

Electronic Supplementary Information

Electrocatalytic Nitrate Reduction by Rhodium Sulfide Compared to Pt and Rh in the Presence of Chloride

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S1 Electrochemically Active Surface Area Determination for Rh/C, Pt/C, and Rh_xS_y/C

All reported current densities are normalized to the electrochemically active surface area (ECSA) of the catalyst. For Rh and Pt, we estimate ECSA using hydrogen underpotential deposition (H_{upd}). The hydrogen adsorption or desorption charge is used with the known charge per metal surface.¹ For materials incapable of H_{upd} , such as non-Pt group metals or metal sulfides such as Rh_xS_y, currents often are normalized to geometric area. However, geometric surface area normalization is inappropriate for normalizing the activity of high surface area or porous materials such as nanoparticles or felts, which can have geometric surface areas that are orders of magnitude smaller than the ECSAs.

S1.1 Comparison of H_{upd} and Capacitance-based ECSA Models

Though two prior studies showed limited charge in the H_{upd} region for rhodium sulfide (Rh_xS_y),^{2,3} we did not detect H_{upd} peaks on Rh_xS_y/C (**Figure S1**). Therefore, the H_{upd} charge cannot be used to compare the Rh_xS_y/C activity with the activity of Pt/C and Rh/C. Instead, we measure the double-layer capacitance in the non-faradaic region to determine the total surface area (catalyst plus carbon support) using a specific capacitance which is then used to estimate the surface area of the Rh_xS_y nanoparticles.⁴ The nanoparticles are modeled as a cube with five exposed sides and one side in contact with the carbon support. X-ray diffraction (XRD) is used to measure the average crystallite size of the particles and this value is used as the cube side length (see **Section S1.2** for XRD analysis).⁵ We refer to this method as the "capacitance & XRD" method. This method accounts for variations in the amount of catalyst deposited onto the glassy carbon disk from run to run and allows us to compare Rh_xS_y/C to Rh/C and Pt/C on an even basis.

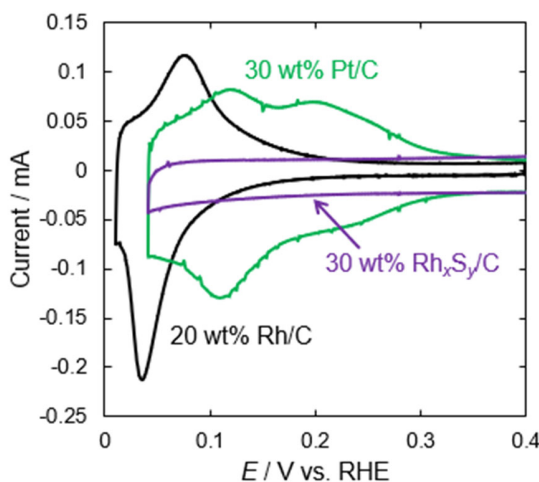


Figure S1. Hydrogen underpotential deposition currents for 30 wt% Pt/C in 1 M HClO₄ and 20 wt% Rh/C and 30 wt% Rh_xS_y/C in 1 M H₂SO₄. All measurements taken in de-aerated solution under a N₂ blanket. The scan rate was 50 mV s⁻¹ for each material. A Pt wire counter electrode and Ag/AgCl reference electrode were used.

An example calculation using the capacitance & XRD method is shown below for Pt/C deposited onto glassy carbon:

$$\text{ECSA}_{\text{cap\&XRD}} (\text{Pt}) = \text{Capacitance} \times \frac{1 \text{ cm}^2}{20 \text{ } \mu\text{F}} \times \frac{1 \text{ m}^2}{10^4 \text{ cm}^2} \times \frac{1 \text{ g}_{\text{cat}}}{250 \text{ m}^2} \times \frac{0.3 \text{ g}_{\text{Pt}}}{1 \text{ g}_{\text{cat}}} \\ \times \frac{1 \text{ cm}^3}{21.45 \text{ g}_{\text{Pt}}} \times \frac{10^{21} \text{ nm}^3}{1 \text{ cm}^3} \times \frac{5(2.2 \text{ nm})^2}{(2.2 \text{ nm})^3} \quad (\text{S1})$$

where the capacitance is the total capacitance of the deposited catalyst and carbon support in μF . The specific capacitance of the Vulcan XC-72 carbon support is approximated as $20 \text{ } \mu\text{F cm}^{-2}$,⁶ the mass per area of Vulcan XC-72 carbon is $250 \text{ m}^2 \text{ g}^{-1}$, the metal loading is 30 wt% of Pt on Vulcan carbon, the density of Pt is 21.45 g cm^{-3} , and each nanoparticle is approximated as a cube with five faces showing and side lengths equal to the average size of the nanoparticle as determined by XRD (2.2 nm). If for a particular deposition of a sample there is, for example, 10% more catalyst exposed to the electrolyte, the capacitance will be 10% higher, and will be normalized out by this method.

The average ECSAs of Rh/C and Pt/C, and $\text{Rh}_x\text{S}_y/\text{C}$ from the geometric area, H_{upd} , and capacitance & XRD method are shown in **Table S1**. These averages are determined from the ECSA values from ink depositions used for steady-state NO_3RR current measurements in **Figure 1** of the main text. The ECSA values for Pt/C and Rh/C through the H_{upd} and capacitance & XRD method are similar, and both 5–9 times larger than the geometric area, highlighting both the importance of measuring ECSA and the relative accuracy of the capacitance & XRD technique.

Table S1. Geometric area, H_{upd} ECSA, crystallite size from the Scherrer equation analysis of XRD, and capacitance & XRD ECSA for Rh/C, Pt/C, and $\text{Rh}_x\text{S}_y/\text{C}$ supported nanoparticles. The projected area of the glassy carbon rotating disk was used for the geometric area. The difference in ECSA methods is calculated by subtracting the capacitance & XRD ECSA by the H_{upd} ECSA and normalizing to the H_{upd} ECSA for each ink deposition.

Catalyst	Geometric Area (cm^2)	H_{upd} ECSA (cm^2)	XRD Crystallite Size (nm)	Capacitance & XRD ECSA (cm^2)	(H_{upd} ECSA – Capacitance & XRD ECSA)/ H_{upd} ECSA
Rh/C	0.196	1.02 ± 0.10	2.3 ± 0.4	1.56 ± 0.43	–0.53
Pt/C	0.196	1.47 ± 0.21	2.2 ± 0.1	1.74 ± 0.24	–0.18
$\text{Rh}_x\text{S}_y/\text{C}$	0.196	N/A	12	1.02 ± 0.11	N/A

No observable H_{upd} charge for $\text{Rh}_x\text{S}_y/\text{C}$ in **Figure S1** suggests that the $\text{Rh}_x\text{S}_y/\text{C}$ is not simply reduced to form metallic Rh/C. The ECSA of $\text{Rh}_x\text{S}_y/\text{C}$ for the samples is comparable to that of Rh/C (**Table S1**). Based on the similar ECSA, if $\text{Rh}_x\text{S}_y/\text{C}$ was metallic Rh under reaction conditions, the H_{upd} current would be visible.

S1.2 X-Ray Diffraction of $\text{Rh}_x\text{S}_y/\text{C}$, Pt/C, and Rh/C for Crystallite Sizes

X-ray powder diffraction was used to estimate the crystallite sizes of Rh/C, Pt/C, and $\text{Rh}_x\text{S}_y/\text{C}$. The diffraction patterns are shown in **Figure S2**. The powder XRD patterns were collected using a PANalytical Empyrean diffractometer operating at 45 kV and 40 mA ranging from 10° to 90° for Rh/C and $\text{Rh}_x\text{S}_y/\text{C}$ and 30° to 90° for Pt/C with a 0.008° step size. No metallic Rh is observed in the $\text{Rh}_x\text{S}_y/\text{C}$ sample, in agreement with our cyclic voltammetry results. The Scherrer equation was used to determine the mean crystallite size τ in nm:

$$\tau = \frac{K\lambda}{\beta \cos(\theta)} \quad (\text{S2})$$

where K is the shape factor (0.9), λ is the X-ray wavelength (Cu K- α has a wavelength of 0.15405 nm), β is the line broadening at the full width half max of the peak in radians, and θ is the Bragg angle of the peak in radians.

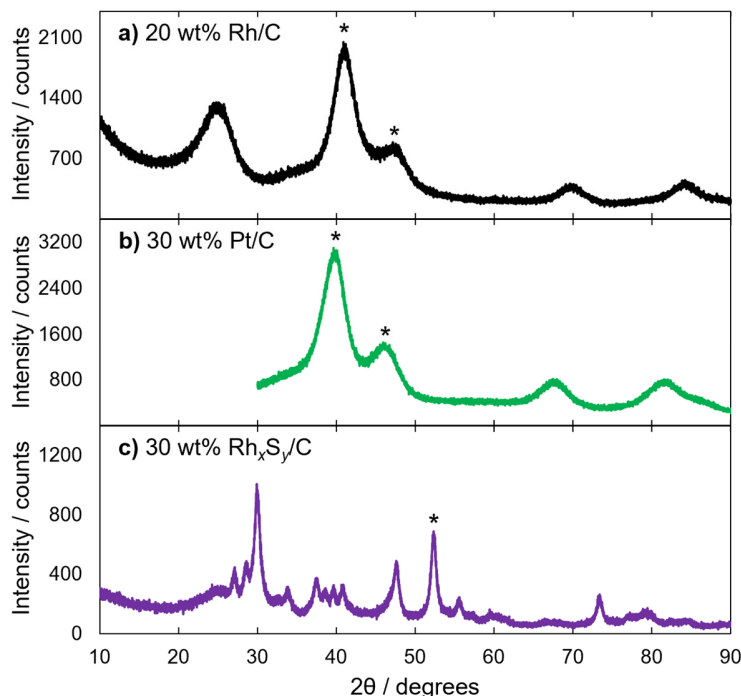


Figure S2. XRD spectra of a) 20 wt% Rh/C, b) 30 wt% Pt/C, and c) 30 wt% Rh_xS_y/C. Peaks used for estimating the crystallite sizes are marked (*).

The average crystallite size from the two highest intensity diffraction peaks for Rh and Pt is taken as the catalyst's approximate particle size. The Rh/C particle size is 2.3 ± 0.4 nm approximated from the (111) peak at 41° and (200) peak at 47° . The Pt/C particle size is 2.2 ± 0.1 nm using the (111) peak at 40° and (200) peak at 46° . The standard deviation reported is from the particle sizes from the two peaks. The Rh_xS_y/C particle size is 12 nm approximated from the peak at 52° .

S1.3 Transmission Electron Microscopy for Particle Size Distribution

Transmission electron microscopy (TEM) was used to find the particle size distribution for 30 wt% Rh_xS_y/C and 20 wt % Rh/C. TEM was performed on a JOEL 2010F electron microscope operating with 200 kV accelerating voltage. Samples were prepared by dispersing a small amount of catalyst powder in Millipore water and dropping on a gold grid. TEM images for Rh_xS_y/C are shown in **Figure S3**. TEM images for the 20 wt% Rh/C are included in ref. ⁷. Since we normalize the Rh/C activity to the ECSA measured using H_{upd} , the accuracy of the particle size from the XRD crystallites does not affect the reported current density. For Rh_xS_y/C, we normalize the currents to the ECSA estimated using the XRD crystallite size, but could also use the particle sizes from TEM. If we use the average particle size from TEM micrographs (9.8 nm, **Figure S3**) instead of from XRD (12 nm), the calculated ECSA would increase by $< 20\%$ and decrease the reported current density accordingly. Though the Rh_xS_y/C activity would decrease as a result of using this TEM particle size, Rh_xS_y/C would still be more active than Rh/C. However, when trying to estimate the total

number of surface sites from a distribution of particle sizes, it is more accurate to weight each nanoparticle by the number of atoms present, rather than weighting a small and large nanoparticle equally.

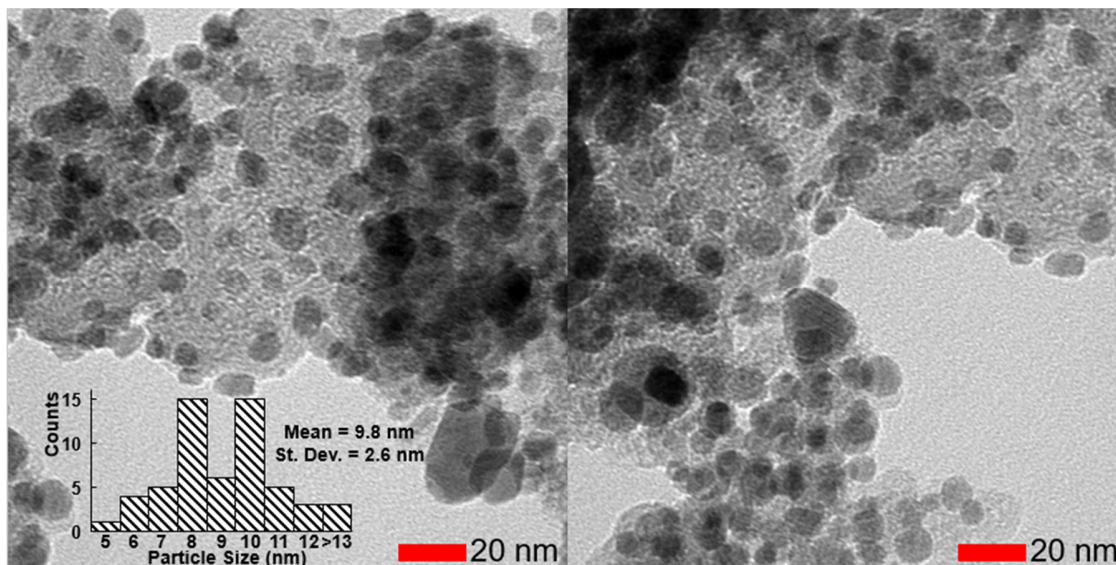


Figure S3. Particle size distribution from TEM for 30 wt% Rh_xS_y/C from three micrographs (two shown here). The red scale bar indicates 20 nm in the micrograph. Histogram bins: [5,6], (6,7], (7,8], (8,9], (9,10], (10,11], (11,12], (12,13], >13.

S2 Analysis of Electrolyte and Rotation Rate Effects for NO₃RR on Rh/C and Rh_xS_y/C in 1 M HNO₃

In the main text, nitrate reduction measurements on Rh/C and Rh_xS_y/C were taken with sodium nitrate added to sulfuric acid (1 M H₂SO₄ + 1 M NaNO₃) to distinguish the background current (H₂SO₄ only) from the nitrate reduction current (**Figure 1** and **Figure S22**) and to measure the ECSA in the supporting electrolyte more accurately. We also measure considerable reduction currents on Rh_xS_y/C and Rh/C in 1 M HNO₃ (**Figure S4**), but because we are unable to measure a background current nor measure the ECSA in the supporting electrolyte of interest, we do not focus on pure nitric acid electrolyte in the main text. At 2500 rpm, the reduction currents on both Rh_xS_y/C and Rh/C are more negative in 1 M HNO₃ (**Figure S4**) than in 1 M H₂SO₄ + 1 M NaNO₃ (**Figure 1**) which could be due to unwanted surface interactions (site blocking) of spectator ions (Na⁺, HSO₄⁻, SO₄⁻), faster kinetics of nitrate reduction from nitric acid compared to the nitrate anion, issues with the inability to subtract the background current, or inaccuracies in the surface area measurements. In 1 M HNO₃, the ECSAs were measured in a separate electrolyte and then the electrode was transferred to 1 M HNO₃ for kinetic measurements, rather than adding sodium nitrate without moving the electrode as explained in the main text.

When adding chloride to the nitric acid solution, the current density decreased (open diamonds in **Figure S4**), similar to the effect observed in the sulfuric acid with sodium nitrate in **Figure 1**. Though the NO₃RR currents are greater for both Rh/C and Rh_xS_y/C in 1 M HNO₃ than in 1 M H₂SO₄ + 1 M NaNO₃, when 1 mM chloride is added the current densities become approximately the same in both electrolytes. This is rationalized by similar site blocking of chloride in both solutions. For NO₃RR in 1 M H₂SO₄ + 1 M NaNO₃ at 0.1 V vs. RHE, there may be site blocking by spectator anions and when chloride is added to the solution, the chloride will adsorb to the surface and block additional sites and displace the more weakly bound ions. In 1 M HNO₃, there are no spectator ions to occupy sites until chloride is added. On these

surfaces it makes sense that once a strongly bound anion like chloride is added to solution there would be similar site blocking for this surface reaction.

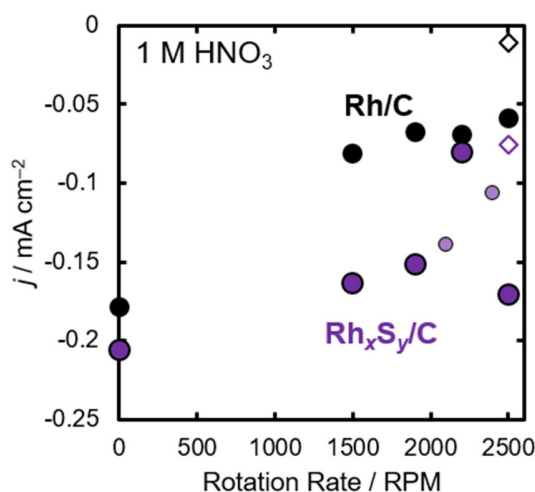


Figure S4. NO₃RR on Rh/C (black circles) and Rh_xS_y/C (purple circles) in 1 M HNO₃ at 0.1 V vs. RHE at various rotation rates. The data points shown are averages of two individual measurements which were each taken following the procedure in Section 2.3 of the main text. Open diamonds represent the current density after 1 mM chloride was added. Smaller, light purple circles represent individual measurements on Rh_xS_y/C.

The rotation rate was observed to affect the current density of nitrate reduction at 0.1 V vs. RHE in 1 M HNO₃ (**Figure S4**) and 1 M H₂SO₄ + 1 M NaNO₃ on Rh/C and Rh_xS_y/C. The rotation rate effects for NO₃RR on Pt/C were not distinguishable from overall measurement error. For both Rh/C and Rh_xS_y/C, the current densities at 0 rpm were more negative (higher rates) than at 2500 rpm. At low rotation rates the local surface concentration of nitrate will be lower than in the bulk due to the reaction at the electrode surface depleting nitrate, and higher rotation rates will minimize this concentration gradient. Although typically a lower concentration of the reactant at the surface reduces the reaction rate, we see the opposite effect here. We attribute this to a negative reaction order in nitrate at 1 M nitrate. At high concentrations of nitrate (>0.1 M), on Pt the reaction order is less than 0 for nitrate meaning that the reaction would be faster when nitrate concentrations are lower.⁸ As Rh adsorbs nitrate more strongly than Pt, we believe this to be the case here as well. Thus, greater reduction current at low rotation rates could be due to the decrease in the local concentration of nitrate near the electrode surface, causing an increase in the rate for Rh/C and Rh_xS_y/C. In the main text, we report current densities at 2500 rpm because, though it is not the rotation rate with the most negative NO₃RR current at 0.1 V, it is the rotation rate where the concentration of species at the surface most closely matches the bulk solution.

S3 Detection of Nitrate, Nitrite, and Ammonium

Nitrate (NO₃⁻)

For NO₃⁻, 10 μL from the aliquot at each time point was diluted to 3 mL with Millipore water then 1 mL of that solution was further diluted to 3 mL. The absorbance was detected at 220 nm and compared to a nitric acid calibration (**Figure S5a**).

Nitrite (NO₂⁻)

For NO_2^- , a color reagent was prepared by adding 100 mL of 85% H_3PO_4 (85%, ACROS Organics) and 10 g sulfanilamide ($\geq 98\%$, Fisher Chemical) to 800 mL of distilled water. 1 g N-(1-naphthyl)-ethylenediamine dihydrochloride ($\geq 98\%$, Sigma Aldrich) was added to the color reagent solution, mixed, and diluted to 1 L. 0.3 mL from aliquots at each time point were adjusted to a pH of 7 using 1 M NaOH and then diluted to 1 mL with Millipore water. 0.04 mL of the prepared color reagent was added to the aliquot dilution, mixed, and left covered for 30 minutes. The absorbance for nitrite was measured at 543 nm and compared to sodium nitrite standards in 0.1 M HNO_3 (**Figure S5b**).

Ammonium (NH_4^+)

For NH_4^+ quantification, a 0.25 mL aliquot from each time point was pH adjusted by adding 1 M NaOH solution until pH 12 was reached and diluted to 1 mL using Millipore water. 122 μL of 5 wt% sodium salicylate solution (99.5%, Sigma Life Science), 27.3 μL of 1 wt% sodium nitroprusside dihydrate ($\geq 99\%$, Sigma-Aldrich), and 40 μL of sodium hypochlorite solution (4–4.99%, Sigma-Aldrich) were added to the diluted aliquot sequentially, stirred, and left covered for 40 minutes. The NH_4^+ peak appeared around 650 nm and concentrations were determined using a calibration curve prepared from ammonium chloride calibration standards in 0.1 M HNO_3 (**Figure S5c**).

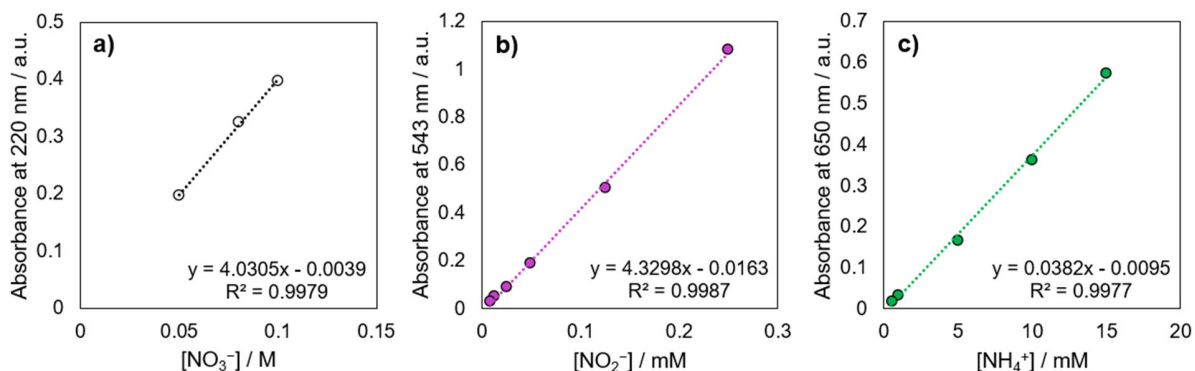


Figure S5. UV-Vis absorbance calibration curves prepared for quantifying a) nitrate, b) nitrite, and c) ammonium. The nitrate calibration curve is for a set of standards prepared by diluting 0.1 M HNO_3 . The nitrite calibration curve was prepared by diluting 25 mM NaNO_2 (with a background of 0.1 M HNO_3). The ammonium calibration curve was prepared by diluting 15 mM NH_4Cl (with a background of 0.1 M HNO_3). For NO_2^- and NH_4^+ , a baseline measurement of only 0.1 M HNO_3 was subtracted from the absorbance measurements.

The faradaic efficiency was calculated by taking the number of moles of ammonia produced multiplied by 8 moles of electrons per mole of ammonia, multiplying by Faraday's constant, and dividing by the total charge passed during the measurement.

S4 Calculating Adsorption Free Energies of NO_3^- , H^+ , and Cl^-

S4.1 Calculating the Gibbs Energy of NO_3^- Adsorption

The Gibbs energy of nitrate adsorption at 0 V vs. SHE ($\Delta G_{\text{NO}_3}(E = 0 \text{ V vs. SHE})$) was computed using a thermodynamic cycle to include solvation and temperature effects, while avoiding the explicit DFT calculation of a nitrate anion in the aqueous phase.^{9,10} For this correction, all tabulated values correspond to standard conditions (298.15 K, 1 bar). We use the generalized computational hydrogen electrode model

(CHE)¹¹ to compute the potential-dependent adsorption free energy of nitrate, ΔG_{NO_3} . The adsorption of nitrate to a catalyst surface is:



Figure S6 illustrates the thermodynamic cycle used to obtain ΔG_{NO_3} , which breaks the adsorption process into three steps:

- (1) The formation of liquid HNO_3 from its aqueous ion constituents, denoted as $\Delta G_{\text{assoc}}(\text{HNO}_3)$.
- (2) The vaporization of liquid HNO_3 to form gaseous HNO_3 , denoted as $\Delta G_{\text{vap}}(\text{HNO}_3)$.
- (3) The dissociative adsorption of gaseous HNO_3 to surface-adsorbed NO_3^* and $\frac{1}{2} \text{H}_2$ on a bare metal surface (in vacuum), denoted as $\Delta G_{\text{diss-ads}}(\text{NO}_3^*)$. At 0 V vs. SHE and pH = 0, $\frac{1}{2} \text{H}_2$ is equilibrated with aqueous $\text{H}^+ + \text{e}^-$.

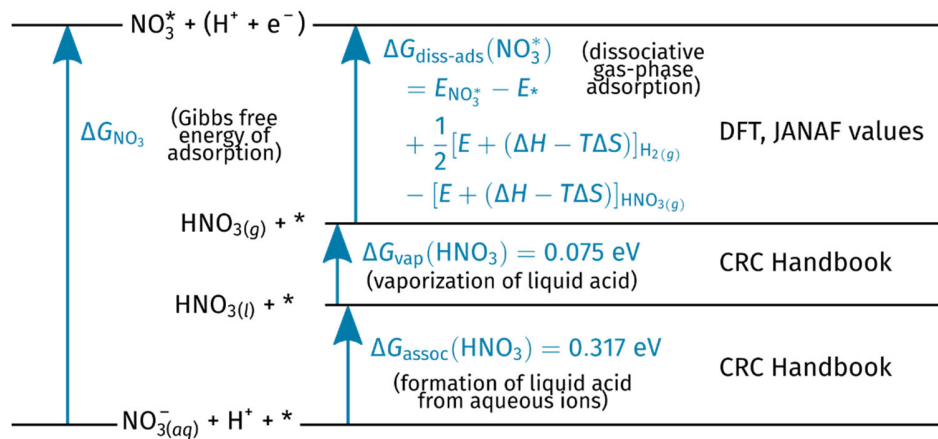


Figure S6. Thermodynamic cycle used for calculation of Gibbs energy of nitrate adsorption at 0 V vs. SHE. Adapted from Calle-Vallejo and coworkers.⁹ Values were retrieved from the CRC handbook¹² and the JANAF Thermochemical Tables.¹³ The Gibbs energies of formation needed to calculate $\Delta G_{\text{assoc}}(\text{HNO}_3)$ and $\Delta G_{\text{vap}}(\text{HNO}_3)$ are given in **Table Error! Reference source not found.**

Table S2. Gibbs energies of formation used to calculate $\Delta G_{\text{assoc}}(\text{HNO}_3)$ and $\Delta G_{\text{vap}}(\text{HNO}_3)$. Values taken from the CRC handbook.¹² Tabulated at 298.15 K and 1 bar.

Quantity	kJ mol ⁻¹	eV
$\Delta G_f(\text{H}_{(\text{aq})}^+)$	0.0	0.000
$\Delta G_f(\text{NO}_{3(\text{aq})}^-)$	-111.3	-1.153
$\Delta G_f(\text{HNO}_{3(\text{l})})$	-80.7	-0.836
$\Delta G_f(\text{HNO}_{3(\text{g})})$	-73.5	-0.762

The energy of forming $\text{HNO}_{3(\text{l})}$ from its aqueous ions is:

$$\begin{aligned} \Delta G_{\text{assoc}}(\text{HNO}_3) &= \Delta G_f(\text{HNO}_{3(\text{l})}) - \Delta G_f(\text{NO}_{3(\text{aq})}^-) - \Delta G_f(\text{H}_{(\text{aq})}^+) \\ &= -0.836 \text{ eV} - (-1.153 \text{ eV}) - 0 \text{ eV} = \boxed{0.317 \text{ eV}}. \end{aligned} \quad (\text{S4})$$

The energy required to vaporize $\text{HNO}_{3(l)}$ to $\text{HNO}_{3(g)}$ is:

$$\Delta G_{\text{vap}}(\text{HNO}_3) = \Delta G_f(\text{HNO}_{3(g)}) - \Delta G_f(\text{HNO}_{3(l)}) = -0.762 \text{ eV} - (-0.836 \text{ eV}) = \boxed{0.075 \text{ eV}}. \quad (\text{S5})$$

The term $\Delta G_{\text{diss-ads}}(\text{NO}_3^*)$ is defined as:

$$\begin{aligned} \Delta G_{\text{diss-ads}}(\text{NO}_3^*) = & E_{\text{NO}_3^*} + \frac{1}{2}(E_{\text{H}_2} + \Delta H_{\text{H}_2} - T\Delta S_{\text{H}_2})_{(g)} \\ & - E_* - (E_{\text{HNO}_3} + \Delta H_{\text{HNO}_3} - T\Delta S_{\text{HNO}_3})_{(g)} \end{aligned} \quad (\text{S6})$$

where E_i denotes a DFT-computed electronic energy and ΔH_i and ΔS_i represents enthalpic and entropic ideal-gas corrections (**Table S3**), respectively, required to convert the electronic energies of the gaseous species i to standard conditions. Ultimately, the Gibbs energy of nitrate adsorption is:

$$\Delta G_{\text{NO}_3}(E = 0 \text{ V}) = \Delta G_{\text{diss-ads}}(\text{NO}_3^*) + \Delta G_{\text{vap}}(\text{HNO}_3) + \Delta G_{\text{assoc}}(\text{HNO}_3) \quad (\text{S7})$$

The Gibbs energy of nitrate adsorption as a function of applied potential E (vs. SHE) within the CHE framework is:¹⁰

$$\Delta G_{\text{NO}_3} = \Delta G_{\text{NO}_3}(E = 0 \text{ V}) - FE \quad (\text{S8})$$

Table S3. Thermodynamic parameters used to correct gas-phase molecular DFT energies, taken from the JANAF thermodynamic tables.¹³ All parameters are with respect to the reference state $T_{\text{ref}} = 298.15 \text{ K}$ and $P = 1 \text{ bar}$.

Quantity	$\text{H}_2(g)$	$\text{HNO}_{3(g)}$	$\text{Cl}_2(g)$
T	298.15 K	298.15 K	298.15 K
$H(T)$	0.000 kJ/mol	0.000 kJ/mol	0.000 kJ/mol
$H(0 \text{ K})$	-8.467 kJ/mol	-11.780 kJ/mol	-9.181 kJ/mol
$S(T)$	130.680 J/mol-K	266.400 J/mol-K	223.079 J/mol-K
$S(0 \text{ K})$	0.000 J/mol-K	0.000 J/mol-K	0.000 J/mol-K
$\Delta H - T\Delta S$ (kJ/mol)	-30.495 kJ/mol	-67.647 kJ/mol	-57.330 kJ/mol
$\Delta H - T\Delta S$ (eV)	-0.316 eV	-0.701 eV	-0.594 eV

S4.2 Dependence of Adsorption Gibbs Energies of Cl^- and H^+ on Applied Potential

The generalized CHE model was used to model the effect of applied potential on the adsorption free energies of Cl^* and H^* .¹⁴ This model gives a thermodynamic approximation of the change in adsorption free energy that occurs in the aqueous phase at an applied potential compared to the gaseous phase with no applied potential. At standard conditions, H_2 molecules at the surface of the solution are in equilibrium with dissolved protons and electrons at the Fermi level of the metal electrode.¹⁵

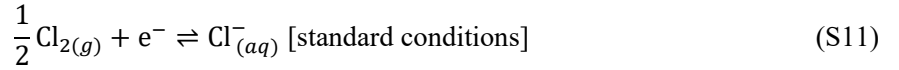
$$\frac{1}{2}\text{H}_{2(g)} \rightleftharpoons \text{H}_{(aq)}^+ + \text{e}^- [\text{standard conditions}] \quad (\text{S9})$$

At equilibrium, the Gibbs energies of the species are related by a reaction quotient and a potential shift:

$$\begin{aligned}
G_{\text{H}^+} + G_{\text{e}^-} &= \frac{1}{2} G_{\text{H}_2(g)} + RT \ln \left[\frac{a_{\text{H}^+} a_{\text{e}^-}}{\sqrt{a_{\text{H}_2}}} \right] - nF(E - E^\circ(\text{H}_2)) \\
&= \frac{1}{2} G_{\text{H}_2(g)} - RT \ln 10 (\text{pH}) - nF(E - 0 \text{ V vs. SHE})
\end{aligned} \tag{S10}$$

where G_i is the Gibbs energy of species i and a_i is the dimensionless thermodynamic activity. These activities are referenced to a concentration of 1 mol/L (for protons this implies pH = 0) and 1 bar (for gaseous species). E is the applied cell potential, $E^\circ(\text{H}_2) = 0 \text{ V vs. SHE}$ is the standard redox potential for the $\frac{1}{2} \text{H}_2(g) \rightleftharpoons \text{H}_{(aq)}^+ + \text{e}^-$ equilibrium, and n is the number of electrons transferred. Here, we have assumed activity coefficients of unity, and $n = +1$ for proton reduction.

The formalism for the CHE model is intuitively extended to other aqueous adsorbates formed from dissociation of a gaseous dimer.¹⁵ For the adsorption of Cl^- , the pertinent equilibrium reaction is:



and the corresponding shift in Gibbs energy is given by:

$$\begin{aligned}
G_{\text{Cl}^-} - G_{\text{e}^-} &= \frac{1}{2} G_{\text{Cl}_{2(g)}} + RT \ln \left[\frac{a_{\text{Cl}^-}}{a_{\text{e}^-} \sqrt{a_{\text{Cl}_2}}} \right] - nF(E - E^\circ(\text{Cl}_2)) \\
&= \frac{1}{2} G_{\text{Cl}_{2(g)}} - RT \ln a_{\text{Cl}^-} - nF(E - 1.36 \text{ V})
\end{aligned} \tag{S12}$$

where we again assume activity coefficients of unity, but here $n = -1$ and we use the reduction potential of the chlorine redox couple, $E^\circ(\text{Cl}_2) = 1.36 \text{ V vs. SHE}$.

Using the CHE, the adsorption free energy of hydrogen (ΔG_{H}) as a function of potential to a site $*$ at pH = 0 is:

$$\Delta G_{\text{H}} = G_{\text{H}^*} - G_* - \frac{1}{2} G_{\text{H}_2(g)} + FE = \Delta G_{\text{H}}(E = 0 \text{ V}) + FE \tag{S13}$$

$$\Delta G_{\text{H}} \approx [E_{\text{H}^*} + \Delta \text{ZPE}_{\text{H}^*}] - E_* - \frac{1}{2} G_{\text{H}_2(g)} + FE \tag{S14}$$

where $\Delta \text{ZPE}_{\text{H}^*}$ is the zero-point energy correction for H adsorbed on the surface, and where we have assumed that the enthalpic and entropic contributions to the Gibbs energy of adsorbed H are small compared to those of gaseous H_2 . Also, the Gibbs energy of the bare slab is assumed to have negligible difference from the bare slab's electronic energy ($G_* \approx E_*$). The adsorption energy of Cl^- at $[\text{Cl}^-] = 1 \text{ mol/L}$ as a function of applied potential (ΔG_{Cl}) is modeled as:

$$\begin{aligned}
\Delta G_{\text{Cl}} &= G_{\text{Cl}^*} - G_* - \frac{1}{2} G_{\text{Cl}_{2(g)}} - F(E - E^\circ(\text{Cl}_2)) \\
&= E_{\text{Cl}^*} - E_* - \frac{1}{2} G_{\text{Cl}_{2(g)}} - F(E - 1.36 \text{ V}) = \Delta G_{\text{Cl}}(E = 0 \text{ V}) - FE
\end{aligned} \tag{S15}$$

where G_{Cl^*} is the Gibbs energy of adsorbed chloride. We neglect rotational and translational free energy contribution for adsorbed species and include zero-point corrections only for G_{H^*} , thus we assume that $G_{\text{Cl}^*} \approx E_{\text{Cl}^*}$. We did not treat solvation of metal surfaces or the Rh_xS_y surfaces with either explicit or implicit

solvation methods. We note that the JANAF thermochemical data for gas-phase species is based on available experimental data (such as spectroscopic constants).¹³

S5 DFT Benchmarking Tests

S5.1 Metal Surface Benchmarking

Several calculation parameters were benchmarked using a $p(3 \times 1)$ supercell of the Ag(211) surface, with a single N atom adsorbed at the middle surface atom (**Figure S7**). Benchmarking included altering DFT calculation parameters and geometric properties of the base slab model. The parameters tested include: (1) the plane-wave energy cutoff; (2) the k -point grid density; (3) the Gaussian smearing parameter σ ; (4) the surface cell size; (5) the total number of layers in the slab; (6) thickness of the vacuum layer in the z direction; (7) the effect of spin polarization; and (8) the choice of dipole corrections in the x , y , and z directions. Spin polarization was included for all calculations. Dipole corrections were converged only in the z direction for all calculations.

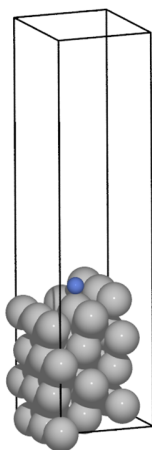


Figure S7. Prototype Ag(211) surface with a single adsorbed N atom used for metal surface benchmarking calculations.

The data in **Figure S8** shows benchmarking results for the cut-off parameters. Based on the results in **Figure S8a–f**, a plane-wave cutoff of 400 eV, a $6 \times 6 \times 1$ k -point grid, a Gaussian smearing constant of $\sigma = 0.05$ eV, and a vacuum thickness of 15 Å are chosen. These choices offer a balance between accuracy and computational tractability. Based on **Figure S8d–e**, there is no clear convergence pattern for the parameters tested. To keep the number of atoms in the supercell computationally tractable, $3 \times 4 \times 4$ FCC(211) supercells with four layers of atoms are chosen. To maintain consistency between metal and Rh_xS_y calculations, the settings identified via benchmarking on Ag(211) were used for both metal and Rh_xS_y surface calculations, except for the k -point grid, which was $3 \times 3 \times 1$ for Rh_xS_y surfaces.

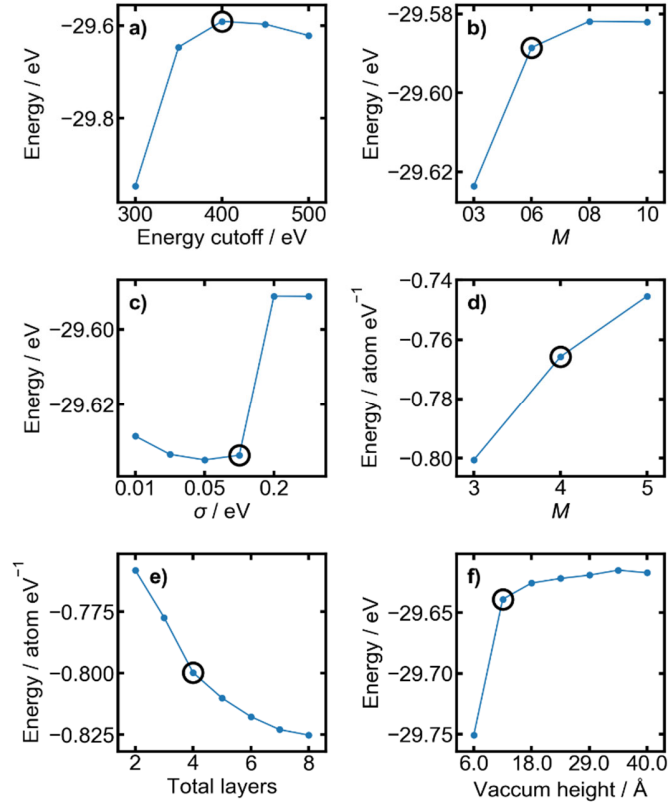


Figure S8. Benchmarking results on the Ag(211) surface (with the chosen setting indicated by a bold black circle) for a) the plane-wave energy cutoff; b) k -point grids of density $M \times M \times 1$, where M ranges from 3 to 10; c) the Gaussian smearing parameter σ , d) FCC(211) supercell sizes of $3 \cdot \text{floor}(M/3) \times M \times 4$, where M ranges from 3 to 5 and $\text{floor}(\cdot)$ rounds its argument down to the nearest integer; e) the total number of layers in the slab; and f) the thickness of the vacuum layer in the z direction.

S6 Selection of Stable Rh_xS_y Surface Terminations

The structures of Rh_2S_3 , Rh_3S_4 , and $\text{Rh}_{17}\text{S}_{15}$ phases are such that different surface terminations of a given facet result in different stoichiometries of atoms exposed to the surface. This leads to different surface chemistry depending on which termination is used for further calculations (**Figure S9**), unlike that of pure face-centered cubic (FCC) metals.

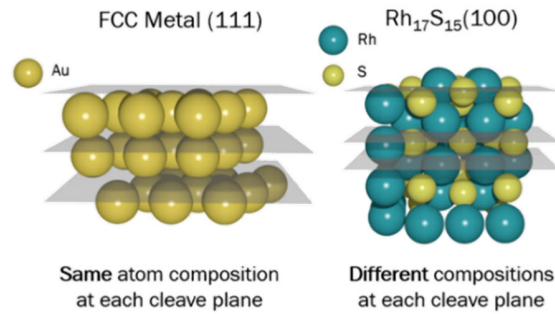


Figure S9. Comparison of termination cuts for an FCC(111) surface and a $\text{Rh}_{17}\text{S}_{15}$ (100) surface.

The stable surface terminations were searched by computing atom-normalized surface energies of symmetric surfaces for $\text{Rh}_2\text{S}_3(001)$, $\text{Rh}_3\text{S}_4(100)$, and $\text{Rh}_{17}\text{S}_{15}(100)$. The metric used for surface termination searching is an atom-normalized version of the normal surface energy metric for symmetric slabs:¹⁶

$$\frac{\gamma}{n_*} = \frac{1}{2A} \left(\frac{E_*}{n_*} - \frac{E_{\text{bulk}}}{n_{\text{bulk}}} \right) \quad (\text{S16})$$

where γ/n_* is the surface energy per surface atom, $2A$ is the combined geometric area of the top and bottom faces of the slab supercell, and E_*/n_* and $E_{\text{bulk}}/n_{\text{bulk}}$ are the DFT-predicted electronic energies per atom of the slab supercell and bulk primitive cell, respectively. Atom-normalized electronic energies were used for comparison because the bulk primitive has a fixed number of atoms, whereas the number of atoms in each generated termination may vary to keep the termination symmetric between the top and bottom surfaces. Thus, atom-normalized electronic energies yield a fairer comparison of which termination surface is lowest in energy relative to the bulk material. The $\frac{1}{2A}$ factor indicates calculation of a surface energy from a symmetric termination. Keeping both the top and bottom surfaces symmetric is a more accurate way to measure the cost of creating a surface from a bulk structure.¹⁷ The atom-normalized surface energies and the minimum-energy surface terminations appear in **Figure S10**.

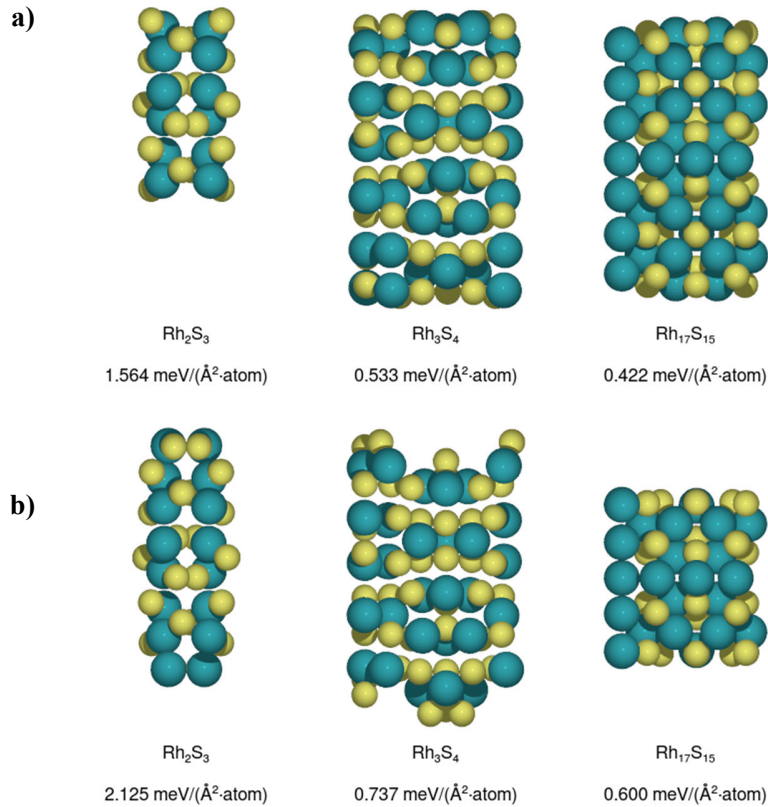


Figure S10. Side views of the three Rh_xS_y facets ($\text{Rh}_2\text{S}_3(001)$, $\text{Rh}_3\text{S}_4(100)$, and $\text{Rh}_{17}\text{S}_{15}(100)$) studied. a) The most stable predicted surface terminations. b) The second most stable predicted surface terminations. The corresponding surface energies are given. Color legend: Teal = Rh; Yellow = S.

S7 DFT-Predicted Geometries

S7.1 Bulk cell dimensions

Table S4 shows the lattice constants and cell angles of the sulfide and Pt bulk structures used to derive catalyst surfaces. Lattice constant calculation was done using a $10 \times 10 \times 10$ k point grid for Pt (FCC) and a $4 \times 4 \times 4$ k point grid for the sulfide crystals, in accordance with a $k_1a \approx k_2b \approx k_3c \geq 24$ rule of thumb.

Table S4. Lattice constants (Å) and cell angles (degrees) for each of the bulk structures used in the study.

Composition	a	b	c	α	β	γ
Rh ₂ S ₃	6.085	6.242	8.617	90.000	90.000	90.000
Rh ₃ S ₄	10.564	10.958	6.352	90.000	107.978	90.000
Rh ₁₇ S ₁₅	10.085	10.085	10.085	90.000	90.000	90.000
Pt (FCC)	4.002	—	—	90.000	90.000	90.000

S7.2 Sampling of adsorption sites on transition metal surfaces

For both the transition metal and Rh sulfide surfaces, we extensively sampled the surface for possible adsorption sites. We used the AdsorbateSiteFinder module within the Pymatgen Python library to enumerate all possible single adsorption sites (for H⁺ and Cl⁻ adsorbates) and all nearby pairs of single adsorption sites (for NO₃⁻).

For the six transition metal catalysts consider (Au, Ag, Cu, Pd, Pt, and Rh), we used the FCC(211) step surface. We chose this surface based on our previous computational work, which showed that a microkinetic model for nitrate reduction built on data from FCC(211) step surfaces successfully reproduced key experimental trends.¹⁰ This shows that the choice of the FCC(211) surface is a valid one for obtaining computational data that mirrors experimental results. Although previous literature has identified step surfaces as more active than terrace surfaces,^{9,18} we extensively sampled adsorption energies on symmetrically distinct adsorption sites on this surface to ensure that we calculated binding energies at the most active site on the FCC(211) surface. These sites are shown in **Figure S11**.

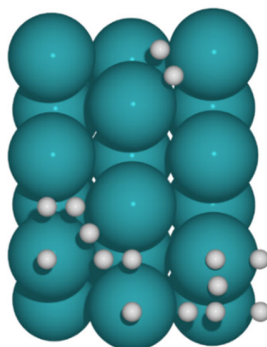


Figure S11. Location of adsorption sites sampled on metal FCC(211) surfaces. Atom key: teal = metal, white = adsorption site.

S7.3 Adsorption Energies and Predicted Binding Geometries

Figure S12 shows the adsorption site geometries of the strongest predicted free energy for Cl^- , H^+ , and NO_3^- on Rh_xS_y model surfaces. The predicted hydrogen adsorption energies for $\text{Rh}_2\text{S}_3(001)$, $\text{Rh}_3\text{S}_4(100)$, and $\text{Rh}_{17}\text{S}_{15}(100)$ agree well with a prior study.¹⁹ We show the adsorption sites geometries for the strongest predicted free energy for Cl^- , H^+ , and NO_3^- on S-defected Rh_xS_y model surfaces in **Figure S13**.

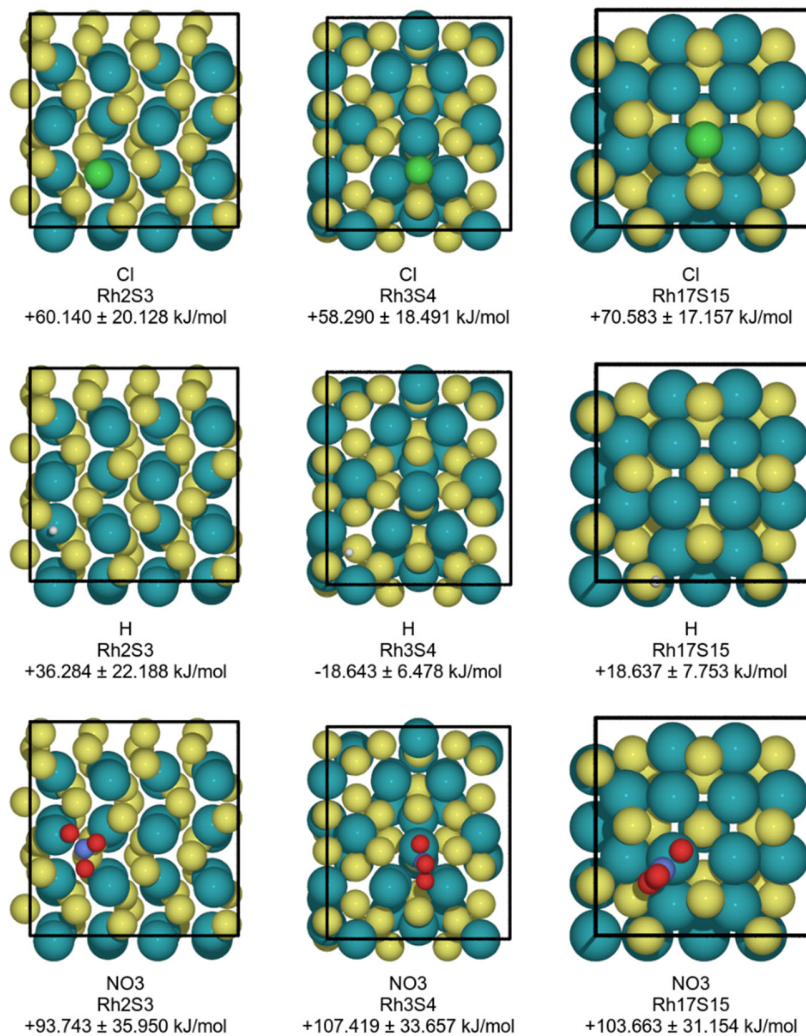


Figure S12. Adsorption sites where Cl^- , H^+ , and NO_3^- bind the strongest on pristine Rh_xS_y facets ($\text{Rh}_2\text{S}_3(001)$, $\text{Rh}_3\text{S}_4(100)$, and $\text{Rh}_{17}\text{S}_{15}(100)$). The caption underneath each image indicates the adsorbate, the bulk composition of the Rh_xS_y slab, and the electronic binding energy with its BEEF-vdW uncertainty in kJ mol^{-1} calculated at 298.15 K and 0 V vs. SHE. Teal = Rh, yellow = S, green = Cl, white = H, red = O, indigo = N.

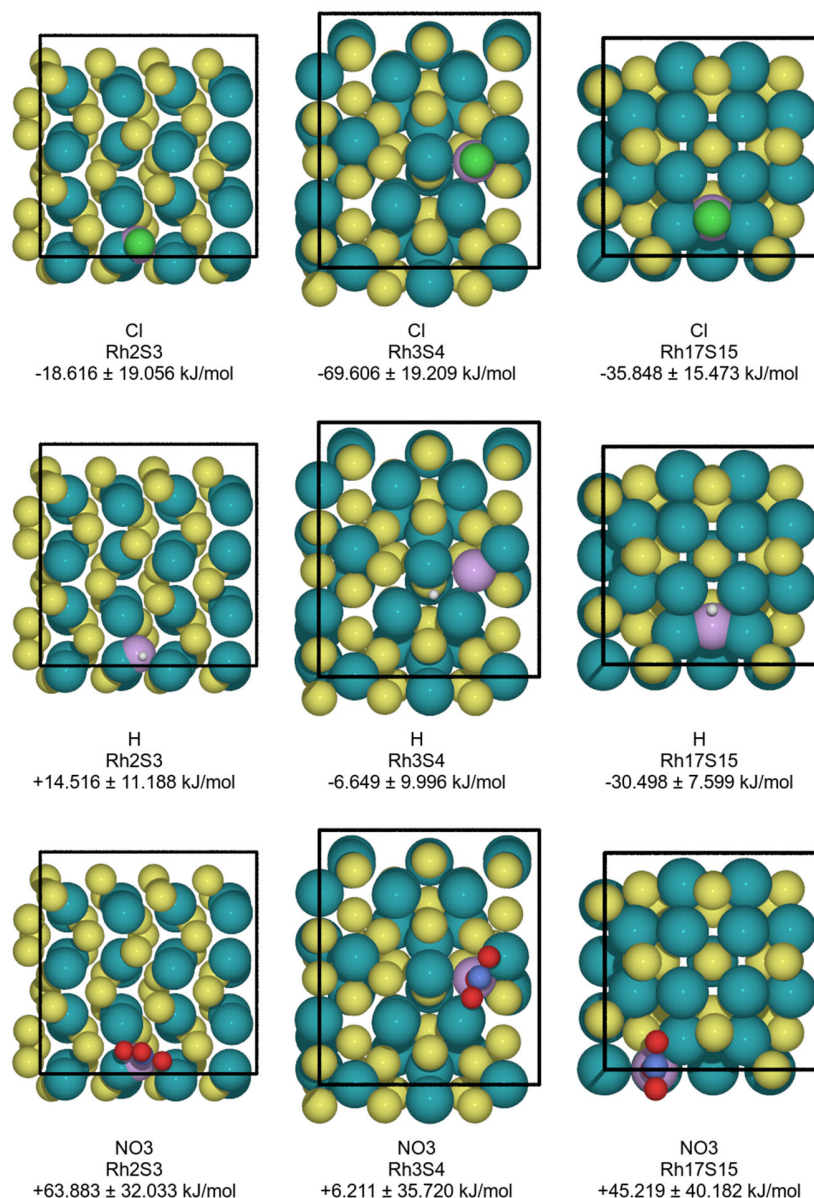


Figure S13. Adsorption sites where Cl^- , H^+ , and NO_3^- bind the strongest on S-defected Rh_xS_y facets ($\text{Rh}_2\text{S}_3(001)$, $\text{Rh}_3\text{S}_4(100)$, and $\text{Rh}_{17}\text{S}_{15}(100)$). The caption underneath each image indicates the adsorbate, the bulk composition of the Rh_xS_y slab, and the electronic binding energy with its BEEF-vdW uncertainty in kJ mol^{-1} calculated at 298.15 K and 0 V vs. SHE and pH = 0. Teal = Rh, yellow = S, green = Cl, white = H, red = N, indigo = O, purple = S defect location.

S7.4 Transition State Geometries

The initial, transition state, and final geometries for $\text{NO}_3^* \rightarrow \text{NO}_2^* + \text{O}^*$ and $\text{NO}_3^* + \text{H}^* \rightarrow \text{HNO}_3^* \rightarrow \text{NO}_2^* + \text{HO}^*$ nudged elastic band calculations appear in **Figures S14–S17**.

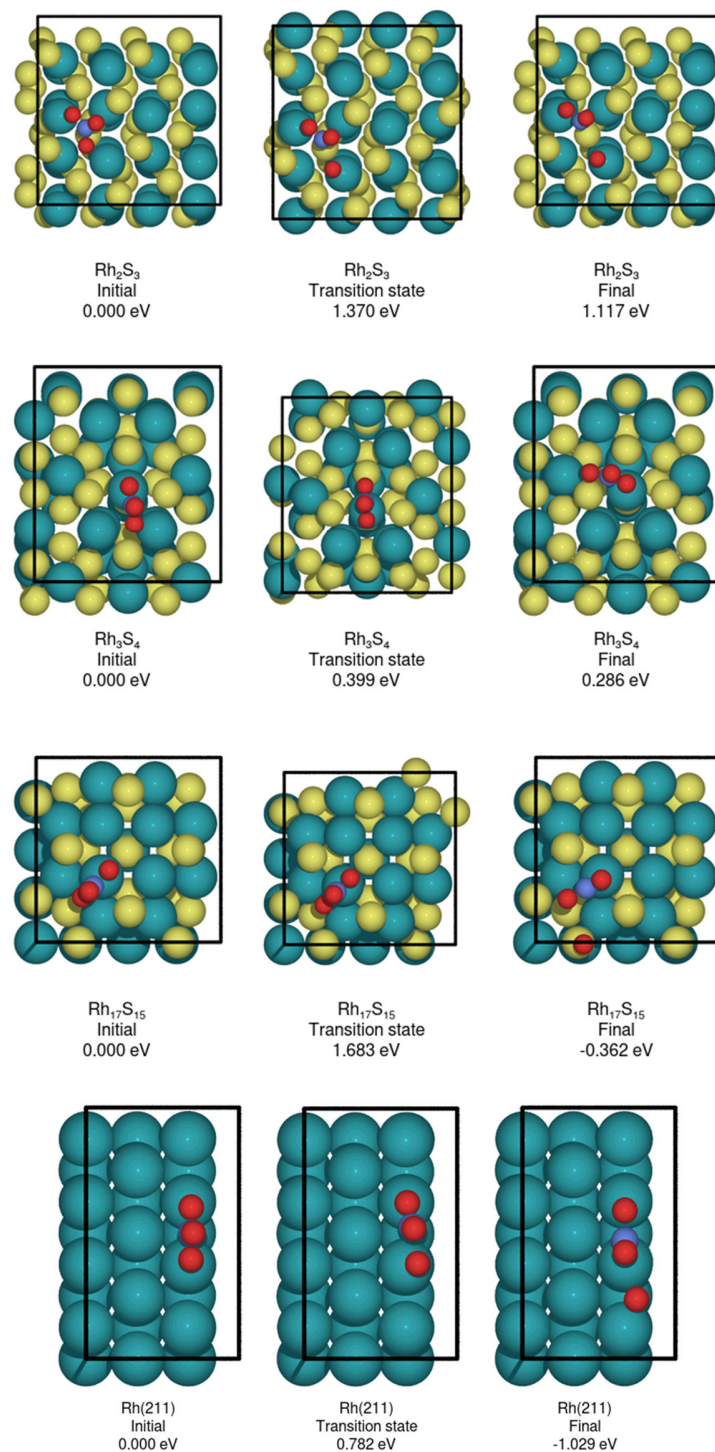


Figure S14. Initial, transition state, and final geometries for direct nitrate reduction ($\text{NO}_3^* \rightarrow \text{NO}_2^* + \text{O}^*$) on $\text{Rh}_2\text{S}_3(001)$, $\text{Rh}_3\text{S}_4(100)$, $\text{Rh}_{17}\text{S}_{15}(100)_y$, and $\text{Rh}(211)$ surfaces. Energies are relative to the initial state for each surface.

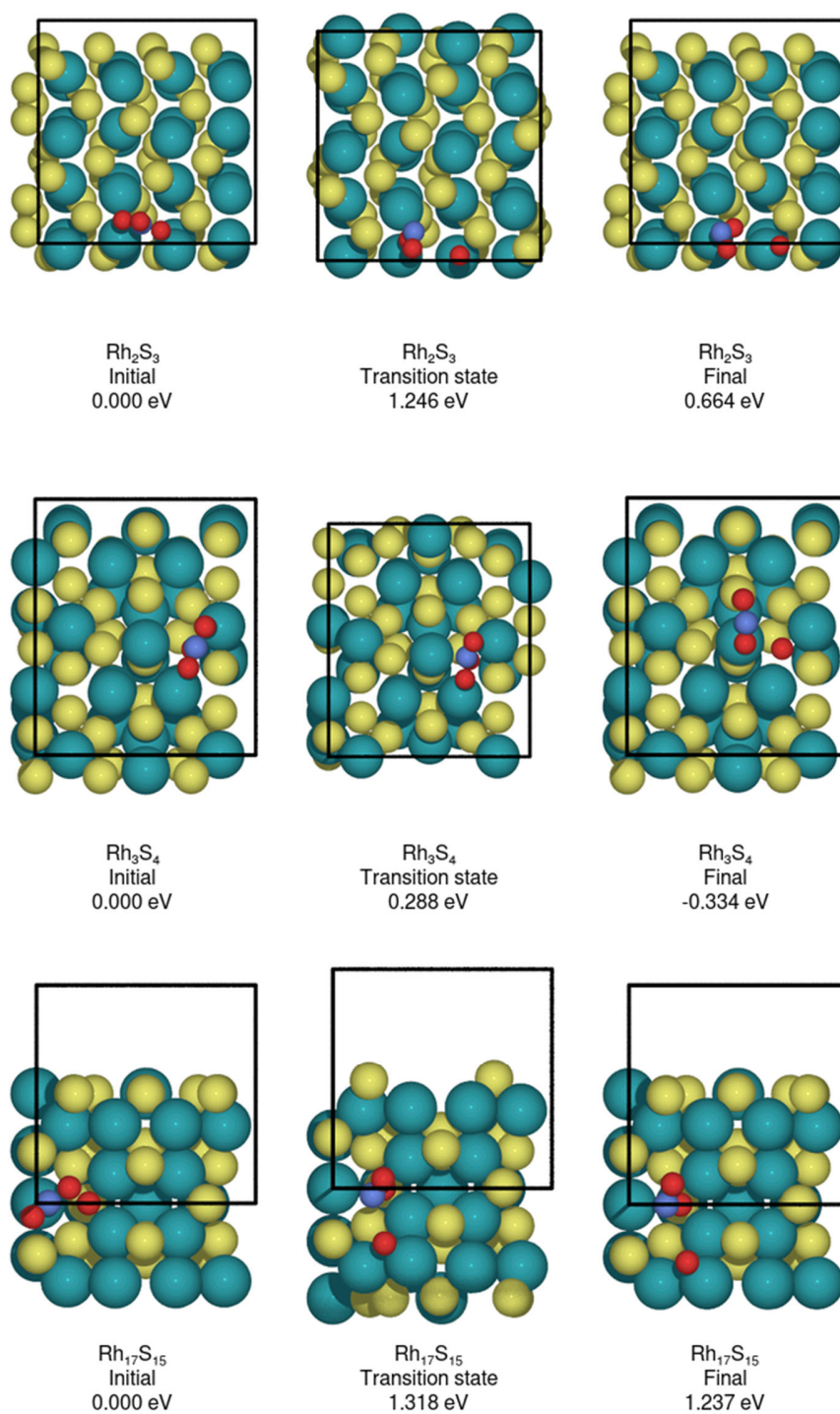
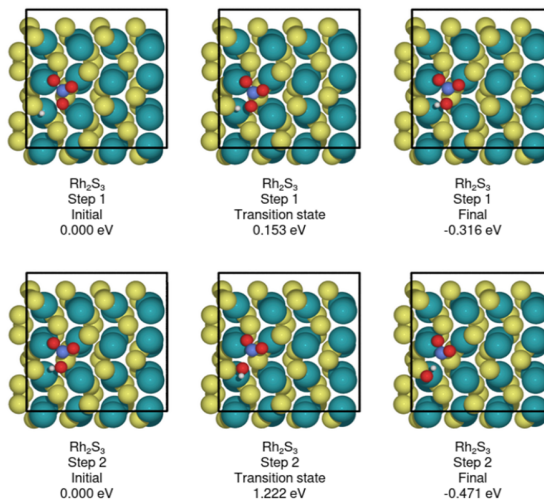
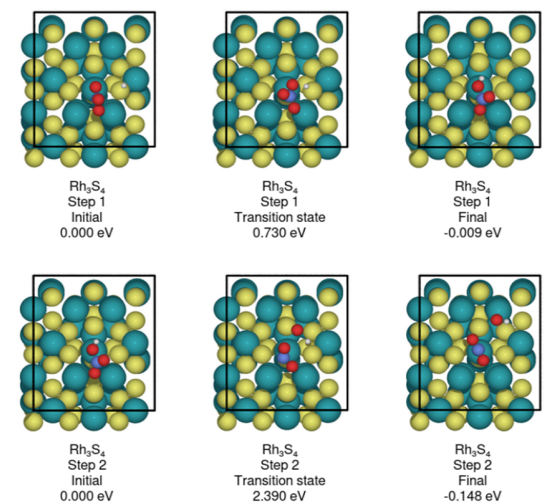


Figure S15. Initial, transition state, and final geometries for direct nitrate reduction ($\text{NO}_3^* \rightarrow \text{NO}_2^* + \text{O}^*$) on S-defected $\text{Rh}_2\text{S}_3(001)$, $\text{Rh}_3\text{S}_4(100)$, $\text{Rh}_{17}\text{S}_{15}(100)$ surfaces. Energies are relative to the initial state for each surface.

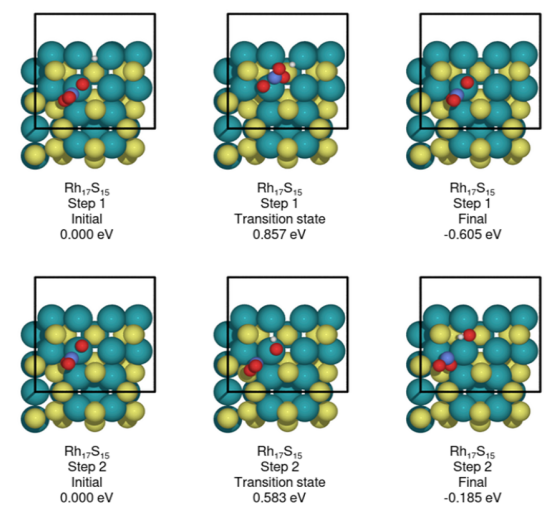
Rh_2S_3



Rh_3S_4



$\text{Rh}_{17}\text{S}_{15}$



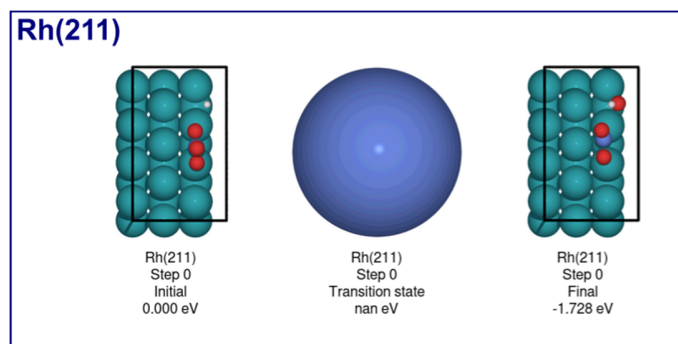


Figure S16. Initial, transition state, and final geometries for H-assisted nitrate reduction ($\text{NO}_3^* + \text{H}^* \rightarrow \text{HNO}_3^* \rightarrow \text{NO}_2^* + \text{HO}^*$) on $\text{Rh}_2\text{S}_3(001)$, $\text{Rh}_3\text{S}_4(100)$, $\text{Rh}_{17}\text{S}_{15}(100)$ and $\text{Rh}(211)$ surfaces. Energies are relative to the initial state for each surface. A large blue sphere and a nan transition state energy indicate a transition state that could not be identified.

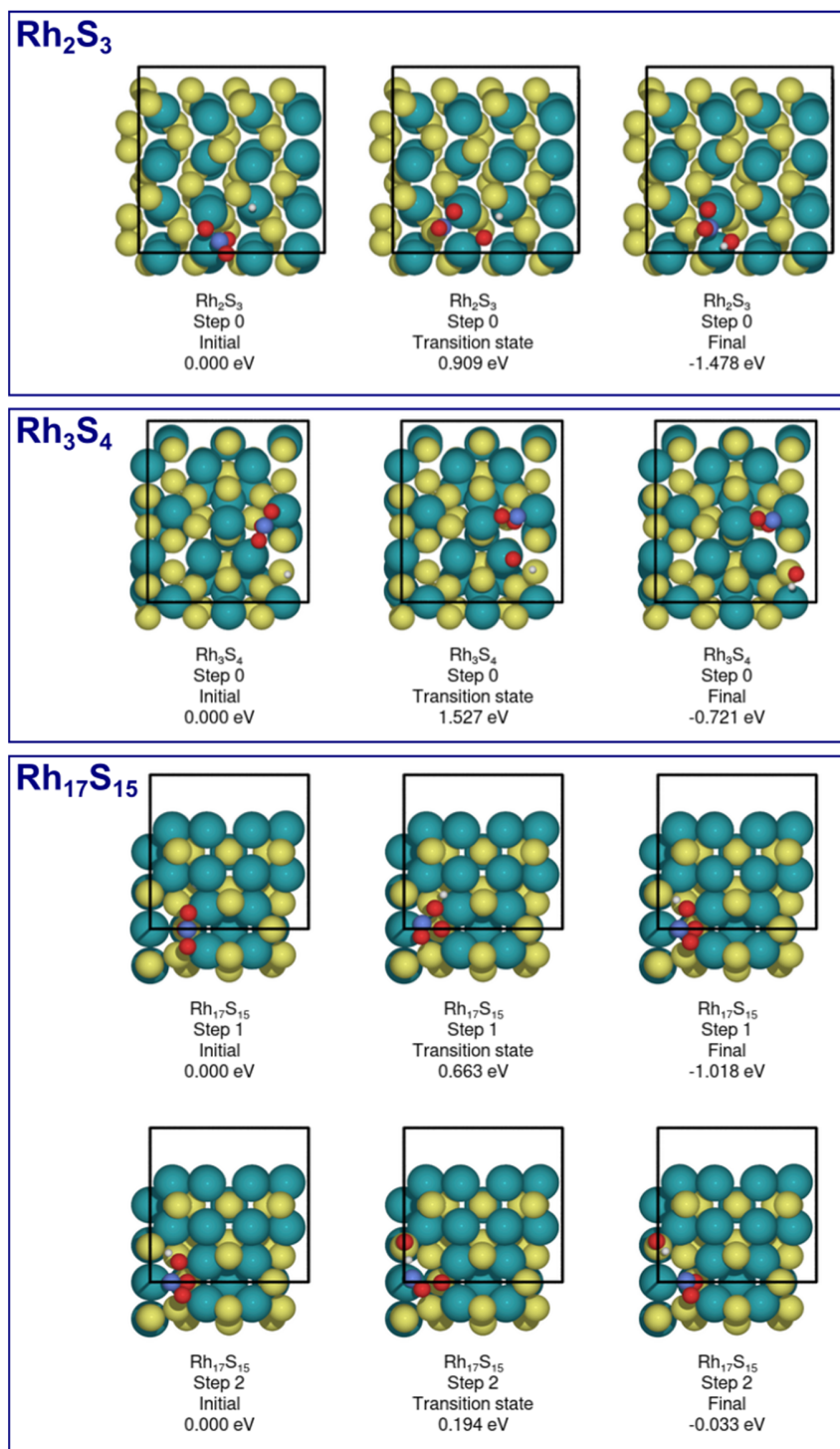


Figure S17. Initial, transition state, and final geometries for H-assisted nitrate reduction ($\text{NO}_3^* + \text{H}^* \rightarrow \text{HNO}_3^* \rightarrow \text{NO}_2^* + \text{HO}^*$) on S-defected Rh₂S₃(001), Rh₃S₄(100), and Rh₁₇S₁₅(100) surfaces. Energies are relative to the initial state for each surface.

S8 Charge from Cyclic Voltammograms with Nitrate and Chloride on Pt and Rh

Like chloride, nitrate also adsorbs on the surface of Rh and Pt in what appears to be a charge transfer process (Eq. 2). Using cyclic voltammograms in the H_{upd} region with different concentrations of nitrate,¹⁰ the anodic charge on Pt and Rh changes with nitrate concentration (Figure S18a). On Rh, the charge decreases with increasing nitrate concentration, mirroring the behavior with chloride concentration (Figure S18b). On Pt, the charge increases at low concentrations of nitrate and decreases at concentrations greater than 0.1 M NO_3^- , also mirroring the behavior with Cl^- concentration on Pt. This additional anodic charge must come from an additional charge transfer reaction, indicating nitrate adsorption involves an electron transfer. For Pt and Rh, the potential region where chloride is adsorbed is the same in which nitrate adsorbs and nitrate reduction occurs.^{8,20,21}

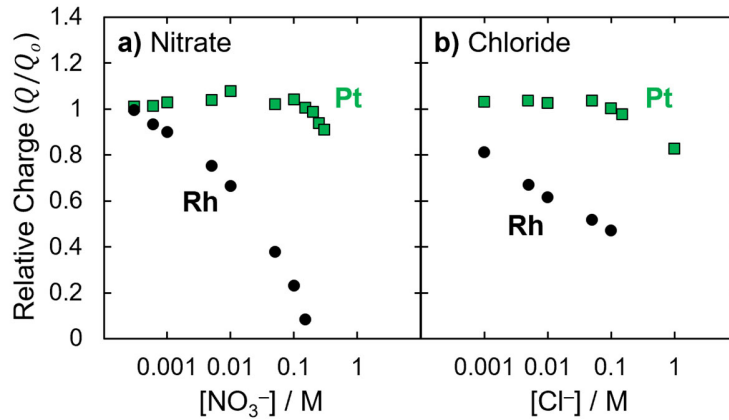


Figure S18. The charge (Q) of the anodic scan from 0.05 to 0.4 V vs. RHE on a Pt RDE in 1 M HClO_4 and Rh wire in 1 M H_2SO_4 with a) 0.3 mM to 0.3 M NO_3^- (reproduced with permission from Ref. ¹⁰) or b) 1 mM to 1 M Cl^- relative to the charge at the same potentials without nitrate or chloride (Q_0). Data in b) is reproduced from Figure 2c.

S9 Coverage Model and Computational CVs

A Langmuir adsorption isotherm is used to analyze the competitive adsorption between hydrogen and chloride on Pt and Rh (Section 3.2 of the main text) and to rationalize the change in H_{upd} charge in the experimental cyclic voltammograms (CVs) when chloride is added to the electrolyte (Figure 2a–b). To construct computational CVs, we use the predicted adsorption free energy (ΔG_i) of each species “i” and the applied potential (E) to calculate the coverage (θ_i) using adsorption equilibrium expressions. For the system with just hydrogen and chloride, the Langmuir isotherm considers two species which achieve an adsorption/desorption equilibrium while competing for active sites (indicated by *), as shown in Eqs. S17 and S18 where $K_i(E)$ is the potential-dependent equilibrium constant for the adsorption/desorption reaction of the species indicated, F is Faraday’s constant, ΔG_{H} and ΔG_{Cl} are as defined in Eqs. S13 and S15, R is the ideal gas constant, and T is the temperature. $[\text{H}^+]_0$ and $[\text{Cl}^-]_0$ are the concentrations of each species in the solution. For Eqs. S17 and S18 we refer to the adsorption reactions in Eqs. 1 and 3, respectively. The site balance includes the coverage of hydrogen and chloride and the remaining active sites (Eq. S19).

$$K_{\text{H}}(E) = \exp\left(-\frac{\Delta G_{\text{H}}}{RT}\right) = \exp\left(-\frac{\Delta G_{\text{H}}(E = 0 \text{ V}) + FE}{RT}\right) = \frac{\theta_{\text{H}}}{[\text{H}^+]_0 \theta_*} \quad (\text{S17})$$

$$K_{\text{Cl}}(E) = \exp\left(-\frac{\Delta G_{\text{Cl}}}{RT}\right) = \exp\left(-\frac{\Delta G_{\text{Cl}}(E = 0 \text{ V}) - FE}{RT}\right) = \frac{\theta_{\text{Cl}}}{[\text{Cl}^-]_0 \theta_*} \quad (\text{S18})$$

$$1 = \theta_* + \theta_{\text{H}} + \theta_{\text{Cl}} \quad (\text{S19})$$

The equilibrium constants, and thus adsorbate coverages, are each a function of the applied potential. The coverages can be expressed as a function of potential and concentration, as shown in **Eqs. S20–S22**.

$$\theta_{\text{Cl}} = \frac{K_{\text{Cl}}(E)[\text{Cl}^-]_0}{1 + K_{\text{H}}(E)[\text{H}^+]_0 + K_{\text{Cl}}(E)[\text{Cl}^-]_0} \quad (\text{S20})$$

$$\theta_{\text{H}} = \frac{K_{\text{H}}(E)[\text{H}^+]_0}{1 + K_{\text{H}}(E)[\text{H}^+]_0 + K_{\text{Cl}}(E)[\text{Cl}^-]_0} \quad (\text{S21})$$

$$\theta_* = \frac{1}{1 + K_{\text{H}}(E)[\text{H}^+]_0 + K_{\text{Cl}}(E)[\text{Cl}^-]_0} \quad (\text{S22})$$

Once the coverage of each species is known as a function of applied potential, computational cyclic voltammograms were approximated by time differentiation of each coverage:

$$j_{\text{theo},i} = nF \frac{dN_i}{dt} = ne\sigma \frac{d\theta_i}{dE} \frac{dE}{dt} \quad (\text{S23})$$

where N_i is the number of sites with species “i” adsorbed, n is the number of electrons needed to adsorb/desorb from a single surface site (with positive sign when desorption reduces the adsorbed species and negative sign when desorption oxidizes it), e is the charge of an electron, σ is the areal dispersion of surface sites (1.5×10^{15} sites cm^{-2} geometric area), $d\theta_i/dE$ is the derivative of the coverage in **Eqs. S20–S22**, and dE/dt is the CV scan rate. The derivatives may be approximated by finite differences. For example, the average current density for the desorption of a monolayer of H^* over a potential window of 0.2 V at a scan rate of 100 mV s^{-1} would be:

$$\begin{aligned} j_{\text{theo}, \text{H}^*} &= ne\sigma \frac{d\theta_{\text{H}}}{dE} \frac{dE}{dt} \approx ne\sigma \frac{\Delta\theta_{\text{H}}}{\Delta E} \frac{\Delta E}{\Delta t} \\ &= \frac{1 \text{ e}^-}{1 \text{ atom Pt}} \times \frac{1.602 \times 10^{-19} \text{ C}}{1 \text{ e}^-} \times \frac{1.5 \times 10^{15} \text{ atoms Pt}}{1 \text{ cm}^2} \times \frac{1}{0.2 \text{ V}} \times \frac{0.1 \text{ V}}{\text{s}} \\ &= 0.12 \frac{\text{mA}}{\text{cm}^2} \end{aligned} \quad (\text{S24})$$

Theoretical coverages for hydrogen and chloride between 0.05–0.4 V vs. RHE for Rh(211) and Pt(211) surfaces are shown in **Figure S19a–b**. The integrals of the coverages were used to create computational CVs for desorbing hydrogen and adsorbing chloride on these surfaces (**Figure S19c–d**). Qualitatively comparing the experimental CVs on a Rh wire with adding chloride (**Figure 2a**) and the computational CVs on Rh(211) where we set $[\text{H}^+]$ to 1 M then increase the chloride concentration (**Figure S19c**), the theoretical current for Rh(211) is close to zero at concentrations above 10^{-6} M Cl^- , whereas for the Rh wire the measured current is still significant even at 0.1 M Cl^- . The difference between the experimental and computational CVs may be because the saturation coverage of chloride experimentally is less than one monolayer and in experimental results we study polycrystalline surfaces and calculations are only on the (211) surfaces.²² In the application of the adsorption isotherm, we have assumed that chloride can block all

available sites in the computational model which would cause the current from hydrogen adsorption to be lower at even small chloride concentrations.

For the Pt CVs in **Figures 2b and S19d**, the relative charges between 0 to 0.4 V vs. RHE are due to chloride adsorbing on the surface as hydrogen is desorbing from the surface. In the computational Pt(211) CV, there is a shift in the peak in anodic current towards more negative potentials at higher chloride coverages. This shift in current is less obvious in the experimental CVs on the Pt RDE due to the two characteristic Pt H_{upd} peaks but the accumulation of charge across the potentials also indicates that the charge is transferred at more negative potentials on the Pt RDE with increasing chloride concentrations.

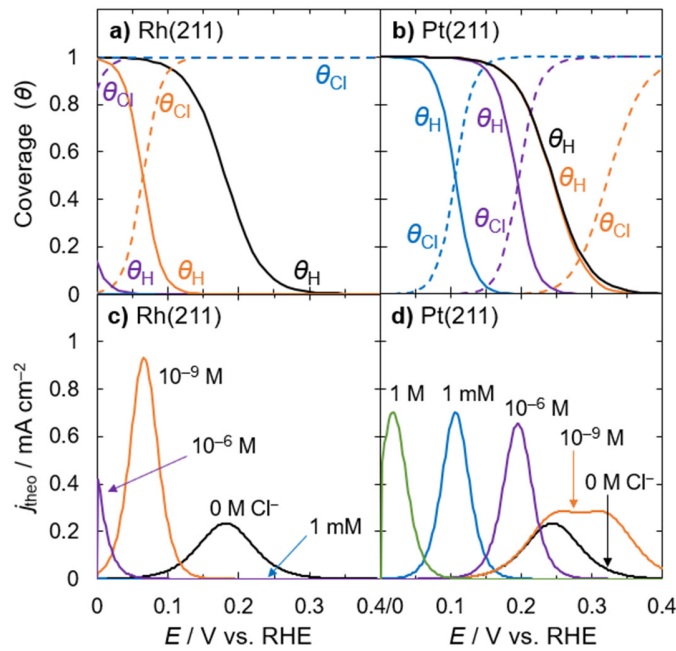


Figure S19. Theoretical coverage plots generated using the Langmuir adsorption model for a) Rh(211) and b) Pt(211). These coverage plots are used to calculate the computational CVs for c) Rh(211) and d) Pt(211). Solid and dashed lines indicate the hydrogen and chloride coverages at each concentration, respectively.

The Langmuir adsorption model was expanded to include hydrogen, nitrate, and chloride species competing for the same active surface sites (**Eqs. 1–3**). We assume for simplicity that each molecule adsorbs only to one site, although NO₃ binds to two sites.²³ Using **Eqs. S17, S18, S25, and S26**, we fully describe the adsorption thermodynamics of all species in the system.

$$K_{\text{NO}_3}(E) = \exp\left(-\frac{\Delta G_{\text{NO}_3}}{RT}\right) = \exp\left(-\frac{\Delta G_{\text{NO}_3}(E = 0 \text{ V}) - FE}{RT}\right) = \frac{\theta_{\text{NO}_3}}{[\text{NO}_3^-]_0 \theta_*} \quad (\text{S25})$$

$$1 = \theta_* + \theta_H + \theta_{Cl} + \theta_{\text{NO}_3} \quad (\text{S26})$$

The coverages as a function of potential and concentration from **Eqs. S20–S22** are adjusted to include the contribution from nitrate in **Eqs. S27–S30**.

$$\theta_{Cl} = \frac{K_{Cl}(E)[\text{Cl}^-]_0}{1 + K_H(E)[\text{H}^+]_0 + K_{Cl}(E)[\text{Cl}^-]_0 + K_{\text{NO}_3}(E)[\text{NO}_3^-]_0} \quad (\text{S27})$$

$$\theta_H = \frac{K_H(E)[H^+]_0}{1 + K_H(E)[H^+]_0 + K_{Cl}(E)[Cl^-]_0 + K_{NO_3}(E)[NO_3^-]_0} \quad (S28)$$

$$\theta_{NO_3} = \frac{K_{NO_3}(E)[NO_3^-]_0}{1 + K_H(E)[H^+]_0 + K_{Cl}(E)[Cl^-]_0 + K_{NO_3}(E)[NO_3^-]_0} \quad (S29)$$

$$\theta_* = \frac{1}{1 + K_H(E)[H^+]_0 + K_{Cl}(E)[Cl^-]_0 + K_{NO_3}(E)[NO_3^-]_0} \quad (S30)$$

The coverages of hydrogen, nitrate, and chloride on Rh(211) and Pt(211) are shown in **Figure 3** for potentials between 0.05–0.4 V vs. RHE with 1 M H^+ , 1 M NO_3^- , and 0, 10^{-10} , and 10^{-9} M Cl^- .

S10 Microkinetic Models for Nitrate Reduction

Four rate laws for nitrate reduction were considered to understand the effects of chloride on the reduction rate. The model approximating the rate determining step (RDS) as the dissociation of nitrate to nitrite via adsorbed hydrogen most closely matched our experimental observations and is written in **Section 2.7** of the main text and referred to here as model 1 (M1). Reactions from **Section 2.7** are rewritten below, where * represents an active site or adsorbed species. All four rate laws begin with the same adsorption steps.



The equilibrium constants K_H , K_{NO_3} , and K_{Cl} as defined in **Eqs. S17, S25, and S18**, respectively, correspond to the reactions in **Eqs. 1–3** and are a function of potential. Following hydrogen, nitrate, and chloride adsorption, we modeled four rate laws. The rates predicted from the four models are presented in **Figure S20** from 0 to 0.4 V vs. RHE for Rh(211) and 0 to 0.6 V vs. RHE for Pt(211). The rate from M1 is also in **Figure 3** in the main text.

Microkinetic Model 1 (M1)—H-assisted Nitrate Reduction

The rate equation for M1 is given in **Eqs. 10 and 11** when **Eqs. 1–3** are considered in quasi-equilibrium, **Eq. 9** is considered irreversible and rate determining, and the reactions in **Eqs. 6 and 7** are assumed to be infinitely fast. The rate constant k_9 is the rate constant for the forward reaction of **Eq. 9**, θ_i is the coverage of species i , and $[NO_3^-]_0$, $[H^+]_0$, and $[Cl^-]_0$ are the concentrations of each species in the solution. M1 is the microkinetic model we use throughout the main text. We do not know the value of the rate constant k_9 so we plot the rate in **Eq. 11** divided by k_9 in **Figure S20**.



$$\text{rate}_{M1} = k_9 \theta_{NO_3} \theta_H \quad (10)$$

$$\text{rate}_{M1} = \frac{k_9 K_{NO_3} K_H [NO_3^-]_0 [H^+]_0}{(1 + K_H [H^+]_0 + K_{NO_3} [NO_3^-]_0 + K_{Cl} [Cl^-]_0)^2} \quad (11)$$

Alternatively, if we consider the reaction in **Eq. S31** as the RDS following quasi-equilibrated adsorption of nitrate and hydrogen, we attain a rate law identical to **Eqs. 10 and 11** except with k_{S31} as the rate constant

instead of k_9 . Due to the similar dependence on nitrate and hydrogen coverages, the rate law for the formation of adsorbed HNO_3 is only distinguished from the rate law for the formation of adsorbed NO_2 and HO by the rate constant of the RDS.



Microkinetic Model 2 (M2)

The second microkinetic model (M2) considers **Eqs. S33 and S32**. In M2, the reaction of adsorbed nitrate and a proton to form adsorbed nitric acid (**Eq. S33**) is assumed to be the RDS and irreversible. The rate equation for M2 is given in **Eq. S34**, where k_{S33} is the rate constant for the forward reaction of **Eq. S33**. We do not know the value of the rate constant k_{S33} , so when we model M2 from 0 to 0.6 V vs. RHE we normalize to k_{S33} at 0 V vs. RHE (e.g., at 0.2 V vs. RHE, the rate from **Eq. S34** is divided by the value of k_{S33} at 0 V vs. RHE). We approximate the voltage dependence of this rate constant using the Butler-Volmer equation with a symmetry coefficient of 0.5.



$$\text{rate}_{\text{M2}} = k_{\text{S33}} \theta_{\text{NO}_3} [\text{H}^+]_0 = \frac{k_{\text{S33}} K_{\text{NO}_3} [\text{NO}_3^-]_0 [\text{H}^+]_0}{1 + K_{\text{H}} [\text{H}^+]_0 + K_{\text{NO}_3} [\text{NO}_3^-]_0 + K_{\text{Cl}} [\text{Cl}^-]_0} \quad (\text{S34})$$

Microkinetic Model 3 (M3)—Direct Nitrate Reduction

The third microkinetic model (M3) considered **Eqs. 4–7**. In M3, we consider nitrate dissociation to adsorbed nitrite and adsorbed O (**Eq. 4**) as the RDS and the reduction of adsorbed oxygen and nitrite to other products (**Eqs. 5–7**) is infinitely fast. The rate equation for M3 is given in **Eq. S35**, where k_4 is the rate constant for the forward reaction in **Eq. 4**. k_4 was previously calculated¹⁰ on Pt(211) and Rh(211) as 0.2 and 3400 s^{-1} , respectively.



$$\text{rate}_{\text{M3}} = k_4 \theta_{\text{NO}_3} \theta_* = \frac{k_4 K_{\text{NO}_3} [\text{NO}_3^-]_0}{(1 + K_{\text{H}} [\text{H}^+]_0 + K_{\text{NO}_3} [\text{NO}_3^-]_0 + K_{\text{Cl}} [\text{Cl}^-]_0)^2} \quad (\text{S35})$$

Microkinetic Model 4 (M4)

The fourth microkinetic model (M4) considers **Eqs. 4–7** and the rate law was determined by assuming **Eqs. 4 and 5** are irreversible in the forward direction. In this model only, we included adsorbed oxygen in the active site balance. A pseudo-steady state assumption was made for the coverage of oxygen to solve for the rate equation. The rate equation for M4 is given in **Eq. S36**. k_4 and k_5 are the forward rate constants of

the reactions in **Eqs. 4 and 5**. Along with k_4 , k_5 was previously calculated using DFT¹⁰ on Pt(211) and Rh(211) as 14.5 and 23700 s⁻¹, respectively.



$$\text{rate}_{\text{M4}} = k_4 \theta_{\text{NO}_3} \theta_* = \frac{k_4 K_{\text{NO}_3} [\text{NO}_3^-]_0}{\left[1 + K_{\text{H}} [\text{H}^+]_0 + K_{\text{NO}_3} [\text{NO}_3^-]_0 + K_{\text{Cl}} [\text{Cl}^-]_0 + \frac{k_4 K_{\text{NO}_3} [\text{NO}_3^-]_0}{k_5 K_{\text{H}} [\text{H}^+]_0} \right]^2} \quad (\text{S36})$$

The nitrate reduction rates as a function of potential as predicted by the four rate laws are shown in **Figure S20**, with M1 best matching the experimental trends observed on Pt/C in this work. For Pt(211) shown in **Figure S20e–h**, M1 most closely captures what we observe experimentally, where nitrate reduction has a maximum in current between 0 and 0.4 V vs. RHE and when chloride is added, NO₃RR is inhibited. M2 inaccurately predicts that Pt would not have nitrate reduction above 0.1 V vs. RHE. M3 and M4 are very similar for their prediction of NO₃RR on Pt(211) (**Figure S20g–h** and **Figure S21**) and both predict that NO₃RR will be greatest at potentials more positive than 0.4 V, which does not match what we experimentally observe on Pt (**Figure 1**). For all four models, Rh(211) (**Figure S20a–d**) shows a maximum in predicted nitrate reduction rate near 0.1 V vs. RHE which is caused by the desorption of hydrogen allowing for an increase in nitrate coverage at this potential. The amount the rate is suppressed by chloride is dependent on the model, though all modeled rates are similarly affected by chloride.

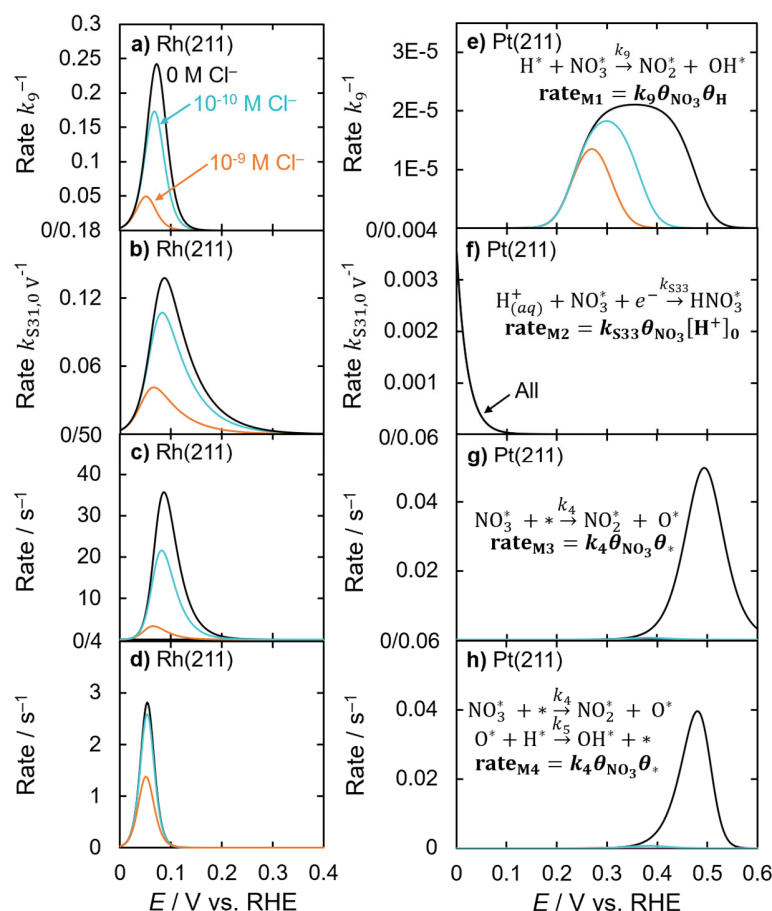


Figure S20. Microkinetic models for nitrate reduction considering the adsorption of nitrate, hydrogen, and chloride with different rate determining steps on Rh(211) (a–d) and Pt(211) (e–h). In all models for both Rh(211) and Pt(211), the proton and nitrate concentration in solution is 1 M and only the concentration of chloride is increasing. The concentration of chloride is labeled in panels a) and e) as 0 M (black), 10^{-10} M (teal), and 10^{-9} M (orange). The data in panels (a) and (e) are shown in **Figure 3**.

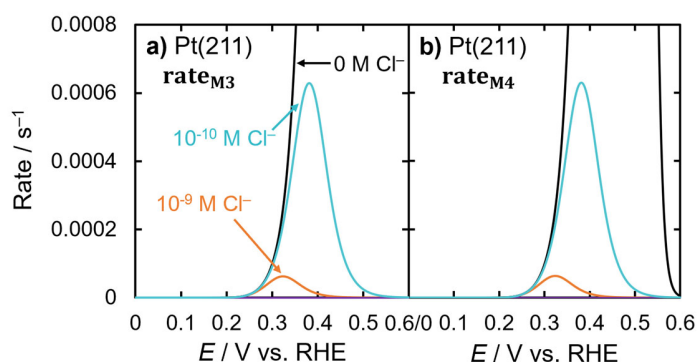


Figure S21. Close up view of microkinetic models a) M3 and b) M4 for nitrate reduction on Pt(211) from **Figure S20g–h**. The proton and nitrate concentration in solution is 1 M and only the concentration of chloride is increasing. The concentration of chloride is 0 M (black), 10^{-10} M (teal), and 10^{-9} M (orange).

S11 Baseline Steady-state Currents (with and without NaNO₃) on Rh_xS_y/C, Rh/C, and Pt/C

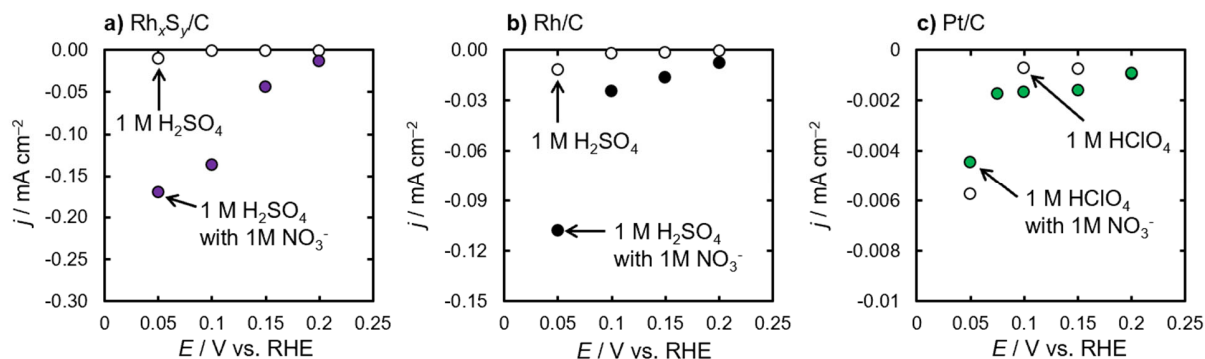


Figure S22. Steady-state current densities for a) 30 wt% Rh_xS_y/C, b) 20 wt% Rh/C, and c) 30 wt% Pt/C in the supporting electrolyte (open circles) and with 1 M NaNO₃ (filled circles). Currents for Rh_xS_y/C are normalized to the capacitance & XRD estimated area. Currents for Rh/C and Pt/C are normalized to H_{upd} determined ECSA. Measurements were taken at 2500 rpm at each potential with 85% IR compensation.

S12 Rh_xS_y/C and Rh/C NO₃RR Faradaic Efficiency to Ammonia

Ammonium was measured as the major nitrate reduction product of Rh_xS_y/C and Rh/C at 0.1 V vs. RHE in 0.1 M HNO₃ (**Figure S23a**). The nitrate faradaic efficiency to ammonium on Rh/C did not significantly change when 1 mM chloride was present (**Figure S23b**), which we postulate arises because chloride only blocks the active site of Rh/C for NH₄⁺ production and does not change the product distribution or reaction mechanism. NO₂⁻ was not detected for the reduction experiment with or without chloride. The total amount of ammonium produced is lower in the presence of chloride proportionally to the decrease in current. NO₃⁻ could not be quantified in the presence of Cl⁻ due to overlapping UV absorbance wavelengths. The concentration of nitrate in the solution did not change significantly over the experiment time of 6 hours (**Figure S23c**).

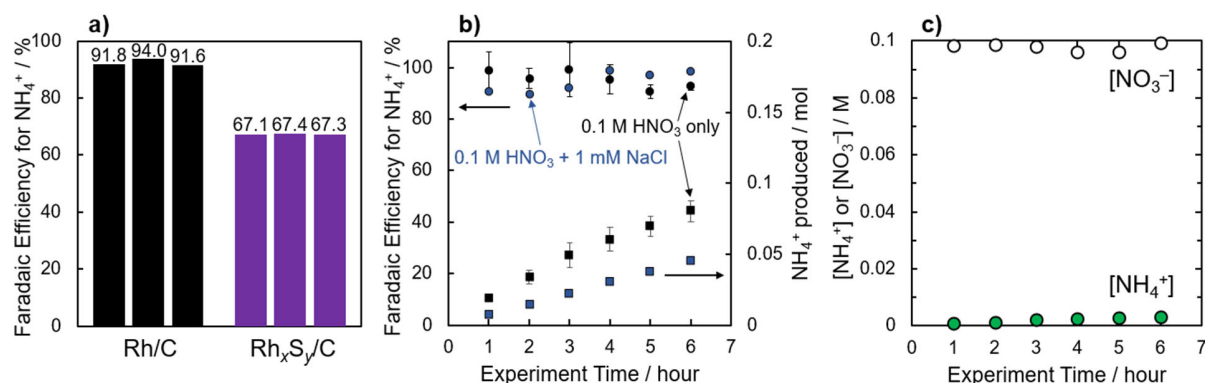


Figure S23. a) Faradaic efficiency towards ammonium for Rh/C and Rh_xS_y/C at 0.1 V vs. RHE. The results from three experiments for each catalyst are shown. Electrolysis time was 6 hours for each experiment. The average faradaic efficiency towards NH₄⁺ was 92.5 ± 1.3 for Rh/C and 67.3 ± 0.1 for Rh_xS_y/C. b) FE towards ammonium and total ammonium produced for Rh/C at 0.1 V vs. RHE in 0.1 M HNO₃ (black) and 0.1 M HNO₃ + 1 mM NaCl (blue). For Rh/C without chloride, the error bars for the measurements without chloride are the standard deviation from the average of the three separate experiments shown in panel a. Conversion measurements with chloride were performed

once. c) Concentration of nitrate and ammonium as detected by colorimetry/UV-Vis spectrophotometry for one of the $\text{Rh}_x\text{S}_y/\text{C}$ NO_3RR measurements over 6 hours. Measurements were taken in N_2 sparged 0.1 M HNO_3 and the catalysts were deposited on carbon felt as described in the Methods. Stirring at 400 rpm with a stir bar was used to decrease mass transfer limitations.

S13 Comparison to Previous Reports of the Effect of Chloride on NO_3RR on Pt and Rh

The effect of chloride on NO_3RR current has been shown for Pt and Rh at pH 0. In **Figure S24**, the percent nitrate reduction current remaining when Cl^- is added is shown for our measurements and from those reported in literature. Experimental conditions are given in **Table S5** for the data in **Figure S24**.

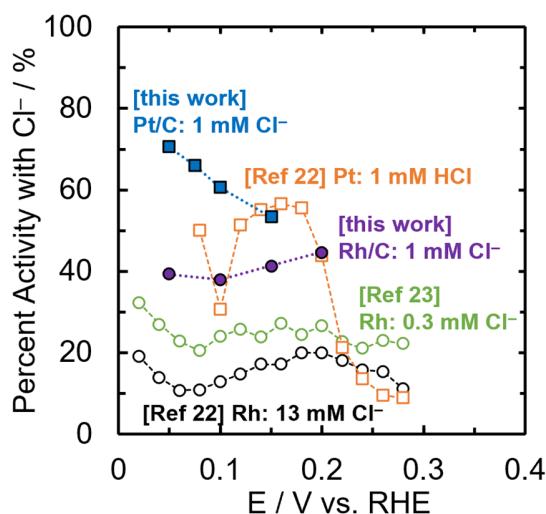


Figure S24. Literature reports of the current density for NO_3RR activity on polycrystalline Pt and Rh from Horányi et al.²⁴ and Wasberg et al.²⁵, respectively, in different concentrations of chloride were extracted and normalized to the current density in the absence of chloride as a function of potential. Percent activity with Cl^- is also shown for Pt/C and Rh/C data from this work from **Figure 1a**. Other differences in experimental conditions between data series are summarized in **Table S5**. Open data points represent cited works and closed data points are from this work. Circles and squares are used for Rh and Pt, respectively.

Table S5. Experimental conditions for nitrate reduction measurements on Pt and Rh with chloride shown in **Figure S24**.

Electrode (Ref.)	$[\text{NO}_3^-]$ (M)	$[\text{Cl}^-]$ (M)	Supporting Electrolyte	Rotation/Stir Rate (rpm)
Pt (Horányi <i>et al.</i> ²⁴)	0.015	10^{-3}	1 M H_2SO_4	N/A
Rh (Wasberg <i>et al.</i> ²⁵)	0.114	3×10^{-4} , 1.3×10^{-2}	1 M H_2SO_4	N/A
Pt/C (this work)	1.0	10^{-3}	1 M HClO_4	2500 rpm
Rh/C (this work)	1.0	10^{-3}	1 M H_2SO_4	2500 rpm

The decrease in nitrate current in the presence of chloride is similar between the different studies for Pt and Rh. For Rh (Wasberg *et al.*²⁵ and this work), the percent change in current is similar across the studied

potential range (0.05–0.2 V vs. RHE). Assuming nitrate reduction occurs as a Langmuir-Hinshelwood surface reaction between adsorbed nitrate and hydrogen, we attribute this decrease in activity to chloride adsorption beginning at negative potentials on Rh and limiting available surface sites in the potential range studied. The chloride is present on the surface and decreases the available surface sites for nitrate and hydrogen to adsorb and react. For Pt, the percent NO₃RR activity decreases for both ref. ²⁴ and this work show that the NO₃RR rate is more affected by chloride at more positive potentials. We attribute this decrease in activity to the onset of chloride adsorption in the studied potential range, where at 0.05 V the surface has a negligible coverage of chloride and as the potential increases the chloride coverage increases and thus inhibits NO₃RR.

There are a few differences in experimental conditions to consider when comparing this work with the results from ref. ²⁴ and ref. ²⁵, namely that the nitrate concentrations are different and the results from literature may be in the mass transport limited regime. In our measurements on Rh/C and Pt/C, we use 2500 rpm to minimize mass transfer effects. The results on Rh from ref. ²⁴ are taken using a low stirring rate and are likely in the mass transfer limited regime, and therefore nitrate reduction inhibition by chloride could be lower than reported due to mass transport limitations. Ref. ²⁵ does not indicate that stirring or rotation was used, so we can assume that there are mass transport limitations present.

S14 NO₃RR on Pt/C and Rh/C with Different Chloride Concentrations

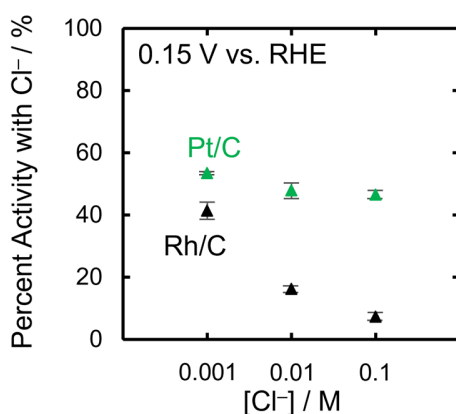


Figure S25. The percent nitrate reduction current from the reduction currents in 1 M H₂SO₄ + 1 M NaNO₃ on Pt/C (green) and or 1 M HClO₄ + 1 M NaNO₃ on Rh/C (black) with and without Cl⁻ at 0.15 V for 0.001–0.1 M Cl⁻.

S15 H^+ and Cl^- Adsorption Energies on Transition Metals, Pristine Rh_xS_y , and S-defected Rh_xS_y Surfaces

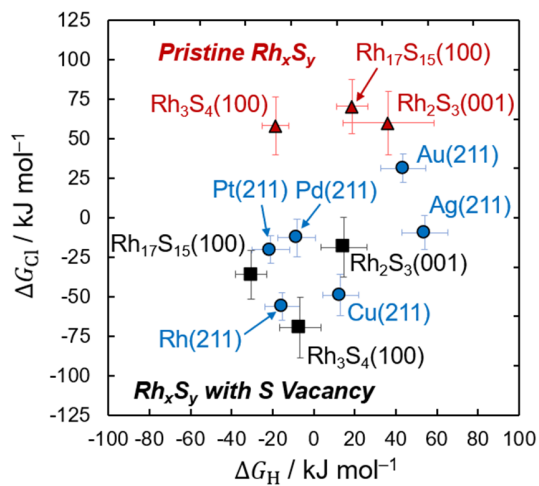


Figure S26. Adsorption free energies at 0 V vs. SHE and 298.15 K for Cl^- and H^+ on pure metals (blue circles), pristine Rh_xS_y surfaces (red triangles), and sulfur-defected Rh_xS_y surfaces (black squares). Error bars are BEEF-vdW uncertainties.

S16 Computed Kinetic and Thermodynamic Parameters for NO₃RR on Rh_xS_y

Table S6. Computed kinetic and thermodynamic parameters for nitrate reduction on Rh₃S₄(100), Rh₁₇S₁₅(100), Rh₂S₃(100), and Rh(211). Adsorption energies are from **Figure 4** and **Figure S26**. Activation barriers are from **Figure 5** as described in the main text.

Surface	Direct			H-assisted			
	E_a / kJ mol ⁻¹	k_4 / s ⁻¹	ΔG_{NO_3} / kJ mol ⁻¹	E_a / kJ mol ⁻¹	k_9 / s ⁻¹	ΔG_{NO_3} / kJ mol ⁻¹	ΔG_{H} / kJ mol ⁻¹
Rh(211)	75.46	5.91×10^{-2}	-1.44	—	—	-1.44	-15.39
Pristine Rh ₃ S ₄ (100)	38.52	1.77×10^5	107.42	70.47	4.44×10^{-1}	107.42	-18.64
Pristine Rh ₁₇ S ₁₅ (100)	162.38	3.44×10^{-17}	103.66	82.66	3.24×10^{-3}	103.66	18.64
Pristine Rh ₂ S ₃ (100)	132.19	6.75×10^{-12}	93.74	117.95	2.11×10^{-9}	93.74	36.28
S-defected Rh ₃ S ₄ (100)	27.78	1.35×10^7	6.21	147.37	1.47×10^{-14}	6.21	-6.65
S-defected Rh ₁₇ S ₁₅ (100)	127.15	5.15×10^{-11}	45.22	63.97	6.12×10^0	45.22	-30.50
S-defected Rh ₂ S ₃ (100)	120.19	8.54×10^{-10}	63.88	87.66	4.31×10^{-4}	63.88	14.52

S17 Calculated TOFs with 10⁻⁹ M Chloride Poisoning

Figure S27 shows computed TOF values assuming trace (10⁻⁹ M) chloride concentrations. It is the same methodology as **Figure 6** in the main text, but with chloride included in the model. The decrease in TOF when including chloride (by comparing **Figure 6** and **Figure S27**) is generally largest for Rh₃S₄(100) and Rh₁₇S₁₅(100), which tend to bind chloride the strongest. Generally, pristine sulfide surfaces are not affected as they bind chloride very weakly. For S-defected sulfide surfaces, both Rh₃S₄(100) and Rh₁₇S₁₅(100) show sharp declines in activity. For S-defected Rh₂S₃(100), the TOF declines near $E = 0.4$ V vs. RHE rather than reaching a plateau as it did in the chloride-free case. Rh(211) also shows a lower TOF with chloride present, as expected. The computed TOF for Rh(211) in **Figure S27a** is the same as that shown in **Figure S20c** above, just on a log plot here.

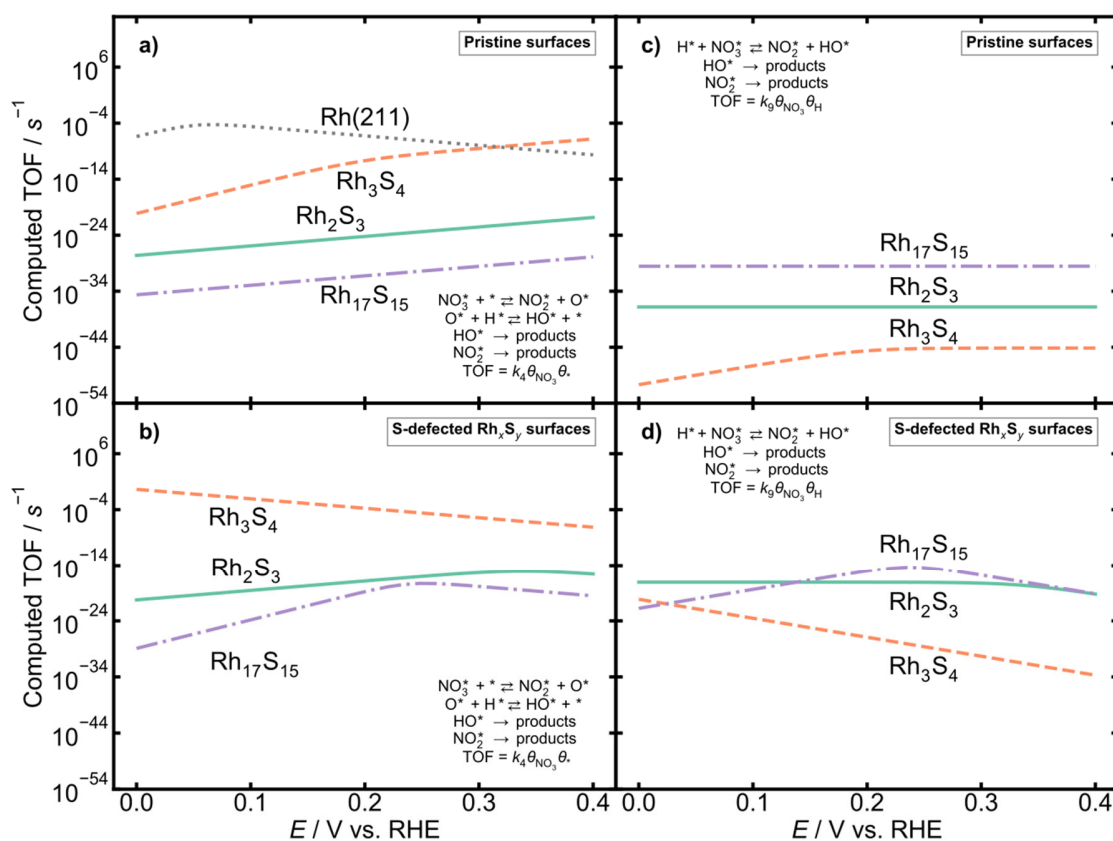


Figure S27. Computed potential-dependent TOFs for pristine (a, c) and S-defected (b, d) surfaces, assuming a direct (a, b) or H-assisted (c, d) reaction mechanism. For all TOF calculations, we assume $[\text{NO}_3^-]_0 = 1 \text{ M}$, $[\text{H}^+]_0 = 1 \text{ M}$, and $[\text{Cl}^-]_0 = 10^{-9} \text{ M}$.

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