

Term	Description	Physical Justification
ε_d	d band center	d-band model
V_{as}^2	adsorbate-surface <i>s</i> coupling matrix	hybridization, perturbation theory
$V_{as}^2 f$	adsorbate-surface <i>s</i> coupling matrix \times band filling	hybridization, perturbation theory
V_{ad}^2	adsorbate-surface <i>d</i> coupling matrix	hybridization, perturbation theory
$V_{ad}^2 f$	adsorbate-surface <i>d</i> coupling matrix \times band filling	hybridization, perturbation theory
$R_p f$	reduction potential \times band filling	ionic contributions

4 Linear model assumptions check

Apart from the scatter plot shown in Figure 3 and the test-train splits shown in Figure 4, we performed other tests to check the appropriateness of a linear model: the mean of residuals, error distributions, multi-collinearity, auto-correlation and homoscedasticity. These checks suggest that the use of a linear model is appropriate.

4.1. The Mean of Residuals

The mean of residuals should be very close to zero. They are indeed quite small, as shown in Table S3.

Table S3: The calculated mean of residuals for O, C, OH and CH₃

Model	Mean of Residuals
O	-1.93×10^{-16}
OH	7.14×10^{-16}
C	-7.13×10^{-16}
CH ₃	-1.93×10^{-17}

4.2. Error distribution

The residuals should approximately follow a normal distribution. As shown in Figure S3, this is true of our fits.

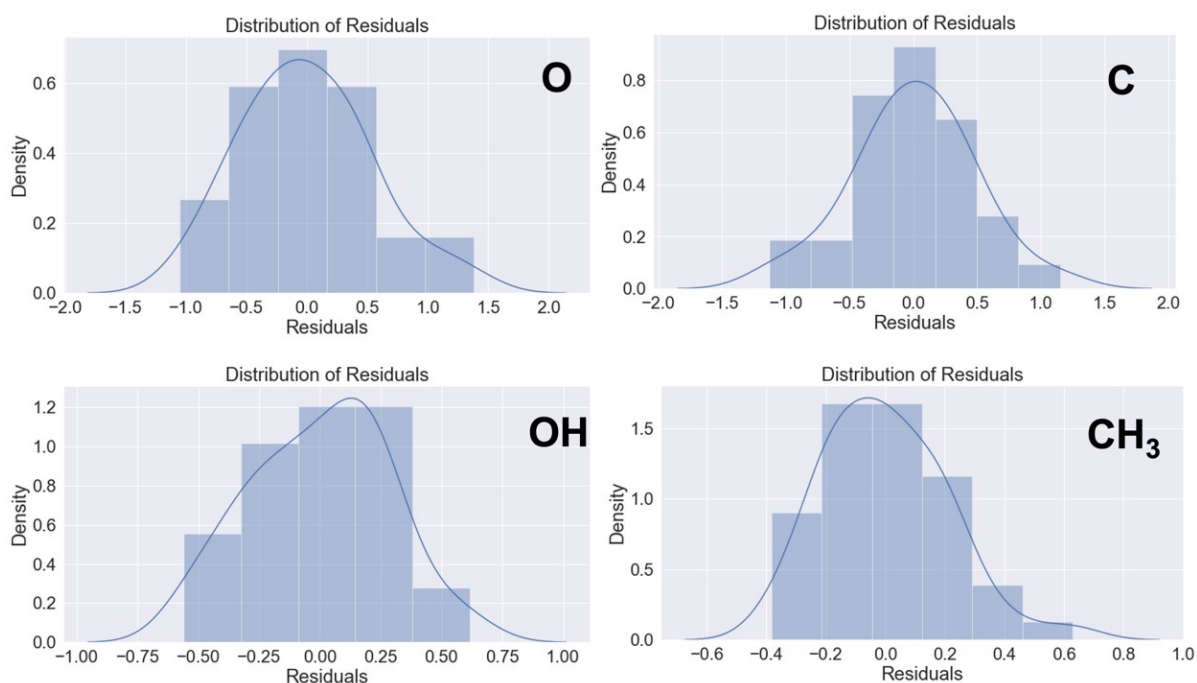


Figure S3 Error distributions for the different linear models. The residuals roughly follow a normal distribution.

4.3. Multi-collinearity

There should not be a high correlation between model inputs. As shown in Figure S4, the correlation is low in nearly all cases. There are few variables that are somewhat correlated, such as V_{ad}^2 and V_{adf}^2 . We expect this rough correlation and their inclusion is justified by physics as discussed in the main text and based on previous work.^{3,4}



Figure S4 Correlation matrix of all the model inputs

4.4. Homoscedasticity

Ideally, the variance of the residuals should not vary significantly across the data range. Figure S5 shows that the variance is indeed fairly constant across the full range with a few outliers. Hence, this assumption is also satisfied.

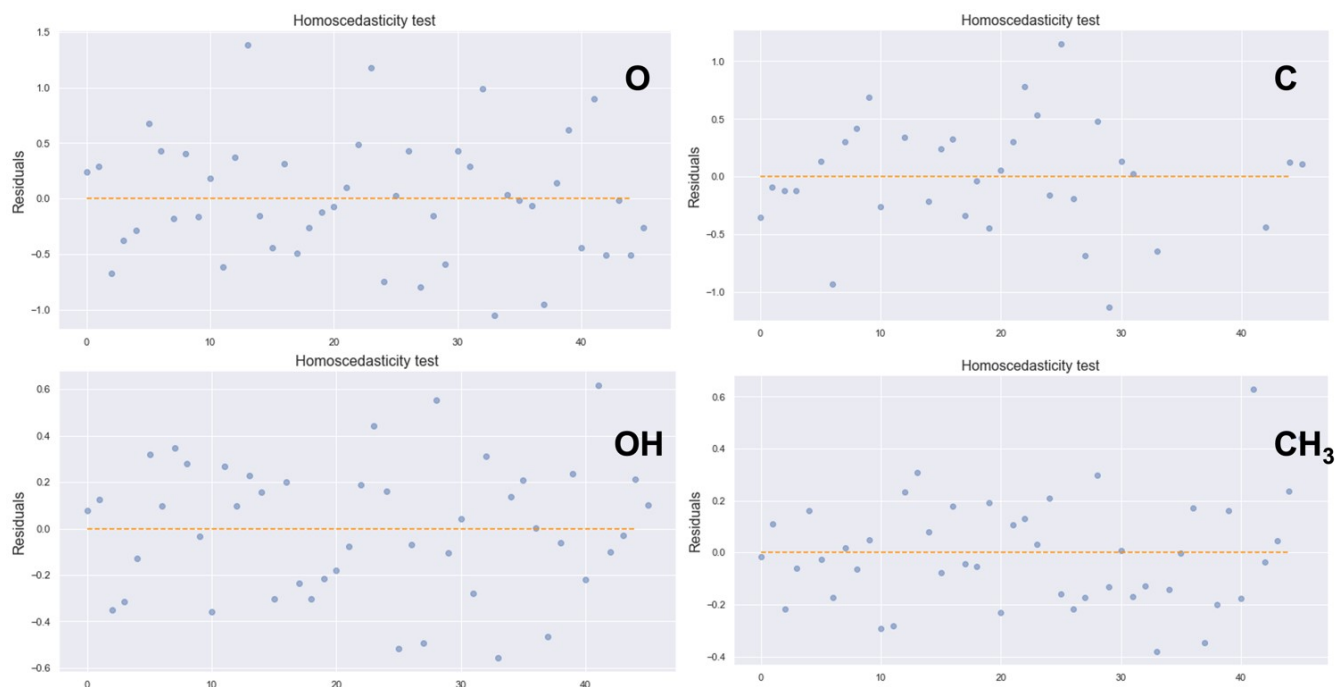


Figure S5 Residual plots for the different models

5 O and C adsorption trends across the periodic table

Here we show that the trends observed for OH and CH₃ adsorption are very similar to that observed for O and C adsorption. O and C trends as well as their quantitative difference are shown in Figure S6.

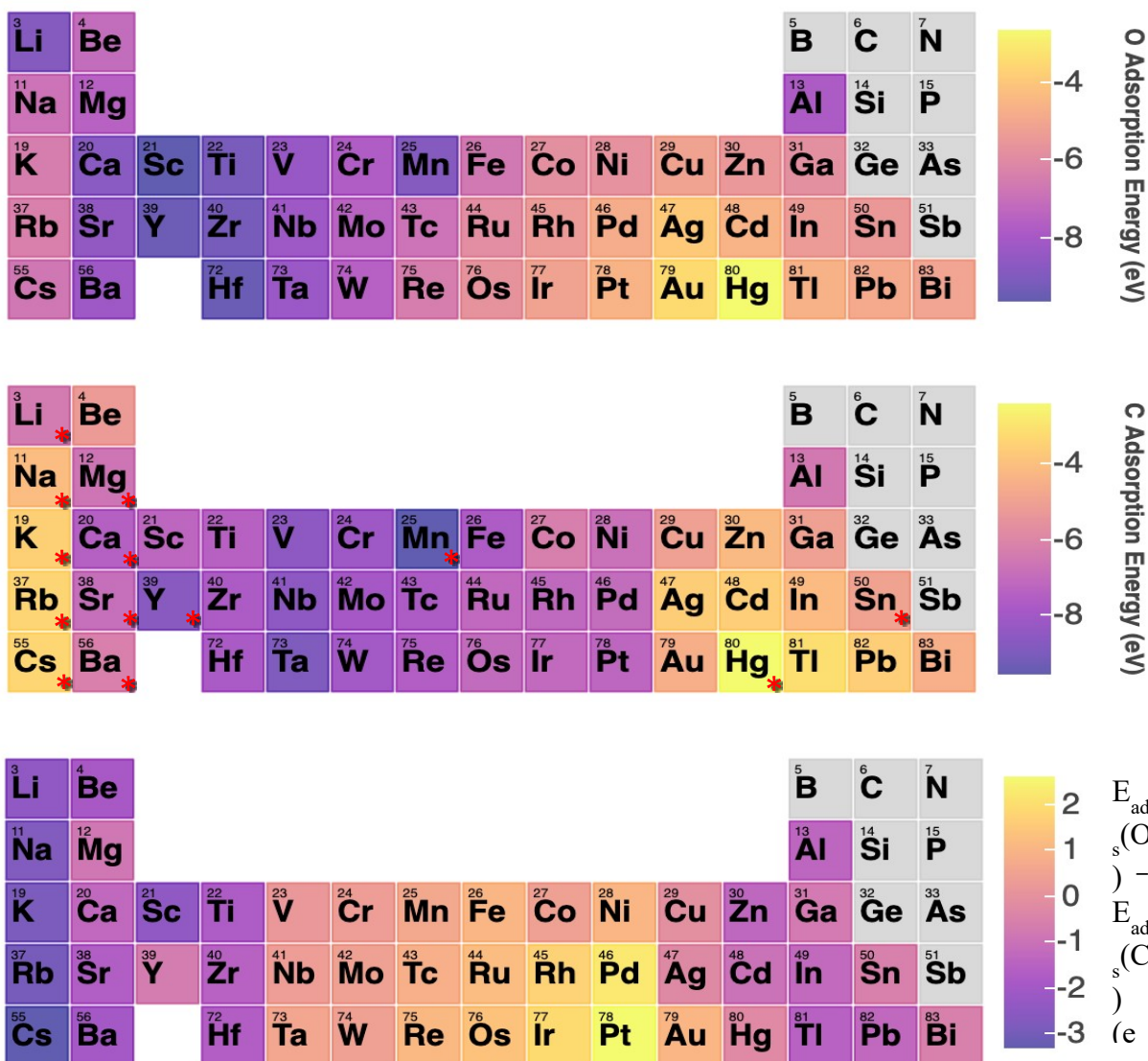


Figure S6 Periodic table of the DFT-calculated, O, C adsorption energies and their quantitative difference for all metals considered in this work. The * marks surfaces where the C atom was not stable on the surface but rather preferred the sub-surface. The resulting energies are given here for completeness, but the adsorption energies of these systems were not included in any model fitting.

6 Surface property trends across the periodic table

The trends across the periodic table of every property used in the final model are shown below in

Figures S7-S12.

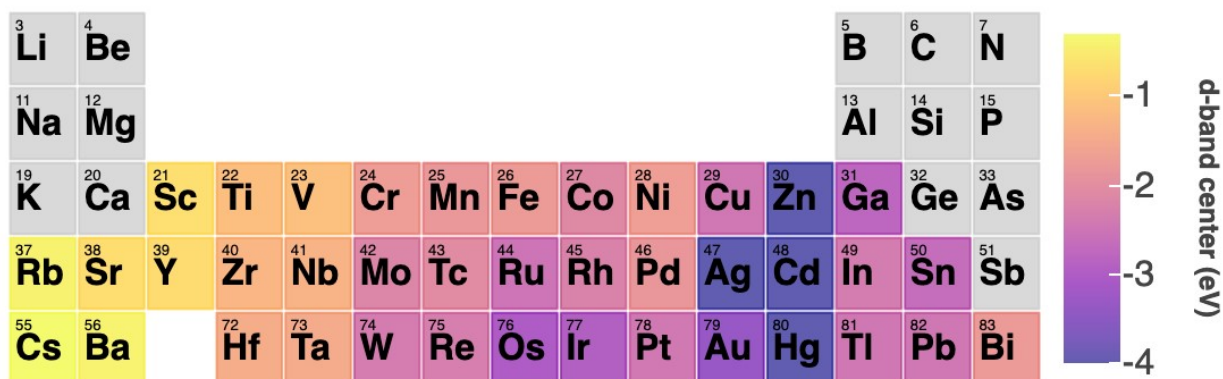


Figure S7 Periodic table trend of the d-band center for all metals considered in this work.

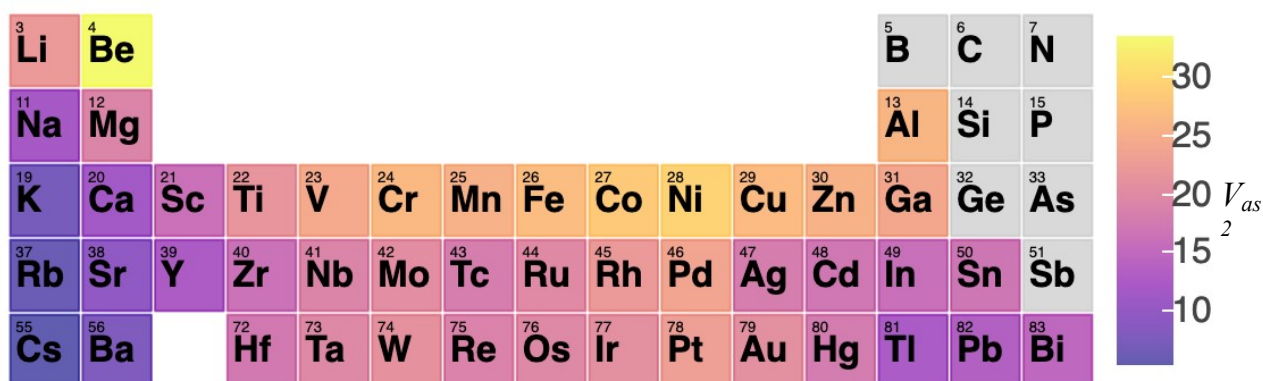


Figure S8 Periodic table trend of V_{as}^2 for all metals considered in this work.

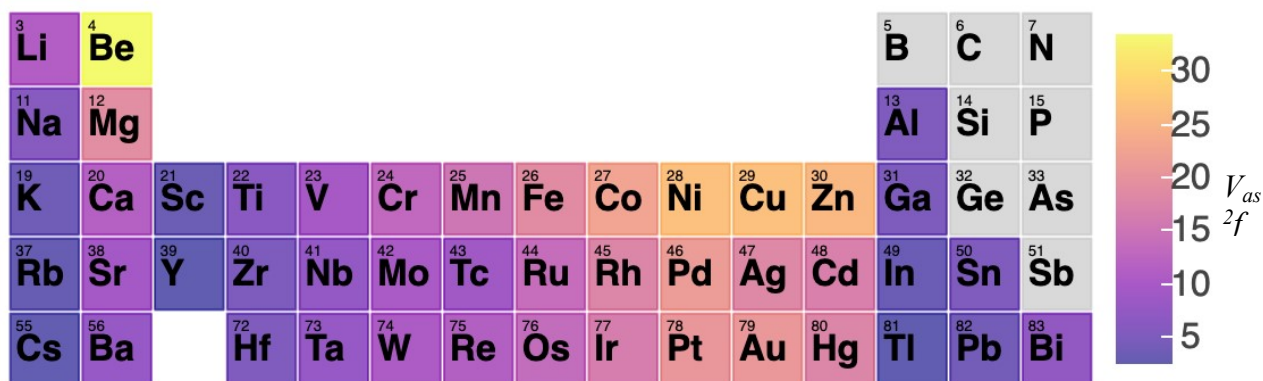


Figure S9 Periodic table trend of V_{as}^{2f} for all metals considered in this work.

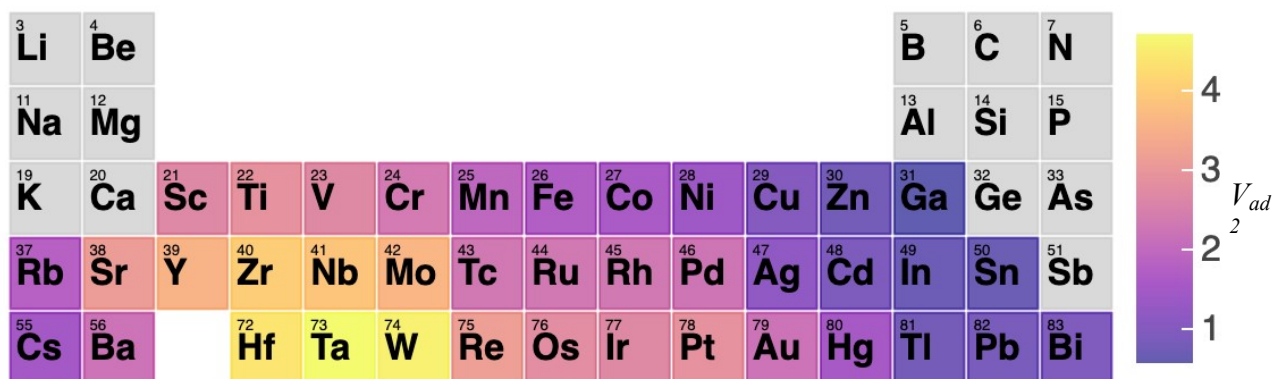


Figure S10 Periodic table trend of V_{ad}^2 for all metals considered in this work.

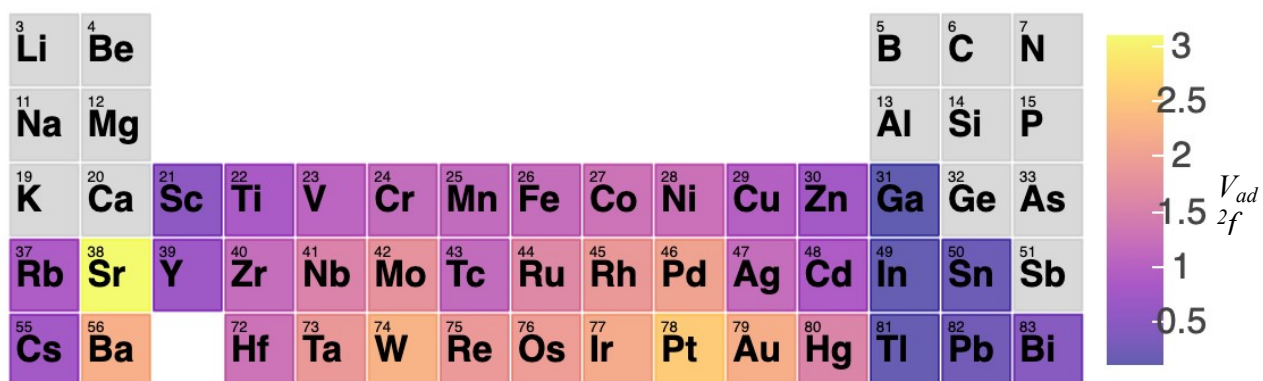


Figure S11 Periodic table trend of $V_{ad}^2 f$ for all metals considered in this work.

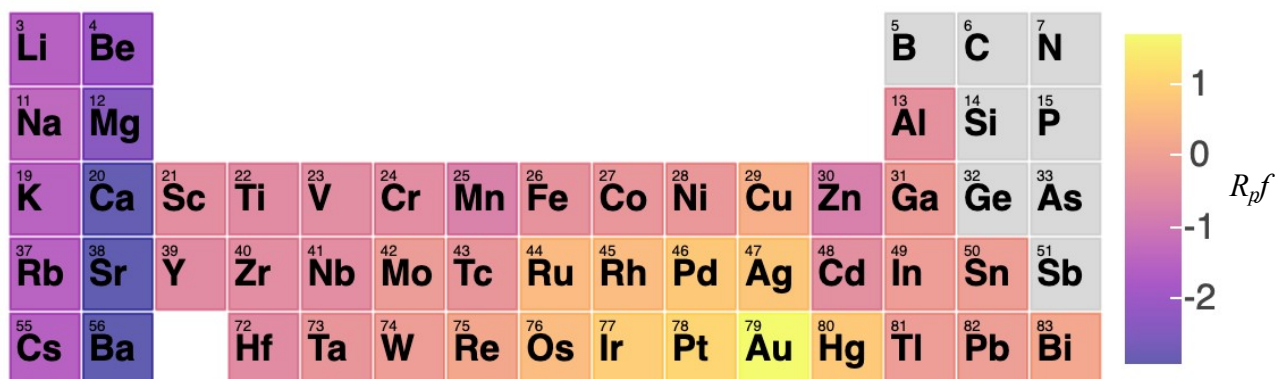


Figure S12 Periodic table trend of R_{pf} for all metals considered in this work.

7. Correlations among adsorption energies and formation energies

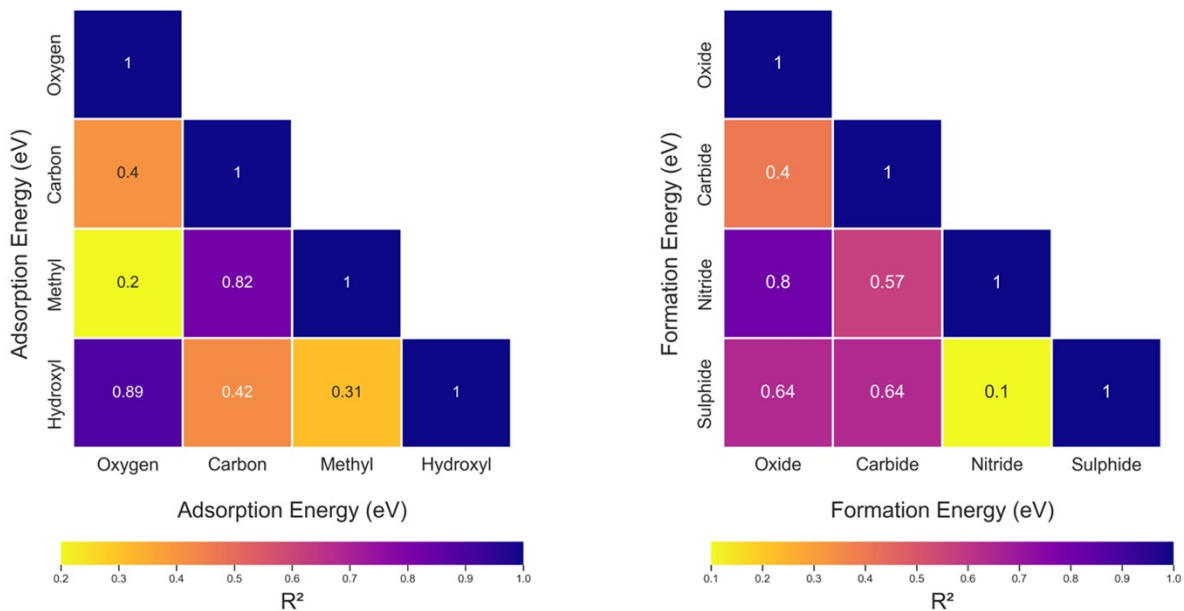


Figure S13 Correlation matrices for adsorption energies and formation energies.

8. V_{as}^2 trends for alkali and alkaline-earth metals

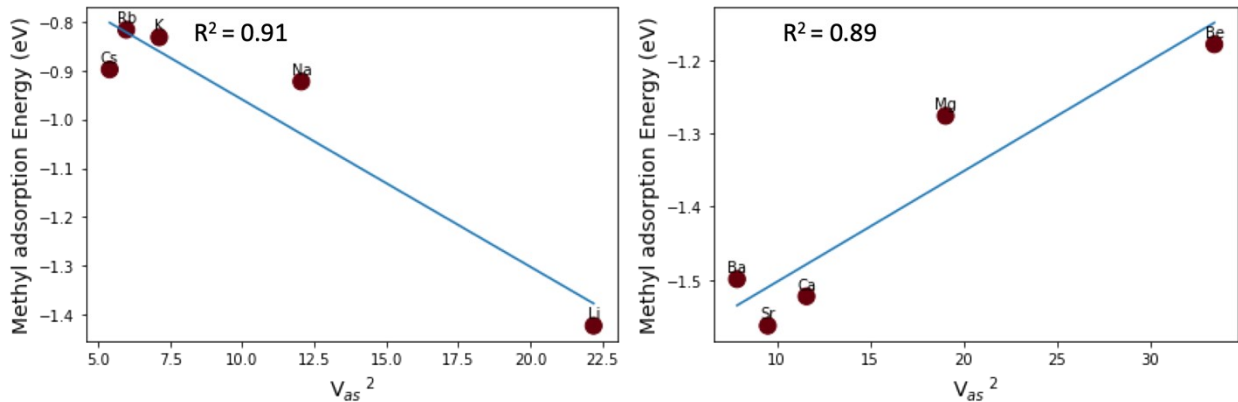


Figure S14 V_{as}^2 trends for alkali and alkaline-earth metals.

Reference:

- 1 K. A. Moltved and K. P. Kepp, *J. Phys. Chem. C*, 2019, **123**, 16.
- 2 K. P. Kepp, *Inorg. Chem*, 2016, **55**, 11.
- 3 M. M. Montemore and J. W. Medlin, *J. Am. Chem. Soc.*, 2014, **136**, 9272–9275.
- 4 M. M. Montemore and J. W. Medlin, *J. Phys. Chem. C*, 2014, **118**, 2666–2672.