

Experimental and Theoretical Characterization of Rh Single Atoms Supported on γ -Al₂O₃ with Varying Hydroxyl Contents during NO Reduction by CO

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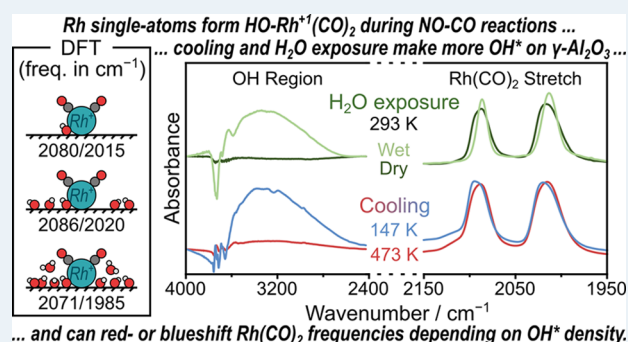
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ABSTRACT: Oxide-supported Rh catalysts are important components of commercial three-way catalysts for pollution abatement. Despite their universal application, many mysteries remain about the active structure of Rh on oxide supports as these materials often contain a mixture of nanoparticles and single-atom Rh species on the same support, even after aging. Probe molecule Fourier transform infrared (FTIR) spectroscopy in this work shows that atomically dispersed Rh on γ -Al₂O₃ prefer to strongly bind CO when exposed to NO and CO mixtures and that light-off of NO reduction occurs at temperatures similar to CO desorption, suggesting that the first and rate-determining step in NO–CO reactions may be the desorption of CO from single-atom Rh dicarbonyl complexes, Rh(CO)₂. Two sets of symmetric and asymmetric stretching frequencies associated with distinct Rh(CO)₂ species are observed in FTIR spectra at 2084/2010 and 2094/2020 cm^{−1}. During temperature ramps, the latter pair of bands at 2094/2020 cm^{−1} converts to the 2084/2010 cm^{−1} bands at 463 K before all symmetric and asymmetric bands disappear at 573 K. Bands then appear in the range of 1975–1985 cm^{−1} associated with Rh monocarbonyl, Rh(CO), species upon the disappearance of the 2084/2010 cm^{−1} bands, suggesting that CO desorbs sequentially from Rh(CO)₂ by forming Rh(CO) intermediates. Combined DFT and FTIR experiments suggest that local OH coverage on the γ -Al₂O₃ surface distinguishes the two Rh(CO)₂ species: the higher frequency species resides on a less hydroxylated region and migrates to a more hydroxylated region at higher temperatures, causing the CO vibrational frequency to decrease by ~10 cm^{−1}. CO desorption occurs from this Rh(CO)₂ structure with high local OH coverage, consistent with the DFT predicted trend of CO binding energies. Because of the coincidence of CO desorption with the light-off of NO reduction, local support hydroxylation of atomically dispersed Rh₁/ γ -Al₂O₃ catalysts likely affects both the Rh structure after CO desorption and the kinetics of NO reduction, studies of which are enabled by the Rh(CO)₂ model developed here.

KEYWORDS: NO_x reduction, three-way catalyst, alumina, single-atom catalyst, rhodium



1. INTRODUCTION

Three-way catalysts (TWCs) in catalytic converters have reduced NO_x emissions by 68% since 1980, after their commercial introduction in 1975.¹ NO_x species are reduced by H₂, CO, NH₃, or uncombusted hydrocarbons in engine effluent streams, ideally to form N₂ and CO₂, but reduction can also produce undesirable N₂O or NH₃.² Despite significant improvements, TWCs do not sufficiently reduce NO_x compounds at low temperatures during engine startup (<600 K).³ As such, TWCs remain actively studied to continue their improvement and reduce emissions. Rh is particularly important because of its high activity for NO_x reduction with CO and uncombusted hydrocarbons as reductants compared to other Pt-group metals present in TWC,^{4,5} which are more active for NO–H₂ reactions.^{6,7}

TWC wash coats typically contain less than 0.5 wt % Rh,⁸ yielding a mixture of Rh structures (and potential active sites) including small Rh nanoparticles and single atoms (Rh₁) on oxide supports.^{9–11} Additionally, Rh clusters can reversibly disperse into single atoms and re-agglomerate via Ostwald ripening at moderate temperatures.^{11–17} These dispersal-ripening processes are facilitated and accelerated by strong interactions between NO and CO reactants and single metal atoms on oxide supports,¹⁸ and more recent studies have

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illustrated that Rh_1 speciation on TiO_2 depends on the gas composition and operating conditions.^{19,20} The mobility of metal atoms during restructuring processes leads to a dynamic distribution of local active site environments under reaction conditions, which complicates rigorous analyses of their catalytic properties but may partly explain why Rh extended surfaces and large supported Rh particles behave differently than low-loading oxide-supported Rh. Therefore, analyzing the behavior of atomically dispersed Rh is required, in addition to studying Rh particles, to understand NO_x reduction in catalytic converters where reactions could occur on Rh nanoparticles, single atoms, or both.

Catalysts solely comprising Rh_1 species (within detection limits) have been synthesized in our prior work on $\gamma\text{-Al}_2\text{O}_3$.^{21,22} These Rh_1 species selectively produce NH_3 (an undesired byproduct of NO_x reduction that contributes to atmospheric particulate formation)²³ during NO reduction in the presence of H_2O , while nanoparticles more selectively produce N_2 (0.05–5 wt % $\text{Rh}/\gamma\text{-Al}_2\text{O}_3$ and Rh/CeO_2 , 373–623 K, 0.5 kPa CO, 0.1 kPa NO, 0–2% H_2O).^{21,24} The structure of Rh_1 species dispersed on $\gamma\text{-Al}_2\text{O}_3$ has been investigated in prior work using both theory and experiment, but none have identified the precise structure of the single Rh atoms in conditions relevant to NO_x reduction and the effects of surface hydroxylation on their characteristics.^{10–13,21,25–28} Probe molecule Fourier transform infrared (FTIR) spectroscopy can help identify these Rh structures and reveal their bonding geometries to reactants—in this case, CO and NO. Early CO probe-molecule FTIR studies of $\text{Rh}_1/\text{Al}_2\text{O}_3$ (0.2–2.2 wt %) identified stretching frequencies characteristic of Rh *gem*-dicarbonyl structures— $\text{Rh}(\text{CO})_2$ —with symmetric and asymmetric vibrations near 2090 and 2020 cm^{-1} , respectively, that did not vary in frequency with CO^* coverage.^{11–13,27,29} Moreover, these IR bands disappeared simultaneously during CO desorption, indicating that the bands were associated with the same species. These studies suggested that the Rh was likely in a +1 oxidation state based on the stoichiometry, X-ray photoelectron spectroscopy (XPS),¹³ and extended X-ray absorption fine structure (EXAFS) data.^{13,25,26}

The $\gamma\text{-Al}_2\text{O}_3$ surface has many local environments to host supported Rh species. Undercoordinated edge sites on $\gamma\text{-Al}_2\text{O}_3$ particles can be critical for some chemistries, such as ethanol dehydration.^{30–33} These edges may also border different facets that are heterogeneously distributed on the $\gamma\text{-Al}_2\text{O}_3$ surface; previous microscopy studies have shown that $\gamma\text{-Al}_2\text{O}_3$ facet sizes approach the nanometer scale on some particles.³⁴ Theoretical studies have suggested the existence of an OH ligand on a $\text{Rh}^+(\text{CO})_2$ species supported on $\gamma\text{-Al}_2\text{O}_3$;¹⁰ however, such studies did not account for a range of possible OH concentrations on the surface or the effects of changing Rh oxidation states through interactions with other ligands or compare calculations with experimental characterization data. OH groups on the surface of $\gamma\text{-Al}_2\text{O}_3$ vary in concentration and structure as conditions change according to density functional theory (DFT) calculations of a $\gamma\text{-Al}_2\text{O}_3$ model derived from dehydrated boehmite,^{35–39} and thermogravimetric and surface area analyses suggest that average coverages can range from 8 to 12 OH nm^{-2} at the temperatures relevant to CO desorption (573–673 K).^{40,41} Neighboring OH may also form hydrogen bonding networks: at high coverage, densely packed OH can form ice-like regions on the support,⁴² and OH gathered in surface depressions can form nest-like structures where water can accumulate,^{43,44} similar to H-bond networks near silanol

nests on zeolites.^{45–50} Furthermore, IR bands associated with hydroxyl groups at 3679 and 3735 cm^{-1} decrease when CO is introduced to a 2.2 wt % $\text{Rh}/\gamma\text{-Al}_2\text{O}_3$ sample while symmetric and asymmetric $\text{Rh}(\text{CO})_2$ peaks grow, indicating that particular OH groups are displaced or consumed during the dissolution and oxidation of Rh clusters to $\text{Rh}^+(\text{CO})_2$.^{28,51} Interestingly, exposing the $\text{Rh}/\gamma\text{-Al}_2\text{O}_3$ to NH_3 mitigates this Rh dispersal process by bonding to $\gamma\text{-Al}_2\text{O}_3$ hydroxyl groups.⁵² A better understanding of the role of OH groups in the behavior and structure of these Rh_1 species is critical to studying these active sites for NO_x reduction.

Rh atoms are likely deposited on several facets and in different OH environments during synthesis but can become mobile and likely reconstruct on $\gamma\text{-Al}_2\text{O}_3$ depending on changing surface environments during catalyst treatment and reaction conditions. CO-induced restructuring of atomically dispersed $\text{Rh}_1/\gamma\text{-Al}_2\text{O}_3$ relies on the migration of $\text{Rh}(\text{CO})_2$ across the $\gamma\text{-Al}_2\text{O}_3$ surface to produce spatially isolated Rh species or to induce their re-agglomeration.^{11–16} Indeed, sintering of atomically dispersed Rh can be suppressed by anchoring organic ligands to limit Rh mobility.^{53,54} Rh cluster fragmentation occurs on the order of seconds when exposed to CO near ambient temperature, according to time-resolved EXAFS, with a low 17 kJ mol^{-1} barrier to form $\text{Rh}(\text{CO})_2$ from adjacent Rh atoms.¹⁴ DFT studies of Pd₁ diffusion indicated an activation barrier between 15 and 72 kJ mol^{-1} for diffusion across dehydrated and hydrated (110) $\gamma\text{-Al}_2\text{O}_3$ surfaces, respectively.⁵⁵ The high mobility of Rh atoms may allow them to traverse the $\gamma\text{-Al}_2\text{O}_3$ surface and sample a range of surface facets, local adsorbate environments, and hydroxyl densities at relevant desorption and reaction conditions until finding a stable bonding geometry.

Here, we use a combination of spectroscopic and theoretical methods to rigorously analyze the structure, adsorption behavior, and spectroscopic properties of Rh_1 supported on $\gamma\text{-Al}_2\text{O}_3$ under conditions relevant for NO reduction by CO. We show that $\text{Rh}(\text{CO})_2$ is the preferred structure when single Rh atoms are exposed to NO reduction reaction conditions (478 K, 0.5 kPa CO and 0.1 kPa NO, Ar balance, 1 bar total). DFT-calculated vibrational frequencies of adsorbed CO^* most closely match experiments when $\text{Rh}(\text{CO})_2$ is coordinated to a single OH^- group—compared to other possible ligands containing H and O—on the $\gamma\text{-Al}_2\text{O}_3$ surface at a variety of water coverages. Furthermore, FTIR spectroscopy reveals shifts in CO frequency that suggest the local Rh environment changes during temperature-programmed desorption (TPD), which is expected for a mobile species on a heterogeneous support like $\gamma\text{-Al}_2\text{O}_3$. We conclude that local OH coverage around $\text{Rh}(\text{CO})_2$ alters the *gem*-dicarbonyl symmetric and asymmetric stretching frequencies and CO binding energies, suggesting that this factor is relevant for CO desorption and subsequent reactions of NO and CO on atomically dispersed $\text{Rh}_1/\gamma\text{-Al}_2\text{O}_3$.

2. MATERIALS AND METHODS

2.1. Computational Methods and Models. Periodic DFT calculations were completed using the Vienna Ab initio Simulation Package^{56–59} in the computational catalysis interface (CCI).⁶⁰ The revised Perdew–Burke–Ernzerhof (RPBE) form of the generalized gradient approximation (GGA) was used for most calculations,^{61,62} and planewaves were composed of projector augmented waves (PAW)^{63,64} with an energy cutoff of 400 eV. Select structures were

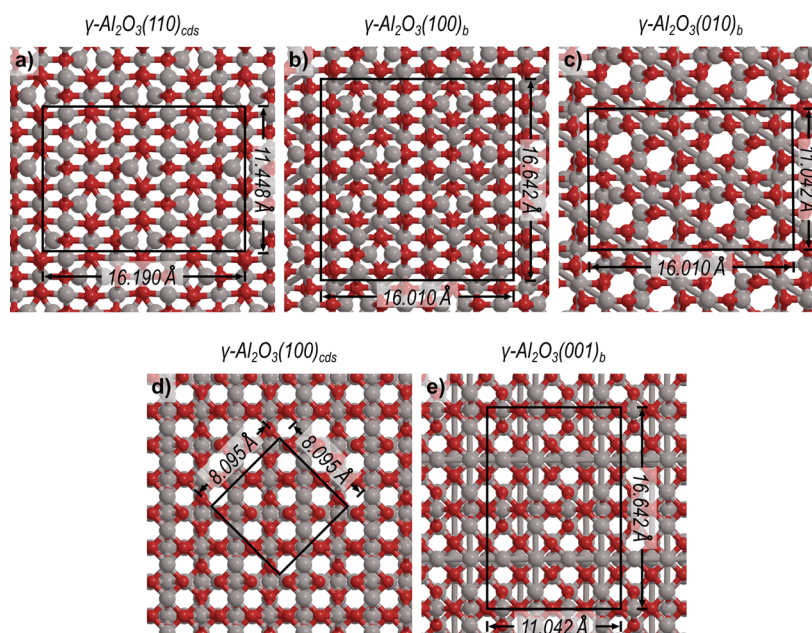


Figure 1. Top views of the (a) $(110)_{\text{cds}}$ surface and the corresponding (b) $(100)_b$ and (c) $(010)_b$ surfaces and the (d) $(100)_{\text{cds}}$ and corresponding (e) $(001)_b$ surface models of $\gamma\text{-Al}_2\text{O}_3$. Lengths of unit cell vectors are labeled in Å. Additional views are shown in Figure S2 of the Supporting Information.

Table 1. Identities and Unit Cell Parameters of Surface Models from $\gamma\text{-Al}_2\text{O}_3$ Tested in This Work

boehmite facet	$\gamma\text{-Al}_2\text{O}_3$ facet ^a	unit cell parameters ($a \times b \times c$)/Å ^b	$\gamma/^\circ$ ^c	supercell
$(100)_b$	$(110)_{\text{cds}}$	$8.321 \times 8.005 \times 21.851$	90.000	$2 \times 2 \times 1$
$(010)_b$	$(110)_{\text{cds}}$	$8.005 \times 5.521 \times 17.066$	90.588	$2 \times 2 \times 1$
$(001)_b$	$(100)_{\text{cds}}$	$5.521 \times 8.321 \times 16.358$	90.000	$2 \times 2 \times 1$

^aThe most similar surface of cds materials. ^bThe c -vector for each facet is perpendicular to the exposed surface and includes the 10 Å of vacuum. ^c α and β values are 90.00° for all surface models.

optimized a second time using the Heyd–Scuseria–Ernzerhof (HSE06) hybrid exchange–correlation functional.^{65–68} Structures were optimized using a multi-step process implemented in CCI. Wavefunctions were converged to within 10^{-4} in the first step with forces calculated using a fast Fourier transform (FFT) grid of $1.5 \times$ the plane-wave cutoff. Wavefunctions were optimized in the second step within 10^{-6} eV and with an FFT grid $2 \times$ the plane-wave cutoff. Structures were optimized such that forces on all atoms were <0.05 eV Å⁻¹ in both steps. Partial charges were estimated using quasiatomic minimum basis orbitals (QUAMBO).⁶⁹ Gas-phase species were modeled in $18 \times 18 \times 18$ Å unit cells surrounded by vacuum with spin polarization for species with partially occupied orbitals in their valence shells.

The $\gamma\text{-Al}_2\text{O}_3$ model employed here was developed from a bulk structure constructed by modeling the dehydration of boehmite [$\gamma\text{-AlO}(\text{OH})$] to form $\gamma\text{-Al}_2\text{O}_3$ ($a = 5.587$ Å, $b = 8.413$ Å, $c = 8.068$ Å; $\alpha = \gamma = 90.00^\circ$, $\beta = 90.59^\circ$).^{35,37–39} This approach is necessary because previous cubic defect spinel-like models were less stable in DFT calculations and as-synthesized $\gamma\text{-Al}_2\text{O}_3$ has low crystallinity, rendering periodic models for DFT difficult to construct from characterization data alone.³⁵ We illustrate the instability of cubic defect spinel models during DFT calculations and compare the boehmite-derived model³⁷ and a cubic defect spinel model⁷⁰ ($a = b = c = 7.887$ Å; $\alpha = \beta = \gamma = 90.00^\circ$) in Section S2 of the Supporting Information. After optimizing the bulk unit cell parameters of the boehmite-derived $\gamma\text{-Al}_2\text{O}_3$ model ($a = 5.521$ Å, $b = 8.321$

Å, $c = 8.005$ Å; $\alpha = \gamma = 90.00^\circ$, $\beta = 90.588^\circ$), surface formation energies were calculated for the (100) , (010) , and (001) surfaces of this dehydrated boehmite surface (Figure 1 and Table 1). We note that in this work we retain the Miller indices for the boehmite from which this $\gamma\text{-Al}_2\text{O}_3$ model was derived because its (100) and (010) surfaces both resemble the (110) facet of $\gamma\text{-Al}_2\text{O}_3$, although they differ in their structures and unit cell sizes (Figure 1).³⁹ These surfaces have distinct Miller indices from cubic defect spinel $\gamma\text{-Al}_2\text{O}_3$ models, as shown in Figure 1 and discussed in Section S2 of the Supporting Information. We denote the surfaces of the models we use in this study with a “b” subscript to show that they are derived from dehydrated boehmite [e.g., $(010)_b$], while indices for the typical cubic defect spinel structure are denoted with a “cds” subscript, including when describing experimental characterization data [e.g., $(110)_{\text{cds}}$, which most closely matches $(100)_b$ and $(010)_b$]. A 10 Å vacuum layer was added above the surface. Supercells were used for each surface to reduce lateral interactions between adsorbates on Rh/ $\gamma\text{-Al}_2\text{O}_3$ systems, as shown in Table 1. Calculations using the RPBE functional for $\gamma\text{-Al}_2\text{O}_3$ and Rh/ $\gamma\text{-Al}_2\text{O}_3$ systems sampled the Brillouin zone using a Γ -centered $2 \times 2 \times 1$ K -point mesh and were performed with spin polarization. Calculations performed with HSE06 only sampled the Γ -point of the Brillouin zone.

We calculate binding energies for H_2O^* or OH^*/H^* pairs on $\gamma\text{-Al}_2\text{O}_3$ surfaces ($\Delta E_{\text{W},n}$) with respect to gas-phase $\text{H}_2\text{O}(\text{g})$

$$\Delta E_{\text{W},n} = E_{\text{W},n} - E_{\text{W},n-1} - E_{\text{W}(\text{g})} \quad (1)$$

where $E_{W,n}$ is the energy of the most stable configuration of n H_2O^* (or n OH^*/H^* pairs) on the surface. Similarly, for CO^* on $Rh_1/\gamma-Al_2O_3$ ($\Delta E_{CO,n}$), differential binding energies were also calculated

$$\Delta E_{CO,n} = E_{Rh(CO)_n} - E_{Rh(CO)_{n-1}} - E_{CO(g)} \quad (2)$$

where $E_{Rh(CO)_n}$ is the most stable configuration of the Rh single atom with n CO adsorbates. Finally, the binding energy of the entire $Rh(CO)_2$ complex was calculated using a gas-phase $Rh(CO)_2$ reference state

$$\Delta E_{Rh(CO)_2} = E_{Rh(CO)_2/Al_2O_3} - E_{Al_2O_3} - E_{Rh(CO)_2(g)} \quad (3)$$

to give insights into the adhesion of these $Rh(CO)_2$ species to $\gamma-Al_2O_3$. This gas-phase $Rh(CO)_2$ structure was calculated with spin polarization, as were $\gamma-Al_2O_3$ and $Rh/\gamma-Al_2O_3$ systems.

Frequency calculations of optimized structures were used to determine zero-point vibrational energies (ZPVE) and rotational, translational, and vibrational enthalpies (H) and free energies (G) at 473 K based on formalisms from statistical mechanics (Section S1, [Supporting Information](#)).⁷¹ Translation and rotation of adsorbates on surfaces were treated as frustrated motions and modeled as vibrations, while translation and rotation of gas-phase species were treated as ideal, and corresponding translational and rotational partition functions were used to calculate enthalpy

$$H = E_0 + ZPVE + H_{vib} + H_{rot} + H_{trans} \quad (4)$$

and free energy

$$G = E_0 + ZPVE + G_{vib} + G_{rot} + G_{trans} \quad (5)$$

Frequencies were calculated using a fixed displacement method (two displacements) where all adsorbate atoms (H_2O^* , H^* , OH^* , Rh, and anything bound to Rh) were displaced. All frequencies below 60 cm^{-1} were replaced with 60 cm^{-1} in estimations of enthalpy or free energies, consistent with prior work,^{6,72,73} because low-frequency vibrations are inaccurately predicted by DFT, but their exclusion would exacerbate errors in computed adsorbate entropies. CO stretch frequencies were scaled based on the gas-phase CO stretching frequency (2143 cm^{-1})⁷⁴ and the DFT-calculated CO stretching frequency. For example, the calculated CO frequency is 2102 cm^{-1} using the RPBE functional and PAW potentials, and therefore, all calculated frequencies using those methods were scaled by a factor of 1.019. Frequencies were not adjusted when calculating enthalpies and free energies.

2.2. Experimental Methods. 2.2.1. Catalyst Synthesis.

Atomically dispersed 0.1 and 0.05 wt % Rh catalysts were synthesized using incipient wetness impregnation by dissolving Rh(III) nitrate hydrate precursor [$Rh(NO_3)_3 \cdot xH_2O$, Sigma-Aldrich, CAS: 10139-58-9] in 80 cm^3 of high-performance liquid chromatograph-grade water (J.T. Baker, CAS: 7732-18-15) and adding the diluted precursor solution 0.2 cm^3 at a time to dry $\gamma-Al_2O_3$ support powder (Sasol, Puralox TH100/150, CAS: 9529248-35-0) in a 10 cm^3 ceramic evaporation dish. The mixtures were dried overnight in an oven at 373 K. The catalyst powders were then treated in dry air in a tube furnace at 623 K for 4 h.

2.2.2. Probe Molecule FTIR Spectroscopy. Catalysts were loaded in a Harrick low-temperature reaction chamber mounted inside a ThermoScientific Praying Mantis diffuse reflectance adapter set in a Nicolet iS10 FTIR spectrometer with a mercury cadmium telluride (MCT) detector, and mass flow controllers (Teledyne Hastings) were used to control the

gas flow rates across the reactor bed. Catalysts were pretreated in situ for 0.5 h at 623 K in pure O_2 at 1 bar and subsequently in 10 kPa H_2/Ar at 373 K in a Harrick reaction chamber for 1 h. FTIR spectra were taken with 12 scans and 0.482 cm^{-1} data spacing. IR spectra collected under reaction conditions were taken after samples were pretreated in situ, heated to a reaction temperature of 478 K in flowing Ar, while continuously exposed to flowing 0.1 kPa NO, 0.5 kPa CO, and balance Ar until spectra remained unchanging. CO probe molecule IR spectra were taken after samples were pretreated in situ, brought to the CO adsorption temperature (298 or 423 K) in flowing Ar, exposed to flowing 1 kPa CO in Ar until Rh sites were saturated—indicated when spectra remained unchanging—and purged with Ar. Isotopically labeled CO ($>99\%$ ^{13}CO , $<5\%$ ^{18}O) was used to identify NCO^* by saturating the catalyst with 10 kPa ^{13}CO and pulsing with 1 kPa NO at 463 K. The predominant Rh species was probed by saturating the catalyst with 0.5 kPa CO prior to exposure to 0.5 kPa CO and 0.1 kPa NO at 463 K and by allowing the catalyst to remain in 0.5 kPa CO and 0.1 kPa NO at 523 K for 1.5 h. Cryogenic temperatures were achieved by adding liquid N_2 to a dewar attached to the reaction chamber. The area of the H-bonding OH region ($3600\text{--}2500\text{ cm}^{-1}$) was computed with a linear baseline between 4000 and 2400 cm^{-1} , and the full width at half max (fwhm) was taken as the width of each CO peak at half the distance from peak maximum to a linear baseline between the end points of the peak. In experiments where the material was exposed to variable water concentrations, the CO-saturated Rh catalyst was exposed to a water-saturated Ar stream by diverting the Ar through a water bubbler at ambient temperature and pressure prior to entering the reaction chamber.

TPD measurements were executed by heating the sample in Ar at a rate (β) of 0.33 K s^{-1} (20 K min^{-1}) until all CO desorbed while taking spectra continuously. The rate of band intensity loss was traced using the change in peak areas of deconvoluted spectra, integrated and fit using Origin by fixing constant peak fwhm and positions. We estimate the CO binding energy range by solving the following form of the Redhead analysis equation numerically in MATLAB, similar to our prior work⁵³

$$\ln\left(\frac{\beta}{k_B T_p^2}\right) = \frac{-E}{k_B T_p} + \ln\left(\frac{A}{E}\right) \quad (6)$$

where E is the binding energy, T_p is the peak desorption temperature, k_B is the Boltzmann constant, β is the temperature ramp rate (0.33 K s^{-1}), and A is the pre-exponential factor. When estimating the CO binding energy without an entropic barrier ($\Delta S = 0$), we use a preexponential factor (A) of 10^{13} ,⁷⁵ based on a previous analysis of flat Rh surfaces where single molecular desorption occurs.⁷⁶ When estimating the upper limit of the CO binding energy, the pre-exponential factor (A) used is $6 \times 10^{11}\text{ s}^{-1}$ for a CO entropic desorption barrier of $52\text{ J mol}^{-1}\text{ K}^{-1}$ from $Rh(CO)_2$, as calculated in a previous work.⁵³ From these energies, we can estimate desorption enthalpy, ΔH

$$\Delta H = E - RT_p \quad (7)$$

where R is the ideal gas constant.

2.2.3. NO Reduction Light-Off Experiment. “Light-off” experiments were performed to test the reactivity of atomically dispersed Rh catalysts, where the reactor was heated at a

constant rate under reactive environments from ambient temperature, mimicking engine start-up conditions. Catalysts were diluted with purified SiO₂ (Sigma-Aldrich, CAS: 84878) to 2 (mg Rh) g_{cat}^{−1} in a home-built, temperature-controlled reactor system with mass flow controllers (Teledyne Hastings) to precisely control CO, NO, H₂O, and Ar gas flow concentrations. After pretreatment identical to that used before CO FTIR characterization, catalysts were heated by 0.0833 K s^{−1} from 293 to 723 K, while 4.17 cm³ s^{−1} of 0.5 kPa CO and 0.1 kPa NO in Ar gas (1 bar total) flowed over a packed bed. Gas-phase product compositions were identified by flowing outlet effluent through a Thermo Scientific Antaris IGS 2 m Gas Cell set in a Nicolet iS10 FTIR spectrometer with an MCT detector and using OMNIC Series Software to take 5 spectral scans every 10 s at high 0.5 resolution and 0.241 cm^{−1} data spacing. Reactants and products were calibrated with the TQ Analyst Pro Edition Software to identify established spectral signatures of known mixtures of CO, NO, N₂O, NH₃, CO₂, and H₂O in Ar at set pressure and temperature.

3. RESULTS AND DISCUSSION

3.1. CO–NO Mixtures over Atomically Dispersed Rh.

Designing structural models that coincide with characterization data of working catalytic active sites first requires the identification of structural elements present under reaction conditions. In situ FTIR provides insights into the Rh structure during NO reduction by CO and the predominant adsorbate that saturates the active sites. Upon exposure to conditions of realistic TWC operation, 0.5 kPa CO and 0.1 kPa NO (5000 and 1000 ppm, respectively) at 478 K, atomically dispersed Rh exists predominantly as Rh(CO)₂ with characteristic frequencies at 2084 and 2102 cm^{−1} and without peaks associated with NO* on Rh expected in the range of 1700–1800 cm^{−1} (Figure 2).^{11,12,25,27} Additionally, exposing a CO-saturated catalyst to

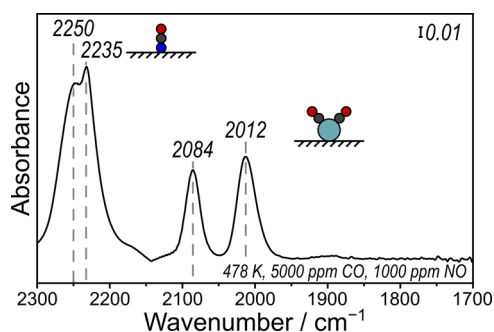


Figure 2. In situ IR spectra of 0.1 wt % Rh/γ-Al₂O₃ during NO–CO reactions at 478 K for 600 s (0.5 kPa CO and 0.1 kPa NO, Ar balance, 1 bar total). Inset cartoons show the assigned species associated with the observed bands where O is red, C is gray, N is blue, and Rh is cyan.

the mixture of NO and CO does not cause the intensity of Rh(CO)₂ bands to decrease (Figure S2a, Supporting Information). These data indicate that atomically dispersed Rh is exclusively coordinated to CO, rather than NO, at conditions similar to those in automotive exhaust treatment. This preference for CO* on Rh₁ contrasts with Rh nanoparticles and surfaces, where NO adsorbs more strongly than CO, resulting in NO*-saturated Rh surfaces under similar conditions.⁷⁷ The differences in the preferred most abundant surface intermediates (MASI) between Rh₁ and Rh nano-

particles may contribute to differences in their selectivities and reactivities during NO_x reduction. Therefore, we focus on Rh₁ coordinated to CO* in this study to guide DFT-calculated structures with experimental characterization data. The models developed herein can then be used to study the mechanistic differences between these active site structures more rigorously in future work.

Notably, other peaks appear at 2250 and 2235 cm^{−1} during exposure of the catalysts to CO and NO, which are assigned to adsorbed NCO* species on γ-Al₂O₃. The shoulders at 2130 and 2170 cm^{−1} in Figure 2 correspond to the P and R branches of gas-phase CO, respectively. These features are visible in the IR spectrum of the 0.05 wt % Rh/γ-Al₂O₃ catalyst during CO exposure in the absence of NO (Figure S2a, Supporting Information), but they do not appear in spectra of the catalysts that had been exposed to the NO/CO mixture and then purged with Ar (Figure S2b, Supporting Information). IR spectra of the 0.05 wt % Rh/γ-Al₂O₃ sample show similar but shifted bands when exposed to ¹²CO and isotopically labeled ¹³CO mixed with NO (Figure S2b, Supporting Information). Both the sets of symmetric and asymmetric Rh(CO)₂ stretches, and the features near 2230–2250 red-shift by ~50 cm^{−1}, indicating that each is associated with species containing C, which further indicates that the 2230–2250 cm^{−1} bands are caused by NCO*. Prior work^{21,78–81} has indicated that such NCO* species can spill over onto the γ-Al₂O₃ support once formed during NO reduction by CO on Rh/γ-Al₂O₃, which is confirmed in this work by the slow growth of these features without loss of Rh(CO)₂ in IR spectra collected at 523 K (Figure S2c, Supporting Information). Al₂O₃ also favors the formation of NCO* species more than other more inert materials such as SiO₂ and MgO,^{81,82} further indicating the importance of the support in forming and stabilizing these NCO*. Although these earlier studies used higher weight loadings of Rh, their findings indicate that understanding support effects is crucial to understanding the mechanism of NO_x reduction on both Rh₁ and nanoparticles. Notably, the precise mechanism by which these NCO* species form on Rh₁ remains unknown, and additional data are needed to determine the preferred path. While prior studies have suggested that NCO* can form through N* on Rh nanoparticles,⁷⁸ the same mechanism may not be possible on Rh₁. Thus, we conclude that NCO* is adsorbed only on the γ-Al₂O₃ support, while atomically dispersed Rh species exist almost exclusively as Rh(CO)₂ species under reaction conditions.

Prior studies have indicated that oxide-supported Rh(CO)₂ species are in a +1 oxidation state and are bound to an OH on the surface of the oxide.^{20,83,84} We explore different coordinating ligands that lead to different Rh oxidation states using DFT calculations, but we first compare the binding energies of CO and NO to confirm the observed preponderance of Rh(CO)₂ in IR spectra observed below 573 K in Figure 3 in an NO/CO mixture. Electronic binding energies for the first CO are weaker (−268 kJ mol^{−1}) than for NO (−299 kJ mol^{−1}), while the second NO binds more weakly (−169 kJ mol^{−1}) than the second CO (−174 kJ mol^{−1}) when calculated using the RPBPE exchange–correlation functional (Figure 3). Previous work has used HSE06 hybrid functionals to improve predictions from GGA functionals for NO binding to single-atom Cu^{85–87} and Pd⁸⁸ within zeolites because GGA functionals overpredict NO binding energies on these cationic metal sites. While Rh differs from Cu and Pd, we repeat these binding energy calculations using HSE06 for comparison to

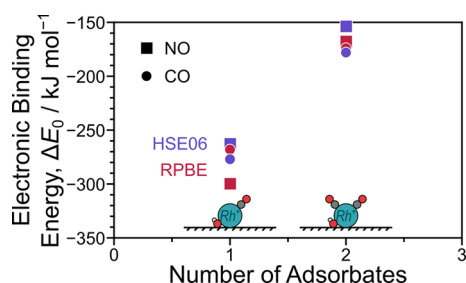


Figure 3. Electronic binding energies (ΔE_0) for CO (●) and NO (■) on an Rh single atom coordinated to an OH ligand on the γ -Al₂O₃ using the RPBE exchange–correlation functional (red) and the HSE06 exchange–correlation functional (purple).

RPBE for these adsorbates with more complex electronic structures. CO binding energies from HSE06 (−277 and −178 kJ mol^{−1}) remain similar to those from RPBE (−268 and −174 kJ mol^{−1}) for the first and second CO, respectively. In contrast, NO binding energies are much weaker when calculated with HSE06 (−262 and −153 kJ mol^{−1} for the first and second NO, respectively) than with RPBE (−299 and −167 kJ mol^{−1}) (Figure 3). These findings indicate that more accurate computational approaches are needed for molecules with challenging electronic structures like NO and that RPBE is appropriate for CO calculations on these Rh models. Additionally, these data corroborate the experimental observation that Rh single atoms are saturated by CO* pairs rather than NO* or CO*–NO* mixtures in situ, which is in contrast to the preference of extended Rh surfaces to be saturated by NO* under similar conditions.⁷⁷ While the differences in these computed binding energies are close to DFT error (typically considered ± 10 kJ mol^{−1}), their agreement with experimental observations and the change in the binding trends indicate that HSE06 more accurately predicts adsorption behavior on Rh₁. Based on the absence of any other features between 1700 and 2300 cm^{−1} in the in situ IR and initial calculations suggesting the preference for CO rather than NO to adsorb on Rh₁, we focus on understanding the characteristics of Rh(CO)₂ as the catalyst approaches reaction conditions.

3.2. FTIR Measurements of CO on γ -Al₂O₃-Supported Atomically Dispersed Rh. The CO stretching bands

characteristic of the symmetric and asymmetric frequencies of Rh(CO)₂ species at 2094 and 2020 cm^{−1} are observed in CO probe molecule FTIR measurements in Ar at 298 K, after a 0.1 wt % Rh/ γ -Al₂O₃ catalyst was pretreated in situ for 0.5 h at 623 K in pure O₂ at 1 bar, followed by 10 kPa H₂/Ar at 373 K for 1 h and saturated by flowing 1% CO/Ar at 1 bar for 0.5 h at 298 K (Figure 4a). The absence of CO bands in experimental FTIR spectra at frequencies characteristic of linear (~ 2080 – 2040 cm^{−1}) and bridge- or threefold bound (~ 1950 – 1850 cm^{−1}) CO* on Rh clusters confirms that Rh exists primarily as atomically dispersed species following CO exposure in this sample.^{77,89} Both the symmetric and asymmetric Rh(CO)₂ vibrational bands are broad and non-symmetric (>20 cm^{−1} fwhm), suggesting the presence of multiple Rh(CO)₂ coordination environments.^{11,90,91} TPD of CO from the 0.1 wt % Rh catalyst proceeds nonuniformly across both the symmetric and asymmetric Rh(CO)₂ bands, as the peak centers shift to lower frequency within each band. This suggests that there are distinct Rh(CO)₂ species on the γ -Al₂O₃, each with its own set of symmetric and asymmetric Rh(CO)₂ frequencies. Deconvolution of the FTIR spectra yields good fits to the data by including two pairs of peaks at 2094/2020 and 2084/2010 cm^{−1} (Figure 4b). As the temperature increases from 293 to 493 K, the bands at 2094 and 2020 cm^{−1} decrease in intensity together, while the bands at 2084 and 2010 cm^{−1} grow, suggesting that both species are Rh(CO)₂ and that the first species converts to the second species as temperature increases (Table 2). At 493 K, the 2084

Table 2. Vibrational Frequencies and fwhm Parameters for Deconvoluted FTIR Stretches Associated with CO Bound to Atomically Dispersed Rh₁/ γ -Al₂O₃

species	temperature range/K ^a	wavenumber/cm ^{−1}	fwhm/cm ^{−1}
Rh(CO) ₂	293–493 K	2094/2020	11/12
	493–603 K	2084/2010	22/29
Rh(CO)	>603 K	1985 and 1975	49 and 36

^aThe temperature range at which the species dominates the surface based on IR bands.

and 2010 cm^{−1} peaks reach maximum area before decreasing. The peak positions and widths of the 2084 and 2010 cm^{−1}

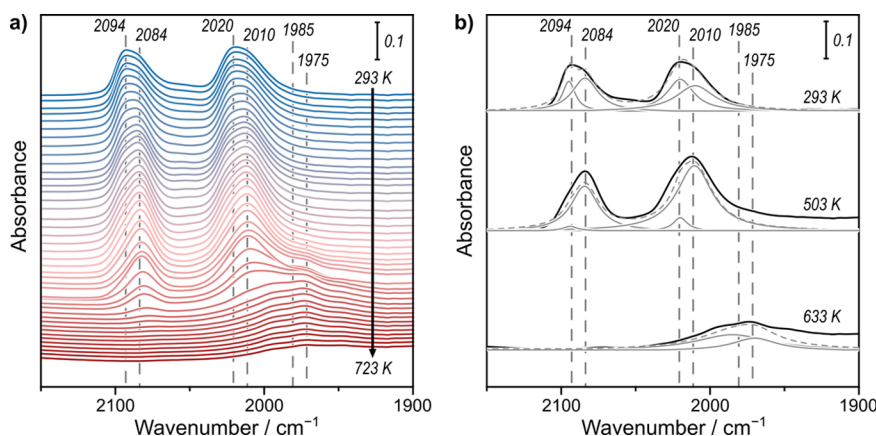


Figure 4. (a) IR spectra taken of 0.1 wt % Rh/ γ -Al₂O₃ every 10 K after the sample is fully saturated with CO, and as temperature increases at a rate of 0.33 K s^{−1} (20 K min^{−1}) from 293 K (blue) to 723 K (red). (b) Deconvolution spectra from (a) at 293, 503, and 633 K. Deconvoluted peaks (solid gray lines) are shown at each noted wavelength (2094, 2084, 2020, 2010, 1985, and 1975 cm^{−1}) with their sum (dashed gray lines) at each temperature.

features were identified following complete loss of the 2094/2020 cm^{-1} features, to enable deconvolution of the $\text{Rh}(\text{CO})_2$ peaks in each spectrum during the TPD. The loss of 2084 and 2010 cm^{-1} peaks occurs concurrently with the emergence and growth of bands at $\sim 1975\text{--}1985\text{ cm}^{-1}$, which reach a maximum area at 603 K. Previous work on Rh_1/TiO_2 suggests that these bands appear because CO desorbs sequentially from $\text{Rh}(\text{CO})_2$ to form an $\text{Rh}(\text{CO})$ intermediate when the Rh is complexed to an OH species on the support.^{20,83,84} Consistent with this finding, we observe that CO desorbs sequentially from $\text{Rh}_1/\gamma\text{-Al}_2\text{O}_3$; after the first CO desorbs, a $\text{Rh}(\text{CO})$ species remains with CO vibrational stretches of 1975–1985 cm^{-1} . The most prominent $\text{Rh}(\text{CO})$ peaks appear at 1985 and 1975 as distinct species; however, the large fwhm of these peaks (39 and 45 cm^{-1} , respectively) indicate that the local environment around $\text{Rh}(\text{CO})$ varies.

The new CO vibrational frequency that appears at 1975–1985 cm^{-1} does not coincide with the growth of any additional CO vibrational frequencies expected for terminal and bridging vibrational modes on small clusters, such as $\text{Rh}_2(\text{CO})_3$,⁹² $\text{Rh}_4(\text{CO})_{12}$,⁹³ or $\text{Rh}_6(\text{CO})_{16}$.⁹³ Furthermore, larger Rh nanoparticles, such as those formed on 10 wt % $\text{Rh}/\gamma\text{-Al}_2\text{O}_3$ that we studied in our prior work,⁷⁷ would have a bridge-bound CO^* mode far below this frequency at $\sim 1870\text{ cm}^{-1}$ and a linearly bound CO^* stretch that shifts from 2067 cm^{-1} at high CO coverage to 1989 cm^{-1} at the lowest observed coverage. The latter frequency is above the observed frequencies at 1985 and 1975 cm^{-1} , which suggests that they are likely not attributable to CO^* linearly bound to Rh nanoparticles. In situ X-ray absorption spectroscopy (XAS) on the same material showed a significant increase in the Rh oxidation state and Rh–O coordination with minimal Rh–Rh coordination following the same TPD procedure.⁹⁴ These XAS data indicate that Rh oxidizes rather than sinters during thermal CO desorption. Additionally, we characterized the final Rh structure here by cooling to 143 K and re-exposing the catalyst to CO to probe the final Rh structure following TPD and mitigate Rh dispersion commonly caused by CO.⁹⁵ $\text{Rh}(\text{CO})_2$ intensity increased after this CO exposure, indicating that atomically dispersed Rh species remain after TPD, but the original intensity was not fully recovered (Figure S4, Supporting Information). Rh that became oxidized after CO desorption likely would not bind CO at this temperature. No new features of linearly or bridge-bound CO were detected; therefore, metallic Rh clusters did not form or formed in an undetectably small amount. The intensity of the 1975–1985 cm^{-1} feature also decreased following CO exposure, likely because $\text{Rh}(\text{CO})_2$ formed from $\text{Rh}(\text{CO})$. As such, we assign the 1975–1985 cm^{-1} feature to an atomically dispersed Rh monocarbonyl, $\text{Rh}(\text{CO})$, formed from the sequential desorption of CO molecules from $\text{Rh}(\text{CO})_2$.

Interestingly, the disappearance of peaks at 2084 and 2010 cm^{-1} closely corresponds to light-off of NO reduction by CO over atomically dispersed Rh sites (Figure 5). The coincidence of CO desorption with reactivity light-off suggests that NO–CO reactions on $\text{Rh}(\text{CO})_2$ sites begin with the desorption of CO and that this CO desorption is a kinetically relevant step of the NO–CO reaction. This is in direct contrast to NO reduction over Rh nanoparticles, where the Rh particle surface is NO^* saturated and NO^* is consumed by dissociating during light-off (10 wt % $\text{Rh}/\gamma\text{-Al}_2\text{O}_3$, 273–673 K, 0.5 kPa CO and 0.1 kPa NO).^{21,77} These data also indicate that NO^* reacts rapidly once CO^* is displaced from $\text{Rh}_1/\gamma\text{-Al}_2\text{O}_3$. As such,

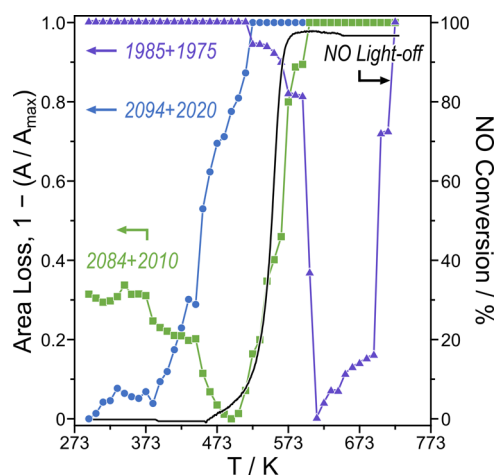


Figure 5. Total peak area loss for the sum of peak areas associated with the 2094 and 2020 cm^{-1} peaks (blue, ●), 2084 and 2010 cm^{-1} peaks (green, ■), and 1985 and 1975 cm^{-1} peaks (purple, ▲) normalized by the maximum sum of absorbance (A_{max}) as a function of temperature during TPD overlaid with NO conversion (%) as a function of temperature at a ramp rate of 0.083 K s^{-1} in 0.5 kPa of CO and 0.1 kPa of NO over 200 mg of diluted 0.1% $\text{Rh}/\gamma\text{-Al}_2\text{O}_3$ catalyst (0.2 mg Rh).

even if NO were to bind more strongly than CO—as RPBE binding energies would suggest (Figure 3)— NO^* is not stable on Rh_1 at relevant reaction temperatures and is quickly consumed. This kinetic behavior also indicates the importance of the stability of adsorbates on the observed MASI: even if one species binds more strongly than another, its presence on the surface may be brief if it reacts rapidly. This result highlights the first distinct mechanistic feature of NO reduction by CO on Rh nanoparticles and Rh_1 : the MASI on each active site structure differs.

The activation energy of desorption for each CO on Rh_1 in the experimental system can be estimated using Redhead analysis based on the temperature of the maximum desorption rate (Table 3). The 2094/2020 cm^{-1} peaks associated with

Table 3. Desorption Energy and Enthalpy (ΔH) Values for CO Bound to Atomically Dispersed Rh on $\gamma\text{-Al}_2\text{O}_3$

adsorbate	peak desorption temperature, T_p/K	desorption energy, $E/\text{kJ mol}^{-1}$	desorption enthalpy, $\Delta H/\text{kJ mol}^{-1}$
CO from $\text{Rh}(\text{CO})_2$	573	148 ^b –161 ^a	144 ^b –157 ^a
CO from $\text{Rh}(\text{CO})$	703	199 ^b	193 ^b
difference		38–51	36–49

^aUpper limit of the CO binding energy calculated using preexponential factor (A) of $6 \times 10^{11}\text{ s}^{-1}$ to account for the entropic barrier of desorption from $\text{Rh}(\text{CO})_2$. ^bLower limit and first-order single molecule desorption were calculated with a preexponential factor (A) of 10^{13} s^{-1} .

one type of $\text{Rh}(\text{CO})_2$ species disappear at 493 K, while the 2084/2010 cm^{-1} peaks grow, indicating that the 2094/2020 cm^{-1} species reconstructs to form the second species rather than desorbing. Therefore, the CO desorption energy for the 2094/2020 cm^{-1} $\text{Rh}(\text{CO})_2$ species cannot be computed from the TPD. Furthermore, our prior work found that the desorption of CO from $\text{Rh}(\text{CO})_2$ had an entropic barrier,

altering the appropriate rate constant for the pre-exponential factor used in Redhead analysis (see Section 2.2.2),⁵³ justifying the use of two pre-exponential factors here— $6 \times 10^{11} \text{ s}^{-1}$ (yielding an upper limit for the adsorption energy) and the canonical 10^{13} s^{-1} —to calculate a range of possible CO binding energies from eqs 6 and 7. The 2084/2010 cm^{-1} peaks reach maximum rate of change at 573 K, from which the desorption energy for the first CO molecule from $\text{Rh}(\text{CO})_2$ can be estimated as 148–161 kJ mol^{-1} , varying with the different possible pre-exponential factors. The peaks associated with $\text{Rh}(\text{CO})$ species at 1985 cm^{-1} and 1975 cm^{-1} grow as the 2084/2010 cm^{-1} peaks disappear, then reach their maximum rate of desorption at 703 K, yielding a desorption energy of 199 kJ mol^{-1} for the second CO. Additionally, previous measurements for CO desorption from $\text{Rh}(\text{CO})_2$ on a different Al_2O_3 sample, which was reduced by CO rather than H_2 , showed simultaneous desorption of both CO species without $\text{Rh}(\text{CO})$ formation.⁵³ This suggests that the nature of the support (and likely the concentration of bound OH^* or H_2O^*) is critical for stabilizing $\text{Rh}(\text{CO})$.

The $\text{Rh}(\text{CO})_2$ with CO frequencies at 2084 and 2010 cm^{-1} is the presumptive Rh_1 site from which CO desorbs to catalyze NO–CO reactions based on the comparison between in situ NO/CO reactivity during a temperature ramp and probe molecule CO TPD FTIR spectroscopy. The experimentally observed CO frequencies and CO desorption energies described here can be compared with DFT calculations of $\text{Rh}(\text{CO})_2$ in a wide variety of environments to find a suitable model. We use this reconstruction and resulting frequency shift from 2094/2020 cm^{-1} to 2084/2010 cm^{-1} to further clarify the structure and local environment of the $\text{Rh}(\text{CO})_2$ at 2084 and 2010 cm^{-1} , which is the species most relevant to NO reduction.

3.3. Preferred $\gamma\text{-Al}_2\text{O}_3$ Surfaces and Model Considerations. There are many factors that could influence the behavior of supported Rh_1 active sites, including the structure of the $\gamma\text{-Al}_2\text{O}_3$ support, the surface facet to which the Rh_1 is bound, the presence of chemisorbed species that may alter the Rh_1 oxidation state, and the coverage of surface hydroxyl groups on the support. The high mobility of $\text{Rh}(\text{CO})_2$ species on $\gamma\text{-Al}_2\text{O}_3$ makes this range of environments available to Rh during catalysis, so we vary many of these factors to determine their effect on the adsorption and vibrational frequencies of CO^* bound to Rh_1 .

The bulk $\gamma\text{-Al}_2\text{O}_3$ structure is typically considered a cubic defect spinel with spacegroup $Fd\bar{3}m$;^{70,96–98} however, the precise crystal structure—particularly the location of defects within the spinel model—remains undetermined.^{99,100} The surfaces of the cubic defect spinel model studied here⁷⁰ restructure during optimization (Figure S1, Supporting Information). Recently, reconstruction of prevailing $\gamma\text{-Al}_2\text{O}_3(110)_{\text{cds}}$ facets has been detected using high-resolution transmission electron microscopy when $\gamma\text{-Al}_2\text{O}_3$ is heated above 673 K for 1 h or more and particularly above 773 K.^{99,101} $\gamma\text{-Al}_2\text{O}_3$ is often formed from the dehydration of boehmite ($\gamma\text{-AlOOH}$) during calcination, which can leave lingering hydroxyl groups on the surface that stabilize $\gamma\text{-Al}_2\text{O}_3(110)_{\text{cds}}$ facets.^{35,38,39,99} Heating $\gamma\text{-Al}_2\text{O}_3$ samples above 773 K drives off any remaining OH groups as H_2O , which causes the surfaces to restructure to $(100)_{\text{cds}}$ and $(111)_{\text{cds}}$ facets, which are more stable without any remaining OH groups than the $(110)_{\text{cds}}$ facets. Critically, none of the samples in this work were exposed to such high temperatures for

extended periods, suggesting that some lingering OH groups should remain on the $\gamma\text{-Al}_2\text{O}_3$ surfaces and that $(110)_{\text{cds}}$ surfaces may still dominate.

Because of the instability of cubic defect spinel $\gamma\text{-Al}_2\text{O}_3$ structures, another $\gamma\text{-Al}_2\text{O}_3$ model based on the dehydration of boehmite was developed.³⁷ This structure has slightly different surfaces from the original cubic defect spinel, as emphasized in Figure 1, and does not match the $Fd\bar{3}m$ spacegroup, but its behavior is consistent with experimental observations.^{35,36} Furthermore, this structure is more stable [by 5 $\text{kJ mol}^{-1} (\text{Al}_2\text{O}_3 \text{ unit})^{-1}$] than the cubic defect spinel structure. Because this boehmite-derived model is more stable by our DFT methods and has been used and validated by many DFT studies,^{35,36} we use this model in our study of supported Rh_1 instead of a defect spinel model, although we acknowledge that the low crystallinity of $\gamma\text{-Al}_2\text{O}_3$ may require a more precise model for specific cases. However, our goal is to develop a model that is guided by experimental observations and that is useful for future mechanistic studies of $\text{Rh}_1/\gamma\text{-Al}_2\text{O}_3$ catalysts, similar to earlier work on $\gamma\text{-Al}_2\text{O}_3$ models themselves.

Rh atoms can bind to many different facets of the $\gamma\text{-Al}_2\text{O}_3$ support. As described in Section 2.1, the differences between these cubic defect spinel (cds) and boehmite-derived (b) structures cause their Miller indices to be distinct: the $(100)_{\text{cds}}$ surface of the cubic defect spinel is similar to the $(001)_b$ surface of the boehmite-derived structure, and the $(110)_{\text{cds}}$ surface is similar to both the $(100)_b$ and $(010)_b$ surfaces of the boehmite-derived structure. Experimental X-ray diffraction studies show that the $(110)_{\text{cds}}$ and $(100)_{\text{cds}}$ facets dominate $\gamma\text{-Al}_2\text{O}_3$ supports of various provenances,^{31,98,102} so we focus our analysis of supported Rh atoms on the three similar boehmite-derived surfaces [$(010)_b$, $(100)_b$, and $(001)_b$]. While Rh has been shown to occupy vacancies on the surfaces of reducible oxide supports, such as TiO_2 ,¹⁹ $\gamma\text{-Al}_2\text{O}_3$ is irreducible and thus should have no or few such vacancies. Therefore, we exclude Rh structures situated in vacancies of the $\gamma\text{-Al}_2\text{O}_3$ support from consideration. Surface formation energies for the dehydrated $(100)_b$ and $(010)_b$ surfaces are 13.2 and 12.2 $\text{kJ mol}^{-1} \text{ \AA}^{-2}$, both higher than that for the $(001)_b$ facet (7.3 $\text{kJ mol}^{-1} \text{ \AA}^{-2}$). While this indicates that the $(001)_b$ surface is more stable than the $(100)_b$ or $(010)_b$ surfaces, prior work has shown that these $(010)_b$ and $(100)_b$ surfaces remain hydroxylated up to temperatures $>700 \text{ K}$.^{35,36,38,39}

3.4. DFT Calculations of $\text{Rh}(\text{CO})_2$ on $\gamma\text{-Al}_2\text{O}_3$. Prior work has suggested that Rh_1 species in $\text{Rh}(\text{CO})_2$ on $\gamma\text{-Al}_2\text{O}_3$ occupy a +1 oxidation state based on the agreement between in situ IR studies of $\text{Rh}(\text{CO})_2/\gamma\text{-Al}_2\text{O}_3$ and homogeneous $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ complexes;^{12,13} however, the precise structure, vibrational modes, and charge of this species could change depending on conditions. Surface ligands derived from H_2O —which can be present on the surface from boehmite dehydration, deposited during catalyst pre-treatment in air and H_2 , or formed from H_2O in typical TWC conditions—can alter observed frequencies and binding energies. Therefore, we consider a range of O_xH_y^* ($x = 0-1$, $y = 0-1$) ligands attached to Rh_1 to alter the oxidation state and coordination of the Rh_1 species to the surface of $\gamma\text{-Al}_2\text{O}_3$. No calculations in this work were run with a net charge; instead, the ligand attached to Rh_1 sets its oxidation state. For example, an O^* has an oxidation state of -2 , forcing the Rh_1 into an oxidation state of $+2$, while an OH^* has a net oxidation state of -1 , forcing the Rh_1 into a $+1$ oxidation state.

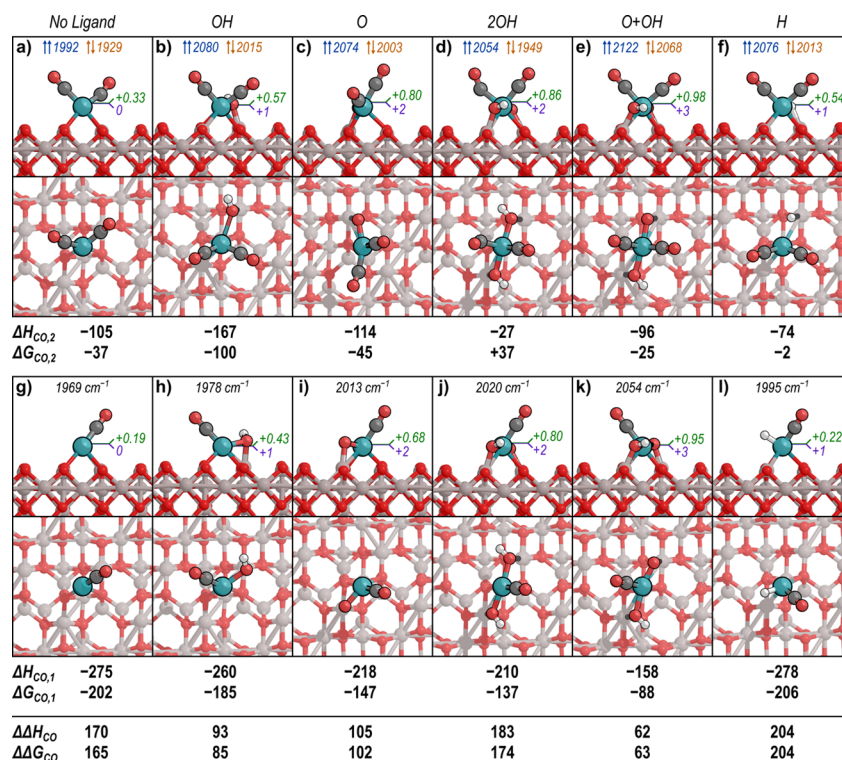


Figure 6. Models of (a–f) $Rh_1(CO)_2$ and (g–l) $Rh_1(CO)$ on $\gamma-Al_2O_3(010)_b$ [corresponding to the $(110)_{cds}$ surface of spinel defect $\gamma-Al_2O_3$] shown parallel to (top) and perpendicular to (bottom) the $\gamma-Al_2O_3$ surface. The Rh_1 is shown with different co-adsorbed species in each column: (a,g) $Rh(0)$ with no ligands, (b,h) $Rh(I)$ with an OH ligand, (c,i) $Rh(II)$ with an O ligand, (d,j) $Rh(III)$ with two OH ligands, (e,k) $Rh(III)$ with O and OH ligands, and (f,l) $Rh(I)$ with an H ligand. CO^* vibrational frequencies are shown above each structure in cm^{-1} , including symmetric (blue, $\uparrow\uparrow$) and asymmetric (orange, $\uparrow\downarrow$) stretches above the $Rh(CO)_2$ species. Calculated binding enthalpies (ΔH_{CO}) and free energies (ΔG_{CO}) at 473 K are shown below their corresponding structures. The Rh oxidation state and estimated partial charges from QUAMBO are shown for each structure in purple and green, respectively. The difference in the binding enthalpy ($\Delta \Delta H_{CO}$) and free energy ($\Delta \Delta G_{CO}$) between the first and second CO^* is shown beneath each set of structures in $kJ\ mol^{-1}$. Additional images are shown in Figures S13 and S14 of the Supporting Information.

We begin by analyzing models with Rh_1 on the $(010)_b$ surface of the boehmite-derived model, which is similar to the most abundant $\gamma-Al_2O_3(110)_{cds}$ facet and has a lower surface formation energy than the $(100)_b$ surface. While previous work has shown the macroscopic $(110)_{cds}$ facet to be comprised of nanosized $(111)_{cds}$ and $(100)_{cds}$ facets on some forms of $\gamma-Al_2O_3$,¹⁰¹ we still consider the $(010)_b$ facet [equivalent to the $(110)_{cds}$ facet] to develop a DFT model suitable for examining the effects of Rh oxidation state, types of Rh ligands, and local hydroxyl concentration on $Rh(CO)_2$ desorption behavior. We validate this model with FTIR spectroscopy of $Rh(CO)_2$ in commercially available $\gamma-Al_2O_3$ found in catalytic converters to capture behavior relevant to NO_x reduction.

To minimize the complexity of the DFT model, we begin these studies absent hydroxyls on the $\gamma-Al_2O_3$ surface, apart from those coordinated to Rh_1 , and examine the role of surface hydroxyls in Section 3.5. The structures of the most stable $Rh(CO)$ and $Rh(CO)_2$ analyzed in this work with different ligands on otherwise de-hydroxylated $\gamma-Al_2O_3(010)_b$ are shown in Figure 6. Partial charges estimated by QUAMBO⁶⁹ indicate that, despite ostensibly having an oxidation state of 0, Rh_1 carries partial charge of +0.33 e in the $Rh(CO)_2$ structure without any ligands, with this charge balanced by the $\gamma-Al_2O_3$ support (−0.18 e) and CO ligands (−0.15 e). As various O^* and OH^* ligands are added, the formal charge assigned to Rh_1 increases up to +3, and the computed partial charges increase linearly up to +0.98, as shown in Figure 7, presenting a strong correlation between the formal charge assignments and the

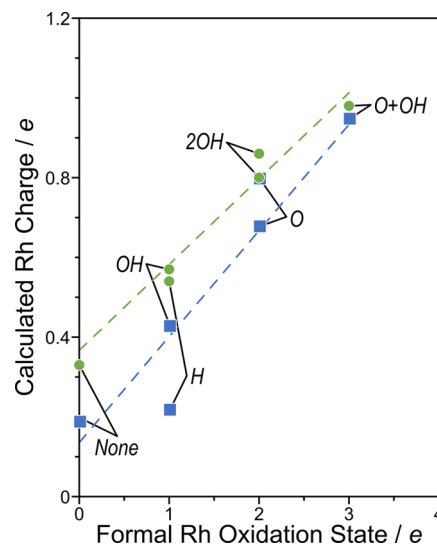


Figure 7. Relationship between the calculated partial charge and formal oxidation state of the Rh single atom on $\gamma-Al_2O_3$ as an $Rh(CO)$ (■, blue) and $Rh(CO)_2$ (●, green) with a variety of ligands attached. Each point is labeled with its corresponding ligand(s). Dashed lines are to guide the eye.

partial charges obtained by QUAMBO. Additionally, partial charge estimates of the Rh_1 in $Rh(CO)_2$ appear to be systematically higher than those in $Rh(CO)$ across all ligands tested in this work. These higher charges on the Rh_1 in

Table 4. Summary of the Characteristics from Experimental Observations of CO* on a 0.1 wt % Rh/ γ -Al₂O₃ Sample and the DFT-Studied Model That Most Closely Matches Those Observations on the (010)_b Surface without Nearby OH* Groups Derived from H₂O on the Support

species	Rh(CO) ₂ frequencies/cm ⁻¹	Rh(CO) frequency/cm ⁻¹	$\Delta\Delta H_{\text{CO}}$ /kJ mol ⁻¹
experiment	2094/2020 and 2084/2010	1975 and 1985	36–49
HO–Rh ⁺¹ (DFT)	2080/2015	1978	93

Rh(CO)₂ indicate that the additional CO* helps to stabilize a more ionic Rh center by accepting some electrons, despite CO being formally neutral. This correlation without exact quantitative agreement between calculated partial charges and formal oxidation states corroborates prior work that has shown that computed partial charges do not quantitatively match formal oxidation state assignments in bulk materials.^{103–105} Notably, adding H* to the Rh₁ results in an increase in the partial charge on Rh₁, suggesting that it behaves as a hydride rather than as a proton when bound to these Rh(CO)_x species. As such, the charge on the Rh₁ in H–Rh(CO)_x is similar to the partial charges on Rh₁ in HO–Rh(CO)_x, supporting a +1 formal charge assignment for this species (Figures 6f and 6l).

On the dehydrated (010)_b surface, the binding enthalpy ($\Delta H_{\text{CO},2}$) and free energy ($\Delta G_{\text{CO},2}$) of CO* to form Rh(CO)₂ from Rh(CO) with no additional ligands on Rh are –105 and –37 kJ mol⁻¹ respectively, as shown in Figure 6a. The adsorption free energy is less negative than the enthalpy because of a 106 J mol⁻¹ K⁻¹ entropy loss of CO upon adsorption. The binding enthalpies for the second CO* [to form Rh(CO)₂ from Rh(CO)] vary from –167 to –27 kJ mol⁻¹ when additional ligands are present on the Rh₁ (Figure 6a–f), indicating that these ligands can either make Rh₁ bind CO* more (e.g., OH ligand) or less (e.g., H ligand) strongly, with similar trends seen for the binding free energies. Critically, the partial charge on the Rh₁ does not predict CO* binding energies, as the partial charges on Rh₁ in Rh(CO)₂ in the presence of OH* and H* ligands are nearly identical (+0.57 and +0.54, respectively), while the CO* binding enthalpies are very different (–167 and –74 kJ mol⁻¹). Adding a second O* or OH* ligand results in significantly weaker CO* binding energies (Figure 6d,e). In each case where there is an additional ligand bound to the Rh₁ (O, OH, or H), the remaining CO* prefers to be oriented away from the ligand. These data show that the Rh₁ oxidation state and the presence of charge-altering Rh₁ ligands significantly change the adsorption energies of CO* in Rh(CO)₂ complexes.

The CO* in the monocarbonyl, Rh(CO), binds much more strongly than the first CO* when no ligand is present, with $\Delta H_{\text{CO},1}$ of –275 kJ mol⁻¹ compared to $\Delta H_{\text{CO},2}$ of –105 kJ mol⁻¹ for the second CO* to form Rh(CO)₂ from Rh(CO). The binding energies of CO* in Rh(CO) ($\Delta H_{\text{CO},1}$ and $\Delta G_{\text{CO},1}$) are generally less exothermic with added O_xH_x ligands, except for the H ligand, which slightly strengthens the CO* binding energy. These data suggest that strong co-adsorbate interactions between the CO* in Rh(CO)₂ weaken the binding of the second CO* relative to the first. The result of this interaction, in turn, suggests that CO would desorb from Rh(CO)₂ sequentially through a monocarbonyl intermediate when additional ligands are coordinated to Rh₁. This sequential desorption process is in qualitative agreement with FTIR–TPD data (Figure 4 and Section 3.1). The adsorption energies calculated here, particularly for the second CO*, are near those estimated by Redhead analysis of the TPD data

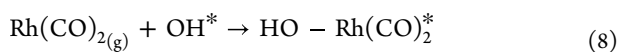
collected in this work (Table 3). While the absolute values for these adsorption energies are difficult to accurately determine from experiment, their differences ($\Delta\Delta G_{\text{CO}}$ and $\Delta\Delta H_{\text{CO}}$) are instructive: CO* desorption from Rh(CO)₂ has a Redhead-estimated binding energy from experimental data that is ~50 kJ mol⁻¹ weaker than for CO* desorption from Rh(CO), while the $\Delta\Delta H_{\text{CO}}$ estimated from DFT ranges from 62 kJ mol⁻¹ [for Rh³⁺(CO)₂ with O and OH ligands] to 170 kJ mol⁻¹ [for Rh⁰(CO)₂ without additional ligands]. For the Rh⁺(CO)₂ with an OH ligand, the model embraced by prior work on TiO₂,²⁰ the $\Delta\Delta H_{\text{CO}}$ is 93 kJ mol⁻¹, larger than the 50 kJ mol⁻¹ suggested by Redhead estimates (Table 3). These discrepancies likely arise from the instability of the “bare” Rh atom that would result from CO* desorption from Rh(CO) in the calculations. This bare Rh₁ would reconstruct upon the second CO* desorption to coordinate with species native to the support and may also change its oxidation state—details absent from the current DFT study and unobservable from FTIR studies. The vibrational frequency data from the FTIR, furthermore, provides a reliable characterization against which these DFT models can be compared.

While CO* binding energies can either increase or decrease upon the addition of these ligands to Rh₁, the vibrational frequencies always increase relative to the structure without additional ligands (Figure 6). The symmetric and asymmetric stretches of Rh(CO)₂ increase by 60–130 and 20–138 cm⁻¹, respectively, and the single CO* stretch frequency for the Rh(CO) increases by 8–85 cm⁻¹ upon ligand addition (Figure 6). An O²⁻ ligand (O), a combination of two OH⁻ ligands (2OH), and a combination of O²⁻ and OH⁻ ligands (O + OH) place Rh₁ into +2, +2, and +3 oxidation states, respectively. These states do not match with prior XPS and FTIR studies of Rh₁/ γ -Al₂O₃ that indicated that Rh is in a +1 oxidation state.^{11–13} Our data confirm these results: calculated stretching frequencies for the Rh(CO)₂ species with these ligands generally differ by >10 cm⁻¹ from those observed experimentally (Table 2). When H is coordinated to Rh₁, the symmetric and asymmetric stretching frequencies for the gem-dicarbonyl structure (2076 and 2013 cm⁻¹) are similar to those from IR spectra (~2090/~2015 cm⁻¹), but the binding enthalpies (–278 and –74 kJ mol⁻¹) disagree with experimental values (–193 and –150 kJ mol⁻¹). When an OH ligand is present, the symmetric and asymmetric stretching frequencies for Rh(CO)₂ (2080 and 2015 cm⁻¹, respectively) are in close agreement to the second set of frequencies observed during IR TPD (2084 and 2010 cm⁻¹). These data suggest that the presence of ligands can alter the Rh₁ oxidation state, CO* adsorption energies, and CO* stretch frequencies. Furthermore, these data suggest that the Rh(CO)₂ species observed during both in situ FTIR and CO probe molecule FTIR experiments is most likely coordinated to OH⁻, as summarized in Table 4, consistent with prior work examining Rh single atoms on other oxide supports, such as TiO₂^{19,20,83} and ZrO₂.⁸⁴

We now turn to other facets of γ -Al₂O₃ also prevalent on γ -Al₂O₃ supports: (100)_b—which, like (010)_b, resembles (110)_{cds}—and (001)_b, which resembles (100)_{cds}.^{31,35,36,38} Rh₁ may behave differently on these other facets; for example, 0.5 wt % Rh/CeO₂ samples contain three different sets of peaks that may correspond to Rh₁ on different facets with different activities for NO reduction.²⁴ The most stable termination of the (001)_b surface has Al sites that are all fivefold coordinated and therefore have lower Lewis acid strength than the Al of the (100)_b and (010)_b surfaces of Al.^{38,106} Meanwhile, the most stable (100)_b surface, after optimization, has a threefold coordinated Al site, which is a stronger Lewis acid than other fourfold coordinated Al on the (100)_b and (010)_b surfaces.³⁵ Again, for simplicity, we begin by examining γ -Al₂O₃ surfaces absent hydroxyls apart from an OH ligand directly bound to Rh.

CO binding strengths to Rh₁ are similar when Rh₁ resides on the (010)_b and (100)_b surface facets (both of which correspond to the (110)_{cds} facet of the cubic defect spinel γ -Al₂O₃), with differences of 5 and 16 kJ mol⁻¹ for the first and second CO adsorption (Figure 8). CO binding energies to Rh₁ on the (001)_b surface [corresponding to the (100)_{cds} facet of the cubic defect spinel γ -Al₂O₃], however, are $\sim$ 50 kJ mol⁻¹ less exothermic than those on the other facets. The differences between the first and second CO adsorption energies remain near 100 kJ mol⁻¹ across all three facets for these OH⁻-coordinated Rh⁺(CO)₂ species, with the smallest gap (in closest agreement with the Redhead analysis) observed on the (010)_b surface.

Additionally, we calculate the interaction energy between the Rh(CO)₂ and each facet (ΔE_{int}), which is the energy to bind a gas-phase Rh(CO)₂ to the alumina facet with one OH group



This interaction energy is the strongest on the (010)_b facet at -388 kJ mol⁻¹, followed closely by the (100)_b facet (-387 kJ mol⁻¹), both of which are much stronger than ΔE_{int} on the (001)_b surface (-334 kJ mol⁻¹) (Figure 8). This further indicates that HO–Rh(CO)₂ is likely to form on (010)_b or (100)_b facets during synthesis.

The symmetric and asymmetric stretching frequencies of the HO–Rh(CO)₂ species on the (001)_b and (100)_b surfaces are higher than those on the (010)_b surface by 6–14 cm⁻¹, with larger differences for the symmetric stretch between surfaces (Figure 8). Critically, these vibrational frequencies do not directly correlate to CO* binding energies (as also observed when we altered ligands, Figure 6). Frequencies of the HO–Rh(CO)₂ on each surface agree relatively well with measured values, given the range of frequencies observed in FTIR spectroscopy (2084 and 2094 cm⁻¹ for symmetric and 2010 and 2020 cm⁻¹ for asymmetric). Stretching frequencies for the HO–Rh(CO) species are also larger on the (100)_b and (001)_b surfaces (2007 and 2013 cm⁻¹, respectively) than on the (010)_b surface (1978 cm⁻¹), with the latter being more similar to measured values (1975 and 1985 cm⁻¹). This suggests that the shift in frequencies observed in the IR TPD from 2094/2020 to 2084/2010 cm⁻¹ may be explained by HO–Rh(CO)₂ moving from the (001)_b surface (frequencies of 2093/2020 cm⁻¹) or the (100)_b surface (frequencies of 2094/2027 cm⁻¹) to the (010)_b surface (frequencies of 2080/2015 cm⁻¹), from which CO* desorbs to form a monocarbonyl with a CO* stretch frequency measured near 1980 cm⁻¹; however, these

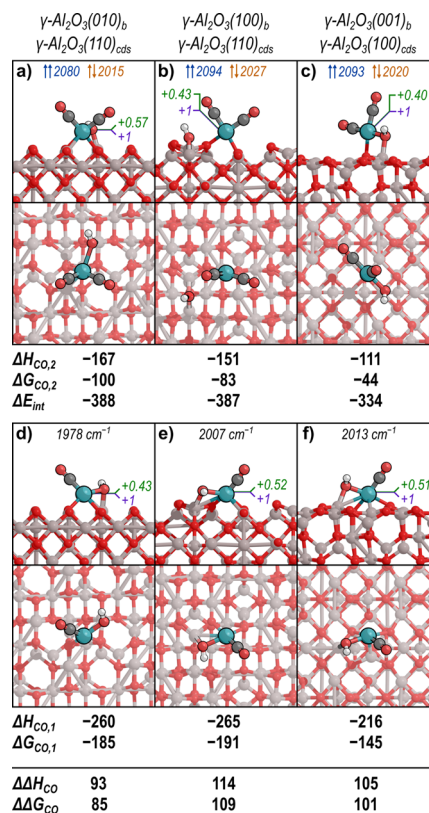
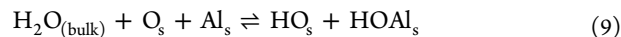


Figure 8. Models of (a–c) HO–Rh₁(CO)₂ and (d–f) HO–Rh₁(CO) on (a,d) γ -Al₂O₃ (010)_b [equivalent to γ -Al₂O₃(110)_{cds}], (b,e) γ -Al₂O₃ (100)_b [equivalent to γ -Al₂O₃(110)_{cds}], and (c,f) γ -Al₂O₃(001)_b [equivalent to γ -Al₂O₃(100)_{cds}], surfaces shown from the top and from the side. For each structure, the CO* vibrational frequencies are shown in cm⁻¹, including symmetric (blue, $\uparrow\uparrow$), asymmetric (orange, $\uparrow\downarrow$), and monocarbonyl (black) stretches where appropriate. The assigned formal Rh oxidation state (purple) and partial charges from QUAMBO analysis (green) are also shown in e. Binding enthalpies (ΔH_{CO}) and free energies (ΔG_{CO}) for each CO*, the interaction energy between the Rh(CO)₂ and each facet (ΔE_{int}), as well as the differences for each between the first and second CO* ($\Delta\Delta H_{\text{CO}}$ and $\Delta\Delta G_{\text{CO}}$) at 473 K are shown in kJ mol⁻¹ below their corresponding structures. Additional images are shown in Figures S15 and S16 in the Supporting Information.

calculations neglect the role of OH coverage, which may also lead to the FTIR spectroscopy evolution during the TPD.

3.5. Effects of H₂O Adsorption to γ -Al₂O₃ on Rh(CO)₂ Frequencies. Hydroxyl species (OH) likely exist at high coverages on γ -Al₂O₃ surfaces formed from H₂O-derived H* and OH* species bound to Brønsted basic O atoms or Lewis acidic Al of the support,³⁸ respectively



where H₂O_(bulk) is H₂O in the bulk (gas or liquid phase, gas modeled here), while O_s and Al_s are atoms on the support surface. In addition to these dissociated complexes, H₂O may also adsorb molecularly



The coverage of these H*/OH* (abbreviated herein as OH*) and H₂O* can be described in terms of total (dissociated and molecular) water content (θ_w), in units of OH nm⁻² (when H₂O adsorbs dissociatively, with 2 OH per H₂O adsorbed) or H₂O nm⁻² (when H₂O begins to adsorb

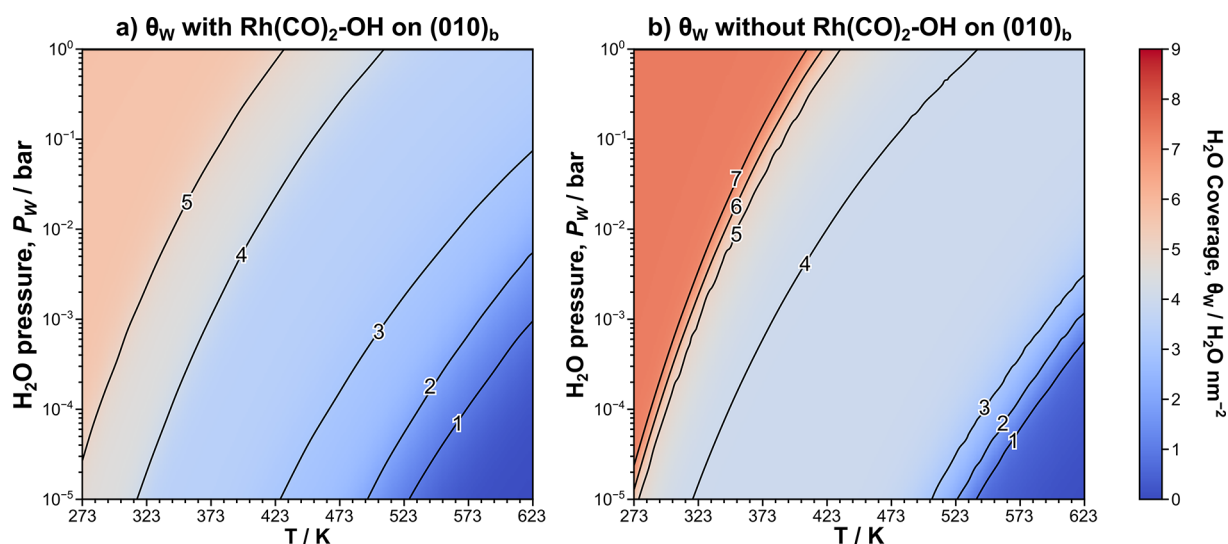


Figure 9. H₂O coverage on (010)_b surfaces both (a) with and (b) without HO–Rh(CO)₂ present as a function of H₂O pressure and temperature based on equilibrium constants for dissociative or associative H₂O adsorption under standard conditions (473 K, 1 bar H₂O). All coverages are presented in units of H₂O nm^{−2}, although H₂O dissociatively adsorbs to form H*/OH* pairs below 3.96 H₂O nm^{−2} (7.92 OH nm^{−2}) in (a) and below 4.52 H₂O nm^{−2} (9.05 OH nm^{−2}) in (b).

molecularly). These OH* and H₂O* may influence the CO* adsorption energies and/or vibrational frequency of CO* on Rh₁. As the coverages of OH* and H₂O* are expected to decrease with increasing temperature, understanding how these influence CO* behavior is critical for understanding the CO FTIR TPD data and likely the species involved in the CO–NO reaction. As such, we systematically evaluate the effects of changing θ_W on CO* frequencies and binding energies using DFT, including coverages above which the surface saturates and where H₂O molecularly physisorbs in bilayers above the support.

We calculate θ_W on the γ -Al₂O₃ surface in a range of temperatures and water pressures to explore possible hydroxylated and hydrated environments (for details, see Section S5, Supporting Information). We also assess θ_W with and without a HO–Rh(CO)₂ complex to determine the most stable environment around HO–Rh(CO)₂, how adsorbed H₂O* affects CO* stretch frequencies, and the extent to which Rh₁ species displace OH* and H₂O* upon adsorption. Equilibrium constants for H₂O adsorption were calculated on each facet tested in this work based on the sequential adsorption free energies of H₂O, ΔG_{W_i} , at 473 K and 1 bar H₂O (standard pressure). Prior DFT studies^{35,38} indicated that the (001)_b surface of this γ -Al₂O₃ model had no OH* above 600 K but that OH* remained on the (100)_b and (010)_b surfaces up to 1100 K. Here, we also examine the coverage of dissociatively and molecularly adsorbed H₂O* on the (010)_b surface and how the HO–Rh(CO)₂ species may influence those coverages. Then, we address the effects of θ_W on the behavior of this HO–Rh(CO)₂ species because it is the most likely candidate structure for a Rh single atom.

Calculations of OH* and H₂O* on γ -Al₂O₃(010)_b confirm previous results,^{38,39} indicating that the surfaces corresponding to γ -Al₂O₃(110)_{cds} are partly covered with OH* even above 500 K and with water pressures below 10^{−4} bar when studied at 373–623 K and 10^{−5} to 10⁰ bar (Figure 9). We examined concentrations of 0–15.27 and 0–9.05 H₂O nm^{−2} on (010)_b with and without HO–Rh(CO)₂, respectively, where the model has a surface area of 1.77 nm². We explored higher

coverages around HO–Rh(CO)₂ to determine how water solvating the Rh₁ altered the vibrational frequencies of the bound CO*. Notably, there are 8 exposed Al atoms on this γ -Al₂O₃(010)_b model, and H₂O prefers to adsorb dissociatively until each Al atom is covered. When there is no HO–Rh(CO)₂ present, this saturation occurs with 8 H₂O molecules at a coverage of 9.05 OH nm^{−2} (NB: each adsorbed H₂O* produces two OH* species in these units of coverage). When HO–Rh(CO)₂ is present, its OH occupies one Al and H₂O stops adsorbing dissociatively at 7.92 OH nm^{−2}, not counting the OH attached to the Rh₁. The ΔG_w values remain negative—indicating favorable binding—up to 9.05 OH nm^{−2} on γ -Al₂O₃(010)_b when HO–Rh(CO)₂ is absent (473 K and 1 bar H₂O, Figure S5, Supporting Information). Specifically, OH concentrations do not drop below 1.2 OH nm^{−2} on (010)_b without HO–Rh(CO)₂ at 623 K and 10^{−4} bar H₂O (presented in Figure 9 in units of total H₂O nm^{−2}) and peak at 7.35 H₂O nm^{−2} at 273 K and 1 bar (although H₂O forms ice under these conditions). The H₂O-derived adlayer at this maximum coverage comprises 8 dissociated H₂O in the form of H*/OH* pairs (a coverage of 9.05 OH nm^{−2}) and 5 molecularly adsorbed H₂O (an additional coverage of 2.83 molecular H₂O nm^{−2}) (see Figures S5–S12 in the Supporting Information for images of all hydrated γ -Al₂O₃ structures studied in this work). While water is not co-fed under most conditions in this work, trace water in the feed and residual hydroxyls from the hydrothermal synthesis and reduction of the initially oxidized Rh by H₂ are expected during TPD experiments. Moreover, the conditions under which TWCs typically operate include ~10% water,⁸ which leads to support hydroxylation and water adsorption. Even trace amounts of water can lead to significant changes in catalytic behavior, perhaps best illustrated by the behavior of Au/TiO₂ during CO oxidation, during which trace H₂O shuttles H atoms to facilitate O₂ dissociation at the Au interface with TiO₂.^{107,108} Next, we evaluate surface hydroxylation in the presence of HO–Rh(CO)₂ species on γ -Al₂O₃(010)_b.

When HO–Rh(CO)₂ is present on the γ -Al₂O₃ surface, surface hydroxylation decreases (Figure 9a). The coverages are

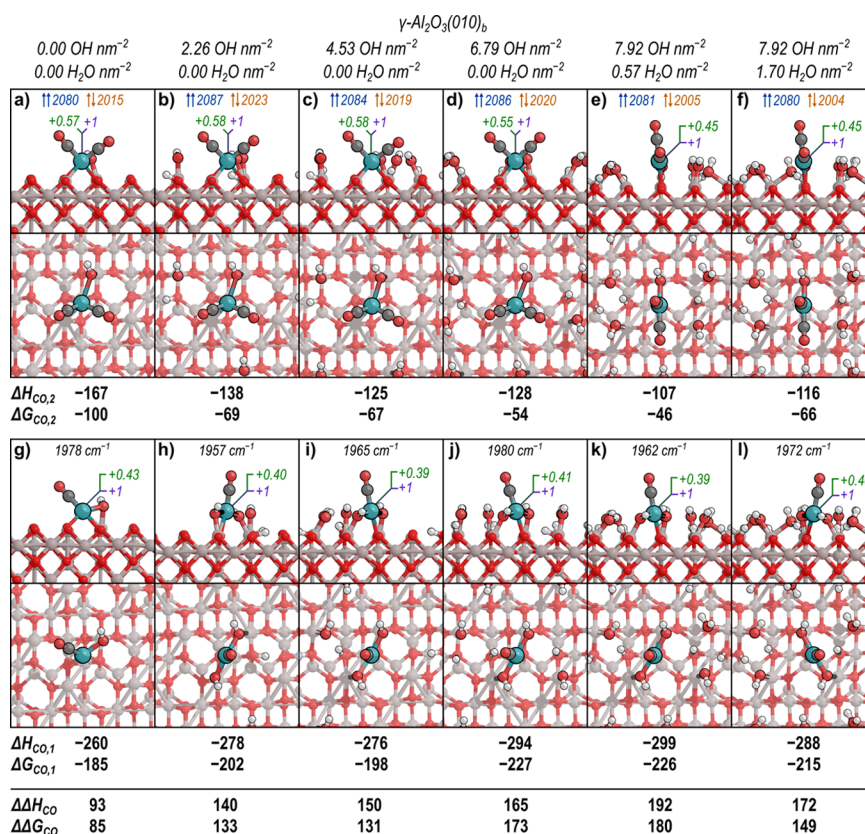


Figure 10. Models of (a–f) HO–Rh₁(CO)₂ and (g–l) HO–Rh₁(CO) on γ -Al₂O₃(010)_b with adsorbed H₂O coverages of (a,g) 0.0 OH nm⁻², (b,h) 2.26 OH nm⁻², (c,i) 4.53 OH nm⁻², (d,j) 6.79 OH nm⁻², (e,k) 7.92 OH nm⁻² and 0.57 H₂O nm⁻² (where H₂O first adsorbs molecularly), and (f,l) 7.92 OH nm⁻² and 1.70 H₂O nm⁻² from additional H₂O dissociated on the γ -Al₂O₃ surface. For each structure, the CO* vibrational frequencies are shown in cm⁻¹, including symmetric (blue, ↑↑), asymmetric (orange, ↑↓), and monocarbonyl (black) stretches where appropriate. The assigned formal Rh oxidation state (purple) and partial charges from QUAMBO analysis (green) are also shown in e. Binding enthalpies (ΔH_{CO}) and free energies (ΔG_{CO}), as well as the differences for each between the first and second CO* (ΔΔH_{CO} and ΔΔG_{CO}) at 473 K, are shown in kJ mol⁻¹ below their corresponding structures. Additional views of these structures and other structures with varying OH coverages are shown in Figures S5–S10 of the [Supporting Information](#).

0.05–7.35 H₂O nm⁻² without HO–Rh(CO)₂ (373–623 K, 10⁻⁵–10⁰ bar H₂O), which drops to 0.02–5.73 H₂O nm⁻² when the HO–Rh(CO)₂ is present. This decrease in coverage indicates that OH groups are locally displaced by the HO–Rh(CO)₂ (NB: these coverages exclude the OH group to which the Rh₁ is attached). Dilute Rh₁ on γ -Al₂O₃ likely negligibly affects sample-averaged θ_w , except in their immediate vicinities. For the IR spectra that were recorded under “dry” conditions in this work, DFT predicts that hydroxyl coverages on the (010)_b surface should be low if adsorption and desorption of H₂O are quasi-equilibrated, although their relative density would still decrease with increasing temperature according to these data. Previous experimental studies, however, suggest that average hydroxyl coverages may be 8–12 OH nm⁻², with OH distributed heterogeneously, such that some regions of γ -Al₂O₃ exceed this range.^{40,41}

Rh(CO)₂ remains bound to two surface O atoms of the γ -Al₂O₃ support at coverages where H₂O adsorbs dissociatively (≤ 7.92 OH nm⁻²; [Figure 10a–d](#)). The presence of these H*/OH* pairs on γ -Al₂O₃(010)_b weakens the binding energy for the second CO* to form Rh(CO)₂ from Rh(CO), shifting ΔH_{CO,2} from –167 to –116 kJ mol⁻¹ as the surface becomes increasingly hydrated ([Figure 10a–f](#)). Hydration, however, strengthens binding for the first CO [to form Rh(CO), [Figure 10](#)] with ΔH_{CO,1} decreasing from –260 to –288 kJ mol⁻¹ over

this same range. These additional H*/OH* can coordinate to the Rh₁ without altering its oxidation state, which confers some additional stability when the Rh is bare and when only one CO* is adsorbed but more so for the latter. When the second CO adsorbs to form Rh(CO)₂, these additional OH* both stabilize the preceding state and repel the additional CO* on the now-saturated Rh₁; as such, binding energies for the second CO* weaken with additional OH* on the surface. These contradicting trends cause the ΔΔH_{CO} to increase from 93 to 172 kJ mol⁻¹, far above the experimentally estimated ΔΔH_{CO} of 36–49 kJ mol⁻¹. However, desorption from Rh(CO) to form a “bare” Rh, as modeled here, is unlikely to occur in experiments, leading to some doubts in DFT-derived ΔΔH_{CO} energies. Instead, it is likely that new ligands (water- or surface-derived OH*) take the place of desorbed CO* on the resulting Rh₁/γ-Al₂O₃ species. These structural changes of the bare Rh cannot be fully described by FTIR spectroscopy alone; here, we focus on that which FTIR can describe, which are the frequencies of the Rh(CO)₂ and Rh(CO) species, and the binding energy of the second CO* to form Rh(CO)₂ and how those metrics may be influenced by the hydration of the surface. The coincidence of the TPD and reactivity light-off suggest that the loss of CO* from Rh(CO)₂ to form Rh(CO) is kinetically relevant, which is a step that our calculations seem to capture accurately.

The presence of additional H*/OH* groups on the (010)_b surface generally increases the frequencies of the symmetric and asymmetric stretches of Rh(CO)₂ below 7.92 OH nm⁻² (Figures 10 and 11). At very low coverage (0, 1.13, and 2.26

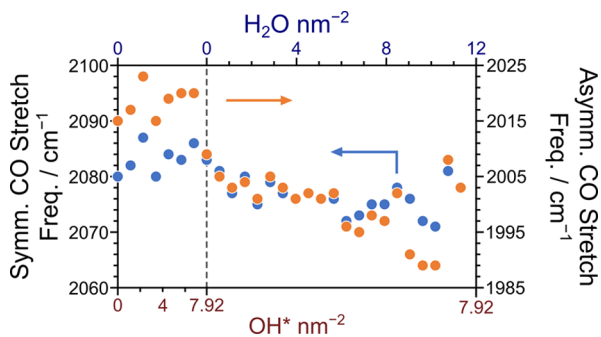


Figure 11. Changes in the symmetric (blue) and asymmetric (orange) stretches of the Rh(CO)₂ with different surface concentrations of H*/OH* pairs and of molecular H₂O on γ -Al₂O₃(010)_b. The coverages within which H₂O adsorbs dissociatively to form H*/OH* pairs (in OH nm⁻²) and molecularly (in H₂O nm⁻²) are labeled along the bottom and top ordinate, respectively.

OH nm⁻²), the symmetric stretch frequency increases from 2080 to 2082 and 2087 cm⁻¹ and asymmetric from 1978 to 2025 and 2027 cm⁻¹, respectively. This trend breaks at 7.92 OH nm⁻²; at this coverage, Rh(CO)₂ rotates such that Rh₁ coordinates only to one surface O atom and subsequent H₂O adsorption occurs molecularly (Figure 10e–f). This configurational shift causes both the symmetric and asymmetric stretching frequencies to decrease despite the increase in θ_W (Figure 11). As H₂O continues to adsorb, the symmetric and asymmetric frequencies further decrease to lower bounds of 2071 and 1989 cm⁻¹, respectively, at 7.92 OH nm⁻² and 10.18 H₂O nm⁻². While it is unlikely that the entire γ -Al₂O₃ surface reaches this level of hydroxylation, the heterogeneity of γ -

Al₂O₃ and likelihood of attractive OH–OH interactions suggest that OH* could aggregate to form these high coverage regimes under the probed experimental conditions. Notably, this shift in CO* frequency as γ -Al₂O₃ reaches high θ_W is of similar magnitude to the decrease in CO* frequency observed in IR spectra during TPD (2094 and 2020 to 2084 and 2010 cm⁻¹).

Changes in the Rh(CO) frequencies trend differently than those for the Rh(CO)₂ with θ_W . When only one CO* is adsorbed, the Rh₁ can coordinate to two OH* on the surface, which reduces the stretching frequency of the CO* from 1978 cm⁻¹ with only the OH ligand to 1957 cm⁻¹ at 2.26 OH nm⁻² (the OH ligand with an additional dissociated H₂O on γ -Al₂O₃). After introducing this additional OH* from an H*/OH* pair to which the Rh₁ bonds at 2.26 OH nm⁻², the CO* frequency increases with higher OH* coverages, increasing to 1958–1985 cm⁻¹ at θ_W coverages between 1.70 and 7.92 OH nm⁻². Similar to that of Rh(CO)₂, the frequencies of Rh(CO) begin to decrease once molecular H₂O begins adsorbing on γ -Al₂O₃, dropping from 1985 to 1962 cm⁻¹ when the first H₂O adsorbs molecularly (Figure 10k). Such changes again implicate denser OH* adlayers as a possible cause for increases in stretching frequencies despite Rh(CO) occupying less space on the support than Rh(CO)₂. Finally, QUAMBO-calculated charges are relatively insensitive to OH concentration for the Rh(CO)₂, remaining between +0.55 and +0.59 *e* until the Rh(CO)₂ rearranges at 7.92 OH nm⁻² coverage, when the charge drops to +0.44 *e*.

In summary, DFT predicts that increasing local θ_W around HO–Rh(CO)₂ can increase CO* frequencies by ~ 7 cm⁻¹ from 2080/2015 cm⁻¹ at 0 OH nm⁻² to 2086/2020 cm⁻¹ at 6.79 OH nm⁻², after which they significantly decrease to as low as 2071/1989 cm⁻¹ at 7.92 OH nm⁻² and 10.18 H₂O nm⁻². These shifts are similar to the 10 cm⁻¹ range observed in FTIR spectroscopy and decrease CO binding energies. This approach also predicts that the γ -Al₂O₃ facet affects CO* frequency of Rh(CO)₂, directly through Rh-support inter-

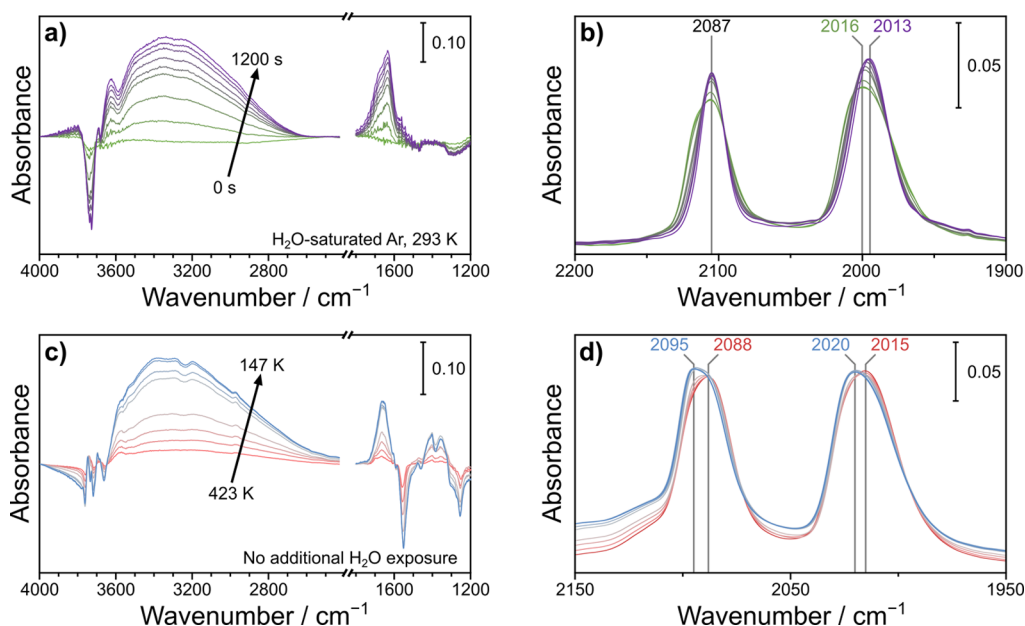


Figure 12. FTIR spectra of 0.1 wt % Rh/ γ -Al₂O₃ (a,b) saturated with CO at 298 K and exposed to a water-saturated Ar stream at 298 K for 1200 s and (c,d) saturated with CO at 423 K and cooled to 147 K, highlighting the O–H stretch and H–O–H bending regions in (a,c) and the Rh(CO)₂ stretch region in (b,d).

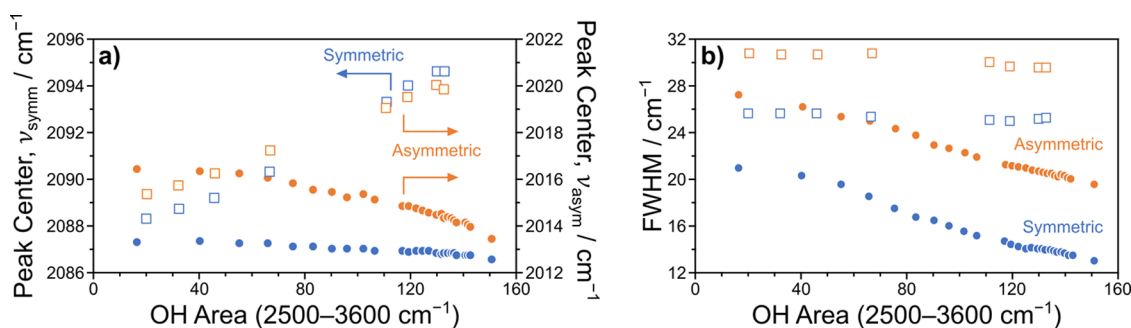


Figure 13. (a) Peak center and (b) fwhm of $\text{Rh}(\text{CO})_2$ peaks as the area of the OH band changes for symmetric (blue) and asymmetric (orange) stretches in samples brought to cryogenic temperatures (■, hollow) and exposed to H_2O at 298 K (●, filled).

actions but also indirectly by equilibrium θ_{W} . Therefore, we investigate the effect of θ_{W} on CO^* frequency using FTIR spectroscopy next.

Exposing 0.1 wt % $\text{Rh}/\gamma\text{-Al}_2\text{O}_3$ first saturated with CO to form $\text{Rh}(\text{CO})_2$ to an Ar feed saturated with H_2O at 293 K increases the surface hydroxylation of $\gamma\text{-Al}_2\text{O}_3$ (Figure 12a). This increase in θ_{W} is evidenced by the loss of isolated OH groups ($>3700\text{ cm}^{-1}$)^{30,109,110} and growth of the broad hydrogen bonding OH band from 3600 to 2500 cm^{-1} ,^{30,42} indicating the formation of OH-dense regions on $\gamma\text{-Al}_2\text{O}_3$ (Figure 12a). The growth of the H–O–H bending band at 1650 cm^{-1} also indicates the presence of molecularly adsorbed water (Figure 12a).⁴² Water exposure noticeably tightens the bands ($\sim 8\text{ cm}^{-1}$ reduction of fwhm) around centers at 2087/2013 cm^{-1} as OH^* density increases (Figures 12b and 13b), thus causing the peak centers to decrease. The reduction of the fwhm is likely because physisorbed water molecules near Rh_1 sites homogenize the local coordination environment, indicating that the lower frequency $\text{Rh}(\text{CO})_2$ species with peaks near 2087 and 2013 cm^{-1} formed during H_2O exposure exist in a highly hydroxylated environment.

Separately, 0.1 wt % $\text{Rh}/\gamma\text{-Al}_2\text{O}_3$ was exposed to 10 kPa CO at 423 K to form $\text{Rh}(\text{CO})_2$ and cooled to 147 K (Figure 12c,d). The $\text{Rh}(\text{CO})_2$ bands initially appear similar in shape and position after CO adsorption to those at 423 K during TPD, but cooling to 147 K induces a shift in maximum intensity from 2088/2015 to 2095/2020 cm^{-1} for the $\text{Rh}(\text{CO})_2$ peaks—the reverse effect of heating during TPD, indicating that the conversion between $\text{Rh}(\text{CO})_2$ species observed during TPD prior to desorption is reversible. During cooling, the hydrogen bonding OH^* region and the H–O–H bending peak (1650 cm^{-1}) grow, indicating that trace water in the Ar feed adsorbs on the $\gamma\text{-Al}_2\text{O}_3$ during cooling. This H_2O adsorption does not cause as substantial a loss of isolated OH^* groups ($3800\text{--}3700\text{ cm}^{-1}$) as observed during water exposure at room temperature, which presumably consumes most isolated OH^* by condensing water on the surface. Assuming that water molecularly adsorbs only on OH-saturated surfaces because of hydrogen bonding, the persistence of isolated OH^* groups suggests that during cooling to cryogenic temperatures, water preferentially deposits onto some regions of $\gamma\text{-Al}_2\text{O}_3$, leaving other regions drier. Despite increasing absorbance in the OH^* region, the fwhm of each CO^* peak does not tighten and the positions of maximum intensity of the CO^* peaks shift to higher frequencies during cooling, opposite to the behavior observed when water was fed at room temperature (Figure 13). This can be explained by $\text{OH}^*\text{--OH}^*$ interactions on the support: at low temperature, densely packed OH^* form ice-like

layers on $\gamma\text{-Al}_2\text{O}_3$ from which $\text{Rh}(\text{CO})_2$ is excluded by the strengthening hydrogen bonding networks. Whether this exclusion occurs by Rh_1 migration out of dense OH^* regions or by OH^* agglomeration away from $\text{Rh}(\text{CO})_2$ is unclear. Altogether, these results suggest that θ_{W} indeed alters the frequency of CO bound to Rh_1 , as DFT predicts, and that the effects are moderated by temperature.

DFT also predicts that the second CO binding enthalpy ($\Delta H_{\text{CO},2}$) weakens from -167 to -122 kJ mol^{-1} as the coverage of H^*/OH^* pairs and molecular H_2O increase, suggesting that CO desorption from $\text{HO--Rh}(\text{CO})_2$ occurs more readily in high θ_{W} environments rather than low. The facet supporting $\text{HO--Rh}(\text{CO})_2$ also affects CO frequency, both directly through Rh-support interactions and indirectly by equilibrium θ_{W} . For instance, $\text{HO--Rh}(\text{CO})_2$ on dehydrated $(001)_\text{b}$ has frequencies of 2090 and 2020 cm^{-1} , and the $(001)_\text{b}$ facet retains fewer OH than the $(010)_\text{b}$ or $(100)_\text{b}$ facets.^{38,39} The facet dependence of θ_{W} and the likeliness of $\text{OH}^*\text{--OH}^*$ interactions may lead to distinct patches of high and low θ_{W} on $\gamma\text{-Al}_2\text{O}_3$ rather than a continuous distribution, which would lead to the appearance of the two relatively distinct sets of $\text{Rh}(\text{CO})_2$ observed in FTIR.

Taken together, these data indicate that $\text{Rh}(\text{CO})_2$ is in the +1 state, coordinated to charge-balancing OH , and present on $\gamma\text{-Al}_2\text{O}_3$ surfaces in areas of varying θ_{W} . At ambient conditions, $\text{HO--Rh}(\text{CO})_2$ exists in heterogeneous areas of the support that contain a range of θ_{W} , leading to broad and non-symmetric CO^* stretching bands, and as temperature increases, these $\text{HO--Rh}(\text{CO})_2$ species migrate to more hydroxylated regions of $\gamma\text{-Al}_2\text{O}_3$ (conversion of 2094/2020 cm^{-1} bands to 2084/2010 cm^{-1} bands). Sequential CO desorption then occurs from these $\text{HO--Rh}(\text{CO})_2$ species in high hydroxyl coverage regions to form a $\text{Rh}(\text{CO})$ species with a CO^* band in the range 1985–1975 cm^{-1} . Thus, we propose that $\text{Rh}(\text{CO})$ species form in high θ_{W} regions, which are the likely active site models for the CO–NO reaction on Rh_1 .

4. CONCLUSIONS

Our combined theoretical and experimental approach rigorously characterizes atomically dispersed $\text{Rh}_1/\gamma\text{-Al}_2\text{O}_3$ to enable mechanistic investigations of NO reduction. CO probe-molecule FTIR spectroscopy on low weight-loading (0.05–0.1 wt %) $\text{Rh}/\gamma\text{-Al}_2\text{O}_3$ catalysts shows distinct peaks at ~ 2090 and $\sim 2015\text{ cm}^{-1}$, corresponding to symmetric and asymmetric vibrations of atomically dispersed $\text{Rh}(\text{CO})_2$. At least two $\text{Rh}(\text{CO})_2$ species exist on $\gamma\text{-Al}_2\text{O}_3$ at ambient temperature with CO stretching bands at 2094/2020 and 2084/2010 cm^{-1} . The 2094/2020 cm^{-1} species convert to those at 2084/2010 cm^{-1}

as temperature increases, after which CO desorption occurs from the lower frequency $\text{Rh}(\text{CO})_2$ species to form intermediate $\text{Rh}(\text{CO})$ with frequencies at 1985–1975 cm^{-1} . The conversion of lower frequency $\text{Rh}(\text{CO})_2$ to $\text{Rh}(\text{CO})$ coincides with light-off in the NO–CO reaction. Characterizing this conversion process and the $\text{Rh}(\text{CO})_2$ species at 2084 and 2010 cm^{-1} is therefore critical to modeling NO reduction over Rh_1 active sites.

DFT calculations for Rh_1 on $\gamma\text{-Al}_2\text{O}_3$ are complicated by the presence of multiple $\gamma\text{-Al}_2\text{O}_3$ facets, charge-balancing ligands that can coordinate to Rh, and the local hydroxyl concentration on $\gamma\text{-Al}_2\text{O}_3$. We computed the CO binding energies and frequencies for $\text{Rh}(\text{CO})$ and $\text{Rh}(\text{CO})_2$ on three $\gamma\text{-Al}_2\text{O}_3$ surfaces on a previously developed model of $\gamma\text{-Al}_2\text{O}_3$ from boehmite:^{35,37,38} (010)_b, (100)_b, and (001)_b. We also studied $\text{Rh}(\text{CO})$ and $\text{Rh}(\text{CO})_2$ surface species with various water-derived ligands: H, O, OH, O + OH, and 2OH. These ligands alter the oxidation state of $\text{Rh}(\text{CO})$ and $\text{Rh}(\text{CO})_2$ and, in turn, the binding energies of CO^* and the corresponding C–O stretch frequencies. Results suggest that $\text{Rh}(\text{CO})_2$ with the Rh in a +1 oxidation state and bound to a charge-compensating OH^- ligand supported on a (010)_b surface is most consistent with the experimental FTIR and TPD data.

Critically, the local OH^* concentration affects the stretching frequencies of $\text{Rh}(\text{CO})_2$. At OH^* coverages above 7.4 OH nm^{-2} , the nearby OH^* groups disrupt one of the bonds of the Rh to surface O atoms. This disruption decreases $\text{Rh}(\text{CO})_2$ symmetric and asymmetric stretching frequencies from a maximum of 2087 and 2023 cm^{-1} at 2.26 OH nm^{-2} to 2083 and 2009 cm^{-1} at 7.92 OH nm^{-2} . Experimentally observed $\text{Rh}(\text{CO})_2$ frequencies substantially tighten around 2086/2014 cm^{-1} when 0.1 wt % $\text{Rh}_1/\gamma\text{-Al}_2\text{O}_3$ is exposed to a water-saturated Ar stream at 298 K, confirming that $\text{Rh}(\text{CO})_2$ frequencies red-shift in high OH^* coverage environments. Alternatively, CO^* frequencies blue-shift when $\text{Rh}(\text{CO})_2$ is cooled from 423 to 147 K, likely because ice-like high OH^* coverage areas exclude $\text{Rh}(\text{CO})_2$ to areas of predominantly low OH^* coverage. DFT also predicts that CO^* desorption occurs more readily from $\text{Rh}(\text{CO})_2$ in high OH^* coverage areas. DFT suggests that these shifts in frequency do not correspond to a change in the oxidation state of the $\text{Rh}(\text{CO})_2$ but only in changes to the local environment around the catalyst active site. While $\gamma\text{-Al}_2\text{O}_3$ in aged TWC converts to more thermodynamically stable phases, we believe that the effects of these OH^* coverages are important to consider for any Al_2O_3 that can accommodate surface hydroxyls on which Rh is atomically dispersed.

This combined theoretical and experimental approach uses rigorous DFT calculations of binding enthalpies and free energies with corresponding frequencies in conjunction with probe molecule FTIR spectroscopy and temperature-programmed experiments to identify the structure of Rh_1 on $\gamma\text{-Al}_2\text{O}_3$ under conditions consistent with NO reduction by CO. We conclude that CO^* desorption from atomically dispersed $\text{Rh}_1/\gamma\text{-Al}_2\text{O}_3$ occurs from $\text{Rh}(\text{CO})_2$ bound to an OH ligand with additional OH^* nearby on the support. NO reduction occurs after desorption of CO^* from these $\text{Rh}(\text{CO})_2$ species and interaction of NO with the now unsaturated Rh_1 sites, so the $\text{Rh}(\text{CO})_2$ model presented here can be applied to future mechanistic studies of NO reduction.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acscatal.2c02813>.

Details of statistical mechanics treatments for calculating free energies and enthalpies, additional information about $\gamma\text{-Al}_2\text{O}_3$ models tested in this work, IR spectra used to identify NCO^* , IR spectra of cooled $\text{Rh}/\gamma\text{-Al}_2\text{O}_3$ samples after TPD, DFT-calculated structures with different H_2O content, and additional images of DFT-calculated Rh structures with different ligands and on different $\gamma\text{-Al}_2\text{O}_3$ surfaces (PDF)

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Notes

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