Supporting Information

for

Experimental and theoretical characterization of Rh single-atoms supported on γ-Al₂O₃ with varying hydroxyl content during NO reduction by CO

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S1. Additional computational details

Enthalpies ($H$) and Gibb’s free energies ($G$) can be calculated from density functional theory (DFT)-derived energies using statistical mechanics. Specifically, each is a sum of the electronic energy ($E_0$), the zero-point vibrational energy (ZPVE), and the respective vibrational, translational, and rotational components of the species:

$$ H = E_0 + ZPVE + H_{vib} + H_{rot} + H_{trans} $$ \hspace{1cm} (S1)

$$ G = E_0 + ZPVE + G_{vib} + G_{rot} + G_{trans} $$ \hspace{1cm} (S2)

at 473 K. Adsorbed species are not considered to have translational or rotational contributions; all such motions are modeled as frustrated vibrations on the surface. Metal atoms of the Rh(111) surfaces and on the Rh$_{201}$ nanoparticles are frozen in place during frequency calculations. All atoms of the support were frozen during frequency calculations on γ-Al$_2$O$_3$, while atoms attached to the support (the Rh single-atom and species bound to it; H and OH bound to the γ-Al$_2$O$_3$ support) were unfrozen. Vibrational, rotational, and translational enthalpies and free energies are estimated from other statistical mechanics formalisms:

$$ ZPVE = \sum_i \left( \frac{1}{2} h \nu_i \right) $$ \hspace{1cm} (S3)

$$ H_{vib} = \sum_i \left( h \nu_i \exp \left( - \frac{h \nu_i}{kT} \right) \right) \left( 1 - \exp \left( - \frac{h \nu_i}{kT} \right) \right) $$ \hspace{1cm} (S4)

$$ G_{vib} = \sum_i \left( -kT \ln \left( \frac{1}{1 - \exp \left( - \frac{h \nu_i}{kT} \right)} \right) \right) $$ \hspace{1cm} (S5)

$$ H_{trans} = \frac{5}{2} kT $$ \hspace{1cm} (S6)

$$ H_{rot,linear} = kT $$ \hspace{1cm} (S7)

$$ H_{rot,nonlinear} = \frac{3}{2} kT $$ \hspace{1cm} (S8)

$$ G_{trans} = -kT \ln \left( \left( \frac{2\pi m k T}{h^2} \right)^\frac{3}{2} V \right) $$ \hspace{1cm} (S9)

$$ G_{rot} = -kT \ln \left( \frac{\pi^2}{\sigma} \left( \frac{T}{\Theta} \right)^3 \right) $$ \hspace{1cm} (S10)

$$ \Theta_i = \frac{h^2}{6\pi^2 I_i k} $$ \hspace{1cm} (S11)

where $I_i$ is the moment of inertia about the $i$ axis (either x, y, or z) and $\sigma$ is the symmetry number of the species.$^1$
S2. Models of γ-Al₂O₃ employed

All surface models of γ-Al₂O₃ used in this work were developed from the structure first published by Digne et al.²⁻⁵ The unit cell of this γ-Al₂O₃ model contained 8 Al₂O₃ units. Surface formation energies were calculated by adding 10 Å of vacuum above various terminations of the preferred surfaces of γ-Al₂O₃. All surface models contained four times the number of Al₂O₃ units as in the bulk (32 Al₂O₃ units) and were fully dehydrated. Therefore, the surface formation energy was calculated as

\[ \Delta E_{surf} = \frac{1}{A}(4 \times E_{bulk} - E_{surface}) \]  

(S12)

where \( A \) is the area of the exposed surface, \( E_{bulk} \) is the energy of the bulk γ-Al₂O₃, and \( E_{surface} \) is the energy of the surface. The surface energies for the models used in this work are shown in Table S1. The (001)₀ surface has the lowest formation energy, likely because the exposed Al on this facet are most highly coordinated among all those tested in this work. Moreover, the Lewis acidity of the Al of the (100)₀ and (010)₀ facets of this γ-Al₂O₃ model is well-established, and these two facets bind OH groups derived from H₂O during the dehydration of boehmite up to 800 K.² As such, the bare (100)₀ and (010)₀ facets are likely to be more stable when covered with OH groups and XRD¹ and computational² data indicate that these facets are more common than (001)₀.

<table>
<thead>
<tr>
<th>γ-Al₂O₃ facet</th>
<th>Corresponding boehmite facet</th>
<th>( \Delta E_{surf} ) (kJ mol⁻¹ Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(110)_{cds}</td>
<td>(100)₀</td>
<td>13.2</td>
</tr>
<tr>
<td>(110)_{cds}</td>
<td>(010)₀</td>
<td>12.2</td>
</tr>
<tr>
<td>(100)_{cds}</td>
<td>(001)₀</td>
<td>7.3</td>
</tr>
</tbody>
</table>

The structures of these γ-Al₂O₃ models absent water are shown in Figure 1 of the main text and compared with models from a cubic defect spinel (cds) model based on XRD studies of γ-Al₂O₃.⁶ The images of the cds model in the main text are not optimized, simply the structures of the initial cleaved surfaces. Upon optimization, these surfaces restructure significantly (Fig. S1), indicating the instability of these models and their inappropriateness for density functional theory (DFT) studies of catalysts supported on γ-Al₂O₃.
Additional views of the $\gamma$-Al$_2$O$_3$ models employed in this work are shown in Figure S2. A 10 Å vacuum layer was added above each surface. The bottom half of each slab was frozen during optimization calculations (corresponding to 160, 80, and 80 frozen atoms for the (100)$_b$, (010)$_b$, and (001)$_b$ slabs, respectively). The slabs for the (100)$_b$, (010)$_b$, and (001)$_b$ surfaces are 11.85, 7.07, and 16.36 Å thick, respectively.

**Figure S1.** Initial and optimized surfaces for the most stable terminations of (a) $\gamma$-Al$_2$O$_3$(110)$_{cds}$ and (b) $\gamma$-Al$_2$O$_3$(100)$_{cds}$ derived from the cubic defect spinel model based on XRD studies.$^5$
Figure S2. Detailed views of the γ-Al₂O₃ models used in this work for (a, d) the (100)b, (b, e) the (010)b, and (c, f) the (001)b surfaces shown (a–c) perpendicular to and (d–f) parallel to the surface. The total number of atoms in each γ-Al₂O₃ is shown above the respective structure. The horizontal dashed light blue lines in d–f indicate the point below which atoms were frozen during optimization calculations.
S3. IR spectra for identification of NCO*

*In situ* IR spectra of atomically dispersed Rh/γ-Al₂O₃ contain features near 2250 and 2230 cm⁻¹ that have been assigned to adsorbed isocyanate species (NCO*).⁷,⁸ We confirm that Rh exists predominantly as Rh(CO)₂ by collecting a series of IR spectra to demonstrate that Rh is saturated with CO during reaction conditions (Fig. S2a), that the features near 2250 and 2230 cm⁻¹ correspond to NCO* rather than N₂O* (Fig. S2b), and that NCO* is spilling over onto the support rather than sitting on Rh sites (Fig. S2c).

Figure S3. IR spectra of 0.05 wt.% Rh/γ-Al₂O₃ (a) after saturation with 0.5 kPa CO for 20 min (black), during exposure to 0.5 kPa CO and 0.1 kPa NO after 2 min (red) and 25 min (blue) at 463 K; (b) after 25 minutes in 0.5 kPa ¹²CO and 0.1 kPa NO at 463 K (purged with Ar) (black) and after saturation with 10 kPa ¹³CO and a pulse of 1 kPa NO at 463 K (purged with Ar) (red); and (c) during exposure to 0.5 kPa CO and 0.1 kPa NO at 523 K after exposure to the same mixture at 473 K. All gas mixtures were balanced with Ar to 1 bar.
S4. IR spectra for cooled Rh/γ-Al₂O₃ sample after temperature-programmed desorption

We investigated the resulting Rh structure produced following the thermal desorption of CO from atomically dispersed Rh(CO)₂ complexes by cooling down to cryogenic temperature and re-exposing the catalyst to CO after conducting the temperature-programmed desorption (TPD). Cryogenic temperature was used to ensure that CO-induced fragmentation or restructuring of Rh complexes was minimized. During the TPD, the catalyst was heated at 0.33 K s⁻¹ (20 K min⁻¹) from 298 K to 623 K, at which a significant portion of Rh(CO)₂ disappeared and the new shoulder at 1985/1975 cm⁻¹ assigned to Rh(CO) appeared. The catalyst was then cooled to 143 K and CO was introduced to the cell for 20 minutes before purging with Ar.

Figure S4. CO-DRIFTS spectra of 0.2 wt% Rh/Al₂O₃ collected after TPD with heating from 298 to 623 K at 0.33 K s⁻¹ and cooling to 183 K in Ar (black), and again after flowing 10% CO in Ar for 1200 s at 143 K and purging to collect a final spectrum at 183 K (red).
S5. DFT calculations with different OH coverages on $\gamma$-Al$_2$O$_3$

The coverages of adsorbed water can be estimated based on equilibrium constants ($K_{W,x}$) from H$_2$O adsorption free energies ($\Delta G_{W,x}$) at 1 bar (standard pressure) and 473 K:

$$K_{W,x} = e^{-\frac{\Delta G_{W,x}}{kT}} = e^{-\frac{\Delta H_{W,x} - T\Delta S_{W,x}}{kT}} \quad \text{(S12)}$$

where $x$ is the number of H$_2$O that have adsorbed, $\Delta H_{W,x}$ is the enthalpy of adsorption, and $\Delta S_{W,x}$ is the entropy of adsorption for the $x^{th}$ H$_2$O. These can then be applied to the Langmuirian adsorption isotherm to predict the coverage of OH groups at a range of temperatures ($T$) and water pressures ($P_w$):

$$\theta_W = \left(\frac{1}{A}\right)\sum_i K_{W,i}P_{W,i} \quad \frac{1}{\sum_j K_{W,j}P_{W,j}} \quad \text{(S13)}$$

where $A$ is the surface area of the unit cell of the $\gamma$-Al$_2$O$_3$ surface to give coverage in units of OH nm$^{-2}$ and $i$ and $j$ are the number of adsorbed H$_2$O.
Figure S5. γ-Al₂O₃ with dissociatively adsorbed H₂O at (a) 1.13 OH nm⁻², (b) 2.26 OH nm⁻², (c) 3.39 OH nm⁻², (d) 4.53 OH nm⁻², (e) 5.66 OH nm⁻², (f) 6.79 OH nm⁻², (g) 7.92 OH nm⁻², and (h) 9.05 OH nm⁻² (from 1-8 dissociatively adsorbed H₂O molecules), shown parallel (top) and perpendicular (bottom) to the surface. Adsorption enthalpies (ΔHₖ) and free energies (ΔGₖ) in kJ mol⁻¹ and entropies (ΔSₖ) in J mol⁻¹ K⁻¹ are shown beneath each structure.
Figure S6. $\gamma$-Al$_2$O$_3$ with 9.05 OH nm$^{-2}$ from dissociatively adsorbed H$_2$O and with (a) 0.56 H$_2$O nm$^{-2}$, (b) 1.13 H$_2$O nm$^{-2}$, (c) 1.70 H$_2$O nm$^{-2}$, (d) 2.26 H$_2$O nm$^{-2}$, (e) 2.83 H$_2$O nm$^{-2}$, (f) 3.39 H$_2$O nm$^{-2}$, (g) 3.96 H$_2$O nm$^{-2}$, and (h) 4.53 H$_2$O nm$^{-2}$ (from dissociatively and 1-8 more molecularly adsorbed H$_2$O molecules), shown parallel (top) and perpendicular (bottom) to the surface. Adsorption enthalpies ($\Delta H_w$) and free energies ($\Delta G_w$) in kJ mol$^{-1}$ and entropies ($\Delta S_w$) in J mol$^{-1}$ K$^{-1}$ are shown beneath each structure.
Calculations of H$_2$O adsorption near the HO–Rh(CO)$_2$ were completed with 0–7 dissociated H$_2$O (0–7.92 OH nm$^{-2}$) and, once H$_2$O begins to adsorb molecularly above this coverage, 0–20 molecularly adsorbed H$_2$O (0–11.31 H$_2$O nm$^{-2}$). The Rh, CO molecules, and all H*, OH*, and H$_2$O* on the $\gamma$-Al$_2$O$_3$ were permitted to vibrate in frequency calculations up to a total coverage of 7.92 OH nm$^{-2}$ and 2.83 H$_2$O nm$^{-2}$ (Fig. S7–S8). Above this coverage, only the Rh(CO)$_2$ was permitted to vibrate to test the effects of an H$_2$O overlayer on CO* frequencies (Fig. S9–S10). We exclude H$_2$O vibrational frequencies from these high coverages because the surface was predicted to saturate below this coverage under most conditions (absent the presence of liquid H$_2$O) and because such calculations are computationally expensive. Similarly, calculations for H$_2$O adsorption around HO–Rh(CO) (Fig. S11–S12) and HO–Rh were only performed up to a total coverage of 7.92 OH nm$^{-2}$ and 2.83 H$_2$O nm$^{-2}$ because H$_2$O is unlikely to exist above these coverages near these Rh structures.
Figure S7. γ-Al₂O₃(010) with Rh(CO)₂ and with (a) 1.13 OH nm⁻², (b) 2.26 OH nm⁻², (c) 3.39 OH nm⁻², (d) 4.53 OH nm⁻², (e) 5.66 OH nm⁻², (f) 6.79 OH nm⁻², (g) 7.92 OH nm⁻², and (h) 7.92 OH nm⁻² and 0.57 H₂O nm⁻² from 1–7 dissociatively and 0–1 more molecularly adsorbed H₂O molecules, shown parallel (top) and perpendicular (bottom) to the surface. Adsorption enthalpies (ΔH) and free energies (ΔG) in kJ mol⁻¹ and entropies (ΔS) in J mol⁻¹ K⁻¹ are shown beneath each structure for water (W subscript) and the second CO (CO₂ subscript). Calculated symmetric (blue) and asymmetric (orange) stretching frequencies are shown above each structure.
Figure S8. γ-Al$_2$O$_3$(010)$_h$ with Rh(CO)$_2$ and with 7.92 OH nm$^{-2}$ from 7 dissociatively adsorbed H$_2$O and (a) 1.13 H$_2$O nm$^{-2}$, (b) 1.70 H$_2$O nm$^{-2}$, (c) 2.26 H$_2$O nm$^{-2}$, (d) 2.83 H$_2$O nm$^{-2}$ from 2–5 more molecularly adsorbed H$_2$O molecules, shown parallel (top) and perpendicular (bottom) to the surface. Adsorption enthalpies ($\Delta H$) and free energies ($\Delta G$) in kJ mol$^{-1}$ and entropies ($\Delta S$) in J mol$^{-1}$ K$^{-1}$ are shown beneath each structure for water (W subscript) and the second CO (CO$_2$ subscript). Calculated symmetric (blue) and asymmetric (orange) stretching frequencies are shown above each structure.
Figure S9. γ-Al₂O₃(010), with Rh(CO)₂ and with 7.92 OH nm⁻² from 7 dissociatively adsorbed H₂O and (a) 3.39 H₂O nm⁻², (b) 3.96 H₂O nm⁻², (c) 4.53 H₂O nm⁻², (d) 5.09 H₂O nm⁻², (e) 5.66 H₂O nm⁻², (f) 6.22 H₂O nm⁻², (g) 6.79 H₂O nm⁻², and (h) 7.35 H₂O nm⁻² from 6–13 molecularly adsorbed H₂O molecules, shown parallel (top) and perpendicular (bottom) to the surface. Calculated symmetric (blue) and asymmetric (orange) stretching frequencies for the Rh(CO)₂ are shown above each structure.
Figure S10. γ-Al₂O₃(010) with Rh(CO)₂ and with 7.92 OH nm² from 7 dissociatively adsorbed H₂O and (a) 7.92 H₂O nm², (b) 8.49 H₂O nm², (c) 9.05 H₂O nm², (d) 9.62 H₂O nm², (e) 10.18 H₂O nm², (f) 10.75 H₂O nm², and (g) 11.31 H₂O nm² from 14–20 molecularly adsorbed H₂O molecules, shown parallel (top) and perpendicular (bottom) to the surface. Calculated symmetric (blue) and asymmetric (orange) stretching frequencies for the Rh(CO)₂ are shown above each structure.
Figure S11. γ-Al₂O₃(010)ₙ with Rh(CO) and with (a) 1.13 OH nm⁻², (b) 2.26 OH nm⁻², (c) 3.39 OH nm⁻², (d) 4.53 OH nm⁻², (e) 5.66 OH nm⁻², (f) 6.79 OH nm⁻², (g) 7.92 OH nm⁻², and (h) 7.92 OH nm⁻² and 0.57 H₂O nm⁻² from 1–7 dissociatively and 0–1 more molecularly adsorbed H₂O molecules, shown parallel (top) and perpendicular (bottom) to the surface. Adsorption enthalpies (ΔH_CO,1) and free energies (ΔG_CO,1) in kJ mol⁻¹ and entropies (ΔS_CO,1) in J mol⁻¹ K⁻¹ are shown beneath each structure for the first CO. Calculated CO stretching frequencies are shown above each structure.
Figure S12. γ-Al₂O₃(010)ₜ with Rh(CO) and with 7.92 OH nm⁻² from 7 dissociatively adsorbed H₂O and (a) 1.13 H₂O nm⁻², (b) 1.70 H₂O nm⁻², (c) 2.26 H₂O nm⁻², (d) 2.83 H₂O nm⁻² from 2–5 more molecularly adsorbed H₂O molecules, shown parallel (top) and perpendicular (bottom) to the surface. Adsorption enthalpies (ΔH_{CO,1}) and free energies (ΔG_{CO,1}) in kJ mol⁻¹ and entropies (ΔS_{CO,1}) in J mol⁻¹ K⁻¹ are shown beneath each structure for the first CO. Calculated CO stretching frequencies are shown above each structure.
S6. DFT structures of Rh(CO) and Rh(CO)$_2$ with different ligands and γ-Al$_2$O$_3$ surfaces

Figure S13. γ-Al$_2$O$_3$(010)$_h$ with Rh(CO)$_2$ and with (a) no ligand, (b) an OH$^-$, (c) an H$^-$, (d) an O$_2^-$, (e) two OH$^-$, and (f) an O$_2^-$ and OH$^-$, shown parallel (top) and perpendicular (bottom) to the surface. Calculated symmetric (blue) and asymmetric (orange) stretching frequencies for the Rh(CO)$_2$ are shown above each structure.
Figure S14. γ-Al₂O₃(010)₆ with Rh(CO) and with (a) no ligand, (b) an OH⁻, (c) an H⁻, (d) an O²⁻, (e) two OH⁻, and (f) an O²⁻ and OH⁻, shown parallel (top) and perpendicular (bottom) to the surface. Calculated stretching frequencies for the Rh(CO) are shown above each structure.
Figure S15. Rh(CO)$_2$ with an OH$^-$ ligand on (a) γ-Al$_2$O$_3$(100)$_b$ and (b) γ-Al$_2$O$_3$(001)$_b$ shown parallel (top) and perpendicular (bottom) to the surface. Calculated symmetric (blue) and asymmetric (orange) stretching frequencies for the Rh(CO)$_2$ are shown above each structure.
Figure S16. Rh(CO) with an OH− ligand on (a) γ-Al$_2$O$_3$(100)$_b$ and (b) γ-Al$_2$O$_3$(001)$_b$ shown parallel (top) and perpendicular (bottom) to the surface. Calculated stretching frequencies for the Rh(CO) are shown above each structure.
References


(5) Pigeon, T.; Chizallet, C.; Raybaud, P. *J. Catal.* **2021**.

