

Exploring the Synergistic Performance of a Pt-Rh/ γ -Al₂O₃ Catalyst for the Reduction of NO with H₂

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Introduction

Several researchers have shown that Pt-Rh bimetallic catalysts can perform synergistically for the NO/H₂, NO/CO, CO/O₂, and NO/CO/HC reactions [1-5]. Lakis and coworkers clarified some of the mystery surrounding the synergistic performance of Pt-Rh catalysts for the NO + H₂ reaction by using analytical electron microscopy (AEM) to show that the synergistic performance of a Pt(95%)Rh(5%)/ γ -Al₂O₃ was due to the presence of a single-phase of supported Pt-rich nanoparticles while non-synergistic Pt-Rh catalysts with increased Rh fractions contained both Pt-rich and Rh-rich nanoparticles [2, 3]. This study uses *in-situ* FTIR spectroscopy with NO and NO + H₂ as probes to explore the synergistic performance of a Pt(95%)-Rh(5%)/ γ -Al₂O₃ catalyst for the reduction of NO with H₂, with the goal of verifying the presence of surface segregated Rh on the synergistic catalyst under reaction conditions.

Materials and Methods

All catalysts were prepared by incipient wetness impregnation of aqueous precursor solutions into Norton SA 6375D γ -Al₂O₃ stabilized by calcining at 500°C for 3 h. The precursors for Pt and Rh were Platinum(IV) chloride (98% pure, Aldrich) and Rhodium(III) chloride (38-41 weight percent Rh, Strem Chemicals), respectively. Following impregnation, catalysts were air dried at room temperature for 12 h. Monometallic Rh catalysts were stored in a desiccator following drying while monometallic Pt catalysts were calcined at 500°C for 3 h prior to storage in a desiccator. Bimetallic Pt-Rh catalysts were prepared by incipient wetness impregnation of an aqueous RhCl₃ solution into a calcined Pt catalyst then air dried at room temperature for 12 h and stored in a desiccator. A summary of all prepared catalysts and their compositions is presented in Table 1.

The activity of each catalyst for the reduction of NO with H₂ was tested with a feed composition of 3500 ppm NO, 3500 ppm H₂, and 99.3% N₂ with a space velocity of 20,000 h⁻¹. Prior to activity testing the catalysts were reduced in flowing 0.7% H₂ in N₂ for 12 h at 300°C then conditioned by exposing the catalyst to reaction conditions for 10 h at 250°C. The feed and product NO composition was analyzed using a Siemens Ultramat 6 analyzer. Between activity tests and thermal treatments, the catalysts were kept at room temperature under flowing N₂.

In-situ FTIR studies were conducted using a temperature-controlled Harrick Scientific demountable liquid cell modified for gas flow in a Thermo-Mattson Satellite FTIR instrument with 2 cm⁻¹ resolution. FTIR samples were prepared by pressing ~40 mg of previously reacted catalyst into a 13 mm wafer using an International Crystal Laboratories die and a Carver hydraulic press using a pressing force of 1.5 metric tons and a pressing time of 30 s. For the

studies where the catalyst was interacted with NO, the catalyst wafer was reduced *in-situ* at 250°C for 12 h under 30 ml/min of 0.7% H₂ then cooled to the desired temperature under flowing N₂. Following equilibration, a minimum of 2 h, 0.7% NO in N₂ was introduced into the cell at 12 mL/min and spectra were recorded at determined intervals for 1 h. The sample was then allowed to cool to room temperature and was stored under flowing N₂. If multiple adsorption studies were performed on a given sample, the sample was reduced prior to each subsequent test. NO + H₂ FTIR studies were performed using the same reduction, equilibration and storage procedure, except the catalyst was exposed to a 1:1 blend of 0.7% NO in N₂ and 0.7% H₂ in N₂ with a total flowrate of 12 mL/min giving a feed composition of 0.35% NO, 0.35% H₂, and 99.3% N₂. The 95/5 catalyst was further probed by exposing the catalyst 12 mL/min of 0.7% H₂ in N₂ for 30 minutes followed by re-exposure to NO + H₂.

Annular dark field (ADF) electron micrographs of 95/5 and 90/10 were acquired with a JEOL JEM 2200 FS aberration-corrected scanning transmission electron microscope (STEM) and were used to determine the particle size of several hundred supported metal nanoparticles from each sample. Particle sizes were measured digitally and were determined by the averaging the longest and shortest particle diameter. This method allows particle sizes to be reported to 0.1 nm. Electron microscopy samples were prepared by grinding the catalyst with a mortar and pestle and dispersing it on a continuous-carbon-coated 300 mesh Cu grid (Structure Probe, Inc).

Results and Discussion

The activity of the prepared catalysts is presented on an Arrhenius plot using activity as the y-axis and 1000/T(K) as the x-axis (Figure 1) [6]. The following relative order of catalyst activity was observed: 95/5 > Pt/ γ -Al₂O₃ \approx 90/10 >> Rh/ γ -Al₂O₃. The maximum activity of 95/5, a five-fold increase over Pt/ γ -Al₂O₃, was observed after conditioning the catalyst by equilibrating under reaction conditions for 10 h at 250°C. Prior to conditioning the activity of 95/5 was slightly greater than Pt/ γ -Al₂O₃. The activity of conditioned 95/5 was stable to a 24 h reduction at 300°C under flowing 0.7% H₂ in N₂ with a space velocity of 20,000 h⁻¹. Size distributions of the supported metal nanoparticles on 95/5 and 90/10 were compiled by measuring several hundred supported nanoparticles in ADF STEM images (Figure 2). It was determined with 99% confidence that the difference between the mean particle size of 95/5 and 90/10 is zero; therefore, particle size was not responsible for the activity difference between 95/5 and 90/10 [6].

The interaction of NO with Pt/ γ -Al₂O₃, Rh/ γ -Al₂O₃, 90/10, and 95/5 with 0.7% NO in N₂ resulted in several peaks between 1200 cm⁻¹ and 1950 cm⁻¹ being observed in the FTIR spectra[6]. Peaks between 1200 cm⁻¹ and 1675 cm⁻¹ correspond to nitrates and nitrites bound to the Al₂O₃ support. It is well known that NO does not readily interact with Al₂O₃ to form nitrates and nitrites [7], so the formation of nitrates and nitrites results from gas-phase species produced by the supported metal nanoparticles. A trend of increasing magnitude of the peaks associated with alumina bound nitrates and nitrites during exposure to 0.7% NO in N₂ was observed with increasing temperature for all of the examined catalysts, and at each temperature the following relative order of nitrate and nitrite peak magnitude was observed: 95/5 > 90/10 > Rh/ γ -Al₂O₃ > Pt/ γ -Al₂O₃ [6].

Comparing the peaks present in the NO-metal region (1675 cm^{-1} - 1950 cm^{-1}) of the FTIR spectra for Pt/ γ - Al_2O_3 , Rh/ γ - Al_2O_3 , 90/10, and 95/5 allows a qualitative comparison of the exposed metal atoms on the catalyst surface (Figure 3) [6]. The peak intensities cannot be used to quantify the amount of each metal on the surface because there are other adsorbed species, mainly O_{ads} and N_{ads} , that cannot be detected with FTIR spectroscopy. The broad peak at 1760 cm^{-1} is assigned to linearly adsorbed NO on Pt [8], and the peaks at 1695 cm^{-1} and 1905 cm^{-1} are assigned to anionic NO adsorbed on metallic Rh and cationic NO on oxidized Rh (or Rh nitrosyl) [9, 10]. The primary difference between the spectra of 95/5 and 90/10 is the presence of a peak representative of cationic NO on oxidized Rh in the spectra for 90/10 at 150°C and 200°C [6]. Analyzing the NO-metal region under NO + H_2 yields a similar result, as the Rh nitrosyl peak was observed on 90/10 at 150°C and 200°C and it was not present on 95/5 (Figure 4) [6]. Thus, the non-synergistic performance of 90/10 can be attributed to the presence of oxidized Rh on the catalyst surface.

Since the interaction of NO and NO + H_2 with 95/5 did not present any significant spectroscopic evidence of Rh being on the catalyst surface as was suggested by previous researchers [2, 3, 11], an additional *in-situ* FTIR test was performed where, following exposure to NO + H_2 for 60 minutes, the reacted catalyst was exposed to reducing conditions for 30 minutes and re-exposed to reaction conditions (Figure 5) [6]. Exposing the reacted catalyst to H_2 resulted in the disappearance of the peak related to NO linearly bound to Pt and the emergence of a peak at 1695 cm^{-1} which corresponds to NO linearly bound on Rh. After 30 minutes of reduction, the peak representative of linearly bound NO on Rh remained present at all four temperatures. Following re-exposure to reaction conditions, the peak associated with NO linearly bound to Rh remains and the peak associated with NO linearly bound to Pt returns. These results prove the presence of both Pt and Rh on the surface of the synergistic 95/5 catalyst. Observation of the peak representative of anionic NO on Rh under reducing conditions provides insight into the stability of the conditioned 95/5 catalyst to a 24 h reduction at 300°C : Rh on the nanoparticles surface adsorbs NO allowing it to remain surface segregated. These results imply that the conditioning step facilitates diffusion of Rh to the nanoparticle surface where it binds with NO_{ads} or O_{ads} to form a highly active surface.

Conclusions

Metallic Pt and Rh are both present on the surface of 95/5, while the surface of 90/10 contains oxidized Rh in addition to metallic Pt. The non-synergistic performance of 90/10 is attributed to the presence of oxidized Rh on the catalyst surface.

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Table 1. Summary of Prepared Catalysts [11].

Catalyst	Pt (wt %)	Rh (wt %)	Pt/(Pt + Rh) mass ratio
Pt/ γ -Al ₂ O ₃	0.83	0	N/A
Rh/ γ -Al ₂ O ₃	0	0.89	N/A
95/5	0.83	0.04	0.95
90/10	0.83	0.09	0.90

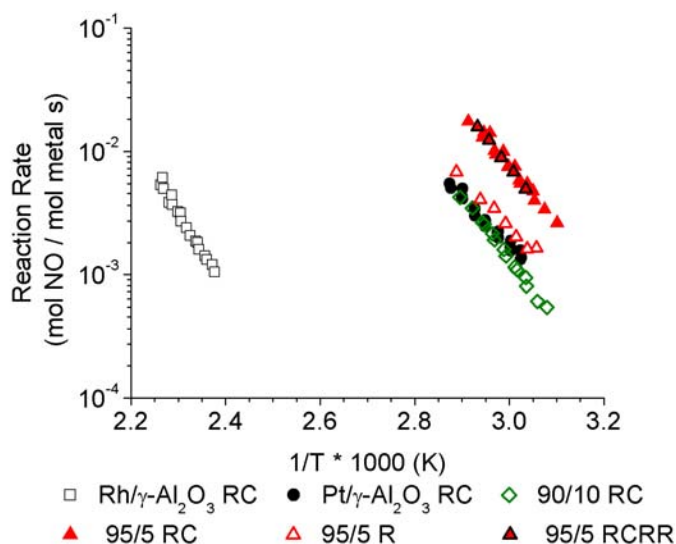


Figure 1. Arrhenius plot of reaction rate (mmol NO/ mol metal s) vs. 1000/T for the reduction of NO with H₂ using a feed composition of 3500 ppm NO, 3500 ppm H₂, and 99.7% N₂ with a space velocity of 20 000 h⁻¹ [6]. The sequence of alphanumeric characters following the catalyst identification corresponds to the thermal treatments other than activity testing that the catalyst received once placed in the reactor where R = reduction at 300°C for 12 h and C = conditioning by equilibrating under reaction conditions at 250°C for 12 h. For example, the notation 90/10 RC indicates that 90/10 was reduced for 12 h at 300°C then exposed to reaction conditions at 250°C for 12 h prior to activity testing.

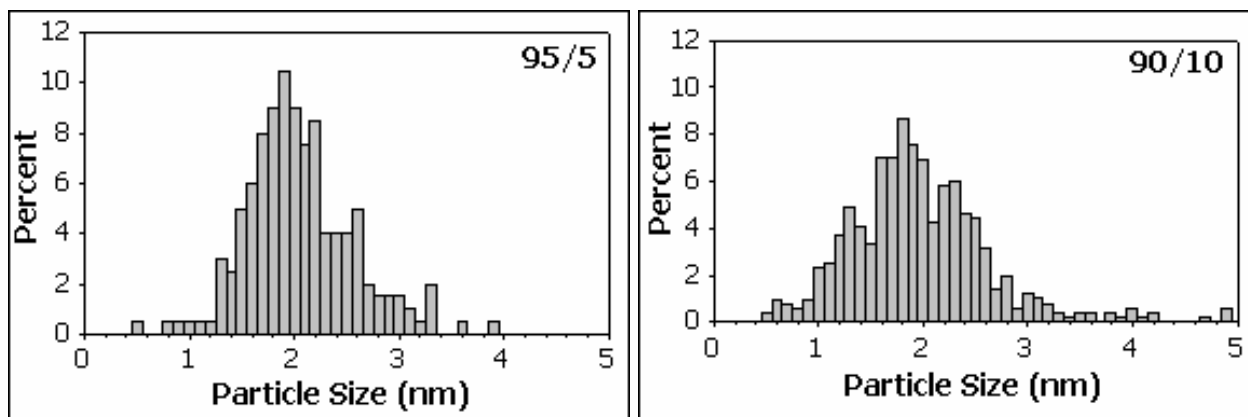


Figure 2. Particle-size distributions of 95/5 (Left) and 90/10 (Right) [6]. The particle-size distribution histograms are reported using percent of total particles as the y-axis. For 95/5 the sample size is 200 particles, and for 90/10 the sample size is 576. The mean particle sizes of 95/5 and 90/10 were found to be $2.05 \text{ nm} \pm 0.07 \text{ nm}$ and $1.96 \pm 0.05 \text{ nm}$, respectively, where the error represents the 95% confidence interval on the mean.

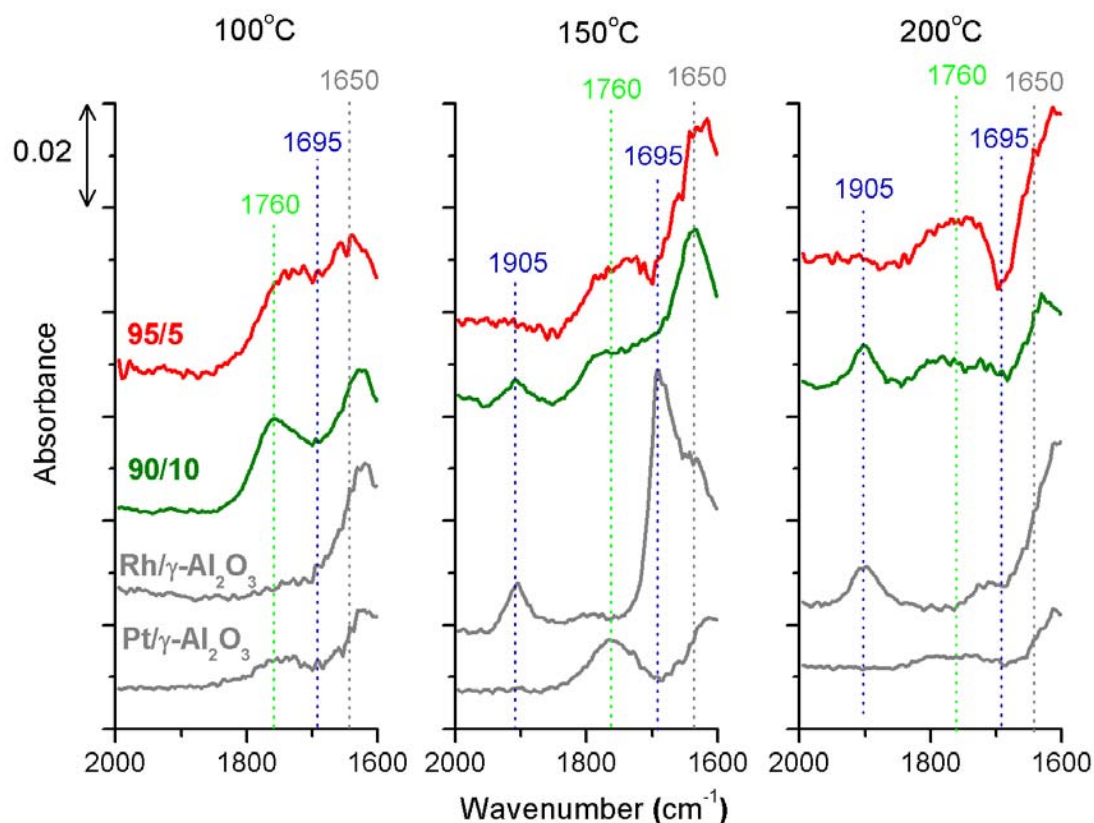


Figure 3. Comparison of NO-metal region from the FTIR spectra obtained from exposing Pt/ γ -Al₂O₃, Rh/ γ -Al₂O₃, 95/5, and 90/10 to 0.7% NO in N₂ at 100°C, 150°C, and 200°C for 60 minutes [6]. The peak at 1650 cm⁻¹ is assigned to bridged bidentate nitrate on Al₂O₃ [8]. The

broad peak at 1760 cm^{-1} is assigned to linear NO on Pt [8]. The peaks at 1695 cm^{-1} and 1905 cm^{-1} are assigned to $\text{NO}^{\delta-}\text{-Rh}^0$ and $\text{NO}^{\delta+}\text{-Rh}^+$, respectively [9].

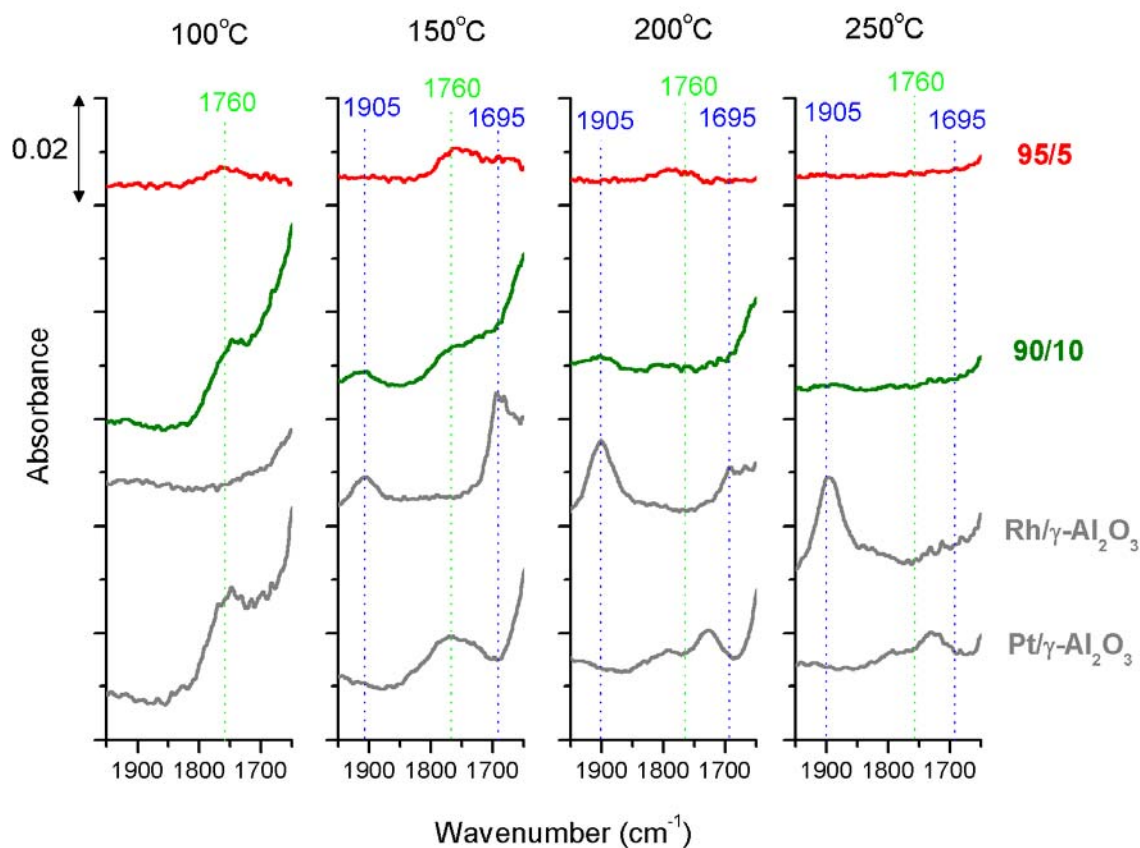


Figure 4. Comparison of NO-Metal Region from the FTIR spectra obtained from exposing Pt/ $\gamma\text{-Al}_2\text{O}_3$, Rh/ $\gamma\text{-Al}_2\text{O}_3$, 95/5, and 90/10 to 0.35% NO, 0.35% H₂, and 99.7% N₂ at 100°C, 150°C, 200°C, and 250°C for 40 min [6]. The broad peak at 1760 cm^{-1} is assigned to linear NO on Pt [8]. The peaks at 1695 cm^{-1} and 1905 cm^{-1} are assigned to $\text{NO}^{\delta-}\text{-Rh}^0$ and $\text{NO}^{\delta+}\text{-Rh}^+$ [9].

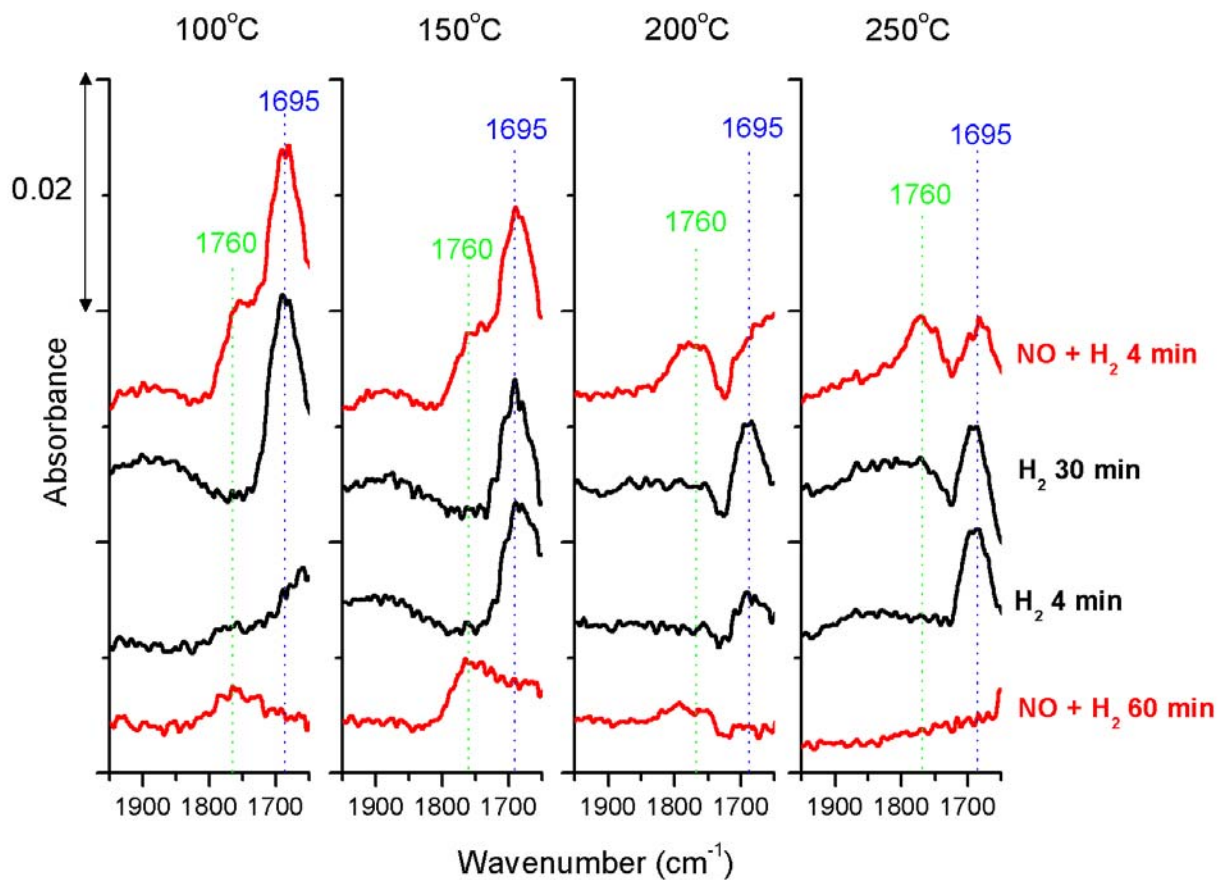


Figure 5. FTIR spectra obtained from 95/5 following exposure to 0.35% NO in N₂ and 0.35% H₂ in N₂ for 60 min followed by 0.7% H₂ in N₂ for 30 min and re-exposure to NO + H₂ [6]. The broad peak at 1760 cm⁻¹ is assigned to linear NO on Pt [8]. The peak at 1695 cm⁻¹ is assigned to NO^{δ-}-Rh⁰ [9].